Using voltammetry to analyse hydrogen bonding interactions of donors and acceptors in non-aqueous solvents

Tessensohn, Malcolm Eugene

2017

Tessensohn, M. E. (2017). Using voltammetry to analyse hydrogen bonding interactions of donors and acceptors in non-aqueous solvents. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/69488>

<https://doi.org/10.32657/10356/69488>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**USING VOLTAMMETRY TO ANALYSE HYDROGEN
BONDING INTERACTIONS OF DONORS AND
ACCEPTORS IN NON-AQUEOUS SOLVENTS**

MALCOLM EUGENE TESSENSOHN

SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES
NANYANG TECHNOLOGICAL UNIVERSITY

2016

This page has been intentionally left blank

**Using Voltammetry to Analyse Hydrogen
Bonding Interactions of Donors and
Acceptors in Non-Aqueous Solvents**

MALCOLM EUGENE TESSENSOHN

School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2016

This page has been intentionally left blank

Acknowledgements

First and above all, I thank my **Lord Jesus Christ** for blessing this journey and giving me the strength and courage to face each day. I owe everything that I have learnt and achieved to His grace.

I would also like to express utmost gratitude to my academic father, **Professor Richard Webster**, who was always believing, supporting and guiding me. Thank you for being more than a wonderful supervisor, I will never forget the positive impact that you have in my life!

The past four years are unforgettable because of **Sherman Lauw**, **Jazreen Lee** and **Kwok Kiong Chan**, who have brought so much joy and laughter. I will always cherish the wonderful memories that we have created together!

This thesis is also recognition of the efforts of **Yu Zhi Lim**, **Melvyn Lee**, **Sher Li Gan**, **Miechie**, **Sihao Lim**, **Yan Feng Yee**, **Yu Rong Koh** and **Quan Li Poh**. Thank you for your contributions and trust.

I would also like to thank my good friends, **Bahareh Khezri**, **Ying Shan Tan**, **Ya Yun Chan** and **Shu Jun Ng** for their support and advice over the past six years. As well as to **Yanni Yue**, **Gwendeline Wong**, **Serena Tan**, **Xiuhui Xu**, **Diane Tiong**, **Maria Novianti** and **Dejan Urbancok** for creating a vibrant atmosphere in the lab.

A special thanks is extended to our collaborator **Dr Hajime Hirao** for his assistance over the past five years.

I am always grateful to have received unwavering support from **Jinyan Zhang**, **Her Shuang Toh**, **Rabi'ah Nisha Khanizeman**, **Mu Jing**, **Sally** and **Guo Hao Chan**.

Words cannot describe my love and appreciation for my dearest **Mummy**, **Por Por**, **Mei Mei**, aunts, **Gladys**, **Cecilia**, **Shirley** and **Jessie**, uncles, **Alfred**, **Wilfred**, **Matthew** and **Garry**, cousins, **Germaine**, **Leonard**, **Timothy**, **Joshua**, **Brandon**, **Petrina**, and **Jared**, and cuties, **Mimi** and **Mao Mao**. Thank you for the sacrifices and overflowing love.

Lastly, to my love, **Genever Tan**, thank you for your love and prayers! I love you!

This page has been intentionally left blank

Table of Contents

		Page
	Acknowledgements	I
	Table of Contents	III-XI
	Abstract	XIII
	List of Publications	XV
Chapter 1	Introduction	1-14
1.1	Background Information	3
1.2	Objectives	4
1.3	Rationale	4
	References	10
Chapter 2	Hydrogen Bonding Analysis	15-44
2.1	The Hydrogen Bond	17
2.2	Cyclic and Square-Wave Voltammetry	18
	2.2.1 Theory	18
	2.2.2 Electrochemical and Chemical Reversibility	19
	2.2.3 Cyclic voltammetry	21
	2.2.4 Square-wave voltammetry	22
2.3	Methods for Hydrogen Bonding Analysis in Non-Aqueous Solvents	25
	2.3.1 Non-electrochemical methods	25
	2.3.2 Electrochemical methods	27
2.4	Summary	36
	References	37

Chapter 3	Measuring the Water Content of Non-Aqueous Solvents	45-72
3.1	The Importance of Measuring Water Content	47
3.2	Types of Water	47
3.3	Significance of Aquametry	49
	3.3.1 Food and pharmaceutical industry	49
	3.3.2 Petrochemical industry	50
	3.3.3 Research industry	50
3.4	Karl Fischer Titrations	51
	3.4.1 The Karl Fischer reaction	51
	3.4.2 Volumetric Karl Fischer titration	53
	3.4.3 Coulometric Karl Fischer titration	53
	3.4.4 Advantages and limitations of coulometric Karl Fischer titration	57
3.5	Alternative Aquametric Methods	61
	3.5.1 Non-electrochemical methods	61
	3.5.2 Electrochemical methods	65
3.6	Summary	68
	References	68
Chapter 4	Electrochemical Applications of Quinones and Phenylenediamines	73-85
4.1	Why Quinones and Phenylenediamines?	75
4.2	Electrochemical Applications of Quinones	75
4.3	Electrochemical Applications of Phenylenediamines	79
4.4	Summary	81
	References	82
Chapter 5	Experimental Methods	87-98
5.1	Purchased Chemicals	89

5.2	Synthesis Procedures	91
	5.2.1 Synthesis of tetra- <i>n</i> -butylammonium hexafluorophosphate	91
	5.2.2 Synthesis of 3,3',5,5'-tetra- <i>tert</i> -butyl-4,4'-diphenoquinone	92
5.3	Voltammetry	92
5.4	Preparation of Dried Solvents and Dried Solutions	93
5.5	Voltammetric Procedure	93
5.6	Karl Fischer Titration	94
5.7	Computational Methods	94
5.8	Nuclear Magnetic Resonance Spectroscopy	96
5.9	Purge and Trap Gas Chromatography-Mass Spectrometry	96
	References	97
Chapter 6	Electrochemical Properties of Quinones, Phenols and Phenylenediamines in Organic Solvents are Strongly Influenced by Hydrogen Bonding with Water	99-127
6.1	Interference of Quinones, Phenols and Phenylenediamines in Karl Fischer Titrations	101
6.2	Effect of Water on the Reduction of Quinones	102
6.3	Effect of Water on the Oxidation of Phenols	110
6.4	Effect of Water on the Oxidation of Hydroquinone	115
6.5	Effect of Water on the Oxidation of Phenylenediamine	119
6.6	Effect of Water on the Oxidation of Ferrocene	124
6.7	Summary	125
	Notes	126
	References	126

Chapter 7	Measuring the Relative Hydrogen Donor Abilities of Alcohols in Organic Solvents via the Voltammetry of Quinones	129-150
7.1	Introduction	131
7.2	Steric Effects of Simple Alcohols	131
7.3	Electronic Effect of Fluorinated Alcohols	139
7.4	The Role of the Additional Hydroxyl Group of Diols	143
7.5	Interesting Comparisons	146
7.6	Hydrogen Bonding or Proton-Transfer?	147
7.7	Summary	148
	Notes	149
	References	149
Chapter 8	Measuring the Relative Basicity and Hydrogen Acceptor Strengths of Pyridine and Its Derivatives in Aprotic Organic Solvents via the Voltammetry of Phenylenediamines	151-200
8.1	Introduction	153
8.2	Hydrogen Bonding or Proton-Transfer?	154
	8.2.1 Hydrogen bonding or deprotonation?	155
	8.2.2 Hydrogen bonding or protonation?	158
8.3	Measuring the Relative Basicity and Hydrogen Acceptor Abilities of Pyridine and Its Derivatives	161
	8.3.1 Steric and electronic effects of pyridine derivatives	161
	8.3.2 Mesomeric and ring effects of quinoline and isoquinoline	172
	8.3.3 Presence of two heteroatoms: The diazines and bipyridyls	175
	8.3.4 Interesting comparisons	179
	8.3.5 Pi-stacking effects	180
	8.3.6 Oxygen and sulfur heterocycles	181
8.4	Measuring the Hydrogen Donor and Acceptor Abilities of Alcohols and Diols	183
	8.4.1 The effect of the simple alcohols on the electrochemical behavior of TMPD	183

	8.4.2 The effect of the diols on the voltammetric behavior of TMPD	189
	8.4.3 The effect of trifluoroethanol and acetic acid on the electrochemical behavior of TMPD	192
8.5	Summary	198
	Notes	199
	References	199
Chapter 9	Optimizing the Selectivity of Quinones for the Detection of Water in Organic Solvents via Structural Modifications	201-215
9.1	Introduction	203
9.2	Selectivity of Quinones for Water	204
	9.2.1 General results	204
	9.2.2 Positional isomers: <i>para</i> and <i>ortho</i> quinones	208
	9.2.3 Steric and electronic effects	210
9.3	Measuring the Moisture Content of Carbonyl Solvents	210
9.4	Measuring the Moisture Content of Protic Organic Solvents	212
9.5	Summary	213
	Notes	214
	References	214
Chapter 10	Detection of Impurities in Nitrile Solvents Commonly Used for Electrochemistry via the Voltammetry of Quinones and Phenylenediamines	217-229
10.1	Introduction	219
10.2	Electrochemical Behavior of Quinones and Phenylenediamines in Nitrile Solvents	221
10.3	Qualitative and Quantitative Analysis with Purge and Trap Gas Chromatography-Mass Spectrometry	224

10.4	Purification Techniques	226
10.5	Summary	228
	References	229
Chapter 11	Conclusion	231-235
11.1	Conclusion	233
Appendix A	Supporting Information for Chapter 6	237-303
A.1	Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 1,4-Benzoquinone	239
	A.1.1 Gas-phase calculations	239
	A.1.2 MeCN-solvated calculations	244
A.2	Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,5-Di-<i>tert</i>-butyl-1,4-benzoquinone	249
A.3	Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,6-Di-<i>tert</i>-butyl-1,4-benzoquinone	256
A.4	Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,4,6-Trimethylphenol	263
A.5	Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2, 6-Di-<i>tert</i>-butyl-4-methylphenol	270
A.6	Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,4,6-Tri-<i>tert</i>-butylphenol	280
A.7	Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of Hydroquinone	291
A.8	Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,3,5,6-Tetramethyl-1,4-phenylenediamine	297

Appendix B	Supporting Information for Chapter 7	305-402
B.1	Supporting Information for 9,10-Anthraquinone	307
	B.1.1 Cyclic voltammograms	307
	B.1.2 Plots of $\Delta E_Q = E_{Q1} - E_{Q2} $ against concentration of simple alcohols	315
	B.1.3 Computational data: Geometries, energies and coordinates of hydrogen-bonded complexes	316
B.2	Supporting Information for 1,4-Benzoquinone	359
	B.2.1 Cyclic voltammograms	359
	B.2.2 Plots of $\Delta E_Q = E_{Q1} - E_{Q2} $ against concentration of simple alcohols	367
	B.2.3 Computational data: Geometries, energies and coordinates of hydrogen-bonded complexes	368
Appendix C	Supporting Information for Chapter 8	403-491
C.1	Supporting Information for Pyridine and Its Derivatives	405
	C.1.1 Plots of $\Delta E_P = E_{P1} - E_{P3} $ against concentration of bases	405
	C.1.2 Plots of $\Delta E_P = E_{P1} - E_{P2} $ against concentration of hydrogen acceptors	405
	C.1.3 Energies of phenylenediamine-base/hydrogen acceptor complexes	406
	C.1.4 Geometries of phenylenediamine-base/hydrogen acceptor complexes	406
	C.1.5 Coordinates of phenylenediamine-base/hydrogen acceptor complexes	414
C.2	Supporting Information for Oxygen and Sulfur Heterocycles	430
	C.2.1 Cyclic voltammograms of 2,3,5,6-tetramethyl-1,4-phenylenediamine at different concentrations of tetrahydrothiophene and thiophene	430
C.3	Supporting Information for the Simple Alcohols	431
	C.3.1 Cyclic voltammograms of 2,3,5,6-tetramethyl-1,4-phenylenediamine at different concentrations of the simple alcohols	431
	C.3.2 Plots of E_{P1} , E_{P2} and $\Delta E_P = E_{P1} - E_{P2} $ against concentration of simple alcohols	433
	C.3.3 Energies of phenylenediamine-alcohol hydrogen-bonded complexes	434
	C.3.4 Geometries of phenylenediamine-alcohol hydrogen-bonded complexes	435

	C.3.5 Coordinates of phenylenediamine-alcohol hydrogen-bonded complexes	439
C.4	Supporting Information for the Diols	447
	C.4.1 Cyclic voltammograms of 2,3,5,6-tetramethyl-1,4-phenylenediamine at different concentrations of the diols	447
	C.4.2 Plots of E_{P1} , E_{P2} and $\Delta E_P = E_{P1} - E_{P2} $ against concentration of diols	449
	C.4.3 Energies of phenylenediamine-diol hydrogen-bonded complexes	450
	C.4.4 Geometries of phenylenediamine-diol hydrogen-bonded complexes	450
	C.4.5 Coordinates of phenylenediamine-diol hydrogen-bonded complexes	453
C.5	Supporting Information for 2,2,2-Trifluoroethanol and Acetic Acid	459
	C.5.1 Plots of E_{P1} , E_{P2} and $\Delta E_P = E_{P1} - E_{P2} $ against concentration of hydrogen donors	459
C.6	Computational Data for Calculations of Adiabatic Ionization Energies	460
	C.6.1 Energies of phenylenediamine-base/hydrogen acceptor/hydrogen donor complexes	460
	C.6.2 Geometries of phenylenediamine- phenylenediamine-base/hydrogen acceptor/hydrogen donor complexes	461
	C.6.3 Coordinates of phenylenediamine-diol hydrogen-bonded complexes	469
Appendix D	Supporting Information for Chapter 9	493-523
D.1	Supporting Information for 9,10-Anthraquinone	495
	D.1.1 Cyclic voltammograms	495
	D.1.2 Plots of E_{Q1} , E_{Q2} and $\Delta E_Q = E_{Q1} - E_{Q2} $ against concentration of simple alcohols	497
D.2	Supporting Information for 9,10-Phenanthrenequinone	499
	D.2.1 Cyclic voltammograms	499
	D.2.2 Plots of E_{Q1} , E_{Q2} and $\Delta E_Q = E_{Q1} - E_{Q2} $ against concentration of simple alcohols	501
D.3	Supporting Information for Duroquinone	503
	D.3.1 Cyclic voltammograms	503

	D.3.2 Plots of E_{Q1} , E_{Q2} and $\Delta E_Q = E_{Q1} - E_{Q2} $ against concentration of simple alcohols	505
D.4	Supporting Information for 3,3',5,5'-Tetra-<i>tert</i>-butyl-4,4'-diphenquinone	507
	D.4.1 Cyclic voltammograms	507
	D.4.2 Plots of E_{Q1} , E_{Q2} and $\Delta E_Q = E_{Q1} - E_{Q2} $ against concentration of simple alcohols	509

This page has been intentionally left blank

Abstract

The electrochemical behavior of phenols, quinones and phenylenediamines in non-aqueous solvents is strongly influenced by hydrogen bonding interactions, especially to the trace water that is present in the solvents. Hence, it is recommended that voltammetric studies on electroactive hydrogen donors and hydrogen acceptors measure and report the moisture content of their working solutions to enable accurate comparisons and better understanding of the data. The voltammetry of quinones and phenylenediamines were used in hydrogen bonding analysis of several compounds. In the case of quinones, their electrochemical parameter $\Delta E_Q = |E_{Q1} - E_{Q2}|$ (where E_{Q1} was the first reduction potential and E_{Q2} was the second reduction potential) was found to be sensitive to the steric and electronic effects of hydrogen donors as well as the number of hydroxyl groups present thus, could differentiate the binding abilities of alcohols and diols. As for phenylenediamines, their oxidized forms are such strong hydrogen donors that pyridine and its derivatives and even the alcohols and diols could be categorized as bases or hydrogen acceptors. Yet, their voltammetric response could also measure the hydrogen donor strengths of trifluoroethanol and acetic acid because the neutral species predominantly behaves as a hydrogen acceptor. Finally, the voltammetric behavior of quinones and phenylenediamines were explored for the purpose of measuring the moisture content of carbonyl and protic organic solvents as well as applied to detect impurities in nitrile solvents that were commonly used for electrochemistry.

This page has been intentionally left blank

List of Publications

The results in this thesis project were published in the following research articles.

Research Articles:

CHAPTER 2

M. E. Tessensohn, R. D. Webster, Using Voltammetry to Measure Hydrogen-Bonding Interactions in Non-Aqueous Solvents: A Mini-Review. *Electrochemistry Communications* **2016**, 62, 38-43.

CHAPTER 6

M. E. Tessensohn, H. Hirao, R. D. Webster, Electrochemical Properties of Phenols and Quinones in Organic Solvents are Strongly Influenced by Hydrogen-Bonding with Water. *Journal of Physical Chemistry C* **2013**, 117, 1081-1090.

CHAPTER 7

M. E. Tessensohn, M. Lee, H. Hirao, R. D. Webster, Measuring the Relative Hydrogen-Bonding Strengths of Alcohols in Aprotic Organic Solvents. *ChemPhysChem* **2015**, 16, 160-168.

CHAPTER 10

M. E. Tessensohn, S. J. Ng, K. K. Chan, S. L. Gan, N. F. Sims, Y. R. Koh, R. D. Webster, Impurities in Nitrile Solvents Commonly Used for Electrochemistry, and their Effects on Voltammetric Data. *ChemElectroChem* **2016**, 3, 1753-1759.

OTHERS

Y. Yue, M. L. Novianti, M. E. Tessensohn, H. Hirao, R. D. Webster, Optimizing the Lifetimes of Phenoxonium Cations derived from Vitamin E via Structural Modifications. *Organic & Biomolecular Chemistry* **2015**, 13, 11732-11739

This page has been intentionally left blank

Chapter 1

Introduction

1.1 Background Information

1.2 Objectives

1.3 Rationale

References

This page has been intentionally left blank

1.1 Background Information

Hydrogen bonds are one of the most valuable intermolecular interactions by virtue of their ubiquitous nature, selectivity, strength and directionality. They have an influence on the physical properties and chemical reactivity of numerous molecules and play a part in determining the pathways that some reactions undertake. These important interactions are also responsible for maintaining the structures of biomolecules like proteins and DNA as much as they are contributing to their biological functions. Hence, it is unsurprising that a significant amount of attention and resources have been devoted into understanding the hydrogen bond and expending its unique properties for application purposes.

Voltammetry is an important electroanalytical technique and is widely used because it enables the mechanism of a redox process to be thoroughly investigated, to which the presence and stability of intermediates and products, thermodynamic and kinetic properties as well as chemical and electrochemical reversibility of individual reactions can be established. Phenols, quinones and phenylenediamines are popular subjects of such studies in light of their biological, medicinal, and industrial properties. For instance, *N,N,N',N'*-tetramethyl-1,4-phenylenediamine and *N,N*-dimethyl-1,4-phenylenediamine have been used as redox indicators in the oxidase test while the radical cations of numerous phenylenediamines have enjoyed successful applications as dyes and also as key molecules in electrochromic devices.^[1]

α -Tocopherol, the biologically active form of vitamin E, contains a phenol functional group and is almost always recognized as an anti-oxidant.^[2] However, there are arguments that it may also possess a non-anti-oxidant role as a cellular signaling molecule,^[3] but no detailed mechanisms of this function are presently available. Cyclic voltammetry has shown that the general electrochemical behavior of phenols in non-aqueous solvents (Scheme 1.1) involves a $-2e^-/-H^+$ oxidation following the ECE type of mechanism (with E and C representing electron-transfer and proton transfer reactions, respectively).^[4]

Vitamin K comprises a series of naphthoquinone compounds with an aliphatic side chain in the 3-position whose functions as a cofactor in the blood clotting process^[5] and also as electron

carriers in oxidative phosphorylation^[6] are well documented. The quinone functional group is primarily responsible for the biological properties by partaking in electron and proton transfers whereas the aliphatic side group provides compatibility and solubility within hydrophobic regions. Phylloquinone, or vitamin K₁ (VK₁), that can be found in the cell membrane, is believed to aid the transfer of electrons across the photosynthetic cell membrane in photosystem I via the formation of the semiquinone radical anion (VK₁^{•-}).^[7] Therefore, voltammetry studies conducted in non-aqueous systems are useful in providing information about the electrochemical properties and associated biological functions of molecules for comparisons to those recorded under aqueous conditions.

1.2 Objectives

It is more significant to this work that voltammetry has been previously applied to gather information about the strength of hydrogen bonds, binding abilities of hydrogen donors and acceptors, constituents and stability of the hydrogen-bonded complex as well as association constants and kinetic data; it has also been used to perturb hydrogen bonds for the purpose of molecular sensing and measurement of physical properties like temperature and relative humidity. Thus, the primary objective of this thesis is to utilize voltammetry to analyze hydrogen bonding interactions of donors and acceptors such as phenols, quinones and phenylenediamines in non-aqueous solvents and investigate the effects of hydrogen bonding on their electrochemical properties. The knowledge obtained will subsequently be used to develop voltammetric methods for detecting and quantifying trace water and impurities in organic solvents as well as for measuring the relative hydrogen bonding abilities of hydrogen donors and acceptors in non-aqueous solvents.

1.3 Rationale

Voltammetry is particularly suited for this project because the hydrogen bond carries some electrostatic character and so is susceptible to electrochemical perturbation. Additionally, voltammetry only requires one component of the donor-acceptor pair to be electroactive to enable

the hydrogen bond system to be investigated. Therefore, voltammetry measurements allow the assessment of the hydrogen bonding abilities of alcohols and pyridine and its derivatives despite them being electroinactive.

Furthermore, it is not mandatory for the same group of atoms in the molecule to be involved in both the hydrogen bond and redox center, but the redox center should preferably reside close to the hydrogen bond to exert its influence either by mesomeric and/or inductive effects. The voltammetric technique is also not overwhelmed by a large excess of hydroxyl groups unlike the case of infrared (IR) and ^1H nuclear magnetic resonance (NMR) spectroscopy, and has greater sensitivity than ultraviolet-visible (UV-vis) spectroscopy.^[8] Its results were also shown to agree with the findings from theoretical calculations.^[9]

Nevertheless, there are several criteria that must be satisfied prior to using voltammetry to study any hydrogen bond system. First and foremost, one component of the donor-acceptor pair has to be electroactive and, secondly, their oxidized and reduced forms should preferably be chemically long-lived under the timescale and conditions of the experiments. Next, the electron-transfer kinetics should be reasonably fast and the redox center must be able to significantly affect the interaction between the hydrogen donor and acceptor via a resonance and/or inductive effect. Finally, it is important that the effects of proton-transfer can be distinguished from hydrogen bonding.

We were interested in the quinones, phenols and phenylenediamines because of their biological and industrial importance and that they are susceptible to hydrogen bonding with acceptors or donors in aprotic organic solvents. The neutral quinone (Q) undergoes an EE reduction mechanism to first give a radical anion or semiquinone ($\text{Q}^{\bullet-}$) at potential E_{Q1} followed by an aromatic dianion (Q^{2-}) at a more negative potential E_{Q2} (Scheme 1.2).^[10] Phenylenediamines, on the other hand, participate in EE oxidation reactions where the neutral species (P) is first oxidized to the radical cation ($\text{P}^{\bullet+}$) at potential E_{P1} before another oxidation to the quinonediimine dication (P^{2+}) at a more positive potential E_{P2} (Scheme 1.3).^[11] On the other hand, the oxidation of phenols in aprotic organic solvents is not as simple. Its neutral species

(PhOH) is converted into the phenoxonium cation (PhO^+) through the intermediates PhOH^{*+} and $\text{PhO}^\bullet$ via a series of electron and proton transfers that follow the ECE mechanism (Scheme 1.1).^[12]

Scheme 1.1. Electrochemical oxidation of phenol in aprotic organic solvents.

Scheme 1.2. Electrochemical reduction of 1,4-benzoquinone in aprotic organic solvents.

Scheme 1.3. Electrochemical oxidation of 1,4-phenylenediamine in aprotic organic solvents.

Quinones and phenylenediamines exhibit clear voltammetric responses (Figures 1.1 and 1.2, respectively) that are chemically reversible on the voltammetric timescale ($\leq$ seconds) with reasonably fast heterogeneous electron-transfer rates (k_{et}). Their electrochemical behavior are widely known to be responsive to the presence of acids, bases, hydrogen donors and acceptors, of which it has been reported that the characteristics of hydrogen bonding are shifts in the formal potentials without any loss in the chemical reversibility of the electrochemical processes. This is unlike proton-transfer with acids and bases that may lead to chemically irreversible electron-transfer reactions and/or the loss of the EE behavior.^[8-9, 11b, 11c, 11f, 11j, 13]

Figure 1.1. Cyclic voltammogram of 1 mM 1,4-benzoquinone with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as supporting electrolyte in acetonitrile (MeCN) recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode.

Figure 1.2. Cyclic voltammogram of 1 mM 1,4-phenylenediamine with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode.

The general oxidation profiles of phenols (see Figure 1.3 for 2,4,6-trimethylphenol) show a single chemically irreversible anodic peak on the forward scan even though two electrons are transferred per molecule because the intermediate deprotonation reaction occurs rapidly and the second 1e^- -oxidation process converting $\text{PhO}^\bullet$ into the phenoxonium cation PhO^+ takes place at a potential that is less positive than the first 1e^- -oxidation reaction of PhOH to PhOH^{++} . The chemical irreversibility occurs because the phenoxonium cation is highly reactive and can undergo dealkylation, hydrolysis and self-reactions (e.g. dimerization) depending on the nature and type of the substituents at the vital *ortho* and *para* positions as well as the amount of trace

water present in the solvent.^[4, 12, 14] It may therefore be a challenge to differentiate the effects of hydrogen bonding from those that are a result of these homogeneous chemical reactions.

Figure 1.3. Cyclic voltammogram of 1 mM 2,4,6-trimethylphenol with 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode.

It is advantageous that quinones and phenylenediamines possess dissimilar chemical properties for it allows them to interact with different species and in so doing assists with the applied aspects of this thesis; that is, in using their voltammetric properties for sensing other molecules. Quinones being hydrogen acceptors would only interact with acids and hydrogen donors. The order of their hydrogen bond strengths and basicity follows $Q < Q^{\cdot-} < Q^{2-}$ because of the accumulation of negative charge at the oxygen atoms after each reduction reaction that ultimately results in hydrogen bonding exerting a greater effect on E_{Q2} than E_{Q1} .

The neutral form of the phenylenediamines is both a hydrogen acceptor and hydrogen donor through the corresponding nitrogen and hydrogen atoms of the amine groups. But their oxidized forms ($P^{\cdot+}$ and P^{2+}) are strictly hydrogen donors and so will only interact with bases and hydrogen acceptors. This suggests that the phenylenediamines are more versatile than the quinones for they might enable the examination of the binding abilities of both hydrogen donors and acceptors. The order of acidity and hydrogen donor abilities of the phenylenediamines is $P < P^{\cdot+} < P^{2+}$.

Phenylenediamines might however be less sensitive towards hydrogen bonding than the quinones because their positive charges in the dication are dispersed across a number of atoms whereas the negative charges in the dianion of the quinones are localized at the oxygen atoms. The phenols are expected to be the least affected because only a monocation is produced, as compared to the dication of phenylenediamines and dianion of quinones, and the single positive charge is mainly contained within the ring.

It is more important and beneficial, however, that both the quinones and phenylenediamines undergo two consecutive electron-transfer reactions that are well spaced apart (in terms of potential applied) because that is where the novelty of this project resides in. Although several electrochemical and non-electrochemical methods and models have been proposed for similar purposes, few of them have utilized the electrochemical parameter ΔE , which is the difference in potential between the first and second electron-transfer reactions e.g. for quinones, $\Delta E_Q = |E_{Q1} - E_{Q2}|$ and for phenylenediamines, $\Delta E_P = |E_{P1} - E_{P2}|$, to measure trace water content and hydrogen bond strengths. The use of ΔE implies that the phenols are uninvolved in the applied aspects of this thesis. Nonetheless, there is on-going work in our laboratories to synthesize structurally modified vitamin E compounds that will produce stable and long-lived phenoxonium cations upon oxidation, to which their biological properties can also be explored.^[15]

It is believed that ΔE affords greater accuracy and reproducibility than the use of absolute potentials because the effects of uncompensated solution resistance, heterogeneous electron-transfer rates (assuming similar k_{et} values for both processes), migration effects, the condition of the working electrode surface and changes in the potential of the reference electrode are cancelled. Therefore, the electrochemical parameter is only dependent on the interaction between the hydrogen donor and acceptor and the measurements are accurate and reliable. In addition, the analyses can be easily conducted and the results quickly obtainable without significant data processing. The use of differences in formal potentials (either between two molecules or within a single molecule containing two redox centers) has been reported for measurements of temperature^[16] and humidity^[16b].

Lastly, the sensitivity of our analytical technique for molecular sensing and measuring of hydrogen bonding interactions can be adjusted accordingly by changing the type (e.g. electron-withdrawing or electron-donating), size and number of substituents that are attached to the quinones and phenylenediamines. Such changes would alter the strength of their hydrogen bonds and affect their acidity and basicity, and so also creates the opportunity of doing away with unwanted proton-transfer reactions that would interfere with the analyses. The selectivity of the measurements is, on the other hand, regulated by the size of the substituents. As with all other analytical measurements, our proposed voltammetric techniques are not without their limitations and these will be carefully addressed in the following chapters. The use of quinones and phenylenediamines would also enable the development of a “dipstick” sensor, with the compounds chemically attached onto the surface of the electrode, or an injection device for commercial applications.

References

- [1] (a) L. Michaelis, M. P. Schubert, S. Granick, *J. Am. Chem. Soc.* **1939**, *61*, 1981-1992; (b) J. Yang, S. Kai, K. Ogura, *J. Mater. Sci. Lett.* **1993**, *12*, 1791-1792; (c) J. Yano, K. Terayama, S. Yamasaki, *J. Mater. Sci.* **1996**, *31*, 4785-4792; (d) H.-M. Wang, S.-H. Hsiao, *J. Polym. Sci. Pol. Chem.* **2011**, *49*, 337-351; (e) H. Wei, X. Yan, Y. Li, H. Gu, S. Wu, K. Ding, S. Wei, Z. Guo, *J. Phys. Chem. C* **2012**, *116*, 16286-16293; (f) T. Suzuki, Y. Sakano, Y. Tokimize, Y. Miura, R. Katoono, K. Fujiwara, N. Yoshioka, N. Fujii, H. Ohno, *Chem. Asian J.* **2014**, *9*, 1841-1846; (g) S. J. L. Lauw, X. Xu, R. D. Webster, *ChemPlusChem* **2015**, *80*, 1288-1297.
- [2] (a) G. W. Burton, K. U. Ingold, *Acc. Chem. Res.* **1986**, *19*, 194-201; (b) T. Finkel, N. J. Holbrook, *Nature* **2000**, *408*, 239-247; (c) X. Wang, P. Quinn, *Molec. Membr. Biol.* **2000**, *17*, 143-156; (d) E. Niki, N. Noguchi, *Acc. Chem. Res.* **2004**, *37*, 45-51; (e) M. G. Traber, J. Atkinson, *Free Radic. Biol. Med.* **2007**, *43*, 4-15.
- [3] A. Azzi, *Free Radic. Biol. Med.* **2007**, *43*, 16-21.

- [4] R. D. Webster, *Acc. Chem. Res.* **2007**, *40*, 251-257.
- [5] (a) *Vitamin K and Vitamin K-Dependent Proteins: Analytical, Physiological, and Clinical Aspects*; M. J. Shearer, M. J. Seghatchian, Eds.; CRC Press, Boca Raton, Florida, **1993**;
(b) D. Josic, L. Hoffer, A. Buchacher, *J. Chromatogr. B* **2003**, *790*, 183-197.
- [6] D. Voet, J. G. Voet, *Biochemistry*, 4th ed., John Wiley & Sons, **2010**.
- [7] (a) *Function of Quinones in Energy Conserving Systems*; B. L. Trumpower, Eds.; Academic Press, New York, **1982**; (b) M. C. Thurnauer, J. W. Brown, P. Gast, L. L. Feezel, *Radiat. Phys. Chem.* **1989**, *34*, 647-651; (c) S. E. J. Rigby, M. C. W. Evans, P. Heathcote, *Biochim. Biophys. Acta* **2001**, *1507*, 247-259; (d) A. van der Est, *Biochim. Biophys. Acta* **2001**, *1507*, 212-225; (e) R. E. Blankenship, *Molecular Mechanisms of Photosynthesis*, 2nd ed., Wiley-Blackwell, **2014**.
- [8] Y. Hui, E. L. K. Chng, C. Y. L. Chng, H. L. Poh, R. D. Webster, *J. Am. Chem. Soc.* **2009**, *131*, 1523-1534.
- [9] (a) M. Gómez, F. J. González, I. González, *J. Electrochem. Soc.* **2003**, *150*, E527-E534;
(b) J. Garza, R. Vargas, M. Gómez, I. González, F. J. González, *J. Phys. Chem. A* **2003**, *107*, 11161-11168; (c) C. Costentin, M. Robert, J.-M. Savéant, C. Tard, *Angew. Chem. Int. Ed.* **2010**, *49*, 3803-3806; (d) J.-M. Savéant, C. Tard, *J. Am. Chem. Soc.* **2014**, *136*, 8907-8910.
- [10] J. Q. Chambers, In *The Chemistry of the Quinonoid Compounds*; S. Patai, Z. Rappoport, Eds.; Wiley, New York, **1988**; Vol. II, Chapter 12, pp 719-757.
- [11] (a) M. T. Melchior, A. H. Maki, *J. Chem. Phys.* **1961**, *34*, 471-476; (b) V. Dvořák, I. Němec, J. Zýka, *Microchem. J.* **1967**, *12*, 324-349; (c) V. Dvořák, I. Němec, J. Zýka, *Microchem. J.* **1967**, *12*, 350-370; (d) G. Cauquis, H. Delhomme, D. Serve, *Tetrahedron Lett.* **1972**, *13*, 1965-1968; (e) T. Yao, S. Musha, M. Munemori, *Chem. Lett.* **1974**, *3*, 939-944; (f) V. Solís, T. Iwasita, M. C. Giordano, *J. Electroanal. Chem.* **1976**, *73*, 91-

- 104; (g) H. Fernández, M. A. Zón, *J. Electroanal. Chem.* **1990**, 283, 251-270; (h) K. Hu, D. H. Evans, *J. Electroanal. Chem.* **1997**, 423, 29-35; (i) O. V. Klymenko, D. Giovanelli, N. S. Lawrence, N. V. Rees, L. Jiang, T. G. J. Jones, R. G. Compton, *Electroanalysis* **2003**, 15, 949-960; (j) U. Nickel, M. d. G. García-Angel, U. Ramminger, B. Weidinger, *Z. Phys. Chem.* **2006**, 220, 497-509; (k) J. R. Quinn, F. W. J. Foss, L. Venkataraman, R. Breslow, *J. Am. Chem. Soc.* **2007**, 129, 12376-12377; (l) S. Ernst, H. Baltruschat, J. Hönes, M. Lungu, *Electrochim. Acta* **2009**, 54, 3129-3138; (m) P. Rapta, A. Vargová, J. Polovková, A. Gatíal, L. Omelka, P. Majzlík, M. Breza, *Polym. Degrad. Stabil.* **2009**, 94, 1457-1466.
- [12] (a) *Organic Electrochemistry*, 3rd ed.; H. Lund, M. M. Baizer, Eds.; Marcel Dekker, New York, **1991**; (b) H. Eickhoff, G. Jung, A. Rieker, *Tetrahedron* **2001**, 57, 353-364.
- [13] (a) Y. Ge, R. R. Lilienthal, D. K. Smith, *J. Am. Chem. Soc.* **1996**, 118, 3976-3977; (b) N. Gupta, H. Linschitz, *J. Am. Chem. Soc.* **1997**, 119, 6384-6391; (c) M. B. Moressi, M. A. Zón, H. Fernández, *Electrochim. Acta* **1997**, 42, 303-314; (d) F. J. González, *Electroanalysis* **1998**, 10, 638-642; (e) M. Aguilar-Martínez, N. A. Macías-Ruvalcaba, I. González, *J. Mex. Chem. Soc.* **2000**, 44, 74-81; (f) Y. Ge, L. Miller, T. Ouimet, D. K. Smith, *J. Org. Chem.* **2000**, 65, 8831-8838; (g) M. W. Lehmann, D. H. Evans, *J. Phys. Chem. B* **2001**, 105, 8877-8884; (h) M. W. Lehmann, D. H. Evans, *J. Electroanal. Chem.* **2001**, 500, 12-20; (i) G. Cooke, H. A. de Cremiers, F. M. A. Duclairoir, J. Leonardi, G. Rosair, V. M. Rotello, *Tetrahedron* **2003**, 59, 3341-3347; (j) G. Cooke, V. Sindelar, V. M. Rotello, *Chem. Commun.* **2003**, 752-753; (k) M. Gómez, F. J. González, I. González, *Electroanalysis* **2003**, 15, 635-645; (l) M. Gómez, I. González, F. J. González, R. Vargas, J. Garza, *Electrochem. Commun.* **2003**, 5, 12-15; (m) M. Aguilar-Martínez, N. A. Macías-Ruvalcaba, J. A. Bautista-Martínez, M. Gómez, F. J. González, I. González, *Curr. Org. Chem.* **2004**, 8, 1721-1738; (n) J. A. Bautista-Martínez, I. González, M. Aguilar-Martínez, *J. Electroanal. Chem.* **2004**, 573, 289-298; (o) J. B. Carroll, M. Gray, G. Cooke, V. M. Rotello, *Chem. Commun.* **2004**, 442-443; (p) C. Frontana, B. A. Frontana-

Uribe, I. González, *J. Electroanal. Chem.* **2004**, 573, 307-314; (q) M. Gómez, C. Z. Gómez-Castro, I. I. Padilla-Martínez, F. J. Martínez-Martínez, F. J. González, *J. Electroanal. Chem.* **2004**, 567, 269-276; (r) N. A. Macías-Ruvalcaba, I. González, M. Aguilar-Martínez, *J. Electrochem. Soc.* **2004**, 151, E110-E118; (s) M. Gómez, F. J. González, I. González, *J. Electroanal. Chem.* **2005**, 578, 193-202; (t) C. Frontana, I. González, *J. Braz. Chem. Soc.* **2005**, 16, 299-307; (u) S. Ahmed, A. Y. Khan, R. Qureshi, *J. Chem. Soc. Pak.* **2006**, 28, 542-548; (v) G. Cooke, J. Couet, J. F. Garety, C.-Q. Ma, S. Mabruk, G. Rabani, V. M. Rotello, V. Sindelar, P. Woisel, *Tetrahedron Lett.* **2006**, 47, 3763-3766; (w) D. K. Smith, J. E. Woods, *ECS Trans.* **2006**, 3, 31-43; (x) S. Ahmed, A. Y. Khan, R. Qureshi, M. S. Subhani, *Russ. J. Electrochem.* **2007**, 43, 811-819; (y) P. D. Astudillo, J. Tiburcio, F. J. González, *J. Electroanal. Chem.* **2007**, 604, 57-64; (z) C. Frontana, I. González, *J. Electroanal. Chem.* **2007**, 603, 155-165; (aa) C. Frontana, M. Gómez, I. González, *ECS Trans.* **2007**, 3, 37-44; (ab) C. E. Frontana, I. González, *ECS Trans.* **2007**, 3, 13-23; (ac) I. González, C. Frontana, M. Gómez, M. Aguilar, J. A. Bautista, N. A. Macías, M. Salas, P. D. Astudillo, F. J. González, *ECS Trans.* **2007**, 2, 25-36; (ad) M. Quan, D. Sanchez, M. F. Wasyliw, D. K. Smith, *J. Am. Chem. Soc.* **2007**, 129, 12847-12856; (ae) A. Rahman, R. Qureshi, S. Ahmed, *J. Chem. Soc. Pak.* **2008**, 30, 655-663; (af) J. E. Woods, Y. Ge, D. K. Smith, *J. Am. Chem. Soc.* **2008**, 130, 10070-10071; (ag) L. S. Hernández-Muñoz, M. Gómez, F. J. González, I. González, C. Frontana, *Org. Biomol. Chem.* **2009**, 7, 1896-1903; (ah) L. Zhang, H. Zhou, X. Li, Y. Lin, P. Yu, L. Su, L. Mao, *Electrochem. Commun.* **2009**, 11, 808-811; (ai) L. A. Clare, L. E. Rojas-Sligh, S. M. Maciejewski, K. Kangas, J. E. Woods, L. J. Deiner, A. Cooksy, D. K. Smith, *J. Phys. Chem. C* **2010**, 114, 8938-8949; (aj) Y. Hui, E. L. K. Chng, L. P.-L. Chua, W. Z. Liu, R. D. Webster, *Anal. Chem.* **2010**, 82, 1928-1934; (ak) A. Galano, M. Gómez, F. J. González, I. González, *J. Phys. Chem A* **2012**, 116, 10638-10645; (al) J. Katsumi, T. Nakayama, Y. Esaka, B. Uno, *Anal. Sci.* **2012**, 28, 257-265; (am) A. René, D. H. Evans, *J. Phys. Chem. C* **2012**, 116, 14454-14460; (an) S. Ahmed, A. Y. Khan, *Russ. J. Electrochem.* **2013**, 49, 336-343; (ao) Z. H. Lim, E. L. K. Chng, Y. Hui, R. D. Webster, *J.*

- Phys. Chem. B* **2013**, *117*, 2396-2402; (ap) P. A. Staley, E. M. Lopez, L. A. Clare, D. K. Smith, *J. Phys. Chem. C* **2015**, *119*, 20319-20327; (aq) B. T. Tamashiro, M. R. Cedano, A. T. Pham, D. K. Smith, *J. Phys. Chem. C* **2015**, *119*, 12865-12874; (ar) N. Gamboa-Valero, P. D. Astudillo, M. A. González-Fuentes, M. A. Leyva, M. de J. Rosales-Hoz, F. J. González, *Electrochim. Acta* **2016**, *188*, 602-610.
- [14] (a) A. Ronlán, V. D. Parker, *J. Chem. Soc. (C)* **1971**, 3214-3218; (b) A. Nilsson, A. Ronlán, V. D. Parker, *J. Chem. Soc., Perkin Trans. 1* **1973**, 2337-2345; c) J. A. Richards, P. E. Whitson, D. H. Evans, *J. Electroanal. Chem.* **1975**, *63*, 311-327.
- [15] Y. Yue, M. L. Novianti, M. E. Tessensohn, H. Hirao, R. D. Webster, *Org. Biomol. Chem.* **2015**, *13*, 11732-11739.
- [16] (a) L. Xiong, A. M. Fletcher, S. Ernst, S. G. Davies, R. G. Compton, *Analyst* **2012**, *137*, 2567-2573; (b) L. Xiong, A. M. Fletcher, S. Ernst, S. G. Davies, S. E. Norman, C. Hardacre, R. G. Compton, *Analyst* **2012**, *137*, 4951-4957; (c) M. Zhang, L. Xiong, R. G. Compton, *Anal. Methods* **2013**, *5*, 3473-3481.

Chapter 2

Hydrogen Bonding Analysis

2.1 *The Hydrogen Bond*

2.2 *Cyclic and Square-Wave Voltammetry*

2.2.1 Theory

2.2.2 Electrochemical and Chemical Reversibility

2.2.3 Cyclic voltammetry

2.2.4 Square-wave voltammetry

2.3 *Methods for Hydrogen Bonding Analysis in Non-Aqueous Solvents*

2.3.1 Non-electrochemical methods

2.3.2 Electrochemical methods

2.4 *Summary*

References

This page has been intentionally left blank

2.1 The Hydrogen Bond

The hydrogen bond, according to the recommendation by the International Union of Pure and Applied Chemistry (IUPAC), is defined as *an attractive interaction between a hydrogen atom from a molecule or a molecular fragment D–H in which D is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is experimental and/or theoretical evidence of bond formation.*^[1]

The hydrogen bond is typically represented as a series of three dots such as in D–H•••A, where D–H and A are the hydrogen donor and hydrogen acceptor, respectively. Traditionally, nitrogen, oxygen and fluorine were the only atoms to be thought of as hydrogen donors, but there are now reports of carbon, phosphorus, sulfur, and halogens atoms as well; the only criteria is that the elements are more electronegative than hydrogen.^[2] As for hydrogen acceptors, A can be any electron rich atom or anion with available lone pairs, another hydrogen atom (as in metal hydrides and is known as dihydrogen bonding),^[3] a sigma (σ)^[4] or pi (π)^[2c, 2e, 2h, 5] bond, a single electron,^[6] and even rare gas elements^[7] and transition metals^[8].

The above definition requires some evidence of bond formation with the condition that the forces leading to the formation of the hydrogen bond are not purely based on dispersion forces because the hydrogen bond is isotropic whereas dispersion forces are anisotropic. The D–H covalent bond also has to be polarized and the strength of the hydrogen bond should increase with greater electronegativity of D and shorter H•••A distance. In addition, the strength of the interaction should increase as the hydrogen bond angle approaches 180°. The formation of a hydrogen bond usually lengthens the D–H bond and so will result in a bathochromic shift of its stretching frequency, and deshielding of the proton in ¹H NMR spectroscopy. Lastly, the hydrogen bond has to be thermally stable, that is the Gibbs energy of formation should be larger than the thermal energy of the system so that it can be observed.^[9]

A set of characteristic features of the hydrogen bond is also provided in the recommendation. Namely, that hydrogen bonds display directionality, exhibit cooperativity and are precursors to proton-transfer reactions. The pK_a of the hydrogen donor and pK_b of the

hydrogen acceptor have been found to parallel the energy of the hydrogen bond that they are associated in, which is a particularly useful relationship and knowledge for our study because the measurement of hydrogen donor and acceptor abilities would correspondingly reflect, to a certain extent, the acidity and basicity of their constituents.^[8c] Finally, there would be an observation of a (3,-1) bond critical point between the hydrogen acceptor and the hydrogen atom in electron density topological analysis.^[10]

2.2 Cyclic and Square-wave Voltammetry

Voltammetry, or the measurement of the current response of an analyte as a function of the applied potential, is a popular analytical method to obtain mechanistic and kinetic information of chemical reactions, especially those that follow an electron-transfer reaction. It is also widely used to study adsorption processes and electron-transfer reactions on bare and chemically modified electrode surfaces. The concepts and workings of cyclic voltammetry and square-wave voltammetry will be briefly described in this section.

2.2.1 Theory

It is not uncommon to find voltammetric experiments using a three-electrode setup to minimize the effects of the iR -drop and allow for accurate and simultaneous measurement of the current and control of the applied potential. The working electrode, or the electrode where the electrochemical phenomena of interest (e.g. a reduction reaction) occurs, is typically made of platinum or glassy carbon material but can also include silver, gold, mercury and diamond for specialized purposes, or be modified via self-assembled monolayers (such as thiolates) or coated with physisorbed materials (such as nanoparticles). The auxiliary electrode closes this circuit by allowing the opposite reaction (e.g. an oxidation reaction) to take place at its surface. It is usually made of an inert metal such as platinum and has a much larger surface area to allow its half-reaction to occur quickly without affecting the desired studied reaction at the working electrode. The reference electrode is the third electrode in the setup whose primary role is to provide a constant potential to monitor the potential of the working electrode. It is able to accurately achieve

this feat because negligible current flows through the circuit consisting of the working electrode and reference electrode thus the IR-drop between the two electrodes is insignificant. A potentiostat is used to adjust the potential between the working and auxiliary electrodes to give the desired potential difference between the working and reference electrodes. The bubbler is present to supply nitrogen or argon into the solution to remove any dissolved oxygen, ensure homogeneity and limit evaporation by providing an inert atmosphere directly above the solution.

The electrochemical solution consists of an analyte and a supporting electrolyte, with the latter in a hundred-fold excess of the former, in an organic solvent with low resistivity. The supporting electrolyte is present to prevent the migration of ions and reduce the resistance of the solvent. It is typically inert towards any chemical reactions with the analyte and its charged products, merely stabilizing the oxidized and reduced products via weak ion-pairing.

In this study, glassy carbon was selected as the working electrode material to avoid unwanted reactions, such as the reduction of water that may occur on a platinum surface. In addition, it has been reported that the second $1e^-$ -reduction reaction of quinones in non-aqueous solvents is difficult to detect on platinum surfaces because the relative high reduction potential suffers interference from the concurrent reduction of trace water (due to the low overpotential for hydrogen evolution on platinum).^[11] Unless otherwise stated, acetonitrile (MeCN) was used in the experiments because it is highly miscible with water, alcohols (hydrogen donors), pyridine and its derivatives (hydrogen acceptors). Yet, it does not form strong hydrogen bonding interactions with the compounds, unlike *N,N*-dimethylformamide and dimethyl sulfoxide, and so the competing interactions with the solvent are less significant.^[11-12] It can also be easily dried by storing over molecular sieves.

2.2.2 Electrochemical and Chemical Reversibility

An electron-transfer or “electrochemical” process can be described as chemically and electrochemically reversible depending on the conditions which the experiments were performed. Reaction 2.1 can be termed as electrochemically reversible but only if the

kinetics of the forward and reverse heterogeneous electron-transfer reactions are facile and allow for equilibrium to be rapidly achieved at every potential that is applied on the time-scale of the experiment. The electrochemical reversibility of a reaction in cyclic voltammetry experiments can be qualitatively determined through the potential separation between the forward and reverse peaks (e.g. $\Delta E_p = |E_p^{\text{ox}} - E_p^{\text{red}}|$). $\Delta E_p = 57/n$ for an electrochemically reversible reaction where n is the number of electrons transferred, and increases with greater irreversibility.

Chemical reversibility, on the other hand, is associated with the stability of the product of the reaction and is often indicated via the ratio of the peak currents of the forward and reverse electron-transfer processes (e.g. $|i_p^{\text{ox}}/i_p^{\text{red}}|$). If the forward and backward steps of Reaction 2.2 are sufficiently fast to maintain equilibrium on the time-scale of the experiment then the entire process may be considered as chemically reversible when $|i_p^{\text{red}}/i_p^{\text{ox}}| \approx 1$; values lesser than 1 indicate that Ox is unstable under the experimental conditions and so the reaction would be termed as chemically irreversible.

It is noted that the chemical and electrochemical reversibility of the overall process (encompassing Reactions 2.1 and 2.2) is dependent on the kinetics of the forward and reverse heterogeneous electron-transfer reactions of Reaction 2.1, kinetics of the forward and backward chemical reactions in Reaction 2.2 as well as the applied the potential scan rate (v).

2.2.3 Cyclic voltammetry

In cyclic voltammetry, the working electrode is excited by a triangular potential waveform and the current response is then measured as a function of the applied potential. The rate at which the potential of the working electrode is varied with time is termed the potential scan rate (v) and it enables the technique to unravel reaction mechanisms, detect intermediates and observe follow-up reactions of products that are produced within the vicinity of the electrode surface. The input waveform can also be cycled to examine the stability of the electrochemically-generated species. The excitation waveform and the resulting cyclic voltammogram, adopting the IUPAC convention for current, are shown in Figure 2.1 for a chemically and electrochemically reversible reaction.

Figure 2.1. Excitation waveform and resulting voltammogram in cyclic voltammetry for a chemically and electrochemically reversible reaction.

Cyclic voltammetry experiments are more often than not conducted under stationary conditions with diffusion as the only mode of mass transfer. The resulting characteristic feature in the voltammograms is the observation of peak currents (i_p) instead of limiting currents. As the potential of the working electrode is swept towards larger magnitudes, the reactant molecules undergo an electron-transfer reaction with the electrode surface only if the potential is sufficient for it to occur. At this instance, the reactant molecules within the immediate vicinity of the electrode surface will be the first to convert into charged products and will subsequently diffuse out into the bulk solution because of the concentration gradient, while unreacted molecules from the bulk solution will at the same time move towards the electrode surface for reaction. With an increase in potential and time, a greater number of reactant molecules would have approached the surface of the electrode and be converted into product molecules and so the current will increase.

However, in light of the fixed rate of mass transfer, there will come a point where the supply of reactant molecules to the electrode surface is unable to keep up with their consumption in the electrochemical reaction and so the current will decrease. It is this phenomenon of concentration polarization where the maximum rate of diffusion does not permit sufficient replenishment of the analyte within the Nernst diffusion layer that is responsible for the occurrence of peak currents. Peak currents are useful for our study because their magnitudes are dependent on n , the number of electrons transferred in the reaction, and c , the concentration of the analyte (mol L^{-1}), according to the Randles-Sevcik equation (Equation 2.1). The other factors are A the area of the electrode (cm^2), D the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and ν (V s^{-1}). Equation 2.1 is only valid for an electrochemically reversible reaction where the Nernst equation applies at the electrode surface.

$$i_p = 2.686 \times 10^5 \times n^{3/2} \times A \times c \times D^{1/2} \times \nu^{1/2} \quad (\text{Eqn 2.1})$$

2.2.4 Square-wave voltammetry

The excitation waveform in square-wave voltammetry is a superposition of a square-wave pulse and a staircase signal (Figure 2.2). The current is sampled at the end of the forward (point 1)

and reverse (point 2) pulses. After which the differential current $\Delta i = |i_{\text{forward}} - i_{\text{reverse}}|$, that is the difference in magnitude of the forward and reverse current waveforms, is plotted against the applied potential to give the square-wave voltammogram (Figure 2.3), with the maximum value of Δi occurring at the half-wave potential, $E_{1/2}$, of the electrochemical process if the reaction is electrochemically reversible.

The advantage of using square-wave voltammetry in our study of the quinones and phenylenediamines, whose redox behavior exhibit electrochemical reversibility, is its rapidity and ability in distinguishing faradaic and non-faradaic currents. The procedure is much faster than cyclic voltammetry because of the short pulse period (τ) and therefore our proposed methods of measuring moisture content and hydrogen bond strengths as well as detecting impurities can be achieved rather quickly. Also, detection limits as low as the nanomolar scale have been reported because of the manner that the current is sampled; sufficient time is allowed to elapse between the switching of the pulse direction and sampling of the current and so minimizes contribution from capacitive (or non-faradaic) current. The use of Δi also suppresses the background current.

Figure 2.2. Excitation waveform for square-wave voltammetry.

Figure 2.3. A square-wave voltammogram.

2.3 Methods for Hydrogen Bonding Analysis in Non-Aqueous Solvents

This section covers some qualitative and quantitative electrochemical and non-electrochemical methods for hydrogen bonding analysis, which includes the characterization of hydrogen bond complexes as well as determination of the binding abilities of hydrogen donors and acceptors.

2.3.1 Non-electrochemical methods

Physical and Thermodynamic Properties

The occurrence of hydrogen bonding between the hydrogen donor (D) and acceptor (A), as in $D-H\cdots A$, has traditionally been determined via a comparison of the distance between the D and A atoms (and ignoring the hydrogen atom) against the sum of their respective van der Waals radii, of which a hydrogen bond is considered to be present only if the distance between D and A is shorter than the sum of their van der Waals radii.^[13] Unfortunately, this method is inaccurate because of the incorrect assumption that the hydrogen atom does not occupy a finite volume.^[14]

Dissociation energies were also suggested as indicators of hydrogen bonding and limits were given to weak ($<17\text{ kJ mol}^{-1}$), moderate ($17\text{-}63\text{ kJ mol}^{-1}$) and strong ($63\text{-}167\text{ kJ mol}^{-1}$) hydrogen bonds.^[2f, 13a, 15] However, energy alone was insufficient to differentiate hydrogen bonds from ionic, covalent and especially London dispersion interactions and so directionality was included as an additional and critical requirement. Hydrogen bonds, unlike van der Waals forces, are anisotropic.^[13a, 16] Thus, H_2O in ice has four neighbors in a tetrahedral arrangement whereas H_2S has twelve neighbors ordered in a spherical arrangement.

Spectral Methods

Spectroscopic techniques like infrared (IR)^[13b, 17] and nuclear magnetic resonance (NMR)^[18] spectroscopy are more popularly used in the detection and characterization of hydrogen bonds because the intensity of the D–H stretch and magnetic resonance of the related proton are heavily affected by hydrogen bonding.^[19] Microwave,^[2d, 20] electronic^[19] and Raman^[21]

spectroscopy are also utilized but only in specific circumstances or if they are useful to the cause. A concern with using spectroscopy to analyze hydrogen bonds is that the targeted signal may be overwhelmed by other inconsequential signals, such as the O–H stretching and proton NMR signal of trace water in the solvent. Therefore, care must be taken to ensure that there is little or no interference.

In IR spectroscopy, the D–H stretching frequency is often found to red-shift upon hydrogen bonding because of bond lengthening,^[17] but blue-shifts and non-shifting have also been observed.^[22] Such shifting or non-shifting of the D–H stretching frequency has been found to be dependent on the D–H distance where the energy of the D–H...A complex is a minimum, of which the optimum distance may be longer (resulting in a red-shift), shorter (blue-shift) or equal (no shift) than the non-hydrogen-bonded donor.^[23]

In the case of NMR spectroscopy, hydrogen bonding almost always shifts the magnetic resonance of the donor proton downfield as a result of deshielding from the acceptor. Information about the presence of a hydrogen bond may also be sought from the through-bond coupling, if there is any, between the donor and acceptor atoms.^[18]

Computational Chemistry

Theoretical chemistry is another useful tool for studying hydrogen bonding, of which the density functional theory (DFT) approach is recently popular because of its lower computational cost.^[24] It however lacks the proper consideration of dispersion forces, which could be an important contributor to hydrogen bonding.^[25] Hydrogen-bonded systems are usually, and directly, analyzed via their interaction energies, which is the amount of energy needed to separate the donor and acceptor. Therefore, there is a challenge to study intramolecular hydrogen bonds because the donor and acceptor components can never be fully separated.^[14a, 26] The counterpoise procedure must also be applied in all calculations to correct for the basis set superposition error.^[27]

Computational chemistry can also indirectly assist in the understanding of hydrogen-bonded complexes by enabling the determination of the lowest-energy geometry, from which important structural information can be extracted. The calculation of vibrational spectra as well as NMR chemical shifts and coupling constants can also be performed to support experimental findings.^[28] Lastly, the Quantum Theory of Atoms in Molecules model is widely used in electron density topological analysis to predict the existence of hydrogen bonding via the observation of a (3,-1) bond critical point between the hydrogen and A atoms.^[10, 29]

2.3.2 Electrochemical methods

Characterization of the Hydrogen Bond Complex

Gonzalez and co-workers suggested that the formation of hydrogen bonds could be revealed through changes in the peak current magnitude (i_p) because of its dependence on the diffusion coefficient of the redox-active species approaching the electrode surface (see Equation 2.1).^[30] A smaller i_p value will be obtained for the hydrogen-bonded complex because it is comparatively larger, and so its diffusion coefficient is smaller, than its unbound electroactive constituent. Yet, it appears that this technique may not accurately define the existence of hydrogen bonding, as compared to changes in absolute potentials (E), because the diffusion coefficient, and consequently i_p , would decrease in the event of ion-pairing interactions. The diffusion coefficients are also dependent on the viscosity of the solution, which would vary in the presence and absence of the additional component.

It is common to use an electrochemical “square scheme” mechanism, analogous to the reaction scheme for proton-coupled electron transfer (PCET) reactions, to describe the series of electron-transfer reactions and hydrogen bonding interactions that can occur between a pair of electroactive hydrogen acceptor (A_{act}) and electroinactive hydrogen donor (D_{inact}) as in Scheme 2.1, or as shown in Scheme 2.2 between an electroactive hydrogen donor (D_{act}) and electroinactive hydrogen acceptor (A_{inact}); the observed potential E_{obs} can represent either $E_{1/2}$ or peak, E_p , potentials while K is the association constant for the formation of the hydrogen bond. These

square schemes can be extended horizontally and vertically to incorporate more electron-transfer and association reactions, respectively, and have diagonal arrows to represent concerted pathways as opposed to the stepwise routes shown.

Scheme 2.1. Nine-membered square scheme mechanism for the reduction of an electroactive hydrogen acceptor (A_{act}).

The shifting of E_{obs} is an indicator of hydrogen bonding as well as the binding efficiency of the oxidized and reduced species and therefore, is more often used than i_p . To illustrate this consider the upper left square of Scheme 2.1, where if the electroinactive hydrogen donor (D_{inact}) has preferred binding to the reduced form of the electroactive hydrogen acceptor ($A_{\text{act}}^{\bullet-}$) than its oxidized form (A_{act}), then the reduction of the $A_{\text{act}}D_{\text{inact}}$ complex would require less energy than the reduction of A_{act} . Therefore, $E^{\circ}(AD/AD^{\bullet-})$ will be less negative than $E^{\circ}(A/A^{\bullet-})$, where $E^{\circ}(A/A^{\bullet-})$ and $E^{\circ}(AD/AD^{\bullet-})$ are the standard electrode potentials of the $A/A^{\bullet-}$ and $AD/AD^{\bullet-}$ redox couples, respectively. This means that the E_{obs} for the reduction of A_{act} will continuously shift towards less negative potentials with increasing amounts of D_{inact} .

Scheme 2.2. Nine-membered square scheme mechanism for the oxidation of an electroactive hydrogen donor (D_{act}).

On the other hand, if D_{inact} has stronger binding to A_{act} then the E_{obs} for the reduction of A_{act} will shift in the opposite direction (i.e. towards more negative potentials) with increasing concentration of D_{inact} . This arises because the reduction of the $A_{\text{act}}D_{\text{inact}}$ complex requires more energy than the reduction of A_{act} , and $E^{\circ(A^{\bullet-}/A)}$ occurs at a more negative potential than $E^{\circ(A^{\bullet-}/A)}$. It should be noted that E_{obs} for the reduction of A_{act} would not vary with increasing amounts of D_{inact} if no hydrogen bonding is occurring between the three species (D_{inact} , A_{act} and $A_{\text{act}}^{\bullet-}$).

In a similar qualitative fashion, if the upper left square of Scheme 2.2 is considered, then E_{obs} for the oxidation of D_{act} will shift towards less positive potentials if A_{inact} has greater interaction with the oxidized form (D_{act}^{*+}), and in the direction of more positive potentials if there is stronger binding to D_{act} . It will also remain unchanged if A_{inact} does not interact with D_{act} and D_{act}^{*+} .

Quantitatively, these shifts of E_{obs} can be explained via the equilibrium expressions of the Nernst equation. If the electron-transfer steps and association reactions are fast and reversible, then a four-membered square scheme can be shown to behave as a one-electron redox couple with E_{obs} dependent on the standard electrode potentials and association constants.

For example, in the upper left square of Scheme 2.1, if given that $[A]_{\text{total}} = [A] + [AD]$ and $[A^{\bullet-}]_{\text{total}} = [A^{\bullet-}] + [AD^{\bullet-}]$, with $K_1^{(A)} = \frac{[AD]}{[A][D]}$ and $K_1^{(A^{\bullet-})} = \frac{[AD^{\bullet-}]}{[A^{\bullet-}][D]}$. Then a substitution of these

equations into the Nernst equation $E_{\text{obs}} = E^{\circ}(\text{A}/\text{A}^{\cdot-}) - \frac{RT}{F} \ln \frac{[\text{A}^{\cdot-}]}{[\text{A}]}$, assuming that the activities are equal to concentrations, and replacement of $E_f^{\circ}(\text{A}/\text{A}^{\cdot-})$ with $E^{\circ}(\text{A}/\text{A}^{\cdot-}) - \frac{RT}{F} \ln \frac{[\text{A}^{\cdot-}]_{\text{total}}}{[\text{A}]_{\text{total}}}$ would give Equation 2.2.

$$E_{\text{obs}} = E_f^{\circ}(\text{A}/\text{A}^{\cdot-}) + \frac{RT}{F} \ln \frac{1+K_1^{(\text{A}^{\cdot-})}[\text{D}]}{1+K_1^{(\text{A})}[\text{D}]} \quad (\text{Eqn 2.2})$$

If D_{inact} is present in a significant excess so that the amount of unbound D_{inact} may be taken as its added concentration and also such that only $\text{A}_{\text{act}}\text{D}_{\text{inact}}$ exists in solution (because all the A_{act} molecules are hydrogen bonded to D_{inact}) then E_{obs} will be equal to $E_f^{\circ}(\text{AD}/\text{AD}^{\cdot-})$. Furthermore, if $K_1^{(\text{A})}$, $K_1^{(\text{A}^{\cdot-})}$ and/or $[\text{D}]$ is large so that $K_1^{(\text{A})}[\text{D}] \gg 1$ and $K_1^{(\text{A}^{\cdot-})}[\text{D}] \gg 1$ then Equation 2.3 showing the relative binding affinities of A and $\text{A}^{\cdot-}$ to D_{inact} via the ratio of the association constants to the maximum difference in potential can be obtained.

$$\frac{K_1^{(\text{A}^{\cdot-})}}{K_1^{(\text{A})}} = e^{\frac{\{E_f^{\circ}(\text{AD}/\text{AD}^{\cdot-}) - E_f^{\circ}(\text{A}/\text{A}^{\cdot-})\}_F}{RT}} \quad (\text{Eqn 2.3})$$

For the upper left square in Scheme 2.2, Equation 2.4 can be obtained via the same mathematical treatment as above but with $[\text{D}]_{\text{total}} = [\text{D}] + [\text{DA}]$, $[\text{D}^{\cdot+}]_{\text{total}} = [\text{D}^{\cdot+}] + [\text{DA}^{\cdot+}]$, $K_1^{(\text{D})} = \frac{[\text{DA}]}{[\text{D}][\text{A}]}$, $K_1^{(\text{D}^{\cdot+})} = \frac{[\text{DA}^{\cdot+}]}{[\text{D}^{\cdot+}][\text{A}]}$ and $E_f^{\circ}(\text{D}/\text{D}^{\cdot+}) = E^{\circ}(\text{D}/\text{D}^{\cdot+}) - \frac{RT}{F} \ln \frac{[\text{D}^{\cdot+}]_{\text{total}}}{[\text{D}]_{\text{total}}}$. Also, if A_{inact} is present in great excess so that the amount of unbound A_{inact} may be taken as its added concentration and that only $\text{D}_{\text{act}}\text{A}_{\text{inact}}$ exists in solution (because all the D_{act} molecules are hydrogen bonded to A_{inact}) then E_{obs} will be equal to $E_f^{\circ}(\text{DA}/\text{DA}^{\cdot+})$. Equation 2.5, which indicates the relative hydrogen bonding abilities of D and $\text{D}^{\cdot+}$ to A_{inact} , will be obtained if $K_1^{(\text{D})}$, $K_1^{(\text{D}^{\cdot+})}$ and/or $[\text{A}]$ are large so that $K_1^{(\text{D})}[\text{A}] \gg 1$ and $K_1^{(\text{D}^{\cdot+})}[\text{A}] \gg 1$.

$$E_{\text{obs}}^{(\text{D}/\text{D}^{\cdot+})} = E_f^{\circ}(\text{D}/\text{D}^{\cdot+}) + \frac{RT}{F} \ln \frac{1+K_1^{(\text{D}^{\cdot+})}[\text{A}]}{1+K_1^{(\text{D})}[\text{A}]} \quad (\text{Eqn 2.4})$$

$$\frac{K_1^{(\text{D}^{\cdot+})}}{K_1^{(\text{D})}} = e^{\frac{\{E_f^{\circ}(\text{DA}/\text{DA}^{\cdot+}) - E_f^{\circ}(\text{D}/\text{D}^{\cdot+})\}_F}{RT}} \quad (\text{Eqn 2.5})$$

Measurement of the Binding Abilities of Hydrogen Donors and Acceptors in Non-Aqueous Solvents

Qualitative knowledge about the binding ability of a series of D_{inact} or A_{inact} can also be determined indirectly through the E_{obs} of a reference electroactive partner. For example, the hydrogen donor ability of alcohols can be investigated with quinones where the absolute value of E_{obs} for the reduction of the quinone-alcohol complex is compared, to which the stronger hydrogen donor would give a smaller E_{obs} . Hydrogen acceptor abilities may also be analyzed in a similar fashion using phenylenediamines.

It is often the case that the E_{obs} of the electroactive component will shift towards smaller potentials (i.e. less negative for reduction processes and less positive for oxidation reactions) with increasing concentration and hydrogen bonding ability of the electroinactive component probably because the hydrogen-bonded complexes have greater electron affinity (for compounds that partake in reduction) and decreased ionization energy (for those that undergo oxidation) than their corresponding non-hydrogen-bonded forms.^[12f, 31] This, of course, is only possible if hydrogen bonding to the higher charged entity (e.g. dication and dianion) is preferred over the lesser-charged species (e.g. monocation and monoanion). Having said that, the opposite trend of E_{obs} moving towards larger potentials is also possible but would occur because of the greater tendency of the electroinactive component to interact with the lesser-charged species; in this scenario, the electron affinity and ionization energy should correspondingly decrease and increase as the amount and binding ability of the electroinactive species is raised.

Although absolute potentials can be easily obtained, we do not recommend their use in hydrogen bonding analysis because they are affected by changes in the iR-drop and kinetics of the heterogeneous electron transfer and so have to be referenced against a constant potential such as the potential of the reference electrode (whose internal filling solution is difficult to keep completely dry). Instead, the difference in potentials (ΔE) is preferred as the abovementioned factors can be cancelled out. There are at least three known descriptions of ΔE in the literature; the first expresses it as the difference between the potentials recorded in the absence and presence of

the electroinactive species.^[32] The second describes it as the difference in potential of two species in solution, one of which can hydrogen bond to the electroinactive additive while the other has no interaction.^[33] The third definition of ΔE is unique to electroactive compounds such as quinones and phenylenediamines that undergo more than one successive electron-transfer reaction for it exploits the potential separation between each process.^[11, 12h] This is especially useful since the potential of the first electron-transfer process is more often than not unaffected by hydrogen bonding and hence can be applied as a reference potential for the subsequent electron-transfer reactions.

Quantitative data such as the number of donor or acceptor molecules in the hydrogen-bonded complex, association constants and kinetic information can also be obtained from voltammetric data by simulating the results with available software (e.g. DigiElch and Digisim CV simulation) or treating them with one of the three working models (e.g. model for a single global equilibrium, model for equilibria in two successive global stages, and model for equilibria of n and m successive stages). In the model of a single global equilibrium, with consideration of the step-wise reduction processes of Scheme 2.1, the formation of a particular hydrogen-bonded species is taken to occur through a single association step as shown in Reactions 2.3 and 2.4. With the assumption that only the reduced species $A^{\bullet-}$ and A^{2-} (and not neutral A) can interact with p and q molecules of D to form $(AD_p)^{\bullet-}$ and $(AD_q)^{2-}$ hydrogen-bonded complexes, respectively; $\beta^{(A^{\bullet-})}$ and $\beta^{(A^{2-})}$ represent the global equilibrium constants of Reactions 2.3 and 2.4.

Equations 2.6 and 2.7 relating $E_{1/2}^{(A/A^{\bullet-})}$ and $E_{1/2}^{(A^{\bullet-}/A^{2-})}$ to the concentration of D may then be established, with $E_{1/2}^{o(A/A^{\bullet-})}$ and $E_{1/2}^{o(A^{\bullet-}/A^{2-})}$ denoting the half-wave potentials of the first and second electron-transfer processes in the absence of D . The number of molecules of D interacting with $A^{\bullet-}$ (p) and A^{2-} (q) together with the global equilibrium constants, $\beta^{(A^{\bullet-})}$ and $\beta^{(A^{2-})}$, may subsequently be determined by first measuring $E_{1/2}^{(A/A^{\bullet-})}$ and $E_{1/2}^{(A^{\bullet-}/A^{2-})}$ at different concentrations of D before applying linear regression analysis. One concern with using the model of a single global equilibrium in hydrogen bond analysis is that fractional values of p and q , which are most likely the average number of associated molecules, are more often obtained. In addition, it

requires that $\beta^{(A^{\star-})}[D]^p$ is significantly greater than 1, which is only possible if $\beta^{(A^{\star-})}$ and/or $[D]$ is very large.

$$E_{1/2}^{(A/A^{\star-})} = E_{1/2}^{\circ(A/A^{\star-})} + \frac{RT}{F} \ln(1 + \beta^{(A^{\star-})}[D]^p) \quad (\text{Eqn 2.6})$$

$$E_{1/2}^{(A^{\star-}/A^{2-})} = E_{1/2}^{\circ(A^{\star-}/A^{2-})} + \frac{RT}{F} \ln\left(\frac{1 + \beta^{(A^{2-})}[D]^q}{1 + \beta^{(A^{\star-})}[D]^p}\right) \quad (\text{Eqn 2.7})$$

Because of steric and electronic effects, Gonzalez et al. proposed the model for equilibria of n and m successive stages to account for a more realistic picture of hydrogen bonding where the association of D to $A^{\star-}$ and A^{2-} occurs in n and m successive steps as opposed to a single step (Reactions 2.5 to 2.7).^[34] An association constant, $K_i^{(A^{\star-})}$, is assigned to each association reaction from which the global association constant, $\beta_i^{(A^{\star-})}$, is derived via the product of the necessary association constants. The neutral species A is assumed to not participate in hydrogen bonding. The total concentration of $A^{\star-}$ (Equation 2.8) is typically expressed as a function of the concentration of its different forms to account for the many hydrogen-bonded species that can simultaneously exist in solution. Equation 2.9 can then be obtained by assuming that the electrochemical reaction is reversible, applying the Nernst equation to obtain Equation 2.8 and substituting for the total concentration of $A^{\star-}$ and $[A] = [A^{\star-}]_{\text{total}}$ when $E_{\text{obs}}^{(A/A^{\star-})} = E_{1/2}^{(A/A^{\star-})}$. Equation 2.9 is also only valid when the concentration of D is much greater than that of A so that the concentration of the former at the electrode surface can be taken to be equal to its bulk concentration. Subsequently, the value of n can be determined via a non-linear regression analysis of the experimental values of $E_{1/2}^{(A/A^{\star-})}$ at different concentrations of D.

$$[A^{\cdot-}]_{\text{total}} = [A^{\cdot-}] \times \left(1 + \beta_1^{(A^{\cdot-})}[D] + \beta_2^{(A^{\cdot-})}[D]^2 + \cdots + \beta_n^{(A^{\cdot-})}[D]^n \right) \quad (\text{Eqn 2.7})$$

$$E_{\text{obs}}^{(A/A^{\cdot-})} = E_{1/2}^{\circ(A/A^{\cdot-})} + \frac{RT}{F} \ln \left(\frac{[A]}{[A^{\cdot-}]} \right) \quad (\text{Eqn 2.8})$$

$$E_{1/2}^{(A/A^{\cdot-})} = E_{1/2}^{\circ(A/A^{\cdot-})} + \frac{RT}{F} \ln \left(1 + \beta_1^{(A^{\cdot-})}[D] + \cdots + \beta_n^{(A^{\cdot-})}[D]^n \right) \quad (\text{Eqn 2.9})$$

The association constant, $K_i^{(A^{2-})}$, global association constant, $\beta_i^{(A^{2-})}$, and value of m for the second electron-transfer process can be obtained in a similar manner. The important reactions and equations are shown below.

$$[A^{2-}]_{\text{total}} = [A^{2-}] \times \left(1 + \beta_1^{(A^{2-})}[D] + \beta_2^{(A^{2-})}[D]^2 + \cdots + \beta_m^{(A^{2-})}[D]^m \right) \quad (\text{Eqn 2.10})$$

$$E_{1/2}^{(A^{\cdot-}/A^{2-})} = E_{1/2}^{\circ(A^{\cdot-}/A^{2-})} + \frac{RT}{F} \ln \left(\frac{1 + \beta_1^{(A^{2-})}[D] + \cdots + \beta_m^{(A^{2-})}[D]^m}{1 + \beta_1^{(A^{\cdot-})}[D] + \cdots + \beta_n^{(A^{\cdot-})}[D]^n} \right) \quad (\text{Eqn 2.11})$$

The biggest advantage of this model is that it allows for the evaluation of the association constants for each step as well as the global constants and number of molecules of D interacting with $A^{\cdot-}$ and A^{2-} across a wide concentration range.

The last model, that is, the one for equilibria in two successive global stages, is a combination of the previous two models and so it will not be discussed in depth. This model essentially breaks up a single global step into two consecutive steps, and is particularly applicable to molecules that offer more than one site for hydrogen bonding. The treatment of its results is similar to those described above.

It should be noted that even though the preceding equations were derived from the reduction processes in Scheme 2.1, the same treatment and analysis could also be performed for the oxidation processes of Scheme 2.2.

The disadvantage of using these working models for hydrogen bonding analysis is the presence of many unknown interactions such as those between the electroactive species with the solvent molecules, and also ion-pairing with the supporting electrolyte. An accurate evaluation can only be possible if there is knowledge of all the conceivable interactions, which may not always be available. It is also common that the hydrogen bonding interactions between the neutral species as well as those with trace water are ignored. Knowledge of the trace moisture content is important for compounds that undergo strong hydrogen bonding interactions with water and also because it is often much higher than the concentration of the electroactive substrates, yet it is not regularly measured or reported. Moreover, the effects of iR-drop and slow k_{et} will undermine the accuracy of using absolute potentials.

Electroactive Hydrogen Donors and Hydrogen Acceptors

Besides the quinones and phenylenediamines, there are other compounds such as flavins,^[35] arylimides,^[36] tetrazines^[37] and nitrobenzenes^[36a, 38] that have been studied and used in hydrogen bonding analysis. These hydrogen acceptors are particularly useful because their reduced forms are capable of two- or three-point interactions. The flavins and arylimides can also function as hydrogen donors through their N–H group. Rotello et al. synthesized a mellitic triimide that is capable of undergoing three consecutive electron-transfer reactions,^[39] which is especially useful since more than one type of ΔE (e.g. $\Delta E_{12} = |E_1 - E_2|$, $\Delta E_{13} = |E_1 - E_3|$ and $\Delta E_{23} = |E_2 - E_3|$) can be measured, potentially providing a more accurate assessment of the relative strength of the hydrogen donors. The *para* isomer of the nitrobenzenes is preferred over its *ortho* and *meta* isomers because of the chemical reversibility of the electron-transfer processes. Nitrobenzenes are however weaker hydrogen acceptors than quinones because of the greater spread of the negative charge in the respective reduced states (six atoms in the former as compared to two atoms in the latter). Alternatively, an electroactive group such as the phenylenediamines,^[40] cobaltocenium^[41] or ferrocene^[30b, 35e, 42], or a molecule like tetrathiofulvalene^[43] that is incapable of hydrogen bonding, can be incorporated into an

electroinactive compound to modulate the strength of its hydrogen bond via an inductive or mesomeric effect.

2.4 Summary

A number of methods for hydrogen bonding analysis have been summarized in this chapter, to which the electrochemical approach is especially useful because it is able to provide information about the nature and constituents of the hydrogen-bonded complexes, thermodynamic constants towards their formation, binding abilities of the hydrogen donors and hydrogen acceptors as well as the strength of their interactions. However, it is only applicable if the compounds (either the hydrogen donor or hydrogen acceptor) are capable of undergoing electron-transfer reactions and so there is a limit to its use. Furthermore, accurate evaluation is only possible if there is knowledge of all potential interactions, such as those with trace water and the solvent molecules as well as ion pairing with the supporting electrolyte, which may not be available. There is also some degree of inaccuracy in the measurements depending on the methodology (e.g. shifts in absolute potentials or differences in potentials ΔE) and model used (e.g. model of a single global equilibrium or that involving equilibria of n and m successive stages) and assumptions taken (e.g. neutral species does not participate in hydrogen bonding). Lastly, as will be addressed in the next chapter, there is the interference from other hydrogen donors and hydrogen acceptors, of which water, either from the atmosphere or present in trace amounts in solution, is the primary concern. Non-electrochemical techniques like NMR and IR spectroscopy and computational chemistry may be employed in cases where the hydrogen donors and hydrogen acceptors of interests are electroinactive. It is anticipated that this study will shed light on the hydrogen bonding ability of quinones, phenols and phenylenediamines and the effects of the interactions on their electrochemical behaviors in non-aqueous solutions, from which a method of measuring the hydrogen bonding abilities of hydrogen donors and hydrogen acceptors based on the voltammetric behaviors of the quinones and phenylenediamines might be developed.

References

- [1] (a) E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci, D. J. Nesbitt, *Pure Appl. Chem.* **2011**, *83*, 1637-1641; (b) E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci, D. J. Nesbitt, *Pure Appl. Chem.* **2011**, *83*, 1619-1636.
- [2] (a) W. D. Kumler, *J. Am. Chem. Soc.* **1935**, *57*, 600-605; (b) P. A. Kollman, L. C. Allen, *Chem. Rev.* **1972**, *72*, 283-303; (c) P. D. Aldrich, A. C. Legon, W. H. Flygare, *J. Chem. Phys.* **1981**, *75*, 2126-2134; (d) A. C. Legon, P. D. Soper, W. H. Flygare, *J. Chem. Phys.* **1981**, *74*, 4944-4950; (e) W. G. Read, E. J. Campbell, G. Henderson, W. H. Flygare, *J. Am. Chem. Soc.* **1981**, *103*, 7670-7672; (f) G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond*, Oxford University Press, Oxford, **1999**; (g) J. S. Loveday, R. J. Nelmes, S. Klotz, J. M. Besson, G. Hamel, *Phys. Rev. Lett.* **2000**, *85*, 1024-1027; (h) M. Goswami, P. K. Mandal, D. J. Ramdass, E. Arunan, *Chem. Phys. Lett.* **2004**, *393*, 22-27.
- [3] R. H. Crabtree, P. E. M. Siegbahn, O. Eisenstein, A. L. Rheingold, T. F. Koetzle, *Acc. Chem. Res.* **1996**, *29*, 348-354.
- [4] (a) S. J. Grabowski, W. A. Sokalski, J. Leszczynski, *Chem. Phys. Lett.* **2006**, *432*, 33-39; (b) B. Raghavendra, E. Arunan, *Chem. Phys. Lett.* **2008**, *467*, 37-40.
- [5] (a) O. R. Wulf, U. Liddel, S. B. Hendricks, *J. Am. Chem. Soc.* **1936**, *58*, 2287-2293; (b) E. Arunan, T. Emilsson, H. S. Gutowsky, G. T. Fraser, G. de Oliveira, C. E. Dykstra, *J. Chem. Phys.* **2002**, *117*, 9766-9776.
- [6] (a) G. R. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441-449; (b) I. Alkorta, J. Elguero, *Arkivoc* **2003**, 31-36; (c) J. M. Merritt, S. Rudić, R. E. Miller, *J. Chem. Phys.* **2006**, *124*, 084301.

- [7] (a) F. A. Baiocchi, T. A. Dixon, C. H. Joyner, W. Klemperer, *J. Chem. Phys.* **1981**, *75*, 2041-2046; (b) S. A. C. McDowell, *J. Chem. Phys.* **2003**, *118*, 4066-4072; (c) S.-Y. Yen, C.-H. Mou, W.-P. Hu, *Chem. Phys. Lett.* **2004**, *383*, 606-611; (d) V. Aquilanti, E. Cornicchi, M. M. Teixidor, N. Saendig, F. Pirani, D. Cappelletti, *Angew. Chem. Int. Ed.* **2005**, *44*, 2356-2360; (e) J. Cukras, J. Sadlej, *Chem. Phys. Lett.* **2008**, *459*, 44-48.
- [8] (a) G. Gilli, P. Gilli, *J. Mol. Struc.* **2000**, *552*, 1-15; (b) E. S. Kryachko, A. Karpfen, F. Remacle, *J. Phys. Chem. A* **2005**, *109*, 7309-7318; (c) P. Gilli, L. Pretto, V. Bertolasi, G. Gilli, *Acc. Chem. Res.* **2009**, *42*, 33-44.
- [9] M. Goswami, E. Arunan, *Phys. Chem. Chem. Phys.* **2009**, *11*, 8974-8983.
- [10] R. A. Klein, *Chem. Phys. Lett.* **2006**, *429*, 633-637.
- [11] Y. Hui, E. L. K. Chng, C. Y. L. Chng, H. L. Poh, R. D. Webster, *J. Am. Chem. Soc.* **2009**, *131*, 1523-1534.
- [12] (a) J. R. Jezorek, H. B. Mark Jr, *J. Phys. Chem.* **1970**, *74*, 1627-1633; (b) T. Tokuhiro, L. Menafrá, H. H. Szmant, *J. Chem. Phys.* **1974**, *61*, 2275-2282; (c) T. M. Krygowski, W. R. Fawcett, *J. Am. Chem. Soc.* **1975**, *97*, 2143-2148; (d) V. Gutmann, *Electrochim. Acta* **1976**, *21*, 661-670; (e) C. Reichardt, VCH Publishers, New York, **1988**, p. 105; (f) N. Gupta, H. Linschitz, *J. Am. Chem. Soc.* **1997**, *119*, 6384-6391; (g) J. Catalán, *J. Phys. Chem. B* **2009**, *113*, 5951-5960; (h) Y. Hui, E. L. K. Chng, L. P.-L. Chua, W. Z. Liu, R. D. Webster, *Anal. Chem.* **2010**, *82*, 1928-1934; (i) Y. Hui, R. D. Webster, *Anal. Chem.* **2011**, *83*, 976-981.
- [13] (a) L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, United States, Ithaca, **1960**; (b) G. C. Pimentel, A. L. McClellan, *The Hydrogen Bond*, W. H. Freeman, San Francisco, **1960**; (c) W. C. Hamilton, J. A. Ibers, *Hydrogen Bonding in Solids: Methods of Molecular Structure Determination*, W. A. Benjamin, **1968**; (d) A. D. Buckingham, P. W. Fowler, *Can. J. Chem.* **1985**, *63*, 2018-2025.

- [14] (a) S. Scheiner, Eds., *Molecular Interactions: From van der Waals to Strongly Bound Complexes*, Wiley, **1997**; (b) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, **1997**; (c) G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond: In Structural Chemistry and Biology*, Oxford University Press, Oxford, **2001**; (d) R. A. Klein, *J. Am. Chem. Soc.* **2002**, *124*, 13931-13937; (e) B. Lakshmi, A. G. Samuelson, K. V. Jovan Jose, S. R. Gadre, E. Arunan, *New J. Chem.* **2005**, *29*, 371-377; (f) R. A. Klein, *Chem. Phys. Lett.* **2006**, *425*, 128-133; (g) B. Raghavendra, P. K. Mandal, E. Arunan, *Phys. Chem. Chem. Phys.* **2006**, *8*, 5276-5286.
- [15] (a) J. Emsley, *Chem. Soc. Rev.* **1980**, *9*, 91-124; (b) G. A. Jeffrey, W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer Verlag, Berlin, **1991**.
- [16] T. Steiner, G. R. Desiraju, *Chem. Commun.* **1998**, 891-892.
- [17] (a) G. E. Hilbert, O. R. Wulf, S. B. Hendricks, U. Liddel, *J. Am. Chem. Soc.* **1936**, *58*, 548-555; (b) R. M. Badger, S. H. Bauer, *J. Chem. Phys.* **1937**, *5*, 605-608; (c) R. M. Badger, S. H. Bauer, *J. Chem. Phys.* **1937**, *5*, 839-851; (d) L. P. Kuhn, *J. Am. Chem. Soc.* **1952**, *74*, 2492-2499; (e) L. P. Kuhn, *J. Am. Chem. Soc.* **1954**, *76*, 4323-4326; (f) L. P. Kuhn, *J. Am. Chem. Soc.* **1958**, *80*, 5950-5954; (g) A. V. Iogansen, *Spectrochim. Acta Mol. Biomol. Spectrosc.* **1999**, *55*, 1585-1612; (h) D. L. Howard, P. Jørgensen, H. G. Kjaergaard, *J. Am. Chem. Soc.* **2005**, *127*, 17096-17103; (i) D. L. Howard, H. G. Kjaergaard, *J. Phys. Chem. A* **2006**, *110*, 9597-9601.
- [18] (a) A. J. Dingley, S. Grzesiek, *J. Am. Chem. Soc.* **1998**, *120*, 8293-8297; (b) M. Pecul, J. Leszczynski, J. Sadlej, *J. Chem. Phys.* **2000**, *112*, 7930-7938.
- [19] A. S. N. Murthy, C. N. R. Rao, *Appl. Spectrosc. Rev.* **1968**, *2*, 69-191.
- [20] E. Arunan, S. Dev, P. K. Mandal, *Appl. Spectrosc. Rev.* **2004**, *39*, 131-181.
- [21] Z. Xue, M. A. Suhm, *J. Chem. Phys.* **2009**, *131*, 054301.

- [22] (a) P. Hobza, V. Špirko, Z. Havlas, K. Buchhold, B. Reimann, H.-D. Barth, B. Brutschy, *Chem. Phys. Lett.* **1999**, *299*, 180-186; (b) P. Hobza, Z. Havlas, *Chem. Rev.* **2000**, *100*, 4253-4264; (c) B. J. van der Veken, W. A. Herrebout, R. Szostak, D. N. Shchepkin, Z. Havlas, P. Hobza, *J. Am. Chem. Soc.* **2001**, *123*, 12290-12293; (d) S. Scheiner, T. Kar, *J. Phys. Chem. A* **2002**, *106*, 1784-1789; (e) I. V. Alabugin, M. Manoharan, S. Peabody, F. Weinhold, *J. Am. Chem. Soc.* **2003**, *125*, 5973-5987; (f) S. K. Sikka, *High Press. Res.* **2007**, *27*, 313-319.
- [23] (a) J. Joseph, E. D. Jemmis, *J. Am. Chem. Soc.* **2007**, *129*, 4620-4632; (b) A. Karpfen, E. S. Kryachko, *J. Phys. Chem. A* **2007**, *111*, 8177-8187.
- [24] (a) G. Fitzgerald, J. Andzelm, *J. Phys. Chem.* **1991**, *95*, 10531-10534; (b) Z. Latajka, Y. Bouteiller, *J. Phys. Chem.* **1994**, *101*, 9793-9799; (c) S. Tsuzuki, H. P. Lüthi, *J. Phys. Chem.* **2001**, *114*, 3949-3957; (d) E. M. Cabaleiro-Lago, J. R. Otero, *J. Phys. Chem.* **2002**, *117*, 1621-1632; (e) Y. Zhao, O. Tishchenko, D. G. Truhlar, *J. Phys. Chem. B* **2005**, *109*, 19046-19051; (f) Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157-167; (g) S. J. Arey, P. C. Aeberhard, I.-C. Lin, U. Rothlisberger, *J. Phys. Chem. B* **2009**, *113*, 4726-4732; (h) L. Rao, H. Ke, G. Fu, X. Xu, Y. Yan, *J. Chem. Theory Comput.* **2009**, *5*, 86-96; (i) J. K. Labanowski, J. W. Andzelm, *Density Functional Methods in Chemistry*, Springer, **2012**.
- [25] (a) S. Kristyán, P. Pulay, *Chem. Phys. Lett.* **1994**, *229*, 175-180; (b) J. Antony, S. Grimme, *Phys. Chem. Chem. Phys.* **2006**, *8*, 5287-5293; (c) P. Jurečka, J. Černý, P. Hobza, D. R. Salahub, *J. Comput. Chem.* **2007**, *28*, 555-569.
- [26] (a) H. Umeyama, K. Morokuma, *J. Am. Chem. Soc.* **1977**, *99*, 1316-1332; (b) J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211-7218; (c) A. E. Reed, F. Weinhold, L. A. Curtiss, D. J. Pochatko, *J. Chem. Phys.* **1986**, *84*, 5687-5705; (d) E. D. Glendening, A. Streitwieser, *J. Chem. Phys.* **1994**, *100*, 2900-2909; (e) B. Jeziorski, R. Moszynski, K. Szalewicz, *Chem. Rev.* **1994**, *94*, 1887-1930; (f) R. Moszynski, P. E. S. Wormer, B. Jeziorski, A. van der Avoird, *J. Chem. Phys.* **1995**, *103*, 8058-8074; (g) K. Kitaura, K.

- Morokua, *Int. J. Quantum Chem.* **2004**, *10*, 325-340; (h) M. Deshmukh, S. R. Gadre, *J. Phys. Chem. A* **2009**, *113*, 7927-7932; (i) K. Wendler, J. Thar, S. Zahn, B. Kirchner, *J. Phys. Chem. A* **2010**, *114*, 9529-9536.
- [27] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 552-566.
- [28] (a) K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251-8260; (b) J. E. Del Bene, S. A. Perera, R. J. Bartlett, M. Yanez, O. Mó, J. Elguero, I. Alkorta, *J. Phys. Chem. A* **2003**, *107*, 3222-3227; (c) J. E. Del Bene, S. A. Perera, R. J. Bartlett, M. Yanez, O. Mó, J. Elguero, I. Alkorta, *J. Phys. Chem. A* **2003**, *107*, 3121-3125; (d) J. E. Del Bene, S. A. Perera, R. J. Bartlett, M. Yanez, O. Mó, J. Elguero, I. Alkorta, *J. Phys. Chem. A* **2003**, *107*, 3126-3131.
- [29] (a) R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press, **1994**; (b) U. Koch, P. L. A. Popelier, *J. Phys. Chem.* **1995**, *99*, 9747-9754; (c) P. Coppens, *X-Ray Charge Densities and Chemical Bonding*, International Union of Crystallography, **1997**; (d) J. J. Novoa, F. Mota, *Chem. Phys. Lett.* **2000**, *318*, 345-354; (e) P. Kollandaivel, V. Nirmala, *J. Mol. Struct.* **2004**, *694*, 33-38; (f) P. Munshi, T. N. Guru Row, *J. Phys. Chem. A* **2005**, *109*, 659-672; (g) L. J. Farrugia, C. Evans, M. Tegel, *J. Phys. Chem. A* **2006**, *110*, 7952-7961; (h) A. Martín Pendás, E. Francisco, M. A. Blanco, C. Gatti, *Chem. Eur. J.* **2007**, *13*, 9362-9371; (i) R. F. W. Bader, *J. Phys. Chem. A* **2009**, *113*, 10391-10396; (j) E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen, W. Yang, *J. Am. Chem. Soc.* **2010**, *132*, 6498-6506.
- [30] (a) J. Garza, R. Vargas, M. Gómez, I. González, F. J. González, *J. Phys. Chem. A* **2003**, *107*, 11161-11168; (b) M. Salas, B. Gordillo, F. J. González, *J. Electroanal. Chem.* **2004**, *574*, 33-39; (c) L. Zhang, H. Zhou, X. Li, Y. Lin, P. Yu, L. Su, L. Mao, *Electrochem. Commun.* **2009**, *11*, 808-811.

- [31] (a) N. Gupta, H. Linschitz, *J. Am. Chem. Soc.* **1997**, *119*, 6384-6391; (b) Y. S. Tan, S. Chen, W. M. Hong, J. M. Kan, E. S. H. Kwek, S. Y. Lim, Z. H. Lim, M. E. Tessensohn, Y. Zhang, R. D. Webster, *Phys. Chem. Chem. Phys.* **2011**, *13*, 12745-12754.
- [32] (a) H.-S. Kim, T. D. Chung, H. Kim, *J. Electroanal. Chem.* **2001**, *498*, 209-215; (b) J. Kim, T. D. Chung, H. Kim, *J. Electroanal. Chem.* **2001**, *499*, 78-84; (c) S. K. Gupta, *Analyst* **1984**, *109*, 793-794.
- [33] (a) L. Xiong, A. M. Fletcher, S. G. Davies, S. E. Norman, C. Hardacre, R. G. Compton, *Analyst* **2012**, *137*, 4951-4957; (b) L. Xiong, A. M. Fletcher, S. Ernst, S. G. Davies, R. G. Compton, *Analyst* **2012**, *137*, 2567-2573; (c) M. Zhang, L. Xiong, R. G. Compton, *Anal. Methods* **2013**, *5*, 3473-3481.
- [34] M. Gómez, F. J. González, I. González, *Electroanalysis* **2003**, *15*, 635-645.
- [35] (a) A. Niemcz, J. Imbriglio, V. M. Rotello, *J. Am. Chem. Soc.* **1997**, *119*, 887-892; (b) A. K. Boal, V. M. Rotello, *J. Am. Chem. Soc.* **1999**, *121*, 4914-4915; (c) T. Kajiki, H. Moriya, K. Hoshino, T. Kuroi, S.-I. Kondo, T. Nabeshima, Y. Yano, *J. Org. Chem.* **1999**, *64*, 9679-9689; (d) C. Bourgel, A. S. F. Boyd, G. Cooke, H. A. de Cremiers, F. M. A. Duclairoir, V. M. Rotello, *Chem. Commun.* **2001**, 1954-1955; (e) G. Cooke, H. A. de Cremiers, F. M. A. Duclairoir, J. Leonardi, G. Rosair, V. M. Rotello, *Tetrahedron* **2003**, *59*, 3341-3347; (f) G. Cooke, F. M. A. Duclairoir, P. John, N. Polwart, V. M. Rotello, *Chem. Commun.* **2003**, 2468-2469; (g) Y.-M. Legrand, M. Gray, G. Cooke, V. M. Rotello, *J. Am. Chem. Soc.* **2003**, *125*, 15789-15795; (h) G. Cooke, J. Garety, S. Mabruk, V. Rotello, G. Surpateanu, P. Woisel, *Chem. Commun.* **2004**, 2722-2723; (i) M. Gray, A. J. Goodman, J. B. Carroll, K. Bardson, M. Markey, G. Cooke, V. M. Rotello, *Org. Lett.* **2004**, *6*, 385-388; (j) A. S. F. Boyd, J. B. Carroll, G. Cooke, J. F. Garety, B. J. Jordan, S. Mabruk, G. Rosair, V. M. Rotello, *Chem. Commun.* **2005**, 2468-2470; (k) J. B. Carroll, G. Cooke, J. F. Garety, B. J. Jordan, S. Mabruk, V. M. Rotello, *Chem. Commun.* **2005**, 3838-3840; (l) G. Cooke, J. F. Garety, B. Jordan, N. Kryvokhyzha, A. Parkin, G. Rabani, V. M. Rotello, *Org. Lett.* **2006**, *8*, 2297-2300.

- [36] (a) Y. Ge, R. R. Lilienthal, D. K. Smith, *J. Am. Chem. Soc.* **1996**, *118*, 3976-3977; (b) R. Deans, A. Niemz, E. C. Breinlinger, V. M. Rotello, *J. Am. Chem. Soc.* **1997**, *119*, 10863-10864; (c) M. Gray, A. O. Cuello, G. Cooke, V. M. Rotello, *J. Am. Chem. Soc.* **2003**, *125*, 7882-7888.
- [37] B. J. Jordan, M. A. Pollier, L. A. Miller, C. Tiernan, G. Clavier, P. Audebert, V. M. Rotello, *Org. Lett.* **2007**, *9*, 2835-2838.
- [38] (a) M. F. Nielsen, V. D. Parker, *Acta Chem. Scand.* **1988**, *42B*, 93-100; (b) J. Bu, N. D. Lilienthal, J. E. Woods, C. E. Nohrden, K. T. Hoang, D. Truong, D. K. Smith, *J. Am. Chem. Soc.* **2005**, *127*, 6423-6429; (c) C. Chan-Leonor, S. L. Martin, D. K. Smith, *J. Org. Chem.* **2005**, *70*, 10817-10822.
- [39] J. B. Carroll, M. Gray, K. A. McMenimen, D. G. Hamilton, V. M. Rotello, *Org. Lett.* **2003**, *5*, 3177-3180.
- [40] (a) D. K. Smith, J. E. Woods, *ECS Trans.* **2006**, *3*, 31-43; (b) J. E. Woods, Y. Ge, D. K. Smith, *J. Am. Chem. Soc.* **2008**, *130*, 10070-10071.
- [41] (a) P. D. Beer, A. D. Keefe, *J. Organomet. Chem.* **1989**, *375*, C40-C42; (b) P. D. Beer, D. Heseck, J. Hodacova, S. E. Stokes, *J. Chem. Soc. Chem. Commun.* **1992**, 270-272; (c) P. D. Beer, C. Hazlewood, D. Heseck, J. Hodacova, S. E. Stokes, *J. Chem. Soc. Dalton Trans.* **1993**, 1327-1332; (d) P. D. Beer, M. G. B. Drew, A. R. Graydon, D. K. Smith, S. E. Stokes, *J. Chem. Soc. Dalton Trans.* **1995**, 403-408.
- [42] (a) C. Valério, J.-L. Fillaut, J. Ruiz, J. Guittard, J.-C. Blais, D. Astruc, *J. Am. Chem. Soc.* **1997**, *119*, 2588-2589; (b) M.-C. Daniel, J. Ruiz, S. Nlate, J.-C. Blais, D. Astruc, *J. Am. Chem. Soc.* **2003**, *125*, 2617-2628; (c) D. Astruc, M.-C. Daniel, J. Ruiz, *Chem. Commun.* **2004**, 2637-2649; (d) F. Otón, A. Tárraga, A. Espinosa, M. D. Velasco, P. Molina, *J. Org. Chem.* **2006**, *71*, 4590-4598.

- [43] (a) L. M. Goldenberg, O. Neilands, *J. Electroanal. Chem.* **1999**, *463*, 212-217; (b) M. B. Nielsen, C. Lomholt, J. Becher, *Chem. Soc. Rev.* **2000**, *29*, 153-164; (c) A. S. F. Boyd, G. Cooke, F. M. A. Duclairoir, V. M. Rotello, *Tetrahedron Lett.* **2003**, *44*, 303-306.

Chapter 3

Measuring the Water Content of Non-Aqueous Solvents

3.1 *The Importance of Measuring Water Content*

3.2 *Types of Water*

3.3 *Significance of Aquametry*

3.3.1 Food and pharmaceutical industry

3.3.2 Petrochemical industry

3.3.3 Research industry

3.4 *Karl Fischer Titration*

3.4.1 The Karl Fischer reaction

3.4.2 Volumetric Karl Fischer titration

3.4.3 Coulometric Karl Fischer titration

3.4.4 Advantages and limitations of coulometric Karl Fischer titration

3.5 *Alternative Aquametric Methods*

3.5.1 Non-electrochemical methods

3.5.2 Electrochemical methods

3.6 *Summary*

References

This page has been intentionally left blank

3.1 The Importance of Measuring Water Content

It is critical in this study on hydrogen bonding and its effects on the electrochemistry of quinones, phenols and phenylenediamines in non-aqueous solvents that the trace moisture content of the working solutions (consisting of the analyte and supporting electrolyte in an organic solvent) are taken into account, minimized and maintained over the course of their experiments because of the possible interference that water might pose. Water is peculiar for it is able to take on the role of both hydrogen donor and hydrogen acceptor and is capable of forming up to a maximum of four direct hydrogen bonds. Its propensity for hydrogen bonding is enhanced in solvents of low polarity, such as acetonitrile (MeCN) and dichloromethane (DCM) that are commonly used in organic electrochemistry experiments, and the phenomenon of cooperativity allows the development of a strong hydrogen bond network.

The task of reducing the interference from water begins with removing its presence in solution and limiting absorption from the environment; the amount of trace water in solution is dependent on the type of solvent used. This is especially challenging in a tropical country like Singapore where the natural humidity can vary from >90% in the early morning to ~60% in the late afternoon, with a mean relative humidity of about 80%,^[1] and so carefully designed procedures (see Chapter 5 for experimental procedures) were put into practice. First and foremost, all glassware and chemicals were dried before use. The glassware were dried at 100 °C in a conventional oven for at least an hour before cooling to room temperature (25±2 °C) under an argon atmosphere. The supporting electrolyte was also dried but at 160 °C and under vacuum for at least 6 h before cooling to room temperature for subsequent use while the solvents were dried by storing over freshly activated molecular sieves (heated at 160 °C under a vacuum) in air-tight bottles for at least 24 h prior to use. When permitted, the working solutions and electrolyte solutions (consisting only of the supporting electrolyte in the solvent) were prepared by dissolving the analyte and dried supporting electrolyte in dried solvent before storage in air-tight bottles or vacuum syringes containing activated molecular sieves for a minimum period of 24 h before use.

It was preferred for all experiments to be carried out in a glove box to reduce the interference from the humidity, but practical limitations restricted this choice and so a number of experiments were performed in the fume cupboard. In such circumstances, care was taken to limit the concentration of water in the solution by the use of argon gas to provide an inert atmosphere in the electrochemical cell. The internal filling solution of the reference electrode was also replaced with dried reference solution at the start of each experiment to reduce the amount of water it contributed into the working solution, and the uptake of water over the duration of the experiments was monitored with a dummy setup. Karl Fischer titrations were also performed to which the measured water contents were reported along with their associated voltammetric results. As a prelude to the results of this thesis and much in the same way that potentials are reported relative to a reference electrode or standard compound like ferrocene, we recommend that the water content of non-aqueous working electrochemical solutions be measured and reported for all compounds that are capable of hydrogen bonding.

At present, the Karl Fischer titration is the preferred method for measuring water content and it is used in this study because of its high accuracy and wide working range; it is also easy to operate and does not require the use of calibration curves. However, the procedure is significantly disadvantaged by the requirement for large sample volumes in addition to its high cost, acute toxicity, and poor shelf life of the reagents and so other methods have been developed. The succeeding sections of this chapter will describe both the Karl Fischer titration and its alternatives in greater detail.

3.2 Types of Water

Water may exist in three different forms, e.g. free, trapped or bound, in a sample. Free water, as the name suggests, is that which is unrestricted or loosely adsorbed and thus is most easily extractable from the sample. Trapped water molecules, on the other hand, are those that are physically confined such as in solids and crystals and prevented from escaping. Bound water is similar to trapped water except that the molecules are either physically or chemically attached, and so are the hardest to remove. Both free and trapped water display physiochemical properties

that are identical to bulk water whereas bound water has a vastly different behavior. The extraction of trapped and bound water from solid samples can be improved by increasing the surface area of the samples.

3.3 Significance of Aquametry

The measurement of water content, also known as aquametry, is one of the most common tests performed today. It is an important analytical procedure for the food, petrochemical, pharmaceutical and chemical industries because water is ubiquitous and its amount affects the shelf life and productivity of the various products. Moisture content also serves as a quality control factor and has been directly linked to human health.

3.3.1 Food and pharmaceutical industry

The measurement of moisture content is critical in the food industry at almost every point of the assembly line because the concentration of water influences the growth, texture, taste and appearance of food. It also governs the performance of processing and handling procedures such as the speed of mixing and flow of materials, which are dependent on viscosity that is in turn regulated by the water content. Furthermore, the amount of water affects storage and shelf life, whereby it is typical of food products that contain higher amounts of moisture to have shorter shelf lives because of the activity of microorganisms. It is for this reason that the United States Food and Drug Administration requires all food products to be fitted with labels specifying the ingredients present in descending order of predominance by weight, of which water is not exempted unless it has been purposefully removed. Such regulation also safeguards consumers against the exploitation of the mass of water and provides them with knowledge to make informed choices.

The activity of water (a_w), which is the measure of the energy of free water in a specified system, is of greater importance for the pharmaceutical industry than water content because of its bearings on dissolution rates, compactness and hardness of solid prescription drugs. It is also a

prime indicator of the extent of microbial growth, microbial and chemical stability as well as component compatibility. Water activity is defined as the ratio of the vapor pressure of water in the substance (p) to the vapor pressure of pure water (p_o), or alternatively as the product of the activity coefficient (l_w) and mole fraction of water in the aqueous fraction (x_w) (Equation 3.1). The activity of water can be measured with a dew point or capacitance hygrometer but the process is affected by hysteresis and vapor and thermal equilibration. The measurements are also longer than the Karl Fischer titration, with each analysis taking up to 5 min.

$$a_w = \frac{p}{p_o} = l_w \cdot x_w \quad (\text{Eqn 3.1})$$

3.3.2 Petrochemical industry

The petrochemical industry is heavily dependent on aquametry because of the inverse relationship between fuel efficiency and the concentration of water. Fuels containing lower moisture content tend to ignite readily and burn efficiently and so are sought after. Aside from corroding metallic parts, the presence of water may restrict the working temperature range of the petroleum products as well as suppress their desired properties. For example, the formation of ice will interfere with anti-wear abilities and the presence of even minute amounts of water will render transformer oil some electrical conductivity. Sludge can also be formed when large amounts of water are present during the treatment of petroleum products and so would incur costs for repairs, replacements and disposal of waste.

3.3.3 Research industry

Aquametry is also important in research laboratories. Residual water can interfere with IR and NMR spectroscopic measurements by masking out important structural information while numerous organic, inorganic and organometallic reactions require the use of dry solvents and reagents for completion and prevention of unwanted side reactions. Liquid reagents are typically treated with drying agents such as sodium metal, calcium chloride, benzophenone and molecular

sieves while solid compounds are vacuum dried at elevated temperatures. The Karl Fischer titration is applied thereafter to ensure that the desired low moisture levels are obtained.

3.4 Karl Fischer Titration

The Karl Fischer titration is an analytical method for quantifying both free and bound water in solid, liquid and gaseous samples.^[2] It is usually the first option for aquametry because of its wide linear working range, that spans from the parts-per-million regime up to the milligram level, and linear response, which means that only a single-point calibration is needed and calibration plots are unnecessary.^[3] The measurements also provide absolute instead of relative results. This section will cover the chemistry, concepts, equipment, titration method, endpoint detection procedure, advantages and limitations of the Karl Fischer titration.

3.4.1 The Karl Fischer reaction

Reactions 3.1 to 3.3 represent the generally accepted version of the Karl Fischer reaction through which water is quantified via the amount of iodine that has reacted.^[2b, 4] The identity of the solvent is very important here because it greatly influences the stoichiometry between iodine and water in the reaction that serves as the basis of the measurement. Methanol is almost always used for it affords higher sensitivity, with one mole of water consuming one mole of iodine, whereas other solvents, such as chloroform or *N,N*-dimethylformamide, may either give unclear stoichiometry or expend less than one mole of iodine, which would complicate the measurement and make it less sensitive.^[2b, 5] It is also imperative to have sufficient methanol present to produce methyl sulfite ($\text{CH}_3\text{OSO}_2^-$) and the corresponding $\text{CH}_3\text{OSO}_2^-\text{RNH}^+$ species to prevent the unwanted Bunsen reaction (Reaction 3.4) from taking place. Sulfur dioxide must also be present in large excess, with water existing as the limiting reagent, to retain this chemistry.

RN is a base, which nowadays is usually imidazole, whose purpose is to act as a buffer and maintain the pH of the solution between 5 and 7.5 since the rate constant (k) of the Karl Fischer reaction is pH-dependent.^[6] Pyridine is no longer used because of its toxicity. The dependence of k on pH can be attributed to Reaction 3.1, where the formation of $\text{CH}_3\text{OSO}_2^-$ is facilitated by the deprotonation of methanol. The rate of the Karl Fischer reaction is reflected in the $\log k$ versus pH curve shown in Figure 3.1 where the rate of the reaction increases up to pH 5 and reaches a constant between pH 5 and 8 before increasing further at pH >8.

Figure 3.1. Dependence of $\log k$ of the Karl Fischer reaction on pH of the medium.

Despite having faster rates of reaction, it is not possible to perform the Karl Fischer titration at pH >8 because of the occurrence of unwanted side reactions between iodine and hydroxide or methoxide that would bring about sluggish endpoints and compromise the accuracy of the titration. The optimum rate of the Karl Fischer reaction occurs between pH 5 and 7.5 where the $\log k$ versus pH graph is constant because most of the sulfur dioxide has already been converted into $\text{CH}_3\text{OSO}_2^-$. Serendipitously, this is also the buffering region of imidazole. Within this pH window, it has been found that the kinetics of the Karl Fischer reaction are independent on the concentration and identity of the base and first-order with respect to iodine, sulfur dioxide and water.

3.4.2 Volumetric Karl Fischer titration

The choice of using the volumetric or coulometric method is dependent on several factors that include the expected moisture content of the sample that is to be analyzed.^[4, 5b, 7] The volumetric Karl Fischer titration is generally preferred for solid samples and also those suspected of containing large amounts of water ($\geq 0.05\%$ w/w or v/v) whereas the coulometric method is ideal for trace moisture content analysis (parts-per-million level).

Volumetric titration can be readily performed with available glassware in the laboratory such as a burette, conical flask and stirrer bar that should preferably be dried before use. The procedure begins with dissolving the sample in a solution of imidazole and sulfur dioxide in methanol before transferring into a conical flask. Thereafter, the titer containing iodine in methanol is slowly added until the first appearance of a persistent brown color due to excess iodine. The endpoint can then be detected visually or through photometry but that is only suitable for uncolored solutions. Otherwise, potentiometric,^[8] thermometric,^[9] spectrophotometric^[10] or flow injection analysis^[11] detection methods can be used.

The biggest disadvantage of the volumetric Karl Fischer method is the stability of the titer; it has to be freshly prepared on the day of the analysis. The precision and accuracy of the volumetric titration is also affected by atmospheric moisture. Hence, steps should be taken to minimize the uptake of moisture by drying all glassware before use and limiting the exposure times of all samples and solutions. It is also best to carry out a blank analysis after each titration to determine the amount of titer that has reacted with water that is not contributed by the sample. Finally, effort should be put into expediting the measurements.

3.4.3 Coulometric Karl Fischer titration

The coulometric Karl Fischer titration is the interest of our study because of its extensive use and capacity for measuring trace amounts of water. It is based on coulometry, which is the measure of the amount of matter transformed by production or consumption of charge. In this method, the iodine that is carefully generated through the electrochemical oxidation of iodide

(Reaction 3.5) reacts with water from the sample. The amount of charge that is required to produce all the iodine to reach the endpoint is then determined and used to calculate the amount of water via Faraday's law of electrolysis (Equation 3.2), where m is the mass of iodine produced (g); M the molar mass (g mol^{-1}); Q the total amount of charge (C); z the dimensionless number of electrons transferred per mole of iodine produced; and F is the Faraday Constant (96485 C mol^{-1}).

$$m = \frac{M \times Q}{z \times F} \quad (\text{Eqn 3.2})$$

The important assumptions taken are that iodine is produced only from the electrochemical oxidation of iodide, with the measured charge solely related to this electrochemical reaction, and that iodine does not participate in any side reactions. It can then be determined that 1.32 mg or 5.18 μmol of iodine is formed for every coulomb of charge passed and consequently 93.4 μg of water is present; alternatively, every 10.72 mC of charge passed correlates with the presence of 1 μg of water in the sample. Consequently, it is the easily measurable parameters of current and time of the coulometric Karl Fischer titration that enables it to measure trace water content with high precision and accuracy in the absence of calibration plots.

A setup of the Karl Fischer coulometer is shown in Figure 3.2. The titration cell consists of an anodic compartment housing the anolyte solution that is kept separated from the catholyte solution by a diaphragm. The anolyte solution, or working medium of the Karl Fischer reaction, is made up of potassium iodide, sulfur dioxide and imidazole with methanol as the solvent. The primary purpose of the anolyte solution is to supply iodide for the production of iodine by the generator electrode. The magnetic stirrer ensures homogeneity inside the anodic compartment by transferring the iodine produced at the generator electrode to the bulk solution for reaction with water from the sample and also to the measuring electrode for endpoint detection. Because of the hygroscopic nature of the anolyte solution, a tube containing desiccant material such as molecular sieves is also present to reduce the amount of moisture that enters the titration cell. Samples are

introduced into the titration cell via the Teflon™-silicon septum of the injection port to minimize the interference from atmospheric humidity.

Figure 3.2. Setup of a Karl Fischer coulometer.

The generator electrodes consist of two platinum mesh electrodes that are kept apart by the diaphragm. A constant current is supplied by a galvanostat to simultaneously oxidize iodide to iodine at the anode (Reaction 3.5) and reduce the ammonium salt to an amine together with the evolution of hydrogen gas at the cathode (Reaction 3.6).^[7b] It is necessary to control the rate of production of iodine throughout the analysis to prevent any overproduction and, consequently, an over-estimation of the concentration of water.

The purpose of the diaphragm is to allow the electrochemically-generated iodine to participate in the Karl Fischer reaction instead of undergoing reduction at the cathode of the generator electrode.^[12] Generator electrodes with the diaphragm separating the anolyte and

catholyte solutions are preferred for measurements of samples with low conductivities and containing less than 0.005% of water.

However, this does not imply that a diaphragm is always needed. A diaphragmless generator electrode can also be used so long as the undesirable reduction reaction of iodine to iodide can be prevented. The most efficient way of achieving this is to decrease the surface area of the cathode and stream it with a constant flow of hydrogen gas bubbles. Large sample volumes are also used to reduce the total amount of iodine that has been reconverted into iodide. The advantages of using generator electrodes without a diaphragm are the absence of contamination and easier cleaning. In addition, the drift, that is the amount of water that enters the coulometer over a specific period of time, is lower. Having said that, nascent hydrogen is a good reducing agent and so generator electrodes without diaphragms cannot be used to analyze samples containing easily reducible functionalities such as nitro groups.

The measuring electrode acts to determine the endpoint of the Karl Fischer titration by using either the bivalentammetric or biamperometric methods to detect a slight excess of iodine. In the case of the bivalentammetric detection method, a constant polarization current is applied to the double platinum pins and the voltage required to maintain this current is monitored. A certain voltage is needed to keep this polarization current at its preset value when there is no free iodine around because of the reaction with water. But when some free iodine exists at the end of the titration, the phenomenon of ionic conduction occurs and it results in a significant drop in the measured voltage. This drop in measured potential is used to indicate the endpoint of the titration.

The biamperometric or “dead-stop” method is similar to the previous method except that a constant voltage is applied to the double platinum pins and the current flowing through them is examined.^[13] The endpoint is determined when the current increases because of ionic conduction.

The earlier mentioned phenomenon of ionic conduction occurs when free iodine, that is present after all the water has been consumed, undergoes reduction to iodide at the cathodic platinum pin of the measuring electrode. Subsequently, iodide, that is either from the bulk solution or produced from the earlier mentioned reduction of iodine, would undergo oxidation to

iodine at the anodic platinum pin, which in so doing decreases the applied voltage for the bivalentammetric method and increases the current in the biamperometric method to indicate the endpoint of the titration.

Both the bivalentammetric and biamperometric methods require a sufficient yet small amount of free iodine to determine the endpoint, which as a result will lead to an inherent overestimation of the actual moisture content of the sample. Nonetheless, they remain preferred over the visual and photometric detection methods of the volumetric Karl Fischer titration because the same amount is overestimated across all experiments and so reproducibility is not compromised. Therefore, it is important to ensure good mixing within the anolyte compartment of which the magnetic stirrer is present for that purpose.

3.4.4 Advantages and limitations of coulometric Karl Fischer titration

The coulometric Karl Fischer titration offers many advantages such as its high accuracy, sensitivity and reproducibility, wide working range and provision of absolute results without the need for calibration plots.^[14] It is capable of measuring the various forms of trapped water and is applicable to gaseous samples as well as viscous and volatile liquids. Solid samples can also be analyzed with the use of external extraction, dissolution procedures or drying in an oven. The coulometer is automated, easy to operate and relatively cheap to afford. The procedure is still safe although hydrogen gas is liberated because only trace quantities of water are analyzed and so only small amounts of the gas are produced; there is also a lack of ignition sources. The toxic chemicals are all tightly sealed in the titration cell. Lastly, the Karl Fischer titration can also be applied to indirectly quantify organic and inorganic compounds via their reactions that liberate or consume water.

In spite of its advantages, this coulometric Karl Fischer procedure has a number of limitations of which the main disadvantage is interference from atmospheric humidity. In high humidity environments, it is recommended that the Karl Fischer coulometer be operated in a controlled humidity chamber to limit the effects of fluctuating atmospheric humidity. Titration

cells should also preferably be made of glass. It is advisable to swirl the titration cell to remove any moisture that has collected on the walls of the cell and to ensure that the drift is low before each measurement.

The minimum amount of charge that can be accurately measured by the coulometer is another drawback because it imposes the requirement for a minimum amount of sample for accurate analysis. This means that larger volumes are needed for samples with lower expected moisture contents. It has been found that at least 10 g of sample is needed to accurately quantify 1 ppm (or 0.056 mM) of water, which is not economical because modern day Karl Fischer coulometers are only capable of analyzing about 100 mL of sample before the anolyte solution is exhausted or the drift is too high for accurate measurements. Therefore, a large amount of waste will be generated for only a small number of samples analyzed. Furthermore, the Karl Fischer reagents are expensive.

As mentioned previously, the stoichiometry between iodine and water in the Karl Fischer reaction is strongly dependent on the type of solvent employed. Methanol is used to avoid the Bunsen reaction (Reaction 3.4) and to provide the 1:1 iodine to water stoichiometry that affords the measurement its high sensitivity. However, this solvent also brings about the issue of insolubility for samples that are based on non-polar solvents. In such cases, it is common for additives (such as chloroform and octanol) to be added into the anolyte solution to improve sample solubility but their volumes are limited to a maximum of 30% of the total amount so as to retain the desired important stoichiometry between iodine and water. Additionally, a smaller volume of sample can be used but this, as mentioned earlier, may compromise the accuracy of the measurement.

Then there is the concern of interference from acids and bases and other side reactions that consume or produce iodine, or react with the Karl Fischer reagents to produce water. It is necessary to ensure that the Karl Fischer reaction takes place in a well-buffered solution to achieve an optimum rate of reaction and to avoid any inaccuracies in the measurements. This would also prevent an overestimation of the true moisture content by the action of acids through

protonation (Reaction 3.7) and esterification (Reaction 3.8) of methanol. Alternatively, other buffers such as sodium acetate or aliphatic amines can be used. It is also possible to neutralize the samples with imidazole for acidic samples and salicylic acid or benzoic acid for basic samples prior to the analysis.

Over-titrations and overestimation of the moisture content occur when iodine reacts with some other species besides water. This tends to take place in the presence of samples that contain reducing agents, ammonia, bicarbonates, iron(III) and copper(II) salts, and thiols^[15]. On the other hand, an under-titration ensues when iodine is produced by a chemical reaction aside from the electrochemical oxidation of iodide. The oxidation of iodide can occur in the presence of oxidants like elemental bromine and chlorine, nitrites, and quinones but their actions tend to be suppressed by the large excess of sulfur dioxide, which is itself a reducing agent. Only those compounds that are not reduced by sulfur dioxide, such as sodium dichromate, and are strong enough to oxidize iodide will lead to an underestimation of the moisture content.

There is also a possibility that the reaction between iodine and iodide to form the triiodide (I_3^-) (Reaction 3.9) may occur but it is often ignored at the operating pH because the rate of Reaction 3.3 is 10,000 times faster.^[16]

There are several compounds that are incompatible with the Karl Fischer reagents. For instance, ketones and aldehydes may react with methanol to give ketals (Reaction 3.10) and acetals (Reaction 3.11), respectively, with the liberation of water and so may require the titration to be conducted at lower temperatures.^[7a, 17] Alternatively, other alcohols such as isopropanol or *tert*-butyl alcohol,^[18] propylene glycol with pyridine,^[19] 2-chloroethanol or 3,3,3-trifluoroethanol,^[17] or a mixture of chloroform and propylene carbonate^[20] can be used. 2-Methoxyethanol (commercial name: Methyl Cellosolve[®]) is another solvent that is quite often

used in place of methanol because it retains the desired reaction stoichiometry between iodine and water.^[21]

Figure 3.3. Advantages and disadvantages of the coulometric Karl Fischer titration method.

Alternative aquametric methods are continuously developed to address the other disadvantages such as safety, toxicity, cost and shelf life of the Karl Fischer reagents. Among these, the shelf life of the anolyte solutions is a particular concern because their hygroscopic natures mean that water will inadvertently be drawn into the cell and so has to be removed from the anolyte solution before any analysis. Xylene-based reagent systems are currently the most stable titrants available. Finally, there are some areas such as the response time of the analysis, miniaturization of the instrument and ability to distinguish between the different forms of trapped water that can be investigated to improve the overall efficiency of the technique. The advantages and disadvantages of the coulometric Karl Fischer titration technique are summarized in Figure 3.3.

3.5 Alternative Aquametric Methods

Aside from the Karl Fischer titration, there are many other methods that have been developed to measure moisture content. These differ in their selectivity, sensitivity as well as working concentration range. The proposed methods may make use of the chemical reactivity, spectral, physical, radiochemical and electrochemical properties of specific molecules or be based on gravimetric and separation techniques.

3.5.1 Non-electrochemical methods

Thermogravimetric methods

The thermogravimetric procedure for quantifying moisture content looks at the changes in mass of the sample or that of a drying agent as thermal energy, either in the form of heat or electromagnetic radiation, is supplied. The mass of the sample or drying agent is continuously monitored over a time duration to which the measurement is deemed complete only when it remains constant for a specified period. The efficiency of this method is mainly dependent on the surface area of the sample as well as type of water present. In general, samples with large surface areas will provide for greater accuracy because of the better rate and extent of drying. Some common sources of heat are halogen heaters, vacuum ovens, microwave ovens and infrared lamps.

The disadvantages of the thermogravimetric method are its destructive nature, poor selectivity and restriction to solid samples,. Decomposition or volatilization can occur when high temperatures are used or when the drying is prolonged. The sources of thermal energy are also incapable of differentiating between water and other volatile species and so the difference in mass may not necessarily arise from the removal of water. However, this procedure is still used today because it offers multiple sample analysis with low cost and high precision. It is also able to analyze all the different types of water although it is unable to distinguish between them, and is applicable for samples containing medium to high amounts of water.

Distillation methods

In 1920, Ernest Dean and David Stark developed the Dean-Stark method of measuring moisture content through the use of the distillation setup shown in Figure 3.4.^[22] The sample is introduced into the reaction flask after which an organic solvent, that is insoluble with water, is added and the mixture is heated to reflux. The resulting vapor subsequently condenses into the Dean-Stark receiver, of which two immiscible liquids (water and the chosen organic solvent) are obtained.

Figure 3.4. Apparatus for the Dean-Stark distillation procedure.

The amount of water extracted from the sample can be directly read off the measuring scale of the receiver if water is the denser of the two liquids. Or through a subtraction method if the organic solvent were instead denser; the organic liquid can also be carefully drained out. It is recommended to perform several rounds of distillation to ensure that all the water from the sample has been completely removed.

There is presently no known interference to the Dean-Stark aquametric method and it can be used for solid and liquid samples that contain large amounts of water. The apparatus is also cheap to purchase if not readily available in the laboratory. Nevertheless, the analysis is not

economical and so is not often employed. Alternatively, centrifugation and extraction methods can also be used.

Physical Methods

Methods that are based on the physical properties of water or other compounds have also been developed which they may be based on changes in color, conductivity, density, dew point temperature and refractive index to measure water content. Color indication tubes or those containing molecular sieves with indicators as well as dew point meters and piezoelectric sensors are some examples of such physical devices. But they are not usually employed because of their limited applicability, numerous restrictions and sample-specific nature.

Spectral methods

The water content of organic solvents can also be quantified, directly and indirectly, through IR,^[23] near-infrared (NIR),^[24] UV-vis,^[25] and NMR^[26] spectroscopy. Direct analysis can be obtained with NIR spectroscopy, where a calibration plot is derived from the intensity of the O–H stretching overtone and if possible its combination bands, or NMR spectroscopy to which the calibration curve is constructed from the ratio of the integration of the singlet signal from water to that of a reference compound.

Indirect analysis, on the other hand, is achieved by building a calibration plot from the spectroscopic signal of a reference compound, usually a reactant or product of a chemical reaction that involves water. The intensity of the C–H stretching of acetylene that is produced from the reaction between calcium carbide and water (Reaction 3.12) has been applied to quantify water.^[23a] While UV-vis spectroscopy has exploited the absorbance of lead dioxide at 396-402 nm,^[25a, 27] tin tetrachloride at 300 nm^[25b] and antimony pentachloride at 350-420 nm^[25b] for the same purpose. *N*-Heteroaryl-1,8-naphthalimides^[28] and acridinyl-based^[29] fluorescent sensors have also been utilized.

^{19}F NMR spectroscopy has also been applied to which the signal of the bifluoride product, from the reaction between water and difluoro(aryl)- λ^3 -iodanes, is compared to that of the tetrafluoroborate reference standard.^[26c] This procedure does not require calibration and has enabled detection limits of 100 ng to be acquired. It can be used in alcohols and aprotic solvents but is not compatible with carbonyls and halogenated alkanes; it is also restricted by the basicity and nucleophilicity of the bifluoride species.

The difficulties with using spectral methods for the detection and quantification of water are interference from the solvent and residual moisture that may lead to larger than preferred background noise and less ideal detection limits. A background scan prior to sample analysis is therefore recommended. Nonetheless, spectral aquametric methods are still employed because of their high selectivity and ease of interchangeability.

Chemical methods

Aquametry can also be carried out through a chemical reaction between water and a chosen molecule that results in a measurable physical change of the system. These chemical methods are highly selective towards water and are especially useful for they allow the three forms of water to be analyzed. They are also applicable to volatile and viscous liquids as well as solids and gases. The Karl Fischer titration is one such example that depends on the reaction between iodine and water to bring about a change in color, applied current or potential to signal the end of the reaction.

Reaction 3.12, discovered by Friedrich Wöhler, is another example of an aquametric method that is based on a chemical reaction, but one that measures the amount of water indirectly through the amount of acetylene released.^[23a, 30] This chemical method is generally quicker and cheaper than the Karl Fischer titration and had been successfully linked to gas chromatography^[30] and IR spectroscopy^[23a] to improve the accuracy and detection limit. However, it is no longer used because of its applicability only to dry solvents, associated risks with handling acetylene and development of safer and more sensitive techniques.

Alternative chemical methods based on the reaction of water with acid anhydrides, acetyl chloride, antimony pentachloride,^[25b] difluoro(aryl)- λ^3 -iodanes,^[26c] lead tetraacetate,^[25a, 27] magnesium nitride, *tert*-butyl-*o*-vanadate and tin tetrachloride^[25b] have also been developed.

Radiochemical methods

Isotope exchange reactions, β - and γ -ray counting as well as neutron scattering have also been applied for moisture content analysis but are not popular in light of their associated risks and hazards.

3.5.2 Electrochemical methods

Electrochemical methods such as amperometry, conductivity, voltammetry as well as electrochemical impedance spectroscopy have been developed to measure moisture content.

Wang et al. utilized amperometry and the ability of tyrosinase to catalyze the hydroxylation of phenols to *o*-quinones to determine the moisture content of solvents such as MeCN, ethanol, isopropanol and *n*-butanol.^[31] A poly(ester-sulfonic acid) polymer containing the enzyme and the phenol was coated onto the electrode surface and immersed in those solvents, from which linear calibration plots of the cathodic current from the reduction of the quinone to the amount of water were built. Some advantages of this amperometric method are its speed, selectivity, reproducibility, detection limit of $\sim 0.05\%$ (v/v) and low applied potential ($\sim +0.25$ V vs. Ag/AgCl) that would prevent interference from other electroactive species. The accuracy and precision of the measurements may however be affected by the extent of surface coverage and condition of the electrode surface.

A chemoresistor using electrochemical impedance spectroscopy and two cross-linked networks of polyelectrolytes, poly(4-vinylpyridine) with 1,4-dibromobutane and poly(glycidyl methacrylate) with diethylenetriamine, was devised by Zanelli et al. to measure the moisture content of organic solvents.^[32] The conductivity of the interpenetrated polymer network was established to increase with greater amounts of water because of the increase in ionic mobility and dielectric constant.^[33] Interestingly, it was reported that the interference from electroactive

impurities is insignificant. Yet, the most important feature of this polyelectrolyte-based chemoresistor is its ability to cater for individual solvents by changing the ion density. The conductivity and hence sensitivity of the measurement can be improved at the expense of kinetic performance with a higher ion concentration. Detection limits as low as 10 ppm were obtained, but they share an inverse relationship to the dielectric constant of the solvent.^[33a]

Shim et al. designed a chronoamperometric water sensor with poly(1,5-diaminonaphthalene) nanofibers coated in the gap between two split gold electrodes and were able to quantify 0.05% to 20% of moisture in MeCN with a detection limit of 0.1 ppm and average shelf life of 40 days for the device.^[34] The moisture content is measured through a calibration plot of the anodic current of the reverse potential step (of the applied double-step chronoamperometric technique), which enables the earlier mentioned detection limit to be achieved because the current is monitored over a long period and so better signal-to-noise ratios are obtained. It is suspected that the mechanism of sensing water occurs via the increase in conductivity, and consequently the increase in current, as it accumulates in the polymer matrix. Unfortunately, the conductivity was also found to increase through the production of radical cations from nucleophilic reactions involving water. In addition, the sensor must be activated before use.

There is the dual-band gold electrode/polyallylammonium ferrocyanide film conductive device fabricated by Cammarata et al. to determine the trace water content of halogenated solvents like DCM, chloroform, 1,2-dichloroethane and 1,2-dichlorobenzene.^[35] The polymer film is conductive in these solvents only when trace amounts of water are present and so low detection limits of 0.0002% to 0.002% can be obtained. The advantages of this procedure are its simplicity and scalability. It also does not require the use of supporting electrolytes and can be miniaturized and adapted for flow processing.

The microgap impedance sensor prepared by Long et al. is particularly useful because detection limits as low as 68 μM in acetone, 75 μM in MeCN, 54 μM in chloroform and 30 μM in tetrahydrofuran have been reported.^[36] It consists of an indium tin oxide electrode coated with a film of poly(dimethyldiallylammonium chloride) polymer that contains ferricyanide and

ferrocyanide. Water is detected through changes in the ionic and electronic conduction, dielectric constant as well as swelling of the film. A satisfactory linear range and repeatability with response time of 100 s was obtained.

Ohira et al. constructed a flow-through capacitive sensor for water from a glass capillary by coating a thin film of Nafion on the inner bore.^[37] The researchers found that the presence of ~20% of phosphoric acid permitted a linear response in the low-concentration regime with a detection limit of 0.075%, of which no reagent was consumed in the process of the measurement. Ohira's capacitive sensor has a quicker response of 60 ms, but like Long's microgap impedance sensor, it is affected by the thickness and composition of the film. Also, it appears that the capacitive sensor is preferable but not restricted for use in aprotic solvents since protic solvents offer an interference of about 10% of the response with respect to water. The accuracy of the results are also comparable to those obtained from gas chromatography with thermal conductivity detection when the capacitive sensor was used with a prevaporizer-flow injection analysis system.

Finally, the research groups of Webster and Mao had independently developed a voltammetric method using quinones to measure the trace moisture content of aprotic organic solvents. Mao et al. utilized the shift in the potential of the $Q^{\cdot-}/Q^{2-}$ redox couple for the analyses and showed that their voltammetric procedure could be applied over a wide concentration range.^[38] They also found that the sensitivity of their measurements could be modified through the basicity and nucleophilicity of the quinones, where weakly basic and poorly nucleophilic quinones were beneficial for measuring high moisture content while strongly basic and highly nucleophilic quinones were more appropriate for analyzing trace moisture levels. Webster et al., on the other hand, employed ΔE that is, the difference in the reduction potentials of the two electron-transfer steps.^[39] Measurements using ΔE , as explained in Section 1.3, are more accurate and reproducible because the effects of the heterogeneous electron-transfer rates (assuming similar k_{et} values for both processes) and uncompensated solution resistance are cancelled. Hence, the magnitude of ΔE , which reflects the moisture content, is only dependent on the hydrogen bonding interaction between water and the quinone. Webster et al. carefully measured the trace

water content of the solvent (using Karl Fischer titrations) prior to experiments performed with the addition of water; thus the exact water content was known (whereas Mao et al. did not take into account the background water levels in their calibration measurements). The team also successfully established working curves for the following aprotic organic solvents: MeCN, butyronitrile, 1,2-dichloroethane, DCM, *N,N*-dimethylformamide and dimethyl sulfoxide, which enabled the water content of solvents used for electrochemistry to be estimated from one voltammetric scan in the presence of the natural quinone, vitamin K₁.

3.6 Summary

The measurement of the trace moisture content of the working solution in the electrochemical cell is critical for this study because of the potential interference that water might pose in the analysis of the effects of hydrogen bonding on the electrochemistry of quinones, phenols and phenylenediamines in non-aqueous solvents. This can be achieved with coulometric Karl Fischer titration because of its high accuracy, wide linear working range and provision of absolute results that are not based on calibration curves. However, in spite of its advantages, the Karl Fischer titration suffers from a number of shortcomings that are related to its cost, toxicity, short shelf life of the reagents and large sample volume requirements, so has led to the development of alternative aquametric procedures. Therefore, in addition to hydrogen bonding analysis, it is also the interest of this study to apply the electrochemistry of quinones and phenylenediamines, given their sensitivity towards hydrogen bonding, for the purpose of measuring the moisture content of non-aqueous solvents and detecting impurities in analytical grade solvents. Some applications of the electrochemical properties of the quinones and phenylenediamines are covered in the next chapter.

References

- [1] Y. Hui, R. D. Webster, *Anal. Chem.* **2011**, 83, 976-981.
- [2] (a) K. Fischer, *Angew. Chem.* **1935**, 48, 394-396; (b) D. M. Smith, W. M. D. Bryant, J. Mitchell Jr., *J. Am. Chem. Soc.* **1939**, 61, 2407-2412.

- [3] (a) J. Mitchell Jr., D. M. Smith, *Aquametry, Part III*, 2nd ed., John Wiley & Sons, New York, **1980**; (b) E. Scholz, *Karl Fischer Titration*, Springer-Verlag, Berlin, **1984**.
- [4] J. Mitchell Jr., *Anal. Chemistry* **1951**, *23*, 1069-1075.
- [5] (a) F. B. Sherman, *Talanta* **1967**, *27*, 1067-1072; (b) A. Cedergren, C. Orädd, *Fresen. J. Anal. Chem.* **1993**, *346*, 539-542; (c) K. Schmitt, H.-D. Isengard, *Fresen. J. Anal. Chem.* **1997**, *357*, 806-811.
- [6] (a) A. Cedergren, *Talanta* **1974**, *21*, 265-271; (b) J. C. Verhoef, W. P. Cofino, E. Barendrecht, *J. Electroanal. Chem.* **1978**, *93*, 75-80; (c) C. Orädd, A. Cedergren, *Anal. Chem.* **1994**, *66*, 2603-2607; (d) A. Cedergren, *Anal. Chem.* **1996**, *68*, 784-791; (e) A. Cedergren, *Anal. Chem.* **1996**, *68*, 3682-3687.
- [7] (a) S. K. MacLeod, *Anal. Chem.* **1991**, *63*, 557A-566A; (b) E. Scholz, *Fresen. J. Anal. Chem.* **1994**, *348*, 269-271; (c) B. King, *Metrologia* **1997**, *34*, 77-82; (d) S. A. Margolis, *Anal. Chem.* **1997**, *69*, 4864-4871.
- [8] (a) A. Cedergren, *Talanta* **1974**, *21*, 367-375; (b) A. Cedergren, *Talanta* **1974**, *21*, 553-563.
- [9] J. C. Wasilewski, C. D. Miller, *Anal. Chem.* **1966**, *38*, 1750-1751.
- [10] I. Nordin-Andersson, A. Cedergren, *Anal. Chem.* **1985**, *57*, 2571-2575.
- [11] (a) I. Kågevall, O. Åström, A. Cedergren, *Anal. Chim. Acta* **1980**, *114*, 199-208; (b) I. Nordin-Andersson, O. Åström, A. Cedergren, *Anal. Chim. Acta* **1984**, *162*, 9-18; (c) R. E. A. Escott, A. F. Taylor, *Analyst* **1985**, *110*, 847-849; (d) C. Liang, P. Vácha, W. E. van der Linden, *Talanta* **1988**, *35*, 59-61.
- [12] (a) U. Nordmark, A. Cedergren, *Anal. Chem.* **2000**, *72*, 172-179; (b) A. Cedergren, S. Jonsson, *Anal. Chem.* **2001**, *73*, 5611-5615.

- [13] (a) H. H. Willard, F. Fenwick, *J. Am. Chem. Soc.* **1922**, *44*, 2516-2529; (b) G. Wernimont, F. Hopkinson, *Ind. Eng. Chem., Anal. Ed.* **1943**, *15*, 272-274.
- [14] R. Karlsson, K. J. Karrman, *Talanta* **1971**, *18*, 459-465.
- [15] H. J. J. Francis, D. D. Persing, *Talanta* **1978**, *25*, 282-283.
- [16] J. C. Verhoef, E. Barendrecht, *J. Electroanal. Chem.* **1977**, *75*, 705-717.
- [17] E. Scholz, *Anal. Chem.* **1985**, *57*, 2965-2971.
- [18] T. P. G. Shaw, T. Bruce, *Anal. Chem.* **1947**, *19*, 884-885.
- [19] K. Muroi, K. Ogawa, Y. Ishii, *Bull. Chem. Soc. Jpn.* **1976**, *38*, 1176-1181.
- [20] K. Muroi, H. Fujino, *J. Jpn. Pet. Inst.* **1983**, *26*, 97-101.
- [21] E. D. Peters, J. L. Jungnickel, *Anal. Chem.* **1955**, *27*, 450-453.
- [22] E. W. Dean, D. D. Stark, *J. Ind. Eng. Chem.* **1920**, *12*, 486-490.
- [23] (a) J. W. Forbes, *Anal. Chem.* **1962**, *34*, 1125-1128; (b) A. Borin, R. J. Poppi, *Vib. Spectrosc.* **2005**, *37*, 27-32; (c) F. R. van de Voort, J. Sedman, R. Cocciardi, S. Juneau, *Talanta* **2007**, *72*, 289-295; (d) F. B. Xiong, W. Z. Zhu, H. F. Lin, X. G. Meng, *Appl. Phys. B - Lasers O.* **2014**, *115*, 129-135.
- [24] (a) R. L. Meeker, F. E. Critchfield, E. T. Bishop, *Anal. Chem.* **1962**, *34*, 1510-1511; (b) S. Garrigues, M. Gallignani, M. de la Guardia, *Anal. Chim. Acta* **1993**, *281*, 259-264; (c) M. Li, G. E. Pacey, *Talanta* **1997**, *44*, 1949-1958; (d) H. Büning-Pfaue, *Food Chem.* **2003**, *82*, 107-115.
- [25] (a) C. D. Thompson, F. D. Bogar, R. T. Foley, *Anal. Chem.* **1970**, *42*, 1474-1477; (b) J.-S. Rhee, P. K. Dasgupta, *Anal. Chim. Acta* **1989**, *220*, 55-63; (c) T. Gupta, M. E. van der Boom, *J. Am. Chem. Soc.* **2006**, *128*, 8400-8401.

- [26] (a) S. J. Schmidt, in *Advances in Experimental Medicine and Biology*, Springer, US, **1991**, pp. 599-613; (b) S. J. Schmidt, H.-M. Lai, in *Water Relationships in Foods*, Springer, US, **1991**, pp. 405-452; (c) H. Sun, B. Wang, S. G. DiMagno, *Org. Lett.* **2008**, *10*, 4413-4416.
- [27] M. Guzman, J. L. P. Pavón, E. R. Gonzalo, C. Hatfield, J. Růžicka, G. D. Christian, *Analyst* **1991**, *116*, 1043-1049.
- [28] (a) C.-G. Niu, P.-Z. Qin, G.-M. Zeng, X.-Q. Gui, A.-L. Guan, *Anal. Bioanal. Chem.* **2007**, *387*, 1067-1074; (b) C.-G. Niu, L. Li, P.-Z. Qin, G.-M. Zeng, Y. Zhang, *Anal. Sci.* **2010**, *26*, 671-674; (c) Z. Li, Q. Yang, R. Chang, G. Ma, M. Chen, W. Zhang, *Dyes Pigm.* **2010**, *88*, 307-314; (d) H. Niu, D. Huang, C. Niu, *Sens. Actuat. B Chem.* **2014**, *192*, 812-817.
- [29] D. Citterio, K. Minamihashi, Y. Kuniyoshi, H. Hisamoto, S.-I. Sasaki, K. Suzkui, *Anal. Chem.* **2001**, *73*, 5339-5345.
- [30] H. S. Knight, F. T. Weiss, *Anal. Chem.* **1962**, *34*, 749-751.
- [31] J. Wang, A. J. Reviejo, *Anal. Chem.* **1993**, *65*, 845-847.
- [32] G. Casalbore-Miceli, Y. S. Chen, E. M. Girotto, Y. Li, A. W. Rinaldi, M. J. Yang, A. Zanelli, *Sens. Actuat. B Chem.* **2006**, *119*, 577-582.
- [33] (a) G. Casalbore-Miceli, A. Zanelli, A. W. Rinaldi, E. M. Girotto, M. J. Yang, Y. S. Chen, Y. Li, *Langmuir* **2005**, *21*, 9704-9708; (b) G. Casalbore-Miceli, A. Zanelli, A. W. Rinaldi, N. Camaioni, M. J. Yang, Y. Li, E. M. Girotto, *Sens. Actuat. B Chem.* **2007**, *125*, 120-125.
- [34] M. A. Rahman, M.-S. Won, N.-H. Kwon, J.-H. Yoon, D.-S. Park, Y.-B. Shim, *Anal. Chem.* **2008**, *80*, 5307-5311.
- [35] J. Liang, M. C. Elliot, V. Cammarata, *Electroanalysis* **2009**, *21*, 2542-2548.
- [36] J. Liang, B.-Q. Chen, Y.-T. Long, *Analyst* **2011**, *136*, 4053-4058.

- [37] S.-I. Ohira, K. Goto, K. Toda, P. K. Dasgupta, *Anal. Chem.* **2012**, *84*, 8891-8897.
- [38] L. Zhang, H. Zhou, X. Li, Y. Lin, P. Yu, L. Su, L. Mao, *Electrochem. Commun.* **2009**, *11*, 808-811.
- [39] (a) Y. Hui, E. L. K. Chng, C. Y. L. Chng, H. L. Poh, R. D. Webster, *J. Am. Chem. Soc.* **2009**, *131*, 1523-1534; (b) Y. Hui, E. L. K. Chng, L. P.-L. Chua, W. Z. Liu, R. D. Webster, *Anal Chem.* **2010**, *82*, 1928-1934.

Chapter 4

Electrochemical Applications of Quinones and Phenylenediamines

4.1 Why Quinones and Phenylenediamines?

4.2 Electrochemical Applications of Quinones

4.3 Electrochemical Applications of Phenylenediamines

4.4 Summary

References

This page has been intentionally left blank

4.1 Why Quinones and Phenylenediamines?

Quinones and phenylenediamines are widely studied because of their numerous industrial functions and biological applications. Quinones, for instance, play important roles in photosynthetic reaction centers,^[1] are used in pest control^[2] and have been found to exhibit antibiotic,^[3] anticancer,^[3-4] antifungal,^[3, 5] antimalarial,^[6] antimicrobial^[7] and other medicinal^[8] properties. They have also been regularly used as dyes^[9] and oxidizing agents in chemical synthesis. More recently, their electrochemical behavior has been considered for pH measurements,^[10] redox switches in molecular electronics^[11] and sensing^[10c, 12]. Phenylenediamines, likewise, have seen much use especially as dyes, e.g. Wurster's blue (the radical cation of *N,N,N',N'*-tetramethyl-1,4-phenylenediamine),^[13] antioxidants in rubber and fuels^[14] and organic materials for spin electronic devices^[11, 15]. The stability of their radical cations have also enabled applications in electrochromism^[16] as well as detection of pollutants^[17]. The electrochemical applications of both classes of compounds will be briefly described in the following sections.

4.2 Electrochemical Applications of Quinones

Compton et al. developed an electroanalytical method for detecting cysteine via the reaction of the thiol with 2,3-dimethoxy-5-methyl-1,4-benzoquinone^[12a] because of the important role that sulfhydryl thiols play as biomarkers. This reaction generates a quinone-cysteine adduct that produces a more defined voltammetric peak than the direct oxidation of the sulfhydryl thiols would and is also clearly resolved from the peak arising from the unreacted quinone. A linear response was obtained within the concentration range of 5 to 47 μM to which there was little interference from 4-aminophenol, ascorbic acid, homocysteine, glutathione, lysine and paracetamol. The applicability of the method was tested in urine to which a recovery of 91% and relative standard deviation of 5% was obtained. A similar procedure was also employed for the detection of hydrogen sulfide.^[12b]

The same researchers then investigated the capability of quinones for pH measurements and designed a reagentless voltammetric pH probe based on anthraquinone-derivatized carbon powder with the potential of the peak, arising from the reduction of quinone on the derivatized material, showing a linear trend with Nernstian response between pH 1 to 9 and over a temperature range of 20 to 70 °C.^[10a] The derivatized material was found to be stable in the presence of surfactants and complexing metal ions. The sensitivity of the method was subsequently improved by immobilizing both the quinone and phenylenediamine onto the basal plane of a pyrolytic graphite electrode to enable simultaneous monitoring of the redox potentials of the independently occurring oxidation of the phenylenediamine and reduction of the quinone;^[10b] a change of ~120 mV per pH unit at 25 °C was obtained with this doubly derivatized electrode as compared to the 58 mV per pH unit sensitivity acquired with the quinone-derivatized carbon powder.

Lawrence et al. were also observant to apply the definition of ΔE that involves the difference in potential of two components in a single molecule for measuring pH by building upon the pH-sensitive reduction reaction of anthraquinone and the pH-insensitive oxidation of ferrocene.^[10c] Measurements with this single molecule pH probe were highly stable because of the poor solubility of the charged products and use of small molecules instead of polymers, which prevents electron hopping from occurring. The function of the single molecule probe was also extended to the sensing of dissolved oxygen given that the reduction of quinones are oxygen-sensitive but not the oxidation of ferrocene.

Anthraquinone and its derivatives have also enjoyed successful use in lithium ion batteries because of their well-spaced (in terms of potential) sequential uptake of electrons and electrochemical reversibility, as well as possible production from biomass.^[18] Gutel et al. however showed that monothioanthraquinone is a better organic active material in terms of cyclability, working potential and specific gravimetry.^[19]

Smith et al. proposed that the perturbation of hydrogen bonds via electron transfer may be useful and important in supramolecular chemistry as well as for studies on molecular recognition

and self-assembly.^[20] They showed with voltammetry that 9,10-phenanthrenequinone and acenaphthenequinone were capable redox-dependent receptors for urea and arylureas in aprotic organic solvents,^[21] to which the first definition of ΔE , that is the difference between the potentials recorded in the presence and absence of the compounds, was utilized for that purpose. The quinones were concluded to be more responsive than flavins.

Through a combination of electrochemistry, spectroelectrochemistry and spectrophotometry techniques, Yilmaz et al. was able to quantify barium and calcium cations as well as trace water in MeCN with their synthesized multisensor molecule.^[22] This multisensor molecule contains ferrocene, quinone and crown ether functionalities to which the amount of trace water was determined on the basis of hydrogen bonding to the quinone and through the difference in potentials of the second $1e^-$ -reduction of the quinone and oxidation of ferrocene, with the latter serving as an internal reference potential. The sensing of the cations occurs via the ion-dipole interactions with the macrocyclic ring whereas the quantification of Ca^{2+} and Ba^{2+} ions is achieved with UV-vis spectrophotometry through changes in the intensity and wavelength of the absorbance at 666 nm, which involves the intramolecular charge-transfer reaction between the donor (ferrocene) and acceptor (quinone) components. It is speculated that the multisensor molecule might also be capable of measuring pH.

Kim et al. applied a variation of ΔE to determine the pK_a of various organic acids in MeCN, DCM and dimethyl sulfoxide, to which they claim to be the first to report for trichloroacetic acid and 1-naphthoic acid.^[23] In their voltammetric study, ΔE was defined as the difference between the reduction potential of the $Q/Q^{\bullet-}$ couple and that for the EPE process converting Q directly to QH^- . An inverse linear relationship was found to exist between ΔE and the aqueous pK_a values and the order of acidity in each of the organic solvents was found to follow: protonated amines > phenols > carboxylic acids. The studied compounds were also most acidic in dimethyl sulfoxide and least acidic in DCM. This work is valuable because it enables the determination of pK_a values in non-aqueous media, unlike potentiometric titration, spectrophotometry and conductometry that are meant for use in water. Furthermore, the relative

acidity in water may not necessarily be translated to non-aqueous solvents, as is the case of acetic acid and the ammonium ion. Acetic acid ($pK_a = 4.8$) is more acidic than the ammonium ion ($pK_a = 9.2$) in water but is less acidic in dimethyl sulfoxide ($pK_a = 12.6$ for $\text{CH}_3\text{CO}_2\text{H}$ vs. $pK_a = 10.5$ for NH_4^+) and even more so in MeCN ($pK_a = 22.3$ for $\text{CH}_3\text{CO}_2\text{H}$ vs. $pK_a = 16.5$ for NH_4^+).^[24] Their voltammetric method is also advantageous for it is simple to use, convenient and does not require large amounts of sample. The work was subsequently extended to analyze and detect the biologically active pyruvic acid, maleic acid and histamine in a 9:1 (v/v) solution of MeCN and water for which a detection limit of 10 μM and sensitivity of $\sim 18 \mu\text{A mM}^{-1}$ was obtained with linear sweep voltammetry.^[25]

Also using voltammetry, Mao et al. created a method for detecting melamine via the decrease in i_p of the first $1e^-$ -reduction process for chloranil.^[26] A $n-\pi$ charge-transfer reaction between melamine and chloranil would occur in the bulk solution thereby leading to the consumption of the quinone before the electrochemical reaction converting Q to $Q^{\cdot-}$ can take place, which results in the decrease in i_p . This change in i_p was found to respond linearly to the amount of melamine in solution, for which a concentration range of 10 to 1000 μM of the triamine was successfully determined with 0.5 mM of quinone.

Salazar et al. reported using quinone-rich polydopamine-modified iron oxide magnetic nanoparticles in what was the first amperometric magneto-biosensor for glucose in blood samples.^[27] The quinone-rich coat containing immobilized glucose oxidase was found to be stable to pH and temperature and could last for up to 45 days without any significant loss in response. The biosensor exhibited a linear response with sensitivity of $8.7 \text{ mA M}^{-1} \text{ cm}^{-2}$ and detection limit of 0.02 mM. In addition, because of the low applied potential, it suffered only minor interference (1-3%) from reducing agents like ascorbic acid and uric acid that may be present in biological samples. Recovery was reported to be satisfactory after comparison to a commercial glucometer.

Lastly, Hatton et al. employed the reduction of 1,4-naphthoquinone in the ionic liquid, 1-ethyl-3-methylimidazolium tricyanomethanide, for electrochemical separation of carbon dioxide from a dilute gas mixture.^[28] The reduced states of the quinone have higher affinity for CO_2 than

the neutral form has and so, in the presence of the gas, would render the reduction of the quinone to proceed via an ECEC mechanism (with C representing a chemical reaction) at the cathode with the uptake of two molecules of CO_2 to produce the dicarboxylated dianion species, $\text{Q}(\text{CO}_2)^{2-}$. The “bound” CO_2 molecules are then subsequently released upon the oxidation of $\text{Q}(\text{CO}_2)^{2-}$ back into Q at the anode. This electrochemical separation method exploits the electrochemical stability and low volatility of ionic liquids and is particularly advantageous because it operates under mild conditions of temperature and applied potential. The slow diffusion of the quinone and $\text{Q}(\text{CO}_2)^{2-}$ complex was however a setback and so alternative electrode designs and arrangements are currently explored by the researchers.

4.3 Electrochemical Applications of Phenylenediamines

Webster et al. showed that the radical cations of phenylenediamines could display the primary colors of red (*N,N'*-di-*sec*-butyl-1,4-phenylenediamine), blue (*N,N,N',N'*-tetramethyl-1,4-phenylenediamine), green (*N,N,N',N'*-tetraphenyl-1,4-phenylenediamine) and yellow (tetramethyl-1,4-phenylenediamine) and revert back into their uncolored state after reduction into the neutral species thereby leading to their potential use as electrochromic materials.^[16] The radical cations were easily produced at ambient conditions and stable in the presence of both water and oxygen; their voltammetric responses also displayed good cycle life with negligible loss in signal intensity after repeated cycling. Good electrochromic properties in terms of contrast ratios, chromatic efficiency and optical memory were also obtained.

Pearson et al. synthesized a couple of crown-annulated *para*-phenylenediamine derivatives and explored their potential as electrochemical and fluorescence-responsive chemosensors for metal cations.^[29] These compounds were found to reversibly oxidize into their radical cations for which the potential would be shifted in the positive direction in the event that a metal cation is coordinated, and with the extent of the shift dependent on the degree of interaction between the aza-crown and the metal cation. Changes in the fluorescence spectra were also reported; a larger blue shift occurred in the presence of the alkaline earth metals (Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) as compared to the alkali metal cations (Li^+ , Na^+ and K^+) and varied fluorescence

enhancements were detected. It was concluded that the compounds were more selective for dications as compared to monocations.

In a similar fashion to the quinones, Compton et al. developed an electrochemical procedure for detecting chlorine, because of its high toxicity and prevalence in commercial and industrial formulations, through its reaction with *N,N*-diethyl-1,4-phenylenediamine to produce a phenylenediamine-chlorine adduct.^[17] The phenylenediamine-chlorine adduct is able to successfully overcome the interference of the direct reduction of chlorine when performed at pH 0 and in addition the sensitivity can be improved if square-wave voltammetry is used because the product exhibits chemically reversible behavior on a glassy carbon electrode; therefore, an enhanced signal is obtained as compared to electrochemical irreversibility observed for the direct reduction of chlorine. The electroanalytical parameter i_p showed a linear relationship to the concentration of the phenylenediamine between 17 to 495 μM with a 6.8 μM limit of detection. The researchers also successfully developed an electrochemical method for the detection of ammonia through its reaction with *N,N'*-diphenyl-1,4-phenylenediamine.^[30]

Sibert et al. were also interested in the sensing of cations in organic solvents and achieved this with several *ortho* and *para* Wurster's type-containing crown ethers.^[31] These phenylenediamine-containing macrocycles were found to have stronger affinity for alkali metal cations but did not show improved selectivity when compared to their parent crown ethers. The electrochemical behavior of the *para*-Wurster's crown ethers displayed two chemically reversible oxidation processes to which the quinonediimine dication had no affinity for the alkali metals and so only the first oxidation potential was affected upon coordination. On the other hand, the *ortho*-Wurster's crowns were more difficult to oxidize and showed chemically irreversible oxidation processes because the coulombic repulsion between the amino group of the radical cation and guest alkali metal cation disrupts the planarity of the phenylenediamine and so destabilizes the molecule. The group eventually synthesized crownophanes, where both nitrogen atoms of the phenylenediamine are incorporated within the macrocyclic framework as opposed to the above mentioned crowns where only one of the nitrogen atoms was involved,^[32] and found their EE

oxidation behavior to be unresponsive towards alkali metal cations despite some selectivity for alkaline earth metal cations.

Using cyclic voltammetry and linear sweep voltammetry, Peng et al. constructed an electrochemical sensor from an electropolymerized molecularly imprinted *ortho*-phenylenediamine film on a multi-walled carbon nanotube modified glassy carbon electrode for the detection of paracetamol for medical control and quality control analysis.^[33] The linear sweep i_p showed a linear relationship to the concentration of the drug between the range of 0.2 to 40 μM with a detection limit of 0.05 μM . The sensor was also reported to show good repeatability, high selectivity for paracetamol, with little interference from dopamine, phenacetin, ascorbic acid, adrenaline and noradrenaline, and excellent recoveries of 94 to 105% when applied to real samples.

Finally, using a combination of UV-vis spectroscopy and electrochemical impedance spectroscopy, Parsa et al. reported on the antioxidant ability of 1,4-phenylenediamine through its reaction with the free radical 1,1-diphenyl-2-picrylhydrazyl in a zinc chloride medium.^[34] The polyphenylenediamine was found to be 1.67 times more effective at radical scavenging than the corresponding polyaniline film owing to its lower charge transfer resistance.

4.4 Summary

The versatility of the quinones and phenylenediamines has led to their applications in numerous fields and industries, with the unique properties and reactivity of their charged forms being at the center of many of their uses. Therefore, it is in our interest, after understanding their hydrogen bonding interactions, to determine the efficacy of the electrochemical behavior of quinones and phenylenediamines for measurements of hydrogen donor and hydrogen acceptor strengths as well as the detection of similar-type impurities in organic solvents. It is also in our purpose to improve on the established voltammetric method for measuring the moisture content of organic solvents with vitamin K₁ by exploring other types of quinones, some of which have to be

synthesized; this component of the study will also be extended to the phenylenediamines in light of the limitations of the quinones.

The next chapter of this thesis (Chapter 5) will outline the experimental procedures, synthetic routes as well as computational parameters that were used. After which, the results of the different components of the study will be discussed through Chapters 6 to 10 before the conclusion and elaboration of future plans in Chapter 11. The supporting information for the individual Results chapters is provided in the appendices that can be found at the end of the thesis.

References

- [1] (a) D. Kleinfeld, M. Y. Okamura, G. Feher, *Biochim. Biophys. Acta* **1984**, 766, 126-140; (b) J. Breton, C. Boullais, J.-R. Burie, E. Navedryk, C. Misokowski, *Biochemistry* **1994**, 33, 14378-14386; (c) J. S. van den Brink, R. J. Hulsebosch, P. Gast, P. J. Hore, A. J. Hoff, *Biochemistry* **1994**, 33, 13668-13677.
- [2] K. A. L. Ribeiro, C. M. de Carvalho, M. T. Molina, E. P. Lima, E. López-Montero, J. R. M. Reys, M. B. F. de Oliveira, A. V. Pinto, A. E. G. Santana, M. O. F. Goulart, *Acta Trop.* **2009**, 111, 44-50.
- [3] V. K. Tandon, R. V. Singh, D. B. Yadav, *Bioorg. Med. Chem. Lett.* **2004**, 14, 2901-2904.
- [4] (a) S. Hayashi, H. Ueki, Y. Ueki, H. Aoki, K. Tanaka, J. Fujimoto, K. Katsukawa, M. Mori, *Chem. Pharm. Bull.* **1963**, 11, 948-951; (b) E. M. Hodnett, C. Wongwiechintana, W. J. Dunn III, P. Marrs, *J. Med. Chem.* **1983**, 26, 570-574; (c) A. Ashnagar, J. M. Bruce, P. L. Dutton, R. C. Prince, *Biochim. Biophys. Acta* **1984**, 801, 351-359.
- [5] (a) N. G. Clark, *Pestic. Sci.* **1985**, 16, 23-32; (b) G. Meazza, F. E. Dayan, D. E. Wedge, *J. Agr. Food Chem.* **2003**, 51, 3824-3828; (c) D. N. Singh, N. Verma, S. Raghuwanshi, P. K. Shukla, D. K. Kulshreshtha, *Bioorg. Med. Chem. Lett.* **2006**, 16, 4512-4514.
- [6] B. Prescott, *J. Med. Chem.* **1969**, 12, 181-182.

- [7] J. L. Howland, *Biochim. Biophys. Acta* **1963**, 73, 665-667.
- [8] E. N. da Silva Júnior, T. T. Guimarães, R. F. S. Menna-Barreto, M. d. C. F. R. Pinto, C. A. de Simone, C. Pessoa, B. C. Cavalcanti, J. R. Sabino, C. K. Z. Andrade, M. O. F. Goulart, S. L. de Castro, A. V. Pinto, *Bioorg. Med. Chem.* **2010**, 18, 3224-3230.
- [9] C. Ibis, Z. O. Gunes, *Dyes Pigments* **2008**, 77, 39-42.
- [10] (a) G. G. Wildgoose, M. Pandurangappa, N. S. Lawrence, L. Jiang, T. G. J. Jones, R. G. Compton, *Talanta* **2003**, 60, 887-893; (b) I. Streeter, H. C. Leventis, G. G. Wildgoose, M. Pandurangappa, N. S. Lawrence, L. Jiang, T. G. J. Jones, R. G. Compton, *J. Solid State Electrochem.* **2004**, 8, 718-721; (c) V. G. H. Lafitte, W. Wang, A. S. Yashina, N. S. Lawrence, *Electrochem. Commun.* **2008**, 10, 1831-1834.
- [11] (a) A. Ito, Y. Nakano, M. Urabe, T. Kato, K. Tanaka, *J. Am. Chem. Soc.* **2006**, 128, 2948-2953; (b) A. Ito, R. Kurata, D. Sakamaki, S. Yano, Y. Kono, Y. Nakano, K. Furukawa, T. Kato, K. Tanaka, *J. Phys. Chem. A* **2013**, 117, 12858-12867.
- [12] (a) G. Hignett, S. Threlfell, A. J. Wain, N. S. Lawrence, S. J. Wilkins, J. Davis, R. G. Compton, M. F. Cardosi, *Analyst* **2001**, 126, 353-357; (b) D. Giovanelli, N. S. Lawrence, L. Jiang, T. G. J. Jones, R. G. Compton, *Anal. Lett.* **2003**, 36, 2941-2959; (c) Q. Li, C. Batchelor-McAuley, N. S. Lawrence, R. S. Hartshorne, R. G. Compton, *ChemPhysChem* **2011**, 12, 1255-1257.
- [13] R. D. Theys, G. Sosnovsky, *Chem. Rev.* **1997**, 97, 83-132.
- [14] (a) J. Pospíšil, *Aromatic and Heterocyclic Amines in Polymer Stabilization, Vol. 124*, Springer Berlin Heidelberg, **1995**; (b) F. Cataldo, *Polym. Degrad. Stabil.* **2001**, 72, 287-296; (c) F. Cataldo, *Eur. Polym. J.* **2002**, 38, 885-893; (d) N. M. Huntink, R. N. Datta, J. W. M. Noordermeer, *Rubber Chem. Technol.* **2004**, 77, 476-511.
- [15] A. Ito, M. Urabe, K. Tanaka, *Polyhedron* **2003**, 22, 1829-1836.

- [16] (a) K. Ogino, A. Kanegae, R. Yamaguchi, H. Sato, J. Kurjata, *Macromol. Rapid Commun.* **1999**, *20*, 103-106; (b) W.-L. Yu, J. Pei, W. Huang, A. J. Heeger, *Chem. Commun.* **2000**, 681-682; (c) M.-Y. Chou, M.-K. Leung, Y. O. Su, C. L. Chiang, C.-C. Lin, J.-H. Liu, C.-K. Kuo, C.-Y. Mou, *Chem. Mater.* **2004**, *16*, 654-661; (d) G.-S. Liou, C.-W. Chang, *Macromolecules* **2008**, *41*, 1667-1674; (e) C.-W. Chang, G.-S. Liou, *J. Mater. Chem.* **2008**, *18*, 5638-5646; (f) W.-H. Chen, K.-L. Wang, D.-J. Liaw, K.-R. Lee, J.-Y. Lai, *Macromolecules* **2010**, *43*, 2236-2243; (g) L.-T. Huang, H.-J. Yen, C.-W. Chang, G.-S. Liou, *J. Polym. Sci. A Polym. Chem.* **2010**, *48*, 4747-4757; (h) H.-Y. Wu, K.-L. Wang, D.-J. Liaw, K.-R. Lee, J.-Y. Lai, *J. Polym. Sci. A Polym. Chem.* **2010**, *48*, 1469-1476; (i) S. J. L. Lauw, X. Xu, R. D. Webster, *ChemPlusChem* **2015**, *80*, 1288-1297.
- [17] E. H. Seymour, N. S. Lawrence, R. G. Compton, *Electroanalysis* **2003**, *15*, 689-694.
- [18] (a) H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot, J.-M. Tarascon, *ChemSusChem* **2008**, *1*, 348-355; (b) M. Armand, J.-M. Tarascon, *Nature* **2008**, *451*, 652-657; (c) H. Chen, M. Armand, M. Courty, M. Jiang, C. P. Grey, F. Dolhem, J.-M. Tarascon, P. Poizot, *J. Am. Chem. Soc.* **2009**, *131*, 8984-8988.
- [19] A. Iordache, V. Maurel, J.-M. Mouesca, J. Pécaut, L. Dubois, T. Gutel, *J. Power Sources* **2014**, *267*, 553-559.
- [20] D. K. Smith, in *Electrochemistry of Functional Supramolecular Systems* (Eds.: P. Ceroni, A. Credi, M. Venturi), John Wiley & Sons, Inc., Hoboken, New Jersey, **2010**, pp. 1-30.
- [21] (a) Y. Ge, R. R. Lilienthal, D. K. Smith, *J. Am. Chem. Soc.* **1996**, *118*, 3976-3977; (b) Y. Ge, L. Miller, T. Ouimet, D. K. Smith, *J. Org. Chem.* **2000**, *65*, 8831-8838.
- [22] M. Dagdevren, I. Yilmaz, B. Yucel, M. Emirik, *J. Phys. Chem. B* **2015**, *119*, 12464-12479.
- [23] H.-S. Kim, T. D. Chung, H. Kim, *J. Electroanal. Chem.* **2001**, *498*, 209-215.
- [24] I. M. Kolthoff, M. K. Chantooni Jr., S. Bhowmik, *J. Am. Chem. Soc.* **1968**, *90*, 23-28.

- [25] J. Kim, T. D. Chung, H. Kim, *J. Electroanal. Chem.* **2001**, 499, 78-84.
- [26] L. Zhang, T. Li, P. Yu, T. Ohsaka, L. Mao, *Electrochem. Commun.* **2013**, 26, 89-92.
- [27] M. Martín, A. G. Orive, P. Lorenzo-Luis, A. H. Creus, J. L. González-Mora, P. Salazar, *ChemPhysChem* **2014**, 15, 3742-3752.
- [28] B. Gurkan, F. Simeon, T. A. Hatton, *ACS Sus. Chem. Eng.* **2015**, 3, 1394-1405.
- [29] (a) A. J. Pearson, J.-J. Hwang, *Tetrahedron Lett.* **2001**, 42, 3533-3536; (b) A. J. Pearson, J.-J. Hwang, M. E. Ignatov, *Tetrahedron Lett.* **2001**, 42, 3537-3540; (c) A. J. Pearson, J.-J. Hwang, *Tetrahedron Lett.* **2001**, 42, 3541-3543.
- [30] X. Ji, R. G. Compton, *Anal. Sci.* **2007**, 23, 1317-1320.
- [31] (a) J. W. Sibert, P. B. Forshee, *Inorg. Chem.* **2002**, 41, 5928-5930; (b) J. W. Sibert, P. B. Forshee, G. R. Hundt, A. L. Sargent, S. G. Bott, V. Lynch, *Inorg. Chem.* **2007**, 46, 10913-10925.
- [32] J. W. Sibert, G. R. Hundt, A. L. Sargent, V. Lynch, *Tetrahedron* **2005**, 61, 12350-12357.
- [33] Y. Peng, Z. Wu, Z. Liu, *Anal. Methods* **2014**, 6, 5673-5681.
- [34] A. Parsa, M. Sadeghi, M. Maleki, S. Parhizkar, S. A. Ghani, *Electrochim. Acta* **2014**, 127, 34-38.

This page has been intentionally left blank

Chapter 5

Experimental Methods

5.1 *Purchased Chemicals*

5.2 *Synthesis Procedures*

5.2.1 Synthesis of tetra-n-butylammonium hexafluorophosphate

5.2.2 Synthesis of 3,3',5,5'-tetra-tert-butyl-4,4'-diphenquinone

5.3 *Voltammetry*

5.4 *Preparation of Dried Solvents and Dried Solutions*

5.5 *Voltammetric Procedure*

5.6 *Karl Fischer Titration*

5.7 *Computational Methods*

5.8 *Nuclear Magnetic Resonance Spectroscopy*

5.9 *Purge and Trap Gas Chromatography-Mass Spectrometry*

References

This page has been intentionally left blank

5.1 Purchased Chemicals

The following compounds were used as received of which some of their structures are shown in Figure 5.1.

Quinones: 9,10-anthraquinone (AQ, Sigma-Aldrich, 97%), 1,4-benzoquinone (BQ, Alfa Aesar, $\geq 98\%$), 2,5-di-*tert*-butyl-1,4-benzoquinone (2,5-DTBBQ, Aldrich, 99%), 2,6-di-*tert*-butyl-1,4-benzoquinone (2,6-DTBBQ, Acros Organics, 98%), duroquinone (DQ, Sigma-Aldrich, 97%), 9,10-phenanthrenequinone (PQ, Sigma-Aldrich, $\geq 99\%$) and hydroquinone (QH₂, Sigma-Aldrich, ReagentPlus[®], $\geq 99\%$).

Phenols: 2,6-di-*tert*-butyl-4-methylphenol (DTBMP, Alfa Aesar, 99%), 2,4,6-trimethylphenol (TMP, Aldrich, 97%) and 2,4,6-tri-*tert*-butylphenol (TTBP, Aldrich, 98%).

Phenylenediamines: 1,2-phenylenediamine (*o*PD, Tokyo Industry Co. Limited, $>98\%$), 1,4-phenylenediamine (*p*PD or PD, Tokyo Industry Co. Limited, $>98\%$), 2,3,5,6-tetramethyl-1,4-phenylenediamine (TMPD, Sigma-Aldrich, 99%), and *N,N,N',N'*-tetramethyl-1,4-phenylenediamine (NTMPD, Alfa Aesar, 98+%).

Hydrogen donors: methanol (MeOH, Fulltime, HPLC grade), ethanol (EtOH, Merck, ACS grade), *n*-propanol (*n*-PrOH, Fischer, AR grade), isopropanol (*i*-PrOH, Panreac, ACS grade), *n*-butanol (*n*-BuOH, Alfa Aesar, 99+%), *sec*-butanol (*s*-BuOH, Alfa Aesar, 99+%), isobutanol (*i*-BuOH, Fischer, AR grade), *tert*-butanol (*t*-BuOH, Alfa Aesar, 99+%), 2-fluoroethanol (FE, Sigma-Aldrich, 95%), 2,2-difluoroethanol (DFE, Alfa Aesar, 97%), 2,2,2-trifluoroethanol (TFE, Alfa Aesar, 99+%), 3,3,3-trifluoro-*n*-propanol (TFP, Alfa Aesar, 97%), 1,3-difluoroisopropanol (DFIP, Alfa Aesar, 98%), ethylene glycol (EG, Alfa Aesar, 99+%), 1,3-propanediol (PD, Alfa Aesar, 99+%), and 1,4-butanediol (BD, Sigma-Aldrich, 99%), and glycerol (Sigma, $\geq 99\%$).

Hydrogen acceptors: pyridine (Py, Alfa Aesar, 99.5+%), 2-picoline (Merck, $\geq 98\%$), 3-picoline (Alfa Aesar, 99%), 4-picoline (Alfa Aesar, 98%), 2-(trifluoromethyl)pyridine (2-CF₃-Py, Alfa Aesar, 99%), 3-(trifluoromethyl)pyridine (3-CF₃-Py, Alfa Aesar, 97%), 4-(trifluoromethyl)pyridine (4-CF₃-Py, Alfa Aesar, 97%), 2,6-lutidine (Alfa Aesar, 98+%), 2,6-di-

tert-butylpyridine (Aldrich, $\geq 97\%$), quinoline (Alfa Aesar, 97%), isoquinoline (Alfa Aesar, 98%), acridine (Alfa Aesar, 98%), phenanthridine (Aldrich, 98%), pyridazine (Alfa Aesar, 98+%), pyrimidine (Alfa Aesar, 99%), pyrazine (Aldrich, 99+%), 2,2'-bipyridyl (Sigma-Aldrich, $\geq 99\%$), 4,4'-bipyridyl (Sigma-Aldrich, 98%), tetrahydrofuran (THF, Tedia, HPLC grade), tetrahydropyran (THP, Alfa Aesar, 98+%), thiophene (Aldrich, 99+%), and tetrahydrothiophene (THT, Aldrich, 99%).

For electrochemistry experiments: glacial acetic acid ($\text{CH}_3\text{CO}_2\text{H}$, Schedelco, AR grade), acetonitrile (MeCN, RCI Labscan Limited, AR grade), butyronitrile (PrCN, Alfa Aesar, Lot# 10111037, 99%), dichloromethane (DCM, Fischer, HPLC grade), ferrocene (Fc, Sigma-Aldrich, 98%), lithium perchlorate (LiClO_4 , Alfa Aesar, 99%, anhydrous), 2-methyl-2-pentenal (Aldrich, 97%), perchloric acid (HClO_4 , Sigma-Aldrich, ACS reagent, 70% conc.), propionitrile (EtCN, Acros Organics, 99%, extra pure: Lot# A0324874; Aldrich, 99%: Lot# BCBQ1587V (denoted as #1) and purum, $\geq 99.0\%$ (GC): Lot# BCBQ1587V (denoted as #2); Alfa Aesar, 99%: Lot# 10135507 (denoted as #1) and 10177320 (denoted as #2); Fluka, $\geq 99.0\%$: Lot# BCBG6203V; and Merck, assay (GC, area%) $\geq 99\%$: Lot# S6485568 325), toluene (Tedia, Absolv grade), and trifluoroacetic acid ($\text{CF}_3\text{CO}_2\text{H}$, Alfa Aesar, 99%).

For synthesis use: chloroform-*d* (CDCl_3 , Aldrich, ≥ 99.8 atom % D, contains 0.05% v/v TMS), 2,6-di-*tert*-butylphenol (Aldrich, 99%), hexafluorophosphoric acid (HPF_6 , Alfa Aesar, 60% w/w aqueous solution), potassium hydroxide (KOH, Merck, EMSURE[®]), tetra-*n*-butylammonium hydroxide (*n*- Bu_4NOH , Alfa Aesar, 40% w/w aqueous solution).

Miscellaneous: 1/16 in. rods with 3 Å pore size molecular sieves (CAS: 308080-99-1) were obtained from Fluka. Calcium hydride (CaH_2) (reagent grade, 95% (gas-volumetric)) and phosphorus pentoxide (P_2O_5) (ReagentPlus[®], 99%) were purchased from Sigma-Aldrich. SilicaFlash[®] F60 silica gels (Silicycle, ultrapure) and aluminum oxide (Sigma-Aldrich, activated, basic, Brockmann I) were used as the stationary phases in flash column chromatography. Purified water with a resistivity of $\geq 18 \text{ M}\Omega \text{ cm}$ was obtained from an ELGA Purelab Option-Q water purification system.

Figure 5.1. Structures of several compounds used in the project.

5.2 Synthesis Procedures

Tetra-*n*-butylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$),^[1] and 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenylquinone (DPQ)^[2] were synthesized in accordance to published procedures.

5.2.1 Synthesis of tetra-*n*-butylammonium hexafluorophosphate

The supporting electrolyte used in most of the electrochemistry experiments was prepared by reacting equal molar amounts of $n\text{-Bu}_4\text{NOH}$ and HPF_6 at room temperature (25 ± 2 °C). The precipitate was then washed with hot water until the washings had a pH ≥ 5 , and recrystallized three times from hot EtOH before drying under vacuum at 160 °C for 6 h and storing under vacuum.^[1]

5.2.2 Synthesis of 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone

The synthetic route towards DPQ is shown in Scheme 5.1. KOH (2 g, 35.6 mmol) in water (3 mL) was added to a solution of 2,6-di-*tert*-butylphenol (2.07 g, 10.0 mmol) in *t*-BuOH (25 mL). Air was then bubbled through the solution for 48 h at room temperature following which the reaction mixture was diluted with water (25 mL) and a brown precipitate was collected after filtration. Recrystallization from *i*-PrOH yielded brown needles of DPQ (1.5 g, 76%, melting point = 246 °C). ¹H NMR (CDCl₃, 400 MHz): δ = 1.36 (36H, s), 7.71 (4H, s); ¹³C NMR (CDCl₃, 100 MHz): δ = 29.8, 36.2, 126.2, 136.3, 150.7, 186.7.^[2]

Scheme 5.1. Synthesis of 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone.

5.3 Voltammetry

Cyclic voltammetry and square-wave voltammetry experiments were conducted with a computer-controlled Eco Chemie Autolab PGSTAT302N potentiostat in a three-electrode cell where a 1 mm diameter planar glassy carbon disk (Cypress Systems) was used as the working electrode and a platinum wire (Metrohm) as the auxiliary electrode. As for the reference electrode, a platinum wire (Metrohm) was used when the experiments were performed in a Precise[®] Controlled Atmosphere Glove Box (Labconco Corporation) or in the presence of 3 Å molecular sieves. Where a very low water content of the solvent was not required, a silver wire (Cypress Systems) miniature reference electrode that was connected to the electrochemical solution through a salt bridge containing 0.5 M *n*-Bu₄NPF₆ in MeCN (also known as the reference solution) was employed and the experiments were conducted in a Faraday cage that was located inside the fume cupboard. The internal filling solution of the silver wire reference electrode was replaced with dried reference solution prior to the start of each experiment to reduce the amount of moisture it contributed. All voltammetric experiments were conducted at room temperature (25±2 °C).

Unless otherwise stated, the cyclic voltammograms (CVs) were typically recorded at a scan rate (v) of 0.1 V s^{-1} whereas square-wave voltammograms (SWVs) were recorded with a pulse period (τ) of 25 Hz, potential step of 5 mV, and pulse amplitude of 20 mV. Fc was used as an internal standard when accurate potentials were needed by adding it to the test solution at the end of the experiments.

5.4 Preparation of Dried Solvents and Dried Solutions

Dried DCM and MeCN were prepared by storing the solvents over 3 Å molecular sieves that were activated prior to use. The molecular sieves were heated at 160 °C for 6 h under vacuum before cooling to room temperature. Dried solutions containing $n\text{-Bu}_4\text{NPF}_6$ were prepared in three steps with the first involving the heating of the electrolyte under vacuum at 160 °C for 6 h before cooling to room temperature and dissolving with the necessary dried solvent; following which the solutions were stored over activated molecular sieves. The dried solvents and dried $n\text{-Bu}_4\text{NPF}_6$ solutions were kept in airtight reagent bottles that were in turn stored under a nitrogen atmosphere. Dried solutions containing the quinones and $n\text{-Bu}_4\text{NPF}_6$ were prepared in a similar fashion except that the freshly prepared dried electrolyte solution was subsequently used to dissolve the desired quinone before transfer and storage in a vacuum syringe (SGE Analytical Science) containing activated molecular sieves. The syringe was then shielded from light and kept under a nitrogen atmosphere. All dried solutions were prepared at least 24 h prior to use.

5.5 Voltammetric Procedure

The general procedure used for the voltammetric experiments in the fume cupboard is as follows: 15 mL of the dried quinone/ $n\text{-Bu}_4\text{NPF}_6$ solution was accurately injected into an electrochemical cell that was previously heated at 100 °C for an hour before cooling under an argon atmosphere to room temperature. The solution was deoxygenated with argon gas following which consecutive cyclic voltammetry and square-wave voltammetry scans were performed. A vacuum syringe (SGE Analytical Science) was subsequently used to extract a 5 mL aliquot for Karl Fischer titration to determine the initial moisture content. The working electrode was then

systematically polished on a Buehler polishing pad to obtain an electrode surface that was free of any artifacts, and this was followed by careful additions of accurately controlled microliter volumes of the desired additive before mixing with a steady stream of argon bubbles. The voltammetric procedure for working within the glove box is largely similar to that used in the fume cupboard except that nitrogen gas was used in place of argon and that the electrochemical cell was gently swirled after the addition of the additive to ensure homogeneity.

As for the phenylenediamines, it was found that their voltammetric behavior were altered, much like that observed with hydroquinone, when they were stored over molecular sieves. Hence, their electrochemical solutions had to be freshly prepared before the start of each experiment, which was done by dissolving the desired phenylenediamine with dried $n\text{-Bu}_4\text{NPF}_6$ solution inside the humidity chamber that was maintained at 30% relative humidity.

5.6 Karl Fischer Titration

Karl Fischer titrations to measure moisture content were made with a Mettler Toledo DL32 coulometer located inside a (122 cm $\times$ 61 cm $\times$ 61 cm) humidity control box (Coy Laboratory Products) that was regulated at 30% relative humidity. A HYDRANAL[®]-Coulomat CG solution was used in the catholyte compartment while HYDRANAL[®]-Coulomat A and AG solutions were used in the anolyte compartment for DCM and MeCN solutions, respectively. The coulometer was allowed to stabilize before each measurement by ensuring that a steady drift value close to 0 $\mu\text{g min}^{-1}$ of water was obtained. Drift from atmospheric water was found to be insignificant since all the measurements concluded within 1 min.

5.7 Computational Methods

Molecular geometries were drawn using GaussView 5 and optimized with the B3LYP hybrid density functional^[3] with the 6-311+G(2df,p) Pople-style Gaussian basis set^[4] (triple ζ quality with one set of diffuse s and p functions on heavy atoms, two additional d -type polarization functions and an additional f -type polarization function on heavy atoms, and one set of p -type polarization function on hydrogen) with solvation effects taken into account by the

default solvent model implemented within the Gaussian suite of programs.^[5] The final geometries of the compounds were verified to stay at true energy minima through frequency calculations that were performed at the B3LYP/6-311+G(2df,p) level from which no imaginary frequencies were detected. Zero-point energies were scaled by a factor of 0.9889.^[6]

In many cases, the relative hydrogen bond strengths were calculated by simply subtracting the ground state energies (single point energy plus zero-point correction) of the constituent molecules from the ground state energy of the hydrogen-bonded complex e.g. relative hydrogen bond strength between D–H and A = ground state energy of D–H...A complex – (ground state energy of D–H + ground state energy of A).

However, when additional modes of interactions are possible, such as the bidentate and 2:1 form of hydrogen bonding for diols and bipyridyls, the relative hydrogen bond strengths were computed differently. In the case of the bidentate mode of hydrogen bonding where, for example, one molecule of D–H is interacting with another molecule of A via two hydrogen bonds, the strength of each interaction was determined by: relative hydrogen bond strength = $\frac{1}{2} \times$ overall interaction energy, where the overall interaction energy = ground state energy of bidentate complex – (ground state energy of D–H + ground state energy of A). As for the case of the 2:1 mode of interaction where, for instance, two molecules of D–H are interacting with one molecule of A, the strength of each hydrogen bond can be calculated as follows: relative hydrogen bond strength = $\frac{1}{2} \times$ overall interaction energy, but the overall interaction energy = ground state energy of D–H...A...H–D complex – (2 $\times$ ground state energy of D–H + ground state energy of A).

The methods for computing the adiabatic electron affinity (AEA) of the quinones and adiabatic ionization energy (AIE) of the phenols and phenylenediamines are similar to those used in the literature.^[7] In general, the calculations were based on the difference in ground state energies of the compounds and their respective oxidized or reduced states. For example, the AEA of Q can be obtained by subtracting the ground state energy of Q^{•–} from the ground state energy of Q whereas the AEA of Q^{•–} can be acquired through the difference in ground state energies of Q^{•–} and Q^{2–}. In a similar fashion, the AIE of P will involve the difference in ground state energies of P

and P^{*+} while the AIE of P^{*+} requires the subtraction of the ground state energy of P^{2+} from the ground state energy of P^{*+} . The AIE of PhOH can be obtained through the difference in ground state energies of PhOH and $PhOH^{*+}$ whereas that of PhO^* is calculated from the difference in ground state energies of PhO^* and PhO^+ .

5.8 Nuclear Magnetic Resonance Spectroscopy

1H and ^{13}C NMR spectra were measured with a Bruker AV 400 (400 MHz for 1H NMR and 100 MHz for ^{13}C NMR) nuclear magnetic resonance (NMR) spectrometer, with tetramethylsilane (TMS, 0.00 ppm) as the internal reference standard and referenced to the solvent $CDCl_3$. Multiplicity is given as s (singlet) or m (multiplet) and the number of protons (n) for a given resonance is indicated by nH .

5.9 Purge and Trap Gas Chromatography-Mass Spectrometry

The EtCN solvent samples were analysed by a purge and trap gas chromatography-mass spectrometry (PAT GC-MS) system for qualitative determination of probable organic impurities via matching with the library provided by the National Institute of Standards and Technology (NIST). Quantitative analyses were confirmed by running calibration standards with neat chemicals. The solvent delay of the GC-MS system was set to 11 min after the retention time of EtCN. A 200 μL aliquot of each sample was diluted with ultrapure water to 50 mL before analysis.

The Atomx purge and trap (PAT) system (Teledyne Tekmar) is equipped with an analytical trap (#9) made of proprietary material and a 5 mL sparger using nitrogen (99.999% from Air Products) as sparging gas. The samples were held at 40 $^{\circ}C$ for analysis before purging at 50 $mL\ min^{-1}$ for 10.4 min followed by dry purging at 100 $mL\ min^{-1}$ (0.25 min). The trap was subsequently desorbed at 250 $^{\circ}C$ for 1.5 min and baked for 15 min at 260 $^{\circ}C$ to reduce carryover for the next run.

An Agilent J & W 122-1564 533 K 60 m x 250 μm x 1.4 μm DB-VRX 1219.45766 column was utilized in the gas chromatography-mass spectrometry (GC-MS) system (7890A GC system and 5975C inert MSD with triple-axis detector) from Agilent Technologies to maximize separation resolution while helium gas with purity of 99.999% from Air Products was used as the carrier gas. Electron ionization mode, employed as the ionization source with impact energy of 70 eV, was kept at 230 °C whereas the quadrupole, set to perform scans from 35 to 300 amu, was maintained at 150 °C. For optimal separation of the organic compounds, the oven temperature of the GC-MS system was set to hold at 30 °C for 7 min before ramping at 40 °C min⁻¹ to 145 °C with a holding time of 3 min, 40 °C min⁻¹ to 30 °C with a holding time of 5.8 min and lastly 60 °C min⁻¹ to 200 °C with a holding time of 4 min. The data obtained were processed with the data analysis program, Environmental Data Analysis.

References

- [1] A. J. Fry, W. E. Britton in *Laboratory Techniques in Electroanalytical Chemistry*. P. T. Kissinger, W. R. Heineman, Eds. Marcel Dekker: New York, **1984**.
- [2] A. Krasovskiy, A. Tishkov, V. del Amo, H. Mayr and P. Knochel, *Angew. Chem. Int. Ed.* **2006**, *45*, 5010-5014.
- [3] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.
- [4] (a) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650-654; (b) A. D. McLean and G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639-5648.
- [5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. J. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken,

C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, Revision B.01, Gaussian, Inc., Wallingford CT, **2010**.

- [6] J. P. Merrick, D. Moran, L. Radom, *J. Phys. Chem. A* **2007**, *111*, 11683-11700.
- [7] (a) L. T. Sein Jr., J. M. Pagillo, *J. Mol. Struc.* **2011**, *985*, 299-306; (b) L. T. Sein Jr., A. L. Cederberg-Crossley, *J. Mol. Struc.* **2011**, *1004*, 319-328; (c) N. Seeburrun, H. H. Abdallah, P. Ramasami, *J. Phys. Chem. A* **2012**, *116*, 3215-3223.

Chapter 6

Electrochemical Properties of Quinones, Phenols and Phenylenediamines in Organic Solvents are Strongly Influenced by Hydrogen Bonding with Water

-
- 6.1 *Interference of Quinones, Phenols and Phenylenediamines in Karl Fischer Titrations*
 - 6.2 *Effect of Water on the Reduction of Quinones*
 - 6.3 *Effect of Water on the Oxidation of Phenols*
 - 6.4 *Effect of Water on the Oxidation of Hydroquinone*
 - 6.5 *Effect of Water on the Oxidation of Phenylenediamine*
 - 6.6 *Effect of Water on the Oxidation of Ferrocene*
 - 6.7 *Summary*

Notes

References

This page has been intentionally left blank

6.1 Interference of Quinones, Phenols and Phenylenediamines in Karl Fischer Titrations

As addressed in Chapter 3, it is important in hydrogen bonding analyses that the trace moisture content of the working solutions is measured, minimized and maintained across the duration of the experiment to limit the interference from water. All glassware and solvents were dried prior to use and additional steps were taken to reduce the absorption from the surrounding environment. A dummy setup was also employed in this study to enable the initial and final concentrations of trace water as well as the amount of water absorbed over the course of the experiment to be determined.

Coulometric Karl Fischer titration was employed for this purpose because of its high accuracy and sensitivity, and wide working range. But there is the possibility that the quinones may oxidize iodide and lead to an underestimation of the true moisture content, or that the phenols and phenylenediamines may reduce iodine and so result in an overestimation. Therefore, the interference of 1,4-benzoquinone (BQ), 2,4,6-trimethylphenol (TMP) and 1,4-phenylenediamine (*p*PD) on the Karl Fischer reaction (Eqn. 3.3) was investigated. BQ, TMP and *p*PD were selected because they were suspected to be the easiest, within their own class of compounds, in undergoing oxidation, reduction and/or some chemical reaction with the Karl Fischer reagents.

Three solutions of 1, 2 and 5 mM concentrations of the respective analytes were prepared from a stock solution of 0.2 M *n*-Bu₄NPF₆ in MeCN (electrolyte solution) to which the moisture contents were measured and compared. We found that the concentration of water in the various solutions (BQ, TMP and *p*PD at the three concentrations) was no different and highly similar to that obtained for the stock electrolyte solution thereby indicating that BQ, TMP and *p*PD imposed no significant interference on the Karl Fischer procedure. Consequently, the measured moisture contents can be regarded as accurate and true and unaffected by their presence in the working solutions.

The effect of water on the electrochemical behavior of BQ, 2,5-di-*tert*-butyl-1,4-benzoquinone (2,5-DTBQ) and 2,6-di-*tert*-butyl-1,4-benzoquinone (2,6-DTBQ), TMP, 2,6-di-

tert-butyl-4-methylphenol (DTBMP), 2,4,6-tri-*tert*-butylphenol (TTBP), 2,3,5,6-tetramethyl-1,4-phenylenediamine (TMPD), hydroquinone (QH₂) and ferrocene (Fc) in MeCN was then investigated with cyclic voltammetry and square-wave voltammetry. Water was chosen to reduce the complexity and number of competing interactions that have to be considered.

6.2 Effect of Water on the Reduction of Quinones

The effect of water on the reduction of BQ, 2,5-DTBQ and 2,6-DTBQ in MeCN was examined and their cyclic voltammograms are shown in Figures 6.1 and 6.2. For all three quinones, it was found that the two 1e⁻-reduction processes representing their EE electrochemical behavior were evident, even under ultra-dry conditions, and would shift towards less negative potentials as the concentration of water was increased, which is a result of hydrogen bonding and not protonation because the latter would lead to chemically irreversible behavior and the occurrence of electrochemical processes at more positive potentials (see Section 7.6 in Chapter 7).^[1] The shifts of E_{Q2} are much larger than E_{Q1} because Q²⁻ with its greater charge density and consequently better hydrogen acceptor ability, would form stronger hydrogen bonding interactions with water than those that are formed by Q⁻ and Q. As a result, the difference in potentials between the first and second 1e⁻-reduction processes, $\Delta E_Q = |E_{Q1} - E_{Q2}|$, was found to decrease with increasing moisture content so that a single reduction process representing the direct 2e⁻-reduction of Q to Q²⁻ was obtained for BQ and 2,5-DTBQ at approximately 13 and 6 M of water, respectively. In this situation, the cathodic peak currents, i_p^{red} , increased but fell short of a two-fold magnitude that was expected for the transfer of two electrons per molecule of quinone. The merger of the two 1e⁻-reduction processes of 2,5-DTBQ occurred at a lower concentration of water than that found for BQ because the former is more basic and a stronger hydrogen acceptor as a result of the electron-donating inductive effect of the *tert*-butyl groups.

It was not a surprise that two 1e⁻-reduction processes of 2,6-DTBQ did not merge even at 6 M of water because only one oxygen atom could effectively participate in hydrogen bonding as compared to the availability of both oxygen atoms in 2,5-DTBQ. In addition, the formation of its first hydrogen bond would reduce the charge density at the oxygen atom and consequently its

propensity to form a second hydrogen bond (anticooperativity effect of hydrogen bonding). As for 2,5-DTBQ, the formation of the second hydrogen bond is unhindered by the first. Alternatively, it can be viewed that the second hydrogen bond would have a greater effect on the electrochemical behavior of 2,5-DTBQ than 2,6-DTBQ.

Figure 6.1. Cyclic voltammograms of 2 mM BQ at different concentrations of water with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The cyclic voltammogram recorded under ultra-dry conditions with a platinum wire reference electrode is shown in dashed line.

Figure 6.3 depicts the plots of ΔE_Q that were obtained through square-wave voltammetry against the concentration of water for the three quinones. The combination of the ΔE_Q values obtained in the ultra-dry experiments (where $[\text{H}_2\text{O}] < [\text{Quinone}]$) with the use of a Pt wire pseudo reference electrode with those obtained with the liquid-junction reference electrode is permissible because ΔE_Q is highly accurate and unaffected by the effects of the iR drop, rate of heterogeneous electron-transfer (k_{et}) and drift in potential of the reference electrode. ΔE_Q generally decreases as the concentration of water is increased to which a logarithmic relationship was found to exist between the two entities. Therefore, the largest changes were observed at the lowest water concentrations. Interestingly, the plots of ΔE_Q for the three quinones were found to closely

overlap thereby indicating that some leverage was obtained between the reduction in hydrogen acceptor ability because of steric effect and enhancement of the hydrogen acceptor ability as a result of the electronic effect of the *tert*-butyl groups of 2,5-DTBQ and 2,6-DTBQ.

Figure 6.2. Cyclic voltammograms of 2 mM (a) 2,5-DTBQ and (b) 2,6-DTBQ at different concentrations of water with 0.2 M *n*-Bu₄NPF₆ as supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The cyclic voltammograms recorded under ultra-dry conditions with a platinum wire reference electrode are shown in dashed lines.

The ease of the reduction of quinones, observed through the shifts of their potentials towards less negative values, with increasing concentrations of a hydrogen donor has often been attributed to thermodynamic stabilization of the difference forms. The Nernst equation (Equation 6.1) (with concentrations used in place of activities, the charge of the molecules ignored and assumption that the electrochemical reaction is kinetically favorable) can be used to predict the shifts in peak potentials for electrochemical reactions (such as that in Reaction 6.1.) where the equilibrium constants strongly favor the forward process and the hydrogen bonding interactions to water are strong so that all the reduced species are only existing in their hydrogen-bonded states. With equal amounts of Ox and Red(H₂O)_y species at the surface of the electrode, the observed voltammetric potential E_{obs} will be dependent on $\log [\text{H}_2\text{O}]^{-y}$ and the voltammetric wave will shift

by +59.2 mV for every ten-fold increase in the concentration of water; E_f° is the formal potential, R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature and F is the Faraday constant (96485 C mol^{-1}).

Figure 6.3. Plots of ΔE_Q against concentration of water as measured by square-wave voltammetry during the reduction of 2 mM BQ (red ×), 2,5-DTBQ (blue +) and 2,6-DTBQ (black ○) with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

However, in situations where the equilibrium constant does not favor the forward process, or if multiple hydrogen bonding steps and species are involved, then the individual equilibrium constants will have to be incorporated into the logarithmic term of Equation 6.1.^[2] Nonetheless, even if the equilibrium in Reaction 6.1 strongly favors the product, the shifts of both E_{Q1} and E_{Q2} observed in Figures 6.1 and 6.2 are too large to be accounted for by the Nernst equation alone and hence a more detailed understanding of the effects of hydrogen bonding interactions on the voltammetry of the quinones were sought through density functional theory (DFT) calculations.

$$E_{\text{obs}} = E_f^\circ - \frac{2.303RT}{nF} \log \frac{[\text{Red}(\text{H}_2\text{O})_y]}{[\text{Ox}][\text{H}_2\text{O}]^y} \quad (\text{Eqn 6.1})$$

The adiabatic electron affinity (AEA), or propensity of a molecule to accept an electron, of Q and $Q^{\cdot-}$ for the three quinones with hydrogen bonding up to four molecules of water were

computed, with the solvent effects from MeCN taken into consideration for BQ, and tallied in Table 6.1. In general, the AEAs of Q and $Q^{\cdot-}$ increased with more water molecules added thereby indicating that lesser energy was needed to initiate the respective $1e^-$ -reduction processes in the event of more extensive hydrogen bonding, and that the higher hydrogen-bonded states were more receptive towards the addition of an electron than the lower hydrogen-bonded forms. In addition, the changes in the AEA of $Q^{\cdot-}$ was more often than not much greater in magnitude than those for Q and so the merger of the two $1e^-$ -reduction processes were theoretically plausible.

Interestingly, only one primary direct hydrogen bond was found to exist between Q and water in the $Q(H_2O)_n$ hydrogen-bonded complexes (with the remaining molecules of water engaged in secondary indirect hydrogen bonding interactions to the primary-bonded water molecule) whereas no secondary indirect hydrogen bonding interactions between Q^{2-} and water were found in the $Q^{2-}(H_2O)_n$ hydrogen-bonded complexes (see Figure 6.4 for BQ; the geometries of the various hydrogen-bonded complexes of all the compounds can be found in Appendix A). The tendency to form secondary indirect hydrogen bonding interactions may be a result of the phenomenon of cooperativity whereby the indirect interactions impart greater stabilization than that obtainable through direct hydrogen bonding. As for 2,5-DTBQ and 2,6-DTBQ, steric obstruction from the *tert*-butyl groups is likely to further promote the formation of such indirect hydrogen bonds.

Besides hydrogen bonding, the quinones and their reduced forms as well as water may also undergo other interactions such as with the solvent molecules (solvation) and the supporting electrolyte (ion pairing).^[3] However, it appears that the effects of these competing interactions are minor because the shifts in reduction potentials of the quinones were observed even when small amounts of water were added in the presence of a large excess of solvent and supporting electrolyte. Nonetheless, DFT calculations for BQ were repeated with the solvation effects from MeCN taken into consideration and the AEA values were compared to the gas-phase results (Table 6.1). It was found that solvation only affected the absolute values of AEA and the magnitudes to which they increase by but not the trends in which they varied.

Table 6.1. Adiabatic electron affinities of $Q(H_2O)_n$ and $Q^-(H_2O)_n$ of BQ, 2,5-DTBQ and 2,6-DTBQ.

No. of H ₂ O molecules (<i>n</i>)	Adiabatic electron affinity (eV)							
	BQ (Gas-phase)		BQ (Solvated)		2,5-DTBQ		2,6-DTBQ	
	$Q(H_2O)_n$	$Q^-(H_2O)_n$	$Q(H_2O)_n$	$Q^-(H_2O)_n$	$Q(H_2O)_n$	$Q^-(H_2O)_n$	$Q(H_2O)_n$	$Q^-(H_2O)_n$
0	2.185	-3.205	4.183	2.822	2.088	-2.678	2.098	-2.679
1	2.504	-2.594	4.325	3.028	2.377	-2.184	2.379	-2.154
2	2.689	-2.040	4.414	3.226	2.574	-1.719	2.545	-1.710
3	2.810	-1.570	4.476	3.374	2.692	-1.392	2.730	-1.395
4	2.864	-1.315	4.553	3.495	2.627	-1.077	2.795	-1.043

Figure 6.4. Secondary indirect (left) and primary direct (right) hydrogen bonding interactions in $Q(H_2O)_4$ and $Q^{2-}(H_2O)_4$ of BQ, respectively.

The DFT calculations also provided insights into the structural features of the $Q(H_2O)_n$, $Q^-(H_2O)_n$ and $Q^{2-}(H_2O)_n$ hydrogen-bonded complexes of the three quinones to which hydrogen bonding had affected. Firstly, the C-O bond lengths progressively increased with greater extent of reduction, changing from a C=O double bond in Q into a C-O single bond in Q^{2-} (see Tables 6.2 to 6.4), as supported by the shifting of the C=O stretch towards smaller wavenumbers in infrared spectroscopy.^[4]

Table 6.2. Calculated C-O bond lengths of $Q(H_2O)_n$, $Q^-(H_2O)_n$ and $Q^{2-}(H_2O)_n$ for BQ.

No. of H ₂ O molecules (<i>n</i>)	Bond length (Å)					
	C=O in $Q(H_2O)_n$		C=O in $Q^-(H_2O)_n$		C-O in $Q^{2-}(H_2O)_n$	
	1 ^[a]	2 ^[b]	1	2	1	2
0	1.22	1.22	1.26	1.26	1.31	1.31
1	1.22	1.22	1.27	1.26	1.33	1.30
2	1.23	1.22	1.27	1.27	1.32	1.32
3	1.23	1.22	1.28	1.27	1.36	1.31
4	1.22	1.22	1.28	1.27	1.33	1.33

[a] Carbonyl group is involved in hydrogen bonding interactions. [b] Carbonyl group is not involved in hydrogen bonding interactions.

Table 6.3. Calculated C-O bond lengths of $Q(H_2O)_n$, $Q^+(H_2O)_n$ and $Q^{2-}(H_2O)_n$ for 2,5-DTBQ.

No. of H ₂ O molecules (<i>n</i>)	Bond length (Å)					
	C=O in $Q(H_2O)_n$		C=O in $Q^+(H_2O)_n$		C-O in $Q^{2-}(H_2O)_n$	
	1 ^[a]	2 ^[b]	1	2	1	2
0	1.22	1.22	1.27	1.27	1.31	1.31
1	1.23	1.22	1.28	1.26	1.33	1.31
2	1.23	1.22	1.27	1.27	1.32	1.32
3	1.23	1.22	1.28	1.27	1.34	1.32
4	1.23	1.22	1.29	1.27	1.33	1.333

[a] Carbonyl group is involved in hydrogen bonding interactions. [b] Carbonyl group is not involved in hydrogen bonding interactions.

Table 6.4. Calculated C-O bond lengths of $Q(H_2O)_n$, $Q^+(H_2O)_n$ and $Q^{2-}(H_2O)_n$ for 2,6-DTBQ.

No. of H ₂ O molecules (<i>n</i>)	Bond length (Å)					
	C=O in $Q(H_2O)_n$		C=O in $Q^+(H_2O)_n$		C-O in $Q^{2-}(H_2O)_n$	
	1 ^[a]	2 ^[b]	1 ^[a]	2 ^[b]	1 ^[a]	2 ^[b]
0	1.22	1.22	1.26	1.27	1.30	1.32
1	1.23	1.22	1.27	1.27	1.32	1.31
2	1.23	1.22	1.28	1.26	1.36	1.30
3	1.23	1.22	1.29	1.26	1.37	1.30
4	1.23	1.22	1.29	1.26	1.37	1.30

[a] Carbonyl group is involved in hydrogen bonding interactions. [b] Carbonyl group is not involved in hydrogen bonding interactions.

Secondly, it was noticed in the $Q(H_2O)_n$ series, where only one primary direct hydrogen bonding occurred between the quinone and water molecules (Table 6.5), that the distance between the oxygen and hydrogen atoms in the $O_{\text{quinone}} \cdots H_{\text{water}}$ interaction was generally unchanged in BQ and 2,5-DTBQ whereas there was a systematic decrease in 2,6-DTBQ with increasing *n*, which may be linked to the asymmetry caused by the positioning of both *tert*-butyl groups at one of its carbonyl groups.

Table 6.5. Calculated $O_{\text{quinone}} \cdots H_{\text{water}}$ distance in $Q(H_2O)_n$ for BQ, 2,5-DTBQ and 2,6-DTBQ.

No. of H ₂ O molecules (<i>n</i>)	$O_{\text{quinone}} \cdots H_{\text{water}}$ distance in $Q(H_2O)_n$ (Å)		
	BQ	2,5-DTBQ	2,6-DTBQ
1	1.97	1.94	1.93
2	1.88	1.85	1.84
3	1.86	1.92	1.81
4	1.97	1.93	1.77

On the other hand, the distances between the oxygen and hydrogen atoms in the $O_{\text{quinone}} \cdots H_{\text{water}}$ interaction for the $Q^{2-}(H_2O)_n$ series of all three quinones in Table 6.6 showed a

general elongation with increasing number of interactions as a result of the anticooperativity nature of hydrogen bonding. The formation of the first hydrogen bond between the dianion and water reduces the electron density of the oxygen atom and discourages it to function again as a hydrogen acceptor for the second molecule of water. Therefore, the second hydrogen bond is formed with the other oxygen atom and also that the third and fourth hydrogen bonds are approximately 0.2 Å longer than the first and second hydrogen bonds. Since the oxygen atoms of the dianions have three lone electron pairs available for hydrogen bonding, it can be expected that the fifth and sixth primary direct hydrogen bonds will be longer than the preceding ones but only if the secondary indirect interactions are not preferred.

Table 6.6. Calculated $O_{\text{quinone}} \cdots H_{\text{water}}$ distance in $Q^{2-}(H_2O)_n$ for BQ, 2,5-DTBQ and 2,6-DTBQ.

No. of H ₂ O molecules (<i>n</i>)	$O_{\text{quinone}} \cdots H_{\text{water}}$ distance in $Q^{2-}(H_2O)_n$ (Å)				
	BQ		2,5-DTBQ		2,6-DTBQ ^[a]
	1	2	1	2	1
1	1.46		1.53		1.50
2	1.50	1.50	1.55	1.55	1.03
3	1.03	1.55	1.57/1.76 ^[b]	1.56	1.01
4	1.54/1.75 ^[b]	1.54/1.75 ^[b]	1.59/1.78 ^[b]	1.59/1.78 ^[b]	1.00

[a] Only one primary direct hydrogen bond was present between the quinone dianion and water molecules. [b] More than one primary direct hydrogen bond was present between the quinone dianion and water molecules.

It is likely that the asymmetric distribution of the *tert*-butyl groups in 2,6-DTBQ is responsible for the formation of only one primary direct hydrogen bond between Q^{2-} and water in its $Q^{2-}(H_2O)_n$ hydrogen-bonded complexes. In addition, the ~1 Å distance between the oxygen and hydrogen atoms in the $O_{\text{quinone}} \cdots H_{\text{water}}$ interaction for $Q^{2-}(H_2O)_4$ was also midway between that found in $Q^{2-}(H_2O)$ (1.5 Å) and the O-H bond length of water (0.96 Å). Yet no protonation effects were observed in the cyclic voltammograms of 2,6-DTBQ.

The trends for the $O_{\text{quinone}} \cdots H_{\text{water}}$ interactions in the $Q^{\cdot-}(H_2O)_n$ series were generally similar to those found for the $Q^{2-}(H_2O)_n$ series but not as clearly defined because of the mixture of primary direct and secondary indirect hydrogen bonding interactions in the optimized geometrical structures. Nonetheless, it may be concluded for the quinones that the computational results are highly supportive of the experimental findings.

6.3 Effect of Water on the Oxidation of Phenols

Limited information about the oxidation of phenols in organic solvents at trace amounts of water is currently available even as concerted proton-coupled electron transfer (PCET) reactions are reported to occur in the presence of higher amounts of water.^[5] As such, our attention was turned towards TMP, DTBMP and TBP for some insight.

The cyclic voltammograms of TMP (Figure 6.5) and DTBMP (Figure 6.6) show more than one chemically irreversible oxidation processes as compared to TBP (Figure 6.6). These extra electrochemical processes may arise from compounds formed via the interaction of their phenols with the molecular sieves (since only one oxidation wave is seen for TMP in Figure 1.3) or through side reactions involving their highly reactive phenoxonium cations PhO^+ . The significant steric bulk imposed by the *tert*-butyl groups at the *ortho* and *para* positions of TBP limits both of the abovementioned processes and so would assist in retaining the typical $-2\text{e}^-/-\text{H}^+$ electrochemical oxidation behavior of phenols that is usually presented as a single voltammetric wave. The methyl groups, on the other hand, are not sufficient to stabilize the PhO^+ and prevent the unwanted side reactions and so additional electrochemical processes are detected. The decrease in the anodic peak currents, i_p^{ox} , may be explained by the decrease in concentration of the phenols as more water was added.

Unlike the quinones, it was not possible to compare the shifts of the absolute potentials for the oxidation of the phenols (E_{PhOH}) between the experiments conducted under ultra-dry and normal conditions because different reference electrodes were used. Nevertheless, it might be interesting to note that significant changes in the appearance of the voltammograms of TMP and DTBMP were found for water concentrations less than 50 mM, which is the range that is considered as trace and is usually unaccounted for.

Figure 6.5. Cyclic voltammograms of 2 mM TMP at different concentrations of water with 0.2 M *n*-Bu₄NPF₆ as supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The cyclic voltammogram recorded under ultra-dry conditions with a platinum wire reference electrode is shown in dashed line.

It was common among the three phenols that their E_{PhOH} shifted towards less positive potentials as the concentration of water was increased. The shifts were however less substantial than those detected for the quinones because a monocation (and not a doubly charged species) was formed and that the neutral phenol molecules may already be involved in hydrogen bonding interactions to each other. It is reasonable to suspect that deprotonation of the phenols rather than hydrogen bonding effects are responsible for the experimental data. But this is unlikely to be true as a previous study using voltammetry and UV-vis spectroscopy showed that the oxidation of phenolate anions occurred more easily than the phenols by about 1 V.^[6] Therefore, the shifting of E_{PhOH} of the three phenols are due to hydrogen bonding effects and the progression towards less positive potentials with increasing moisture content indicates that hydrogen bonding has facilitated their oxidation. It should be noted that the extent of the variations in E_{PhOH} with concentration of water are also dependent on the stability of PhO^+ , which is determined by the size of the substituents at the *ortho* (that primarily influences the extent of hydrogen bonding) and

para positions (that predominantly controls its chemical reactivity). The shifts of E_{PhOH} were largest for TMP and the least for TBP.

Figure 6.6. Cyclic voltammograms of 2 mM (a) DTBMP and (b) TBP at different concentrations of water with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The cyclic voltammograms recorded under ultra-dry conditions with a platinum wire reference electrode are shown in dashed lines.

The shifting of E_{PhOH} can also be predicted by the Nernst equation (Equation 6.2) if the equilibrium constant of the electrochemical reaction (Reaction 6.2) is assumed to strongly favor the forward process so that all the oxidized forms exist in their hydrogen-bonded states (Reaction 6.2). In this context, E_{obs} will shift towards less positive potentials as $\log [\text{H}_2\text{O}]^y$ increases.

$$E_{\text{obs}} = E_f^\circ - \frac{2.303RT}{nF} \log \frac{[\text{Red}][\text{H}_2\text{O}]^y}{[\text{Ox}(\text{H}_2\text{O})_y]} \quad (\text{Eqn 6.2})$$

DFT calculations were also performed for the phenols and their adiabatic ionization energies (AIEs), which is the minimum amount of energy needed for a molecule to give up its electron, were computed and reflected in Table 6.7. In line with the experimental findings, the

AIEs of PhOH and PhO[•] were found to decrease with increased hydrogen bonding to water and the changes in the AIEs of TMP were greater than those for DTBMP and TBP.

Table 6.7. Gas-phase adiabatic ionization energies of PhOH(H₂O)_n and PhO[•](H₂O)_n for TMP, DTBMP and TBP.

No. of H ₂ O molecules (<i>n</i>)	Adiabatic ionization energy (eV)					
	PhOH(H ₂ O) _n			PhO [•] (H ₂ O) _n		
	TMP	DTBMP	TBP	TMP	DTBMP	TBP
0	7.549	7.307	7.240	6.902	7.329	7.233
1	7.112	7.015	6.965	6.699	7.325	7.239
2	6.957	6.859	6.809	6.315	7.279	7.058
3	6.892	6.861	6.831	6.267	7.088	7.005
4	6.822	6.613	6.702	6.344	7.156	7.062

Although bond lengths are an inaccurate measure of hydrogen bonding strengths, we found that the changes in the O-H bond lengths (Table 6.8), PhOH•••O_{water} (Table 6.9) and Ph(H)O•••H_{water} (Table 6.10) distances of the various hydrogen-bonded complexes were in good agreement with the expectation from more extensive hydrogen bonding and cooperativity/anticooperativity effects. The O-H bond length in the PhOH(H₂O)_n and PhOH^{•+}(H₂O)_n hydrogen-bonded complexes were found to increase while the PhOH•••O_{water} distance concomitantly shortened as more water molecules were included. In addition, the O-H bond length and PhOH•••O_{water} distance were measured to be always shorter and longer, respectively, in the reduced state (PhOH) than in the oxidized state (PhOH^{•+}). These variations in interatomic distances would collectively increase the electron density of the oxygen atom and facilitate the deprotonation of the phenol. Hence, assists the electron-transfer and consequently shifts E_{PhOH} towards less positive potentials; a similar phenomenon was observed with phenolate anions.^[6a, 7]

The effect of cooperativity was also observed through the Ph(H)O•••H_{water} distance in the PhOH(H₂O)_n hydrogen-bonded complexes where it was found to decrease with more extensive hydrogen bonding (see Table 6.10). Such a simultaneous decrease in both PhOH•••O_{water} and Ph(H)O•••H_{water} distances is cooperative, which implies that the initial hydrogen donor function of the phenol had assisted its ability to subsequently act as an hydrogen acceptor.

Table 6.8. Calculated O-H bond length of $\text{PhOH}(\text{H}_2\text{O})_n$ and $\text{PhOH}^{++}(\text{H}_2\text{O})_n$ for TMP, DTBMP and TBP.

No. of H_2O molecules (n)	O-H bond length (Å)					
	$\text{PhOH}(\text{H}_2\text{O})_n$			$\text{PhOH}^{++}(\text{H}_2\text{O})_n$		
	TMP	DTBMP	TBP	TMP	DTBMP	TBP
0	0.96	0.96	0.96	0.97	0.97	0.97
1	0.97	0.96	0.96	1.00	0.98	0.98
2	0.98	0.98	0.97	1.03	1.00	1.00
3	0.98	0.98	0.98	1.07	1.01	1.01
4	0.99	0.99	0.99	1.33	1.46	1.45

Table 6.9. Calculated $\text{PhOH}\cdots\text{O}_{\text{water}}$ distance in $\text{PhOH}(\text{H}_2\text{O})_n$ and $\text{PhOH}^{++}(\text{H}_2\text{O})_n$ for TMP, DTBMP and TBP.

No. of H_2O molecules (n)	$\text{PhOH}\cdots\text{O}_{\text{water}}$ distance (Å)					
	$\text{PhOH}(\text{H}_2\text{O})_n$			$\text{PhOH}^{++}(\text{H}_2\text{O})_n$		
	TMP	DTBMP	TBP	TMP	DTBMP	TBP
1	1.98	2.15	2.16	1.66	1.83	1.84
2	1.93	1.92	2.13	1.53	1.66	1.68
3	1.79	1.79	1.79	1.39	1.59	1.60
4	1.73	1.78	1.75	1.10	1.03	1.04

Table 6.10. Calculated $\text{Ph}(\text{H})\text{O}\cdots\text{H}_{\text{water}}$ distance in $\text{PhOH}(\text{H}_2\text{O})_n$ for TMP, DTBMP and TBP.

No. of H_2O molecules (n)	$\text{Ph}(\text{H})\text{O}\cdots\text{H}_{\text{water}}$ distance (Å)		
	TMP	DTBMP	TBP
2	1.97	1.97	2.12
3	1.82	1.84	1.84
4	1.78	1.81	1.80

Finally, there are three other interesting observations, which were only apparent through computational chemistry, that are worth mentioning. The first is that the overall change in the $\text{PhOH}\cdots\text{O}_{\text{water}}$ and $\text{Ph}(\text{H})\text{O}\cdots\text{H}_{\text{water}}$ distances followed the trend $\text{TMP} < \text{DTBMP} < \text{TBP}$ whereas the O-H bond lengths of the $\text{PhOH}(\text{H}_2\text{O})_n$ and $\text{PhOH}^{++}(\text{H}_2\text{O})_n$ hydrogen bonded complexes are comparable across the three phenols. Secondly, it was observed in the $\text{PhOH}^{++}(\text{H}_2\text{O})_n$ hydrogen-bonded complex series that the incorporation of the fourth molecule of water would bring about much greater changes to the O-H bond length and $\text{PhOH}\cdots\text{OH}_2$ distance than that which are borne by the first three molecules of water. Lastly, it was to our surprise that the DFT calculations indicated that the water molecules would preferentially interact with other portions of the phenols and not only at the carbonyl group for the $\text{PhO}^+(\text{H}_2\text{O})_n$ hydrogen-bonded complexes (see 114

Appendix A). The computational results were therefore supportive of the experimental findings that extensive hydrogen bonding with water would facilitate the oxidation of the phenols.

6.4 Effect of Water on the Oxidation of Hydroquinone

The effect of water on the oxidation of QH_2 , which proceeds via a $-2\text{e}^-/-2\text{H}^+$ ECEC mechanism to Q (Scheme 6.1), was subsequently studied. In unbuffered organic solvents, the cyclic voltammogram of QH_2 would typically show a single oxidation peak on the forward scan because the second 1e^- -oxidation reaction that converts QH^+ to QH^{++} occurs at a potential that is less positive than the initial 1e^- -oxidation of QH_2 to QH_2^{++} and deprotonation of QH_2^{++} to QH^+ occurs rapidly. As compared to the phenols, it is expected for the oxidation of QH_2 to be more susceptible to the effects of hydrogen bonding as well as interactions with the molecular sieves because of the lack of substantial steric bulk on the aromatic ring.

Scheme 6.1. Electrochemical oxidation of hydroquinone in aprotic organic solvents.

Figure 6.7 shows two oxidation reactions of approximately equal heights at low concentrations of water ($< 55 \text{ mM}$) that shift to less positive potentials with increasing moisture content before merging at about 0.2 M of water. The eventual single oxidation process was also found to move towards less positive potentials with increasing moisture content with the overall shift being more significant than that observed for the phenols. Interestingly, the i_p^{ox} (which is directly proportional to concentration) for the oxidation of QH_2 was much smaller than those obtained with the phenols and quinones, and so, like the case of the phenols, is indicative of surface based adsorption interactions with the molecular sieves (rather than a smaller diffusion coefficient) that consequently decreased its bulk concentration. The molecular sieves were required as part of the drying procedure to minimize the moisture content of the working solutions at the start of the experiments.

Figure 6.7. Cyclic voltammograms of 2 mM QH_2 at different concentrations of water with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode.

The AIE for $\text{QH}_2(\text{H}_2\text{O})_n$ was then computed through the difference in ground state energies of $\text{QH}_2(\text{H}_2\text{O})_n$ and $\text{QH}_2^{+\bullet}(\text{H}_2\text{O})_n$ while that for $\text{QH}^+(\text{H}_2\text{O})_n$ was obtained via the difference in ground state energies of $\text{QH}^+(\text{H}_2\text{O})_n$ and $\text{QH}^{\bullet+}(\text{H}_2\text{O})_n$, of which both AIEs were found to decrease as the number of water molecules increased and also by a larger magnitude than calculated for TMP (see Table 6.11). Although two hydroxyl groups are available for interactions, only the $\text{QH}_2^{+\bullet}(\text{H}_2\text{O})_n$ hydrogen-bonded complexes had both groups participating in hydrogen bonding whereas the neutral species QH_2 and the neutral radical $\text{QH}^{\bullet}$ utilized only one. The optimized structures of the QH_2 and $\text{QH}^{\bullet}$ hydrogen-bonded complexes showed that secondary indirect hydrogen bonding interactions among the water molecules was much preferred over direct hydrogen bonding interactions between water and the second hydroxyl group of the hydroquinone.

The changes in the O-H bond length of the hydroquinone and $\text{H}_{\text{hydroquinone}} \cdots \text{O}_{\text{water}}$ distance in $\text{QH}_2(\text{H}_2\text{O})_n$, $\text{QH}^+(\text{H}_2\text{O})_n$ and $\text{QH}^{\bullet+}(\text{H}_2\text{O})_n$ (Table 6.12) as well as $\text{O}_{\text{hydroquinone}} \cdots \text{H}_{\text{water}}$ distance in $\text{QH}_2(\text{H}_2\text{O})_n$ and $\text{QH}^{\bullet+}(\text{H}_2\text{O})_n$ (Table 6.13) with increasing number of water molecules followed a

similar trend to that reported earlier for the phenols. In general, the O-H bond of the hydroquinone was found to lengthen with greater hydrogen bonding while the distance between the hydrogen and oxygen atoms in the $\text{H}_{\text{hydroquinone}} \cdots \text{O}_{\text{water}}$ interaction had decreased. The $\text{O}_{\text{hydroquinone}} \cdots \text{H}_{\text{water}}$ distance had also shortened as a result of cooperativity.

Table 6.11. Gas-phase adiabatic ionization energies of $\text{QH}_2(\text{H}_2\text{O})_n$ and $\text{QH}^+(\text{H}_2\text{O})_n$.

No. of H_2O molecules (n)	Adiabatic ionization energy (eV)	
	$\text{QH}_2(\text{H}_2\text{O})_n$	$\text{QH}^+(\text{H}_2\text{O})_n$
0	7.711	7.867
1	7.198	7.230
2	6.843	6.917
3	6.789	6.701
4	6.545	6.613

Table 6.12. Calculated O-H bond length of hydroquinone and $\text{H}_{\text{hydroquinone}} \cdots \text{O}_{\text{water}}$ distance for $\text{QH}_2(\text{H}_2\text{O})_n$, $\text{QH}^+(\text{H}_2\text{O})_n$ and $\text{QH}^+(\text{H}_2\text{O})_n$.

No. of H_2O molecules (n)	O-H bond length (Å)			$\text{H}_{\text{hydroquinone}} \cdots \text{O}_{\text{water}}$ distance (Å)		
	$\text{QH}_2(\text{H}_2\text{O})_n$	$\text{QH}^+(\text{H}_2\text{O})_n$	$\text{QH}^+(\text{H}_2\text{O})_n$	$\text{QH}_2(\text{H}_2\text{O})_n$	$\text{QH}^+(\text{H}_2\text{O})_n$	$\text{QH}^+(\text{H}_2\text{O})_n$
0	0.96	0.97	0.97			
1	0.97	0.98	1.03	1.90	1.82	1.53
2	0.98	0.99	1.08	1.85	1.75	1.38
3	0.99	1.00	1.44	1.74	1.66	1.05
4	0.99	1.00	1.48	1.71	1.63	1.04

Table 6.13. Calculated $\text{O}_{\text{hydroquinone}} \cdots \text{H}_{\text{water}}$ distance for $\text{QH}_2(\text{H}_2\text{O})_n$ and $\text{QH}^+(\text{H}_2\text{O})_n$.

No. of H_2O molecules (n)	$\text{O}_{\text{hydroquinone}} \cdots \text{H}_{\text{water}}$ distance (Å)	
	$\text{QH}_2(\text{H}_2\text{O})_n$	$\text{QH}^+(\text{H}_2\text{O})_n$
2	2.01	2.22
3	1.83	1.93
4	1.79	1.85

The anticooperativity effects of hydrogen bonding were also observed. Table 6.14 carries the O-H bond lengths and the $\text{H}_{\text{hydroquinone}} \cdots \text{O}_{\text{water}}$ distances for the two hydroxyl groups in the $\text{QH}_2^{*+}(\text{H}_2\text{O})_n$ hydrogen-bonded complexes where it can be seen that both O-H bonds are of equal lengths in the absence of any hydrogen bonding ($n = 0$). However, after interaction with one molecule of water, it was found that the O-H bond of the 1st hydroxyl group (that was involved in the hydrogen bond) had elongated whereas the O-H bond of the 2nd hydroxyl group (that was not involved in the hydrogen bond) had shortened and hence became less receptive as a hydrogen

donor, and probably more inclined to function as a hydrogen acceptor. Yet the interaction of the $\text{QH}_2^{++}(\text{H}_2\text{O})$ complex with another molecule of water (to give $\text{QH}_2^{++}(\text{H}_2\text{O})_2$) occurred at this second hydroxyl group, to which the two O-H bonds resumed to be of equal lengths and the distance between the hydrogen and oxygen atoms in both $\text{H}_{\text{hydroquinone}} \cdots \text{O}_{\text{water}}$ interactions were almost identical.

The inclusion of another molecule of water into the $\text{QH}_2^{++}(\text{H}_2\text{O})_2$ complex, via indirect hydrogen bonding to an existing hydrogen bonded water molecule, to give $\text{QH}_2^{++}(\text{H}_2\text{O})_3$ again resulted in unequal O-H bond lengths. The O-H bond in the 1st hydroxyl group (the site where the 3rd molecule of water interacts) became longer than those found previously for the $\text{QH}_2^{++}(\text{H}_2\text{O})_2$ hydrogen-bonded complex, while the O-H bond in the 2nd hydroxyl group once more became shorter. The distances between the hydrogen and oxygen atoms in the $\text{H}_{\text{hydroquinone}} \cdots \text{O}_{\text{water}}$ interactions were also found to vary according to the changes in the O-H bond lengths. The $\text{H}_{\text{hydroquinone}} \cdots \text{O}_{\text{water}}$ distance involving the 1st hydroxyl group had decreased, thereby suggesting that its hydrogen bond had been strengthened, whereas the $\text{H}_{\text{hydroquinone}} \cdots \text{O}_{\text{water}}$ distance for the 2nd hydroxyl group had increased, and so its hydrogen bond had most probably weakened.

Nonetheless, the $\text{QH}_2^{++}(\text{H}_2\text{O})_4$ hydrogen-bonded complex was found to be symmetric with two molecules of water located at each hydroxyl group with the above mentioned distances being equal. Interestingly, it appears that the 2nd hydroxyl group is the preferred site for additional hydrogen bonding even if its propensity to do so is reduced through anticooperativity effects. The stabilization derived from extending the hydrogen bond network at the 2nd hydroxyl group (via secondary indirect hydrogen bonding interactions) is apparently greater than that which would be obtained at the 1st hydroxyl group (also via secondary indirect hydrogen bonding interactions).

The results computed for hydroquinone are in good agreement with the experimental data and, more importantly, have provided insights into the effects of cooperativity and anticooperativity from hydrogen bonding that may be useful in understanding complex hydrogen bond systems.

Table 6.14. Calculated O-H bond lengths and $H_{\text{hydroquinone}} \cdots O_{\text{water}}$ distances for both hydroxyl groups in $QH_2^{++}(H_2O)_n$.

No. of H ₂ O molecules (<i>n</i>)	O-H bond length (Å)		$H_{\text{hydroquinone}} \cdots O_{\text{water}}$ distance (Å)	
	1 st	2 nd	1 st	2 nd
0	0.97	0.97		
1	1.01	0.97	1.61	
2	1.00	1.00	1.64	1.64
3	1.02	1.00	1.54	1.66
4	1.02	1.02	1.56	1.56

6.5 Effect of Water on the Oxidation of Phenylenediamine

TMPD was chosen for study from among 1,2-phenylenediamine (*o*PD), 1,4-phenylenediamine (*p*PD) and *N,N,N',N'*-tetramethyl-1,4-phenylenediamine (NTMPD) because it exhibited the recognizable EE oxidation behavior of phenylenediamines that was not observed for *o*PD, to prevent unwanted side reactions that might occur with the ring carbon atoms of the quinonediimine dications of *p*PD and NTMPD especially at high concentrations of water, and to allow for both the hydrogen donor and hydrogen acceptor abilities of the phenylenediamines to be explored (see Figure 6.8). Smith et al. have found that the mechanism for the oxidation of TMPD is complex and involves a series of adsorption and desorption processes, hydrogen bonding and proton transfer steps to give a mixed valent hydrogen-bonded dimer as the kinetic product of the first $1e^-$ -oxidation reaction. Therefore, care had to be taken in the interpretation of our results. The researchers had verified that the radical cation $P^{+\bullet}$ was the thermodynamic product and also that oxidized to the quinonediimine dication P^{2+} in the second $1e^-$ -oxidation process.^[8]

The voltammetric behavior of TMPD in MeCN was altered much like that observed for the phenols and hydroquinone if the working solution was dried over molecular sieves. For this reason, the electrochemical solutions were freshly prepared before the start of each experiment by dissolving TMPD with dried electrolyte solution inside the humidity chamber that was maintained at 30% relative humidity.

Figure 6.8. Cyclic voltammograms of 2 mM phenylenediamines with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode.

Figure 6.9. Cyclic voltammograms of 1 mM TMPD at different concentrations of water with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode.

The cyclic voltammograms of TMPD at different concentrations of water are depicted in Figure 6.9 and it can be seen that E_{P1} and E_{P2} were shifted to less positive potentials as the water content increased, but only after a sizeable amount had been added (e.g. E_{P2} shifted by -60 mV only after 0.6 M of water was added). Such shifting of the potentials is indicative of the decrease in the AIEs of P and P^{*+} with more extensive hydrogen bonding and that the changes in the AIEs of P^{*+} are probably more significant than those for P. ΔE_P decreased because the shifts of E_{P2} are much larger than those of E_{P1} .

Surprisingly, the two $1e^-$ -oxidation processes of TMPD (present at a concentration of 1 mM) were found to be still separated by about 200 mV at a ~9 M concentration of water. Thus, indicating that the hydrogen bonding interactions between the various oxidized species of TMPD and water were not very extensive or, in other words, the electrochemical behavior of TMPD is not particularly sensitive towards the hydrogen bonding effects of water. This insensitivity could arise from the stability of the oxidized species as a result of the greater spread of the positive charges in the P^{2+} state of the phenylenediamine (e.g. each positive charge is spread across two hydrogen atoms and one carbon atom even though it is formally assigned to the nitrogen atom) and electron-donating inductive effect of the methyl groups. The steric effect of the methyl groups are also likely to prevent the phenylenediamine and water from coming into close proximity and so reduces the extent of hydrogen bonding. On the other hand, the quinones BQ, 2,5-DTBQ and 2,6-DTBQ are more sensitive towards hydrogen bonding effects because the negative charges in the Q^{2-} state are localized on the oxygen atoms and the electron-donating inductive effects of the *tert*-butyl groups would only serve to increase their basicity and hydrogen-acceptor ability.

It was found through DFT calculations that P behaved more like a hydrogen acceptor through its nitrogen atom rather than a hydrogen donor through the hydrogen atoms of the amino group, unlike P^{*+} and P^{2+} that consistently performed as hydrogen donors. Such knowledge is particularly useful for it suggests that the electrochemistry of phenylenediamines and the electrochemical parameter $\Delta E_P = |E_{P1} - E_{P2}|$ may have wider applications than the related ΔE_Q

parameter of quinones by serving as a measure of both the hydrogen donor and hydrogen acceptor abilities of compounds in non-aqueous solvents.

In addition, only two direct hydrogen bonds existed between the neutral phenylenediamine and the water molecules in the $P(H_2O)_n$ hydrogen-bonded complexes regardless if $n = 2, 3$ or 4 ; one has the nitrogen atom functioning as a hydrogen acceptor while the other hydrogen bond involved the hydrogen (of the same amino group) acting as a hydrogen donor. The remaining water molecules were then engaged in secondary indirect hydrogen bonding interactions to the “primary” hydrogen-bonded water molecules instead of neither interacting with the adjacent hydrogen atom of the same amino group or those of the second amino group. As for the $P^{2+}(H_2O)_n$ hydrogen-bonded complexes, no indirect hydrogen bonding interactions were discovered and all the water molecules were interacting directly with the hydrogen atoms of the dication; the second molecule of water however interacted with the non-hydrogen-bonded amino group instead of the amino group already involved in hydrogen bonding. Both direct and indirect hydrogen bonding interactions were found for the $P^{++}(H_2O)_n$ series of hydrogen-bonded complexes.

The gas-phase AIEs of $P(H_2O)_n$ and $P^{++}(H_2O)_n$ (Table 6.15) were found to decrease with greater number of water molecules in the hydrogen-bonded complexes. Moreover, the changes to the AIE of $P^{++}(H_2O)_n$ were significantly larger than those observed for the AIE of $P(H_2O)_n$; the overall change in the AIE of $P^{++}(H_2O)_n$ was approximately five times greater than the overall change that the AIE of $P(H_2O)_n$ underwent. This suggests that the merger of the two $1e^-$ -oxidation processes into a single $2e^-$ -oxidation process may be possible at higher concentrations of water or if a stronger hydrogen acceptor was present.

Table 6.15. Gas-phase adiabatic ionization energies of $P(H_2O)_n$ and $P^{++}(H_2O)_n$ of TMPD.

No. of H_2O molecules (n)	Adiabatic ionization energy (eV)	
	$P(H_2O)_n$	$P^{++}(H_2O)_n$
0	6.063	10.982
1	5.877	10.568
2	5.793	10.180
3	5.820	9.889
4	5.806	9.621

In comparison to the phenols and hydroquinone, the AIE of $P^{++}(H_2O)_n$ for TMPD was found to be about 3 to 4 eV greater than the AIEs of $QH^+(H_2O)_n$ and $PhO^+(H_2O)_n$, with the similarity among them being the removal of the second electron from their respective initial neutral molecules. This larger energy required for the second $1e^-$ -oxidation of the phenylenediamine was not unexpected since it concerns the removal of an electron from a positively charged radical, whereas those for the hydroquinone and phenols involve a neutral radical. The effect of hydrogen bonding on the AIE of $P^{++}(H_2O)_n$ was comparable to that found for $QH^+(H_2O)_n$ but far exceeded those observed for $PhO^+(H_2O)_n$ of the three phenols; on the other hand, the AIE of $P(H_2O)_n$ was the least affected by hydrogen bonding to water.

With regards to the bond lengths and interatomic distances, it was not possible to determine a trend in their variations in the $P^{++}(H_2O)_n$ hydrogen-bonded complexes because of the existence of both direct and indirect hydrogen bonding interactions whose manifestations were highly dependent on the number of water molecules. But it was found that the distances between the nitrogen and hydrogen atoms in the $N_{TMPD} \cdots H_{water}$ interaction and hydrogen and oxygen atoms in the $H_{TMPD} \cdots O_{water}$ interaction in the $P(H_2O)_n$ hydrogen-bonded complexes had decreased with more water molecules in the secondary hydrogen bond network as a result of cooperativity. Although the N-H bond (containing the hydrogen atom involved in the $H_{TMPD} \cdots O_{water}$ hydrogen bonding interaction) was expectedly found to elongate, there was no significant change in the adjacent N-H bond (whose hydrogen atom was not participating in any form of hydrogen bonding) as well as those of the other “free” amino group. The $N_{TMPD} \cdots H_{water}$ and $H_{TMPD} \cdots O_{water}$ distances as well as the significant N-H bond lengths are shown in Table 6.16.

As for the $P^{2+}(H_2O)_n$ hydrogen-bonded complexes, the $H_{TMPD} \cdots O_{water}$ distance were consistently found to increase (Table 6.17). Although the various N-H bond lengths did not vary in a systematic manner, their changes agreed with the cooperativity/anticooperativity effects of hydrogen bonding (Table 6.18). It may be concluded that the computational results for TMPD and its oxidized forms are supportive of the experimental findings that extensive hydrogen bonding with water assists in the oxidation reactions.

Table 6.16. Calculated N-H bond length, $N_{\text{TMPD}} \cdots H_{\text{water}}$ and $H_{\text{TMPD}} \cdots O_{\text{water}}$ distances for $P(\text{H}_2\text{O})_n$.

No. of H_2O molecules (n)	N-H bond length (Å)	$N_{\text{TMPD}} \cdots H_{\text{water}}$ distance (Å)	$H_{\text{TMPD}} \cdots O_{\text{water}}$ distance (Å)
0	1.01		
1	1.01	1.99	
2	1.02	1.90	2.35
3	1.02	1.83	2.11
4	1.02	1.81	2.05

Table 6.17. Calculated $H_{\text{TMPD}} \cdots O_{\text{water}}$ distance for $P^{2+}(\text{H}_2\text{O})_n$.

No. of H_2O molecules (n)	$H_{\text{TMPD}} \cdots O_{\text{water}}$ distance (Å)			
	1 st	2 nd	3 rd	4 th
1	1.72			
2	1.75	1.75		
3	1.81	1.77	1.82	
4	1.83	1.83	1.83	1.83

Table 6.18. Calculated N-H bond lengths for $P^{2+}(\text{H}_2\text{O})_n$.

No. of H_2O molecules (n)	N-H bond length (Å)			
	1 st	2 nd	3 rd	4 th
0	1.02	1.02	1.02	1.02
1	1.05	1.02	1.02	1.02
2	1.04	1.04	1.02	1.02
3	1.04	1.04	1.04	1.02
4	1.03	1.03	1.03	1.03

6.6 Effect of Water on the Oxidation of Ferrocene

Finally, the influence of water on the $1e^-$ -oxidation reaction of Fc was investigated to determine if changes in the solution resistance as well as liquid-junction potential of the reference electrode are responsible for the aforementioned results. Figure 6.10 shows the cyclic voltammograms of Fc in MeCN to which a difference of 25 mV was obtained between the starting (5 mM) and final (5.1 M) concentrations of water thereby indicating that the effects of the variations in solution resistance and liquid-junction potential of the reference electrode can be ignored and also that the results in the previous sections were mainly arising from the effects of hydrogen bonding to water.

Figure 6.10. Cyclic voltammograms of 2 mM Fc with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode.

6.7 Summary

The results in this chapter have shown the critical role that water has on the electrochemical properties of the quinones, phenols and hydroquinone in non-aqueous solutions where significantly different voltammetric behavior were obtained at the ultra-dry and moderate-to-high moisture concentration levels. Such hydrogen bonding to water did not however have much effect on the electrochemistry of phenylenediamines, specifically TMPD. Nevertheless, the results obtained in this chapter emphasize the importance of measuring and reporting the trace water content of organic solvents used in electrochemistry studies, especially when compounds that are capable of forming strong hydrogen bonds are involved, in a similar way that potentials are reported against a reference compound such as Fc.

Through DFT calculations, we have found that the variations in adiabatic electron affinities of the quinones and adiabatic ionization energies of the phenols, hydroquinone and phenylenediamines were consistent with the experimental results and therefore should be

considered in the explanation of the shifts in redox potentials with more extensive hydrogen bonding. The effects of cooperativity and anticooperativity were also evident through changes in the relevant bond lengths and interatomic distances.

Finally, the sensitivity of the voltammetric behavior of the quinones and, to some extent, the phenylenediamines towards hydrogen bonding suggests their usefulness as measures of hydrogen bonding strength (Chapters 7 and 8) and moisture content (Chapter 9) as well as for detecting impurities in organic solvents (Chapter 10).

Notes

The Cartesian coordinates and visualizations of the optimized geometries of the various hydrogen-bonded complexes are included in Appendix A.

References

- [1] (a) J. Q. Chambers, *Vol. 2* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1988**; (b) N. Gupta, H. Linschitz, *J. Am. Chem. Soc.* **1997**, *119*, 6384-6391.
- [2] (a) M. Gómez, F. J. González, I. González, *Electroanalysis* **2003**, *15*, 635-645; (b) M. Aguilar-Martínez, N. A. Macías-Ruvalcaba, J. A. Bautista-Martínez, M. Gómez, F. J. González, I. González, *Curr. Org. Chem.* **2004**, *8*, 1721-1738.
- [3] (a) J. E. Woods, Y. Ge, D. K. Smith, *J. Am. Chem. Soc.* **2008**, *130*, 10070-10071; (b) Y. Hui, E. L. K. Chng, C. Y. L. Chng, H. L. Poh, R. D. Webster, *J. Am. Chem. Soc.* **2009**, *131*, 1523-1534; (c) Y. Hui, E. L. K. Chng, L. P.-L. Chua, W. Z. Liu, R. D. Webster, *Anal. Chem.* **2010**, *82*, 1928-1934; (d) A. René, D. H. Evans, *J. Phys. Chem. C* **2012**, *116*, 14454-14460.
- [4] Z. H. Lim, E. L. K. Chng, Y. Hui, R. D. Webster, *J. Phys. Chem. B* **2013**, *117*, 2396-2402.

- [5] (a) M. H. V. Huynh, T. J. Meyer, *Chem. Rev.* **2007**, *107*, 5004-5064; (b) C. Costentin, *Chem. Rev.* **2008**, *108*, 2145-2179; (c) J. M. Mayer, *Acc. Chem. Res.* **2011**, *44*, 36-46.
- [6] (a) H. Lund, M. M. Baizer, *Organic Electrochemistry*, 3rd ed., Marcel Dekker, New York, **1991**; (b) R. D. Webster, *Electrochem. Commun.* **1999**, *1*, 581-584; (c) L. L. Williams, R. D. Webster, *J. Am. Chem. Soc.* **2004**, *126*, 12441-12450; (d) R. D. Webster, *Acc. Chem. Res.* **2007**, *40*, 251-257; (e) Y. S. Tan, S. Chen, W. M. Hong, J. M. Kan, E. S. H. Kwek, S. Y. Lim, Z. H. Lim, M. E. Tessensohn, Y. Zhang, R. D. Webster, *Phys. Chem. Chem. Phys.* **2011**, *13*, 12745-12754.
- [7] (a) E. Mueller, A. Rieker, K. Scheffler, *Justus Liebigs Annalen der Chemie* **1961**, *645*, 92-100; (b) J. A. Richards, P. E. Whitson, D. H. Evans, *J. Electroanal. Chem.* **1975**, *63*, 311-327; (c) J. A. Richards, D. H. Evans, *J. Electroanal. Chem.* **1977**, *81*, 171-187; (d) E. J. Nanni Jr., M. D. Stallings, D. T. Sawyer, *J. Am. Chem. Soc.* **1980**, *102*, 4481-4485; (e) D. H. Evans, P. J. Jimenez, M. J. Kelly, *J. Electroanal. Chem.* **1984**, *163*, 145-157; (f) P. Hapiot, J. Pinson, *J. Electroanal. Chem.* **1993**, *362*, 257-265; (g) N. Seeburrun, H. H. Abdallah, P. Ramasami, *J. Phys. Chem. A* **2012**, *116*, 3215-3223.
- [8] L. A. Clare, L. E. Rojas-Sligh, S. M. Maciejewski, K. Kangas, J. E. Woods, L. J. Deiner, A. Cooksy, D. K. Smith, *J. Phys. Chem. C* **2010**, *114*, 8938-8949.

This page has been intentionally left blank

Chapter 7

Measuring the Relative Hydrogen Donor Abilities of Alcohols in Organic Solvents via the Voltammetry of Quinones

7.1 *Introduction*

7.2 *Steric Effects of Simple Alcohols*

7.3 *Electronic Effects of Fluorinated Alcohols*

7.4 *The Role of the Additional Hydroxyl Group of Diols*

7.5 *Interesting Comparisons*

7.6 *Hydrogen Bonding or Proton-Transfer?*

7.7 *Summary*

Notes

References

This page has been intentionally left blank

7.1 Introduction

The results presented in the preceding chapter have suggested that the voltammetric behavior of quinones may be useful in analyzing the binding abilities of hydrogen donors, like alcohols, via the electrochemical parameter $\Delta E_Q = |E_{Q1} - E_{Q2}|$. ΔE_Q is believed to be more accurate and reproducible than using absolute potentials because the effects of uncompensated solution resistance and heterogeneous electron-transfer rates (assuming similar k_{et} values for both processes) are cancelled. Therefore, the magnitude of ΔE_Q is only dependent on the hydrogen bonding between the hydrogen donor and the different reduced forms of the quinones (e.g. Q, $Q^{\cdot-}$ and Q^{2-}), which in turn is affected by the steric and electronic properties of both constituents.

ΔE_Q is unfortunately only a relative indicator of hydrogen donor strengths and is also unable to determine the number of hydrogen donor molecules that are involved in the various hydrogen-bonded complexes. Nevertheless, this chapter investigates the effects of hydrogen bonding of several simple alcohols, fluorinated alcohols and diols on the voltammetric behavior of 9,10-anthraquinone (AQ) and 1,4-benzoquinone (BQ) in acetonitrile (MeCN) and dichloromethane (DCM) and the capability of ΔE_Q in distinguishing them. The alcohols were selected because they exist as non-viscous liquids and so can be easily added into the working solutions by micropipettes. They are also electroinactive within the potential window that the glassy carbon working electrode is cycled and are weakly acidic in aprotic organic solvents therefore would not lead to unwanted protonation of the quinones.

7.2 Steric Effects of Simple Alcohols

The cyclic voltammograms of AQ and BQ in the two solvents at different concentrations of MeOH are shown in Figures 7.1 and 7.2, respectively, with the initial scans (in dashed lines) acquired in the absence of the alcohol and the subsequent ones (those in solid lines) obtained at their stated MeOH concentrations; the moisture content of the working solution was measured by Karl Fischer titration from an aliquot that was extracted before the addition of MeOH. The cyclic voltammograms of the quinones in the presence of the other alcohols, namely EtOH, *n*-PrOH, *i*-

PrOH, *n*-BuOH, *s*-BuOH, *i*-BuOH and *t*-BuOH, as well as with the fluorinated alcohols and diols are included in Appendix B that can be found at the end of the thesis.

Figure 7.1. Cyclic voltammograms of 2 mM AQ in (a) MeCN and (b) DCM with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of MeOH. The voltammograms were recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of MeOH are indicated in dashed lines with their measured trace moisture content.

Much like the results in Chapter 7, E_{Q1} and E_{Q2} of AQ and BQ in both solvents were seen to shift towards less negative potentials, with a concomitant decrease in ΔE_Q , as the amount of MeOH was increased; this was also observed for the other simple alcohols (see Appendix B). As previously explained, the shifts of E_{Q1} and E_{Q2} to less negative potentials occur because of thermodynamic stabilization, that can be predicted by the Nernst equation, and the increase in the electron affinities of Q and Q^{•-} with extended hydrogen bonding. ΔE_Q decreases because the changes in the electron affinity of the radical anion were almost always much greater than those observed for the neutral compound.

Figure 7.2. Cyclic voltammograms of 2 mM BQ in (a) MeCN and (b) DCM with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of MeOH. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of MeOH are indicated in dashed lines with their measured trace moisture content.

Interestingly, a closer examination of the cyclic voltammograms of both quinones in DCM found that their second 1e^- -reduction process was chemically irreversible at low concentrations of the alcohols, while the chemical and electrochemical reversibility of the same electron-transfer reaction in MeCN was unaffected throughout the experiment. Moreover, an unknown oxidation reaction was detected along the reverse scan at a potential more positive than the first 1e^- -reduction reaction. The chemical reversibility of the second reduction reaction was however regained with increasing amounts of hydrogen donor, to which the unknown oxidation reaction gradually disappeared. This implies that accurate comparisons of the hydrogen donor abilities of the alcohols in DCM can only be performed at concentrations $\geq 0.1 \text{ M}$ where the second 1e^- -reduction process is chemically reversible and the unknown chemicals steps consuming Q^{2-} and leading to the formation of additional electroactive products are suppressed.

The contrasting voltammetric response of the quinones in MeCN and DCM at low moisture concentrations is almost certainly a result of the difference in stability and reactivity of Q^{2-} , which is dependent on the extent of solvation by the solvent molecules and the different amounts and reactivity of trace water in the two solvents. DCM being less polar is expected to be less effective in solvating the reduced quinone forms when compared to MeCN and thus would enhance the reactivity of Q^{2-} . Furthermore, the average concentration of water in the dried MeCN working solutions was measured to be ~ 8.6 mM, which is about three times larger than the amount found in the dried DCM working solutions (~ 2.5 mM). The greater availability of water molecules in MeCN is likely to afford greater kinetic and thermodynamic stability to Q^{2-} through hydrogen bonding and so prevents it from undergoing undesirable side reactions. Smith et al. have verified that hydrogen bonding to water affords kinetic stabilization to Q^{2-} and prevents it from undergoing a nucleophilic reaction with the DCM solvent molecules, which would produce a chloromethyl ether that is responsible for the unknown oxidation process.^[1] It was also noted that the trace water in DCM is more reactive than those found in MeCN even if it exists in a lower quantity because the water-DCM interactions are much weaker than the water-MeCN interactions.^[2] The voltammetric results obtained thus far have led to the conclusion that it is unlikely for Q^{2-} to exist in a non-hydrogen-bonded state in organic solutions even at what is considered to be low moisture conditions, and that a minimum amount of water is needed to stabilize and improve the solubility of Q^{2-} for its existence in DCM at least on the timescale of voltammetry experiments ($\leq$ seconds).

It was observed in Figure 7.3 that ΔE_Q has an inverse relationship with the concentration of the alcohols regardless of the identities of the quinones, alcohols and solvents. The plots were also highly reproducible for most of the alcohols, which was only possible if similar water contents were obtained at the start of each experiment. The poor reproducibility obtained for *t*-BuOH (Figure 7.3d) is likely to be an outcome of its weaker hydrogen donor ability so permitting greater interference from atmospheric moisture. The complete set of plots of ΔE_Q against concentration of the various alcohols from three experiments for both quinones in both solvents are provided in Appendix B.

Figure 7.3. Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of alcohol obtained over three experiments (red +, blue O and black x) as measured by square-wave voltammetry during the reduction of 2 mM quinone with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN/DCM recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

The spread of ΔE_Q for AQ was smaller than that for BQ thereby indicating that the former is a weaker hydrogen acceptor as expected from its greater steric effect and unfavorable electronic effect on the oxygen atoms; the resonance structures bearing a negative charge on the oxygen atoms have lesser contributions to the resonance hybrid because aromaticity in the rings are disrupted. BQ is expected to be the stronger hydrogen acceptor because of its greater basicity (aqueous pK_a values for protonated anthraquinone and benzoquinone are -8.2 and -7, respectively)^[3] and lower steric impediment towards hydrogen bonding.

The spread of ΔE_Q for both quinones was expectedly larger in DCM than in MeCN because the latter has inherent hydrogen acceptor ability and so would form competing alcohol–MeCN solvent interactions.^[2c] More importantly, ΔE_Q was found to be sensitive to the size of the alkyl group at the α -carbon atom and could effectively distinguish between the primary, secondary and tertiary alcohols as seen in the average plots of ΔE_Q against concentration of alcohols for both quinones in the two solvents (Figure 7.4). The individual plots were obtained by fitting a logarithmic best fit line to the results of three combined experiments.

The hydrogen donor ability of the alcohols is apparently inversely proportional to the magnitude of ΔE_Q (when compared at sufficiently high concentrations e.g. ~0.1 M) with the primary alcohols MeOH, EtOH, *n*-PrOH, *n*-BuOH and *i*-BuOH displaying smaller ΔE_Q -values than the secondary alcohols *i*-PrOH and *s*-BuOH and the tertiary alcohol *t*-BuOH. The smallest and largest ΔE_Q -values were rightfully found for MeOH and *t*-BuOH, respectively. The bulky

tert-butyl group prevents *t*-BuOH from coming into close proximity to the quinone and therefore would result in the formation of weaker hydrogen bonding interactions whereas the methyl group offers little disruption and so stronger hydrogen bonds can be made. It was unexpected that ΔE_Q could separate *i*-BuOH, a primary alcohol, from *s*-BuOH and *t*-BuOH thereby suggesting that ΔE_Q had some sensitivity towards the steric effects at the β -carbon. This sensitivity and efficiency in separating the alcohols based on steric effects at the β -carbon is probably only limited to the butyl and heavier classes of alcohols because of the lack of consistency in the ordering of EtOH, *n*-PrOH and *n*-BuOH. It is likely that the characterization of such similarly structured alcohols would require the use of quinones with stronger hydrogen acceptor abilities (an electronic effect) and/or bulky substituents near the carbonyl groups (a steric effect). A comparison of the secondary alcohols indicates that *i*-PrOH is a stronger hydrogen donor than *s*-BuOH.

Figure 7.4. Plots of average $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of MeOH (red solid line), EtOH (blue solid line), *n*-PrOH (green solid line), *i*-PrOH (green dashed line), *n*-BuOH (black solid line), *s*-BuOH (black dashed line), *i*-BuOH (pink solid line) and *t*-BuOH (brown dashed line) as measured by square-wave voltammetry during the reduction of 2 mM quinone with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN/DCM recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

The relative hydrogen bond strengths of the quinone-alcohol hydrogen-bonded complexes were subsequently calculated via the difference in ground state energies of the hydrogen-bonded complex and their constituents (see Section 5.7) to verify the experimental findings, to which the results are given in Tables 7.1 and 7.2 for AQ and BQ, respectively. The distances between the oxygen and hydrogen atoms in the $O_{\text{quinone}} \cdots H_{\text{alcohol}}$ interactions for AQ and BQ are given in Tables 7.3 and 7.4, respectively. In general, the strength of the hydrogen bonds are dependent on the extent of reduction and amount of electron density at the oxygen atoms and so followed the order $Q\text{-alcohol} < Q^{\cdot-}\text{-alcohol} < Q^{2-}\text{-alcohol}$ regardless of the identities of the quinones, alcohols

or solvents; the $O_{\text{Quinone}} \cdots H_{\text{Alcohol}}$ distance correspondingly follows the reverse trend $Q\text{-alcohol} > Q^{\cdot-}\text{-alcohol} > Q^{2-}\text{-alcohol}$. The interactions between the neutral species Q and the alcohols may also be regarded as weak hydrogen bonds whereas those of $Q^{\cdot-}$ and Q^{2-} can be considered as moderate strength (see Section 2.3.1 in Chapter 2). In addition, the hydrogen bonds formed in DCM were shorter and about 0.6 to 4.7 kJ mol⁻¹ stronger than those made in MeCN. An interesting question to pose at this point is whether the weak hydrogen bonding interactions of the neutral quinone should be considered in voltammetric analysis of hydrogen bonds or left ignored.

Table 7.1. Relative hydrogen bond strengths between the alcohols and AQ and its reduced forms in MeCN and DCM.

Alcohol	Relative hydrogen bond strengths (kJ mol ⁻¹)					
	MeCN			DCM		
	Q	Q ^{·-}	Q ²⁻	Q	Q ^{·-}	Q ²⁻
MeOH	-8.93	-20.35	-38.27	-10.24	-22.50	-38.57
EtOH	-8.12	-18.41	-34.73	-9.20	-20.17	-38.47
<i>n</i> -PrOH	-8.62	-18.86	-33.13	-9.54	-21.11	-36.33
<i>i</i> -PrOH	-7.88	-17.44	-33.43	-8.80	-19.39	-34.65
<i>n</i> -BuOH	-8.41	-18.71	-35.76	-9.45	-20.69	-36.38
<i>s</i> -BuOH	-8.37	-18.07	-34.12	-9.31	-19.95	-34.16
<i>i</i> -BuOH	-8.86	-19.13	-35.74	-9.79	-20.98	-36.12
<i>t</i> -BuOH	-7.49	-15.75	-28.78	-8.63	-17.78	-29.27

Table 7.2. Relative hydrogen bond strengths between the alcohols and BQ and its reduced forms in MeCN and DCM.

Alcohol	Relative hydrogen bond strengths (kJ mol ⁻¹)					
	MeCN			DCM		
	Q	Q ^{·-}	Q ²⁻	Q	Q ^{·-}	Q ²⁻
MeOH	-9.09	-22.90	-42.34	-9.90	-25.28	-46.06
EtOH	-7.93	-21.33	-40.27	-8.87	-23.27	-44.11
<i>n</i> -PrOH	-8.64	-21.66	-40.87	-9.58	-23.85	-45.06
<i>i</i> -PrOH	-7.84	-20.15	-38.25	-8.79	-22.60	-42.04
<i>n</i> -BuOH	-8.58	-21.44	-40.32	-9.51	-23.74	-44.97
<i>s</i> -BuOH	-4.83	-16.93	-34.23	-5.81	-18.68	-38.06
<i>i</i> -BuOH	-9.03	-21.92	-40.53	-9.64	-23.85	-44.08
<i>t</i> -BuOH	-7.21	-18.54	-33.57	-8.19	-20.41	-37.59

The relative hydrogen bond strengths of BQ and its $O_{\text{Quinone}} \cdots H_{\text{Alcohol}}$ distances were stronger and shorter than those obtained for AQ and so supports that BQ was by and large the stronger hydrogen acceptor out of the two quinones. As for the alcohols, their calculated hydrogen bond strengths and $O_{\text{Quinone}} \cdots H_{\text{Alcohol}}$ distances were in agreement with the voltammetric results. MeOH was the strongest hydrogen donor among the simple alcohols and was followed in second

by the other primary alcohols; the order of the other primary alcohols was however inconsistent between the two quinones and two solvent conditions. The secondary alcohols *i*-PrOH and *s*-BuOH were next but, unlike the experiments, *s*-BuOH was found to be the stronger hydrogen donor. *t*-BuOH completed the list as the weakest hydrogen donor.

Table 7.3. Calculated $O_{\text{Quinone}} \cdots H_{\text{Alcohol}}$ distance in the various AQ-alcohol hydrogen-bonded complexes in MeCN and DCM.

Alcohol	$O_{\text{Quinone}} \cdots H_{\text{Alcohol}}$ distance (Å)					
	MeCN			DCM		
	Q	Q ^{•-}	Q ²⁻	Q	Q ^{•-}	Q ²⁻
MeOH	1.89	1.73	1.57	1.89	1.73	1.58
EtOH	1.91	1.75	1.58	1.91	1.74	1.57
<i>n</i> -PrOH	1.91	1.75	1.60	1.92	1.74	1.59
<i>i</i> -PrOH	1.92	1.76	1.59	1.92	1.75	1.60
<i>n</i> -BuOH	1.91	1.75	1.58	1.92	1.75	1.60
<i>s</i> -BuOH	1.93	1.76	1.59	1.93	1.76	1.60
<i>i</i> -BuOH	1.91	1.75	1.58	1.91	1.75	1.59
<i>t</i> -BuOH	1.95	1.79	1.62	1.95	1.78	1.63

Table 7.4. Calculated $O_{\text{Quinone}} \cdots H_{\text{Alcohol}}$ distance in the various BQ-alcohol hydrogen-bonded complexes in MeCN and DCM.

Alcohol	$O_{\text{Quinone}} \cdots H_{\text{Alcohol}}$ distance (Å)					
	MeCN			DCM		
	Q	Q ^{•-}	Q ²⁻	Q	Q ^{•-}	Q ²⁻
MeOH	1.92	1.72	1.53	1.92	1.71	1.52
EtOH	1.94	1.73	1.54	1.95	1.73	1.52
<i>n</i> -PrOH	1.94	1.73	1.54	1.94	1.73	1.52
<i>i</i> -PrOH	1.95	1.74	1.56	1.95	1.74	1.54
<i>n</i> -BuOH	1.94	1.73	1.54	1.95	1.73	1.52
<i>s</i> -BuOH	1.95	1.74	1.56	1.95	1.74	1.54
<i>i</i> -BuOH	1.94	1.73	1.54	1.95	1.73	1.53
<i>t</i> -BuOH	1.97	1.77	1.58	1.99	1.76	1.56

It was mentioned in Chapter 2 that dissociation energies are better indicators of the strength of hydrogen bonding than the distance between the hydrogen donor and hydrogen acceptor and the calculations apparently support this. A greater difference was observed among the relative hydrogen bond strengths than among the $O_{\text{Quinone}} \cdots H_{\text{Alcohol}}$ distances.

The results from the theoretical calculations, which took the solvation effects of MeCN and DCM into consideration, are therefore a testament to the accuracy of ΔE_Q as an indicator of the hydrogen donor strengths of the alcohols. It showed that ΔE_Q is sensitive to the steric effects

of both the alcohols and the quinones as well as representative of the environment in which the hydrogen-bonded complex exists. Although they were in general agreement, some deviations between the experimental and calculated results existed because it was not possible to take into account all the other important interactions (such ion pairing with the supporting electrolyte and competing hydrogen bonding interactions to trace water) that would affect the true extent of hydrogen bonding between the alcohols and quinone species. The numerous conformational possibilities also mean that the optimized structures of the hydrogen-bonded complexes may not necessarily correspond to the global energy minima. Hence, the voltammetric method and ΔE_Q might possibly be more accurate in measuring the hydrogen acceptor abilities of the alcohols because the matrix effects are taken into consideration.

7.3 Electronic Effects of Fluorinated Alcohols

The dependence of ΔE_Q on electronic effects of the hydrogen donors was subsequently investigated through the fluorinated alcohols, 2-fluoroethanol (FE), 2,2-difluoroethanol (DFE), 2,2,2-trifluoroethanol (TFE), 3,3,3-trifluoro-*n*-propanol (TFP) and 1,3-difluoroisopropanol (DFIP), whose structures can be found in Figure 5.1 of Chapter 5. These fluorinated alcohols are useful because the presence of the fluorine atoms would greatly polarize the O-H bond yet not impose any considerable steric impediment to hydrogen bonding and so would significantly strengthen the interactions with the quinones and their reduced species.

The electrochemical behavior of the quinones in MeCN with increasing concentrations of the fluorinated alcohols was similar to that observed with the simple alcohols; E_{Q1} and E_{Q2} shifted to less negative potentials with a concomitant decrease in ΔE_Q as the amount of hydrogen donor was increased (see Appendix B for the cyclic voltammograms of AQ and BQ in MeCN at different concentrations of the various fluorinated alcohols). More importantly, it was found that the extent by which ΔE_Q decreases as the concentration of the hydrogen donor was increased is dependent on the degree of fluorination, as depicted in the plots of ΔE_Q versus concentration of the fluorinated derivatives of ethanol (Figures 7.5), and hence ΔE_Q is expectedly also sensitive to electronic effects of the hydrogen donor.

The substitution of a single hydrogen atom with a fluorine atom in EtOH was sufficient to cause the plot of ΔE_Q versus concentration of FE to lie lower than that of MeOH thereby indicating that the fluorinated derivatives of EtOH were stronger hydrogen donors than all of the simple alcohols. In fact, it was only with TFE (at approximately ~ 0.11 M), out of all the alcohols investigated in this study, that the two $1e^-$ -reduction processes of the quinones had merged into a single $2e^-$ -reduction process with Q directly reduced to Q^{2-} . Similar results were also obtained for TFP and DFIP when compared against *n*-PrOH and *i*-PrOH, respectively (see Figure 7.6).

Figure 7.5. Plots of average $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of MeOH (red solid line), EtOH (blue solid line), FE (green solid line), DFE (black solid line) and TFE (pink solid line) as measured by square-wave voltammetry during the reduction of 2 mM (a) AQ and (b) BQ with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure 7.6. Plots of average $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of *n*-PrOH (red solid line), *i*-PrOH (blue solid line), TFP (red dashed line) and DFIP (blue dashed line) as measured by square-wave voltammetry during the reduction of 2 mM (a) AQ and (b) BQ with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Table 7.5. Relative hydrogen bond strengths of the fluorinated alcohols with AQ and BQ in MeCN.

Fluorinated Alcohol	Relative hydrogen bond strengths (kJ mol ⁻¹)					
	Q	AQ Q ⁻	Q ²⁻	Q	BQ Q ⁻	Q ²⁻
FE	-9.91	-22.22	-42.44	-5.18	-21.85	-46.11
DFE	-14.64	-29.64	-54.13	-14.36	-33.22	-61.39
TFE	-16.47	-32.16	-60.59	-16.61	-36.52	-70.59
TFP	-10.81	-23.95	-44.99	-10.71	-27.15	-50.63
DFIP	-13.35	-28.04	-52.47	-5.57	-25.17	-56.13

The hydrogen bond strengths (Table 7.5) and O_{Quinone}...H_{FluorinatedAlcohol} distances (Table 7.6) of the fluorinated alcohols agrees with the electrochemical data that the order of hydrogen donor strengths is FE < TFP < DFIP < DFE < TFE (Figure 7.7). Also indicating that they are

stronger and shorter than their non-fluorinated counterparts and are more significant for BQ than AQ.

Table 7.6. Calculated $O_{\text{Quinone}} \cdots H_{\text{FluorinatedAlcohol}}$ distance in the various AQ-fluorinated alcohol and BQ-fluorinated alcohol hydrogen-bonded complexes in MeCN.

Fluorinated Alcohol	$O_{\text{Quinone}} \cdots H_{\text{FluorinatedAlcohol}}$ distance (Å)					
	Q	AQ			BQ	
		Q^+	$Q^{\cdot+}$	Q^{2-}	Q^+	Q^{2-}
FE	1.87	1.71	1.53	1.89	1.68	1.47
DFE	1.83	1.67	1.48	1.86	1.65	1.42
TFE	1.81	1.64	1.42	1.84	1.62	1.33
TFP	1.87	1.70	1.52	1.89	1.68	1.48
DFIP	1.83	1.67	1.47	1.84	1.63	1.38

Figure 7.7. Plots of average $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of FE (red solid line), DFE (blue solid line), TFE (green solid line), TFP (black solid line) and DFIP (pink solid line) as measured by square-wave voltammetry during the reduction of 2 mM (a) AQ and (b) BQ with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

7.4 The Role of the Additional Hydroxyl Group of Diols

The role of the additional hydroxyl group of the diols ethylene glycol (EG), 1,3-propanediol (PD) and 1,4-butanediol (BD) in hydrogen bonding to the quinones and its effect on ΔE_Q was then investigated in MeCN. The cyclic voltammograms of the quinones in MeCN at different concentrations of the three diols are provided in Appendix B.

The ΔE_Q -values of the diols (from the plots of ΔE_Q against their concentrations in Figure 7.8) were found to be significantly smaller than the ΔE_Q -values of their alcoholic counterparts across the entire concentration range and so indicates that their additional hydroxyl groups are actively engaged in hydrogen bonding, which would be different in the case that the additional hydroxyl group was not participating in any form of hydrogen bonding because the plots of the diols and their related alcohols would overlap.

DFT calculations indicate that each of the different reduced forms (Q , $Q^{\cdot-}$ and Q^{2-}) have preference for the bidentate form of hydrogen bonding (see Appendix B) to all three diols, where a single oxygen atom of the quinone is simultaneously interacting with both hydroxyl groups of the diol, as compared to the normal mode of interaction, where the oxygen atom is only interacting with one hydroxyl group. However, the calculations of the hydrogen bond strengths (Table 7.7) as well as $O_{\text{Quinone}} \cdots H_{\text{Diol}}$ distances (Table 7.8) have also revealed that each hydrogen bond in the bidentate hydrogen-bonded complex was weaker than the normal mode of interaction and the case when two diol molecules are simultaneously interacting to different oxygen atoms of the quinone but through only one of their hydroxyl groups. The differences in interaction energies and $O_{\text{Quinone}} \cdots H_{\text{Diol}}$ distances between the bidentate, single and double normal modes of hydrogen bonding arise from the anticooperativity effects of hydrogen bonding.

The voltammetric results have also indicated that the hydrogen donor abilities of the diols is $EG > PD > BD$. It is likely that the shorter alkyl chain in EG has positioned the second hydroxyl group in closer proximity to the oxygen atom of the quinone to which the stabilization gained from bidentate hydrogen bonding is sufficient to overcome the energy required to distort the diol to assume the bidentate structure and maintain the structural integrity of the quinone-EG

hydrogen-bonded complexes. As for PD and BD, a greater amount of energy is probably required to alter their longer alkyl chains to bring the additional hydroxyl group close to the oxygen atom of the quinone, of which the energy derived from the bidentate form of hydrogen bonding is apparently unable to fully compensate it. Hence, less extensive bidentate hydrogen bonding interactions are formed with the heavier diols.

Figure 7.8. Plots of average $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of EtOH (red solid line), *n*-PrOH (blue solid line), *n*-BuOH (black solid line), EG (red dashed line), PD (blue dashed line) and BD (black dashed line) as measured by square-wave voltammetry during the reduction of 2 mM (a) AQ and (b) BQ with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

There is a possibility that the diols are simultaneously interacting with two quinone molecules and so it might be worthy to investigate the effects of such hydrogen bonding on the electron affinity of the quinones. It was unfortunate that glycerol is immiscible with MeCN and its high viscosity impaired accurate usage with a micropipette and so could not be included into this

study for it would enable other forms of hydrogen bonding as well as the influence of the third hydroxyl group on ΔE_Q to be investigated.

Table 7.7. Relative hydrogen bond strengths of the diols with AQ and BQ in MeCN.

Diol	Relative hydrogen bond strengths (kJ mol ⁻¹)					
	Q	AQ Q ^{•-}	Q ²⁻	Q	BQ Q ^{•-}	Q ²⁻
EG - Normal ^[a]	-9.80	-22.09	-40.97	-9.84	-24.93	-46.38
EG - Bidentate ^[b]	-8.10	-18.79	-33.48	-8.36	-20.34	-38.03
	(-16.19)	(-37.57)	(-66.95)	(-16.71)	(-40.68)	(-76.06)
Two EG ^[c]	-11.48	-21.62	-38.70	-12.11	-24.39	-45.31
	(-22.96)	(-43.23)	(-77.39)	(-24.21)	(-48.78)	(-90.62)
PD - Normal	-8.42	-18.47	-36.13	-8.33	-21.47	-40.01
PD - Bidentate	-5.70	-16.24	-30.08	-6.31	-18.38	-35.13
	(-11.40)	(-32.47)	(-60.16)	(-12.62)	(-36.75)	(-70.26)
Two PD	-7.67	-19.49	-34.57	-7.93	-21.88	-41.66
	(-15.34)	(-38.97)	(-69.14)	(-15.86)	(-43.75)	(-83.31)
BD - Normal	-9.49	-20.05	-36.24	-4.65	-18.35	-36.91
BD - Bidentate	-1.50	-10.40	-23.84	-1.80	-12.51	-27.82
	(-2.99)	(-20.79)	(-47.68)	(-3.59)	(-25.02)	(-55.63)
Two BD	-9.22	-16.73	-34.72	-8.65	-22.10	-24.60
	(-18.43)	(-33.45)	(-69.44)	(-17.30)	(-44.20)	(-49.19)

[a] Diols are engaged in normal hydrogen bonding to the quinones. [b] Diols are engaged in bidentate hydrogen bonding to the quinones. [c] Two diol molecules are individually engaged in normal hydrogen bonding to each oxygen atom of the quinones. The overall interaction energies are reflected in parentheses.

Table 7.8. Calculated O_{Quinone}...H_{Diol} distance in the various AQ-diol and BQ-diol hydrogen-bonded complexes in MeCN.

Diol	O _{Quinone} ...H _{Diol} distance (Å)					
	Q	AQ Q ^{•-}	Q ²⁻	Q	BQ Q ^{•-}	Q ²⁻
EG - Normal ^[a]	1.88	1.71	1.54	1.91	1.70	1.51
EG - Bidentate ^[b]	1.97/1.97	1.78/1.78	1.63/1.65	1.97/1.98	1.76/1.77	1.61/1.62
Two EG ^[c]	1.88/1.97	1.72/1.74	1.56/1.59	1.92/1.93	1.71/1.73	1.52/1.53
PD - Normal	1.91	1.74	1.57	1.93	1.73	1.54
PD - Bidentate	1.98/1.98	1.80/1.80	1.64/1.65	1.99/1.99	1.78/1.78	1.62/1.63
Two PD	1.91/1.93	1.75/1.74	1.59/1.60	1.94/1.95	1.73/1.73	1.54/1.54
BD - Normal	1.91	1.74	1.58	1.93	1.73	1.54
BD - Bidentate	2.10/2.10	1.84/1.84	1.65/1.66	2.05/2.11	1.80/1.83	1.63/1.64
Two BD	1.91/1.94	1.75/1.75	1.59/1.60	1.99/2.03	1.70/1.73	1.05/1.50

[a] Diols are engaged in normal hydrogen bonding to the quinones. [b] Diols are engaged in bidentate hydrogen bonding to the quinones. [c] Two diol molecules are individually engaged in normal hydrogen bonding to each oxygen atom of the quinones.

7.5 Interesting Comparisons

Thus far, we have seen that the ΔE_Q of the quinones offers an accurate and reproducible measure of the relative hydrogen donor abilities of alcohols and diols in aprotic organic solvents. This electrochemical parameter is able to respond accordingly to the surrounding environment, sensitive to both the steric and electronic effects of the alcohols and can differentiate them from diols. The results are also in good agreement with those obtained from theoretical calculations and, in fact, may be more accurate because the effects of solvation, interactions with trace water and ion pairing with the supporting electrolyte are considered.

Nevertheless, revisiting Figure 7.6 and comparing the hydrogen donor abilities within each group of alcohols (non-fluorinated versus fluorinated) will perhaps better illustrate the usefulness of ΔE_Q as a measure of hydrogen bond strengths. In the case of the non-fluorinated alcohols, *n*-PrOH and *i*-PrOH, it is possible to arrive at the conclusion that the secondary alcohol will be a weaker hydrogen donor than the primary alcohol as a result of greater steric impediment and, to some extent, stronger electron-donating inductive effect of the isopropyl group. A similar comparison between TFP and DFIP is however not as simple because the combined electronic effects of the two fluorine atoms in DFIP, which are two bonds away from their hydroxyl group, have to be considered against (i) the larger steric effects of its own isopropyl-like structure, (ii) the combined electronic effects of the three fluorine atoms in TFP, which are three bonds away from their hydroxyl group, and also (iii) the lower steric effects of the *n*-propyl-like backbone in TFP. The ΔE_Q of both quinones, with support from DFT calculations, indicates that DFIP is the stronger hydrogen donor.

It may also be purposeful to extend the current discussion by comparing the hydrogen donor abilities of TFE and EG, which if based solely on theoretical considerations is challenging to perform because of the lack of any grounds for judging the combined electronic effects of the three fluorine atoms in TFE against the availability of the two hydroxyl groups in the diol for hydrogen bonding. Although the calculations indicate that EG would form slightly stronger hydrogen bonds, the comparison of ΔE_Q of both compounds, which we believe is a more accurate

assessment, suggests that TFE is the better hydrogen donor; noting that the merger of the two $1e^-$ -reduction processes for both quinones was only achieved with TFE.

The above examples clearly highlight the value of ΔE_Q as a measure of hydrogen donor ability, especially for situations where there are no common grounds for comparisons.

7.6 Hydrogen Bonding or Proton-Transfer?

It was necessary to verify that the changes in the cyclic voltammograms of the quinones were a result of hydrogen bonding interactions to the alcohols and not a situation of proton-transfer. Hence, the electrochemical response of BQ in the presence of acetic acid and trifluoroacetic acid was investigated and are presented in Figure 7.9.

It was noticed that both the first and second $1e^-$ -reduction processes of BQ were lost in the presence of acetic acid and replaced by a chemically irreversible reduction reaction that was approximately twice the height and occurring at a potential less negative than the initial first $1e^-$ -reduction process. This new reduction reaction progressively shifted to more positive potentials as the concentration of the weak acid was increased. In view of the available aqueous pK_a values of the neutral (-7), radical anion (4) and dianion (11-12) species of BQ and acetic acid (4.76),^[4] this new reduction reaction may then be assigned, as Gupta et al. similarly did,^[5] to the reduction of hydrogen-bonded Q to $Q^{\cdot-}$ with a fast disproportionation reaction to give Q^{2-} that is then protonated to give QH^- . As a consequence of a slow deprotonation step, this QH^- species is then oxidized on the reverse scan and is responsible for the chemically irreversible oxidation reaction occurring at potentials more positive than the oxidation of $Q^{\cdot-}$ to Q.

The electrochemical behavior of BQ in the presence of trifluoroacetic acid was found to be quite similar to that obtained with acetic acid. However, trifluoroacetic acid (aqueous $pK_a = 0.3$) is sufficiently acidic to protonate the radical anion of BQ. The reduction process then follows an ECEC mechanism with QH_2 as the final product.

Nonetheless, it is clear that the results obtained with the acids (at millimolar equivalents) are very different from those observed with the alcohols (at molar concentrations) and so it is highly likely that hydrogen bonding with the alcohols, rather than proton-transfer, are responsible for the changes in the voltammograms of the quinones.

Figure 7.9. Cyclic voltammograms of 2 mM BQ at different concentrations of (a) acetic acid and (b) trifluoroacetic acid with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the acids are indicated in dashed lines.

7.7 Summary

The results presented in this chapter of the thesis are sufficient to conclude that the $\Delta E_Q = |E_{Q1} - E_{Q2}|$ of the quinones can effectively serve as a measure of the hydrogen donor abilities of compounds like alcohols in non-aqueous solvents. This electrochemical parameter offers qualitative and useful results that are highly accurate and reproducible provided that the interference from trace water in the solvent is minimized. ΔE_Q is also easy to obtain and is unaffected by uncompensated solution resistance, the condition of the working electrode surface, migration effects, the heterogeneous electron transfer rate and drifts in the liquid-junction potential of the reference electrode.

This procedure to determine hydrogen bond strengths of hydrogen donors is unfortunately unable to provide quantitative data, such as formation constants and the number of hydrogen donors involved in the hydrogen-bonded complex, that will have to be obtained with available working models (see Section 2.3.2 in Chapter 2); a universal standard may also be required to enable easy comparisons. Lastly, this technique is not applicable for very strong hydrogen donors that might lead to the possible protonation of $Q^{\cdot-}$ and Q^{2-} and loss of the EE reduction behavior. The unwanted protonation may however be somewhat addressed by changing the basicity and hydrogen acceptor ability of the quinones through structural modifications.

Notes

The cyclic voltammograms of the quinones in the presence of the simple alcohols, fluorinated alcohols and diols are provided in Appendix B along with their plots of ΔE_Q against concentration of the simple alcohols in both solvents. The Cartesian coordinates and visualizations of the optimized geometries of the various hydrogen-bonded complexes are also included.

References

- [1] P. A. Staley, E. M. Lopez, L. A. Clare, D. K. Smith, *J. Phys. Chem. C* **2015**, *119*, 20319-20327.
- [2] (a) Y. Hui, E. L. K. Chng, C. Y. L. Chng, H. L. Poh, R. D. Webster, *J. Am. Chem. Soc.* **2009**, *131*, 1523-1534; (b) Y. Hui, E. L. K. Chng, L. P.-L. Chua, W. Z. Liu, R. D. Webster, *Anal. Chem.* **2010**, *82*, 1928-1934; (c) J.-Y. Le Questel, M. Berthelot, C. Laurence, *J. Phys. Org. Chem.* **2000**, *13*, 347-358.
- [3] (a) J. Q. Chambers, In *The Chemistry of the Quinonoid Compounds*; S. Patai, Z. Rappoport, Eds.; Wiley, New York, **1988**; Vol. II, Chapter 12, pp 719-757; (b) E. Laviron, *J. Electroanal. Chem.* **1984**, *164*, 213-227; (c) Q. Zhao, H. Wang, H. Zheng, Z. Sun, W. Shi, S. Wang, X. Wang, Z. Jiang, *Catal. Sci. Technol.* **2013**, *3*, 2004-2209.

- [4] A. J. Swallow in *Function of Quinones in Energy Conserving Systems*. B. L. Trumpower, Ed. Academic Press: New York, **1982**, p. 66.
- [5] N. Gupta, H. Linschitz, *J. Am. Chem. Soc.* **1997**, *119*, 6384-6391.

Chapter 8

Measuring the Relative Basicity and Hydrogen Acceptor Strengths of Pyridine and Its Derivatives in Aprotic Organic Solvents via the Voltammetry of Phenylenediamines

8.1 *Introduction*

8.2 *Hydrogen Bonding or Proton-Transfer?*

8.2.1 *Hydrogen bonding or deprotonation?*

8.2.2 *Hydrogen bonding or protonation?*

8.3 *Measuring the Relative Basicity and Hydrogen Acceptor Abilities of Pyridine and Its Derivatives*

8.3.1 *Steric and electronic effects of pyridine and its derivatives*

8.3.2 *Mesomeric and ring effects of quinoline and isoquinoline*

8.3.3 *Presence of two heteroatoms: The diazines and bipyridyls*

8.3.4 *Interesting comparisons*

8.3.5 *Pi-stacking effects*

8.3.6 *Oxygen and sulfur heterocycles*

8.4 *Measuring the Hydrogen Donor and Acceptor Abilities of Alcohols and Diols*

8.4.1 *The effect of the simple alcohols on the electrochemical behavior of TMPD*

8.4.2 *The effect of the diols on the voltammetric behavior of TMPD*

8.4.3 *The effect of trifluoroethanol and acetic acid on the electrochemical behavior of TMPD*

8.5 *Summary*

Notes

References

This page has been intentionally left blank

8.1 Introduction

This chapter investigates the efficacy of the voltammetric behavior of phenylenediamines and their electrochemical parameter $\Delta E_p = |E_{p1} - E_{p2}|$ for measuring basicity and the hydrogen acceptor ability of pyridine and its derivatives. We postulate that their standard EE electrochemical behavior would be retained in the presence of hydrogen acceptors but lost in the case of both weak and strong bases. In this work, very weak bases that do not undergo any proton-transfer reactions with P, P^{*+} and P^{2+} are considered as hydrogen acceptors of which E_{p1} and E_{p2} would progressively shift towards less positive potentials with increasing concentrations of the hydrogen acceptor. ΔE_p would concomitantly decrease because the changes in E_{p2} and the ionization energy of P^{*+} are more sensitive to the effects of hydrogen bonding than the changes in E_{p1} and ionization energy of P. But the overall EE oxidation mechanism as well as the chemical and electrochemical reversibility of both $1e^-$ -oxidation processes would be unaffected. The bases, on the other hand, may compromise the chemical reversibility of the second and/or first $1e^-$ -oxidation process depending if P^{*+} (in the case of strong bases) or P^{2+} (for weak bases) is deprotonated. Hence, we propose to use changes in the overall voltammetric behavior of the phenylenediamines to differentiate between a base and a hydrogen acceptor and the magnitude of ΔE_p to determine basicity and hydrogen acceptor ability.

It is also our interest to explore the efficacy of ΔE_p for measuring hydrogen donor ability because the neutral compound was found to function predominantly as a hydrogen acceptor. The alcohols studied in the previous chapter would be re-employed for this part of the study. In this role, E_{p1} would shift to more positive potentials with increasing concentrations and binding ability of the hydrogen donor because of the increase in ionization energy of P, while E_{p2} would be unaffected owing to the lack of any lone electron pairs on the nitrogen atoms in the P^{2+} state and so minimal changes, if any, to the ionization energy of P^{*+} are expected. Therefore, ΔE_p would also decrease with increasing amounts of hydrogen donor.

8.2 Hydrogen Bonding or Proton-Transfer?

As with the quinones, it is important that the effects of proton-transfer are distinguished from hydrogen bonding to ensure the validity of the studies and accuracy of the measurements. Therefore, cyclic voltammetry experiments for 2,3,5,6-tetramethyl-1,4-phenylenediamine (TMPD) in the presence of pyridine (Py) and the strong base tetra-*n*-butylammonium hydroxide (*n*-Bu₄NOH) as well as MeOH (a hydrogen donor) and the acids acetic acid, trifluoroacetic acid (TFA) and perchloric acid (HClO₄) were conducted and compared. The various protonated, deprotonated and oxidation states of TMPD along with their reported aqueous pK_a values are shown in Scheme 8.1 together with the pK_a values of pyridinium, MeOH, and the acids.^[1]

Scheme 8.1. Nine-membered “parallelogram scheme” representing possible electron-transfer and proton-transfer reactions for TMPD.

8.2.1 Hydrogen bonding or deprotonation?

The cyclic voltammograms of TMPD at different concentrations of pyridine are shown in Figure 8.1a where a third chemically reversible oxidation process at E_{P3} ($\sim +0.65$ V vs. reference electrode) was detected at sub-stoichiometric concentrations at the expense of the second $1e^-$ -oxidation process but without any effect on the first. The occurrence of this new oxidation process at 250 mV negative of E_{P2} is indicative that a species more easily oxidizable than P^{*+} and stable on the voltammetric timescale ($\leq$ seconds) is existing in solution. This new oxidation process should not be related to the oxidation of the quinoneimine radical to the quinoneimine cation because pyridine (aqueous pK_a value of pyridinium is 5.1) is unable to deprotonate P^{*+} (aqueous pK_a value of 12) in aqueous conditions and so is also unlikely to do the same under organic conditions. Instead, it is more likely that the third oxidation process represents the conversion of P^{*+} to P^{2+} with strong hydrogen bonding between P^{2+} and pyridine. It is also possible that a proton-transfer reaction between P^{2+} and pyridine follows after the electron-transfer reaction to give the quinonediimine cation and pyridinium that may be held together by hydrogen bonding interactions. The rate of proton-transfer between P^{2+} and pyridine would have to be fast to maintain the chemical reversibility of the newly detected oxidation process.

This third oxidation process was also found to shift to less positive potentials with increasing amounts of pyridine and eventually merged with the first $1e^-$ -oxidation process (which was unchanged in its position and chemical reversibility throughout the experiment) at about 200 equivalents (200 mM) to give a single chemically reversible oxidation process. The shifts of E_{P3} suggests that strong hydrogen bonding between P^{2+} and pyridine or the quinonediimine cation and pyridinium are occurring while the lack of any changes to the position and chemical reversibility of the first oxidation process is supportive that P and P^{*+} are not deprotonated and indicative that any hydrogen bonding interactions between pyridine and P or P^{*+} are weak. The computational results in Chapter 6 have revealed that the neutral compound of TMPD has a greater tendency to function as a hydrogen acceptor and so may explain why the first $1e^-$ -oxidation process is seemingly unaffected by the presence of pyridine.

Figure 8.1. Cyclic voltammograms of 1 mM TMPD at different concentrations of (a) pyridine and (b) *n*-Bu₄NOH with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the bases are indicated in dashed lines with their measured trace moisture content.

The new oxidation process, obtained from the merger of the first and third oxidation processes, was twice in height of the initial first 1e⁻-oxidation reaction (e.g. $i_p^{\text{ox}} \approx 2 \times i_p^{\text{ox}(1)}$) as well as approximately equal to the sum of the initial two 1e⁻-oxidation processes (e.g. $i_p^{\text{ox}} \approx i_p^{\text{ox}(1)} + i_p^{\text{ox}(2)}$) thereby indicating that it is likely to involve the transfer of two electrons per molecule of TMPD and may represent either the 2e⁻-oxidation of P to P²⁺ in the case of hydrogen bonding, or the -2e⁻/-H⁺-oxidation to the quinoneimine cation via the EEC mechanism in the event of proton-transfer.

It is presently unclear if hydrogen bonding or a proton-transfer reaction has occurred between pyridine and P²⁺. But the voltammetric response of the phenylenediamine can still be applied to assess the extent of interaction of the various pyridine derivatives and differentiate hydrogen acceptors and bases because the resulting oxidation processes are chemically reversible. Even so, a reference compound would be required because the measurements only yield

qualitative results. As pyridine is generally regarded as a weak base therefore any of its derivatives that bring about the third oxidation process at sub-stoichiometric concentrations would also be regarded as weak bases. On the other hand, the derivatives would be considered as hydrogen acceptors (very weak bases) if they do not alter the standard EE oxidation behavior and no additional oxidation processes other than the $1e^-$ -oxidation reactions of P to $P^{\bullet+}$ and $P^{\bullet+}$ to P^{2+} are detected across the studied concentration range.

The measurement of hydrogen acceptor ability would proceed via the electrochemical parameter $\Delta E_p = |E_{p1} - E_{p2}|$ with the magnitude inversely proportional to the strength of the interaction. As for bases, their strengths can be ranked by comparing their values of $\Delta E_p = |E_{p1} - E_{p3}|$ across their concentrations. If needed, the concentration at which a single chemically reversible oxidation process is obtained as well as the observation of any deprotonation features at high concentrations of the base (defined as 200 mM in this study) would then be used to further distinguish them.

It is important to highlight that the voltammetric behavior of TMPD is more complex than its isomeric counterpart *N,N,N',N'*-tetramethyl-1,4-phenylenediamine (NTMPD). Smith et al. have found that a mixed valent hydrogen-bonded dimer is the kinetic product of the first $1e^-$ -oxidation reaction, whereas the radical cation $P^{\bullet+}$ is the thermodynamically favored product that is oxidized to the quinonediimine dication P^{2+} in the second $1e^-$ -oxidation process.^[1c]

The effect of *n*-Bu₄NOH on the voltammetry of TMPD is shown in Figure 8.1b where it can be seen that both the first and second $1e^-$ -oxidation processes are affected by its presence. *n*-Bu₄NOH may thus be classified as a strong base, that is, one that can deprotonate the radical cation $P^{\bullet+}$ of TMPD at sub-stoichiometric concentrations.

8.2.2 Hydrogen bonding or protonation?

Our density functional theory (DFT) calculations in Chapter 6 have found that the neutral form of TMPD preferably functions as a hydrogen acceptor and so suggests that its electrochemical behavior may be used to measure hydrogen donor strengths. Hence, in the presence of a hydrogen donor, it is likely that E_{p1} would shift to more positive potentials whereas E_{p2} would remain unaffected because the quinonediimine dication can only serve as a hydrogen donor. The voltammetric response of TMPD at different concentrations of MeOH was subsequently investigated and are presented in Figure 8.2 to which a number of similarities to the response with water are recognized.

Figure 8.2. Cyclic voltammograms of 1 mM TMPD at different concentrations of MeOH with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that was acquired before the introduction of MeOH is indicated in dashed line with its measured trace moisture content.

E_{p1} and E_{p2} were found to shift towards less positive potentials, rather than to more positive potentials, without any loss in the chemical reversibility of both 1e⁻-oxidation processes as the concentration of MeOH was increased. It was noted that a significant amount of the alcohol

was needed to elicit observable shifts and that both oxidation processes remained separated ($\Delta E_p = |E_{p1} - E_{p2}| = 380 \text{ mV}$) even after 7 M of MeOH was present. These results suggest that the interactions between MeOH and the various oxidized states of TMPD are weak. In addition, the hydrogen donor abilities of P^{++} and P^{2+} were apparently stronger and dominating the hydrogen acceptor role of P. Therefore, the changes in the electrochemical behavior of TMPD were arising from the alcohol functioning as a hydrogen acceptor rather than a hydrogen donor, which is surprising and unexpected because MeOH is a relatively weak hydrogen donor and even weaker hydrogen acceptor. Hence, it appears that the ability of TMPD to measure relative hydrogen donor strengths may be limited to only strong hydrogen donors such as the fluorinated alcohols and weak carboxylic acids and that the assessment of the hydrogen donor abilities of the simple alcohols may require a phenylenediamine such as NTMPD that can only function as a hydrogen acceptor.

The electrochemical response of TMPD in MeCN to increasing amounts of the simple alcohols as well as water (in Chapter 6) was confirmed to be a consequence of hydrogen bonding and not proton-transfer through experiments with acetic acid, TFA and HClO_4 as shown in Figure 8.3. Acetic acid, the weakest acid in the series with an aqueous pK_a value of 4.76, would be sufficiently acidic to protonate the neutral species to give PH^+ yet no changes were observed in the electrochemical response even after ten equivalents had been added. This apparent inactivity can be explained by the relative acidities of acetic acid and PH^+ in water and an organic solvent such as MeCN. Acetate, the conjugate base of acetic acid, is charged and so would be better stabilized in water as compared to the less polar environment of MeCN, which is unlike the case for P, the conjugate base of PH^+ , which is better stabilized in the organic solvent. Therefore, even though the aqueous pK_a values suggest that acetic acid is a stronger acid than PH^+ in water, the reverse order should in fact be expected in MeCN, that is, acetic acid should be a weaker acid than PH^+ and thus is unable to protonate the neutral phenylenediamine species. Still it was surprising that acetic acid did not show any hydrogen bonding effects on the electrochemical behavior of the phenylenediamine by functioning as a hydrogen donor through the hydrogen atom of its carboxyl group or as a hydrogen acceptor through either one of its oxygen atoms. It was believed and put

forward by Smith et al. that self hydrogen bonding interactions are preventing acetic acid from interacting with the phenylenediamine.^[2]

Figure 8.3. Cyclic voltammograms of 1 mM TMPD in the presence of (a) acetic acid, (b) TFA and (c) HClO₄ with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode.

In the presence of TFA, the first $1e^-$ -oxidation reaction of P to P^{*+} was lost and replaced by a new oxidation reaction at a more positive potential that is suspected to involve the conversion of PH^+ to PH^{*2+} . This is a reasonable deduction given that TFA (aqueous pK_a value of 0.5) appears to be sufficiently acidic, after taking into consideration the effect of the organic solvent, to protonate the neutral phenylenediamine. The second $1e^-$ -oxidation reaction of P^{*+} to P^{2+} was however not inhibited by the presence of the acid probably because of the fast deprotonation of PH^{*2+} to P^{*+} . $HClO_4$, the strongest acid in the series, is capable of protonating the neutral phenylenediamine as well as its conjugate acid PH^+ to give the electroinactive doubly protonated phenylenediamine dication (PH_2^{2+}) and so two equivalents of it are sufficient to render the loss of the electrochemical signal.

Hence, the replacements of the first $1e^-$ -oxidation process with one occurring at a more positive potential or the loss of electrochemical activity are signs of protonation of TMPD.

8.3 Measuring the Relative Basicity and Hydrogen Acceptor Abilities of Pyridine and Its Derivatives

Our study subsequently focused on utilizing the voltammetric data of TMPD to determine the relative basicity and hydrogen acceptor abilities of several derivatives of pyridine in MeCN based on the guidelines listed in Section 8.2.1. A diverse series was selected to cover the possible influence from steric and electronic effects, mesomeric and ring donating effects, the presence of two heteroatoms, positional isomerism and the bidentate mode of interaction. The structures of the derivatives can be found in Figure 5.1 of Chapter 5.

8.3.1 Steric and electronic effects of pyridine and its derivatives

The cyclic voltammograms of TMPD at different concentrations of 2-picoline, 2,6-lutidine and 2,6-di-*tert*-butylpyridine are shown in Figures 8.4 and 8.5, respectively. In the case of 2-picoline and 2,6-lutidine (Figure 8.4), it can be seen that the addition of sub-stoichiometric amounts would bring about effects similar to those obtained with pyridine. That is, a third oxidation process appeared at the expense of the second $1e^-$ -oxidation reaction at potential E_{P3}

($\sim +0.6$ V vs. reference electrode) between E_{P1} and E_{P2} . After which, further increments of either additive would see the disappearance of the second $1e^-$ -oxidation process with a concomitant development of the third oxidation reaction as well as shifting of the third oxidation reaction towards less positive potentials. The third oxidation reaction eventually merged with the first $1e^-$ -oxidation process, which was unaffected throughout the experiment, to give one chemically reversible oxidation process at approximately 5 mM and 20 mM of 2,6-lutidine and 2-picoline, respectively. Subsequent increments of either additive would then result in the shifting of the oxidation process towards less positive potentials with some signs of deprotonation detected (e.g. a loss in chemical reversibility or occurrence of a shoulder peak at less positive potentials). Both additives can therefore be classified as bases that are stronger than pyridine because of the observation of deprotonation effects at high concentrations (200 mM).

Figure 8.4. Cyclic voltammograms of 1 mM TMPD at different concentrations of (a) 2-picoline and (b) 2,6-lutidine with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the additives are indicated in dashed lines with their measured trace moisture content.

2,6-Di-*tert*-butylpyridine, on the other hand, in Figure 8.5 gave a rather subdued effect on the voltammetric behavior of TMPD by gradually shifting E_{P2} towards less positive potentials as its concentration was increased without the occurrence of a third oxidation process nor shifting of E_{P1} . The two oxidation processes were also found to remain separated by about 150 mV at 200 mM of the additive. Thus, 2,6-di-*tert*-butylpyridine may be considered as a hydrogen acceptor.

Figure 8.5. Cyclic voltammograms of 1 mM TMPD at different concentrations of 2,6-di-*tert*-butylpyridine with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that was acquired before the introduction of 2,6-di-*tert*-butylpyridine is indicated in dashed line with its measured trace moisture content.

If based on steric considerations alone, one might expect the binding abilities of the additives to follow the trend: 2-picoline > 2,6-lutidine > 2,6-di-*tert*-butylpyridine, that is opposite to the order that would be expected for pure electronic considerations: 2-picoline < 2,6-lutidine < 2,6-di-*tert*-butylpyridine. The electrochemical results of TMPD however indicate that the hydrogen acceptor ability of 2,6-lutidine is so strong that it functions as a base towards P^{2+} instead of a hydrogen acceptor whereas 2,6-di-*tert*-butylpyridine is purely a hydrogen acceptor. These

findings can be understood by considering both the steric and electronic effects of the three additives as well as the ease of their approach to the phenylenediamine for hydrogen bonding.

The nitrogen atom of 2,6-lutidine carries a greater electron density than that found in 2-picoline as a result of the additional methyl group at the 6-position and the general electron-donating inductive effect of alkyl groups. Thus, it is expected to be a better hydrogen acceptor and base than 2-picoline. Yet, the presence of the additional methyl group would also impose a greater steric impediment for 2,6-lutidine to approach TMPD that should then result in it being a poorer hydrogen acceptor and base. However, this would only be true if the phenylenediamine and additives are approaching in a manner that has their rings coplanar to each other so that their methyl substituents encounter each other head-on as seen in Figure 8.6. The significance of the steric repulsion between the two sets of methyl groups would be reduced if the phenylenediamine and the additives are interacting in an orthogonal fashion.

Figure 8.6. Co-planar (left) and orthogonal (right) approaches to hydrogen bond formation.

However, this does not apply to 2,6-di-*tert*-butylpyridine, probably because the steric repulsion arising from its *tert*-butyl groups with the methyl groups of the phenylenediamine are similar in the co-planar and orthogonal approaches and so their steric effects outweigh their electronic contributions. DFT calculations for the hydrogen-bonded complexes of TMPD and its oxidized forms (P^{+} and P^{2+}) with 2-picoline and 2,6-lutidine support the preference for the orthogonal arrangement (see Appendix C).

The relative interaction energies of pyridine, 2-picoline, 2,6-lutidine and 2,6-di-*tert*-butylpyridine with TMPD shown in Table 8.1 do not entirely agree with the electrochemical findings. The interaction energies of pyridine, 2-picoline and 2,6-lutidine with the various

oxidized states of the phenylenediamine were found to be negative, so indicating that the formation of the hydrogen-bonded complexes is spontaneous, and the magnitude expectedly increases from P to P^{2+} in line with the greater hydrogen donor ability of the dication. On the other hand, the interaction energies of 2,6-di-*tert*-butylpyridine were not only positive, thereby indicating that the formation of the hydrogen-bonded complexes are not favorable, but also increasing from P to P^{2+} and so indicates that more energy is needed for it to interact with the higher oxidized states of TMPD. The calculations apparently suggest that the hydrogen-bonded complexes formed between 2,6-di-*tert*-butylpyridine and the various oxidized forms of TMPD are unstable. Yet, E_{P2} was observed to shift by about 100 mV at sub-stoichiometric concentrations of 2,6-di-*tert*-butylpyridine. The calculations also suggest that the order of hydrogen acceptor ability and basicity is 2,6-lutidine < 2-picoline < pyridine that is unlike the trend obtained from the experimental data.

Table 8.1. Relative interaction energies of pyridine, 2-picoline, 2,6-lutidine and 2,6-di-*tert*-butylpyridine with TMPD in MeCN.

Oxidation state	Relative interaction energies (kJ mol ⁻¹)			
	Pyridine	2-Picoline	2,6-Lutidine	2,6-Di- <i>tert</i> -butylpyridine
P	-4.17	-3.57	-1.66	3.04
P ^{•+}	-15.19	-14.28	-11.59	3.88
P ²⁺	-37.16	-35.24	-30.41	7.77

One possible explanation for the disagreement between the calculated and experimental results could be the failure of accounting for some important interactions such as the trace water-phenylenediamine interactions, which are present in the actual experiments and may have some significance, as well as solvation effects and ion pairing with the supporting electrolyte that might be critical for the phenylenediamine and its oxidized forms. Also, any interactions between the additives and trace water in the organic solvent would certainly reduce their binding ability with the phenylenediamine. Thus, it was necessary to measure and report the moisture content of the working solutions and to perform the electrochemical experiments with minimum interference from trace water that is present in the solvent as well as that absorbed from the atmosphere over the course of the experiment. The electrochemical results were found to be highly reproducible across different experiments.

Both 3-picoline and 4-picoline were found to affect the electrochemical behavior of TMPD in the same way that 2-picoline did and so can be regarded as stronger bases than pyridine. The electrochemical data also indicates that 2-picoline and 3-picoline are correspondingly the strongest and weakest bases among the picolines through the observations that only 2-picoline exhibited deprotonation effects at high concentrations, and that the $\Delta E_p = |E_{p1} - E_{p3}|$ value of 3-picoline was consistently the largest among the three positional isomers across the entire concentration range. The cyclic voltammograms of TMPD at different concentrations of 3-picoline and 4-picoline are shown in Figure 8.7.

Figure 8.7. Cyclic voltammograms of 1 mM TMPD at different concentrations of (a) 3-picoline and (b) 4-picoline with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the picolines are indicated in dashed lines with their measured trace moisture content.

The greater hydrogen acceptor ability and basicity of 2-picoline and 4-picoline over 3-picoline can be partially explained through stabilization of the different mesomeric structures via the electron-donating inductive effect of the methyl group (Figure 8.8). The methyl groups in 2-picoline and 4-picoline are well positioned to stabilize the partially positively charged carbon

atoms that come about because of the greater electronegativity of the nitrogen atom, thereby rendering those resonance structures greater contribution to the final resonance hybrid. On the other hand, the methyl group in 3-picoline is unable to stabilize the partially positively charged carbon atom and so its resonance structures with a partially negatively charged nitrogen atom would not significantly contribute to the final resonance hybrid.

Figure 8.8. Resonance structures of the different picolines.

2-Picoline is a stronger base than 4-picoline probably because the electronic effect of its methyl group has outweighed its own steric effect as a result of the orthogonal approach. Although it imposes lesser steric effects by virtue of its position, the methyl group in 4-picoline is nonetheless further from the nitrogen atom than the methyl group in 2-picoline and so its electron-donating inductive effect will be reduced.

DFT calculations were performed for the neutral, radical cationic and dicationic picoline-phenylenediamine hydrogen-bonded complexes for which the interaction energies and distances between the hydrogen and nitrogen atoms in their $\text{H}_{\text{TMPD}} \cdots \text{N}_{\text{picoline}}$ interactions are tabulated in Tables 8.2 and 8.3, respectively. The magnitudes of the interaction energies of the picolines were found, as expected, to increase from P to P^{2+} in line with the greater hydrogen donor ability of the dication while the $\text{H}_{\text{TMPD}} \cdots \text{N}_{\text{picoline}}$ interactions became progressively shorter so supporting that hydrogen bonding of the picolines to the dication are the strongest and weakest to the neutral species. Interestingly, it was found that the relative hydrogen acceptor strengths followed the order 4-picoline < 3-picoline < 2-picoline while the distance between the hydrogen and nitrogen

atoms in $H_{\text{TMPD}} \cdots N_{\text{picoline}}$ interactions were the shortest in 4-picoline and longest in 2-picoline as opposed to the electrochemical findings. This as explained earlier may be due to the lack of consideration of the other important interactions in the calculations.

Table 8.2. Relative interaction energies of the picolines and (trifluoromethyl)pyridines with TMPD in MeCN.

Oxidation state	Relative interaction energies (kJ mol ⁻¹)					
	2-Picoline	3-Picoline	4-Picoline	2-CF ₃ -Py	3-CF ₃ -Py	4-CF ₃ -Py
P	-3.57	-3.83	-3.70	-2.98	-3.50	-3.40
P ^{•+}	-14.28	-16.14	-16.41	-10.12	-13.11	-13.08
P ²⁺	-35.24	-39.06	-41.12	-22.32	-29.31	-29.56

Table 8.3. Calculated $H_{\text{TMPD}} \cdots N_{\text{picoline}}$ distance of the various picolines and (trifluoromethyl)pyridines TMPD-hydrogen-bonded complexes in MeCN.

Oxidation state	$H_{\text{TMPD}} \cdots N_{\text{picoline}}$ distance (Å)					
	2-Picoline	3-Picoline	4-Picoline	2-CF ₃ -Py	3-CF ₃ -Py	4-CF ₃ -Py
P	2.23	2.26	2.26	2.38	2.30	2.30
P ^{•+}	1.99	1.96	1.95	2.10	2.01	2.01
P ²⁺	1.65	1.61	1.58	1.84	1.74	1.73

The (trifluoromethyl)pyridines were then investigated for which the cyclic voltammograms for 2-(trifluoromethyl)pyridine (2-CF₃-Py) (Figure 8.9), 3-(trifluoromethyl)pyridine (3-CF₃-Py) (Figure 8.10) and 4-(trifluoromethyl)pyridine (Figure 8.9) did not show the occurrence of the third oxidation process at sub-stoichiometric concentrations, so assigning them as hydrogen acceptors. This is unsurprising because the trifluoromethyl group exerts an electron-withdrawing inductive effect and reduces the electron density of the nitrogen atom in each substituted pyridine therefore weakening their interaction energies (Table 8.2) and lengthening their $H_{\text{TMPD}} \cdots N_{\text{picoline}}$ distances (Table 8.3) when compared to the picolines. The order of the hydrogen acceptor ability was determined to be 4-CF₃-Py > 3-CF₃-Py >> 2-CF₃-Py through the plots of $\Delta E_p = |E_{p1} - E_{p2}|$ against concentration (Figure 8.11).

2-CF₃-Py is the weakest hydrogen acceptor because its trifluoromethyl group is closest to the nitrogen atom of the pyridine ring and so both the steric and electron-withdrawing inductive effects are more extensive than that exerted by the trifluoromethyl groups of 3-CF₃-Py and 4-CF₃-Py. Furthermore, mesomeric effects will assign a partial positive charge on the carbon atoms that

are directly bonded to the trifluoromethyl groups in 2-CF₃-Py and 4-CF₃-Py and so destabilizes that resonance structure, unlike the case for 3-CF₃-Py where the trifluoromethyl group exerts a stabilizing effect and so the resonance structure (with a partial negative charge on the nitrogen atom) will have greater contributions to the resonance hybrid. The important resonance structures of the (trifluoromethyl)pyridines are shown in Figure 8.12.

Figure 8.9. Cyclic voltammograms of 1 mM TMPD at different concentrations of (a) 2-CF₃-Py and (b) 4-CF₃-Py with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the additives are indicated in dashed lines with their measured trace moisture content.

Both the electron-withdrawing inductive effect and steric effect of the trifluoromethyl group in 4-CF₃-Py is decreased by virtue of its position as compared to that borne in 3-CF₃-Py and so explains why the former is a stronger hydrogen acceptor than the latter. The experimental results and theoretical calculations also suggest that the inductive effects are more significant than the mesomeric effects as purely mesomeric considerations would result in 3-CF₃-Py being a stronger hydrogen acceptor than 4-CF₃-Py.

In summary, the basicity and hydrogen acceptor abilities of the compounds studied in this section can first be determined based on the presence of a third oxidation process at sub-stoichiometric concentrations, which would be observed in the presence of a base and absent in the case of hydrogen acceptors. As for the bases (that can also be considered as strong hydrogen acceptors), their relative basicity (as well as hydrogen acceptor ability) can be differentiated via the plots of $\Delta E_p = |E_{p1} - E_{p3}|$ against concentration (0.25 to 200 mM) and also the concentration at which a single chemically reversible oxidation process is obtained from the merger of the first and third oxidation reactions. If required, the observation of deprotonation effects at high concentrations of the additives (200 mM) can also be used. As for the hydrogen acceptors, their binding abilities are determined through their plots of $\Delta E_p = |E_{p1} - E_{p2}|$ against concentration for which the ΔE_p -value at a given concentration is inversely proportional to the strength of the hydrogen bond.

Figure 8.10. Cyclic voltammograms of 1 mM TMPD at different concentrations of 3-CF₃-Py with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that was acquired before the introduction of the additive is indicated in dashed line with its measured trace moisture content.

Figure 8.11. Plots of $\Delta E_p = |E_{p1} - E_{p2}|$ against concentration of the 2- CF_3 -Py (red solid line), 3- CF_3 -Py (blue solid line) and 4- CF_3 -Py (black solid line) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at $25 \pm 2^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure 8.12. Resonance structures of the different (trifluoromethyl)pyridines.

The order of the pyridine derivatives based on their basicity/hydrogen acceptor strengths is: 2,6-lutidine > 2-picoline > 4-picoline > 3-picoline > pyridine > 2,6-di-*tert*-butylpyridine > 4- CF_3 -Py > 3- CF_3 -Py >> 2- CF_3 -Py.

8.3.2 Mesomeric and ring effects of quinoline and isoquinoline

The sensitivity of the electrochemical response of TMPD to mesomeric and fused ring effects was subsequently explored with quinoline and its isomer isoquinoline (that can be considered as nitrogen analogs of naphthalene). It was unfortunate that acridine and phenanthrenedine (in what are nitrogen analogs of anthracene) were insoluble in MeCN and so were not included in the study. The cyclic voltammograms of TMPD at different concentrations of quinoline and isoquinoline are shown in Figure 8.13 to which both quinoline and isoquinoline gave a third oxidation process and so can be considered as bases.

Figure 8.13. Cyclic voltammograms of 1 mM TMPD at different concentrations of (a) quinoline and (b) isoquinoline with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the additives are indicated in dashed line with their measured trace moisture content.

The results indicate that quinoline is a weaker base than isoquinoline (and even pyridine), as supported by the literature,^[3] because the first and third oxidation processes of TMPD remained separated at 200 mM of the base, whereas a single chemically reversible oxidation process was found for the same concentration of isoquinoline. The weaker basicity of quinoline is most likely

a consequence of the steric effects from the adjacent ring as well as the *peri* hydrogen that prevents it from coming into close proximity with the phenylenediamine rather than electronic effects because both quinoline and isoquinoline have the same number of resonance structures to accommodate and spread the partial positive charge that arises from the greater electronegativity of the nitrogen atom.^[4] Isoquinoline probably approaches TMPD in a similar way that pyridine does, with lesser steric impediment than that encountered by quinoline, for the reason that its adjacent ring is positioned on the side “opposite” to the nitrogen atom.

The plots of $\Delta E_p = |E_{P1} - E_{P3}|$ against concentration of pyridine and isoquinoline (Figure 8.14) indicates that isoquinoline is a stronger base than pyridine, which should rightfully be the case because the presence of the additional fused ring would increase the electron density of the nitrogen atom by distributing the partial positive charge (as a result of the electron-withdrawing character of the nitrogen atom) through mesomeric effects (Figure 8.15). The computed interaction energies and distances between the hydrogen and nitrogen atoms in their $H_{\text{TMPD}} \cdots N_{\text{PyridineDerivative}}$ interactions in Tables 8.4 and 8.5, respectively, are supportive of the experimental findings and show trends that are similar to the earlier studied compounds.

Figure 8.14. Plots of $\Delta E_p = |E_{P1} - E_{P3}|$ against concentration of pyridine (black solid line), 3-picoline (blue solid line), 4-picoline (red solid line), quinoline (blue dashed line), isoquinoline (red dashed line), pyridazine (green solid line) and 2,2'-bipyridyl (pink solid line) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure 8.15. Resonance structures of quinoline, isoquinoline and pyridine.

Table 8.4. Relative interaction energies of quinoline, isoquinoline and pyridine with TMPD in MeCN.

Oxidation state	Relative interaction energies (kJ mol ⁻¹)		
	Quinoline	Isoquinoline	Pyridine
P	-3.59	-4.17	-4.17
P ^{•+}	-13.14	-15.49	-15.19
P ²⁺	-32.73	-36.98	-37.16

Table 8.5. Calculated H_{TMPD}•••N_{PyridineDerivative} distance of the quinoline, isoquinoline and pyridine TMPD-hydrogen-bonded complexes in MeCN.

Oxidation state	H _{TMPD} •••N _{PyridineDerivative} distance (Å)		
	Quinoline	Isoquinoline	Pyridine
P	2.30	2.27	2.27
P ^{•+}	2.00	1.96	1.97
P ²⁺	1.68	1.62	1.63

The lack of any deprotonation effects at high concentrations of isoquinoline makes it a weaker base than 2-picoline. It can also be established that the basicity of isoquinoline lies between those of 4-picoline and 3-picoline through the plots of $\Delta E_P = |E_{P1} - E_{P3}|$ against concentration in Figure 8.14. From the results gathered, it is thus possible to suspect that acridine, with two fused rings and two *peri* hydrogen atoms, would be a poorer base/hydrogen acceptor than both quinoline and phenanthrenedine, and that phenanthrenedine would be a stronger base than quinoline because of its greater mesomeric stability. The updated order of basicity and

hydrogen acceptor ability for the studied compounds is: 2,6-lutidine > 2-picoline > 4-picoline > isoquinoline > 3-picoline > pyridine > quinoline > 2,6-di-*tert*-butylpyridine > 4-CF₃-Py > 3-CF₃-Py >> 2-CF₃-Py.

8.3.3 Presence of two heteroatoms: The diazines and bipyridyls

The additional heteroatom within the aromatic rings of the diazines and bipyridyls may enhance or abate their basicity and hydrogen acceptor abilities and so their effects on the electrochemical behavior of TMPD in MeCN were investigated. The cyclic voltammograms of TMPD in response to increasing concentration of pyridazine are given in Figure 8.16 whereas those for pyrimidine and pyrazine can be found in Figure 8.17 to which it is obvious that pyrimidine and pyrazine can be considered as hydrogen acceptors while pyridazine may be regarded as a base. Although pyridazine shows a third oxidation process at sub-stoichiometric concentrations, it is unable to merge the first and third oxidation reactions of TMPD at high concentrations and so is a weaker base than pyridine.

The weaker basicity of pyridazine, as compared to pyridine, can be explained by the decrease in electron density at one nitrogen atom because of the electron-withdrawing inductive effect exerted by the neighboring nitrogen atom. This may then suggest that a greater separation between the two nitrogen atoms would lead to an increase in electron density and basicity because of the diminishing electron-withdrawing inductive effect. However, this is not the case for the diazines because the equally important mesomeric effects must be taken into consideration. Figure 8.18 shows the various important resonance structures of the diazines and it can be seen that it is only in pyrimidine that the partial positive charge does not reside on any of the nitrogen atoms. Hence, it is a better hydrogen acceptor than pyrazine.

However, the paradigms seem to fail when pyridazine is considered. Pyrimidine would be a better hydrogen acceptor than pyridazine by inductive considerations alone because the nitrogen atoms in the former are not adjacent to each other. The same outcome will also be obtained if only mesomeric effects are considered, given that the partial positive charge will reside on one of the

nitrogen atoms of pyridazine in its resonance structures but not for pyrimidine. Yet, according to the electrochemical response of TMPD, pyridazine may be regarded as a base whereas pyrimidine can be considered as a hydrogen acceptor and this is because the electrochemical data has not ignored the greater tendency of pyridazine to utilize one of its lone electron pair for either hydrogen bonding with P and P^{*+} or to receive a proton from P^{2+} to reduce the electronic repulsion with the lone electron pair on the adjacent nitrogen atom. The electronic repulsion between the lone electron pairs is however not sufficient to entirely outweigh the electron-withdrawing inductive effect of the adjacent nitrogen atom and so pyridazine remains a weaker base than pyridine and even quinoline.

Figure 8.16. Cyclic voltammograms of 1 mM TMPD at different concentrations of pyridazine with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that was acquired before the introduction of pyridazine is indicated in dashed line with its measured trace moisture content.

The computational results for the interaction energies of the diazines and the distances between the hydrogen and nitrogen atoms in their $\text{H}_{\text{TMPD}} \cdots \text{N}_{\text{diazine}}$ interactions strongly support the experimental findings and are shown in Tables 8.6 and 8.7, respectively. Interestingly, only one nitrogen atom of the diazines was found to be interacting with the hydrogen atoms of the

phenylenediamine and its oxidized forms, even though two are available, so indicating that anticooperativity effects are at play.

Figure 8.17. Cyclic voltammograms of 1 mM TMPD at different concentrations of (a) pyrimidine and (b) pyrazine with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the diazines are indicated in dashed lines with their measured trace moisture content.

Figure 8.18. Resonance structures of the various diazines.

The effect of 2,2'-bipyridyl on the electrochemical behavior of TMPD was also worth studying since it may engage in bidentate hydrogen bonding interactions with the phenylenediamine, in the

same way that the diols had interacted with the quinones, if it was not functioning as a base. It was unfortunate that 4,4'-bipyridyl was insoluble in MeCN as it would enable easier and direct comparisons within the bipyridyl class of molecules. Nonetheless, the cyclic voltammograms of TMPD at different concentrations of 2,2'-bipyridyl as shown in Figure 8.19 display the third oxidation process at sub-stoichiometric concentrations and so classifies it as a base. 2,2'-Bipyridyl is however weaker than pyridine because the first and third oxidation processes did not merge at high concentrations thereby suggesting that either the bidentate mode of hydrogen bonding was not transpiring or its effect on the electrochemical behavior of TMPD was weak.

Table 8.6. Relative interaction energies of diazines and 2,2'-bipyridyl with TMPD in MeCN.

Oxidation state	Relative interaction energies (kJ mol ⁻¹)			
	Pyridazine	Pyrimidine	Pyrazine	2,2'-Bipyridyl
P	-3.87	-3.43	-3.34	-12.59
P ^{•+}	-15.00	-12.51	-11.85	-19.89
P ²⁺	-35.14	-28.27	-25.99	-34.06

Table 8.7. Calculated H_{TMPD}...N_{PyridineDerivative} distance of the diazines and 2,2'-bipyridyl TMPD-hydrogen-bonded complexes in MeCN.

Oxidation state	H _{TMPD} ...N _{PyridineDerivative} distance (Å)			
	Pyridazine	Pyrimidine	Pyrazine	2,2'-Bipyridyl
P	2.29	2.32	2.32	2.39
P ^{•+}	1.98	2.03	2.03	2.05
P ²⁺	1.68	1.76	1.77	1.75

As mentioned, 2,2'-bipyridyl may either interact with TMPD via the typical 1:1 interaction, the bidentate mode where each nitrogen atom is simultaneously interacting with the hydrogen atoms of a single amino group of the phenylenediamine, or a 1:2 interaction with one molecule of 2,2'-bipyridyl simultaneously interacting with two molecules of TMPD. DFT calculations revealed that the bidentate mode of interaction was not preferred, possibly because the basicity of one pyridyl ring was reduced by the electron-withdrawing mesomeric effect of the other pyridyl ring and that the two pyridyl rings are not coplanar to each other.

The interaction energy of 2,2'-bipyridyl with TMPD and its oxidized forms as well as the distances between the hydrogen and nitrogen atoms in its H_{TMPD}...N_{2,2'-Bipyridyl} interactions are given in Tables 8.6 and 8.7, respectively, to which a comparison of the energies suggest that 2,2'-bipyridyl is a stronger base than pyridazine whereas the H_{TMPD}...N distances indicate otherwise.

The experimental plots of $\Delta E_p = |E_{p1} - E_{p3}|$ against their concentrations in Figure 8.14 indicate that 2,2'-bipyridyl is the stronger base.

Figure 8.19. Cyclic voltammograms of 1 mM TMPD at different concentrations of 2,2'-bipyridyl with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that was acquired before the introduction of 2,2'-bipyridyl is indicated in dashed line with its measured trace moisture content.

8.3.4 Interesting comparisons

It is worthy to highlight that the results obtained with the diazines show that the mesomeric effects are more significant than inductive effects whereas those achieved with the (trifluoromethyl)pyridines indicate otherwise, that the inductive effects are more important than the mesomeric effects. Such dissimilar yet accurate results are a demonstration of the sensitivity of the electrochemical behavior of TMPD, and probably phenylenediamines in general, towards apparent subtle structural changes that may have large electronic and/or steric consequences.

It is difficult to compare the basicity and hydrogen acceptor abilities of 2,6-di-*tert*-butylpyridine, the (trifluoromethyl)pyridines and the diazines in the absence of a common basis. For example, in the case of 4-CF₃-Py and 2,6-di-*tert*-butylpyridine, the former has lesser steric

obstruction towards hydrogen bonding but its nitrogen atom has a low electron density because of the electron-withdrawing inductive effect of the trifluoromethyl group, whereas the latter has a nitrogen atom with a high electron density because of the strong electron-donating inductive character of the *tert*-butyl groups, but their large size also hampers hydrogen bonding. Or the case of the diazines against the (trifluoromethyl)pyridines, where the inductive and mesomeric effects have opposite trends. Therefore, the voltammetric response of TMPD is useful for such purposes. Through the plots of $\Delta E_p = |E_{p1} - E_{p2}|$ against concentration of the above mentioned compounds in Figure 8.20 and the previously established trend, a new order of basicity and hydrogen acceptor strength in MeCN can then be proposed: 2,6-lutidine > 2-picoline > 4-picoline > isoquinoline > 3-picoline > pyridine > 2,2'-bipyridyl > quinoline > pyridazine > 2,6-di-*tert*-butylpyridine > 4-CF₃-Py > pyrimidine > 3-CF₃-Py > pyrazine >> 2-CF₃-Py.

Figure 8.20. Plots of $\Delta E_p = |E_{p1} - E_{p2}|$ against concentration of the 2,6-di-*tert*-butylpyridine (black solid line), 2-CF₃-Py (red dashed line), 3-CF₃-Py (blue dashed line), 4-CF₃-Py (green dashed line), pyrimidine (pink solid line) and pyrazine (brown solid line) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

8.3.5 Pi-stacking effects

It was possible that the changes in the voltammetric behavior of TMPD with increasing concentration of pyridine and its derivatives had contributions from pi-stacking interactions

between the aromatic rings of the phenylenediamine and the bases/hydrogen acceptors. Therefore, the experiments were performed with toluene as an additive. However, as seen in Figure 8.21, there was no observable change to the voltammograms even after 200 mM of toluene was added and so it can be presumed that pi-stacking interactions, if it existed between the compounds, had little influence on the results of the study.

Figure 8.21. Cyclic voltammograms of 1 mM TMPD at different concentrations of toluene with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that was acquired before the introduction of toluene is indicated in dashed line with its measured trace moisture content.

8.3.6 Oxygen and sulfur heterocycles

The positive results with the pyridine derivatives subsequently led to an extension of the scope of this study towards oxygen and sulfur heterocycles, namely tetrahydrofuran (THF), tetrahydropyran (THP), thiophene and tetrahydrothiophene (THT). Both THF and THP are expected to be weaker hydrogen acceptors than the pyridine derivatives in light of the greater electronegativity of the oxygen atom. In addition, their different ring sizes would affect the

energies of the lone electron pairs of the oxygen atoms, according to Bent's rule,^[5] and so influence their hydrogen acceptor abilities.

The sulfur heterocycles are also expected to possess weak hydrogen acceptor abilities because of the differences in energies of their lone electron pairs and sizes of the orbitals that would lead to poor overlap with the σ^* orbital of the N-H bond residing on the hydrogen atom. The different hybridization of the orbitals of the lone electron pairs on the sulfur atom in THT and thiophene would also affect their hydrogen acceptor abilities which we hope that the voltammetric behavior of TMPD is sensitive and responsive to.

Figure 8.22. Cyclic voltammograms of 1 mM TMPD at different concentrations of (a) THF and (b) THP with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of THF and THP are indicated in dashed lines with their measured trace moisture content.

Unfortunately, as seen in the cyclic voltammograms of TMPD in MeCN at different concentrations of THF and THP in Figure 8.22 and also for THT and thiophene in Appendix C, the voltammetric behavior of the phenylenediamine and its $\Delta E_p = |E_{p1} - E_{p2}|$ parameter were unchanged over the entire concentration range of the compounds. Therefore, little information

about their relative hydrogen acceptor strengths can be obtained. Nonetheless, it can be concluded that the four compounds are very poor hydrogen acceptors with respect to the pyridine derivatives. It appears that a phenylenediamine with a much greater hydrogen donor ability than TMPD is necessary to elicit information about the hydrogen acceptor abilities of these oxygen and sulfur heterocycles.

8.4 Measuring the Hydrogen Donor and Acceptor Abilities of Alcohols and Diols

The other aim of our study is to utilize the voltammetric behavior of phenylenediamines and the electrochemical parameter $\Delta E_p = |E_{P1} - E_{P2}|$ to measure the hydrogen donor strengths of alcohols and diols, which is based on the fact that the neutral phenylenediamine species has preference to function as a hydrogen acceptor whereas the oxidized forms (P^{*+} and P^{2+}) are only capable of serving as hydrogen donors. Hence, only E_{P1} should be affected by hydrogen bonding interactions to the alcohols and diols. In addition, the impact of bidentate hydrogen bonding from the diols to TMPD might yield unexpected results because it would require one hydroxyl group to function as a hydrogen donor and the other as a hydrogen acceptor given that each amino group of the phenylenediamine has only one available lone pair of electrons to accept a hydrogen atom. The alcohols are expected to behave as hydrogen donors unlike their alkoxides that are strictly hydrogen acceptors.

8.4.1 The effect of the simple alcohols on the electrochemical behavior of TMPD

The electrochemical response of TMPD at different concentrations of the alcohols, as found with MeOH in Figure 8.3 in Section 8.2.2 and also with *t*-BuOH in Figure 8.23, shows that E_{P2} is more affected by the increase in alcohol concentration than E_{P1} is, with both shifting towards less positive potentials thereby causing $\Delta E_p = |E_{P1} - E_{P2}|$ to decrease. Hence, the plots of $\Delta E_p = |E_{P1} - E_{P2}|$ against the concentration of the alcohols (Figure 8.24) were a measure of the hydrogen acceptor abilities of the alcohols instead of their desired hydrogen donor abilities, which was only possible if the hydrogen donor abilities of P^{*+} and P^{2+} are more pronounced than the

hydrogen acceptor ability of P. The cyclic voltammograms of TMPD at different concentrations of the other simple alcohols can be found in Appendix C. It should be noted that a large concentration of the alcohols was required to elicit an observable shift in E_{P1} and E_{P2} and change in $\Delta E_P = |E_{P1} - E_{P2}|$. Also, no other electrochemical processes were detected over the course of the experiments therefore indicating that the hydrogen bonds between the alcohols and the various oxidation states of TMPD are not very strong. The cationic forms of TMPD are generally quite stable because of greater charge dispersal and the electron-donating inductive effects of the methyl groups. The methyl groups also pose steric hindrance and so collectively reduces the extent of hydrogen bonding between the alcohols and the phenylenediamine.

The plots of E_{P1} and E_{P2} against concentration of MeOH and *t*-BuOH are given in Figure 8.25 where it can be seen that E_{P1} had shifted towards more positive potentials with increasing concentration of the alcohols whereas E_{P2} moved towards less positive potentials so that $\Delta E_P = |E_{P1} - E_{P2}|$ decreased; the changes in E_{P2} were more significant than those for E_{P1} . The absolute potentials also show very poor reproducibility across three experiments as compared to the plots of $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration in Figure 8.26. This, as emphasized throughout the thesis, is because $\Delta E_P = |E_{P1} - E_{P2}|$ is unaffected by the drifts in the potential of the reference electrode, the condition of the working electrode surface, migration effects and kinetics of the heterogeneous electron transfer.

The shifts of E_{P1} and E_{P2} are in line with changes in the electron density and stability of the phenylenediamine species as a result of hydrogen bonding. The electron densities of the nitrogen atoms in P are reduced when the phenylenediamine functions as a hydrogen acceptor and so diminishes the ability of the lone electron pairs to stabilize the cations and shifts E_{P1} to more positive potentials. As for the quinonediimine dication, functioning as a hydrogen donor would impart greater stability and cause E_{P2} to move towards less positive potentials with increasing amounts of the alcohols.

Figure 8.23. Cyclic voltammograms of 1 mM TMPD at different concentrations of *t*-BuOH with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that was acquired before the introduction of *t*-BuOH is indicated in dashed line with its measured trace moisture content.

Figure 8.24. Plots of $\Delta E_p = |E_{p1} - E_{p2}|$ against concentration of water (red dashed line), MeOH (red solid line), EtOH (blue solid line), *n*-PrOH (green solid line), *i*-PrOH (green dashed line), *n*-BuOH (black solid line), *s*-BuOH (black dashed line), *i*-BuOH (pink solid line) and *t*-BuOH (brown dashed line) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure 8.25. Plots of E_{P1} and E_{P2} against concentration of MeOH and t -BuOH obtained over three experiments (red +, blue O and black $\times$) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M n -Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure 8.26. Plots of $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration of MeOH and t -BuOH obtained over three experiments (red +, blue O and black $\times$) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M n -Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Table 8.8. Calculated adiabatic ionization energies of P and P⁺⁺ hydrogen-bonded complexes of TMPD in MeCN.

No. of additives (n)	Adiabatic ionization energy (eV)							
	P				P ⁺⁺			
	Py ^[a]	H ₂ O ^[b]	MeOH ^[b]	t -BuOH ^[b]	Py	H ₂ O ^[b]	MeOH ^[b]	t -BuOH ^[b]
0	4.460	4.460	4.460	4.460	5.739	5.739	5.739	5.739
1	4.345	4.506	4.498	4.481	5.511	5.627	5.624	5.601
2	4.226	4.516	4.517	4.451	5.317	5.543	5.538	5.501
3	4.135	4.521	4.529	4.474	5.168	5.496	5.504	5.442
4	4.046	4.589	4.548	4.470	5.033	5.438	5.478	5.383

[a] Neutral phenylenediamine acts as a hydrogen donor. [b] Neutral phenylenediamine acts as a hydrogen acceptor.

DFT calculations of the adiabatic ionization energies (AIEs) of the P and P⁺⁺ hydrogen-bonded complexes with MeOH and t -BuOH (Table 8.8) showed that hydrogen bonding to the alcohols would increase the AIE of P and decrease the AIE of P⁺⁺ in agreement with the experimental results. The changes in the AIE of P were larger for MeOH than t -BuOH whereas

the AIE of P^{*+} was more affected by hydrogen bonding to *t*-BuOH than MeOH. These differences can be rationalized by considering the acidity and hydrogen acceptor abilities of the alcohols (for the AIEs of P) as well as the electron density of the oxygen atom as a result of the different electron-donating inductive effects of the methyl and *tert*-butyl groups (for the AIEs of P^{*+}). Water was found to be a better hydrogen donor than MeOH and poorer hydrogen acceptor than *t*-BuOH; the latter finding was unexpected because it was thought that the smaller size of water would enable the formation of stronger hydrogen bonds as compared to the larger steric effect imposed by the *tert*-butyl group. The calculations apparently suggest that the electronic effects (i.e. greater electron density at the oxygen atom of *t*-BuOH as compared to water) have outweighed the steric effects whereas the experimental results in Figure 8.24 show otherwise (i.e. the steric effect of *t*-BuOH is more significant than water). The calculations for both the AIEs of P and P^{*+} of the TMPD-pyridine hydrogen-bonded complexes are in good agreement with the experimental results obtained in Section 8.3. Both AIEs decreased with more pyridine molecules added into the hydrogen-bonded complex with the overall change in the AIE of P^{*+} being approximately two times of that obtained for the AIE of P.

A comparison of the plots of $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration for the simple alcohols in Figure 8.24 showed that there was an inverse relationship between ΔE_P and their hydrogen acceptor abilities. At sufficiently high concentrations (> 5 M), ΔE_P was found to follow the order: water $< t$ -BuOH $< i$ -PrOH $< s$ -BuOH $< n$ -BuOH $\approx i$ -BuOH $\approx n$ -PrOH $\approx$ EtOH $<$ MeOH (in a general reverse sequence to that found with the quinones) and so the order of their hydrogen acceptor strengths is water $> t$ -BuOH $> i$ -PrOH $> s$ -BuOH $> n$ -BuOH $\approx i$ -BuOH $\approx n$ -PrOH $\approx$ EtOH $>$ MeOH. The lower sensitivity of the voltammetric response of TMPD towards hydrogen bonding is evident in the inability of its ΔE_P to properly distinguish the primary alcohols (as also found for the quinones in Chapter 7). This trend can be explained through the ability of the alkyl groups to inductively increase the electron density and enhance the hydrogen acceptor ability of the oxygen atom.

Hence, it may be concluded that ΔE_P of TMPD is able to distinguish between the different alcohols based on the collective extent of their hydrogen donor and hydrogen acceptor strengths but primarily the latter because of the strong hydrogen donor abilities of the P^{*+} and P^{2+} forms of TMPD. The stronger hydrogen donor abilities of the oxidized forms are also evident at high concentrations of the alcohols where the electronic effects of the alkyl groups are outweighing their steric effects. The apparent disagreement between the theoretical and experimental findings for water may be due to the effects of cooperativity within the extended hydrogen bonded network as opposed to the electronic effects that govern the strength of the interactions for the alcohols.

However, DFT calculations of the relative hydrogen bond strengths of the alcohols to TMPD and its oxidized forms (Table 8.9) as well as the distances between the nitrogen and hydrogen atoms in $N_{\text{TMPD}} \cdots H_{\text{Alcohol}}$ and hydrogen and oxygen atoms in $H_{\text{TMPD}} \cdots O_{\text{Alcohol}}$ interactions (Table 8.10) do not fully agree with the experimental results. Although the order of their hydrogen donor strengths with P are in line with the expectations and agree with that obtained for the quinones, it is their hydrogen acceptor strengths with P^{*+} and P^{2+} that fall short. The $H_{\text{TMPD}} \cdots O_{\text{Alcohol}}$ interactions in P^{2+} were also shorter than the $N_{\text{TMPD}} \cdots H_{\text{Alcohol}}$ interactions in P. Nonetheless, there is work presently on-going to determine the AIEs of P and P^{*+} for each alcohol for comparisons against the experimental results.

Table 8.9. Relative hydrogen bond strengths of the alcohols with TMPD in MeCN.

Alcohol	Relative hydrogen bond strengths (kJ mol ⁻¹)		
	P ^[a]	P ^{*+} [b]	P ²⁺ [b]
Water	-12.79	-8.32	-19.18
MeOH	-14.22	-10.56	-21.65
EtOH	-13.75	-11.30	-22.22
<i>n</i> -PrOH	-12.31	-11.00	-23.44
<i>i</i> -PrOH	-12.86	-9.50	-23.56
<i>n</i> -BuOH	-12.78	-10.54	-22.99
<i>s</i> -BuOH	-14.01	-9.53	-21.14
<i>i</i> -BuOH	-13.79	-10.79	-22.99
<i>t</i> -BuOH	-10.85	-8.76	-22.10
TFE	-24.51	-10.53	-16.55

[a] Neutral phenylenediamine functions as a hydrogen acceptor. [b] Radical cation and quinonediimine dication are functioning as hydrogen donors.

Table 8.10. Calculated $N_{\text{TMPD}} \cdots H_{\text{Alcohol}}$ distance in P and $H_{\text{TMPD}} \cdots O_{\text{Alcohol}}$ distance in P^{+} and P^{2+} in TMPD-alcohol hydrogen-bonded complexes in MeCN.

Alcohol	$N_{\text{TMPD}} \cdots H_{\text{Alcohol}}$ distance (Å)	$H_{\text{TMPD}} \cdots O_{\text{Alcohol}}$ distance (Å)	
	P ^[a]	P ⁺⁺ [b]	P ²⁺ [b]
Water	1.92	1.97	1.76
MeOH	1.92	1.95	1.73
EtOH	1.93	1.96	1.72
<i>n</i> -PrOH	1.93	1.94	1.73
<i>i</i> -PrOH	1.95	1.95	1.72
<i>n</i> -BuOH	1.93	1.94	1.73
<i>s</i> -BuOH	1.96	1.94	1.74
<i>i</i> -BuOH	1.93	1.94	1.72
<i>t</i> -BuOH	2.00	1.98	1.74
TFE	1.82	2.05	1.85

[a] Neutral phenylenediamine functions as a hydrogen acceptor. [b] Radical cation and quinonediimine dication are functioning as hydrogen donors.

8.4.2 The effect of the diols on the voltammetric behavior of TMPD

Cyclic voltammetry experiments were conducted on TMPD in the presence of the diols ethylene glycol (EG), 1,3-propanediol (PD) and 1,4-butanediol (BD) to which the cyclic voltammograms can be found in Appendix C. As with the simple alcohols, E_{P1} was found to be unchanged whereas E_{P2} moved towards less positive potentials with increasing concentrations of the diols. The plots of $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration of the diols in Figure 8.27 point out that at high concentrations (> 5 M) the order of the ΔE_P -values follows $BD < PD < EG$, which is opposite to that obtained with the quinones in Section 7.4 of Chapter 7, thereby indicating that BD and EG are respectively the strongest and weakest hydrogen acceptors. The diols were also generally stronger hydrogen acceptors than their related simple alcohols.

The hydrogen acceptor ability of a diol is affected by the length of its alkyl chain in three ways. Firstly, the extent of the electron-withdrawing inductive effect that one oxygen atom exerts over the other is dependent on the distance between the two hydroxyl groups. The oxygen atoms of the hydroxyl groups in BD are more willing to serve as hydrogen acceptors because its longer alkyl chain positions the hydroxyl groups furthest apart and so reduces their electron-withdrawing inductive effect. Secondly, the longer alkyl chain in BD will also provide a greater electron-donating inductive effect onto both its oxygen atoms, which in so doing adds onto their hydrogen

acceptor abilities. Lastly, the longer chain might also facilitate bidentate hydrogen bonding and appears to be the case given that the plots of ΔE_p for the diols lie lower than their corresponding alcohols.

Figure 8.27. Plots of $\Delta E_p = |E_{p1} - E_{p2}|$ against concentration of EG (red solid line), PD (blue solid line), BD (black solid line), EtOH (red dashed line), *n*-PrOH (blue dashed line) and *n*-BuOH (black dashed line) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

The neutral phenylenediamine species has only one available lone pair of electrons at each amino group that it can utilize to interact with a hydrogen atom. Therefore, any bidentate hydrogen bonding interactions that the diols partake with the neutral compound would involve one hydroxyl group acting as a hydrogen donor (to the nitrogen atom of P) and the other serving as a hydrogen acceptor (to the hydrogen atom of the amino group). Cooperativity effects appear to support the formation of the second hydrogen bond and bidentate hydrogen bonding between the diols and P. It is unlikely that bidentate hydrogen bonding is occurring between the diols and P⁺ and P²⁺ because both hydroxyl groups will be serving as hydrogen acceptors to which anticooperativity effects do not appear to favor the formation of the second hydrogen bond.

DFT calculations of the relative hydrogen bond strengths (Table 8.11) and distances (Table 8.12) of the diols with the neutral and cationic forms of TMPD indicate that normal

hydrogen bonding is preferred for BD with P whereas the bidentate mode of hydrogen bonding (with one $N_{\text{TMPD}} \cdots H_{\text{Diol}}$ and one $H_{\text{TMPD}} \cdots O_{\text{Diol}}$ interaction) is more stable between EG and P; the bidentate and normal hydrogen bonding modes to P were indifferent in terms of relative energy for PD. However, a comparison of the interaction energies of the P-diol hydrogen-bonded complexes shows little difference among the three diols even though the distances between the nitrogen and hydrogen atoms in the $N_{\text{TMPD}} \cdots H_{\text{Diol}}$ interaction generally increased from EG to BD. Much like the quinones, it is possible that the shorter alkyl chain of EG positions its second hydroxyl group in close proximity to the hydrogen atom of the amino group and so the energy required to maintain the hydrogen-bonded complex is compensated by the stability gained from the bidentate interaction. The longer alkyl chains in PD and BD would require greater energy for distortion and so the energy derived from bidentate interactions may not be sufficient to stabilize the hydrogen-bonded complexes.

Table 8.11. Relative hydrogen bond strengths of the diols with TMPD in MeCN.

Diol	Relative hydrogen bond strengths (kJ mol ⁻¹)					
	P		P ^{•+}		P ²⁺	
	Normal ^[a]	Bidentate ^[b]	Normal ^[c]	Bidentate ^[d]	Normal ^[c]	Bidentate ^[d]
EG	-14.70	-9.72 (-19.43)	-6.89	-8.55 (-17.10) -5.15 (-10.29) ^[e]	-17.27	-17.73 (-35.47) -13.57 (-27.13) ^[f]
PD	-13.28	-6.77 (-13.53)	-9.12	-7.75 (-15.51)	-20.74	-19.13 (-38.26)
BD	-14.83	-2.80 (-5.59)	-10.43	-3.59 (-7.17)	-23.27	-13.08 (-26.15)

[a] Neutral phenylenediamine functions as a hydrogen acceptor with one $N_{\text{TMPD}} \cdots H_{\text{Diol}}$ interaction. [b] Neutral phenylenediamine functions as a hydrogen donor and hydrogen acceptor correspondingly with a $N_{\text{TMPD}} \cdots H_{\text{Diol}}$ and $H_{\text{TMPD}} \cdots O_{\text{Diol}}$ interaction [c] Radical cation and quinonediimine dication are acting as hydrogen donors with one $H_{\text{TMPD}} \cdots O_{\text{Diol}}$ interaction. [d] Radical cation and quinonediimine dication are acting as hydrogen donors with two $H_{\text{TMPD}} \cdots O_{\text{Diol}}$ interactions. [e] Radical cation functions as a hydrogen donor and hydrogen acceptor with a $N_{\text{TMPD}} \cdots H_{\text{Diol}}$ and $H_{\text{TMPD}} \cdots O_{\text{Diol}}$ interaction. [f] Quinonediimine dication functions as a hydrogen donor with bifurcated hydrogen bonding (two $H_{\text{TMPD}} \cdots O_{\text{Diol}}$ interactions but with both oxygen atoms of EG interacting to the same hydrogen atom of the amino group). The overall interaction energies are reflected in parentheses.

As for the P^{•+}-diol and P²⁺-diol hydrogen-bonded complexes, it was found that the relative hydrogen bond strengths of the normal mode of hydrogen bonding increased from EG to BD in line with the results obtained through the electrochemistry experiments. This supports that the hydrogen acceptor ability of the diols is mainly governed by the electron density of their oxygen atoms. Interestingly, the bidentate mode of hydrogen bonding is not preferred for BD unless it involves the P²⁺ species and even so the difference in stability between the normal and bidentate

hydrogen-bonded complexes is only $\sim 3 \text{ kJ mol}^{-1}$ in favor of the latter. It is worth mentioning that the bidentate P^{++} -EG hydrogen-bonded complex with the radical cation apparently acting as both a hydrogen donor and hydrogen acceptor and the bifurcated P^{2+} -EG hydrogen-bonded complex were found to be more stable than their respective normal hydrogen-bonded complexes but less stable than the corresponding bidentate hydrogen-bonded complexes. Nonetheless, the greater amount of diol molecules in solution relative to the phenylenediamine molecules would make such unique hydrogen-bonded complexes less likely to occur.

Table 8.12. Calculated $N_{\text{TMPD}} \cdots H_{\text{Diol}}$ and $H_{\text{TMPD}} \cdots O_{\text{Diol}}$ distances in the various TMPD-diol hydrogen-bonded complexes in MeCN.

Diol	$N_{\text{TMPD}} \cdots H_{\text{Diol}}$ and $H_{\text{TMPD}} \cdots O_{\text{Diol}}$ distances (Å)					
	P		P^{++}		P^{2+}	
	Normal ^[a]	Bidentate ^[b]	Normal ^[c]	Bidentate ^[d]	Normal ^[c]	Bidentate ^[d]
EG	1.91	1.91/2.37	1.99	2.05/2.08 (1.99/2.63) ^[e]	1.78	1.86/1.86 (1.79/2.57) ^[f]
PD	1.93	1.91/3.76	1.98	1.99/2.09	1.74	1.82/1.82
BD	1.95	1.97/2.70	1.97	2.09/2.11	1.73	1.80/1.84

[a] Neutral phenylenediamine functions as a hydrogen acceptor with one $N_{\text{TMPD}} \cdots H_{\text{Diol}}$ interaction. [b] Neutral phenylenediamine functions as a hydrogen donor and hydrogen acceptor correspondingly with a (shorter) $N_{\text{TMPD}} \cdots H_{\text{Diol}}$ and (longer) $H_{\text{TMPD}} \cdots O_{\text{Diol}}$ interaction. [c] Radical cation and quinonediimine dication are acting as hydrogen donors with one $H_{\text{TMPD}} \cdots O_{\text{Diol}}$ interaction. [d] Radical cation and quinonediimine dication are acting as hydrogen donors with two $H_{\text{TMPD}} \cdots O_{\text{Diol}}$ interactions. [e] Radical cation functions as a hydrogen donor and apparently also a hydrogen acceptor with a $H_{\text{TMPD}} \cdots O_{\text{Diol}}$ and $N_{\text{TMPD}} \cdots H_{\text{Diol}}$ interaction. [f] Quinonediimine dication functions as a hydrogen donor with bifurcated hydrogen bonding (i.e. two $H_{\text{TMPD}} \cdots O_{\text{Diol}}$ interactions but with both oxygen atoms of EG interacting with the same hydrogen atom of the amino group). The overall interaction energies are reflected in parentheses.

8.4.3 The effect of trifluoroethanol and acetic acid on the electrochemical behavior of TMPD

It is in our interest to utilize the voltammetric behavior of TMPD and particularly its $\Delta E_p = |E_{p1} - E_{p2}|$ parameter, to measure the hydrogen donor strengths of the alcohols. However, the hydrogen donor abilities of P^{++} and especially P^{2+} were overly dominant so that even the hydrogen acceptor abilities of the simple alcohols could be differentiated (recalling that alcohols are weak acids and even weaker bases and nucleophiles!). Therefore, experiments with TFE (a very strong hydrogen donor that does not participate in proton-transfer reactions with 9,10-anthraquinone and 1,4-benzoquinone nor their reduced forms) and acetic acid (a weak acid that could protonate the

dianion of 1,4-benzoquinone) were recorded as a proof-of-concept that $\Delta E_p = |E_{P1} - E_{P2}|$ of the phenylenediamines can be applied for measuring hydrogen donor strengths.

The cyclic voltammograms of TMPD at different concentrations of TFE are shown in Figure 8.28, and it was observed that both E_{P1} and E_{P2} had shifted towards more positive potentials with increasing concentrations so indicating that the hydrogen donor strengths can be measured, although significantly large amounts of the hydrogen donor relative to the phenylenediamine were needed. The average overall shifts of E_{P1} was about 1.7 times larger than that of E_{P2} thus $\Delta E_p = |E_{P1} - E_{P2}|$ decreased. Interestingly, no effects of protonation were observed even when ~ 7 M of TFE was present. For comparison purposes, the cyclic voltammetric data of TMPD in the presence of EtOH is also provided in Figure 8.28, where it is clear that both E_{P1} and E_{P2} had shifted to less positive potentials with increasing concentrations yet $\Delta E_p = |E_{P1} - E_{P2}|$ also decreased because the average overall change to E_{P2} was approximately 30 times greater than that found for E_{P1} . It should be noted that any comparisons of the hydrogen donor/acceptor strengths of EtOH and TFE directly through their ΔE_p versus concentration plots are not valid because different hydrogen bonding roles of the phenylenediamine are dominant and in play. In the case of EtOH, it is the interaction between the alcohol (the hydrogen acceptor) and the quinonediimine dication P^{2+} (the hydrogen donor) that dictates the overall change in ΔE_p , whereas for the fluorinated alcohol, it is the hydrogen bonding between the neutral species P (the hydrogen acceptor) and TFE (the hydrogen donor) that results in the decrease in ΔE_p .

A comparison of the relative hydrogen bond strengths between TFE and EtOH in Table 8.9 as well as the $N_{\text{TMPD}} \cdots H_{\text{Alcohol}}$ distance in P-alcohol and $H_{\text{TMPD}} \cdots O_{\text{Alcohol}}$ distance in P^{++} -alcohol and P^{2+} -alcohol hydrogen-bonded complexes in Table 8.10 indicate that TFE is the stronger hydrogen donor by about 10.8 kJ mol^{-1} with a shorter $N_{\text{TMPD}} \cdots H_{\text{Alcohol}}$ distance in the P-TFE hydrogen-bonded complex by $0.11 \text{ \AA}$. EtOH is however a better hydrogen acceptor with the interaction energies being about 0.8 kJ mol^{-1} and 5.7 kJ mol^{-1} stronger for the P^{++} -EtOH and P^{2+} -EtOH hydrogen-bonded complexes, respectively, with likewise shorter $H_{\text{TMPD}} \cdots O_{\text{Alcohol}}$ distance by $0.09 \text{ \AA}$ and $0.13 \text{ \AA}$.

The shifts of E_{P1} and E_{P2} to more positive potentials indicate that the first and second $1e^-$ oxidation reactions are becoming increasingly difficult to occur in the presence of hydrogen bonding to TFE. Such shifting of E_{P1} can be understood by recalling that P is preferably a hydrogen acceptor and so TFE, being a strong hydrogen donor, would strongly interact with the lone electron pairs of its nitrogen atoms and compete with their availability for use in stabilizing the oxidized forms. In addition, the interactions between TFE and P are more favored than those with P^{++} . Hence, greater energy is required for the removal of an electron from the TFE-hydrogen-bonded complex as compared to the free P.

Figure 8.28. Cyclic voltammograms of 1 mM TMPD at different concentrations of (a) TFE and (b) EtOH with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of TFE and EtOH are indicated in dashed lines with their measured trace moisture content.

The shifts of E_{P2} to more positive potentials implies that the interactions between the radical cation P^{++} and TFE are much stronger than those between the quinonediimine dication P^{2+} and TFE. Although the computations indicate that the radical cation is preferably a hydrogen donor, it appears that the dominant interaction between P^{++} and TFE involves the radical being a

hydrogen acceptor and the alcohol serving as a hydrogen donor because this form of interaction would result in a greater amount of energy needed to remove an electron from the P^{++} -TFE hydrogen-bonded complex.

DFT calculations were also performed to determine the effect that hydrogen bonding to TFE would have on the AIE of the $P(TFE)_n$ and $P^{++}(TFE)_n$ hydrogen-bonded complexes of TMPD. As for the AIE of the $P(TFE)_n$ hydrogen-bonded complex, the results in Table 8.13 show that it increases quite significantly with hydrogen bonding (+0.25 eV for TFE as compared to +0.09 eV for MeOH and +0.01 eV for *t*-BuOH). On the other hand, the AIE of $P^{++}(TFE)_n$ hydrogen-bonded complex had decreased, which is in contrast to the experimental findings where E_{P2} shifted to more positive potentials. It is possible that the lack of provisions for interactions with trace water in the solvent and the supporting electrolyte are responsible for the disagreement between the experimental and calculated results. The difference in the change of AIE of $P^{++}(TFE)_n$ was smaller than those obtained for MeOH and *t*-BuOH (-0.13 eV for TFE, -0.26 eV for MeOH and -0.36 eV for *t*-BuOH). More importantly, the computational work indicates that the changes to the AIE of $P(TFE)_n$ are approximately two times greater than the changes in the AIE of $P^{++}(TFE)_n$ and so the decrease of $\Delta E_P = |E_{P1} - E_{P2}|$ may be regarded as a measure of the hydrogen donor ability of TFE instead of its hydrogen acceptor strength.

Table 8.13. Calculated adiabatic ionization energies of P and P^{++} hydrogen-bonded complexes of TMPD in MeCN.

No. of TFE molecules (<i>n</i>)	Adiabatic ionization energy (eV)	
	$P(TFE)_n^{[a,b]}$	$P^{++}(TFE)_n^{[b]}$
0	4.460	5.739
1	4.604	5.677
2	4.659	5.639
3	4.691	5.611
4	4.708	5.608

[a] Neutral phenylenediamine acts as a hydrogen acceptor for up to two molecules of TFE, after which the remaining TFE molecules interacted with the primary hydrogen-bonded TFE molecules via secondary indirect hydrogen bonding interactions. [b] Radical cation and quinonediimine dication act as hydrogen donors with only one primary direct hydrogen bonding interaction to one molecule of TFE whereas the remaining TFE molecules were connected by secondary hydrogen bonding interactions.

Interestingly, only two primary direct hydrogen bonds between the phenylenediamine and TFE molecules were found to exist in the $P(TFE)_4$ hydrogen-bonded complex. The nitrogen atoms

of the phenylenediamine were functioning as hydrogen acceptors while the remaining two molecules of TFE were involved in secondary indirect hydrogen bonding interactions to the primary hydrogen-bonded TFE molecules. As for the $P^{++}(TFE)_4$ and $P^{2+}(TFE)_4$ hydrogen-bonded complexes, only one primary direct hydrogen bond was found with the phenylenediamine species acting as hydrogen donors and TFE acting as a hydrogen acceptor; the remaining three molecules of TFE were engaged in secondary indirect hydrogen bonding interactions to the primary hydrogen bonded TFE molecule. It should be noted that the $P^{2+}(Py)_4$, $P^{2+}(water)_4$, $P^{2+}(MeOH)_4$ and $P^{2+}(t-BuOH)_4$ hydrogen-bonded complexes showed four primary direct hydrogen bonds between the quinonediimine dication and the additives whereas the $P^{2+}(TFE)_4$ hydrogen-bonded complex only had one.

Although acetic acid does not undergo proton-transfer reactions with TMPD (see Section 8.2.2) because of its lower acidity in MeCN, it may still function as a hydrogen donor to P and/or a hydrogen acceptor to P^{++} and P^{2+} . Thus, cyclic voltammetry experiments for TMPD in the presence of this weak acid were repeated with the concentration of the acid varied by much larger amounts (than that in Figure 8.3) to explore these possibilities. The cyclic voltammograms of TMPD in Figure 8.29 show both E_{P1} and E_{P2} shifting to more positive potentials with increasing concentration of acetic acid, similar to that found for TFE. The average shift of E_{P1} (+250 mV) was more significant than that of E_{P2} (+30 mV) and also two times larger than the value obtained with TFE (average shift of E_{P1} = +110 mV). More importantly, the plot of $\Delta E_p = |E_{P1} - E_{P2}|$ against concentration of acetic acid was found to lie lower than the plot with TFE (Figure 8.30) thereby indicating that TMPD is more affected by hydrogen bonding interactions with the acid than the fluorinated alcohol; it may thus be concluded that acetic acid is a stronger hydrogen donor. $\Delta E_p = |E_{P1} - E_{P2}|$ can be directly used for comparing the hydrogen bonding abilities of TFE and acetic acid because the same interaction, that is with P as the hydrogen acceptor and the additives being the hydrogen donor, is underlying and dominating the overall change of the electrochemical parameter; unlike the case between TFE and EtOH where two different interactions, $P\cdots TFE$ and $P^{2+}\cdots EtOH$, are causing the changes in their respective ΔE_p -values.

Figure 8.29. Cyclic voltammograms of 1 mM TMPD at different concentrations of acetic acid with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that was acquired before the introduction of acetic acid is indicated in dashed line with its measured trace moisture content.

Figure 8.30. Plots of $\Delta E_p = |E_{p1} - E_{p2}|$ against concentration of TFE (black solid line) and acetic acid (black dashed line) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Hence, the aim of using $\Delta E_p = |E_{p1} - E_{p2}|$ of TMPD to measure hydrogen donor strengths has been achieved, but the procedure is only applicable for very strong hydrogen donors that do not undergo proton-transfer reactions with the neutral phenylenediamine. Another limitation of the voltammetric technique is that it requires very large amounts of the hydrogen donors to elicit observable changes. It is possible that the use of phenylenediamines, such as NTMPD, with stronger hydrogen acceptor and weaker hydrogen donor abilities than TMPD would improve the sensitivity of the measurements.

8.5 Summary

The results of this chapter have shown that specific changes to the voltammetric behavior of TMPD can be used to distinguish bases and hydrogen acceptors among pyridine and its derivatives in a non-aqueous solution. The differentiation is mainly based on the occurrence of the third oxidation process between the two main $1e^-$ -oxidation processes at sub-stoichiometric concentrations that would indicate that they are bases. The strength of the bases may subsequently be assessed via the value of $\Delta E_p = |E_{p1} - E_{p3}|$ at a chosen concentration and the concentration at which the third process merges with the first $1e^-$ -oxidation reaction. Very strong bases might also be revealed if the chemical reversibility of the peak formed through the merger of first and third processes is compromised. The bases in this study were suspected to be able to only deprotonate P^{2+} and not P or P^{*+} .

As for hydrogen acceptors, their ability to hydrogen bond can be determined through $\Delta E_p = |E_{p1} - E_{p2}|$ that is inversely related to the strength and extent of their interactions. The electrochemical parameter $\Delta E_p = |E_{p1} - E_{p2}|$ has also been shown to be able to measure the hydrogen acceptor strengths of alcohols and diols, which are very poor hydrogen acceptors, because the hydrogen donor abilities of the radical cation P^{*+} and quinonediimine dication P^{2+} are superior to the hydrogen acceptor ability of P. Nonetheless, the assessment of hydrogen donor strengths using $\Delta E_p = |E_{p1} - E_{p2}|$ could be achieved but only with very strong hydrogen donors such as TFE and acetic acid.

The electrochemical behavior of TMPD is sensitive to steric and electronic (both inductive and mesomeric) effects and can distinguish within and between the different picolines, (trifluoromethyl)pyridines and the diazines. It was however not responsive towards oxygen and sulfur heterocycles and so may require the use of other phenylenediamines with stronger hydrogen donor abilities in their oxidized states. Lastly, the results gathered thus far suggest that the voltammetric behavior of the quinones and phenylenediamines can be applied for aquametry and the detection of impurities in organic solvents and are explored in the succeeding two chapters.

Notes

The cyclic voltammograms of TMPD in the presence of the THT, thiophene, the simple alcohols not shown in this chapter and the diols are provided in Appendix C along with the complete set of the plots of ΔE_p against concentration of the simple alcohols, diols, TFE and acetic acid. The Cartesian coordinates and visualizations of the optimized geometries of the various hydrogen-bonded complexes are also included.

References

- [1] (a) J. F. Corbett, *J. Chem. Soc. B* **1969**, 213-216; (b) M. Jonsson, J. Lind, T. E. Eriksen, G. Merenyi, *J. Am. Chem. Soc.* **1994**, *116*, 1423-1427; (c) L. A. Clare, L. E. Rojas-Sligh, S. M. Maciejewski, K. Kangas, J. E. Woods, L. J. Deiner, A. Cooksy, D. K. Smith, *J. Phys. Chem. C* **2010**, *114*, 8938-8949; (d) A. Trummel, L. Lipping, I. Kaljurand, I. A. Koppel, I. Leito, *J. Phys. Chem. A* **2016**, *120*, 3663-3669.
- [2] T. R. Franco, L. A. Clare, D. K. Smith, in 218th ECS Meeting, Las Vegas, Nevada, **2010**, Abstract 79.
- [3] R. S. Hosmane, J. F. Liebman, *Struct. Chem.* **2009**, *20*, 693-697.
- [4] P. G. Seybold, K. B. Lipkowitz, *Int. J. Quantum Chem.* **1987**, *31*, 847-853.

- [5] H. A. Bent, *Chem. Rev.* **1961**, *61*, 275-311.

Chapter 9

Optimizing the Selectivity of Quinones for the Detection of Water in Organic Solvents via Structural Modifications

9.1 *Introduction*

9.2 *Selectivity of Quinones for Water*

9.2.1 *General results*

9.2.2 *Positional isomers: ortho and para quinones*

9.2.3 *Steric and electronic effects*

9.3 *Measuring the Moisture Content of Carbonyl Solvents*

9.4 *Measuring the Moisture Content of Protic Organic Solvents*

9.5 *Summary*

Notes

References

This page has been intentionally left blank

9.1 Introduction

The EE reduction behavior of quinones and the difference in basicity of their reduced forms Q, $Q^{\cdot-}$ and Q^{2-} has made them useful for measuring the moisture content of aprotic organic solvents.^[1] As reported in the literature^[1a, 1c] and shown in Chapter 6, the electrochemical parameter $\Delta E_Q = |E_{Q1} - E_{Q2}|$ of the quinones is inversely proportional to the concentration of water in the solvent because the shifting of E_{Q2} towards less negative potentials with increasing moisture content occurs in larger steps than that of E_{Q1} . E_{Q2} is more sensitive than E_{Q1} because the oxygen atoms in Q^{2-} carry a higher electron density than those in $Q^{\cdot-}$ and Q and so their basicity follows the order $Q^{2-} > Q^{\cdot-} > Q$ to which the strength of their hydrogen bonds is then $Q \cdots H_2O < Q^{\cdot-} \cdots H_2O < Q^{2-} \cdots H_2O$. The electron affinity of $Q^{\cdot-}$ is subsequently more sensitive to hydrogen bonding than the electron affinity of Q.

In addition to their voltammetric behavior, the quinones are particularly suited for aquametry because slight structural modifications would alter their basicity, hydrogen acceptor ability as well as selectivity for water and so enables accurate measurements in both the low and high water concentration regimes. Mao et al. have shown that the more basic duroquinone (DQ) is better suited for lower concentration measurements as compared to the less basic chloranil that is preferred for higher levels of water.^[1b] Furthermore, quinones have reportedly been functionalized with thiol groups and attached onto the surface of a gold electrode via S-Au linkages and so may allow for the development of a “dipstick” water sensor.^[2]

Although the sensitivity of the quinones in measuring the moisture content of aprotic organic solvents have been reported, there is little information about their selectivity for water in the presence of other hydrogen donors such as the alcohols, which is surprising because the simple alcohols, as shown in Chapter 7, can form strong hydrogen bonding interactions to the quinones and are often used as stabilizers for a number of organic solvents. The aim of the study in this chapter is therefore to identify a quinone that is selective for water by possessing a $\Delta E_Q = |E_{Q1} - E_{Q2}|$ electrochemical parameter that is responsive only to water and unchanging with variations in the concentration of the alcohols. Any success would also enable the quinone and the

voltammetric technique for measuring moisture content to be extended to carbonyl solvents, which is presently difficult to achieve with the Karl Fischer titration because of side reactions between carbonyl compounds and methanol and poor shelf life of the Karl Fischer reagents.

9.2 Selectivity of Quinones for Water

9.2.1 General results

The quinones 9,10-anthraquinone (AQ), 9,10-phenanthrenequinone (PQ), duroquinone (DQ) and 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone (DPQ) were investigated because they offer a number of comparisons, ranging from positional isomerism to steric and electronic effects, to be made. Voltammetry experiments for these four quinones at different concentrations of the simple alcohols were conducted with a platinum wire reference electrode inside a Precise[®] Controlled Atmosphere Glove Box (Labconco Corporation) to limit the interference of water from the environment. The experiments with varying amounts of water were however performed with a silver wire (Cypress Systems) miniature reference electrode that was connected to the working solution through a salt bridge containing a solution of 0.5 M *n*-Bu₄NPF₆ in MeCN and within a Faraday cage that was located inside the fume cupboard. The internal filling solution of the reference electrode was replaced prior to the start of each experiment. Nevertheless, comparisons between the two sets of experiments using different reference electrodes could still be made because $\Delta E_Q = |E_{Q1} - E_{Q2}|$ was independent of the potential of the reference electrode.

The electrochemical response of all four quinones to increasing amounts of the hydrogen donors was generally no different to that reported in Chapters 6 and 7. As shown in Figure 9.1, regardless of the identity of the quinone, hydrogen donor and reference electrode used, $\Delta E_Q = |E_{Q1} - E_{Q2}|$ decreased as more hydrogen donor was added. The average ΔE_Q -plots in Figure 9.1 comprise the combined results of three experiments for each hydrogen donor (Figure 9.2), which showed greater reproducibility than the plots of absolute potentials in Figure 9.3.

Nonetheless, it must be mentioned that E_{Q1} was at times found to shift towards more negative potentials while E_{Q2} remain unchanged with increasing concentrations of the alcohols

when the platinum wire (Metrohm) reference electrode was used, in contrast to the results in Chapters 6 and 7 where both reduction potentials were found to shift to less negative potentials. This is believed to be a consequence of the drift in the potential of the reference electrode between the scans because of the change in the composition of the working solution. Nevertheless, the absence of any extraordinary effects for ΔE_Q as a result of this drift of the potential of the platinum wire reference electrode shows that it is a useful electrochemical parameter for representing the extent of hydrogen bonding between the quinones and the hydrogen donors. The cyclic voltammograms of the quinones at different concentrations of MeOH can be found in Figure 9.4 while those obtained in the presence of the other simple alcohols and water are provided in Appendix D.

Figure 9.1. Plots of average $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of water (cyan solid line), MeOH (red solid line), EtOH (blue solid line), *n*-PrOH (green solid line), *i*-PrOH (green dashed line), *n*-BuOH (black solid line), *s*-BuOH (black dashed line), *i*-BuOH (pink solid line) and *t*-BuOH (brown dashed line) as measured by square-wave voltammetry during the reduction of 1 mM (a) AQ, (b) PQ, (c) DQ and (d) DPQ with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV. The plot for *i*-BuOH in (d) is not available because a white precipitate was formed upon the addition of the alcohol into the electrochemical solution.

Figure 9.2. Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of MeOH obtained over three experiments (red +, blue O and black x) as measured by square-wave voltammetry during the reduction of 1 mM (a) AQ, (b) PQ, (c) DQ and (d) DPQ with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure 9.3. Plots of E_{Q1} (top) and E_{Q2} (bottom) against concentration of MeOH obtained over three experiments (red +, blue O and black x) as measured by square-wave voltammetry during the reduction of 1 mM quinone with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure 9.4. Cyclic voltammograms of 1 mM (a) AQ, (b) PQ, (c) DQ and (d) DPQ in MeCN with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of MeOH. The voltammograms were recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were obtained before the introduction of MeOH are indicated in dashed lines along with their measured trace moisture content.

9.2.2 Positional isomers: *ortho* and *para* quinones

The different positions of the carbonyl groups in AQ and PQ affects the manner in which they interact with hydrogen donors and so may result in different sensitivities toward the effects of hydrogen bonding. In the case of AQ, where the two carbonyl groups are *para* relative to each other, an incoming hydrogen donor is unlikely to be affected by the steric effects of an existing bound hydrogen donor because the lone electron pairs of the oxygen atoms are oriented away from one other. Therefore, without taking the cooperativity and anticooperativity effects of hydrogen bonding into consideration, the theoretical maximum number of primary direct hydrogen bonds that the Q and Q⁻ states of AQ can form is four whereas its Q²⁻ is able to take up to six because the oxygen atoms are in the sp^3 hybridization state.

However, the same cannot be said for PQ because any hydrogen donor that interacts with one of the two lone electron pairs located between the two oxygen atoms would certainly affect the ability of the other electron pair to function as a hydrogen acceptor. Therefore, based on the steric effects of a bound hydrogen donor, it is likely that PQ would form a lesser number of hydrogen bonds than AQ and so might be less sensitive towards the effects of hydrogen bonding. Then again, it might be argued that the accumulation of charge in PQ, as opposed to even distribution in AQ, as well as electronic repulsion between the lone electron pairs, such as that observed for pyridazine in Chapter 8, might make PQ a better hydrogen acceptor than AQ. Or that the greater number of hydrogen bonds that AQ can form will be balanced by the tendency of PQ to form stronger (albeit lesser) interactions and so both quinones will show the same sensitivity towards hydrogen bonding. It should be noted that PQ may be engaged in bifurcated or three-centered hydrogen bonding interactions where a single hydrogen donor is simultaneously interacting with both oxygen atoms. The stabilization gained from such bifurcated hydrogen bonding may differ from canonical hydrogen bonding and manifest in the voltammetric results.

A comparison of the ΔE_Q -plots of AQ and PQ in Figure 9.1 expectedly show that neither quinone will have good selectivity for water in the presence of the simple alcohols, which can be attributed to the lack of bulky substituents to impede their interactions with the alcohols.

Interestingly, the ΔE_Q -plots for water were found to lie among the primary alcohols when it was thought that the more extensive secondary hydrogen bond network of water would have resulted in a larger effect on $\Delta E_Q = |E_{Q1} - E_{Q2}|$. The results across the four quinones consistently indicate that MeOH is a stronger hydrogen donor than water.

There was little difference in the overall spread of ΔE_Q for AQ and PQ; the difference between the maximum and minimum ΔE_Q -values was ~ 160 mV. This indicates that both quinones are equally sensitive to hydrogen bonding effects. Nonetheless, the *para* quinone was observed to be better at differentiating between the different classes of alcohols since there was a wider separation between the ΔE_Q -plots of the primary, secondary and tertiary alcohols at high concentrations. The difference between the lowest (MeOH) and highest (*t*-BuOH) lying ΔE_Q -plots at a concentration of 0.1 M was about 20 mV larger for AQ than PQ. Unfortunately, it was not apparent from the voltammetric results that PQ was preferably engaged in one form of hydrogen bonding (bifurcated or canonical).

Although the analysis of the results presented in Figure 9.1 suggests that the overall electrochemical behavior of AQ and PQ are equally sensitive to hydrogen bonding effects, a closer look at their cyclic voltammograms in Figure 9.4 shows that the second reduction process of PQ is slightly smaller than the first reduction process. This indicates that some of the $Q^{\cdot-}$ molecules that were formed through the reduction of Q have participated in unknown chemical reactions in addition to undergoing reduction to Q^{2-} . The oxidation of Q^{2-} to $Q^{\cdot-}$ on the reverse scan was also found to be slightly broad in the presence of higher amounts of hydrogen donors. Thus, revealing a slower rate of heterogeneous electron-transfer from Q^{2-} to the electrode surface as compared to the forward reduction where the electron was transferred from the electrode surface to $Q^{\cdot-}$. Yet, the chemical and electrochemical reversibility of the first reduction process was unaffected throughout. René and Evans have previously reported similar findings for 3,5-di-*tert*-butyl-1,2-benzoquinone and 3,6-di-*tert*-butyl-1,2-benzoquinone where a Michael addition reaction occurred between Q^{2-} and $Q^{\cdot-}$ to produce an electroinactive trianion QQ^{3-} .^[3] Hence, the greater complexity in the electrochemical behavior of the *ortho* quinone suggests that *para*

quinones be used instead for the measurement of water content of organic solvents, especially for those that are susceptible to nucleophiles and bases such as the carbonyls.

9.2.3 Steric and electronic effects

A comparison of the ΔE_Q -plots for DQ (Figure 9.1c) and DPQ (Figure 9.1d) clearly shows that the former is more affected by hydrogen bonding effects and is better able to differentiate the steric effects of the alcohols. Both quinones were however, not selective towards water and so other quinones will have to be explored to achieve our goal.

It is clear that the steric effects of the *tert*-butyl groups in DPQ have dominated their electronic effects yet it appears, to some extent, that the quinone is still capable of distinguishing the hydrogen donor strengths of the simple alcohols. This is probably a consequence of the puckered structure of DPQ where the carbonyl groups are oriented out of the plane of the ring of carbon atoms and away from the *tert*-butyl groups thereby making the oxygen atoms susceptible to some interaction with the alcohols.^[4]

9.3 Measuring the Moisture Content of Carbonyl Solvents

It was mentioned in Chapter 3 that the Karl Fischer titration of aldehydes and ketones is difficult to achieve because they react with MeOH and liberate water. Moreover, the Karl Fischer reagents designed specially for use with carbonyl compounds are unstable and have short shelf lives. Therefore, the extension of the current voltammetric technique of measuring the moisture content of aprotic organic solvents with quinones to carbonyl solvents would be useful. The challenge however was to ensure that the reduced forms of the quinone do not react with the carbonyl compounds.

Figure 9.5 shows the cyclic voltammograms of the four quinones in acetone and it can be seen that only DPQ could reproduce the standard EE reduction response and did not react with the solvent. The other quinones either showed additional electrochemical processes, broad peaks or

complex responses that made them not appropriate for use in the measurement of moisture content of carbonyl solvents.

Figure 9.5. Cyclic voltammograms of 1 mM (a) AQ, (b) PQ, (c) DQ and (d) DPQ in acetone with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. Red trace: 1st scan, blue trace: 2nd scan, green trace: 3rd scan, pink trace: 4th trace, black trace: 5th and last scan.

With increasing amounts of water (Figure 9.6), we found that both reduction processes of DPQ in acetone had shifted to less negative potentials with a concomitant decrease in $\Delta E_Q = |E_{Q1} - E_{Q2}|$. Therefore, DPQ can indeed be applied to measure the moisture content of carbonyl solvents. However, the working range appears to be limited to <5 M because of precipitation of the supporting electrolyte at higher amounts of water. It should be noted that the concentrations of water indicated in Figure 9.6 represent the amounts added and does not take the amount of water that was initially present in the solvent into consideration.

Figure 9.6. Cyclic voltammograms of 1 mM DPQ in acetone with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of water recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram obtained before the addition of water is indicated in dashed line.

9.4 Measuring the Moisture Content of Protic Organic Solvents

A limitation of the voltammetric method for determining the moisture content of organic solvents with quinones is that it is only applicable to aprotic organic solvents because the two 1e^- -reduction processes will collapse into a single 2e^- -reduction reaction in protic organic solvents as a result of extensive hydrogen bonding interactions between the quinone and the solvent molecules. The standard electrochemical behavior of 2,3,5,6-tetramethyl-1,4-phenylenediamine (TMPD) was however unaffected by the nature of the solvent as seen in Figure 9.7 where the cyclic voltammograms of the phenylenediamine in the simple alcohols and ethylene glycol (EG) with lithium perchlorate (LiClO_4) as the supporting electrolyte are given. The voltammetric response of TMPD was highly reproducible and each 1e^- -oxidation process was chemically as well as electrochemically reversible. Therefore, it appears that phenylenediamines and their electrochemical parameter $\Delta E_p = |E_{p1} - E_{p2}|$ may be applied for measuring the moisture content of protic organic solvents for which work is currently still in progress.

Figure 9.7. Cyclic voltammograms of 1 mM TMPD in the stated alcohols with 0.1 M LiClO₄ as the supporting electrolyte recorded at a scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. Red trace: 1st scan, blue trace: 2nd scan, green trace: 3rd scan, pink trace: 4th trace, black trace: 5th and last scan.

9.5 Summary

We have shown that the quinones are suitable for measuring the moisture content of carbonyls so long as the nucleophilic reaction between the reduced forms and the solvent can be prevented. This can be achieved by having bulky substituents close to the carbonyl groups. In addition, it appears that *para* quinones are better suited for general use and that the anthraquinone class of molecules may offer greater selectivity for water if appropriate substituents are located at the 1-, 4-, 5- and 8-positions. Work is presently on-going with tetramethyl- and tetrakis(trimethylsilyl)-substituted anthraquinones. Lastly, we have shown that the phenylenediamines may be suitable for measuring the moisture content of protic organic solvents, which cannot be achieved with the quinones. However more studies are needed to ascertain their capability.

Notes

The cyclic voltammograms of the quinones in the presence of water and the other simple alcohols not shown in this chapter are given in Appendix D along with the complete set of plots of ΔE_Q , E_{Q1} and E_{Q2} against concentration of the hydrogen donors.

References

- [1] (a) Y. Hui, E. L. K. Chng, C. Y. L. Chng, H. L. Poh, R. D. Webster, *J. Am. Chem. Soc.* **2009**, *131*, 1523-1534; (b) L. Zhang, H. Zhou, X. Li, Y. Lin, P. Yu, L. Su, L. Mao, *Electrochem. Commun.* **2009**, *11*, 808-811; (c) Y. Hui, E. L. K. Chng, L. P.-L. Chua, W. Z. Liu, R. D. Webster, *Anal. Chem.* **2010**, *82*, 1928-1934.
- [2] (a) C. A. Panetta, P. W.-J. Fan, R. Fattah, J. C. Greever, Z. He, C. L. Hussey, D. Sha, L. D. Wescott Jr, *J. Org. Chem.* **1999**, *64*, 2919-2923; (b) M. Kažemėkaitė, A. Bulovas, Z. Talaikytė, E. Butkus, V. Railaitė, G. Niaura, A. Palaima, V. Razumas, *Tetrahedron Lett.* **2004**, *45*, 3551-3555; (c) A. Bulovas, N. Dirvianskytė, Z. Talaikytė, G. Niaura, S. Valentukonytė, E. Butkus, V. Razumas, *J. Electroanal. Chem.* **2006**, *591*, 175-188; (d) S. A. Trammell, D. A. Lowy, D. S. Seferos, M. Moore, G. C. Bazan, N. Lebedev, *J. Electroanal. Chem.* **2007**, *606*, 33-38; (e) M. Nagata, M. Kondo, Y. Suemori, T. Ochiai, T. Dewa, T. Ohtsuka, M. Nango, *Colloids Surf. B* **2008**, *64*, 16-21; (f) S. A. Trammell, M. Moore, D. Lowy, N. Lebedev, *J. Am. Chem. Soc.* **2008**, *130*, 5579-5585; (g) S. A. Trammell, N. Lebedev, *J. Electroanal. Chem.* **2009**, *632*, 127-132; (h) S. A. Trammell, M. Moore, T. L. Schull, N. Lebedev, *J. Electroanal. Chem.* **2009**, *628*, 125-133; (i) L. Rojas de Astudillo, L. Rivera, R. Brito-Gómez, R. J. Tremont, *J. Electroanal. Chem.* **2010**, *640*, 56-60; (j) A. D. Abhayawardhana, T. C. Sutherland, *J. Electroanal. Chem.* **2011**, *653*, 50-55; (k) C. Liehn, M. Bouvet, R. Meunier-Prest, *ChemElectroChem* **2014**, *1*, 2116-2123.
- [3] A. René, D. H. Evans, *J. Phys. Chem. C* **2012**, *116*, 14454-14460.

- [4] (a) M. A. Jackisch, F. R. Fronczek, C. C. Geiger, P. S. Hale, W. H. Daly, L. G. Butler, *Acta Cryst. C* **1990**, *C46*, 919-922; (b) M. Tümer, M. Aslantaş, E. Şahin, N. Deligönül, *Spectrochim. Acta Mol. Biomol. Spectrosc.* **2008**, *70*, 477-481.

This page has been intentionally left blank

Chapter 10

Detection of Impurities in Nitrile Solvents Commonly Used for Electrochemistry via the Voltammetry of Quinones and Phenylenediamines

10.1 Introduction

10.2 Electrochemical Behavior of Quinones and Phenylenediamines in Nitrile Solvents

10.3 Qualitative and Quantitative Analysis with Purge and Trap Gas Chromatography-Mass Spectrometry

10.4 Purification Techniques

10.5 Summary

References

This page has been intentionally left blank

10.1 Introduction

The results in the previous chapters have shown that the standard EE electrochemical behavior of quinones and phenylenediamines is responsive to their surrounding environment. Thus, leading to the possibility of applying their voltammetric behavior for the detection of impurities in non-aqueous solvents. This method of detecting impurities based on changes in the voltammetric data of quinones and phenylenediamines would be highly sensitive because the analytes are almost always used in millimolar concentrations (ppm) that so happens to coincide with the amount that impurities are often found to exist in organic solvents. In addition, the method is applicable to the full gamut of contaminants because the quinones will only respond to acids whereas the phenylenediamines would display different voltammetric behavior depending if they are interacting with acids or bases.

Quinones can act as bases and hydrogen acceptors, for which their interactions with hydrogen donors in aprotic organic solvents would only cause a shift of E_{Q1} and E_{Q2} to less negative values, with a concomitant decrease in the separation between the two $1e^-$ -reduction processes (e.g. $\Delta E_Q = |E_{Q1} - E_{Q2}|$ decreases), and not affect their overall reduction behavior nor the chemical and electrochemical reversibility of the individual electron-transfer reactions. However, as shown in Section 6.2 in Chapter 6 and Section 7.3 in Chapter 7, it is possible for a single $2e^-$ -reduction behavior to be obtained if a sufficient amount of the hydrogen donor exists in solution. On the other hand, the voltammograms that would arise from proton-transfer reactions with acids are difficult to predict because any one of the three forms (Q , $Q^{\cdot-}$ and Q^{2-}) may be protonated. Nevertheless, the effects of protonation were reported in Section 7.6 in Chapter 7 to cause the voltammetric behaviors of the quinones to depart from the standard response and lead to the detection of a chemically irreversible reduction reaction prior to and greater in height than the first $1e^-$ -reduction process, the absence of the second $1e^-$ -reduction reaction and the occurrence of an oxidation reaction on the reverse scan at a potential more positive than E_{Q1} .^[1]

The voltammetry of the phenylenediamines is more sensitive to their surroundings because of their versatility in behaving as hydrogen acceptors and hydrogen donors as well as

acids and bases. As shown in Section 8.4 in Chapter 8, hydrogen bonding of the phenylenediamines to strong hydrogen donors would cause E_{P1} and E_{P2} to shift towards more positive potentials whereas interactions with hydrogen acceptors would see them move to less positive potentials, with a concomitant decrease in $\Delta E_P = |E_{P1} - E_{P2}|$ in both cases. Their overall EE oxidation response and the chemical and electrochemical reversibility of each $1e^-$ -oxidation process was also unaffected except in the presence of strong hydrogen acceptors, for which a single process involving the $2e^-$ -oxidation of P to P^{2+} would be obtained if a sufficient amount is present. Density functional theory calculations also uncovered that the neutral species P almost always behaves as a hydrogen acceptor while the other oxidized states P^{*+} and P^{2+} were strictly hydrogen donors.

In the case that the phenylenediamines are functioning as bases (see Section 8.2.2 in Chapter 8), it was found that very weak acids such as acetic acid had no effect on their voltammetric behavior unless at very high concentrations whereas the addition of an acid of moderate strength such as trifluoroacetic acid (that is capable of protonating P to give PH^+) would lead to the loss of the first electron-transfer process to be replaced by the $1e^-$ -oxidation of PH^+ to PH^{*2+} that occurs at a potential between E_{P1} and E_{P2} ; the second electron-transfer process converting P^{*+} to P^{2+} was however unaffected because PH^{*2+} is highly acidic and so fast deprotonation to P^{*+} would occur. This is unlike the situation with perchloric acid (a strong acid that can further protonate PH^+ to give PH_2^{2+}) for which both oxidation processes are not detected because PH_2^{2+} is electroinactive.^[2] The phenylenediamines, especially the P^{*+} and P^{2+} species, can also function as acids of which the consequence of proton transfer with bases are the disappearance of the first and second $1e^-$ -oxidation reactions and occurrence of new processes at potentials that are less positive than E_{P2} (if the base can deprotonate P^{2+}) or E_{P1} (if the base is able to deprotonate P^{*+}); there might also be a loss in the chemical reversibility of either one or both new oxidation processes (see Section 8.2.1 in Chapter 8).

Hence, it may be expected that both the quinones and phenylenediamines will always retain their EE electrochemical response in any aprotic organic solvent unless the solvent had

been contaminated by acids, bases, hydrogen donors and/or hydrogen acceptors. A previous study from our laboratories found that the voltammetric behavior of vitamin K₁ in propionitrile (EtCN) shows only one reduction process with the transfer of 1.5 electrons per molecule as opposed to the EE behavior recorded in MeCN and butyronitrile (PrCN).^[3] This difference in behavior can only arise from the presence of impurities because the nitrile solvents possess similar chemical and physical properties and so any electroactive compound, and not just vitamin K₁, should display the same voltammetric response in all of them. 1,4-Benzoquinone (BQ) and 1,4-phenylenediamine (PD) were selected for use to enhance the sensitivity of the detection.

10.2 Electrochemical Behavior of Quinones and Phenylenediamines in Nitrile Solvents

The cyclic voltammograms of BQ and PD as well as the blank scans performed without the analytes in MeCN, PrCN and seven samples of EtCN are shown in Figure 10.1, from which it can be observed that only MeCN and the Fluka brand of EtCN are free of electroactive impurities. In addition, it is only in this Fluka sample that the standard EE electrochemical behavior of the quinone and phenylenediamine are obtained and are similar to those recorded in MeCN.

The impurities that are responsible for the observations are likely to come from the solvents instead of the supporting electrolyte, *n*-Bu₄NPF₆, because the blank scans in MeCN and the Fluka brand of EtCN do not contain any electrochemical processes. Furthermore, the blank scans of the other brands of EtCN were dissimilar even though the same batch of supporting electrolyte was used for all the experiments. The supporting electrolyte was also synthesized in high purity via a highly efficient method that required three recrystallization steps and vacuum drying to remove ethanol and water.

A glassy carbon material was used in all experiments because the second 1e⁻-reduction reaction of quinones was found to be sluggish on a platinum surface even at slow scans rates.^[4] Nonetheless, the effect of the impurities on the electrochemical behavior of BQ and PD are

expected to be the same even if a platinum working electrode was used. It is clear that the glassy carbon working electrode is not responsible for the different voltammetric results.

Figure 10.1. Cyclic voltammograms of 1 mM (a) BQ and (b) PD with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in the labeled solvents recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The blank scans performed without BQ and PD are indicated by the voltammograms in dashed lines.

Trace water in the solvents is also unlikely to be responsible for the different voltammetric behavior of BQ and PD nor the unknown electrochemical processes because water is not known to undergo oxidation and reduction reactions within the potential window that the glassy carbon working electrode was cycled. As mentioned in the previous section and presented in Chapter 6, the effects of hydrogen bonding to water will only lead to the shifting of the redox potentials of the analytes without affecting their overall voltammetric behavior. Therefore, water cannot be held accountable for the altered voltammetric behavior of BQ and PD in the other brands of EtCN. Furthermore, Karl Fischer titrations performed under the experimental conditions revealed that the concentration of trace water in the solvents varied between 10 and 100 mM, which are well below the 13 M amount needed to merge the two 1e^- -reduction reactions of BQ into a single electrochemical process as found in Chapter 6. The measured moisture contents of

the solvents are 11.6 mM and 22.7 mM for MeCN and PrCN, and 25.6 mM (Acros Organics), 98.5 mM (Aldrich #1), 98.3 mM (Aldrich #2), 19.4 mM (Alfa Aesar #1), 57.8 mM (Alfa Aesar #2), 26.4 mM (Fluka) and 36.8 mM (Merck) for the respective brands of EtCN.

The voltammetric response of BQ in the Acros Organics, Aldrich, Merck and Alfa Aesar #2 samples of EtCN may be described as partly similar to those recorded in the Fluka brand and also in MeCN in spite of the broadness of the second reduction process and occurrence of additional oxidation processes after the scan direction had been changed. The biggest contrast was found in the Alfa Aesar #1 sample where only one reduction process was observed; this result was similar to the response of vitamin K₁ in the previous study.^[3]

As for PD in the seven EtCN samples, its cyclic voltammograms would show either one chemically irreversible oxidation reaction or two oxidation processes with an unusually small potential separation that was only noticed in the presence of strong hydrogen acceptors (see Chapter 8). The occurrence of a single oxidation process may be a consequence of strong hydrogen bonding interactions to hydrogen acceptors and involve the transfer of two electrons per molecule (also see Chapter 8).^[2] It was also noticed that the analytes and the blank scans had largely similar responses in the two Aldrich samples of EtCN (that had the same lot numbers despite their different grades of purity) as opposed to substantial contrast between the two Alfa Aesar samples (that had different lot numbers for the same grade of purity).

It is possible to infer from Figure 10.1 that bases and hydrogen acceptors are among the contaminants present in the various samples of EtCN because only they are able to affect the electrochemistry of PD but not BQ. Yet this does not rule out the existence of acids and hydrogen donors. To which it is more likely that hydrogen donors instead of acids are present to account for the observation in the Alfa Aesar #1 sample; noting that weak acids would lead to the protonation of Q⁻ or Q²⁻ and departure of the EE reduction behavior whereas strong acids would produce the electroinactive PH₂²⁺ species.

Lastly, the electrochemical behavior of the analytes in PrCN may be described to be almost similar to the response in MeCN. The smaller ΔE_p -value of ~0.4 V detected in PrCN as

compared to ~ 0.6 V in MeCN suggests that its impurities are strongly interacting with the oxidized forms of PD. A chemically irreversible oxidation process was also detected at +1.2 V vs. Fc/Fc^+ in the blanks scans.

10.3 Qualitative and Quantitative Analysis with Purge and Trap Gas Chromatography-Mass Spectrometry

The individual EtCN samples were then qualitatively and quantitatively analyzed with purge and trap gas chromatography-mass spectrometry (PAT GC-MS) and the impurities detected are listed in Table 10.1. The qualitative probability match specifies the likelihood that an unknown compound is correctly identified and is obtained by comparing the retention times and fragmentation pathways of the unknown compounds against the reference library provided by the National Institute of Standards and Technology (NIST) with values of 90% and higher indicating good matches. Only impurities with a qualitative probability match $\geq 90\%$ are included in Table 10.1 with the values in parentheses referring to their amounts that were accurately obtained through the use of high purity standards. It was noted that poor matching (defined in this work as $\leq 90\%$) could arise because the impurities existed in trace concentrations and so the mass detector is unable to pick up all of their fragmentation peaks.

2-Methyl-2-pentenal was found to be the major contaminant in the Acros Organics, Aldrich, Alfa Aesar and Merck samples of EtCN while 2-methyl-2-butenal was only found in the two Aldrich samples. A number of electroinactive impurities such as benzene, chlorobenzene, ethylbenzene, styrene, toluene and the xylenes were present in the Acros Organics, Alfa Aesar #2 and Merck samples. But it was most surprising that only nitrile contaminants were detected in the Alfa Aesar #1 and Fluka samples of EtCN given that the electrochemical response of BQ and PD were unaffected in the latter yet most significantly affected in the former. In light that bases and hydrogen acceptors were suspected as being responsible for the altered behavior of the phenylenediamine, it was therefore another great surprise that neither of them nor any acids and hydrogen donors were detected in any of the seven EtCN samples. One possible reason to their

absence could be that they have stronger affinity to water and so were not effectively purged onto the analytical trap of the atomx PAT system during the sample preparation step.

Table 10.1. Impurities detected in EtCN by purge and trap gas chromatography-mass spectrometry.

Retention Time (min)	Impurities	Supplier						
		Acros Organics	Aldrich #1	Aldrich #2	Alfa Aesar #1	Alfa Aesar #2	Fluka	Merck
		Qualitative Probability Match (%)						
11.74	2-Butenenitrile				95	92	95	
	Methacrylonitrile				93	93	93	
11.82	Benzene ^[a]					96	95	
12.13	2-Butenenitrile				92			
	Methacrylonitrile				93			
12.32	2-Methylene-butanenitrile				96		97	
	2-Methyl-2-butenenitrile				95		95	
	2-Methyl-3-butenenitrile				95		93	
	2-Methylene-butanenitrile				90	95	80	94
12.68	2-Methyl-2-butenenitrile				96	86		
	2-Methyl-3-butenenitrile				96			
13.00	2-Methyl-2-butenal	97	94	94				
13.45	Toluene ^{[a],[b]}	94 (0.13)			91 (0.05)	94 (0.05)	94 (0.08)	94 (0.26)
14.25	2-Methyl-2-pentenal	93				94		92
	2-Ethyl-2-butenal	90				93		93
14.35	2-Methyl-2-pentenal ^{[a],[b]}	96 (11.15)	96 (2.31)	96 (2.31)		96 (4.78)		97 (4.09)
	2-Ethyl-2-butenal					90		90
14.83	Chlorobenzene						90	
15.02	Ethylbenzene ^[a]	94				94	93	94
15.25	<i>m</i> -Xylene	94				95		
	<i>p</i> -Xylene	94				95		
15.69	Styrene	96				91		96
15.80	<i>o</i> -Xylene	97				95		97

[a] Positively identified with authentic samples. [b] Concentration (mmol L⁻¹) was accurately quantified with a high purity standard and reported in parenthesis.

Among the major impurities detected, it was unlikely that benzene, chlorobenzene, ethylbenzene, styrene and the xylenes were responsible for the voltammetric observations because they lack any functional groups to interact with the analytes. Moreover, the EE oxidation behavior of several phenylenediamines was reported to prevail in a 1:1 MeCN/toluene solvent mixture.^[5] The nitriles are expected to behave no differently from MeCN and PrCN. Therefore, only the

effect of the α,β -unsaturated aldehyde, 2-methyl-2-pentenal, on the voltammetric behavior of BQ and PD was further investigated.

The cyclic voltammograms of the quinone and phenylenediamine in the presence of 5 mM of 2-methyl-2-pentenal are shown in Figure 10.2 with the aldehyde giving rise to the chemically irreversible reduction reaction at about -2.6 V vs. Fc/Fc^+ . This reduction reaction is also present in the two Aldrich samples of EtCN. The presence of the aldehyde did not lead to the formation of one electrochemical process for BQ as found in the Alfa Aesar #2 sample and for PD in the various samples. This led to the conclusion that 2-methyl-2-pentenal is only partly accountable for the general findings and so suggests that other unidentified species are responsible for affecting the voltammetric behavior of BQ and PD in the EtCN solvents.

Figure 10.2. Cyclic voltammogram of 1 mM (a) BQ and (b) PD with 5 mM of 2-methyl-2-pentenal with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte recorded in MeCN at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The cyclic voltammogram in dashed line was collected in the absence of 2-methyl-2-pentenal.

10.4 Purification Techniques

The efficiency of distillation and flash column chromatography in purifying the EtCN solvent was subsequently explored, to which the Alfa Aesar #1 sample was selected for this purpose because the phenylenediamine and, more importantly, the quinone did not display their standard EE electrochemical behavior in it. The cyclic voltammograms of BQ and PD in the samples after each purification procedure are shown in Figure 10.3.

The voltammetric response of BQ and PD in the residual and distillate fractions of the Alfa Aesar #1 sample of EtCN were found to be very much alike the initial untreated sample if

the distillation was performed without a drying agent thereby suggesting that the impurities have boiling points close to that of EtCN. The electroactive, and probably also the electroinactive, impurities could however be removed if the distillation was carried out in the presence of phosphorus pentoxide (P_2O_5), a common drying agent for nitrile solvents, for which the EE oxidation behavior of PD, but not the EE reduction behavior of BQ, could be recovered. On the other hand, distillation over calcium hydride (CaH_2), another desiccating agent, could not remove the electroactive impurities and so neither the electrochemical behavior of the quinone nor the phenylenediamine was fully recaptured.

Although there are reports of P_2O_5 converting primary amides into nitriles and carboxylic acids into anhydrides,^[6] the successful recovery of the standard EE electrochemical behavior of PD but not for BQ indicates that only the base and/or hydrogen acceptor had been removed while the acid and/or hydrogen donor had remained in the Alfa Aesar #1 sample even after distillation with the desiccant. Nonetheless, P_2O_5 has also been reported to cause the polymerization of nitriles and contaminate the distillate fractions with some desiccant residue,^[7] which may be contributing to the slight differences in behavior of BQ in the undistilled and distilled samples. More importantly, the results of the distillation experiments with the drying agents support the earlier claim that trace water is not the cause of the non-ideal voltammetric response of BQ and PD.

The Alfa Aesar #1 sample of EtCN was subsequently purified by flash column chromatography with silica gel and basic activated alumina as the stationary phase. It was to our expectation that only the EE oxidation behavior of PD would be recovered in the eluate that was collected from silica gel flash column since the stationary phase is slightly acidic and so would neutralize bases. Interestingly, both the EE reduction of BQ as well as the EE oxidation of PD could be obtained in the eluate that was gathered from the activated alumina flash column. But additional oxidation processes found in the blank scans indicate that the silica gel stationary phase was more effective than the basic activated alumina stationary phase in removing electroactive impurities.

Figure 10.3. Cyclic voltammogram of 1 mM (a) BQ and (b) PD with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte recorded in the Alfa Aesar #1 sample of EtCN at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The solvent was treated either by distillation over P_2O_5 or CaH_2 , or passing it through a flash column containing silica gel or basic activated Al_2O_3 . The blank scans performed without the quinone and phenylenediamine are represented by the voltammograms in dashed lines.

10.5 Summary

Although the compounds responsible for the deviations of the electrochemical behavior of BQ and PD in the EtCN solvents were not fully determined, it may still be concluded that the voltammetric responses of quinones and phenylenediamines are applicable for the detection of impurities so long as the organic solvents are able to support and dissolve the analytes and supporting electrolyte. This method of detection is highly sensitive and has low sample consumption because only small amounts of the analytes (0.5 to 2 mM), supporting electrolyte (0.1 M) and solvents (about 5 mL) are needed. The results are easy to interpret and the procedures are cheap to setup, quick and simple to perform and also easy to maintain. The main disadvantages, however, are the inability in identifying and characterizing the contaminants as well as limitation to only aprotic organic solvents.

This study has also shown that the purity of EtCN can vary between different suppliers and so it is recommended that the solvent be first treated by flash column chromatography before its use. The passing of the solvent through a flash column with activated alumina as the stationary phase appears to be sufficient to regain both the EE standard electrochemical behavior of BQ and PD but some electroactive impurities lingered and so the use of silica gel is also suggested. Dried EtCN can thereafter be prepared via distillation over P_2O_5 or CaH_2 or storing over 3 Å molecular sieves.

References

- [1] (a) N. Gupta, H. Linschitz, *J. Am. Chem. Soc.* **1997**, *119*, 6384-6391; (b) H.-S. Kim, T. D. Chung, H. Kim, *J. Electroanal. Chem.* **2001**, *498*, 209-215; (c) J. Kim, T. D. Chung, H. Kim, *J. Electroanal. Chem.* **2001**, *499*, 78-84; (d) M. Aguilar-Martínez, N. A. Macías-Ruvalcaba, J. A. Bautista-Martínez, M. Gómez, F. J. González, I. González, *Curr. Org. Chem.* **2004**, *8*, 1721-1738; (e) N. A. Macías-Ruvalcaba, I. González, M. Aguilar-Martínez, *J. Electrochem. Soc.* **2004**, *151*, E110-E118; (f) J. A. Bautista-Martínez, I. González, M. Aguilar-Martínez, *J. Electroanal. Chem.* **2004**, *573*, 289-298; (g) P. D. Astudillo, J. Tiburcio, F. J. González, *J. Electroanal. Chem.* **2007**, *604*, 57-64.
- [2] L. A. Clare, L. E. Rojas-Sligh, S. M. Maciejewski, K. Kangas, J. E. Woods, L. J. Deiner, A. Cooksy, D. K. Smith, *J. Phys. Chem. C* **2010**, *114*, 8938-8949.
- [3] Y. Hui, E. L. K. Chng, L. P.-L. Chua, W. Z. Liu, R. D. Webster, *Anal. Chem.* **2010**, *82*, 1928-1934.
- [4] Y. Hui, E. L. K. Chng, C. Y. L. Chng, H. L. Poh, R. D. Webster, *J. Am. Chem. Soc.* **2009**, *131*, 1523-1534.
- [5] S. J. L. Lauw, X. Xu, R. D. Webster, *ChemPlusChem* **2015**, *80*, 1288-1297.
- [6] M. S. Meier, *e-EROS Encyclopedia of Reagents for Organic Synthesis* **2001**.
- [7] D. R. Burfield, K.-H. Lee, R. H. Smithers, *J. Org. Chem.* **1977**, *42*, 3060-3065.

This page has been intentionally left blank

Chapter 11

Conclusion

11.1 Conclusion

This page has been intentionally left blank

11.1 Conclusion

This thesis has shown that the electrochemical behavior of phenols, quinones and phenylenediamines in aprotic organic solvents can be strongly affected by hydrogen bonding interactions. Of the three compounds, the quinones were the most sensitive to the moisture content of the solvents because the reduced states, the radical anion $Q^{\cdot-}$ and dianion Q^{2-} , undergo strong hydrogen bonding interactions to water. It was found that changes in the concentration of water (relative to the quinones) can significantly impact their voltammetric response such as the loss in the chemical reversibility of the second reduction reaction because of kinetic instability of the dianion at trace water levels, or the convergence of the two $1e^-$ -reduction processes into a single $2e^-$ -reduction reaction at sufficiently high amounts.

The phenols and phenylenediamines were less affected by hydrogen bonding to water because they either produced monocationic species or had greater distribution of their charges and so possessed weaker hydrogen bonding abilities. Nonetheless, the redox processes of all three compounds were found to shift to smaller magnitudes with increasing concentrations of water (e.g. the reduction potentials of quinones moved towards less negative values whereas the oxidation potentials of phenols and phenylenediamines shifted to less positive values) because of the increase in thermodynamic stability as well as favorable changes to the electron affinities and ionization energies of the relevant hydrogen-bonded complexes. More importantly, our findings recommend that electrochemical studies on compounds with the tendency to participate in hydrogen bonding measure and report the moisture content of their working solutions to allow for better understanding of their voltammetric data and facilitate accurate comparisons when desired.

We have shown that voltammetry is useful for hydrogen bond analysis and that the electrochemical behavior of the quinones and phenylenediamines can serve to determine the hydrogen bonding abilities of electroinactive hydrogen donors and hydrogen acceptors especially when there are no common bases for comparisons. The electrochemical parameter $\Delta E_Q = |E_{Q1} - E_{Q2}|$ of the quinones is inversely proportional to the strength of the hydrogen donor such as alcohols and is sensitive to their steric and electronic effects. It is also able to detect the presence

of the additional hydroxyl group in diols and can provide some information regarding the length of the alkyl chain between both its hydroxyl groups. Our voltammetric method indicates that trifluoroethanol is a stronger hydrogen donor than ethylene glycol.

Although less sensitive, the phenylenediamines are more versatile in this aspect because they can function as both hydrogen donors and hydrogen acceptors. We found that bases and hydrogen acceptors exerted different effects on the electrochemical behavior of phenylenediamines and so pyridine and its derivatives could be categorized into their respective classes. In the case of bases like pyridine, defined as compounds that are capable of deprotonating P^{2+} , a third oxidation process occurred at the expense of the oxidation of P^{++} to P^{2+} to which the electrochemical parameter $\Delta E_P = |E_{P1} - E_{P3}|$ was used to determine their order of basicity. As for hydrogen acceptors, or compounds that are unable to deprotonate P^{2+} , their interactions with P^{++} and P^{2+} only shifted E_{P1} and E_{P2} to less positive potentials and so the magnitude of $\Delta E_P = |E_{P1} - E_{P2}|$ was used as the indicator of their binding abilities.

Our initial aim of using the electrochemical behavior of the phenylenediamines to determine the hydrogen donor strengths of the simple alcohols and diols surprisingly became an assessment of their (weaker) hydrogen acceptor abilities instead. This is because the quinonediimine dication P^{2+} is a much stronger hydrogen donor than the neutral phenylenediamine P is as a hydrogen acceptor. Nonetheless, the measurement of hydrogen donor strengths could still be achieved with the phenylenediamines but only for very strong hydrogen donors, such as trifluoroethanol, and weak acids, like acetic acid, that can significantly affect E_{P1} .

The electrochemical behavior of the quinones and phenylenediamines was also employed to explain the differences in the voltammetric responses obtained in propionitrile against the standard EE electrochemical behavior recorded in acetonitrile and butyronitrile. Our simpler voltammetric analyses put forward that impurities such as bases, hydrogen acceptors and hydrogen donors are present in some of the commercial brands of propionitrile and responsible for the differences. It is also substantially sensitive but is unable to identify and characterize the impurities and so cannot stand alone in qualitative analysis. Purification with flash column

chromatography using silica gel and activated alumina as stationary phases was effective in removing the unknown impurities and had assisted in recovering the standard voltammetric behavior of the quinones and phenylenediamines.

The existing voltammetric method of measuring the trace moisture content of aprotic organic solvents using hydrogen bonding interactions was extended to acetone with the use of the sterically hindered 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenoquinone to avoid nucleophilic side reactions with the carbonyl center. This is particularly useful because the measurement of moisture content of carbonyl compounds is difficult to achieve with the Karl Fischer procedure. Lastly, it was also observed that phenylenediamines had retained their standard EE oxidation behavior in protic organic solvents. Thus, their electrochemical behavior and the parameter $\Delta E_p = |E_{p1} - E_{p2}|$ may be applied to determine the moisture content of alcohols, which cannot be achieved with quinones because only one $2e^-$ -reduction process would be observed and so there would not be any $\Delta E_Q = |E_{Q1} - E_{Q2}|$ to work with.

Although more work remains to be done, the results presented in this thesis lead us to believe that the quinones and phenylenediamines have wider applications. Our current motivation is to develop a “dipstick” electrode with the compounds chemically attached onto the surface of an electrode for sensing applications.

This page has been intentionally left blank

Appendix A

A.1 *Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 1,4-Benzoquinone*

A.1.1 Gas-phase calculations

A.1.2 MeCN-solvated calculations

A.2 *Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,5-Di-tert-butyl-1,4-benzoquinone*

A.3 *Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,6-Di-tert-butyl-1,4-benzoquinone*

A.4 *Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,4,6-Trimethylphenol*

A.5 *Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,6-Di-tert-butyl-4-methylphenol*

A.6 *Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,4,6-Tri-tert-butylphenol*

A.7 *Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of Hydroquinone*

A.8 *Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,3,5,6-Tetramethyl-1,4-phenylenediamine*

This page has been intentionally left blank

A.1 Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 1,4-Benzoquinone

A.1.1 Gas-phase calculations

Table A.1. Gas-phase energies of the hydrogen-bonded complexes of 1,4-benzoquinone and its reduced forms.

No. of H ₂ O molecules (<i>n</i>)	Energy (hartrees)		
	Q(H ₂ O) _{<i>n</i>}	Q ^{•-} (H ₂ O) _{<i>n</i>}	Q ²⁻ (H ₂ O) _{<i>n</i>}
0	-381.605	-381.678	-381.531
1	-458.080	-458.154	-458.043
2	-534.555	-534.629	-534.555
3	-611.031	-611.104	-611.067
4	-687.506	-687.580	-687.543

Figure A.1. Optimized geometries for Q(H₂O)_{*n*} for 1,4-benzoquinone (*n* = 1 to 4).

Figure A.2. Optimized geometries for $Q^-(H_2O)_n$ for 1,4-benzoquinone ($n = 1$ to 4).

Figure A.3. Optimized geometries for $Q^{2-}(H_2O)_n$ for 1,4-benzoquinone ($n = 1$ to 4).

Cartesian Coordinates of Hydrogen-Bonded Complexes of 1,4-Benzoquinone

Q							
C	-0.187801	-0.425384	0.000310	O	-0.965541	-2.112743	-0.253864
C	1.293875	-0.391386	0.000544	O	1.486813	2.566647	0.271805
C	1.961837	0.765467	0.000024	O	1.117727	5.365187	0.051108
C	1.250636	2.065771	-0.000835	H	1.201721	4.396611	0.127476
C	-0.231041	2.031773	-0.001479	H	1.659116	5.736891	0.753577
C	-0.899002	0.874921	-0.000960	O	-1.470521	6.197511	-0.397050
H	1.790165	-1.354848	0.001202	H	-0.533087	5.961996	-0.228418
H	3.044367	0.817452	0.000225	H	-1.485559	6.635859	-1.252878
H	-0.727331	2.995236	-0.002362	O	-2.801580	3.777605	-0.079497
H	-1.981533	0.822935	-0.001388	H	-2.406923	4.664555	-0.212151
O	-0.796881	-1.480038	0.000470	H	-3.527806	3.907917	0.536706
O	1.859716	3.120425	-0.001545	Q(H ₂ O) ₄			
Q(H ₂ O)				C	-0.105370	-1.018190	0.349163
C	-0.222102	-0.600872	0.338094	C	1.367068	-1.064848	0.181014
C	1.247280	-0.656177	0.145008	C	2.057272	0.023045	-0.170635
C	1.958530	0.452546	-0.075167	C	1.380181	1.317815	-0.405931
C	1.307673	1.779610	-0.135131	C	-0.089256	1.371630	-0.241927
C	-0.158628	1.842430	0.055889	C	-0.776438	0.280287	0.110582
C	-0.867423	0.730923	0.276509	H	1.836621	-2.024969	0.360083
H	1.696534	-1.641121	0.194021	H	3.133134	0.019773	-0.300402
H	3.032495	0.442662	-0.219517	H	-0.574511	2.326010	-0.419047
H	-0.608645	2.827699	0.007190	H	-1.852524	0.289227	0.238807
H	-1.941484	0.744525	0.419975	O	-0.735043	-2.009820	0.670472
O	-0.869401	-1.612347	0.539412	O	2.028372	2.304320	-0.725921
O	1.970954	2.787599	-0.337964	O	1.019220	5.015410	-1.186549
O	0.190842	5.049975	-0.418366	H	1.478802	4.168995	-1.064740
H	0.982727	4.488348	-0.426507	H	0.072494	4.782253	-1.231376
H	0.501721	5.958225	-0.370593	O	-1.741411	6.145358	1.247499
Q(H ₂ O) ₂				H	-1.907173	5.904533	2.163497
C	2.449801	0.542183	0.006661	H	-0.808423	6.464901	1.206247
C	2.441777	-0.941148	-0.002609	O	-1.713182	4.349936	-0.803912
C	1.294612	-1.624482	-0.010621	H	-2.408478	4.559422	-1.434839
C	-0.010551	-0.928061	-0.010681	H	-1.840221	4.960745	-0.039551
C	-0.013420	0.549752	-0.003292	O	0.882226	6.753402	0.886296
C	1.138594	1.229286	0.006568	H	1.067836	6.144750	0.129109
H	3.412269	-1.423297	-0.002898	H	1.197736	7.622288	0.621784
H	1.255592	-2.707431	-0.017975	Q ⁻			
H	-0.978661	1.048878	-0.004395	C	-0.199763	-0.446062	-0.000040
H	1.169825	2.312510	0.015368	C	1.245401	-0.381280	0.000492
O	3.496368	1.164766	0.013341	C	1.928909	0.802411	-0.000021
O	-1.049855	-1.577315	-0.016010	C	1.262598	2.086450	-0.001068
O	-3.769116	-0.729489	-0.059004	C	-0.182566	2.021667	-0.001471
H	-2.865632	-1.096000	-0.049054	C	-0.866074	0.837976	-0.000958
H	-4.259462	-1.202498	0.619718	H	1.772503	-1.331409	0.001306
O	-3.002784	1.954347	0.065036	H	3.015302	0.820995	0.000354
H	-3.442059	1.082548	0.032170	H	-0.709670	2.971795	-0.002209
H	-3.493655	2.521636	-0.535990	H	-1.952468	0.819393	-0.001255
Q(H ₂ O) ₃				O	-0.831983	-1.540892	0.000611
C	-0.411201	-1.035462	-0.129954	O	1.894819	3.181279	-0.001535
C	1.058765	-0.949111	0.053084	Q ⁻ (H ₂ O)			
C	1.668161	0.231112	0.188795	C	-0.100838	-0.819872	0.112722
C	0.901157	1.495994	0.157436	C	1.331426	-0.616713	0.075429
C	-0.562986	1.420560	-0.016184	C	1.891682	0.621424	-0.062263
C	-1.168882	0.235645	-0.151962	C	1.096540	1.817784	-0.178182
H	1.593768	-1.891397	0.067580	C	-0.331521	1.622818	-0.146964
H	2.739330	0.327589	0.321720	C	-0.893121	0.384700	-0.010366
H	-1.126914	2.349081	-0.022251	H	1.950143	-1.504880	0.163188
H	-2.241222	0.151231	-0.283116	H	2.969694	0.750037	-0.087127
				H	-0.951189	2.509249	-0.242522
				H	-1.971662	0.259798	0.009487

O	-0.619785	-1.962722	0.241943
O	1.632627	2.966505	-0.298476
O	0.324284	5.340496	-0.134969
H	0.785934	4.470317	-0.264459
H	0.188472	5.386420	0.815287

 $Q^-(H_2O)_2$

C	0.026393	-0.625296	0.074035
C	1.440867	-0.354592	0.152403
C	1.938972	0.914354	0.074926
C	1.087719	2.066659	-0.086785
C	-0.326751	1.795951	-0.165203
C	-0.824856	0.527004	-0.087726
H	2.099891	-1.208082	0.275079
H	3.006430	1.101729	0.134389
H	-0.985777	2.649436	-0.287905
H	-1.892312	0.339629	-0.147207
O	-0.450759	-1.800907	0.143053
O	1.564880	3.242267	-0.155842
O	0.153417	5.572110	-0.175611
H	0.634197	4.707253	-0.235016
H	0.344427	5.880139	0.714329
O	0.960507	-4.130862	0.162361
H	0.769059	-4.438864	-0.727494
H	0.479719	-3.266030	0.222036

 $Q^-(H_2O)_3$

C	-0.110038	-0.584646	-0.732927
C	0.238938	-0.046358	0.559411
C	0.330817	1.297728	0.780581
C	0.084413	2.261443	-0.259397
C	-0.261953	1.727132	-1.549735
C	-0.355082	0.384144	-1.773110
H	0.429122	-0.758585	1.355442
H	0.599799	1.683663	1.758656
H	-0.449559	2.442564	-2.343731
H	-0.618983	-0.005697	-2.750713
O	-0.199276	-1.830667	-0.952446
O	0.164806	3.517088	-0.054987
O	0.049493	6.313865	-0.698588
H	0.016854	5.348811	-0.817777
H	0.277200	6.381619	0.239116
O	0.454497	-3.836929	0.791288
H	1.247637	-4.172496	0.365011
H	0.165453	-3.093709	0.206192
O	0.522288	5.128539	2.096436
H	0.455320	4.440848	1.387208
H	-0.320319	5.079752	2.556635

 $Q^-(H_2O)_4$

C	-0.148763	-0.564423	0.029812
C	1.247662	-0.204009	-0.027628
C	1.657303	1.097640	0.000845
C	0.723228	2.185156	0.091355
C	-0.668200	1.833270	0.151528
C	-1.080869	0.532906	0.123314
H	1.964466	-1.015001	-0.098799
H	2.710876	1.351838	-0.050020
H	-1.383016	2.646009	0.227219
H	-2.133805	0.276559	0.172093
O	-0.543690	-1.767557	0.001958
O	1.110304	3.405790	0.117108
O	3.574574	4.528350	0.336352
H	3.792821	4.409211	1.265213
H	2.717985	4.047103	0.216859
O	-0.270325	5.738997	-0.033727

H	0.159206	4.852049	0.061138
H	-0.455133	5.819204	-0.973984
O	1.015149	-3.996006	-0.390930
H	0.663865	-4.298889	-1.232503
H	0.490978	-3.183572	-0.190690
O	2.299447	7.207896	0.236991
H	1.392397	6.859087	0.228858
H	2.847268	6.405666	0.204268

 Q^{2-}

C	-0.218114	-0.477856	-0.000300
C	1.206077	-0.378887	0.000437
C	1.907178	0.835281	-0.000107
C	1.280947	2.118244	-0.001528
C	-0.143242	2.019275	-0.001518
C	-0.844344	0.805105	-0.000973
H	1.764328	-1.318003	0.001461
H	2.999610	0.821352	0.000508
H	-0.701496	2.958389	-0.002044
H	-1.936776	0.819039	-0.001085
O	-0.872687	-1.611405	0.000722
O	1.935525	3.251790	-0.001364

 $Q^{2-}(H_2O)$

C	-0.143615	-0.795364	0.172015
C	1.271218	-0.601393	0.096528
C	1.874282	0.643267	-0.110897
C	1.145502	1.847298	-0.271320
C	-0.258570	1.669530	-0.205167
C	-0.866908	0.425452	0.006723
H	1.897045	-1.487852	0.211126
H	2.962117	0.713314	-0.153782
H	-0.888623	2.549078	-0.342049
H	-1.955468	0.362861	0.044768
O	-0.705960	-1.952440	0.367012
O	1.742699	3.017946	-0.473188
O	0.568331	5.171399	0.136492
H	1.054841	4.263596	-0.143038
H	-0.170807	4.844019	0.657368

 $Q^{2-}(H_2O)_2$

C	-0.068275	-0.596357	0.245266
C	1.336389	-0.396058	0.207807
C	1.924047	0.853454	-0.012726
C	1.177584	2.041414	-0.215351
C	-0.227080	1.841111	-0.177915
C	-0.814735	0.591587	0.042584
H	1.977758	-1.260791	0.374740
H	3.010103	0.941321	-0.026477
H	-0.868471	2.705830	-0.344820
H	-1.900791	0.503726	0.056325
O	-0.644144	-1.766749	0.451974
O	1.753510	3.211803	-0.421835
O	0.491803	5.390090	-0.019471
H	1.005069	4.492648	-0.214313
H	-0.233839	5.088364	0.534550
O	0.616077	-3.944563	0.042325
H	1.341251	-3.641907	-0.511801
H	0.103560	-3.047325	0.240010

 $Q^{2-}(H_2O)_3$

C	-0.257506	-0.458587	0.119518
C	1.154832	-0.580384	0.239085
C	2.004388	0.525312	0.290799
C	1.522418	1.836849	0.228914

Appendix A

C	0.134579	1.988979	0.112274
C	-0.717761	0.885710	0.062553
H	1.575732	-1.580884	0.306977
H	3.078527	0.381157	0.386308
H	-0.269773	2.995163	0.052644
H	-1.790536	1.039986	-0.029264
O	-1.072994	-1.479356	0.067328
O	2.404142	2.873550	0.276260
O	1.434964	5.260952	0.505624
H	1.961712	3.802379	0.350837
H	0.796093	5.260281	1.224885
O	-0.246294	-3.842643	-0.557299
H	0.499737	-3.631897	-1.125840
H	-0.575416	-2.905522	-0.267374
O	1.381538	7.518708	-0.674424
H	1.036714	7.247077	-1.529556
H	1.425655	6.605931	-0.152361

$Q^{2-}(H_2O)_4$

C	-0.240594	-0.508937	0.279228
C	0.994980	0.120735	0.549084
C	1.250042	1.455307	0.221756
C	0.291445	2.284815	-0.402060
C	-0.944346	1.654117	-0.670747
C	-1.197742	0.320904	-0.347313
H	1.768679	-0.466851	1.039515
H	2.225771	1.883017	0.443943
H	-1.719044	2.248123	-1.151394
H	-2.167954	-0.113972	-0.578597
O	-0.491055	-1.774189	0.597793
O	0.531260	3.551451	-0.723570
O	2.075371	5.059820	0.667736
H	1.527563	4.398126	0.088418
H	1.973924	4.699412	1.553360
O	1.308455	-3.605546	0.510116
H	1.884035	-3.295749	-0.195012
H	0.634556	-2.825978	0.613113
O	-0.663644	5.958372	-0.570238
H	0.123117	6.209085	-0.068485
H	-0.452723	4.997859	-0.730050
O	-1.670072	-3.963465	-0.427638
H	-0.805867	-4.374055	-0.293315
H	-1.458485	-3.039291	-0.120991

A.1.2 MeCN-solvated calculations

Table A.2. Energies of the MeCN-solvated hydrogen-bonded complexes of 1,4-benzoquinone and its reduced forms.

No. of H ₂ O molecules (<i>n</i>)	Energy (hartrees)		
	Q(H ₂ O) _{<i>n</i>}	Q ^{•-} (H ₂ O) _{<i>n</i>}	Q ²⁻ (H ₂ O) _{<i>n</i>}
0	-381.605	-381.678	-381.531
1	-458.080	-458.227	-458.337
2	-534.555	-534.702	-534.813
3	-611.031	-611.178	-611.325
4	-687.506	-687.690	-687.800

Figure A.4. Optimized geometries for Q(H₂O)_{*n*} for 1,4-benzoquinone (*n* = 1 to 4).

Figure A.5. Optimized geometries for Q^{•-}(H₂O)_{*n*} for 1,4-benzoquinone (*n* = 1 to 4).

Figure A.6. Optimized geometries for $Q^{2-}(H_2O)_n$ for 1,4-benzoquinone ($n = 1$ to 4).

Cartesian Coordinates of Hydrogen-Bonded Complexes of 1,4-Benzoquinone

Q			
C	-0.185212	-0.421032	-0.000031
C	1.294192	-0.391502	0.000516
C	1.962033	0.765239	0.000017
C	1.248047	2.061420	-0.000989
C	-0.231357	2.031890	-0.001486
C	-0.899199	0.875148	-0.000987
H	1.795674	-1.351760	0.001300
H	3.044380	0.811123	0.000348
H	-0.732839	2.992147	-0.002245
H	-1.981546	0.829264	-0.001292
O	-0.796566	-1.479463	0.000598
O	1.859401	3.119850	-0.001543

Q(H ₂ O)			
C	-0.330274	-0.514663	-0.014433
C	1.149939	-0.507205	0.007509
C	1.835073	0.639238	0.024139
C	1.137520	1.941248	0.021424
C	-0.339234	1.938394	0.000414
C	-1.025001	0.792387	-0.016354
H	1.637421	-1.474477	0.008790
H	2.917717	0.666508	0.039847
H	-0.823759	2.907083	-0.000500
H	-2.107672	0.763710	-0.031856
O	-0.956390	-1.563276	-0.030314
O	1.759470	2.997543	0.035965
O	4.583235	3.588993	0.062526
H	4.636624	4.547981	-0.008531
H	3.632258	3.384156	0.051365

Q(H ₂ O) ₂			
C	-0.348832	-0.446761	-0.135363
C	1.105374	-0.292890	-0.362669
C	1.707121	0.894395	-0.243045
C	0.931645	2.097352	0.122654
C	-0.520027	1.950413	0.350804
C	-1.119311	0.762969	0.230795
H	1.648152	-1.191617	-0.629777
H	2.772045	1.020837	-0.407956
H	-1.059795	2.850842	0.617362
H	-2.181851	0.629122	0.393088
O	-0.894910	-1.533854	-0.246468
O	1.467266	3.195561	0.237460
O	4.183181	3.906941	-0.105494
H	4.240650	4.628853	-0.741301
H	3.231155	3.713410	-0.003660
O	5.144577	1.398659	-0.884794
H	5.848651	1.124256	-0.287902
H	4.912844	2.310802	-0.616391

Q(H ₂ O) ₃			
C	-0.510311	-0.417605	0.104580
C	0.963252	-0.328387	-0.002976
C	1.586678	0.852821	-0.041288
C	0.819103	2.113173	0.023311
C	-0.651694	2.030446	0.124338
C	-1.273691	0.849215	0.163228
H	1.500666	-1.267867	-0.047867
H	2.665081	0.933413	-0.120068
H	-1.185990	2.971606	0.166842
H	-2.350624	0.761808	0.239259
O	-1.076778	-1.499056	0.142958

O	1.377191	3.205890	-0.003114
O	4.137414	3.780166	-0.044141
H	4.322507	4.431280	-0.730229
H	3.171682	3.630748	-0.064299
O	5.218442	1.270967	-0.362054
H	5.781774	1.077484	0.395303
H	4.907744	2.196143	-0.241794
O	6.386093	0.748522	-2.852203
H	5.846700	0.064669	-3.262445
H	5.970942	0.919626	-1.982272

Q(H ₂ O) ₄			
C	-0.674454	-0.550419	0.564387
C	0.785980	-0.429211	0.355496
C	1.371973	0.764209	0.222692
C	0.575096	2.006461	0.281837
C	-0.882708	1.891704	0.486617
C	-1.467425	0.698280	0.619015
H	1.345371	-1.356053	0.317004
H	2.440088	0.868063	0.068023
H	-1.439038	2.820257	0.523364
H	-2.534104	0.587591	0.771131
O	-1.206699	-1.642903	0.686831
O	1.099116	3.110241	0.166721
O	3.827354	3.727677	-0.161697
H	3.932711	4.335794	-0.902045
H	2.867363	3.561629	-0.080083
O	4.952881	1.243719	-0.426816
H	5.593339	1.116699	0.281908
H	4.619788	2.165555	-0.334052
O	5.901484	0.650417	-2.940557
H	5.366164	-0.078119	-3.273206
H	5.558062	0.849722	-2.040369
O	6.061885	2.836650	-4.670937
H	6.018096	2.070940	-4.061581
H	6.988783	2.912066	-4.919990

Q ⁻			
C	-0.194234	-0.436497	0.000892
C	1.248179	-0.382302	0.000591
C	1.931105	0.800483	0.000024
C	1.257068	2.076885	-0.000536
C	-0.185344	2.022689	-0.001425
C	-0.868271	0.839904	-0.000861
H	1.779897	-1.328759	0.000990
H	3.016655	0.813395	0.000024
H	-0.717062	2.969145	-0.002543
H	-1.953820	0.826992	-0.001582
O	-0.829396	-1.536207	0.000258
O	1.892231	3.176594	-0.001625

Q ⁻ (H ₂ O)			
C	-0.352011	-0.523187	-0.001340
C	1.089379	-0.496935	0.079881
C	1.794147	0.672481	0.100157
C	1.142121	1.954583	0.041787
C	-0.295067	1.933902	-0.037607
C	-1.001002	0.765677	-0.058179
H	1.601710	-1.452537	0.125112
H	2.877278	0.662922	0.162500
H	-0.804344	2.891151	-0.081572
H	-2.084535	0.773248	-0.118672
O	-1.006571	-1.608738	-0.020965

Appendix A

O	1.792578	3.053429	0.058790
O	4.473215	3.355825	0.202879
H	4.858956	2.971778	-0.590879
H	3.498528	3.189815	0.130836

$Q^-(H_2O)_2$

C	-0.357694	-0.392600	-0.005175
C	1.079481	-0.391255	0.088706
C	1.799393	0.768526	0.105081
C	1.163903	2.058849	0.030006
C	-0.273419	2.057002	-0.063517
C	-0.992846	0.897801	-0.080571
H	1.579641	-1.352058	0.145725
H	2.881427	0.745428	0.176808
H	-0.769736	3.019926	-0.121072
H	-2.075204	0.915879	-0.151679
O	-1.038635	-1.469774	-0.021426
O	1.827282	3.147030	0.044546
O	4.519664	3.425665	0.216936
H	4.907328	3.058035	-0.583672
H	3.545801	3.270208	0.134430
O	-0.111042	-4.015448	0.085371
H	0.332562	-4.136688	0.930919
H	-0.398002	-3.068413	0.070845

$Q^-(H_2O)_3$

C	-0.333753	-0.375147	0.086264
C	1.102627	-0.380329	0.121975
C	1.824546	0.777494	0.103675
C	1.186760	2.068553	0.049473
C	-0.253686	2.068491	0.015447
C	-0.974186	0.910150	0.032889
H	1.600958	-1.342567	0.162812
H	2.908313	0.753178	0.131483
H	-0.751255	3.031289	-0.025203
H	-2.058036	0.931700	0.006319
O	-1.010581	-1.462783	0.102354
O	1.850183	3.154173	0.032631
O	4.556584	3.440868	0.094700
H	4.910396	3.085274	-0.726798
H	3.581943	3.283790	0.051776
O	-0.003366	-4.009205	0.154785
H	0.286521	-4.186760	1.055382
H	-0.321383	-3.075898	0.160930
O	-3.744873	-1.639515	-0.000950
H	-2.762634	-1.558323	0.023103
H	-3.922454	-2.451479	-0.486592

$Q^-(H_2O)_4$

C	-0.279482	-0.207594	0.156081
C	1.155758	-0.235092	0.191722
C	1.896247	0.908027	0.109712
C	1.278634	2.204271	-0.014945
C	-0.161929	2.225663	-0.047663
C	-0.900315	1.081479	0.032900
H	1.638773	-1.201528	0.285316
H	2.979444	0.868157	0.138270
H	-0.644058	3.192626	-0.140153
H	-1.983818	1.118690	0.007237
O	-0.973674	-1.282864	0.230842
O	1.958796	3.276093	-0.091828
O	4.673130	3.522322	-0.074566
H	5.007061	3.150156	-0.897060
H	3.695996	3.380445	-0.098755
O	-0.275170	-3.889124	0.448951
H	0.181077	-4.043866	1.282909

H	-0.419616	-2.911529	0.395999
O	-3.642185	-1.734040	0.196299
H	-2.691686	-1.459159	0.175997
H	-4.025979	-1.419560	-0.629166
O	-3.072254	-4.544684	0.376121
H	-2.102990	-4.447856	0.424850
H	-3.390117	-3.626079	0.296671

Q^{2-}

C	-0.206607	-0.458188	-0.000045
C	1.211600	-0.379516	0.000474
C	1.910310	0.831028	-0.000060
C	1.269441	2.098576	-0.001139
C	-0.148766	2.019904	-0.001469
C	-0.847476	0.809359	-0.000931
H	1.770076	-1.314618	0.001306
H	2.999327	0.814294	0.000387
H	-0.707242	2.955006	-0.002174
H	-1.936493	0.826094	-0.001251
O	-0.865063	-1.598526	0.000639
O	1.927898	3.238913	-0.001529

$Q^{2-}(H_2O)$

C	-0.258438	-0.499406	-0.133930
C	1.139997	-0.431636	0.111199
C	1.821852	0.770666	0.312421
C	1.177815	2.028781	0.285151
C	-0.213060	1.971089	0.041747
C	-0.897558	0.770553	-0.156799
H	1.694873	-1.367402	0.145404
H	2.893098	0.745046	0.501109
H	-0.763663	2.909296	0.008888
H	-1.970412	0.795236	-0.339295
O	-0.900203	-1.628841	-0.319553
O	1.819279	3.179349	0.477813
O	4.236433	3.485843	-0.294783
H	4.797494	2.906187	0.229159
H	3.273317	3.309254	0.028995

$Q^{2-}(H_2O)_2$

C	-0.416247	-0.355604	-0.003059
C	0.995570	-0.361719	0.085218
C	1.753463	0.810708	0.130675
C	1.170488	2.098744	0.091581
C	-0.241338	2.104038	0.000832
C	-0.998154	0.933247	-0.044063
H	1.505921	-1.321104	0.120033
H	2.835946	0.736353	0.200157
H	-0.747160	3.066529	-0.033931
H	-2.081438	1.002201	-0.112956
O	-1.147972	-1.460637	-0.040944
O	1.877543	3.219247	0.139835
O	4.417679	3.310938	-0.171398
H	4.825516	2.784753	0.523105
H	3.402768	3.214389	-0.033207
O	-0.132209	-3.807613	-0.220097
H	0.495845	-3.919984	0.499959
H	-0.485922	-2.845698	-0.132357

$Q^{2-}(H_2O)_3$

C	-0.428461	-0.309031	-0.053441
C	0.978069	-0.332436	0.037045
C	1.745720	0.832567	0.066089
C	1.171693	2.125349	0.009651
C	-0.240498	2.141285	-0.081506

C	-1.006438	0.976024	-0.112107
H	1.476560	-1.297038	0.084875
H	2.827224	0.750638	0.135114
H	-0.738843	3.106649	-0.129314
H	-2.088179	1.053819	-0.183923
O	-1.162439	-1.425167	-0.082473
O	1.886837	3.237145	0.040251
O	4.454547	3.281093	0.005652
H	4.777034	2.750698	0.740645
H	3.431769	3.203680	0.035329
O	-0.166571	-3.818335	-0.342585
H	0.337078	-4.014797	0.453321
H	-0.503378	-2.870214	-0.223833
O	-3.720831	-1.488500	0.400082
H	-2.731309	-1.410453	0.197009
H	-4.167240	-1.010027	-0.305217

C	-0.449107	-0.372241	-0.044326
C	0.958587	-0.385814	0.044757
C	1.715868	0.784849	0.072667
C	1.127411	2.065616	0.015626
C	-0.280486	2.079443	-0.072601
C	-1.037413	0.908492	-0.101764
H	1.464543	-1.346125	0.092315
H	2.797930	0.715322	0.140128
H	-0.786434	3.039730	-0.118934
H	-2.119479	0.978266	-0.171650
O	-1.172802	-1.491089	-0.072965
O	1.851095	3.184273	0.043186
O	4.461019	3.229619	0.031642
H	4.767383	2.791341	0.831513
H	3.452029	3.158059	0.052501
O	-0.172223	-3.880934	-0.390901
H	0.339546	-4.092560	0.395902
H	-0.509329	-2.937836	-0.249446
O	-3.732421	-1.574567	0.428650
H	-2.746812	-1.489011	0.217809
H	-4.187841	-1.089444	-0.266283
O	0.829334	5.583583	-0.090892
H	1.176264	4.633971	-0.057117
H	0.380962	5.664834	-0.938305

A.2 Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,5-Di-*tert*-butyl-1,4-benzoquinone

Table A.3. Gas-phase energies of the hydrogen-bonded complexes of 2,5-di-*tert*-butyl-1,4-benzoquinone and its reduced forms.

No. of H ₂ O molecules (<i>n</i>)	Energy (hartrees)		
	Q(H ₂ O) _{<i>n</i>}	Q [•] (H ₂ O) _{<i>n</i>}	Q ²⁻ (H ₂ O) _{<i>n</i>}
0	-696.215	-696.289	-696.179
1	-772.691	-772.764	-772.691
2	-849.166	-849.240	-849.166
3	-925.641	-925.715	-925.678
4	-1002.117	-1002.190	-1002.153

Figure A.7. Optimized geometries for Q(H₂O)_{*n*} for 2,5-di-*tert*-butyl-1,4-benzoquinone (*n* = 1 to 4).

Figure A.8. Optimized geometries for Q[•](H₂O)_{*n*} for 2,5-di-*tert*-butyl-1,4-benzoquinone (*n* = 1 to 4).

Figure A.9. Optimized geometries for $Q^{2-}(H_2O)_n$ for 2,5-di-*tert*-butyl-1,4-benzoquinone ($n = 1$ to 4).

Cartesian Coordinates of Hydrogen-Bonded Complexes of 2,5-Di-*tert*-butyl-1,4-benzoquinone

Q							
C	0.272377	-0.495789	0.000088	H	0.771543	4.768634	-0.708607
C	1.608747	-0.426658	-0.093810	H	0.907150	4.696269	1.056023
C	2.397688	0.825004	-0.103201	H	2.082078	5.609603	0.113861
C	1.677332	2.136008	-0.000928	H	4.102443	2.687167	1.138752
C	0.340966	2.066874	0.093016	H	3.923398	4.444499	1.204964
C	-0.447970	0.815209	0.102461	H	2.839850	3.415588	2.144950
H	2.228264	-1.310160	-0.172688	H	3.732728	4.545485	-1.334236
H	-0.278551	2.950374	0.171904	H	3.897647	2.789143	-1.447036
C	-0.514392	-1.805039	0.005214	H	2.505142	3.600876	-2.180860
C	0.418871	-3.020559	-0.107686	O	3.516769	0.779747	-0.189180
C	-1.310087	-1.931123	1.325351	O	-1.753492	0.970689	0.223183
C	-1.487225	-1.831919	-1.196978	O	4.475972	-1.914828	-0.473021
H	0.995245	-3.010871	-1.035680	H	5.374960	-2.105871	-0.191572
H	1.117748	-3.079891	0.729939	H	4.356850	-0.955785	-0.369621
H	-0.178932	-3.933832	-0.101709	Q(H ₂ O) ₂			
H	-2.031567	-1.124881	1.438059	C	0.078747	-0.509353	-0.048293
H	-1.850527	-2.880821	1.333341	C	1.418184	-0.491664	-0.161797
H	-0.638483	-1.922732	2.187616	C	2.237503	0.735490	-0.150715
H	-2.027152	-2.781946	-1.205560	C	1.573638	2.069340	-0.006062
H	-2.214343	-1.024595	-1.143516	C	0.239256	2.046612	0.120826
H	-0.942097	-1.749918	-2.140786	C	-0.590179	0.820880	0.127674
C	2.464095	3.445263	-0.006050	H	1.996822	-1.402758	-0.263039
C	1.530867	4.660743	0.107554	H	-0.346028	2.948664	0.237649
C	3.437416	3.471818	1.195752	C	-0.759446	-1.784874	-0.075072
C	3.259246	3.571725	-1.326479	C	0.113728	-3.024688	-0.318438
H	0.831582	4.720230	-0.729721	C	-1.480708	-1.956726	1.282973
H	0.954942	4.650859	1.035825	C	-1.802149	-1.702578	-1.215176
H	2.128651	5.574028	0.101474	H	0.620804	-2.979231	-1.284943
H	4.164479	2.664475	1.141794	H	0.878060	-3.161273	0.447377
H	3.977387	4.421820	1.204344	H	-0.523345	-3.911598	-0.320721
H	2.892669	3.389608	2.139762	H	-2.155290	-1.128449	1.490309
H	3.799608	4.521468	-1.334459	H	-2.064769	-2.880024	1.265682
H	3.980742	2.765570	-1.439676	H	-0.758134	-2.035527	2.098866
H	2.587293	3.563495	-2.188474	H	-2.364818	-2.638357	-1.253670
O	3.612371	0.747985	-0.193793	H	-2.504715	-0.885601	-1.067054
O	-1.662641	0.892216	0.193228	H	-1.311126	-1.571701	-2.182960
Q(H ₂ O)				C	2.404244	3.352822	-0.005595
C	0.164498	-0.438681	0.006875	C	1.512483	4.594175	0.156494
C	1.502460	-0.387032	-0.091412	C	3.406549	3.330667	1.171980
C	2.296215	0.857718	-0.096313	C	3.166772	3.484928	-1.344507
C	1.597231	2.176764	0.010533	H	0.792718	4.692060	-0.659416
C	0.260865	2.122904	0.110926	H	0.962772	4.584508	1.100447
C	-0.541350	0.878576	0.121207	H	2.138596	5.488178	0.150380
H	2.106587	-1.281008	-0.175410	H	4.113770	2.508843	1.085814
H	-0.348061	3.013043	0.195007	H	3.969012	4.267341	1.186888
C	-0.633578	-1.739998	0.005927	H	2.883300	3.241096	2.127267
C	0.288372	-2.962163	-0.125345	H	3.736896	4.417055	-1.346372
C	-1.421390	-1.869383	1.330805	H	3.859146	2.660466	-1.499399
C	-1.615593	-1.745552	-1.189521	H	2.471168	3.518576	-2.186762
H	0.861654	-2.948359	-1.054617	O	3.456268	0.642488	-0.264516
H	0.993521	-3.036867	0.705187	O	-1.793961	0.939029	0.285171
H	-0.318766	-3.869304	-0.125044	O	5.411385	-1.390710	-0.389787
H	-2.134942	-1.057961	1.457057	H	6.100744	-1.134169	0.229807
H	-1.970252	-2.814142	1.333155	H	4.759470	-0.664858	-0.384235
H	-0.743325	-1.876646	2.187932	O	3.525680	-3.377580	0.165338
H	-2.161394	-2.692002	-1.203728	H	3.697570	-4.189195	-0.320361
H	-2.337624	-0.934487	-1.123034	H	4.293101	-2.798788	-0.006727
H	-1.076555	-1.658409	-2.136241	Q(H ₂ O) ₃			
C	2.398038	3.478323	0.002009	C	0.415932	-0.405872	0.183986
C	1.476168	4.701837	0.123523	C	1.732289	-0.178849	0.050198
C	3.378907	3.497178	1.197723	C	2.346895	1.154602	-0.091017
C	3.183900	3.600733	-1.324322	C	1.474517	2.370472	-0.082359

C	0.159104	2.144070	0.049354
C	-0.464491	0.808013	0.184703
H	2.449486	-0.988252	0.035836
H	-0.565849	2.946783	0.065341
C	-0.191771	-1.798293	0.328785
C	0.890977	-2.888425	0.308972
C	-0.950897	-1.895045	1.673242
C	-1.166058	-2.063390	-0.843123
H	1.454564	-2.900257	-0.626358
H	1.603786	-2.780751	1.129401
H	0.412712	-3.864163	0.415842
H	-1.775380	-1.187064	1.725156
H	-1.355446	-2.903761	1.785499
H	-0.277342	-1.711857	2.514179
H	-1.576730	-3.071373	-0.747785
H	-1.992441	-1.355728	-0.850854
H	-0.645157	-2.006389	-1.021107
C	2.088384	3.763072	-0.221171
C	1.007547	4.855234	-0.187356
C	3.067479	4.022676	0.947217
C	2.838018	3.873499	-1.569370
H	0.293016	4.752530	-1.007367
H	0.452507	4.855374	0.753652
H	1.483182	5.832528	-0.287221
H	3.893977	3.315490	0.946031
H	3.478798	5.030931	0.857518
H	2.552627	3.957283	1.909034
H	3.240812	4.883401	-1.677621
H	3.663514	3.167983	-1.631807
H	2.160544	3.693282	-2.407804
O	3.564567	1.236098	-0.213706
O	-1.677645	0.742516	0.292416
O	5.417549	-0.956520	-0.491070
H	5.371238	-1.435402	0.352326
H	4.852935	-0.171024	-0.386653
O	4.269880	-3.193191	-1.560265
H	4.722846	-3.625066	-2.289959
H	4.710685	-2.323659	-1.427526
O	4.650507	-3.149139	1.216385
H	4.485102	-3.492495	0.317804
H	5.123885	-3.837615	1.691824

 $Q(H_2O)_4$

C	0.169083	-0.303311	0.237240
C	1.494330	-0.108635	0.151446
C	2.142530	1.201681	-0.048849
C	1.294506	2.427565	-0.183872
C	-0.029287	2.234665	-0.086484
C	-0.684136	0.925682	0.135186
H	2.196875	-0.927213	0.229586
H	-0.738186	3.048344	-0.159470
C	-0.475125	-1.672577	0.436839
C	0.580515	-2.789165	0.470581
C	-1.244213	-1.690590	1.778698
C	-1.447961	-1.966904	-0.729256
H	1.136648	-2.848928	-0.468437
H	1.299541	-2.666203	1.282855
H	0.077741	-3.747622	0.615105
H	-2.041860	-0.950725	1.795315
H	-1.687311	-2.678220	1.927380
H	-0.569140	-1.498557	2.616194
H	-1.875467	-2.963749	-0.597652
H	-2.262520	-1.247159	-0.770080
H	-0.922012	-1.955195	-1.687386
C	1.942041	3.792959	-0.411197
C	0.883480	4.902204	-0.517335
C	2.875455	4.134631	0.773910
C	2.750814	3.773068	-1.729160

H	0.200812	4.739820	-1.354631
H	0.291803	4.993382	0.396413
H	1.382886	5.858653	-0.681865
H	3.690566	3.420430	0.866303
H	3.304887	5.127701	0.621344
H	2.319504	4.153238	1.714700
H	3.192447	4.758010	-1.898373
H	3.553254	3.039362	-1.698491
H	2.103209	3.547496	-2.580163
O	3.366100	1.253834	-0.100273
O	-1.899627	0.893249	0.231387
O	5.287194	-0.849805	0.453007
H	4.830182	-1.379740	1.135324
H	4.686581	-0.119623	0.229113
O	5.952887	-2.810296	-1.277236
H	6.900602	-2.796466	-1.439214
H	5.751802	-2.007482	-0.733982
O	4.785192	-4.666183	0.334857
H	5.256179	-4.095790	-0.318358
H	4.174903	-5.211161	-0.170115
O	3.949570	-2.723280	2.079918
H	4.187675	-3.504548	1.529660
H	4.253022	-2.920714	2.971049

 Q^-

C	0.259772	-0.441263	-0.012993
C	1.625059	-0.384909	-0.107538
C	2.418546	0.822079	-0.103313
C	1.689921	2.081494	0.012226
C	0.324633	2.025141	0.106765
C	-0.468853	0.818152	0.102560
H	2.218814	-1.286705	-0.195759
H	-0.269124	2.926938	0.194963
C	-0.513163	-1.767991	-0.027128
C	0.414267	-2.987371	-0.153766
C	-1.315760	-1.919606	1.284726
C	-1.488175	-1.790075	-1.226106
H	0.995267	-2.962901	-1.079000
H	1.115549	-3.053955	0.681756
H	-0.186444	-3.902323	-0.159818
H	-1.999423	-1.081621	1.409830
H	-1.891026	-2.852894	1.272642
H	-0.640202	-1.950864	2.144700
H	-2.058459	-2.726516	-1.235531
H	-2.181043	-0.952266	-1.167731
H	-0.936212	-1.721649	-2.168225
C	2.462862	3.408217	0.026329
C	1.535437	4.627614	0.152841
C	3.437808	3.430363	1.225358
C	3.265535	3.559739	-1.285489
H	0.834182	4.694138	-0.682708
H	0.954408	4.603223	1.078059
H	2.136155	5.542562	0.158839
H	4.130662	2.592534	1.167078
H	4.008112	4.366792	1.234750
H	2.885792	3.362012	2.167452
H	3.840815	4.493019	-1.273429
H	3.949192	2.721735	-1.410502
H	2.590027	3.590955	-2.145503
O	3.679609	0.751105	-0.197055
O	-1.729920	0.889134	0.196247

 $Q^-(H_2O)$

C	0.134928	-0.395015	-0.026737
C	1.493978	-0.353122	-0.191987
C	2.295040	0.843362	-0.189902
C	1.601892	2.108611	-0.004468

Appendix A

C	0.243360	2.068203	0.161388
C	-0.566018	0.871159	0.166485
H	2.063461	-1.261099	-0.346225
H	-0.331286	2.974516	0.305287
C	-0.656054	-1.710068	-0.042829
C	0.246790	-2.935301	-0.258267
C	-1.390548	-1.894472	1.304461
C	-1.692603	-1.680112	-1.188844
H	0.781036	-2.887648	-1.210028
H	0.988705	-3.041497	0.537031
H	-0.366634	-3.841430	-0.264520
H	-2.060428	-1.057124	1.491942
H	-1.973006	-2.822875	1.293694
H	-0.671616	-1.957574	2.126636
H	-2.271618	-2.610672	-1.199628
H	-2.373948	-0.839913	-1.066479
H	-1.190740	-1.584402	-2.156016
C	2.394062	3.424413	0.002423
C	1.489122	4.650214	0.207786
C	3.428746	3.407282	1.150194
C	3.128159	3.601408	-1.345811
H	0.745704	4.746773	-0.587350
H	0.958115	4.609899	1.162038
H	2.101012	5.557333	0.204316
H	4.116109	2.571175	1.035410
H	4.002832	4.340871	1.156146
H	2.925677	3.314896	2.117214
H	3.709125	4.530707	-1.341157
H	3.800340	2.765275	-1.529424
H	2.408979	3.657624	-2.168142
O	3.558903	0.768841	-0.345707
O	-1.816320	0.957157	0.331272
O	5.089949	-1.485017	-0.370171
H	4.983638	-1.783018	0.537266
H	4.521209	-0.674385	-0.421609

Q⁺(H₂O)₂

C	0.119944	-0.396452	0.002585
C	1.474991	-0.350230	-0.187608
C	2.272396	0.849556	-0.187657
C	1.581465	2.112107	0.028112
C	0.226415	2.065888	0.218287
C	-0.570987	0.866102	0.218341
H	2.044114	-1.254687	-0.359953
H	-0.342715	2.970348	0.390590
C	-0.668319	-1.713705	-0.010076
C	0.237676	-2.932817	-0.247332
C	-1.380237	-1.911503	1.347318
C	-1.721049	-1.682402	-1.141056
H	0.755623	-2.878035	-1.207626
H	0.992940	-3.040101	0.535001
H	-0.371525	-3.841453	-0.248388
H	-2.056803	-1.084119	1.552647
H	-1.953245	-2.845316	1.339423
H	-0.648466	-1.972761	2.158006
H	-2.289792	-2.618772	-1.152430
H	-2.411713	-0.852734	-1.002451
H	-1.234292	-1.572566	-2.114343
C	2.369724	3.429361	0.040719
C	1.463740	4.648478	0.277995
C	3.422510	3.398076	1.171648
C	3.081581	3.627127	-1.316712
H	0.708282	4.755600	-0.504174
H	0.946029	4.593839	1.238423
H	2.072908	5.557137	0.278755
H	4.113136	2.568374	1.033054
H	3.991288	4.334425	1.182947
H	2.935798	3.288308	2.144966

H	3.654558	4.560959	-1.308879
H	3.758168	2.799757	-1.522033
H	2.349776	3.688326	-2.127373
O	3.530171	0.778408	-0.369407
O	-1.828770	0.937260	0.400042
O	5.054633	-1.488393	-0.533112
H	5.104015	-1.734011	0.394672
H	4.488151	-0.677033	-0.535134
O	-3.353192	3.203979	0.564452
H	-2.786739	2.392593	0.566370
H	-3.403049	3.449347	-0.363373

Q⁺(H₂O)₃

C	0.107708	-0.430500	0.071935
C	1.472370	-0.417411	-0.036806
C	2.289937	0.766461	-0.047814
C	1.617348	2.050569	0.058400
C	0.252886	2.038795	0.167696
C	-0.567559	0.854312	0.182261
H	2.030553	-1.340400	-0.127713
H	-0.307185	2.960809	0.255180
C	-0.704852	-1.732491	0.077632
C	0.188173	-2.977035	-0.051426
C	-1.492747	-1.851743	1.401737
C	-1.693706	-1.737685	-1.110287
H	0.757097	-2.978769	-0.984042
H	0.897865	-3.058668	0.775281
H	-0.437895	-3.873815	-0.041389
H	-2.160080	-1.002083	1.532804
H	-2.086352	-2.772387	1.404271
H	-0.807430	-1.891376	2.253282
H	-2.276994	-2.664920	-1.109829
H	-2.376728	-0.892583	-1.049017
H	-1.152706	-1.681158	-2.059160
C	2.429768	3.353307	0.049243
C	1.535126	4.597322	0.172683
C	3.416903	3.364552	1.238423
C	3.218119	3.469498	-1.274753
H	0.824998	4.674219	-0.653905
H	0.965999	4.602153	1.105074
H	2.160331	5.494704	0.158861
H	4.101742	2.520595	1.182522
H	3.998671	4.292717	1.235611
H	2.874320	3.310774	2.186517
H	3.812411	4.389654	-1.279235
H	3.884996	2.619309	-1.404609
H	2.533081	3.507656	-2.126493
O	3.558676	0.665007	-0.147171
O	-1.830538	0.957676	0.287093
O	5.013128	-1.540968	-0.046967
H	5.143753	-1.672232	0.896378
H	4.422460	-0.733365	-0.115825
O	-3.316789	3.256934	0.168484
H	-2.761499	2.446025	0.275192
H	-3.498600	3.292092	-0.774526
O	7.460063	-1.111337	-1.349575
H	7.377680	-0.190610	-1.613697
H	6.603493	-1.310024	-0.913393

Q⁺(H₂O)₄

C	0.324222	-0.400303	-0.066112
C	1.687838	-0.363982	-0.177557
C	2.484094	0.830824	-0.190378
C	1.801843	2.104813	-0.062685
C	0.437743	2.072350	0.049498
C	-0.366837	0.876182	0.052210
H	2.261858	-1.277641	-0.262560

H	-0.134957	2.984922	0.148556
C	-0.467884	-1.713870	-0.059093
C	0.444380	-2.943249	-0.198052
C	-1.243398	-1.848417	1.271045
C	-1.465349	-1.730799	-1.239699
H	1.003172	-2.934030	-1.136985
H	1.163361	-3.015465	0.621080
H	-0.166686	-3.850006	-0.184794
H	-1.925527	-1.011767	1.409278
H	-1.820064	-2.779438	1.276019
H	-0.551210	-1.877465	2.117104
H	-2.032220	-2.667863	-1.237894
H	-2.162746	-0.898195	-1.171138
H	-0.933229	-1.662053	-2.192801
C	2.591522	3.422300	-0.049216
C	1.675341	4.643293	0.136073
C	3.604468	3.417875	1.117840
C	3.345159	3.600390	-1.385683
H	0.950723	4.740481	-0.675527
H	1.121954	4.601510	1.076987
H	2.284154	5.551531	0.147563
H	4.312179	2.597573	1.017496
H	4.160534	4.360997	1.134091
H	3.086380	3.316380	2.075646
H	3.903441	4.542355	-1.377889
H	4.045999	2.787455	-1.560709
H	2.640982	3.635157	-2.221533
O	3.760666	0.734211	-0.305816
O	-1.628354	0.962658	0.159866
O	5.223324	-1.209823	0.939981
H	5.616177	-0.732260	1.676094
H	4.649808	-0.544315	0.485525
O	-3.168960	3.239841	0.158120
H	-2.586214	2.445448	0.215337
H	-3.613597	3.144476	-0.688436
O	7.111379	-1.597297	-1.288958
H	6.635117	-0.967204	-1.853732
H	6.569886	-1.610326	-0.481799
O	5.189477	0.230314	-2.622178
H	4.600091	-0.324250	-3.141779
H	4.678373	0.438292	-1.807946

 Q^{2-}

C	0.257179	-0.405094	-0.009896
C	1.655118	-0.352920	-0.103031
C	2.448378	0.827058	-0.100667
C	1.692553	2.045300	0.009085
C	0.294614	1.993125	0.102219
C	-0.498645	0.813149	0.099852
H	2.231887	-1.270033	-0.186518
H	-0.282153	2.910240	0.185708
C	-0.500433	-1.745588	-0.025017
C	0.418390	-2.972479	-0.147487
C	-1.312676	-1.891087	1.283029
C	-1.479198	-1.766440	-1.222521
H	1.004420	-2.947843	-1.070447
H	1.120708	-3.036763	0.688358
H	-0.189204	-3.887715	-0.153189
H	-1.946218	-1.008820	1.398262
H	-1.936262	-2.799276	1.264403
H	-0.634987	-1.960364	2.141015
H	-2.098649	-2.677708	-1.214159
H	-2.118872	-0.882998	-1.163884
H	-0.920586	-1.742425	-2.164637
C	2.450142	3.385807	0.024212
C	1.531278	4.612666	0.146680
C	3.428895	3.406692	1.221726
C	3.262383	3.531341	-1.283832

H	0.828962	4.676927	-0.689168
H	0.945244	4.588007	1.069637
H	2.138843	5.527922	0.152387
H	4.068611	2.523282	1.163087
H	4.048304	4.317990	1.213379
H	2.870277	3.382641	2.163838
H	3.885918	4.439565	-1.265210
H	3.895975	2.649109	-1.399055
H	2.584696	3.600574	-2.141824
O	3.755813	0.781393	-0.191781
O	-1.806080	0.858801	0.190972

 $Q^{2-}(H_2O)$

C	0.178174	-0.378125	-0.046179
C	1.566997	-0.332583	-0.231620
C	2.358124	0.838909	-0.232048
C	1.642332	2.058981	-0.029898
C	0.255113	2.017278	0.152298
C	-0.551070	0.843709	0.160549
H	2.116252	-1.252489	-0.406529
H	-0.303916	2.935019	0.305673
C	-0.593945	-1.709087	-0.065058
C	0.302180	-2.937403	-0.293766
C	-1.322682	-1.899829	1.285712
C	-1.646674	-1.674992	-1.197590
H	0.830516	-2.882618	-1.249435
H	1.053202	-3.044472	0.494034
H	-0.314381	-3.845867	-0.298448
H	-1.942363	-1.021497	1.476824
H	-1.951549	-2.803549	1.271339
H	-0.593177	-2.005547	2.095925
H	-2.271430	-2.581595	-1.184461
H	-2.275029	-0.791986	-1.065976
H	-1.149823	-1.617664	-2.171995
C	2.414327	3.392443	-0.017441
C	1.512253	4.618382	0.205543
C	3.464253	3.371312	1.117308
C	3.140123	3.583993	-1.369156
H	0.758575	4.716096	-0.580595
H	0.987097	4.565684	1.163041
H	2.125518	5.529026	0.203587
H	4.110344	2.501406	0.992711
H	4.073449	4.288064	1.107004
H	2.965412	3.305084	2.090018
H	3.754801	4.497069	-1.359632
H	3.774240	2.717315	-1.561051
H	2.408814	3.674487	-2.179497
O	3.673737	0.797179	-0.415925
O	-1.842615	0.901994	0.339767
O	5.067045	-1.303131	0.068393
H	4.440162	-1.852521	0.547507
H	4.496752	-0.459620	-0.152030

 $Q^{2-}(H_2O)_2$

C	0.297514	-0.719729	0.034292
C	1.654279	-0.533111	-0.256808
C	2.320148	0.715098	-0.306603
C	1.504438	1.856228	-0.034041
C	0.147671	1.669604	0.257053
C	-0.518186	0.421391	0.306866
H	2.279638	-1.389727	-0.485253
H	-0.477736	2.526192	0.485485
C	-0.333226	-2.124374	0.062919
C	0.669686	-3.248690	-0.245038
C	-0.927111	-2.395698	1.464134
C	-1.464858	-2.205321	-0.987501
H	1.112330	-3.138623	-1.238359

Appendix A

H	1.486413	-3.275147	0.481321
H	0.154597	-4.216898	-0.209148
H	-1.631556	-1.602193	1.716143
H	-1.441632	-3.367660	1.490510
H	-0.129780	-2.412836	2.214646
H	-1.973974	-3.179310	-0.940560
H	-2.186158	-1.408288	-0.804693
H	-1.052825	-2.085514	-1.994901
C	2.135126	3.260900	-0.062659
C	1.132144	4.385126	0.245373
C	3.266778	3.341922	0.987742
C	2.728930	3.532316	-1.463894
H	0.315161	4.411297	-0.480708
H	0.689844	4.275208	1.238864
H	1.647073	5.353406	0.209107
H	3.988108	2.544915	0.804929
H	3.775839	4.315939	0.940771
H	2.854767	3.222116	1.995153
H	3.243154	4.504433	-1.490333
H	3.433634	2.739028	-1.715853
H	1.931594	3.549170	-2.214408
O	3.608837	0.803149	-0.590542
O	-1.806873	0.333372	0.590884
O	5.253351	-1.132512	-0.134749
H	4.736536	-1.695338	0.448707
H	4.591253	-0.366353	-0.346705
O	-3.451573	2.266443	0.124309
H	-2.933680	2.827074	-0.460307
H	-2.789600	1.501542	0.340909

$Q^{2-}(H_2O)_3$

C	0.391221	-0.749458	-0.027896
C	1.753165	-0.557272	-0.283074
C	2.410699	0.689428	-0.303551
C	1.601063	1.830208	-0.046586
C	0.237887	1.642421	0.209285
C	-0.429212	0.392485	0.234097
H	2.388109	-1.408919	-0.503610
H	-0.393549	2.496521	0.427170
C	-0.239159	-2.153489	-0.028717
C	0.773566	-3.272439	-0.322944
C	-0.868053	-2.439713	1.354110
C	-1.343178	-2.224800	-1.108773
H	1.240722	-3.151903	-1.303591
H	1.571405	-3.305563	0.423947
H	0.260059	-4.241681	-0.309809
H	-1.580719	-1.651226	1.597600
H	-1.380769	-3.412488	1.356677
H	-0.090607	-2.463605	2.124920
H	-1.850417	-3.200140	-1.085148
H	-2.071970	-1.432365	-0.937150
H	-0.905999	-2.093480	-2.103849
C	2.229837	3.236941	-0.048652
C	1.211354	4.354504	0.233360
C	3.325262	3.320148	1.038272
C	2.864570	3.520693	-1.428526
H	0.416477	4.378591	-0.516607
H	0.741118	4.239971	1.213202
H	1.722234	5.324892	0.214769
H	4.072573	2.545284	0.871534
H	3.814341	4.304653	1.023299
H	2.885346	3.174686	2.030056
H	3.361141	4.501464	-1.434664
H	3.593482	2.745783	-1.664005
H	2.093417	3.525750	-2.205678

O	3.725275	0.766159	-0.545450
O	-1.719047	0.304286	0.484623
O	5.284462	-0.730468	0.889279
H	4.676954	-1.370988	1.270177
H	4.657245	-0.105677	0.367465
O	-3.368315	2.260249	0.074266
H	-2.870010	2.812269	-0.534936
H	-2.709721	1.493747	0.270370
O	5.415162	-0.537654	-2.223344
H	4.678751	-0.014829	-1.805376
H	5.788991	-0.946551	-1.432167

$Q^{2-}(H_2O)_4$

C	0.461145	-0.916485	-0.168318
C	1.817442	-0.642194	-0.372406
C	2.413624	0.633582	-0.286857
C	1.544414	1.714722	0.031722
C	0.188077	1.440444	0.235808
C	-0.408146	0.164671	0.150265
H	2.497252	-1.444379	-0.636645
H	-0.491700	2.242649	0.500096
C	-0.096974	-2.346383	-0.291055
C	0.982605	-3.387346	-0.633115
C	-0.747067	-2.769473	1.045296
C	-1.162118	-2.395303	-1.409678
H	1.471941	-3.170707	-1.585862
H	1.757754	-3.437851	0.136163
H	0.519731	-4.378459	-0.709009
H	-1.521267	-2.054982	1.322630
H	-1.190949	-3.771168	0.960486
H	0.004867	-2.797650	1.840472
H	-1.604677	-3.398800	-1.480509
H	-1.948806	-1.669976	-1.205645
H	-0.707132	-2.156224	-2.376006
C	2.102511	3.144654	0.154395
C	1.022899	4.185614	0.496317
C	3.167588	3.193708	1.273071
C	2.752673	3.567655	-1.181954
H	0.247796	4.236035	-0.273012
H	0.533514	3.969050	1.449055
H	1.485743	5.176746	0.572156
H	3.954366	2.468474	1.069092
H	3.610014	4.197263	1.343918
H	2.712585	2.954573	2.239377
H	3.196628	4.569319	-1.097156
H	3.526815	2.853087	-1.459249
H	2.000761	3.595870	-1.977149
O	3.721764	0.789605	-0.490377
O	-1.716194	0.008621	0.353786
O	5.348439	-0.759397	0.830020
H	4.771977	-1.456003	1.156773
H	4.697323	-0.125164	0.360460
O	-3.342500	1.560364	-0.963755
H	-2.766178	2.256831	-1.290981
H	-2.691208	0.925019	-0.495972
O	5.495024	-0.306411	-2.248109
H	4.732932	0.149524	-1.803567
H	5.879858	-0.758331	-1.486170
O	-3.494472	1.104682	2.108632
H	-3.875703	1.556511	1.344745
H	-2.731143	0.648131	1.667288

A.3 Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,6-Di-*tert*-butyl-1,4-benzoquinone

Table A.4. Gas-phase energies of the hydrogen-bonded complexes of 2,6-di-*tert*-butyl-1,4-benzoquinone and its reduced forms.

No. of H ₂ O molecules (<i>n</i>)	Energy (hartrees)		
	Q(H ₂ O) _{<i>n</i>}	Q [•] (H ₂ O) _{<i>n</i>}	Q ²⁻ (H ₂ O) _{<i>n</i>}
0	-696.215	-696.289	-696.179
1	-772.691	-772.764	-772.691
2	-849.166	-849.240	-849.166
3	-925.641	-925.715	-925.678
4	-1002.117	-1002.190	-1002.153

Figure A.10. Optimized geometries for Q(H₂O)_{*n*} for 2,6-di-*tert*-butyl-1,4-benzoquinone (*n* = 1 to 4).

Figure A.11. Optimized geometries for $Q^{\bullet+}(H_2O)_n$ for 2,6-di-*tert*-butyl-1,4-benzoquinone ($n = 1$ to 4).

Figure A.12. Optimized geometries for $Q^{2-}(H_2O)_n$ for 2,6-di-*tert*-butyl-1,4-benzoquinone ($n = 1$ to 4).

Cartesian Coordinates of Hydrogen-Bonded Complexes of 2,6-Di-*tert*-butyl-1,4-benzoquinone

Q			
C	0.055948	-0.351830	0.081846
C	1.391363	-0.396754	0.200166
C	2.148522	0.910457	0.191369
C	1.402194	2.214113	0.031237
C	0.066335	2.165233	-0.080442
C	-0.692241	0.905982	-0.058957
H	-0.560886	-1.240098	0.081650
H	-0.542877	3.051363	-0.194780
O	3.360114	0.913208	0.314509
O	-1.910251	0.904564	-0.159201
C	2.191753	3.527208	0.004419
C	2.953295	3.717948	1.337161
C	3.189406	3.522441	-1.177782
C	1.257329	4.734643	-0.177728
H	2.260290	3.731677	2.182285
H	3.686426	2.931874	1.500481
H	3.475905	4.677516	1.320633
H	2.665749	3.391998	-2.128332
H	3.710434	4.482266	-1.215044
H	3.931929	2.734417	-1.078379
H	1.854438	5.648048	-0.197342
H	0.700866	4.685927	-1.116491
H	0.541295	4.828597	0.641910
C	2.170609	-1.708866	0.343141
C	3.165182	-1.865098	-0.830895
C	2.932218	-1.731793	1.689052
C	1.225335	-2.921953	0.320634
H	2.639854	-1.855507	-1.789380
H	3.912175	-1.075175	-0.834864
H	3.679811	-2.825121	-0.743911
H	2.240937	-1.625164	2.528966
H	3.442762	-2.691690	1.799050
H	3.675113	-0.940068	1.746956
H	1.815521	-3.834728	4.420443
H	0.510446	-2.901986	1.146307
H	0.667517	-2.992098	-0.615930

Q(H ₂ O)			
C	0.024527	-0.207770	0.092006
C	1.359152	-0.300761	0.202209
C	2.166968	0.975489	0.182892
C	1.469271	2.309119	0.034437
C	0.131952	2.309454	-0.068508
C	-0.666274	1.079025	-0.046977
H	-0.623533	-1.073789	0.098956
H	-0.446076	3.216787	-0.176374
O	3.378837	0.933452	0.287575
O	-1.889321	1.136179	-0.146850
C	2.304628	3.592219	0.008134
C	3.083453	3.746410	1.335785
C	3.291261	3.559165	-1.183003
C	1.412645	4.833804	-0.158328
H	2.398455	3.781969	2.186758
H	3.787898	2.932594	1.489221
H	3.641542	4.685656	1.319310
H	2.755243	3.451516	-2.129442
H	3.843580	4.501239	-1.219790
H	4.007678	2.746191	-1.094244
H	2.042144	5.725160	-0.174754
H	0.848906	4.813036	-1.093782
H	0.706034	4.946953	0.667044
C	2.084227	-1.642571	0.344368
C	3.056107	-1.846973	-0.841441

C	2.861913	-1.688067	1.680690
C	1.087460	-2.814213	0.341618
H	2.518467	-1.824112	-1.792727
H	3.835956	-1.089482	-0.862480
H	3.530984	-2.826978	-0.752804
H	2.186517	-1.547123	2.528370
H	3.331227	-2.668654	1.790410
H	3.639650	-0.929431	1.724537
H	1.640870	-3.750073	0.438946
H	0.383348	-2.759909	1.174488
H	0.512341	-2.865872	-0.585049
O	-3.031884	-1.488552	-0.187283
H	-3.962830	-1.586659	0.030579
H	-2.850572	-0.532804	-0.180331

Q(H ₂ O) ₂			
C	0.164973	-0.340404	0.014554
C	1.500578	-0.364432	0.164780
C	2.236630	0.953379	0.238053
C	1.490150	2.249607	0.020865
C	0.160423	2.182807	-0.136136
C	-0.579194	0.915702	-0.122934
H	-0.435578	-1.242467	-0.003016
H	-0.457017	3.058816	-0.279587
O	3.427861	0.976023	0.485628
O	-1.803360	0.931184	-0.238934
C	2.266418	3.569053	0.005591
C	2.938188	3.808047	1.378662
C	3.338201	3.538295	-1.108989
C	1.333685	4.759299	-0.274558
H	2.192165	3.835042	2.176860
H	3.668506	3.037007	1.610640
H	3.448094	4.774492	1.367244
H	2.879669	3.370150	-2.086858
H	3.850225	4.502819	-1.144449
H	4.081471	2.763799	-0.935313
H	1.923493	5.677359	-0.294384
H	0.832318	4.669610	-1.241020
H	0.571372	4.877498	0.498921
C	2.298185	-1.665564	0.294350
C	3.407668	-1.723781	-0.782450
C	2.925163	-1.757056	1.706000
C	1.394160	-2.892640	0.095764
H	2.980879	-1.643209	-1.785685
H	4.147748	-0.937844	-0.654440
H	3.916868	-2.688214	-0.717916
H	2.149673	-1.736699	2.475460
H	3.461180	-2.704613	1.800263
H	3.626453	-0.946955	1.893087
H	2.000698	-3.795541	0.191842
H	0.588699	-2.950578	0.828419
H	0.939725	-2.903752	-0.897658
O	-3.850589	-0.985109	-0.082480
H	-4.514556	-0.627196	0.513999
H	-3.171696	-0.289574	-0.180511
O	-2.054263	-3.009200	0.587686
H	-2.288517	-3.840050	0.164649
H	-2.793020	-2.398549	0.396679

Q(H ₂ O) ₃			
C	0.360094	-0.427301	-0.615145
C	1.647037	-0.399067	-0.233430
C	2.231542	0.925517	0.196990
C	1.391006	2.181717	0.129295

Appendix A

C	0.120323	2.062063	-0.281549
C	-0.469422	0.776966	-0.670868
H	-0.138376	-1.344476	-0.893102
H	-0.553355	2.904651	-0.355849
O	3.374750	0.985637	0.609189
O	-1.639455	0.735110	-1.048563
C	2.012094	3.521559	0.533516
C	2.442566	3.479164	2.018980
C	3.234171	3.832416	-0.362369
C	1.005341	4.672459	0.369764
H	1.587786	3.264927	2.665461
H	3.209938	2.729918	2.196848
H	2.840786	4.455229	2.306845
H	2.945941	3.870086	-1.416082
H	3.637906	4.811429	-0.093557
H	4.021885	3.092626	-0.243083
H	1.484046	5.609155	0.660474
H	0.670861	4.781705	-0.664398
H	0.126214	4.543014	1.004893
C	2.527823	-1.650743	-0.199814
C	3.769068	-1.448533	-1.100832
C	2.967315	-1.946254	1.254044
C	1.764162	-2.881692	-0.717125
H	3.470862	-1.231152	-2.130010
H	4.408379	-0.643682	-0.745899
H	4.354896	-2.370732	-1.115470
H	2.095927	-2.103457	1.893452
H	3.560086	-2.864039	1.269225
H	3.571002	-1.142104	1.668712
H	2.430532	-3.746156	-0.685501
H	0.889639	-3.111163	-0.106124
H	1.446097	-2.754555	-1.755403
O	-3.534680	-1.135384	-1.879663
H	-4.341207	-0.613547	-1.928127
H	-2.832213	-0.514115	-1.600236
O	-3.488086	-3.412419	-0.333548
H	-3.496815	-4.165780	-0.931154
H	-3.559415	-2.614067	-0.901092
O	-1.180378	-3.036893	1.199904
H	-2.005224	-3.213157	0.703427
H	-1.410651	-3.145176	2.126788

Q(H₂O)₄

C	0.506037	-0.239946	-0.793334
C	1.788294	-0.184334	-0.390802
C	2.344886	1.149698	0.050767
C	1.445099	2.363784	0.111804
C	0.174728	2.216147	-0.289522
C	-0.361775	0.939451	-0.771819
H	0.045806	-1.150114	-1.164458
H	-0.538226	3.029124	-0.288796
O	3.520428	1.256321	0.345774
O	-1.536344	0.886637	-1.141014
C	2.013316	3.696260	0.606640
C	2.550264	3.543349	2.049043
C	3.148561	4.168070	-0.332798
C	0.932825	4.790643	0.621854
H	1.759803	3.210469	2.726552
H	3.374221	2.835967	2.101350
H	2.906696	4.512716	2.405409
H	2.783594	4.282283	-1.356617
H	3.511232	5.143011	0.001801
H	3.985048	3.473785	-0.336545
H	1.373252	5.720415	0.986237
H	0.531639	4.987811	-0.374850
H	0.101218	4.539233	1.284248
C	2.708996	-1.407778	-0.384357
C	3.869973	-1.196327	-1.385675

C	3.272756	-1.641674	1.037865
C	1.950141	-2.677898	-0.799879
H	3.485199	-1.040074	-2.396407
H	4.495246	-0.349036	-1.113323
H	4.494839	-2.092510	-1.404578
H	2.462687	-1.781266	1.758433
H	3.873002	-2.554424	1.037364
H	3.900660	-0.819438	1.372238
H	2.642560	-3.521911	-0.781972
H	1.132640	-2.907742	-0.113387
H	1.528494	-2.611690	-1.803034
O	-3.330389	-0.889079	-2.226667
H	-3.848885	-0.369191	-2.848274
H	-2.672757	-0.276514	-1.830115
O	-4.484978	-2.809370	-0.562378
H	-4.732247	-2.417164	0.280085
H	-4.147957	-2.077064	-1.118023
O	-2.393420	-4.644818	-0.714044
H	-3.188633	-4.087191	-0.588178
H	-2.709470	-5.486836	-1.054336
O	-1.035476	-2.779692	-2.433731
H	-1.823754	-2.274666	-2.674310
H	-1.375670	-3.508153	-1.883109

Q⁺

C	0.043060	-0.311310	0.066407
C	1.406882	-0.343276	0.192068
C	2.167451	0.909653	0.181481
C	1.416506	2.159213	0.029843
C	0.052331	2.121700	-0.090282
C	-0.715166	0.903774	-0.079239
H	-0.548901	-1.218001	0.069977
H	-0.532457	3.025962	-0.203008
O	3.429784	0.912403	0.299577
O	-1.974533	0.901349	-0.191379
C	2.187776	3.492238	0.007065
C	2.957947	3.684194	1.333298
C	3.185512	3.507328	-1.173529
C	1.256625	4.704707	-0.163644
H	2.261731	3.721720	2.176443
H	3.654024	2.863246	1.492583
H	3.515548	4.628051	1.314178
H	2.652258	3.413633	-2.124271
H	3.739315	4.453520	-1.189374
H	3.891619	2.683850	-1.088115
H	1.855132	5.620906	-0.175952
H	0.695702	4.660125	-1.100326
H	0.538086	4.787092	0.655515
C	2.168421	-1.673871	0.343757
C	3.165269	-1.849955	-0.823979
C	2.936498	-1.695946	1.684598
C	1.227398	-2.891131	0.332999
H	2.632165	-1.879014	-1.778935
H	3.875013	-1.025608	-0.845717
H	3.713951	-2.792959	-0.715204
H	2.239746	-1.616076	2.524326
H	3.486279	-2.638597	1.791189
H	3.639100	-0.866639	1.734760
H	1.819370	-3.805300	0.441758
H	0.508894	-2.859535	1.155624
H	0.666481	-2.965898	-0.601736

Q⁺(H₂O)

C	0.134372	-0.323828	-0.047996
C	1.491435	-0.339473	0.138450
C	2.233487	0.925174	0.176712
C	1.475804	2.168069	-0.003110

C	0.119853	2.111764	-0.184940
C	-0.621909	0.884305	-0.212929
H	-0.441993	-1.239209	-0.083863
H	-0.473717	3.006899	-0.318686
O	3.485305	0.944196	0.357437
O	-1.884747	0.881092	-0.377385
C	2.228950	3.510544	0.015249
C	2.934856	3.706611	1.376209
C	3.278631	3.543738	-1.119024
C	1.288997	4.710132	-0.193699
H	2.201184	3.725678	2.187492
H	3.639077	2.898583	1.562612
H	3.474342	4.660694	1.387649
H	2.791127	3.444774	-2.093324
H	3.816973	4.498456	-1.107290
H	3.994224	2.732226	-1.004506
H	1.874450	5.634330	-0.176651
H	0.771646	4.661338	-1.154882
H	0.533657	4.780588	0.592805
C	2.261978	-1.661614	0.308973
C	3.319727	-1.806960	-0.808734
C	2.960165	-1.693243	1.687513
C	1.338710	-2.889521	0.231509
H	2.837172	-1.826100	-1.790281
H	4.023069	-0.977434	-0.782031
H	3.870396	-2.746645	-0.686245
H	2.220088	-1.634114	2.491045
H	3.513608	-2.631534	1.808523
H	3.650781	-0.858569	1.787821
H	1.937234	-3.797420	0.353374
H	0.580900	-2.883012	1.018335
H	0.824081	-2.956103	-0.729749
O	-3.530299	-1.262017	-0.092648
H	-3.646019	-1.251207	0.861281
H	-2.912607	-0.503729	-0.263783

 $Q^+(H_2O)_2$

C	0.221583	-0.548215	-0.103240
C	1.569379	-0.467548	0.125684
C	2.212584	0.849600	0.192076
C	1.371048	2.035718	-0.005157
C	0.029642	1.879886	-0.230632
C	-0.611337	0.601516	-0.285854
H	-0.285374	-1.502762	-0.161885
H	-0.623916	2.729768	-0.378483
O	3.451478	0.959018	0.410730
O	-1.869216	0.497122	-0.488000
C	2.019143	3.430470	0.049114
C	2.656705	3.664650	1.437529
C	3.103805	3.553826	-1.045462
C	0.997651	4.556103	-0.185690
H	1.894010	3.620855	2.220439
H	3.413553	2.911474	1.645820
H	3.121028	4.656414	1.475988
H	2.661424	3.427073	-2.037821
H	3.564916	4.547084	-1.007474
H	3.876150	2.799810	-0.910043
H	1.509190	5.521800	-0.138582
H	0.522222	4.479155	-1.166340
H	0.211000	4.559457	0.572359
C	2.428236	-1.729822	0.317200
C	3.527343	-1.794307	-0.767854
C	3.083383	-1.716993	1.717045
C	1.599445	-3.021122	0.208076
H	3.078394	-1.840106	-1.764277
H	4.172340	-0.919807	-0.716989
H	4.136248	-2.695011	-0.631964
H	2.316655	-1.713222	2.497322

H	3.697131	-2.614421	1.853383
H	3.710414	-0.836730	1.841137
H	2.257198	-3.883491	0.350600
H	0.817159	-3.072094	0.969144
H	1.125617	-3.123174	-0.770998
O	-3.667321	-1.512573	-0.359108
H	-3.716043	-1.707532	0.580961
H	-2.914763	-0.870439	-0.437714
O	-4.565211	1.402422	-0.769746
H	-4.728797	0.449744	-0.735510
H	-3.594459	1.430095	-0.696860

 $Q^+(H_2O)_3$

C	0.242885	-0.367996	-0.024655
C	1.599855	-0.365527	0.158929
C	2.316220	0.914363	0.221817
C	1.536406	2.148561	0.067316
C	0.181445	2.069327	-0.113947
C	-0.524966	0.828622	-0.164284
H	-0.318010	-1.291739	-0.079388
H	-0.426486	2.957814	-0.223209
O	3.563753	0.952603	0.402741
O	-1.798521	0.790624	-0.330674
C	2.262117	3.504276	0.113625
C	2.960222	3.686368	1.480676
C	3.313014	3.580163	-1.017693
C	1.296992	4.687064	-0.073839
H	2.225236	3.669826	2.290496
H	3.685882	2.894499	1.652782
H	3.474268	4.653249	1.513430
H	2.830439	3.489050	-1.995095
H	3.828275	4.546436	-0.986472
H	4.048252	2.784740	-0.917488
H	1.863118	5.622159	-0.038872
H	0.782082	4.646908	-1.036627
H	0.539758	4.728461	0.712421
C	2.393513	-1.675913	0.299929
C	3.451704	-1.777810	-0.822371
C	3.093113	-1.725422	1.677292
C	1.491207	-2.917255	0.195746
H	2.969245	-1.777474	-1.804007
H	4.146814	-0.942439	-0.775978
H	4.012776	-2.713581	-0.724274
H	2.353833	-1.692728	2.482832
H	3.657978	-2.658697	1.777763
H	3.774220	-0.885593	1.795733
H	2.104979	-3.816744	0.298042
H	0.734605	-2.941937	0.983476
H	0.978371	-2.973020	-0.767225
O	-3.578158	-1.230947	-0.104408
H	-3.655654	-1.345269	0.847173
H	-2.863720	-0.551734	-0.216093
O	-5.740951	0.701966	-0.732859
H	-5.130785	-0.042050	-0.593893
H	-5.149405	1.473326	-0.750761
O	-3.584184	2.730013	-0.921922
H	-2.878287	2.081233	-0.666087
H	-3.469496	2.850694	-1.868922

 $Q^+(H_2O)_4$

C	0.211150	-0.200400	-0.191694
C	1.556427	-0.272576	0.054530
C	2.323071	0.967842	0.228104
C	1.607635	2.244803	0.106839
C	0.261087	2.237819	-0.140928
C	-0.493166	1.036379	-0.291955
H	-0.385596	-1.092908	-0.326322

Appendix A

H	-0.300877	3.157860	-0.231307
O	3.558436	0.937177	0.473589
O	-1.765488	1.068898	-0.510107
C	2.388247	3.560444	0.265458
C	3.014578	3.636625	1.676573
C	3.503227	3.647681	-0.801727
C	1.487983	4.795440	0.091462
H	2.234728	3.611414	2.443042
H	3.694764	2.804490	1.844333
H	3.566955	4.575592	1.790592
H	3.073387	3.628593	-1.807210
H	4.053734	4.587953	-0.689999
H	4.199579	2.817664	-0.705556
H	2.092810	5.699147	0.207729
H	1.026855	4.830859	-0.898292
H	0.690806	4.833112	0.837474
C	2.283394	-1.624361	0.153468
C	3.390061	-1.710381	-0.922523
C	2.911621	-1.786761	1.556446
C	1.332598	-2.812864	-0.068487
H	2.957589	-1.630489	-1.923849
H	4.119430	-0.913662	-0.794426
H	3.903245	-2.675656	-0.854525
H	2.136815	-1.761951	2.328124
H	3.425096	-2.751740	1.627426
H	3.626389	-0.991283	1.755360
H	1.899696	-3.744964	0.005668
H	0.537409	-2.849095	0.679836
H	0.866119	-2.786254	-1.055955
O	-3.510149	-0.891414	0.040663
H	-3.532737	-0.941302	1.000518
H	-2.794008	-0.231721	-0.168170
O	-5.440270	0.892057	-1.113917
H	-4.928233	0.164529	-0.712744
H	-5.062445	1.690482	-0.704516
O	-3.648139	3.141060	-0.455888
H	-2.916340	2.501795	-0.312215
H	-3.634306	3.241450	-1.418175
O	-3.354518	1.630476	-3.061843
H	-4.156402	1.266756	-2.645788
H	-2.647567	1.357036	-2.456541

Q^{2-}

C	0.015103	-0.280579	0.054803
C	1.410977	-0.304323	0.186081
C	2.181089	0.909497	0.180792
C	1.420800	2.120260	0.032589
C	0.024629	2.091475	-0.094291
C	-0.761368	0.904116	-0.091012
H	-0.554737	-1.205435	0.059519
H	-0.537434	3.014296	-0.205155
O	3.495524	0.912158	0.302651
O	-2.057602	0.901828	-0.210182
C	2.183863	3.462656	0.011662
C	2.962435	3.642336	1.335968
C	3.187770	3.471340	-1.165143
C	1.268648	4.688381	-0.154995
H	2.262714	3.720120	2.175338
H	3.604585	2.772620	1.485489
H	3.573703	4.558668	1.313941
H	2.648963	3.426539	-2.117975
H	3.796905	4.389412	-1.159082
H	3.835363	2.596876	-1.079664
H	1.879615	5.601196	-0.163447
H	0.704690	4.648613	-1.090813
H	0.547553	4.770734	0.662833
C	2.163222	-1.644701	0.339874
C	3.168236	-1.814280	-0.823258

C	2.937665	-1.655492	1.678412
C	1.236837	-2.873488	0.332417
H	2.631149	-1.889591	-1.775105
H	3.822508	-0.941108	-0.848922
H	3.769778	-2.728567	-0.696578
H	2.235276	-1.620264	2.518384
H	3.544436	-2.569745	1.777811
H	3.583606	-0.776346	1.714416
H	1.839679	-3.784879	0.444853
H	0.514360	-2.841407	1.152419
H	0.674276	-2.951371	-0.601871

$Q^{2-}(H_2O)$

C	0.001461	-0.191064	-0.084845
C	1.387891	-0.251304	0.119140
C	2.184048	0.945345	0.163989
C	1.462451	2.178156	-0.015308
C	0.076431	2.179952	-0.210885
C	-0.719669	1.012822	-0.254787
H	-0.579928	-1.105724	-0.136703
H	-0.462038	3.113017	-0.341525
O	3.482744	0.916966	0.353245
O	-2.025474	1.066003	-0.447447
C	2.254120	3.502432	0.011548
C	2.968442	3.658677	1.374241
C	3.314903	3.497151	-1.113926
C	1.372493	4.746990	-0.192389
H	2.229965	3.742938	2.178785
H	3.588560	2.778671	1.550660
H	3.594506	4.564198	1.388706
H	2.824373	3.467224	-2.092828
H	3.938707	4.403418	-1.071743
H	3.942840	2.611885	-1.003323
H	2.000701	5.646926	-0.163087
H	0.856664	4.725974	-1.156193
H	0.612843	4.840081	0.588542
C	2.097133	-1.610602	0.297827
C	3.160217	-1.795757	-0.810025
C	2.795173	-1.654879	1.677115
C	1.141441	-2.814334	0.225020
H	2.675618	-1.850011	-1.790798
H	3.839387	-0.942201	-0.793387
H	3.728510	-2.726350	-0.658121
H	2.048770	-1.607754	2.477343
H	3.368362	-2.586935	1.799055
H	3.463905	-0.797131	1.762272
H	1.714537	-3.741928	0.352909
H	0.380633	-2.777920	1.009312
H	0.624556	-2.866320	-0.736791
O	-3.563367	-0.827398	0.304150
H	-2.985806	-1.328774	0.886793
H	-2.928613	-0.060130	-0.028585

$Q^{2-}(H_2O)_2$

C	0.196353	-0.392782	0.182956
C	1.585740	-0.343561	0.344190
C	2.296667	0.909240	0.261545
C	1.490570	2.078983	0.009452
C	0.106803	1.966413	-0.148571
C	-0.567207	0.748099	-0.068781
H	-0.341349	-1.330012	0.256596
H	-0.505274	2.839970	-0.343255
O	3.587082	0.983348	0.405868
O	-1.920993	0.734238	-0.226448
C	2.185819	3.450652	-0.087324
C	2.921539	3.759896	1.237105
C	3.213040	3.435922	-1.243208

C	1.208328	4.608255	-0.353986
H	2.201162	3.852446	2.056616
H	3.610685	2.945241	1.460853
H	3.478167	4.705614	1.163706
H	2.700909	3.296497	-2.200977
H	3.766021	4.385646	-1.287364
H	3.911317	2.612415	-1.091588
H	1.766702	5.550890	-0.408120
H	0.673508	4.480335	-1.299023
H	0.463638	4.704266	0.440932
C	2.388273	-1.631424	0.616776
C	3.426714	-1.848589	-0.508177
C	3.128168	-1.510718	1.969398
C	1.506430	-2.889799	0.682807
H	2.918220	-2.012830	-1.463833
H	4.059152	-0.964409	-0.589316
H	4.049470	-2.730185	-0.298118
H	2.405714	-1.435699	2.788695
H	3.756243	-2.395177	2.149946
H	3.750601	-0.615704	1.961122
H	2.137116	-3.764986	0.881930
H	0.759384	-2.825189	1.477636
H	0.974399	-3.066329	-0.255406
O	-3.087508	-1.558556	-0.463533
H	-2.622073	-2.061333	-1.139207
H	-2.330388	-0.212567	-0.300157
O	-5.578783	-1.595069	-1.018840
H	-5.704159	-0.672258	-1.257578
H	-4.554730	-1.621392	-0.774953

 $Q^{2-}(H_2O)_3$

C	0.358035	-0.467422	-0.148307
C	1.729000	-0.335824	0.098495
C	2.328830	0.968249	0.250519
C	1.434527	2.096460	0.135288
C	0.075231	1.900022	-0.115705
C	-0.486596	0.634392	-0.261969
H	-0.092475	-1.446587	-0.254124
H	-0.603295	2.740441	-0.205966
O	3.596604	1.121091	0.479524
O	-1.832485	0.542826	-0.502701
C	2.007692	3.517471	0.296267
C	2.644640	3.668432	1.697326
C	3.087865	3.773059	-0.779823
C	0.942312	4.618314	0.153684
H	1.877919	3.572283	2.473089
H	3.392181	2.887874	1.839058
H	3.117287	4.655089	1.806328
H	2.640593	3.743676	-1.778752
H	3.549421	4.761339	-0.642088
H	3.852461	2.999246	-0.711225
H	1.413375	5.599950	0.284031
H	0.468145	4.602397	-0.831477
H	0.154462	4.521755	0.905625
C	2.626683	-1.582899	0.214939
C	3.729984	-1.536250	-0.867366
C	3.289699	-1.622069	1.611282
C	1.855563	-2.901169	0.032054
H	3.281722	-1.582235	-1.865207
H	4.290171	-0.605988	-0.773354
H	4.414162	-2.390368	-0.762784
H	2.526362	-1.729959	2.388605
H	3.978497	-2.475018	1.690767
H	3.836735	-0.694177	1.777624
H	2.549810	-3.744096	0.130860
H	1.069908	-3.025525	0.781320
H	1.388447	-2.967664	-0.953943

O	-2.944980	-1.827261	-0.998726
H	-2.320120	-2.395034	-1.460874
H	-2.156557	-0.400869	-0.654608
O	-4.481854	-0.721988	-2.840255
H	-4.087777	0.155135	-2.804660
H	-3.943278	-1.216262	-2.134645
O	-3.818340	-3.164604	1.077638
H	-3.519647	-2.666494	0.236634
H	-3.300310	-2.736482	1.765215

 $Q^{2-}(H_2O)_4$

C	0.387333	-0.351389	-0.148926
C	1.753533	-0.252966	0.134627
C	2.387324	1.037886	0.263125
C	1.532507	2.188263	0.078949
C	0.176402	2.023562	-0.207708
C	-0.417028	0.770589	-0.325814
H	-0.089387	-1.320186	-0.234361
H	-0.472720	2.879725	-0.350568
O	3.649617	1.160414	0.529139
O	-1.761627	0.710074	-0.600880
C	2.144443	3.596306	0.206234
C	2.739031	3.782099	1.621366
C	3.267195	3.777050	-0.841373
C	1.119442	4.721711	-0.015347
H	1.945189	3.737053	2.374095
H	3.458528	2.987158	1.817262
H	3.236594	4.758290	1.709578
H	2.852131	3.725715	-1.853252
H	3.756272	4.754378	-0.723236
H	4.004076	2.983022	-0.720496
H	1.616719	5.692983	0.091296
H	0.677195	4.679388	-1.014408
H	0.305623	4.679558	0.713534
C	2.608563	-1.520997	0.320773
C	3.748240	-1.543762	-0.724204
C	3.223019	-1.533452	1.739510
C	1.804442	-2.821567	0.153477
H	3.332906	-1.610869	-1.734957
H	4.334009	-0.628399	-0.642504
H	4.400816	-2.413894	-0.566758
H	2.431075	-1.590501	2.493158
H	3.880466	-2.404320	1.870656
H	3.794084	-0.618183	1.894314
H	2.469889	-3.680640	0.298493
H	0.993742	-2.900779	0.882198
H	1.365763	-2.904640	-0.844396
O	-2.932136	-1.678973	-1.111151
H	-2.287406	-2.330566	-1.401962
H	-2.091703	-0.219725	-0.758378
O	-4.665610	-1.081754	-2.928185
H	-4.591810	-0.123231	-2.953743
H	-3.943478	-1.354177	-2.244933
O	-4.571596	-2.580271	0.658248
H	-3.880551	-2.266851	-0.042403
H	-4.506209	-1.914559	1.348919
O	-6.767803	-2.128325	-1.202091
H	-6.179787	-1.746336	-1.881659
H	-6.138836	-2.339235	-0.485416

A.4 Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,4,6-Trimethylphenol

Table A.5. Gas-phase energies of the hydrogen-bonded complexes of 2,4,6-trimethylphenol and its oxidized forms.

No. of H ₂ O molecules (<i>n</i>)	Energy (hartrees)			
	PhOH(H ₂ O) _{<i>n</i>}	PhOH ⁺⁺ (H ₂ O) _{<i>n</i>}	PhO [•] (H ₂ O) _{<i>n</i>}	PhO ⁺ (H ₂ O) _{<i>n</i>}
0	-425.557	-425.300	-424.932	-424.675
1	-502.032	-501.775	-501.407	-501.150
2	-578.507	-578.250	-577.883	-577.662
3	-654.983	-654.726	-654.358	-654.138
4	-731.495	-731.238	-730.833	-730.613

Figure A.13. Optimized geometries for PhOH(H₂O)_{*n*} for 2,4,6-trimethylphenol (*n* = 1 to 4).

Figure A.14. Optimized geometries for PhOH⁺⁺(H₂O)_{*n*} for 2,4,6-trimethylphenol (*n* = 1 to 4).

Figure A.15. Optimized geometries for $\text{PhO}^\bullet(\text{H}_2\text{O})_n$ for 2,4,6-trimethylphenol ($n = 1$ to 4).

Figure A.16. Optimized geometries for $\text{PhO}^+(\text{H}_2\text{O})_n$ for 2,4,6-trimethylphenol ($n = 1$ to 4).

Cartesian Coordinates of Hydrogen-Bonded Complexes of 2,4,6-Trimethylphenol

PhOH							
C	-0.639619	-0.543572	-0.022972	H	1.004846	3.489247	1.061060
C	0.754843	-0.520274	-0.066732	H	2.205951	2.904257	-0.099234
C	1.392881	0.720920	-0.078971	H	2.229741	2.318553	1.556419
C	0.668676	1.917527	-0.048645	C	-3.108682	0.745866	0.323937
C	-0.718356	1.839884	-0.005638	H	-3.397235	0.614669	1.371806
C	-1.398065	0.620980	0.007931	H	-3.659776	0.007823	-0.261409
H	-1.141705	-1.505845	-0.012967	H	-3.449226	1.737828	0.017760
H	-1.286551	2.764898	0.018219	C	0.862195	-2.036271	-1.089299
O	2.761523	0.832855	-0.121421	H	0.062905	-2.754579	-1.271606
H	3.162551	-0.041681	-0.139074	H	1.585144	-2.506487	-0.416592
C	1.391888	3.235979	-0.062793	H	1.376885	-1.868526	-2.041322
H	0.684782	4.065537	-0.032686	O	4.365222	-1.790497	-0.792145
H	2.009048	3.341174	-0.958896	H	4.803295	-2.017591	-1.617565
H	2.067895	3.327522	0.791326	H	4.933584	-1.131374	-0.349218
C	-2.904588	0.576489	0.055023	O	5.209145	0.524127	0.519698
H	-3.291809	1.066648	0.952828	H	4.264503	0.744128	0.446207
H	-3.270107	-0.451522	0.055356	H	5.435184	0.603955	1.451210
H	-3.347376	1.085773	-0.805664	PhOH(H ₂ O) ₃			
C	1.556387	-1.796005	-0.099756	C	-1.331132	-0.366048	-0.856213
H	0.899401	-2.665355	-0.083975	C	0.042752	-0.512956	-1.026952
H	2.227008	-1.884413	0.762952	C	0.895663	0.111038	-0.111719
H	2.170934	-1.874085	-1.004234	C	0.395718	0.881650	0.942675
PhOH(H ₂ O)				C	-0.988136	0.989234	1.074783
C	-0.636586	-0.434309	-0.066823	C	-1.871650	0.373544	0.192892
C	0.711773	-0.072977	-0.047303	H	-1.996410	-0.850193	-1.564449
C	1.030297	1.286503	0.012796	H	-1.382893	1.586544	1.890822
C	0.026759	2.264096	0.060041	O	2.250541	-0.032764	-0.326642
C	-1.299747	1.851728	0.040946	H	2.790091	-0.049000	0.496220
C	-1.659874	0.505131	-0.024742	C	1.318831	1.600559	1.890524
H	-0.886623	-1.489681	-0.115087	H	0.746005	2.193890	2.603532
H	-2.077407	2.608946	0.077568	H	1.990654	2.276616	1.353113
O	2.318579	1.743105	0.040898	H	1.954882	0.915288	2.455748
H	2.975865	1.038538	-0.066970	C	-3.363507	0.483514	0.380396
C	0.401748	3.718916	0.131404	H	-3.749215	-0.337449	0.993651
H	-0.489104	4.347583	0.160856	H	-3.889495	0.448287	-0.575780
H	1.006013	4.016371	-0.729791	H	-3.634986	1.416033	0.878990
H	1.003708	3.931327	1.018997	C	0.606150	-1.317117	-2.167460
C	-3.109865	0.092234	-0.055622	H	-0.190129	-1.827538	-2.710294
H	-3.659567	0.491901	0.801213	H	1.319793	-2.064549	-1.813674
H	-3.212582	-0.994075	-0.037836	H	1.141669	-0.682616	-2.880507
H	-3.611481	0.456664	-0.957211	O	4.183428	-0.155892	1.609079
C	1.791637	-1.122768	-0.079789	H	4.515409	-1.036021	1.810432
H	1.354704	-2.118335	-0.160540	H	4.908277	0.308421	1.131054
H	2.402152	-1.105792	0.829764	O	5.964868	1.135847	-0.019205
H	2.474770	-0.991908	-0.924178	H	5.387685	1.234886	-0.809173
O	4.837614	0.464983	-0.432864	H	6.315337	2.009726	0.176538
H	5.412193	0.137125	0.266757	O	4.070556	1.230981	-2.002932
H	5.270049	1.253011	-0.779633	H	3.325169	0.801083	-1.533200
PhOH(H ₂ O) ₂				H	4.181800	0.752393	-2.829790
C	-1.071667	-0.581812	-0.366308	PhOH(H ₂ O) ₄			
C	0.303356	-0.756723	-0.523833	C	-1.402412	-0.431878	-0.768236
C	1.145361	0.294426	-0.152192	C	-0.051299	-0.592930	-1.066047
C	0.634648	1.493995	0.355552	C	0.886899	0.076761	-0.275711
C	-0.743894	1.617831	0.490374	C	0.491865	0.907713	0.778144
C	-1.620275	0.591857	0.139510	C	-0.871658	1.028000	1.040703
H	-1.730854	-1.394718	-0.654478	C	-1.837075	0.366567	0.286183
H	-1.143736	2.548734	0.880830	H	-2.134171	-0.951538	-1.378897
O	2.509312	0.211208	-0.278219	H	-1.185263	1.672037	1.856532
H	2.820422	-0.650968	-0.611714	O	2.216507	-0.075276	-0.614664
C	1.565907	2.612135	0.737267	H	2.822463	-0.141697	0.162361
				C	1.504191	1.672434	1.589081
				H	1.004364	2.344713	2.286958

H	2.152597	2.273767	0.945084
H	2.156966	1.010487	2.162978
C	-3.302781	0.494016	0.615417
H	-3.604020	-0.232440	1.377199
H	-3.925387	0.319653	-0.264141
H	-3.540005	1.486735	1.003660
C	0.396085	-1.459284	-2.212475
H	-0.449097	-1.998481	-2.641707
H	1.146086	-2.186435	-1.893560
H	0.851857	-0.864453	-3.009931
O	4.097504	-0.421169	1.302596
H	4.424971	-1.324799	1.340890
H	4.888742	0.152135	1.161862
O	6.246254	1.159898	0.812454
H	6.166359	1.616083	-0.057319
H	6.523720	1.823592	1.449987
O	3.588399	1.160166	-2.660988
H	3.045984	0.726661	-1.965881
H	3.683304	0.514341	-3.367392
O	5.865301	2.269820	-1.652592
H	5.052742	1.876867	-2.048256
H	5.827798	3.211492	-1.842253

PhOH⁺

C	-0.633933	-0.560193	0.017455
C	0.731198	-0.559786	-0.023541
C	1.377122	0.720168	-0.080107
C	0.650167	1.964181	-0.094313
C	-0.719019	1.885588	-0.050865
C	-1.392532	0.647304	0.005066
H	-1.165788	-1.503519	0.061028
H	-1.302471	2.797892	-0.059981
O	2.688086	0.827479	-0.122803
H	3.138697	-0.032158	-0.111864
C	1.396040	3.255132	-0.154293
H	0.710135	4.099513	-0.157837
H	2.020180	3.303949	-1.050720
H	2.073350	3.354476	0.698268
C	-2.875663	0.578319	0.053215
H	-3.201396	0.064717	0.965376
H	-3.256572	-0.023639	-0.779523
H	-3.340673	1.561063	0.019621
C	1.553268	-1.814166	-0.011399
H	0.914375	-2.693921	0.031813
H	2.217694	-1.854228	0.858449
H	2.167380	-1.904739	-0.913839

PhOH⁺(H₂O)

C	-0.561742	-0.443069	0.032330
C	0.760754	-0.098813	-0.021854
C	1.067639	1.306692	-0.094071
C	0.029356	2.313481	-0.122900
C	-1.273321	1.889357	-0.066677
C	-1.605346	0.522001	0.013908
H	-0.831194	-1.491479	0.089031
H	-2.070771	2.622081	-0.084020
O	2.284397	1.771034	-0.141915
H	3.060782	1.141352	-0.094293
C	0.409225	3.754696	-0.209333
H	-0.475143	4.388419	-0.225414
H	0.999327	3.949596	-1.108629
H	1.035547	4.045425	0.638098
C	-3.022297	0.074003	0.082623
H	-3.205843	-0.456088	1.024426
H	-3.237399	-0.645447	-0.714355
H	-3.723796	0.902350	0.008726
C	1.849394	-1.127430	-0.019122

H	1.428130	-2.125673	0.083032
H	2.557918	-0.972380	0.797358
H	2.420217	-1.101730	-0.952088
O	4.608011	0.567662	0.080482
H	5.204977	1.060811	0.656473
H	5.147751	0.232307	-0.645221

PhOH⁺(H₂O)₂

C	-0.489781	-0.424747	-0.336830
C	0.648967	0.277372	-0.050163
C	0.498962	1.682126	0.244935
C	-0.798773	2.324035	0.218699
C	-1.892413	1.552365	-0.078484
C	-1.775621	0.176278	-0.357424
H	-0.412343	-1.482463	-0.561204
H	-2.874214	2.009449	-0.099037
O	1.492413	2.459558	0.545794
H	2.447790	2.099321	0.645218
C	-0.896964	3.783468	0.519446
H	-0.516733	4.002270	1.520646
H	-1.928344	4.124330	0.453811
H	-0.287383	4.367382	-0.174826
C	-2.972051	-0.651785	-0.673896
H	-3.075028	-1.465786	0.052057
H	-2.858714	-1.131005	-1.652090
H	-3.890690	-0.068589	-0.674723
C	1.998146	-0.371803	-0.051167
H	1.907589	-1.432605	-0.277545
H	2.499361	-0.267809	0.913459
H	2.654161	0.077362	-0.802336
O	3.924887	1.907448	0.989604
H	4.286262	2.504665	1.653666
H	4.620818	1.768647	0.307366
O	5.772087	1.427400	-0.941082
H	6.097319	2.074721	-1.576843
H	6.478251	0.781380	-0.825989

PhOH⁺(H₂O)₃

C	-0.441649	-0.440902	-0.290469
C	0.694621	0.283757	-0.050630
C	0.541440	1.704097	0.175388
C	-0.767185	2.327435	0.130618
C	-1.856964	1.533024	-0.116457
C	-1.731204	0.146203	-0.328072
H	-0.356517	-1.507949	-0.462377
H	-2.843026	1.980460	-0.150348
O	1.527181	2.497599	0.421362
H	2.545632	2.179957	0.538796
C	-0.877462	3.799461	0.358700
H	-0.482326	4.072587	1.340391
H	-1.913727	4.126002	0.293729
H	-0.286398	4.353419	-0.374943
C	-2.926490	-0.707331	-0.582170
H	-3.070485	-1.411721	0.245172
H	-2.786450	-1.315677	-1.480489
H	-3.836329	-0.120269	-0.692417
C	2.046285	-0.359260	-0.033420
H	1.957236	-1.431490	-0.199397
H	2.558377	-0.198399	0.917413
H	2.691838	0.050636	-0.815270
O	3.900857	2.021405	0.811413
H	4.312543	2.712641	1.373407
H	4.515876	1.800207	0.081006
O	5.490878	1.236515	-1.286032
H	5.776773	1.804763	-2.010085
H	6.197064	0.593532	-1.155237
O	5.050325	3.897690	2.433005

Appendix A

H 5.454681 3.695016 3.283376
H 5.075617 4.855451 2.336410

PhOH⁺(H₂O)₄

C -0.749721 -0.693952 -0.262118
C 0.401509 0.010545 -0.035612
C 0.294750 1.434823 0.230572
C -1.015219 2.067611 0.243124
C -2.124137 1.294090 0.006703
C -2.028226 -0.086381 -0.247342
H -0.686767 -1.758124 -0.462195
H -3.104621 1.756136 0.015160
O 1.307847 2.167472 0.455319
H 2.614706 1.945800 0.581296
C -1.099804 3.534329 0.513955
H -0.670151 3.775726 1.489474
H -2.132918 3.877549 0.490381
H -0.523070 4.099835 -0.222233
C -3.246879 -0.913047 -0.497754
H -3.345045 -1.693609 0.263831
H -3.174323 -1.428431 -1.460360
H -4.156114 -0.314181 -0.493635
C 1.747041 -0.645418 -0.062256
H 1.652674 -1.710987 -0.266060
H 2.272246 -0.525515 0.888246
H 2.385058 -0.209589 -0.836010
O 3.702718 1.894699 0.742044
H 4.000065 2.462521 1.512674
H 4.232973 2.211614 -0.046200
O 5.227462 2.973607 -1.091557
H 5.805113 3.636045 -0.675610
H 5.707615 2.577786 -1.826020
O 4.681504 3.551388 2.511498
H 4.886238 3.431029 3.444319
H 5.390894 4.080748 2.109974
O 6.480228 4.897938 0.678159
H 6.221897 5.810804 0.494895
H 7.435821 4.920211 0.816924

PhO[•]

C -0.652639 -0.591814 0.002538
C 0.722455 -0.603344 -0.000395
C 1.446901 0.665111 -0.002629
C 0.669775 1.904212 -0.001950
C -0.699634 1.835814 0.000976
C -1.389834 0.605155 0.003273
H -1.191656 -1.534174 0.004361
H -1.277865 2.755208 0.001568
O 2.693750 0.690989 -0.005658
C 1.415752 3.200286 -0.004333
H 0.732302 4.049967 -0.003968
H 2.069127 3.270041 -0.877659
H 2.071915 3.271616 0.866785
C -2.889933 0.587359 0.006153
H -3.286914 1.107736 0.883293
H -3.281514 -0.429798 0.009755
H -3.290131 1.102624 -0.872576
C 1.518675 -1.868688 -0.001412
H 0.869387 -2.744715 0.002286
H 2.179262 -1.911970 0.868286
H 2.172675 -1.914707 -0.875976

PhO[•](H₂O)

C -0.561886 -0.449969 -0.005069
C 0.777662 -0.136834 -0.004238
C 1.172547 1.268186 -0.003411

C 0.126306 2.287855 -0.004597
C -1.186834 1.896740 -0.005406
C -1.563032 0.536170 -0.004981
H -0.860267 -1.493371 -0.006194
H -1.966894 2.651987 -0.006810
O 2.377325 1.606064 -0.002412
C 0.544083 3.723697 -0.005367
H -0.321479 4.386549 -0.006478
H 1.163358 3.946993 -0.877746
H 1.162040 3.948248 0.867624
C -3.014817 0.161590 0.002962
H -3.500434 0.504919 0.922217
H -3.154760 -0.916756 -0.069767
H -3.546955 0.633437 -0.828245
C 1.845039 -1.182530 -0.004969
H 1.412886 -2.183330 -0.005582
H 2.498401 -1.081438 0.865240
H 2.497979 -1.080282 -0.875387
O 4.916520 0.292289 0.020548
H 4.060246 0.754748 0.011220
H 5.581585 0.986120 0.028513

PhO[•](H₂O)₂

C -0.452656 -0.294042 -0.124367
C 0.801547 0.223049 -0.356847
C 0.973613 1.672320 -0.356774
C -0.194253 2.516182 -0.116489
C -1.408853 1.925432 0.109495
C -1.570048 0.522502 0.113244
H -0.586144 -1.370881 -0.123423
H -2.278303 2.549453 0.292298
O 2.091474 2.199737 -0.559994
C -0.004838 3.999759 -0.123665
H -0.947805 4.517926 0.051837
H 0.411782 4.333665 -1.077104
H 0.713014 4.302962 0.642787
C -2.922974 -0.073326 0.362064
H -3.332064 0.269407 1.317228
H -2.888838 -1.162430 0.377040
H -3.633132 0.234177 -0.412244
C 1.989625 -0.647816 -0.602136
H 1.689271 -1.688782 -0.725290
H 2.704578 -0.595700 0.225587
H 2.530706 -0.328635 -1.495996
O 4.866503 -0.415039 1.436099
H 4.960561 0.326839 0.807732
H 5.620978 -0.988350 1.275044
O 4.819875 1.683635 -0.439233
H 5.191520 2.543919 -0.223391
H 3.858042 1.832006 -0.543158

PhO[•](H₂O)₃

C -0.477738 -0.182832 0.168084
C 0.705930 0.352189 -0.279358
C 0.757635 1.773717 -0.607684
C -0.456119 2.570990 -0.451944
C -1.599668 1.964731 0.002014
C -1.641877 0.592749 0.322861
H -0.521577 -1.239616 0.411565
H -2.503579 2.554497 0.118707
O 1.810385 2.309837 -1.019070
C -0.392332 4.024020 -0.797632
H -1.356687 4.508815 -0.644215
H -0.086089 4.162659 -1.837543
H 0.361405 4.533626 -0.192100
C -2.903391 -0.021980 0.850280
H -2.983946 0.136057 1.932034

H	-2.930097	-1.098460	0.676484
H	-3.788237	0.427188	0.395122
C	1.945160	-0.467344	-0.442739
H	1.750853	-1.518352	-0.228249
H	2.740338	-0.120657	0.222507
H	2.339237	-0.381222	-1.458345
O	5.745182	0.169436	0.586676
H	5.306984	0.669331	-0.141130
H	6.416312	-0.380664	0.172965
O	4.633531	2.034716	-1.049666
H	4.937227	2.695916	-0.407267
H	3.663384	2.115875	-1.089051
O	5.938298	2.873826	1.392724
H	6.069772	1.907474	1.367185
H	6.799119	3.259993	1.576465

 $\text{PhO}^+(\text{H}_2\text{O})_4$

C	-0.510233	0.301817	0.838132
C	0.642496	0.937293	0.444321
C	0.547693	2.046116	-0.501369
C	-0.771890	2.431995	-0.994594
C	-1.876769	1.749762	-0.552299
C	-1.779447	0.684251	0.364868
H	-0.444688	-0.526402	1.536687
H	-2.858647	2.033375	-0.918228
O	1.565308	2.658807	-0.893060
C	-0.855105	3.562613	-1.969335
H	-1.887833	3.759678	-2.257832
H	-0.271009	3.344718	-2.867046
H	-0.424340	4.472943	-1.545044
C	-3.015043	-0.011644	0.851602
H	-3.433439	0.511274	1.719548
H	-2.803706	-1.035825	1.162371
H	-3.791819	-0.032714	0.085131
C	1.991491	0.531830	0.944008
H	1.921735	-0.348265	1.583859
H	2.466352	1.334929	1.514154
H	2.665652	0.311065	0.112890
O	6.220607	1.294161	-1.154021
H	5.497267	1.956383	-0.999281
H	6.847603	1.714712	-1.749389
O	4.347483	3.070091	-0.418894
H	4.435696	3.012277	0.551776
H	3.405661	2.917428	-0.612290
O	6.831276	0.777180	1.445801
H	6.711630	0.898126	0.473202
H	6.788249	-0.169671	1.607041
O	4.863024	2.500383	2.305534
H	5.584965	1.857151	2.124645
H	5.236122	3.162322	2.894958

 PhO^+

C	-0.656077	-0.631469	0.002601
C	0.702534	-0.659134	-0.000349
C	1.437495	0.664175	-0.002917
C	0.643951	1.950041	-0.002085
C	-0.709085	1.858771	0.000895
C	-1.374870	0.596316	0.003245
H	-1.220922	-1.556026	0.004553
H	-1.316630	2.756560	0.001590
O	2.643637	0.688990	-0.005608
C	1.399131	3.221125	-0.004527
H	0.737029	4.084287	-0.003909
H	2.061041	3.267758	-0.875537
H	2.064327	3.269092	0.863913
C	-2.852041	0.580955	0.006327
H	-3.224758	1.137883	0.875770

H	-3.272742	-0.421051	0.009386
H	-3.227987	1.133645	-0.864492
C	1.513707	-1.892968	-0.001261
H	0.893313	-2.786412	0.001273
H	2.182772	-1.906938	0.865873
H	2.178033	-1.908692	-0.872022

 $\text{PhO}^+(\text{H}_2\text{O})$

C	-0.792881	-0.568313	-0.034908
C	0.578743	-0.476115	0.050772
C	1.147897	0.815105	0.051281
C	0.277193	1.992058	-0.035380
C	-1.154552	1.783797	-0.121223
C	-1.695302	0.542467	-0.122548
H	-1.227499	-1.563552	-0.036193
H	-1.780791	2.665445	-0.184620
O	2.449311	0.867798	0.131327
C	0.767482	3.252735	-0.036578
H	0.088917	4.094999	-0.101776
H	1.821836	3.490094	0.024920
H	4.548857	3.173516	0.964097
C	-3.171027	0.284583	-0.209518
H	-3.735491	1.213775	-0.271783
H	-3.521026	-0.269263	0.665411
H	-3.409147	-0.319090	-1.089064
C	1.465207	-1.684574	0.140907
H	0.874292	-2.598753	0.128142
H	2.058289	-1.667937	1.057698
H	2.170914	-1.716048	-0.691801
O	4.028236	3.024043	0.164795
H	2.907798	1.747440	0.134109
H	4.637053	3.133495	-0.576596

 $\text{PhO}^+(\text{H}_2\text{O})_2$

C	-0.739406	-0.555449	-0.106088
C	0.602605	-0.464731	0.177946
C	1.166868	0.828599	0.293987
C	0.310021	2.006912	0.110974
C	-1.093138	1.799080	-0.186800
C	-1.623357	0.558936	-0.296196
H	-1.166905	-1.549916	-0.194222
H	-1.707237	2.681757	-0.318486
O	2.436297	0.877169	0.561515
C	0.788525	3.267845	0.214021
H	0.119722	4.108624	0.072121
H	1.821736	3.501563	0.436951
H	4.316764	3.053528	1.756339
C	-3.070285	0.303153	-0.601612
H	-3.624443	1.233537	-0.717122
H	-3.540002	-0.276616	0.197177
H	-3.177388	-0.274280	-1.523578
C	1.471860	-1.674311	0.365143
H	0.892415	-2.588438	0.246638
H	1.928715	-1.679042	1.356976
H	2.289379	-1.685319	-0.358781
O	3.906895	2.973046	0.887619
H	2.918617	1.760178	0.663096
H	4.615328	3.133711	0.219999
O	5.791918	3.424013	-0.997154
H	6.492199	2.815567	-1.257558
H	6.058266	4.297777	-1.303930

 $\text{PhO}^+(\text{H}_2\text{O})_3$

C	-0.724560	-0.553397	-0.106142
C	0.609644	-0.426783	0.186435
C	1.153556	0.883827	0.266881

Appendix A

C	0.270005	2.038687	0.043757
C	-1.125331	1.791455	-0.261673
C	-1.628465	0.538726	-0.339126
H	-1.132670	-1.557984	-0.168085
H	-1.756695	2.656573	-0.425469
O	2.412866	0.966260	0.536791
C	0.720173	3.311409	0.121939
H	0.034037	4.133046	-0.047341
H	1.746673	3.568589	0.349723
H	4.232127	3.160724	1.630003
C	-3.066424	0.243713	-0.651496
H	-3.637839	1.158443	-0.803243
H	-3.533972	-0.319600	0.160380
H	-3.151850	-0.365183	-1.555415
C	1.502461	-1.610958	0.417956
H	0.943410	-2.540658	0.324069
H	1.951752	-1.574442	1.412641
H	2.326203	-1.626942	-0.298870
O	3.810301	3.037122	0.752807
H	2.916747	1.872374	0.608710
H	4.496786	3.157131	0.062220
O	5.629580	3.357604	-1.276608
H	6.318515	2.733414	-1.528943
H	5.872847	4.204234	-1.666588
O	4.874301	3.368694	3.259406
H	5.439223	2.746330	3.729863
H	4.953906	4.211396	3.719251

PhO⁺(H₂O)₄

C	-0.937140	-0.591186	-0.148123
C	0.357369	-0.518427	0.300031
C	0.963126	0.764424	0.385184
C	0.177175	1.951015	0.013018
C	-1.180770	1.759818	-0.457198
C	-1.741369	0.532164	-0.541462
H	-1.391457	-1.575383	-0.215140
H	-1.737366	2.646674	-0.735769
O	2.187043	0.794725	0.794003
C	0.676411	3.203782	0.114938
H	0.060328	4.050121	-0.165444
H	1.674196	3.422750	0.472943
H	4.216270	2.838824	1.825976
C	-3.144489	0.295840	-1.018924
H	-3.637340	1.229325	-1.287348
H	-3.742075	-0.194955	-0.246208
H	-3.152987	-0.357888	-1.895073
C	1.147622	-1.733990	0.688762
H	0.551567	-2.637251	0.568317
H	1.477488	-1.671558	1.727958
H	2.048004	-1.827467	0.077935
O	3.675076	2.792709	1.019110
H	2.740248	1.673644	0.857364
H	4.281136	3.030025	0.261849
O	5.366305	3.578347	-0.849030
H	6.115710	3.939446	-0.328510
H	5.744569	3.049880	-1.558727
O	5.578180	3.190631	3.200234
H	6.042840	2.419921	3.550380
H	5.287441	3.693429	3.971336
O	7.196565	4.361297	1.020913
H	6.803757	4.165297	1.884642
H	7.739004	5.149974	1.120056

A.5 Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,6-Di-*tert*-butyl-4-methylphenol

Table A.6. Gas-phase energies of the hydrogen-bonded complexes of 2,6-di-*tert*-butyl-4-methylphenol and its oxidized forms.

No. of H ₂ O molecules (<i>n</i>)	Energy (hartrees)			
	PhOH(H ₂ O) _{<i>n</i>}	PhOH ⁺⁺ (H ₂ O) _{<i>n</i>}	PhO [•] (H ₂ O) _{<i>n</i>}	PhO ⁺ (H ₂ O) _{<i>n</i>}
0	-697.906	-661.230	-660.863	-660.605
1	-737.963	-737.705	-737.338	-737.081
2	-814.438	-814.217	-813.813	-813.556
3	-890.950	-890.693	-890.289	-890.031
4	-967.389	-967.168	-966.764	-966.507

Figure A.17. Optimized geometries for PhOH(H₂O)_{*n*} for 2,6-di-*tert*-butyl-4-methylphenol (*n* = 1 to 4).

Figure A.18. Optimized geometries for PhOH⁺⁺(H₂O)_{*n*} for 2,6-di-*tert*-butyl-4-methylphenol (*n* = 1 to 4).

Figure A.19. Optimized geometries for $\text{PhO}^\bullet(\text{H}_2\text{O})_n$ for 2,6-di-*tert*-butyl-4-methylphenol ($n = 1$ to 4).

Figure A.20. Optimized geometries for $\text{PhO}^+(\text{H}_2\text{O})_n$ for 2,6-di-*tert*-butyl-4-methylphenol ($n = 1$ to 4).

Cartesian Coordinates of Hydrogen-Bonded Complexes of 2,6-Di-*tert*-butyl-4-methylphenol

PhOH			
C	-0.502807	-0.866747	-0.021157
C	0.898361	-0.823469	-0.156510
C	1.618814	0.389751	-0.172270
C	0.881455	1.563044	-0.042241
C	-0.502839	1.574053	0.098638
C	-1.166563	0.356678	0.104528
H	1.395813	2.513916	-0.051251
H	-2.241924	0.369039	0.208821
C	-1.298615	-2.194532	-0.013099
C	-1.121935	-2.955271	-1.351182
C	-0.886319	-3.081317	1.188454
C	-2.813076	-1.956675	0.138672
H	-1.487010	-2.345356	-2.179930
H	-0.091036	-3.221508	-1.591853
H	-1.699542	-3.883073	-1.334148
H	-1.091281	-2.561356	2.126368
H	-1.462023	-4.010394	1.183916
H	0.169870	-3.357273	1.211565
H	-3.327955	-2.919864	0.138904
H	-3.056894	-1.453031	1.075662
H	-3.218357	-1.367267	-0.685597
C	3.154233	0.429050	-0.331870
C	3.839946	-0.320401	0.833190
C	3.570414	-0.193786	-1.683861
C	3.695332	1.870436	-0.317322
H	3.576409	0.135874	1.790828
H	3.558269	-1.370054	0.865418
H	4.926386	-0.261158	0.722791
H	3.115394	0.353290	-2.513556
H	4.656355	-0.135826	-1.800963
H	3.275137	-1.237448	-1.759870
H	4.780779	1.842651	-0.433624
H	3.293650	2.470439	-1.136909
H	3.479995	2.383367	0.622744
C	-1.250782	2.874564	0.253837
H	-2.328057	2.726753	0.160599
H	-0.947916	3.603557	-0.502211
O	1.643579	-1.971978	-0.287637
H	1.072386	-2.741269	-0.248481
H	-1.064929	3.329526	1.231839

PhOH(H ₂ O)			
C	-0.590528	-0.767742	-0.011795
C	0.812434	-0.760793	-0.148179
C	1.557540	0.440775	-0.162259
C	0.849748	1.631362	-0.031070
C	-0.533732	1.674769	0.108938
C	-1.223389	0.472485	0.113776
H	1.386294	2.569967	-0.038762
H	-2.298165	0.509824	0.218049
C	-1.424335	-2.070231	-0.000796
C	-1.271143	-2.833252	-1.339497
C	-1.031416	-2.961547	1.202725
C	-2.931663	-1.790470	0.154928
H	-1.612926	-2.206236	-2.165882
H	-0.253435	-3.145631	-1.570242
H	-1.886081	-3.737283	-1.326141
H	-1.231335	-2.434789	2.138412
H	-1.626602	-3.878945	1.198659
H	0.017510	-3.256188	1.218674
H	-3.470431	-2.740624	0.158894
H	-3.161075	-1.278677	1.091448
H	-3.325229	-1.193777	-0.670104

C	3.093974	0.449271	-0.323498
C	3.767420	-0.313425	0.840176
C	3.496793	-0.177621	-1.677675
C	3.666878	1.878673	-0.307809
H	3.521929	0.154135	1.797188
H	3.454672	-1.353899	0.879927
H	4.854702	-0.283942	0.723330
H	3.060610	0.387996	-2.504987
H	4.584535	-0.151250	-1.791922
H	3.167601	-1.210376	-1.761765
H	4.751533	1.826966	-0.424852
H	3.277923	2.488049	-1.126520
H	3.463317	2.395502	0.632718
C	-1.252090	2.992351	0.260744
H	-2.334689	2.861386	0.216329
H	-0.969913	3.696330	-0.526857
O	1.542923	-1.912742	-0.277587
H	1.005274	-2.711654	-0.272384
H	-1.017361	3.469750	1.217265
O	1.636787	-4.755152	-0.519302
H	2.585246	-4.586996	-0.534096
H	1.522998	-5.587269	-0.049392

PhOH(H ₂ O) ₂			
C	-0.777387	-0.917405	0.098957
C	0.623419	-1.008433	-0.026886
C	1.450908	0.130677	-0.084284
C	0.821060	1.376011	-0.054645
C	-0.557483	1.514740	0.034857
C	-1.330198	0.364210	0.119200
H	1.416446	2.276641	-0.099729
H	-2.400561	0.482600	0.207938
C	-1.690496	-2.158696	0.227937
C	-1.614085	-3.037119	-1.040787
C	-1.302803	-2.984402	1.474661
C	-3.170589	-1.766940	0.402179
H	-1.867620	-2.453237	-1.929107
H	-0.634855	-3.482694	-1.197710
H	-2.335134	-3.855948	-0.965633
H	-1.405367	-2.383293	2.381494
H	-1.965330	-3.849364	1.568982
H	-0.278350	-3.342898	1.418312
H	-3.767325	-2.675379	0.508121
H	-3.335154	-1.161059	1.295660
H	-3.558265	-1.221016	-0.460618
C	2.992629	0.041786	-0.154654
C	3.545144	-0.659572	1.105805
C	3.449230	-0.708313	-1.425539
C	3.647079	1.435684	-0.209593
H	3.266903	-0.105142	2.005426
H	3.173316	-1.676199	1.202726
H	4.637143	-0.700659	1.062473
H	3.037989	-0.237015	-2.321860
H	4.539682	-0.676300	-1.502411
H	3.151269	-1.753925	-1.419902
H	4.731789	1.315430	-0.247435
H	3.348521	1.998547	-1.096851
H	3.416359	2.035909	0.672864
C	-1.200212	2.878810	0.021969
H	-2.133713	2.886239	0.588135
H	-1.437251	3.195019	-0.999107
O	1.221018	-2.265826	-0.031233
H	1.259128	-2.658996	-0.922554
H	-0.540115	3.635364	0.450628

Appendix A

O	1.749742	-4.178251	-1.989730
H	2.403215	-4.199034	-2.694940
H	2.148725	-4.626927	-1.220152
O	2.536603	-4.683306	0.638370
H	2.150038	-5.300400	1.266981
H	2.099897	-3.827570	0.789515

PhOH(H₂O)₃

C	-0.909053	-0.848586	0.146846
C	0.471531	-0.963065	-0.123213
C	1.321142	0.160894	-0.178172
C	0.728719	1.413487	-0.002733
C	-0.629679	1.575972	0.228586
C	-1.422055	0.438700	0.309510
H	1.341341	2.302330	-0.041798
H	-2.475055	0.572822	0.511196
C	-1.844011	-2.073252	0.291281
C	-1.885250	-2.904524	-1.009450
C	-1.384336	-2.958548	1.470183
C	-3.296644	-1.656826	0.592737
H	-2.176117	-2.279352	-1.857628
H	-0.928039	-3.367311	-1.234903
H	-2.625974	-3.703555	-0.915433
H	-1.394472	-2.392408	2.404575
H	-2.061105	-3.809927	1.585209
H	-0.379842	-3.342574	1.313789
H	-3.908432	-2.555357	0.697604
H	-3.380255	-1.094631	1.524896
H	-3.730003	-1.057503	-0.210872
C	2.847817	0.057523	-0.405032
C	3.505718	-0.783581	0.710807
C	3.162044	-0.547566	-1.790098
C	3.527640	1.440587	-0.369124
H	3.315957	-0.337770	1.690571
H	3.142784	-1.807026	0.726393
H	4.588858	-0.813212	0.562530
H	2.705147	0.049799	-2.583214
H	4.243296	-0.546742	-1.955427
H	2.813561	-1.570539	-1.900757
H	4.601604	1.308479	-0.516002
H	3.169258	2.099645	-1.162876
H	3.388608	1.946530	0.588756
C	-1.234093	2.949811	0.373793
H	-2.039101	2.956838	1.111806
H	-1.659856	3.297429	-0.573073
O	1.018518	-2.232953	-0.284377
H	1.032461	-2.523338	-1.223233
H	-0.487405	3.683127	0.683522
O	2.512531	-5.655236	-1.606391
H	3.437591	-5.848165	-1.785987
H	2.468966	-5.353602	-0.672216
O	2.239387	-4.468012	0.857163
H	1.743520	-4.848171	1.588375
H	1.787407	-3.632870	0.620038
O	1.318929	-3.459764	-2.719707
H	1.749624	-4.302722	-2.449089
H	0.613969	-3.690406	-3.331491

PhOH(H₂O)₄

C	-0.889235	-0.815485	0.198153
C	0.488677	-0.949244	-0.075941
C	1.337622	0.168442	-0.214300
C	0.747578	1.430616	-0.120347
C	-0.609054	1.609362	0.109410
C	-1.400125	0.480832	0.275495
H	1.360103	2.314242	-0.225519
H	-2.451468	0.629412	0.475277

C	-1.824552	-2.024915	0.436635
C	-1.871336	-2.952768	-0.796060
C	-1.359417	-2.817700	1.677899
C	-3.275942	-1.586037	0.711369
H	-2.142805	-2.392249	-1.693827
H	-0.923661	-3.451305	-0.976392
H	-2.624672	-3.731117	-0.647204
H	-1.377416	-2.186189	2.569375
H	-2.027019	-3.666226	1.851716
H	-0.349802	-3.199959	1.551413
H	-3.886950	-2.474362	0.885110
H	-3.357954	-0.954665	1.598396
H	-3.711341	-1.049940	-0.134726
C	2.862754	0.049064	-0.443999
C	3.527232	-0.709047	0.726176
C	3.166742	-0.656642	-1.782643
C	3.543356	1.430537	-0.512870
H	3.340211	-0.194237	1.671980
H	3.164943	-1.728794	0.817190
H	4.609953	-0.747660	0.576157
H	2.707524	-0.119790	-2.616139
H	4.246939	-0.676752	-1.952836
H	2.807691	-1.681187	-1.809753
H	4.616343	1.288624	-0.658993
H	3.177538	2.032225	-1.347673
H	3.411633	2.002337	0.408159
C	-1.212237	2.990398	0.160849
H	-2.039504	3.039423	0.872044
H	-1.607128	3.286551	-0.816471
O	1.037840	-2.226163	-0.154959
H	1.015562	-2.601030	-1.065911
H	-0.472667	3.738390	0.452538
O	2.800812	-5.772969	-1.121182
H	3.681505	-6.157670	-1.091089
H	2.647126	-5.340510	-0.247333
O	2.256436	-4.356530	1.133398
H	1.701008	-4.717824	1.830922
H	1.803682	-3.547183	0.813981
O	1.302165	-3.646275	-2.477404
H	2.096910	-4.155171	-2.252052
H	0.646501	-4.348900	-2.627080
O	0.276596	-6.307448	-2.295582
H	1.156293	-6.421221	-1.893752
H	0.164348	-7.025881	-2.924430

PhOH⁺⁺

C	-0.549723	-0.866231	-0.010385
C	0.889656	-0.810562	-0.161275
C	1.650268	0.427105	-0.187871
C	0.915452	1.581969	-0.061797
C	-0.483104	1.577554	0.085342
C	-1.181605	0.340861	0.108395
H	1.415998	2.538073	-0.075023
H	-2.254845	0.379176	0.223768
C	-1.319138	-2.201230	0.011513
C	-1.143035	-2.955494	-1.332802
C	-0.862673	-3.079286	1.206625
C	-2.829383	-1.963525	0.189640
H	-1.489053	-2.345023	-2.168473
H	-0.119640	-3.262153	-1.565882
H	-1.741342	-3.867286	-1.313091
H	-0.987702	-2.547094	2.151005
H	-1.478572	-3.978566	1.244370
H	0.175942	-3.420081	1.168337
H	-3.340126	-2.926516	0.199247
H	-3.059533	-1.464689	1.132824
H	-3.253204	-1.380607	-0.630016
C	3.173477	0.443577	-0.347697

C	3.843841	-0.316251	0.826065
C	3.573857	-0.193817	-1.703235
C	3.717380	1.882935	-0.336324
H	3.565256	0.121688	1.787003
H	3.595666	-1.374630	0.840113
H	4.926817	-0.229549	0.725565
H	3.107643	0.334969	-2.537379
H	4.655332	-0.111799	-1.823361
H	3.311464	-1.246866	-1.767606
H	4.800502	1.847475	-0.452304
H	3.324587	2.482254	-1.160473
H	3.510703	2.398738	0.603928
C	-1.244703	2.848139	0.222095
H	-2.033557	2.907304	-0.535335
H	-0.607801	3.726163	0.137515
O	1.592238	-1.914638	-0.285334
H	1.031890	-2.705444	-0.257638
H	-1.756515	2.880291	1.191186

PhOH⁺(H₂O)

C	-0.649260	-0.763617	0.001914
C	0.795890	-0.763301	-0.148748
C	1.585603	0.464016	-0.176510
C	0.889879	1.641284	-0.049620
C	-0.506671	1.680555	0.099422
C	-1.237392	0.467115	0.120394
H	1.419711	2.581279	-0.063955
H	-2.308924	0.538393	0.234527
C	-1.483936	-2.053142	0.026962
C	-1.336092	-2.809047	-1.317905
C	-1.076285	-2.928575	1.239115
C	-2.984882	-1.750607	0.192642
H	-1.709937	-2.195816	-2.139974
H	-0.318102	-3.103643	-1.568970
H	-1.936935	-3.719909	-1.286657
H	-1.262357	-2.393869	2.172413
H	-1.687215	-3.833172	1.250496
H	-0.034051	-3.244609	1.247113
H	-3.532574	-2.693482	0.201835
H	-3.204317	-1.240575	1.132472
H	-3.380949	-1.155691	-0.632459
C	3.110930	0.445998	-0.341747
C	3.772957	-0.321801	0.830718
C	3.495765	-0.195656	-1.699109
C	3.688824	1.872989	-0.334099
H	3.512522	0.129933	1.790425
H	3.495959	-1.372423	0.855987
H	4.857206	-0.262383	0.722038
H	3.040463	0.347197	-2.530333
H	4.578726	-0.138158	-1.821828
H	3.205709	-1.240864	-1.767767
H	4.770550	1.811332	-0.453125
H	3.308078	2.480326	-1.157922
H	3.497358	2.395220	0.605744
C	-1.228780	2.974736	0.243758
H	-2.049618	3.043588	-0.476790
H	-0.571778	3.832612	0.114871
O	1.498833	-1.856370	-0.271566
H	1.057032	-2.735362	-0.264007
H	-1.690720	3.039933	1.236058
O	1.441071	-4.519750	-0.382536
H	0.907316	-5.321701	-0.372106
H	2.356679	-4.804972	-0.480758

PhOH⁺(H₂O)₂

C	-0.621600	-0.735842	-0.010888
C	0.825612	-0.724126	-0.167270

C	1.600099	0.516140	-0.169872
C	0.895896	1.683347	-0.006100
C	-0.499265	1.706314	0.155012
C	-1.217722	0.487557	0.145222
H	1.417220	2.628212	0.000100
H	-2.289243	0.546223	0.265918
C	-1.452142	-2.026621	-0.021414
C	-1.298277	-2.743147	-1.386448
C	-1.044241	-2.929214	1.169963
C	-2.955212	-1.736317	0.148299
H	-1.686922	-2.111888	-2.188025
H	-0.276819	-3.012997	-1.645555
H	-1.882133	-3.665146	-1.375816
H	-1.272775	-2.430808	2.114102
H	-1.621263	-3.854913	1.133468
H	0.007542	-3.206319	1.190568
H	-3.496357	-2.683016	0.132135
H	-3.180325	-1.252226	1.100491
H	-3.353654	-1.122842	-0.662077
C	3.124597	0.519244	-0.350090
C	3.807721	-0.264044	0.799436
C	3.504335	-0.088676	-1.724072
C	3.687070	1.952224	-0.318732
H	3.551540	0.165251	1.770612
H	3.541729	-1.317692	0.805885
H	4.890265	-0.190112	0.681755
H	3.033561	0.465735	-2.539021
H	4.585243	-0.014819	-1.856790
H	3.225825	-1.135472	-1.811509
H	4.767910	1.905336	-0.452286
H	3.289087	2.572822	-1.124356
H	3.501365	2.451930	0.634397
C	-1.230435	2.990685	0.344671
H	-2.075879	3.063871	-0.345667
H	-0.585981	3.857158	0.208521
O	1.543859	-1.796895	-0.316938
H	1.168761	-2.724064	-0.333987
H	-1.656419	3.035656	1.354032
O	1.451499	-4.354424	-0.467579
H	0.889094	-5.157026	-0.450028
H	2.362099	-4.646983	-0.575012
O	-0.134448	-6.603250	-0.425714
H	-0.326049	-7.125088	-1.212987
H	-0.167509	-7.215257	0.318031

PhOH⁺(H₂O)₃

C	-0.615587	-0.710707	0.036907
C	0.830566	-0.708042	-0.141994
C	1.607016	0.531941	-0.168450
C	0.909463	1.703159	-0.006126
C	-0.482970	1.732569	0.175444
C	-1.204704	0.516962	0.188893
H	1.433732	2.646381	-0.017039
H	-2.274144	0.580321	0.324917
C	-1.451955	-1.996525	0.052978
C	-1.321931	-2.727727	-1.306826
C	-1.030407	-2.885723	1.249647
C	-2.951489	-1.698911	0.241452
H	-1.726854	-2.104420	-2.106762
H	-0.305308	-2.998894	-1.580698
H	-1.902181	-3.651355	-1.275477
H	-1.265420	-2.382857	2.189944
H	-1.591837	-3.820936	1.218956
H	0.025484	-3.144952	1.270633
H	-3.495014	-2.644438	0.245302
H	-3.161373	-1.202099	1.190640
H	-3.360209	-1.094428	-0.570673
C	3.128945	0.528803	-0.371067

Appendix A

C	3.827109	-0.246543	0.774605
C	3.486774	-0.091321	-1.745226
C	3.696707	1.960145	-0.359941
H	3.588111	0.193342	1.745471
H	3.555947	-1.298616	0.795466
H	4.908050	-0.178817	0.639210
H	3.006032	0.458419	-2.557577
H	4.565939	-0.022889	-1.894535
H	3.202480	-1.137547	-1.819895
H	4.775435	1.908468	-0.508552
H	3.289248	2.575451	-1.164923
H	3.526296	2.468728	0.591390
C	-1.206793	3.022053	0.363409
H	-2.064176	3.090595	-0.312337
H	-0.561759	3.884402	0.204972
O	1.543591	-1.780475	-0.292198
H	1.192360	-2.729478	-0.294091
H	-1.613319	3.081042	1.379924
O	1.414947	-4.297630	-0.403390
H	0.823592	-5.086913	-0.312812
H	2.308103	-4.618330	-0.560578
O	-0.199740	-6.407223	-0.131778
H	-0.400907	-7.026750	-0.861800
H	-0.192988	-6.929029	0.676783
O	-0.791047	-8.158341	-2.199069
H	-0.192582	-8.781036	-2.625054
H	-1.680466	-8.399633	-2.478624

PhOH⁺⁺(H₂O)₄

C	-0.898415	-0.472278	-0.533260
C	0.505359	-0.829260	-0.280614
C	1.430913	0.176520	0.262521
C	0.936071	1.432753	0.516217
C	-0.402574	1.780830	0.275892
C	-1.283891	0.811098	-0.244745
H	1.585342	2.197687	0.916371
H	-2.306777	1.116360	-0.414570
C	-1.895707	-1.495648	-1.092121
C	-1.439950	-1.972777	-2.491150
C	-2.039780	-2.685368	-0.113572
C	-3.301908	-0.893374	-1.267389
H	-1.437077	-1.138793	-3.196492
H	-0.442332	-2.404333	-2.488204
H	-2.137657	-2.724161	-2.867809
H	-2.433340	-2.343567	0.846358
H	-2.745964	-3.412142	-0.521413
H	-1.099843	-3.197211	0.073863
H	-3.968049	-1.659799	-1.666742
H	-3.727643	-0.555571	-0.320458
H	-3.310419	-0.058217	-1.970641
C	2.900727	-0.173104	0.532212
C	2.997240	-1.308290	1.579592
C	3.600483	-0.594748	-0.781973
C	3.680824	1.028975	1.094432
H	2.541574	-1.005123	2.524994
H	2.505046	-2.216453	1.238724
H	4.048861	-1.531362	1.775611
H	3.557801	0.209727	-1.519787
H	4.653935	-0.803167	-0.581382
H	3.149849	-1.483251	-1.217616
H	4.715943	0.730518	1.267414
H	3.698596	1.871535	0.400160
H	3.279205	1.373901	2.049497
C	-0.903606	3.160293	0.563053
H	-1.284085	3.631179	-0.348994
H	-0.126595	3.799747	0.979373
O	0.950180	-1.987485	-0.517183
H	0.895360	-3.381227	-0.956768

H	-1.740201	3.130147	1.267939
O	0.996604	-4.378865	-1.205686
H	1.618984	-4.882321	-0.556080
H	1.274934	-4.504766	-2.156420
O	2.517521	-5.656896	0.342144
H	2.220637	-6.475278	0.801624
H	3.171380	-5.224817	0.900736
O	1.735285	-7.932880	1.575005
H	1.079354	-8.043368	2.271443
H	2.132288	-8.797741	1.425909
O	1.653043	-4.722744	-3.719765
H	2.524119	-4.637025	-4.122174
H	1.086810	-5.174002	-4.355532

PhO[•]

C	-0.575231	-0.864452	-0.035571
C	0.891790	-0.873013	-0.185957
C	1.617594	0.409861	-0.195056
C	0.888666	1.567761	-0.057687
C	-0.507963	1.570535	0.090056
C	-1.205147	0.349153	0.095044
H	1.390276	2.526161	-0.063122
H	-2.280671	0.391549	0.204597
C	-1.349482	-2.187479	-0.033229
C	-1.128537	-2.931081	-1.371537
C	-0.877119	-3.074375	1.143023
C	-2.863133	-1.966519	0.129985
H	-1.472296	-2.324116	-2.213387
H	-0.079388	-3.172665	-1.522535
H	-1.704397	-3.860464	-1.373452
H	-1.040443	-2.569843	2.099084
H	-1.452452	-4.004010	1.154275
H	0.178324	-3.320523	1.055730
H	-3.366842	-2.935165	0.125082
H	-3.109499	-1.474912	1.074196
H	-3.283903	-1.375623	-0.687163
C	3.141063	0.422995	-0.358814
C	3.804790	-0.354503	0.802378
C	3.531790	-0.220339	-1.710399
C	3.709309	1.852744	-0.344759
H	3.553935	0.098041	1.765468
H	3.489664	-1.395001	0.814377
H	4.891883	-0.320230	0.690880
H	3.082147	0.326195	-2.543674
H	4.617532	-0.182510	-1.833922
H	3.212375	-1.258269	-1.762484
H	4.793443	1.805388	-0.463903
H	3.316920	2.460802	-1.163459
H	3.506667	2.369357	0.596581
C	-1.251924	2.861069	0.270087
H	-2.220485	2.837726	-0.234026
H	-0.683381	3.710696	-0.110419
O	1.509144	-1.950357	-0.307956
H	-1.449466	3.048797	1.331925

PhO[•](H₂O)

C	-0.708430	-0.764389	-0.023110
C	0.757347	-0.806608	-0.161963
C	1.519082	0.456076	-0.155114
C	0.821355	1.628642	-0.012922
C	-0.579284	1.667187	0.124173
C	-1.306432	0.467655	0.113533
H	1.347640	2.573836	-0.004328
H	-2.380526	0.536751	0.216287
C	-1.524660	-2.061370	-0.035340
C	-1.320812	-2.804246	-1.377046
C	-1.101532	-2.965726	1.146726

C	-3.032662	-1.790621	0.112321
H	-1.644037	-2.181022	-2.215173
H	-0.283522	-3.085660	-1.534851
H	-1.924910	-3.714771	-1.385044
H	-1.266775	-2.456139	2.099795
H	-1.707528	-3.875058	1.144703
H	-0.056536	-3.256835	1.086681
H	-3.565674	-2.742978	0.095388
H	-3.274517	-1.298300	1.057279
H	-3.425504	-1.182464	-0.706035
C	3.044349	0.432827	-0.306949
C	3.681497	-0.364275	0.855625
C	3.431344	-0.206280	-1.661499
C	3.646001	1.848786	-0.278700
H	3.441285	0.095292	1.817884
H	3.337151	-1.395204	0.870934
H	4.769326	-0.361929	0.747546
H	3.008115	0.363397	-2.492861
H	4.518892	-0.199321	-1.772453
H	3.082395	-1.233144	-1.734740
H	4.729538	1.776178	-0.389232
H	3.275284	2.470941	-1.096740
H	3.448131	2.363886	0.664345
C	-1.275032	2.984914	0.294795
H	-2.357927	2.883632	0.221921
H	-0.944658	3.706917	-0.456882
O	1.355776	-1.896923	-0.286114
H	-1.044601	3.421107	1.272908
O	2.046132	-4.701816	-0.456008
H	1.818536	-3.761143	-0.403184
H	3.004109	-4.727685	-0.531773

PhO[•](H₂O)₂

C	-0.686919	-0.697306	-0.021129
C	0.780474	-0.736053	-0.150081
C	1.538646	0.528727	-0.151565
C	0.837111	1.700095	-0.023101
C	-0.564812	1.735995	0.106896
C	-1.288165	0.534860	0.102553
H	1.360590	2.646818	-0.020545
H	-2.362971	0.600485	0.199531
C	-1.501000	-1.994336	-0.028238
C	-1.292033	-2.740502	-1.367920
C	-1.086315	-2.887814	1.165564
C	-3.011050	-1.729565	0.108717
H	-1.667042	-2.139914	-2.201207
H	-0.246256	-2.966551	-1.554386
H	-1.842270	-3.683148	-1.350129
H	-1.323159	-2.392713	2.111309
H	-1.631936	-3.832380	1.126167
H	-0.025025	-3.118251	1.156229
H	-3.537286	-2.685629	0.096958
H	-3.260605	-1.231353	1.048585
H	-3.402597	-1.130362	-0.716963
C	3.064951	0.510279	-0.297957
C	3.702543	-0.269459	0.875977
C	3.460652	-0.142515	-1.643452
C	3.659923	1.929407	-0.283779
H	3.454364	0.197903	1.832407
H	3.365627	-1.302671	0.899253
H	4.790751	-0.260672	0.772676
H	3.032464	0.411651	-2.482689
H	4.548190	-0.124829	-1.753042
H	3.124310	-1.174382	-1.703994
H	4.744068	1.860500	-0.390410
H	3.288814	2.540405	-1.109960
H	3.457067	2.454456	0.652692
C	-1.264082	3.054372	0.254610

H	-2.348020	2.940771	0.252988
H	-0.989071	3.738405	-0.553521
O	1.388506	-1.824471	-0.258404
H	-0.977119	3.543874	1.191202
O	1.901759	-4.602913	-0.476980
H	1.712935	-3.649934	-0.411758
H	2.672420	-4.756427	0.077379
O	-0.394898	-6.265152	-0.068451
H	0.395963	-5.712753	-0.205155
H	-0.347572	-6.946034	-0.745294

PhO[•](H₂O)₃

C	-1.095537	-0.508358	-0.211361
C	0.344616	-0.813670	-0.173641
C	1.310407	0.284128	0.014820
C	0.818351	1.557549	0.150113
C	-0.558899	1.847888	0.117131
C	-1.479470	0.804717	-0.063943
H	1.498135	2.387757	0.288524
H	-2.528614	1.065214	-0.085457
C	-2.117458	-1.632902	-0.410235
C	-1.879033	-2.330714	-1.770379
C	-2.007962	-2.659427	0.742017
C	-3.561967	-1.101186	-0.414875
H	-1.982197	-1.618140	-2.592934
H	-0.893291	-2.784359	-1.828572
H	-2.626350	-3.115274	-1.913133
H	-2.201182	-2.180945	1.705677
H	-2.755793	-3.444307	0.603676
H	-1.026756	-3.124925	0.779406
H	-4.246817	-1.938953	-0.558899
H	-3.829051	-0.620290	0.529178
H	-3.739214	-0.392211	-1.227095
C	2.813919	-0.012983	0.052097
C	3.137102	-0.966523	1.226614
C	3.263170	-0.647491	-1.285375
C	3.646225	1.264954	0.255662
H	2.851023	-0.515944	2.180583
H	2.621606	-1.918213	1.126487
H	4.213129	-1.156372	1.257078
H	3.064935	0.029249	-2.120578
H	4.339549	-0.835499	-1.257540
H	2.755160	-1.588978	-1.477445
H	4.704884	0.999526	0.274295
H	3.504444	1.983819	-0.554787
H	3.417724	1.761243	1.201889
C	-1.025585	3.262714	0.289693
H	-2.096177	3.361415	0.110277
H	-0.498779	3.937767	-0.390476
O	0.747703	-1.989834	-0.301157
H	-0.820892	3.617549	1.305528
O	1.346197	-4.755022	-0.797946
H	1.146760	-3.823446	-0.618225
H	2.301056	-4.870431	-0.661088
O	1.120246	-6.908722	0.887226
H	0.930122	-6.138110	0.309143
H	0.678912	-7.662083	0.484277
O	3.708299	-6.080666	0.186226
H	4.293263	-5.862400	0.917217
H	2.960438	-6.575222	0.574546

PhO[•](H₂O)₄

C	-1.120871	-0.566994	0.125104
C	0.315630	-0.889911	0.083775
C	1.295093	0.197520	-0.093579
C	0.818279	1.478873	-0.210400
C	-0.554867	1.786293	-0.170388

Appendix A

C	-1.488720	0.752573	-0.002979
H	1.507956	2.302305	-0.339718
H	-2.534501	1.026227	0.023362
C	-2.155669	-1.682694	0.305538
C	-2.056153	-2.692054	-0.862664
C	-1.926038	-2.405868	1.653862
C	-3.594060	-1.135088	0.318108
H	-2.243366	-2.195747	-1.818556
H	-1.079898	-3.167149	-0.905454
H	-2.810561	-3.472450	-0.737034
H	-2.026409	-1.707300	2.488785
H	-2.678190	-3.188589	1.780179
H	-0.942272	-2.864905	1.704107
H	-4.288340	-1.967454	0.447632
H	-3.764134	-0.437386	1.141633
H	-3.854601	-0.635757	-0.618183
C	2.794465	-0.117442	-0.142136
C	3.243453	-0.774935	1.184260
C	3.100126	-1.058836	-1.330994
C	3.640871	1.153310	-0.333135
H	3.052491	-0.109358	2.030198
H	2.731891	-1.716881	1.363841
H	4.318596	-0.968861	1.149170
H	2.812638	-0.592496	-2.276980
H	4.173611	-1.260002	-1.371468
H	2.578191	-2.007786	-1.241313
H	4.696013	0.875147	-0.362026
H	3.413107	1.665232	-1.271215
H	3.512995	1.863015	0.487790
C	-1.004239	3.208978	-0.324558
H	-2.069423	3.321829	-0.122304
H	-0.816540	3.566504	-1.342837
O	0.700115	-2.073153	0.200259
H	-0.453512	3.872525	0.347726
O	1.686713	-4.748833	0.601939
H	1.333490	-3.857979	0.456632
H	0.935394	-5.371284	0.528418
O	1.617176	-7.852973	-1.710200
H	1.428684	-7.846023	-2.653088
H	2.350485	-7.208350	-1.570789
O	-0.172035	-6.785018	0.095728
H	-0.375548	-7.435848	0.773697
H	0.372658	-7.252591	-0.576185
O	3.422705	-5.895727	-1.113612
H	4.234305	-6.104339	-0.642137
H	2.859524	-5.382287	-0.480482

PhO⁺

C	-0.623328	-0.883944	-0.032220
C	0.895378	-0.878227	-0.184422
C	1.656230	0.445763	-0.198166
C	0.914359	1.577579	-0.056606
C	-0.497066	1.545388	0.089089
C	-1.227559	0.327287	0.099534
H	1.390028	2.547801	-0.058593
H	-2.300399	0.395113	0.210600
C	-1.377847	-2.193204	-0.033566
C	-1.130255	-2.936884	-1.377476
C	-0.893341	-3.075272	1.153726
C	-2.891565	-1.973978	0.120130
H	-1.448006	-2.330077	-2.228048
H	-0.087596	-3.213719	-1.507436
H	-1.730004	-3.848157	-1.378388
H	-1.040543	-2.566278	2.108625
H	-1.494012	-3.985832	1.167654
H	0.152028	-3.355727	1.057321
H	-3.389577	-2.943298	0.111276
H	-3.147107	-1.489362	1.065090

H	-3.310975	-1.388699	-0.701301
C	3.157160	0.452539	-0.363229
C	3.814892	-0.331007	0.810083
C	3.536004	-0.212952	-1.717964
C	3.722211	1.882392	-0.358962
H	3.553229	0.110072	1.774188
H	3.534766	-1.380825	0.810695
H	4.897930	-0.263697	0.697686
H	3.071403	0.309402	-2.556934
H	4.617606	-0.141573	-1.841482
H	3.255990	-1.262299	-1.752295
H	4.803793	1.832300	-0.482055
H	3.331604	2.484953	-1.182108
H	3.529301	2.403244	0.581655
C	-1.231993	2.818161	0.262096
H	-2.237980	2.771412	-0.156853
H	-0.688915	3.673645	-0.137106
O	1.495933	-1.919670	-0.286905
H	-1.356219	2.991012	1.342921

PhO⁺(H₂O)

C	-0.744336	-0.795490	-0.189058
C	0.747175	-0.797947	-0.510934
C	1.562496	0.480645	-0.338973
C	0.858635	1.619606	-0.094353
C	-0.550983	1.617475	0.068082
C	-1.311284	0.419098	0.045278
H	1.365756	2.570343	-0.011397
H	-2.373009	0.502307	0.229686
C	-1.515936	-2.092478	-0.169528
C	-1.498511	-2.743585	-1.583991
C	-0.863771	-3.055450	0.862718
C	-2.983350	-1.872303	0.233001
H	-1.920089	-2.069382	-2.332417
H	-0.497575	-3.032656	-1.889667
H	-2.123799	-3.637136	-1.550721
H	-0.898406	-2.629062	1.868087
H	-1.443790	-3.979724	0.877715
H	0.167862	-3.301555	0.621840
H	-3.487065	-2.838377	0.264386
H	-3.077725	-1.425360	1.225286
H	-3.523369	-1.251702	-0.485677
C	3.065057	0.442909	-0.473904
C	3.645058	-0.575382	0.548045
C	3.454405	0.019718	-1.921351
C	3.693242	1.818531	-0.195725
H	3.406015	-0.278069	1.571875
H	3.289215	-1.590165	0.386086
H	4.731874	-0.571957	0.450275
H	3.031451	0.705439	-2.658446
H	4.541111	0.069071	-2.005036
H	3.134152	-0.991931	-2.151418
H	4.777095	1.731387	-0.271908
H	3.380783	2.574197	-0.919993
H	3.467074	2.179967	0.809993
C	-1.245124	2.898513	0.333827
H	-2.272403	2.892376	-0.031424
H	-0.702160	3.755663	-0.062951
O	1.267243	-1.789705	-0.957640
H	-1.302394	3.033710	1.425113
O	2.607332	-4.011426	0.975946
H	2.901948	-4.637748	0.305548
H	2.881543	-4.397181	1.815270

PhO⁺(H₂O)₂

C	-0.765993	-0.721822	-0.205781
C	0.718484	-0.713614	-0.562944

C	1.550363	0.542900	-0.319453
C	0.871445	1.655538	0.072137
C	-0.528596	1.646891	0.301713
C	-1.305964	0.467363	0.178952
H	1.392066	2.590438	0.223303
H	-2.359592	0.542479	0.406937
C	-1.561843	-1.999811	-0.307437
C	-1.545959	-2.526162	-1.772470
C	-0.934035	-3.060350	0.642218
C	-3.028025	-1.789656	0.104234
H	-1.937971	-1.777349	-2.464198
H	-0.550481	-2.818863	-2.091356
H	-2.198444	-3.399189	-1.823665
H	-0.999249	-2.733648	1.682764
H	-1.513470	-3.980612	0.548536
H	0.105963	-3.280919	0.412319
H	-3.550180	-2.744159	0.038653
H	-3.123035	-1.440517	1.134788
H	-3.549414	-1.090934	-0.554195
C	3.044058	0.513746	-0.533646
C	3.667327	-0.553986	0.410383
C	3.366125	0.162690	-2.015598
C	3.689155	1.873489	-0.218649
H	3.502725	-0.287556	1.457108
H	3.277398	-1.555228	0.241677
H	4.745300	-0.567214	0.239470
H	2.900382	0.875962	-2.699153
H	4.446705	0.230451	-2.149907
H	3.046904	-0.841517	-2.276803
H	4.766787	1.791372	-0.360607
H	3.336352	2.665774	-0.883102
H	3.522875	2.181308	0.816106
C	-1.188381	2.900457	0.735908
H	-2.250671	2.916432	0.494933
H	-0.691649	3.785094	0.336445
O	1.219725	-1.678224	-1.083082
H	-1.107149	2.964673	1.831922
O	2.475887	-3.831166	0.909745
H	2.804857	-4.510737	0.295457
H	2.708091	-4.154024	1.786066
O	3.452369	-5.850697	-0.875619
H	4.375166	-5.959593	-1.128306
H	3.034732	-6.707253	-1.014088

PhO⁺(H₂O)₃

C	-0.726326	-0.859920	-0.131261
C	0.659954	-0.851583	-0.763338
C	1.667183	0.218396	-0.358058
C	1.195713	1.236177	0.414192
C	-0.138697	1.269317	0.884249
C	-1.056572	0.223356	0.623101
H	1.841014	2.057026	0.692123
H	-2.043267	0.309778	1.055307
C	-1.694841	-1.979016	-0.440228
C	-2.087201	-1.893015	-1.946246
C	-1.056874	-3.360946	-0.147620
C	-2.981536	-1.859025	0.394235
H	-2.522797	-0.921150	-2.187537
H	-1.236305	-2.073033	-2.597784
H	-2.842837	-2.655716	-2.142725
H	-0.773083	-3.440238	0.901634
H	-1.797568	-4.132308	-0.364319
H	-0.179569	-3.546810	-0.761320
H	-3.626990	-2.707654	0.167353
H	-2.777153	-1.880522	1.466995
H	-3.549802	-0.955526	0.162600
C	3.073345	0.185963	-0.912190
C	3.746116	-1.190386	-0.680905

C	2.994761	0.474183	-2.443198
C	3.959979	1.266525	-0.269319
H	3.821429	-1.412485	0.383349
H	3.207715	-1.998492	-1.168009
H	4.754995	-1.151609	-1.094338
H	2.512055	1.433228	-2.642122
H	4.014151	0.526709	-2.829752
H	2.462017	-0.309514	-2.975522
H	4.970534	1.174724	-0.667771
H	3.619376	2.279117	-0.495249
H	4.023811	1.151356	0.815092
C	-0.577955	2.410193	1.725950
H	-1.638550	2.627861	1.595554
H	0.016340	3.306664	1.554153
O	0.923288	-1.621235	-1.654412
H	-0.444455	2.129923	2.781140
O	2.422180	-4.468793	1.358505
H	3.329030	-4.717667	1.096178
H	2.027797	-5.250534	1.756438
O	5.016185	-5.172526	0.570368
H	5.748774	-5.340980	1.172712
H	5.189567	-5.698098	-0.218114
O	1.388210	-1.953254	1.696872
H	1.774200	-2.849812	1.580648
H	1.656546	-1.670866	2.576654

PhO⁺(H₂O)₄

C	-0.352375	-1.195669	-0.685048
C	0.669979	-0.587703	-1.634354
C	1.778613	0.305912	-1.088721
C	1.853152	0.426287	0.260594
C	0.926190	-0.212094	1.134622
C	-0.154891	-1.000190	0.644624
H	2.624696	1.028959	0.717861
H	-0.813502	-1.431705	1.388440
C	-1.510804	-1.996874	-1.242224
C	-2.315717	-1.133437	-2.251091
C	-0.965772	-3.267699	-1.953120
C	-2.468586	-2.445188	-0.126521
H	-2.685307	-0.219788	-1.779953
H	-1.729549	-0.867919	-3.127107
H	-3.182880	-1.707238	-2.581501
H	-0.390733	-3.886848	-1.261308
H	-1.815996	-3.857583	-2.299751
H	-0.344562	-3.023499	-2.810977
H	-3.287454	-3.009933	-0.573381
H	-1.983328	-3.091216	0.606633
H	-2.905075	-1.596140	0.403657
C	2.736215	0.990352	-2.041300
C	3.548553	-0.080339	-2.823164
C	1.941030	1.878948	-3.036125
C	3.732165	1.889278	-1.290174
H	4.109075	-0.723150	-2.141019
H	2.912148	-0.698536	-3.450262
H	4.268079	0.434622	-3.461923
H	1.345549	2.627049	-2.507917
H	2.652728	2.410461	-3.669646
H	1.286188	1.293717	-3.676526
H	4.387869	2.371357	-2.015401
H	3.231243	2.680923	-0.728315
H	4.369276	1.323910	-0.606379
C	1.081626	-0.058702	2.587315
H	0.111099	0.037299	3.081444
H	1.760421	0.745663	2.863175
O	0.627188	-0.836828	-2.816011
H	1.476759	-1.010031	2.993223
O	2.265105	-5.306171	3.500450
H	3.170569	-5.624564	3.680078

Appendix A

H	1.695448	-6.080973	3.528104
O	4.855975	-6.224380	4.016253
H	5.206114	-6.491454	4.872667
H	5.450864	-6.590316	3.353313
O	1.294279	-2.889713	4.300559
H	1.664757	-3.761805	4.029352
H	1.535180	-2.776657	5.225851
O	-1.256853	-2.152502	3.424862
H	-0.458392	-2.528402	3.844582
H	-2.011529	-2.468402	3.930278

A.6 Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,4,6-Tri-*tert*-butylphenol

Table A.7. Gas-phase energies of the hydrogen-bonded complexes of 2,4,6-tri-*tert*-butylphenol and its oxidized forms.

No. of H ₂ O molecules (<i>n</i>)	Energy (hartrees)			
	PhOH(H ₂ O) _{<i>n</i>}	PhOH ⁺⁺ (H ₂ O) _{<i>n</i>}	PhO [•] (H ₂ O) _{<i>n</i>}	PhO ⁺ (H ₂ O) _{<i>n</i>}
0	-779.489	-779.232	-778.865	-778.571
1	-855.965	-855.707	-855.340	-855.046
2	-932.440	-932.183	-931.815	-931.521
3	-1008.915	-1008.658	-1008.291	-1008.033
4	-1085.391	-1085.133	-1084.766	-1084.509

Figure A.21. Optimized geometries for PhOH(H₂O)_{*n*} for 2,4,6-tri-*tert*-butylphenol (*n* = 1 to 4).

Figure A.22. Optimized geometries for PhOH⁺⁺(H₂O)_{*n*} for 2,4,6-tri-*tert*-butylphenol (*n* = 1 to 4).

Figure A.23. Optimized geometries for $\text{PhO}^\bullet(\text{H}_2\text{O})_n$ for 2,4,6-tri-*tert*-butylphenol ($n = 1$ to 4).

Figure A.24. Optimized geometries for $\text{PhO}^+(\text{H}_2\text{O})_n$ for 2,4,6-tri-*tert*-butylphenol ($n = 1$ to 4).

Cartesian Coordinates of Hydrogen-Bonded Complexes of 2,4,6-Tri-*tert*-butylphenol

PhOH			
C	-0.618135	-0.586149	-0.003140
C	0.772095	-0.611957	-0.022312
C	1.435569	0.632697	-0.037108
C	0.735292	1.851985	-0.033498
C	-0.661971	1.787497	-0.012896
C	-1.365754	0.591384	0.002742
H	-1.146886	-1.526967	0.008131
H	-1.215349	2.711289	-0.008879
O	2.809558	0.587872	-0.055181
H	3.168356	1.477096	-0.061786
C	1.542625	-1.950816	-0.025904
C	2.404024	-2.076572	-1.303072
C	2.435336	-2.064267	1.230811
C	0.589488	-3.160413	-0.008528
H	1.775367	-2.032474	-2.196159
H	3.149975	-1.288355	-1.370856
H	2.922531	-3.039489	-1.307030
H	1.828597	-2.012471	2.138528
H	2.954879	-3.026647	1.230930
H	3.181755	-1.274704	1.272846
H	1.180704	-4.078620	-0.011889
H	-0.037822	-3.178773	0.885527
H	-0.059919	-3.186541	-0.886465
C	1.452670	3.224121	-0.050413
C	2.328108	3.410955	1.213783
C	2.296824	3.396549	-1.337763
C	0.452911	4.397129	-0.044922
H	1.709357	3.354555	2.111545
H	3.119858	2.669106	1.335008
H	2.807970	4.392760	1.194692
H	1.656212	3.330010	-2.219340
H	2.776630	4.378550	-1.341455
H	3.085514	2.653448	-1.470130
H	1.006377	5.338623	-0.057594
H	-0.196474	4.386347	-0.922032
H	-0.174041	4.397011	0.848420
C	-2.902104	0.525623	0.024410
C	-3.406984	-0.221738	-1.228515
C	-3.372082	-0.226719	1.287880
C	-3.549558	1.919431	0.036380
H	-3.101146	0.296372	-2.140465
H	-3.016949	-1.239751	-1.278015
H	-4.498882	-0.283773	-1.223313
H	-3.039317	0.286555	2.193112
H	-4.463754	-0.286873	1.313509
H	-2.983009	-1.245749	1.321696
H	-4.637134	1.817688	0.052529
H	-3.260663	2.495946	0.918315
H	-3.287743	2.499121	-0.851897

PhOH(H ₂ O)			
C	-0.733021	-0.581645	-0.010474
C	0.656827	-0.554902	-0.016834
C	1.280290	0.713206	-0.017040
C	0.532512	1.905451	-0.011906
C	-0.861683	1.787259	-0.004408
C	-1.523082	0.567378	-0.003501
H	-1.228030	-1.540790	-0.010052
H	-1.448497	2.690057	0.000673
O	2.649729	0.703051	-0.025679
H	3.038426	1.583643	-0.003210
C	1.472502	-1.867321	-0.021727
C	2.348653	-1.956880	-1.292152

C	2.356104	-1.960583	1.243237
C	0.563124	-3.110355	-0.021139
H	1.725156	-1.936316	-2.189677
H	3.060388	-1.137216	-1.353513
H	2.905721	-2.898365	-1.294260
H	1.737714	-1.943908	2.144305
H	2.914177	-2.901466	1.238839
H	3.067230	-1.140369	1.303890
H	1.186740	-4.007037	-0.024948
H	-0.071249	-3.156868	0.866849
H	-0.077253	-3.153378	-0.905026
C	1.190747	3.305876	-0.013638
C	2.042353	3.518471	1.261929
C	2.038503	3.515497	-1.292284
C	0.144220	4.437282	-0.014091
H	1.415144	3.418505	2.150391
H	2.875455	2.825217	1.374468
H	2.466948	4.526103	1.261304
H	1.406461	3.430527	-2.178956
H	2.478269	4.516678	-1.286679
H	2.856591	2.805387	-1.411565
H	0.661565	5.399295	-0.019266
H	-0.497208	4.405819	-0.896934
H	-0.489905	4.412239	0.874141
C	-3.055979	0.445713	0.004365
C	-3.523051	-0.314890	-1.255251
C	-3.509335	-0.328233	1.260873
C	-3.753418	1.815165	0.015419
H	-3.228297	0.217485	-2.162659
H	-3.095337	-1.317750	-1.304766
H	-4.612037	-0.416899	-1.259817
H	-3.203586	0.193722	2.170674
H	-4.598292	-0.429170	1.276684
H	-3.082341	-1.332063	1.294517
H	-4.837048	1.675403	0.021190
H	-3.492946	2.398299	0.901829
H	-3.503741	2.407118	-0.868247
O	5.126189	2.119758	0.088582
H	5.481970	1.227467	0.015950
H	5.736407	2.687880	-0.392056

PhOH(H ₂ O) ₂			
C	-0.742372	-0.546856	0.009569
C	0.646712	-0.499916	0.054889
C	1.256074	0.774563	0.010625
C	0.492511	1.955210	-0.058706
C	-0.898777	1.815202	-0.104929
C	-1.545670	0.588316	-0.075598
H	-1.224057	-1.512153	0.038031
H	-1.496003	2.708844	-0.162924
O	2.632594	0.793155	0.055285
H	3.018269	1.654367	-0.159167
C	1.468053	-1.803904	0.158897
C	2.410532	-1.953898	-1.057677
C	2.258104	-1.826465	1.487559
C	0.574060	-3.058761	0.166636
H	1.827752	-2.036721	-1.978280
H	3.083836	-1.108313	-1.173353
H	3.006199	-2.866324	-0.959371
H	1.568073	-1.866537	2.333800
H	2.895354	-2.714143	1.535816
H	2.883245	-0.947171	1.623849
H	1.207860	-3.945112	0.244690
H	-0.110693	-3.072470	1.016929

Appendix A

H	-0.011141	-3.153902	-0.750476
C	1.121457	3.368452	-0.092375
C	1.989655	3.618987	1.164923
C	1.937009	3.568492	-1.392632
C	0.053200	4.479588	-0.088365
H	1.374872	3.543559	2.064768
H	2.821708	2.926787	1.281579
H	2.408913	4.628124	1.129033
H	1.287546	3.443733	-2.261853
H	2.347575	4.581567	-1.421771
H	2.779911	2.889056	-1.511931
H	0.554170	5.450076	-0.090464
H	-0.586942	4.443200	-0.971866
H	-0.580499	4.439548	0.799904
C	-3.075751	0.446216	-0.128281
C	-3.476234	-0.398536	-1.357004
C	-3.576490	-0.253982	1.153242
C	-3.787739	1.803821	-0.234583
H	-3.142077	0.076769	-2.282245
H	-3.041096	-1.398797	-1.321158
H	-4.563013	-0.510418	-1.405828
H	-3.319208	0.328691	2.040878
H	-4.663772	-0.369487	1.126530
H	-3.140044	-1.247503	1.269418
H	-4.868709	1.649637	-0.270643
H	-3.576343	2.443169	0.625590
H	-3.502341	2.344090	-1.140205
O	4.981423	2.414157	-0.454708
H	5.416799	1.590324	-0.166386
H	5.441392	3.135007	-0.015186
O	5.429621	-0.156794	0.466815
H	4.461675	-0.210778	0.444022
H	5.748920	-0.921025	-0.022951

PhOH(H₂O)₃

C	-0.693602	-0.523297	-0.091122
C	0.696068	-0.465679	-0.011626
C	1.286678	0.815152	0.050001
C	0.512515	1.989621	0.071789
C	-0.876141	1.842784	-0.011661
C	-1.504988	0.608419	-0.100097
H	-1.169125	-1.489993	-0.146077
H	-1.484830	2.730417	-0.005049
O	2.671885	0.910386	0.146278
H	3.109702	0.989561	-0.729889
C	1.520114	-1.775034	0.026011
C	2.499631	-1.855104	-1.165523
C	2.297634	-1.878373	1.356431
C	0.623819	-3.025745	-0.058958
H	1.963567	-1.750921	-2.112443
H	3.269825	-1.089828	-1.120000
H	2.999167	-2.828019	-1.170739
H	1.611329	-1.865425	2.206516
H	2.858468	-2.816686	1.391272
H	3.001712	-1.058693	1.472680
H	1.254237	-3.916507	-0.017938
H	-0.080576	-3.086670	0.773087
H	0.059191	-3.067261	-0.992996
C	1.126850	3.404738	0.195792
C	1.921389	3.535148	1.513688
C	2.036192	3.722064	-1.011135
C	0.045997	4.503452	0.226344
H	1.275309	3.338174	2.373001
H	2.765164	2.852614	1.558466
H	2.308072	4.553206	1.613922
H	1.477613	3.637770	-1.946874
H	2.403238	4.749650	-0.935421
H	2.901524	3.069141	-1.079485

H	0.535144	5.474664	0.326323
H	-0.544986	4.530802	-0.691804
H	-0.635653	4.393172	1.072597
C	-3.032309	0.454831	-0.193036
C	-3.399478	-0.289782	-1.494460
C	-3.545062	-0.354339	1.017612
C	-3.759249	1.808905	-0.200555
H	-3.056053	0.265086	-2.370684
H	-2.951541	-1.284154	-1.533746
H	-4.483611	-0.409959	-1.571866
H	-3.306922	0.154091	1.954824
H	-4.630530	-0.475744	0.963591
H	-3.100900	-1.350485	1.057361
H	-4.837310	1.646309	-0.271097
H	-3.572788	2.377024	0.713615
H	-3.463446	2.425832	-1.052157
O	4.341289	1.193737	-2.015301
H	7.097373	2.090898	-0.382963
H	4.431601	0.580746	-2.750518
O	4.939809	1.064735	1.764742
H	4.059881	0.981239	1.344268
H	4.999694	0.357741	2.414101
O	6.571948	1.286856	-0.434558
H	5.216431	1.231611	-1.565905
H	6.109741	1.202505	0.428507

PhOH(H₂O)₄

C	-0.768689	-0.570448	-0.175793
C	0.606515	-0.481835	0.031083
C	1.150492	0.811031	0.199535
C	0.340136	1.962167	0.198209
C	-1.030677	1.783196	-0.016251
C	-1.610695	0.537762	-0.211671
H	-1.207718	-1.545807	-0.314531
H	-1.665003	2.652560	-0.027553
O	2.516574	0.946217	0.428623
H	3.037079	1.035516	-0.403816
C	1.458703	-1.773868	0.065729
C	2.452945	-1.804407	-1.115032
C	2.221538	-1.896784	1.403221
C	0.590462	-3.041893	-0.055599
H	1.918660	-1.748695	-2.066854
H	3.171231	-0.989597	-1.089601
H	3.013584	-2.743802	-1.103078
H	1.530926	-1.853809	2.249403
H	2.743634	-2.856566	1.445360
H	2.959953	-1.108683	1.517027
H	1.239043	-3.918983	-0.005124
H	-0.136615	-3.124823	0.755392
H	0.055042	-3.089765	-1.006012
C	0.892221	3.387761	0.446466
C	1.485549	3.488625	1.868534
C	1.960572	3.771198	-0.600318
C	-0.211350	4.460126	0.351310
H	0.725631	3.255275	2.618466
H	2.325386	2.815759	2.015876
H	1.835738	4.508091	2.055140
H	1.561932	3.670918	-1.613668
H	2.255430	4.815184	-0.462197
H	2.857350	3.163432	-0.519743
H	0.234025	5.440311	0.533775
H	-0.675997	4.490741	-0.636873
H	-0.996123	4.317211	1.096914
C	-3.117004	0.346618	-0.455744
C	-3.334988	-0.330380	-1.825964
C	-3.713528	-0.546787	0.652953
C	-3.885677	1.677489	-0.456614
H	-2.927588	0.283581	-2.632585

H	-2.853002	-1.308072	-1.876038
H	-4.402444	-0.474696	-2.014534
H	-3.581296	-0.088782	1.635969
H	-4.784572	-0.694761	0.488722
H	-3.242836	-1.531066	0.678633
H	-4.946678	1.488145	-0.635669
H	-3.801757	2.196993	0.500603
H	-3.535131	2.350494	-1.242399
O	4.182260	1.189516	-1.712927
H	6.826032	1.621316	0.018418
H	4.010658	1.828117	-2.411010
O	4.264694	1.105229	2.577250
H	3.596649	1.026696	1.863280
H	4.142763	0.339361	3.146100
O	6.769741	1.489119	-0.957482
H	5.132910	1.292897	-1.466412
H	7.394963	0.790654	-1.172108
O	6.770286	1.796078	1.741884
H	5.879774	1.549135	2.081030
H	6.974098	2.656646	2.119712

PhOH⁺⁺

C	-0.605542	-0.572306	-0.011029
C	0.761139	-0.596842	-0.030222
C	1.413582	0.691706	-0.038349
C	0.692382	1.950470	-0.025977
C	-0.680228	1.859436	-0.005856
C	-1.368628	0.631626	0.002209
H	-1.144741	-1.505270	-0.004906
H	-1.258075	2.767172	0.004473
O	2.726096	0.782303	-0.057833
H	3.147529	-0.090514	-0.063392
C	1.417035	3.300835	-0.033633
C	2.307179	3.438725	1.228262
C	2.274466	3.443253	-1.317458
C	0.415430	4.469444	-0.019019
H	1.712043	3.346057	2.139388
H	3.109926	2.706150	1.260701
H	2.761105	4.430980	1.230100
H	1.657011	3.349476	-2.213494
H	2.724521	4.437190	-1.329448
H	3.078984	2.713924	-1.371302
H	0.971762	5.406877	-0.024589
H	-0.231543	4.473591	-0.898845
H	-0.209009	4.470877	0.876945
C	1.557437	-1.917233	-0.041807
C	2.409131	-2.035406	-1.332936
C	2.448169	-2.033271	1.223154
C	0.611773	-3.132042	-0.026495
H	1.778681	-1.973967	-2.221495
H	3.192176	-1.280621	-1.446828
H	2.911098	-3.003713	-1.343816
H	1.844691	-1.971693	2.130253
H	2.951416	-3.000971	1.219831
H	3.233381	-1.277323	1.312705
H	1.207204	-4.045178	-0.034430
H	-0.009713	-3.158124	0.870494
H	-0.035767	-3.159974	-0.904791
C	-2.882731	0.546049	0.023759
C	-3.354328	-0.220658	-1.240725
C	-3.319142	-0.238967	1.289518
C	-3.563626	1.922472	0.043121
H	-3.063424	0.303919	-2.152617
H	-2.959051	-1.235988	-1.287815
H	-4.443190	-0.291605	-1.224455
H	-3.000267	0.270680	2.200540
H	-4.408157	-0.307190	1.304013
H	-2.925727	-1.255909	1.309557

H	-4.645437	1.786710	0.058185
H	-3.298738	2.501387	0.930371
H	-3.325373	2.513350	-0.843772

PhOH⁺⁺(H₂O)

C	-0.672523	-0.485818	0.022856
C	0.692834	-0.396004	0.006982
C	1.238554	0.945907	-0.036798
C	0.391958	2.132369	-0.052600
C	-0.966265	1.921738	-0.033683
C	-1.541668	0.639020	0.001233
H	-1.126124	-1.462602	0.052804
H	-1.622859	2.773845	-0.046146
O	2.520756	1.195983	-0.065986
H	3.167256	0.455832	-0.059379
C	0.982348	3.548800	-0.088766
C	1.854572	3.801621	1.167464
C	1.816143	3.753634	-1.379240
C	-0.124944	4.618202	-0.091807
H	1.271369	3.667255	2.081200
H	2.725381	3.153001	1.214576
H	2.205955	4.834746	1.150131
H	1.205441	3.586236	-2.269205
H	2.168104	4.786236	-1.410710
H	2.684904	3.102444	-1.428617
H	0.342169	5.603000	-0.115706
H	-0.771182	4.547442	-0.969288
H	-0.745564	4.578439	0.805911
C	1.575338	-1.654944	0.033908
C	2.417268	-1.745301	-1.263728
C	2.462151	-1.659155	1.304841
C	0.727178	-2.938875	0.092224
H	1.764125	-1.826443	-2.134605
H	3.085185	-0.902284	-1.435610
H	3.035753	-2.644296	-1.230266
H	1.839840	-1.669436	2.201605
H	3.071202	-2.565081	1.315756
H	3.143488	-0.813978	1.390941
H	1.395990	-3.799940	0.111402
H	0.111076	-2.988576	0.992114
H	0.083637	-3.050391	-0.782506
C	-3.043259	0.414998	0.016285
C	-3.432786	-0.428796	-1.225804
C	-3.418571	-0.365536	1.302976
C	-3.845606	1.724486	-0.012237
H	-3.173727	0.087608	-2.151986
H	-2.952827	-1.407945	-1.234076
H	-4.512038	-0.590856	-1.219955
H	-3.154786	0.199345	2.199008
H	-4.496960	-0.533009	1.314275
H	-2.933277	-1.340572	1.357540
H	-4.911290	1.493413	-0.000033
H	-3.641490	2.351651	0.858027
H	-3.652127	2.306735	-0.915553
O	4.981463	0.149369	-0.088947
H	5.528097	-0.643562	-0.066985
H	5.589515	0.896090	-0.132401

PhOH⁺⁺(H₂O)₂

C	-0.798525	-0.418428	0.031903
C	0.567806	-0.339090	0.003895
C	1.126437	1.000046	-0.047224
C	0.280320	2.189738	-0.068612
C	-1.078760	1.987966	-0.036784
C	-1.660927	0.709373	0.013239
H	-1.257672	-1.392366	0.069387
H	-1.730503	2.843743	-0.050693

Appendix A

O	2.402490	1.252309	-0.078046
H	3.105622	0.543943	-0.065690
C	0.876060	3.604007	-0.124371
C	1.755346	3.870449	1.123830
C	1.703089	3.791114	-1.421567
C	-0.226904	4.678176	-0.134747
H	1.176093	3.748911	2.041949
H	2.623728	3.219080	1.174365
H	2.109688	4.902349	1.092198
H	1.086059	3.616246	-2.305811
H	2.059589	4.821733	-1.467227
H	2.568046	3.134779	-1.468526
H	0.244091	5.660681	-0.174838
H	-0.879274	4.598208	-1.006909
H	-0.842025	4.653141	0.767291
C	1.435293	-1.606722	0.025733
C	2.276163	-1.698170	-1.272087
C	2.316164	-1.624964	1.300097
C	0.575554	-2.883546	0.075250
H	1.619772	-1.785392	-2.140244
H	2.939143	-0.852785	-1.444142
H	2.899748	-2.593172	-1.234554
H	1.686793	-1.661060	2.191525
H	2.938580	-2.521572	1.294866
H	2.983708	-0.772235	1.402463
H	1.237965	-3.749778	0.087475
H	-0.040153	-2.935620	0.975356
H	-0.069872	-2.983260	-0.799659
C	-3.164783	0.493980	0.046067
C	-3.574066	-0.356097	-1.184437
C	-3.530960	-0.272907	1.342798
C	-3.959084	1.808443	0.016061
H	-3.321261	0.151295	-2.117381
H	-3.100025	-1.338187	-1.190395
H	-4.654240	-0.511438	-1.166601
H	-3.254142	0.298244	2.230978
H	-4.609979	-0.435220	1.368120
H	-3.049199	-1.249553	1.400537
H	-5.026180	1.584678	0.042118
H	-3.740726	2.441374	0.878696
H	-3.771669	2.382250	-0.893936
O	4.740079	0.178355	-0.075866
H	5.266478	-0.647618	-0.050807
H	5.363328	0.910602	-0.116264
O	6.217590	-2.146838	-0.001004
H	6.689725	-2.500104	-0.763222
H	6.705839	-2.437664	0.777282

PhOH⁺(H₂O)₃

C	-1.001283	-0.335957	-0.120108
C	0.367096	-0.290098	-0.118287
C	0.961532	1.035945	-0.095050
C	0.141936	2.245214	-0.076306
C	-1.221871	2.076302	-0.080677
C	-1.835368	0.811695	-0.101787
H	-1.484247	-1.299008	-0.136098
H	-1.852674	2.947708	-0.067763
O	2.240154	1.259808	-0.089023
H	2.956601	0.549133	-0.104266
C	0.771838	3.645780	-0.053063
C	1.625307	3.834022	1.226445
C	1.634999	3.872779	-1.319859
C	-0.305314	4.746148	-0.040815
H	1.019877	3.687191	2.123775
H	2.475239	3.158016	1.268823
H	2.006235	4.856701	1.249757
H	1.037448	3.749279	-2.225965
H	2.012395	4.896993	-1.311388

H	2.487635	3.201205	-1.374148
H	0.189246	5.717797	-0.025254
H	-0.937328	4.721242	-0.931113
H	-0.943448	4.695941	0.844033
C	1.201502	-1.578564	-0.139435
C	2.057688	-1.632248	-1.429524
C	2.059718	-1.675237	1.146695
C	0.310698	-2.834895	-0.159859
H	1.409378	-1.692737	-2.306100
H	2.720038	-0.780916	-1.568481
H	2.682611	-2.526682	-1.411078
H	1.412648	-1.749975	2.023135
H	2.672959	-2.576904	1.104392
H	2.735062	-0.837711	1.304900
H	0.952555	-3.716479	-0.176604
H	-0.319997	-2.911000	0.728145
H	-0.323420	-2.880331	-1.047504
C	-3.345204	0.633257	-0.106069
C	-3.752774	-0.139820	-1.386229
C	-3.754627	-0.190228	1.141751
C	-4.105741	1.967641	-0.079986
H	-3.476775	0.413138	-2.286151
H	-3.295841	-1.128654	-1.439588
H	-4.835762	-0.275749	-1.392217
H	-3.475299	0.323689	2.063548
H	-4.838185	-0.321461	1.143445
H	-3.302287	-1.182504	1.153796
H	-5.178508	1.770788	-0.084560
H	-3.887760	2.548644	0.818627
H	-3.886693	2.583581	-0.954699
O	4.498277	0.113498	-0.113273
H	4.965828	-0.756039	-0.181946
H	5.168060	0.802682	-0.073568
O	5.725308	-2.254786	-0.323028
H	6.287378	-2.629468	0.384542
H	6.114874	-2.532410	-1.158043
O	7.308262	-3.329827	1.686682
H	7.191186	-4.203846	2.073741
H	8.171400	-3.016189	1.976539

PhOH⁺(H₂O)₄

C	-1.235528	-0.443945	0.155883
C	0.121669	-0.446841	0.341068
C	0.835600	0.818614	0.134700
C	0.082468	2.021331	-0.242741
C	-1.278934	1.908605	-0.402562
C	-1.975365	0.702178	-0.217238
H	-1.781648	-1.362475	0.301525
H	-1.843784	2.781664	-0.682008
O	2.088886	0.912753	0.272202
H	3.418459	0.415200	0.560295
C	0.800845	3.362227	-0.451427
C	1.504543	3.800488	0.855323
C	1.828400	3.247425	-1.602569
C	-0.180600	4.485970	-0.832623
H	0.781905	3.913604	1.666828
H	2.260782	3.084122	1.168288
H	1.983742	4.770295	0.701404
H	1.335929	2.958566	-2.533924
H	2.301038	4.218728	-1.765909
H	2.604873	2.517904	-1.384984
H	0.377183	5.415050	-0.960503
H	-0.694860	4.285601	-1.774856
H	-0.930309	4.662283	-0.058430
C	0.863651	-1.725972	0.753127
C	1.881214	-2.125671	-0.341387
C	1.561007	-1.519689	2.118586
C	-0.093142	-2.920093	0.922609

H	1.363733	-2.366419	-1.272806
H	2.602423	-1.342338	-0.559441
H	2.430031	-3.015899	-0.025760
H	0.822554	-1.311021	2.895912
H	2.092154	-2.431240	2.401537
H	2.277051	-0.702559	2.110621
H	0.484246	-3.798080	1.216718
H	-0.837515	-2.745862	1.702203
H	-0.612083	-3.169985	-0.005004
C	-3.486585	0.590280	-0.398848
C	-3.786315	-0.459277	-1.495973
C	-4.121681	0.132400	0.936059
C	-4.137651	1.919216	-0.811710
H	-3.349708	-0.164701	-2.452613
H	-3.403280	-1.447733	-1.238988
H	-4.866097	-0.548309	-1.631378
H	-3.927319	0.854119	1.732165
H	-5.203535	0.046627	0.815456
H	-3.747603	-0.839379	1.261328
H	-5.212503	1.773659	-0.929312
H	-3.996388	2.697488	-0.058656
H	-3.753491	2.286805	-1.765798
O	4.414819	0.208765	0.766695
H	4.974779	0.026796	-0.074522
H	4.823507	0.912922	1.344537
O	5.774642	-0.305472	-1.292686
H	6.333368	-1.108473	-1.393920
H	6.015214	0.319680	-1.982639
O	7.284875	-2.533063	-1.579878
H	7.034461	-3.303336	-2.101099
H	8.197250	-2.668721	-1.302995
O	5.536264	2.007014	2.317604
H	5.331619	2.948662	2.329042
H	5.871326	1.780254	3.192483

PhO[•]

C	-0.616393	-0.586296	0.000659
C	0.754750	-0.615530	0.001259
C	1.477615	0.667832	0.000914
C	0.699764	1.916100	-0.000045
C	-0.675574	1.831384	-0.000645
C	-1.367301	0.609370	-0.000335
H	-1.158844	-1.520047	0.000922
H	-1.251144	2.742545	-0.001385
O	2.725289	0.695223	0.001472
C	1.426542	3.266083	-0.000379
C	2.307349	3.393422	1.265146
C	2.308295	3.392284	-1.265361
C	0.443918	4.450649	-0.001267
H	1.698390	3.323704	2.170471
H	3.068569	2.617889	1.297487
H	2.801633	4.368615	1.270207
H	1.699987	3.321863	-2.171069
H	2.802673	4.367428	-1.270878
H	3.069464	2.616652	-1.296480
H	1.011242	5.383528	-0.001500
H	-0.194777	4.457214	-0.887831
H	-0.195387	4.458026	0.884851
C	1.540868	-1.932302	0.002215
C	2.427206	-2.020432	-1.262548
C	2.426471	-2.019100	1.267582
C	0.610547	-3.157943	0.002595
H	1.816530	-1.976567	-2.168321
H	3.154013	-1.212430	-1.293678
H	2.964130	-2.972841	-1.268145
H	1.815270	-1.974289	2.172955
H	2.963389	-2.971504	1.274486
H	3.153265	-1.211071	1.298291

H	1.216823	-4.065898	0.003324
H	-0.027847	-3.191100	0.888880
H	-0.027243	-3.192115	-0.884085
C	-2.897230	0.531503	-0.001003
C	-3.369357	-0.228986	-1.261278
C	-3.370528	-0.227061	1.259990
C	-3.565063	1.915690	-0.002360
H	-3.054984	0.288142	-2.170583
H	-2.973048	-1.244579	-1.299614
H	-4.460197	-0.296784	-1.270200
H	-3.057088	0.291523	2.168788
H	-4.461372	-0.294941	1.267960
H	-2.974160	-1.242553	1.300297
H	-4.650368	1.794768	-0.002823
H	-3.300946	2.498811	0.882549
H	-3.300025	2.497514	-0.887849

PhO[•](H₂O)

C	-0.715937	-0.528844	0.000367
C	0.654414	-0.471020	-0.011223
C	1.287378	0.858235	-0.016401
C	0.431420	2.054023	-0.009244
C	-0.934488	1.879442	0.002401
C	-1.544159	0.614174	0.007497
H	-1.197000	-1.495232	0.004210
H	-1.569130	2.750119	0.007683
O	2.532107	0.976075	-0.026779
C	1.065039	3.450218	-0.014604
C	1.941501	3.639829	1.246122
C	1.923064	3.639012	-1.288110
C	0.005640	4.566639	-0.007408
H	1.341830	3.535277	2.154067
H	2.752327	2.916845	1.284164
H	2.370886	4.645140	1.244804
H	1.310577	3.532176	-2.187186
H	2.350909	4.644960	-1.294494
H	2.734336	2.917208	-1.336834
H	0.510871	5.534489	-0.011805
H	-0.638857	4.532450	-0.889026
H	-0.625531	4.533668	0.883846
C	1.517308	-1.738571	-0.018891
C	2.391057	-1.778895	-1.295116
C	2.414184	-1.778610	1.241237
C	0.660152	-3.016768	-0.010928
H	1.765220	-1.775512	-2.191540
H	3.075906	-0.937096	-1.347844
H	2.982414	-2.697793	-1.303637
H	1.804740	-1.772402	2.148870
H	3.003653	-2.698764	1.240544
H	3.101576	-0.938159	1.280059
H	1.320548	-3.885760	-0.017600
H	0.034354	-3.089955	0.881960
H	0.017344	-3.089413	-0.891690
C	-3.064566	0.434639	0.019221
C	-3.494033	-0.350479	-1.241443
C	-3.474530	-0.360241	1.280263
C	-3.822296	1.771750	0.030323
H	-3.220925	0.189625	-2.150674
H	-3.032414	-1.337772	-1.286566
H	-4.578026	-0.489238	-1.242519
H	-3.185675	0.171779	2.189400
H	-4.558587	-0.497230	1.297812
H	-3.014197	-1.348684	1.309776
H	-4.897336	1.580408	0.038625
H	-3.589564	2.367222	0.915825
H	-3.604475	2.373247	-0.854859
O	5.382437	0.495344	-0.053456
H	4.427272	0.660462	-0.044610

Appendix A

H 5.790799 1.365595 -0.052071

PhO⁺(H₂O)₂

C -0.878856 -0.586623 0.168175
C 0.489039 -0.650292 0.221873
C 1.248513 0.600261 0.056621
C 0.513535 1.856731 -0.154766
C -0.863195 1.804159 -0.193119
C -1.592219 0.615071 -0.037966
H -1.449059 -1.495500 0.288235
H -1.408418 2.719960 -0.349765
O 2.499543 0.580852 0.097036
C 1.271219 3.177145 -0.326319
C 2.100106 3.477905 0.945861
C 2.189333 3.104315 -1.570414
C 0.321816 4.369902 -0.537095
H 1.440843 3.608032 1.808492
H 2.807118 2.685711 1.173825
H 2.664099 4.401722 0.803719
H 1.591077 2.983767 -2.477795
H 2.765058 4.027437 -1.658632
H 2.893357 2.279426 -1.513031
H 0.917936 5.276624 -0.654183
H -0.285432 4.261172 -1.438907
H -0.345522 4.525483 0.314217
C 1.230500 -1.974508 0.447676
C 2.144857 -2.282805 -0.761286
C 2.073283 -1.897262 1.742706
C 0.260477 -3.158946 0.601400
H 1.558140 -2.365464 -1.679857
H 2.897415 -1.511071 -0.901812
H 2.652150 -3.238046 -0.602627
H 1.434248 -1.705692 2.608619
H 2.579885 -2.851865 1.907579
H 2.824076 -1.113136 1.688007
H 0.837299 -4.072139 0.760083
H -0.403843 -3.039948 1.460588
H -0.350984 -3.311225 -0.291186
C -3.121768 0.576273 -0.086029
C -3.570309 -0.347490 -1.242011
C -3.660604 0.018646 1.251661
C -3.746713 1.961806 -0.312847
H -3.207849 0.024485 -2.202821
H -3.205115 -1.367747 -1.117690
H -4.661588 -0.387381 -1.284278
H -3.359513 0.651358 2.089481
H -4.752667 -0.014295 1.227490
H -3.302211 -0.992424 1.449109
H -4.834366 1.869410 -0.339886
H -3.497318 2.659912 0.489047
H -3.431920 2.402220 -1.261231
O 5.568638 4.185219 -0.651903
H 6.205857 4.543567 -0.027802
H 5.453311 3.253196 -0.392476
O 5.190373 1.457218 0.134699
H 4.260406 1.168152 0.126136
H 5.682703 0.772462 -0.327330

PhO⁺(H₂O)₃

C -0.771126 -0.446791 -0.044412
C 0.585756 -0.304126 0.088887
C 1.133235 1.059965 0.174188
C 0.208331 2.201738 0.128730
C -1.138243 1.943243 -0.006874
C -1.665068 0.645003 -0.099369
H -1.186915 -1.440880 -0.110360
H -1.823313 2.773967 -0.043171

O 2.365838 1.238660 0.284064
C 0.745920 3.633800 0.232093
C 1.486843 3.826592 1.577031
C 1.701539 3.929070 -0.948255
C -0.382241 4.679143 0.178536
H 0.813686 3.642385 2.418457
H 2.343585 3.164716 1.669402
H 1.841284 4.857628 1.653289
H 1.179263 3.827730 -1.903187
H 2.065329 4.957047 -0.874810
H 2.560271 3.263247 -0.953304
H 0.054740 5.675998 0.261201
H -0.935617 4.644104 -0.762970
H -1.092207 4.565100 1.001282
C 1.526491 -1.514059 0.151331
C 2.526099 -1.470646 -1.028327
C 2.293153 -1.520116 1.494911
C 0.759763 -2.844814 0.054319
H 1.997284 -1.491008 -1.984841
H 3.146866 -0.578926 -0.996606
H 3.177104 -2.347911 -0.988425
H 1.598309 -1.576491 2.336917
H 2.944167 -2.396924 1.540939
H 2.905988 -0.630215 1.612970
H 1.472559 -3.669839 0.109324
H 0.049197 -2.973062 0.874390
H 0.220248 -2.943593 -0.890699
C -3.164314 0.374814 -0.250476
C -3.411120 -0.421588 -1.552617
C -3.654636 -0.456617 0.957333
C -3.999743 1.663114 -0.315061
H -3.071648 0.140269 -2.425599
H -2.895021 -1.382322 -1.550915
H -4.479481 -0.618777 -1.671214
H -3.498720 0.083949 1.893497
H -4.723457 -0.662117 0.858664
H -3.137381 -1.414128 1.032853
H -5.054689 1.405353 -0.428302
H -3.904446 2.258916 0.595100
H -3.722371 2.289038 -1.166018
O 6.743701 3.211680 -1.290209
H 7.189726 4.008763 -0.989579
H 6.013092 3.049798 -0.654083
O 5.078217 2.121029 0.595742
H 4.162475 1.822697 0.482580
H 5.643972 1.336167 0.509496
O 7.363436 0.640902 -0.351118
H 7.396167 1.491140 -0.831320
H 7.448100 -0.046841 -1.017451

PhO⁺(H₂O)₄

C -0.829996 -0.549588 -0.271306
C 0.533849 -0.431794 -0.348343
C 1.108450 0.922895 -0.396519
C 0.203504 2.081282 -0.364002
C -1.151959 1.847203 -0.286201
C -1.705528 0.557687 -0.237588
H -1.266659 -1.536206 -0.235372
H -1.822453 2.690222 -0.262338
O 2.345873 1.085998 -0.464975
C 0.773940 3.503191 -0.417052
C 1.693152 3.752017 0.802263
C 1.567794 3.708530 -1.729418
C -0.333021 4.571616 -0.381172
H 1.136071 3.636691 1.735819
H 2.539305 3.070386 0.818257
H 2.078736 4.773890 0.767232
H 0.922762 3.558198 -2.599208

H	1.947800	4.732553	-1.768647
H	2.411136	3.027145	-1.803486
H	0.128049	5.560146	-0.424692
H	-1.014328	4.491960	-1.231799
H	-0.921539	4.527968	0.538446
C	1.452642	-1.659139	-0.385163
C	2.268466	-1.671631	-1.699566
C	2.408519	-1.642728	0.831014
C	0.657560	-2.975386	-0.326227
H	1.604372	-1.708424	-2.567191
H	2.904883	-0.795157	-1.788793
H	2.902685	-2.561447	-1.727125
H	1.843475	-1.653700	1.766779
H	3.040276	-2.534369	0.812440
H	3.053407	-0.768085	0.827495
H	1.356554	-3.813224	-0.359634
H	0.080694	-3.069648	0.597015
H	-0.023682	-3.085638	-1.173497
C	-3.214671	0.312939	-0.156326
C	-3.665478	-0.491262	-1.397471
C	-3.533922	-0.497815	1.120831
C	-4.028578	1.615821	-0.109475
H	-3.457164	0.059697	-2.317257
H	-3.163079	-1.457267	-1.464179
H	-4.741352	-0.677482	-1.350263
H	-3.224517	0.044908	2.016787
H	-4.609834	-0.677419	1.187991
H	-3.034850	-1.467518	1.127335
H	-5.092428	1.377312	-0.049026
H	-3.779292	2.223508	0.763117
H	-3.880153	2.223273	-1.004706
O	6.274853	3.727972	0.222497
H	6.798337	4.307309	-0.338714
H	6.909770	3.297657	0.837722
O	7.946617	2.207406	1.802974
H	7.835434	2.190224	2.757942
H	7.669249	1.318682	1.477325
O	6.926970	-0.079521	0.719987
H	7.457845	-0.634047	0.141054
H	6.238203	0.340902	0.144910
O	5.194389	1.343137	-0.778321
H	4.235158	1.275739	-0.655469
H	5.452282	2.252659	-0.526314

PhO⁺

C	-0.622226	-0.608922	0.005869
C	0.733893	-0.660344	0.012529
C	1.467584	0.666877	0.096973
C	0.677994	1.967531	0.006029
C	-0.679924	1.864272	0.007010
C	-1.357327	0.615342	0.037026
H	-1.185345	-1.527648	-0.022651
H	-1.277651	2.759676	-0.019301
O	2.662505	0.695589	0.269134
C	1.407743	3.289068	-0.052635
C	2.196651	3.505626	1.272992
C	2.395084	3.289828	-1.254112
C	0.438214	4.468848	-0.228705
H	1.526748	3.495394	2.135188
H	2.971475	2.757583	1.415192
H	2.668177	4.488662	1.229168
H	1.870541	3.120933	-2.197195
H	2.866238	4.272074	-1.309946
H	3.176972	2.543184	-1.143333
H	1.014884	5.391569	-0.290678
H	-0.146591	4.389759	-1.148018
H	-0.246264	4.575004	0.615735
C	1.519703	-1.954426	-0.030658

C	2.508874	-1.928234	-1.228258
C	2.308451	-2.130162	1.298576
C	0.596416	-3.171561	-0.201279
H	1.980980	-1.788640	-2.174388
H	3.260988	-1.150358	-1.123748
H	3.020112	-2.890778	-1.275036
H	1.633627	-2.146142	2.157018
H	2.825902	-3.090260	1.264472
H	3.047952	-1.347232	1.443210
H	1.207149	-4.072758	-0.253632
H	-0.087135	-3.297002	0.641479
H	0.013170	-3.121631	-1.123758
C	-2.862809	0.547751	0.076914
C	-3.349810	-0.197409	-1.201767
C	-3.281555	-0.269850	1.334296
C	-3.547593	1.921002	0.134700
H	-3.062778	0.340356	-2.106693
H	-2.970336	-1.216358	-1.267626
H	-4.439150	-0.247851	-1.168749
H	-2.943908	0.214874	2.251742
H	-4.370966	-0.319768	1.358889
H	-2.901732	-1.290716	1.321496
H	-4.627280	1.776792	0.176055
H	-3.263537	2.487587	1.023644
H	-3.338987	2.526260	-0.749524

PhO⁺(H₂O)

C	-0.720130	-0.608656	0.090071
C	0.632679	-0.655612	0.193975
C	1.351303	0.673179	0.354666
C	0.567966	1.970726	0.191550
C	-0.786700	1.862937	0.091643
C	-1.459093	0.612374	0.067524
H	-1.276240	-1.529107	0.016201
H	-1.383090	2.756784	0.020146
O	2.518193	0.704724	0.660609
C	1.296360	3.292616	0.167879
C	2.025911	3.523179	1.524371
C	2.332810	3.280110	-0.991834
C	0.335135	4.470568	-0.058672
H	1.320546	3.503201	2.357854
H	2.805236	2.788103	1.700437
H	2.481704	4.514228	1.497786
H	1.835051	3.157570	-1.956719
H	2.839926	4.246452	-1.003728
H	3.082598	2.500008	-0.883961
H	0.914133	5.393049	-0.100690
H	-0.206800	4.386031	-1.003334
H	-0.387703	4.581452	0.752897
C	1.425411	-1.944820	0.180592
C	2.464391	-1.892506	-0.973296
C	2.154220	-2.136888	1.541163
C	0.518540	-3.165446	-0.045724
H	1.966706	-1.793768	-1.941036
H	3.179128	-1.079903	-0.865138
H	3.014697	-2.834988	-0.981346
H	1.442116	-2.152755	2.369162
H	2.662810	-3.102150	1.521778
H	2.892773	-1.361977	1.723885
H	1.137518	-4.061958	-0.080888
H	-0.202672	-3.305134	0.763024
H	-0.021746	-3.108924	-0.993587
C	-2.963801	0.538739	-0.017752
C	-3.336353	-0.193531	-1.341174
C	-3.485657	-0.292032	1.189820
C	-3.656153	1.909469	-0.004645
H	-2.973515	0.354347	-2.212251
H	-2.947727	-1.210293	-1.384375

Appendix A

H	-4.424225	-0.247980	-1.403649
H	-3.235424	0.187731	2.137459
H	-4.572500	-0.352309	1.117879
H	-3.096380	-1.309401	1.203762
H	-4.735386	1.761743	-0.047352
H	-3.443411	2.471196	0.907071
H	-3.382149	2.521391	-0.866131
O	4.849372	0.789468	-1.619878
H	5.617690	0.797243	-1.038488
H	5.211671	0.791923	-2.512645

PhO⁺(H₂O)₂

C	-0.519609	-0.560580	0.080241
C	0.778381	-0.542518	0.476668
C	1.373539	0.814611	0.804408
C	0.571852	2.073761	0.503095
C	-0.721360	1.900515	0.109102
C	-1.298686	0.621409	-0.085906
H	-0.996719	-1.506013	-0.121366
H	-1.338233	2.764455	-0.070502
O	2.433116	0.895305	1.377742
C	1.183101	3.435131	0.741840
C	1.403555	3.611885	2.275524
C	2.540182	3.576650	0.004229
C	0.258989	4.566844	0.261007
H	0.466063	3.504069	2.825013
H	2.128481	2.902455	2.665675
H	1.777716	4.622374	2.449102
H	2.410499	3.446158	-1.070249
H	2.923970	4.581687	0.185747
H	3.275989	2.859855	0.358226
H	0.760159	5.521597	0.420984
H	0.037238	4.488551	-0.805674
H	-0.681798	4.604174	0.814285
C	1.598556	-1.799315	0.689400
C	2.953546	-1.707886	-0.057586
C	1.853983	-1.975874	2.214732
C	0.859849	-3.049534	0.183131
H	2.796810	-1.561773	-1.126747
H	3.572943	-0.898349	0.319519
H	3.490985	-2.646594	0.086295
H	0.914232	-2.039085	2.767454
H	2.393540	-2.912556	2.365498
H	2.451531	-1.164871	2.623050
H	1.502758	-3.918763	0.322609
H	-0.062258	-3.244112	0.735172
H	0.625069	-2.984272	-0.881808
C	-2.748285	0.473886	-0.490994
C	-2.805143	-0.269422	-1.855588
C	-3.470306	-0.381630	0.588747
C	-3.493265	1.809391	-0.631944
H	-2.300980	0.301484	-2.637258
H	-2.362744	-1.264108	-1.813523
H	-3.851918	-0.381899	-2.142376
H	-3.437123	0.103956	1.565487
H	-4.516971	-0.487476	0.299467
H	-3.048924	-1.381429	0.685569
H	-4.527616	1.610023	-0.912674
H	-3.515243	2.370871	0.303989
H	-3.064641	2.442919	-1.410811
O	1.881801	0.927107	-2.069199
H	2.827275	1.030322	-2.287544
H	1.444902	0.770510	-2.912256
O	4.615635	1.229290	-2.718517
H	5.266533	0.523229	-2.791875
H	5.020035	2.008680	-3.114334

PhO⁺(H₂O)₃

C	-0.374969	-0.354350	0.109341
C	0.638598	-0.324394	1.010783
C	1.042684	1.038558	1.540854
C	0.435331	2.289394	0.921790
C	-0.570691	2.105588	0.021818
C	-1.004836	0.821669	-0.391166
H	-0.721528	-1.303730	-0.265354
H	-1.055461	2.964046	-0.410253
O	1.769865	1.130619	2.500716
C	0.883434	3.656981	1.386869
C	0.439023	3.840431	2.869789
C	2.423625	3.807427	1.286221
C	0.238982	4.780220	0.556864
H	-0.642862	3.734719	2.974052
H	0.931328	3.132356	3.531128
H	0.707362	4.851406	3.181916
H	2.759233	3.665354	0.258686
H	2.691420	4.817986	1.598281
H	2.945435	3.102949	1.928245
H	0.620807	5.739439	0.906932
H	0.484157	4.697255	-0.504293
H	-0.847262	4.810362	0.665308
C	1.306658	-1.572673	1.552344
C	2.846961	-1.475243	1.408437
C	0.930989	-1.735175	3.053846
C	0.837437	-2.833425	0.807169
H	3.130518	-1.345708	0.363377
H	3.259291	-0.654287	1.989499
H	3.288626	-2.405112	1.770439
H	-0.151300	-1.800739	3.185038
H	1.367756	-2.666850	3.417953
H	1.311980	-0.916985	3.659341
H	1.368453	-3.697474	1.207102
H	-0.229530	-3.024612	0.941135
H	1.054308	-2.782061	-0.262245
C	-2.131403	0.661637	-1.385821
C	-1.591514	-0.124751	-2.614880
C	-3.265846	-0.157092	-0.707280
C	-2.717927	1.992737	-1.878981
H	-0.745822	0.389420	-3.074301
H	-1.280452	-1.137140	-2.358700
H	-2.395050	-0.200067	-3.349528
H	-3.671879	0.370137	0.157755
H	-4.071808	-0.292252	-1.430318
H	-2.936891	-1.144730	-0.385946
H	-3.527046	1.785469	-2.579739
H	-3.140667	2.586802	-1.066344
H	-1.978699	2.597138	-2.408046
O	1.803301	1.118590	-3.569231
H	2.109142	0.393547	-4.149240
H	1.946927	1.929627	-4.067984
O	2.678846	-0.962560	-5.227242
H	2.202412	-1.295828	-5.995140
H	3.596592	-1.231349	-5.342389
O	2.563161	1.134404	-0.884923
H	2.344750	1.120364	-1.839860
H	3.522069	1.192593	-0.831375

PhO⁺(H₂O)₄

C	-0.347978	-0.693202	0.058643
C	0.605719	-0.598972	1.018392
C	1.094648	0.794747	1.372739
C	0.489236	1.999935	0.667451
C	-0.446551	1.752760	-0.287220
C	-0.881862	0.440832	-0.622904
H	-0.723234	-1.662776	-0.221656

H	-0.886412	2.577963	-0.820461
O	1.933802	0.948053	2.228226
C	0.906209	3.397523	1.072427
C	0.552679	3.614628	2.572172
C	2.432548	3.594121	0.860878
C	0.173326	4.470710	0.250741
H	-0.513398	3.460758	2.754005
H	1.122435	2.958683	3.225173
H	0.786886	4.648051	2.832760
H	2.691903	3.469665	-0.190888
H	2.688611	4.613426	1.155149
H	3.020206	2.906408	1.462886
H	0.509619	5.454423	0.579262
H	0.391701	4.391080	-0.816026
H	-0.909035	4.436027	0.395434
C	1.161104	-1.802896	1.754763
C	2.697198	-1.896114	1.553736
C	0.839310	-1.671397	3.269992
C	0.537596	-3.114329	1.248992
H	2.944233	-1.995832	0.495209
H	3.215160	-1.031865	1.960934
H	3.059639	-2.787716	2.068020
H	-0.236478	-1.586474	3.438835
H	1.183607	-2.574944	3.775821
H	1.336447	-0.816368	3.720693
H	0.971937	-3.947547	1.801818
H	-0.542245	-3.149390	1.409249
H	0.740344	-3.285936	0.189446
C	-1.976797	0.241235	-1.636654
C	-1.813383	-1.074072	-2.432308
C	-3.284968	0.152568	-0.775880
C	-2.114834	1.409723	-2.631210
H	-0.836858	-1.128210	-2.915077
H	-1.947420	-1.962968	-1.815900
H	-2.582084	-1.107875	-3.204803
H	-3.464551	1.072536	-0.218216
H	-4.118715	-0.000823	-1.463863
H	-3.257698	-0.684192	-0.077231
H	-2.902247	1.166017	-3.344960
H	-2.407384	2.343512	-2.149999
H	-1.192648	1.571178	-3.192559
O	2.661726	2.724589	-2.690793
H	2.109160	2.395014	-3.434678
H	3.348937	3.276150	-3.078308
O	1.043824	1.401102	-4.457161
H	1.272769	0.473508	-4.235046
H	1.006346	1.466050	-5.416642
O	2.977939	0.435309	-1.246612
H	2.998503	1.301544	-1.718721
H	3.873104	0.279829	-0.927109
O	1.721541	-0.996506	-3.268606
H	2.271332	-0.643491	-2.536665
H	2.214569	-1.721491	-3.666144

A.7 Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of Hydroquinone

Table A.8. Gas-phase energies of the hydrogen-bonded complexes of hydroquinone and its oxidized forms.

No. of H ₂ O molecules (<i>n</i>)	Energy (hartrees)			
	QH ₂ (H ₂ O) _{<i>n</i>}	QH ₂ ⁺⁺ (H ₂ O) _{<i>n</i>}	QH [•] (H ₂ O) _{<i>n</i>}	QH ⁺ (H ₂ O) _{<i>n</i>}
0	-382.817	-382.560	-382.193	-381.899
1	-459.293	-459.036	-458.668	-458.411
2	-535.768	-535.548	-535.143	-534.886
3	-612.280	-612.023	-611.619	-611.398
4	-688.755	-688.498	-688.094	-687.873

Figure A.25. Optimized geometries for QH₂(H₂O)_{*n*} for hydroquinone (*n* = 1 to 4).

Figure A.26. Optimized geometries for QH₂⁺⁺(H₂O)_{*n*} for hydroquinone (*n* = 1 to 4).

Figure A.27. Optimized geometries for $\text{QH}^-(\text{H}_2\text{O})_n$ for hydroquinone ($n = 1$ to 4).

Figure A.28. Optimized geometries for $\text{QH}^+(\text{H}_2\text{O})_n$ for hydroquinone ($n = 1$ to 4).

Cartesian Coordinates of Hydrogen-Bonded Complexes of Hydroquinone

QH ₂							
C	-0.617183	0.074865	0.093753	C	-0.567437	2.530352	0.799658
C	0.765589	0.074621	-0.072441	C	-1.307522	1.551608	0.143692
C	1.459638	1.274851	-0.154818	H	-1.216461	-0.245723	-1.032849
C	0.762623	2.477480	-0.070109	H	1.253027	-0.331444	-1.049851
C	-0.612899	2.477722	0.095263	H	1.397636	3.232025	1.309371
C	-1.310577	1.275341	0.178050	H	-1.088026	3.328871	1.312977
H	-1.149109	-0.868929	0.156946	O	2.852172	1.435927	0.153446
H	1.297001	-0.869361	-0.137149	H	3.213920	0.631357	-0.289037
H	1.311250	3.408506	-0.135420	O	-2.675688	1.654959	0.184018
H	-1.161022	3.408940	0.162069	H	-3.071276	0.926381	-0.305186
O	2.820046	1.340705	-0.318423	O	4.061022	-0.562030	-1.225983
H	3.187697	0.452243	-0.364674	H	4.714332	-0.034283	-1.742400
O	-2.670944	1.341679	0.341764	H	4.558611	-1.255502	-0.782413
H	-3.039087	0.453349	0.386618	O	5.749241	1.205151	-2.432313
QH ₂ (H ₂ O)				H	5.702099	1.408033	-3.371261
C	-0.373662	0.203132	-0.198287	H	5.466990	2.018111	-1.956157
C	0.948463	0.560420	-0.451107	O	4.677561	3.235630	-0.928710
C	1.362131	1.878859	-0.283183	H	5.171942	3.695470	-0.243763
C	0.437226	2.832763	0.139850	H	3.965375	2.741321	-0.472113
C	-0.878341	2.475918	0.391107	QH ₂ (H ₂ O) ₄			
C	-1.290648	1.157348	0.223047	C	-0.284705	0.558675	-0.938979
H	-0.684591	-0.828441	-0.332630	C	1.060845	0.435820	-0.605939
H	1.658132	-0.190137	-0.779776	C	1.711385	1.475305	0.050125
H	0.764556	3.856941	0.268540	C	1.008127	2.634179	0.367368
H	-1.598600	3.214633	0.719789	C	-0.331308	2.757323	0.029829
O	2.642294	2.290226	-0.514657	C	-0.984551	1.718010	-0.625331
H	3.197004	1.545087	-0.800171	H	-0.785592	-0.258062	-1.449244
O	-2.607089	0.862143	0.487422	H	1.605227	-0.466371	-0.857461
H	-2.764533	-0.075278	0.336411	H	1.516730	3.435976	0.888740
O	4.412176	0.200680	-1.359179	H	-0.884000	3.655366	0.275146
H	4.804589	0.322535	-2.230432	O	3.038196	1.405456	0.398111
H	5.145136	0.023101	-0.759872	H	3.412309	0.508872	0.210970
QH ₂ (H ₂ O) ₂				O	-2.310054	1.894339	-0.932552
C	-0.468507	0.325458	-0.328235	H	-2.650166	1.108538	-1.372554
C	0.920871	0.241891	-0.334210	O	4.253565	-0.888345	-0.309231
C	1.686752	1.360774	-0.026647	H	5.035078	-0.544838	-0.810679
C	1.053667	2.561616	0.283858	H	4.581665	-1.559949	0.295809
C	-0.330238	2.644651	0.285732	O	6.271178	0.371793	-1.599831
C	-1.098482	1.525115	-0.020130	H	5.955861	0.691030	-2.465830
H	-1.058193	-0.553686	-0.568211	H	6.317410	1.189607	-1.083516
H	1.406762	-0.694810	-0.582024	O	4.984064	2.960940	-0.792692
H	1.656678	3.427212	0.529069	H	5.120919	3.816238	-0.374791
H	-0.828573	3.574919	0.527490	H	4.248298	2.521353	-0.312026
O	3.057584	1.334143	-0.019018	O	5.114888	2.130263	-3.491969
H	3.395908	0.433137	-0.198878	H	4.289435	2.089694	-3.983577
O	-2.463569	1.666550	-0.000768	H	4.925285	2.621445	-2.671817
H	-2.881017	0.828371	-0.224068	QH ₂ ⁺⁺			
O	4.458252	-0.806734	-1.057528	C	-0.602468	0.032592	0.092779
H	4.882844	-0.103815	-1.586248	C	0.750957	0.032313	-0.069868
H	5.166793	-1.288212	-0.619905	C	1.447667	1.269440	-0.153421
O	5.051232	1.736788	-2.026001	C	0.749662	2.506911	-0.069454
H	4.854668	2.147655	-2.873225	C	-0.600052	2.507191	0.092643
H	4.332755	1.991809	-1.421346	C	-1.298616	1.270013	0.176468
QH ₂ (H ₂ O) ₃				H	-1.150510	-0.900229	0.158626
C	-0.648131	0.522016	-0.517175	H	1.298609	-0.900729	-0.135849
C	0.742377	0.468382	-0.526996	H	1.318622	3.425002	-0.137811
C	1.480046	1.446026	0.131375	H	-1.168634	3.425507	0.161117
C	0.818085	2.475532	0.794653	O	2.752016	1.344895	-0.310493
				H	3.190122	0.480835	-0.363796
				O	-2.602930	1.346066	0.333569
				H	-3.041425	0.482205	0.386920

QH ₂ ⁺⁺ (H ₂ O)				QH ₂ ⁺⁺ (H ₂ O) ₄			
C	-0.563604	0.116272	0.050694	C	0.107110	-0.349352	0.555619
C	0.774779	0.254843	-0.168072	C	1.357538	0.014258	0.158669
C	1.354548	1.559374	-0.198707	C	1.610747	1.361110	-0.234800
C	0.537147	2.712247	-0.001931	C	0.554652	2.318420	-0.213556
C	-0.797207	2.569804	0.216047	C	-0.695705	1.954892	0.183794
C	-1.369000	1.269308	0.245893	C	-0.948295	0.608649	0.579773
H	-1.019182	-0.867170	0.076925	H	-0.120031	-1.362191	0.862142
H	1.409563	-0.609159	-0.319792	H	2.170739	-0.700034	0.135116
H	1.010304	3.685069	-0.031768	H	0.781881	3.331372	-0.519654
H	-1.446435	3.421976	0.369402	H	-1.509003	2.669114	0.206726
O	2.625624	1.760675	-0.401916	O	2.786074	1.775180	-0.622103
H	3.173063	0.927625	-0.535351	H	3.508932	1.060554	-0.612343
O	-2.669755	1.204674	0.462065	O	-2.121845	0.196046	0.973830
H	-3.012113	0.297975	0.472838	H	-4.291030	2.294255	1.853639
O	4.075516	-0.391632	-0.750337	O	4.618031	-0.029967	-0.587421
H	4.486038	-0.551839	-1.609515	H	5.024633	-0.311004	-1.438483
H	4.735014	-0.627540	-0.085664	H	5.334875	0.062311	0.049574
QH ₂ ⁺⁺ (H ₂ O) ₂				O	-6.032196	1.739995	-0.714520
C	-0.670055	0.672138	-0.155137	H	-6.655893	1.006449	-0.742641
C	0.680246	0.526769	-0.275350	H	-6.412530	2.447302	-1.246420
C	1.535356	1.649135	-0.074679	O	5.694145	-0.813212	-2.957202
C	0.982938	2.921282	0.251129	H	5.870878	-1.724880	-3.213126
C	-0.363441	3.066261	0.370864	H	6.165500	-0.253491	-3.583635
C	-1.220309	1.945815	0.170604	O	-3.941651	2.012843	1.001054
H	-1.337515	-0.167686	-0.303396	H	-2.840992	0.914650	0.981722
H	1.118947	-0.432105	-0.522090	H	-4.709853	1.918594	0.393098
H	1.662169	3.751127	0.396546	QH ⁺			
H	-0.816044	4.017960	0.616937	C	-0.561746	-0.040043	-0.034164
O	2.836993	1.574054	-0.176294	C	0.802265	0.020679	-0.128739
H	3.185570	0.665330	-0.406948	C	1.452133	1.268800	-0.134923
O	-2.505694	2.149080	0.299972	C	0.715139	2.465543	-0.044853
H	-3.072891	1.338613	0.152176	C	-0.646800	2.420289	0.049967
O	3.796856	-0.810103	-0.785186	C	-1.365019	1.161486	0.060784
H	4.233913	-0.937247	-1.636397	H	-1.085870	-0.987370	-0.027262
H	4.332252	-1.279151	-0.133197	H	1.392916	-0.887943	-0.199527
O	-4.037934	0.031008	-0.079463	H	1.255740	3.404026	-0.053223
H	-4.634514	0.011277	-0.838025	H	-1.237379	3.325040	0.120496
H	-4.536630	-0.324531	0.666617	O	2.796499	1.381882	-0.226439
QH ₂ ⁺⁺ (H ₂ O) ₃				H	3.207401	0.510998	-0.283511
C	-0.684573	0.671709	-0.097954	O	-2.610851	1.112708	0.147016
C	0.665577	0.497305	-0.171381	QH ⁺ (H ₂ O)			
C	1.538051	1.614916	-0.006317	C	-0.346885	-0.007354	-0.095947
C	0.994942	2.912100	0.232005	C	0.961218	0.393394	-0.096069
C	-0.351647	3.084168	0.304771	C	1.279493	1.766420	-0.023632
C	-1.221019	1.968604	0.142352	C	0.253291	2.732212	0.049442
H	-1.362553	-0.163996	-0.219842	C	-1.056127	2.344635	0.050479
H	1.096261	-0.479217	-0.353699	C	-1.433846	0.947247	-0.023009
H	1.683437	3.738324	0.352090	H	-0.614882	-1.055304	-0.151093
H	-0.794612	4.054863	0.485618	H	1.766906	-0.330466	-0.151429
O	2.834914	1.508988	-0.062135	H	0.537814	3.776156	0.104244
H	3.181398	0.563385	-0.226436	H	-1.859049	3.069271	0.106129
O	-2.508147	2.199250	0.224723	O	2.546334	2.212075	-0.020119
H	-3.080265	1.390428	0.107137	H	3.189923	1.478269	-0.072918
O	3.712456	-0.862469	-0.469915	O	-2.630404	0.584484	-0.022297
H	4.214974	-1.030121	-1.300765	O	4.487778	0.203497	-0.170777
H	4.200692	-1.287916	0.243691	H	5.049242	0.169583	-0.952945
O	-4.068918	0.075293	-0.078270	H	5.070339	0.074082	0.585562
H	-4.649917	0.024315	-0.847139	QH ⁺ (H ₂ O) ₂			
H	-4.588134	-0.233812	0.674220	C	-0.416524	0.302961	-1.042430
O	5.060205	-1.292666	-2.782064	C	0.919798	0.593954	-1.013429
H	4.980566	-2.077652	-3.334773	C	1.439204	1.420793	0.004528
H	5.853535	-0.829535	-3.072357				

Appendix A

C	0.589955	1.951707	0.996911
C	-0.746283	1.667899	0.979796
C	-1.328719	0.823636	-0.044428
H	-0.838213	-0.330493	-1.812984
H	1.595526	0.192930	-1.760986
H	1.024669	2.587926	1.758823
H	-1.417745	2.066490	1.730163
O	2.747154	1.731763	0.071600
H	3.262400	1.340956	-0.674366
O	-2.550017	0.558752	-0.065649
O	4.547714	0.529252	-1.533744
H	5.098692	0.963699	-2.192215
H	5.097578	0.409157	-0.735558
O	5.321874	0.656962	1.122209
H	5.460851	-0.010270	1.801538
H	4.469167	1.073161	1.314965

QH⁺(H₂O)₃

C	-0.243280	0.196954	-1.046378
C	1.062178	0.603143	-1.088056
C	1.579230	1.417397	-0.058323
C	0.758192	1.819202	1.015250
C	-0.547008	1.418688	1.069164
C	-1.124776	0.580216	0.037728
H	-0.662409	-0.429899	-1.823739
H	1.716792	0.305322	-1.899193
H	1.186042	2.455007	1.781688
H	-1.196567	1.717750	1.882441
O	2.858912	1.836645	-0.059149
H	3.356198	1.547786	-0.874149
O	-2.317318	0.208554	0.081040
O	4.387454	1.017267	-2.061489
H	4.678505	1.633755	-2.740616
H	5.199377	0.704035	-1.594414
O	5.100363	1.428227	1.677297
H	4.939959	1.154675	2.584939
H	4.233346	1.634463	1.285754
O	6.452605	0.315474	-0.463046
H	6.751360	-0.589284	-0.333152
H	6.111954	0.630986	0.400154

QH⁺(H₂O)₄

C	0.119415	1.782691	-1.410392
C	1.321076	1.142352	-1.279580
C	1.758101	0.720221	-0.006283
C	0.966662	0.957864	1.136017
C	-0.235113	1.597173	1.018161
C	-0.730454	2.046990	-0.267379
H	-0.237389	2.116634	-2.376895
H	1.953169	0.953860	-2.139478
H	1.334464	0.623140	2.098899
H	-0.859219	1.789544	1.881987
O	2.930947	0.079653	0.163769
H	3.434775	-0.045222	-0.691537
O	-1.829368	2.631326	-0.383445
O	4.371980	-0.220641	-2.013392
H	5.282863	0.154117	-1.896881
H	4.480401	-1.092830	-2.404600
O	4.807090	0.095322	2.270517
H	4.789774	-0.761349	2.708040
H	4.090970	0.079820	1.607659
O	7.157374	0.934296	1.122870
H	7.491759	1.691412	1.611949
H	6.338821	0.643844	1.582786
O	6.820433	0.766444	-1.575539
H	7.116668	1.569052	-2.014085
H	7.008682	0.877537	-0.614344

QH⁺

C	-0.543217	-0.085386	-0.027841
C	0.795355	-0.025274	-0.124329
C	1.434619	1.264595	-0.137325
C	0.705476	2.501667	-0.051472
C	-0.633796	2.462956	0.045483
C	-1.356348	1.161934	0.064179
H	-1.088206	-1.021976	-0.012365
H	1.408634	-0.917825	-0.192580
H	1.274007	3.423367	-0.068947
H	-1.241590	3.357444	0.113328
O	2.718379	1.383520	-0.227902
H	3.201711	0.540163	-0.285361
O	-2.560595	1.110911	0.150755

QH⁺(H₂O)

C	-0.811653	0.053172	-0.040505
C	0.524006	0.166591	-0.087048
C	1.121739	1.485092	-0.042758
C	0.321602	2.686176	0.050094
C	-1.014830	2.588158	0.097485
C	-1.681215	1.259321	0.055301
H	-1.318211	-0.904207	-0.069870
H	1.178612	-0.693970	-0.157031
H	0.848196	3.632063	0.078076
H	-1.663226	3.453259	0.167325
O	2.386590	1.650658	-0.083292
H	4.373302	-0.586315	-1.050901
O	-2.885474	1.155720	0.097762
O	3.862223	-0.427774	-0.246221
H	4.430322	-0.670657	0.496813
H	2.964184	0.804340	-0.148604

QH⁺(H₂O)₂

C	-1.083958	0.703608	-1.070828
C	0.232661	0.548984	-0.874506
C	0.922288	1.425663	0.056914
C	0.214474	2.466066	0.779401
C	-1.101865	2.629856	0.591919
C	-1.850798	1.757034	-0.349894
H	-1.649870	0.080243	-1.752759
H	0.812288	-0.209732	-1.386100
H	0.797239	3.079723	1.455083
H	-1.676268	3.391009	1.105977
O	2.165440	1.319423	0.277182
H	4.100722	-0.130970	-1.535558
O	-3.040169	1.893227	-0.527022
O	3.427954	-0.424700	-0.909544
H	3.812567	-1.168202	-0.370740
H	2.711689	0.550675	-0.250594
O	4.378440	-2.417228	0.545479
H	5.048919	-2.358679	1.235531
H	4.315937	-3.345893	0.294534

QH⁺(H₂O)₃

C	-1.331087	0.807693	-1.044206
C	-0.024037	0.542076	-0.948820
C	0.822772	1.298057	-0.019237
C	0.220393	2.349878	0.804991
C	-1.085940	2.621993	0.715870
C	-1.962628	1.870185	-0.217128
H	-1.989907	0.272820	-1.717786
H	0.451845	-0.228160	-1.544572
H	0.886956	2.878993	1.474957
H	-1.565439	3.391314	1.309081

O	2.038740	1.070072	0.087749
H	4.220662	-0.130043	-1.610144
O	-3.147593	2.109439	-0.304862
O	3.511891	-0.576738	-1.052144
H	3.902257	-1.244942	-0.408140
H	2.855462	0.105779	-0.592383
O	4.463497	-2.345831	0.577036
H	4.971219	-2.204862	1.383919
H	4.402911	-3.297256	0.434744
O	5.302925	0.544525	-2.544827
H	5.914213	1.253513	-2.316002
H	5.448506	0.323629	-3.471723

 $\text{QH}^+(\text{H}_2\text{O})_4$

C	-1.880480	1.511692	-0.937300
C	-0.661130	0.975813	-0.821768
C	0.322327	1.550913	0.105251
C	-0.052827	2.721807	0.906366
C	-1.270239	3.263506	0.796065
C	-2.278292	2.699495	-0.136255
H	-2.632650	1.116426	-1.609508
H	-0.354958	0.110116	-1.397647
H	0.704947	3.109404	1.576240
H	-1.580561	4.127987	1.370580
O	1.458922	1.073040	0.227059
H	3.452604	-0.560487	-1.373155
O	-3.384064	3.185129	-0.243691
O	2.620078	-0.864870	-0.878212
H	2.935798	-1.545321	-0.194160
H	2.112277	-0.072743	-0.439681
O	6.408210	-2.020667	-0.183827
H	6.960398	-1.549696	0.454685
H	6.964487	-2.728060	-0.535744
O	4.892484	-0.274896	-1.909753
H	5.138279	-0.089935	-2.822293
H	5.589794	-0.819033	-1.503969
O	3.722608	-2.506541	0.754719
H	4.677124	-2.562634	0.574086
H	3.421013	-3.359694	1.084145

A.8 Gas-Phase Geometries, Energies and Coordinates of the Hydrogen-Bonded Complexes of 2,3,5,6-Tetramethyl-1,4-phenylenediamine

Table A.9. Gas-phase energies of the hydrogen-bonded complexes of 2,3,5,6-tetramethyl-1,4-phenylenediamine and its oxidized forms.

No. of H ₂ O molecules (<i>n</i>)	Energy (hartrees)		
	P (H ₂ O) _{<i>n</i>}	P ⁺ (H ₂ O) _{<i>n</i>}	P ²⁺ (H ₂ O) _{<i>n</i>}
0	-500.141	-499.918	-499.514
1	-576.587	-576.371	-575.982
2	-653.035	-652.823	-652.448
3	-729.488	-729.274	-728.911
4	-805.939	-805.725	-805.372

Figure A.29. Optimized geometries for P (H₂O)_{*n*} for 2,3,5,6-tetramethyl-1,4-phenylenediamine (*n* = 1 to 4).

Figure A.30. Optimized geometries for P⁺(H₂O)_{*n*} for 2,3,5,6-tetramethyl-1,4-phenylenediamine (*n* = 1 to 4).

Figure A.31. Optimized geometries for $P^{2+}(H_2O)_n$ for 2,3,5,6-tetramethyl-1,4-phenylenediamine ($n = 1$ to 4).

Cartesian Coordinates of Hydrogen-Bonded Complexes of 2,3,5,6-Tetramethyl-1,4-phenylenediamine

P				P(H ₂ O) ₂			
C	-1.06228300	-0.36119300	-0.01657900	C	-1.02218100	-0.41334700	-0.42564700
C	0.34109800	-0.37684400	0.00266000	C	0.37327700	-0.40499500	-0.27156500
C	1.04197000	0.83581200	-0.00016000	C	1.03747800	0.81165300	-0.06739900
C	0.32764300	2.04401700	0.01552600	C	0.28655300	1.99265600	0.01599100
C	-1.07574400	2.05967500	-0.00368900	C	-1.10784800	1.98664500	-0.13461800
C	-1.77661300	0.84702600	-0.00090000	C	-1.77174000	0.77021200	-0.33643800
N	-1.76899800	-1.58321800	0.01789200	N	-1.68986900	-1.64118300	-0.60395700
N	1.03437000	3.26605900	-0.01896800	N	0.95118500	3.24105000	0.19818000
H	-1.26551500	-2.37001600	-0.36276200	H	-1.13155700	-2.37186900	-1.01770600
H	-2.69865300	-1.54133400	-0.37137300	H	-2.58568700	-1.57501400	-1.06214900
H	1.96397200	3.22416100	0.37043100	H	1.86640700	3.17241000	0.63073600
H	0.53086100	4.05282800	0.36171400	H	0.39992800	3.90577300	0.72593900
C	-3.28385400	0.77065100	0.03988300	C	-3.27384200	0.66293400	-0.44219700
C	-1.76233800	3.40365800	-0.04744600	C	-1.83357300	3.31050900	-0.08264500
C	2.54921000	0.91220200	-0.04099800	C	2.54000400	0.89894100	0.06838400
C	1.02769000	-1.72082400	0.04649000	C	1.09245700	-1.73212100	-0.30572900
H	-3.75146200	1.72799800	0.25192400	H	-3.78417600	1.57967800	-0.16075700
H	-3.70355300	0.41222500	-0.90888800	H	-3.59892400	0.41429000	-1.46062400
H	-3.61312500	0.07683000	0.81906900	H	-3.65098100	-0.12489300	0.21663100
H	-1.32757500	4.03344300	-0.82938500	H	-1.31867900	4.06027100	-0.68901700
H	-2.82568400	3.32984000	-0.25677600	H	-2.85122500	3.24737800	-0.45784600
H	-1.65912900	3.94878600	0.89958700	H	-1.89223500	3.70846500	0.93839900
H	2.87839100	1.60603900	-0.82021700	H	2.94639500	1.75003600	-0.48092100
H	2.96894700	1.27066400	0.90774400	H	2.84985500	1.02545600	1.11224600
H	3.01682500	-0.04513400	-0.25304400	H	3.04324200	0.01400100	-0.31213000
H	2.09099400	-1.64700500	0.25604100	H	2.12188900	-1.66279900	0.03355500
H	0.59276200	-2.35063600	0.82832000	H	0.59259300	-2.45736100	0.34313600
H	0.92468000	-2.26592700	-0.90057800	H	1.11422800	-2.16366400	-1.31476700
P(H ₂ O)				H	1.57463100	4.26277000	-1.27783200
C	-0.95420000	-0.34000700	-0.56391500	O	2.13159300	4.87876900	-1.80983400
C	0.40214500	-0.34414400	-0.19954400	H	2.19690900	4.49813200	-2.69069300
C	0.99253000	0.84093800	0.25790900	O	3.88393000	4.33204800	0.31104400
C	0.20485600	1.99405200	0.37868600	H	4.44009300	5.02982200	0.66764200
C	-1.14865000	2.00252000	0.01438000	H	3.48523900	4.68644300	-0.50589200
C	-1.73974800	0.81785100	-0.44305800	P(H ₂ O) ₃			
N	-1.55545800	-1.53825100	-0.99433800	C	-1.08421000	-0.34308700	-0.36419500
N	0.81379100	3.20764100	0.81128800	C	0.29053100	-0.42507200	-0.09423500
H	-0.92417200	-2.20932200	-1.40386100	C	1.01998000	0.74969500	0.13130900
H	-2.37534400	-1.42158100	-1.56950000	C	0.35171800	1.98197200	0.12610200
H	1.60783400	3.06260300	1.42037000	C	-1.02290900	2.06607000	-0.14320600
H	0.16707300	3.84240900	1.26002300	C	-1.75190000	0.89207000	-0.37165500
C	-3.20298300	0.71322400	-0.79885800	N	-1.82074000	-1.52761100	-0.56433600
C	-1.90434100	3.30565800	0.12654300	N	1.09017200	3.18436900	0.33325900
C	2.45526100	0.94117800	0.62219100	H	-1.28338700	-2.30835300	-0.90865500
C	1.15255100	-1.64956000	-0.30369700	H	-2.66786900	-1.41530900	-1.09965100
H	-3.77432700	1.59046300	-0.50983600	H	1.91817100	3.08863500	0.91792900
H	-3.35421300	0.57366300	-1.87684400	H	0.52347800	3.92201500	0.73177700
H	-3.66094900	-0.14417100	-0.29662700	C	-3.24367900	0.88231000	-0.60399600
H	-1.34698300	4.12227700	-0.34077300	C	-1.65619800	3.43737300	-0.18558100
H	-2.87597300	3.27313000	-0.35752700	C	2.51100100	0.73696800	0.37619100
H	-2.07793800	3.58941800	1.17221000	C	0.91685100	-1.79744300	-0.03177400
H	2.91985600	1.80507300	0.13855400	H	-3.71204900	1.83912700	-0.39220300
H	2.60050900	1.05931000	1.70341400	H	-3.49759000	0.62297500	-1.63983300
H	3.02662100	0.06833800	0.32031000	H	-3.72875100	0.14312900	0.04040600
H	2.13257200	-1.61449500	0.16299800	H	-1.06209200	4.12416800	-0.79459200
H	0.59621500	-2.45415800	0.18641000	H	-2.65536100	3.42613000	-0.61155300
H	1.30564700	-1.95284000	-1.34719800	H	-1.73858300	3.88225700	0.81394300
H	1.52261400	4.22114300	-0.74482100	H	3.00384100	1.56501600	-0.13653200
O	1.88000900	4.75246900	-1.48227000	H	2.75277000	0.83920000	1.44007700
H	1.70574700	4.23821600	-2.27591900	H	2.98098600	-0.17702300	0.02143500
				H	1.91967300	-1.78358100	0.38546500
				H	0.32039700	-2.46462600	0.59751200

H	0.98628500	-2.26530400	-1.02229000
H	1.80004900	3.92125300	-1.18485900
O	2.27340000	4.39149700	-1.92126300
H	2.28761700	3.78681700	-2.66908300
O	4.52035900	5.20353200	-0.58201200
H	4.59861200	6.15986000	-0.64576900
H	3.77276800	4.95111900	-1.17002800
O	3.62090000	3.99934800	1.75836700
H	4.34845300	3.64489900	2.27663500
H	4.03048600	4.46596000	0.99940200

P(H₂O)₄

C	-0.90473300	-0.39154900	-0.86727200
C	0.47697300	-0.41690600	-0.61718900
C	1.10036800	0.71766700	-0.08221600
C	0.32090100	1.83977700	0.23436800
C	-1.05866800	1.86855500	-0.01684900
C	-1.68179400	0.73574900	-0.55764700
N	-1.53388400	-1.54420100	-1.37780400
N	0.96152200	3.00150000	0.76280300
H	-0.93314200	-2.15687100	-1.90739400
H	-2.39669600	-1.37582200	-1.87168900
H	1.74537300	2.80600300	1.38606700
H	0.31644700	3.59410600	1.26918400
C	-3.16904200	0.65101500	-0.80345400
C	-1.81431700	3.13827700	0.30139000
C	2.58978300	0.79575700	0.15679000
C	1.22226700	-1.69435400	-0.92056100
H	-3.72039500	1.47836700	-0.36619800
H	-3.40902500	0.63724200	-1.87441800
H	-3.57918500	-0.26650700	-0.37087100
H	-1.30585500	4.01303200	-0.11399500
H	-2.82111800	3.14215900	-0.10580100
H	-1.90559000	3.30065900	1.38254200
H	2.99516000	1.73130100	-0.23772500
H	2.83880900	0.78073700	1.22222100
H	3.13376000	-0.01280700	-0.32373500
H	2.23077800	-1.69937400	-0.51795400
H	0.70312200	-2.55492500	-0.48812800
H	1.30551800	-1.87702500	-1.99971400
H	1.62253800	4.07254500	-0.53807200
O	1.99205500	4.68753000	-1.22901400
H	1.90522300	4.23147800	-2.07144400
O	4.39332300	5.75090100	-0.52647800
H	4.28125200	6.70589200	-0.53503100
H	3.52911800	5.37102500	-0.81354100
O	5.26644400	4.56947400	1.77400400
H	6.10548000	4.14977800	1.56302600
H	4.97459700	5.02334300	0.94936100
O	3.24032300	2.98507200	2.76951700
H	3.13600900	3.20122400	3.70022200
H	3.98400000	3.54008200	2.44643000

P⁺⁺

C	-1.05542600	-0.34938100	-0.05808300
C	0.37963400	-0.38361000	-0.02737000
C	1.06706000	0.80578800	0.02945500
C	0.32078000	2.03221900	0.05705000
C	-1.11428100	2.06644700	0.02633400
C	-1.80170600	0.87705200	-0.03048900
N	-1.72788400	-1.51277100	-0.11530600
N	0.99324900	3.19560200	0.11427600
H	-1.24885600	-2.39761000	-0.13727200
H	-2.73366800	-1.53852500	-0.13984500
H	1.99903500	3.22134400	0.13881700
H	0.51423200	4.08044600	0.13624400
C	-3.30292000	0.77284100	-0.06626000

C	-1.77410500	3.41892600	0.05938700
C	2.56827300	0.91002300	0.06522800
C	1.03943800	-1.73609900	-0.06042800
H	-3.79626400	1.73759400	-0.03968800
H	-3.64188800	0.27064000	-0.97799600
H	-3.67911000	0.20337100	0.78961300
H	-1.46537100	4.02987600	-0.79487400
H	-2.85600400	3.36309400	0.02771600
H	-1.51315000	3.96350600	0.97250500
H	2.94445300	1.47950500	-0.79064200
H	2.90723000	1.41223100	0.97696400
H	3.06163800	-0.05471800	0.03865500
H	2.12133700	-1.68029000	-0.02877500
H	0.73070400	-2.34704200	0.79383800
H	0.77845700	-2.28067900	-0.97353900

P⁺⁺(H₂O)

C	-1.07772400	-0.45557600	0.11275100
C	0.34894400	-0.58775000	0.18226100
C	1.12622100	0.52828400	-0.01965600
C	0.48084400	1.78407700	-0.29478200
C	-0.94920000	1.91238700	-0.36331100
C	-1.72467800	0.79433900	-0.16227200
N	-1.83901100	-1.54864700	0.31402800
N	1.24326900	2.86899700	-0.49428400
H	-1.42942100	-2.44616600	0.51064300
H	-2.84335600	-1.50440700	0.27731200
H	2.24687700	2.79904000	-0.45253300
H	0.88280500	3.79859700	-0.69202400
C	-3.22951800	0.79432700	-0.21283000
C	-1.50546900	3.27891400	-0.65391700
C	2.63069800	0.52141700	0.02987300
C	0.90132300	-1.95781500	0.47406000
H	-3.64565700	1.76797300	-0.44413300
H	-3.59850500	0.10496000	-0.97905500
H	-3.65728400	0.48711000	0.74701100
H	-1.15936000	3.64783900	-1.62335100
H	-2.58908700	3.29933300	-0.67097500
H	-1.18107000	4.00372300	0.09742600
H	3.05909700	0.83132500	-0.92871100
H	3.00363500	1.20574400	0.79858700
H	3.04303100	-0.45515200	0.25591900
H	1.98453700	-1.98153300	0.50216500
H	0.55276000	-2.32684400	1.44409600
H	0.59069500	-2.67866800	-0.28903700
H	1.09193000	6.14200100	-1.92540100
O	0.99997600	5.72143400	-1.06326700
H	1.07504600	6.43227500	-0.41698800

P⁺⁺(H₂O)₂

C	-1.11809200	-0.40453300	-0.16233700
C	0.31054200	-0.44073200	-0.05558600
C	0.99132800	0.73500000	0.15933500
C	0.24280900	1.95842300	0.27001400
C	-1.19100100	1.99114700	0.14798900
C	-1.86830000	0.81335100	-0.06245500
N	-1.78288100	-1.55941300	-0.36854000
N	0.89613100	3.10636600	0.49128600
H	-1.29892400	-2.43771500	-0.44498800
H	-2.78495800	-1.58210600	-0.45053700
H	1.90603300	3.19617900	0.62635100
H	0.38158800	3.96907900	0.56369400
C	-3.36516800	0.71281700	-0.19414400
C	-1.86370300	3.33290000	0.26592100
C	2.48680700	0.83034800	0.27727700
C	0.97663300	-1.78481900	-0.19088700
H	-3.86578200	1.66966900	-0.10053000

Appendix A

H	-3.64985200	0.30131900	-1.16788100
H	-3.78540100	0.06183500	0.57922400
H	-1.49180500	4.02882300	-0.49278800
H	-2.93893000	3.28007500	0.13976000
H	-1.68143000	3.78208500	1.24751000
H	2.89845000	1.46933900	-0.50891400
H	2.78340100	1.27614000	1.22952600
H	2.97917500	-0.13263200	0.20264200
H	2.05554200	-1.73254400	-0.10304900
H	0.63010900	-2.47769900	0.58283000
H	0.76026700	-2.23620300	-1.16452300
O	3.55325100	3.96092100	1.02924800
H	4.27402100	4.16986600	0.40348800
H	3.79794400	4.36473700	1.86744400
O	5.58076700	4.50500300	-0.80868000
H	6.46698200	4.12927200	-0.77243900
H	5.65452000	5.32150700	-1.31443000

P⁺(H₂O)₃

C	-1.13176500	-0.34202800	-0.01067400
C	0.28306400	-0.43458100	0.21008500
C	1.00878100	0.72179300	0.37970600
C	0.32471400	1.98455600	0.33594100
C	-1.09442300	2.07556700	0.12120200
C	-1.81776300	0.91934000	-0.05229700
N	-1.84261000	-1.46971000	-0.18354000
N	1.02551600	3.11582400	0.50189200
H	-1.44542600	-2.40340100	-0.17823700
H	-2.83574700	-1.42602600	-0.33894700
H	2.03439100	3.16878300	0.64997900
H	0.55620600	4.00585100	0.47293400
C	-3.30519700	0.88675500	-0.28627500
C	-1.70088400	3.45390200	0.09932700
C	2.49380700	0.75391400	0.61444500
C	0.88335300	-1.81401200	0.24289700
H	-3.75324200	1.87344100	-0.31153900
H	-3.54487500	0.40781400	-1.24111900
H	-3.81733300	0.32768100	0.50352900
H	-1.25774200	4.06815700	-0.69105300
H	-2.77058800	3.44411800	-0.07522500
H	-1.54088600	3.97113200	1.05088800
H	3.00222600	1.34453500	-0.15166800
H	2.72962100	1.21934700	1.57520700
H	2.94310400	-0.23264000	0.61370100
H	1.94880200	-1.80563900	0.44176800
H	0.41553400	-2.42821500	1.01709100
H	0.73468900	-2.33277300	-0.70835400
O	3.72401800	3.94976200	0.90490700
H	4.28821700	4.34354100	0.21197700
H	4.13709100	4.17072800	1.74506000
O	5.30769700	5.06037300	-1.11633400
H	6.13818600	4.68988000	-1.43352100
H	5.31375900	5.99054500	-1.36603300
O	-1.49791600	-4.38446700	-0.33263700
H	-1.44298300	-4.90169000	-1.14361300
H	-1.66681000	-5.01997300	0.37154000

P⁺(H₂O)₄

C	-1.08667000	-0.31501000	-0.01199800
C	0.31060900	-0.55398000	0.20591400
C	1.19085500	0.49717300	0.09613100
C	0.68474800	1.80278800	-0.23253700
C	-0.71726600	2.03773500	-0.45379000
C	-1.59528700	0.98520800	-0.34357700
N	-1.95163600	-1.34100800	0.09411900
N	1.54022200	2.82527400	-0.33755000
H	-1.68377200	-2.29241700	0.31952200

H	-2.93539000	-1.19377300	-0.05475700
H	2.53951700	2.72779900	-0.17913000
H	1.24348900	3.77519500	-0.54490100
C	-3.08209200	1.10911700	-0.55305200
C	-1.12957500	3.44319800	-0.79872200
C	2.67672700	0.37035700	0.29837800
C	0.72071200	-1.96228600	0.54324000
H	-3.39149500	2.11640000	-0.80711300
H	-3.42191600	0.45990800	-1.36647300
H	-3.63407400	0.82699600	0.34945600
H	-0.64383700	3.77520500	-1.72100800
H	-2.19906600	3.54818200	-0.94226300
H	-0.83621600	4.14337800	-0.01178800
H	3.21806600	0.63758900	-0.61421000
H	3.02560200	1.04289000	1.08664300
H	2.98176900	-0.63339600	0.57168900
H	1.78789200	-2.06521900	0.70361400
H	0.22193800	-2.31157900	1.45143800
H	0.44590200	-2.65488300	-0.25726500
O	4.37330200	3.41514200	0.11090500
H	4.47251800	4.38037100	0.09731600
H	5.25493200	3.04712900	-0.00160800
O	4.24347800	6.34299000	0.09323400
H	4.81158000	6.85258600	-0.49753900
H	4.33586700	6.74907600	0.96415400
O	-2.01251600	-4.23616900	0.66400000
H	-2.04545500	-4.94296300	0.01020800
H	-2.24538400	-4.64646900	1.50395000
O	1.48499400	5.73286900	-0.67938300
H	2.37225000	6.06601800	-0.47068500
H	1.02912100	6.43993000	-1.14587600

P²⁺

C	-1.05079100	-0.34153800	-0.05768300
C	0.42434900	-0.39807500	-0.02654400
C	1.10185000	0.77432100	0.02910700
C	0.31614000	2.02437900	0.05665000
C	-1.15900000	2.08091600	0.02550700
C	-1.83650100	0.90852000	-0.03014200
N	-1.70050800	-1.46549700	-0.11344300
N	0.96585800	3.14833700	0.11241500
H	-1.22228400	-2.36136200	-0.13517700
H	-2.71545100	-1.49737700	-0.13802000
H	1.98080100	3.18021600	0.13699500
H	0.48763500	4.04420300	0.13414900
C	-3.33016300	0.78000200	-0.06633800
C	-1.79400400	3.43898400	0.05937700
C	2.59551300	0.90284100	0.06530400
C	1.05935100	-1.75614400	-0.06041800
H	-3.83285200	1.73976000	-0.03995800
H	-3.66214800	2.7825400	-0.98166900
H	-3.69922500	0.21051200	0.79343600
H	-1.48113600	4.04442700	-0.79813100
H	-2.87625000	3.39393100	0.02737100
H	-1.53025500	3.97666800	0.97655700
H	2.96457400	1.47233500	-0.79446800
H	2.92749600	1.40458900	0.98063700
H	3.09820300	-0.05691500	0.03892300
H	2.14159800	-1.71109300	-0.02842600
H	0.74649300	-2.36158400	0.79709500
H	0.79559000	-2.29383000	-0.97759300

P²⁺(H₂O)

C	-1.08712300	-0.37887500	-0.06262600
C	0.38136900	-0.46952600	-0.05460000
C	1.09038800	0.68176600	0.04201500
C	0.33834600	1.94614800	0.19345400

C	-1.13083600	2.04153600	0.03040700
C	-1.83640000	0.88990300	-0.06715700
N	-1.76761500	-1.48793500	-0.09934300
N	0.98555400	3.02680600	0.49338900
H	-1.31213400	-2.39472600	-0.10813700
H	-2.78216300	-1.49310600	-0.11930000
H	2.01132900	3.11447200	0.67900600
H	0.47710400	3.89991100	0.60241100
C	-3.33115500	0.80416000	-0.17137500
C	-1.73529300	3.41427400	-0.02152300
C	2.58407700	0.76924600	0.01715800
C	0.98389800	-1.84076100	-0.15589400
H	-3.80550600	1.77866800	-0.17776300
H	-3.63714800	0.29534800	-1.09122600
H	-3.75524100	0.26162700	0.68051400
H	-1.22400800	4.06730200	-0.69148500
H	-2.78104100	3.40290800	-0.26411900
H	-1.68485800	3.87959500	1.01273500
H	2.91405200	1.49104300	-0.73423900
H	2.98302700	1.09991000	0.98050200
H	3.05049300	-0.17975400	-0.22069800
H	2.06727100	-1.82040300	-0.14364900
H	0.67890000	-2.46962300	0.68758900
H	0.68445100	-2.33913800	-1.08357000
O	3.53575200	3.75990500	1.15017700
H	4.19813300	4.15288000	0.56707600
H	3.80365800	3.99427500	2.04821800

 $P^{2+}(H_2O)_2$

C	-1.18200300	-0.23219700	-0.16199600
C	0.28575200	-0.36752900	-0.20183500
C	1.03374200	0.74871800	-0.02207000
C	0.33100300	2.02240300	0.21924900
C	-1.12776200	2.18686700	0.04191000
C	-1.87352000	1.07502700	-0.15385700
N	-1.91243800	-1.30383100	-0.14970100
N	1.01782100	3.05861200	0.58892100
H	-1.57213300	-2.28796700	-0.12146500
H	-2.92423100	-1.22076800	-0.13482500
H	2.04203800	3.09115500	0.77767100
H	0.54449300	3.94212400	0.75071000
C	-3.36421400	1.06432200	-0.32774500
C	-1.67630100	3.58140900	0.12489100
C	2.53105200	0.78827800	-0.04543500
C	0.84018600	-1.73829300	-0.44206200
H	-3.77550300	2.06033400	-0.44553600
H	-3.65503100	0.49683400	-1.21643400
H	-3.86384700	0.62166900	0.54135600
H	-1.16114200	4.25245200	-0.56859000
H	-2.73164700	3.62823800	-0.11788000
H	-1.57380900	3.98849200	1.13709900
H	2.88486700	1.53071100	-0.76553800
H	2.94030100	1.06319800	0.93052400
H	2.96647500	-0.16449400	-0.32257000
H	1.92271900	-1.74565300	-0.48658800
H	0.54379700	-2.43472900	0.34663900
H	0.46881900	-2.14318100	-1.38779600
O	3.60439700	3.67179300	1.29657300
H	4.28391700	4.07024300	0.73791800
H	3.87969800	3.84173200	2.20646500
O	-1.57291900	-4.02854700	0.03134900
H	-1.55575900	-4.66909300	-0.69115800
H	-1.78777700	-4.53427400	0.82552200

 $P^{2+}(H_2O)_3$

C	-1.13965500	-0.23334000	-0.22700400
C	0.32925000	-0.34099400	-0.35496300

C	1.06928200	0.76118000	-0.08633700
C	0.35592800	2.00807100	0.23762400
C	-1.09388300	2.17740600	0.02416700
C	-1.83198700	1.07474900	-0.24207300
N	-1.84029900	-1.31268000	-0.09310400
N	1.03131900	3.02556200	0.67976000
H	-1.42606600	-2.26077200	-0.03105700
H	-2.86834000	-1.31727900	0.03775400
H	2.04907700	3.04689400	0.88544800
H	0.55142200	3.89613400	0.88276900
C	-3.30296800	1.07242300	-0.52208000
C	-1.64889000	3.56790600	0.14055600
C	2.56741000	0.80759100	-0.09923200
C	0.88941400	-1.67229100	-0.75193900
H	-3.68779200	2.06971100	-0.70497000
H	-3.52063400	0.47023400	-1.40747700
H	-3.87392300	0.64394300	0.30658700
H	-1.12924500	4.26171100	-0.52661600
H	-2.70298500	3.61439500	-0.10816100
H	-1.55916600	3.94570700	1.16507600
H	2.92592900	1.54611900	-0.82191100
H	2.96719500	1.09036600	0.87776700
H	3.00737800	-0.14845500	-0.35826600
H	1.93889700	-1.61146600	-1.01803700
H	0.79235100	-2.41024000	0.04955300
H	0.35438700	-2.06706700	-1.61900300
O	3.61897100	3.60114400	1.47724000
H	4.31498000	4.01626100	0.95240200
H	3.87160500	3.73398600	2.39955900
O	-1.17100000	-4.02801100	0.28735900
H	-1.16655900	-4.72684200	-0.37873800
H	-1.27038900	-4.47845500	1.13516700
O	-4.56703900	-1.81597100	0.43690100
H	-5.25209300	-2.05162600	-0.20125700
H	-4.88410100	-2.14029900	1.28889100

 $P^{2+}(H_2O)_4$

C	-1.14963500	-0.25151300	-0.23965700
C	0.31686700	-0.34360400	-0.39230700
C	1.03958700	0.78910900	-0.23037100
C	0.30783000	2.03259500	0.08689100
C	-1.13696400	2.17191200	-0.18726000
C	-1.85969700	1.03927500	-0.35014400
N	-1.83273500	-1.33293600	-0.03498400
N	0.95555200	3.03603000	0.58843400
H	-1.40365500	-2.26721600	0.07507200
H	-2.85768500	-1.34410700	0.10161400
H	1.96156000	3.00528100	0.82513600
H	0.50789800	3.92918100	0.85501200
C	-3.33318500	0.99287700	-0.61904700
C	-1.69480300	3.56156900	-0.24894200
C	2.53226600	0.87659000	-0.33268400
C	0.89258700	-1.69231100	-0.70123400
H	-3.74426200	1.97478600	-0.82444200
H	-3.54402300	0.35857500	-1.48388200
H	-3.88632100	0.57723000	0.22745800
H	-1.10782300	4.17956200	-0.93324700
H	-2.72250400	3.57609300	-0.59373500
H	-1.67050200	4.05116900	0.72832300
H	2.82259500	1.67937200	-1.01544800
H	2.99204900	1.09512500	0.63487500
H	2.97333000	-0.04261000	-0.70117000
H	1.95179700	-1.64499200	-0.92736600
H	0.76722700	-2.38736900	0.13328500
H	0.38952200	-2.13365400	-1.56561100
O	3.60757000	3.39138600	1.53417400
H	4.34639700	3.79329100	1.06055600
H	3.82583700	3.47156600	2.47069900

Appendix A

O	-1.13167000	-4.03324400	0.48326500
H	-1.12362100	-4.76237400	-0.14919400
H	-1.21495400	-4.44468300	1.35215000
O	-4.56092000	-1.85706000	0.54192500
H	-5.24431200	-2.14005800	-0.07821000
H	-4.87078500	-2.13356100	1.41295700
O	0.17768200	5.56826900	1.60563800
H	0.21522400	6.41746700	1.14832800
H	0.17896200	5.78052600	2.54696100

This page has been intentionally left blank

Appendix B

B.1 Supporting Information for 9,10-Anthraquinone

B.1.1 Cyclic voltammograms

B.1.2 Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of simple alcohols

B.1.3 Computational data: Geometries, energies and coordinates of hydrogen-bonded complexes

B.2 Supporting Information for 1,4-Benzoquinone

B.2.1 Cyclic voltammograms

B.2.2 Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of simple alcohols

B.2.3 Computational data: Geometries, energies and coordinates of hydrogen-bonded complexes

This page has been intentionally left blank

B.1 Supporting Information for 9,10-Anthraquinone

B.1.1 Cyclic voltammograms

Figure B.1. Cyclic voltammograms of 2 mM 9,10-anthraquinone (AQ) in (a) MeCN and (b) DCM with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of EtOH. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of EtOH are indicated in dashed lines with their measured trace moisture content.

Figure B.2. Cyclic voltammograms of 2 mM AQ in (a) MeCN and (b) DCM with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of $n\text{-PrOH}$. The voltammograms were recorded at a scan

rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of *n*-PrOH are indicated in dashed lines with their measured trace moisture content.

Figure B.3. Cyclic voltammograms of 2 mM AQ in (a) MeCN and (b) DCM with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of *i*-PrOH. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of *i*-PrOH are indicated in dashed lines with their measured trace moisture content.

Figure B.4. Cyclic voltammograms of 2 mM AQ in (a) MeCN and (b) DCM with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of *n*-BuOH. The voltammograms were recorded at a scan

rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of *n*-BuOH are indicated in dashed lines with their measured trace moisture content.

Figure B.5. Cyclic voltammograms of 2 mM AQ in (a) MeCN and (b) DCM with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of *s*-BuOH. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of *s*-BuOH are indicated in dashed lines with their measured trace moisture content.

Figure B.6. Cyclic voltammograms of 2 mM AQ in (a) MeCN and (b) DCM with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of *i*-BuOH. The voltammograms were recorded at a scan

rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of *i*-BuOH are indicated in dashed lines with their measured trace moisture content.

Figure B.7. Cyclic voltammograms of 2 mM AQ in (a) MeCN and (b) DCM with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of *t*-BuOH. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of *t*-BuOH are indicated in dashed lines with their measured trace moisture content.

Figure B.8. Cyclic voltammograms of 2 mM AQ in MeCN with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of 2-fluoroethanol (FE). The voltammograms were recorded at a scan

rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of FE are indicated in dashed lines with their measured trace moisture content.

Figure B.9. Cyclic voltammograms of 2 mM AQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of 2,2-difluoroethanol (DFE). The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of DFE are indicated in dashed lines with their measured trace moisture content.

Figure B.10. Cyclic voltammograms of 2 mM AQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of 2,2,2-trifluoroethanol (TFE). The voltammograms were recorded at

a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of TFE are indicated in dashed lines with their measured trace moisture content.

Figure B.11. Cyclic voltammograms of 2 mM AQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of 3,3,3-trifluoro- n -propanol (TFP). The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of TFP are indicated in dashed lines with their measured trace moisture content.

Figure B.12. Cyclic voltammograms of 2 mM AQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of 1,3-difluoroisopropanol (DFIP). The voltammograms were

recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of DFIP are indicated in dashed lines with their measured trace moisture content.

Figure B.13. Cyclic voltammograms of 2 mM AQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of ethylene glycol (EG). The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of EG are indicated in dashed lines with their measured trace moisture content.

Figure B.14. Cyclic voltammograms of 2 mM AQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of 1,3-propanediol (PD). The voltammograms were recorded at a scan

rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of PD are indicated in dashed lines with their measured trace moisture content.

Figure B.15. Cyclic voltammograms of 2 mM AQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of 1,4-butanediol (BD). The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of BD are indicated in dashed lines with their measured trace moisture content.

B.1.2 Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of simple alcohols

Figure B.16. Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of alcohols obtained over three experiments (red +, blue ○ and black ×) as measured by square-wave voltammetry during the reduction of 2 mM AQ with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure B.17. Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of alcohols obtained over three experiments (red +, blue ○ and black ×) as measured by square-wave voltammetry during the reduction of 2 mM AQ with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte in DCM recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

B.1.3 Computational data: Geometries, energies and coordinates of hydrogen-bonded complexes

Table B.1. Energies of the solvated hydrogen-bonded complexes of AQ and its reduced forms.

Hydrogen donors	Energy (hartrees)					
	Q	MeCN Q ^{•-}	Q ²⁻	Q	DCM Q ^{•-}	Q ²⁻
MeOH	-804.552	-804.689	-804.792	-804.551	-804.682	-804.766
EtOH	-843.855	-843.992	-844.093	-843.854	-843.984	-844.069
<i>n</i> -PrOH	-883.153	-883.289	-883.390	-883.151	-883.282	-883.366
<i>i</i> -PrOH	-883.159	-883.295	-883.396	-883.157	-883.287	-883.371
<i>n</i> -BuOH	-922.450	-922.587	-922.689	-922.449	-922.579	-922.664
<i>s</i> -BuOH	-922.455	-922.591	-922.693	-922.453	-922.584	-922.667
<i>i</i> -BuOH	-922.452	-922.588	-922.690	-922.450	-922.581	-922.664
<i>t</i> -BuOH	-922.460	-922.596	-922.697	-922.459	-922.588	-922.671
FE	-943.134	-943.271	-943.374			
DFE	-1042.424	-1042.563	-1042.668			
TFE	-1141.720	-1141.859	-1141.965			
TFP	-1181.021	-1181.158	-1181.262			
DFIP	-1081.713	-1081.851	-1081.956			
EG - Normal	-919.094	-919.232	-919.334			
EG - Bidentate	-919.097	-919.238	-919.344			
Two EG	-1149.366	-1149.506	-1149.615			
PD - Normal	-958.393	-958.529	-958.631			
PD - Bidentate	-958.394	-958.535	-958.641			
Two PD	-1227.961	-1228.103	-1228.210			
BD - Normal	-997.692	-997.829	-997.930			
BD - Bidentate	-997.689	-997.828	-997.934			
Two BD	-1306.559	-1306.697	-1306.807

Figure B.18. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(MeOH) hydrogen-bonded complexes.

Figure B.19. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(EtOH) hydrogen-bonded complexes.

Figure B.20. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(*n*-PrOH) hydrogen-bonded complexes.

Figure B.21. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(*i*-PrOH) hydrogen-bonded complexes.

Figure B.22. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(*n*-BuOH) hydrogen-bonded complexes.

Figure B.23. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(*s*-BuOH) hydrogen-bonded complexes.

Figure B.24. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(*i*-BuOH) hydrogen-bonded complexes.

Figure B.25. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(*t*-BuOH) hydrogen-bonded complexes.

Figure B.26. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(Fe) hydrogen-bonded complexes.

Figure B.27. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(DFE) hydrogen-bonded complexes.

Figure B.28. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(TFE) hydrogen-bonded complexes.

Figure B.29. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(TFP) hydrogen-bonded complexes.

Figure B.30. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(DFIP) hydrogen-bonded complexes.

Figure B.31. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(EG) normal hydrogen-bonded complexes.

Figure B.32. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(EG) bidentate hydrogen-bonded complexes.

Figure B.33. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(EG)₂ hydrogen-bonded complexes.

Figure B.34. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(PD) normal hydrogen-bonded complexes.

Figure B.35. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(PD) bidentate hydrogen-bonded complexes.

Figure B.36. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(PD)₂ hydrogen-bonded complexes.

Figure B.37. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(BD) normal hydrogen-bonded complexes.

Figure B.38. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(BD) bidentate hydrogen-bonded complexes.

Figure B.39. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated AQ(BD)₂ hydrogen-bonded complexes.

Cartesian Coordinates of MeCN-Solvated Hydrogen-Bonded Complexes of 9,10-Anthraquinone

Q(MeOH)				Q ²⁻ (MeOH)			
C	-6.18599900	-3.56584800	0.30604800	C	-6.29561100	-3.63570900	0.15004100
C	-4.80052000	-3.49732100	0.31890600	C	-4.96487400	-3.43436800	0.41581500
C	-4.15261800	-2.28650100	0.07930600	C	-4.29762500	-2.22389100	0.08971800
C	-4.91085200	-1.13105800	-0.17569100	C	-5.06607100	-1.16933600	-0.53999700
C	-6.30408400	-1.21069400	-0.18512400	C	-6.44414200	-1.42089000	-0.80368400
C	-6.93850600	-2.42075600	0.05375000	C	-7.04812000	-2.60639000	-0.47585900
C	-2.66586700	-2.24422300	0.09925500	C	-2.89822900	-2.07897900	0.38464400
C	-4.24958700	0.17171300	-0.43426200	C	-4.48303100	0.08069000	-0.89959900
C	-2.76641900	0.21648300	-0.42120700	C	-3.09306500	0.22992700	-0.61993200
C	-2.00825300	-0.93754800	-0.16505500	C	-2.31584200	-0.82148800	0.00262300
C	-0.61621300	-0.86012000	-0.15834200	C	-0.93527500	-0.58473600	0.23551100
H	-0.04479800	-1.75680800	0.04034500	H	-0.36829600	-1.38359100	0.69903000
C	0.01923000	0.34840600	-0.40343100	C	-0.32380900	0.59536300	-0.10516000
C	-0.73285800	1.49369600	-0.65825400	C	-1.08558100	1.62907800	-0.71216300
C	-2.11811100	1.42730600	-0.66678600	C	-2.42119300	1.44128800	-0.95514700
H	-6.68180200	-4.51023300	0.49241600	H	-6.77269800	-4.57417500	0.41170900
H	-4.20387600	-4.37829500	0.51373000	H	-4.37584900	-4.21190800	0.88783800
H	-6.88373200	-0.31884600	-0.38042900	H	-7.01181300	-0.63153300	-1.28095800
H	-8.01989200	-2.47347100	0.04398700	H	-8.09958500	-2.76186100	-0.69426300
H	1.10073100	0.40068200	-0.39688100	H	0.73395900	0.74162700	0.08600100
H	-0.23643800	2.43666800	-0.84984000	H	-0.60775300	2.56523800	-0.98199100
H	-2.71328200	2.30884700	-0.86296000	H	-3.01032500	2.22441600	-1.41668000
O	-4.90008800	1.18789100	-0.65349100	O	-5.18106900	1.04217100	-1.47370700
O	-2.00825000	-3.24903700	0.32457500	O	-2.20911000	-3.01611500	0.95330400
H	-6.61502100	1.97512300	-0.79806000	H	-6.34769700	1.79348400	-0.73673900
O	-7.48582200	2.39792400	-0.86989100	O	-7.09959400	2.32309400	-0.30900800
C	-7.63814500	3.31109900	0.21070700	C	-6.55975900	3.16968300	0.68277100
H	-8.62484200	3.76556700	0.11935400	H	-7.37670700	3.72033400	1.15659800
H	-7.57731500	2.80731600	1.18138800	H	-6.03363200	2.60884800	1.46711300
H	-6.88572200	4.10649200	0.18043500	H	-5.85655600	3.90418800	0.26667200

Q ⁻ (MeOH)				Q(EtOH)			
C	-6.21023400	-3.49554000	0.32156400	C	-6.11930300	-3.73246400	0.22683900
C	-4.83563900	-3.42887300	0.35819500	C	-4.73899400	-3.62429100	0.14071300
C	-4.15206900	-2.22563600	0.09105700	C	-4.13726600	-2.37393400	0.00658600
C	-4.90715600	-1.05944600	-0.22135300	C	-4.93688200	-1.21934400	-0.04264000
C	-6.31600200	-1.15533800	-0.25188000	C	-6.32439900	-1.33923300	0.04593500
C	-6.95813400	-2.34374100	0.01236900	C	-6.91272700	-2.58815900	0.17992500
C	-2.69367600	-2.20468200	0.14030400	C	-2.65491500	-2.28925000	-0.08108100
C	-4.25711400	0.20836900	-0.50601100	C	-4.32577500	0.12509800	-0.18824500
C	-2.80449700	0.23368200	-0.46188400	C	-2.84628700	0.21439800	-0.26209700
C	-2.04754300	-0.92917000	-0.14922800	C	-2.04676200	-0.93901300	-0.21168000
C	-0.64121100	-0.83884800	-0.12024100	C	-0.65960400	-0.81973700	-0.28509800
H	-0.08070600	-1.73317200	0.12004600	H	-0.05613200	-1.71655500	-0.24527400
C	0.00538300	0.34685300	-0.38810000	C	-0.06951800	0.42988300	-0.40606200
C	-0.74308600	1.49836100	-0.69854500	C	-0.86272100	1.57469300	-0.45642200
C	-2.11755300	1.43680000	-0.73309600	C	-2.24356600	1.46667000	-0.38558500
H	-6.71680400	-4.43079900	0.52934200	H	-6.57922600	-4.70716100	0.33106800
H	-4.24534100	-4.30514400	0.59352700	H	-4.11064600	-4.50403300	0.17680900
H	-6.88906900	-0.26891300	-0.48958000	H	-6.93589500	-0.44808900	0.01061100
H	-8.04041600	-2.39366600	-0.01739500	H	-7.99006900	-2.67187500	0.24776500
H	1.08769200	0.39575800	-0.36084100	H	1.00853300	0.51475200	-0.46113000
H	-0.23524200	2.43227600	-0.90980100	H	-0.40169000	2.54980400	-0.55109300
H	-2.70420300	2.31483100	-0.96984200	H	-2.87059600	2.34710100	-0.42456700
O	-4.91524400	1.25797300	-0.78486600	O	-5.01422500	1.13796300	-0.24718500
O	-2.02689700	-3.23509800	0.41795100	O	-1.96113500	-3.29443500	-0.04517600
H	-6.51948100	1.90749500	-0.83599100	H	-6.77738400	1.85328100	-0.41794100
O	-7.39619800	2.35047400	-0.88408800	O	-7.69347600	2.16665900	-0.49054300
C	-7.57422400	3.13183600	0.28582600	C	-7.73803700	3.55467500	-0.15763100
H	-8.55584400	3.60515800	0.22874200	H	-8.79742800	3.81210100	-0.09272100
H	-7.54081200	2.52172800	1.19640800	H	-7.30108400	3.71839200	0.83488200
H	-6.81763200	3.92092700	0.37191000	C	-7.04569800	4.43387500	-1.18780600
				H	-5.98240100	4.19132100	-1.25889600

Appendix B

H -7.49537700 4.30243100 -2.17459100
H -7.13279100 5.48743900 -0.90846300

Q⁺(EtOH)

C -6.12718200 -3.70886800 0.16448500
C -4.75776100 -3.59467400 0.08158100
C -4.13142900 -2.33601700 -0.02024900
C -4.93983900 -1.16399300 -0.03726300
C -6.34186500 -1.30959900 0.04980200
C -6.92779800 -2.55112700 0.14843800
C -2.67642000 -2.26503000 -0.10476800
C -4.35042200 0.16039900 -0.14002500
C -2.90093600 0.23644200 -0.22058900
C -2.09082300 -0.93254700 -0.20268600
C -0.69049700 -0.79202600 -0.28227600
H -0.08860100 -1.69164100 -0.26653400
C -0.10014600 0.44825300 -0.37675200
C -0.90136700 1.60597200 -0.39617800
C -2.27113700 1.49603000 -0.31977400
H -6.58934400 -4.68603200 0.24241800
H -4.12759200 -4.47472700 0.09341300
H -6.95551200 -0.41891000 0.03919500
H -8.00612500 -2.63834600 0.21387200
H 0.97848100 0.53544800 -0.43601700
H -0.43776200 2.58279000 -0.47139400
H -2.89783600 2.37823500 -0.33416200
O -5.05771600 1.21430100 -0.15869900
O -1.96239600 -3.30135400 -0.09312100
H -6.70738100 1.77420400 -0.27040100
O -7.62515700 2.12461600 -0.30712000
C -7.59646700 3.53292700 -0.10601200
H -8.62654300 3.83702800 0.09896300
H -7.00442400 3.77722700 0.78530900
C -7.06164100 4.29639800 -1.31011600
H -6.02595000 4.01921200 -1.52062700
H -7.66108000 4.08441100 -2.19875400
H -7.09280900 5.37395900 -1.12475200

Q²⁻(EtOH)

C -6.47460500 -3.46080100 -0.53501200
C -5.15885500 -3.27519100 -0.87606700
C -4.43658600 -2.10602900 -0.51786600
C -5.13102700 -1.07711400 0.22926100
C -6.49539900 -1.31179600 0.56866400
C -7.15393400 -2.45749200 0.20610800
C -3.05663000 -1.97575100 -0.89840400
C -4.48947800 0.13175200 0.62902000
C -3.11998500 0.26909500 0.25698900
C -2.41690800 -0.75681600 -0.48503700
C -1.05192900 -0.53337700 -0.80640700
H -0.54149300 -1.31158900 -1.36173800
C -0.38753400 0.60966100 -0.43962900
C -1.07574800 1.61685100 0.28794500
C -2.39425400 1.44126400 0.61797800
H -6.99530700 -4.36704300 -0.82556300
H -4.62562000 -4.03267000 -1.43832500
H -7.00840400 -0.54244200 1.13251900
H -8.19315000 -2.60059000 0.48361900
H 0.65622900 0.74671600 -0.70157100
H -0.55559800 2.52321600 0.58026200
H -2.92752100 2.20400500 1.17230900
O -5.11726600 1.06587500 1.31664700
O -2.43247600 -2.89270200 -1.56679300
H -6.38162700 1.82291700 0.76078000
O -7.19704900 2.35692200 0.47998100
C -6.78560500 3.57879600 -0.10308000
H -7.62393500 4.27994000 -0.02280900

H -5.95218500 4.01403300 0.46547100
C -6.38341400 3.43909300 -1.56801600
H -5.53255600 2.76215400 -1.67726000
H -7.21289300 3.04180300 -2.15874300
H -6.10073300 4.41027000 -1.98602500

Q(n-PrOH)

C -6.13730500 -3.64868300 0.39028900
C -4.75498800 -3.53285000 0.40048200
C -4.14851600 -2.30778400 0.12692200
C -4.94527700 -1.18652400 -0.16101500
C -6.33505500 -1.31360500 -0.16790600
C -6.92797200 -2.53727500 0.10609800
C -2.66421400 -2.21409400 0.14722200
C -4.32844200 0.13021900 -0.45706900
C -2.84772800 0.22798300 -0.43475900
C -2.05124500 -0.89192400 -0.14582100
C -0.66279600 -0.76540900 -0.13369400
H -0.06149000 -1.63624000 0.09032900
C -0.06865500 0.45835700 -0.40522300
C -0.85885100 1.56990400 -0.69224700
C -2.24082400 1.45449200 -0.70682800
H -6.60094600 -4.60362500 0.60371400
H -4.12873200 -4.38707300 0.61996300
H -6.94481000 -0.44782200 -0.38755000
H -8.00696500 -2.62684900 0.09888600
H 1.01027900 0.54890100 -0.39416900
H -0.39454500 2.52480000 -0.90423200
H -2.86558600 2.30920400 -0.92819400
O -5.01275600 1.11467700 -0.71382300
O -1.97284200 -3.19019500 0.39665200
H -6.77953200 1.79916800 -0.96616100
O -7.69624600 2.09545700 -1.08673000
C -7.88586800 3.31853700 -0.37694000
H -8.96302900 3.50586900 -0.38014500
H -7.57932900 3.20120000 0.67068100
C -7.15148300 4.49811400 -1.00425900
H -6.07808300 4.28115800 -1.02072400
H -7.46999600 4.59480400 -2.04693000
C -7.40427600 5.80606500 -0.25439700
H -8.46832500 6.05772300 -0.24498800
H -7.06982400 5.73942200 0.78446400
H -6.87148200 6.63697700 -0.72100300

Q⁺(n-PrOH)

C -6.15307500 -3.60371100 0.40472600
C -4.78107400 -3.49054800 0.41429800
C -4.14411200 -2.26484300 0.13381600
C -4.94434700 -1.12546000 -0.16471200
C -6.34946900 -1.26875900 -0.16687200
C -6.94552300 -2.47803000 0.11059200
C -2.68676200 -2.19366500 0.15648600
C -4.34365000 0.16385300 -0.46223400
C -2.89215900 0.24071500 -0.43701000
C -2.09040700 -0.89534200 -0.13782200
C -0.68781800 -0.75535100 -0.12780200
H -0.09269700 -1.62965800 0.10295300
C -0.08736900 0.45306900 -0.40138600
C -0.88025000 1.57797300 -0.69905500
C -2.25205100 1.46783900 -0.71512900
H -6.62352600 -4.55533800 0.62291200
H -4.15697000 -4.34596800 0.63904500
H -6.95692100 -0.40207500 -0.39158800
H -8.02590500 -2.56447900 0.10318700
H 0.99279900 0.54036300 -0.38836800
H -0.40859800 2.52962800 -0.91501700
H -2.87266400 2.32484900 -0.94238900

O	-5.04221000	1.18832300	-0.73389100
O	-1.97972500	-3.20159400	0.41717700
H	-6.67829800	1.72716800	-1.01591500
O	-7.58831900	2.06080500	-1.17889700
C	-7.79591300	3.24178400	-0.41498800
H	-8.87862000	3.39377700	-0.35911200
H	-7.43757200	3.09952900	0.61364600
C	-7.13826200	4.47833800	-1.02129800
H	-6.05870200	4.30965100	-1.09002100
H	-7.50393600	4.60145000	-2.04587700
C	-7.41646600	5.74379100	-0.21007200
H	-8.48942500	5.94626100	-0.14745000
H	-7.03680800	5.65221000	0.81138600
H	-6.94092900	6.61652300	-0.66242500

 $Q^{2-}(n\text{-PrOH})$

C	-6.17187700	-3.55419000	0.42100500
C	-4.80442200	-3.44923000	0.43742300
C	-4.12865800	-2.23532800	0.14234300
C	-4.92798100	-1.07081500	-0.18739200
C	-6.34556800	-1.22262300	-0.19196500
C	-6.95631400	-2.41472400	0.09950800
C	-2.69309000	-2.19658900	0.17973100
C	-4.33471400	0.18898700	-0.49837500
C	-2.90808700	0.23603900	-0.45995500
C	-2.10542900	-0.92272300	-0.12905900
C	-0.69291900	-0.77512700	-0.11438300
H	-0.10838900	-1.65223000	0.13747800
C	-0.07435300	0.41523900	-0.40175600
C	-0.86050600	1.55209300	-0.72876400
C	-2.22740500	1.45235400	-0.75358800
H	-6.65414300	-4.49819400	0.65167300
H	-4.18987100	-4.30789300	0.68088600
H	-6.94595600	-0.35490500	-0.43471200
H	-8.03878000	-2.48988200	0.08585000
H	1.00762500	0.49163900	-0.38056600
H	-0.37703500	2.49622800	-0.95758500
H	-2.83672500	2.31315800	-1.00062500
O	-5.03947000	1.25602100	-0.80553200
O	-1.97791200	-3.23740400	0.47278500
H	-6.56041000	1.70105000	-1.04404000
O	-7.48701700	2.05041600	-1.21860300
C	-7.72369800	3.19198300	-0.41673200
H	-8.80913500	3.28629800	-0.28977700
H	-7.29755400	3.05268000	0.58741600
C	-7.17889000	4.48521300	-1.02144100
H	-6.09632600	4.38821400	-1.15225400
H	-7.60627900	4.60875200	-2.02215600
C	-7.49248700	5.71132700	-0.16403800
H	-8.57131700	5.84079300	-0.03751800
H	-7.05163300	5.62176000	0.83291100
H	-7.10100800	6.62469300	-0.61729900

 $Q(i\text{-PrOH})$

C	-6.07070900	-3.77898000	0.22587000
C	-4.69201500	-3.65416900	0.13685200
C	-4.10580800	-2.39680400	-0.00062500
C	-4.91940200	-1.25202800	-0.05010800
C	-6.30524700	-1.38865400	0.04088600
C	-6.87802400	-2.64447000	0.17818000
C	-2.62482100	-2.29441300	-0.09189200
C	-4.32484200	0.09970300	-0.19807900
C	-2.84659500	0.20648800	-0.27629200
C	-2.03321800	-0.93720100	-0.22611800
C	-0.64775900	-0.80144300	-0.30333700
H	-0.03345800	-1.69089100	-0.26350300
C	-0.07299000	0.45492700	-0.42811500

C	-0.87997300	1.59007500	-0.47833500
C	-2.25922300	1.46564300	-0.40345100
H	-6.51856000	-4.75899100	0.33276200
H	-4.05286700	-4.52608900	0.17317700
H	-6.92775600	-0.50518200	0.00465100
H	-7.95415900	-2.74117500	0.24795300
H	1.00381500	0.55257900	-0.48622300
H	-0.43090200	2.57046000	-0.57593100
H	-2.89694300	2.33838900	-0.44214200
O	-5.02550400	1.10415800	-0.25515900
O	-1.91891200	-3.29115100	-0.05626400
H	-6.81400700	1.79036500	-0.39191200
O	-7.74284600	2.06693100	-0.44893100
C	-7.84461900	3.45293500	-0.09390700
H	-7.41883100	3.59116800	0.90927300
C	-7.07516200	4.32946800	-1.07683900
H	-6.02000600	4.04780900	-1.10663900
H	-7.48772600	4.22697700	-2.08411200
H	-7.13435600	5.38111300	-0.78510300
C	-9.32439300	3.79489900	-0.04610800
H	-9.46898600	4.83484200	0.25333800
H	-9.78032000	3.65478400	-1.03000200
H	-9.84601000	3.15602100	0.66923600

 $Q^{+}(i\text{-PrOH})$

C	-6.08365700	-3.75089400	0.21008100
C	-4.71627900	-3.62027800	0.11814800
C	-4.10702100	-2.35534500	-0.00705900
C	-4.93083600	-1.19445900	-0.03960700
C	-6.33038300	-1.35664200	0.05768400
C	-6.89937400	-2.60400100	0.17985100
C	-2.65349100	-2.26668300	-0.09890100
C	-4.35961200	0.13588300	-0.16770600
C	-2.91130400	0.22951100	-0.25389100
C	-2.08585600	-0.92839000	-0.21971400
C	-0.68769100	-0.77080300	-0.30583600
H	-0.07396700	-1.66211200	-0.27712200
C	-0.11400700	0.47540100	-0.42230000
C	-0.93043600	1.62209600	-0.45805500
C	-2.29841800	1.49542000	-0.37546800
H	-6.53259500	-4.73260500	0.30620000
H	-4.07443000	-4.49166000	0.14097200
H	-6.95532600	-0.47393100	0.03619200
H	-7.97610600	-2.70417600	0.25290700
H	0.96321100	0.57572100	-0.48631800
H	-0.47992800	2.60354000	-0.55062800
H	-2.93688400	2.36890200	-0.40220800
O	-5.08111200	1.17947500	-0.20254200
O	-1.92585900	-3.29334100	-0.07414500
H	-6.74727500	1.70287900	-0.39328200
O	-7.67769200	2.00570900	-0.48432600
C	-7.76881400	3.38400700	-0.12032700
H	-7.30849600	3.52189300	0.86852500
C	-7.03487700	4.27143500	-1.12296900
H	-5.98180200	3.99038500	-1.19029400
H	-7.48137500	4.17367500	-2.11652600
H	-7.08671600	5.32184600	-0.82398900
C	-9.24568400	3.73314000	-0.01843900
H	-9.37820000	4.77451200	0.28275400
H	-9.73743500	3.59098400	-0.98497900
H	-9.74340600	3.09699800	0.71636900

 $Q^{2-}(i\text{-PrOH})$

C	-6.05730500	-3.80846100	-0.02564900
C	-4.80095800	-3.47019400	-0.46073200
C	-4.24532100	-2.17953800	-0.25434600
C	-5.05046900	-1.19281700	0.43623000

331

H	0.45724000	1.18324500	0.20343900	C	-6.36583800	-1.40397900	0.05913800
H	-1.02803900	2.84717900	-0.93324100	C	-6.89769000	-2.67218100	0.11731500
H	-3.37266500	2.26089000	-1.42411500	C	-2.66510600	-2.19591800	-0.16430500
O	-5.41473200	0.87085300	-1.51224100	C	-4.44069500	0.15569700	-0.09522900
O	-2.11898900	-2.83870300	1.05437900	C	-2.99612100	0.29646900	-0.18012200
H	-6.63304800	1.55413600	-0.78260300	C	-2.13692900	-0.83681700	-0.21162300
O	-7.42556500	1.99932400	-0.33383300	C	-0.74427700	-0.63286800	-0.29130600
C	-7.05562200	3.28477300	0.12648400	H	-0.10334800	-1.50501300	-0.31224400
H	-7.72462600	3.54530500	0.95592300	C	-0.20812200	0.63437900	-0.34027000
H	-6.03537700	3.26855700	0.53614800	C	-1.05807300	1.75656300	-0.31196800
C	-7.15043300	4.36636400	-0.94895700	C	-2.42134300	1.58479000	-0.23385800
H	-6.48214200	4.10440500	-1.77730100	H	-6.46835000	-4.79279900	0.12760700
H	-8.16853400	4.36697300	-1.35551500	H	-4.01960900	-4.47145700	-0.03660000
C	-6.80244000	5.76208200	-0.42913800	H	-7.01628600	-0.54003800	0.08844400
H	-7.46209600	6.01004100	0.41049500	H	-7.97052600	-2.80758200	0.19069000
H	-5.78443100	5.75450200	-0.02343800	H	0.86546700	0.76982400	-0.40033200
C	-6.91315000	6.84995900	-1.49730400	H	-0.63722300	2.75458700	-0.35145700
H	-6.24001800	6.64924600	-2.33553400	H	-3.08543500	2.43905800	-0.21175200
H	-7.92957200	6.90780200	-1.89689200	O	-5.19290900	1.17757900	-0.07110000
H	-6.65799400	7.83334200	-1.09465300	O	-1.90831700	-3.20091900	-0.20212800
Q(s-BuOH)				H	-6.86989500	1.65692200	-0.30383500
C	-6.04180300	-3.81013600	0.15818800	O	-7.80363000	1.94661800	-0.40174800
C	-4.66543200	-3.65110500	0.09094000	C	-7.89948000	3.34094800	-0.10466200
C	-4.10800700	-2.37864000	-0.02603500	H	-7.41467400	3.53374600	0.86434600
C	-4.94840200	-1.25349400	-0.07700700	C	-7.17849400	4.17329700	-1.17194600
C	-6.33166100	-1.42452200	-0.00802900	H	-6.17405900	3.75644500	-1.29356700
C	-6.87570100	-2.69507400	0.10912300	H	-7.69381200	4.03237800	-2.12877100
C	-2.62877300	-2.23928800	-0.09338300	C	-7.06774300	5.66370200	-0.84734400
C	-4.38491100	0.11369900	-0.20315700	H	-8.04545200	6.14873400	-0.80894100
C	-2.90866400	0.25721700	-0.25770800	H	-6.57964400	5.82216600	0.11869300
C	-2.06848400	-0.86687400	-0.20607800	H	-6.47515200	6.18236100	-1.60425100
C	-0.68575100	-0.69673000	-0.26147400	C	-9.37911800	3.67148100	0.01994900
H	-0.05044600	-1.57129200	-0.22092200	H	-9.53240100	4.71744200	0.29031600
C	-0.14003200	0.57434200	-0.36621800	H	-9.89102100	3.48309400	-0.92818700
C	-0.97363000	1.69003300	-0.41773700	H	-9.84385000	3.05144000	0.78920500
C	-2.35033900	1.53140800	-0.36441700	Q ²⁻ (s-BuOH)			
H	-6.46716400	-4.80168800	0.24916700	C	-6.06128700	-3.74919800	-0.52853900
H	-4.00582800	-4.50758400	0.12876200	C	-4.82283000	-3.28225500	-0.88923100
H	-6.97477000	-0.55594300	-0.04495700	C	-4.33617200	-2.01442900	-0.47460800
H	-7.95005600	-2.81843400	0.16210100	C	-5.19410500	-1.19148100	0.35350100
H	0.93479200	0.69861400	-0.40764400	C	-6.47035200	-1.71574300	0.71037200
H	-0.54724200	2.68191500	-0.49948600	C	-6.89964000	-2.94803100	0.29174500
H	-3.00858400	2.38870500	-0.40440900	C	-3.02575200	-1.58736800	-0.88205300
O	-5.10926200	1.10107800	-0.26145300	C	-4.79396100	0.09805500	0.81251200
O	-1.89928400	-3.21884200	-0.05594300	C	-3.49332400	0.52782200	0.41670800
H	-6.91526600	1.75371200	-0.40851100	C	-2.62841200	-0.28939000	-0.40908600
O	-7.84990400	2.01062200	-0.46125800	C	-1.35140700	0.22707200	-0.75382900
C	-7.97885700	3.39415300	-0.10506400	H	-0.71844300	-0.39476900	-1.37570700
H	-7.54710800	3.54354400	0.89525100	C	-0.91596300	1.45721900	-0.32990600
C	-7.21613900	4.27902000	-1.09620100	C	-1.76109900	2.25712700	0.48455000
H	-6.19544700	3.89053500	-1.17543600	C	-3.00301100	1.79767900	0.83738400
H	-7.67178600	4.16502700	-2.08595100	H	-6.40087500	-4.72347300	-0.86375500
C	-7.15820400	5.75697200	-0.70783100	H	-4.16903100	-3.88068300	-1.51259200
H	-8.14745800	6.21909400	-0.70994400	H	-7.10440900	-1.09927000	1.33578200
H	-6.73174800	5.88682700	0.29094000	H	-7.87838700	-3.31377000	0.58465000
H	-6.53407500	6.31625400	-1.40799000	H	0.06676100	1.81973000	-0.61229300
C	-9.46778800	3.69235200	-0.04316800	H	-1.42135900	3.23017400	0.82415900
H	-9.65228400	4.71739800	0.28109600	H	-3.65669100	2.39880600	1.45741200
H	-9.92533300	3.55489500	-1.02686000	O	-5.57368300	0.84673500	1.56727500
H	-9.96082500	3.02074000	0.66225200	O	-2.25712400	-2.32091800	-1.62312300
Q ⁺ (s-BuOH)				H	-6.86108800	1.56009200	0.96576700
C	-6.04884000	-3.79458600	0.08186200	O	-7.71041400	2.02691600	0.67464900
C	-4.68647800	-3.61919100	-0.00993300	C	-7.39990300	3.28788200	0.09997900
C	-4.11489600	-2.33204700	-0.07022000	H	-6.64604900	3.79538000	0.72314100
C	-4.97228600	-1.19581300	-0.03631600	C	-6.80478300	3.11810800	-1.30581800
				H	-5.99643900	2.38422600	-1.23515400
				H	-7.57057400	2.67755800	-1.95490500

Appendix B

C	-6.26302500	4.40496600	-1.93052600
H	-7.05203300	5.13936100	-2.10804100
H	-5.51465300	4.87221900	-1.28365700
H	-5.78452300	4.20077200	-2.89124100
C	-8.67171900	4.12706900	0.10838700
H	-8.49782100	5.12994800	-0.28642500
H	-9.44459400	3.64842500	-0.50073800
H	-9.05348100	4.22594900	1.12680400

Q(*i*-BuOH)

C	-6.07397900	-3.77819700	0.16982900
C	-4.69524700	-3.63912600	0.10641200
C	-4.11909100	-2.37482900	-0.00800900
C	-4.94292800	-1.23751300	-0.06017000
C	-6.32870100	-1.38851700	0.00511600
C	-6.89147500	-2.65111700	0.11962500
C	-2.63780800	-2.25706600	-0.07144100
C	-4.35915500	0.12123400	-0.18401100
C	-2.88100600	0.24331800	-0.23463000
C	-2.05735800	-0.89288600	-0.18170900
C	-0.67220100	-0.74283700	-0.23334200
H	-0.04982600	-1.62658300	-0.19188700
C	-0.10779900	0.52027500	-0.33547300
C	-0.92496700	1.64799500	-0.38829700
C	-2.30397800	1.50937500	-0.33889800
H	-6.51391600	-4.76355900	0.25876600
H	-4.04827100	-4.50514100	0.14524500
H	-6.95917800	-0.51081200	-0.03273700
H	-7.96764800	-2.75888600	0.16960700
H	0.96882600	0.62896300	-0.37387200
H	-0.48402500	2.63365300	-0.46810500
H	-2.94952500	2.37621200	-0.38005300
O	-5.06858700	1.11949200	-0.24355600
O	-1.92279500	-3.24716700	-0.03269100
H	-6.85007800	1.78949400	-0.41303500
O	-7.77614900	2.07159000	-0.48517500
C	-7.86792300	3.45422800	-0.14871900
H	-8.93588400	3.67013000	-0.04456700
H	-7.39986000	3.63619600	0.82689000
C	-7.25496700	4.39111500	-1.19386500
H	-6.19975800	4.10938600	-1.30352600
C	-7.31177100	5.83713200	-0.69309400
H	-8.34776500	6.16159400	-0.55301000
H	-6.79294700	5.95238800	0.26210100
H	-6.84705800	6.51760900	-1.41024500
C	-7.93685200	4.24340500	-2.55550900
H	-7.90031700	3.21116300	-2.90725100
H	-8.98872000	4.54137100	-2.49502800
H	-7.45455900	4.87492300	-3.30579700

Q⁺(*i*-BuOH)

C	-6.08416600	-3.75171400	0.12148300
C	-4.71885500	-3.60243500	0.02727500
C	-4.12348400	-2.32664200	-0.04234000
C	-4.95940400	-1.17435700	-0.01554200
C	-6.35649700	-1.35579300	0.08301600
C	-6.91184000	-2.61341500	0.15032700
C	-2.67147900	-2.21830800	-0.13840100
C	-4.40265400	0.16630800	-0.08448100
C	-2.95604200	0.27958500	-0.17249800
C	-2.11819700	-0.86968200	-0.19732900
C	-0.72222500	-0.69262400	-0.28192000
H	-0.09803400	-1.57692400	-0.29859600
C	-0.16256900	0.56399800	-0.34118000
C	-0.99133200	1.70206900	-0.31877200
C	-2.35741200	1.55656400	-0.23663300
H	-6.52225800	-4.74156300	0.17424500

H	-4.06804900	-4.46716400	0.00563700
H	-6.99072100	-0.47976600	0.10719500
H	-7.98693000	-2.72830800	0.22566400
H	0.91319700	0.67899500	-0.40483000
H	-0.55189200	2.69170300	-0.36625900
H	-3.00526300	2.42331800	-0.21936100
O	-5.13554100	1.20263800	-0.06610700
O	-1.93354200	-3.23736600	-0.16803600
H	-6.78803900	1.70153700	-0.34686200
O	-7.70995900	2.01574800	-0.47847600
C	-7.78049400	3.39834900	-0.15874300
H	-8.84155100	3.63501700	-0.01997900
H	-7.27728800	3.59249000	0.79769400
C	-7.19580000	4.32105800	-1.23465500
H	-6.14825900	4.02812600	-1.37841100
C	-7.22339800	5.77286900	-0.74881700
H	-8.25093500	6.10648800	-0.57127000
H	-6.66692500	5.89454200	0.18424900
H	-6.78279600	6.44337200	-1.49048100
C	-7.92601300	4.16493300	-2.56984400
H	-7.90974100	3.12837700	-2.91020800
H	-8.97307900	4.47209100	-2.47646400
H	-7.46577900	4.78389200	-3.34440100

Q²⁻(*i*-BuOH)

C	-6.81750600	-3.46425600	-0.03410800
C	-5.75773100	-3.25803000	-0.88058400
C	-4.92521900	-2.11097900	-0.79260400
C	-5.22014000	-1.13064200	0.23252000
C	-6.32708400	-1.38479000	1.09361300
C	-7.10505100	-2.50642900	0.97465200
C	-3.82777400	-1.95463400	-1.70742200
C	-4.44038800	0.05160600	0.39663100
C	-3.34829100	0.21397700	-0.50475800
C	-3.04442600	-0.76232300	-1.53084600
C	-1.93325100	-0.51587500	-2.38005800
H	-1.72005400	-1.25639500	-3.14212800
C	-1.14884000	0.60316000	-2.25904200
C	-1.44636300	1.56175700	-1.25387500
C	-2.51067700	1.36330400	-0.41368100
H	-7.43299200	-4.35241500	-0.13016100
H	-5.52284600	-3.98087900	-1.65327300
H	-6.54015500	-0.64968200	1.86018300
H	-7.94012000	-2.66590300	1.64894000
H	-0.30636500	0.75868400	-2.92453700
H	-0.83012600	2.44942100	-1.15452400
H	-2.74656400	2.08897400	0.35539100
O	-4.70368000	0.93984700	1.33566800
O	-3.56302900	-2.82764700	-2.62645100
H	-6.01947100	1.80638600	1.25774200
O	-6.85030500	2.38760500	1.26594400
C	-6.48987600	3.72334700	0.97889700
H	-7.26865100	4.37566700	1.39692600
H	-5.54993000	3.98305300	1.48628700
C	-6.34500200	4.03263300	-0.51829700
H	-5.59513800	3.34040000	-0.92067700
C	-5.83015300	5.46151600	-0.71317300
H	-6.53567900	6.19098500	-0.30167900
H	-4.86784400	5.61243300	-0.21650600
H	-5.69882100	5.69268400	-1.77318400
C	-7.65791500	3.80786100	-1.27053300
H	-8.02670800	2.79137800	-1.12433500
H	-8.42966900	4.50041000	-0.91698000
H	-7.53141000	3.97179700	-2.34408900

Q(*t*-BuOH)

C	-6.06277000	-3.77003800	0.18054300
---	-------------	-------------	------------

C	-4.68407400	-3.64763800	0.08843000	H	-6.04370000	3.96497300	-1.15616900
C	-4.09466200	-2.38961700	-0.02838400	H	-7.53276200	3.93477800	-2.11468400
C	-4.90502800	-1.24179700	-0.05252300	H	-7.21080000	5.28652000	-1.01589800
C	-6.29092700	-1.37596200	0.04080900	C	-9.31973900	3.75170200	-0.03648800
C	-6.86692300	-2.63251400	0.15655600	H	-9.50116300	4.81621500	0.12532600
C	-2.61390500	-2.28988100	-0.12588900	H	-9.75621100	3.47091400	-0.99772400
C	-4.30717500	0.11117800	-0.17607500	H	-9.83197500	3.19221400	0.74952200
C	-2.82929900	0.21429500	-0.26915100	C	-7.21524200	3.80399800	1.34047000
C	-2.01924200	-0.93254700	-0.24507000	H	-6.15402300	3.54546600	1.36645500
C	-0.63412300	-0.79994100	-0.33400900	H	-7.30966100	4.87342000	1.54490200
H	-0.02238000	-1.69181600	-0.31391500	H	-7.72175900	3.25587600	2.13815900
C	-0.05652100	0.45635300	-0.44550200	$Q^{2-}(t\text{-BuOH})$			
C	-0.86026900	1.59466300	-0.47000000	C	-6.06254300	-3.87125100	0.24891600
C	-2.23906300	1.47341000	-0.38252400	C	-4.80134900	-3.60281900	-0.21929100
H	-6.51309700	-4.75057900	0.27096000	C	-4.22226900	-2.30759700	-0.14891000
H	-4.04743200	-4.52197700	0.10589200	C	-5.00871100	-1.23944300	0.43420500
H	-6.91066000	-0.48998700	0.02228500	C	-6.31207500	-1.56138900	0.91145200
H	-7.94312000	-2.72745200	0.22796200	C	-6.83099400	-2.82725700	0.82961300
H	1.01995000	0.55152500	-0.51322600	C	-2.89228100	-2.09409000	-0.64848700
H	-0.40900200	2.57502500	-0.55726200	C	-4.51357300	0.09480700	0.54420700
H	-2.87434400	2.34861600	-0.40078100	C	-3.19036800	0.31299600	0.05641000
O	-5.00494600	1.11859200	-0.20119300	C	-2.39737500	-0.75058400	-0.52536700
O	-1.91053400	-3.28893700	-0.10831300	C	-1.09057800	-0.43485100	-0.98397000
H	-6.81018000	1.84316900	-0.21426500	H	-0.51069600	-1.24052300	-1.41862400
O	-7.74888800	2.08874700	-0.24785500	C	-0.56335300	0.82833700	-0.89116000
C	-7.88238100	3.50559700	-0.01761900	C	-1.33834400	1.87103900	-0.31684300
C	-7.13897200	4.27424000	-1.11482200	C	-2.60528500	1.60954900	0.13586900
H	-6.07111600	4.04233700	-1.09340800	H	-6.47320300	-4.87300700	0.17956900
H	-7.52962200	4.00508400	-2.09849600	H	-4.20175100	-4.38847200	-0.66381200
H	-7.25192000	5.35296500	-0.98308200	H	-6.89385100	-0.75961200	1.34939700
C	-9.38069100	3.78917700	-0.07971300	H	-7.82773100	-3.03423900	1.20535600
H	-9.58067500	4.84949800	0.08550600	H	0.43925200	1.03301500	-1.25155500
H	-9.78143000	3.51204500	-1.05714600	H	-0.92542000	2.87154700	-0.23922700
H	-9.90988900	3.21613000	0.68471200	H	-3.20596900	2.39724600	0.57426500
C	-7.32086700	3.85433700	1.36463300	O	-5.22591200	1.06588400	1.07517000
H	-6.25595500	3.61429300	1.42170500	O	-2.18745900	-3.04725600	-1.17264200
H	-7.43741100	4.91956400	1.57770900	H	-6.57137900	1.62537700	0.36653700
H	-7.84231600	3.28940400	2.14029400	O	-7.43751000	1.92266300	-0.05704500
$Q^+(t\text{-BuOH})$				C	-7.50518400	3.34475100	-0.15110900
C	-6.07329400	-3.74804600	0.16269500	C	-6.37392400	3.87033100	-1.04658500
C	-4.70540100	-3.61421100	0.08458300	H	-5.40183700	3.61985900	-0.61732700
C	-4.09762400	-2.34744400	-0.03059900	H	-6.43651500	3.41849900	-2.03956200
C	-4.92389900	-1.18837900	-0.06519200	H	-6.42930900	4.95657100	-1.15976000
C	-6.32396200	-1.35387300	0.01600700	C	-8.86355900	3.66882600	-0.77536400
C	-6.89147100	-2.60296200	0.12736000	H	-9.00022800	4.74740400	-0.88394400
C	-2.64378800	-2.25519600	-0.11135400	H	-8.94717500	3.21168000	-1.76426500
C	-4.35484300	0.14451300	-0.18063900	H	-9.67204100	3.28176900	-0.15045400
C	-2.90588900	0.24098400	-0.26008700	C	-7.40411500	3.96831600	1.24845000
C	-2.07836400	-0.91549000	-0.22544300	H	-6.45354500	3.70142500	1.71497800
C	-0.67998600	-0.75451400	-0.30404100	H	-7.47070400	5.05875900	1.20377200
H	-0.06433700	-1.64449100	-0.27482700	H	-8.21299600	3.60130000	1.88491700
C	-0.10838300	0.49318900	-0.41421800	$Q(\text{FE})$			
C	-0.92697700	1.63836900	-0.45071600	C	-6.23392300	-3.48929400	-0.17803400
C	-2.29505200	1.50842200	-0.37481100	C	-4.85243900	-3.44301800	-0.29547200
H	-6.52087100	-4.73112000	0.25110000	C	-4.17828400	-2.22593200	-0.20962100
H	-4.06205600	-4.48441200	0.11044400	C	-4.90570000	-1.04134400	-0.00251500
H	-6.95008600	-0.47206400	-0.01048600	C	-6.29529300	-1.09909900	0.11266100
H	-7.96871900	-2.70596400	0.18787800	C	-6.95608400	-2.31549400	0.02578500
H	0.96893800	0.59588200	-0.47275200	C	-2.69676200	-2.20838700	-0.34056800
H	-0.47814000	2.62102800	-0.53848400	C	-4.21529900	0.26811600	0.09485700
H	-2.93535700	2.38057800	-0.40194200	C	-2.73714100	0.28921700	-0.02995300
O	-5.07837600	1.18568300	-0.21153200	C	-2.00987700	-0.89394900	-0.23843800
O	-1.91379800	-3.28054400	-0.08410000	C	-0.62143800	-0.83858700	-0.35169000
H	-6.76882700	1.75995000	-0.22495200	H	-0.07396800	-1.75761000	-0.51197400
O	-7.71179500	2.03186200	-0.24406600	C	0.04085500	0.37687400	-0.25912900
C	-7.82335600	3.44572500	-0.02085800				
C	-7.10911200	4.20601000	-1.14506100				

Appendix B

C	-0.68049300	1.55117200	-0.05211300
C	-2.06195000	1.50685800	0.06167800
H	-6.75015600	-4.43869000	-0.24550500
H	-4.27930700	-4.34647000	-0.45449100
H	-6.85254800	-0.18591700	0.26923800
H	-8.03441200	-2.35058500	0.11620600
H	1.11945800	0.41204800	-0.34738000
H	-0.16309000	2.49952300	0.02041800
H	-2.63320100	2.41107400	0.22241500
O	-4.83837500	1.30952200	0.27381600
O	-2.06651600	-3.23858500	-0.52560100
H	-6.51206900	2.11715400	0.50749600
O	-7.36808400	2.55289500	0.65966800
C	-7.42806400	3.74747000	-0.10295700
H	-8.28470200	4.31597900	0.26582600
H	-6.53138400	4.36282600	0.04485400
C	-7.58539200	3.51404000	-1.58659500
H	-6.81752500	2.84225900	-1.97570200
H	-7.55492700	4.46158100	-2.12920700
F	-8.83001600	2.91511600	-1.86215800

Q⁺(FE)

C	-6.24528100	-3.44737800	-0.20500500
C	-4.87513100	-3.39636600	-0.32933700
C	-4.17381000	-2.17833700	-0.22497100
C	-4.90567800	-0.98059400	0.01506800
C	-6.31047000	-1.06118500	0.13726300
C	-6.97044100	-2.26423400	0.03062400
C	-2.72103900	-2.17426900	-0.36516900
C	-4.23618700	0.30298300	0.13380800
C	-2.78952400	0.31272000	-0.00329100
C	-2.05547100	-0.88167200	-0.24325500
C	-0.65323800	-0.80682400	-0.36428400
H	-0.10962000	-1.72525700	-0.54485000
C	0.01119300	0.39424600	-0.25578800
C	-0.71456700	1.57737800	-0.01959900
C	-2.08457000	1.53137700	0.10319600
H	-6.76573000	-4.39428200	-0.28845800
H	-4.30274800	-4.29696600	-0.51063100
H	-6.86757000	-0.15146200	0.31599800
H	-8.04928100	-2.30125100	0.12730100
H	1.09012600	0.43092600	-0.35096800
H	-0.19271200	2.52347700	0.06588400
H	-2.65296200	2.43412600	0.28484900
O	-4.87318600	1.38065700	0.35055900
O	-2.07497600	-3.23208200	-0.58074700
H	-6.44408900	2.02788900	0.53189500
O	-7.30225700	2.49595700	0.66415500
C	-7.31820300	3.66392300	-0.13176900
H	-8.10839700	4.31459200	0.25312800
H	-6.37125800	4.21531200	-0.05656300
C	-7.57055500	3.39826900	-1.59764500
H	-6.88440300	2.64871800	-1.99633000
H	-7.49026700	4.32050200	-2.17785600
F	-8.87580600	2.89987300	-1.79139800

Q²(FE)

C	-6.51626200	-3.39227800	-0.10061400
C	-5.24218600	-3.19113100	-0.56805100
C	-4.51798100	-1.99691500	-0.31345700
C	-5.16331800	-0.95820900	0.46254300
C	-6.48564500	-1.20862400	0.93337300
C	-7.14721600	-2.37887300	0.66869400
C	-3.18204300	-1.85155300	-0.82521800
C	-4.51392400	0.27311900	0.76383600
C	-3.18999100	0.42710000	0.26292900
C	-2.53487600	-0.60578400	-0.51220100

C	-1.21339900	-0.36183000	-0.96988400
H	-0.73734900	-1.14324000	-1.55027800
C	-0.54586600	0.80659700	-0.70139000
C	-1.18556300	1.81884600	0.06212600
C	-2.46136800	1.62471000	0.52261800
H	-7.04081300	-4.31758900	-0.31364700
H	-4.74518300	-3.95455800	-1.15504100
H	-6.96259500	-0.43197300	1.51833500
H	-8.15313400	-2.53380400	1.04499700
H	0.46395800	0.95921300	-1.06704300
H	-0.66143900	2.74386600	0.27944100
H	-2.95682700	2.39022800	1.10736900
O	-5.09858900	1.21869900	1.47992200
O	-2.60315300	-2.77745000	-1.51859100
H	-6.25093200	2.01564800	0.86215000
O	-7.00712000	2.59751200	0.48826900
C	-6.48963400	3.43183700	-0.51711400
H	-7.20476100	4.24197400	-0.69836400
H	-5.54152200	3.89953600	-0.20990700
C	-6.22029500	2.72140800	-1.82474500
H	-5.61591700	1.82466500	-1.67503100
H	-5.73108800	3.38770400	-2.53967600
F	-7.43207900	2.30191500	-2.42053200

Q(DFE)

C	-6.12338000	-3.66674600	0.16222000
C	-4.74548100	-3.54323600	0.26600500
C	-4.13060100	-2.31031000	0.05494400
C	-4.91409300	-1.18810800	-0.26483000
C	-6.29945100	-1.32335400	-0.36585100
C	-6.90107700	-2.55498800	-0.15385500
C	-2.65136200	-2.20928600	0.17403100
C	-4.28716000	0.13575300	-0.49574400
C	-2.81274000	0.24162300	-0.37667900
C	-2.02925500	-0.87908300	-0.05656200
C	-0.64557500	-0.74527400	0.04729500
H	-0.05406300	-1.61657800	0.29420000
C	-0.04313800	0.48651000	-0.16363800
C	-0.82027100	1.59880800	-0.48127200
C	-2.19762900	1.47626200	-0.58725400
H	-6.59342800	-4.62809500	0.32722600
H	-4.12925100	-4.39777700	0.51108200
H	-6.90051000	-0.45848300	-0.61052600
H	-7.97652500	-2.65032100	-0.23452300
H	1.03220800	0.58259300	-0.08123800
H	-0.34963200	2.55992400	-0.64569900
H	-2.81194700	2.33164900	-0.83356800
O	-4.95837800	1.12370500	-0.77801400
O	-1.97175000	-3.18569000	0.45202700
H	-6.62938900	1.79827200	-1.12016700
O	-7.50864400	2.18649700	-1.27896300
C	-7.77682600	3.15438400	-0.28840700
H	-8.85959300	3.27810800	-0.21200000
H	-7.39248000	2.85959800	0.69303700
C	-7.17294900	4.49877400	-0.64453300
H	-6.09386900	4.48033300	-0.80623900
F	-7.75523100	5.00116800	-1.78173400
F	-7.44230600	5.39686900	0.36088200

Q⁺(DFE)

C	-6.14689900	-3.60324900	0.16925400
C	-4.77947800	-3.48382400	0.27587800
C	-4.13148800	-2.25187300	0.05703000
C	-4.91414000	-1.11159000	-0.28244300
C	-6.31520300	-1.26174400	-0.38401200
C	-6.92246800	-2.47713500	-0.16413400
C	-2.67933900	-2.17486500	0.18416200

C	-4.29887800	0.18143600	-0.52088700
C	-2.85453700	0.26546900	-0.39330100
C	-2.06965800	-0.87063800	-0.05338000
C	-0.67206700	-0.72605700	0.05456500
H	-0.08982400	-1.60103300	0.31373100
C	-0.05973600	0.48811100	-0.16186900
C	-0.83571000	1.61371500	-0.49790500
C	-2.20258700	1.49907400	-0.61001400
H	-6.62621700	-4.55982600	0.34129400
H	-4.16796000	-4.33948600	0.53188300
H	-6.91287500	-0.39704400	-0.63914600
H	-7.99926200	-2.56774200	-0.24756300
H	1.01658600	0.57920700	-0.07426200
H	-0.35495000	2.57007100	-0.66808800
H	-2.80923100	2.35724000	-0.86798600
O	-4.97948600	1.21079200	-0.83028700
O	-1.98823800	-3.18162700	0.48414100
H	-6.54000900	1.70775100	-1.13207500
O	-7.43743900	2.09549200	-1.29662400
C	-7.72164600	3.03316700	-0.28909400
H	-8.80602800	3.14769300	-0.20412800
H	-7.33210700	2.72371000	0.68711200
C	-7.13263400	4.39270500	-0.61009700
H	-6.05468400	4.38656900	-0.77854200
F	-7.72507500	4.92340800	-1.73090400
F	-7.40251000	5.26562800	0.41934500

 $Q^2(\text{DFE})$

C	-6.20480300	-3.82687300	-0.07659300
C	-4.91126600	-3.55671000	0.29254300
C	-4.29450300	-2.30324900	0.04132500
C	-5.07345500	-1.27881400	-0.62261300
C	-6.41145400	-1.60199700	-0.99649200
C	-6.96655200	-2.82738200	-0.73806300
C	-2.93139100	-2.08382800	0.44602600
C	-4.53872600	0.00797700	-0.90747600
C	-3.19191100	0.23793600	-0.51214400
C	-2.40242900	-0.77909400	0.14935800
C	-1.06704200	-0.46162600	0.51005200
H	-0.49226800	-1.23410100	1.00744600
C	-0.50684100	0.76370500	0.25002300
C	-1.27844200	1.76131600	-0.40260400
C	-2.57295500	1.49752500	-0.76545800
H	-6.64550400	-4.79576900	0.13211100
H	-4.31526300	-4.30919800	0.79559600
H	-6.98753700	-0.83589200	-1.50102800
H	-7.98795600	-3.03729800	-1.03824700
H	0.51746900	0.97269600	0.53930500
H	-0.84013000	2.73151200	-0.61254500
H	-3.16857900	2.25257000	-1.26402000
O	-5.24929800	0.94275700	-1.52393400
O	-2.22966300	-2.99546000	1.03457800
H	-6.37796400	1.58783200	-0.82592200
O	-7.16263600	2.08600100	-0.35975000
C	-6.68715300	3.26889000	0.21101700
H	-7.32061000	3.56067700	1.05704100
H	-5.65779700	3.17120100	0.57973900
C	-6.69612300	4.41507500	-0.78129900
H	-6.14017400	4.21601100	-1.69870000
F	-7.98465200	4.73999500	-1.14112100
F	-6.16816800	5.54711900	-0.19650000

 $Q(\text{TFE})$

C	-6.15454400	-3.65956200	0.33028000
C	-4.77074600	-3.56134100	0.34272300
C	-4.14896700	-2.33745400	0.10183200
C	-4.93159000	-1.19842200	-0.15486200

C	-6.32289700	-1.30820300	-0.16394200
C	-6.93125400	-2.53122100	0.07683000
C	-2.66335000	-2.26391600	0.12264000
C	-4.29689600	0.11612300	-0.41474000
C	-2.81623300	0.19409200	-0.39656000
C	-2.03359200	-0.94328800	-0.13925500
C	-0.64384200	-0.83543300	-0.12938400
H	-0.05332100	-1.71947400	0.07006700
C	-0.03455700	0.38705500	-0.37234500
C	-0.81083400	1.51579600	-0.62812300
C	-2.19427400	1.41921800	-0.63999100
H	-6.62996700	-4.61409500	0.51792000
H	-4.15530100	-4.42904500	0.53851200
H	-6.92338200	-0.43059200	-0.35943600
H	-8.01125000	-2.60679000	0.06756100
H	1.04551200	0.46296300	-0.36338300
H	-0.33473600	2.46950300	-0.81796200
H	-2.80800600	2.28761400	-0.83729800
O	-4.96598200	1.12022900	-0.64004600
O	-1.98494400	-3.25480900	0.34712100
H	-6.62139800	1.81909500	-0.87063800
O	-7.52088400	2.17596100	-0.99497600
C	-7.70045900	3.30899200	-0.18882600
H	-8.76746600	3.44561800	-0.00555400
H	-7.19004800	3.23127500	0.77536200
C	-7.19729100	4.57260100	-0.87004400
F	-7.81814900	4.80587900	-2.04323400
F	-7.40431800	5.65311900	-0.08695900
F	-5.87494700	4.51922500	-1.13384700

 $Q^-(\text{TFE})$

C	-6.18443700	-3.59443900	0.32025400
C	-4.81151400	-3.50089800	0.36261100
C	-4.15093400	-2.28340900	0.10494800
C	-4.92627800	-1.12962600	-0.20534900
C	-6.33332600	-1.25334800	-0.24108400
C	-6.95269500	-2.45552800	0.01478200
C	-2.69300300	-2.23536800	0.16267600
C	-4.29670900	0.14868700	-0.48062400
C	-2.84676200	0.20386200	-0.42365400
C	-2.06927500	-0.94516900	-0.11202400
C	-0.66577200	-0.82786000	-0.06957600
H	-0.09007700	-1.71253800	0.17049400
C	-0.04039400	0.37221300	-0.32403800
C	-0.80894700	1.51028300	-0.63408300
C	-2.18155700	1.42241100	-0.68148800
H	-6.67357500	-4.54034300	0.52115500
H	-4.20499900	-4.36650500	0.59608600
H	-6.92657100	-0.37936100	-0.47328200
H	-8.03373000	-2.52558600	-0.01856200
H	1.04037800	0.44252300	-0.28651600
H	-0.31791700	2.45537800	-0.83500200
H	-2.78264900	2.29042900	-0.91843000
O	-4.96800000	1.19238300	-0.76381500
O	-2.00895700	-3.25430600	0.43547300
H	-6.50984400	1.71924800	-0.91992000
O	-7.42404600	2.10332200	-0.99929600
C	-7.54802800	3.19501900	-0.13687200
H	-8.57051300	3.25416900	0.24552300
H	-6.86482400	3.14127000	0.71638200
C	-7.27227300	4.51037300	-0.84973100
F	-8.11020000	4.71788300	-1.88695300
F	-7.42299200	5.55618900	-0.00538600
F	-6.01949400	4.57935400	-1.34525400

 $Q^2-(\text{TFE})$

C	-6.12079000	-3.82651900	0.15165200
---	-------------	-------------	------------

Appendix B

C	-4.81678400	-3.51938500	0.44815200
C	-4.23168300	-2.27343700	0.10347600
C	-5.05340900	-1.29712800	-0.58062500
C	-6.40284900	-1.65659200	-0.87354800
C	-6.92649200	-2.87331100	-0.52542400
C	-2.85515900	-2.01435300	0.43497400
C	-4.54874600	-0.02485100	-0.96231900
C	-3.18870900	0.24219800	-0.64840700
C	-2.35564700	-0.72594100	0.03196600
C	-1.00711000	-0.37848900	0.30305500
H	-0.39867900	-1.11725200	0.81095100
C	-0.47428600	0.83429600	-0.05495400
C	-1.28998700	1.78613900	-0.72152800
C	-2.59768300	1.49102600	-1.00376600
H	-6.53592100	-4.78960400	0.42835800
H	-4.18739700	-4.23673700	0.96119100
H	-7.01367300	-0.92636000	-1.38974400
H	-7.95700600	-3.11211000	-0.76720500
H	0.56135300	1.06773400	0.16736400
H	-0.87461700	2.74710700	-1.00703200
H	-3.22427700	2.21199200	-1.51379400
O	-5.30054400	0.86739400	-1.60083000
O	-2.11814200	-2.87758400	1.05030000
H	-6.34168200	1.52749900	-0.88651500
O	-7.11755800	2.03560100	-0.37799800
C	-6.61973000	3.16466200	0.25363600
H	-7.06185900	3.29380200	1.24922100
H	-5.52926700	3.14346900	0.37197200
C	-6.94125900	4.43750600	-0.51546300
F	-8.26996100	4.62276500	-0.68099400
F	-6.47425100	5.53178200	0.13415600
F	-6.39610700	4.45539200	-1.75083300

Q(TFP)

C	-6.21312600	-3.45809100	0.56540700
C	-4.82969500	-3.36446900	0.60840000
C	-4.19064000	-2.18716500	0.22296400
C	-4.95560600	-1.09107500	-0.21148300
C	-6.34673200	-1.19583800	-0.25089500
C	-6.97230000	-2.37209400	0.13516800
C	-2.70592000	-2.11721700	0.28149400
C	-4.30290400	0.17449300	-0.62681400
C	-2.82249200	0.24935700	-0.56727700
C	-2.05757200	-0.84560700	-0.13348500
C	-0.66795200	-0.74191300	-0.09128500
H	-0.09114000	-1.59309200	0.24468900
C	-0.04145500	0.43491700	-0.47497800
C	-0.80018400	1.52174000	-0.90540000
C	-2.18316200	1.42871200	-0.95102000
H	-6.70198000	-4.37595700	0.86695300
H	-4.22764900	-4.19944400	0.94060700
H	-6.93268200	-0.35081100	-0.58557500
H	-8.05207600	-2.44425000	0.10176900
H	1.03829500	0.50785600	-0.43999100
H	-0.31074500	2.43985500	-1.20509300
H	-2.78357100	2.26455000	-1.28364400
O	-4.95770900	1.13853000	-1.01037300
O	-2.04288800	-3.07199500	0.65764600
H	-6.65341500	1.81175300	-1.39962000
O	-7.53502000	2.17065400	-1.60079100
C	-7.87064300	3.14918900	-0.63141300
H	-8.94165700	3.33166300	-0.72849800
H	-7.68466100	2.77689000	0.38083900
C	-7.09416500	4.44974000	-0.86682700
H	-6.02060600	4.27492100	-0.77234800
H	-7.28878600	4.82305400	-1.87362700
C	-7.45634600	5.54390800	0.10104800
F	-7.21477500	5.19992400	1.38786300

F	-8.76534500	5.88114700	0.03582800
F	-6.75594100	6.67692100	-0.13152900

Q⁺(TFP)

C	-6.21792100	-3.43209600	0.55274000
C	-4.84458600	-3.33830000	0.57673300
C	-4.18403000	-2.14959900	0.20717000
C	-4.96061600	-1.02676600	-0.19761200
C	-6.36773100	-1.14988100	-0.21294900
C	-6.98722200	-2.32339300	0.15252000
C	-2.72596300	-2.09882000	0.24883400
C	-4.33341200	0.22377700	-0.58715500
C	-2.88229300	0.28158000	-0.54358900
C	-2.10355600	-0.83798700	-0.14033500
C	-0.69938900	-0.71931600	-0.11928500
H	-0.12207300	-1.58104200	0.19047500
C	-0.07516700	0.45379300	-0.47996300
C	-0.84509600	1.56252800	-0.88026100
C	-2.21809300	1.47242400	-0.90978600
H	-6.70690400	-4.35528800	0.84091500
H	-4.23756400	-4.18073700	0.88254200
H	-6.95880500	-0.29773700	-0.52102300
H	-8.06854400	-2.39448200	0.13284600
H	1.00595100	0.52546600	-0.45695900
H	-0.35483600	2.48622100	-1.16512600
H	-2.82083000	2.31721200	-1.21659400
O	-5.00963100	1.23627800	-0.95223800
O	-2.04030200	-3.09233200	0.60239400
H	-6.58963500	1.72313800	-1.34528100
O	-7.47830400	2.08548000	-1.57871700
C	-7.82864600	3.07863900	-0.63752600
H	-8.89756400	3.27004500	-0.75078000
H	-7.66053200	2.72705200	0.38639700
C	-7.04057000	4.37321700	-0.87847300
H	-5.97037300	4.18810900	-0.76910800
H	-7.21967700	4.73520400	-1.89250200
C	-7.40456500	5.48264800	0.06954600
F	-7.17949100	5.15660700	1.36427600
F	-8.71090700	5.82966800	-0.01333600
F	-6.69437100	6.60944600	-0.17008200

Q²-(TFP)

C	-6.39949600	-3.07416600	0.83425700
C	-5.07296800	-3.18413100	0.50142300
C	-4.26133200	-2.05243600	0.22699900
C	-4.86963900	-0.74012700	0.29962900
C	-6.24903500	-0.66907400	0.65381800
C	-6.99624900	-1.78779600	0.91350100
C	-2.87553000	-2.23523200	-0.11086700
C	-4.13272500	0.44934700	0.03645600
C	-2.76009000	0.27981800	-0.30203000
C	-2.14145500	-1.02696500	-0.37466100
C	-0.76659200	-1.09846500	-0.72084900
H	-0.32039200	-2.08472600	-0.77364000
C	-0.01538300	0.01955800	-0.98237500
C	-0.61997800	1.30257500	-0.90799100
C	-1.94523100	1.41628300	-0.57903700
H	-6.99118200	-3.96033900	1.03750200
H	-4.60025300	-4.15729800	0.43807600
H	-6.69840100	0.31478300	0.71409800
H	-8.04378800	-1.69409400	1.18075400
H	1.03315700	-0.07156300	-1.24505100
H	-0.03017500	2.19014000	-1.11268400
H	-2.41607600	2.39009400	-0.51984500
O	-4.68538600	1.64877600	0.11436800
O	-2.32804000	-3.40513200	-0.17398300
H	-5.44790600	2.22381200	-1.07282300

O	-5.96171800	2.64321600	-1.85555200	H	-3.35686700	-3.01733400	3.07112100
C	-7.21121500	3.09509700	-1.40160500	H	-6.69783700	0.13061100	1.23518400
H	-7.86328400	3.23112700	-2.26925300	H	-7.25171300	-1.21749200	3.21406500
H	-7.68732200	2.35515900	-0.74614600	H	0.40849600	-0.36698000	-2.42682700
C	-7.08130200	4.43111200	-0.65116400	H	-1.26660000	1.21985200	-3.36177600
H	-6.45330500	4.30633100	0.23277800	H	-3.48567800	1.43537300	-2.29395500
H	-6.60981600	5.17378400	-1.29766500	O	-5.25121800	0.95917200	-0.65829200
C	-8.39394600	5.00246500	-0.19341900	O	-1.58411400	-2.52995500	1.42679000
F	-9.05405100	4.18296700	0.65937600	H	-6.79568500	1.54729600	-0.44288500
F	-9.24433800	5.24473200	-1.22032800	O	-7.69029000	1.96914900	-0.38022400
F	-8.23880500	6.18112100	0.45663900	C	-7.73707700	3.08448000	-1.24605900
Q(DFIP)				H	-6.78892700	3.63981500	-1.22740500
C	-5.30762900	-2.27141100	3.29187700	C	-7.98151000	2.59197800	-2.66961500
C	-4.07125500	-2.40656600	2.67733000	H	-7.19355700	1.90184000	-2.97157300
C	-3.74601500	-1.62629000	1.56914400	H	-8.95502400	2.10919000	-2.75777300
C	-4.67896100	-0.69923600	1.07342500	C	-8.79671500	4.05344700	-0.77017300
C	-5.91953200	-0.57139500	1.69954400	H	-8.82283400	4.94450500	-1.39836300
C	-6.23270600	-1.35201100	2.80235600	H	-8.61790600	4.33084600	0.26923200
C	-2.41139900	-1.79219200	0.93368300	F	-10.07449600	3.46556700	-0.82849100
C	-4.36066700	0.14349400	-0.10457900	F	-7.96169700	3.67617600	-3.56798200
C	-3.02980500	-0.01579000	-0.73913600	Q ² (DFIP)			
C	-2.09672000	-0.94128500	-0.24387200	C	-5.47187700	-2.23757100	3.30851300
C	-0.85496800	-1.06707000	-0.86472800	C	-4.18268100	-1.97509800	2.91946600
H	-0.14593700	-1.78390500	-0.47304300	C	-3.87291100	-1.35727500	1.67982900
C	-0.53967400	-0.28383900	-1.96554200	C	-4.96808900	-0.98628700	0.80756600
C	-1.46516400	0.63482200	-2.45707500	C	-6.29264400	-1.28338300	1.24550800
C	-2.70341500	0.76750000	-1.84679600	C	-6.54657700	-1.88678400	2.44890300
H	-5.55244500	-2.88090900	4.15266400	C	-2.49940100	-1.11866200	1.32587100
H	-3.34301800	-3.11586900	3.04693100	C	-4.74977600	-0.35615600	-0.44931300
H	-6.63549000	0.14305100	1.31797900	C	-3.39582100	-0.10736100	-0.80764800
H	-7.19753900	-1.24507200	3.28174800	C	-2.29337100	-0.47729200	0.05452800
H	0.42679200	-0.38735500	-2.44265600	C	-0.97444300	-0.18976600	-0.38336700
H	-1.21864900	1.24580100	-3.31628600	H	-0.16290600	-0.47040900	0.27740000
H	-3.43064000	1.47635800	-2.21884600	C	-0.71492700	0.41778500	-1.58597800
O	-5.16758500	0.95322200	-0.55105900	C	-1.79487000	0.77669900	-2.43546400
O	-1.60201300	-2.59910500	1.36533600	C	-3.08419600	0.51856900	-2.05043500
H	-6.84258000	1.68112300	-0.43520000	H	-5.67307200	-2.71030700	4.26383300
O	-7.72022600	2.09898400	-0.37242700	H	-3.35039300	-2.23796700	3.56161700
C	-7.80108500	3.16879600	-1.30028800	H	-7.10953300	-1.01328000	0.58785000
H	-6.86780100	3.74684500	-1.31767900	H	-7.56812100	-2.09714100	2.74829300
C	-8.04954200	2.59744200	-2.69327100	H	0.30591100	0.62330800	-1.88972600
H	-7.25212800	1.90726200	-2.97058100	H	-1.59580800	1.25545700	-3.38871200
H	-9.01411700	2.09240700	-2.74620100	H	-3.91314500	0.78813500	-2.69318600
C	-8.88295500	4.12696200	-0.85520200	O	-5.74936800	-0.03334700	-1.25785500
H	-8.93848000	4.98704600	-1.52309500	O	-1.51762400	-1.45726400	2.09550200
H	-8.70120400	4.45634300	0.16828200	H	-6.77769300	0.94537700	-0.86477300
F	-10.14133900	3.49981200	-0.87378800	O	-7.51236700	1.64808700	-0.64436600
F	-8.05848300	3.63639800	-3.64021500	C	-7.32226800	2.79071200	-1.43487500
Q ⁺ (DFIP)				H	-6.25647200	2.94382600	-1.66440600
C	-5.33234200	-2.21274700	3.27435700	C	-8.06812200	2.60198900	-2.75356000
C	-4.09685500	-2.33168300	2.67870800	H	-7.69688400	1.71855600	-3.27293800
C	-3.75315600	-1.57020600	1.54402000	H	-9.14241900	2.51389300	-2.58889600
C	-4.70980900	-0.66207000	1.00719000	C	-7.76266200	4.03523800	-0.69264900
C	-5.96924600	-0.55929500	1.63852000	H	-7.58377800	4.93581800	-1.28199200
C	-6.27863500	-1.31432400	2.74682600	H	-7.24804600	4.10420500	0.26646000
C	-2.42955200	-1.73044400	0.94980100	F	-9.14549000	3.99365000	-0.41576800
C	-4.40997500	0.14482000	-0.16183800	F	-7.86253000	3.70841600	-3.60649700
C	-3.09505200	-0.01083600	-0.75862900	Q(EG - normal)			
C	-2.13670800	-0.91592800	-0.22489000	C	-5.93775300	-3.59429800	0.45820000
C	-0.87829200	-1.02264900	-0.85011900	C	-4.56146100	-3.43544000	0.52843600
H	-0.16048700	-1.71626800	-0.43145700	C	-3.98117100	-2.19490900	0.26854600
C	-0.56472000	-0.27034300	-1.95995500	C	-4.79788200	-1.10168000	-0.06766400
C	-1.51232600	0.62676800	-2.48850400	C	-6.18145300	-1.27224100	-0.13497200
C	-2.74877200	0.74957600	-1.89680900	C	-6.74835200	-2.51086000	0.12668900
H	-5.57719900	-2.80753700	4.14651600	C	-2.50289500	-2.05532700	0.35455600

Appendix B

C	-4.20817600	0.22978300	-0.35140700
C	-2.73444800	0.37504800	-0.25826900
C	-1.91815300	-0.71687200	0.07859500
C	-0.53656100	-0.54652500	0.15568500
H	0.08026400	-1.39613300	0.41607200
C	0.03147600	0.69336000	-0.09816600
C	-0.77828500	1.77722500	-0.43237300
C	-2.15367000	1.61810600	-0.51213600
H	-6.38105200	-4.56103700	0.66142700
H	-3.91964000	-4.26746400	0.78506100
H	-6.80818000	-0.42930600	-0.39214700
H	-7.82268800	-2.63384100	0.07253700
H	1.10526000	0.81811700	-0.03632400
H	-0.33438300	2.74478200	-0.63013000
H	-2.79318100	2.45100000	-0.77117200
O	-4.90868700	1.18981000	-0.65528700
O	-1.79403200	-3.00776100	0.64301600
H	-6.65443200	1.75963600	-1.06390300
O	-7.56759000	2.02276400	-1.26833500
C	-7.90462400	3.17449600	-0.50581500
H	-8.99292200	3.26468100	-0.52308700
H	-7.59662000	3.05588200	0.54084900
C	-7.28218800	4.43998500	-1.08944500
H	-6.19022700	4.34711400	-1.11059000
H	-7.62791500	4.57898200	-2.11505900
O	-7.67803700	5.60966900	-0.37235400
H	-7.27448300	5.59073600	0.50280100

Q⁺(EG - normal)

C	-5.95567700	-3.54547700	0.48090100
C	-4.58987000	-3.38681800	0.54999000
C	-3.98121000	-2.14472300	0.27962800
C	-4.80319000	-1.03689500	-0.07340700
C	-6.20150200	-1.22678300	-0.13602100
C	-6.76990200	-2.45086700	0.13426000
C	-2.52949400	-2.02449600	0.36874300
C	-4.23095300	0.26624600	-0.36418400
C	-2.78615700	0.39278600	-0.27236300
C	-1.96237400	-0.71160600	0.08036400
C	-0.56699100	-0.52576600	0.15043300
H	0.04534200	-1.37677200	0.42012900
C	0.00591900	0.69791400	-0.11452900
C	-0.80874300	1.79207100	-0.46317100
C	-2.17415500	1.63687000	-0.53900400
H	-6.40437200	-4.50900400	0.69247400
H	-3.94911300	-4.21786900	0.81560800
H	-6.82677700	-0.38512900	-0.40270400
H	-7.84549200	-2.57293800	0.08022700
H	1.08105000	0.82077500	-0.05538900
H	-0.35889100	2.75590400	-0.67149300
H	-2.81082600	2.47011500	-0.80653700
O	-4.94866000	1.26406900	-0.68578500
O	-1.80328300	-3.00362800	0.67961200
H	-6.55105200	1.68857400	-1.12517400
O	-7.45584800	1.98697800	-1.37812900
C	-7.83272900	3.07611300	-0.55455300
H	-8.92343100	3.15133200	-0.57777800
H	-7.53587900	2.90245600	0.48863600
C	-7.23020500	4.39080300	-1.04412600
H	-6.13663900	4.32154900	-1.05253000
H	-7.56330100	4.58941800	-2.06426100
O	-7.66175700	5.50587600	-0.26051500
H	-7.28798000	5.42640100	0.62448200

Q²-(EG - normal)

C	-6.17813800	-3.23150000	0.63730600
C	-4.82377900	-3.22693000	0.41745500

C	-4.08255600	-2.02683900	0.25776700
C	-4.79693900	-0.76878800	0.32666500
C	-6.20192500	-0.81685400	0.56377000
C	-6.87880900	-1.99847800	0.71480700
C	-2.66361000	-2.08898600	0.03390000
C	-4.13876600	0.48457000	0.16965600
C	-2.73304100	0.43391000	-0.05635700
C	-2.00880600	-0.81830300	-0.12147500
C	-0.60799400	-0.77115100	-0.34817100
H	-0.08388300	-1.71852000	-0.39556000
C	0.07223900	0.41015400	-0.50347200
C	-0.63631300	1.63935000	-0.43860900
C	-1.98969000	1.63855400	-0.22365600
H	-6.71325100	-4.16798800	0.75313100
H	-4.27372900	-4.15864500	0.35849400
H	-6.72784400	0.12832900	0.62165600
H	-7.94917000	-1.99575100	0.89327900
H	1.14341000	0.40978200	-0.67480100
H	-0.10369100	2.57691100	-0.56046100
H	-2.53806700	2.57128200	-0.17407100
O	-4.79112600	1.63187000	0.24107100
O	-2.02046600	-3.21013100	-0.02532700
H	-5.54863600	2.17464100	-0.99019100
O	-6.04161200	2.56018200	-1.79676500
C	-7.34988300	2.92063400	-1.41987300
H	-7.97064000	2.97867000	-2.32087400
H	-7.79981600	2.15967100	-0.76439500
C	-7.38674400	4.27259100	-0.70899600
H	-6.75023000	4.24224100	0.18265100
H	-6.99992000	5.04842800	-1.37246600
O	-8.71780600	4.67324000	-0.36615700
H	-9.06291400	4.06133300	0.29390300

Q(EG - bidentate)

C	-6.00628700	-3.59249400	0.19990000
C	-4.62300200	-3.52721000	0.11362400
C	-3.97862000	-2.29301600	0.05522300
C	-4.73740000	-1.11040500	0.08288600
C	-6.12797300	-1.18752900	0.17397400
C	-6.75943300	-2.42098200	0.23107100
C	-2.49488600	-2.25308600	-0.03142000
C	-4.08057100	0.21594600	0.02310300
C	-2.60253300	0.26390400	-0.05924500
C	-1.84248800	-0.91796700	-0.08384600
C	-0.45334500	-0.84320600	-0.16304500
H	0.11784700	-1.76150800	-0.18140100
C	0.18044400	0.38985900	-0.21781900
C	-0.57177200	1.56219800	-0.19727100
C	-1.95503500	1.49888900	-0.11978100
H	-6.49952900	-4.55532600	0.24462400
H	-4.02582500	-4.42880600	0.09152500
H	-6.70824300	-0.27592100	0.20289800
H	-7.83864000	-2.47120300	0.30075000
H	1.26035600	0.43969500	-0.27797300
H	-0.07818200	2.52468300	-0.24281100
H	-2.54265900	2.40615700	-0.10852800
O	-4.74565600	1.25058800	0.04141600
O	-1.83511000	-3.28066900	-0.05799800
H	-4.75329700	3.19122700	0.39459800
H	-6.49816700	2.03229500	-0.39010100
O	-7.34283600	2.50714400	-0.38246800
O	-4.83910200	4.15442600	0.33400200
C	-7.11265100	3.90111800	-0.58350000
C	-6.21101000	4.52483400	0.46700700
H	-8.09404000	4.37859400	-0.53604500
H	-6.24143900	5.61147500	0.35936300
H	-6.69353900	4.08386800	-1.58076800
H	-6.58432100	4.27129300	1.46694300

$Q^-(EG - bidentate)$							
C	-6.01060600	-3.57826400	0.20985200	H	-7.34477400	4.33272600	-1.36464800
C	-4.64192000	-3.49601100	0.08072200	H	-6.14195000	5.43718500	0.37012600
C	-3.98399400	-2.25139600	0.04599500	H	-5.62533200	3.99880400	-1.62076600
C	-4.75523900	-1.05984500	0.14360600	H	-6.98894700	4.06810300	1.10715100
C	-6.15679500	-1.17205700	0.28048000	$Q(EG)_2$			
C	-6.77497800	-2.40122900	0.31254700	C	-6.23175600	-3.67743800	0.28961000
C	-2.53013900	-2.21096600	-0.08532100	C	-4.84680100	-3.58869300	0.26450200
C	-4.13074800	0.24762800	0.11200500	C	-4.22718600	-2.34869200	0.11142200
C	-2.68854900	0.30005500	-0.01724400	C	-5.01106800	-1.18866800	-0.02291400
C	-1.91109700	-0.88834100	-0.11174000	C	-6.40176700	-1.29187500	0.00617200
C	-0.51257100	-0.78222400	-0.23722100	C	-7.00955900	-2.52923200	0.16243200
H	0.06111400	-1.69724800	-0.30871700	C	-2.74470300	-2.27660200	0.09352300
C	0.11200900	0.44473500	-0.27026400	C	-4.38016600	0.14245000	-0.19868600
C	-0.65455900	1.62124800	-0.18002200	C	-2.89853200	0.21432100	-0.22027100
C	-2.02328300	1.54582600	-0.05766900	C	-2.11538800	-0.94313900	-0.08120600
H	-6.49908100	-4.54522000	0.23452000	C	-0.72496000	-0.84176700	-0.10509200
H	-4.03862800	-4.39140700	0.00370000	H	-0.13376600	-1.74089900	0.00363600
H	-6.74152500	-0.26597200	0.36477900	C	-0.11591400	0.39427500	-0.26553200
H	-7.85177000	-2.46372800	0.41805100	C	-0.89281200	1.54275400	-0.40411200
H	1.18957100	0.50615600	-0.36660000	C	-2.27680100	1.45242400	-0.38167200
H	-0.16590300	2.58816400	-0.20845500	H	-6.70710800	-4.64309000	0.40871500
H	-2.61219600	2.45057700	0.00693700	H	-4.23891200	-4.47928800	0.35812700
O	-4.83032000	1.31341800	0.19776300	H	-7.00169600	-0.39791200	-0.09339400
O	-1.84662800	-3.26054000	-0.16941900	H	-8.08980300	-2.59971100	0.18377500
H	-4.72072900	3.06740400	0.47993900	H	0.96434700	0.46532500	-0.28283500
H	-6.39338700	1.94505100	-0.36062400	H	-0.41691100	2.50716600	-0.52954400
O	-7.21968200	2.43670400	-0.55069500	H	-2.89106800	2.33618000	-0.48847800
O	-4.79271500	4.04400800	0.51480200	O	-5.05326600	1.15973100	-0.32579200
C	-6.92562100	3.82031700	-0.70770800	O	-2.05572600	-3.28075000	0.22052600
C	-6.16399900	4.42300200	0.46265300	H	-6.78090000	1.87156900	-0.53955200
H	-7.88772500	4.33163300	-0.80097500	O	-7.68700400	2.20862400	-0.63870600
H	-6.17949700	5.51240400	0.36899800	C	-7.73276100	3.56484200	-0.21407500
H	-6.36109900	3.99569100	-1.63379200	H	-8.78472600	3.82136900	-0.07156800
H	-6.67665500	4.15929300	1.39800400	H	-7.22510700	3.69099200	0.75070300
$Q^2(EG - bidentate)$				C	-7.11813600	4.50226100	-1.24994000
C	-5.99947500	-3.63227700	0.24979100	H	-6.07132300	4.23070700	-1.42890500
C	-4.65286400	-3.49903100	0.02259200	H	-7.65627200	4.40830800	-2.19456300
C	-4.00219500	-2.23840000	0.03144000	O	-7.22768900	5.87229400	-0.86257100
C	-4.79831700	-1.05759500	0.28574200	H	-6.65819400	6.02804700	-0.10057400
C	-6.19400300	-1.23823600	0.52071100	O	-0.88133500	-5.83372700	0.91640000
C	-6.78179300	-2.47561600	0.50616900	H	-1.48130700	-5.11156700	0.67701400
C	-2.58508100	-2.16600400	-0.20792700	C	-1.60517500	-6.86143100	1.58090900
C	-4.22726600	0.24346700	0.30662000	H	-0.86394900	-7.54184600	2.00556700
C	-2.82999800	0.33380700	0.06853300	H	-2.19439600	-6.44817800	2.40860800
C	-2.02142500	-0.84220700	-0.18052200	C	-2.51223300	-7.64919800	0.66114200
C	-0.63115100	-0.66685000	-0.40376300	H	-1.94011800	-8.01168600	-0.19959900
H	-0.04212000	-1.55825200	-0.58494700	H	-2.91039600	-8.51432800	1.20528800
C	-0.03492700	0.56878500	-0.39465600	O	-3.57582400	-6.79483900	0.22990400
C	-0.82554500	1.72328700	-0.15528600	H	-4.07710500	-7.24126900	-0.46069000
C	-2.17174100	1.60039200	0.06662800	$Q^+(EG)_2$			
H	-6.46614100	-4.61128400	0.23549600	C	-5.58290100	-3.71717900	-0.10497000
H	-4.03870200	-4.37012000	-0.17311400	C	-4.23730400	-3.43147200	-0.06112800
H	-6.78843200	-0.35429200	0.71590000	C	-3.77118400	-2.10045300	-0.05805300
H	-7.84663200	-2.57444400	0.68993900	C	-4.71934100	-1.04016800	-0.10378700
H	1.03113500	0.66712700	-0.56857800	C	-6.09305300	-1.36107100	-0.14572100
H	-0.36111000	2.70395100	-0.14915800	C	-6.52141300	-2.66922800	-0.14670000
H	-2.77106900	2.48390200	0.24526500	C	-2.34017300	-1.84352800	-0.00596800
O	-4.97677000	1.31481800	0.54801100	C	-4.29425100	0.34952100	-0.10503600
O	-1.87022400	-3.21714500	-0.43247700	C	-2.86363700	0.60666600	-0.05043800
H	-4.84241800	2.93278100	0.85346900	C	-1.91546600	-0.45345800	-0.00380000
H	-6.11066100	1.90815600	-0.45745500	C	-0.54192200	-0.13315800	0.04326700
O	-6.80945900	2.41320300	-0.97042400	H	0.17680000	-0.94115500	0.07604500
O	-4.91772600	3.92270800	0.94404900	C	-0.11333600	1.17495600	0.04677400
C	-6.48145700	3.79347100	-0.96042600	C	-1.05163000	2.22298000	0.00212300
C	-6.17037600	4.34394400	0.42540300	C	-2.39716400	1.93768000	-0.04579700

Appendix B

H	-5.92112200	-4.74673200	-0.10645600
H	-3.50384200	-4.22632500	-0.02687700
H	-6.81281200	-0.55400200	-0.17467200
H	-7.58120000	-2.89319300	-0.17901500
H	0.94633000	1.39878800	0.08341500
H	-0.71327000	3.25249900	0.00502800
H	-3.13007600	2.73291100	-0.08165400
O	-5.12174900	1.30775200	-0.15078700
O	-1.51272800	-2.80118600	0.03726200
H	-6.77661700	1.67066300	-0.47220500
O	-7.70809000	1.94875800	-0.62657600
C	-7.86589200	3.29233400	-0.20397500
H	-8.93423100	3.47105100	-0.05517700
H	-7.36524000	3.46339900	0.75844700
C	-7.33215700	4.27842900	-1.24042400
H	-6.26963400	4.08681800	-1.42750900
H	-7.86872700	4.14803600	-2.18182500
O	-7.54116200	5.63713000	-0.84840300
H	-6.98241800	5.82987500	-0.08692500
O	1.10555900	-3.49931300	0.24135400
H	0.17634900	-3.18840600	0.16539800
C	1.36754800	-4.40937700	-0.81400900
H	0.68607900	-5.26929900	-0.76835800
H	1.22969800	-3.92722700	-1.79121700
C	2.77965300	-4.93343900	-0.71773800
H	2.95840600	-5.31894400	0.29253500
H	2.89656700	-5.75988500	-1.42848300
O	3.70272500	-3.88313200	-1.02072000
H	4.59834300	-4.21545900	-0.89897200

$Q^2(EG)_2$

C	-5.77182400	-3.98983300	0.73919400
C	-4.44292000	-3.65692500	0.77758500
C	-4.00143400	-2.30896100	0.88985000
C	-5.00470000	-1.26856400	0.95426800
C	-6.37340000	-1.65795100	0.91325200
C	-6.75703700	-2.96931000	0.81211500
C	-2.60368900	-2.01537100	0.93730600
C	-4.65530500	0.11040200	1.06191800
C	-3.26059700	0.40456400	1.11655600
C	-2.25445100	-0.63492400	1.05440100
C	-0.88726100	-0.24421000	1.11814400
H	-0.13902100	-1.02547300	1.06991500
C	-0.50607300	1.06698600	1.23427600
C	-1.49299600	2.08629900	1.29804600
C	-2.82055600	1.75296300	1.24126200
H	-6.07413900	-5.02816400	0.65386300
H	-3.68231100	-4.42623800	0.72348500
H	-7.11597200	-0.87139300	0.96721900
H	-7.80952000	-3.23107900	0.78585800
H	0.54568500	1.32852800	1.28026200
H	-1.19280900	3.12445300	1.39325500
H	-3.58229900	2.52114600	1.29353700
O	-5.56636400	1.05732200	1.11843700
O	-1.70508100	-2.96788200	0.89070700
H	-6.36520000	1.45176700	-0.16144800
O	-6.92004700	1.75080000	-0.95882600
C	-6.33695300	2.89620400	-1.53788300
H	-7.11715700	3.46205900	-2.05900900
H	-5.91383300	3.55839200	-0.76820600
C	-5.24153500	2.53323900	-2.53881600
H	-4.46311100	1.94272900	-2.04274100
H	-5.66295800	1.92695200	-3.34287100
O	-4.67618500	3.68774200	-3.16869800
H	-4.20435600	4.20060400	-2.50275900
O	0.50072000	-3.25378500	-0.44518800
H	-0.35641800	-3.07290600	0.05503200
C	0.37096400	-2.78535700	-1.76892100

H	-0.48294500	-3.25870300	-2.27591900
H	0.20090700	-1.69862300	-1.79200300
C	1.60850100	-3.09895100	-2.57674400
H	1.84873900	-4.16402200	-2.47918100
H	1.40560900	-2.88562600	-3.63308900
O	2.70318900	-2.29937900	-2.11367700
H	3.49645600	-2.55606000	-2.59549100

$Q(PD - normal)$

C	-5.91325600	-3.60195900	0.53438600
C	-4.53640300	-3.43810700	0.57486500
C	-3.96598500	-2.19720200	0.29514500
C	-4.79331300	-1.10911800	-0.03127300
C	-6.17738100	-1.28457700	-0.06873800
C	-6.73434700	-2.52333500	0.21292300
C	-2.48682500	-2.05180200	0.35017300
C	-4.21457500	0.22288300	-0.33627300
C	-2.73966600	0.37452800	-0.27045000
C	-1.91280900	-0.71239700	0.05663000
C	-0.53065800	-0.53616100	0.10703200
H	0.09442100	-1.38196800	0.36002600
C	0.02745500	0.70470700	-0.16334900
C	-0.79287700	1.78368200	-0.48752800
C	-2.16884300	1.61862200	-0.54100200
H	-6.34892500	-4.56877000	0.75321900
H	-3.88646600	-4.26627000	0.82346200
H	-6.81178400	-0.44490000	-0.31785500
H	-7.80917100	-2.65024700	0.18228900
H	1.10168600	0.83408500	-0.12206700
H	-0.35672400	2.75210600	-0.69793100
H	-2.81664500	2.44767700	-0.79168100
O	-4.92490100	1.17662900	-0.63533000
O	-1.76862200	-3.00038600	0.62834400
H	-6.70570800	1.73671600	-1.02692400
O	-7.62958100	1.96697000	-1.21787500
C	-7.93732300	3.21335000	-0.59475000
H	-9.02546500	3.31242700	-0.63442000
H	-7.64719900	3.19300500	0.46038600
C	-7.28666300	4.39756600	-1.30424400
H	-6.19687100	4.29417500	-1.27334500
H	-7.58174900	4.38199000	-2.35795900
C	-7.67608900	5.74398000	-0.72035300
H	-7.27472700	6.54907500	-1.34505900
H	-8.76817400	5.84694800	-0.70086800
O	-7.15119100	5.84683400	0.60993900
H	-7.40847700	6.69899100	0.97782900

$Q^-(PD - normal)$

C	-5.90304200	-3.61222800	0.51416800
C	-4.53968400	-3.42708000	0.56153400
C	-3.96014600	-2.17124500	0.28972900
C	-4.80985900	-1.07778700	-0.04160500
C	-6.20483100	-1.29478100	-0.08197700
C	-6.74456700	-2.53163100	0.18906100
C	-2.51002100	-2.02268100	0.35488600
C	-4.26910700	0.23899800	-0.33388000
C	-2.82518500	0.39307100	-0.26623400
C	-1.97403200	-0.69730700	0.06475300
C	-0.58142500	-0.48444000	0.11137600
H	0.05204000	-1.32507500	0.36416100
C	-0.03731000	0.75190200	-0.15526000
C	-0.87919700	1.83224200	-0.48186400
C	-2.24244500	1.65061100	-0.53485900
H	-6.32901000	-4.58591100	0.72632600
H	-3.87819500	-4.24700300	0.81051600
H	-6.85032000	-0.46295200	-0.33053200
H	-7.81832300	-2.67455600	0.15243700

H	1.03611700	0.89541200	-0.11410800	C	-2.68459000	0.38931500	0.01233400
H	-0.45204400	2.80619400	-0.69090800	C	-1.92063600	-0.79049600	0.01564500
H	-2.90012800	2.47299300	-0.78475500	C	-0.52981200	-0.71214200	0.04368200
O	-5.01236200	1.22250000	-0.63715500	H	0.04385600	-1.62909100	0.04558000
O	-1.75916600	-2.98925200	0.64761300	C	0.10258500	0.52257200	0.07012000
H	-6.66437500	1.65249500	-0.98528000	C	-0.65300900	1.69278600	0.07153800
O	-7.58495400	1.92754000	-1.19438700	C	-2.03808800	1.62620100	0.04380700
C	-7.85618900	3.17377100	-0.56586600	H	-6.57431400	-4.44479300	-0.08388300
H	-8.94480500	3.28816000	-0.54951900	H	-4.09658700	-4.30835400	-0.04129800
H	-7.51476400	3.16018800	0.47471800	H	-6.79795500	-0.16627500	-0.06917600
C	-7.23431700	4.35450400	-1.30955300	H	-7.92208000	-2.36538800	-0.09878600
H	-6.14432600	4.25250200	-1.31885000	H	1.18383700	0.57516900	0.09141700
H	-7.56857900	4.32711800	-2.35161400	H	-0.16065900	2.65671600	0.09518800
C	-7.60601400	5.70673700	-0.72829800	H	-2.62677500	2.53304600	0.04829000
H	-7.22925900	6.50631400	-1.37536400	O	-4.83340300	1.37029300	-0.02500200
H	-8.69718500	5.80735700	-0.67150500	O	-1.90667600	-3.15315100	-0.00366400
O	-7.03605400	5.82824800	0.58234600	H	-4.67890800	3.22868700	-0.70132000
H	-7.28276400	6.68482000	0.94712000	H	-6.59702400	2.01435000	0.61312400
Q ² -(PD - normal)				O	-7.45638000	2.44843900	0.71733400
C	-6.61142700	-2.89974600	0.61161800	O	-4.71386700	4.19014800	-0.81119700
C	-5.27946700	-3.08466000	0.33971700	C	-7.61130300	3.38759800	-0.35057800
C	-4.37436300	-2.00033900	0.19361000	C	-5.50061000	4.72896500	0.25522600
C	-4.89262400	-0.65498000	0.33457100	H	-8.68540700	3.50321500	-0.51020400
C	-6.28080200	-0.50634200	0.62166600	H	-5.14927400	5.75012700	0.41759500
C	-7.11959300	-1.58144000	0.75745100	H	-7.18925500	2.97473000	-1.27278100
C	-2.98846000	-2.26097600	-0.08631900	H	-5.30986200	4.16946700	1.17674700
C	-4.06111600	0.49467100	0.20009500	C	-6.99582100	4.75146700	-0.04944000
C	-2.68563300	0.24633300	-0.07879000	H	-7.18068300	5.40429600	-0.90965500
C	-2.15781300	-1.09518400	-0.21923000	H	-7.50930300	5.19863500	0.80898400
C	-0.77333000	-1.24269800	-0.49810000	Q ² -(PD - bidentate)			
H	-0.39429000	-2.25229800	-0.60377800	C	-6.09144900	-3.43607500	-0.12201500
C	0.06865900	-0.16777700	-0.63262700	C	-4.71662200	-3.36720600	-0.08427100
C	-0.44665400	1.14813200	-0.49011600	C	-4.04661400	-2.12911400	-0.04257500
C	-1.77761400	1.33531700	-0.22339300	C	-4.81213300	-0.92946100	-0.03871100
H	-7.27470300	-3.75171100	0.71666800	C	-6.22088600	-1.02800000	-0.08129200
H	-4.87500500	-4.08362900	0.22739900	C	-6.85046900	-2.25115900	-0.12116900
H	-6.66062900	0.50193600	0.73269700	C	-2.58704200	-2.10434000	-0.00786200
H	-8.17134600	-1.42898900	0.97679400	C	-4.17453200	0.37185900	-0.00019600
H	1.12157500	-0.31784900	-0.84637800	C	-2.72588200	0.40771100	0.03419600
H	0.21520300	2.00182400	-0.59328300	C	-1.95499400	-0.78846800	0.03033700
H	-2.18050800	2.33468400	-0.11236900	C	-0.55022900	-0.69656800	0.06775500
O	-4.53408200	1.71919400	0.33757700	H	0.01872500	-1.61732400	0.06477000
O	-2.52108400	-3.46227500	-0.20923000	C	0.08631600	0.52391300	0.10844700
H	-5.01905200	2.52884400	-0.91871000	C	-0.67380600	1.70812500	0.11542800
O	-5.31926600	3.06982800	-1.72323000	C	-2.04819000	1.64665900	0.08004900
C	-6.64775900	3.51310300	-1.52678400	H	-6.58886000	-4.39827500	-0.15379300
H	-7.05341600	3.78858200	-2.50783900	H	-4.11736300	-4.26853400	-0.08702900
H	-7.27389600	2.70066400	-1.13798100	H	-6.80310000	-0.11648100	-0.08204500
C	-6.73620300	4.72463700	-0.59599900	H	-7.93257500	-2.30261600	-0.15282000
H	-6.34302300	4.45911300	0.39070000	H	1.16840500	0.57432600	0.13635700
H	-6.09427300	5.51775000	-0.99345500	H	-0.17533000	2.66986600	0.14990000
C	-8.13811600	5.28563100	-0.44130200	H	-2.63379500	2.55601900	0.08713700
H	-8.10472700	6.22533200	0.12119300	O	-4.86395600	1.44829700	0.00355500
H	-8.57130500	5.50043700	-1.42646400	O	-1.90942500	-3.16155100	-0.01093200
O	-8.95552400	4.33170300	0.25244200	H	-4.69544400	3.10586000	-0.67809600
H	-9.84416200	4.69292600	0.33855400	H	-6.46122300	1.98148900	0.63835600
Q(PD - bidentate)				O	-7.31726200	2.41632800	0.83086800
C	-6.08319000	-3.47994700	-0.06947400	O	-4.74833900	4.05803500	-0.90043900
C	-4.69774400	-3.40914500	-0.04488500	C	-7.59676100	3.30869400	-0.24569000
C	-4.05603400	-2.17238800	-0.02545300	C	-5.47025100	4.70357400	0.14633200
C	-4.81932000	-0.99217200	-0.03044200	H	-8.68395700	3.40236800	-0.31294400
C	-6.21237500	-1.07498700	-0.05948700	H	-5.11887600	5.73791800	0.19036200
C	-6.84100700	-2.31118500	-0.07753700	H	-7.25025100	2.87185800	-1.18834400
C	-2.57027700	-2.12769400	-0.00465600	H	-5.22562200	4.23714300	1.10670200
C	-4.16472900	0.33683100	-0.01518400	C	-6.98403100	4.69626500	-0.06242200
				H	-7.23406200	5.29536600	-0.94569500
				H	-7.44679300	5.18934300	0.80029900

$Q^2(\text{PD} - \text{bidentate})$							
C	-6.06304600	-3.48196700	-0.22911200	H	-8.73683300	3.95462400	-0.20661800
C	-4.70018500	-3.38138500	-0.10659600	H	-7.19966900	3.83659800	0.65039800
C	-4.03122100	-2.13081300	-0.06159200	C	-7.00911600	4.34061500	-1.44683300
C	-4.82742300	-0.92484400	-0.14444100	H	-5.98107700	3.97634300	-1.54088800
C	-6.24076200	-1.07199800	-0.27261600	H	-7.52524400	4.10807800	-2.38306200
C	-6.84569000	-2.30041300	-0.31505500	O	-0.81268300	-5.72935800	1.63780400
C	-2.59805500	-2.09368500	0.06186200	H	-1.34080100	-4.97580700	1.33421100
C	-4.23783400	0.36766000	-0.10508300	C	-1.64988300	-6.87827500	1.73705100
C	-2.82339900	0.42139500	0.01893200	H	-1.05457600	-7.64051800	2.24552400
C	-2.01611000	-0.77817500	0.09766200	H	-2.51691900	-6.66313000	2.37383800
C	-0.60931900	-0.63363200	0.21606800	C	-2.11019200	-7.39267200	0.37616500
H	-0.02092700	-1.54195100	0.27169700	H	-1.23357300	-7.60583200	-0.24272800
C	0.00227900	0.59375500	0.26134700	C	-6.98551500	5.84518200	-1.24575500
C	-0.78782800	1.77126600	0.18828000	C	-2.96092200	-8.64472600	0.49256000
C	-2.14947800	1.67804100	0.07065900	H	-2.68789300	-6.61408500	-0.13252000
H	-6.54261900	-4.45434200	-0.26087400	H	-8.00786200	6.23428700	-1.17002300
H	-4.08677500	-4.27218900	-0.04061800	H	-6.46107600	6.09755900	-0.31654600
H	-6.83529000	-0.16931700	-0.33561200	H	-2.39347500	-9.44507400	0.98217000
H	-7.92383800	-2.37319800	-0.41381300	H	-3.85145100	-8.44523200	1.10032200
H	1.08056000	0.66832700	0.35217500	O	-6.31581600	6.43958300	-2.36352600
H	-0.31009400	2.74486500	0.22536100	H	-6.29852000	7.39488300	-2.24047100
H	-2.75379600	2.57450800	0.01094500	O	-3.34755200	-9.05255700	-0.82465600
O	-4.97538100	1.46916300	-0.18393700	H	-3.89055600	-9.84526700	-0.75514700
O	-1.88459300	-3.16771800	0.13558500	$Q^*(\text{PD})_2$			
H	-4.85496200	2.93952000	-0.92147400	C	-5.60949600	-3.71339700	-0.15073600
H	-6.24112700	2.00664100	0.71520900	C	-4.26398500	-3.42569000	-0.11948400
O	-7.02469100	2.48131800	1.11604800	C	-3.79996400	-2.09384500	-0.11207700
O	-4.91822400	3.88684900	-1.23011700	C	-4.75047200	-1.03502600	-0.13837000
C	-7.55427300	3.33073000	0.10863800	C	-6.12380400	-1.35803100	-0.16929200
C	-5.35854700	4.66089600	-0.12362400	C	-6.55021800	-2.66683000	-0.17556600
H	-8.62056900	3.46995900	0.31535700	C	-2.36887400	-1.83485900	-0.07651900
H	-4.98869200	5.68193700	-0.26358100	C	-4.32851700	0.35619200	-0.13304800
H	-7.47684100	2.83901500	-0.86795400	C	-2.89710400	0.61494500	-0.09849400
H	-4.90674400	4.27828800	0.79894000	C	-1.94680200	-0.44401300	-0.07177700
C	-6.88020800	4.70278700	0.03756300	C	-0.57318300	-0.12155200	-0.04153200
H	-7.32336800	5.25322000	-0.80131700	H	0.14675500	-0.92895100	-0.02301400
H	-7.10760800	5.27133300	0.94759900	C	-0.14663000	1.18720000	-0.03627300
$Q(\text{PD})_2$				C	-1.08710200	2.23402700	-0.06158300
C	-6.34971100	-3.61347600	1.15683100	C	-2.43271400	1.94657600	-0.09211100
C	-4.96744300	-3.55031400	1.05794500	H	-5.94599300	-4.74351800	-0.15594400
C	-4.34123400	-2.36201600	0.68442100	H	-3.52878000	-4.21942100	-0.09935000
C	-5.11845700	-1.22402400	0.40669400	H	-6.84448800	-0.55155400	-0.18671800
C	-6.50738800	-1.29842600	0.50989600	H	-7.60989900	-2.89236100	-0.19939700
C	-7.12030000	-2.48598200	0.88269100	H	0.91309900	1.41268400	-0.01273000
C	-2.86057300	-2.32151500	0.58655900	H	-0.75037200	3.26408400	-0.05710300
C	-4.48090500	0.05495100	0.00629800	H	-3.16766200	2.74050300	-0.11228000
C	-3.00039400	0.09707200	-0.08469900	O	-5.15847500	1.31189500	-0.15804300
C	-2.22425800	-1.04023800	0.19307000	O	-1.53889200	-2.79116900	-0.05042400
C	-0.83497800	-0.96737700	0.09799800	H	-6.86453300	1.70488900	-0.24586600
H	-0.24893300	-1.85039600	0.31411100	O	-7.80775300	1.97729800	-0.26811900
C	-0.22007900	0.22101800	-0.26825600	C	-7.88973400	3.38010400	-0.05136400
C	-0.98986300	1.34935800	-0.54379800	H	-8.94453800	3.60993700	0.10938600
C	-2.37267700	1.28686900	-0.45249000	H	-7.35120900	3.65955600	0.86476900
H	-6.82840800	-4.54014400	1.44723300	C	-7.34891000	4.19128400	-1.22729200
H	-4.35858400	-4.41891300	1.26845900	H	-6.30176600	3.92022600	-1.39527100
H	-7.10119600	-0.42004400	0.29789300	H	-7.89964100	3.92691200	-2.13576200
H	-8.19911100	-2.53428300	0.96012800	O	1.08738300	-3.48393300	0.15017900
H	0.85912900	0.27042600	-0.33975900	H	0.15581200	-3.18087100	0.07682600
H	-0.50945500	2.27661000	-0.82958000	C	1.35986900	-4.38489900	-0.91604600
H	-2.98135400	2.15557500	-0.66373500	H	0.66790500	-5.23574500	-0.88566400
O	-5.14844700	1.05201000	-0.24367900	H	1.21897500	-3.88485500	-1.88467500
O	-2.18229300	-3.31298600	0.82366800	C	2.78635900	-4.89956400	-0.80667700
H	-6.87651000	1.83150300	-0.43261100	H	2.92350200	-5.38561300	0.16452200
O	-7.77038700	2.20431000	-0.50170600	H	2.93950000	-5.66350500	-1.57571200
C	-7.70287100	3.61332300	-0.29865300	C	-7.41830700	5.69252800	-1.01406200
				C	3.83167000	-3.81242800	-0.97880200
				H	-6.91737500	6.20914600	-1.83993800

H	-6.90419000	5.96801900	-0.08489100
H	3.69671500	-3.31358000	-1.94663600
H	3.73269100	-3.05877400	-0.19257700
O	5.12871600	-4.42178700	-0.91720800
H	5.79670600	-3.72938900	-0.96209800
O	-8.79407200	6.09309800	-0.94794000
H	-8.83129500	7.04395700	-0.79928500

 $Q^2(\text{PD})_2$

C	-5.68665000	-4.07219900	0.80956000
C	-4.36286100	-3.72123900	0.86170500
C	-3.93952500	-2.36413800	0.92366600
C	-4.95645500	-1.33479700	0.92107300
C	-6.31894800	-1.74261500	0.86671200
C	-6.68524200	-3.06201400	0.81471900
C	-2.54686300	-2.05172500	0.98819600
C	-4.62624300	0.05288200	0.97728100
C	-3.23511200	0.36541700	1.04343600
C	-2.21651000	-0.66350500	1.05250800
C	-0.85579600	-0.25321100	1.13329500
H	-0.09866100	-1.02728700	1.14258700
C	-0.49266300	1.06685600	1.19439500
C	-1.49200900	2.07609100	1.18075000
C	-2.81398200	1.72336100	1.10985500
H	-5.97484200	-5.11708800	0.76395800
H	-3.59180300	-4.48204500	0.85842100
H	-7.07110200	-0.96323300	0.86904600
H	-7.73369400	-3.33805200	0.77591300
H	0.55456900	1.34353900	1.25502300
H	-1.20592000	3.12143900	1.22882000
H	-3.58671600	2.48218900	1.10365300
O	-5.54750600	0.98838200	0.98258600
O	-1.63484800	-2.99363500	1.00054000
H	-6.34347000	1.37620500	-0.33404700
O	-6.89370900	1.64799700	-1.13673000
C	-6.48346700	2.92649000	-1.58417300
H	-7.31417100	3.35923300	-2.15476100
H	-6.29782800	3.59218800	-0.73309300
C	-5.24397100	2.87187200	-2.47899900
H	-4.39696200	2.47153700	-1.91246000
H	-5.43809100	2.17481000	-3.30086200
O	0.56637700	-3.27465400	-0.35482400
H	-0.28956700	-3.10224200	0.14954200
C	0.39057000	-2.90233500	-1.70788900
H	-0.44818500	-3.45170300	-2.15785800
H	0.14912200	-1.83126200	-1.78734400
C	1.65307300	-3.19564800	-2.50686500
H	1.89220700	-4.26134300	-2.42949500
H	1.45719500	-2.98294100	-3.56310200
C	2.84951100	-2.37833800	-2.05594100
C	-4.85838500	4.21189000	-3.07879300
H	-4.04578000	4.07795400	-3.80134600
H	-5.71289600	4.64754300	-3.61215500
H	2.61758500	-1.30795100	-2.12133900
H	3.09864600	-2.60777900	-1.01627700
O	-4.43760300	5.09673500	-2.03015300
H	-4.19431300	5.94275400	-2.42087300
O	3.96081200	-2.69152100	-2.90911400
H	4.73760300	-2.22256600	-2.58609300

 $Q(\text{BD} - \text{normal})$

C	-5.86255200	-3.65514000	0.51724400
C	-4.48821600	-3.46715300	0.52120900
C	-3.94858000	-2.20717900	0.26685200
C	-4.80449900	-1.12410000	0.00328200
C	-6.18577800	-1.32394900	0.00257600
C	-6.71195000	-2.58163600	0.25845600

C	-2.47127600	-2.03636400	0.28204400
C	-4.25871200	0.22789000	-0.27363600
C	-2.78530700	0.40437500	-0.24768200
C	-1.92998600	-0.67746900	0.01717500
C	-0.55021300	-0.47772000	0.03169400
H	0.09683900	-1.31997400	0.23674400
C	-0.02219000	0.78146400	-0.21321600
C	-0.87068700	1.85536900	-0.47589900
C	-2.24456600	1.66694700	-0.49334100
H	-6.27414100	-4.63675200	0.71583300
H	-3.81647000	-4.29099700	0.72141900
H	-6.84271900	-0.48853000	-0.19701400
H	-7.78484200	-2.72717400	0.25636900
H	1.05040200	0.92902500	-0.19986000
H	-0.45808200	2.83809100	-0.66656400
H	-2.91387800	2.49188500	-0.69648500
O	-4.99450700	1.17799700	-0.51814500
O	-1.72830100	-2.98019700	0.50600100
H	-6.80273600	1.70140700	-0.83347500
O	-7.74431700	1.89441600	-0.97236400
C	-8.02607700	3.21143600	-0.50399000
H	-9.11543300	3.29831100	-0.48329000
H	-7.66930100	3.33334200	0.52649300
C	-7.43421700	4.29944300	-1.39365600
H	-6.34525800	4.18192100	-1.42381200
H	-7.79784600	4.15123600	-2.41580600
C	-7.79050100	5.70579900	-0.90879000
H	-8.87881000	5.82403700	-0.87649200
H	-7.42490100	5.85346800	0.11289300
C	-7.20807900	6.78971200	-1.79662500
H	-6.11500200	6.70789200	-1.82542500
H	-7.58052700	6.67904800	-2.82194600
O	-7.59119300	8.06599500	-1.27013100
H	-7.22004600	8.75570300	-1.83089500

 $Q^*(\text{BD} - \text{normal})$

C	-5.83447900	-3.67143500	0.52913300
C	-4.47660700	-3.44470800	0.53450900
C	-3.94550600	-2.16528500	0.27379300
C	-4.83938500	-1.09131000	-0.00032600
C	-6.22758500	-1.35100100	0.00225400
C	-6.71950000	-2.61037100	0.26023800
C	-2.49918400	-1.97292700	0.29163800
C	-4.34993300	0.24860600	-0.27773700
C	-2.90982600	0.44557300	-0.25991800
C	-2.01460200	-0.62528200	0.01371400
C	-0.62829700	-0.37071900	0.01451900
H	0.03890100	-1.19716300	0.22317500
C	-0.13160800	0.88751200	-0.24207900
C	-1.01697800	1.94842500	-0.51240100
C	-2.37517600	1.72606500	-0.52030800
H	-6.22275600	-4.66282500	0.73134800
H	-3.78237100	-4.24927900	0.74066300
H	-6.90670500	-0.53417300	-0.20211900
H	-7.78900700	-2.78599600	0.25663200
H	0.93783400	1.06299600	-0.23650500
H	-0.62722800	2.93945500	-0.71414500
H	-3.06565700	2.53315500	-0.72783700
O	-5.13378200	1.21585700	-0.52662400
O	-1.70902700	-2.92164100	0.53523900
H	-6.80568700	1.59201300	-0.83746700
O	-7.74156200	1.83970100	-1.01067700
C	-7.97623100	3.15168600	-0.51857100
H	-9.06204000	3.27891200	-0.47062100
H	-7.59391700	3.25065900	0.50619700
C	-7.37084100	4.24025800	-1.40124300
H	-6.28682200	4.09238400	-1.45324700
H	-7.75651300	4.11823500	-2.41908300

Appendix B

C	-7.68048100	5.64803000	-0.88960000	H	-6.20420500	-5.00493300	0.31600000
H	-8.76458200	5.79757700	-0.84269400	H	-3.92381000	-4.50284600	-0.52492900
H	-7.29991400	5.76802300	0.13043500	H	-6.74239100	-0.86588500	1.28920900
C	-7.07670600	6.73010600	-1.76502300	H	-7.61135100	-3.17930800	1.22486200
H	-5.98653600	6.61975300	-1.80457500	H	0.56915800	1.05339900	-1.37641800
H	-7.46031500	6.64610500	-2.78882400	H	-0.84510700	2.88425300	-0.48943300
O	-7.42072400	8.00865700	-1.21598800	H	-3.11702100	2.39032100	0.35488100
H	-7.03311800	8.69624600	-1.76812700	O	-1.98513100	-3.05011100	-1.04447600
Q ² -(BD - normal)				C	-5.42725500	3.57976700	3.64594600
C	-5.92775700	-3.53690800	0.69732900	C	-8.38859200	2.81278900	1.21779700
C	-4.57513500	-3.39462100	0.51825100	O	-5.04670300	0.92440600	0.92013500
C	-3.96505600	-2.13192300	0.29412300	H	-7.09156100	1.38899100	0.77184600
C	-4.81745100	-0.96093300	0.24751500	O	-8.03992300	1.44793700	0.95876300
C	-6.21645400	-1.15137200	0.44275800	C	-6.78389700	3.05020300	3.19933100
C	-6.76346400	-2.38878400	0.66143100	C	-7.25639600	3.60856400	1.85378300
C	-2.54039500	-2.04959400	0.12425100	H	-5.44649000	4.66901100	3.74181400
C	-4.29559000	0.34683900	0.02245600	H	-7.51812600	3.27811800	3.97920500
C	-2.88283100	0.43729700	-0.15162300	H	-6.72447600	1.95845500	3.14563400
C	-2.02426700	-0.72795500	-0.10352400	H	-6.41824700	3.63521400	1.15003300
C	-0.62936400	-0.53858000	-0.29035200	H	-7.58721600	4.64562500	1.97308000
H	-0.00272300	-1.42193800	-0.25341500	H	-8.69621200	3.29831500	0.28392700
C	-0.07759400	0.69835900	-0.50912300	H	-9.26096200	2.78278000	1.87681200
C	-0.91813300	1.84265700	-0.55203900	O	-4.37638400	3.28342800	2.71952200
C	-2.27048300	1.70370600	-0.37798200	H	-4.55503600	2.43040800	2.29734500
H	-6.35997600	-4.51751000	0.86614400	H	-5.18041800	3.16573900	4.63100700
H	-3.92283900	-4.25965600	0.54393200	Q ⁺ -(BD - bidentate)			
H	-6.84912300	-0.27305200	0.40686400	C	-5.77867200	-3.97310500	0.50652700
H	-7.83375800	-2.49474500	0.80546600	C	-4.53567600	-3.67550900	-0.00626900
H	0.99290000	0.80609200	-0.64814100	C	-4.04893400	-2.35399000	-0.02411000
H	-0.48711700	2.82367800	-0.72331600	C	-4.86395500	-1.31114500	0.49878900
H	-2.92064800	2.56964000	-0.40858700	C	-6.13315500	-1.64369700	1.02236500
O	-5.06287400	1.41767400	-0.00974000	C	-6.58499800	-2.94367900	1.02702500
O	-1.77455000	-3.09347200	0.17431400	C	-2.72253700	-2.08480000	-0.57216000
H	-6.34669200	1.63178900	-0.91053500	C	-4.41156800	0.06618100	0.51160300
O	-7.16691000	1.82647300	-1.47105000	C	-3.10099700	0.34494600	-0.04220100
C	-7.79392800	2.99828100	-0.99054900	C	-2.28091900	-0.69303700	-0.56602100
H	-8.84625200	2.96170600	-1.29721900	C	-1.01692100	-0.36396600	-1.09305000
H	-7.78492300	3.01868600	0.10873600	H	-0.40645800	-1.16649500	-1.48668700
C	-7.16382600	4.28508900	-1.52494800	C	-0.56663500	0.93740400	-1.11212500
H	-6.10923300	4.31174100	-1.23070100	C	-1.37842000	1.96620500	-0.59880100
H	-7.18546800	4.25415800	-2.62003600	C	-2.61722300	1.67163500	-0.07679300
C	-7.87734700	5.54198000	-1.02401300	H	-6.13594800	-4.99615200	0.51172900
H	-8.93348400	5.51155000	-1.31396100	H	-3.90129700	-4.45515900	-0.40806100
H	-7.85087700	5.57565100	0.07055500	H	-6.74896200	-0.84939900	1.42254100
C	-7.26086900	6.81777800	-1.56573700	H	-7.56271100	-3.17630900	1.43273600
H	-6.21054900	6.88998100	-1.25955200	H	0.40873200	1.17099500	-1.52250600
H	-7.29201100	6.81693100	-2.66183100	H	-1.02707900	2.99132000	-0.61666500
O	-7.99773000	7.93751800	-1.05610900	H	-3.24682700	2.45785400	0.31799600
H	-7.59967100	8.74766700	-1.39229300	O	-1.99791800	-3.00444600	-1.02680000
Q(BD - bidentate)				C	-5.46528700	3.25930900	3.76383900
C	-5.82576400	-3.99083300	0.34315900	C	-8.15788000	2.93377200	0.96426200
C	-4.55066900	-3.71522500	-0.12903600	O	-5.13828100	1.00048400	0.99324500
C	-4.05464700	-2.41307700	-0.09865100	H	-6.91068500	1.40076000	0.71401900
C	-4.85368200	-1.37608800	0.41271500	O	-7.87293200	1.57050600	0.64883800
C	-6.13317500	-1.66496400	0.88977900	C	-6.82046000	2.92751500	3.14978700
C	-6.61713600	-2.96438000	0.85395300	C	-7.07163200	3.60407500	1.79769200
C	-2.68175200	-2.14834400	-0.60404200	H	-5.37722300	4.33780800	3.93618900
C	-4.35175200	0.01799500	0.46479700	H	-7.60185100	3.21126600	3.86292000
C	-2.98700600	0.28937700	-0.04653100	H	-6.88665800	1.84219500	3.03429900
C	-2.18642700	-0.74724800	-0.55556200	H	-6.14814900	3.60976000	1.21174500
C	-0.90784300	-0.46130000	-1.03068700	H	-7.34899200	4.65296300	1.94796300
H	-0.30296100	-1.26958500	-1.41900900	H	-8.30265400	3.50294600	0.03686600
C	-0.42528300	0.83925400	-1.00546500	H	-9.11287500	2.94263700	1.50138300
C	-1.22006600	1.86872700	-0.50592800	O	-4.36011200	2.87955900	2.94342700
C	-2.49369500	1.59499000	-0.03007200	H	-4.63184400	2.18566000	2.30805000
				H	-5.38302000	2.76707000	4.74151200

$Q^2-(BD - \text{bidentate})$							
C	-5.74351200	-3.98694300	0.56873900	H	-6.71372400	1.75694000	-0.55508100
C	-4.53084500	-3.66543400	0.01330300	O	-7.61917500	2.09980900	-0.62790600
C	-4.03615300	-2.33589500	-0.01421500	C	-7.62763800	3.47445500	-0.24858800
C	-4.84928400	-1.28944800	0.56841900	H	-8.67965200	3.75607100	-0.15633700
C	-6.10202300	-1.66546300	1.13846700	H	-7.16850000	3.59888000	0.74033200
C	-6.54199600	-2.96275300	1.14289600	C	-6.93352500	4.37719700	-1.26292300
C	-2.75525000	-2.06524300	-0.61092100	H	-5.88932500	4.06112400	-1.36450800
C	-4.42951500	0.06850800	0.58232100	H	-7.40533100	4.23340000	-2.24054300
C	-3.16850700	0.35220200	-0.00975800	O	-1.02878500	-5.82711100	2.12411400
C	-2.34503700	-0.08640700	-0.59177400	H	-1.47506000	-5.06846500	1.71912000
C	-1.09771200	-0.31624700	-1.15844200	C	-1.89695200	-6.95736100	2.08137500
H	-0.49526400	-1.10868800	-1.58668400	H	-1.42558500	-7.72217800	2.70366700
C	-0.65431300	0.98199100	-1.17467800	H	-2.86289100	-6.71291000	2.54137700
C	-1.46262500	2.00322000	-0.60911900	C	-2.11173400	-7.49423100	0.67025500
C	-2.67314500	1.68945400	-0.04977200	H	-1.13660100	-7.73529300	0.23439400
H	-6.09241300	-5.01396600	0.57269800	C	-6.99128600	5.85280500	-0.86373200
H	-3.90616900	-4.43373000	-0.42674400	C	-3.01551400	-8.72832400	0.65012500
H	-6.70949700	-0.88139300	1.57251100	H	-2.54982000	-6.70381900	0.05054300
H	-7.50138400	-3.21072500	1.58514100	H	-8.03426200	6.17036800	-0.75998800
H	0.30489400	1.23074700	-1.61579500	H	-6.51767800	5.99476500	0.11341400
H	-1.11909700	3.03246300	-0.62173800	H	-2.58166200	-9.51823000	1.27237200
H	-3.29042400	2.46481500	0.38575900	H	-3.99158300	-8.48397900	1.08227100
O	-2.02460600	-2.99571700	-1.12901900	C	-3.22441900	-9.27107500	-0.75134900
C	-5.52181600	3.13854100	3.80796100	C	-6.30523900	6.75394000	-1.87351900
C	-7.99889200	2.98652700	0.81816600	H	-5.25154600	6.46956900	-1.97940800
O	-5.17788900	1.02524500	1.12200900	H	-6.78126100	6.65194500	-2.85599900
H	-6.73420900	1.42208700	0.69024400	H	-2.26141700	-9.54641100	-1.19757000
O	-7.68858800	1.64062100	0.48083400	H	-3.68348200	-8.50589100	-1.38866800
C	-6.86646800	2.92294700	3.11849400	O	-6.40487600	8.10859800	-1.41779900
C	-6.99262300	3.63448500	1.76493200	H	-5.96792600	8.68257100	-2.05613600
H	-5.36899600	4.20747600	4.00659400	O	-4.07598300	-10.42057900	-0.67328200
H	-7.66063400	3.25636600	3.79590600	H	-4.20874800	-10.76788800	-1.56191600
H	-7.00592300	1.84882400	2.97628400	$Q^-(BD)_2$			
H	-6.01872500	3.64658000	1.27006700	C	-5.56727000	-3.71735500	-0.08267000
H	-7.28228000	4.68071400	1.91410300	C	-4.22517300	-3.41297500	-0.10050300
H	-8.06462000	3.59230400	-0.09698500	C	-3.77767100	-2.07552800	-0.09856800
H	-8.99810600	2.99226700	1.27336600	C	-4.74131800	-1.02852600	-0.07871600
O	-4.40953600	2.68065500	3.05098200	C	-6.11084000	-1.36845600	-0.05888200
H	-4.69553900	2.02826100	2.34534800	C	-6.52098600	-2.68247500	-0.06069300
H	-5.54089300	2.63468800	4.78519600	C	-2.34938100	-1.79909600	-0.11491700
$Q(BD)_2$				C	-4.33653300	0.36770200	-0.07670600
C	-6.31707500	-3.43691600	1.59608600	C	-2.90815000	0.64406400	-0.08935200
C	-4.94209600	-3.46054800	1.41366400	C	-1.94458700	-0.40297800	-0.10862500
C	-4.28254000	-2.35409300	0.88047200	C	-0.57485500	-0.06361100	-0.12291300
C	-5.01894500	-1.21015400	0.52588200	H	0.15507700	-0.86205500	-0.13930600
C	-6.40108100	-1.19663800	0.71407200	C	-0.16445000	1.25032400	-0.11699200
C	-7.04690200	-2.30338000	1.24622100	C	-1.11801400	2.28539300	-0.09681100
C	-2.81011900	-2.40511000	0.69825600	C	-2.46027200	1.98136400	-0.08400900
C	-4.34559800	-0.01724400	-0.04539300	H	-5.89112000	-4.75154500	-0.08429600
C	-2.87247100	-0.06500900	-0.21866700	H	-3.47981700	-4.19731800	-0.11578900
C	-2.13728100	-1.20785600	0.13659500	H	-6.84149000	-0.57094800	-0.03973300
C	-0.75407200	-1.22087300	-0.03983800	H	-7.57793100	-2.92123600	-0.04468900
H	-0.19991200	-2.10729200	0.23776400	H	0.89260600	1.48894500	-0.12784800
C	-0.10497400	-0.11197300	-0.56280100	H	-0.79394000	3.31950900	-0.09185500
C	-0.83418400	1.02181800	-0.91549200	H	-3.20530900	2.76596600	-0.06921100
C	-2.21064800	1.04427400	-0.74442000	O	-5.17868600	1.31309100	-0.06341000
H	-6.82153900	-4.30024300	2.01129800	O	-1.50742800	-2.74465300	-0.13293900
H	-4.36492400	-4.33453700	1.68249500	H	-6.88127500	1.67627000	-0.25347100
H	-6.96404100	-0.31406400	0.44274800	O	-7.82846700	1.92581000	-0.32724200
H	-8.11992100	-2.28371300	1.38921200	C	-7.95520700	3.32896300	-0.13527100
H	0.96930000	-0.12878400	-0.69659700	H	-9.02240600	3.52300100	-0.00286000
H	-0.32708400	1.88693000	-1.32379200	H	-7.45286800	3.63683800	0.79217900
H	-2.78800700	1.91793800	-1.01479400	C	-7.40032200	4.13689300	-1.30809100
O	-4.97791200	0.98220500	-0.36764300	H	-6.35605900	3.84630300	-1.45645300
O	-2.16661000	-3.40166500	1.00212400	H	-7.93644400	3.85221400	-2.22008200
				O	1.13780700	-3.41753100	-0.02861400
				H	0.20297900	-3.12154200	-0.07130500

Appendix B

C	1.36262500	-4.37301800	-1.05924200	H	3.01947300	-2.45158000	-1.06109800
H	0.66335800	-5.21309300	-0.95726200	H	-4.62767400	4.87467200	-2.24839200
H	1.18603000	-3.91857400	-2.04487100	C	4.08070100	-2.77285500	-2.87270900
C	2.78950800	-4.89349200	-0.98351800	C	-3.57270300	4.13702000	-3.95463100
H	2.95213000	-5.33405600	0.00420400	H	-2.72779000	3.73700200	-3.38193000
H	2.89188400	-5.70562700	-1.71251000	H	-3.74113800	3.47441600	-4.81194700
C	-7.46432700	5.65661200	-1.11428900	H	4.43127300	-3.78385300	-2.63026500
C	3.85127100	-3.82807300	-1.26261200	H	4.85970900	-2.06460400	-2.56825400
H	-6.90791700	6.14421000	-1.92041000	O	3.85061600	-2.66328700	-4.28512100
H	-6.96745400	5.93467700	-0.17844100	H	4.66977500	-2.87031900	-4.74716100
H	3.67543500	-3.39109300	-2.25219800	O	-3.27123400	5.46241800	-4.41189100
H	3.76389600	-3.01260600	-0.53965600	H	-2.47438100	5.42821300	-4.95198500
C	-8.87534500	6.22029900	-1.11077700				
C	5.27517000	-4.35407100	-1.23865200				
H	-9.39559500	5.93242800	-2.03266100				
H	-9.45246500	5.83258900	-0.26479600				
H	5.37916800	-5.19877100	-1.93124300				
H	5.96826900	-3.56825000	-1.55982200				
O	-8.78748100	7.64842900	-1.02172300				
H	-9.67919300	8.01119200	-0.98753400				
O	5.60021100	-4.77388900	0.09403800				
H	6.49775600	-5.12297900	0.09656400				

$Q^{2-}(\text{BD})_2$

C	-5.63453300	-4.09783900	0.88371300
C	-4.31517000	-3.73247000	0.94818500
C	-3.90532700	-2.37023300	0.97378000
C	-4.93137800	-1.35116100	0.92263900
C	-6.28890100	-1.77368100	0.85616400
C	-6.64208900	-3.09759800	0.83767600
C	-2.51635600	-2.04317400	1.05013400
C	-4.61478700	0.04066800	0.94452000
C	-3.22750300	0.36795000	1.01896600
C	-2.19973500	-0.65035000	1.07372200
C	-0.84408400	-0.22492400	1.15801000
H	-0.08052900	-0.99156600	1.20110800
C	-0.49348700	1.09979600	1.18135800
C	-1.50178000	2.09863900	1.12351400
C	-2.81951900	1.73120200	1.04793100
H	-5.91236500	-5.14638400	0.86649600
H	-3.53680900	-4.48499600	0.98319900
H	-7.04821400	-1.00202400	0.82043700
H	-7.68705700	-3.38480500	0.78763100
H	0.55037900	1.38812400	1.24532300
H	-1.22576200	3.14766600	1.14225900
H	-3.59959100	2.48151300	1.00836200
O	-5.54438200	0.96719800	0.91348000
O	-1.59621400	-2.97471500	1.10798900
H	-6.33664000	1.33435900	-0.41265900
O	-6.88830800	1.60030700	-1.21606500
C	-6.47174100	2.87044700	-1.67767400
H	-7.29829100	3.29757100	-2.25761400
H	-6.29293300	3.54929500	-0.83161900
C	-5.22062800	2.81599600	-2.55471300
H	-4.39885500	2.38365200	-1.97410500
H	-5.41046700	2.13410900	-3.39091200
O	0.62095100	-3.29075900	-0.22641400
H	-0.23954200	-3.10776100	0.26270500
C	0.39359900	-3.19245500	-1.61987400
H	-0.38558500	-3.90160300	-1.93503400
H	0.03387400	-2.18550100	-1.88316200
C	1.67297200	-3.48563700	-2.39091500
H	2.02048500	-4.49196700	-2.12767300
H	1.43436800	-3.50330300	-3.45830400
C	2.79135500	-2.47524300	-2.13004200
C	-4.81427200	4.19227100	-3.08468700
H	-5.63440200	4.62429600	-3.66864300
H	2.45175600	-1.46865400	-2.40092800

Figure B.40. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated AQ(MeOH) hydrogen-bonded complexes.

Figure B.41. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated AQ(EtOH) hydrogen-bonded complexes.

Figure B.42. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated AQ(*n*-PrOH) hydrogen-bonded complexes.

Figure B.43. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated AQ(*i*-PrOH) hydrogen-bonded complexes.

Figure B.44. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated AQ(*n*-BuOH) hydrogen-bonded complexes.

Figure B.45. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated AQ(*s*-BuOH) hydrogen-bonded complexes.

Figure B.46. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated AQ(*i*-BuOH) hydrogen-bonded complexes.

Figure B.47. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated AQ(*t*-BuOH) hydrogen-bonded complexes.

Cartesian Coordinates of DCM-Solvated Hydrogen-Bonded Complexes of 9,10-Anthraquinone

Q(MeOH)				Q ²⁻ (MeOH)			
C	-6.12156100	-3.72650300	0.21628300	C	-6.13004600	-3.68358400	0.17349500
C	-4.74068900	-3.63047000	0.12640600	C	-4.76730600	-3.57809100	0.05555400
C	-4.12805300	-2.38447100	0.00205600	C	-4.10392800	-2.32623000	-0.03194200
C	-4.91694100	-1.22200400	-0.03270300	C	-4.90957200	-1.12031100	0.00279300
C	-6.30530600	-1.32991300	0.05912500	C	-6.32139200	-1.27479600	0.12450000
C	-6.90452800	-2.57457800	0.18273600	C	-6.92098400	-2.50460800	0.20918100
C	-2.64500500	-2.31367300	-0.09137700	C	-2.67145300	-2.29290100	-0.14924000
C	-4.29328700	0.11798900	-0.16600800	C	-4.32728400	0.18011400	-0.07860900
C	-2.81345900	0.19320800	-0.25171400	C	-2.90459200	0.22175800	-0.19247000
C	-2.02486300	-0.96797400	-0.21612800	C	-2.09496100	-0.97842900	-0.22575100
C	-0.63719200	-0.86191300	-0.29902200	C	-0.68744200	-0.83350800	-0.33749500
H	-0.04334400	-1.76557900	-0.27025200	H	-0.09963000	-1.74403800	-0.35613900
C	-0.03609900	0.38273300	-0.41534400	C	-0.07788500	0.39337300	-0.41783200
C	-0.81849800	1.53555900	-0.45114100	C	-0.87077500	1.57159700	-0.38695700
C	-2.19960200	1.44064500	-0.37017900	C	-2.23392900	1.47535100	-0.27702800
H	-6.59025100	-4.69789200	0.31275200	H	-6.60302200	-4.65807800	0.23926800
H	-4.11949500	-4.51570700	0.15157000	H	-4.14600200	-4.46561300	0.02597000
H	-6.90929900	-0.43348300	0.03353800	H	-6.92901600	-0.37965900	0.14948600
H	-7.98245900	-2.64869200	0.25281100	H	-7.99989300	-2.57845000	0.30198900
H	1.04233500	0.45765100	-0.47818400	H	1.00154000	0.46671000	-0.50232800
H	-0.34861300	2.50683900	-0.54234900	H	-0.39544300	2.54550300	-0.44952000
H	-2.81886500	2.32701600	-0.39746900	H	-2.84837000	2.36712500	-0.25023100
O	-4.97082900	1.13885300	-0.20527100	O	-5.03609200	1.28735600	-0.04836600
O	-1.96086300	-3.32500700	-0.06553800	O	-1.95285500	-3.36858700	-0.18235900
H	-6.71384900	1.87170500	-0.27761300	H	-6.55802300	1.70494700	-0.04948300
O	-7.61533400	2.22887600	-0.31471100	O	-7.49831900	2.07636400	-0.04758700
C	-7.55601400	3.64293200	-0.17838300	C	-7.44178600	3.46134200	-0.30083200
H	-8.57878500	4.01877900	-0.21496500	H	-8.46099200	3.85842400	-0.31008400
H	-7.11112400	3.94227200	0.77688800	H	-6.87616800	4.00322000	0.46981200
H	-6.98707900	4.10726000	-0.99131700	H	-6.98333100	3.68815300	-1.27329800

Q ⁻ (MeOH)				Q(EtOH)			
C	-6.11154900	-3.73488900	0.21082000	C	-6.13094900	-3.70627800	0.21298300
C	-4.74267300	-3.62151700	0.11866800	C	-4.74940700	-3.60878500	0.13617800
C	-4.11781800	-2.36423800	-0.00285400	C	-4.13766400	-2.36309500	0.00412100
C	-4.92657700	-1.19274700	-0.03087300	C	-4.92821200	-1.20258200	-0.05215100
C	-6.32798300	-1.33750200	0.06531100	C	-6.31732700	-1.31171600	0.02691800
C	-6.91273800	-2.57769700	0.18367900	C	-6.91542400	-2.55615400	0.15865000
C	-2.66271200	-2.29471000	-0.09578600	C	-2.65388300	-2.29051700	-0.07409900
C	-4.33842900	0.13041100	-0.15397800	C	-4.30569600	0.13716500	-0.19489500
C	-2.88940700	0.20549100	-0.24278600	C	-2.82479000	0.21430500	-0.26220600
C	-2.07881600	-0.96260500	-0.21301000	C	-2.03466000	-0.94493400	-0.20496700
C	-0.67911800	-0.82339600	-0.29958700	C	-0.64622800	-0.83707300	-0.27183100
H	-0.07929300	-1.72419500	-0.27279300	H	-0.05119100	-1.73928500	-0.22657400
C	-0.08936400	0.41546500	-0.41341200	C	-0.04592900	0.40743900	-0.39331700
C	-0.89119500	1.57262500	-0.44555500	C	-0.82989900	1.55835100	-0.45061900
C	-2.26051700	1.46377800	-0.36153500	C	-2.21172900	1.46157000	-0.38603800
H	-6.57293900	-4.71122800	0.30430400	H	-6.59896100	-4.67737600	0.31559500
H	-4.11065800	-4.50023200	0.13789400	H	-4.12700300	-4.49255700	0.17778300
H	-6.94167500	-0.44699600	0.04510900	H	-6.92242300	-0.41646900	-0.01428000
H	-7.99081600	-2.66398000	0.25591400	H	-7.99388900	-2.63148300	0.21884400
H	0.98916300	0.50207400	-0.47799500	H	1.03307000	0.48376400	-0.44352100
H	-0.42818900	2.54861000	-0.53616400	H	-0.36063600	2.52954700	-0.54592000
H	-2.88850900	2.34496100	-0.38433100	H	-2.83236900	2.34629800	-0.43038600
O	-5.04513000	1.18393100	-0.18235100	O	-4.98485800	1.15565500	-0.25649300
O	-1.94854600	-3.32938000	-0.07530300	O	-1.96818700	-3.30026500	-0.03091800
H	-6.67023700	1.76379600	-0.25117100	H	-6.76025300	1.85753400	-0.39850700
O	-7.56145500	2.17826000	-0.29056200	O	-7.68482300	2.15041000	-0.44099200
C	-7.41110000	3.58346400	-0.19557700	C	-7.74663700	3.54248400	-0.13406100
H	-8.40597700	4.03198600	-0.22507600	H	-8.80845700	3.78042900	-0.04007700
H	-6.92816300	3.88302900	0.74248800	H	-7.28188500	3.73546400	0.84070300
H	-6.82653000	3.99188700	-1.02899100	C	-7.10534500	4.41457300	-1.20299500
				H	-6.04009800	4.19143200	-1.30326300

Appendix B

H -7.58273900 4.25319900 -2.17209800
H -7.20499800 5.47191400 -0.94235900

Q⁺(EtOH)

C -6.12610600 -3.69266000 0.30892500
C -4.75549600 -3.57469900 0.25646200
C -4.13444800 -2.32563000 0.05563400
C -4.94914900 -1.16786100 -0.09657000
C -6.35218200 -1.31655700 -0.03705300
C -6.93290000 -2.54853700 0.16081700
C -2.67749900 -2.24996200 0.00949100
C -4.36598100 0.14651400 -0.30829700
C -2.91497700 0.22801100 -0.34929500
C -2.09857000 -0.92610000 -0.19379800
C -0.69751100 -0.78072900 -0.23902200
H -0.09309400 -1.67033400 -0.11569800
C -0.11202000 0.45028800 -0.43192100
C -0.91952300 1.59322900 -0.58919200
C -2.29032100 1.47827100 -0.54784900
H -6.58460000 -4.66249200 0.46416100
H -4.11929000 -4.44333700 0.36894100
H -6.96953500 -0.43523300 -0.14909300
H -8.01232600 -2.63848000 0.20258600
H 0.96761100 0.54162800 -0.46293400
H -0.45968300 2.56287100 -0.74236800
H -2.92298800 2.34833200 -0.66680900
O -5.07824400 1.18656500 -0.45100800
O -1.95750300 -3.27279200 0.13844800
H -6.72055900 1.72939700 -0.66741200
O -7.62815300 2.09553000 -0.76516900
C -7.66807200 3.38341700 -0.16596000
H -8.72477800 3.64890600 -0.07024900
H -7.25190400 3.34390600 0.84921500
C -6.93917700 4.44318800 -0.98215300
H -5.87882000 4.19826200 -1.07758600
H -7.36525900 4.51786800 -1.98560800
H -7.02042400 5.42218100 -0.50042700

Q²⁻(EtOH)

C -6.59041000 -3.51248600 -0.27162700
C -5.27848300 -3.33454500 -0.63291100
C -4.56443000 -2.14215700 -0.34517500
C -5.26171300 -1.08004200 0.35101700
C -6.62162600 -1.30563600 0.71102600
C -7.27346200 -2.47457900 0.41654900
C -3.18782700 -2.02179400 -0.74524400
C -4.62830700 0.15344200 0.68323400
C -3.26369600 0.28144100 0.29184000
C -2.55729900 -0.77519000 -0.40271200
C -1.19934500 -0.55551100 -0.75063000
H -0.68963900 -1.35757400 -1.27160400
C -0.54187300 0.61133800 -0.45094600
C -1.23251700 1.64780400 0.23224700
C -2.54568600 1.47663000 0.58560800
H -7.10510600 -4.43828000 -0.50731300
H -4.74077000 -4.11659800 -1.15651900
H -7.13455800 -0.50868400 1.23531200
H -8.31044100 -2.60897200 0.70780900
H 0.49770100 0.74427700 -0.73231700
H -0.71824600 2.57298400 0.47288000
H -3.08267400 2.25983700 1.10722000
O -5.25840900 1.11493000 1.32858200
O -2.56162900 -2.96613100 -1.36789200
H -6.32304700 2.04828200 0.65912600
O -7.01802500 2.69990300 0.30569100
C -6.37520200 3.72097000 -0.42759000
H -7.06743400 4.56934600 -0.48580900

H -5.48160400 4.07627500 0.10596200
C -5.98335000 3.29044900 -1.83828500
H -5.27066700 2.46269500 -1.80779200
H -6.86358200 2.96120500 -2.39703800
H -5.52013500 4.11932100 -2.38348500

Q(n-PrOH)

C -6.14287400 -3.65012200 0.35038900
C -4.76033500 -3.53920500 0.36782300
C -4.14910300 -2.31193900 0.11568100
C -4.94112900 -1.18364600 -0.15747800
C -6.33141400 -1.30573400 -0.17156300
C -6.92886800 -2.53178400 0.08069800
C -2.66428000 -2.22420800 0.14265200
C -4.31874800 0.13572900 -0.43039000
C -2.83727300 0.22687400 -0.40488400
C -2.04578100 -0.89989000 -0.13034900
C -0.65685600 -0.77919100 -0.11337600
H -0.06046100 -1.65611500 0.09986100
C -0.05763000 0.44586400 -0.36653500
C -0.84297000 1.56437800 -0.63985700
C -2.22520800 1.45475700 -0.65876800
H -6.61048000 -4.60688000 0.54674400
H -4.13673600 -4.39823400 0.57604500
H -6.93784000 -0.43476600 -0.37982900
H -8.00815900 -2.61756800 0.06751400
H 1.02168000 0.53213800 -0.35195200
H -0.37443000 2.52029300 -0.83784300
H -2.84702900 2.31430500 -0.86957800
O -4.99813700 1.12725300 -0.67040500
O -1.97731700 -3.20551700 0.38078400
H -6.77381100 1.80508900 -0.92317200
O -7.69675200 2.08478900 -1.03339000
C -7.88831100 3.32669100 -0.36009300
H -8.96681800 3.50641800 -0.35894000
H -7.57173700 3.24449600 0.68822000
C -7.16799300 4.49196800 -1.02948600
H -6.09353800 4.28058500 -1.05098800
H -7.49744700 4.55577500 -2.07119000
C -7.42071000 5.81969100 -0.31507200
H -8.48590300 6.06637900 -0.30261900
H -7.07644300 5.78447000 0.72216400
H -6.89689100 6.63993600 -0.80992200

Q⁺(n-PrOH)

C -6.17777200 -3.54671000 0.46147600
C -4.80661000 -3.42919800 0.49761600
C -4.16583300 -2.21703600 0.17153200
C -4.96083500 -1.09655300 -0.20241000
C -6.36511300 -1.24413200 -0.23186700
C -6.96509100 -2.43976100 0.09196000
C -2.70907700 -2.14086700 0.22603400
C -4.35617000 0.17898200 -0.54862000
C -2.90568300 0.26147800 -0.49075800
C -2.10915900 -0.85541800 -0.11587700
C -0.70782200 -0.71017900 -0.07647800
H -0.11835400 -1.57055000 0.21366100
C -0.10335800 0.48522600 -0.39442900
C -0.89106100 1.59106500 -0.76805600
C -2.26169200 1.47560900 -0.81314800
H -6.65151700 -4.48771300 0.71637600
H -4.18497800 -4.26951200 0.77945300
H -6.96816100 -0.39191000 -0.51615200
H -8.04496000 -2.52963400 0.06268700
H 0.97608800 0.57687400 -0.35817600
H -0.41623100 2.53251800 -1.01968000
H -2.87962100 2.31713400 -1.09854500

O	-5.04926200	1.18625100	-0.88722400
O	-2.00671000	-3.13202300	0.55111200
H	-6.68415600	1.71370200	-1.19032400
O	-7.59092900	2.05730000	-1.35417900
C	-7.81488500	3.17903600	-0.51317400
H	-8.89224300	3.37387100	-0.52990100
H	-7.54745200	2.93991500	0.52570800
C	-7.06150200	4.42899300	-0.95998900
H	-5.98872900	4.21167700	-0.96140600
H	-7.33936700	4.65225200	-1.99508800
C	-7.34863700	5.63592600	-0.06690500
H	-8.41425900	5.88297100	-0.06441400
H	-7.05143900	5.44372000	0.96785600
H	-6.80515300	6.51977800	-0.40777400

 $Q^{2-}(n\text{-PrOH})$

C	-6.16917100	-3.57981200	0.39259900
C	-4.80262300	-3.46235700	0.42487900
C	-4.13468700	-2.24221100	0.14099100
C	-4.94051800	-1.08453600	-0.19859700
C	-6.35606200	-1.24934800	-0.22112000
C	-6.95977100	-2.44692500	0.06290200
C	-2.69904100	-2.19075700	0.19827700
C	-4.35655600	0.18175100	-0.50266400
C	-2.93065500	0.24145000	-0.44592800
C	-2.12121000	-0.90992700	-0.10467000
C	-0.71117500	-0.75007700	-0.07308400
H	-0.12429600	-1.62283900	0.18862100
C	-0.09892300	0.44527400	-0.35471900
C	-0.89140000	1.57519700	-0.69101300
C	-2.25730200	1.46369700	-0.73053600
H	-6.64550100	-4.52893600	0.61608300
H	-4.18198700	-4.31563200	0.67285700
H	-6.96094000	-0.38730400	-0.47255500
H	-8.04163100	-2.53099600	0.03583900
H	0.98243100	0.53053800	-0.32144900
H	-0.41376900	2.52389400	-0.91491600
H	-2.87245400	2.31884800	-0.98357600
O	-5.06653300	1.24088500	-0.81991000
O	-1.97776300	-3.22180400	0.50218300
H	-6.57893400	1.68590200	-1.04804400
O	-7.50635100	2.04845800	-1.20462500
C	-7.70263300	3.19782800	-0.40819500
H	-8.78259700	3.30813500	-0.24504000
H	-7.24392200	3.06511600	0.58248500
C	-7.16396900	4.47944100	-1.04437900
H	-6.08818500	4.36714500	-1.21060000
H	-7.62314800	4.59689000	-2.03174200
C	-7.43362600	5.71806100	-0.18988500
H	-8.50600000	5.86266300	-0.02735300
H	-6.96007800	5.63261100	0.79246400
H	-7.04675500	6.62275600	-0.66468000

 $Q(i\text{-PrOH})$

C	-6.08475900	-3.75352300	0.21261600
C	-4.70441400	-3.63779500	0.14016100
C	-4.10916600	-2.38488300	0.00107800
C	-4.91509000	-1.23559100	-0.06648300
C	-6.30292300	-1.36304900	0.00791400
C	-6.88449900	-2.61457500	0.14662500
C	-2.62627800	-2.29281000	-0.07266700
C	-4.31021500	0.11163500	-0.21582300
C	-2.83017800	0.20803200	-0.28027400
C	-2.02479400	-0.94005000	-0.21199100
C	-0.63772300	-0.81407700	-0.27582700
H	-0.03075700	-1.70783400	-0.22178500
C	-0.05380800	0.43737200	-0.40556400

C	-0.85295400	1.57719800	-0.47405200
C	-2.23352200	1.46238500	-0.41218900
H	-6.53994500	-4.73010400	0.32072700
H	-4.07014200	-4.51262800	0.19056900
H	-6.92010300	-0.47653800	-0.04247300
H	-7.96207700	-2.70412300	0.20317000
H	1.02420400	0.52775900	-0.45349600
H	-0.39647100	2.55381400	-0.57579500
H	-2.86593300	2.33828300	-0.46499700
O	-5.00278300	1.12046100	-0.28477000
O	-1.92713300	-3.29283900	-0.01956000
H	-6.80044600	1.79628600	-0.39835900
O	-7.73459900	2.05844200	-0.42673900
C	-7.84441000	3.44700600	-0.08957400
H	-7.39172100	3.60679400	0.89884300
C	-7.11566100	4.31903300	-1.10727900
H	-6.05807100	4.05066700	-1.16333000
H	-7.55495800	4.19495900	-2.10066200
H	-7.18070600	5.37434300	-0.82998900
C	-9.32677200	3.76990100	-0.00357700
H	-9.47777500	4.81236500	0.28405300
H	-9.80864000	3.60726900	-0.97137100
H	-9.81791100	3.13450600	0.73592000

 $Q^{+}(i\text{-PrOH})$

C	-6.08347800	-3.75055600	0.21411100
C	-4.71663100	-3.61895400	0.11672200
C	-4.10912200	-2.35334700	-0.00763100
C	-4.93376900	-1.19302900	-0.03475200
C	-6.33271700	-1.35605200	0.06833800
C	-6.90006800	-2.60407900	0.19032700
C	-2.65545100	-2.26434800	-0.10368900
C	-4.36434300	0.13836000	-0.16314900
C	-2.91602600	0.23258500	-0.25161900
C	-2.08970000	-0.92459300	-0.22126100
C	-0.69191200	-0.76623700	-0.30824400
H	-0.07953500	-1.65859300	-0.28121500
C	-0.11912100	0.48045700	-0.42286100
C	-0.93657000	1.62669800	-0.45563300
C	-2.30427500	1.49910800	-0.37153600
H	-6.53141300	-4.73297500	0.30964900
H	-4.07267200	-4.48900500	0.13432300
H	-6.95788200	-0.47340500	0.05153500
H	-7.97657100	-2.70475800	0.26788300
H	0.95813700	0.58161200	-0.48770700
H	-0.48683400	2.60880500	-0.54696400
H	-2.94457700	2.37141700	-0.39535100
O	-5.08591900	1.18114500	-0.19567500
O	-1.92744800	-3.28969500	-0.08471500
H	-6.75034900	1.69444500	-0.40595000
O	-7.67958700	2.00146800	-0.50012300
C	-7.76606200	3.37495600	-0.12618500
H	-7.31229200	3.50421800	0.86718900
C	-7.02032800	4.26744200	-1.11622600
H	-5.96841900	3.98104200	-1.17641000
H	-7.45855400	4.17762700	-2.11423200
H	-7.06999100	5.31630600	-0.81044200
C	-9.24216400	3.73106100	-0.03210600
H	-9.37264400	4.77051000	0.27733300
H	-9.72701600	3.59862100	-1.00346600
H	-9.74783000	3.08983500	0.69278100

 $Q^{2-}(i\text{-PrOH})$

C	-6.07414300	-3.79255300	0.14935700
C	-4.72164100	-3.62855400	-0.01293400
C	-4.10896800	-2.34877600	-0.05889200
C	-4.95794600	-1.17997100	0.06623000

355

H	0.92107200	0.63819300	-0.36915300	C	-6.37397400	-1.40819300	0.04451100
H	-0.52824400	2.61893300	-0.86992200	C	-6.89953700	-2.67804500	0.11916400
H	-2.98263200	2.36379600	-0.89634000	C	-2.66811900	-2.18636200	-0.15155100
O	-5.15146000	1.23404600	-0.71723200	C	-4.45619000	0.15858100	-0.12614900
O	-1.94102700	-3.19828800	0.40351900	C	-3.01158100	0.30430400	-0.20515700
H	-6.69152100	1.63683500	-0.84070500	C	-2.14672400	-0.82491900	-0.21458900
O	-7.64036800	1.96466300	-0.93408000	C	-0.75473500	-0.61557800	-0.28796800
C	-7.77068700	3.22173700	-0.30350000	H	-0.11080700	-1.48584700	-0.29082100
H	-8.83757200	3.37699700	-0.09896700	C	-0.22444800	0.65334500	-0.35274300
H	-7.25890200	3.22189300	0.67002900	C	-1.08015500	1.77165600	-0.34741000
C	-7.24873800	4.38359100	-1.14875900	C	-2.44293200	1.59442800	-0.27518800
H	-6.18774200	4.21510600	-1.36204000	H	-6.45993200	-4.79636700	0.16177500
H	-7.76824600	4.37352700	-2.11406100	H	-4.01061200	-4.46406600	0.00291700
C	-7.43105200	5.74598900	-0.47817400	H	-7.02848000	-0.54698700	0.05919600
H	-8.49252000	5.89931100	-0.25018300	H	-7.97215300	-2.81725900	0.19042700
H	-6.90999900	5.74797500	0.48584000	H	0.84902000	0.79314600	-0.40772200
C	-6.92403900	6.91042900	-1.32944100	H	-0.66390700	2.77120500	-0.39980200
H	-5.85752900	6.80380000	-1.54610900	H	-3.11263400	2.44462600	-0.27051500
H	-7.45129500	6.95717300	-2.28659400	O	-5.21231800	1.17705500	-0.12291800
H	-7.06655300	7.86912600	-0.82400200	O	-1.90719700	-3.18750700	-0.17233000
Q(s-BuOH)				H	-6.89348100	1.63805600	-0.33719100
C	-6.05536600	-3.78962000	0.13192700	O	-7.82627200	1.93627000	-0.42298000
C	-4.67739100	-3.63958900	0.08102900	C	-7.90368300	3.32487600	-0.10528600
C	-4.11081500	-2.37074300	-0.03090700	H	-7.42826700	3.49644000	0.87279300
C	-4.94336600	-1.24032800	-0.09296300	C	-7.15512300	4.16223600	-1.14983200
C	-6.32855200	-1.40228200	-0.04051600	H	-6.15846800	3.72624100	-1.26659700
C	-6.88152800	-2.66936200	0.07138600	H	-7.66195700	4.04771500	-2.11474000
C	-2.62974900	-2.24163800	-0.08139000	C	-7.01926600	5.64420000	-0.79733700
C	-4.36950800	0.12329000	-0.21326400	H	-7.98800800	6.14735300	-0.75806800
C	-2.89147300	0.25647600	-0.25492000	H	-6.53671400	5.77570800	0.17558200
C	-2.05944200	-0.87278200	-0.19217400	H	-6.41019900	6.16583400	-1.53915500
C	-0.67509600	-0.71232700	-0.23454700	C	-9.37954900	3.67730500	0.00634600
H	-0.04718900	-1.59179900	-0.18520800	H	-9.52040000	4.72147100	0.29100300
C	-0.12006600	0.55465800	-0.33776500	H	-9.88220500	3.51008000	-0.95063400
C	-0.94567900	1.67578800	-0.40065200	H	-9.86287000	3.05206200	0.75981700
C	-2.32373000	1.52669600	-0.35991400	Q ²⁻ (s-BuOH)			
H	-6.48812800	-4.77841100	0.21892700	C	-6.04615900	-3.80726100	0.16261900
H	-4.02274600	-4.49949400	0.12760700	C	-4.69584900	-3.61048200	0.01936500
H	-6.96605900	-0.53002000	-0.08645900	C	-4.11837900	-2.31587000	-0.05661300
H	-7.95728500	-2.78565300	0.11124300	C	-5.00102500	-1.16839700	0.02226800
H	0.95597800	0.67171600	-0.36930000	C	-6.39648500	-1.41598500	0.16813100
H	-0.51179600	2.66457500	-0.48146000	C	-6.91262500	-2.68413100	0.23700400
H	-2.97660200	2.38768200	-0.40866700	C	-2.69434900	-2.18334200	-0.20376200
O	-5.08573600	1.11574400	-0.27688100	C	-4.50972900	0.17026900	-0.03741200
O	-1.90722900	-3.22514900	-0.03258000	C	-3.09625500	0.31065400	-0.18246800
H	-6.89985800	1.76258700	-0.38952100	C	-2.20824000	-0.83144400	-0.25788500
O	-7.83863200	2.00762200	-0.41509100	C	-0.81586800	-0.58589700	-0.38793500
C	-7.97184000	3.39568800	-0.08398300	H	-0.16378600	-1.45020500	-0.43572400
H	-7.51493900	3.57071200	0.90123000	C	-0.29457700	0.68206900	-0.45112000
C	-7.24553100	4.26796800	-1.11326400	C	-1.16571600	1.80240300	-0.38740800
H	-6.22295800	3.88876400	-1.21137800	C	-2.51655200	1.60927200	-0.25665200
H	-7.72520800	4.12725300	-2.08802400	H	-6.45285500	-4.81178700	0.21905100
C	-7.19447700	5.75445700	-0.75805700	H	-4.01704700	-4.45376600	-0.03639400
H	-8.18863800	6.20572600	-0.74403400	H	-7.05520100	-0.55824600	0.22369100
H	-6.74383000	5.91083300	0.22624600	H	-7.98217300	-2.83179600	0.34826900
H	-6.59535800	6.30576100	-1.48590300	H	0.77575300	0.83141000	-0.54995200
C	-9.46165600	3.68010600	0.01258100	H	-0.75961200	2.80753100	-0.44251800
H	-9.64889000	4.70914500	0.32254600	H	-3.19401800	2.45381200	-0.20942300
H	-9.94362400	3.51821500	-0.95547100	O	-5.29343400	1.22095600	0.04836200
H	-9.92766300	3.01624400	0.74312000	O	-1.90752500	-3.20837300	-0.28158600
Q ⁺ (s-BuOH)				H	-6.79103700	1.59790700	-0.37364900
C	-6.04509000	-3.79668700	0.10322100	O	-7.72249800	1.92121700	-0.58412500
C	-4.68329400	-3.61597300	0.01433900	C	-7.84871500	3.27677100	-0.18646700
C	-4.11822000	-2.32710700	-0.06218600	H	-7.44598100	3.39512800	0.83267400
C	-4.98117400	-1.19478700	-0.04867400	C	-7.04178400	4.19717700	-1.11384800
				H	-6.03045200	3.78655000	-1.17430600
				H	-7.46818100	4.13318000	-2.12186400

Appendix B

C	-6.96850700	5.65770000	-0.66517000
H	-7.94782200	6.14222200	-0.67667300
H	-6.57061300	5.73831700	0.35081200
H	-6.31142700	6.23455100	-1.32073000
C	-9.33418500	3.61497500	-0.15730200
H	-9.50956800	4.63991400	0.17621500
H	-9.76702700	3.49951000	-1.15557700
H	-9.86215600	2.94199300	0.52165100

Q(*i*-BuOH)

C	-6.09732100	-3.72866900	0.19149200
C	-4.71579400	-3.61423200	0.14369900
C	-4.11706200	-2.36230200	0.01101700
C	-4.92068000	-1.21259000	-0.07532900
C	-6.30976200	-1.33872200	-0.02539700
C	-6.89475500	-2.58932900	0.10724200
C	-2.63301100	-2.27161900	-0.03549100
C	-4.31192200	0.13342500	-0.21915500
C	-2.83094600	0.22870300	-0.25472100
C	-2.02790700	-0.91974400	-0.16740300
C	-0.63980400	-0.79495700	-0.20496800
H	-0.03467800	-1.68898000	-0.13671800
C	-0.05251100	0.45568200	-0.32714900
C	-0.84929800	1.59587300	-0.41443600
C	-2.23088400	1.48222900	-0.37905300
H	-6.55517700	-4.70453000	0.29470400
H	-4.08329400	-4.48937400	0.20879000
H	-6.92541500	-0.45203100	-0.08960700
H	-7.97325000	-2.67780600	0.14481600
H	1.02629300	0.54512600	-0.35461700
H	-0.39019900	2.57185900	-0.51025000
H	-2.86143600	2.35841700	-0.44690900
O	-5.00202800	1.14266400	-0.30674700
O	-1.93579200	-3.27200900	0.03360800
H	-6.79132700	1.79990000	-0.48712400
O	-7.72634900	2.05118300	-0.55567100
C	-7.87125800	3.41621700	-0.17394700
H	-8.94659800	3.58648600	-0.06075600
H	-7.40779900	3.58563500	0.80631100
C	-7.29995000	4.41066900	-1.18945800
H	-6.23411700	4.17680400	-1.30887800
C	-7.41667800	5.83678300	-0.64399100
H	-8.46523800	6.11241600	-0.49320400
H	-6.90152800	5.94469500	0.31411200
H	-6.98294500	6.55871700	-1.33975100
C	-7.97829300	4.27628800	-2.55417800
H	-7.90284000	3.25657000	-2.93460600
H	-9.04087500	4.53103700	-2.48381200
H	-7.52281400	4.94751900	-3.28657700

Q⁺(*i*-BuOH)

C	-6.08061100	-3.75708500	0.11640200
C	-4.71556200	-3.60369600	0.02568700
C	-4.12448000	-2.32617300	-0.04364900
C	-4.96412600	-1.17662700	-0.02105000
C	-6.36076800	-1.36207700	0.07433300
C	-6.91201900	-2.62137500	0.14193400
C	-2.67196900	-2.21421500	-0.13479800
C	-4.41193800	0.16608000	-0.09113800
C	-2.96511700	0.28322600	-0.17302400
C	-2.12341300	-0.86317700	-0.19202000
C	-0.72781300	-0.68191600	-0.26940300
H	-0.10215200	-1.56532200	-0.28038800
C	-0.17194600	0.57633500	-0.32816900
C	-1.00469400	1.71175600	-0.31245100
C	-2.37057800	1.56200800	-0.23679600
H	-6.51571200	-4.74845000	0.16900900

H	-4.06055700	-4.46540600	0.00690400
H	-6.99723400	-0.48758800	0.09598100
H	-7.98709200	-2.73923000	0.21472700
H	0.90393700	0.69465300	-0.38626200
H	-0.56829400	2.70293200	-0.35978200
H	-3.02264000	2.42575100	-0.22445100
O	-5.14740100	1.19979900	-0.07872200
O	-1.93128100	-3.23015700	-0.16151000
H	-6.80067100	1.69265900	-0.35482100
O	-7.72103100	2.01588200	-0.47835900
C	-7.77243200	3.39697500	-0.15702400
H	-8.82932200	3.64667100	-0.00681500
H	-7.25658500	3.58604000	0.79390200
C	-7.18869100	4.31354000	-1.23935000
H	-6.14755600	4.00556200	-1.39591800
C	-7.19047300	5.76541900	-0.75320500
H	-8.21087100	6.11278400	-0.56042600
H	-6.61905600	5.87946700	0.17179400
H	-6.75195500	6.43102400	-1.50071900
C	-7.93714900	4.16662900	-2.56529200
H	-7.94241000	3.12853900	-2.90080100
H	-8.97790400	4.49175100	-2.46076700
H	-7.47567600	4.77501900	-3.34767400

Q²⁻(*i*-BuOH)

C	-6.10544700	-3.72368600	0.16689000
C	-4.74660400	-3.57883100	0.04467400
C	-4.11952400	-2.30784600	-0.03500400
C	-4.96008000	-1.12691000	0.00826000
C	-6.36586400	-1.32115700	0.13861800
C	-6.92979300	-2.56820600	0.21714700
C	-2.68854500	-2.23121800	-0.15138300
C	-4.41788000	0.19098900	-0.06980200
C	-2.99680800	0.27601300	-0.17878000
C	-2.15074600	-0.89937300	-0.21312000
C	-0.74721100	-0.70914200	-0.31010600
H	-0.12828800	-1.59885200	-0.32622500
C	-0.17579800	0.53678800	-0.37795700
C	-1.00507600	1.68980700	-0.35135700
C	-2.36532400	1.55026000	-0.25423100
H	-6.55016100	-4.71182000	0.22612900
H	-4.10079700	-4.44848300	0.00763000
H	-6.99489800	-0.44070700	0.17643700
H	-8.00543700	-2.67410400	0.31688000
H	0.90168700	0.64394700	-0.45018500
H	-0.55976000	2.67821000	-0.40665000
H	-3.00824800	2.42198200	-0.23145800
O	-5.16282400	1.27348700	-0.03147100
O	-1.93944200	-3.28580700	-0.19550700
H	-6.65443400	1.64170900	-0.43899000
O	-7.58716500	1.96818000	-0.64730400
C	-7.70640100	3.31163200	-0.23319600
H	-8.77232800	3.51431900	-0.05737500
H	-7.18808100	3.46497700	0.72402700
C	-7.17568900	4.32967500	-1.25313200
H	-6.12445200	4.07713700	-1.43543700
C	-7.23870400	5.74522500	-0.67399000
H	-8.27187900	6.03016100	-0.44750800
H	-6.66125800	5.82554400	0.25089700
H	-6.84213400	6.48010100	-1.37950800
C	-7.92968300	4.23383900	-2.58016500
H	-7.90294200	3.21483300	-2.96846300
H	-8.98039500	4.51675100	-2.45041700
H	-7.49682800	4.89858400	-3.33298200

Q(*t*-BuOH)

C	-6.08886200	-3.72051700	0.17223200
---	-------------	-------------	------------

B.2 Supporting Information for 1,4-Benzoquinone

B.2.1 Cyclic voltammograms

Figure B.48. Cyclic voltammograms of 2 mM 1,4-benzoquinone (BQ) in (a) MeCN and (b) DCM with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of EtOH. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of EtOH are indicated in dashed lines with their measured trace moisture content.

Figure B.49. Cyclic voltammograms of 2 mM BQ in (a) MeCN and (b) DCM with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of $n\text{-PrOH}$. The voltammograms were recorded at a scan

rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of *n*-PrOH are indicated in dashed lines with their measured trace moisture content.

Figure B.50. Cyclic voltammograms of 2 mM BQ in (a) MeCN and (b) DCM with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of *i*-PrOH. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of *i*-PrOH are indicated in dashed lines with their measured trace moisture content.

Figure B.51. Cyclic voltammograms of 2 mM BQ in (a) MeCN and (b) DCM with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of *n*-BuOH. The voltammograms were recorded at a scan

rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of *n*-BuOH are indicated in dashed lines with their measured trace moisture content.

Figure B.52. Cyclic voltammograms of 2 mM BQ in (a) MeCN and (b) DCM with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of *s*-BuOH. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of *s*-BuOH are indicated in dashed lines with their measured trace moisture content.

Figure B.53. Cyclic voltammograms of 2 mM BQ in (a) MeCN and (b) DCM with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of *i*-BuOH. The voltammograms were recorded at a scan

rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of *t*-BuOH are indicated in dashed lines with their measured trace moisture content.

Figure B.54. Cyclic voltammograms of 2 mM BQ in (a) MeCN and (b) DCM with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of *t*-BuOH. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of *t*-BuOH are indicated in dashed lines with their measured trace moisture content.

Figure B.55. Cyclic voltammograms of 2 mM BQ in MeCN with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of FE. The voltammograms were recorded at a scan rate of 0.1 V s^{-1}

at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of FE are indicated in dashed lines with their measured trace moisture content.

Figure B.56. Cyclic voltammograms of 2 mM BQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of DFE. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of DFE are indicated in dashed lines with their measured trace moisture content.

Figure B.57. Cyclic voltammograms of 2 mM BQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of TFE. The voltammograms were recorded at a scan rate of 0.1 V s^{-1}

at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of TFE are indicated in dashed lines with their measured trace moisture content.

Figure B.58. Cyclic voltammograms of 2 mM BQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of TFP. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of TFP are indicated in dashed lines with their measured trace moisture content.

Figure B.59. Cyclic voltammograms of 2 mM BQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of DFIP. The voltammograms were recorded at a scan rate of 0.1 V s^{-1}

¹ at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of DFIP are indicated in dashed lines with their measured trace moisture content.

Figure B.60. Cyclic voltammograms of 2 mM BQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of EG. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of EG are indicated in dashed lines with their measured trace moisture content.

Figure B.61. Cyclic voltammograms of 2 mM BQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of PD. The voltammograms were recorded at a scan rate of 0.1 V s^{-1}

at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of PD are indicated in dashed lines with their measured trace moisture content.

Figure B.62. Cyclic voltammograms of 2 mM BQ in MeCN with 0.2 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of BD. The voltammograms were recorded at a scan rate of 0.1 V s^{-1} at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of BD are indicated in dashed lines with their measured trace moisture content.

B.2.2 Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of simple alcohols

Figure B.63. Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of alcohols obtained over three experiments (red +, blue ○ and black ×) as measured by square-wave voltammetry during the reduction of 2 mM BQ with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure B.64. Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of alcohols obtained over three experiments (red +, blue ○ and black ×) as measured by square-wave voltammetry during the reduction of 2 mM BQ with 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte in DCM recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

B.2.3 Computational data: Geometries, energies and coordinates of hydrogen-bonded complexes

Table B.2. Energies of the solvated hydrogen-bonded complexes of BQ and its reduced forms.

Hydrogen donors	Energy (hartrees)					
	MeCN			DCM		
	Q	Q ^{•-}	Q ²⁻	Q	Q ^{•-}	Q ²⁻
MeOH	-497.236	-497.396	-497.506	-497.235	-497.388	-497.480
EtOH	-536.539	-536.698	-536.809	-536.538	-536.690	-536.782
<i>n</i> -PrOH	-575.837	-575.996	-576.107	-575.835	-575.988	-576.080
<i>i</i> -PrOH	-575.843	-576.001	-576.112	-575.841	-575.994	-576.085
<i>n</i> -BuOH	-615.135	-615.293	-615.404	-615.133	-615.286	-615.378
<i>s</i> -BuOH	-615.138	-615.296	-615.406	-615.136	-615.288	-615.380
<i>i</i> -BuOH	-615.136	-615.294	-615.405	-615.134	-615.286	-615.379
<i>t</i> -BuOH	-615.144	-615.302	-615.412	-615.143	-615.295	-615.385
FE	-635.816	-635.976	-636.089			
DFE	-735.108	-735.269	-735.384			
TFE	-834.405	-834.566	-834.682			
TFP	-873.705	-873.865	-873.977			
DFIP	-774.394	-774.555	-774.671			
EG - Normal	-611.779	-611.938	-612.050			
EG - Bidentate	-611.781	-611.944	-612.061			
Two EG	-842.051	-842.214	-842.333			
PD - Normal	-651.077	-651.236	-651.346			
PD - Bidentate	-651.079	-651.242	-651.358			
Two PD	-920.646	-920.810	-920.929			
BD - Normal	-690.374	-690.533	-690.643			
BD - Bidentate	-690.374	-690.536	-690.651			
Two BD	-999.243	-999.407	-999.512

Figure B.65. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(MeOH) hydrogen-bonded complexes.

Figure B.66. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(EtOH) hydrogen-bonded complexes.

Figure B.67. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(*n*-PrOH) hydrogen-bonded complexes.

Figure B.68. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(*i*-PrOH) hydrogen-bonded complexes.

Figure B.69. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(*n*-BuOH) hydrogen-bonded complexes.

Figure B.70. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(*s*-BuOH) hydrogen-bonded complexes.

Figure B.71. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(*i*-BuOH) hydrogen-bonded complexes.

Figure B.72. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(*t*-BuOH) hydrogen-bonded complexes.

Figure B.73. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(FE) hydrogen-bonded complexes.

Figure B.74. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(DFE) hydrogen-bonded complexes.

Figure B.75. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(TFE) hydrogen-bonded complexes.

Figure B.76. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(TFP) hydrogen-bonded complexes.

Figure B.77. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(DFIP) hydrogen-bonded complexes.

Figure B.78. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(EG) normal hydrogen-bonded complexes.

Figure B.79. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(EG) bidentate hydrogen-bonded complexes.

Figure B.80. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(EG)₂ hydrogen-bonded complexes.

Figure B.81. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(PD) normal hydrogen-bonded complexes.

Figure B.82. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(PD) bidentate hydrogen-bonded complexes.

Figure B.83. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(PD)₂ hydrogen-bonded complexes.

Figure B.84. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(BD) normal hydrogen-bonded complexes.

Figure B.85. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(BD) bidentate hydrogen-bonded complexes.

Figure B.86. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) MeCN-solvated BQ(BD)₂ hydrogen-bored complexes.

Cartesian Coordinates of MeCN-Solvated Hydrogen-Bonded Complexes of 1,4-Benzoquinone

Q(MeOH)							
C	-4.18233300	-2.18630000	-0.53716500	C	-4.88995600	-0.94928700	-0.13560900
C	-4.87927600	-1.05338700	-0.41553100	C	-2.77344000	-2.16477800	0.12006300
C	-2.70347200	-2.18725400	-0.46686900	C	-4.13961000	0.29452100	-0.40456700
C	-4.19676500	0.23991000	-0.20700900	C	-2.66379200	0.23147700	-0.39354100
C	-2.72119800	0.24381600	-0.13938100	C	-2.02559300	-0.91610900	-0.14928600
C	-2.02369300	-0.88877200	-0.26024900	O	-4.71841500	1.35103600	-0.63089000
O	-4.82951800	1.28339600	-0.09180200	O	-2.19092000	-3.21481600	0.34376700
O	-2.06683300	-3.22394200	-0.57561700	H	-6.61784300	1.72975600	-0.73966400
H	-6.71120300	1.66470500	-0.06539400	O	-7.57441000	1.88970900	-0.79412200
O	-7.65377000	1.89551700	-0.03672000	C	-7.86750400	3.15346800	-0.19739300
C	-7.77757100	3.26700000	0.32201300	H	-8.95670900	3.21190000	-0.14253500
H	-8.84163700	3.50159400	0.35676900	H	-7.48724700	3.18238200	0.83098000
H	-7.34542800	3.47075700	1.30757500	C	-7.31727400	4.32661900	-0.99394700
H	-5.96113400	-1.03115200	-0.46276300	H	-6.22657600	4.28497800	-1.05027600
H	-2.24763500	1.20602200	0.01242400	H	-7.71464100	4.32421100	-2.01145800
H	-4.65874100	-3.14700800	-0.69001000	H	-7.59409700	5.27200700	-0.51940800
H	-0.94177500	-0.91221300	-0.21372800	H	-5.97067900	-0.87808000	-0.14816500
H	-7.30140900	3.92475300	-0.41304000	H	-2.13960500	1.15808800	-0.59304900
				H	-4.77912000	-3.02218500	0.30896000
				H	-0.94488800	-0.98807000	-0.13611700
Q ⁻ (MeOH)				Q ⁻ (EtOH)			
C	-4.38883900	-1.87192300	-0.22945700	C	-4.26838100	-2.04056200	0.08493400
C	-4.92282300	-0.62900700	-0.41523400	C	-4.90464700	-0.86377300	-0.18880900
C	-2.96541100	-2.08688800	-0.11754000	C	-2.82906200	-2.13954600	0.14389400
C	-4.09752800	0.54664300	-0.51165800	C	-4.17764800	0.35410000	-0.43670100
C	-2.67769900	0.33775500	-0.40207300	C	-2.74229700	0.26081800	-0.37842800
C	-2.14249700	-0.90424100	-0.21579400	C	-2.10493400	-0.91501600	-0.10481600
O	-4.58848800	1.71299900	-0.68393500	O	-4.76391900	1.45839700	-0.69491000
O	-2.46941700	-3.24073100	0.05587300	O	-2.23848000	-3.23255000	0.39772200
H	-6.26846500	2.05004300	-0.78124900	H	-6.47745700	1.67953600	-0.76579700
O	-7.22092900	2.30744500	-0.84524800	O	-7.45224500	1.83623300	-0.80723700
C	-7.68515300	2.65444500	0.44789300	C	-7.75082800	3.07358000	-0.17399500
H	-8.73742700	2.93302700	0.36729800	H	-8.83303600	3.09071200	-0.01728400
H	-7.60716900	1.81689500	1.15202400	H	-7.28145200	3.11676900	0.81763400
H	-5.99641600	-0.49489800	-0.49656800	C	-7.32894200	4.28316700	-0.99822900
H	-2.03955200	1.21254500	-0.47300000	H	-6.24696900	4.29394800	-1.15014400
H	-5.02952500	-2.74499500	-0.15953400	H	-7.81276500	4.27059000	-1.97794800
H	-1.06872100	-1.03900500	-0.13533100	H	-7.60888700	5.21039500	-0.48979800
H	-7.13732900	3.50733400	0.86703600	H	-5.98794900	-0.81663500	-0.22699500
				H	-2.17780100	1.16927700	-0.56224300
				H	-4.83549200	-2.94752500	0.26832600
				H	-1.02141300	-0.96215300	-0.06624300
Q ²⁻ (MeOH)				Q ²⁻ (EtOH)			
C	-4.43626000	-1.77108400	-0.14655700	C	-4.27593000	-1.75447000	0.56166200
C	-4.94069300	-0.49008100	-0.38337300	C	-4.98510100	-0.75244600	-0.10517700
C	-3.04651300	-2.05491800	-0.05733600	C	-2.86146400	-1.87930000	0.49914400
C	-4.10779900	0.63948300	-0.55463200	C	-4.35307800	0.22957700	-0.90241400
C	-2.72375000	0.36675200	-0.46844800	C	-2.94592300	0.11258800	-0.97106400
C	-2.21784100	-0.91303600	-0.23134900	C	-2.23566200	-0.88913800	-0.30672100
O	-4.57636700	1.86457000	-0.77867100	O	-5.01560900	1.18771800	-1.54423100
O	-2.57247400	-3.25886800	0.16518100	O	-2.19536900	-2.82103100	1.12630700
H	-6.08284600	2.14510600	-0.81498000	H	-6.47517900	1.55261500	-1.22149200
O	-7.07193600	2.41604900	-0.87224800	O	-7.44538000	1.84035100	-1.05736500
C	-7.61292400	2.46839700	0.42779500	C	-7.47156600	2.89606700	-0.11857300
H	-8.67371600	2.72677100	0.36197400	H	-8.44063100	2.86744700	0.39395200
H	-7.53589300	1.50475300	0.95100500	H	-6.70257000	2.74283400	0.65191900
H	-6.01753100	-0.34780900	-0.43928400	C	-7.28355300	4.27061000	-0.75516200
H	-2.03159900	1.19759600	-0.59198000	H	-6.30929700	4.34444200	-1.24481600
H	-5.13209300	-2.59913000	-0.02363000	H	-8.05715100	4.45566500	-1.50517000
H	-1.14009600	-1.05443300	-0.17462800	H	-7.34461100	5.06030100	0.00034300
H	-7.12305700	3.22732500	1.05466300	H	-6.06832600	-0.72074400	-0.01324000
				H	-2.40342000	0.84067000	-1.57125200
Q(EtOH)							
C	-4.25228800	-2.09706500	0.10918800				

Appendix B

H -4.82281700 -2.48133200 1.15963800
H -1.15197000 -0.92266100 -0.40335500

Q(*n*-PrOH)

C -4.22563200 -2.13795000 -0.18192200
C -4.89813900 -0.98420700 -0.15707000
C -2.74591500 -2.16132000 -0.21767700
C -4.18674900 0.31056200 -0.16420300
C -2.71013000 0.29150000 -0.19845000
C -2.03710000 -0.86189500 -0.22345700
O -4.79750600 1.37299300 -0.14286000
O -2.13129700 -3.21665000 -0.24139300
H -6.69599700 1.76300400 -0.13276800
O -7.64834100 1.95310500 -0.12888400
C -7.84202400 3.34983400 0.08846800
H -8.91401900 3.48278200 0.25711100
H -7.32683200 3.66705600 1.00456500
C -7.39099400 4.21091000 -1.08602000
H -6.32235600 4.04569200 -1.25965000
H -7.91294900 3.87526100 -1.98761900
C -7.65375200 5.69822700 -0.84950900
H -8.71888900 5.89239600 -0.69635500
H -7.12019600 6.06019300 0.03355900
H -7.32694800 6.29671400 -1.70214900
H -5.98023500 -0.94499700 -0.13123900
H -4.72353300 -3.09990500 -0.17776600
H -0.95497700 -0.90238400 -0.24873600
H -2.21491400 1.25477900 -0.20197600

Q⁻(*n*-PrOH)

C -4.24998100 -2.06444200 -0.20760700
C -4.90893300 -0.86835200 -0.20908300
C -2.80861200 -2.14678100 -0.18283700
C -4.20521900 0.38762500 -0.18640100
C -2.76790600 0.31074800 -0.16171200
C -2.10794000 -0.88421600 -0.15999500
O -4.81206300 1.51053600 -0.18835800
O -2.19685100 -3.25740100 -0.18140500
H -6.52696800 1.73244800 -0.19487400
O -7.49981400 1.90199100 -0.16970200
C -7.72218900 3.28206100 0.08359000
H -8.77874600 3.38749600 0.35058400
H -7.13714000 3.61129700 0.95384500
C -7.40581800 4.17688200 -1.11199500
H -6.35418200 4.04326600 -1.38576400
H -7.99953900 3.84018100 -1.96812100
C -7.68547500 5.65258000 -0.82761800
H -8.73677000 5.81506600 -0.57354200
H -7.08271300 6.01644000 0.00918000
H -7.45519000 6.27389200 -1.69563600
H -5.99336300 -0.83508300 -0.22776200
H -4.79979900 -2.99995300 -0.22524700
H -1.02336600 -0.91840800 -0.14121900
H -2.22084700 1.24782900 -0.14432200

Q²⁻(*n*-PrOH)

C -4.33546100 -1.83711500 0.32410700
C -4.93152400 -0.71441800 -0.25565500
C -2.93055000 -1.97230700 0.49177000
C -4.18430900 0.38992700 -0.72636400
C -2.78591500 0.26516800 -0.56171200
C -2.18851400 -0.85659700 0.01663000
O -4.73868900 1.46238500 -1.28451600
O -2.37029600 -3.02860500 1.03481000
H -6.25918000 1.70561400 -1.26925700
O -7.26346100 1.90949000 -1.29693500

C -7.55444600 2.99533600 -0.44286200
H -8.58862300 2.88455400 -0.09097700
H -6.91342600 2.96709700 0.45127400
C -7.40793800 4.35829500 -1.12030800
H -6.37764500 4.46829300 -1.47462500
H -8.04831700 4.37507700 -2.00888100
C -7.76848400 5.51992900 -0.19453500
H -8.80170700 5.44079200 0.15611100
H -7.12171100 5.54022600 0.68736600
H -7.66479300 6.48168300 -0.70194500
H -6.01417600 -0.68079900 -0.35322400
H -4.96818800 -2.65439100 0.66574400
H -1.10472800 -0.88871700 0.11284900
H -2.15734500 1.08478500 -0.90486700

Q(*i*-PrOH)

C -4.25896700 -2.08155200 0.10615900
C -4.89545200 -0.92884900 -0.11772000
C -2.78106300 -2.15990500 0.07164400
C -4.14463300 0.31024600 -0.40691700
C -2.66961700 0.23639500 -0.44137400
C -2.03268500 -0.91622700 -0.21842500
O -4.72250300 1.37125400 -0.61315700
O -2.19961100 -3.21460400 0.27558000
H -6.63303900 1.75814800 -0.69085100
O -7.59186000 1.90592800 -0.73563600
C -7.89879500 3.17678500 -0.14578300
H -7.52912300 3.18314600 0.88874300
C -7.23007000 4.31411400 -0.91124500
H -6.14517400 4.18679300 -0.93014500
H -7.59138900 4.34416500 -1.94267200
H -5.97551000 -0.84965500 -0.09760800
H -4.78611700 -3.00324800 0.32040000
H -0.95264000 -0.99616200 -0.23851300
H -2.14498000 1.15950900 -0.65539000
C -9.41280400 3.30457500 -0.12246200
H -9.71210300 4.24143900 0.35158400
H -9.81219000 3.29211600 -1.14023100
H -9.86191400 2.47957300 0.43394200
H -7.44763600 5.27654500 -0.44118000

Q⁻(*i*-PrOH)

C -4.30378100 -2.02367200 0.02328500
C -4.93385200 -0.83805000 -0.22561400
C -2.86553100 -2.12822300 0.09697400
C -4.20115000 0.38452100 -0.43075200
C -2.76669000 0.28527500 -0.35897900
C -2.13559000 -0.89946300 -0.11026400
O -4.78192300 1.49703400 -0.66410900
O -2.28063600 -3.22917000 0.32875800
H -6.50579600 1.72581900 -0.72570000
O -7.48187400 1.87140000 -0.76091100
C -7.79298700 3.13108900 -0.16661700
H -7.34039900 3.17445800 0.83482600
C -7.23757500 4.28723400 -0.99583000
H -6.15444100 4.19966500 -1.10414000
H -7.68379100 4.28851500 -1.99436500
H -6.01650100 -0.78719200 -0.27565500
H -4.87549000 -2.93362300 0.17489800
H -1.05268400 -0.95062300 -0.06075800
H -2.19747600 1.19659000 -0.51144900
C -9.30461500 3.20846000 -0.01530600
H -9.60009100 4.14635100 0.46006400
H -9.78819700 3.15389400 -0.99484800
H -9.67439000 2.38246800 0.59576000
H -7.45441700 5.24777400 -0.52052500

$Q^{2-}(i\text{-PrOH})$							
C	-4.29991800	-2.02634800	-0.03338900	C	-7.76249100	3.14196600	-0.08718000
C	-4.94706900	-0.82412000	-0.33034000	H	-8.80194900	3.16890800	0.25521900
C	-2.89384400	-2.12900100	0.14517500	H	-7.13146200	3.35843300	0.78580900
C	-4.25486200	0.40034600	-0.47977900	C	-7.54783000	4.21236000	-1.15386100
C	-2.85526000	0.30737400	-0.30106300	H	-6.51126100	4.16208500	-1.50617200
C	-2.20690000	-0.89344300	-0.00528000	H	-8.18430500	3.98122700	-2.01560200
O	-4.85650300	1.54936700	-0.76924500	C	-7.85110700	5.62498700	-0.65130100
O	-2.28573500	-3.25966900	0.42185800	H	-8.88444100	5.66577200	-0.28850000
H	-6.40451600	1.72352500	-0.78194600	H	-7.21584800	5.84638100	0.21369800
O	-7.41426600	1.88153700	-0.80362800	H	-5.99567100	-0.80715000	-0.12589200
C	-7.72392200	3.12152900	-0.19033200	H	-4.79093200	-2.91510400	0.33961500
H	-7.20372400	3.18782500	0.77838900	H	-1.02601900	-0.88731100	-0.22107000
C	-7.26904500	4.30220300	-1.05080000	H	-2.23473900	1.22152400	-0.68701600
H	-6.19427200	4.25081600	-1.23560800	C	-7.64566600	6.69980400	-1.71856800
H	-7.78401700	4.28792200	-2.01616700	H	-6.61248600	6.70638700	-2.07675300
H	-6.02767000	-0.82206800	-0.45455900	H	-8.29367700	6.52634100	-2.58219100
H	-4.89129400	-2.93488900	0.06657100	H	-7.86917100	7.69625800	-1.32992100
H	-1.12513300	-0.89542600	0.11628400	$Q^{2-}(n\text{-BuOH})$			
H	-2.26770200	1.21800500	-0.40289900	C	-4.25991800	-1.05532000	1.01988800
C	-9.22406600	3.16533200	0.07392200	C	-4.88979400	-0.14789300	0.16419700
H	-9.50997900	4.09781700	0.56706600	C	-2.94147300	-1.54022600	0.80446300
H	-9.77673600	3.09345000	-0.86769500	C	-4.26732700	0.36825000	-0.99582800
H	-9.52791600	2.33272200	0.71225900	C	-2.95580200	-0.10962200	-1.21853000
H	-7.48552700	5.25572400	-0.56004900	C	-2.32420300	-1.01489100	-0.36377300
$Q(n\text{-BuOH})$				O	-4.85299500	1.23650300	-1.81521900
C	-4.21765500	-2.05132700	0.14523100	O	-2.34889100	-2.39301100	1.60841700
C	-4.88495000	-0.91325100	-0.06316300	H	-6.36665600	1.53576800	-1.78717500
C	-2.74201400	-2.10435000	0.03965600	O	-7.36677600	1.74653300	-1.85408500
C	-4.17164000	0.33417400	-0.40619400	C	-7.70842700	2.73716300	-0.90695900
C	-2.69904100	0.28568000	-0.51173400	H	-8.77979800	2.63966000	-0.69006700
C	-2.03124100	-0.85217100	-0.30367000	H	-7.17870500	2.56301000	0.04186800
O	-4.77799400	1.38191400	-0.59880900	C	-7.42553800	4.16226300	-1.38371100
O	-2.13231200	-3.14559600	0.22963500	H	-6.35557800	4.25840100	-1.60080200
H	-6.68703600	1.72481800	-0.53823500	H	-7.95346800	4.32647900	-2.33057100
O	-7.64787900	1.85405600	-0.48054700	C	-7.84151500	5.22944000	-0.37017300
C	-7.91178100	3.19258200	-0.06107700	H	-8.91021300	5.12306900	-0.15073600
H	-8.98013000	3.23084000	0.16737000	H	-7.31823800	5.05329500	0.57659100
H	-7.37211500	3.41117800	0.86945400	H	-5.90068200	0.18138800	0.39416300
C	-7.56832000	4.23345100	-1.12037800	H	-4.79504700	-1.41375800	1.89732600
H	-6.50073800	4.16264200	-1.35955300	H	-1.31128000	-1.33999500	-0.59430300
H	-8.11380900	3.99356200	-2.03976000	H	-2.42417800	0.25189000	-2.09667200
C	-7.89995800	5.66014900	-0.67818000	C	-7.56154000	6.65533200	-0.84484700
H	-8.96469900	5.72195800	-0.42698800	H	-6.49536200	6.80354800	-1.03798800
H	-7.35509600	5.88983500	0.24418800	H	-8.09827500	6.87462100	-1.77223900
H	-5.96398200	-0.85281500	0.00919500	H	-7.86990800	7.39328800	-0.10008500
H	-4.71701800	-2.97871900	0.39794400	$Q(s\text{-BuOH})$			
H	-0.95215300	-0.91348700	-0.37504400	C	-4.02164000	-2.15416300	-0.40351400
H	-2.20229500	1.21451500	-0.76406800	C	-4.72695800	-1.02369400	-0.31094600
C	-7.56702200	6.70896200	-1.73887500	C	-2.54848600	-2.15183900	-0.25745800
H	-6.50254800	6.69257000	-1.98861700	C	-4.05992000	0.27041100	-0.05994000
H	-8.12603400	6.52793700	-2.66105400	C	-2.58986100	0.27682500	0.08622700
H	-7.81212600	7.71607800	-1.39357800	C	-1.88409000	-0.85337100	-0.00594100
$Q^+(n\text{-BuOH})$				O	-4.70125400	1.31126000	0.02524500
C	-4.24607800	-2.00392000	0.11454900	O	-1.90381600	-3.18596600	-0.34152000
C	-4.91129500	-0.83949300	-0.14268900	H	-6.61885000	1.64491300	-0.11991400
C	-2.80444200	-2.08385700	0.10064600	O	-7.58056200	1.77341900	-0.14960600
C	-4.21440900	0.38375500	-0.44489600	C	-7.86528300	3.17927300	-0.15154300
C	-2.77688400	0.30900100	-0.46104500	H	-7.42652200	3.62624000	0.75117300
C	-2.11060200	-0.85442100	-0.20384800	C	-7.24748000	3.86313000	-1.36844800
O	-4.82781500	1.47688100	-0.68719400	H	-6.16107600	3.74779500	-1.36008800
O	-2.18695900	-3.16504500	0.34093500	H	-7.62609000	3.43433400	-2.29823800
H	-6.54440600	1.67668500	-0.61663100	H	-5.80490800	-1.00351300	-0.41427100
O	-7.51964300	1.82273000	-0.55699200	H	-4.48685900	-3.11494300	-0.58733900
				H	-0.80606200	-0.87486300	0.09740900
				H	-2.12724600	1.23883100	0.26984500

383

Appendix B

C	-4.90853300	-0.87475100	-0.23842100
C	-2.83644100	-2.16186900	0.07055100
C	-4.18144600	0.35983400	-0.37279800
C	-2.74879800	0.27009900	-0.27465000
C	-2.11275300	-0.91934000	-0.06510400
O	-4.76558500	1.47943100	-0.56968300
O	-2.24710100	-3.26705100	0.26513100
H	-6.42952500	1.68052600	-0.61364600
O	-7.40744900	1.85767900	-0.62549200
C	-7.65256300	3.13863700	-0.08125700
H	-8.69408200	3.17640300	0.24947400
H	-7.01702300	3.33606900	0.79019000
C	-7.42158900	4.21303100	-1.13200800
H	-6.38025600	4.23811200	-1.45802700
H	-8.07473400	4.06825600	-1.99413800
H	-5.99032400	-0.83077500	-0.30916000
H	-2.18501100	1.19198800	-0.37374600
H	-4.84077600	-2.98567700	0.06854700
H	-1.03088600	-0.96427300	0.00617600
F	-7.71954300	5.47816300	-0.58486100

Q²(FE)

C	-4.36517500	-1.88891900	0.22125400
C	-4.96877300	-0.75715000	-0.33160600
C	-2.96033000	-2.01057500	0.40186800
C	-4.22911500	0.36812400	-0.75831800
C	-2.83240300	0.25865200	-0.58311400
C	-2.22683300	-0.87235000	-0.03250400
O	-4.79087800	1.45347400	-1.29206100
O	-2.39367300	-3.07367600	0.92161400
H	-6.24470300	1.66481300	-1.20347800
O	-7.26777700	1.87618100	-1.17146500
C	-7.51730100	2.85604700	-0.19755700
H	-8.54592000	2.75476000	0.16844000
H	-6.84898500	2.75108100	0.66834300
C	-7.34412300	4.24586100	-0.79096300
H	-6.31513600	4.41740800	-1.11173900
H	-8.02360800	4.40283400	-1.63064800
H	-6.05031300	-0.73379000	-0.44197100
H	-2.21168600	1.09652500	-0.89454900
H	-4.99077200	-2.72400500	0.53102100
H	-1.14392200	-0.89417200	0.07449800
F	-7.64680700	5.22779300	0.18045700

Q(DFE)

C	-4.21340300	-2.17865500	-0.17720400
C	-4.88791700	-1.02673900	-0.22322100
C	-2.73539500	-2.19806800	-0.09145800
C	-4.17996800	0.26862200	-0.19118700
C	-2.70602800	0.25477300	-0.10691400
C	-2.03074500	-0.89661300	-0.06026700
O	-4.79108400	1.33144900	-0.23230100
O	-2.11935500	-3.25160100	-0.04799200
H	-6.60944300	1.71479500	-0.31186700
O	-7.55140700	1.96360100	-0.32789500
C	-7.67980400	3.33834800	-0.03890100
H	-8.69240400	3.51868600	0.32922900
H	-6.97006400	3.66897600	0.72565300
C	-7.46945600	4.19064900	-1.27504800
H	-6.50350200	4.04846700	-1.76257700
H	-5.96865200	-0.99132600	-0.28505100
H	-2.21456500	1.21967700	-0.08547500
H	-4.70833200	-3.14185100	-0.19920100
H	-0.95003800	-0.93385900	0.00180400
F	-7.58906200	5.51755200	-0.93608900
F	-8.44592900	3.93656300	-2.20596200

Q⁺(DFE)

C	-4.25945900	-2.07208100	-0.04812800
C	-4.89823600	-0.87911400	-0.23035000
C	-2.82152700	-2.16568000	0.04746000
C	-4.17484600	0.35967000	-0.33874100
C	-2.74217900	0.27325100	-0.24524300
C	-2.10184300	-0.91824000	-0.06256700
O	-4.76246200	1.48261100	-0.50988600
O	-2.22850400	-3.27270700	0.21713400
H	-6.39900900	1.66665400	-0.57693600
O	-7.37917100	1.85160400	-0.60378800
C	-7.62074600	3.13462800	-0.08652800
H	-8.64775100	3.18411300	0.28730900
H	-6.94448200	3.38373100	0.73911700
C	-7.46119100	4.20483400	-1.14874500
H	-6.48432100	4.21375800	-1.63480300
H	-5.98028000	-0.83735700	-0.29839500
H	-2.18184800	1.19899900	-0.32576800
H	-4.82321900	-2.99589600	0.03121500
H	-1.01972800	-0.96122400	0.00556500
F	-7.67399900	5.44469300	-0.58930200
F	-8.41175300	4.05719800	-2.13054400

Q²(DFE)

C	-4.37437400	-1.83932600	0.26106000
C	-4.97605500	-0.74376700	-0.36249600
C	-2.97253400	-1.93591900	0.47799400
C	-4.23691900	0.36536100	-0.82662700
C	-2.84455100	0.28295500	-0.61518500
C	-2.24065500	-0.81164500	0.00524900
O	-4.79605300	1.41870200	-1.42896100
O	-2.40551100	-2.96561600	1.05878200
H	-6.20236400	1.62708300	-1.34097500
O	-7.23794900	1.85974900	-1.29988800
C	-7.46832200	2.75669800	-0.25820500
H	-8.48118000	2.62993400	0.14521700
H	-6.76002500	2.62490600	0.57161200
C	-7.34239300	4.19629900	-0.71741400
H	-6.38806500	4.43174100	-1.19095600
H	-6.05448800	-0.73859100	-0.50069600
H	-2.22627100	1.11206700	-0.95333500
H	-4.99838600	-2.66542500	0.59678900
H	-1.16062800	-0.81586900	0.13850700
F	-7.51199900	5.05088400	0.35276200
F	-8.33783400	4.51322600	-1.61515700

Q(TFE)

C	-4.09972800	-1.86962500	-0.81603000
C	-4.79068200	-0.77889600	-0.47406200
C	-2.63602600	-1.94723700	-0.60545600
C	-4.11587600	0.38741400	0.12902300
C	-2.65620600	0.31672600	0.33840300
C	-1.96442600	-0.77345400	-0.00339300
O	-4.74211000	1.39181000	0.45206600
O	-2.00543100	-2.94512600	-0.91805900
H	-6.53464700	1.78562100	0.40205500
O	-7.47809900	2.02759600	0.46292400
C	-7.63974000	3.38703600	0.15954500
H	-8.56109500	3.74449400	0.62215600
H	-6.81025200	4.00451600	0.51560700
C	-7.77093900	3.61886700	-1.33796700
H	-5.86103800	-0.70273300	-0.62069000
H	-2.18939500	1.18803600	0.78101700
H	-4.57015900	-2.73877800	-1.25924300
H	-0.89384100	-0.85083200	0.14157200
F	-7.94135600	4.93101800	-1.60617400

F	-8.82258900	2.96399500	-1.86869700
F	-6.67695500	3.21170200	-2.01581500

Q⁺(TFE)

C	-4.13999000	-1.73800700	-0.84196100
C	-4.81913100	-0.62970400	-0.42360600
C	-2.71373200	-1.87701300	-0.66239900
C	-4.15254600	0.46739400	0.22481200
C	-2.73211700	0.33617800	0.40606500
C	-2.05132800	-0.77041900	-0.01208700
O	-4.77797200	1.50932900	0.62523700
O	-2.08278700	-2.90485100	-1.05091400
H	-6.37547700	1.72657700	0.46353100
O	-7.35471200	1.93678800	0.43216200
C	-7.53059500	3.28580900	0.12046400
H	-8.42220100	3.67373000	0.62071800
H	-6.67669400	3.90472000	0.41413200
C	-7.74192000	3.49871700	-1.37092400
H	-5.89096600	-0.55082800	-0.57186000
H	-2.21488000	1.15634300	0.89297800
H	-4.66116200	-2.55594300	-1.32856600
H	-0.97921700	-0.85005400	0.13477000
F	-7.92789600	4.80935500	-1.64891900
F	-8.82438200	2.84051100	-1.83650100
F	-6.69088400	3.08351700	-2.10834900

Q²⁻(TFE)

C	-4.20804500	-1.48765800	-0.98202600
C	-4.88221500	-0.42174800	-0.38319600
C	-2.81047100	-1.70492600	-0.83410300
C	-4.22308900	0.53087100	0.41911000
C	-2.83777600	0.33136600	0.57507400
C	-2.16198500	-0.73422100	-0.02066800
O	-4.85075100	1.55920200	1.00892900
O	-2.17891600	-2.70569800	-1.39558900
H	-6.13843800	1.73607900	0.73904800
O	-7.21877600	1.95042000	0.58718500
C	-7.39329200	3.21777500	0.06852600
H	-8.24889800	3.73602300	0.52387400
H	-6.51203500	3.86243800	0.19766100
C	-7.67657600	3.19573100	-1.42724700
H	-5.95294600	-0.31790200	-0.53585700
H	-2.28358700	1.03955600	1.18721700
H	-4.76944200	-2.19137100	-1.59313300
H	-1.09023000	-0.83632500	0.13721400
F	-7.86735600	4.44903300	-1.91173400
F	-8.78794000	2.49011600	-1.73766600
F	-6.66782500	2.65338900	-2.14383500

Q(TFP)

C	-4.22023800	-2.14436300	-0.19342200
C	-4.90589600	-0.99852100	-0.22344800
C	-2.74056800	-2.15055300	-0.14454400
C	-4.20929400	0.30369000	-0.20961700
C	-2.73335900	0.30252200	-0.16203900
C	-2.04703400	-0.84287900	-0.13168800
O	-4.83145000	1.36006500	-0.23623700
O	-2.11412800	-3.19857500	-0.11589700
H	-6.68807700	1.72612600	-0.28535900
O	-7.63696900	1.94136000	-0.29464900
C	-7.81225000	3.30231000	0.06206000
H	-8.87101900	3.43163200	0.29032500
H	-7.24261300	3.54692600	0.96397200
C	-7.40809000	4.23189800	-1.08774700
H	-6.34588000	4.12088400	-1.31415600
H	-7.97354900	3.97907100	-1.98624100

C	-7.65350900	5.68730300	-0.79327100
H	-5.98811800	-0.97246000	-0.25832100
H	-4.70687100	-3.11200700	-0.20234900
H	-0.96480300	-0.87057500	-0.09677300
H	-2.24987300	1.27167500	-0.15356400
F	-8.95745500	5.95324100	-0.54746700
F	-7.28786400	6.47985200	-1.82601400
F	-6.96509400	6.12289200	0.28777800

Q⁺(TFP)

C	-4.25922500	-2.04529500	-0.14863900
C	-4.93061300	-0.85769500	-0.20669500
C	-2.81701700	-2.11070300	-0.11810700
C	-4.23966200	0.40425600	-0.24115000
C	-2.80234700	0.34530200	-0.21034800
C	-2.12960300	-0.84100300	-0.15218100
O	-4.85845000	1.52087300	-0.29710600
O	-2.19368200	-3.21307700	-0.06483700
H	-6.53215500	1.69095600	-0.33593000
O	-7.51016400	1.86391900	-0.35122500
C	-7.74591700	3.20098600	0.03495500
H	-8.81289200	3.29599900	0.24716500
H	-7.20179100	3.44817900	0.95355900
C	-7.35095800	4.17838000	-1.08079000
H	-6.28235000	4.10111500	-1.28981100
H	-7.89276900	3.93497800	-1.99653100
C	-7.64254900	5.61691100	-0.75299400
H	-6.01526600	-0.83728900	-0.22831200
H	-4.79924100	-2.98623300	-0.12341600
H	-1.04484000	-0.86288000	-0.13037100
H	-2.26553700	1.28802200	-0.23584500
F	-8.95820600	5.84170300	-0.52396100
F	-7.28241600	6.44935000	-1.75757800
F	-6.98634900	6.04476000	0.35148300

Q²⁻(TFP)

C	-4.38333000	-1.72993100	0.37200000
C	-5.06868700	-0.77993300	-0.38866200
C	-2.98315400	-1.66915700	0.61148500
C	-4.42628300	0.32806800	-0.98429400
C	-3.03495200	0.39788500	-0.75381000
C	-2.34686000	-0.55214900	0.00288800
O	-5.07093400	1.23813000	-1.71582500
O	-2.33786900	-2.55929500	1.32740800
H	-6.49185100	1.53829700	-1.43205900
O	-7.48470900	1.80642000	-1.26537800
C	-7.53357500	2.86425700	-0.34640500
H	-8.52163200	2.87414900	0.12496300
H	-6.79291200	2.73215600	0.45293800
C	-7.29360400	4.21661300	-1.03976800
H	-6.30278400	4.23207300	-1.49760300
H	-8.03282500	4.36268300	-1.82989400
C	-7.38029200	5.39971000	-0.11725700
H	-6.14082300	-0.89075300	-0.53419500
H	-4.93775500	-2.56086800	0.80429600
H	-1.27308200	-0.44099000	0.14150200
H	-2.48557400	1.23078600	-1.18843200
F	-8.58806100	5.50392400	0.48871700
F	-7.18111500	6.57177200	-0.76822800
F	-6.46133600	5.35766800	0.87695000

Q(DFIP)

C	-4.36550700	-2.06592700	-0.02049800
C	-4.95478800	-0.89093000	-0.25726200
C	-2.89632400	-2.16895900	0.13262300
C	-4.15832900	0.34657400	-0.37536400

Appendix B

C	-2.69342000	0.25017300	-0.22036300
C	-2.10326800	-0.92438300	0.01633000
O	-4.69075300	1.42962800	-0.59682400
O	-2.35801300	-3.24373600	0.34771300
H	-6.46664800	1.83612800	-0.88475400
O	-7.40211400	2.06704100	-1.03413300
C	-7.73452800	3.21843400	-0.27188500
H	-7.15133600	3.26530300	0.65485100
C	-7.42231400	4.45218000	-1.11429700
H	-6.39372500	4.40083700	-1.47481500
H	-8.10457800	4.53565600	-1.96311000
H	-6.02747500	-0.79377300	-0.37146500
H	-4.92615500	-2.98819400	0.07030600
H	-1.03085900	-1.02241100	0.13245200
H	-2.13632000	1.17454700	-0.31060300
C	-9.20600300	3.05200900	0.07967500
H	-9.82517100	3.05155000	-0.82018300
H	-9.35285900	2.12110200	0.62817400
F	-7.54180000	5.62671100	-0.35587000
F	-9.64630700	4.10181500	0.89634800

$Q^*(DFIP)$

C	-4.45762600	-1.91917800	0.07193200
C	-5.00665000	-0.71397300	-0.26030500
C	-3.03287700	-2.09652700	0.22735100
C	-4.19595600	0.45426600	-0.47685000
C	-2.77618600	0.28507600	-0.32274300
C	-2.22546800	-0.91890100	0.00930100
O	-4.69875200	1.58815400	-0.79058900
O	-2.52318700	-3.21497500	0.53551300
H	-6.29630400	1.84326000	-1.01035900
O	-7.26386600	2.05644000	-1.14797300
C	-7.63585500	3.12056800	-0.29580900
H	-7.04236300	3.12184600	0.62730100
C	-7.38664500	4.43131300	-1.03721400
H	-6.36035900	4.45251800	-1.40652400
H	-8.08041100	4.55113100	-1.87249400
H	-6.08063700	-0.60760300	-0.37041500
H	-5.08621100	-2.78924100	0.23076300
H	-1.15133500	-1.02561400	0.12011300
H	-2.15104900	1.15742600	-0.48226800
C	-9.09449800	2.87062100	0.05967700
H	-9.72781900	2.92382400	-0.82886500
H	-9.19831800	1.89105000	0.52736100
F	-7.54839000	5.54249400	-0.19122800
F	-9.56783100	3.82740200	0.97137000

$Q^2(DFIP)$

C	-4.62523500	-1.53565400	0.50133200
C	-5.07357600	-0.32995600	-0.04270100
C	-3.26294400	-1.94155500	0.47372500
C	-4.20402900	0.58619800	-0.66971600
C	-2.84932600	0.19770100	-0.70322700
C	-2.39820400	-1.00520300	-0.15842600
O	-4.61210800	1.74696100	-1.19619900
O	-2.84226200	-3.07367400	0.98238600
H	-5.95633600	1.99818000	-1.34143300
O	-6.99365400	2.26522800	-1.50988900
C	-7.49863600	2.96094100	-0.40479900
H	-6.93724500	2.73147200	0.51404400
C	-7.36334900	4.45572300	-0.68443300
H	-6.33038500	4.68127300	-0.95246700
H	-8.02993900	4.76767200	-1.49219100
H	-6.13100700	-0.08435400	0.01408800
H	-5.34456900	-2.20287100	0.97190700
H	-1.33903700	-1.24840000	-0.21526800
H	-2.13585400	0.86985700	-1.17529000

C	-8.93672000	2.49521400	-0.21986900
H	-9.54915200	2.76955800	-1.08218200
H	-8.95792700	1.41347200	-0.08341400
F	-7.67877200	5.24200500	0.44396800
F	-9.53832600	3.07158600	0.91710000

$Q(EG - normal)$

C	-4.03150300	-2.06829300	-0.10219100
C	-4.76604700	-0.95369900	-0.14862000
C	-2.56239600	-2.01110700	0.07275900
C	-4.13611500	0.37666800	-0.02660400
C	-2.67094700	0.43839500	0.14944600
C	-1.93571900	-0.67571500	0.19544900
O	-4.80308300	1.40453700	-0.06953900
O	-1.89132800	-3.03070500	0.11444900
H	-6.66905400	1.68696100	-0.33466700
O	-7.61966600	1.83965900	-0.46969000
C	-7.91261800	3.21031700	-0.23129200
H	-8.99687600	3.29348300	-0.13038900
H	-7.46320100	3.54973400	0.71070200
C	-7.44083100	4.09850200	-1.37942600
H	-6.35788800	3.99571300	-1.51446100
H	-7.92638300	3.78857500	-2.30622100
O	-7.79905500	5.46605500	-1.17835800
H	-7.28749700	5.81783100	-0.44091600
H	-2.23667700	1.42679700	0.23666300
H	-5.84145400	-0.97428900	-0.27589500
H	-4.46889900	-3.05540600	-0.18922800
H	-0.86023500	-0.65692500	0.32282200

$Q^*(EG - normal)$

C	-4.09731800	-1.97331200	0.01915400
C	-4.77500400	-0.80171200	-0.16083400
C	-2.66687000	-2.01115400	0.21355800
C	-4.10344400	0.47142900	-0.16695700
C	-2.67760400	0.43969700	0.02682600
C	-1.99858100	-0.73091400	0.20639500
O	-4.72891400	1.57280200	-0.33479800
O	-2.03784600	-3.09916100	0.37966200
H	-6.40421100	1.67255400	-0.59494200
O	-7.38129600	1.77233200	-0.72978000
C	-7.78355400	3.05494700	-0.28615900
H	-8.86032700	3.02337400	-0.09661200
H	-7.29065700	3.31807600	0.65993500
C	-7.49196500	4.13179400	-1.32887000
H	-6.41887500	4.15875800	-1.54976300
H	-8.02043900	3.89803500	-2.25477500
O	-7.95750500	5.42030900	-0.92004600
H	-7.43192600	5.71581500	-0.16799300
H	-2.15408100	1.39022400	0.02458500
H	-5.85038000	-0.80300000	-0.30480500
H	-4.62377000	-2.92223500	0.02084800
H	-0.92290600	-0.73157000	0.35016800

$Q^2(EG - normal)$

C	-4.11542400	-1.93098300	0.13503000
C	-4.78558300	-0.74258800	-0.16568000
C	-2.71035900	-2.00158700	0.33684200
C	-4.11895800	0.49700600	-0.29462500
C	-2.72185500	0.43806100	-0.09243000
C	-2.05037800	-0.74874700	0.20774700
O	-4.74294800	1.63636300	-0.58662600
O	-2.08061000	-3.11884800	0.61518700
H	-6.23378200	1.68100300	-0.79421600
O	-7.25310700	1.77616300	-0.94673300
C	-7.70969100	2.96758900	-0.35508900

H	-8.78065000	2.87258600	-0.13957700
H	-7.20296500	3.15642400	0.60415400
C	-7.50153300	4.17465800	-1.26905000
H	-6.43774900	4.27878900	-1.51084200
H	-8.04671400	4.02685000	-2.20330200
O	-8.01140200	5.38731600	-0.70282300
H	-7.49714900	5.59895900	0.08457200
H	-2.15498200	1.36324500	-0.17776500
H	-5.86361300	-0.76526400	-0.30759600
H	-4.68671300	-2.85377100	0.21869900
H	-0.97130800	-0.72613600	0.34892000

Q(EG - bidentate)

C	-4.01174900	-2.22467500	-0.14318200
C	-4.72866000	-1.09774700	-0.14774600
C	-2.53825400	-2.19341600	0.00203000
C	-4.07324700	0.21630000	-0.00807600
C	-2.60588400	0.25580500	0.13780200
C	-1.88784900	-0.87041700	0.14246700
O	-4.73275900	1.25164100	-0.01341500
O	-1.88221900	-3.22295300	0.00584400
H	-4.63498200	3.23192100	0.00096000
H	-6.57440000	1.96209900	-0.03705400
O	-7.36693900	2.47915400	0.17043000
O	-4.78749100	4.16117000	-0.22563300
C	-7.22847000	3.80405400	-0.34088200
C	-6.06449700	4.57514000	0.25835900
H	-8.15781400	4.32080400	-0.08989600
H	-6.16210000	5.62789300	-0.01695700
H	-7.13325600	3.79608800	-1.43372600
H	-6.10512000	4.50571200	1.35248200
H	-2.15439800	1.23507400	0.23872100
H	-5.80663300	-1.09337400	-0.25230100
H	-4.46645100	-3.20250100	-0.24415800
H	-0.80984900	-0.87113100	0.24727400

Q⁺(EG - bidentate)

C	-4.04772800	-2.09458400	0.02652300
C	-4.75665500	-0.96857500	-0.27841000
C	-2.62637300	-2.05840900	0.28238200
C	-4.12820700	0.32016100	-0.36260900
C	-2.71504800	0.36619500	-0.10982800
C	-2.00334200	-0.75790900	0.19542900
O	-4.79388000	1.37549200	-0.65607500
O	-1.96726600	-3.10185500	0.56517900
H	-4.60542900	3.09267400	-0.30080100
H	-6.46169200	1.88479000	-0.35455100
O	-7.29535800	2.32910400	-0.08887200
O	-4.70812200	4.06121800	-0.17712900
C	-7.15676000	3.73613200	-0.25351200
C	-5.95136700	4.32923500	0.46142700
H	-8.06431400	4.18562500	0.15928000
H	-6.05867300	5.41740500	0.48318400
H	-7.10690400	4.00072600	-1.31886500
H	-5.94054300	3.97328500	1.50090900
H	-2.22671000	1.33308200	-0.17109300
H	-5.82376200	-1.01831000	-0.46791700
H	-4.53885400	-3.06019300	0.08575500
H	-0.93603200	-0.70512800	0.38293700

Q²⁻(EG - bidentate)

C	-4.15702200	-1.86013600	0.17439300
C	-4.80917100	-0.76877900	-0.40122200
C	-2.78219800	-1.83538700	0.54021900
C	-4.15412500	0.44962000	-0.66861400
C	-2.78983700	0.48767200	-0.31835200

C	-2.13360300	-0.60096000	0.25770400
O	-4.78298400	1.49637700	-1.22458400
O	-2.16979200	-2.85464300	1.08709900
H	-4.58718000	2.96022700	-0.57338200
H	-6.28389100	1.83586500	-0.71133600
O	-7.15885700	2.16547300	-0.33637900
O	-4.63337800	3.89234800	-0.19328200
C	-7.07386900	3.56572800	-0.12614200
C	-5.80616800	4.00261000	0.59679600
H	-7.94053700	3.85767200	0.47725300
H	-5.90976600	5.05567000	0.88024800
H	-7.13829300	4.11033300	-1.08082900
H	-5.71020200	3.41889500	1.52503200
H	-2.23516600	1.40395600	-0.50891400
H	-5.86268400	-0.85327800	-0.65886200
H	-4.71593000	-2.77551600	0.35819400
H	-1.07836500	-0.51358600	0.50830200

Q(EG)₂

C	-3.42640200	-2.18469600	-0.13456200
C	-4.24955900	-1.16107300	-0.38013200
C	-1.96035600	-2.00422800	-0.18553400
C	-3.72311300	0.17872600	-0.70982100
C	-2.25707300	0.35651300	-0.76345200
C	-1.43195300	-0.66488400	-0.51962100
O	-4.47293600	1.12207700	-0.93450400
O	-1.19879600	-2.93594100	0.04345500
H	-6.38233800	1.20527200	-1.01879600
O	-7.35148400	1.24703100	-1.08215700
C	-7.83890500	2.21438600	-0.16133100
H	-8.91569900	2.05642700	-0.07100800
H	-7.39634500	2.06822200	0.83243100
C	-7.57390500	3.63850100	-0.64179700
H	-6.49719800	3.79796400	-0.77182000
H	-8.05608600	3.79540700	-1.60807200
O	-8.12731400	4.61240800	0.24373300
H	-7.63674200	4.59509400	1.07336400
O	-1.25710800	-5.71719200	0.84568400
H	-1.43278700	-4.80414000	0.56819000
C	-2.27322100	-6.15252700	1.74000700
H	-1.87461400	-7.01802200	2.27444100
H	-2.49666000	-5.37598800	2.48110700
C	-3.55066000	-6.57115200	1.04472100
H	-3.31996700	-7.29698400	0.25767600
H	-4.21425700	-7.04818800	1.77604500
O	-4.17685200	-5.41210000	0.48428200
H	-4.92990000	-5.69042900	-0.04794600
H	-5.32731000	-1.26556700	-0.34944700
H	-3.78065800	-3.18063800	0.10824300
H	-0.35416800	-0.56340800	-0.55208100
H	-1.89922100	1.34882000	-1.00886500

Q⁺(EG)₂

C	-4.17969500	-1.83909100	-0.34134500
C	-4.80492600	-0.68094100	0.01976800
C	-2.78065800	-2.06142100	-0.08287500
C	-4.10049300	0.38672600	0.68174200
C	-2.70189200	0.16402100	0.94155000
C	-2.07640400	-0.99369400	0.57963000
O	-4.67492100	1.47271600	1.02273100
O	-2.20579400	-3.14615400	-0.42546200
H	-6.32174400	1.83518600	0.72231600
O	-7.26512800	2.10856200	0.60314900
C	-7.30807300	3.33198200	-0.10873100
H	-8.28750000	3.78652600	0.06480300
H	-6.54876800	4.03275100	0.26453500
C	-7.11306600	3.12249800	-1.60856600

Appendix B

H	-6.14689800	2.64090400	-1.79740700
H	-7.89662500	2.46693100	-1.99258100
O	-7.22149800	4.34442700	-2.34256400
H	-6.47506000	4.91032900	-2.11488200
O	0.40164000	-3.78464800	-0.05389700
H	-0.53998500	-3.51016500	-0.17142000
C	1.15155900	-3.33525200	-1.16862600
H	0.78335200	-3.78891400	-2.09905200
H	1.07696600	-2.24480400	-1.27969500
C	2.60469500	-3.71451700	-1.01545300
H	2.68133300	-4.78451700	-0.79082100
H	3.12001400	-3.52323200	-1.96407100
O	3.19515000	-2.94182400	0.03434000
H	4.10229200	-3.23865600	0.16209200
H	-2.15605300	0.95776300	1.44041300
H	-1.02171700	-1.14050300	0.78579900
H	-4.72582100	-2.63317300	-0.83934800
H	-5.85983700	-0.53468900	-0.18547700

Q²-(EG)₂

C	-3.42330900	-1.89087100	-0.34871300
C	-4.15605300	-0.75218100	-0.69026800
C	-2.01245000	-1.88790300	-0.24591200
C	-3.54578200	0.49407100	-0.96152400
C	-2.13513200	0.49615800	-0.86234200
C	-1.40325700	-0.64134300	-0.52088200
O	-4.23024100	1.58489700	-1.28323500
O	-1.30495400	-2.96015300	0.08281300
H	-5.73300500	1.55089700	-1.45951300
O	-6.75367100	1.59012400	-1.60528600
C	-7.38190000	1.98608700	-0.41053900
H	-8.39313800	1.56312600	-0.37737900
H	-6.84244000	1.60130400	0.46858700
C	-7.48498900	3.50670800	-0.30079500
H	-6.48492700	3.95186500	-0.35588900
H	-8.07340500	3.89711700	-1.13346200
O	-8.15963900	3.92687900	0.89038300
H	-7.62461300	3.67400700	1.65135800
O	-2.28511500	-5.31650800	0.25065700
H	-1.94309600	-4.35045800	0.19097100
C	-2.91688200	-5.51812600	1.49110400
H	-2.19659700	-5.46407100	2.32291100
H	-3.68276200	-4.75043000	1.67961800
C	-3.57378400	-6.87829900	1.55681900
H	-2.84773000	-7.64906300	1.27269700
H	-3.89377100	-7.06892300	2.58844500
O	-4.70317200	-6.91381100	0.67620200
H	-5.07764000	-7.80077100	0.69257500
H	-5.23921400	-0.81862200	-0.75191900
H	-3.95212300	-2.82002700	-0.15194300
H	-0.31897900	-0.57949200	-0.46057600
H	-1.60981700	1.42750300	-1.06253100

Q(PD - normal)

C	-4.00312200	-2.02395400	0.16851700
C	-4.75288100	-0.92111900	0.09363400
C	-2.52805800	-1.95617600	0.06191600
C	-4.13464800	0.40676200	-0.09839500
C	-2.66285000	0.47906700	-0.20187300
C	-1.91259100	-0.62346200	-0.12765000
O	-4.81671700	1.42247900	-0.17138300
O	-1.84309100	-2.96531800	0.12816600
H	-6.73246500	1.67538400	-0.14630600
O	-7.69708900	1.78798100	-0.13103700
C	-8.00219300	3.18203000	-0.11600300
H	-9.07150000	3.25570000	0.09932300
H	-7.46714000	3.67992700	0.69875600

C	-7.69654800	3.86276200	-1.44734300
H	-6.62827100	3.77380700	-1.67122000
H	-8.23695000	3.34077500	-2.24298700
H	-2.23680000	1.46517200	-0.34056800
H	-5.83305400	-0.94880800	0.16839700
H	-4.43190800	-3.00877200	0.30846500
H	-0.83225300	-0.59683000	-0.20150900
C	-8.09181300	5.32835900	-1.48477500
H	-7.95754900	5.72263300	-2.49770600
H	-9.14965100	5.44270100	-1.21738800
O	-7.27224400	6.05738900	-0.56144000
H	-7.53349600	6.98421500	-0.58208900

Q⁺(PD - normal)

C	-4.07238500	-1.93644200	-0.00365800
C	-4.77829100	-0.76760900	-0.00756700
C	-2.62883400	-1.96143700	-0.01905800
C	-4.12537900	0.51556200	-0.02744400
C	-2.68597400	0.49596200	-0.04211400
C	-1.97902500	-0.67195700	-0.03824400
O	-4.77805700	1.61277800	-0.03244400
O	-1.97313100	-3.04667300	-0.01591600
H	-6.50255500	1.70861300	-0.04220000
O	-7.48723600	1.79153600	-0.02313100
C	-7.84056100	3.16762800	-0.04886700
H	-8.88657500	3.23274600	0.26794800
H	-7.24534300	3.73027900	0.67866600
C	-7.69369200	3.78690000	-1.43813600
H	-6.64865600	3.72815400	-1.75940400
H	-8.28155800	3.19708400	-2.14867200
H	-2.17558200	1.45353000	-0.05695100
H	-5.86320000	-0.77795600	0.00415000
H	-4.58549200	-2.89258300	0.01130100
H	-0.89384400	-0.66347600	-0.04991500
C	-8.16101900	5.22901400	-1.51843600
H	-8.14007400	5.56943600	-2.55943700
H	-9.19437100	5.31324200	-1.15910800
O	-7.29771100	6.04863500	-0.71801800
H	-7.60633800	6.95973700	-0.76584400

Q²-(PD - normal)

C	-4.16224400	-1.84598600	-0.17572900
C	-4.81558300	-0.64121200	0.09584000
C	-2.76140300	-1.93811200	-0.39585700
C	-4.13511200	0.59614700	0.17325400
C	-2.74098900	0.51411300	-0.04619500
C	-2.08639000	-0.68933700	-0.31613200
O	-4.74377600	1.74878000	0.43557100
O	-2.14764100	-3.07076400	-0.64926800
H	-6.27735100	1.84468000	0.44724000
O	-7.29492500	1.97383400	0.48730900
C	-7.60953700	3.32444700	0.21916900
H	-8.55886500	3.55919900	0.71840800
H	-6.85094600	3.99060400	0.64809600
C	-7.75931900	3.61045200	-1.27727000
H	-6.81024900	3.41341900	-1.78698500
H	-8.49542800	2.91365500	-1.69165900
H	-2.16349500	1.43553500	0.00012500
H	-5.89141000	-0.64771400	0.25619400
H	-4.74378500	-2.76509900	-0.22071700
H	-1.00920600	-0.68341300	-0.47352800
C	-8.21694100	5.02177500	-1.59679900
H	-8.42589300	5.11397600	-2.66844100
H	-9.14308900	5.25125800	-1.05433700
O	-7.18950900	5.95030100	-1.21948200
H	-7.49179900	6.84216400	-1.42130400

Q(PD - bidentate)							
C	-4.13688700	-2.02249700	0.17773400	O	-4.51203400	4.08011500	0.35533600
C	-4.85340500	-0.89542800	0.19316600	C	-7.08162600	3.15701400	-0.88686900
C	-2.66929100	-1.99346200	-0.01807900	C	-5.74752100	4.68842300	0.69881500
C	-4.20394700	0.41688200	0.01507400	H	-7.92975800	3.17395900	-1.57931500
C	-2.74228500	0.45405600	-0.18030200	H	-5.55454400	5.74675400	0.90360700
C	-2.02459300	-0.67230400	-0.19609600	H	-6.21138200	2.80636300	-1.45458400
O	-4.86405300	1.45272700	0.02907400	H	-6.13306700	4.24857700	1.62657200
O	-2.01361700	-3.02304300	-0.03231700	H	-2.55132100	1.61221300	0.03745400
H	-4.51206700	3.40568000	-0.13450000	H	-5.91241600	-0.88979400	0.89041900
H	-6.79617200	1.91854100	0.15676400	H	-4.69411200	-2.83510400	0.00685400
O	-7.64319800	2.36830700	0.02377400	H	-1.32774400	-0.32545300	-0.84925200
O	-4.58948900	4.36683300	-0.04752000	C	-6.81708200	4.58149800	-0.39168600
C	-7.41999400	3.49737500	-0.82586400	H	-6.52326400	5.19018100	-1.25566100
C	-5.74173900	4.65303000	0.75045100	H	-7.74532800	5.01330900	0.00216500
H	-8.35547200	3.67552500	-1.36074300	Q(PD) ₂			
H	-5.54904900	5.60740600	1.24542200	C	-5.03369800	-1.93367200	0.29577100
H	-6.65928100	3.25553200	-1.57514500	C	-5.59577900	-0.80297700	-0.13929400
H	-5.84878900	3.89714200	1.53529200	C	-3.78120900	-2.43948600	-0.30458100
H	-2.29288700	1.43103200	-0.30872100	C	-4.98382200	-0.02050300	-1.23379900
H	-5.92707000	-0.89154200	0.33485000	C	-3.73265500	-0.52710300	-1.83488300
H	-4.58800700	-2.99873800	0.30623700	C	-3.17168200	-1.65882500	-1.40137700
H	-0.95088100	-0.67415200	-0.33811400	O	-5.49403500	1.01808800	-1.63539500
C	-7.02917100	4.75964600	-0.06234000	O	-3.25801900	-3.47391800	0.09044600
H	-6.93171200	5.57732300	-0.78521800	H	-7.14864600	1.89238700	-1.12471900
H	-7.84056600	5.03171900	0.62192900	O	-8.00399900	2.30047100	-0.91215100
Q ⁺ (PD - bidentate)				C	-7.81858800	3.24730700	0.13659400
C	-4.12711400	-1.97357900	0.12756700	H	-8.82090300	3.54134500	0.45748600
C	-4.85285900	-0.81835400	0.17241400	H	-7.32787600	2.77213800	0.99541800
C	-2.69293500	-1.97078500	-0.04630400	C	-7.02835800	4.47405300	-0.30930000
C	-4.23059400	0.47047400	0.04840700	H	-6.03314900	4.16528000	-0.64530300
C	-2.80459700	0.48326400	-0.12574000	H	-7.53299900	4.93504600	-1.16355800
C	-2.07628900	-0.67040500	-0.17084100	O	-3.92497100	-5.32582300	2.24199800
O	-4.91302400	1.55358200	0.09117800	H	-3.70315300	-4.70958100	1.52533400
O	-2.01817900	-3.04163900	-0.08671100	C	-3.59934400	-6.65216900	1.83027700
H	-4.55068400	3.29110600	-0.08058700	H	-3.99913200	-7.31375800	2.59943800
H	-6.65342800	1.91159200	0.14897700	H	-4.10870700	-6.89573500	0.88869700
O	-7.54178300	2.31802100	0.05736200	C	-2.09657900	-6.86839100	1.67476000
O	-4.58354100	4.27099900	-0.05958400	H	-1.59531900	-6.63289900	2.61872900
C	-7.40821800	3.44453400	-0.80604600	H	-6.51294100	-0.41216100	0.28400700
C	-5.71555700	4.64407000	0.72289700	H	-5.46311500	-2.52318100	1.09637400
H	-8.37456000	3.59287500	-1.29576400	H	-2.25615700	-2.05384100	-1.82409000
H	-5.49870900	5.62347100	1.15805300	H	-3.30675200	0.06478500	-2.63555300
H	-6.67736700	3.22489300	-1.59186100	H	-1.70880500	-6.17449600	0.92174100
H	-5.83977900	3.94073700	1.55334600	C	-6.88108700	5.49876500	0.80104100
H	-2.32043100	1.44947100	-0.22155900	C	-1.73059600	-8.27838200	1.24668000
H	-5.92948300	-0.84415000	0.30403300	H	-7.86790200	5.83649600	1.13919900
H	-4.61447500	-2.93820600	0.22289600	H	-6.36483300	5.05707800	1.66159700
H	-0.99981300	-0.64206300	-0.30326500	H	-2.25543200	-8.54227000	0.32026100
C	-7.01404400	4.72988500	-0.07879300	H	-0.65461600	-8.33920000	1.05144500
H	-6.92944700	5.52864600	-0.82488400	O	-6.12972300	6.60822300	0.29542900
H	-7.81671400	5.01915200	0.60961900	H	-6.03560700	7.26197400	0.99671900
Q ²⁻ (PD - bidentate)				O	-2.09300500	-9.19065500	2.29156300
C	-4.21086800	-1.86002100	0.00579600	H	-1.87837200	-10.08575200	2.00806000
C	-4.90301900	-0.75635100	0.50709600	Q ⁺ (PD) ₂			
C	-2.88709100	-1.77548000	-0.50854600	C	-4.12253800	-1.91276300	-0.38681900
C	-4.34364700	0.53669900	0.54159900	C	-4.78455400	-0.76426100	-0.06225400
C	-3.03303300	0.63685700	0.03261400	C	-2.71689800	-2.08179700	-0.12332700
C	-2.33804500	-0.46385000	-0.46978300	C	-4.11477300	0.34678400	0.56398000
O	-5.00608900	1.59283600	1.03310700	C	-2.70931300	0.17730500	0.82854200
O	-2.23238800	-2.80996300	-0.97302800	C	-2.04724300	-0.97100900	0.50334400
H	-4.59391500	3.10188300	0.57862800	O	-4.72400400	1.42332900	0.87064800
H	-6.50907800	1.91193500	0.52506000	O	-2.10755700	-3.15801600	-0.43154200
O	-7.38525000	2.23499000	0.14841300	H	-6.39698300	1.73887200	0.55110400
				O	-7.34955900	1.97006600	0.43235500
				C	-7.44579900	3.27448300	-0.11893300

391

[illegible]

393

Figure B.87. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated BQ(MeOH) hydrogen-bonded complexes.

Figure B.88. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated BQ(EtOH) hydrogen-bonded complexes.

Figure B.89. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated BQ(*n*-PrOH) hydrogen-bonded complexes.

Figure B.90. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated BQ(*i*-PrOH) hydrogen-bonded complexes.

Figure B.91. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated BQ(*n*-BuOH) hydrogen-bonded complexes.

Figure B.92. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated BQ(*s*-BuOH) hydrogen-bonded complexes.

Figure B.93. Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated BQ(*i*-BuOH) hydrogen-bonded complexes.

Figure B.94 Optimized geometries for neutral (top left), radical anion (top right) and dianion (bottom) DCM-solvated BQ(*t*-BuOH) hydrogen-bonded complexes.

Q(MeOH)							
				C	-4.88190900	-0.92750000	-0.11042100
C	-4.19941200	-2.19318500	-0.12754500	C	-2.78214800	-2.18762200	0.05719000
C	-4.87380800	-1.04034700	-0.10933700	C	-4.11641700	0.30692900	-0.38150000
C	-2.71985300	-2.21518200	-0.18094400	C	-2.64241600	0.21507800	-0.42077700
C	-4.16489200	0.25552400	-0.14109700	C	-2.01929300	-0.94844800	-0.21602500
C	-2.68862500	0.23826100	-0.19231300	O	-4.68098700	1.37832200	-0.56819600
C	-2.01374500	-0.91418200	-0.21102100	O	-2.21343900	-3.25152800	0.24486000
O	-4.77652800	1.31725800	-0.12628500	H	-6.58919600	1.75525500	-0.60660900
O	-2.10391900	-3.26910500	-0.19859800	O	-7.55127400	1.88633000	-0.61849200
H	-6.66621200	1.68241300	-0.09812600	C	-7.84798800	3.19123700	-0.12332600
O	-7.61827900	1.87071000	-0.09099700	H	-8.93461600	3.23094100	-0.02070400
C	-7.80759300	3.27991400	-0.11136300	H	-7.42121400	3.32166000	0.87893000
H	-8.88183400	3.46577900	-0.10525100	C	-7.36607900	4.29995300	-1.04675800
H	-7.36758400	3.76348300	0.76766100	H	-6.27853600	4.27608900	-1.15324000
H	-5.95566700	-1.00223400	-0.07137700	H	-7.81075200	4.19773500	-2.03916100
H	-2.19613000	1.20274400	-0.21369500	H	-7.64356300	5.27823300	-0.64458500
H	-4.69487900	-3.15618600	-0.10531400	H	-5.96091600	-0.83480600	-0.08739200
H	-0.93191600	-0.95399400	-0.24863400	H	-2.10757500	1.13522500	-0.62219700
H	-7.38251600	3.73577000	-1.01226500	H	-4.79673900	-3.00997300	0.29567700
				H	-0.94036900	-1.04210800	-0.23910000
Q ⁻ (MeOH)					Q ⁻ (EtOH)		
C	-4.21367600	-2.12296100	-0.12412100	C	-4.26498400	-2.02400500	0.13942500
C	-4.88787600	-0.93572300	-0.14874300	C	-4.91559400	-0.85800500	-0.14675000
C	-2.77101000	-2.18815200	-0.14174700	C	-2.82400200	-2.12195600	0.13466600
C	-4.20083800	0.32884600	-0.19390800	C	-4.20366700	0.35042100	-0.47306800
C	-2.76264200	0.26963300	-0.21084900	C	-2.76702300	0.25863800	-0.47829700
C	-2.08727600	-0.91654100	-0.18584800	C	-2.11522800	-0.90637900	-0.19223900
O	-4.82206900	1.44356500	-0.21814700	O	-4.80266300	1.44416600	-0.74435100
O	-2.14529000	-3.28962100	-0.11995900	O	-2.22084200	-3.20419700	0.40051900
H	-6.52695600	1.61087300	-0.16399000	H	-6.51481300	1.65713200	-0.76292200
O	-7.50251900	1.76999700	-0.12861800	O	-7.48885900	1.82761800	-0.76513800
C	-7.73259000	3.16564700	-0.07861800	C	-7.73568700	3.07372500	-0.13146300
H	-8.81067000	3.33063800	-0.02575000	H	-8.81259500	3.12278300	0.05453000
H	-7.27308700	3.62825800	0.80377200	H	-7.23838800	3.10978100	0.84715300
H	-5.97276200	-0.91574400	-0.13480400	C	-7.30115600	4.26703900	-0.97347400
H	-2.22820500	1.21364500	-0.24434400	H	-6.22462500	4.23997300	-1.15735700
H	-4.75116700	-3.06526300	-0.09049000	H	-7.81352500	4.26478600	-1.93866300
H	-1.00218000	-0.93851400	-0.19939800	H	-7.53554900	5.20543700	-0.46192200
H	-7.35258100	3.67885800	-0.97093900	H	-5.99960400	-0.81110700	-0.13580900
				H	-2.21439900	1.16059700	-0.72124200
				H	-4.82046100	-2.92442100	0.38177100

H	-5.00396900	-2.46837500	0.91828900	C	-7.51854200	3.00619300	-0.32346500
H	-1.13693300	-1.02596300	-0.21868000	H	-8.50525800	2.94668000	0.15711900
$Q(n\text{-PrOH})$				H	-6.77462400	3.01594900	0.48780400
C	-4.24638400	-2.12380000	-0.17770300	C	-7.42839000	4.32458800	-1.09526800
C	-4.89237400	-0.95511500	-0.14417300	H	-6.45002600	4.38017100	-1.58331800
C	-2.76772100	-2.18137400	-0.22719400	H	-8.17720600	4.31124400	-1.89480200
C	-4.15174400	0.32341000	-0.15501800	C	-7.63856200	5.54748200	-0.20231900
C	-2.67608800	0.27040700	-0.20219700	H	-8.61953000	5.52101400	0.28198500
C	-2.02970100	-0.89792900	-0.23625100	H	-6.88324400	5.59601000	0.58749600
O	-4.73742800	1.39924300	-0.12645500	H	-7.57785400	6.47687100	-0.77369200
O	-2.17777500	-3.24982100	-0.25913500	H	-6.05673500	-0.76667700	-0.40548300
H	-6.63967100	1.79525700	-0.12834100	H	-4.94342000	-2.68886000	0.64857100
O	-7.59712800	1.95575400	-0.12755600	H	-1.14413900	-0.80107500	0.06379800
C	-7.83493700	3.34525400	0.08549700	H	-2.26448700	1.11918700	-0.98859400
H	-8.91314100	3.44665200	0.23572100	$Q(i\text{-PrOH})$			
H	-7.34531400	3.67828800	1.01029500	C	-4.25420700	-2.05068400	-0.47789800
C	-7.38904600	4.21934400	-1.08152000	C	-4.88159000	-0.88400400	-0.30628400
H	-6.31320200	4.08498800	-1.23668800	C	-2.77901100	-2.14719100	-0.39642200
H	-7.88517000	3.86803000	-1.99158900	C	-4.12330100	0.35383200	-0.02996100
C	-7.69848400	5.69856900	-0.85094500	C	-2.65110400	0.26157200	0.05374700
H	-8.77123900	5.86232000	-0.71647900	C	-2.02337100	-0.90490700	-0.11743100
H	-7.19111000	6.07645100	0.04089200	O	-4.69219900	1.42784200	0.12505200
H	-7.37442200	6.30618000	-1.69819600	O	-2.20598200	-3.21376800	-0.55354300
H	-5.97307300	-0.89058200	-0.10835800	H	-6.60590800	1.82048200	0.09170500
H	-4.76544800	-3.07453400	-0.17109900	O	-7.56692300	1.95520000	0.12079800
H	-0.94906500	-0.96386800	-0.27156400	C	-7.85189000	3.35170700	-0.03031600
H	-2.15975800	1.22257700	-0.20794100	H	-7.33292700	3.90589000	0.76397200
$Q^-(n\text{-PrOH})$				C	-7.36928200	3.86876600	-1.38205200
C	-4.24845500	-2.06705700	-0.11481400	H	-6.29334300	3.71671900	-1.49586800
C	-4.91240000	-0.87741600	-0.20780100	H	-7.87885900	3.34482900	-2.19506600
C	-2.80645900	-2.14247200	-0.08442300	H	-5.95944400	-0.79140300	-0.36137900
C	-4.21452300	0.37992300	-0.28227900	H	-4.78656400	-2.97176100	-0.68190500
C	-2.77679400	0.31034500	-0.25236600	H	-0.94565500	-0.99884600	-0.06178800
C	-2.11174500	-0.87823500	-0.15881300	H	-2.12143400	1.18398800	0.25841700
O	-4.82580900	1.49644800	-0.37095400	C	-9.35023000	3.52380100	0.15534400
O	-2.19057800	-3.24637400	0.00221700	H	-9.62861000	4.57721600	0.08319400
H	-6.53857000	1.70774300	-0.35658000	H	-9.89501800	2.97087900	-0.61465300
O	-7.51003800	1.88571400	-0.31592900	H	-9.66357900	3.15170100	1.13258900
C	-7.71118000	3.24657500	0.03048100	H	-7.56944100	4.93866800	-1.48150400
H	-8.75965800	3.34580100	0.33131200	$Q^-(i\text{-PrOH})$			
H	-7.10030200	3.51502200	0.90422300	C	-4.26574800	-2.00007700	-0.45828300
C	-7.41522400	4.21325100	-1.11390000	C	-4.92798500	-0.82487800	-0.24608000
H	-6.37195900	4.08788800	-1.42085700	C	-2.82402800	-2.08448900	-0.44048100
H	-8.03185500	3.93456500	-1.97462400	C	-4.22868400	0.40786900	0.00996900
C	-7.67474800	5.67036100	-0.73167700	C	-2.79121700	0.32874500	0.03072800
H	-8.71839100	5.82514100	-0.44280500	C	-2.12791100	-0.84549800	-0.18166500
H	-7.04948600	5.97677300	0.11168300	O	-4.83905900	1.51057400	0.20811100
H	-7.45917100	6.34356800	-1.56423700	O	-2.20968700	-3.17490800	-0.63914800
H	-5.99700200	-0.84923600	-0.22802600	H	-6.55954600	1.71522900	0.10917300
H	-4.79383000	-3.00384800	-0.06001300	O	-7.53533400	1.87010800	0.08520100
H	-1.02694800	-0.90752800	-0.13806200	C	-7.78468400	3.26831000	-0.03074100
H	-2.23430000	1.24875000	-0.30775300	H	-7.26287900	3.79431400	0.78253600
$Q^2(n\text{-PrOH})$				C	-7.27133300	3.81518700	-1.36170500
C	-4.33974400	-1.85495700	0.29382800	H	-6.20013800	3.63047600	-1.46458500
C	-4.97343800	-0.76384200	-0.30599600	H	-7.78526200	3.32950700	-2.19606800
C	-2.93024000	-1.93962400	0.46471900	H	-6.01234600	-0.78938200	-0.26505400
C	-4.26585800	0.35783400	-0.79622200	H	-4.81221800	-2.91822800	-0.64912800
C	-2.86404100	0.28325600	-0.63193600	H	-1.04335000	-0.88160800	-0.16229600
C	-2.22845000	-0.80726200	-0.03394100	H	-2.24754100	1.24832300	0.22249000
O	-4.85876200	1.40060000	-1.37178400	C	-9.28102800	3.48498000	0.13896800
O	-2.33467900	-2.96240600	1.02920300	H	-9.52922400	4.54762500	0.08537000
H	-6.34873700	1.64589900	-1.21854400	H	-9.83155300	2.96375100	-0.64944400
O	-7.35345900	1.86742700	-1.13515800	H	-9.61951200	3.10108700	1.10358200
				H	-7.43960600	4.89351100	-1.43270300

$Q^{2-}(i\text{-PrOH})$							
C	-4.22006100	-1.98175700	-0.53311800	C	-7.74901000	3.27923500	0.19897300
C	-4.94655500	-0.82720300	-0.22931700	H	-8.77681100	3.37951900	0.56359600
C	-2.79937700	-2.03679400	-0.50696600	H	-7.08737300	3.62039400	1.00752400
C	-4.32932800	0.39322800	0.13157900	C	-7.55412400	4.16366200	-1.03011400
C	-2.91629300	0.34793900	0.15979700	H	-6.52987300	4.03854300	-1.39887600
C	-2.18885300	-0.80523500	-0.14206600	H	-8.21952400	3.80888600	-1.82542100
O	-5.00839100	1.49590600	0.42775400	C	-7.82254600	5.64359800	-0.75198500
O	-2.11553000	-3.11862400	-0.79380400	H	-8.84368200	5.76147200	-0.37136100
H	-6.51448800	1.65052500	0.15752200	H	-7.15796900	5.98845800	0.04825200
O	-7.51761500	1.83827100	0.03248900	H	-6.00671100	-0.82140300	-0.17054700
C	-7.72165000	3.23223100	-0.08921100	H	-4.78626200	-2.97252300	-0.17670000
H	-7.11242100	3.75614300	0.66453600	H	-1.03711500	-0.84617700	-0.28639300
C	-7.30120800	3.74483000	-1.46969600	H	-2.26183300	1.30709900	-0.28104200
H	-6.25013900	3.51815000	-1.65670200	C	-7.63523400	6.53084500	-1.98260500
H	-7.89946700	3.26396600	-2.24945400	H	-6.61380800	6.46043900	-2.36681900
H	-6.03345600	-0.85863200	-0.26882700	H	-8.31183600	6.23417200	-2.78891900
H	-4.75589200	-2.89095200	-0.80226000	H	-7.83222500	7.58084700	-1.75250000
H	-1.10141800	-0.77544900	-0.09989900	$Q^{2-}(n\text{-BuOH})$			
H	-2.38514900	1.25948600	0.42956400	C	-4.25833400	-1.84860600	0.42442600
C	-9.18908900	3.53492100	0.19432300	C	-4.98049800	-0.81860400	-0.18314500
H	-9.39041800	4.60819600	0.13691100	C	-2.83715200	-1.88831800	0.45830000
H	-9.82773000	3.02847000	-0.53578800	C	-4.35855400	0.28164800	-0.81717200
H	-9.46846200	3.18478100	1.19051100	C	-2.94563600	0.25088800	-0.78949700
H	-7.43688300	4.82813100	-1.54913100	C	-2.22171900	-0.77882300	-0.18457800
$Q(n\text{-BuOH})$				O	-5.03537700	1.26701000	-1.40065700
C	-4.23129300	-2.07636900	-0.17063800	O	-2.15840700	-2.85473200	1.02813700
C	-4.90416300	-0.92347000	-0.12304000	H	-6.49956800	1.53408000	-1.07978700
C	-2.75665700	-2.09865600	-0.30301900	O	-7.48479700	1.76988300	-0.89137600
C	-4.19852400	0.37241100	-0.20070100	C	-7.55391600	3.02206800	-0.24969500
C	-2.72690900	0.35463300	-0.33166200	H	-8.47166900	3.04653900	0.35411400
C	-2.05367700	-0.79792500	-0.37975200	H	-6.71335900	3.14248400	0.45057300
O	-4.80905300	1.43381100	-0.15859300	C	-7.56879600	4.20824300	-1.21693000
O	-2.14217300	-3.15272100	-0.34709000	H	-6.65345300	4.18525600	-1.81867800
H	-6.71852000	1.79307900	-0.03936700	H	-8.40536200	4.08236000	-1.91478700
O	-7.67343500	1.94362300	0.04919100	C	-7.68527400	5.55864200	-0.50838800
C	-7.90629500	3.33741900	0.24309200	H	-8.59760300	5.57137300	0.09972100
H	-8.96853200	3.43357100	0.48265100	H	-6.85147300	5.67123000	0.19409000
H	-7.34270500	3.69914800	1.11318400	H	-6.06772400	-0.85440700	-0.17248600
C	-7.56970600	4.18000900	-0.98203800	H	-4.79747100	-2.66880400	0.89589500
H	-6.50932400	4.04692900	-1.22671000	H	-1.13376000	-0.74237600	-0.19755500
H	-8.14001900	3.80130900	-1.83731400	H	-2.41099800	1.07281200	-1.26277300
C	-7.86454300	5.66738400	-0.77912700	C	-7.70018000	6.74881700	-1.46783900
H	-8.92354700	5.79531900	-0.52845900	H	-6.78442800	6.78389400	-2.06460800
H	-7.30009400	6.03461600	0.08518300	H	-8.54319400	6.68555400	-2.16195500
H	-5.98237300	-0.88482300	-0.02660300	H	-7.78287700	7.69706600	-0.93020200
H	-4.72438300	-3.03928400	-0.11556900	$Q(s\text{-BuOH})$			
H	-0.97547000	-0.83798400	-0.47589400	C	-4.11982200	-2.12346200	-0.18154700
H	-2.23652300	1.31891600	-0.38605700	C	-4.74555900	-0.94627500	-0.26463300
C	-7.52694800	6.51742300	-2.00371700	C	-2.64690600	-2.20139600	-0.05242400
H	-6.46616700	6.43906200	-2.25734600	C	-3.98736800	0.32176000	-0.23185100
H	-8.10024500	6.19506300	-2.87725200	C	-2.51729800	0.24839800	-0.10355700
H	-7.75030500	7.57268800	-1.83020500	C	-1.89133900	-0.92853000	-0.01974100
$Q^+(n\text{-BuOH})$				O	-4.55508200	1.40489900	-0.30799500
C	-4.24846400	-2.03002900	-0.19907800	O	-2.07546900	-3.27758400	0.02472400
C	-4.92205700	-0.84216400	-0.19584800	H	-6.47985400	1.71809000	-0.43803500
C	-2.80609800	-2.09570800	-0.23244000	O	-7.44852200	1.77463900	-0.46067300
C	-4.23482800	0.42293600	-0.22596900	C	-7.84758500	3.12179900	-0.17713700
C	-2.79670200	0.36296800	-0.25869400	H	-7.43006900	3.41392500	0.79644100
C	-2.12204100	-0.82387700	-0.26152000	C	-7.31298000	4.08723700	-1.23209700
O	-4.85550000	1.53768300	-0.22503800	H	-6.22067900	4.06844800	-1.24833400
O	-2.18077800	-3.19775600	-0.23572300	H	-7.67020700	3.82118000	-2.22867300
H	-6.56919500	1.73401700	-0.14484900	H	-5.82185700	-0.86654400	-0.35792600
O	-7.53998300	1.90004400	-0.06275600	H	-4.65199000	-3.06670500	-0.20328200
				H	-0.81527700	-1.00946400	0.07477900
				H	-1.98773200	1.19304800	-0.08206700

C	-9.37063100	3.13516600	-0.03693200
H	-9.67014000	4.13921000	0.28033100
H	-9.63275500	2.46042400	0.78395300
H	-7.62654200	5.11153000	-1.01338000
C	-10.15135500	2.73377400	-1.28954700
H	-9.85837300	1.74106800	-1.63540700
H	-11.22298300	2.71179200	-1.07853900
H	-9.99542300	3.43575200	-2.11155500
Q ⁻ (<i>s</i> -BuOH)			
C	-4.09763500	-2.05845400	0.09485000
C	-4.77760600	-0.90733200	-0.18317700
C	-2.65466900	-2.10971700	0.13235900
C	-4.09695900	0.33185200	-0.45738200
C	-2.65824300	0.28635000	-0.42053800
C	-1.97725700	-0.86397500	-0.14290100
O	-4.72390600	1.41184800	-0.71915600
O	-2.02390600	-3.17833000	0.38980900
H	-6.45610700	1.56560400	-0.79804200
O	-7.43624200	1.67907300	-0.83866700
C	-7.78814000	2.91262900	-0.21816600
H	-7.33912100	2.94708700	0.78565900
C	-7.25011200	4.10437100	-1.01083800
H	-6.16095400	4.05659400	-1.06934300
H	-7.64177400	4.10822000	-2.03017900
H	-5.86239000	-0.89592200	-0.20517100
H	-4.63056900	-2.98186800	0.29825200
H	-0.89216600	-0.87502900	-0.12106700
H	-2.12802900	1.21114000	-0.62463100
C	-9.30752000	2.93888200	-0.02740100
H	-9.56230500	3.83574600	0.54741000
H	-9.57638200	2.08235300	0.59887100
H	-7.52289400	5.04893500	-0.53096400
C	-10.13352600	2.90113800	-1.31457600
H	-9.88623900	2.02485100	-1.91628600
H	-11.20065000	2.85831900	-1.08316600
H	-9.96849500	3.78781500	-1.93066200
Q ²⁻ (<i>s</i> -BuOH)			
C	-4.21714800	-1.53992000	0.68714000
C	-4.85289300	-0.49277600	0.01506800
C	-2.83500000	-1.83806700	0.53707300
C	-4.17429300	0.36711900	-0.87950200
C	-2.79810400	0.08022900	-1.03235500
C	-2.16039500	-0.96448200	-0.36009600
O	-4.76447200	1.36623500	-1.52664900
O	-2.24011100	-2.82362900	1.16567600
H	-6.27738000	1.64637900	-1.50106900
O	-7.27697600	1.87674200	-1.55468200
C	-7.65887400	2.60535500	-0.40499900
H	-7.17787500	2.16082300	0.48089900
C	-7.20043700	4.06636800	-0.48784400
H	-6.11172300	4.11588800	-0.55283400
H	-7.61079200	4.55571300	-1.37453800
H	-5.91565500	-0.32667800	0.17767000
H	-4.79701700	-2.16654600	1.36253500
H	-1.09628400	-1.12779800	-0.52266300
H	-2.22218000	0.70961800	-1.70843300
C	-9.17333800	2.46569900	-0.19778200
H	-9.44155700	2.95487900	0.74565300
H	-9.39041500	1.40024000	-0.06904800
H	-7.51369500	4.63214100	0.39571300
C	-10.04120000	3.01972300	-1.32926200
H	-9.77586500	2.56152900	-2.28346800
H	-11.09865100	2.81579400	-1.14115900
H	-9.93146500	4.10160100	-1.43614700
Q(<i>i</i> -BuOH)			
C	-4.14763100	-2.16119600	-0.16329700
C	-4.81148100	-1.00496600	-0.24461400
C	-2.67344900	-2.19111500	-0.02739100
C	-4.09592400	0.28708200	-0.20208300
C	-2.62490200	0.26176300	-0.06599500
C	-1.96063100	-0.89413700	0.01520300
O	-4.69818800	1.35147500	-0.27677200
O	-2.06721100	-3.24821600	0.04716000
H	-6.60390300	1.69567400	-0.46355700
O	-7.56341800	1.83067900	-0.52269000
C	-7.86425400	3.17161200	-0.14547100
H	-8.95188900	3.21668400	-0.03087700
H</			

[illegible]

Appendix C

C.1 Supporting Information for Pyridine and Its Derivatives

C.1.1 Plots of $\Delta E_P = |E_{P1} - E_{P3}|$ against concentration of bases

C.1.2 Plots of $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration of hydrogen acceptors

C.1.3 Energies of phenylenediamine-base/hydrogen acceptor complexes

C.1.4 Geometries of phenylenediamine-base/hydrogen acceptor complexes

C.1.5 Coordinates of phenylenediamine-base/hydrogen acceptor complexes

C.2 Supporting Information for Oxygen and Sulfur Heterocycles

C.2.1 Cyclic voltammograms of 2,3,5,6-tetramethyl-1,4-phenylenediamine at different concentrations of tetrahydrothiophene and thiophene

C.3 Supporting Information for the Simple Alcohols

C.3.1 Cyclic voltammograms of 2,3,5,6-tetramethyl-1,4-phenylenediamine at different concentrations of the simple alcohols

C.3.2 Plots of E_{P1} , E_{P2} and $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration of simple alcohols

C.3.3 Energies of phenylenediamine-alcohol hydrogen-bonded complexes

C.3.4 Geometries of phenylenediamine-alcohol hydrogen-bonded complexes

C.3.5 Coordinates of phenylenediamine-alcohol hydrogen-bonded complexes

C.4 Supporting Information for the Diols

C.4.1 Cyclic voltammograms of 2,3,5,6-tetramethyl-1,4-phenylenediamine at different concentrations of the diols

C.4.2 Plots of E_{P1} , E_{P2} and $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration of diols

C.4.3 Energies of phenylenediamine-diol hydrogen-bonded complexes

C.4.4 Geometries of phenylenediamine-diol hydrogen-bonded complexes

C.4.5 Coordinates of phenylenediamine-diol hydrogen-bonded complexes

C.5 Supporting Information for 2,2,2-Trifluoroethanol and Acetic Acid

C.5.1 Plots of E_{P1} , E_{P2} and $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration of hydrogen donors

C.6 *Computational Data for Calculations of Adiabatic Ionization Energies*

C.6.1 Energies of phenylenediamine-base/hydrogen acceptor/hydrogen donor complexes

C.6.2 Geometries of phenylenediamine-base/hydrogen acceptor/hydrogen donor complexes

C.6.3 Coordinates of phenylenediamine-base/hydrogen acceptor/hydrogen donor complexes

C.1 Supporting Information for Pyridine and Its Derivatives

C.1.1 Plots of $\Delta E_P = |E_{P1} - E_{P3}|$ against concentration of bases

Figure C.1. Plots of $\Delta E_P = |E_{P1} - E_{P3}|$ against concentration of bases obtained over three experiments (red +, blue $\circ$ and black $\times$) as measured by square-wave voltammetry during the oxidation of 1 mM 2,3,5,6-tetramethyl-1,4-phenylenediamine (TMPD) with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

C.1.2 Plots of $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration of hydrogen acceptors

Figure C.2. Plots of $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration of hydrogen acceptors obtained over three experiments (red +, blue $\circ$ and black $\times$) as measured by square-wave voltammetry during the oxidation of

1 mM TMPD with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

C.1.3 Energies of phenylenediamine-base/hydrogen acceptor complexes

Table C.1. Energies of the MeCN-solvated phenylenediamine-base/hydrogen acceptor complexes.

Base/hydrogen acceptor	Energy (hartrees)		
	P	P ^{•+}	P ²⁺
Pyridine	-748.433	-748.274	-748.071
2-Picoline	-787.739	-787.579	-787.376
3-Picoline	-787.737	-787.577	-787.375
4-Picoline	-787.738	-787.579	-787.377
2,6-Lutidine	-827.044	-826.884	-826.680
2,6-Di- <i>tert</i> -butylpyridine	-1062.822	-1062.658	-1062.445
2-(Trifluoromethyl)pyridine	-1085.596	-1085.434	-1085.228
3-(Trifluoromethyl)pyridine	-1085.594	-1085.434	-1085.229
4-(Trifluoromethyl)pyridine	-1085.593	-1085.433	-1085.229
Quinoline	-902.077	-901.917	-901.713
Isoquinoline	-902.075	-901.916	-901.713
Pyridazine	-764.458	-764.298	-764.095
Pyrimidine	-764.490	-764.320	-764.124
Pyrazine	-764.483	-764.322	-764.117
2,2'-Bipyridyl	-995.535	-995.378	-995.173

C.1.4 Geometries of phenylenediamine-base/hydrogen acceptor complexes

Figure C.3. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(pyridine) complexes.

Figure C.4. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(2-picoline) complexes.

Figure C.5. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(3-picoline) complexes.

Figure C.6. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(4-picoline) complexes.

Figure C.7. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(2,6-lutidine) complexes.

Figure C.8. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(2,6-di-*tert*-butylpyridine) complexes.

Figure C.9. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(2-[trifluoromethyl]pyridine) complexes.

Figure C.10. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(3-[trifluoromethyl]pyridine) complexes.

Figure C.11. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(4-[trifluoromethyl]pyridine) complexes.

Figure C.12. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(quinoline) complexes.

Figure C.13. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(isoquinoline) complexes.

Figure C.14. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(pyridazine) complexes.

Figure C.15. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(pyrimidine) complexes.

Figure C.16. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(pyrazine) complexes.

Figure C.17. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(2,2'-bipyridyl) complexes.

C.1.5 Coordinates of phenylenediamine-base/hydrogen acceptor complexes

P(Pyridine)							
C	-1.33167300	-0.47380600	-0.09751500	H	2.91025600	1.58895400	-0.71162600
C	0.04973800	-0.69407800	-0.22383900	H	2.83944400	1.49735100	1.04024500
C	0.92403700	0.40209000	-0.24003100	H	3.04880300	0.03474100	0.09152300
C	0.40860800	1.70125200	-0.08450300	H	2.15986400	-1.60187600	0.02068100
C	-0.97607000	1.91986200	0.04151500	H	0.76134800	-2.30868700	0.80178800
C	-1.85111500	0.82346200	0.04810000	H	0.85576100	-2.23948200	-0.95966200
N	-2.20980800	-1.58288400	-0.04870300	C	4.09844700	4.61258200	1.62931600
N	1.28602500	2.80336500	-0.12578700	C	5.29329800	5.28770400	1.84056100
H	-1.87081700	-2.39875800	-0.53834700	C	6.06685700	5.63015800	0.73871100
H	-3.15082000	-1.37681600	-0.35236200	C	5.61430300	5.28484600	-0.52842500
H	2.22470200	2.65151600	0.23259300	C	4.40595800	4.60988000	-0.64112400
H	0.90790100	3.64712700	0.27847600	N	3.65561800	4.27491200	0.41364500
C	-3.34519300	0.96436700	0.22423100	H	7.00483700	6.15652100	0.86528500
C	-1.45396200	3.34918600	0.14568300	H	3.47004200	4.32916300	2.46707500
C	2.41310200	0.25439700	-0.44371700	H	5.60583500	5.53619600	2.84638400
C	0.52963400	-2.12339900	-0.32035700	H	6.18309300	5.53108500	-1.41549900
H	-3.64780100	1.96845500	0.50577700	H	4.02291200	4.32486400	-1.61527300
H	-3.89041800	0.70966700	-0.69272400	P ²⁺ (Pyridine)			
H	-3.70962200	0.29102600	1.00587600	C	-1.10192400	-0.25536400	-0.36231400
H	-1.04611800	3.95725700	-0.66795800	C	0.36016400	-0.37654600	-0.36830300
H	-2.53470400	3.44131400	0.09589800	C	1.09246700	0.68999400	0.02319400
H	-1.13360500	3.81950400	1.08310800	C	0.38045000	1.93715700	0.36190700
H	2.77162000	0.97967200	-1.17943500	C	-1.09161600	2.00145500	0.50229200
H	2.97624000	0.44209300	0.47693200	C	-1.82088600	0.93209500	0.11659400
H	2.69359100	-0.73203900	-0.80282200	N	-1.80148700	-1.26826700	-0.77519100
H	1.60735800	-2.21472900	-0.22112300	N	1.05596100	3.02348200	0.52645700
H	0.08372400	-2.73612300	0.46877700	H	-1.36763800	-2.11884400	-1.11322100
H	0.25233300	-2.58644100	-1.27520000	H	-2.81412200	-1.25390900	-0.77944500
C	5.30830900	3.47943500	0.36384700	H	2.12850800	3.20275800	0.40900800
C	6.51706600	3.92467300	0.88509000	H	0.54511000	3.87323600	0.74611000
C	6.61863500	4.11511500	2.25740100	C	-3.31869900	0.86628000	0.12949000
C	5.50852500	3.85289900	3.05025600	C	-1.67069600	3.27737400	1.03266500
C	4.34301800	3.41092700	2.43587800	C	2.58527000	0.69880000	0.11822700
N	4.23395100	3.22406400	1.11692800	C	0.93639700	-1.68644000	-0.81583500
H	7.54460100	4.46110000	2.70022200	H	-3.76723600	1.78402500	0.48958900
H	5.19678200	3.32066200	-0.70388400	H	-3.70956100	0.69719000	-0.87793700
H	7.35512900	4.11598900	0.22730100	H	-3.67056700	0.05538700	0.77264300
H	5.54000700	3.98659600	4.12392500	H	-1.55189400	4.09290300	0.31201500
H	3.45826100	3.19772200	3.02725400	H	-2.72932000	3.18914200	1.24529000
P ⁺ (Pyridine)				H	-1.17834100	3.57033100	1.96292200
C	-1.04745800	-0.36241200	-0.09416200	H	3.02565500	1.27527500	-0.69924600
C	0.38475000	-0.35421900	-0.02516800	H	2.90764700	1.15593100	1.05373700
C	1.04034800	0.85232800	0.05171600	H	3.00033300	-0.30187000	0.08112300
C	0.26814100	2.06463900	0.06597800	H	2.01945100	-1.68237300	-0.80517900
C	-1.16909700	2.05165700	-0.00810800	H	0.60283100	-2.50512400	-0.17225700
C	-1.82268500	0.84460200	-0.08594700	H	0.63240600	-1.91260100	-1.84185800
N	-1.68707000	-1.54322200	-0.17064700	C	4.35698200	4.09299100	1.36596000
N	0.89834400	3.24408600	0.15044800	C	5.58487100	4.73463000	1.31224800
H	-1.18735400	-2.41650400	-0.18220800	C	6.05610500	5.16799900	0.07937500
H	-2.69040600	-1.59908800	-0.22110600	C	5.28258700	4.94466600	-1.05270300
H	1.91558200	3.37961900	0.21854100	C	4.06623000	4.29491800	-0.90874000
H	0.36111200	4.09660800	0.16262100	N	3.61086800	3.87393900	0.27692300
C	-3.31921700	0.70040300	-0.16340700	H	7.01081200	5.67283400	0.00222600
C	-1.87285800	3.38193500	0.00674200	H	3.95238100	3.74138400	2.30825600
C	2.53552300	0.98915300	0.12164100	H	6.15431000	4.88931800	2.21875200
C	1.08133900	-1.68862800	-0.04129500	H	5.61112800	5.26702500	-2.03155700
H	-3.83722400	1.65233800	-0.14831200	H	3.43175300	4.10244600	-1.76630200
H	-3.61722100	0.18736200	-1.08292700	P(2-Picoline)			
H	-3.70092500	0.11531400	0.67889700	C	-1.37891400	-0.49013700	-0.14355000
H	-1.54556600	4.00973500	-0.82764800	C	0.00537800	-0.72719100	-0.11924200
H	-2.94999500	3.28951100	-0.07034300	C	0.89056100	0.36025800	-0.10728600
H	-1.66322500	3.92816100	0.93165700				

415

N	-2.18903200	-1.56928600	0.16316900	C	6.54387100	4.21863600	1.76845700
N	1.29770600	2.79819300	-0.31570800	C	5.67028500	3.85787000	2.79504600
H	-1.82079100	-2.44194100	-0.18774600	C	4.42097100	3.37308500	2.41364400
H	-3.11169800	-1.41675400	-0.21836800	N	4.02525000	3.23788600	1.14355900
H	2.21692700	2.70663100	0.10824000	H	7.53001300	4.60250300	2.00521000
H	0.89544900	3.68465400	-0.04966700	H	4.53093500	3.47218900	-0.84323100
C	-3.34274300	0.97831900	0.01150200	H	6.80672700	4.35921800	-0.36623500
C	-1.45232900	3.35018800	-0.27617200	H	3.70157900	3.07825000	3.17196400
C	2.44651400	0.24017400	-0.20959100	C	6.05290500	3.98243600	4.24348600
C	0.56116000	-2.11667300	0.12418300	H	6.32133800	5.01228900	4.49082100
H	-3.66616500	2.00908700	0.12022800	H	5.23450700	3.67936600	4.89705800
H	-3.83029800	0.58237700	-0.88760800	H	6.91968000	3.35827000	4.47460900
H	-3.75101200	0.42407900	0.86203000				
H	-1.00693400	3.84348500	-1.14600000				
H	-2.52962900	3.42663100	-0.38758900				
H	-1.17736200	3.94801500	0.60111900	C	-1.20283400	-0.39323300	-0.26513900
H	2.84928900	0.86124700	-1.01439800	C	0.22373600	-0.67836000	-0.07543900
H	2.95103800	0.55799000	0.70928900	C	1.04739600	0.35028500	0.22653700
H	2.75016200	-0.78339400	-0.41128400	C	0.47388800	1.70833500	0.31458100
H	1.63262500	-2.18482000	0.28785500	C	-0.96559300	1.98463700	0.09890400
H	0.07693800	-2.61753500	0.96790500	C	-1.78506800	0.95278100	-0.19779500
H	0.33267400	-2.71028100	-0.76946800	N	-1.99983500	-1.39093000	-0.49965000
C	5.08274500	4.04408800	0.25576300	N	1.25074600	2.70284200	0.58096000
C	6.26644600	4.54756800	0.78226900	H	-1.66456200	-2.34498400	-0.55222600
C	6.51886700	4.37745300	2.13520900	H	-2.99556400	-1.26205300	-0.63087400
C	5.58883700	3.71083100	2.93355900	H	2.33507000	2.73245500	0.77092500
C	4.43658500	3.24709500	2.30018300	H	0.83445800	3.62781600	0.63041900
N	4.17810900	3.40264900	0.99806100	C	-3.25713300	1.07170000	-0.46120400
H	7.43456400	4.76031900	2.57242000	C	-1.41185200	3.40922700	0.22433600
H	4.85322200	4.15949300	-0.79851700	C	2.51384900	0.21032100	0.48116000
H	6.97243100	5.06113000	0.14201600	C	0.65692500	-2.10737800	-0.21887200
H	3.68164200	2.72058000	2.87754900	H	-3.59879900	2.09890400	-0.43509400
C	5.81231400	3.49984200	4.40546700	H	-3.50941500	0.67535200	-1.44852200
H	5.92447800	4.45388300	4.92655000	H	-3.83487800	0.52080500	0.28633600
H	4.97854200	2.96333600	4.85946800	H	-0.92261300	4.03956400	-0.52360400
H	6.72355100	2.92417500	4.58593100	H	-2.48041700	3.52003700	0.08843500
				H	-1.17226600	3.80756500	1.21395100
				H	3.08836500	0.77899700	-0.25267100
				H	2.76980800	0.59734400	1.46902600
				H	2.84447700	-0.82003400	0.43653100
				H	1.73140700	-2.22060900	-0.14653300
				H	0.21143000	-2.73146500	0.56121400
				H	0.35959500	-2.51022900	-1.19054200
				C	4.68970300	3.52815700	0.12445800
				C	5.96643300	4.00014400	0.38970100
				C	6.37162000	4.12360700	1.71000400
				C	5.50018100	3.77693300	2.74397200
				C	4.24179600	3.31377500	2.37370100
				N	3.84450600	3.18887400	1.10161200
				H	7.36513800	4.49071500	1.94092400
				H	4.33076700	3.41764800	-0.89228400
				H	6.62627600	4.26509800	-0.42558900
				H	3.51835500	3.02932800	3.13078400
				C	5.89626600	3.89468700	4.18853800
				H	6.19683600	4.91717300	4.42801000
				H	5.07507700	3.61774100	4.84962000
				H	6.74658400	3.24623800	4.41294900

Appendix C

H	-3.18136900	-1.38309900	-0.24571200
H	2.21783200	2.64663800	0.09599600
H	0.90964900	3.64879300	-0.01342400
C	-3.36978100	1.00860200	0.05397600
C	-1.44695700	3.35719400	-0.20447000
C	2.40183700	0.18536600	-0.29341300
C	0.48547600	-2.14910700	0.01230500
H	-3.67417900	2.04077900	0.19830000
H	-3.87954800	0.64681500	-0.84718500
H	-3.77200600	0.43650800	0.89550400
H	-1.00978600	3.86706900	-1.06887800
H	-2.52475200	3.45324900	-0.29367300
H	-1.14641400	3.92638800	0.68335700
H	2.80080900	0.82523900	-1.08524200
H	2.92800900	0.46509500	0.62576800
H	2.68414900	-0.83606800	-0.53337700
H	1.55853400	-2.23799900	0.15435500
H	0.00879000	-2.66533800	0.85103800
H	0.23168600	-2.71462200	-0.89262400
C	5.10864400	3.94090500	0.22166200
C	6.30435500	4.43167100	0.72745700
C	6.60016300	4.26699700	2.08046400
C	5.65129600	3.59770200	2.85359500
C	4.48253200	3.14070900	2.26137400
N	4.19938400	3.30239300	0.96483100
H	4.87123200	4.06393500	-0.83037100
H	6.99981700	4.93607000	0.06709200
H	5.81932200	3.42888700	3.91069100
H	3.73962800	2.61765300	2.85543300
C	7.86774000	4.80479700	2.68134400
H	7.70630600	5.81609100	3.06675100
H	8.20478100	4.18807200	3.51552000
H	8.66634100	4.86008600	1.94077900

P⁺(4-Picoline)

C	-1.29210500	-0.42434500	-0.32454100
C	0.09925200	-0.68827100	-0.09943500
C	0.93308200	0.35953300	0.21408200
C	0.38218000	1.68390100	0.30712700
C	-1.01570300	1.94353300	0.08171100
C	-1.84753600	0.89483200	-0.23174500
N	-2.10544400	-1.44989300	-0.63429400
N	1.18640300	2.71057300	0.61279500
H	-1.76216600	-2.39246300	-0.71147700
H	-3.08806000	-1.31372600	-0.80170900
H	2.19900400	2.65529700	0.79120900
H	0.80184600	3.63970800	0.67774100
C	-3.32409700	1.03848100	-0.48960900
C	-1.48072100	3.36982300	0.20508300
C	2.40653500	0.20869100	0.47132400
C	0.55605000	-2.11749400	-0.22395400
H	-3.67336500	2.05956000	-0.38920600
H	-3.57980400	0.70941700	-1.50158900
H	-3.90556500	0.43125900	0.21078200
H	-0.96092700	4.01614400	-0.50878000
H	-2.54265900	3.48421600	0.02119600
H	-1.28474500	3.76253600	1.20745300
H	2.98822800	0.81921600	-0.22377000
H	2.66264400	0.54531300	1.47924300
H	2.74984700	-0.81475600	0.37158700
H	1.61705200	-2.23870900	-0.03928200
H	0.03108100	-2.76100000	0.48868500
H	0.35814700	-2.50732600	-1.22709900
C	4.85923500	3.61447900	0.23070800
C	6.13165900	4.10658600	0.47885800
C	6.58396100	4.21974900	1.79369000
C	5.70471500	3.81525500	2.79858900
C	4.44904100	3.33484700	2.45930800

N	4.01893400	3.23016000	1.19735700
H	4.49760900	3.52137400	-0.78815200
H	6.76512600	4.39672200	-0.35061600
H	5.99362500	3.87016700	3.84121900
H	3.75727400	3.01722700	3.23262200
C	7.94265500	4.77392400	2.11323800
H	7.88589600	5.85776500	2.25244100
H	8.33963000	4.34672800	3.03482500
H	8.64941800	4.58436000	1.30468100

P²⁺(4-Picoline)

C	-1.19086800	-0.36803300	-0.31017900
C	0.22194000	-0.66755200	-0.05351900
C	1.04694600	0.35593800	0.26169800
C	0.47959200	1.71728200	0.34620700
C	-0.95510200	2.00109900	0.10514900
C	-1.77327300	0.97585600	-0.21687800
N	-1.97297000	-1.35038700	-0.64131700
N	1.25450800	2.70409500	0.64293400
H	-1.63345700	-2.30067500	-0.72497100
H	-2.95735500	-1.21109300	-0.83304400
H	2.34713400	2.73875000	0.84986500
H	0.83604700	3.62798100	0.69696600
C	-3.24178800	1.10133200	-0.49707400
C	-1.39710800	3.42695900	0.23016500
C	2.50951900	0.20872500	0.53358800
C	0.64161000	-2.10316600	-0.16710700
H	-3.60110000	2.11504800	-0.37079100
H	-3.46872000	0.80333800	-1.52477700
H	-3.82375000	0.46863300	0.17835400
H	-0.86590400	4.06379500	-0.48266400
H	-2.45579200	3.54853100	0.03811600
H	-1.20504600	3.80962300	1.23627800
H	3.09081000	0.80836100	-0.16928100
H	2.75146700	0.55726300	1.53939500
H	2.84531600	-0.81740600	0.44755200
H	1.69070800	-2.24537500	0.05976000
H	0.07510700	-2.73023800	0.52681300
H	0.47649300	-2.47974100	-1.18040300
C	4.63877100	3.59057500	0.18659900
C	5.91751300	4.06330600	0.42316700
C	6.39986100	4.13057800	1.73124000
C	5.54244500	3.70216600	2.74605000
C	4.27704500	3.24182700	2.42724800
N	3.82597000	3.18223700	1.16845800
H	4.24599300	3.53167200	-0.82224700
H	6.53362500	4.37513400	-0.41067200
H	5.85691200	3.72374900	3.78183500
H	3.59649000	2.90516400	3.20114800
C	7.76904900	4.66360000	2.03473300
H	7.72290200	5.74494400	2.19551100
H	8.17856100	4.21507800	2.94014400
H	8.45713100	4.48442300	1.20824800

P(2,6-Lutidine)

C	-1.34860000	-0.47535000	0.00840400
C	0.03040900	-0.72674200	-0.07834300
C	0.92125300	0.34966200	-0.19701200
C	0.42417200	1.66478600	-0.17953100
C	-0.95818400	1.91486300	-0.09229700
C	-1.85008700	0.83723400	0.01327200
N	-2.24324900	-1.56130900	0.16084800
N	1.31980800	2.74475400	-0.32251400
H	-1.91170700	-2.42789900	-0.23838300
H	-3.17867800	-1.37505400	-0.17141700
H	2.24288300	2.61909600	0.08260500
H	0.94500900	3.63052500	-0.01655700

C	-3.71041100	0.03601100	-0.91611100
C	-2.11793800	2.55039000	-0.19775300
C	2.03483800	-0.26399900	0.44219200
C	0.44301700	-2.77948000	-0.27510600
H	-4.13212700	1.03150100	-0.97798600
H	-3.86865500	-0.43836400	-1.88804600
H	-4.28750200	-0.51611200	-0.16855500
H	-1.63099100	3.19711500	-0.93290500
H	-3.18000600	2.56844100	-0.40862200
H	-1.98136900	2.99349600	0.79249300
H	2.61411100	0.28688300	-0.30456900
H	2.19289300	0.21388200	1.41231300
H	2.45689500	-1.25917200	0.50746200
H	1.50435700	-2.79744100	-0.06054500
H	-0.04654200	-3.42640800	0.45813900
H	0.30978100	-3.22235100	-1.26596100
C	4.88651500	3.48184100	0.23223700
C	5.44473200	2.20453800	0.09112000
C	5.52491500	1.38465400	1.20071000
C	5.05430800	1.84296300	2.42692300
C	4.51445100	3.12352100	2.50252400
N	4.43835100	3.90734700	1.41317300
H	5.95329100	0.39240600	1.11862500
H	5.81397500	1.86190700	-0.86617300
H	5.11823300	1.20873000	3.29888200
C	4.80004700	4.43188600	-0.97191700
C	3.99076800	3.73979900	3.80675300
C	2.51354200	4.13910500	3.61975800
H	1.89092800	3.26130500	3.42597600
H	2.13823100	4.62319200	4.52496200
H	2.39942300	4.83134900	2.78580200
C	4.82089400	5.00073900	4.12455800
H	4.44934400	5.47377400	5.03704600
H	5.87326200	4.74862600	4.27894200
H	4.75954000	5.72319500	3.31062700
C	4.09278100	2.77049900	4.99340700
H	5.12644000	2.48165600	5.19686700
H	3.70346500	3.25351500	5.89225000
H	3.50978300	1.86135200	4.82816300
C	4.09717600	5.74601300	-0.60824400
H	4.05922600	6.39109800	-1.48958500
H	3.07494200	5.57167200	-0.26897000
H	4.62317000	6.27859600	0.18444000
C	4.01495000	3.75498100	-2.11514400
H	3.95719600	4.42584500	-2.97582100
H	4.48872900	2.82971700	-2.44733500
H	2.99402200	3.52007700	-1.80316700
C	6.23082200	4.75223800	-1.45743300
H	6.81285100	5.23278200	-0.66732400
H	6.76417800	3.85255500	-1.76993000
H	6.19331900	5.43309800	-2.31156300

P(2-[Trifluoromethyl]pyridine)

C	-1.40732200	-0.50258400	-0.16331900
C	-0.02417700	-0.74664500	-0.13353700
C	0.86582500	0.33662000	-0.10933500
C	0.35847600	1.64737700	-0.07610800
C	-1.02682400	1.89041000	-0.10670300
C	-1.91683100	0.80662100	-0.13839200
N	-2.30454700	-1.59637400	-0.14934700
N	1.25554200	2.73630700	-0.08291700
H	-1.93135400	-2.44297500	-0.55434800
H	-3.20660400	-1.39703900	-0.55747500
H	2.14557700	2.57851800	0.37607000
H	0.85693400	3.59978800	0.25509400
C	-3.41835500	0.97309100	-0.12925900
C	-1.48638100	3.32939800	-0.11973500
C	2.36589400	0.16485300	-0.13937300

C	0.43602900	-2.18533300	-0.11373800
H	-3.73295600	1.99653500	0.05094200
H	-3.86853900	0.66178400	-1.07967500
H	-3.87329300	0.35698200	0.65226700
H	-0.99091000	3.89054600	-0.91833500
H	-2.55549000	3.43383400	-0.27754600
H	-1.24930900	3.84128800	0.82064800
H	2.81226400	0.82315300	-0.89029300
H	2.82720600	0.42637500	0.81902400
H	2.67105300	-0.84929500	-0.38105800
H	1.49905600	-2.28738700	0.08330100
H	-0.08814000	-2.75014500	0.66310900
H	0.23421900	-2.69325200	-1.06474700
C	5.06682900	3.70601600	0.39418500
C	6.31177100	4.24998300	0.69777200
C	6.67703700	4.37131000	2.02885400
C	5.78928100	3.94667700	3.01215800
C	4.57487000	3.41993400	2.60138600
N	4.20822400	3.29559000	1.32557700
H	7.63661000	4.78924900	2.30474600
H	4.74862100	3.59683700	-0.63662900
H	6.97264800	4.56833800	-0.09745900
H	6.03607200	4.02399200	4.06111300
C	3.54879300	2.92968200	3.60058500
F	2.37205500	3.57434200	3.46759000
F	3.28959000	1.61451800	3.44595000
F	3.95315100	3.10420800	4.87210400

P⁺(2-[Trifluoromethyl]pyridine)

C	-1.34293300	-0.46082100	-0.41505400
C	0.03269500	-0.74681500	-0.12598000
C	0.86053800	0.28385600	0.25256400
C	0.32033000	1.61233100	0.33859700
C	-1.05776400	1.89695200	0.04089500
C	-1.88652100	0.86414500	-0.32811900
N	-2.15110600	-1.47025500	-0.78225300
N	1.12025600	2.62354600	0.70579400
H	-1.81561000	-2.41609000	-0.85573400
H	-3.12257100	-1.31964300	-0.99679100
H	2.10607000	2.52854100	0.94673000
H	0.75359000	3.55898800	0.77679900
C	-3.34722300	1.03102100	-0.65177100
C	-1.50608000	3.32915700	0.15560700
C	2.31725200	0.11034100	0.58226900
C	0.47990800	-2.17783900	-0.26123700
H	-3.69140000	2.05227800	-0.53656900
H	-3.55800000	0.73403900	-1.68377400
H	-3.96635900	0.41008400	0.00280200
H	-0.92630400	3.97579200	-0.51014500
H	-2.55017600	3.46592400	-0.10090600
H	-1.37365200	3.70301800	1.17548200
H	2.94345700	0.68198500	-0.10837900
H	2.53689000	0.47061700	1.59007800
H	2.64044300	-0.92312900	0.53187300
H	1.53277100	-2.31345700	-0.04294400
H	-0.07660700	-2.82977800	0.41918500
H	0.31426600	-2.54523700	-1.27851500
C	4.72438800	3.54060500	0.26167700
C	5.99425300	4.10796800	0.29586900
C	6.58349400	4.34386100	1.52721300
C	5.88629600	4.00765800	2.68317400
C	4.62730000	3.44790400	2.54008200
N	4.04709600	3.21264200	1.36122600
H	7.57024600	4.78327900	1.59458200
H	4.23398800	3.34348800	-0.68494700
H	6.50134000	4.35572500	-0.62693600
H	6.31035100	4.17671400	3.66219900
C	3.80090700	3.04847400	3.74392200

Appendix C

F 2.60084300 3.66317700 3.75248900
F 3.55509000 1.72091900 3.76025400
F 4.41085000 3.35115900 4.90184000

P²⁺(2-[Trifluoromethyl]pyridine)

C -1.25132700 -0.40013600 -0.44119200
C 0.14405500 -0.72889600 -0.12241400
C 0.94752000 0.26019000 0.32794600
C 0.39024800 1.62211200 0.41516100
C -1.03068200 1.93340700 0.15187100
C -1.83447500 0.93982300 -0.28509100
N -2.01838200 -1.35365400 -0.86991200
N 1.17312100 2.60247700 0.72368200
H -1.67841700 -2.30025800 -0.99222600
H -2.99290800 -1.19777400 -1.09830600
H 2.20030300 2.55703200 0.93361000
H 0.79679200 3.54360300 0.76980000
C -3.28470300 1.09574100 -0.63021000
C -1.47413600 3.34580700 0.38080100
C 2.37907000 0.07078200 0.71868700
C 0.57459300 -2.14933300 -0.32959200
H -3.63461500 2.11128900 -0.49250900
H -3.46353600 0.83522100 -1.67722200
H -3.90745200 0.44896200 -0.00585600
H -0.97999500 4.03097700 -0.31469300
H -2.54153900 3.46731000 0.24471800
H -1.24081100 3.66643300 1.39949300
H 3.04435100 0.50691900 -0.03123600
H 2.59214100 0.55101900 1.67370200
H 2.63773700 -0.97675900 0.81874400
H 1.62200500 -2.29867200 -0.09880300
H -0.00148800 -2.83159900 0.30177800
H 0.43306000 -2.44679100 -1.37250900
C 4.64108800 3.36865200 0.16920200
C 5.91367800 3.92641100 0.21163800
C 6.46136500 4.23968300 1.44442900
C 5.72150400 3.98732900 2.5935000
C 4.46333800 3.43013300 2.44968400
N 3.92381500 3.12056400 1.26595900
H 7.44901400 4.67581100 1.51722700
H 4.18100500 3.11520600 -0.77875500
H 6.45381100 4.10851500 -0.70734300
H 6.11276300 4.21944200 3.57497000
C 3.59745400 3.11697900 3.65124900
F 2.37393500 3.67379900 3.53893500
F 3.40324300 1.78645900 3.78715900
F 4.13605000 3.55890900 4.79522200

P(3-[Trifluoromethyl]pyridine)

C -1.31371500 -0.47636100 0.00897000
C 0.07422700 -0.69058600 -0.00749500
C 0.93964900 0.40685600 -0.12252800
C 0.40541800 1.70635000 -0.17687200
C -0.98563600 1.91910100 -0.16073000
C -1.85109100 0.82033900 -0.05472000
N -2.18413100 -1.58166800 0.16135900
N 1.27389500 2.80789700 -0.31965400
H -1.81091100 -2.45242700 -0.18891800
H -3.10844600 -1.43511600 -0.21845800
H 2.19508200 2.71367000 0.09592700
H 0.87069500 3.68999800 -0.04053700
C -3.35401000 0.95872900 0.01325700
C -1.47862300 3.34218000 -0.27747300
C 2.43964700 0.25675400 -0.21294000
C 0.56898700 -2.11238800 0.11857300
H -3.68326500 1.98762800 0.12208600
H -3.84092500 0.55931500 -0.88464900

H -3.75721400 0.40251700 0.86491600
H -1.03220600 3.83985600 -1.14418000
H -2.55587200 3.41165300 -0.39390500
H -1.21179500 3.94008300 0.60231500
H 2.83982300 0.88012400 -1.01727400
H 2.94130400 0.57561800 0.70733000
H 2.74992200 -0.76468600 -0.41502100
H 1.64130300 -2.17442500 0.27892500
H 0.09027200 -2.61603000 0.96379100
H 0.34114400 -2.70727700 -0.77437400
C 5.12085200 4.05071100 0.26613500
C 6.31149900 4.53375500 0.79858800
C 6.54859200 4.36500500 2.15192300
C 5.58208500 3.71923300 2.91782600
C 4.42173000 3.26996600 2.29886300
N 4.19057400 3.43062100 0.99479200
H 7.46299300 4.72830900 2.60378600
H 4.90617500 4.16750500 -0.79060200
H 7.03249500 5.03026300 0.16341200
H 3.65259900 2.76505500 2.87060400
C 5.81271200 3.50939700 4.38562400
F 4.74234000 2.98709400 5.01029100
F 6.11426000 4.66550300 5.01809200
F 6.84980800 2.67103800 4.61762100

P⁺(3-[Trifluoromethyl]pyridine)

C -1.30089400 -0.45776400 -0.31841200
C 0.09443600 -0.71287400 -0.10590700
C 0.92449600 0.34135000 0.19521300
C 0.36589600 1.66210200 0.28703800
C -1.03497700 1.91352700 0.07557100
C -1.86334000 0.85877800 -0.22636300
N -2.11110200 -1.48906700 -0.61467600
N 1.16846400 2.69503600 0.57841600
H -1.76352100 -2.43032400 -0.68961400
H -3.09641900 -1.35951500 -0.77167100
H 2.17726800 2.63384800 0.74457000
H 0.78578500 3.62471800 0.64313300
C -3.34267600 0.99310900 -0.47232000
C -1.50653900 3.33750100 0.19998700
C 2.40131600 0.20118700 0.44030800
C 0.55886400 -2.13957300 -0.22913500
H -3.69537300 2.01368300 -0.37932000
H -3.60544200 0.65308200 -1.47882300
H -3.91532600 0.39023200 0.23899000
H -1.00544200 3.98305100 -0.52784800
H -2.57276400 3.44394200 0.03740400
H -1.29320200 3.73690300 1.19610700
H 2.97342000 0.81091100 -0.26366000
H 2.66380500 0.54253400 1.44517900
H 2.75020400 -0.82046800 0.34227700
H 1.62309900 -2.25276800 -0.05846700
H 0.04800100 -2.78278700 0.49393400
H 0.35008000 -2.53583900 -1.22751300
C 4.90626100 3.59572500 0.20349500
C 6.17258000 4.10352400 0.46634100
C 6.56648500 4.25376600 1.78543100
C 5.67432900 3.89006100 2.78938400
C 4.42754000 3.39054500 2.43418200
N 4.04727900 3.24424200 1.16375900
H 7.54399800 4.64939400 2.02964200
H 4.56640500 3.46657500 -0.81807400
H 6.83106400 4.37566700 -0.34712400
H 3.71065900 3.10161700 3.19304300
C 6.07361000 4.01414700 4.23150200
F 5.02119100 3.94192600 5.06627800
F 6.69962100 5.18340700 4.48053100
F 6.93310100 3.03604500 4.60188700

P²⁺(3-[Trifluoromethyl]pyridine)

C	-1.22170600	-0.41075000	-0.27961900
C	0.20795200	-0.69214900	-0.09714200
C	1.02761000	0.33750900	0.21157100
C	0.44710600	1.69081300	0.30227500
C	-0.99209600	1.96634000	0.09877200
C	-1.80895900	0.93373500	-0.20248500
N	-2.01594700	-1.40952600	-0.51286300
N	1.22328800	2.69012900	0.55927800
H	-1.67796800	-2.36262800	-0.57083400
H	-3.01328000	-1.28375200	-0.63711600
H	2.27475000	2.68542200	0.73647400
H	0.82133900	3.62056600	0.61301700
C	-3.28135100	1.05021400	-0.46159800
C	-1.44117600	3.38865000	0.23847100
C	2.49499700	0.20260600	0.46692400
C	0.64777900	-2.11700400	-0.25424800
H	-3.62402100	2.07707700	-0.43555100
H	-3.53520200	0.65324600	-1.44828200
H	-3.85622600	0.49853300	0.28760900
H	-0.97530200	4.02233000	-0.52167300
H	-2.51361800	3.49388000	0.13168100
H	-1.17819000	3.78632700	1.22229700
H	3.07015500	0.75323100	-0.28062700
H	2.75422800	0.60808000	1.44652900
H	2.82377700	-0.82906800	0.44415600
H	1.72395600	-2.22305700	-0.19746100
H	0.21636000	-2.74861600	0.52778200
H	0.34055700	-2.51560100	-1.22452700
C	4.75873700	3.53444900	0.15339900
C	6.02730900	4.02766900	0.42415000
C	6.41663000	4.17094200	1.74556300
C	5.51808900	3.81562000	2.74678800
C	4.26841400	3.33034100	2.38937800
N	3.89619400	3.19042900	1.11466700
H	7.39733700	4.55852000	1.99365200
H	4.41887500	3.41057600	-0.86814300
H	6.69154800	4.29454800	-0.38592700
H	3.54403000	3.04792200	3.14303100
C	5.91298900	3.93561700	4.19195600
F	4.85563300	3.86867400	5.01996200
F	6.54393700	5.10047700	4.44188100
F	6.76370700	2.95150500	4.56150600

P(4-[Trifluoromethyl]pyridine)

C	-1.36342400	-0.47322300	-0.02233500
C	0.02170800	-0.70453700	-0.04503000
C	0.90066300	0.38353400	-0.14529900
C	0.38283200	1.69038700	-0.17828300
C	-1.00545200	1.92030600	-0.15553600
C	-1.88453600	0.83098700	-0.06507100
N	-2.24729000	-1.56983100	0.11480700
N	1.26502400	2.78280100	-0.30585500
H	-1.88588300	-2.43954600	-0.25013200
H	-3.17051000	-1.40572200	-0.26045200
H	2.18490800	2.67146900	0.10862200
H	0.87263200	3.66597700	-0.01502900
C	-3.38551500	0.98700200	0.00712600
C	-1.48065900	3.35119500	-0.24843000
C	2.39837500	0.21580800	-0.24181300
C	0.49897500	-2.13416800	0.05811200
H	-3.70204600	2.01812400	0.13148700
H	-3.87819100	0.60697300	-0.89601300
H	-3.79465500	0.42329600	0.85099500
H	-1.03312800	3.85596300	-1.11047400
H	-2.55758900	3.43638500	-0.35699300
H	-1.20075700	3.93234400	0.63844700

H	2.80480000	0.84855800	-1.03557400
H	2.90609700	0.51146300	0.68289100
H	2.69488300	-0.80573500	-0.46317400
H	1.57086000	-2.21204600	0.21454900
H	0.01614800	-2.64468800	0.89684000
H	0.26152200	-2.71246100	-0.84317500
C	5.08149700	4.01782600	0.24195100
C	6.29777100	4.48201400	0.72723300
C	6.60763500	4.23583100	2.05768800
C	5.69960900	3.54544300	2.85002600
C	4.51105300	3.12479600	2.26825800
N	4.19990800	3.35114800	0.98983000
H	4.80889800	4.18902600	-0.79349700
H	6.97883400	5.01343800	0.07730500
H	5.90512200	3.33126000	3.88978300
H	3.78082800	2.58040500	2.85671700
C	7.89521200	4.74542600	2.65119500
F	7.72726600	5.95569700	3.23200900
F	8.86191500	4.89003300	1.72672200
F	8.37426800	3.92342200	3.60400100

P⁺⁺(4-[Trifluoromethyl]pyridine)

C	-1.30262800	-0.42692800	-0.33110600
C	0.08591300	-0.69328100	-0.08995400
C	0.91865900	0.35434000	0.22635200
C	0.36890200	1.67952000	0.30795700
C	-1.02530200	1.94216900	0.06784100
C	-1.85637800	0.89394400	-0.24899900
N	-2.11442800	-1.45156900	-0.64565700
N	1.17317200	2.70572700	0.61775600
H	-1.77208200	-2.39503600	-0.71686200
H	-3.09467900	-1.31388600	-0.82571000
H	2.17838900	2.63711800	0.80274200
H	0.79601500	3.63804500	0.67693100
C	-3.33009000	1.03974100	-0.52073500
C	-1.48699100	3.37036400	0.18021900
C	2.38946700	0.20229600	0.49878700
C	0.54040400	-2.12412500	-0.20155500
H	-3.67863800	2.06135900	-0.42339100
H	-3.57691400	0.71100500	-1.53500700
H	-3.91876200	0.43347000	0.17441100
H	-0.95658800	4.01194500	-0.53008000
H	-2.54626800	3.48761900	-0.01671000
H	-1.30136000	3.76617600	1.18331200
H	2.97888100	0.81633400	-0.18679500
H	2.63414400	0.53065800	1.51250800
H	2.73427000	-0.82026300	0.39556900
H	1.59809000	-2.24766100	-0.00011400
H	0.00287500	-2.76278100	0.50601100
H	0.35629400	-2.51770100	-1.20584300
C	4.86378000	3.64819000	0.24602200
C	6.13902400	4.14440000	0.47941700
C	6.58480000	4.21249600	1.79238900
C	5.74887200	3.79003000	2.81741900
C	4.49090600	3.30998500	2.48039400
N	4.05057500	3.23666100	1.22181100
H	4.48297000	3.57734800	-0.76646700
H	6.76110200	4.46103400	-0.34594000
H	6.06042500	3.82484900	3.85203100
H	3.81182600	2.96928400	3.25356800
C	7.94563200	4.77979200	2.10619500
F	7.88391300	6.11272900	2.32540500
F	8.81862800	4.59158100	1.10007600
F	8.48279300	4.22940100	3.21022900

P²⁺(4-[Trifluoromethyl]pyridine)

C	-1.21408900	-0.37661400	-0.32322300
---	-------------	-------------	-------------

Appendix C

C	0.19545300	-0.67830000	-0.04224300
C	1.01692000	0.34572100	0.27985700
C	0.44578900	1.70436300	0.35156500
C	-0.98083500	1.99446200	0.08684100
C	-1.79701900	0.96913400	-0.23988600
N	-1.99010500	-1.35693400	-0.66915100
N	1.21557400	2.69318600	0.66203100
H	-1.64944800	-2.30760500	-0.74826400
H	-2.97126900	-1.21704200	-0.87818500
H	2.26392000	2.68423200	0.86568000
H	0.81530800	3.62436800	0.71560200
C	-3.26164300	1.09617500	-0.53499900
C	-1.41734400	3.42331200	0.19411000
C	2.47670600	0.20116500	0.57016000
C	0.61483600	-2.11405100	-0.14351300
H	-3.62230000	2.10883900	-0.40415600
H	-3.47798000	0.80568200	-1.56709600
H	-3.84969800	0.45821100	0.13014600
H	-0.86906900	4.05201100	-0.51316000
H	-2.47128300	3.54868600	-0.02014600
H	-1.24364900	3.81174500	1.20132100
H	3.06689000	0.79470600	-0.13089600
H	2.70895800	0.55338700	1.57717200
H	2.81289800	-0.82550300	0.49355500
H	1.65802500	-2.25776200	0.10827500
H	0.03091500	-2.73906500	0.53767800
H	0.47269100	-2.49118300	-1.16010600
C	4.66924900	3.63138000	0.21358200
C	5.94932100	4.11763000	0.43140500
C	6.42988100	4.13926100	1.73370000
C	5.62320500	3.68247900	2.76726200
C	4.35692700	3.21393000	2.45201800
N	3.88740500	3.18530500	1.20133800
H	4.25757100	3.59577000	-0.78810600
H	6.54888600	4.46231600	-0.39904400
H	5.96335600	3.68261700	3.79310200
H	3.69657000	2.84713100	3.22881400
C	7.80193300	4.69387000	2.02874700
F	7.74890100	6.02110400	2.27531300
F	8.64887400	4.52084600	0.99900000
F	8.35838200	4.11741300	3.10832700

P(Quinoline)

C	-1.40077800	-0.48089200	0.05919800
C	-0.03153100	-0.76141600	-0.07987200
C	0.87631700	0.29560200	-0.23809800
C	0.40695700	1.62085900	-0.21146800
C	-0.96529700	1.89994600	-0.07113000
C	-1.87405100	0.84180300	0.07834900
N	-2.31152900	-1.54733000	0.25121000
N	1.31675400	2.68148000	-0.39730400
H	-2.01289200	-2.42227900	-0.15568000
H	-3.25436100	-1.34323200	-0.04817900
H	2.26120900	2.53342500	-0.05448800
H	0.98076800	3.57498300	-0.06979100
C	-3.35624600	1.05322200	0.28142900
C	-1.39491600	3.34798500	-0.10690600
C	2.35303600	0.07540800	-0.46434200
C	0.40025400	-2.20866600	-0.03533800
H	-3.61646300	2.09115100	0.46582000
H	-3.93898100	0.72496800	-0.58784300
H	-3.71668600	0.47722800	1.13899900
H	-0.98893200	3.85404200	-0.98839500
H	-2.47315900	3.47065500	-0.14249700
H	-1.03654800	3.90175500	0.76915600
H	2.71028000	0.69636100	-1.29062700
H	2.95043500	0.35136400	0.41152100
H	2.59256200	-0.95520800	-0.71111800

H	1.47669700	-2.32548300	0.04944800
H	-0.04427000	-2.72008900	0.82359000
H	0.08472900	-2.75919200	-0.92996800
C	5.40216600	3.56820200	0.16008200
C	6.59682500	3.95632100	0.83653900
C	6.61041500	3.86779800	2.24741600
C	5.49544500	3.42060000	2.90352200
C	4.36074000	3.05914100	2.14530500
N	4.30167300	3.12418200	0.83377800
H	7.50302800	4.15502400	2.79165100
H	5.46774500	3.33965600	3.98232800
H	3.46981400	2.70236100	2.65441400
C	5.35737300	3.64640200	-1.25225900
C	7.70451300	4.40786500	0.07889200
H	4.44469700	3.34992800	-1.75421100
H	8.60972800	4.70138400	0.59823900
C	6.44754800	4.08810000	-1.95795800
C	7.63124500	4.47209100	-1.28880900
H	6.40494200	4.14455600	-3.03893100
H	8.48156700	4.81818600	-1.86341500

P⁺(Quinoline)

C	-1.36397800	-0.45255600	-0.44827300
C	0.01395500	-0.71278900	-0.14768900
C	0.82882400	0.33854200	0.20177800
C	0.26917700	1.66072600	0.26598700
C	-1.11261200	1.91828600	-0.04358900
C	-1.92553100	0.86623000	-0.39299700
N	-2.15706400	-1.48098800	-0.79709300
N	1.04931500	2.68951100	0.62455800
H	-1.80711000	-2.42265500	-0.85337100
H	-3.12797400	-1.34734800	-1.02463100
H	2.03705000	2.62858800	0.89562100
H	0.65872600	3.61686200	0.67635900
C	-3.38785600	1.00536000	-0.72341800
C	-1.58344200	3.34544600	0.04074000
C	2.29028000	0.19224700	0.52352300
C	0.47790800	-2.14218800	-0.23740900
H	-3.74749400	2.02324600	-0.62741800
H	-3.59193000	0.68651900	-1.75029200
H	-3.99929200	0.38722800	-0.05901900
H	-1.00412700	3.99003700	-0.62733800
H	-2.62561800	3.46249800	-0.23292100
H	-1.47135200	3.73844300	1.05595600
H	2.89588600	0.83403900	-0.12089300
H	2.49740400	0.48887900	1.55504900
H	2.64958300	-0.82278300	0.39761500
H	1.52335000	-2.26380000	0.02122900
H	-0.09475100	-2.78305900	0.44003200
H	0.34839600	-2.53529800	-1.25046700
C	4.65681800	3.57657800	0.42989800
C	5.97056800	4.06150500	0.59507800
C	6.46170700	4.21097800	1.86398000
C	5.64464300	3.88216000	2.96931900
C	4.32869400	3.40074200	2.70294200
N	3.86231000	3.25434100	1.42778500
H	7.46703500	4.57858600	2.03490700
H	4.25470500	3.45236400	-0.57132300
H	6.56532700	4.30477100	-0.27534500
C	3.48662600	3.06846800	3.79020500
C	6.07459200	4.01173200	4.31201100
C	3.93283900	3.20588400	5.08001000
C	5.23668800	3.68012800	5.34512800
H	7.07585400	4.37796100	4.50772500
H	5.57035200	3.78131700	6.37039400
H	3.28114600	2.94977600	5.90643800
H	2.48715700	2.70804300	3.58187000

P ²⁺ (Quinoline)							
C	-1.26821700	-0.39560000	-0.37262300	H	-0.97972500	3.95849700	-0.74683000
C	0.13709900	-0.68427300	-0.06147400	H	-2.49132500	3.47347200	-0.00775500
C	0.95093500	0.35098600	0.24460300	H	-1.10946200	3.85632200	1.00394900
C	0.37184900	1.70820500	0.28961700	H	2.82539800	0.92421800	-1.08526800
C	-1.04697600	1.98703000	-0.03024400	H	2.97132600	0.43898800	0.59310700
C	-1.85530800	0.94985000	-0.33853500	H	2.71961700	-0.77354700	-0.65669600
N	-2.03487500	-1.38722600	-0.70888800	H	1.59712100	-2.23128600	-0.10697300
N	1.12066000	2.70259200	0.63113200	H	0.05258700	-2.72221100	0.55822300
H	-1.68998800	-2.33836800	-0.75615300	H	0.26251500	-2.60964000	-1.18401800
H	-3.01172600	-1.25590700	-0.94184100	C	5.27166900	3.55783200	0.37581100
H	2.16474300	2.71762000	0.91877100	C	6.53073300	3.99418900	0.85693300
H	0.70311500	3.62763700	0.66135900	C	6.71035600	4.06929100	2.26683300
C	-3.31710800	1.06350900	-0.65396900	C	5.61382300	3.70099800	3.08136000
C	-1.48932500	3.41734300	0.02109800	C	4.44527500	3.29422900	2.49617800
C	2.41030700	0.21699500	0.54185300	N	4.26524200	3.21935600	1.14911300
C	0.56305500	-2.12099700	-0.11840100	H	5.11235900	3.49409200	-0.69788800
H	-3.68288700	2.07765100	-0.55197800	H	5.70014700	3.74103700	4.16058600
H	-3.52327300	0.74548000	-1.67995100	H	3.59327000	3.00753300	3.10232200
H	-3.90937400	0.44133700	0.02261200	C	7.95867100	4.50212600	2.77531800
H	-0.89023700	4.03579000	-0.65280700	C	7.59430700	4.35089800	-0.00537700
H	-2.52404900	3.53894100	-0.27429100	H	8.10111200	4.56040700	3.84802800
H	-1.39111600	3.82200400	1.03250700	H	7.44814300	4.29080300	-1.07778400
H	2.99635800	0.84367500	-0.13229100	C	8.97286900	4.84195400	1.91628000
H	2.63195000	0.53450300	1.56271200	C	8.79227000	4.76679400	0.51603100
H	2.76149300	-0.80131200	0.42882800	H	9.92609800	5.17266300	2.31072300
H	1.59803000	-2.25636400	0.16964900	H	9.60756500	5.04043500	-0.14214700
H	-0.03883400	-2.73204200	0.55987400	P ⁺ (Isoquinoline)			
H	0.45201500	-2.52273400	-1.12948000	C	-1.22445400	-0.37284300	-0.36380600
C	4.49507300	3.57122700	0.34652300	C	0.15507200	-0.67540800	-0.11544800
C	5.80427400	4.05410700	0.52418900	C	1.00588700	0.34401900	0.24266700
C	6.29734800	4.16308300	1.79705700	C	0.48238300	1.67720300	0.36347000
C	5.48659000	3.79808800	2.89480600	C	-0.90310100	1.97613000	0.11283300
C	4.17151100	3.31998500	2.62351000	C	-1.75188500	0.95585600	-0.24579100
N	3.70915100	3.21251100	1.34151100	N	-2.05281900	-1.37033700	-0.72143100
H	7.30177000	4.52854700	1.97617500	N	1.30153700	2.67527000	0.72046300
H	4.08592400	3.47995400	-0.65463600	H	-1.72774600	-2.31733100	-0.82072900
H	6.39485000	4.32796100	-0.33931700	H	-3.02779500	-1.20738400	-0.90881400
C	3.33451100	2.95546100	3.70252100	H	2.30561800	2.58765100	0.92560300
C	5.92313400	3.89109000	4.23804800	H	0.93671600	3.61044000	0.80813700
C	3.78769600	3.05948500	4.99311200	C	-3.21912100	1.14024100	-0.52836500
C	5.09112600	3.52908700	5.26525500	C	-1.33690300	3.40991200	0.26086400
H	6.92424700	4.25441000	4.43803600	C	2.47094900	0.15359300	0.52010600
H	5.42879000	3.60315900	6.29127700	C	0.58112100	-2.11157700	-0.26591100
H	3.13978200	2.78032500	5.81472900	H	-3.55102900	2.16303500	-0.39220200
H	2.33268900	2.59975300	3.49816800	H	-3.45946600	0.85802200	-1.55812200
P(Isoquinoline)				H	-3.82704800	0.51692900	0.13436800
C	-1.32537900	-0.45731000	-0.09730500	H	-0.77280000	4.06202100	-0.41292200
C	0.05679200	-0.69424800	-0.17683900	H	-2.38725200	3.55729200	0.03807700
C	0.94309400	0.39239400	-0.18720000	H	-1.17098500	3.76871200	1.28130700
C	0.43705300	1.69971900	-0.07488800	H	3.07627700	0.77954400	-0.14029300
C	-0.94840300	1.93492400	0.00480700	H	2.71571700	0.44433200	1.54507100
C	-1.83508700	0.84789900	0.00564600	H	2.79694000	-0.87144000	0.38442200
N	-2.21649700	-1.55611200	-0.05253700	H	1.63044900	-2.26549900	-0.04291500
N	1.32634100	2.79216400	-0.11294300	H	0.01251900	-2.76117300	0.40653400
H	-1.87126700	-2.38605400	-0.51326900	H	0.41302200	-2.46708000	-1.28719600
H	-3.14546200	-1.34738700	-0.38962600	C	4.98838500	3.49861000	0.48176700
H	2.25503400	2.63852700	0.26963100	C	6.29692600	3.95900500	0.76152000
H	0.94701600	3.64704800	0.26601500	C	6.71001300	3.99359800	2.12330500
C	-3.33252400	1.00708700	0.13030800	C	5.77768400	3.56410600	3.09685400
C	-1.41315200	3.37093600	0.06868900	C	4.53816700	3.13938700	2.70379000
C	2.43640400	0.22604200	-0.33881600	N	4.13815100	3.10329000	1.40285300
C	0.52310600	-2.13025600	-0.23254000	H	4.65020200	3.46295600	-0.55059300
H	-3.63446800	2.02140200	0.37297000	H	6.04465900	3.57196300	4.14656800
H	-3.85043500	0.73100300	-0.79621000	H	3.80754100	2.80625400	3.43166700
H	-3.72850200	0.35949500	0.91839700	C	8.01373900	4.45018500	2.43118000
				C	7.18909400	4.37802400	-0.25362700
				H	8.33325500	4.47854000	3.46619000

Appendix C

H	6.86531600	4.34814000	-1.28756900
C	8.85840000	4.85073200	1.42708600
C	8.44594400	4.81554600	0.07515000
H	9.85537300	5.19938200	1.66773900
H	9.13097200	5.13687500	-0.69950900

P²⁺(Isoquinoline)

C	-1.11477900	-0.31456500	-0.34973500
C	0.28503700	-0.65534100	-0.07197100
C	1.12679500	0.33898600	0.28879800
C	0.58745000	1.70925000	0.40066100
C	-0.83071500	2.03760300	0.12658400
C	-1.66782800	1.04018600	-0.23188100
N	-1.91075500	-1.26864600	-0.72580600
N	1.37426700	2.66780300	0.75547200
H	-1.58919800	-2.22326800	-0.83021200
H	-2.88773400	-1.10245500	-0.93375600
H	2.44463100	2.65390400	0.99061500
H	0.98032500	3.60057200	0.83222600
C	-3.12841800	1.20680700	-0.52966200
C	-1.23689700	3.47260200	0.26678900
C	2.57928700	0.15104000	0.58792000
C	0.67298700	-2.09677600	-0.21668800
H	-3.47023700	2.22126400	-0.36554000
H	-3.34534600	0.95530600	-1.57185200
H	-3.73254600	0.55898300	0.11118100
H	-0.64761400	4.11083000	-0.39756000
H	-2.27868100	3.63143900	0.01777900
H	-1.09097000	3.82235500	1.29270800
H	3.18918200	0.77756100	-0.06523300
H	2.80060500	0.43928400	1.61771100
H	2.90022700	-0.87469700	0.45354300
H	1.71048200	-2.27191200	0.03877800
H	0.06973900	-2.73003100	0.43967600
H	0.53037700	-2.43790000	-1.24607700
C	4.80753900	3.46748000	0.44475100
C	6.11981900	3.90961200	0.71950200
C	6.55067200	3.90798600	2.07702200
C	5.62983300	3.46317300	3.05469000
C	4.38220100	3.05664300	2.67411800
N	3.97218000	3.05602300	1.37497700
H	4.44950100	3.45802800	-0.58040700
H	5.91168400	3.44549100	4.09990800
H	3.65596100	2.71325900	3.40037800
C	7.86100600	4.34726800	2.37826600
C	7.00062600	4.34616800	-0.29836900
H	8.19449400	4.34869400	3.40897300
H	6.66289800	4.34346600	-1.32797000
C	8.69440000	4.76543500	1.37197800
C	8.26431000	4.76594400	0.02508200
H	9.69700400	5.10101200	1.60717500
H	8.94182400	5.10085600	-0.75019300

P(Pyridazine)

C	-1.32485000	-0.47600000	-0.12574100
C	0.06095000	-0.68141200	-0.22690400
C	0.92443400	0.42333200	-0.21241400
C	0.39269400	1.71528000	-0.05234000
C	-0.99612800	1.91916600	0.04843700
C	-1.86012800	0.81429100	0.02444700
N	-2.19271100	-1.59398400	-0.10754400
N	1.25963200	2.82654800	-0.06344100
H	-1.83639000	-2.40046100	-0.60042700
H	-3.12968700	-1.39324300	-0.42682200
H	2.19366900	2.67492300	0.30479200
H	0.86857000	3.65992300	0.34999500
C	-3.35882400	0.93845500	0.17138600

C	-1.48961300	3.34259200	0.15979900
C	2.41889500	0.29326900	-0.38693800
C	0.55656200	-2.10478100	-0.33136700
H	-3.67759400	1.93728900	0.45373200
H	-3.88252500	0.68496600	-0.75834300
H	-3.73214900	0.25554800	0.94049800
H	-1.07008700	3.96429300	-0.63740200
H	-2.56987300	3.42558600	0.08807000
H	-1.19374900	3.80412600	1.10958000
H	2.78481300	1.02648100	-1.11101000
H	2.96105900	0.48128700	0.54625600
H	2.71762200	-0.68788600	-0.74561900
H	1.63295300	-2.18725500	-0.21198400
H	0.10117800	-2.73157600	0.44113400
H	0.30269600	-2.55830100	-1.29723100
N	4.21136100	3.23277700	1.22241900
H	7.63149700	4.38291100	2.51496300
C	6.65255100	4.06062400	2.18534000
H	5.68415100	4.13129900	4.11208900
C	5.59374300	3.92380000	3.05406100
H	7.20122800	3.84968000	0.10204000
C	6.41557300	3.76469800	0.84359300
H	3.50206100	3.37023600	3.13412200
N	5.23571500	3.36514100	0.38016700
C	4.38046800	3.50125300	2.51310100

P⁺(Pyridazine)

C	-1.27422400	-0.41636400	-0.35417700
C	0.11583800	-0.68037500	-0.12049000
C	0.93518800	0.35682200	0.25907900
C	0.36891500	1.66824100	0.41777800
C	-1.02677400	1.92858200	0.18284000
C	-1.84343500	0.89134200	-0.20079700
N	-2.07251500	-1.43050300	-0.73245100
N	1.15819300	2.68205700	0.79735900
H	-1.71876600	-2.36425300	-0.85632800
H	-3.05368100	-1.29418000	-0.90833300
H	2.16430800	2.61515000	0.98683800
H	0.76855700	3.60444200	0.90911000
C	-3.31626500	1.03663000	-0.47760500
C	-1.50597200	3.34259300	0.37379800
C	2.40739600	0.20713300	0.52519700
C	0.58724900	-2.09764700	-0.30914200
H	-3.67770400	2.04659800	-0.32286800
H	-3.54951600	0.76644100	-1.51219700
H	-3.90452200	0.38329600	0.17382400
H	-0.97316200	4.03081400	-0.28947100
H	-2.56373700	3.46052900	0.16910900
H	-1.33852200	3.68002800	1.40123500
H	2.98891700	0.87711200	-0.11291400
H	2.64538900	0.46717400	1.56022300
H	2.76709100	-0.80058900	0.35090500
H	1.64277600	-2.22258600	-0.09741400
H	0.04559800	-2.78169400	0.35128500
H	0.42309500	-2.43389100	-1.33755700
N	4.02459400	3.17410500	1.36321400
H	7.60723800	4.50918600	1.52342800
C	6.59469800	4.12809300	1.51571600
H	6.40877400	3.82141500	3.64311400
C	5.94333200	3.75427100	2.66890800
H	6.34337300	4.27203300	-0.63024100
C	5.89430400	3.99706200	0.31666300
H	4.06214800	2.96327700	3.39633500
N	4.65113300	3.53532500	0.24487500
C	4.64045800	3.27720500	2.53564700

P ²⁺ (Pyridazine)							
C	-1.20755600	-0.38546600	-0.24089900	H	0.05229900	-2.75307100	0.44017100
C	0.23550800	-0.63980100	-0.16165700	H	0.25050900	-2.58288400	-1.29888300
C	1.05451800	0.40358100	0.09909300	C	5.32556200	3.48233000	0.41598000
C	0.44422300	1.72587700	0.33719700	C	4.39541300	3.44971100	2.48383500
C	-0.99531300	1.99406900	0.12694800	N	4.25612500	3.23692800	1.17212900
C	-1.80871600	0.95180700	-0.14840800	H	5.21795800	3.31104500	-0.65024600
N	-1.99829000	-1.39832400	-0.42369100	H	3.52911500	3.25238500	3.10635900
N	1.18899100	2.69445800	0.75178200	H	7.59696400	4.47739200	2.50411500
H	-1.64757300	-2.34559600	-0.49778500	C	6.63379500	4.12376100	2.15155700
H	-3.00301200	-1.28981700	-0.49090200	H	5.69194000	4.07173800	4.09467300
H	2.23824300	2.67946100	0.98972800	N	6.51226300	3.91614600	0.83713500
H	0.75875200	3.59863400	0.91936300	C	5.58595600	3.90137700	3.03215100
C	-3.29079900	1.05010500	-0.35429700	P ⁺ (Pyrimidine)			
C	-1.45044500	3.41488100	0.26093600	C	-1.30781800	-0.44221000	-0.31480500
C	2.54389600	0.31086300	0.18840700	C	0.08911600	-0.70806700	-0.12711100
C	0.69249800	-2.05333900	-0.36517000	C	0.92689200	0.33433800	0.19319400
H	-3.64627500	2.07170300	-0.30011600	C	0.37314800	1.65252600	0.33626100
H	-3.57662300	0.65673300	-1.33375000	C	-1.02854200	1.91547400	0.14599800
H	-3.82958000	0.48523100	0.41189800	C	-1.86416100	0.87313500	-0.17820200
H	-0.86022900	4.07574700	-0.37875700	N	-2.12514900	-1.46157200	-0.63189800
H	-2.48914800	3.54172100	-0.01874800	N	1.18136800	2.67210400	0.65805500
H	-1.35048500	3.76139500	1.29418100	H	-1.78191600	-2.40135300	-0.73883900
H	3.01651400	1.09601800	-0.40368900	H	-3.11211000	-1.32460700	-0.77130800
H	2.87654700	0.43625800	1.22215500	H	2.19026100	2.60044600	0.81173400
H	2.91707300	-0.64232200	-0.16714400	H	0.80282000	3.59989300	0.76184700
H	1.77030900	-2.14703700	-0.31543600	C	-3.34535200	1.02002500	-0.40462900
H	0.28195400	-2.70906100	0.40832000	C	-1.49290700	3.33723300	0.31518800
H	0.37617500	-2.43437200	-1.33983400	C	2.40687000	0.18293000	0.41111700
N	3.82656600	3.08602600	1.37776000	C	0.54654400	-2.13262000	-0.29385200
H	7.44040900	4.26786500	1.67498600	H	-3.69396600	2.03793100	-0.27421700
C	6.41310100	3.93241600	1.62824200	H	-3.61935400	0.71406300	-1.41904800
H	6.07632100	3.81710300	3.75583300	H	-3.91289000	0.39592500	0.29227500
C	5.67194900	3.68755200	2.76131800	H	-0.98556900	4.00290700	-0.38979200
H	6.31254000	3.90466200	-0.53645100	H	-2.55781100	3.45459300	0.15164100
C	5.78927500	3.73113600	0.39573900	H	-1.28141300	3.70343400	1.32449700
H	3.70619700	3.04563600	3.41924600	H	2.96957000	0.83247900	-0.26405600
N	4.53414400	3.31992300	0.27680100	H	2.68195000	0.46601500	1.43084000
C	4.35811000	3.25914900	2.58129500	H	2.75563600	-0.83077900	0.24998000
P(Pyrimidine)				H	1.61046500	-2.25548300	-0.12812700
C	-1.35151000	-0.48302300	-0.12589800	H	0.03464900	-2.79376400	0.41213100
C	0.03194000	-0.70304600	-0.22924900	H	0.33352500	-2.49935600	-1.30264400
C	0.90678200	0.39278500	-0.21644200	C	4.79758200	3.80746100	0.23514200
C	0.38836500	1.69014200	-0.05768900	C	4.65301900	3.14488400	2.40330400
C	-0.99782800	1.90875500	0.04578200	N	4.08510500	3.21710200	1.19516700
C	-1.87312000	0.81284500	0.02480300	H	4.33782900	3.86768900	-0.74587100
N	-2.23091900	-1.59161900	-0.10569800	H	4.07712300	2.66638300	3.18779700
N	1.26630100	2.79308300	-0.07304100	H	7.56240800	4.67011800	1.68891800
H	-1.88367900	-2.40267500	-0.59749600	C	6.56959000	4.24790200	1.57617400
H	-3.16631800	-1.38159800	-0.42360400	H	6.37321600	3.59479900	3.62567200
H	2.20178600	2.62961100	0.28404600	N	6.01503700	4.32850300	0.36322900
H	0.88860000	3.62880400	0.34812000	C	5.91745200	3.65545600	2.64722900
C	-3.37005900	0.95267700	0.17513000	P ²⁺ (Pyrimidine)			
C	-1.47624400	3.33732200	0.15683300	C	-1.21147100	-0.36620800	-0.41668000
C	2.39991100	0.24761500	-0.39045500	C	0.18787100	-0.68965900	-0.11095900
C	0.51210200	-2.13164800	-0.33404000	C	0.98571500	0.29801600	0.35235300
H	-3.67770700	1.95493600	0.45766200	C	0.41353400	1.65134500	0.48117800
H	-3.89854000	0.70406400	-0.75319600	C	-1.02662900	1.93487100	0.30022300
H	-3.74854800	0.27409200	0.94552000	C	-1.81940100	0.94807500	-0.17095400
H	-1.05012900	3.95430600	-0.64048100	N	-1.95908000	-1.30396800	-0.91122500
H	-2.55556800	3.43149300	0.08510500	N	1.19690600	2.64207400	0.74992500
H	-1.17558400	3.79586900	1.10655300	H	-1.60051900	-2.23412300	-1.09215100
H	2.77228700	0.96962900	-1.12269400	H	-2.93382200	-1.15074500	-1.14004600
H	2.94385100	0.44012100	0.54091100	H	2.25227700	2.62968000	0.87211900
H	2.69030300	-0.73969600	-0.73864500	H	0.80165300	3.57388600	0.82742400
H	1.58784300	-2.22576600	-0.21782000	C	-3.27999600	1.09383700	-0.47486700

Appendix C

C	-1.50092400	3.31926500	0.62195000
C	2.42410800	0.11858200	0.72161600
C	0.62985000	-2.10133800	-0.35289400
H	-3.64273200	2.09528600	-0.27828200
H	-3.47835400	0.88754900	-1.53032900
H	-3.87746500	0.40320300	0.12626900
H	-1.14732200	4.04009900	-0.12203700
H	-2.58231200	3.38377800	0.64253400
H	-1.14404500	3.63761900	1.60388600
H	3.07593500	0.59000100	-0.01858000
H	2.63557600	0.57481300	1.68903600
H	2.70074000	-0.92715300	0.78616400
H	1.66847900	-2.25752400	-0.08922400
H	0.03309500	-2.80584900	0.23267200
H	0.52735100	-2.36272800	-1.41024600
C	4.68585700	3.47415200	0.05884800
C	4.44882200	3.30179800	2.31915800
N	3.92032100	3.14119800	1.10036800
H	4.25137400	3.34515500	-0.92665200
H	3.82468100	3.03448400	3.16416900
H	7.45771500	4.48189700	1.39776800
C	6.44492300	4.09822400	1.34219400
H	6.16044200	3.91474400	3.47617200
N	5.92554700	3.94529800	0.12046400
C	5.73351900	3.78630200	2.49163100

P(Pyrazine)

C	-1.35621600	-0.48255100	-0.11415900
C	0.02674800	-0.70584100	-0.21747300
C	0.90345800	0.38857600	-0.21493200
C	0.38728800	1.68809600	-0.06712800
C	-0.99830100	1.91000900	0.03623200
C	-1.87545200	0.81543300	0.02609400
N	-2.23740800	-1.58940200	-0.08313100
N	1.26701600	2.78962200	-0.09312000
H	-1.89211800	-2.40551700	-0.56786500
H	-3.17290100	-1.38071600	-0.40162100
H	2.20297500	2.62601600	0.26227700
H	0.89228800	3.62850600	0.32447700
C	-3.37190400	0.95919900	0.17749600
C	-1.47412400	3.34030200	0.13562500
C	2.39630900	0.23950600	-0.38828600
C	0.50412200	-2.13617000	-0.31076800
H	-3.67722500	1.96418800	0.45275800
H	-3.90223100	0.70439000	-0.74809200
H	-3.75048000	0.28733400	0.95369500
H	-1.04713600	3.94986900	-0.66688800
H	-2.55330900	3.43575300	0.06351100
H	-1.17229000	3.80615900	1.08140700
H	2.76936200	0.95276900	-1.12871800
H	2.94090900	0.44139600	0.54074400
H	2.68530300	-0.75193800	-0.72563600
H	1.58003000	-2.23125600	-0.19706100
H	0.04558800	-2.74980900	0.47038700
H	0.23872200	-2.59559500	-1.27068800
C	5.31661400	3.53823200	0.36249500
C	6.51226600	3.99531500	0.90622200
C	5.62336500	3.84897100	2.98654700
C	4.42720000	3.39199000	2.44382000
N	4.26910900	3.23474000	1.12937500
H	5.20498600	3.41619100	-0.70904500
H	7.35394100	4.23768900	0.26698300
H	5.73397900	3.97055000	4.05835200
H	3.58474000	3.14986500	3.08212100
N	6.67134300	4.15274900	2.22052800

P⁺⁺(Pyrazine)

C	-1.31242400	-0.43401300	-0.28776500
C	0.09359300	-0.69546900	-0.17740500
C	0.94306500	0.34746000	0.10863700
C	0.39361300	1.66343900	0.28481000
C	-1.01637900	1.92320200	0.16557700
C	-1.86472500	0.87923600	-0.11794300
N	-2.14268100	-1.45528900	-0.56196600
N	1.21463300	2.68418300	0.56883400
H	-1.80365700	-2.39457400	-0.68551500
H	-3.13672500	-1.32180700	-0.64174600
H	2.22770100	2.60968000	0.68701300
H	0.84017900	3.61068200	0.69627700
C	-3.35641200	1.02189000	-0.26331100
C	-1.47563400	3.34295500	0.36301800
C	2.43252000	0.19957500	0.25111700
C	0.54746900	-2.11602400	-0.38311000
H	-3.69850500	2.04166000	-0.13006900
H	-3.68705000	0.70046000	-1.25564600
H	-3.88302400	0.40841000	0.47415500
H	-1.00967500	4.01203100	-0.36689400
H	-2.54822500	3.45679900	0.25770200
H	-1.21145200	3.70771600	1.36038700
H	2.95783300	0.82095100	-0.47911400
H	2.76409000	0.52009000	1.24211900
H	2.77082000	-0.82081100	0.11141800
H	1.62196400	-2.23090500	-0.30102900
H	0.09608400	-2.78409000	0.35691400
H	0.26145700	-2.48074000	-1.37437600
C	5.00490400	3.53264900	0.15350500
C	6.27439200	4.00223600	0.47109400
C	5.80357600	3.79122400	2.67957500
C	4.53325500	3.32137000	2.36580800
N	4.13125500	3.19030300	1.10104900
H	4.69015800	3.43159200	-0.87877800
H	6.97366700	4.27619200	-0.31069400
H	6.11593700	3.89163400	3.71283200
H	3.83200500	3.04743900	3.14565700
N	6.67896300	4.13328300	1.73439700

P²⁺(Pyrazine)

C	-1.25113700	-0.40396100	-0.17647900
C	0.19002000	-0.68640700	-0.17168000
C	1.04092400	0.34581100	0.02138600
C	0.47033900	1.69202300	0.21780000
C	-0.97394300	1.98273600	0.08778100
C	-1.82196500	0.94714100	-0.09211800
N	-2.06850700	-1.40614500	-0.27389800
N	1.25846900	2.66977800	0.51840100
H	-1.73988300	-2.36228000	-0.33693200
H	-3.07352100	-1.28011600	-0.28275200
H	2.30631700	2.63937700	0.67750500
H	0.86410900	3.59496900	0.65447300
C	-3.31225700	1.06547800	-0.20310400
C	-1.39621900	3.41647900	0.19152300
C	2.53033200	0.22060300	0.06541400
C	0.60342100	-2.11394400	-0.36803300
H	-3.64816400	2.09390500	-0.15550300
H	-3.66771000	0.64980400	-1.14990100
H	-3.80774300	0.53109000	0.61270900
H	-0.84302100	4.03939400	-0.51575400
H	-2.44957000	3.54939600	-0.02262900
H	-1.22088300	3.80528000	1.19921500
H	2.99592900	0.89495200	-0.65561300
H	2.91056600	0.48092600	1.05586100
H	2.86571300	-0.78441400	-0.15972000
H	1.67924200	-2.22846100	-0.41467100

H	0.24976700	-2.73940700	0.45715400
H	0.19515700	-2.51427200	-1.29988900
C	4.81748200	3.56829000	0.18641400
C	6.07649300	4.02927600	0.55178800
C	5.61851300	3.57909200	2.72865700
C	4.35746400	3.11683000	2.37216200
N	3.95869500	3.11040100	1.09891300
H	4.49912200	3.56889700	-0.84909100
H	6.76643700	4.39901800	-0.19768600
H	5.93268300	3.57882400	3.76581200
H	3.66293500	2.74841500	3.11762200
N	6.48096100	4.03584300	1.82140000

P(2,2'-Bipyridyl)

C	-1.47245400	-0.60880500	-0.46970600
C	-0.12354600	-0.81263200	-0.13483200
C	0.74691100	0.28549100	-0.08371400
C	0.24588400	1.57641100	-0.32598100
C	-1.10456000	1.77919200	-0.66287100
C	-1.97349100	0.67955800	-0.72095600
N	-2.35681100	-1.71301000	-0.48843500
N	1.12836900	2.67748300	-0.29848400
H	-1.91203200	-2.59510400	-0.69884900
H	-3.15911800	-1.58929300	-1.08934100
H	1.90908300	2.60133300	0.34349500
H	0.67289000	3.56822200	-0.16435100
C	-3.44732800	0.81173700	-1.02600500
C	-1.54907500	3.19041700	-0.96826900
C	2.22376300	0.14464600	0.19958200
C	0.32125100	-2.22288700	0.17405900
H	-3.79034100	1.84199200	-1.02752000
H	-3.70233600	0.38606900	-2.00410900
H	-4.04698000	0.27770900	-0.28283700
H	-0.88743700	3.65643800	-1.70500300
H	-2.55519700	3.23989000	-1.37362700
H	-1.52936300	3.82821900	-0.07641600
H	2.80873400	0.72266500	-0.52122600
H	2.49090700	0.52127200	1.19327700
H	2.56858800	-0.88382000	0.13940200
H	1.31450200	-2.26585300	0.61130200
H	-0.36096800	-2.69729000	0.88568100
H	0.33476700	-2.85541800	-0.72190100
C	4.55679300	3.82440200	0.42411400
C	5.88764000	4.21208400	0.51837300
C	6.45910500	4.28235600	1.78203100
C	5.68536500	3.96784100	2.88821400
C	4.35300700	3.58942200	2.70251200
N	3.80281700	3.51904400	1.48006500
H	7.49327200	4.58009800	1.90514200
H	4.07440600	3.75342000	-0.54562700
H	6.45263500	4.44938500	-0.37352900
H	6.09013300	4.01100900	3.88859500
C	3.48569100	3.25428600	3.86666200
C	2.11406100	3.03839500	3.71072500
N	4.08077500	3.17839000	5.06682500
C	1.34851800	2.73264700	4.82570300
H	1.66743100	3.11576900	2.73068600
C	3.33569000	2.88362000	6.13054400
C	1.96686500	2.65035500	6.06631300
H	0.28329800	2.56282800	4.72689600
H	3.85636800	2.83003900	7.08162500
H	1.40888000	2.41394500	6.96292900

P⁺(2,2'-Bipyridyl)

C	-1.32987200	-0.59322800	-0.60164500
C	-0.04303500	-0.75791600	0.01040500
C	0.70384000	0.36011900	0.29867800

C	0.16652900	1.65490800	-0.01619300
C	-1.12118200	1.81602100	-0.63691700
C	-1.86643200	0.69744200	-0.92524900
N	-2.05822800	-1.68729200	-0.88417500
N	0.88113000	2.75142800	0.27535700
H	-1.72295400	-2.61335600	-0.67782200
H	-2.96494100	-1.62277200	-1.31575100
H	1.79386000	2.75407600	0.73605400
H	0.51056900	3.66385900	0.06298700
C	-3.22866900	0.73571700	-1.56479400
C	-1.57418600	3.22095800	-0.92994500
C	2.06714400	0.31578000	0.93128600
C	0.40518100	-2.16551700	0.29891800
H	-3.56734000	1.74325100	-1.77655500
H	-3.23341200	0.18966500	-2.51311600
H	-3.98018100	0.27606400	-0.91559400
H	-0.86606200	3.73235300	-1.58892600
H	-2.54281100	3.25913300	-1.41470700
H	-1.65200400	3.80960800	-0.01062800
H	2.80804500	0.80731700	0.29568000
H	2.06964200	0.83829000	1.89173000
H	2.41570100	-0.69473000	1.11139800
H	1.38148300	-2.20972900	0.76742500
H	-0.29574600	-2.66988700	0.97103900
H	0.46235700	-2.75640700	-0.62037800
C	4.25628200	3.85946600	0.25727500
C	5.60474200	4.18759700	0.24720400
C	6.29495300	4.15599300	1.45195900
C	5.61415200	3.80546100	2.60704500
C	4.25413000	3.49825000	2.53041300
N	3.58935900	3.52199000	1.36352400
H	7.34822900	4.40487900	1.49197400
H	3.68555000	3.86024900	-0.66586900
H	6.09397700	4.45626200	-0.67959300
H	6.11261300	3.77168400	3.56490700
C	3.48896100	3.14590200	3.75656600
C	2.10858700	3.34446600	3.83132500
N	4.19212900	2.65145600	4.78612000
C	1.44229300	3.00745200	5.00023800
H	1.57671400	3.77010500	2.99273400
C	3.54097700	2.32828200	5.90250600
C	2.16841200	2.48247900	6.06062900
H	0.37295600	3.15800700	5.08295100
H	4.14370400	1.92549200	6.71031600
H	1.69021600	2.20334100	6.99037600

P²⁺(2,2'-Bipyridyl)

C	-1.21277200	-0.54559200	-0.52949600
C	0.10190500	-0.72863600	0.09833100
C	0.83710800	0.37133100	0.37565700
C	0.25999200	1.69357500	0.06902600
C	-1.07675300	1.86817900	-0.54074500
C	-1.80834100	0.76647600	-0.81572900
N	-1.88331000	-1.60573100	-0.86004200
N	0.93640500	2.75696900	0.35323800
H	-1.52505200	-2.53918000	-0.69664000
H	-2.79165400	-1.54988600	-1.30475900
H	1.90929100	2.83315100	0.78306100
H	0.52768800	3.66276100	0.14529100
C	-3.18580100	0.77672900	-1.40780900
C	-1.52619900	3.27139500	-0.80988500
C	2.20286900	0.34373200	0.98284200
C	0.53345400	-2.13802300	0.37048000
H	-3.58004200	1.77968900	-1.51534500
H	-3.18940200	0.31842600	-2.40116200
H	-3.88558000	0.22581100	-0.77398600
H	-0.82055700	3.78616500	-1.46755300
H	-2.49394000	3.30760900	-1.29436000

Appendix C

H	-1.60637800	3.84321800	0.11899000
H	2.92177600	0.85466500	0.33971800
H	2.20343000	0.85170800	1.95001700
H	2.56430600	-0.66517800	1.13916800
H	1.47549400	-2.18521000	0.90234000
H	-0.20654800	-2.65968500	0.98280400
H	0.65846600	-2.69556500	-0.56238000
C	4.18606400	3.78019700	0.13361800
C	5.53455600	4.09791600	0.15995400
C	6.19559200	4.05321800	1.38065300
C	5.48491300	3.70564400	2.51827100
C	4.12515600	3.41481600	2.41219900
N	3.49162300	3.44397000	1.22631800
H	7.24991400	4.29088500	1.44621500
H	3.63920600	3.78375800	-0.80319600
H	6.04779000	4.36619000	-0.75341200
H	5.96045000	3.66462700	3.48751300
C	3.33045800	3.07737900	3.62184200
C	1.99319800	3.45957300	3.73988300
N	3.97390300	2.41909800	4.59677200
C	1.29970100	3.12910900	4.89580500
H	1.51777700	4.03317700	2.95665400
C	3.29701300	2.10487500	5.70018200
C	1.95947400	2.43108700	5.89717400
H	0.26390900	3.42160500	5.01459600
H	3.84815100	1.56657400	6.46441700
H	1.45865900	2.15137000	6.81463400

C.2 Supporting Information for Oxygen and Sulfur Heterocycles

C.2.1 Cyclic voltammograms of 2,3,5,6-tetramethyl-1,4-phenylenediamine at different concentrations of tetrahydrothiophene and thiophene

Figure C.18. Cyclic voltammograms of 1 mM TMPD at different concentrations of (a) tetrahydrothiophene and (b) thiophene with $0.1 \text{ M } n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the sulfur heterocycles are indicated in dashed lines with their measured trace moisture content.

C.3 Supporting Information for the Simple Alcohols

C.3.1 Cyclic voltammograms of 2,3,5,6-tetramethyl-1,4-phenylenediamine at different concentrations of the simple alcohols

Figure C.19. Cyclic voltammograms of 1 mM TMPD at different concentrations of (a) n -propanol ($n\text{-PrOH}$) and (b) isopropanol ($i\text{-PrOH}$) with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the alcohols are indicated in dashed lines with their measured trace moisture content.

Figure C.20. Cyclic voltammograms of 1 mM TMPD at different concentrations of (a) n -butanol ($n\text{-BuOH}$) and (b) sec -butanol ($s\text{-BuOH}$) with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the alcohols are indicated in dashed lines with their measured trace moisture content.

Figure C.21. Cyclic voltammograms of 1 mM TMPD at different concentrations of isobutanol ($i\text{-BuOH}$) with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that was acquired before the introduction of $i\text{-BuOH}$ is indicated in dashed lines with its measured trace moisture content.

C.3.2 Plots of E_{P1} , E_{P2} and $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration of the simple alcohols

Figure C.22. Plots E_{P1} against concentration of the simple alcohols obtained over three experiments (red +, blue $\circ$ and black $\times$) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure C.23. Plots of E_{P2} against concentration of the simple alcohols obtained over three experiments (red +, blue $\circ$ and black $\times$) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure C.24. Plots of $\Delta E_p = |E_{p1} - E_{p2}|$ against concentration of the simple alcohols obtained over three experiments (red +, blue ○ and black ×) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

C.3.3 Energies of phenylenediamine-alcohol hydrogen-bonded complexes

Table C.2. Energies of the MeCN-solvated phenylenediamine-alcohol hydrogen-bonded complexes.

Alcohol	Energy (hartrees)		
	P	P ^{•+}	P ²⁺
MeOH	-615.879	-615.714	-615.507
EtOH	-655.182	-655.017	-654.811
<i>n</i> -PrOH	-694.479	-694.315	-694.109
<i>i</i> -PrOH	-694.485	-694.320	-694.115
<i>n</i> -BuOH	-733.777	-733.612	-733.406
<i>s</i> -BuOH	-733.782	-733.616	-733.410
<i>i</i> -BuOH	-733.778	-733.613	-733.407
<i>t</i> -BuOH	-733.786	-733.622	-733.416

C.3.4 Geometries of phenylenediamine-alcohol hydrogen-bonded complexes

Figure C.25. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(MeOH) hydrogen-bonded complexes.

Figure C.26. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(EtOH) hydrogen-bonded complexes.

Figure C.27. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(*n*-PrOH) hydrogen-bonded complexes.

Figure C.28. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(*i*-PrOH) hydrogen-bonded complexes.

Figure C.29. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(*n*-BuOH) hydrogen-bonded complexes.

Figure C.30. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(*s*-BuOH) hydrogen-bonded complexes.

Figure C.31. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(*i*-BuOH) hydrogen-bonded complexes.

Figure C.32. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated TMPD(*t*-BuOH) hydrogen-bonded complexes.

C.3.5 Coordinates of phenylenediamine-alcohol hydrogen-bonded complexes

P(MeOH)							
C	-0.95012600	-0.33228000	-0.57264700	H	0.75061100	-2.34120300	-1.02160200
C	0.40119800	-0.33906800	-0.18527500	O	3.81551500	3.83066100	1.15638000
C	0.98380500	0.84433300	0.29061200	H	4.38565600	3.45841600	1.83794100
C	0.19526700	1.99954600	0.39747700	C	4.62937800	4.34826400	0.09796600
C	-1.15382000	2.00972500	0.01302600	H	5.23468800	3.56224500	-0.36050900
C	-1.73750300	0.82707500	-0.46327500	H	3.95258000	4.75645800	-0.65081400
N	-1.54613600	-1.53075800	-1.01625200	H	5.28280100	5.14628100	0.45820400
N	0.79869900	3.21290000	0.84447100	P ²⁺ (MeOH)			
H	-0.90439800	-2.19171600	-1.42915500	C	-1.02473300	-0.32826600	-0.27671700
H	-2.34553600	-1.40449000	-1.61985600	C	0.38406000	-0.50228900	0.10315400
H	1.57085400	3.05786600	1.48048500	C	1.08181100	0.59380000	0.47492800
H	0.14097600	3.83745000	1.29388000	C	0.38870000	1.89532700	0.45446800
C	-3.19258500	0.72731500	-0.85469900	C	-1.06704300	2.03111000	0.24731300
C	-1.91167000	3.31226000	0.12222100	C	-1.76189300	0.93484800	-0.12617100
C	2.43882300	0.94079700	0.68663100	N	-1.65942000	-1.35229700	-0.75551000
C	1.15493800	-1.64335400	-0.28918500	N	1.07952700	2.97362000	0.62426600
H	-3.76564600	1.61079000	-0.59027700	H	-1.20826000	-2.25036100	-0.88379200
H	-3.31509100	0.57526400	-1.93383100	H	-2.63186500	-1.29940700	-1.03476300
H	-3.66998600	-0.12336000	-0.35912500	H	2.11185100	3.03252600	0.75406800
H	-1.35522500	4.12836600	-0.34704100	H	0.61489600	3.87539800	0.61087200
H	-2.88443500	3.27726500	-0.35861100	C	-3.22976500	0.91036900	-0.42637200
H	-2.07978000	3.59946100	1.16704600	C	-1.66028300	3.39442400	0.43002300
H	2.91922700	1.79531800	0.20187100	C	2.51842700	0.58923100	0.89148000
H	2.55848500	1.07835700	1.76790600	C	0.94461400	-1.89022200	0.02612900
H	3.01123500	0.05986500	0.41279000	H	-3.71340800	1.85001600	-0.18867400
H	2.13391400	-1.60708600	0.17889100	H	-3.40574900	0.71957400	-1.48944600
H	0.59975000	-2.45217500	0.19528500	H	-3.73516400	0.13057100	0.14845500
H	1.30797600	-1.94399200	-1.33262400	H	-1.32515800	4.07590900	-0.35836900
H	1.52622700	4.19070800	-0.64067100	H	-2.74292000	3.37736000	0.39546000
O	1.89303400	4.67550400	-1.41163800	H	-1.37353500	3.81996800	1.39435200
C	2.44738600	5.90077500	-0.95521600	H	3.13541300	1.13785800	0.17564500
H	2.85241400	6.42594600	-1.82108100	H	2.63553400	1.06936900	1.86520400
H	1.69278100	6.54268000	-0.48606400	H	2.92033500	-0.41374500	0.96836400
H	3.26161800	5.74086900	-0.23883400	H	1.95823300	-1.94498200	0.40378100
P ⁺ (MeOH)				H	0.34194800	-2.59013500	0.61009500
C	-1.09862600	-0.39185200	-0.18687200	H	0.96979600	-2.24243300	-1.00961900
C	0.31116100	-0.52008300	0.04503100	O	3.68626700	3.73115400	0.93329000
C	1.04478600	0.61017600	0.31967900	H	4.25322600	3.49228800	1.67517800
C	0.37310700	1.87929200	0.36997200	C	4.49456600	4.18099500	-0.16559100
C	-1.04104100	2.00399500	0.13987100	H	5.16217700	3.38947400	-0.51132100
C	-1.77212900	0.87413100	-0.14083900	H	3.81250600	4.45247700	-0.96866100
N	-1.81493800	-1.49698100	-0.45650300	H	5.07801100	5.05730700	0.12086300
N	1.08191700	2.98428000	0.64018300	P(EtOH)			
H	-1.38925100	-2.40797900	-0.49500000	C	-0.94386100	-0.32008600	-0.59959000
H	-2.80709300	-1.45765700	-0.61992000	C	0.37941100	-0.38532700	-0.12967400
H	2.08668300	3.00036700	0.80420600	C	0.97783400	0.76887800	0.39554100
H	0.62756000	3.88223800	0.68025000	C	0.23073500	1.95410400	0.46741700
C	-3.25368900	0.87479500	-0.40650600	C	-1.09044300	2.02248300	0.00054500
C	-1.63402200	3.38486100	0.22272400	C	-1.68995200	0.86896000	-0.52505800
C	2.52615100	0.60447900	0.57917500	N	-1.55800600	-1.48932900	-1.09424400
C	0.89692100	-1.90475100	-0.02879900	N	0.85350100	3.13718500	0.96504300
H	-3.68885600	1.86664300	-0.36862900	H	-0.91837100	-2.16929600	-1.47861700
H	-3.47463900	0.46634900	-1.39740000	H	-2.31435600	-1.32418100	-1.74229500
H	-3.78524900	0.26246100	0.32843700	H	1.57616500	2.94510500	1.64731100
H	-1.17308500	4.05592100	-0.50844400	H	0.19519600	3.78644300	1.37672200
H	-2.70164600	3.39711800	0.03642200	C	-3.12025800	0.83173300	-1.00766200
H	-1.47787400	3.82038600	1.21436300	C	-1.80108900	3.35359200	0.07910500
H	3.04997500	1.25600200	-0.12502200	C	2.40749400	0.80243100	0.88300000
H	2.74727200	0.97327600	1.58480300	C	1.08571400	-1.71797100	-0.20364700
H	2.96484600	-0.38293400	0.49272500	H	-3.67237300	1.73655900	-0.77249800
H	1.96152900	-1.92377400	0.17335200	H	-3.18044600	0.69115700	-2.09360100
H	0.42170900	-2.57104400	0.69755200				

H	-3.66265100	-0.00133900	-0.55043500
H	-1.18385600	4.15112600	-0.34385400
H	-2.74259500	3.36363200	-0.46145700
H	-2.02246800	3.63656100	1.11513000
H	2.95140100	1.64108900	0.43947500
H	2.46395100	0.92541700	1.97117300
H	2.96040400	-0.09855500	0.63556400
H	2.03234900	-1.72790300	0.32797900
H	0.46744500	-2.50924400	0.23078900
H	1.29510600	-2.01156200	-1.23932200
H	1.72841400	4.08098400	-0.47757700
O	2.16931800	4.52966800	-1.23083100
C	2.67551900	5.78601100	-0.78771700
H	1.85649800	6.41794000	-0.42013000
H	3.37614800	5.64163000	0.04500100
C	3.37906100	6.47229500	-1.94182000
H	4.21216700	5.86527200	-2.30379000
H	2.68892700	6.63806900	-2.77240400
H	3.77341800	7.44098700	-1.62639700

P⁺(EtOH)

C	-1.13139200	-0.47369200	0.03764800
C	0.28938600	-0.60706100	0.18326500
C	1.06547300	0.52798600	0.19304200
C	0.42710200	1.80704900	0.04883800
C	-0.99740600	1.93710700	-0.10005400
C	-1.77275800	0.80190700	-0.10410300
N	-1.88904700	-1.58402200	0.03242800
N	1.17815300	2.91727900	0.05116300
H	-1.48489000	-2.50025900	0.13048600
H	-2.88990300	-1.54158400	-0.06240600
H	2.19198900	2.92759400	0.15024700
H	0.74516800	3.82085500	-0.05037900
C	-3.27070000	0.80510200	-0.25100900
C	-1.55104200	3.32939700	-0.24314800
C	2.56177200	0.51911400	0.34159900
C	0.83888900	-2.00234400	0.31444000
H	-3.68410000	1.80230900	-0.34764600
H	-3.57948200	0.24255900	-1.13750600
H	-3.75111200	0.34204500	0.61630900
H	-1.13176700	3.83112200	-1.12069500
H	-2.62902700	3.34512500	-0.35391100
H	-1.30980400	3.94095400	0.63179100
H	3.04293900	0.93132000	-0.55005700
H	2.87465000	1.13227900	1.19058500
H	2.96471400	-0.47525100	0.49633300
H	1.91827300	-2.02333400	0.40974200
H	0.42806700	-2.50649500	1.19463700
H	0.58352600	-2.60820000	-0.56046600
O	4.00819500	3.62952200	0.35780100
H	4.73249500	3.16568300	-0.07883500
C	4.22225200	5.04675100	0.23080900
H	4.20199300	5.32782900	-0.82702200
H	3.36192700	5.50965300	0.71595800
C	5.51489400	5.49876600	0.88356400
H	5.62191600	6.58233100	0.79132400
H	5.52730600	5.24055400	1.94428300
H	6.38042300	5.03538400	0.40276400

P²⁺(EtOH)

C	-1.05443600	-0.42653000	-0.02532000
C	0.38441600	-0.54093500	0.24288800
C	1.11392200	0.59427200	0.32206200
C	0.42955900	1.87280100	0.06128300
C	-1.03885700	1.98998500	-0.05681400
C	-1.76847600	0.85508000	-0.11396200
N	-1.73765700	-1.51942800	-0.16812900

N	1.13317200	2.94633700	-0.08376100
H	-1.30260600	-2.43267200	-0.11405400
H	-2.73484000	-1.51223900	-0.34662500
H	2.17479900	3.02107500	-0.04557700
H	0.66495300	3.82451300	-0.28157700
C	-3.25657000	0.79883500	-0.27981600
C	-1.60934000	3.37312800	-0.13028300
C	2.58199100	0.62373200	0.61446400
C	0.94947700	-1.92084900	0.39453800
H	-3.70548600	1.78413400	-0.30826000
H	-3.52449700	0.29984500	-1.21567400
H	-3.72154500	0.25104300	0.54407300
H	-1.32873300	3.86528500	-1.06655900
H	-2.69156100	3.37147400	-0.08389000
H	-1.25033100	3.98710000	0.69924300
H	3.15889200	0.66339100	-0.31449800
H	2.85632300	1.49013300	1.21356600
H	2.89501700	-0.26074100	1.15956500
H	2.01280200	-1.90477600	0.60119300
H	0.46116500	-2.46199400	1.20943900
H	0.81635400	-2.49719400	-0.52578300
O	3.79655200	3.60019000	0.00196900
H	4.40095900	3.27052200	-0.67428800
C	4.10127900	4.98614600	0.27670200
H	3.95178500	5.57550200	-0.63204600
H	3.35882500	5.30045100	1.01045600
C	5.50599200	5.16214300	0.81720000
H	5.68557400	6.21570300	1.04342300
H	5.64750700	4.58414400	1.73216000
H	6.25269400	4.84573100	0.08451200

P(*n*-PrOH)

C	-0.97909100	-0.36496100	-0.61418800
C	0.29355000	-0.47754700	-0.02763300
C	0.89056000	0.65827600	0.53779400
C	0.18984400	1.87362800	0.53166200
C	-1.08045400	1.98950000	-0.05250600
C	-1.67867000	0.85434500	-0.61802500
N	-1.59509500	-1.51493600	-1.15004400
N	0.81302200	3.03679900	1.07351600
H	-0.95275200	-2.22414500	-1.47210600
H	-2.28579100	-1.32799100	-1.86221800
H	1.46827100	2.82359500	1.81495900
H	0.14701100	3.71261700	1.42606900
C	-3.06126900	0.86865400	-1.22501900
C	-1.73834000	3.34969700	-0.05239100
C	2.27174200	0.64048800	1.15017600
C	0.94762900	-1.83859400	-0.02495000
H	-3.59568600	1.79632000	-1.04402800
H	-3.03112400	0.72113900	-2.31126100
H	-3.67430800	0.06156500	-0.81272100
H	-1.05389700	4.11348900	-0.43201000
H	-2.62985300	3.38890600	-0.67095200
H	-2.03404400	3.65919300	0.95712200
H	2.88555200	1.45363400	0.75268800
H	2.23628800	0.76987200	2.23850300
H	2.80858300	-0.28321000	0.95681600
H	1.84618100	-1.87757900	0.58344400
H	0.26308700	-2.59696700	0.36675400
H	1.22941100	-2.15742600	-1.03562600
H	1.83725200	3.96747200	-0.27821700
O	2.34672700	4.43104000	-0.97680900
C	2.74141100	5.70810500	-0.48261000
H	3.37834200	5.59163200	0.40587500
C	3.50141000	6.46644600	-1.55899700
H	2.85359200	6.57372700	-2.43559100
H	3.68988600	7.47814500	-1.18503700
C	4.82198700	5.81136400	-1.96287300

Appendix C

H	5.33717600	6.40215700	-2.72379100
H	5.49184500	5.71884200	-1.10299200
H	4.65957600	4.81143600	-2.36858700
H	1.85902400	6.28724400	-0.18089900

P⁺(*n*-PrOH)

C	-1.13556700	-0.39975400	-0.16375500
C	0.26157300	-0.55154000	0.12350600
C	1.01523800	0.57220000	0.36907400
C	0.37708300	1.85896100	0.33015200
C	-1.02547600	2.00705800	0.04859400
C	-1.77716300	0.88300300	-0.19932600
N	-1.87083600	-1.49868600	-0.40647800
N	1.10708500	2.95843800	0.56388100
H	-1.46656300	-2.42007200	-0.39241400
H	-2.85422500	-1.44258700	-0.61232700
H	2.10730500	2.95815800	0.75675300
H	0.67535600	3.86814700	0.54271200
C	-3.24990000	0.90635400	-0.50942600
C	-1.58386200	3.40464600	0.04164800
C	2.48555600	0.54281800	0.68339200
C	0.81254100	-1.95225800	0.13734200
H	-3.66117800	1.90887300	-0.53150600
H	-3.45291000	0.45620600	-1.48594600
H	-3.81743100	0.34261600	0.23745900
H	-1.08743100	4.02293100	-0.71242600
H	-2.64571900	3.43287300	-0.17359000
H	-1.44158200	3.89036300	1.01189600
H	3.05369000	1.12951700	-0.04320100
H	2.68207700	0.97429000	1.66893100
H	2.89687500	-0.46008700	0.68186600
H	1.87031900	-1.98682400	0.37076200
H	0.30005900	-2.56826700	0.88246400
H	0.68301000	-2.43590900	-0.83583600
O	3.85353600	3.73843400	1.10844600
H	4.39593600	3.37849300	1.81989700
C	4.71293900	4.19624200	0.05193100
H	5.30385200	3.35827800	-0.33472900
H	4.04130300	4.52440100	-0.74390000
C	5.62280200	5.33512100	0.48566200
H	5.00629700	6.15247200	0.87124500
H	6.25172900	4.99299400	1.31498800
C	6.50569900	5.83444000	-0.65828000
H	7.14620700	5.03657200	-1.04295900
H	5.90273700	6.20850400	-1.48983100
H	7.15281100	6.64779100	-0.32518800

P²⁺(*n*-PrOH)

C	-1.06549300	-0.34405000	-0.21402300
C	0.34720800	-0.53882900	0.14075400
C	1.08173000	0.55136700	0.45511100
C	0.43158800	1.87283800	0.38180700
C	-1.00622600	2.05392900	0.09645500
C	-1.73902900	0.96266700	-0.21402200
N	-1.76539900	-1.38959200	-0.52747700
N	1.14821600	2.93166800	0.56690700
H	-1.36460800	-2.32004500	-0.54117100
H	-2.74694700	-1.32650200	-0.77059300
H	2.17376700	2.96387000	0.75438800
H	0.71385000	3.84680200	0.51375800
C	-3.19593500	0.97943300	-0.56464600
C	-1.54290200	3.45123200	0.15420300
C	2.51767000	0.51867400	0.87245400
C	0.86587300	-1.94508300	0.12925600
H	-3.60719700	1.98120400	-0.56964500
H	-3.36192500	0.56263800	-1.56199300
H	-3.77704800	0.39231500	0.15203300

H	-1.10875400	4.06954100	-0.63715300
H	-2.61861100	3.48396600	0.03228500
H	-1.31518200	3.91771200	1.11605800
H	3.14581900	1.06009700	0.16153300
H	2.63981800	0.99203700	1.84914000
H	2.90167000	-0.49102600	0.94953500
H	1.92134600	-1.99597500	0.36619400
H	0.33820800	-2.56287100	0.86126900
H	0.74016000	-2.40000300	-0.85729200
O	3.74704900	3.62472500	1.02831200
H	4.27979500	3.33080400	1.77700200
C	4.61572700	4.09676700	-0.02255100
H	5.23868200	3.26983000	-0.37799400
H	3.94936500	4.39018500	-0.83528200
C	5.47434000	5.26900100	0.42111200
H	4.82213200	6.07123500	0.77781000
H	6.09144900	4.95761100	1.27091900
C	6.37195800	5.77949500	-0.70643400
H	7.04619500	4.99657200	-1.06258500
H	5.78081200	6.12520600	-1.55824500
H	6.98459800	6.61576200	-0.36571000

P(*i*-PrOH)

C	-0.89214900	-0.32496600	-0.62900500
C	0.41601100	-0.20368900	-0.12946500
C	0.85542800	1.03935200	0.34804800
C	-0.03197700	2.12599500	0.34620800
C	-1.33797300	2.00851400	-0.15242900
C	-1.77889000	0.76566300	-0.62914800
N	-1.34622700	-1.58335400	-1.07605800
N	0.42745900	3.39775600	0.79943800
H	-0.61747900	-2.20030000	-1.40422400
H	-2.09322100	-1.54396700	-1.75422600
H	1.14176900	3.32807600	1.51330900
H	-0.31776600	3.98270200	1.15587000
C	-3.18299400	0.53058100	-1.13277600
C	-2.20811200	3.24399900	-0.16208600
C	2.25864700	1.27035400	0.85835600
C	1.28254500	-1.44055700	-0.11876200
H	-3.85282600	1.35867800	-0.92152200
H	-3.20656200	0.36452100	-2.21647700
H	-3.61830300	-0.35811400	-0.66642900
H	-1.67881500	4.09050000	-0.60813600
H	-3.12375400	3.11055600	-0.73019200
H	-2.49871500	3.54649200	0.85103600
H	2.69407500	2.16765900	0.41034400
H	2.27966100	1.41360400	1.94527300
H	2.93026800	0.44786000	0.63160400
H	2.20849000	-1.30502700	0.43193200
H	0.75538500	-2.27955700	0.34517500
H	1.55372400	-1.75755300	-1.13294200
H	1.22876100	4.42861900	-0.65485600
O	1.60628800	4.89610400	-1.43006900
C	2.74694300	5.65367400	-1.01549700
H	3.44876700	4.98464400	-0.49779000
C	3.42034300	6.18164700	-2.27222000
H	3.70193800	5.35984000	-2.93361700
H	2.74279400	6.84485100	-2.81712300
H	4.32176300	6.74456000	-2.02105000
C	2.34930900	6.77416500	-0.05798200
H	1.65940600	7.46699100	-0.54737300
H	1.85816000	6.37218800	0.83133000
H	3.22860200	7.33587800	0.26832600

P⁺(*i*-PrOH)

C	-1.09676900	-0.41857700	-0.15207900
C	0.28256000	-0.56235700	0.21415900

C	1.02307500	0.56759100	0.47066700	O	3.75620700	3.55198200	1.21607400
C	0.39165400	1.85313200	0.35554500	H	4.20212800	3.38270800	2.05534600
C	-0.99340500	1.99348000	-0.00524300	C	4.65085700	4.26797200	0.32566100
C	-1.73285700	0.86295000	-0.26071300	H	4.05375400	4.41051200	-0.57761800
N	-1.82023100	-1.52440500	-0.39897000	C	5.00808000	5.62254000	0.91698200
N	1.11153800	2.95919100	0.58974500	H	5.58403000	5.50293800	1.83920400
H	-1.41810500	-2.44472600	-0.33696000	H	4.10814900	6.19736700	1.14075200
H	-2.79092800	-1.47497500	-0.65934200	C	5.86762800	3.41532100	-0.00028000
H	2.09725300	2.96557600	0.84499500	H	6.50441800	3.92596200	-0.72556100
H	0.68320100	3.86786800	0.51764300	H	6.46313000	3.22941800	0.89832800
C	-3.18586800	0.87850600	-0.65356200	H	5.56776200	2.45530300	-0.42314200
C	-1.54865900	3.39038000	-0.08160900	H	5.61644200	6.19467100	0.21359300
C	2.47196500	0.54704900	0.87167700				
C	0.83146700	-1.96184200	0.29308300				
H	-3.59125300	1.88052700	-0.73316700				
H	-3.33518600	0.39627600	-1.62438000	C	-0.98510200	-0.37600900	-0.68948900
H	-3.79716500	0.34166100	0.07840400	C	0.23553100	-0.49542400	-0.00260300
H	-1.02230300	3.98326300	-0.83594100	C	0.78540100	0.63418100	0.62018400
H	-2.60136500	3.41119300	-0.33847500	C	0.08752700	1.85020900	0.57030200
H	-1.44365400	3.90793600	0.87682500	C	-1.13045000	1.97308100	-0.11486600
H	3.08712400	1.08679200	0.14706200	C	-1.68156600	0.84410400	-0.73768500
H	2.61501300	1.03500400	1.83960600	N	-1.55531500	-1.51973700	-1.28606100
H	2.87272300	-0.45676200	0.95432000	N	0.66353600	3.00641600	1.17570400
H	1.88045900	-1.98788400	0.56416400	H	-0.88868800	-2.22843800	-1.55562900
H	0.29219600	-2.55509000	1.03793500	H	-2.17907200	-1.32507500	-2.05568600
H	0.73697100	-2.47520800	-0.66879200	H	1.24718300	2.78424500	1.97236000
O	3.80001900	3.78075400	1.32625900	H	-0.02970600	3.68184800	1.47201400
H	4.24632700	3.54594500	2.14930200	C	-3.01200900	0.86672500	-1.45171700
C	4.75823700	4.38471800	0.42958500	C	-1.78655100	3.33362000	-0.15611800
H	4.17805400	4.58109300	-0.47533500	C	2.11414400	0.60810300	1.33923800
C	5.26330800	5.70336000	0.99815400	C	0.88795700	-1.85670300	0.03989600
H	5.83183900	5.53484000	1.91768100	H	-3.56415800	1.78793400	-1.29172800
H	4.43035000	6.37148300	1.22320500	H	-2.89673300	0.74417200	-2.53542800
C	5.88200300	3.41056900	0.10462000	H	-3.65072700	0.04817900	-1.10674700
H	6.56227400	3.84253700	-0.63263500	H	-1.07130500	4.10232300	-0.46161900
H	6.46335500	3.17742100	1.00190800	H	-2.61717900	3.38092000	-0.85383200
H	5.48281800	2.47946800	-0.30094300	H	-2.17389500	3.62981900	0.82607200
H	5.92141700	6.20207100	0.28319500	H	2.75072300	1.43489700	1.01234800
				H	1.99322200	0.70809600	2.42457600
				H	2.67160900	-0.30702400	1.16375900
				H	1.73081600	-1.90246400	0.72295500
				H	0.17313100	-2.61947900	0.36320600
				H	1.25547900	-2.16390100	-0.94664000
				H	1.82480900	3.94066200	-0.05576600
				O	2.42619200	4.39136800	-0.68639900
				C	2.73317900	5.68836100	-0.18118400
				H	3.14558300	5.61264100	0.83475000
				C	3.73952500	6.37201000	-1.09254600
				H	3.32242700	6.41737500	-2.10544800
				H	3.85014600	7.40913000	-0.75547000
				C	5.11304000	5.69997700	-1.12923500
				H	5.51912800	5.66364700	-0.11166200
				H	4.99848700	4.66155800	-1.45149500
				H	1.82154600	6.29720900	-0.12013600
				C	6.10246100	6.41615600	-2.04784700
				H	5.73607500	6.44165800	-3.07810600
				H	6.26174900	7.45036200	-1.72905600
				H	7.07454300	5.91726300	-2.05412500

Appendix C

H	-1.50766900	-2.46970600	-0.17965600
H	-2.88968000	-1.50076600	-0.46384100
H	2.10273300	2.94835600	0.60967400
H	0.67678400	3.85095900	0.33180600
C	-3.26979000	0.85408900	-0.51563800
C	-1.58159500	3.37177000	-0.15018900
C	2.46592200	0.52991300	0.68874600
C	0.77188800	-1.98413100	0.32428000
H	-3.67793000	1.85570200	-0.58617200
H	-3.47717200	0.35599900	-1.46774600
H	-3.83733000	0.33109500	0.26009900
H	-1.07163700	3.93325200	-0.93887000
H	-2.64041500	3.39296800	-0.38036300
H	-1.44600200	3.92166800	0.78621000
H	3.03471500	1.07435500	-0.06931200
H	2.66636800	1.01313700	1.64919800
H	2.87342500	-0.47329600	0.73991100
H	1.82721100	-2.01022700	0.56943900
H	0.24857700	-2.54481200	1.10472400
H	0.64639700	-2.53135000	-0.61517900
O	3.84872900	3.73432800	0.93697700
H	4.40264000	3.38752400	1.64608700
C	4.69293000	4.21535800	-0.12228300
H	5.29804400	3.39112200	-0.51585100
H	4.00968900	4.53295100	-0.91227900
C	5.58043800	5.37033700	0.31443800
H	4.94864800	6.17375700	0.70748300
H	6.22050500	5.03716800	1.14028500
C	6.45480700	5.90455100	-0.82255800
H	7.07550400	5.09208000	-1.21548700
H	5.81385700	6.22833000	-1.64981500
C	7.35035100	7.06444800	-0.38924400
H	7.95899100	7.42715300	-1.22055700
H	6.75605500	7.90449200	-0.01975900
H	8.02880900	6.76028000	0.41242900

P²⁺(n-BuOH)

C	-1.15815300	-0.38192200	0.01005900
C	0.26885200	-0.61427100	0.27039600
C	1.09381300	0.45562600	0.31121900
C	0.50307100	1.79580300	0.14297900
C	-0.92931900	2.02063000	-0.14045700
C	-1.75063300	0.94923400	-0.18338400
N	-1.93890100	-1.41429100	-0.06801800
N	1.26362700	2.83310800	0.26362600
H	-1.59096700	-2.35925600	0.04375500
H	-2.93084900	-1.32501500	-0.25393000
H	2.28503400	2.83600100	0.47279200
H	0.86504400	3.76091400	0.16650000
C	-3.22926500	1.01099900	-0.42016400
C	-1.36891100	3.43627100	-0.35584600
C	2.57036500	0.37654500	0.54103300
C	0.70200600	-2.03398400	0.47807900
H	-3.59581800	2.02892000	-0.46858300
H	-3.49659500	0.52278400	-1.36181000
H	-3.77309600	0.51634100	0.38887200
H	-0.80695600	3.89588800	-1.17322100
H	-2.41804600	3.50534100	-0.61529900
H	-1.21697900	4.03787500	0.54510400
H	3.11430500	0.97712100	-0.18893700
H	2.82359400	0.75254200	1.53633100
H	2.94054600	-0.63900100	0.46709700
H	1.75858800	-2.11185500	0.70255900
H	0.16442600	-2.48203600	1.31824000
H	0.51164600	-2.64030800	-0.41202800
O	3.86427600	3.47187800	0.77174100
H	4.43483500	3.11423300	1.46236900
C	4.67320100	4.11590100	-0.23475900

H	5.34349800	3.37820200	-0.68652800
H	3.96913900	4.44436900	-1.00095400
C	5.45570800	5.29358700	0.32064000
H	4.75653400	6.00275400	0.77541000
H	6.11542000	4.93947800	1.12157500
C	6.28910700	5.99798100	-0.75235600
H	6.97095700	5.27580300	-1.21394300
H	5.62724500	6.34908500	-1.55139900
C	7.09185500	7.17597600	-0.20212500
H	7.67528500	7.65876400	-0.98910800
H	6.43414200	7.93133300	0.23620900
H	7.78731300	6.84974900	0.57587200

P(s-BuOH)

C	-0.88834900	-0.33460600	-0.65470300
C	0.36745000	-0.32695300	-0.02326500
C	0.85540000	0.87026400	0.51983900
C	0.06291100	2.02599600	0.45240700
C	-1.19082600	2.02153400	-0.17713200
C	-1.68027100	0.82474000	-0.71925900
N	-1.39266100	-1.54537100	-1.17436400
N	0.57048200	3.25117100	0.97789600
H	-0.68436700	-2.20746100	-1.45641800
H	-2.07036500	-1.43402300	-1.91449500
H	1.23043500	3.11319500	1.73270500
H	-0.15970700	3.86988300	1.30793400
C	-3.04230100	0.71454000	-1.36225700
C	-1.95450700	3.32327900	-0.25216400
C	2.21524900	0.97670000	1.17025600
C	1.12548800	-1.63088000	0.05414200
H	-3.65822200	1.59411200	-1.20018700
H	-2.97260300	0.56393000	-2.44624100
H	-3.59397400	-0.13933400	-0.95804500
H	-1.30205600	4.13913900	-0.57359800
H	-2.78045400	3.28502900	-0.95622400
H	-2.37164000	3.61080200	0.72038300
H	2.76878100	1.83516800	0.78004100
H	2.13981900	1.11083500	2.25591100
H	2.83334000	0.10049700	0.99889400
H	1.97019600	-1.58858900	0.73520500
H	0.47429100	-2.43672700	0.40486500
H	1.51381300	-1.93847300	-0.92423700
H	1.51029600	4.26461300	-0.40599000
O	1.97025300	4.71465700	-1.14565400
C	2.73617800	5.80745300	-0.63136200
H	3.36878800	5.44252200	0.19170000
C	3.64608400	6.31006600	-1.74837700
H	3.01487000	6.62202700	-2.58836300
H	4.15749700	7.20942800	-1.39163700
C	1.82686500	6.91045600	-0.09509900
H	1.19840500	7.31004000	-0.89562600
H	1.17389700	6.52902900	0.69335300
H	2.41566400	7.73090600	0.32352900
C	4.67701700	5.28675500	-2.22088000
H	5.30293400	5.69923200	-3.01569000
H	5.33647900	4.98715800	-1.40115100
H	4.19331700	4.38764600	-2.60572100

P⁺⁺(s-BuOH)

C	-1.22485800	-0.41401900	0.04228700
C	0.11027500	-0.65085100	0.50986400
C	0.98957400	0.40453500	0.57081900
C	0.54215900	1.70648900	0.15921100
C	-0.79751500	1.94059000	-0.30830000
C	-1.67558400	0.88448400	-0.36908400
N	-2.08529000	-1.44549200	-0.01052600
N	1.39636600	2.73800600	0.21141200

H	-1.81653400	-2.37314400	0.27174800
H	-3.03359000	-1.32819100	-0.32573700
H	2.36386200	2.67010500	0.52302500
H	1.09850400	3.65774800	-0.07104000
C	-3.09925500	0.99881100	-0.84492700
C	-1.15378700	3.34813300	-0.70497300
C	2.40920100	0.28576300	1.05256900
C	0.45977100	-2.05986500	0.90853900
H	-3.36331700	2.00458500	-1.15052500
H	-3.27929000	0.34596200	-1.70452200
H	-3.80098600	0.70751800	-0.05734700
H	-0.53109300	3.69364100	-1.53593600
H	-2.18649000	3.44842500	-1.01810700
H	-1.00453000	4.04083100	0.12873200
H	3.11365700	0.60091700	0.27841600
H	2.57801200	0.92608800	1.92298800
H	2.67392900	-0.72527100	1.34009300
H	1.49141500	-2.16490800	1.22350100
H	-0.16609500	-2.40106800	1.73896200
H	0.30784000	-2.75270300	0.07540100
O	4.15748200	3.24170200	0.98749200
H	4.77030800	2.70434400	1.50443200
C	4.90727700	4.24582800	0.26753200
H	4.14764000	4.76480300	-0.32413700
C	5.52973600	5.23674200	1.25182800
H	6.28232800	4.71111900	1.85172400
C	6.15790000	6.46513900	0.59218400
H	7.01171700	6.20077300	-0.03440800
H	5.43208300	6.99049300	-0.03454200
H	6.51086500	7.16798400	1.34929100
H	4.74321800	5.55481800	1.94193300
C	5.90847900	3.58631900	-0.67084000
H	6.40667500	4.32705100	-1.29842000
H	6.67795500	3.05302000	-0.10414800
H	5.40414100	2.87343600	-1.32520900

P²⁺(s-BuOH)

C	-1.15431000	-0.37290800	0.02680500
C	0.20400900	-0.63434200	0.52091900
C	1.05636300	0.40943000	0.62438100
C	0.58379800	1.74068200	0.20188400
C	-0.78775900	1.99838100	-0.28130100
C	-1.63755000	0.95339100	-0.38400900
N	-1.98149600	-1.36914900	-0.03986900
N	1.40761200	2.73515500	0.24478800
H	-1.71723000	-2.30777400	0.23503900
H	-2.93407200	-1.25392600	-0.36448400
H	2.40494600	2.70008600	0.54471500
H	1.09881700	3.65749600	-0.04394600
C	-3.04786700	1.03968600	-0.88491600
C	-1.13437800	3.41143600	-0.63664400
C	2.45621400	0.31532400	1.14256600
C	0.53760800	-2.04992500	0.88305700
H	-3.31599000	2.04338000	-1.19069100
H	-3.19209300	0.39130000	-1.75380900
H	-3.75791800	0.73672900	-0.11019400
H	-0.54302600	3.75742100	-1.48947900
H	-2.17806500	3.52310800	-0.90287100
H	-0.94571100	4.08277200	0.20493800
H	3.17474300	0.63308000	0.38369800
H	2.58176300	0.96227100	2.01443900
H	2.71812300	-0.69122100	1.44424400
H	1.57447900	-2.16636700	1.17259300
H	-0.07460400	-2.39488200	1.72120100
H	0.36548200	-2.71922800	0.03613100
O	4.02703200	3.19108400	0.92123400
H	4.60824300	2.68535000	1.50286300
C	4.81138800	4.18680900	0.21192100

H	4.07520500	4.70904400	-0.40462700
C	5.41261800	5.17263500	1.21220500
H	6.13865700	4.64108900	1.83865100
C	6.07910800	6.38682100	0.56401200
H	6.94692800	6.10503400	-0.03486300
H	5.38055700	6.91986000	-0.08643600
H	6.42013100	7.08737200	1.32835900
H	4.60863100	5.50650900	1.87387500
C	5.82948700	3.50191900	-0.68725100
H	6.35574900	4.23077700	-1.30532600
H	6.57352700	2.96432800	-0.09201600
H	5.33500900	2.79065600	-1.35053200

P(*i*-BuOH)

C	-0.97246500	-0.33288100	-0.62412100
C	0.29524500	-0.45696800	-0.02932200
C	0.89508200	0.67155600	0.54763700
C	0.20178400	1.89116300	0.54446700
C	-1.06378500	2.01842600	-0.04756100
C	-1.66477100	0.89059100	-0.62470700
N	-1.59145800	-1.47550800	-1.17206800
N	0.82899300	3.04711400	1.09705500
H	-0.95109500	-2.18662600	-1.49386600
H	-2.27554300	-1.27964300	-1.88822100
H	1.47507400	2.82594700	1.84420200
H	0.16539900	3.72768700	1.44482700
C	-3.04303300	0.91684600	-1.24112500
C	-1.71372300	3.38242100	-0.04301900
C	2.27195000	0.64161000	1.16924000
C	0.94151800	-1.82173800	-0.03128700
H	-3.57341400	1.84639300	-1.05794700
H	-3.00622500	0.77602300	-2.32805800
H	-3.66349400	0.11067400	-0.83823800
H	-1.02329300	4.14439000	-0.41547900
H	-2.60219800	3.43009200	-0.66531600
H	-2.01220800	3.68806300	0.96684400
H	2.89268600	1.45448900	0.78217500
H	2.22980900	0.76289100	2.25827200
H	2.80517300	-0.28343700	0.97232600
H	1.83527200	-1.86991200	0.58348000
H	0.24991600	-2.57894900	0.35010000
H	1.22903000	-2.13510700	-1.04207200
H	1.87764600	3.95055900	-0.25213600
O	2.40305300	4.37957600	-0.96091900
C	2.81316400	5.66708100	-0.51339900
H	3.43681000	5.57868600	0.38872500
C	3.60633700	6.37715100	-1.60643900
H	2.96689100	6.40844000	-2.49739600
C	4.88802000	5.61958700	-1.96151100
H	5.42389000	6.11848400	-2.77305000
H	5.55979600	5.57199700	-1.09808400
H	4.67135700	4.59791600	-2.27633100
H	1.93679300	6.27369200	-0.24865500
C	3.90990000	7.81734000	-1.18393000
H	4.45297600	8.34717200	-1.96983300
H	2.99396400	8.37605000	-0.97494800
H	4.52922300	7.84000800	-0.28173300

P⁺(*i*-BuOH)

C	-1.12429600	-0.46922600	-0.15623800
C	0.26884900	-0.56933000	0.17041600
C	0.98445700	0.58428500	0.39014000
C	0.31432600	1.85003200	0.27425400
C	-1.08482800	1.94640400	-0.04434500
C	-1.79924700	0.79232700	-0.26306900
N	-1.82316400	-1.59833400	-0.36556900
N	1.00979300	2.97928600	0.46758800

Appendix C

H	-1.39375000	-2.50591800	-0.29970300
H	-2.80262900	-1.58015000	-0.59545800
H	2.00713900	3.01782300	0.67196600
H	0.55488400	3.87428700	0.38805800
C	-3.26289400	0.76239000	-0.61326300
C	-1.68187600	3.32610000	-0.12020000
C	2.44393000	0.60853100	0.75170300
C	0.85936600	-1.95189600	0.24971200
H	-3.69468300	1.75201600	-0.70762100
H	-3.42777100	0.25092200	-1.56633400
H	-3.83988000	0.23079200	0.14984700
H	-1.19175900	3.92648900	-0.89282200
H	-2.74081500	3.31418600	-0.35053500
H	-1.56790900	3.85574300	0.83055100
H	3.02881700	1.13423900	-0.00792200
H	2.60082400	1.13271000	1.69817700
H	2.86785600	-0.38336000	0.85894400
H	1.91510700	-1.94546400	0.49442400
H	0.35564100	-2.55280600	1.01309900
H	0.75589800	-2.47735700	-0.70468100
O	3.72748400	3.87272900	0.96808100
H	4.25687100	3.59385000	1.72436800
C	4.60392100	4.15853900	-0.13329000
H	5.19002300	3.26599400	-0.37741500
H	3.94508100	4.36902000	-0.97948700
C	5.53292000	5.34559300	0.11778800
H	6.12631000	5.11199800	1.01168800
C	6.49659100	5.50137100	-1.06259200
H	7.08454700	4.59441100	-1.22371400
H	5.95149100	5.71742700	-1.98651700
H	7.19184800	6.32516800	-0.88839400
C	4.75228800	6.63533600	0.37907900
H	4.16587700	6.91689700	-0.50129100
H	4.06533700	6.52355300	1.21944100
H	5.43136400	7.46082400	0.60491300

P²⁺(*i*-BuOH)

C	-1.05196100	-0.38675300	-0.21915600
C	0.35860400	-0.54151700	0.16217700
C	1.06553100	0.57216800	0.45670100
C	0.39187500	1.87725000	0.32912400
C	-1.04678600	2.01954700	0.02639400
C	-1.75371400	0.90454600	-0.25864000
N	-1.72365300	-1.45487700	-0.51786900
N	1.08648600	2.95584600	0.48057400
H	-1.30124400	-2.37569300	-0.50560100
H	-2.70266600	-1.41993800	-0.77655500
H	2.11011000	3.01660800	0.67373700
H	0.63437300	3.85929900	0.38924200
C	-3.20820200	0.88068500	-0.61843500
C	-1.61352100	3.40623500	0.03799300
C	2.49452200	0.58134700	0.89813600
C	0.90767400	-1.93571500	0.19762100
H	-3.63632900	1.87402000	-0.67110300
H	-3.36161700	0.41720600	-1.59673500
H	-3.78325600	0.31574800	0.12071900
H	-1.18627800	4.00982100	-0.76849600
H	-2.68859400	3.41155400	-0.09328600
H	-1.40435600	3.90668200	0.98706200
H	3.12931100	1.07352500	0.15749000
H	2.59888900	1.12730900	1.83785900
H	2.88300300	-0.41736200	1.05545400
H	1.95911300	-1.95614200	0.45595300
H	0.37851300	-2.54680300	0.93405000
H	0.81199600	-2.41764200	-0.77946100
O	3.66741300	3.71338900	0.91898300
H	4.14719500	3.55659100	1.74099500
C	4.60473000	4.00192200	-0.13810400

H	5.28700800	3.15470500	-0.25546600
H	3.99940200	4.07820700	-1.04410500
C	5.38937800	5.29165100	0.08875900
H	5.92824200	5.18369400	1.03922000
C	6.42662600	5.45806500	-1.02624700
H	7.10514000	4.60301800	-1.07543500
H	5.94039400	5.55962300	-2.00107100
H	7.02808600	6.35410400	-0.86123000
C	4.46998100	6.51079700	0.18763800
H	3.92726800	6.66275300	-0.75064000
H	3.73632000	6.39658500	0.98718700
H	5.04833400	7.41537300	0.38834200

P(*t*-BuOH)

C	-0.96793400	-0.27005500	-0.74751800
C	0.42935500	-0.33369300	-0.60823000
C	1.10722400	0.73104300	0.00263500
C	0.37150100	1.82255600	0.48913900
C	-1.02334800	1.88834000	0.35185600
C	-1.70234500	0.82329100	-0.25682900
N	-1.65434500	-1.35576000	-1.33092300
N	1.06396700	2.92121600	1.07630500
H	-1.10585700	-1.89728000	-1.98313200
H	-2.54193600	-1.11458700	-1.74738800
H	1.93687200	2.65139800	1.51126900
H	0.50870700	3.41868000	1.76077000
C	-3.20528400	0.78211000	-0.39906900
C	-1.72890300	3.12320500	0.86177000
C	2.61033500	0.76642800	0.15310800
C	1.13035000	-1.57090900	-1.11650200
H	-3.70564100	1.56880700	0.15757200
H	-3.51983800	0.87695100	-1.44540500
H	-3.60301100	-0.16956100	-0.03413800
H	-1.22843000	4.02991100	0.51170700
H	-2.76135600	3.18567500	0.53137800
H	-1.73790100	3.16581100	1.95749500
H	3.01583300	1.71685400	-0.20467500
H	2.91804900	0.66237400	1.20050700
H	3.10976200	-0.01948300	-0.40526300
H	2.17241800	-1.62220300	-0.81602600
H	0.64450700	-2.47514300	-0.73790000
H	1.10721100	-1.63286400	-2.21114800
H	1.52399900	4.25051000	-0.34294600
O	1.67987500	4.79392000	-1.14286200
C	2.28599400	6.04539700	-0.77657500
C	3.64038900	5.78774400	-0.10606200
H	3.51301600	5.20664100	0.81088300
H	4.29723900	5.23014100	-0.77723100
H	4.13363000	6.72690600	0.15626700
C	2.47214300	6.80973600	-2.08541100
H	3.11325800	6.24682300	-2.76742900
H	1.50849700	6.97094700	-2.57368100
H	2.93289000	7.78294100	-1.90502100
C	1.35572000	6.81493500	0.16817500
H	1.77496200	7.79151100	0.42234900
H	0.38193600	6.97015200	-0.30126100
H	1.20430900	6.26206300	1.09872100

P⁺(*t*-BuOH)

C	-1.21179200	-0.48924400	-0.00181900
C	0.11888200	-0.61977300	0.51747700
C	0.91253900	0.50027000	0.59855800
C	0.38341700	1.76045300	0.15606800
C	-0.95344600	1.88905800	-0.35788900
C	-1.74505700	0.76811300	-0.44126400
N	-1.98820800	-1.58390900	-0.07733100
N	1.15523800	2.85457800	0.22273600

H	-1.66052300	-2.48710500	0.22186800	C	2.91320200	5.90827200	-0.19479500
H	-2.93116300	-1.54049600	-0.42582800	C	4.37219100	5.67568200	-0.58355200
H	2.12081700	2.86164400	0.54456000	H	5.00073100	5.57628200	0.30530200
H	0.79642200	3.74651700	-0.07738600	H	4.47082700	4.76722300	-1.18036400
C	-3.15350700	0.76994600	-0.97269300	H	4.75103700	6.51594600	-1.16855600
C	-1.40164000	3.26257000	-0.77938200	C	2.01572500	5.97527700	-1.42466100
C	2.31678600	0.49498900	1.13651000	H	2.09554400	5.05911800	-2.01304300
C	0.55844300	-1.99440600	0.94504100	H	0.97209700	6.12015200	-1.13797800
H	-3.48021900	1.75065200	-1.29847800	H	2.31139700	6.81282200	-2.05783600
H	-3.24877200	0.09954000	-1.83233800	C	2.75985400	7.15595200	0.67319500
H	-3.86284500	0.43148400	-0.21113200	H	3.08335900	8.04399800	0.12670400
H	-0.78373200	3.64548100	-1.59742900	H	1.71810000	7.29350800	0.96811500
H	-2.43033300	3.28380700	-1.11996200	H	3.36952600	7.07917900	1.57712400
H	-1.32674200	3.97183400	0.05038300				
H	3.02604200	0.85951900	0.38887300				
H	2.39860500	1.15069800	2.00821000				
H	2.64734400	-0.49081100	1.44283300				
H	1.58199600	-2.01856400	1.30054900				
H	-0.07220900	-2.37539900	1.75426000				
H	0.49245500	-2.70333100	0.11416300				
O	3.89802100	3.58825800	1.03344100				
H	4.40978700	3.05835300	1.65680200				
C	4.81428800	4.42233000	0.27101800				
C	5.62137300	5.28546000	1.24096300				
H	6.22755400	4.66305800	1.90483300				
H	4.95618800	5.89748200	1.85293400				
C	5.72940500	3.52622800	-0.56489000				
H	6.40807600	4.12731900	-1.17391600				
H	6.33628300	2.88228700	0.07684500				
H	5.14024400	2.89259000	-1.23062700				
C	3.92607600	5.28370500	-0.62019200				
H	4.53495500	5.95438600	-1.22847500				
H	3.33304800	4.66087400	-1.29295200				
H	3.24743300	5.88939200	-0.01629800				
H	6.29698000	5.94833900	0.69633300				

$P^{2+}(t\text{-BuOH})$

C	-1.02928400	-0.31453200	-0.91449700
C	0.41167300	-0.08006300	-0.75141900
C	0.80835300	1.10456300	-0.23530600
C	-0.23207700	2.08718100	0.12095900
C	-1.67295700	1.76456200	0.13739300
C	-2.06785700	0.59079900	-0.40127500
N	-1.40839800	-1.39422400	-1.52414800
N	0.12203900	3.29007300	0.43184800
H	-0.74419700	-2.06324000	-1.89503700
H	-2.38733000	-1.61376100	-1.66495400
H	1.09075300	3.67333900	0.42570400
H	-0.58505400	3.97440400	0.67930500
C	-3.49225100	0.14306000	-0.53076300
C	-2.59690800	2.78902300	0.72057100
C	2.23117900	1.50098800	-0.00377900
C	1.33488500	-1.17638900	-1.19004000
H	-4.18599900	0.85285100	-0.09708000
H	-3.77041100	0.03091200	-1.58289900
H	-3.65029500	-0.81671100	-0.03179100
H	-2.64777300	3.67974800	0.08677300
H	-3.60802900	2.41476300	0.82683200
H	-2.25926000	3.09483300	1.71367300
H	2.50602700	2.35728900	-0.62349900
H	2.38043900	1.79197900	1.03840900
H	2.92284300	0.69764600	-0.22614900
H	2.37004000	-0.95928100	-0.95666700
H	1.08212400	-2.11934600	-0.69833100
H	1.27628500	-1.32749900	-2.27221800
H	2.97991000	4.65717700	1.36332300
O	2.44575900	4.74992400	0.56468600

C.4 Supporting Information for the Diols

C.4.1 Cyclic voltammograms of 2,3,5,6-tetramethyl-1,4-phenylenediamine at different concentrations of the diols

Figure C.33. Cyclic voltammograms of 1 mM TMPD at different concentrations of (a) ethylene glycol (EG) and (b) 1,3-propanediol (PD) with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the diols are indicated in dashed lines with their measured trace moisture content.

Figure C.34. Cyclic voltammograms of 1 mM TMPD at different concentrations of 1,4-butanediol (BD) with 0.1 M n -Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at a scan rate of 0.1 V s⁻¹ at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that was acquired before the introduction of BD is indicated in dashed lines with its measured trace moisture content.

C.4.2 Plots of E_{P1} , E_{P2} and $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration of the diols

Figure C.35. Plots E_{P1} against concentration of the diols obtained over three experiments (red +, blue O and black x) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure C.36. Plots of E_{P2} against concentration of the diols obtained over three experiments (red +, blue O and black x) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure C.37. Plots of $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration of the diols obtained over three experiments (red +, blue O and black x) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

C.4.3 Energies of phenylenediamine-diol hydrogen-bonded complexes

Table C.3. Energies of the MeCN-solvated phenylenediamine-diol hydrogen-bonded complexes.

Diol	Energy (hartrees)		
	P	P ^{•+}	P ²⁺
EG - Normal		-730.256	-730.051
EG - Bidentate		-730.258	-730.054
PD - Normal		-769.554	-769.348
PD - Bidentate		-769.557	-769.354
BD - Normal		-808.853	-808.647
BD - Bidentate		-808.852	-808.648

C.4.4 Geometries of phenylenediamine-diol hydrogen-bonded complexes

Figure C.38. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated normal TMPD(EG) hydrogen-bonded complexes.

Figure C.39. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated bidentate TMPD(EG) hydrogen-bonded complexes.

Figure C.40. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated normal TMPD(PD) hydrogen-bonded complexes.

Figure C.41. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated bidentate TMPD(PD) hydrogen-bonded complexes.

Figure C.42. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated normal TMPD(BD) hydrogen-bonded complexes.

Figure C.43. Optimized geometries for neutral (top left), radical cation (top right) and quinonediimine dication (bottom) MeCN-solvated bidentate TMPD(BD) hydrogen-bonded complexes.

C.4.5 Coordinates of phenylenediamine-diol hydrogen-bonded complexes

P(EG) - Normal							
C	-1.03841700	-0.33033400	-0.04924200	C	-3.30079500	0.40802200	-0.90813300
C	0.36604200	-0.36878900	-0.00479900	C	0.91934100	-1.84968800	0.57486600
C	1.08329800	0.83379100	0.06747600	C	2.30095700	0.86454600	0.78368600
C	0.38311600	2.04922500	0.05911000	H	-1.39070800	3.67435100	-1.45845600
C	-1.01813800	2.09169000	0.01355200	H	-2.94808400	3.00172300	-1.02939700
C	-1.73656100	0.88976000	-0.05926100	H	-1.96974000	3.76842000	0.20617500
N	-1.75896800	-1.53788700	-0.15465700	H	-3.36097900	-0.19910800	-1.81666200
N	1.11297100	3.27178000	0.16822100	H	-3.88065500	-0.10074900	-0.13212800
H	2.03982600	3.21307300	-0.23489300	H	-3.80472000	1.34457400	-1.11677500
H	0.63424200	4.05421500	-0.26025300	H	2.86712900	1.37394600	-0.00119000
H	-1.28635900	-2.34416700	0.22726100	H	2.38057600	1.47308500	1.68815600
H	-2.70429100	-1.49536800	0.19738700	H	2.80291900	-0.07567100	0.98086300
H	1.33958800	3.73891900	2.00126700	H	1.93658100	-1.72872800	0.92872300
O	1.39941800	3.97052300	2.95515600	H	0.37533600	-2.39774000	1.35011000
C	2.27298600	5.07647600	3.11317300	H	0.95990500	-2.48878600	-0.31266500
H	2.03384900	5.55206500	4.06788200	P ²⁺ (EG) - Normal			
H	2.11755200	5.82172400	2.32391700	C	-1.03966800	-0.54743200	-0.20476600
C	3.73147100	4.64121700	3.12199600	C	0.29301300	-0.45309900	0.40214700
H	3.88772100	3.90600000	3.91918800	C	0.79981100	0.77681300	0.64289500
H	3.98544800	4.16951700	2.16550900	C	0.01456300	1.94770600	0.21220700
O	4.53244400	5.80503300	3.33870900	C	-1.35234700	1.84833200	-0.33742600
H	5.45959700	5.54612200	3.35997100	C	-1.86222900	0.61791400	-0.56248000
C	-1.69093100	3.44420000	0.05762500	N	-1.53218800	-1.72855800	-0.41842200
C	-3.24174500	0.83850900	-0.16852400	N	0.54847400	3.11966200	0.29970500
C	2.59009400	0.88250600	0.16825000	H	1.51194900	3.33113700	0.62347100
C	1.03570200	-1.72147900	-0.05540900	H	0.02811800	3.93633000	-0.00190600
H	-1.55380000	3.99904300	-0.87813400	H	-1.02079800	-2.57215200	-0.18880600
H	-2.76000600	3.37685000	0.23540200	H	-2.45204400	-1.86141400	-0.82140100
H	-1.27541200	4.06131800	0.85871400	H	0.85207600	4.29129500	3.62977400
H	-3.54815100	0.18519100	-0.99083700	O	1.60215300	4.00325400	3.09797300
H	-3.70517600	0.44086600	0.74237300	C	2.47348400	5.11571600	2.87747900
H	-3.68665700	1.81142100	-0.35479100	H	2.90642000	5.46584600	3.82016500
H	2.10801900	-1.65744800	-0.21394100	H	1.92680100	5.94481900	2.41637800
H	0.87923500	-2.28994800	0.86921400	C	3.59017600	4.66906500	1.97163200
H	0.62873100	-2.32529800	-0.87177100	H	4.29250700	5.49425900	1.83102600
H	2.90545700	1.54812300	0.97622200	H	4.12201500	3.82193800	2.41468300
H	3.03083500	-0.08901600	0.37072500	O	3.02512900	4.28445000	0.70592800
H	3.04941200	1.25871000	-0.75364200	H	3.73470500	4.05969000	0.09304100
P ⁺ (EG) - Normal				C	-2.06768700	3.13197000	-0.62896600
C	-1.12266600	-0.58739500	-0.15750300	C	-3.20851300	0.34329600	-1.16166600
C	0.24659100	-0.53850500	0.26917400	C	1.00128600	-1.73715900	0.71519900
C	0.86558300	0.68495700	0.37228500	C	2.11435200	1.03723700	1.30749700
C	0.11586900	1.86982400	0.06213100	H	-1.57031500	3.68691500	-1.43035000
C	-1.25346700	1.81834800	-0.37086100	H	-3.09204100	2.96844600	-0.94036500
C	-1.87126600	0.59498100	-0.47657200	H	-2.09974700	3.77051200	0.25732700
N	-1.72453200	-1.78290900	-0.26752900	H	-3.11017200	-0.23361800	-2.08554000
N	0.70709600	3.07012700	0.18765000	H	-3.83814500	-0.22363200	-0.47036000
H	1.67359800	3.20242600	0.47236200	H	-3.74187300	1.25203500	-1.41180000
H	0.21786700	3.90808800	-0.08367200	H	2.85482800	1.38098400	0.57926800
H	-1.23971300	-2.64005100	-0.05965200	H	2.01309000	1.81155600	2.07016800
H	-2.68124700	-1.86821100	-0.56819500	H	2.50831400	0.14870800	1.78731700
H	0.92551900	4.04338300	2.62413600	H	2.00961800	-1.56760700	1.07287800
O	1.32695900	4.41463000	3.41790600	H	0.46978800	-2.30810500	1.48230800
C	2.27746600	5.40902300	3.03800800	H	1.08530700	-2.36201100	-0.17802500
H	2.55234300	5.93241200	3.95516700	P(EG) - Bidentate			
H	1.82319100	6.13600400	2.35582600	C	-1.12774900	-0.59093300	-0.18020000
C	3.53284800	4.83868500	2.41799500	C	0.22879900	-0.58250200	0.18758200
H	4.26732200	5.64224900	2.30209000	C	0.88619800	0.64389300	0.36319700
H	3.95420000	4.06645900	3.06943600	C	0.18326000	1.83725200	0.13628900
O	3.21291800	4.28037300	1.13334600	C	-1.17158900	1.83069700	-0.23104100
H	4.02666500	3.97517000	0.71685800	C	-1.82887700	0.60518400	-0.40978200
C	-1.92999800	3.12683000	-0.67937500				

Appendix C

H	3.80431000	7.09199300	2.56586800
H	4.23011400	6.64197600	4.22571800
O	5.73203500	6.35081500	2.81548000
H	6.09196600	7.23199700	2.96408300
C	-1.36965500	3.47330300	0.21156000
C	-3.20104100	1.06461000	-0.13608800
C	2.60224900	0.45789800	0.15821900
C	0.76804800	-1.94904000	-0.19083100
H	-1.14214500	4.06672800	-0.68211600
H	-2.44427100	3.51971500	0.35938400
H	-0.90980600	3.98704600	1.06030600
H	-3.54153300	2.08975600	-0.24536400
H	-3.57794700	0.50891600	-0.99994700
H	-3.70035300	0.65205700	0.74882800
H	1.84474400	-1.99992300	-0.32117400
H	0.52172100	-2.55277200	0.69095600
H	0.31805600	-2.45024600	-1.05309500
H	2.98696200	1.01914800	1.01425800
H	2.93927100	-0.56735600	0.27613400
H	3.09729800	0.85804100	-0.73460400

P⁺⁺(PD) - Normal

C	-1.36194300	-0.39383700	0.15135500
C	0.05489100	-0.60818100	0.08532800
C	0.87783100	0.46370000	-0.16932100
C	0.28999300	1.76089600	-0.35917300
C	-1.13075100	1.97269400	-0.29089000
C	-1.95226900	0.90043900	-0.03552400
N	-2.16544400	-1.44296800	0.39775900
N	1.08593100	2.81074300	-0.60665500
H	2.10023000	2.76348700	-0.66920000
H	0.69103900	3.72709500	-0.74351700
H	-1.79835300	-2.37010700	0.53297000
H	-3.16566700	-1.34381100	0.44557800
O	3.92746700	3.51161900	-0.80589700
H	4.40933200	3.44287600	0.02610400
C	4.86487500	3.42192100	-1.89120300
H	5.65348200	4.16852500	-1.75369400
H	5.33143400	2.43096800	-1.89581500
C	4.12028400	3.66889500	-3.19022400
H	3.33297000	2.91895700	-3.30953900
H	3.63735900	4.64945200	-3.14929200
C	5.04471100	3.61537100	-4.39402100
H	5.82801200	4.37713600	-4.30580900
H	5.53341800	2.63607600	-4.45650000
O	4.25988200	3.84930400	-5.56703000
H	4.83855600	3.81810900	-6.33659400
C	-1.62966400	3.37627600	-0.50509900
C	-3.45142800	0.99354300	0.06371600
C	0.54828400	-2.01367200	0.30147700
C	2.37557800	0.36587200	-0.26303200
H	-1.33666400	3.75213400	-1.49011800
H	-2.70900100	3.45365400	-0.44488700
H	-1.21717100	4.05885000	0.24414900
H	-3.93509300	0.36779300	-0.69257600
H	-3.80119600	0.65550800	1.04384800
H	-3.82169100	2.00274100	-0.07432800
H	1.62732300	-2.09576300	0.24251700
H	0.25225600	-2.38700800	1.28658500
H	0.13344700	-2.69518500	-0.44753000
H	2.73036100	0.71702100	-1.23545000
H	2.85594500	0.98618200	0.49861000
H	2.74038000	-0.64657200	-0.13326700

P²⁺(PD) - Normal

C	-1.10885000	-0.43330900	0.10560900
C	0.31138100	-0.73853600	-0.12027700

C	1.18817200	0.28811300	-0.09987200
C	0.66930500	1.63500600	0.20950500
C	-0.76915700	1.95890700	0.21639600
C	-1.64697000	0.93179300	0.18232500
N	-1.93800900	-1.42426000	0.21338600
N	1.52239400	2.56242400	0.49341300
H	2.51431500	2.34889100	0.49626600
H	1.30023900	3.53958000	0.78234700
H	-1.63268700	-2.38924500	0.16638000
H	-2.92937500	-1.27860600	0.36252000
H	1.45519400	5.88065700	0.81514200
O	1.37375100	5.14728500	1.43706800
C	2.06095900	5.47113200	2.66119200
H	1.84410500	4.64386300	3.33805600
H	1.61963900	6.37701900	3.08573100
C	3.55989300	5.63252700	2.45879900
H	3.96935900	4.71519300	2.02656300
H	3.74923600	6.44386800	1.74865200
C	4.28037500	5.93804400	3.76140000
H	3.89896200	6.86815700	4.19815400
H	4.11295400	5.13254500	4.48601200
O	5.67597300	6.06219700	3.47624200
H	6.14179600	6.26500400	4.29481600
C	-1.14546600	3.40500800	0.27717900
C	-3.13784500	1.07648600	0.23795900
C	2.66376500	0.15320700	-0.31981200
C	0.67890700	-2.17456000	-0.33857900
H	-0.64252400	3.96163000	-0.51672000
H	-2.21245700	3.55497300	0.16347300
H	-0.84494400	3.85202600	1.22775400
H	-3.45024500	2.11270700	0.19332000
H	-3.61468700	0.55546800	-0.59586800
H	-3.53392600	0.66401600	1.17104100
H	1.73800200	-2.30224800	-0.52715000
H	0.44131400	-2.77639800	0.54356400
H	0.13834900	-2.59127100	-1.19251700
H	3.21354600	0.25732100	0.62123200
H	2.92481400	-0.81208300	-0.73787800
H	3.02621800	0.91364700	-1.01467800

P(PD) - Bidentate

C	-1.32968900	-0.63716400	-0.24197800
C	0.07013400	-0.63219900	-0.37103300
C	0.75694100	0.58995900	-0.34169100
C	0.02772100	1.78150000	-0.21469400
C	-1.36918300	1.78016400	-0.08513100
C	-2.05728700	0.55894300	-0.11570000
N	-2.02376800	-1.86272100	-0.30915100
N	0.72820800	3.02346800	-0.14969500
H	1.61319800	3.00232200	-0.64048800
H	0.18704400	3.79833700	-0.51280600
H	-1.48802000	-2.66660500	-0.01595200
H	-2.92331700	-1.86283500	0.14916100
H	1.13463200	3.51852000	1.65576100
O	1.31483600	3.79436400	2.57955500
C	1.86122800	5.11157300	2.57935000
H	1.26896600	5.72915500	3.26286100
H	1.77683400	5.55492700	1.58271800
C	3.31713800	5.12540100	3.03761100
H	3.63922800	6.16566900	3.15810000
H	3.38159900	4.65527100	4.02416800
C	4.27869000	4.41121900	2.10619500
H	5.27630300	4.37667200	2.55777700
H	3.94660200	3.38095000	1.94024500
O	4.33012800	5.11851400	0.85903600
H	4.89503100	4.62999200	0.25110700
C	-2.06613300	3.10877100	0.09412400
C	-3.56202100	0.46113900	-0.03505200

C	0.76340000	-1.96105500	-0.55507800	H	1.91201800	2.90997100	-0.74481800
C	2.26225700	0.68565600	-0.43066100	H	0.42414800	3.67262100	-1.10245100
H	-2.04765200	3.70664400	-0.82495000	H	-1.25262100	-2.44744700	0.94220400
H	-3.10698700	3.00340300	0.38501400	H	-2.74180100	-1.69337500	0.53286600
H	-1.57752500	3.70334400	0.87072600	O	3.42428400	3.85288200	-1.12047700
H	-3.89100200	0.00513200	0.90646300	H	4.11945500	4.11387400	-0.50513500
H	-4.05516100	1.42542500	-0.11247700	C	3.29175400	4.83300200	-2.16629600
H	-3.95415100	-0.16313900	-0.84350400	H	4.24149400	4.93221800	-2.69710300
H	1.81151500	-1.86018800	-0.82025300	H	2.56819600	4.40590800	-2.86064900
H	0.71817100	-2.57418100	0.35304700	C	2.82140700	6.19713000	-1.67451600
H	0.28686900	-2.53981200	-1.35196400	H	3.60939200	6.67713100	-1.08411800
H	2.58679200	1.12370700	-1.38203700	H	2.66704800	6.83024500	-2.55492900
H	2.66078300	1.32048300	0.36546100	C	1.55848800	6.17078300	-0.82167300
H	2.75348100	-0.27829500	-0.33931000	H	1.24623300	7.18978800	-0.58129700
P ⁺ (PD) - Bidentate				H	1.74149100	5.65087400	0.11876300
C	-1.11948500	-0.61044000	0.24312700	O	0.46368500	5.46287800	-1.43199700
C	0.30774100	-0.57594100	0.38165300	H	0.18241000	5.91549500	-2.23583000
C	0.98083000	0.57104700	0.03214600	C	-1.86290000	2.93829900	-1.16396900
C	0.23207800	1.69648700	-0.45826100	C	-3.36597900	0.40902800	-0.31668500
C	-1.19908100	1.65724600	-0.59539000	C	1.01329400	-1.79687000	0.89515300
C	-1.87042600	0.50938000	-0.24606200	C	2.52883100	0.70319600	-0.00171800
N	-1.77723500	-1.73386500	0.58222200	H	-1.49382800	3.15649700	-2.16957900
N	0.88416100	2.81421900	-0.79880400	H	-2.94032500	2.84657200	-1.22403700
H	1.89227100	2.91099300	-0.72907300	H	-1.64150500	3.80437500	-0.53555600
H	0.41175800	3.65123700	-1.12739800	H	-3.63655700	-0.44494900	-0.94336600
H	-1.29431400	-2.54460300	0.93109500	H	-3.77699400	0.24233500	0.68308000
H	-2.77776800	-1.80527300	0.50340000	H	-3.86663800	1.27666600	-0.72810500
O	3.58270700	4.08833400	-1.05724600	H	2.08978800	-1.70391500	0.96913800
H	4.30859200	3.49616400	-1.27981600	H	0.64283700	-2.01655600	1.90040800
C	3.35045400	4.97323000	-2.17059500	H	0.80484900	-2.66137500	0.25832300
H	4.27845800	5.11772900	-2.72790100	H	2.90792600	1.03835200	-0.96925000
H	2.61964300	4.51760400	-2.84616500	H	2.82771800	1.44356100	0.74577500
C	2.84611200	6.31622700	-1.66833800	H	3.02953000	-0.22674000	0.23866000
H	3.62598500	6.80018000	-1.07178300	P(BD) - Normal			
H	2.67067200	6.95768000	-2.53896500	C	-1.24891500	-0.37474300	-0.10401400
C	1.58244600	6.25006200	-0.81867200	C	0.14376800	-0.56054000	-0.14626600
H	1.29535100	7.25754100	-0.50345200	C	0.98769500	0.55339700	-0.03208700
H	1.75827800	5.65912200	0.08041300	C	0.42116200	1.83098700	0.08985700
O	0.47861800	5.61288500	-1.47855100	C	-0.96809600	2.01996300	0.13277300
H	0.23664400	6.11778400	-2.26353900	C	-1.81309400	0.90692800	0.01782400
C	-1.87234500	2.89395600	-1.12496200	N	-2.09824500	-1.49046400	-0.25450200
C	-3.36367000	0.34502300	-0.34412300	N	1.28058200	2.95976300	0.24129000
C	0.97785700	-1.81740300	0.90716200	H	2.17448700	2.83851100	-0.21798700
C	2.47388500	0.72914500	0.12888800	H	0.86563500	3.81822300	-0.09871600
H	-1.50530500	3.13965400	-2.12587900	H	-1.69484600	-2.36792600	0.03988800
H	-2.94932400	2.79144800	-1.19289300	H	-3.01458700	-1.37906800	0.15445600
H	-1.66746300	3.75741700	-0.48619600	H	1.69394000	3.28128700	2.10362300
H	-3.62458100	-0.48703000	-1.00512300	O	1.85817900	3.43158900	3.05968600
H	-3.80099200	0.13574500	0.63706500	C	2.42502700	4.72528900	3.23325200
H	-3.86084500	1.22642500	-0.73229200	H	2.32630400	4.96723000	4.29528900
H	2.05299300	-1.71161800	0.99475100	H	1.84638400	5.47396500	2.67627600
H	0.59937100	-2.07826600	1.90031400	C	3.89340700	4.79633800	2.82323900
H	0.79263500	-2.67253800	0.24968100	H	4.44981200	4.03732500	3.38314900
H	2.91113100	0.90984600	-0.85759700	H	3.98083700	4.53507400	1.76278900
H	2.73791200	1.57914300	0.76426700	C	4.50065100	6.17889200	3.06825800
H	2.96510100	-0.14411300	0.54258500	H	3.94462800	6.93641500	2.50569900
P ²⁺ (PD) - Bidentate				H	4.41178300	6.44214300	4.12763800
C	-1.09337800	-0.55425600	0.24036200	C	5.96260700	6.25017500	2.66876300
C	0.37114300	-0.55535000	0.35262200	H	6.54699100	5.52053800	3.24179600
C	1.03965700	0.55389400	-0.03289000	H	6.07588300	6.00999400	1.60481000
C	0.25630400	1.71645900	-0.49662100	O	6.44283000	7.57538400	2.92673300
C	-1.21492900	1.70161500	-0.62472200	H	7.37251700	7.62125200	2.67881100
C	-1.87809100	0.58302300	-0.25797200	C	-1.48673300	3.42726800	0.31537300
N	-1.73286700	-1.62702200	0.59287500	C	-3.31916100	1.01638500	-0.00005900
N	0.88588300	2.80104600	-0.79477700	C	0.65950000	-1.96761500	-0.33173500
				C	2.49460800	0.44252400	-0.02164600
				H	-1.31094400	4.04565800	-0.57294600

Appendix C

H	-2.55209300	3.46115100	0.52182800
H	-0.98543200	3.92163300	1.15213100
H	-3.66930900	2.04103800	-0.08024500
H	-3.73709800	0.46869500	-0.84993300
H	-3.77046800	0.59129200	0.90451100
H	1.72829000	-2.00696600	-0.51871800
H	0.46266000	-2.59367800	0.54687400
H	0.16879800	-2.45173400	-1.18146900
H	2.92070800	1.00179700	0.81567700
H	2.84219100	-0.58166000	0.07358500
H	2.93981000	0.84951800	-0.93739900

P⁺⁺(BD) - Normal

C	-1.33748300	-0.34185600	-0.14307900
C	0.07137600	-0.60715700	-0.19312100
C	0.94418900	0.45233200	-0.27423700
C	0.41402500	1.78730500	-0.30957100
C	-0.99863100	2.05019600	-0.24991300
C	-1.87002700	0.99018400	-0.16744900
N	-2.18981700	-1.37849800	-0.06817400
N	1.25839000	2.82444100	-0.39891000
H	2.27005800	2.74060900	-0.47078600
H	0.90446600	3.76691600	-0.42670700
H	-1.86479700	-2.33063500	-0.05029000
H	-3.18610800	-1.24228800	-0.03290300
O	4.11842700	3.40860800	-0.60292700
H	4.62339300	3.24473900	0.20151000
C	5.01637400	3.38703100	-1.72607300
H	5.83533500	4.09194400	-1.55070100
H	5.44647500	2.38555600	-1.83635000
C	4.24759000	3.77443000	-2.97520800
H	3.42320400	3.06906800	-3.12165800
H	3.80031100	4.76175600	-2.82219100
C	5.14263600	3.79176400	-4.21551900
H	5.96362100	4.50193200	-4.07387600
H	5.59571400	2.80624800	-4.36416400
C	4.37863200	4.17176500	-5.47065700
H	3.56407900	3.45929200	-5.64710100
H	3.93532600	5.16806600	-5.35634600
O	5.28933300	4.16189400	-6.57540300
H	4.81032600	4.40904500	-7.37373100
C	-3.36714400	1.13337900	-0.10098400
C	-1.43420000	3.49053800	-0.28486900
C	2.43991500	0.30414000	-0.32421400
C	0.50129600	-2.04932600	-0.15273700
H	-1.09675500	3.98142400	-1.20276100
H	-2.51092100	3.60596300	-0.24093800
H	-1.01709000	4.04777300	0.55945900
H	-3.84816900	0.62745000	-0.94374200
H	-3.76310500	0.69116400	0.81833700
H	-3.69414800	2.16647700	-0.12255200
H	1.57805600	-2.16905100	-0.18046800
H	0.14750300	-2.53943200	0.75936800
H	0.09459000	-2.60401000	-1.00395800
H	2.84929500	0.75074400	-1.23398700
H	2.90964200	0.81252100	0.52236500
H	2.76219700	-0.73053200	-0.29986400

P²⁺(BD) - Normal

C	-1.17014500	-0.53125500	0.16911200
C	0.23179700	-0.81452200	-0.17134300
C	1.09619500	0.22235100	-0.20319800
C	0.58741000	1.56120800	0.15519900
C	-0.84848400	1.86264700	0.30253200
C	-1.71254800	0.82384400	0.33514300
N	-1.98122700	-1.53456000	0.29769000
N	1.44862100	2.50309500	0.35462300

H	2.43929900	2.30341700	0.26475100
H	1.24165800	3.48271600	0.65164800
H	-1.67224600	-2.49307600	0.18761900
H	-2.95973200	-1.40625100	0.52641900
H	1.41433700	5.81195900	0.56747300
O	1.35760800	5.10619500	1.22308800
C	2.11104100	5.47354300	2.39633900
H	1.93429000	4.66983000	3.11243700
H	1.69099000	6.39339400	2.81275800
C	3.59639900	5.63303700	2.11366500
H	3.97805100	4.70249000	1.68172800
H	3.73439800	6.41615500	1.35986800
C	4.38332600	5.98806200	3.37681600
H	3.99560700	6.91539100	3.81044200
H	4.25233400	5.20459200	4.13016000
C	5.86626100	6.15937900	3.10218000
H	6.28297600	5.23470500	2.68547100
H	6.02501600	6.95989100	2.37000000
O	6.51921500	6.48216600	4.33426200
H	7.46027700	6.59883400	4.16474700
C	-1.23846800	3.30143300	0.42017700
C	-3.19245000	0.94809600	0.53942000
C	0.59549000	-2.24250500	-0.44282700
C	2.55184000	0.10813100	-0.53795900
H	-0.80439600	3.88069800	-0.39736100
H	-2.31284600	3.43701100	0.38767000
H	-0.87432400	3.73512100	1.35436600
H	-3.51430900	1.98139500	0.58244000
H	-3.74370400	0.46761700	-0.27295600
H	-3.49508000	0.48150500	1.48187700
H	1.64078200	-2.35714200	-0.70244700
H	0.41843500	-2.86427100	0.43972300
H	0.00437800	-2.64578500	-1.26947700
H	3.17240800	0.24527800	0.35306700
H	2.79939400	-0.86158800	-0.95333600
H	2.84277500	0.85899800	-1.27584700

P(BD) - Bidentate

C	-1.41586900	-0.71616800	-0.13877000
C	-0.01304300	-0.79204900	-0.18062900
C	0.74032600	0.38951900	-0.12580400
C	0.07574100	1.62340200	-0.06430000
C	-1.32469700	1.70212400	-0.02370500
C	-2.07913400	0.52153700	-0.07880100
N	-2.17442300	-1.90208500	-0.22713600
N	0.83968500	2.82495400	0.02323200
H	1.74575700	2.76109800	-0.42738500
H	0.35318900	3.62165400	-0.36874600
H	-1.70274200	-2.72802800	0.11153800
H	-3.09609000	-1.84225300	0.18077700
H	1.15934800	3.37959400	1.88182700
O	1.27141800	3.68452300	2.80670400
C	1.80998700	5.00441200	2.80389500
H	1.51371800	5.46638200	3.74909300
H	1.34950600	5.59502400	2.00358300
C	3.33639800	5.03563200	2.69457200
H	3.66045500	6.08155000	2.75353200
H	3.75238400	4.53262400	3.57261800
C	3.90742100	4.37350400	1.43617400
H	4.99186800	4.27286000	1.53598800
H	3.51128200	3.35790800	1.35241600
C	3.60115700	5.11826700	0.14744000
H	4.18725800	6.04268100	0.09285200
H	2.54285000	5.39437900	0.09434100
O	3.92736100	4.25759900	-0.95331000
H	3.79806900	4.74330000	-1.77531700
C	-1.95616800	3.07038500	0.08969100
C	-3.58917900	0.51221100	-0.09585900

C	0.61397000	-2.16085700	-0.30106300
C	2.25089400	0.39573800	-0.11533200
H	-1.85353600	3.64554000	-0.83830500
H	-3.01579000	3.02752400	0.32305100
H	-1.48052900	3.65506200	0.88169500
H	-4.00646600	0.10447200	0.83275700
H	-4.01742200	1.50070300	-0.23183000
H	-3.96400900	-0.11227100	-0.91228700
H	1.67677200	-2.12256900	-0.52030700
H	0.49484600	-2.74712600	0.61799100
H	0.14325700	-2.73346600	-1.10565700
H	2.67591500	-0.59412700	0.02005200
H	2.66464800	0.80069800	-1.04616300
H	2.63231300	1.01806100	0.69869000

P⁺⁺(BD) - Bidentate

C	-1.39573400	-0.69542300	0.14171100
C	0.02615600	-0.86566100	0.21645800
C	0.83932000	0.20469600	-0.07331300
C	0.23844000	1.46183200	-0.43104200
C	-1.18848000	1.62558100	-0.50943600
C	-1.99982500	0.55184200	-0.22640700
N	-2.19019500	-1.74299100	0.42491600
N	1.03178600	2.50870000	-0.69973600
H	2.04529700	2.43591300	-0.68624900
H	0.66433400	3.42904000	-0.92479800
H	-1.81220500	-2.63841500	0.68492500
H	-3.19314400	-1.67217700	0.38740400
C	3.38836000	5.03212700	-1.99964300
H	4.13197700	5.08258600	-2.79869400
H	2.61223100	4.34581400	-2.34734700
C	2.76615600	6.41599900	-1.78701600
H	3.50184700	7.11151200	-1.36766700
H	2.48049900	6.82687800	-2.76058000
C	1.54328500	6.42136300	-0.87238500
H	1.12094600	7.42953600	-0.82271400
H	1.80553100	6.12777800	0.14442300
O	0.52827200	5.48878000	-1.27653400
H	0.17687100	5.75946300	-2.13319500
C	4.02847500	4.43909300	-0.75197800
H	5.04245300	4.82559400	-0.61466000
H	3.45422500	4.68757300	0.14605900
O	4.06374500	3.00829600	-0.90552600
H	4.63373800	2.63564500	-0.22320500
C	-1.70632700	2.97739400	-0.91655700
C	-3.50374800	0.59577800	-0.28150300
C	2.34158300	0.14671200	-0.02686400
C	0.53476100	-2.22456200	0.61835000
H	-1.36391700	3.23673700	-1.92274200
H	-2.78897900	3.02947900	-0.92008300
H	-1.34480700	3.75972600	-0.24506600
H	-3.89141200	-0.13052800	-1.00251200
H	-3.93990200	0.35650700	0.69325200
H	-3.88799000	1.56663900	-0.57194300
H	2.77667000	0.44139400	-0.98531300
H	2.73434500	0.83101100	0.73093200
H	2.71803600	-0.84284500	0.20542700
H	1.61638100	-2.27397300	0.66506600
H	0.15933700	-2.50683100	1.60679000
H	0.20820100	-2.99266500	-0.08955300

P²⁺(BD) - Bidentate

C	-1.37660300	-0.59283900	0.24567000
C	0.07596000	-0.79857300	0.25006100
C	0.86468400	0.20321300	-0.19705000
C	0.22548700	1.48062900	-0.56944600
C	-1.23962300	1.62877400	-0.69972700

C	-2.02627400	0.61413100	-0.27807700
N	-2.13157400	-1.54525900	0.70204500
N	0.97173800	2.51371900	-0.77123100
H	2.00417300	2.50255700	-0.69172800
H	0.60112100	3.45561100	-0.99407900
H	-1.74634800	-2.40650200	1.07027800
H	-3.14160900	-1.46979800	0.71332700
C	3.46747600	5.13989500	-1.95636200
H	4.20415300	5.40623600	-2.71641500
H	2.79064900	4.42862900	-2.43545400
C	2.68734400	6.39989400	-1.56268000
H	3.34637400	7.10856200	-1.04964000
H	2.34766900	6.90651400	-2.47190700
C	1.48663600	6.15170400	-0.65963700
H	0.98969100	7.09596100	-0.42320100
H	1.78111100	5.69058200	0.28399400
O	0.52664100	5.24209600	-1.23309400
H	0.16756400	5.62219300	-2.04399200
C	4.16612600	4.43054900	-0.79132300
H	5.25105900	4.47647000	-0.90012500
H	3.90742900	4.88718200	0.16804200
O	3.76618000	3.03952600	-0.76864300
H	4.35626400	2.56233400	-0.17333200
C	-1.74738100	2.90839200	-1.28458100
C	-3.52544100	0.62631000	-0.29826500
C	2.35648500	0.11078400	-0.28835400
C	0.58545500	-2.11258900	0.76152100
H	-1.27569000	3.09665500	-2.25153400
H	-2.81894400	2.89060000	-1.44141200
H	-1.51902100	3.75744600	-0.63535800
H	-3.91424300	-0.19295200	-0.90866400
H	-3.92925000	0.51999700	0.71259000
H	-3.92531600	1.54859100	-0.70125600
H	2.73296800	0.62029100	-1.17464200
H	2.82545500	0.56263000	0.59110600
H	2.68852000	-0.92036500	-0.34470900
H	1.66806300	-2.15165200	0.77844500
H	0.24966800	-2.28547600	1.78771900
H	0.23177000	-2.94170300	0.14257100

C.5 Supporting Information for 2,2,2-Trifluoroethanol and Acetic Acid

C.5.1 Plots of E_{P1} , E_{P2} and $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration of hydrogen donors

Figure C.44. Plots E_{P1} and E_{P2} against concentration of the 2,2,2-trifluoroethanol (TFE) and acetic acid obtained over three experiments (red +, blue O and black x) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

Figure C.45. Plots $\Delta E_P = |E_{P1} - E_{P2}|$ against concentration of the TFE and acetic acid obtained over three experiments (red +, blue O and black x) as measured by square-wave voltammetry during the oxidation of 1 mM TMPD with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

C.6 Computational Data for Calculations of Adiabatic Ionization Energies

C.6.1 Energies of phenylenediamine-base/hydrogen acceptor/hydrogen donor complexes

Table C.4. Energies of the MeCN-solvated phenylenediamine-base/hydrogen acceptor/hydrogen donor complexes.

Compound	No. of molecules (<i>n</i>)	Energy (hartrees)		
		P(compound) _{<i>n</i>}	P ^{•+} (compound) _{<i>n</i>}	P ²⁺ (compound) _{<i>n</i>}
-	-	-500.149	-499.985	-499.774
Water	1	-576.601	-576.435	-576.228
	2	-653.052	-652.886	-652.683
	3	-729.504	-729.338	-729.136
	4	-805.957	-805.789	-805.589
Pyridine	1	-748.433	-748.274	-748.071
	2	-996.717	-996.562	-996.367
	3	-1245.001	-1245.849	-1244.659
	4	-1493.284	-1493.135	-1492.950
MeOH	1	-615.879	-615.714	-615.507
	2	-731.610	-731.444	-731.241
	3	-847.342	-847.175	-846.973
	4	-963.073	-962.906	-962.705
<i>t</i> -BuOH	1	-733.786	-733.622	-733.416
	2	-967.423	-967.260	-967.058
	3	-1201.062	-1200.897	-1200.697
	4	-1434.698	-1434.534	-1434.336
TFE	1	-953.048	-952.879	-952.670
	2	-1405.947	-1405.776	-1405.569
	3	-1858.845	-1858.673	-1858.467
	4	-2311.744	-2311.571	-2311.365

C.6.2 Geometries of phenylenediamine-base/hydrogen acceptor/hydrogen donor complexes

Figure C.46. Optimized geometries for $P(H_2O)_n$ for TMPD ($n = 1$ to 4).

Figure C.47. Optimized geometries for $P^{+\bullet}(H_2O)_n$ for TMPD ($n = 1$ to 4).

Figure C.48. Optimized geometries for $P^{2+}(H_2O)_n$ for TMPD ($n = 1$ to 4).

Figure C.49. Optimized geometries for $P(\text{pyridine})_n$ for TMPD ($n = 2$ to 4).

Figure C.50. Optimized geometries for $P^+(pyridine)_n$ for TMPD ($n = 2$ to 4).

Figure C.51. Optimized geometries for $P^{2+}(pyridine)_n$ for TMPD ($n = 2$ to 4).

Figure C.52. Optimized geometries for $P(\text{MeOH})_n$ for TMPD ($n = 2$ to 4).

Figure C.53. Optimized geometries for $P^{*+}(\text{MeOH})_n$ for TMPD ($n = 2$ to 4).

Figure C.54. Optimized geometries for $P^{2+}(MeOH)_n$ for TMPD ($n = 2$ to 4).

Figure C.55. Optimized geometries for $P(t-BuOH)_n$ for TMPD ($n = 2$ to 4).

Figure C.56. Optimized geometries for $P^{*+}(t\text{-BuOH})_n$ for TMPD ($n = 2$ to 4).

Figure C.57. Optimized geometries for $P^{2+}(t\text{-BuOH})_n$ for TMPD ($n = 2$ to 4).

Figure C.58. Optimized geometries for $P(TFE)_n$ for TMPD ($n = 1$ to 4).

Figure C.59. Optimized geometries for $P^{++}(TFE)_n$ for TMPD ($n = 1$ to 4).

Figure C.61. Optimized geometries for $P^{2+}(TFE)_n$ for TMPD ($n = 1$ to 4).

C.6.3 Coordinates of phenylenediamine-base/hydrogen acceptor/hydrogen donor complexes

P				P ²⁺			
C	-1.06309800	-0.36256700	-0.01261900	C	-1.05007100	-0.34069200	-0.05591300
C	0.34198500	-0.37837500	0.00391100	C	0.42095000	-0.39368800	-0.02444100
C	1.04379200	0.83580700	-0.00134200	C	1.09648600	0.77511200	0.02780400
C	0.32844500	2.04540900	0.01158000	C	0.31542000	2.02353300	0.05487900
C	-1.07663700	2.06121800	-0.00494100	C	-1.15560200	2.07653000	0.02340600
C	-1.77844500	0.84703600	0.00030300	C	-1.83113700	0.90773000	-0.02883900
N	-1.77023300	-1.58579600	0.02812800	N	-1.69722200	-1.46083200	-0.11232500
N	1.03558300	3.26864000	-0.02917800	N	0.96257000	3.14367400	0.11129300
H	-1.26783500	-2.36911700	-0.36422100	H	-1.22133500	-2.35552500	-0.13717400
H	-2.69623900	-1.54394400	-0.37286500	H	-2.70992900	-1.49684800	-0.13661100
H	1.96157600	3.22679400	0.37184600	H	1.97527800	3.17969000	0.13557900
H	0.53317500	4.05196700	0.36314800	H	0.48668300	4.03836600	0.13614200
C	-3.28665600	0.77251500	0.03732800	C	-3.32263700	0.78094700	-0.06304500
C	-1.76513700	3.40522300	-0.04493200	C	-1.79049500	3.43229500	0.05615300
C	2.55200300	0.91031900	-0.03837300	C	2.58798600	0.90189500	0.06201000
C	1.03049200	-1.72237700	0.04391600	C	1.05584400	-1.74945300	-0.05718900
H	-3.75326700	1.73152000	0.24227400	H	-3.81856300	1.74297600	-0.02717900
H	-3.70226900	0.40677100	-0.90933400	H	-3.64973700	0.28170500	-0.97952000
H	-3.62164900	0.08204400	0.81696200	H	-3.68402400	0.20106000	0.79079600
H	-1.33633700	4.03797100	-0.82770100	H	-1.46039300	4.03944000	-0.79157800
H	-2.82951200	3.32988000	-0.24665800	H	-2.87117300	3.38124100	0.00986400
H	-1.65300000	3.95063400	0.89983100	H	-1.53077700	3.96048100	0.97813500
H	2.88700000	1.60080200	-0.81799200	H	2.94937300	1.48178400	-0.79183000
H	2.96762500	1.27603700	0.90829500	H	2.91508600	1.40113500	0.97848600
H	3.01860200	-0.04868800	-0.24334300	H	3.08391200	-0.06013500	0.02614200
H	2.09485000	-1.64702800	0.24573400	H	2.13652200	-1.69840000	-0.01090200
H	0.60163500	-2.35515000	0.82663200	H	0.72574400	-2.35659700	0.79054400
H	0.91843600	-2.26776200	-0.90087200	H	0.79612300	-2.27764000	-0.97916900
P ⁺				P(H ₂ O)			
C	-1.05661400	-0.35155500	-0.05740900	C	-0.95614900	-0.34118600	-0.56024600
C	0.37834600	-0.38268100	-0.02635900	C	0.40292400	-0.34332000	-0.20137100
C	1.06564300	0.80652800	0.02810900	C	0.99444400	0.84502900	0.25054700
C	0.32196200	2.03439700	0.05637500	C	0.20673100	2.00002900	0.36577400
C	-1.11299700	2.06552300	0.02532400	C	-1.14983600	2.00569800	0.00873500
C	-1.80029400	0.87631400	-0.02914400	C	-1.74245800	0.81797700	-0.44330300
N	-1.72794900	-1.51295000	-0.11572200	N	-1.56027200	-1.54457000	-0.98033200
N	0.99329800	3.19579100	0.11468900	N	0.81826400	3.21757600	0.78951900
H	-1.25227400	-2.39964700	-0.14136500	H	-0.92641700	-2.20699100	-1.40324400
H	-2.73374300	-1.54245100	-0.14125200	H	-2.37227700	-1.42358500	-1.56814600
H	1.99909200	3.22529200	0.14022000	H	1.60355000	3.06889900	1.41081800
H	0.51762300	4.08248800	0.14033400	H	0.16966100	3.84626600	1.24640500
C	-3.30112500	0.77363200	-0.06220900	C	-3.20634000	0.71338300	-0.79925800
C	-1.77391900	3.41694800	0.05571700	C	-1.90794300	3.30783400	0.12206600
C	2.56647400	0.90921000	0.06117400	C	2.45770800	0.94561800	0.61419700
C	1.03926800	-1.73410600	-0.05675400	C	1.15589800	-1.64791600	-0.30740600
H	-3.79125200	1.73964300	-0.02525200	H	-3.77505900	1.59564900	-0.52156700
H	-3.64030100	0.27550700	-0.97560600	H	-3.35517900	0.55929000	-1.87480600
H	-3.67308800	0.19357500	0.78774100	H	-3.66869300	-0.13775600	-0.29053700
H	-1.45079400	4.03112100	-0.79026300	H	-1.35903400	4.12281500	-0.35770900
H	-2.85513300	3.35800800	0.00970000	H	-2.88651600	3.26895600	-0.34674200
H	-1.52003200	3.95771700	0.97263200	H	-2.06340500	3.59946700	1.16759700
H	2.93843700	1.48926900	-0.78877400	H	2.92512000	1.80132200	0.11905700
H	2.90564900	1.40733300	0.97457200	H	2.60118400	1.08349900	1.69252300
H	3.05660100	-0.05680100	0.02421500	H	3.02599600	0.06614000	0.32719100
H	2.12048200	-1.67516700	-0.01074100	H	2.14189600	-1.60714000	0.14545400
H	0.71614700	-2.34827800	0.78922900	H	0.60880200	-2.45309300	0.19197300
H	0.78537600	-2.27487600	-0.97366600	H	1.29304100	-1.95676000	-1.35067900
				H	1.51586700	4.20047900	-0.70133800
				O	1.88476600	4.73305400	-1.44194400
				H	1.71427800	4.21638400	-2.23652600

P(H ₂ O) ₂							
C	-1.05651200	-0.39821900	-0.52167300	H	2.63926800	3.43450300	-2.16363600
C	0.30398200	-0.46021100	-0.17295700	O	4.22439200	5.94249900	-0.79954900
C	0.95994500	0.70846600	0.23916000	H	3.89626600	6.80361600	-1.08011600
C	0.23352400	1.90488800	0.32594000	H	3.54080200	5.28869100	-1.07510300
C	-1.12343800	1.97134800	-0.02134700	O	5.00312600	5.80088600	1.87547800
C	-1.78094900	0.80323500	-0.43274200	H	5.94220600	5.58892600	1.86879200
N	-1.72443600	-1.57895400	-0.90380200	H	4.74109900	5.84986200	0.93261800
N	0.91172300	3.10199500	0.71495500	P(H ₂ O) ₄			
H	-1.13041500	-2.28687700	-1.31024900	C	-0.90402700	-0.39998500	-0.86291300
H	-2.53630300	-1.43414900	-1.48612900	C	0.48212900	-0.40655100	-0.63819400
H	1.68321600	2.92482300	1.34680900	C	1.10096700	0.73727800	-0.11412600
H	0.29592400	3.77280700	1.15813600	C	0.31426100	1.84715800	0.22625200
C	-3.25183200	0.76491600	-0.77243100	C	-1.07232100	1.85780100	0.00025700
C	-1.81373200	3.31353100	0.05619000	C	-1.69014100	0.71943400	-0.53763000
C	2.43009100	0.74222700	0.58742100	N	-1.52739500	-1.56222200	-1.36302600
C	0.98818400	-1.80441500	-0.24441000	N	0.94514900	3.01491000	0.75390400
H	-3.77337100	1.67843700	-0.50292500	H	-0.92803800	-2.15134000	-1.92270300
H	-3.42027100	0.60070900	-1.84356200	H	-2.39705000	-1.39762900	-1.84877600
H	-3.74982700	-0.05370200	-0.24446100	H	1.72495200	2.82295800	1.38189600
H	-1.21932500	4.08835800	-0.43538100	H	0.29387800	3.60402600	1.25732800
H	-2.78792600	3.31410300	-0.42326300	C	-3.17948200	0.62113900	-0.76900400
H	-1.96455700	3.63567200	1.09332800	C	-1.83865400	3.11584000	0.34033300
H	2.93265400	1.57137100	0.08220100	C	2.59738800	0.81595100	0.08368900
H	2.59171500	0.87862600	1.66329100	C	1.24834700	-1.66873300	-0.95566900
H	2.95265500	-0.16475000	0.29874900	H	-3.73330400	1.44819200	-0.33535700
H	1.97637300	-1.80153500	0.20541200	H	-3.42562900	0.59393700	-1.83732900
H	0.40209000	-2.56578600	0.27879300	H	-3.58074900	-0.29620900	-0.32795800
H	1.10524000	-2.14901700	-1.27887100	H	-1.36169500	3.99731400	-0.09756300
H	1.65814000	3.97877500	-0.73534800	H	-2.86016000	3.09938900	-0.02676000
O	2.07021600	4.47565400	-1.48709800	H	-1.88870400	3.28325800	1.42263600
H	1.89672200	3.95213200	-2.27717500	H	2.96801400	1.81747300	-0.14067800
O	4.75261500	5.15951400	-1.13481900	H	2.89094000	0.59349200	1.11496700
H	4.79515700	6.11839900	-1.20957600	H	3.13312100	0.12678400	-0.56491900
H	3.80809600	4.93072700	-1.26064800	H	2.25977800	-1.65515100	-0.55966300
P(H ₂ O) ₃				H	0.74928100	-2.54272000	-0.52697700
C	-1.24723900	-0.47082100	-0.53372700	H	1.32439900	-1.84459900	-2.03561600
C	0.09562200	-0.68311400	-0.17572900	H	1.61195000	4.10301700	-0.53712400
C	0.88147500	0.40991100	0.21650700	O	1.98669600	4.73449800	-1.21047400
C	0.29872700	1.68401900	0.27466900	H	1.90392800	4.29596300	-2.06448200
C	-1.03985900	1.90043900	-0.08221400	O	4.49820100	5.59180000	-0.58927400
C	-1.82726600	0.80830400	-0.47339000	H	4.48925500	6.55385300	-0.63917100
N	-2.04649800	-1.57336900	-0.89637000	H	3.58822000	5.29623100	-0.83260700
N	1.10846900	2.80297700	0.64621500	O	5.27412000	4.56462600	1.82697800
H	-1.53688700	-2.35355900	-1.28463200	H	6.09605100	4.08211000	1.68690300
H	-2.83367200	-1.34729500	-1.48663800	H	5.02519400	4.94055000	0.95055900
H	1.86020700	2.54713000	1.27486300	O	3.19036400	3.06179200	2.87574900
H	0.57278300	3.53938300	1.09007400	H	2.88902500	3.51873900	3.66821100
C	-3.29176200	0.93444900	-0.81953900	H	3.93944000	3.59553300	2.53206200
C	-1.57019300	3.31469000	-0.03475200	P ⁺ (H ₂ O)			
C	2.34454400	0.27920100	0.57234800	C	-1.10403200	-0.39115000	-0.15539400
C	0.61926900	-2.09887400	-0.21656100	C	0.32307500	-0.45223300	-0.02298300
H	-3.70214900	1.90951300	-0.57493800	C	1.02240900	0.71506800	0.17481200
H	-3.47600800	0.76483400	-1.88714600	C	0.29840100	1.95368400	0.25344500
H	-3.88357200	0.19335500	-0.27414700	C	-1.13266200	2.01113300	0.12421300
H	-0.88270000	4.00655200	-0.52829800	C	-1.82956700	0.84481100	-0.08503500
H	-2.53090300	3.42016800	-0.52959500	N	-1.78658400	-1.53224000	-0.35258100
H	-1.69689800	3.66918200	0.99510100	N	0.97396100	3.09407100	0.45361300
H	2.94366600	1.02848200	0.04780300	H	-1.32293300	-2.42349500	-0.40939100
H	2.51838800	0.42491100	1.64498600	H	-2.78857200	-1.54011900	-0.44462900
H	2.75623100	-0.69096700	0.31130300	H	1.98393300	3.15324700	0.55635800
H	1.59473700	-2.20354700	0.24863300	H	0.48448600	3.97225400	0.51269800
H	-0.05871000	-2.77773800	0.30908600	C	-3.32451600	0.77452400	-0.24570600
H	0.70925900	-2.47232500	-1.24376000	C	-1.78086800	3.36528000	0.23180200
H	1.91325500	3.61812500	-0.79093900	C	2.51799700	0.78221500	0.31684100
O	2.33370400	4.10735300	-1.54518900	C	0.96459400	-1.81115700	-0.11229600

Appendix C

H	-3.79975000	1.74802200	-0.21050100
H	-3.59485900	0.32200500	-1.20466600
H	-3.77673600	0.16694000	0.54427800
H	-1.40459400	4.04614600	-0.53788500
H	-2.85844300	3.32627700	0.12260900
H	-1.57439200	3.82137200	1.20483700
H	2.95362100	1.42915400	-0.44925200
H	2.80137200	1.19794200	1.28768700
H	2.99413700	-0.18756300	0.22774700
H	2.03841000	-1.78029700	0.03104300
H	0.56068600	-2.48675400	0.64788900
H	0.78273300	-2.26847800	-1.08979400
O	3.70625300	4.07047200	0.83760600
H	4.35136200	4.09599500	0.12113500
H	4.21835900	3.88071100	1.63249200

P⁺(H₂O)₂

C	-1.08188900	-0.38563000	-0.18957700
C	0.34390000	-0.40659600	-0.03525400
C	1.00199100	0.77302400	0.22243400
C	0.23891300	1.98657300	0.32515000
C	-1.19077100	2.00396400	0.16670200
C	-1.84710300	0.82395000	-0.09128100
N	-1.72481000	-1.54074200	-0.43519300
N	0.87315700	3.13985700	0.57613100
H	-1.23195700	-2.41470700	-0.51049200
H	-2.72414700	-1.57674800	-0.54648300
H	1.88047100	3.23741100	0.70533600
H	0.35026200	3.99757900	0.65017400
C	-3.33642300	0.71194900	-0.27929200
C	-1.88316900	3.33376800	0.29984900
C	2.49027600	0.87921800	0.40768900
C	1.03020300	-1.73978200	-0.16996300
H	-3.84448700	1.66704200	-0.21222200
H	-3.57735400	0.29006500	-1.25983600
H	-3.77979600	0.05852400	0.47840400
H	-1.51081800	4.04860500	-0.44038500
H	-2.95619700	3.26546200	0.16361400
H	-1.71312900	3.76704600	1.29030600
H	2.92916300	1.55228400	-0.33342000
H	2.73274200	1.28712400	1.39255800
H	2.99582200	-0.07567000	0.31914100
H	2.10460300	-1.67557300	-0.04302800
H	0.66097200	-2.45040400	0.57598400
H	0.84938100	-2.17560900	-1.15737200
O	3.52396900	4.16747100	1.04828800
H	4.19459300	4.24891900	0.34041200
H	4.01394900	3.97287400	1.85440500
O	5.32539800	4.42917600	-1.07588800
H	5.97362400	3.72609900	-1.20255400
H	5.82873400	5.25128400	-1.11350600

P⁺(H₂O)₃

C	-1.13531700	-0.34608000	-0.19388200
C	0.28549300	-0.50879200	-0.08115600
C	1.05964600	0.59417900	0.19200200
C	0.41942500	1.87132900	0.35039800
C	-1.00452200	2.03106200	0.23457500
C	-1.77729200	0.92727100	-0.03866100
N	-1.89307500	-1.42630000	-0.45493300
N	1.17130000	2.94630000	0.61177300
H	-1.48996700	-2.34170800	-0.56418700
H	-2.89438800	-1.36412300	-0.53195600
H	2.17874200	2.90689400	0.70532900
H	0.78816000	3.87786300	0.73181100
C	-3.27467800	0.96616500	-0.18895900
C	-1.55686100	3.41769800	0.42418800

C	2.55663400	0.55390700	0.33869600
C	0.83684100	-1.89614400	-0.27416800
H	-3.68282200	1.96398900	-0.07771600
H	-3.57926000	0.60348400	-1.17536600
H	-3.76234500	0.33358200	0.55918000
H	-1.14687500	4.10788200	-0.31909000
H	-2.63675800	3.45745000	0.33892000
H	-1.29575100	3.81067200	1.41094600
H	3.04088500	1.19274500	-0.40578000
H	2.86280200	0.91414500	1.32514600
H	2.96474000	-0.44330500	0.22103300
H	1.91603300	-1.93775200	-0.18213600
H	0.42496700	-2.59025200	0.46486700
H	0.58488500	-2.28342900	-1.26611900
O	3.79605500	4.26024300	1.13124200
H	4.47826200	4.43335600	0.44733100
H	4.27186000	4.16126800	1.96362800
O	5.60769900	4.76749100	-0.90001800
H	6.27012000	4.09082000	-1.08455600
H	6.09592800	5.59796000	-0.84845900
O	1.43841600	5.79364800	1.21222400
H	2.35403400	5.45301400	1.18190200
H	1.41387000	6.54432500	0.60922200

P⁺(H₂O)₄

C	-1.10727600	-0.30060700	-0.03517200
C	0.28217000	-0.53816900	0.23254000
C	1.16159400	0.51816000	0.18030600
C	0.66455600	1.82804600	-0.14373200
C	-0.72798400	2.06211900	-0.41667900
C	-1.60669700	1.00580600	-0.36033400
N	-1.97108800	-1.32848600	0.01739400
N	1.52062400	2.85663200	-0.19217200
H	-1.70981300	-2.28532900	0.23569100
H	-2.94968400	-1.18015500	-0.16533600
H	2.51512400	2.75728400	-0.00176600
H	1.23214200	3.80738200	-0.41184700
C	-3.08488000	1.13014600	-0.62079800
C	-1.13457400	3.47253600	-0.74765600
C	2.63789400	0.39039300	0.44209800
C	0.68527800	-1.95116000	0.55754000
H	-3.38809400	2.14305600	-0.85906500
H	-3.39136100	0.49783700	-1.45986500
H	-3.66583100	0.81981600	0.25330300
H	-0.58419800	3.84557500	-1.61530800
H	-2.19122600	3.56604600	-0.97082200
H	-0.91564100	4.14748400	0.08469500
H	3.21751700	0.68282400	-0.43827200
H	2.94933100	1.04410000	1.26097600
H	2.93413900	-0.61897800	0.70372000
H	1.74786800	-2.05492500	0.74506600
H	0.16049700	-2.31333500	1.44590600
H	0.43194700	-2.62850700	-0.26266100
O	4.38295400	3.37962200	0.31715900
H	4.45544300	4.32885800	0.10938600
H	5.14544600	2.96033200	-0.09609900
O	4.25402700	6.18928200	-0.23171200
H	4.76375300	6.53476400	-0.97568100
H	4.48068600	6.75030300	0.52097900
O	-2.05070300	-4.22591800	0.52624200
H	-1.69368400	-4.86377300	-0.10288400
H	-1.89070100	-4.61202500	1.39540400
O	1.48075800	5.74657800	-0.79047600
H	2.39615400	6.01052500	-0.58559000
H	0.91797900	6.42721400	-0.40579300

$P^{2+}(H_2O)$				H	-1.57934300	-4.43825400	0.89223800
C	-1.08250200	-0.37320300	-0.05251600	$P^{2+}(H_2O)_3$			
C	0.38416900	-0.45594300	-0.06819800	C	-1.13618600	-0.23507500	-0.23260000
C	1.08690900	0.69473900	0.02202800	C	0.32985100	-0.34006400	-0.34989700
C	0.33482000	1.95096500	0.19403600	C	1.06481800	0.76472800	-0.09647400
C	-1.12929100	2.04309600	0.02819500	C	0.34881500	2.00600800	0.23481500
C	-1.83022800	0.89317200	-0.07383100	C	-1.09813000	2.17117000	0.01704100
N	-1.75684700	-1.48053200	-0.05116800	C	-1.83102400	1.06675500	-0.24004100
N	0.97956800	3.02444200	0.51200000	N	-1.83448600	-1.31522000	-0.12128100
H	-1.30101400	-2.38530300	-0.04178300	N	1.01651600	3.01310500	0.69991900
H	-2.76995900	-1.49378400	-0.05188900	H	-1.41869300	-2.25910000	-0.07366800
H	1.99951900	3.08969700	0.70270700	H	-2.86015900	-1.31991200	0.00077300
H	0.47733100	3.89661200	0.63945500	H	2.03058200	3.02025100	0.91135700
C	-3.32138800	0.80511900	-0.19168100	H	0.53702200	3.87832800	0.92131000
C	-1.73387800	3.41364900	0.02268000	C	-3.30636700	1.05844800	-0.49305800
C	2.57910000	0.78908800	-0.02143400	C	-1.65439700	3.55877300	0.12937100
C	0.99140900	-1.82190800	-0.17608400	C	2.56085700	0.81969100	-0.11491900
H	-3.78786900	1.78084700	-0.25110800	C	0.89303600	-1.67954900	-0.71034500
H	-3.61029200	0.24970900	-1.08778100	H	-3.68883300	2.05248400	-0.69566100
H	-3.75139200	0.29920100	0.67781800	H	-3.54411600	0.42993100	-1.35308400
H	-1.23310600	4.05694600	-0.70449800	H	-3.85276100	0.66117300	0.36635200
H	-2.78558500	3.39431200	-0.23621300	H	-1.11988200	4.25039600	-0.52641800
H	-1.65469000	3.88367300	1.00814400	H	-2.70474000	3.60106200	-0.13380500
H	2.89161200	1.53845100	-0.75202300	H	-1.57168200	3.93132800	1.15491600
H	2.98445100	1.08611500	0.94890700	H	2.90714000	1.60392100	-0.79222600
H	3.03947800	-0.15154100	-0.29911900	H	2.95749700	1.04443800	0.87761300
H	2.07348300	-1.78776900	-0.20703100	H	3.00012700	-0.11744100	-0.43552800
H	0.71844700	-2.43732500	0.68648600	H	1.94897400	-1.62694500	-0.94949000
H	0.65202900	-2.33261600	-1.08093300	H	0.77456200	-2.39108300	0.11085500
O	3.58884600	3.59599300	1.26853800	H	0.37410000	-2.09052100	-1.57876800
H	4.25985100	3.86935200	0.63102000	O	3.65080000	3.43517500	1.53931600
H	3.60430000	4.26258400	1.96627100	H	4.34374700	3.70929500	0.92621400
$P^{2+}(H_2O)_2$				H	3.68472800	4.06517800	2.26952000
C	-1.20783600	-0.21722100	-0.17927300	O	-1.32265100	-4.06724000	0.17860000
C	0.25528300	-0.36111800	-0.23746100	H	-0.80855000	-4.67312900	-0.36793900
C	1.01056200	0.74056500	-0.03081800	H	-1.31774900	-4.44585600	1.06577800
C	0.31958500	2.01453600	0.22617100	O	-4.52595300	-1.96021500	0.38233500
C	-1.13130400	2.19431400	0.03414100	H	-5.32487600	-1.73268100	-0.10773100
C	-1.88562200	1.09234900	-0.16370800	H	-4.80415600	-2.07189900	1.29920100
N	-1.94090600	-1.28256100	-0.15437100	$P^{2+}(H_2O)_4$			
N	1.01042300	3.03395800	0.62172000	C	-1.15019100	-0.25876300	-0.25700200
H	-1.59115600	-2.25773700	-0.13087800	C	0.31432500	-0.34896400	-0.39476800
H	-2.95120100	-1.20308200	-0.11852100	C	1.03299300	0.78355800	-0.23946500
H	2.02869400	3.03957600	0.82043100	C	0.30017500	2.02340400	0.07453500
H	0.54830100	3.91948500	0.79617000	C	-1.14280600	2.15984500	-0.19236500
C	-3.37470000	1.09320900	-0.33027000	C	-1.86147100	1.02830300	-0.35584600
C	-1.66439600	3.59284700	0.11368800	N	-1.83228600	-1.34020400	-0.06937600
C	2.50702900	0.76340600	-0.03135800	N	0.94422000	3.02289100	0.58038000
C	0.79779000	-1.73047700	-0.50588300	H	-1.40212000	-2.27180200	0.03353000
H	-3.77725800	2.09518300	-0.41880000	H	-2.85621900	-1.35087500	0.05696500
H	-3.66830000	0.54236100	-1.22700700	H	1.94784100	2.98774800	0.81975700
H	-3.86445600	0.62828500	0.53097000	H	0.49120400	3.90868000	0.85666700
H	-1.11489700	4.26039000	-0.55442200	C	-3.33943500	0.98072100	-0.59338500
H	-2.71009800	3.64833400	-0.16418200	C	-1.70873000	3.54592900	-0.22701300
H	-1.58306100	3.98629100	1.13170200	C	2.52554800	0.87128800	-0.32510800
H	2.87887000	1.50951400	-0.73781300	C	0.89697700	-1.70188600	-0.66452200
H	2.89517100	1.02314800	0.95629000	H	-3.74360600	1.95739800	-0.83464800
H	2.93138400	-0.19458900	-0.30666000	H	-3.57505700	0.30612300	-1.41873900
H	1.86933400	-1.72118400	-0.66546700	H	-3.86810600	0.61536200	0.29089800
H	0.59464000	-2.40387900	0.33059200	H	-1.10076800	4.19278400	-0.86257300
H	0.33306400	-2.15995300	-1.39577000	H	-2.72257200	3.55959200	-0.61059700
O	3.65108100	3.47932000	1.39163000	H	-1.72616600	3.99081000	0.77105900
H	4.32497300	3.74498500	0.75400900	H	2.82243000	1.70567200	-0.96389800
H	3.69567700	4.12862700	2.10419300	H	2.96849100	1.03805900	0.65994800
O	-1.63346400	-4.02755700	0.02087200	H	2.96327100	-0.03263500	-0.73341300
H	-1.16282400	-4.61901600	-0.57844200				

H	1.95596100	-1.65112300	-0.89014200				
H	0.77664500	-2.36022800	0.19952300				
H	0.39447900	-2.17570900	-1.51061500	C			
O	3.58615100	3.31601200	1.58252300	C	-1.24088000	-0.00965100	0.47048500
H	4.33917800	3.55811300	1.02993100	C	0.12419000	-0.32476400	0.33556100
H	3.60658300	3.92636400	2.32952400	C	1.05245600	0.69590400	0.08213500
O	-1.27494000	-4.06863000	0.39616100	C	0.61620800	2.03000700	0.01429800
H	-0.74536200	-4.69638100	-0.10928200	C	-0.74690500	2.34852500	0.15299300
H	-1.26988100	-4.39333900	1.30444200	C	-1.67665600	1.32735100	0.40028300
O	-4.52605700	-1.99533600	0.46843900	N	-2.16964800	-1.02972400	0.74790800
H	-5.30527000	-1.84904000	-0.08085000	N	1.54880500	3.05478700	-0.26378000
H	-4.84461000	-1.99576800	1.37893400	H	-1.90320800	-1.96865400	0.47263400
O	0.10704800	5.51063900	1.66536300	H	-3.12670800	-0.85487900	0.46062600
H	0.12612800	6.32643500	1.15043800	H	2.48865700	2.91379800	0.09623500
H	0.56828900	5.71249800	2.48840600	H	1.23167600	3.97541700	0.00245900
				C	-3.14442500	1.59803800	0.63069100
				C	-1.14900600	3.79844500	0.00785800
				C	2.51939200	0.41935700	-0.15065300
				C	0.53469000	-1.76930600	0.49642300
C	-1.50219800	-0.00879600	0.33336500	H	-3.36376800	2.65246100	0.77288900
C	-0.15996300	-0.35721800	0.09770400	H	-3.76530200	1.24156600	-0.19843000
C	0.820243100	0.65092400	-0.06025200	H	-3.49464600	1.07320500	1.52443300
C	0.402571200	1.99843300	0.06223800	H	-0.72681500	4.23069000	-0.90474300
C	-0.92176100	2.34694100	0.29730400	H	-2.22474600	3.93585700	-0.04903700
C	-1.88436300	1.33874400	0.45461900	H	-0.78917300	4.41077800	0.84370700
N	-2.46382800	-1.02547900	0.51777800	H	2.89004500	1.00729600	-0.99450600
N	1.38340900	3.01459500	-0.12031400	H	3.13567200	0.69282400	0.71299400
H	-2.19740000	-1.91599700	0.12428700	H	2.71846000	-0.62514100	-0.37599100
H	-3.41362800	-0.80669500	0.22990100	H	1.61043700	-1.89342300	0.58495300
H	2.33049100	2.79646200	0.17741300	H	0.08711800	-2.19950900	1.39718400
H	1.11393700	3.90652900	0.26784200	H	0.19911600	-2.39030000	-0.34146000
C	-3.32914200	1.63890800	0.77800700	C	5.61908900	3.65694000	0.04770100
C	-1.27200100	3.81616000	0.35134800	C	6.87917300	4.01731100	0.50975600
C	2.24676000	0.34986200	-0.38516100	C	7.05984100	4.19495800	1.87561400
C	0.19076000	-1.82628800	0.04407200	C	5.97432700	4.00529100	2.72139200
H	-3.47406900	2.64867600	1.15304400	C	4.75326800	3.64511500	2.16423900
H	-3.98232100	1.51464800	-0.09268700	N	4.56781000	3.47133000	0.85201700
H	-3.70088700	0.95485700	1.54517300	H	8.02755600	4.47562600	2.27306900
H	-0.86231500	4.34697300	-0.51359100	H	5.44543300	3.51045500	-1.01349700
H	-2.34344600	3.99364300	0.34988000	H	7.69543200	4.15405300	-0.18785800
H	-0.86399600	4.30451900	1.24471200	H	6.06689100	4.13214400	3.79236300
H	2.62085900	1.04048800	-1.14520400	H	3.8861		

C	0.41870700	2.04048700	0.16052800	N	1.22779600	6.32103300	0.64637000
C	-0.96222200	2.31142400	0.17920800				
C	-1.87374800	1.26512500	0.38614700				
N	-2.31767200	-1.09806800	0.76563100				
N	1.33316500	3.08662300	-0.07318900	C	-1.20932300	-0.00021700	-0.36179700
H	-2.00342600	-2.03173300	0.52524700	C	0.22053200	-0.11944400	-0.27159000
H	-3.25593200	-0.95915700	0.40593100	C	0.97689900	1.01286600	-0.07806000
H	2.27347600	2.94346500	0.27918300	C	0.31473200	2.28279800	0.02628300
H	1.02082500	4.01816400	0.17890400	C	-1.11514800	2.40200000	-0.06372400
C	-3.36304500	1.49241500	0.49419200	C	-1.87152300	1.26967900	-0.25713000
C	-1.40115900	3.73754600	-0.05614200	N	-1.93945300	-1.11027300	-0.54866600
C	2.37919700	0.49488700	0.19510700	N	1.04488200	3.39291300	0.21269800
C	0.41638200	-1.75171400	0.73986100	H	-1.47867300	-2.00292800	-0.62191100
H	-3.62550200	2.54288900	0.58351400	H	-2.96207800	-1.14911100	-0.62856300
H	-3.90697600	1.08942000	-0.36713000	H	2.06754700	3.43186000	0.29249600
H	-3.76502600	0.98405900	1.37570100	H	0.58405800	4.28557000	0.28564800
H	-0.89038300	4.15749800	-0.92769800	C	-3.37175100	1.27129800	-0.36607500
H	-2.46843500	3.82661200	-0.23872200	C	-1.69881100	3.78430200	0.06484100
H	-1.15580800	4.39068700	0.78838600	C	2.47709800	1.01117900	0.03129700
H	2.78136400	1.00174700	-0.68718100	C	0.80419800	-1.50173500	-0.40021600
H	2.92282000	0.89942500	1.05588600	H	-3.79905600	2.26532600	-0.29917000
H	2.64218000	-0.55558100	0.10762300	H	-3.69542700	0.83878100	-1.31617800
H	1.48448200	-1.84311500	0.91607900	H	-3.82119400	0.66682800	0.42642800
H	-0.08984300	-2.17311800	1.61332800	H	-1.31658700	4.44845000	-0.71659900
H	0.16593900	-2.40265900	-0.10507400	H	-2.77989500	3.79447200	-0.01120500
C	5.34766800	3.93400000	0.01286900	H	-1.44178200	4.23101700	1.03025200
C	6.63145800	4.37017400	0.31795000	H	2.92687500	1.61486600	-0.76162000
C	7.02315900	4.40121000	1.65032700	H	2.80051700	1.44454600	0.98109600
C	6.11577300	3.99513700	2.62062100	H	2.90429500	0.01703200	-0.03452300
C	4.85433500	3.57494200	2.21581200	H	1.88522600	-1.51201000	-0.32337300
N	4.46629100	3.54081600	0.93744300	H	0.42135600	-2.16616100	0.38067700
H	8.01579400	4.73510100	1.92688700	H	0.54785100	-1.94805200	-1.36599900
H	5.01164700	3.89861800	-1.01850000	C	4.28340700	4.50482800	1.79469600
H	7.30378400	4.67678000	-0.47307300	C	5.49120600	5.13571400	2.06229300
H	6.37541100	4.00201500	3.67148000	C	6.31455200	5.47418100	0.99587200
H	4.12315200	3.25142600	2.94983200	C	5.89705900	5.16859200	-0.29333500
C	-7.03732000	-2.07963300	-1.98223200	C	4.67204200	4.53673500	-0.46270400
C	-5.78851900	-1.63881300	-1.56055600	N	3.87341800	4.20649600	0.55747600
C	-6.32914500	-1.94339000	0.63955400	H	7.26368800	5.96713400	1.16632600
C	-7.60233500	-2.39795400	0.31739400	H	3.61609200	4.22684800	2.60372000
C	-7.96344600	-2.46719500	-1.02214700	H	5.77498300	5.35421900	3.08350000
H	-7.27304800	-2.11633300	-3.03809400	H	6.50518900	5.41316400	-1.15442500
H	-5.04313400	-1.32935000	-2.28628700	H	4.31505800	4.28464600	-1.45566000
H	-6.01674800	-1.87838300	1.67688300	C	-6.38442700	-2.85772100	-2.39749300
H	-8.29011100	-2.68912700	1.10092900	C	-5.17718600	-2.22554900	-2.13040500
H	-8.94702600	-2.81624300	-1.31203400	C	-5.56731600	-2.25298300	0.12679000
N	-5.43000200	-1.56758400	-0.27510700	C	-6.79183500	-2.88593700	-0.04207700
C	-2.62662300	-6.25324000	-1.27472600	C	-7.20828000	-3.19447100	-1.33092200
C	-2.89512300	-7.05832500	-0.17503400	H	-6.66738200	-3.07853500	-3.41843200
C	-2.85182500	-6.49080700	1.09205500	H	-4.50950300	-1.94885500	-2.93956500
C	-2.54194900	-5.14064300	1.20480400	H	-5.21115900	-1.99861500	1.11946200
C	-2.32654500	-4.91337900	-1.05959900	H	-7.40039400	-3.12908300	0.81911500
H	-2.64824100	-6.65089700	-2.28127800	H	-8.15699800	-3.68836700	-1.50098100
H	-3.13349000	-8.10717200	-0.30299900	N	-4.76819600	-1.92438700	-0.89353900
H	-3.05375300	-7.07828700	1.97853400				
H	-2.50065300	-4.66772400	2.18077100				
H	-2.11272100	-4.25833100	-1.89816700				
N	-2.28252400	-4.35615500	0.15437300				
C	1.09113100	7.23754600	-0.31672000	C	-1.10698900	-0.01328600	-0.42703500
C	1.57704600	6.74975100	1.86301900	C	0.32950100	-0.08403200	-0.38543900
C	1.80103600	8.08738400	2.16657000	C	1.05411700	1.06156800	-0.14930000
C	1.65623100	9.03059400	1.15715900	C	0.35822700	2.30250000	0.03507500
C	1.29352300	8.59722800	-0.11182100	C	-1.07534600	2.37963100	-0.01535800
H	0.80696500	6.86774900	-1.29675200	C	-1.80136700	1.23420100	-0.24556100
H	1.68340300	5.98879300	2.62953400	N	-1.81308200	-1.13232300	-0.63793000
H	2.08211000	8.37741000	3.17089600	N	1.05991100	3.42615300	0.25859700
H	1.82255700	10.08238000	1.35555300	H	-1.38475700	-2.05433300	-0.75226300
H	1.16878100	9.29491400	-0.93000000	H	-2.83496300	-1.15312500	-0.68380100
				H	2.08176200	3.49162800	0.31104500
				H	0.57548300	4.29977300	0.38529300

Appendix C

C	-3.30336100	1.20063900	-0.31782900	H	-3.61871400	0.69884900	-1.59691400
C	-1.69687700	3.73563400	0.19590300	H	-3.83183000	0.56516200	0.13908800
C	2.55613100	1.10187700	-0.06998800	H	-1.32680000	4.34870800	-1.17853500
C	0.95748800	-1.43238100	-0.61064000	H	-2.84272500	3.71845100	-0.56255600
H	-3.75439500	2.17864700	-0.19438900	H	-1.61323500	4.29409500	0.55168400
H	-3.64056700	0.80385100	-1.27864800	H	2.95378200	1.62884300	-0.65773100
H	-3.71849300	0.54861400	0.45536100	H	2.69256300	1.64689700	1.07680300
H	-1.35834900	4.44794700	-0.56311200	H	2.89811800	0.12016200	0.23651200
H	-2.77956800	3.71576800	0.15222700	H	1.93806600	-1.44973200	0.05443900
H	-1.42442500	4.14439800	1.17384300	H	0.41287900	-2.08514200	0.64537400
H	2.97311500	1.74449100	-0.85035500	H	0.72501900	-2.01710100	-1.07990100
H	2.88502200	1.51392700	0.88738100	C	4.38250400	4.72002300	1.40236100
H	3.01153800	0.12370800	-0.17448500	C	5.60883400	5.36211500	1.51866400
H	2.04090000	-1.39616500	-0.62094600	C	6.35413000	5.58430000	0.36776100
H	0.65847100	-2.14160100	0.16584900	C	5.84353500	5.15581000	-0.85089400
H	0.63705500	-1.85672500	-1.56541500	C	4.60744000	4.52245000	-0.86724100
C	4.30717300	4.58682000	1.80112500	N	3.88270300	4.30340100	0.23460700
C	5.50038300	5.24605800	2.06624800	H	7.31466100	6.08201800	0.41952500
C	6.29130300	5.64427700	0.99594800	H	3.77484100	4.53173000	2.28127500
C	5.85730000	5.36768300	-0.29434800	H	5.96632900	5.67861400	2.48992900
C	4.64900400	4.70363000	-0.46083200	H	6.38845500	5.30738600	-1.77361000
N	3.88143000	4.31595800	0.56294200	H	4.17967300	4.17600600	-1.80236500
H	7.22822500	6.16081500	1.16420600	C	-6.32613700	-2.86444500	-2.69544500
H	3.66525900	4.26198400	2.61327400	C	-5.12596300	-2.24704700	-2.36717700
H	5.79807300	5.43993700	3.08847600	C	-5.55700500	-2.41341700	-0.12509000
H	6.44006900	5.65904200	-1.15843800	C	-6.77619000	-3.03829700	-0.35453200
H	4.28014300	4.47257400	-1.45460600	C	-7.16827700	-3.26819600	-1.66715300
C	-6.39309300	-2.69735800	-2.49998400	H	-6.58975000	-3.02234000	-3.73317900
C	-5.16303200	-2.12138600	-2.20946400	H	-4.44507300	-1.91984600	-3.14610800
C	-5.51491100	-2.30585500	0.04509600	H	-5.22081900	-2.21918800	0.88809700
C	-6.76049200	-2.89014100	-0.14613600	H	-7.39930700	-3.33577500	0.47886700
C	-7.20839400	-3.08950500	-1.44585800	H	-8.11213900	-3.75284700	-1.88458200
H	-6.69995200	-2.83275700	-3.52895700	N	-4.73979400	-2.02083000	-1.10749000
H	-4.50180500	-1.80425000	-3.00917400	C	-1.20283700	-6.12263700	-2.11646100
H	-5.13549900	-2.13594500	1.04730500	C	-1.30023500	-6.94867500	-1.00389300
H	-7.36083700	-3.18006600	0.70640100	C	-1.40234500	-6.36567200	0.25284400
H	-8.17435900	-3.54188400	-1.63366000	C	-1.40245600	-4.97967700	0.34419300
N	-4.72337800	-1.92449500	-0.96243400	C	-1.21112400	-4.74690500	-1.92494500
C	-1.24587700	-6.07424200	-2.32826000	H	-1.12180100	-6.53155400	-3.11522100
C	-1.30491600	-6.87873500	-1.19733700	H	-1.29683000	-8.02610100	-1.11411300
C	-1.35199100	-6.27184600	0.05133700	H	-1.48091500	-6.96896300	1.14792600
C	-1.33779400	-4.88454000	0.11634100	H	-1.48114400	-4.49253000	1.31051800
C	-1.23589700	-4.69514800	-2.16283000	H	-1.13703700	-4.07340100	-2.77245000
H	-1.20799700	-6.50225400	-3.32154600	N	-1.30831900	-4.17615000	-0.72000100
H	-1.31415900	-7.95800400	-1.28730700	C	0.37470400	7.07841000	1.21164500
H	-1.39909400	-6.85774800	0.96007000	C	0.49511000	7.21381400	-1.07026700
H	-1.37366300	-4.37885500	1.07569300	C	0.49883000	8.60246200	-1.03833100
H	-1.19042800	-4.03810600	-3.02507500	C	0.43645800	9.23869300	0.19495600
N	-1.28043400	-4.10167000	-0.96581000	C	0.37333000	8.46107600	1.34428000
P ⁺ (Pyridine) ₄				H	0.32645200	6.44185300	2.08903600
C	-1.17239500	-0.04725900	-0.40525600	H	0.54333500	6.68565600	-2.01688700
C	0.24886400	-0.11011100	-0.19696200	H	0.54986800	9.16688600	-1.96035500
C	0.96309200	1.05832800	-0.06252900	H	0.43719000	10.31985100	0.25915600
C	0.27332500	2.31788000	-0.13480900	H	0.32354200	8.91238300	2.32670500
C	-1.15045700	2.38014400	-0.32558600	N	0.43384000	6.45663100	0.02970000
C	-1.86575800	1.21146800	-0.45185600	P ²⁺ (Pyridine) ₂			
N	-1.86543700	-1.18562900	-0.55813500	C	-1.20834200	-0.08369900	-0.07638400
N	0.97143700	3.45745500	-0.01753500	C	0.25232600	-0.29014400	-0.05252800
H	-1.43220900	-2.11125700	-0.55321300	C	1.04719100	0.77129200	0.20504100
H	-2.87409500	-1.21079200	-0.72182400	C	0.40610100	2.06795200	0.47951100
H	1.98727600	3.48471400	0.09305700	C	-1.04610200	2.20008200	0.70826500
H	0.54217000	4.38428500	-0.05051100	C	-1.84009200	1.13943200	0.44600800
C	-3.35761200	1.16421200	-0.64260400	N	-1.95176000	-1.01743100	-0.57297200
C	-1.77426500	3.74846900	-0.38212500	N	1.13374000	3.13438800	0.54603100
C	2.45061200	1.10454900	0.15911600	H	-1.50149100	-1.85190200	-0.93441100
C	0.87200100	-1.47868600	-0.13968200	H	-3.01875300	-1.02514500	-0.71510500
H	-3.81843800	2.14525900	-0.62165500	H	2.19140200	3.24442400	0.37692600

H	0.67302500	4.01710500	0.74117800	H	0.72030100	-1.78319900	-1.39351100
C	-3.32708800	1.12412600	0.62069400	C	4.36268800	4.26408100	0.98518500
C	-1.54144900	3.53308200	1.18403300	C	5.56881200	4.88334000	0.68977300
C	2.54349100	0.73080800	0.20475300	C	5.88181800	5.12926800	-0.64109100
C	0.75395900	-1.66811500	-0.36760000	C	4.97702500	4.74758800	-1.62356800
H	-3.68102700	1.97986200	1.18417300	C	3.79419900	4.13462400	-1.23518200
H	-3.83428900	1.13132200	-0.34701100	N	3.48742800	3.89320000	0.04417200
H	-3.64310000	0.22370700	1.14907700	H	6.81451300	5.61039100	-0.90793300
H	-1.42381400	4.29260100	0.40428000	H	4.08492000	4.05581100	2.01260300
H	-2.59271500	3.51052400	1.44495500	H	6.24326600	5.16432100	1.48771200
H	-0.99094900	3.86541900	2.06725800	H	5.17918100	4.91971300	-2.67242100
H	2.94400800	1.29784800	-0.63881100	H	3.06305400	3.82424500	-1.97359100
H	2.94375600	1.17516600	1.11700100	C	-6.57037600	-2.71190000	-1.26727100
H	2.92640700	-0.28017600	0.12906000	C	-5.33618800	-2.33346300	-0.76014900
H	1.79882100	-1.78989300	-0.10650500	C	-4.91879700	-0.98193000	-2.57214300
H	0.19359200	-2.42622900	0.18320300	C	-6.13653300	-1.30457700	-3.15295300
H	0.66253900	-1.88531300	-1.43668500	C	-6.97840600	-2.18637400	-2.48686800
C	4.54711200	4.08687200	1.19565100	H	-7.19351600	-3.40283600	-0.71538200
C	5.79431500	4.68099100	1.07269300	H	-4.98247200	-2.72208100	0.18829500
C	6.22521400	5.06842100	-0.18990100	H	-4.23354100	-0.29855600	-3.06132800
C	5.39320800	4.84816400	-1.28033700	H	-6.41353500	-0.87251800	-4.10524300
C	4.16149600	4.24792900	-1.06570800	H	-7.93614600	-2.46011700	-2.91145300
N	3.74341300	3.87095000	0.14802100	N	-4.52283300	-1.48291900	-1.39641800
H	7.19330400	5.53509800	-0.32187300	C	0.28274600	6.60504200	1.90899300
H	4.17392400	3.77189800	2.16376100	C	-0.32714100	6.41443300	-0.29563400
H	6.40944000	4.83458200	1.94913700	C	-0.50963000	7.78497300	-0.41400700
H	5.68841300	5.13508300	-2.28073400	C	-0.27821200	8.58494100	0.69783500
H	3.48296200	4.06026600	-1.89032600	C	0.12647600	7.98361400	1.88290100
C	-6.63422000	-2.60810200	-0.73964100	H	0.59766300	6.10114800	2.81614800
C	-5.36578800	-2.18345600	-0.37287200	H	-0.49756400	5.75859000	-1.14232300
C	-5.07576100	-1.07514600	-2.36683800	H	-0.82509600	8.21019900	-1.35754300
C	-6.33218100	-1.45507800	-2.81430500	H	-0.41034800	9.65824100	0.64170700
C	-7.12649500	-2.23566400	-1.98400800	H	0.31879400	8.56756000	2.77317700
H	-7.21816300	-3.21646200	-0.06208500	N	0.06065400	5.82871000	0.84275600
H	-4.94542200	-2.45450400	0.58902400				
H	-4.42544500	-0.46669800	-2.98516000				
H	-6.67556700	-1.14397200	-3.79179700				
H	-8.11282700	-2.54945600	-2.30200800				
N	-4.59857800	-1.42865800	-1.16783900				
P ²⁺ (Pyridine) ₃							
C	-1.23173300	-0.19328800	0.04308900				
C	0.23337600	-0.33250300	0.11670100				
C	0.95523700	0.73371000	0.52202600				
C	0.22843800	1.98933800	0.79915300				
C	-1.21505400	1.97828700	1.10735700				
C	-1.93945400	0.91104000	0.70681800				
N	-1.90847600	-1.09797300	-0.58829800				
N	0.86177800	3.11104400	0.76056200				
H	-1.40536000	-1.86036700	-1.02894400				
H	-2.96072800	-1.12260900	-0.777110900				
H	1.88055600	3.21012800	0.50212600				
H	0.40159300	4.05349600	0.87958000				
C	-3.42148600	0.78130600	0.87824600				
C	-1.78804100	3.17319300	1.80736200				
C	2.44655000	0.74698800	0.66220700				
C	0.82459400	-1.64259100	-0.31267300				
H	-3.83256600	1.58473800	1.47932900				
H	-3.92993500	0.80301600	-0.08806200				
H	-3.67332700	-0.16719400	1.35686500				
H	-2.02519500	3.97062200	1.09851600				
H	-2.70052800	2.92101300	2.33922000				
H	-1.08146700	3.57677000	2.53169600				
H	2.92419800	1.19493200	-0.21277300				
H	2.74680600	1.32983600	1.53310100				
H	2.84521200	-0.25579600	0.77996400				
H	1.88443500	-1.70092000	-0.09181400				
H	0.33411900	-2.48136000	0.18655300				
P ²⁺ (Pyridine) ₄							
C	-1.40258400	-0.05330600	0.52949100				
C	-0.02182600	-0.32465400	0.50873400				
C	0.88985100	0.72192100	0.30284800				
C	0.41870700	2.04048700	0.16052800				
C	-0.96222200	2.31142400	0.17920800				
C	-1.87374800	1.26512500	0.38614700				
N	-2.31767200	-1.09806800	0.76563100				
N	1.33316500	3.08662300	-0.07318900				
H	-2.00342600	-2.03173300	0.52524700				
H	-3.25593200	-0.95915700	0.40593100				
H	2.27347600	2.94346500	0.27918300				
H	1.02082500	4.01816400	0.17890400				
C	-3.36304500	1.49241500	0.49419200				
C	-1.40115900	3.73754600	-0.05614200				
C	2.37919700	0.49488700	0.19510700				
C	0.41638200	-1.75171400	0.73986100				
H	-3.62550200	2.54288900	0.58351400				
H	-3.90697600	1.08942000	-0.36713000				
H	-3.76502600	0.98405900	1.37570100				
H	-0.89038300	4.15749800	-0.92769800				
H	-2.46843500	3.82661200	-0.23872200				
H	-1.15580800	4.39068700	0.78838600				
H	2.78136400	1.00174700	-0.68718100				
H	2.92282000	0.89942500	1.05588600				
H	2.64218000	-0.55558100	0.10762300				
H	1.48448200	-1.84311500	0.91607900				
H	-0.08984300	-2.17311800	1.61332800				
H	0.16593900	-2.40265900	-0.10507400				
C	5.34766800	3.93400000	0.01286900				
C	6.63145800	4.37017400	0.31795000				
C	7.02315900	4.40121000	1.65032700				
C	6.11577300	3.99513700	2.62062100				

Appendix C

C	4.85433500	3.57494200	2.21581200	H	0.59975000	-2.45217500	0.19528500
N	4.46629100	3.54081600	0.93744300	H	1.30797600	-1.94399200	-1.33262400
H	8.01579400	4.73510100	1.92688700	H	1.52622700	4.19070800	-0.64067100
H	5.01164700	3.89861800	-1.01850000	O	1.89303400	4.67550400	-1.41163800
H	7.30378400	4.67678000	-0.47307300	C	2.44738600	5.90077500	-0.95521600
H	6.37541100	4.00201500	3.67148000	H	2.85241400	6.42594600	-1.82108100
H	4.12315200	3.25142600	2.94983200	H	1.69278100	6.54268000	-0.48606400
C	-7.03732000	-2.07963300	-1.98223200	H	3.26161800	5.74086900	-0.23883400
C	-5.78851900	-1.63881300	-1.56055600	P(MeOH) ₂			
C	-6.32914500	-1.94339000	0.63955400	C	-0.81538100	-0.19359500	-0.72428400
C	-7.60233500	-2.39795400	0.31739400	C	0.53085200	-0.21567800	-0.31974600
C	-7.96344600	-2.46719500	-1.02214700	C	1.09485000	0.93541700	0.24872200
H	-7.27304800	-2.11633300	-3.03809400	C	0.29228600	2.07122200	0.42909800
H	-5.04313400	-1.32935000	-2.28628700	C	-1.05086100	2.09746800	0.02689500
H	-6.01674800	-1.87838300	1.67688300	C	-1.61630600	0.94702400	-0.54113600
H	-8.29011100	-2.68912700	1.10092900	N	-1.39232400	-1.36118600	-1.26324200
H	-8.94702600	-2.81624300	-1.31203400	N	0.87530700	3.25508200	0.97900000
N	-5.43000200	-1.56758400	-0.27510700	H	-0.73848100	-1.98464500	-1.71360600
C	-2.62662300	-6.25324000	-1.27472600	H	-2.18598400	-1.19954400	-1.86587200
C	-2.89512300	-7.05832500	-0.17503400	H	1.64044300	3.05524400	1.61162900
C	-2.85182500	-6.49080700	1.09205500	H	0.20195600	3.82481500	1.47666900
C	-2.54194900	-5.14064300	1.20480400	C	-3.06560100	0.86287500	-0.95666000
C	-2.32654500	-4.91337900	-1.05959900	C	-1.82546500	3.38050300	0.21907200
H	-2.64824100	-6.65089700	-2.28127800	C	2.54341500	1.01456100	0.67179900
H	-3.13349000	-8.10717200	-0.30299900	C	1.30026000	-1.50130200	-0.50769400
H	-3.05375300	-7.07828700	1.97853400	H	-3.65097600	1.71741700	-0.63107600
H	-2.50065300	-4.66772400	2.18077100	H	-3.17483600	0.79333500	-2.04564100
H	-2.11272100	-4.25833100	-1.89816700	H	-3.53904200	-0.02816300	-0.53363300
N	-2.28252400	-4.35615500	0.15437300	H	-1.26040900	4.23786700	-0.15629600
C	1.09113100	7.23754600	-0.31672000	H	-2.77819400	3.37999900	-0.30160900
C	1.57704600	6.74975100	1.86301900	H	-2.03689800	3.57507600	1.27732200
C	1.80103600	8.08738400	2.16657000	H	3.02162100	1.90961100	0.26472900
C	1.65623100	9.03059400	1.15715900	H	2.64727000	1.06402600	1.76225700
C	1.29352300	8.59722800	-0.11182100	H	3.12882600	0.16463200	0.33477100
H	0.80696500	6.86774900	-1.29675200	H	2.26562200	-1.49484200	-0.01092100
H	1.68340300	5.98879300	2.62953400	H	0.74067600	-2.35071800	-0.10485700
H	2.08211000	8.37741000	3.17089600	H	1.48423200	-1.71577800	-1.56733600
H	1.82255700	10.08238000	1.35555300	H	1.59794200	4.36053200	-0.33577000
H	1.16878100	9.29491400	-0.93000000	O	1.98475700	4.93953400	-1.03652200
N	1.22779600	6.32103300	0.64637000	C	1.82155400	6.30367200	-0.65883300
P(MeOH)				H	2.26456800	6.91999400	-1.44095400
C	-0.95012600	-0.33228000	-0.57264700	H	0.76348900	6.56689300	-0.56611800
C	0.40119800	-0.33906800	-0.18527500	H	2.32574800	6.52487500	0.28737000
C	0.98380500	0.84433300	0.29061200	O	4.48194500	4.16706600	-1.97064500
C	0.19526700	1.99954600	0.39747700	H	3.60187700	4.43272600	-1.63374700
C	-1.15382000	2.00972500	0.01302600	C	4.36023700	3.82211200	-3.34291600
C	-1.73750300	0.82707500	-0.46327500	H	5.34646500	3.52270800	-3.70012700
N	-1.54613600	-1.53075800	-1.01625200	H	3.67029400	2.98428200	-3.49486000
N	0.79869900	3.21290000	0.84447100	H	4.01736600	4.66855600	-3.94901600
H	-0.90439800	-2.19171600	-1.42915500	P(MeOH) ₃			
H	-2.34553600	-1.40449000	-1.61985600	C	-1.19988200	-0.30838500	-0.51486800
H	1.57085400	3.05786600	1.48048500	C	0.20076700	-0.30138100	-0.40246500
H	0.14097600	3.83745000	1.29388000	C	0.86091500	0.90072600	-0.11046000
C	-3.19258500	0.72731500	-0.85469900	C	0.10554200	2.06300500	0.10546400
C	-1.91167000	3.31226000	0.12222100	C	-1.29413600	2.05829800	-0.00463200
C	2.43882300	0.94079700	0.68663100	C	-1.95520700	0.85796100	-0.30303200
C	1.15493800	-1.64335400	-0.28918500	N	-1.86542000	-1.52399000	-0.77879300
H	-3.76564600	1.61079000	-0.59027700	N	0.77821200	3.29042400	0.38030000
H	-3.31509100	0.57526400	-1.93383100	H	-1.31495500	-2.20229500	-1.28508500
H	-3.66998600	-0.12336000	-0.35912500	H	-2.76967100	-1.42116300	-1.21585600
H	-1.35522500	4.12836600	-0.34704100	H	1.64636200	3.18948700	0.90258100
H	-2.88443500	3.27726500	-0.35861100	H	0.19407400	3.94633300	0.88352600
H	-2.07978000	3.59946100	1.16704600	C	-3.45883500	0.74664000	-0.39150100
H	2.91922700	1.79531800	0.20187100	C	-2.02683700	3.36497500	0.19390900
H	2.55848500	1.07835700	1.76790600	C	2.36609900	1.00200000	-0.02987200
H	3.01123500	0.05986500	0.41279000				
H	2.13391400	-1.60708600	0.17889100				

C	0.93060800	-1.61088300	-0.58577200	H	3.52805600	5.07375100	-1.07012400
H	-3.97193000	1.63708000	-0.04110900	C	5.48506300	5.39655500	-1.09307600
H	-3.79521200	0.56412500	-1.41924000	H	6.17044200	6.07598400	-0.58682400
H	-3.82241100	-0.08924600	0.21360300	H	5.78514700	4.36728300	-0.87348800
H	-1.57855200	4.16025100	-0.40811000	H	5.55912200	5.56532800	-2.17112900
H	-3.07340400	3.30935200	-0.08955000	O	3.63805300	5.53751600	2.05655500
H	-1.99353000	3.69756500	1.23821800	C	4.21058900	6.63950100	2.75544300
H	2.72590000	1.87981800	-0.57179000	H	3.86402500	5.60212000	1.10033100
H	2.71478700	1.10532900	1.00349400	H	3.84313000	7.59650400	2.37202900
H	2.86702000	0.13799200	-0.45717500	H	3.92659200	6.55168500	3.80402200
H	1.97085600	-1.56051400	-0.27796900	H	5.30256800	6.62711000	2.68842400
H	0.46139700	-2.40156600	0.00689600	O	1.01216400	4.75218500	2.43114000
H	0.91757700	-1.94605000	-1.63001400	H	1.93573600	5.06129600	2.31592300
H	1.40564600	4.23494800	-1.07813100	C	0.16841400	5.88415800	2.59900500
O	1.86432900	4.75483300	-1.78628000	H	0.20030000	6.54859000	1.72858300
C	0.96908000	5.72485100	-2.32490000	H	-0.85340600	5.52345800	2.71925100
H	1.51537800	6.30351300	-3.06947200	H	0.43767800	6.46141000	3.49008800
H	0.11471300	5.24669400	-2.81277000				
H	0.60038100	6.40734600	-1.55279900		P ⁺⁺ (MeOH)		
O	4.12978900	5.49579000	-0.44854400	C	-1.09862600	-0.39185200	-0.18687200
H	3.34314300	5.28391900	-1.00137600	C	0.31116100	-0.52008300	0.04503100
C	5.31583500	5.21978000	-1.18935600	C	1.04478600	0.61017600	0.31967900
H	6.16769600	5.44656400	-0.54851500	C	0.37310700	1.87929200	0.36997200
H	5.37112200	4.16777900	-1.48639300	C	-1.04104100	2.00399500	0.13987100
H	5.37773700	5.84423300	-2.08552600	C	-1.77212900	0.87413100	-0.14083900
O	3.39326600	4.08100500	1.83761600	N	-1.81493800	-1.49698100	-0.45650300
C	4.47198100	3.50483900	2.56271400	N	1.08191700	2.98428000	0.64018300
H	3.74770100	4.57652200	1.07048300	H	-1.38925100	-2.40797900	-0.49500000
H	5.15275100	4.26947700	2.95208200	H	-2.80709300	-1.45765700	-0.61992000
H	4.05027800	2.95806000	3.40661600	H	2.08668300	3.00036700	0.80420600
H	5.04742600	2.80319900	1.94905100	H	0.62756000	3.88223800	0.68025000
	P(MeOH) ₄			C	-3.25368900	0.87479500	-0.40650600
C	-1.57119100	-0.41346800	-0.95574300	C	-1.63402200	3.38486100	0.22272400
C	-0.20895200	-0.74281000	-0.84738900	C	2.52615100	0.60447900	0.57917500
C	0.70293200	0.23824600	-0.43255800	C	0.89692100	-1.90475100	-0.02879900
C	0.23275400	1.52021500	-0.10292500	H	-3.68885600	1.86664300	-0.36862900
C	-1.12530500	1.85132800	-0.21650400	H	-3.47463900	0.46634900	-1.39740000
C	-2.03881300	0.86906000	-0.62552200	H	-3.78524900	0.26246100	0.32843700
N	-2.49534400	-1.40854900	-1.33771300	H	-1.17308500	4.05592100	-0.50844400
N	1.16947600	2.52088300	0.29446200	H	-2.70164600	3.39711800	0.03642200
H	-2.10559600	-2.14819400	-1.90376800	H	-1.47787400	3.82038600	1.21436300
H	-3.33764200	-1.05515400	-1.76803800	H	3.04997500	1.25600200	-0.12502200
H	1.99216500	2.12197200	0.72989900	H	2.74727200	0.97327600	1.58480300
H	0.79786700	3.21836300	0.93664600	H	2.96484600	-0.38293400	0.49272500
C	-3.52514300	1.12429300	-0.70740200	H	1.96152900	-1.92377400	0.17335200
C	-1.55621700	3.26428500	1.0228600	H	0.42170900	-2.57104400	0.69755200
C	2.18871400	-0.02137700	-0.33418900	H	0.75061100	-2.34120300	-1.02160200
C	0.19905800	-2.16106700	-1.16918400	O	3.81551500	3.83066100	1.15638000
H	-3.81821300	2.05610400	-0.23247500	H	4.38565600	3.45841600	1.83794100
H	-3.87926000	1.16312200	-1.74469700	C	4.62937800	4.34826400	0.09796600
H	-4.08331100	0.32465700	-0.21183100	H	5.23468800	3.56224500	-0.36050900
H	-0.83178300	3.98995100	-0.27227500	H	3.95258000	4.75645800	-0.65081400
H	-2.51413400	3.51574900	-0.34562200	H	5.28280100	5.14628100	0.45820400
H	-1.64502500	3.43247300	1.18115700				
H	2.75828300	0.77021200	-0.82860100		P ⁺⁺ (MeOH) ₂		
H	2.52958500	-0.05757000	0.70734500	C	-1.08501800	-0.36927100	-0.15563000
H	2.48405200	-0.95714200	-0.79902700	C	0.34329200	-0.47965600	-0.08897900
H	1.22517900	-2.38062300	-0.89061800	C	1.08700100	0.65095500	0.15594000
H	-0.43517300	-2.87696500	-0.63794700	C	0.40833200	1.90601000	0.32746900
H	0.10044600	-2.38242600	-2.23879900	C	-1.02507400	2.01177400	0.26406200
H	1.91829400	3.46916200	-1.08980700	C	-1.76720700	0.88007300	0.02199900
O	2.39761900	3.98134900	-1.79123400	N	-1.81069800	-1.47655500	-0.39145200
C	1.46462100	4.49055300	-2.74126200	N	1.12628500	3.01468400	0.55185400
H	2.02337500	5.06056400	-3.48335000	H	-1.37733600	-2.37559900	-0.51947000
H	0.93613600	3.67899300	-3.24938700	H	-2.81527000	-1.45055000	-0.44187300
H	0.73095900	5.15338600	-2.27215900	H	2.14596900	3.05534800	0.60230400
O	4.16875500	5.67298100	-0.61907400	H	0.66055400	3.89992700	0.67042800

C	-3.26945900	0.86273000	-0.07263700	H	5.96311200	1.39958200	2.85412900
C	-1.62530100	3.37669000	0.46979400	H	7.41622100	2.41923000	2.93821500
C	2.58728400	0.66020700	0.25559200	O	2.05433300	5.71088500	1.24674000
C	0.93727500	-1.84706100	-0.29841800	H	2.92010800	5.25860000	1.24234500
H	-3.71215700	1.84302100	0.06023800	C	1.94544400	6.51683000	2.41635200
H	-3.59691800	0.49326600	-1.04919500	H	2.70898500	7.30061300	2.43584600
H	-3.70406500	0.20833500	0.68923300	H	0.96367900	6.98944000	2.39912800
H	-1.27248600	4.08113600	-0.28978100	H	2.02896000	5.91898800	3.32965300
H	-2.70799400	3.37251800	0.42097200				
H	-1.35102100	3.78236300	1.44825600				
H	3.02742100	1.28204500	-0.52867000				
H	2.91233700	1.07591900	1.21247300	C	-1.08138100	-0.19522100	-0.34131500
H	3.02056600	-0.32954100	0.16812000	C	0.33014600	-0.44937800	-0.37088800
H	2.01978300	-1.84925900	-0.24576800	C	1.19285500	0.55327600	0.00420000
H	0.57662900	-2.55348900	0.45563400	C	0.65076600	1.81952400	0.41571200
H	0.66468900	-2.24553300	-1.28040400	C	-0.76462500	2.07083300	0.44302500
O	3.84918600	3.86412000	0.77597300	C	-1.62606800	1.06729300	0.06772100
H	4.31876200	3.83477300	1.63337100	N	-1.92472500	-1.17577600	-0.71096800
C	4.80254000	3.95396400	-0.27934800	N	1.48770100	2.79444000	0.78643900
H	5.45358900	3.07472200	-0.31074900	H	-1.59080200	-2.07626100	-1.01077800
H	4.25157300	4.01331800	-1.21779000	H	-2.92216400	-1.04436300	-0.70720900
H	5.42148200	4.85068300	-0.18153800	H	2.49580100	2.68855300	0.79547100
O	5.12166300	3.80647800	3.24841200	H	1.17627300	3.71243500	1.08700300
H	5.40459700	4.67133800	3.56598400	C	-3.12519900	1.20645300	0.05659000
C	6.13218900	2.83754800	3.55700700	C	-1.20901200	3.43723700	0.88923700
H	6.29036400	2.76948600	4.63538000	C	2.69092600	0.41270600	0.01482700
H	5.77171000	1.87852900	3.18977200	C	0.77320500	-1.81752200	-0.81601400
H	7.07678700	3.07778400	3.06358800	H	-3.45977800	2.18599400	0.37806800
				H	-3.52780500	1.04330700	-0.94788500
				H	-3.59283400	0.47397200	0.72175900
				H	-0.79061100	4.21465700	0.24344800
				H	-2.28642800	3.55589400	0.87790100
				H	-0.87012900	3.64498700	1.90837900
				H	3.15810700	1.15468100	-0.63932700
				H	3.09124800	0.56811800	1.02104700
				H	3.02571600	-0.56334200	-0.31724800
				H	1.85084400	-1.93393300	-0.81226400
				H	0.36467600	-2.59418700	-0.16220900
				H	0.43083600	-2.02988400	-1.83342800
				O	4.22412300	3.82726800	1.27720000
				H	4.68338400	3.53690000	2.10024000
				C	5.20055900	4.14484300	0.28392900
				H	5.80908000	3.27114000	0.03547200
				H	4.66991000	4.46855600	-0.61084800
				H	5.85681300	4.95420100	0.61586000
				O	5.42430800	3.01210600	3.56618400
				H			

C	0.38870000	1.89532700	0.45446800
C	-1.06704300	2.03111000	0.24731300
C	-1.76189300	0.93484800	-0.12617100
N	-1.65942000	-1.35229700	-0.75551000
N	1.07952700	2.97362000	0.62426600
H	-1.20826000	-2.25036100	-0.88379200
H	-2.63186500	-1.29940700	-1.03476300
H	2.11185100	3.03252600	0.75406800
H	0.61489600	3.87539800	0.61087200
C	-3.22976500	0.91036900	-0.42637200
C	-1.66028300	3.39442400	0.43002300
C	2.51842700	0.58923100	0.89148000
C	0.94461400	-1.89022200	0.02612900
H	-3.71340800	1.85001600	-0.18867400
H	-3.40574900	0.71957400	-1.48944600
H	-3.73516400	0.13057100	0.14845500
H	-1.32515800	4.07590900	-0.35836900
H	-2.74292000	3.37736000	0.39546000
H	-1.37353500	3.81996800	1.39435200
H	3.13541300	1.13785800	0.17564500
H	2.63553400	1.06936900	1.86520400
H	2.92033500	-0.41374500	0.96836400
H	1.95823300	-1.94498200	0.40378100
H	0.34194800	-2.59013500	0.61009500
H	0.96979600	-2.24243300	-1.00961900
O	3.68626700	3.73115400	0.93329000
H	4.25322600	3.49228800	1.67517800
C	4.49456600	4.18099500	-0.16559100
H	5.16217700	3.38947400	-0.51132100
H	3.81250600	4.45247700	-0.96866100
H	5.07801100	5.05730700	0.12086300

 $P^{2+}(\text{MeOH})_2$

C	-1.20491400	-0.17634600	-0.17303100
C	0.20518000	-0.41596500	0.17439200
C	0.96602400	0.64620100	0.52086700
C	0.34274900	1.97939000	0.50779700
C	-1.10969000	2.18645900	0.36014600
C	-1.87126400	1.12519700	0.01909800
N	-1.90514200	-1.15054400	-0.65657500
N	1.09470000	3.02390500	0.63587500
H	-1.56215800	-2.10909900	-0.86706900
H	-2.87964200	-1.00116500	-0.89367800
H	2.13174200	3.02838200	0.71745800
H	0.67647300	3.94761500	0.63058600
C	-3.34940800	1.17884900	-0.22197500
C	-1.62661100	3.57943700	0.55852400
C	2.41135600	0.57315400	0.90411400
C	0.69493100	-1.82881200	0.10357200
H	-3.77440700	2.13869400	0.04533600
H	-3.57701500	1.01246300	-1.27950800
H	-3.87166300	0.41781000	0.36262800
H	-1.29912200	4.23708800	-0.25290500
H	-2.70925500	3.61536200	0.57863500
H	-1.27213900	3.99967200	1.50258500
H	3.03988700	1.06176600	0.15543400
H	2.58062400	1.07763200	1.85770200
H	2.75744800	-0.44825000	1.00676800
H	1.71755800	-1.92735500	0.44708200
H	0.07237700	-2.48285500	0.71770400
H	0.65631400	-2.20354400	-0.92234900
O	3.76235700	3.64147500	0.79857900
H	4.36364500	3.35874100	1.49667900
C	4.51907400	4.03432700	-0.35708600
H	5.10157900	3.19785300	-0.74807100
H	3.80182700	4.35561700	-1.10961700
H	5.18316500	4.86613200	-0.11699600
O	-1.57411200	-3.74482800	-1.48750500

C	-1.47703100	-4.05521800	-2.88638500
H	-0.43771200	-4.20697400	-3.18418200
H	-2.06252600	-4.94475600	-3.12416500
H	-1.88518400	-3.20422600	-3.42800700
H	-1.23541200	-4.48312900	-0.96882800

 $P^{2+}(\text{MeOH})_3$

C	-1.23349000	-0.35214400	-0.09992500
C	0.20281700	-0.60307000	0.10308500
C	0.98639600	0.43942900	0.45583900
C	0.35764900	1.76283300	0.60908000
C	-1.10169800	1.96491800	0.60015200
C	-1.88527100	0.92243300	0.24938500
N	-1.96897100	-1.29439600	-0.59622200
N	1.11862500	2.79248300	0.76940800
H	-1.64036100	-2.22869000	-0.90980600
H	-2.96106000	-1.13867600	-0.73485900
H	2.14159900	2.74341600	0.77691400
H	0.78438800	3.76453000	0.88823800
C	-3.38023000	0.97658800	0.15144600
C	-1.60257600	3.33218100	0.95185600
C	2.46377700	0.35818300	0.69338900
C	0.68763600	-2.00365700	-0.10805500
H	-3.78206600	1.90522500	0.53849000
H	-3.70696400	0.89722300	-0.89006700
H	-3.84076200	0.16279700	0.71671700
H	-1.35743100	4.04866900	0.16254400
H	-2.67766400	3.35349600	1.08561400
H	-1.14765900	3.68814800	1.87819500
H	3.01409200	0.91449500	-0.07070500
H	2.72287400	0.77882800	1.66802900
H	2.82752300	-0.66188000	0.67126600
H	1.74020200	-2.11403100	0.12319000
H	0.13228600	-2.70059700	0.52368000
H	0.54501600	-2.31406600	-1.14568700
O	3.70212500	4.00078800	0.91958100
H	4.21122900	3.89526000	1.73215100
C	4.61127300	4.17984500	-0.18125700
H	5.25856100	3.30878700	-0.29616200
H	4.00249500	4.29655400	-1.07537200
H	5.21906400	5.07493800	-0.03956200
O	-1.68827500	-3.81915900	-1.64678000
C	-1.61785500	-4.05356500	-3.06150400
H	-0.58910400	-4.23440100	-3.37925500
H	-2.24495900	-4.90113800	-3.34281200
H	-1.99132800	-3.15549300	-3.54950500
H	-1.36801300	-4.59587500	-1.17468600
O	1.24541300	5.46520400	1.27249000
C	0.83263000	6.76448700	0.83973900
H	2.20415000	5.35758400	1.15888700
H	1.32542800	7.54412000	1.42486500
H	1.04622400	6.91743300	-0.22102000
H	-0.24226600	6.82950800	0.99881800

 $P^{2+}(\text{MeOH})_4$

C	-1.01782300	-0.40445600	-0.31871800
C	0.44834800	-0.53773300	-0.27810500
C	1.17516300	0.53332300	0.11020100
C	0.46041300	1.76357500	0.48957900
C	-1.00620500	1.84168200	0.59975500
C	-1.73272900	0.77000500	0.21594100
N	-1.71964000	-1.35520100	-0.84421700
N	1.15187300	2.82088300	0.75657200
H	-1.36426300	-2.24337800	-1.27706300
H	-2.72898100	-1.26543800	-0.87908700
H	2.17368400	2.85318100	0.71077600
H	0.75475300	3.73515700	1.03227100

C	-3.22967800	0.69780200	0.26453300	H	0.64450700	-2.47514300	-0.73790000
C	-1.58070700	3.12588400	1.11495100	H	1.10721100	-1.63286400	-2.21114800
C	2.67187900	0.57371400	0.16771800	H	1.52399900	4.25051000	-0.34294600
C	1.02734900	-1.85456300	-0.69241100	O	1.67987500	4.79392000	-1.14286200
H	-3.66032900	1.52796300	0.81143100	C	2.28599400	6.04539700	-0.77657500
H	-3.65710000	0.71956900	-0.74263500	C	3.64038900	5.78774400	-0.10606200
H	-3.56320800	-0.21889700	0.75614800	H	3.51301600	5.20664100	0.81088300
H	-1.36421400	3.94774300	0.42682400	H	4.29723900	5.23014100	-0.77723100
H	-2.65675600	3.07939800	1.23089900	H	4.13363000	6.72690600	0.15626700
H	-1.15183900	3.38310700	2.08594000	C	2.47214300	6.80973600	-2.08541100
H	3.06812000	1.28550300	-0.56233200	H	3.11325800	6.24682300	-2.76742900
H	3.01645700	0.87952900	1.15849100	H	1.50849700	6.97094700	-2.57368100
H	3.11863300	-0.38877200	-0.04940600	H	2.93289000	7.78294100	-1.90502100
H	2.09838700	-1.89940300	-0.53573800	C	1.35572000	6.81493500	0.16817500
H	0.57319300	-2.66954300	-0.12599900	H	1.77496200	7.79151100	0.42234900
H	0.83919400	-2.04745300	-1.75119400	H	0.38193600	6.97015200	-0.30126100
O	3.64836900	4.20794600	1.00024600	H	1.20430900	6.26206300	1.09872100
H	4.18655800	4.03659200	1.78231500				
C	4.51112200	4.59182400	-0.08531800				
H	5.21445800	3.79201400	-0.32292700				
H	3.87099500	4.77558500	-0.94560600	C	-0.84200900	0.06672500	-0.11662800
H	5.05801900	5.50408800	0.15837100	C	0.54111200	0.07061300	0.12159300
O	-1.35260000	-3.73553200	-2.04381500	C	1.19447200	1.29303600	0.33297400
C	-1.23060900	-3.91067300	-3.45664000	C	0.44274800	2.47814300	0.33578000
H	-0.18933200	-4.06876100	-3.74975900	C	-0.94038000	2.47425500	0.09756300
H	-1.83294700	-4.75634200	-3.79657900	C	-1.59373700	1.25183500	-0.11382500
H	-1.59779200	-3.00345600	-3.93474400	N	-1.50961000	-1.17619200	-0.30084800
H	-1.02666900	-4.53623500	-1.57738000	N	1.11033000	3.72106700	0.51999500
O	1.11220600	5.41991800	1.60242800	H	-0.91729400	-1.89007600	-0.70500700
C	0.61461900	6.70963600	1.23395800	H	-2.34625400	-1.09814200	-0.86457700
H	2.07070900	5.37321600	1.44751600	H	1.94701000	3.64303700	1.08367100
H	1.08988500	7.49416000	1.82702100	H	0.51801700	4.43493700	0.92418300
H	0.77597600	6.91013700	0.17176500	C	-3.08538400	1.14785300	-0.32972400
H	-0.45480700	6.71242600	1.43746400	C	-1.65953800	3.80256300	0.06844500
O	-0.48460500	-5.92834300	-0.66458700	C	2.68612300	1.39699300	0.54886900
H	0.41731700	-6.21933600	-0.84001100	C	1.26028700	-1.25768700	0.15072700
C	-1.33493300	-7.07650400	-0.53168300	H	-3.60916700	2.07232800	-0.10598600
H	-1.01864400	-7.69707300	0.30895800	H	-3.33029200	0.88042000	-1.36457100
H	-2.33939000	-6.70359900	-0.34139300	H	-3.51873600	0.37506800	0.31066500
H	-1.34066100	-7.67322800	-1.44634100	H	-1.12979900	4.51851400	-0.56568400
				H	-2.67073300</		

H	3.57207500	5.30240500	-4.10966400
H	2.06996800	6.22762400	-4.26685200
H	3.57413200	7.04980800	-3.82280100
H	2.39614800	7.97842200	-1.69098200
H	0.92109200	7.14191600	-2.20411000
H	1.60150000	6.84046700	-0.59694200
H	4.59937700	6.61767500	-1.46801200
H	3.77241700	5.50437400	-0.37255800
H	4.57298700	4.88276000	-1.82514300

P(*t*-BuOH)₃

C	-1.28997200	-0.29201000	-0.66673400
C	0.09043300	-0.29053900	-0.92458800
C	0.85472700	0.83312100	-0.58007300
C	0.23573900	1.91442900	0.06592000
C	-1.14427000	1.91010700	0.33428000
C	-1.91320700	0.79396300	-0.02794700
N	-2.05224100	-1.43429100	-0.99391700
N	1.01240700	3.05954000	0.40317200
H	-1.68096800	-1.97767200	-1.75978500
H	-3.03338800	-1.25255300	-1.14823600
H	1.95264600	2.85362100	0.73676900
H	0.56343400	3.63590600	1.10251800
C	-3.39312300	0.68268000	0.25338400
C	-1.74062200	3.12573100	1.00638000
C	2.32999500	0.92711200	-0.89134900
C	0.69546300	-1.52313600	-1.55384100
H	-3.76979800	1.48243900	0.88342200
H	-3.98463500	0.69596100	-0.67000400
H	-3.62232600	-0.25847400	0.76230300
H	-1.47445400	4.04305800	0.47370700
H	-2.82473700	3.09619300	1.05124000
H	-1.37977200	3.23822200	2.03543500
H	2.59403500	1.93564100	-1.21347500
H	2.95159000	0.70122700	-0.01810600
H	2.62890000	0.24988000	-1.68767200
H	1.78121100	-1.15969900	-1.52389900
H	0.36428500	-2.42576400	-1.03200300
H	0.39970000	-1.63714900	-2.60389100
H	1.55105800	4.31369200	-1.00104300
O	1.99708200	4.89603100	-1.65796000
C	1.05442900	5.84870600	-2.19768100
O	4.64675500	4.94587500	-0.63210500
H	3.79417500	5.00442500	-1.10939700
C	5.73691400	4.76344300	-1.56446700
O	3.89685600	3.27482000	1.55701600
C	4.15797900	3.75681800	2.89009400
H	4.26800100	3.88862100	0.89264900
C	5.66940200	3.78412800	3.13930600
C	3.55868300	5.15659000	3.06112500
C	3.47872600	2.76029300	3.82651100
C	6.99307200	4.62033000	-0.70979900
C	5.49817100	3.49837900	-2.39341100
C	5.83937000	5.99479300	-2.46840200
C	1.80242300	6.61284800	-3.28655200
C	-0.13681100	5.09288500	-2.79299100
C	0.59909900	6.80313100	-1.08895900
H	1.45907000	7.31318000	-0.65022900
H	-0.08488900	7.55888100	-1.48237700
H	0.08056000	6.26032300	-0.29551400
H	0.19876100	4.40927200	-3.57567900
H	-0.65026800	4.50870000	-2.02587200
H	-0.85920400	5.78677900	-3.22879700
H	2.16295100	5.92903300	-4.05775700
H	1.14540500	7.34626800	-3.75777000
H	2.65893700	7.14352900	-2.86626400
H	6.68499800	5.90346800	-3.15404200
H	4.93312400	6.11420200	-3.06577400

H	5.97859500	6.89680700	-1.86880500
H	6.32605900	3.32582300	-3.08501100
H	5.40734000	2.62680300	-1.74214600
H	4.58078500	3.58676400	-2.97976300
H	7.87393500	4.49815900	-1.34279600
H	7.13714600	5.50739400	-0.08929400
H	6.91829800	3.74930000	-0.05598800
H	5.89055400	4.10712000	4.15946700
H	6.09670700	2.78986100	2.99280600
H	6.16318600	4.47545600	2.45265400
H	4.01600800	5.86042400	2.36158900
H	2.48277500	5.13765500	2.87541600
H	3.72523800	5.53059200	4.07402900
H	3.62459600	3.04894800	4.86919600
H	2.40556100	2.71830900	3.62868600
H	3.89367700	1.75980400	3.68602900

P(*t*-BuOH)₄

C	-0.93237200	-0.32465900	-0.42377400
C	0.45417900	-0.20538500	-0.59510600
C	1.07431600	1.02411000	-0.33191600
C	0.30244800	2.09445200	0.14710100
C	-1.08626400	1.97015300	0.32851200
C	-1.70901500	0.74447000	0.04893000
N	-1.55601700	-1.58015100	-0.67096300
N	0.93114000	3.34393300	0.39702000
H	-1.07565900	-2.13010800	-1.37156800
H	-2.52687400	-1.49482300	-0.94326700
H	1.86883100	3.28348800	0.78764000
H	0.38637000	3.94050300	1.00515000
C	-3.18814700	0.50736400	0.24696100
C	-1.85002900	3.17872400	0.81799200
C	2.55134100	1.24468300	-0.55644400
C	1.22605800	-1.42263100	-1.04842200
H	-3.67891900	1.31230700	0.78506700
H	-3.71295700	0.39364300	-0.70914100
H	-3.36336900	-0.40872400	0.81762900
H	-1.64224300	4.05570700	0.19857100
H	-2.92577100	3.03507600	0.80224300
H	-1.57613100	3.44254000	1.84619500
H	2.73541000	2.23150600	-0.98425900
H	3.12157500	1.19294900	0.37757200
H	2.97969700	0.51649700	-1.24044300
H	2.30006500	-1.29927800	-0.94420300
H	0.94865400	-2.30104100	-0.45956000
H	1.02817600	-1.66642000	-2.09918900
H	1.43986100	4.48958700	-1.13308500
O	1.86736900	5.02300000	-1.84007000
C	0.89159500	5.88415600	-2.46837700
O	4.53164300	5.33421300	-0.83958600
H	3.68145900	5.27803100	-1.31977100
C	5.64104400	5.14561400	-1.74680900
O	3.58871100	4.21546200	1.61748700
C	4.33229800	4.24641700	2.85093600
H	4.11578500	4.57972400	0.88123200
O	-1.52514200	-3.09491000	1.88925900
H	-1.57322500	-2.68539700	1.00107000
C	-2.03005600	-4.44062600	1.83985000
C	0.35571000	6.88645400	-1.44122800
C	1.63036600	6.61119800	-3.58820200
C	-0.24096100	5.02720900	-3.04105400
C	5.62077800	6.24728900	-2.80974500
C	6.89910500	5.25466800	-0.89003300
C	5.54472100	3.76200900	-2.39556100
C	4.86105700	5.66245800	3.09674900
C	5.48514400	3.23952700	2.78142300
C	3.33708600	3.84582300	3.93765500
C	-3.49684500	-4.42749600	1.39451700

483

H	6.32495900	5.11046200	1.83932700
H	6.42764900	2.65218600	1.13779800
H	5.46167700	2.09201700	-0.23896200
H	6.88439900	3.11087300	-0.50491500
H	2.43381800	5.26666800	3.91233200
H	1.23139600	6.36534900	4.59734600
H	0.71032600	4.86687100	3.81122900

 $P^{++}(t\text{-BuOH})_3$

C	-1.10342700	-0.70188400	0.04753500
C	0.27055400	-0.81244900	-0.34824100
C	1.07595300	0.29909500	-0.26869500
C	0.51308300	1.53439200	0.20463400
C	-0.86709700	1.64214600	0.59416100
C	-1.67060500	0.52928400	0.51562600
N	-1.88752300	-1.79269600	-0.02252100
N	1.29257200	2.61879100	0.28417500
H	-1.53349500	-2.67792300	-0.34408500
H	-2.85601300	-1.76628000	0.24872500
H	2.27376700	2.61566100	0.03308900
H	0.95851700	3.52080500	0.60956300
C	-3.12773700	0.51575100	0.89390900
C	-1.34128700	2.98810000	1.06954700
C	2.53000400	0.30941900	-0.65306100
C	0.73990600	-2.15968300	-0.82875600
H	-3.48576100	1.48304400	1.22688600
H	-3.75148500	0.21802900	0.04542200
H	-3.31666800	-0.19333000	1.70577800
H	-1.20003900	3.74827900	0.29606000
H	-2.39078800	2.99500600	1.34069200
H	-0.77660900	3.31350900	1.94790100
H	2.71157100	1.01175200	-1.47169200
H	3.15597200	0.61997700	0.18808300
H	2.88817600	-0.66123300	-0.97643400
H	1.78168500	-2.16239100	-1.12789000
H	0.62757900	-2.91670300	-0.04625500
H	0.15760900	-2.49245500	-1.69352000
O	3.98343800	4.02456700	0.15895500
H	4.44175600	3.83128700	1.00029100
C	4.95970100	4.32375900	-0.87291800
O	5.00996600	3.64290700	2.78444900
H	5.22008700	4.49974100	3.17594300
C	5.56848400	2.59400600	3.62336000
O	1.56099400	5.40787500	0.89588000
H	2.48787500	5.22591800	0.65510100
C	1.41737500	6.74792000	1.41442100
C	-0.03768200	6.86018800	1.85983200
C	2.36635200	6.93902400	2.60053000
C	1.72294700	7.75713800	0.30402100
C	4.94637900	2.69283300	5.01672300
C	5.18288500	1.28586900	2.94249100
C	7.08740600	2.75918300	3.68500500
C	5.79355100	5.53340000	-0.44395800
C	5.85168500	3.09997900	-1.09246800
C	4.15146900	4.63745400	-2.12824100
H	-0.23974700	7.85364800	2.26411100
H	-0.71038900	6.69004200	1.01666000
H	-0.25964500	6.12231500	2.63340800
H	3.40679800	6.82344800	2.28616900
H	2.25520500	7.93701000	3.03042400
H	2.15742900	6.20318600	3.37965500
H	2.75607500	7.65852600	-0.03791400
H	1.06133600	7.59533400	-0.54938300
H	1.58319700	8.78083800	0.65886800
H	6.52310000	5.79139600	-1.21463400
H	5.15312900	6.40108000	-0.27440200
H	6.33908600	5.32107600	0.47851800
H	7.53731000	1.96930500	4.29017700

H	7.51938300	2.71461300	2.68362300
H	7.35539700	3.71900000	4.13469100
H	5.18522100	3.65277000	5.48206300
H	3.86054700	2.59772300	4.95822600
H	5.32794400	1.90232800	5.66630100
H	5.55910400	0.43643400	3.51468100
H	4.09731200	1.19655700	2.86965400
H	5.60452100	1.23452500	1.93697900
H	4.81785500	4.87449000	-2.95941100
H	3.53782100	3.78149000	-2.41608800
H	3.49469200	5.49342300	-1.96184900
H	6.40658100	2.85521600	-0.18391800
H	5.25121000	2.23316300	-1.37455600
H	6.57624700	3.28917700	-1.88754100

 $P^{++}(t\text{-BuOH})_4$

C	-1.02579400	-0.38001300	-0.57965200
C	0.38622600	-0.52111700	-0.78775600
C	1.22103700	0.49610100	-0.38885000
C	0.65238300	1.66440600	0.22687500
C	-0.76497600	1.80545800	0.42434300
C	-1.59825300	0.78608900	0.02810300
N	-1.84240300	-1.37485700	-0.97105900
N	1.46328000	2.65029100	0.62933600
H	-1.48842300	-2.21073700	-1.40517600
H	-2.83981100	-1.31928500	-0.85079100
H	2.47024400	2.60673000	0.53625600
H	1.13320200	3.50400700	1.07214600
C	-3.09425900	0.81103400	0.19438000
C	-1.24490000	3.07817900	1.06595200
C	2.71446000	0.47005700	-0.56413400
C	0.86200000	-1.79141600	-1.44059400
H	-3.45025600	1.71491000	0.67505200
H	-3.59990200	0.74094500	-0.77362400
H	-3.43447400	-0.03086300	0.80504800
H	-0.91799500	3.95123500	0.49474100
H	-2.32483200	3.13104000	1.14292800
H	-0.84033500	3.18259900	2.07685600
H	3.04590000	1.30079600	-1.19362300
H	3.22538100	0.56508400	0.39771800
H	3.07004300	-0.44370500	-1.02623300
H	1.94017700	-1.83548200	-1.54181800
H	0.55957200	-2.66840000	-0.86031200
H	0.44058800	-1.89920300	-2.44494400
O	4.22023200	3.95121600	1.14013800
H	4.68954500	3.60402900	1.92720400
C	5.18931100	4.43969300	0.17637200
O	5.44052600	3.01698800	3.52354300
H	6.00943100	3.63896100	4.01553300
C	5.56012700	1.69155800	4.09338900
O	1.75293700	5.29828700	1.76222700
H	2.68487700	5.01404600	1.69891400
C	1.55434200	6.12222000	2.93263700
O	7.24844400	4.81151300	4.82939400
H	8.09804500	4.79320100	4.37190700
C	7.19308500	5.99873300	5.66752900
C	1.72704100	5.26708100	4.19137500
C	2.55894400	7.27680900	2.91723000
C	0.12639700	6.65011800	2.82712700
C	5.82626700	5.95344200	6.34072700
C	7.33298200	7.23965400	4.78511400
C	8.31878600	5.92604100	6.70007700
C	4.37711300	4.99797900	-0.98872500
C	6.07047700	3.27562700	-0.28307800
C	6.03652900	5.53930600	0.82087800
C	4.69899000	0.78405700	3.22085500
C	7.02611400	1.25167900	4.05195300
C	5.03868400	1.71394500	5.53248400

H	5.22694400	2.61315900	-1.57031600
H	6.32483800	3.99370400	-1.72142200
H	5.94264900	6.07140900	-0.18778000
H	4.59508400	6.04347500	0.96108400
H	6.01224300	5.01034000	1.22170300

 $P^{2+}(t\text{-BuOH})_3$

C	-1.07527700	-0.42621100	-0.01189400
C	0.33697100	-0.73223900	0.25836700
C	1.10953100	0.25090500	0.76982700
C	0.49575100	1.57800100	0.96312600
C	-0.96847500	1.75057300	1.04002000
C	-1.74330700	0.76603000	0.53643200
N	-1.77724800	-1.25076600	-0.72151300
N	1.25836300	2.61509100	1.06589400
H	-1.42396100	-2.10550300	-1.19153000
H	-2.75698900	-1.05737200	-0.89516700
H	2.28797600	2.57725200	0.96618400
H	0.89922500	3.57930800	1.16676200
C	-3.23975500	0.81529900	0.45160900
C	-1.48033000	3.02467500	1.63372500
C	2.55646000	0.10113400	1.12335500
C	0.81572800	-2.11420700	-0.06194400
H	-3.65251500	1.64824000	1.00882000
H	-3.56885700	0.93309300	-0.58556600
H	-3.68691200	-0.09897100	0.84781900
H	-1.27252000	3.87902700	0.98494600
H	-2.55041600	2.99278100	1.80396700
H	-0.99366100	3.21870800	2.59126000
H	3.19755200	0.57165800	0.37402600
H	2.76893100	0.57961500	2.08065900
H	2.84545100	-0.94111600	1.20219300
H	1.85121100	-2.26286300	0.22109600
H	0.21049000	-2.85968100	0.45947900
H	0.73642000	-2.31887000	-1.13218000
O	4.03613300	3.50331700	0.76996900
H	4.60991200	2.88075900	1.52677200
C	4.84754300	3.54661500	-0.33801100
O	-1.33598100	-3.54674500	-2.21718900
C	-1.44739900	-3.75288100	-3.65905100
H	-1.07765100	-4.37657300	-1.79736200
O	0.85286800	5.41663700	1.07907000
H	0.61505000	5.76981300	0.21274700
C	0.92389500	6.51765200	2.03427900
C	-2.48447100	-4.84480600	-3.91656600
C	-0.07601700	-4.14690400	-4.20625600
C	-1.90444700	-2.41356600	-4.22472800
C	-0.47560000	7.10361000	2.22145900
C	1.89383500	7.56846300	1.49614000
C	1.44410300	5.89996400	3.32683000
C	3.86439900	3.80055000	-1.47439700
C	5.53735400	4.83828600	0.09842200
C	5.86966300	2.47552100	-0.71778700
H	-2.17226700	-5.79310700	-3.47138600
H	-3.45037300	-4.56426100	-3.49272400
H	-2.61173300	-5.00532400	-4.98884400
H	-1.99995300	-2.47810700	-5.30942700
H	-2.87594600	-2.13020900	-3.81496700
H	-1.18236300	-1.62775200	-3.99378800
H	0.66040800	-3.36959400	-3.99437100
H	0.26816000	-5.08245200	-3.75800200
H	-0.12273300	-4.29164500	-5.28740300
H	2.42486100	5.44736100	3.16973200
H	1.53964700	6.66642900	4.09729300
H	0.76005600	5.13340500	3.69561600
H	-0.45626700	7.91719500	2.94952900
H	-0.85748500	7.50537000	1.27952100
H	-1.16878900	6.34009500	2.57845900

H	2.88605400	7.13807200	1.35144400
H	1.54478700	7.96615200	0.53944000
H	1.97888500	8.40410000	2.19340400
H	4.39214100	4.17818200	-2.35126700
H	3.35357000	2.87758600	-1.75624200
H	3.11722100	4.53968700	-1.17954600
H	6.53699400	2.25892500	0.12044300
H	5.36961700	1.55017800	-1.00935600
H	6.48393200	2.81173800	-1.55558300
H	6.14278100	5.24409200	-0.71454600
H	4.79896300	5.58837900	0.38582300
H	6.19806100	4.65833200	0.95052000

 $P^{2+}(t\text{-BuOH})_4$

C	-1.35528300	-0.43959900	0.40403200
C	0.09872300	-0.64941200	0.54652700
C	0.88250600	0.44354500	0.66897600
C	0.22982800	1.76121000	0.70690800
C	-1.21762700	1.91739400	0.92406800
C	-1.99994800	0.82241600	0.81124800
N	-2.08055300	-1.38418600	-0.09662700
N	0.95683900	2.82383900	0.59271700
H	-1.68635800	-2.26360300	-0.47285300
H	-3.10049500	-1.30431100	-0.24735400
H	1.96952900	2.80688700	0.43439600
H	0.58744600	3.78374800	0.63621200
C	-3.48267500	0.80758200	1.01717600
C	-1.71676800	3.29726500	1.22344800
C	2.37805800	0.41906900	0.75349100
C	0.59427000	-2.06116600	0.51939400
H	-3.82657700	1.69663600	1.53436700
H	-4.01754200	0.74776100	0.06611800
H	-3.77727400	-0.05839100	1.61122100
H	-1.56682300	3.95648600	0.36410600
H	-2.77531000	3.30934800	1.45524900
H	-1.18082900	3.72985900	2.07099900
H	2.82412100	0.82946700	-0.15658500
H	2.73109900	1.01544500	1.59719400
H	2.76506600	-0.58626300	0.87269800
H	1.63962400	-2.13076500	0.79808600
H	0.01926200	-2.67844500	1.21335400
H	0.48298400	-2.50232900	-0.47381300
O	3.56100600	4.00308600	0.22959300
H	4.02856400	4.01870000	1.07533100
C	4.54927700	4.11048100	-0.84641600
O	-1.45223600	-3.81406300	-1.40278600
C	-1.35962700	-4.13701000	-2.82285000
H	-1.31506900	-4.61772200	-0.88596900
O	1.09664600	5.56824500	0.60399600
C	0.83138100	6.98174000	0.80492600
H	2.04032000	5.42572900	0.42105300
O	-4.77016400	-1.66259300	-0.91268400
H	-4.99760200	-1.17286100	-1.71279300
C	-5.95948900	-2.35703500	-0.42990700
C	-0.62659300	7.07092400	1.24096500
C	1.76289000	7.51126100	1.89624700
C	3.73900900	4.09621700	-2.13674700
C	1.05280600	7.72042700	-0.51620200
C	5.31004000	5.42510200	-0.67956400
C	5.49711100	2.91459000	-0.77221500
C	-1.58883000	-2.81748300	-3.55048100
C	-2.44532700	-5.15564800	-3.16709300
C	0.03372900	-4.69529600	-3.11124500
C	-6.50454300	-3.23232400	-1.55755700
C	-6.99459300	-1.32294100	0.01299900
C	-5.48434000	-3.20474100	0.74415000
H	-0.78672600	6.51632900	2.16751300
H	-0.90626400	8.11157700	1.41270300

H	-1.28576100	6.66433800	0.47137100	H	0.84124400	-2.32560600	0.77410500
H	2.80948500	7.40644300	1.59885400	H	0.57223000	-2.31798800	-0.96460600
H	1.57299500	8.56992200	2.08413800	H	3.04851800	1.21465500	-0.78403100
H	1.61145700	6.96340000	2.82836100	H	2.92155500	1.48507000	0.95027900
H	6.04671100	5.54338900	-1.47647600	H	3.01415300	-0.14579600	0.32443700
H	4.62731700	6.27565200	-0.71512800				
H	5.84299400	5.44824900	0.27458500			P(TFE) ₂	
H	6.03606500	2.89977400	0.17851800	C	-0.91210700	0.07481500	0.08421600
H	4.94843200	1.97703500	-0.87470300	C	0.47836100	0.01710200	-0.08935100
H	6.23611300	2.96633700	-1.57407900	C	1.21460600	1.21039300	-0.08493500
H	2.08914600	7.62223000	-0.84770200	C	0.54398100	2.42284300	0.13131300
H	0.40207500	7.31524800	-1.29351100	C	-0.84648800	2.48055100	0.30477700
H	0.83492400	8.78473500	-0.40498600	C	-1.58275300	1.28729300	0.30029900
H	4.40399500	4.17662800	-2.99780100	N	-1.65862100	-1.14183000	0.10602200
H	3.17313800	3.16704300	-2.22937800	N	1.29063300	3.63947500	0.11030700
H	3.04052700	4.93443400	-2.16556900	H	-1.24065600	-1.86748300	-0.46353600
H	-6.59077200	-0.68474700	0.80064500	H	-2.61642600	-1.01861500	-0.19909300
H	-7.29553000	-0.68985200	0.82563400	H	2.24822900	3.51580700	0.41596100
H	-7.88927200	-1.81778100	0.39642200	H	0.87264400	4.36451100	0.68067100
H	-5.75445400	-3.95658200	-1.87925300	C	-3.07495000	1.24711000	0.53300000
H	-7.39017500	-3.77741000	-1.22525200	C	-1.49056400	3.83619400	0.47889400
H	-6.79097700	-2.62284800	-2.41890300	C	2.70672400	1.25079600	-0.31796600
H	-0.82902700	-2.08448900	-3.27179100	C	1.12235900	-1.33860700	-0.26333900
H	-1.53587100	-2.96880900	-4.62948900	H	-3.62498200	1.00233100	-0.38335500
H	-2.57283600	-2.41059900	-3.31004700	H	-3.33425600	0.48679800	1.27420700
H	-2.30451900	-6.08084500	-2.60227000	H	-3.46783000	2.19033300	0.90011300
H	-3.43383800	-4.75584100	-2.93561800	H	-1.12084400	4.54373200	-0.26773400
H	-2.41425200	-5.40485900	-4.22963100	H	-2.57062400	3.80376900	0.37197200
H	0.20917800	-5.61480700	-2.54672100	H	-1.27578500	4.26630900	1.46410900
H	0.14089300	-4.92903300	-4.17235300	H	2.96529200	2.00932300	-1.06133500
H	0.80353800	-3.97071400	-2.83944700	H	3.25685300	1.49838300	0.59755900
H	-5.07580400	-2.57762800	1.53900500	H	3.10018400	0.30687800	-0.68262400
H	-6.31772100	-3.77442700	1.15771600	H	2.20245700	-1.30622200	-0.15682600
H	-4.71343900	-3.90794400	0.42378700	H	0.75286800	-2.04597300	0.48357600
				H	0.90720900	-1.76894700	-1.24837800
				H	1.38696200	4.30790000	-1.59773800
				H	1.39065800	4.64781100	-2.52780100
				C	1.91803800	5.94346000	-2.55558100
				H	1.50835800	6.48237000	-3.41241300
				H	1.69288200	6.51538800	-1.64986900
				O	-1.75855200	-2.13646400	2.74879400
				H	-1.75404200	-1.80288200	1.81637600
				C	-2.39590000	-3.38078700	2.

C	-3.03334400	1.31865300	0.32990000	H	2.95254000	1.25294500	-0.89263400
C	-1.39710800	3.86788900	0.29795000	H	2.06716700	0.62447700	-2.27251600
C	2.65681700	1.25241400	-1.00175600	H	0.94134100	-0.87277900	-1.85315100
C	1.02039600	-1.29835800	-0.97178300	H	-0.37148200	-1.49967600	-0.88250800
H	-3.66592900	1.18017500	-0.55478000	H	-0.71269200	-0.70930300	-2.41852400
H	-3.26021500	0.50065900	1.01793600	H	1.41554600	4.87526000	-1.43164200
H	-3.35746800	2.23418100	0.81556900	O	1.20524600	5.45968500	-2.21514200
H	-1.05701400	4.61723500	-0.42114600	C	1.81978100	6.71405100	-2.07100900
H	-2.48231100	3.86549400	0.25780300	H	1.22738300	7.47118700	-2.58730200
H	-1.11061600	4.22392900	1.29456500	H	1.92611800	7.01055500	-1.02402700
H	2.88097300	2.06701600	-1.69508800	O	-1.90458500	-1.90348800	1.95857300
H	3.28821400	1.39927600	-0.11761600	H	-2.11665100	-1.25427900	1.22877200
H	2.98454900	0.33486400	-1.48109000	C	-2.53045500	-3.13684000	1.71359500
H	2.10566400	-1.29458200	-0.93664100	H	-2.64120800	-3.34507000	0.64603200
H	0.68569500	-2.04762100	-0.25025200	H	-1.94196100	-3.93792200	2.16365600
H	0.72987900	-1.65572000	-1.96675200	C	3.20695800	6.72356600	-2.69349300
H	1.31339200	4.43657100	-1.95873500	C	-3.91594200	-3.18731200	2.33771800
O	1.25711800	4.85032000	-2.85662000	F	-4.73830600	-2.24483300	1.83198000
C	1.66854600	6.18584300	-2.78710000	F	-3.88459100	-3.00194000	3.67153300
H	1.19754200	6.75148000	-3.59368300	F	-4.49417800	-4.38572200	2.11305500
H	1.41070100	6.66290700	-1.83623400	F	3.18183700	6.43257100	-4.00829600
O	-1.63884600	-2.24491400	2.14476200	F	4.03325900	5.82958300	-2.11156700
H	-1.69086500	-1.82655300	1.23762500	F	3.77750700	7.93963500	-2.56291700
C	-2.38632900	-3.43267600	2.18182500	H	-0.26365700	-1.88085700	2.61903500
H	-2.41790800	-3.93710100	1.21235700	O	0.64120200	-1.94032700	2.99192000
H	-1.94913200	-4.11468000	2.91298400	C	0.62628100	-1.55901000	4.33964800
C	3.17280700	6.32397000	-2.96713200	H	-0.29946700	-1.83795600	4.85128900
C	-3.82141300	-3.16865800	2.60990000	H	1.46278200	-2.03516200	4.85474200
F	-4.46891600	-2.35515700	1.74991400	C	0.79999400	-0.05665400	4.50271000
F	-3.89549600	-2.59021300	3.82410500	F	0.81405500	0.28556400	5.80967000
F	-4.51949100	-4.32187000	2.67217500	F	-0.19716700	0.64071400	3.91953500
F	3.59709700	5.83095200	-4.14785900	F	1.95241300	0.38863500	3.96314300
F	3.86546300	5.67684200	-2.00540500	H	-0.47990600	5.34365100	-2.79182000
F	3.54608400	7.62152900	-2.92055000	O	-1.41393700	5.32970700	-3.08832400
H	-0.15083100	-2.07883900	3.08367700	C	-1.89412700	4.01294900	-3.09565400
O	0.66222400	-2.04583500	3.63067900	H	-1.48668300	3.40489900	-2.28226100
C	0.44344800	-1.24441600	4.75834300	H	-2.98149900	4.03235900	-3.00185700
H	-0.57963400	-1.31436300	5.13906200	C	-1.57287100	3.30041900	-4.40013400
H	1.12874100	-1.54985900	5.55128700	F	-2.08523400	2.05018500	-4.40115500
C	0.71982200	0.22353100	4.47065800	F	-0.24441300	3.18599500	-4.60863100
F	0.51917900	0.97445800	5.57594600	F	-2.08053200	3.93754600	-5.47444700
F	-0.08253200	0.71570000	3.50413000				
F	1.98886400	0.43921700	4.06930300				
				P ⁺ (TFE)			
P(TFE) ₄				C	-1.32982500	-0.50059700	0.23934400
C	-1.38734300	0.90682400	-0.09886800	C	0.07815600	-0.70818700	0.05705400
C	-0.20289700	0.64905800	-0.80289500	C	0.87605200	0.37302700	-0.23461200
C	0.81432600	1.61366000	-0.79609800	C	0.26954000	1.66923100	-0.35783900
C	0.63039100	2.78879700	-0.05372600	C	-1.14284900	1.87319400	-0.18504000
C	-0.55521700	3.04808400	0.64850300	C	-1.93752300	0.79384400	0.11990600
C	-1.57391000	2.08424700	0.63915100	N	-2.10859500	-1.55613700	0.53112700
N	-2.40844400	-0.09371300	-0.07856600	N	1.04236600	2.72674600	-0.64610000
N	1.65891700	3.78209800	-0.06845000	H	2.04859200	2.67663500	-0.75663900
H	-2.44167400	-0.63201000	-0.93667400	H	0.64215200	3.64646600	-0.73473200
H	-3.33067500	0.29485900	0.07821600	H	-1.73037100	-2.48410400	0.62347100
H	2.58265600	3.38225200	-0.18404000	H	-3.10165700	-1.46053400	0.66303400
H	1.66897000	4.34502700	0.77395600	O	3.95439100	3.41782700	-0.86821800
C	-2.86521800	2.25057100	1.40540900	H	4.13782700	4.15685000	-0.27557400
C	-0.68031400	4.36437700	1.37890300	C	4.90607200	3.38930300	-1.90997000
C	2.10552900	1.44421700	-1.56177000	H	5.91865500	3.58634800	-1.55215700
C	-0.07431300	-0.66946300	-1.52814200	H	4.87822500	2.39978600	-2.36442000
H	-3.71850300	2.40634600	0.73515900	C	4.58193900	4.40763900	-2.99134400
H	-3.08422300	1.36117200	2.00222500	F	3.37754800	4.19247800	-3.55278300
H	-2.84150600	3.09005600	2.09308500	F	5.50076300	4.36102700	-3.97503000
H	-0.39088400	5.19871100	0.73479500	F	4.56972500	5.66734200	-2.50806700
H	-1.69309800	4.56491500	1.71413900	C	-1.66226100	3.27617900	-0.34921800
H	-0.03453300	4.40142700	2.26395800	C	-3.42379100	0.87949700	0.34274300
H	2.34443200	2.34491000	-2.13274900	C	2.36256200	0.28395700	-0.44765000
				C	0.59000300	-2.11670100	0.19700800

Appendix C

H	-1.42485300	3.66824400	-1.34276800
H	-2.73759100	3.34395000	-0.23178200
H	-1.21534400	3.95112600	0.38729500
H	-3.80635200	1.88915700	0.24974800
H	-3.96679700	0.26159300	-0.37887800
H	-3.68972200	0.52735500	1.34412800
H	1.65822800	-2.19542700	0.03161800
H	0.38917200	-2.51127600	1.19769700
H	0.10588300	-2.78292500	-0.52357500
H	2.89845400	0.96404500	0.21915900
H	2.75335500	-0.71160700	-0.27127600
H	2.62560500	0.56093200	-1.47291900

P⁺(TFE)₂

C	-1.18903600	-0.39627300	0.09523100
C	0.22663100	-0.62829400	0.09516000
C	1.07649000	0.45257500	0.11189100
C	0.51596900	1.77516300	0.13313600
C	-0.90334000	2.00477600	0.12762500
C	-1.75185300	0.92343900	0.10935100
N	-2.01868900	-1.45359800	0.07989100
N	1.33849200	2.83334100	0.15642600
H	-1.67166000	-2.39808300	0.06998900
H	-3.01867200	-1.34149900	0.07957100
H	2.35188700	2.77022200	0.18573200
H	0.96569800	3.76864500	0.17579900
C	-3.25339700	1.03097300	0.10433200
C	-1.36983600	3.43560100	0.14446400
C	2.57633200	0.34129800	0.10711000
C	0.68826800	-2.06096000	0.07672400
H	-3.60314900	2.05669700	0.11591800
H	-3.67781500	0.55736400	-0.78621300
H	-3.68551300	0.53499700	0.97887900
H	-0.99462200	3.98124200	-0.72666800
H	-2.44971500	3.52707700	0.13551000
H	-1.01140200	3.95547300	1.03819900
H	3.00241600	0.85498800	-0.75908600
H	3.00760500	0.80471800	0.99841000
H	2.92236200	-0.68547300	0.07613400
H	1.76783500	-2.15632300	0.08090300
H	0.31523700	-2.60442800	0.95026600
H	0.32297100	-2.58020000	-0.81465800
O	4.22797800	3.41170900	0.39137400
H	4.48166800	3.76084300	1.26842000
C	5.09591700	3.90782300	-0.59679400
H	5.06063800	3.24297100	-1.46045900
H	6.12942700	3.97456200	-0.24841600
O	4.99240000	4.37219400	2.88629600
H	5.40761300	3.76209400	3.50804800
C	4.42382500	5.46854100	3.57341700
H	4.23158100	6.25438800	2.84464300
H	5.08807100	5.85436800	4.34853700
C	4.67589500	5.29176900	-1.06729900
C	3.10085700	5.09441600	4.22215900
F	3.43497100	5.29924800	-1.59241600
F	5.51661500	5.74868900	-2.01663100
F	4.67821200	6.19190600	-0.06130900
F	3.24888200	4.10878800	5.13113100
F	2.57043900	6.15571400	4.85749000
F	2.19567500	4.66528800	3.32316600

P⁺(TFE)₃

C	-1.21752400	-0.07729300	-0.12244100
C	0.19803700	-0.30921700	-0.10510500
C	1.04774000	0.77179900	-0.08891700
C	0.48726300	2.09455800	-0.08875400
C	-0.93201600	2.32393900	-0.10987900

C	-1.78036600	1.24245100	-0.12560800
N	-2.04710200	-1.13474300	-0.13739300
N	1.30933000	3.15303900	-0.07125800
H	-1.70017700	-2.07930500	-0.13524300
H	-3.04699400	-1.02256200	-0.14993000
H	2.32281400	3.09212400	-0.03278800
H	0.93558800	4.08813300	-0.06426800
C	-3.28180700	1.34986200	-0.14561000
C	-1.39863900	3.75482100	-0.11213300
C	2.54751300	0.66061300	-0.07369700
C	0.65971000	-1.74199800	-0.10611300
H	-3.63167400	2.37560800	-0.14301300
H	-3.69782200	0.87116500	-1.03740900
H	-3.72214700	0.85884100	0.72762600
H	-1.01870100	4.29032600	-0.98752200
H	-2.47845100	3.84613600	-0.12783500
H	-1.04499300	4.28506800	0.77738600
H	2.98421100	1.15646100	-0.94499400
H	2.96764800	1.14254900	0.81298800
H	2.89377500	-0.36654700	-0.07871400
H	1.73924100	-1.83732400	-0.09560200
H	0.28171200	-2.27675200	0.77069400
H	0.29940100	-2.27008900	-0.99429600
O	4.19468200	3.74882000	0.16219300
H	4.47843100	4.05519000	1.04976200
C	5.00837300	4.32302200	-0.82859300
H	4.99088900	3.68683100	-1.71446600
H	6.04477400	4.43769100	-0.50164400
O	5.06408300	4.55337000	2.63465500
H	5.68634100	3.97052700	3.11715500
C	4.41619200	5.43512100	3.52047900
H	4.05967200	6.29724800	2.95673200
H	5.08219600	5.78308600	4.31285800
C	4.50177600	5.69543800	-1.24472200
C	3.20938100	4.78216100	4.17655900
F	3.24561500	5.65033500	-1.73221500
F	5.28622800	6.22181700	-2.20706700
F	4.48841000	6.56779100	-0.21571900
F	3.54919100	3.69534600	4.89853600
F	2.59778500	5.64582400	5.01079100
F	2.29462100	4.37947800	3.27253100
H	7.77225900	3.17112700	3.94146000
O	6.84117700	2.91862500	3.96292800
C	6.71364300	1.51019400	3.98877900
H	5.70887000	1.25748900	3.65370800
H	7.44071400	1.01744300	3.34135800
C	6.88651000	0.96984900	5.39916900
F	6.74950100	-0.36970000	5.40668400
F	5.98059800	1.47535600	6.25477800
F	8.10495400	1.25608900	5.90109300

P⁺(TFE)₄

C	-1.40998200	0.07706700	-0.24048800
C	-0.14252100	-0.07035300	0.41491100
C	0.76596900	0.95938900	0.34221300
C	0.41034300	2.14828900	-0.38169600
C	-0.85792800	2.29037600	-1.04377100
C	-1.76205300	1.25698100	-0.97695900
N	-2.30106300	-0.92628300	-0.16271100
N	1.28749400	3.16000000	-0.44609900
H	-2.10453800	-1.77121000	0.34719800
H	-3.20483900	-0.86562000	-0.60099900
H	2.20180200	3.15242000	-0.00267800
H	1.05791700	4.00691600	-0.94017700
C	-3.11715800	1.27969700	-1.63212700
C	-1.11364800	3.58093300	-1.77447000
C	2.12537300	0.92559100	0.98505100
C	0.10614900	-1.36044500	1.14942100

490

Appendix C

P ²⁺ (TFE) ₃							
C	-1.24412600	-0.25419400	0.45918900	H	-2.91969300	-1.25330000	1.01829700
C	0.17565200	-0.58418800	0.27286500	H	2.40460700	2.74114900	0.32763200
C	1.03966200	0.42924500	0.04331500	H	1.00144400	3.71893800	0.51619400
C	0.50309200	1.80198000	0.01586400	C	-3.19724300	1.08499500	0.90165400
C	-0.94144200	2.10698400	0.04059100	C	-1.30451500	3.47247500	0.61945200
C	-1.80326700	1.09172500	0.26493500	C	2.59490900	0.30180700	0.02653500
N	-2.05283100	-1.20887400	0.79812200	C	0.69369600	-2.07908500	0.30969800
N	1.32958400	2.79377500	-0.03526000	H	-3.54467700	2.11063000	0.89438300
H	-1.72909100	-2.15751400	0.94649700	H	-3.72885400	0.55615700	0.10607700
H	-3.04256400	-1.04825000	0.94309200	H	-3.49850600	0.65227500	1.86007300
H	2.36564400	2.72887200	-0.03588000	H	-0.94966400	4.00374800	-0.26720700
H	0.97810600	3.74530400	-0.04961200	H	-2.38189900	3.57887400	0.64563900
C	-3.29267800	1.23217500	0.35092600	H	-0.90901900	3.98033000	1.50399300
C	-1.34179000	3.53597300	-0.16021400	H	2.86477100	0.85984200	-0.87248600
C	2.51097500	0.26465000	-0.16908600	H	3.17227200	0.71343500	0.85710100
C	0.55611500	-2.03039400	0.36945600	H	2.91129500	-0.72394300	-0.11742300
H	-3.62326900	2.24098000	0.13597500	H	1.75346300	-2.19440300	0.11959800
H	-3.78816500	0.56787100	-0.36173600	H	0.47616300	-2.61572900	1.23770900
H	-3.65173800	0.98628200	1.35467400	H	0.16097900	-2.57595800	-0.50581200
H	-0.90915900	3.93672600	-1.08016400	O	4.10790800	3.23120300	0.30242300
H	-2.41606600	3.65448100	-0.23172100	H	4.50748500	3.52194900	1.15632800
H	-1.00554100	4.15749200	0.67547900	C	4.84650000	3.73616700	-0.78509800
H	2.82237500	0.75466600	-1.09385400	H	4.70144300	3.08583000	-1.64816200
H	3.07727400	0.71801400	0.64762500	H	5.91382600	3.79020700	-0.56173400
H	2.80191900	-0.77693400	-0.23196300	O	5.24810400	3.98535400	2.61644300
H	1.60208300	-2.19574800	0.14258900	H	5.79215600	3.33901300	3.12251400
H	0.38314100	-2.41155600	1.38045600	C	4.88539600	5.08059600	3.42187800
H	-0.02864000	-2.63507600	-0.32838700	H	4.68448300	5.93926600	2.78105400
O	4.07292400	3.18347700	0.07646800	H	5.67349400	5.34599000	4.12945100
H	4.40878600	3.45108200	0.96351000	C	4.37659200	5.12892800	-1.17424800
C	4.95503900	3.60952100	-0.93503200	C	3.62081300	4.79233800	4.21575700
H	4.82554700	2.97390900	-1.81123900	F	4.53774400	6.01840800	-0.17380500
H	5.99744500	3.55701500	-0.61453800	F	3.06879300	5.14699700	-1.50401700
O	5.01452400	3.88713600	2.49938300	F	5.06606600	5.58602600	-2.23636800
H	5.53261300	3.25574400	3.04120300	F	3.27207800	5.86018500	4.95912900
C	4.56629200	4.97339700	3.27487700	F	2.57509300	4.50014100	3.41590500
H	4.36303000	5.81509700	2.61305500	F	3.77288800	3.74797700	5.05490900
H	5.30625500	5.27882000	4.01730000	H	6.35850400	1.49037500	4.47472700
C	4.66718900	5.04218800	-1.35683400	O	6.77650400	2.23742500	3.99769300
C	3.27667400	4.63685600	4.00697700	C	8.13119300	1.96430000	3.72598500
F	4.78558300	5.90693700	-0.32897300	H	8.64918400	2.90741500	3.55274800
F	3.41946100	5.18770100	-1.84659600	H	8.61593000	1.44183200	4.55315700
F	5.52498400	5.43587600	-2.31728900	C	8.28983000	1.11349900	2.47535500
F	2.84588300	5.69371700	4.72144100	F	9.59135000	0.87860000	2.22318300
F	2.28633200	4.29178200	3.15969200	F	7.76721600	1.70717900	1.38513000
F	3.43376200	3.60628300	4.86275100	F	7.67960300	-0.08451600	2.59691000
H	6.20627900	1.65521300	4.71666400	H	5.34443500	0.31747100	6.29853800
O	6.53093200	2.12083300	3.93662100	O	5.63356600	0.16293500	5.39086300
C	7.89478700	1.82652700	3.70946900	C	5.02423900	-0.99886500	4.86519900
H	8.29791200	2.59251800	3.04874100	H	5.58067800	-1.29341600	3.97697900
H	8.47128100	1.81414100	4.63585800	H	5.03120500	-1.82236700	5.58114600
C	8.05938000	0.47912100	3.02477200	C	3.58437900	-0.73436200	4.45441900
F	9.36157500	0.21453600	2.81305000	F	3.02489800	-1.85011400	3.95055800
F	7.43682000	0.43355300	1.83256500	F	3.49103000	0.22557300	3.51405000
F	7.55558800	-0.52595400	3.77004000	F	2.82897000	-0.33544700	5.49741500
P ²⁺ (TFE) ₄							
C	-1.13476100	-0.36588200	0.66501800				
C	0.28648100	-0.64043600	0.41246300				
C	1.12715000	0.41097200	0.29121700				
C	0.56672600	1.76767500	0.43297600				
C	-0.87653400	2.03740000	0.59041300				
C	-1.71393100	0.98480500	0.71204500				
N	-1.92888900	-1.37474400	0.84488400				
N	1.37076600	2.77926500	0.41733100				
H	-1.59544800	-2.33126600	0.82508800				

This page has been intentionally left blank

Appendix D

D.1 *Supporting Information for 9,10-Anthraquinone*

D.1.1 Cyclic voltammograms

D.1.2 Plots of E_{Q1} , E_{Q2} and $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of simple alcohols

D.2 *Supporting Information for 9,10-Phenanthrenequinone*

D.2.1 Cyclic voltammograms

D.2.2 Plots of E_{Q1} , E_{Q2} and $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of simple alcohols

D.3 *Supporting Information for Duroquinone*

D.3.1 Cyclic voltammograms

D.3.2 Plots of E_{Q1} , E_{Q2} and $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of simple alcohols

D.4 *Supporting Information for 3,3',5,5'-Tetra-tert-butyl-4,4'-diphenoquinone*

D.4.1 Cyclic voltammograms

D.4.2 Plots of E_{Q1} , E_{Q2} and $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of simple alcohols

This page has been intentionally left blank

D.1 Supporting Information for 9,10-Anthraquinone

D.1.1 Cyclic voltammograms

Figure D.1. Cyclic voltammograms of 1 mM 9,10-anthraquinone (AQ) in MeCN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of (a) water and (b) EtOH. The voltammograms were recorded at scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of water and EtOH are indicated in dashed lines with their measured trace moisture content.

Figure D.2. Cyclic voltammograms of 1 mM AQ in MeCN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of (a) $n\text{-PrOH}$ and (b) $i\text{-PrOH}$. The voltammograms were recorded at

scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the alcohols are indicated in dashed lines with their measured trace moisture content.

Figure D.3. Cyclic voltammograms of 1 mM AQ in MeCN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of (a) $n\text{-BuOH}$ and (b) $s\text{-BuOH}$. The voltammograms were recorded at scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the alcohols are indicated in dashed lines with their measured trace moisture content.

Figure D.4. Cyclic voltammograms of 1 mM AQ in MeCN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of (a) $i\text{-BuOH}$ and (b) $t\text{-BuOH}$. The voltammograms were recorded at

scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the alcohols are indicated in dashed lines with their measured trace moisture content.

D.1.2 Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of simple alcohols

Figure D.5. Plots of E_{Q1} against concentration of alcohols obtained over three experiments (red +, blue $\bigcirc$ and black $\times$) as measured by square-wave voltammetry during the reduction of 1 mM AQ with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV. A platinum wire (Metrohm) reference electrode was used for the alcohol experiments whereas a silver wire (Cypress Systems) miniature reference electrode that was connected to the working solution through a salt bridge containing 0.5 M $n\text{-Bu}_4\text{NPF}_6$ in MeCN was utilized for the experiments with water.

Figure D.6. Plots of E_{Q2} against concentration of alcohols obtained over three experiments (red +, blue $\circ$ and black $\times$) as measured by square-wave voltammetry during the reduction of 1 mM AQ with 0.1 M n -Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV. A platinum wire (Metrohm) reference electrode was used for the alcohol experiments whereas a silver wire (Cypress Systems) miniature reference electrode that was connected to the working solution through a salt bridge containing 0.5 M n -Bu₄NPF₆ in MeCN was utilized for the experiments with water.

Figure D.7. Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of alcohols obtained over three experiments (red +, blue $\circ$ and black $\times$) as measured by square-wave voltammetry during the reduction of 1 mM AQ with 0.1 M n -Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

D.2 Supporting Information for 9,10-Phenanthrenequinone

D.2.1 Cyclic voltammograms

Figure D.8. Cyclic voltammograms of 1 mM 9,10-phenanthrenequinone (PQ) in MeCN with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of (a) water and (b) EtOH. The voltammograms were recorded at scan rate of 0.1 V s⁻¹ at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that were acquired before the introduction of water and EtOH are indicated in dashed lines with their measured trace moisture content.

Figure D.9. Cyclic voltammograms of 1 mM PQ in MeCN with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of (a) *n*-PrOH and (b) *i*-PrOH. The voltammograms were recorded at

scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the alcohols are indicated in dashed lines with their measured trace moisture content.

Figure D.10. Cyclic voltammograms of 1 mM PQ in MeCN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of (a) $n\text{-BuOH}$ and (b) $s\text{-BuOH}$. The voltammograms were recorded at scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the alcohols are indicated in dashed lines with their measured trace moisture content.

Figure D.11. Cyclic voltammograms of 1 mM PQ in MeCN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of (a) $i\text{-BuOH}$ and (b) $t\text{-BuOH}$. The voltammograms were recorded at

scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the alcohols are indicated in dashed lines with their measured trace moisture content.

D.2.2 Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of simple alcohols

Figure D.12. Plots of E_{Q1} against concentration of alcohols obtained over three experiments (red +, blue O and black x) as measured by square-wave voltammetry during the reduction of 1 mM PQ with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV. A platinum wire (Metrohm) reference electrode was used for the alcohol experiments whereas a silver wire (Cypress Systems) miniature reference electrode that was connected to the working solution through a salt bridge containing 0.5 M $n\text{-Bu}_4\text{NPF}_6$ in MeCN was utilized for the experiments with water.

Figure D.13. Plots of E_{Q2} against concentration of alcohols obtained over three experiments (red +, blue $\circ$ and black $\times$) as measured by square-wave voltammetry during the reduction of 1 mM PQ with 0.1 M n -Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV. A platinum wire (Metrohm) reference electrode was used for the alcohol experiments whereas a silver wire (Cypress Systems) miniature reference electrode that was connected to the working solution through a salt bridge containing 0.5 M n -Bu₄NPF₆ in MeCN was utilized for the experiments with water.

Figure D.14. Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of alcohols obtained over three experiments (red +, blue $\circ$ and black $\times$) as measured by square-wave voltammetry during the reduction of 1 mM PQ with 0.1 M n -Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

D.3 Supporting Information for Duroquinone

D.3.1 Cyclic voltammograms

Figure D.15. Cyclic voltammograms of 1 mM duroquinone (DQ) in MeCN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of (a) water and (b) EtOH. The voltammograms were recorded at scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that were acquired before the introduction of water and EtOH are indicated in dashed lines with their measured trace moisture content.

Figure D.16. Cyclic voltammograms of 1 mM DQ in MeCN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of (a) $n\text{-PrOH}$ and (b) $i\text{-PrOH}$. The voltammograms were recorded at

scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the alcohols are indicated in dashed lines with their measured trace moisture content.

Figure D.17. Cyclic voltammograms of 1 mM DQ in MeCN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of (a) $n\text{-BuOH}$ and (b) $s\text{-BuOH}$. The voltammograms were recorded at scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the alcohols are indicated in dashed lines with their measured trace moisture content.

Figure D.18. Cyclic voltammograms of 1 mM DQ in MeCN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of (a) $i\text{-BuOH}$ and (b) $t\text{-BuOH}$. The voltammograms were recorded at

scan rate of 0.1 V s^{-1} at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the alcohols are indicated in dashed lines with their measured trace moisture content.

D.3.2 Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of simple alcohols

Figure D.19. Plots of E_{Q1} against concentration of alcohols obtained over three experiments (red +, blue O and black x) as measured by square-wave voltammetry during the reduction of 1 mM DQ with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at $25 \pm 2 \text{ }^\circ\text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV. A platinum wire (Metrohm) reference electrode was used for the alcohol experiments whereas a silver wire (Cypress Systems) miniature reference electrode that was connected to the working solution through a salt bridge containing 0.5 M $n\text{-Bu}_4\text{NPF}_6$ in MeCN was utilized for the experiments with water.

Figure D.20. Plots of E_{Q2} against concentration of alcohols obtained over three experiments (red +, blue $\circ$ and black $\times$) as measured by square-wave voltammetry during the reduction of 1 mM DQ with 0.1 M n -Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV. A platinum wire (Metrohm) reference electrode was used for the alcohol experiments whereas a silver wire (Cypress Systems) miniature reference electrode that was connected to the working solution through a salt bridge containing 0.5 M n -Bu₄NPF₆ in MeCN was utilized for the experiments with water.

Figure D.21. Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of alcohols obtained over three experiments (red +, blue $\circ$ and black $\times$) as measured by square-wave voltammetry during the reduction of 1 mM DQ with 0.1 M n -Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV.

D.4 Supporting Information for 3,3',5,5'-Tetra-*tert*-butyl-4,4'-diphenoquinone

D.4.1 Cyclic voltammograms

Figure D.22. Cyclic voltammograms of 1 mM 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone (DPQ) in MeCN with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte at different concentrations of (a) water and (b) EtOH. The voltammograms were recorded at scan rate of 0.1 V s⁻¹ at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that were acquired before the introduction of water and EtOH are indicated in dashed lines with their measured trace moisture content.

Figure D.23. Cyclic voltammograms of 1 mM DPQ in MeCN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of (a) $n\text{-PrOH}$ and (b) $i\text{-PrOH}$. The voltammograms were recorded at scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the alcohols are indicated in dashed lines with their measured trace moisture content.

Figure D.24. Cyclic voltammograms of 1 mM DPQ in MeCN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of (a) $n\text{-BuOH}$ and (b) $s\text{-BuOH}$. The voltammograms were recorded at scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammograms that were acquired before the introduction of the alcohols are indicated in dashed lines with their measured trace moisture content.

Figure D.25. Cyclic voltammograms of 1 mM DPQ in MeCN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte at different concentrations of $t\text{-BuOH}$. The voltammograms were recorded at scan rate of 0.1 V s^{-1} at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The initial cyclic voltammogram that was acquired before the introduction of $t\text{-BuOH}$ is indicated in dashed lines with its measured trace moisture content. The plot for $i\text{-BuOH}$ is not available because a white precipitate was formed upon the addition of the alcohol into the electrochemical solution.

D.4.2 Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of simple alcohols

Figure D.26. Plots of E_{Q1} against concentration of alcohols obtained over three experiments (red +, blue O and black x) as measured by square-wave voltammetry during the reduction of 1 mM DPQ with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at $25 \pm 2^\circ \text{C}$ with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5

mV and pulse amplitude of 20 mV. A platinum wire (Metrohm) reference electrode was used for the alcohol experiments whereas a silver wire (Cypress Systems) miniature reference electrode that was connected to the working solution through a salt bridge containing 0.5 M n -Bu₄NPF₆ in MeCN was utilized for the experiments with water. The plot for i -BuOH is not available because a white precipitate was formed upon the addition of the alcohol into the electrochemical solution.

Figure D.27. Plots of E_{Q2} against concentration of alcohols obtained over three experiments (red +, blue ○ and black ×) as measured by square-wave voltammetry during the reduction of 1 mM DPQ with 0.1 M n -Bu₄NPF₆ as the supporting electrolyte in MeCN recorded at 25±2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV. A platinum wire (Metrohm) reference electrode was used for the alcohol experiments whereas a silver wire (Cypress Systems) miniature reference electrode that was connected to the working solution through a salt bridge containing 0.5 M n -Bu₄NPF₆ in MeCN was utilized for the experiments with water. The plot for i -BuOH is not available because a white precipitate was formed upon the addition of the alcohol into the electrochemical solution.

Figure D.28. Plots of $\Delta E_Q = |E_{Q1} - E_{Q2}|$ against concentration of alcohols obtained over three experiments (red +, blue ○ and black ×) as measured by square-wave voltammetry during the reduction of 1 mM DPQ with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte in MeCN recorded at 25 ± 2 °C with a 1 mm diameter planar glassy carbon working electrode. The scans were carried out with a pulse period (τ) of 25 Hz, potential step of 5 mV and pulse amplitude of 20 mV. The plot for $i\text{-BuOH}$ is not available because a white precipitate was formed upon the addition of the alcohol into the electrochemical solution.