Study of the aromatic boron rich inorganic benzene and its isomers

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2021

Ota, K. (2021). Study of the aromatic boron rich inorganic benzene and its isomers.
Doctoral thesis, Nanyang Technological University, Singapore.
<https://hdl.handle.net/10356/152162>

<https://hdl.handle.net/10356/152162>

<https://doi.org/10.32657/10356/152162>

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**STUDY OF THE AROMATIC BORON RICH INORGANIC
BENZENE AND ITS ISOMERS**

OTA KEI

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2021

STUDY OF THE AROMATIC BORON RICH INORGANIC BENZENE AND ITS ISOMERS

OTA KEI

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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

2021

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Authorship Attribution Statement

This thesis contains material from 4 paper(s) published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 1 and introduction of all chapters are published as K. Ota, R. Kinjo. Inorganic Benzene Valence Isomers. *Chem. Asian J.* **15**, 2558-2574 (2020). doi:10.1002/asia.202000535.

The contributions of the co-authors are as follows:

- Prof Kinjo provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.

Chapter 2 is published as K. Ota, R. Kinjo. A Neutral and Aromatic Boron-Rich Inorganic Benzene. *Angew. Chem. Int. Ed.* **59**, 6572-6575 (2020). doi:10.1002/anie.201915790.

The contributions of the co-authors are as follows:

- Prof Kinjo provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
- I performed all the laboratory work and theoretical calculations.

Chapter 4 is published as B. Su, K. Ota, K. Xu, H. Hirao, R. Kinjo. Zwitterionic Inorganic Benzene Valence Isomer with sigma-Bonding between Two pi-Orbitals. *J. Am. Chem. Soc.* **140**, 11921-11925 (2018). doi:10.1021/jacs.8b08025.

The contributions of the co-authors are as follows:

- Prof Kinjo provided the initial project direction and edited the manuscript drafts.
- Dr Su prepared the manuscript drafts.
- Dr. Su and I performed the laboratory work.
- Prof Hirao and Xu conducted all theoretical calculations.

Chapter 5 is published as K. Ota, R. Kinjo. Aromatic nature of neutral and dianionic 1,4-diaza-2,3,5,6-tetraborinine derivatives. *RSC Adv.* **11**, 592-598 (2021). doi:10.1039/D0RA09040A.

The contributions of the co-authors are as follows:

- Prof Kinjo provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
- I performed all the theoretical calculations.

Note: If published materials are not inserted as thesis chapters, students must acknowledge co-worker contributions in the acknowledgement section of their thesis.

04 Mar 2021

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Ota Kei

Abstract

As with the great progress on the chemistry of benzene (C_6H_6), “carbon-free” inorganic benzenes have also been explored. However, the isolated examples are limited to the heteroatomic systems ($E_3E'_3$ or BP_2N_3), and other skeletal systems have not been developed. My thesis mainly focused on the synthesis and characterization of neutral and anionic B_4N_2 benzene analogues with 6π -electron systems by the reduction of 1,4-diaza-2,3,4,5-tetraborinane derivatives bearing a variety of substituents on both boron (B) and nitrogen (N). We isolated neutral and aromatic B_4N_2 benzene analogue with trimethylphosphine (PMe_3) and Chlorine (Cl). By employing the bulky substituents on B, we successfully synthesized Dewar-type isomer of B_4N_2 benzene analogue with bridged B–B bond. We also developed the reactivity of strained B atoms towards unsaturated carbon-carbon bonds. Moreover, we explored dianionic B_4N_2 benzene analogue regards as a zwitterionic inorganic benzene valence isomer. Based on the experimental results, we investigated the aromaticity of neutral and anionic B_4N_2 benzene analogue by computational studies.

Acknowledgements

Firstly, I would like to express my gratitude towards my supervisor, Professor Rei Kinjo, for accepting me as his Ph.D student and leading me into the main group research area. During my Ph.D journey, he always supported me by giving me a lot of valuable advice and opportunities, which have encouraged me to be a better researcher. Without his continuous supports, this Ph.D thesis would not have been possible. I would like to thank my colleagues in these years through my Ph.D study. I have learnt a lot from them. Without their help, it would be tough for me.

I want to thanks to Professor Hajime Hirao for calculation support. Thanks to my thesis advisor committee (TAC) members, Prof. Han Vinh Huynh and Prof. Pak Hing Leung for their monitoring on my progress and timely advice. I would like to thank all CBC technical and administrative staffs: especially, Dr. Yongxin Li and Dr. Ganguly Rakesh for their help in X-ray crystallography analysis, Ms. Goh Ee Ling and Mr. Keith Leung for their support in NMR analysis. I would also like to thank Nanyang Technological University for providing me a research scholarship to support me to pursue my degree.

I want to thank the former and current members; Dr. Baolin Wang, Dr. Wei Lu, Dr. Bin Rao, Dr. Yuanting Su, Dr. Soichiro Nakatsuka, Dr. Takahiro Asada, Dr. Di Wu, Dr. Bochao Su, Dr. Gillian Goh Kor Hwee, Dr. Dinh Cao Huan Do, Dr. Chenting Yan, Dr. Lizhao Zhu, and Mr. Kota Koshino. Specially, I appreciate Dr. Bochao Su for your kind help. I want to thank Ph. D and exchange students in NTU-CBC, Dr. Atsushi Kaga, Mr. Yoshiya Sekiguchi, Mr. Yosuke Hamamoto, Ms. Rie Fujita, Ms. Ayaka Yubuta, Mr. Kotaro Ochiai. My deepest thanks to my close and supportive circle of friends; the members of Sekiguchi group, Sparrows family, and NTU handball team. Lastly, I would like to express my sincere thanks to my family for their always support.

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Chapter 1: Introduction

Since the discovery of benzene by Faraday from an oil mixture in 1825,¹ the structure of benzene has attracted a considerable attention due to its unusual reactivity as aliphatic compounds. 40 years after this discovery, Kekulé proposed the ring structure of benzene, which contains six carbon atoms with alternating single and double bonds (Figure 1.1, **I**). Many other structures of benzene had also been proposed,²⁻⁷ among which three valence isomers (CH)₆: prismane, Dewar benzene, and benzvalene (Figure 1.1, **II** – **IV**), have been isolated experimentally.⁸⁻¹⁰ In 1867, Dewar benzene was proposed by Dewar, and synthesized in 1962 by van Tamelen and Pappas. Ladenburg proposed prismane in 1869, which was synthesized by Kats and Acton in 1973. In 1937, Hückel proposed benzvalene, which was also synthesized by Katz and Wang in 1971. Decades later, Lonsdale revealed the cyclic structure of benzene and clarified the unusual stability.¹¹ To date, about 30 isomers of C₆H₆ are experimentally synthesized or observed. Significantly, computational studies indicate that benzene **I** among the most stable isomers in the more than 200 possible isomeric structures for C₆H₆ molecules.^{12,13} This outstanding stability of benzene is now explained by “aromaticity”.

Figure 1.1 Historically proposed and synthesized valence isomers of benzene.

Besides benzene chemistry have been widely explored, those involving heteroatoms have also been extensively developed. Some notable examples include group 13,¹⁴⁻¹⁶ heavier group 14,¹⁷⁻²² group 15,²³⁻²⁶ and mixing group 13/15 elements²⁷⁻²⁹ have been reported. These compounds show combination of aromaticity and unique electronic state by incorporating heteroatoms. Hence, they are of great importance for both in fundamental research and application area.

1.1 Preparation of various inorganic benzenes

Inorganic cyclic ring systems which are isoelectronic with benzene **I** have been known for many years. During the late 19th and early 20th centuries, borazine, boroxine and cyclophosphazene have come forward. A large number of studies have focused on fundamental interests such as their bonding modes and industrial applications e.g. material science. The heavier analogues of boroxine have been explored from the middle of the 20th century. In the 1980s and 90s, the Power group has dramatically developed this field by the synthesis of several “heavier” analogues of borazines. While inorganic benzenes have a six-membered six-p-electron system, the presence of aromaticity is still discussed.

1.1.1 Inorganic benzenes containing Group 13/15 elements

In 1926, the parent compound of borazine (HBNH_3) **I-BN1** was originally prepared by Stock and Pohland by pyrolysis of the mixture of borane (B_2H_6) and ammonia (NH_3) (Scheme 1.1, **A**).³⁰ Since that, further synthetic procedures have been developed.³¹ Schlesinger and co-workers discovered that the high temperature (300 °C) solid-state reaction of lithium borohydride (LiBH_4) with ammonium chloride (NH_4Cl) yields **I-BN1** (Scheme 1.1, **B**).³² One of the laboratory syntheses of **I-BN1** involves the preparation of B-trichloroborazine **I-BN2** and its subsequent reduction by metal borohydrides (Scheme 1.1, **C**).^{33,34} The group of Sneddon reported improvement of the laboratory preparation of **I-BN1** by the thermal dehydrogenation of ammonia—borane (H_3NBH_3) (Scheme 1.1, **D**) or reaction of sodium borohydride (NaBH_4) with ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) in tetraglyme solution (Scheme 1.1, **E**).³⁵ The structure of borazine was investigated by electron diffraction in 1969.³⁶ **I-BN1** has a planar hexagonal structure with the equalized B–N bond length of 1.4355(21) Å, which is between B–N single

and double bonds. The studies of the formation, functionalization, and application of borazine derivatives have been summarized in several review articles.^{31,37,38}

Scheme 1.1 Synthesis of borazine **I-BN1**.

English reported the first stable boron–phosphorous analogue of borazine **I-BP1** in a mixture of compounds $(\text{PhBPPh})_n$ ($n = 3$ or 4) (Scheme 1.2, **A**).³⁹ Later, the Power group succeeded the first isolation of $(\text{MesBPCy})_3$ **I-BP2** during the synthesis of $\text{MesB}(\text{PHCy})_2$ by the reaction of MesBBR_2 with two equivalents of $\text{C}_6\text{H}_{11}\text{PHLi}$ (Scheme 1.2, **B**).⁴⁰ A series of phosphaborazines **I-BP3–I-BP6** with variable substituents were also synthesized by the same methods.⁴¹ The structural features of these phosphaborazines **I-BP2–I-BP6** were characterized by X-ray and NMR analysis. The solid-state structures of **I-BP2–I-BP6** show that the B_3P_3 array and the six *ipso*-carbon atoms of the substituents are coplanar. All the B–P distances in **I-BP2** and **I-BP3** are essentially equal and shortening about 1.84 Å length relative to the reported B–P single-bond.⁴² These structural data suggest considerable delocalization of the phosphorus lone pairs over the six-membered ring system.

Scheme 1.2 Synthesis of phosphaborazines.

In 1988, the Power group developed an aluminum-nitrogen analogue of borazine (MeAlNDip)₃ **I-AIN1**, via a two-step alkane elimination reaction between AlMe_3 and DipNH_2 (Scheme 1.3).⁴³ The crystal structure of **I-AIN1** consists of the planar Al_3N_3 six-membered ring with an average Al–N bond length of 1.78 Å. The C atoms bonded to Al and N are coplanar with the central ring.

Scheme 1.3 Formation of the alumazene **I-AIN1**.

Other formal valence analogues of the heavier borazine, Al_3P_3 **I-AIP1** and Al_3As_3 **I-AIAs1**, were prepared through dehydrogenation of $(\text{Mes}^*\text{AlH}_2)_2$ with the corresponding H_2EPH (E = P, As) under the heating conditions (Scheme 1.4).⁴⁴ The six-membered rings of **I-AIP1** and **I-AIAs1** arrange in a nonplanar boat conformation. The aluminum atoms have planar coordination whereas the phosphorus and arsenic atoms are pyramidally coordinated. The average Al–P and Al–As distances are 2.328(3) Å and 2.430(5) Å, respectively, and the average sums of the bond angles (Σ°) at the phosphorus and arsenic atoms are 329.1(3.0)° and

319.7(3.0)°, respectively. These features are consistent with the negligible delocalization of π -electrons over the central ring. The major reasons for the lack of delocalization in either **I-AIP1** or **I-AIAs1** could be the high inversion barriers of P or As atoms and the relatively large sizes of Al, P, or As atoms which hampers the efficient side-on p-p π -type overlap.

Scheme 1.4 Synthesis of **I-AIP1** and **I-AIAs1** from $(\text{Mes}^*\text{AlH}_2)_2$.

The Power group reported the construction of the six-membered ring exclusively composed of heavier main-group elements. In 1991, they successfully prepared the Ga_3P_3 ring compound, $[\text{triphGaP}(\text{C}_6\text{H}_{11})]_3$ **I-GaP1** (triph = 2,4,6-triphenylphenyl) by treatment of triphGaCl_2 with $\text{Li}_2\text{P}(\text{C}_6\text{H}_{11})$ (Scheme 1.5).⁴⁵ The Ga_3P_3 six-membered ring is not planar, but exhibits a twist-boat geometry with normal single Ga-P bond lengths (2.279(4)–2.338(5) Å). The P atoms adopt pyramidal geometry and the sum of the bond angles at the P centers are in the range from 315.7° to 331.1°. It may be envisaged that the energy gained by forming Ga-P π -bonds is insufficient to overcome the energy required for the planarization of phosphorus atoms.

Scheme 1.5 Formation of **I-GaP1**.

In 1994, the Manners group reported the synthesis of the first hybrid borazine phosphazene cation **I-BNP1** by the dechlorination of precursor (Scheme 1.6).⁴⁶ The B–N bond length is 1.429(10) Å and the average distance of P–N bond is 1.624(6) Å.

Scheme 1.6 Synthesis of **I-BNP1**.

1.1.2 Inorganic benzenes containing Group 13/16 elements

In 1936, Kinney and Pontz reported the first preparation of boroxines by heating the corresponding boric acids RB(OH)₂ (R = aryl) (Scheme 1.7, **A**).⁴⁷ Cyclic structure of boroxine was proposed based on its molecular weight. Considering the selective formation of the six-membered ring regardless of the nature of the organic substituents on the B atoms, the Snyder group hypothesized the presence of the resonance stabilization effect of the conjugated six π -electron system.⁴⁸ The simple hydrides of boroxine (HBO)₃ **I-BO1** was synthesized by explosive oxidation of diborane (Scheme 1.7, **B**),⁴⁹ and its structure in the gas phase was determined by electron diffraction,⁵⁰ disclosing that the boron and oxygen atoms are arranged in a planar D_{3h} symmetry. The B–O bond lengths of 1.3758(21) Å are found to be identical.

The general procedure for the formation of boroxine (RBO)₃ is dehydrogenation of boronic acid (Scheme 1.7, **A**). The dehydration and hydrolysis processes proceed reversibly.⁵¹ Trimethylboroxin (MeBO)₃ **I-BO2** was prepared by the carbonylation of borane dimethylsulfide (Me₂S•BH₃) in the presence of tetrabutylammonium borohydride (nBu₄NBH₄) (Scheme 1.7, **C**).⁵² The reaction of triorganoboranes (BR₃) with boric oxide (B₂O₃) gives the corresponding boroxine (Scheme 1.7, **D**, R = alkyl, phenyl).^{53,54} The detailed boroxine chemistry and their applications have been covered in several review articles.^{55,56}

A (R = aryl)

B (R = H)

C (R = Me)

D (R = alkyl, phenyl)

300 °C

Scheme 1.7 Synthesis of boroxines.

In 1953, Wiberg and Sturm reported the series of borthiin (RBS)₃, the heavier analog of boroxine.⁵⁷⁻⁵⁹ The reaction of BBr₃ and H₂S gave [(HS)BS]₃ **I-BS1** (Scheme 1.8). Subsequent treatment with boron trihalides afforded (XBS)₃ (X = Cl: **I-BS2**, Br: **I-BS3**). The structures of **I-BS1** and **I-BS3** were determined by the Schwarz group in the 1970s by X-ray diffraction analysis.^{60,61} The B₃S₃ six-membered rings are nearly planar and the values of the cyclic B–S bond length are almost identical. The detailed discussion of the structural feature of other relevant boron-sulfur compounds is shown in the Krebs's review.⁶²

Scheme 1.8 Synthesis and functionalization of borthiins **I-BS1--BS3**.

In 1971, Schmidt and Kiewert reported the first preparation of triphenylboroselenol (PhBSe)₃ **I-BSe1**.⁶³ The reaction of phenyl boron dibromide PhBBr_2 with hexamethyldisilselenan TMS_2Se afforded **I-BSe1** in moderate yield (Scheme 1.9). The B-Se bond length is 1.93 Å.⁶²

Scheme 1.9 Formation of triphenylboroselenol **I-BSe1**.

1.1.3 Inorganic benzenes containing Group 14/15 elements

Recently, the Scheer group reported the pure heavier borazine analogues, thus, pnictogen–silicon analogues of benzene.⁶⁴ The reactions of $[\text{Cp}^{\text{**}}_2\text{Zr}(\text{h}^{1:1}\text{E}_4)]$ ($\text{E} = \text{P}, \text{As}$) with the monochlorosilylene $[(\text{PhC}(\text{NtBu})_2)\text{SiCl}]$ resulted in the formation of triarsa- and triphospha-trisilabenzenes $[(\text{PhC}(\text{NtBu})_2)\text{SiE}]_3$ ($\text{E} = \text{P}$ (**I-SiP1**), As (**I-SiAs1**)) accompanied with the four-membered ring derivatives $[(\text{PhC}(\text{NtBu})_2)\text{SiE}]_2$ ($\text{E} = \text{P}, \text{As}$) (Scheme 1.10). The solid-state structures of **I-SiP1** and **I-SiAs1** display the nearly planar six-membered Si_3P_3 and Si_3As_3 ring systems with Si–P and Si–As distances falling between the respective single and double bonds.

Scheme 1.10 Formation of heavier borazines **I-SiP1** and **I-SiAs1**.

The Power group also achieved the preparation of the heavier group 14 element-containing borazine. The first “germanazene”, (GeNDip)₃ **I-GeN1**, was synthesized through aggregation of Ge(NTMS₂)₂ with H₂NDip under the mild conditions in good yield (Scheme 1.11).⁶⁵ The solid-state structure of **I-GeN1** exhibits the essentially planar Ge₃N₃ array, including the three *ipso*-carbons of the Dip substituents. The Ge–N bonds are essentially equal, and the average distance is 1.859(2) Å. These data indicate that the p-orbitals on the N and Ge atoms have the correct orientation to induce some degree of delocalization over the ring.

Scheme 1.11 Synthesis of the germanazene **I-GeN1**.

1.1.4 Inorganic benzenes containing Group 15/15 elements

In 1834, Liebig, Wöhler, and Rose reported the synthesis of hexachlorocyclotriphosphazene (Cl₂PN)₃ **I-PN1** which was gained by the reaction of ammonium chloride (NH₄Cl) or ammonia (NH₃) with phosphorus pentachloride (PCl₅) (Scheme 1.12, A).^{66,67} The chemical formula was established based on the vapor density by

Gladstone and Holmes in 1864.⁶⁸ Its cyclic structure was proposed in 1985 by Stokes,⁶⁹ and confirmed by using X-ray diffraction analysis by Bullen in 1971.⁷⁰ To date, **I-PN1** is commonly prepared by treatment of PCl_5 with NH_4Cl at 150 °C (Scheme 1.12, **B**) or the reaction of PCl_5 with tris(trimethylsilyl)amine at 40 °C (Scheme 1.12, **C**).⁷¹ The geometry of cyclophosphazene ring $(\text{R}_2\text{PN})_3$ mainly depends on the substituents. For example, **I-PN1** has the nearly planer P_3N_3 ring, while derivatives bearing the alkyl and alkoxy groups exhibit distorted structure. All the P–N bond lengths of **I-PN1** are equal (1.58 Å) and lies in between the P–N single and double bond lengths. A variety of cyclophosphazene derivatives have been reported so far, and the most convenient synthetic route is the direct functionalization of the commercially available halide derivatives, such as **I-PN1**. There are reviews summarizing the preparation, structure, reactivity and application of cyclophosphazenes.⁷¹⁻⁷⁵

Scheme 1.12 Synthesis of hexachlorocyclotriphosphazene **I-PN1**.

In 2020, the group of Zhu and Eckhardt demonstrated the preparation of cyclotriphosphazene **I-PN2** by exposing low-temperature (5 K) ammonia (NH_3)-phosphine (PH_3) ices to ionizing radiation in the form of energetic electrons (Scheme 1.13).⁷⁶ **I-PN2** was identified via photoionization reflection time-of-flight mass spectrometry (PI-ReTOF-MS).

Scheme 1.13 Synthesis of hexachlorocyclotriphosphazene **I-PN2**.

1.2 Objectives

Since the initial report of the borazine, boroxine and cyclophosphazene in the late 19th and early 20th centuries, a variety of “carbon-free” inorganic benzenes have been explored. Until now, more than 10 examples of inorganic benzenes have been reported. However, the isolated examples are limited to the heteroatomic systems ($\text{E}_3\text{E}'_3$ or BP_2N_3), and other skeletal systems have not been developed. This motivated us to design and synthesize a new skeletal framework, 1,4-diaza-2,3,4,5-tetraborinane derivative (B_4N_2 , Figure 1.2). In order to construct a 6π -electron system with the B_4N_2 ring, the addition of two electrons is a prerequisite. This project mainly focuses on the synthesis and characterization of the neutral and dianionic B_4N_2 rings with 6π -electron system by the reduction of 1,4-diaza-2,3,4,5-tetraborinane derivatives with a variety of substituents. Besides, the properties and reactivities of these compounds are systematically investigated. The second chapter describes the synthesis, characterization and reactivity of a neutral and aromatic B_4N_2 benzene analogue, which has moderate aromatic nature as examined by both experiments and computational studies. The third chapter investigates the synthesis, characterization and reactivity of an inorganic Dewar benzene isomer with a bridged B–B bond by employing bulky ligands. The fourth chapter presents a dianionic B_4N_2 benzene, regarded as a zwitterionic inorganic benzene valence isomer. Finally, the aromaticity of neutral and anionic B_4N_2 benzene derivatives is evaluated by the theoretical calculations in the fifth chapter.

Figure 1.2 The core structures of 1,4-diaza-2,3,4,5- tetraborinane derivatives (B₄N₂).

1.3 References

- 1 M. Faraday. On new compounds of carbon and hydrogen, and on certain other products obtained during the decomposition of oil by heat. *Trans. R. Soc. London B Biol. Sci.* **115**, 440-466 (1825).
- 2 E. Huckel. Main features of the theory of unsaturated and aromatic compounds. *Z. Electrochem.* **43**, 827-849 (1937).
- 3 E. Huckel. Main feature of the theory of unsaturated and aromatic compounds. *Z. Electrochem.* **43**, 752-788 (1937).
- 4 A. Ladenburg. Zur Constitution des Benzols. *Ber. Dtsch. Chem. Ges* **5**, 322-323 (1872). doi:10.1002/cber.187200501100.
- 5 A. Ladenburg. Bemerkungen zur aromatischen Theorie. *Ber. Dtsch. Chem. Ges* **2**, 140-142 (1869). doi:10.1002/cber.18690020171.
- 6 J. Dewar. 5. On the Oxidation of Phenyl Alcohol, and a Mechanical Arrangement adapted to illustrate Structure in the Nonsaturated Hydrocarbons. *P. Roy. Soc. Edinb. A* **6**, 82-86 (1869). doi:doi:10.1017/S0370164600045387.
- 7 A. K. L. Claus. 207 (1867).
- 8 E. E. Van Tamelen, S. P. Pappas. Bicyclo [2.2.0]hexa-2,5-diene. *J. Am. Chem. Soc.* **85**, 3297-3298 (1963). doi:10.1021/ja00903a056.
- 9 T. J. Katz, E. J. Wang, N. Acton. A benzvalene synthesis. *J. Am. Chem. Soc.* **93**, 3782-3783 (1971). doi:10.1021/ja00744a045.
- 10 T. J. Katz, N. Acton. Synthesis of prismane. *J. Am. Chem. Soc.* **95**, 2738-2739 (1973). doi:10.1021/ja00789a084.
- 11 K. Lonsdale, R. Whiddington. The structure of the benzene ring in C₆ (CH₃)₆. *Proc. R. Soc. Lond.* **123**, 494-515 (1929). doi:10.1098/rspa.1929.0081.

- 12 T. C. Dinadayalane, U. D. Priyakumar, G. N. Sastry. Exploration of C₆H₆ Potential Energy Surface: A Computational Effort to Unravel the Relative Stabilities and Synthetic Feasibility of New Benzene Isomers. *J. Phys. Chem. A* **108**, 11433-11448 (2004). doi:10.1021/jp0467696.
- 13 H. Tokoyama, H. Yamakado, S. Maeda, K. Ohno. Isomers of Benzene on Its Global Network of Reaction Pathways. *Bull. Chem. Soc. Jpn.* **88**, 1284-1290 (2015). doi:10.1246/bcsj.20150088.
- 14 G. C. Fu. in *Adv. Organomet. Chem.* Vol. 47 101-119 (Academic Press, 2001).
- 15 A. J. Ashe. Aromatic Borataheterocycles: Surrogates for Cyclopentadienyl in Transition-Metal Complexes. *Organometallics* **28**, 4236-4248 (2009). doi:10.1021/om900308e.
- 16 R. Kinjo, B. Su. Construction of Boron-Containing Aromatic Heterocycles. *Synthesis* **49**, 2985-3034 (2017). doi:10.1055/s-0036-1588832.
- 17 N. Tokitoh. New Progress in the Chemistry of Stable Metallaaromatic Compounds of Heavier Group 14 Elements. *Acc. Chem. Res.* **37**, 86-94 (2004). doi:10.1021/ar020093k.
- 18 N. Tokitoh. Synthesis of Aromatic Species Containing a Heavier Group 14 Element by Taking Advantage of Kinetic Stabilization. *Bull. Chem. Soc. Jpn.* **77**, 429-441 (2004). doi:10.1246/bcsj.77.429.
- 19 V. Y. Lee, A. Sekiguchi. Cyclic polyenes of heavy group 14 elements: new generation ligands for transition-metal complexes. *Chem. Soc. Rev.* **37**, 1652-1665 (2008). doi:10.1039/B800580J.
- 20 V. Y. Lee, A. Sekiguchi. Aromaticity of Group 14 Organometallics: Experimental Aspects. *Angew. Chem. Int. Ed.* **46**, 6596-6620 (2007). doi:10.1002/anie.200604869.
- 21 R. West. Novel aromatic species containing group 14 atoms. *Pure Appl. Chem.* **80**, 563-569 (2008). doi:10.1351/pac200880030563.

- 22 V. Y. Lee, A. Sekiguchi. *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds*. (2010).
- 23 A. J. Ashe. The Group 5 heterobenzenes. *Acc. Chem. Res.* **11**, 153-157 (1978). doi:10.1021/ar50124a005.
- 24 A. J. Ashe. in *Organic Chemistry*. 125-155 (Springer Berlin Heidelberg).
- 25 M. J. Gallagher. in *Phosphorus-Carbon Heterocyclic Chemistry* (ed François Mathey) 463-483 (Elsevier Science Ltd, 2001).
- 26 M. Nicolas, F. Pascal Le. The Chemistry of Phosphinines: Syntheses, Coordination Chemistry and Catalysis. *Curr. Org. Chem.* **10**, 3-25 (2006). doi: 10.2174/138527206775193004.
- 27 Z. Liu, T. B. Marder. B-N versus C-C: how similar are they? *Angew. Chem. Int. Ed. Engl.* **47**, 242-244 (2008). doi:10.1002/anie.200703535.
- 28 M. J. D. Bosdet, W. E. Piers. B-N as a C-C substitute in aromatic systems. *Can. J. Chem.* **87**, 8-29 (2009). doi:10.1139/v08-110.
- 29 G. Bélanger-Chabot, H. Braunschweig, D. K. Roy. Recent Developments in Azaborinine Chemistry. *Eur. J. Inorg. Chem.* **2017**, 4353-4368 (2017). doi:10.1002/ejic.201700562.
- 30 A. Stock, E. Pohland. Borwasserstoffe, IX.: B₃N₃H₆. *Ber. Dtsch. Chem. Ges.* **59**, 2215-2223 (1926). doi:10.1002/cber.19260590907.
- 31 D. Bonifazi, F. Fasano, M. M. Lorenzo-Garcia, D. Marinelli, H. Oubaha, J. Tasseroul. Boron–nitrogen doped carbon scaffolding: organic chemistry, self-assembly and materials applications of borazine and its derivatives. *Chem. Commun.* **51**, 15222-15236 (2015). doi:10.1039/C5CC06611E.

- 32 G. W. Schaeffer, R. Schaeffer, H. I. Schlesinger. The Preparation of Borazole and its Reactions with Boron Halides1. *J. Am. Chem. Soc.* **73**, 1612-1614 (1951). doi:10.1021/ja01148a059.
- 33 C. A. Brown, A. W. Laubengayer. B-Trichloroborazole1. *J. Am. Chem. Soc.* **77**, 3699-3700 (1955). doi:10.1021/ja01619a007.
- 34 L. F. Hohnstedt, D. T. Haworth. Preparation of N-Trisubstituted Borazines by Reduction of B-Trichloroborazines1. *J. Am. Chem. Soc.* **82**, 89-92 (1960). doi:10.1021/ja01486a019.
- 35 T. Wideman, L. G. Sneddon. Convenient Procedures for the Laboratory Preparation of Borazine. *Inorg. Chem.* **34**, 1002-1003 (1995). doi:10.1021/ic00108a039.
- 36 W. Harshbarger, G. H. Lee, R. F. Porter, S. H. Bauer. Structure of borazine. *Inorg. Chem.* **8**, 1683-1689 (1969). doi:10.1021/ic50078a023.
- 37 G. Moussa, C. Salameh, A. Bruma, S. Malo, B. U. Demirci, S. Bernard, P. Miele. Nanostructured Boron Nitride: From Molecular Design to Hydrogen Storage Application. *Inorganics* **2**, 396-409 (2014). doi:10.3390/inorganics2030396.
- 38 V. Salles, S. Bernard. A review on the preparation of borazine-derived boron nitride nanoparticles and nanopolyhedrons by spray-pyrolysis and annealing process. *Nanomater. Nanotechnol.* **6**, 1-13 (2016).
- 39 E. W. David. Organo-phosphorus-boron compound and method of making same. United States patent US3035095A (1962).
- 40 H. V. R. Dias, P. P. Power. Synthesis and X - Ray Structure of (2,4,6 - Me₃C₆H₂BPC₆H₁₁)₃: A Boron-Phosphorus Analogue of Borazine. *Angew. Chem. Int. Ed. Engl.* **26**, 1270-1271 (1987). doi:10.1002/anie.198712701.
- 41 H. V. R. Dias, P. P. Power. Boron-phosphorus analogs of benzene and cyclobutadiene. Synthesis and characterization of the boraphosphabenzenes (RBPR')₃ (R = Mes, Ph; R'

- = Ph, Mes, C₆H₁₁, tert-Bu) and the diphosphadiboretane (thexylBPMe_s)₂. *J. Am. Chem. Soc.* **111**, 144-148 (1989). doi:10.1021/ja00183a025.
- 42 D. C. Pestana, P. P. Power. Nature of the boron-phosphorus bond in monomeric phosphinoboranes and related compounds. *J. Am. Chem. Soc.* **113**, 8426-8437 (1991). doi:10.1021/ja00022a034.
- 43 K. M. Waggoner, H. Hope, P. P. Power. Synthesis and Structure of [MeAlN(2,6-iPr₂C₆H₃)]₃: An Aluminum-Nitrogen Analogue of Borazine. *Angew. Chem. Int. Ed. Engl.* **27**, 1699-1700 (1988). doi:10.1002/anie.198816991.
- 44 R. J. Wehmschulte, P. P. Power. Reactions of (H₂AlMe_s*)₂ (Me_s* = 2,4,6-(t-Bu)₃C₆H₂) with H₂EAr (E = N, P, or As; Ar = aryl): Characterization of the Ring Compounds (Me_s*AlNPh)₂ and (Me_s*AlEPh)₃ (E = P or As). *J. Am. Chem. Soc.* **118**, 791-797 (1996). doi:10.1021/ja952021c.
- 45 H. Hope, D. C. Pestana, P. P. Power. Synthesis and Structure of the Novel Ga₃P₃ Ring Compound [(2,4,6-Ph₃C₆H₂)GaP(cyclo-C₆H₁₁)]₃. *Angew. Chem. Int. Ed.* **30**, 691-693 (1991). doi:10.1002/anie.199106911.
- 46 D. P. Gates, R. Ziembinski, I. Manners, A. L. Rheingold, B. S. Haggerty. Synthesis and Structure of the First Hybrid Borazine—Phosphazene Ring. *Angew. Chem. Int. Ed.* **33**, 2277-2279 (1994). doi:10.1002/anie.199422771.
- 47 C. R. Kinney, D. F. Pontz. The Structure of the Organoboron Oxides. *J. Am. Chem. Soc.* **58**, 197-197 (1936). doi:10.1021/ja01293a005.
- 48 H. R. Snyder, J. A. Kuck, J. R. Johnson. Organoboron Compounds, and the Study of Reaction Mechanisms. Primary Aliphatic Boronic Acids¹. *J. Am. Chem. Soc.* **60**, 105-111 (1938). doi:10.1021/ja01268a033.
- 49 L. Barton, F. A. Grimm, R. F. Porter. Boroxine: A Simplified Preparation. *Inorg. Chem.* **5**, 2076-2078 (1966). doi:10.1021/ic50045a062.

- 50 C.-H. Chang, R. F. Porter, S. H. Bauer. Molecular structure of boroxin, $\text{H}_3\text{B}_3\text{O}_3$, determined by electron diffraction. *Inorg. Chem.* **8**, 1689-1693 (1969). doi:10.1021/ic50078a024.
- 51 Y. Tokunaga, H. Ueno, Y. Shimomura, T. Seo. Formation of Boroxine: Its Stability and Thermodynamic Parameters in Solution. *Heterocycles* **57**, 787-790 (2002). doi:10.3987/COM-02-9464.
- 52 H. C. Brown, T. E. Cole. Organoboranes. 39. Convenient procedures for the preparation of methylboronic acid and trimethylboroxin. *Organometallics* **4**, 816-821 (1985). doi:10.1021/om00124a002.
- 53 J. Goubeau, H. Keller. Über Boroxol-Verbindungen Darstellung, physikalische und chemische Eigenschaften. *Z. Anorg. Allg. Chem.* **267**, 1-26 (1952). doi:10.1002/zaac.19522670102.
- 54 G. F. Hennion, P. A. McCusker, E. C. Ashby, A. J. Rutkowski. Organoboron Compounds. VIII. The Reaction of Triorganoboranes with Boric Oxide¹. *J. Am. Chem. Soc.* **79**, 5194-5196 (1957). doi:10.1021/ja01576a032.
- 55 A. L. Korich, P. M. Iovine. Boroxine chemistry and applications: A perspective. *Dalton Trans.* **39**, 1423-1431 (2010). doi:10.1039/B917043J.
- 56 Y. Tokunaga. Boroxine Chemistry: From Fundamental Studies to Applications in Supramolecular and Synthetic Organic Chemistry. *Heterocycles* **87**, 991-1021 (2013). doi:10.3987/rev-13-767.
- 57 E. Wiberg, W. Sturm. Über Derivate eines „Borsulfols“ $\text{B}_3\text{H}_3\text{S}_3$ II. Zur Kenntnis einer trimeren Metathioborsäure $[\text{B}(\text{SH})\text{S}]_3$. *Z. Naturforsch. B Chem. Sci.* **8**, 530-531 (1953).
- 58 W. Egon, S. Winfried. Notizen: Über Derivate eines „Borsulfols“ $\text{B}_3\text{H}_3\text{S}_3$. I. Zur Kenntnis trimerer Halogenborsulfide $(\text{BXS})_3$. *Z. Naturforsch. B Chem. Sci.* **8**, 529-530 (1953). doi: 10.1515/znb-1953-0916.

- 59 E. Wiberg, W. Sturm. Die Chemie des Borsulfols [BHS]₃ und seiner Derivate. *Angew. Chem.* **67**, 483-493 (1955). doi:10.1002/ange.19550671707.
- 60 W. Schwarz, H. D. Hausen, H. Hess. Neubestimmung der Kristallstruktur von Tribromborsulfol. *Z. Naturforsch. B Chem. Sci.* **B 29**, 596-598 (1974). doi:10.1515/znb-1974-9-1004.
- 61 W. Schwarz, H. D. Hausen, J. Hess, J. Mandt, W. Schmelzer, B. Krebs. Trimere Metathioborsäure (HSBS)₃. *Acta Crystallogr. B* **29**, 2029-2031 (1973). doi:doi:10.1107/S0567740873006035.
- 62 O. Conrad, C. Jansen, B. Krebs. Boron-sulfur and boron-selenium compounds - From unique molecular structural principles to novel polymeric materials. *Angew. Chem. Int. Ed.* **37**, 3208-3218 (1998). doi:10.1002/(sici)1521-3773(19981217)37:23<3208::Aid-anie3208>3.0.Co;2-5.
- 63 M. Schmidt, E. Kiewert. Notizen: Zur Kenntnis des ersten Vertreters eines „Borselenol“-Systems / Triphenylboroselenol — The First Representative of the “Boroselenol”-System. *Z. Naturforsch. B Chem. Sci.* **26**, 613-613 (1971). doi:10.1515/znb-1971-0623.
- 64 A. E. Seitz, M. Eckhardt, A. Erlebach, E. V. Peresypkina, M. Sierka, M. Scheer. Pnictogen–Silicon Analogues of Benzene. *J. Am. Chem. Soc.* **138**, 10433-10436 (2016). doi:10.1021/jacs.6b07389.
- 65 R. A. Bartlett, P. P. Power. Synthesis and structural characterization of the cyclic species [GeN(2,6-iso-Pr₂C₆H₃)]₃: the first "germanazene". *J. Am. Chem. Soc.* **112**, 3660-3662 (1990). doi:10.1021/ja00165a062.
- 66 L. Justus. Nachtrag der Redaktion. *Ann. Chem.* **11**, 139-150 (1834). doi:doi:10.1002/jlac.18340110203.

- 67 H. Rose. Ueber eine Verbindung des Phosphors mit dem Stickstoff. *Ann. Chem.* **11**, 129-139 (1834). doi:doi:10.1002/jlac.18340110202.
- 68 J. H. Gladstone, J. D. Holmes. XXVII.—On chlorophosphuret of nitrogen, and its products of decomposition. *J. Chem. Soc.* **17**, 225-237 (1864). doi:10.1039/JS8641700225.
- 69 H. N. Stokes. *Am. Chem. J.* **17**, 275-290 (1895).
- 70 G. J. Bullen. An improved determination of the crystal structure of hexachlorocyclotriphosphazene (phosphonitrilic chloride). *J. Chem. Soc. A*, 1450-1453 (1971). doi:10.1039/J19710001450.
- 71 V. Chandrasekhar, B. Murugesapandian. Phosphorus-Supported Ligands for the Assembly of Multimetal Architectures. *Acc. Chem. Res.* **42**, 1047-1062 (2009). doi:10.1021/ar800221e.
- 72 H. R. Allcock. Recent advances in phosphazene (phosphonitrilic) chemistry. *Chem. Rev.* **72**, 315-356 (1972). doi:10.1021/cr60278a002.
- 73 C. W. Allen. Regio- and stereochemical control in substitution reactions of cyclophosphazenes. *Chem. Rev.* **91**, 119-135 (1991). doi:10.1021/cr00002a002.
- 74 V. Chandrasekhar, P. Thilagar, B. Muruges Pandian. Cyclophosphazene-based multi-site coordination ligands. *Coord. Chem. Rev.* **251**, 1045-1074 (2007). doi:10.1016/j.ccr.2006.07.005.
- 75 A.-M. Caminade, A. Hameau, J.-P. Majoral. The specific functionalization of cyclotriphosphazene for the synthesis of smart dendrimers. *Dalton Trans.* **45**, 1810-1822 (2016). doi:10.1039/C5DT03047A.
- 76 C. Zhu, A. K. Eckhardt, A. Bergantini, S. K. Singh, P. R. Schreiner, R. I. Kaiser. The elusive cyclotriphosphazene molecule and its Dewar benzene-type valence isomer (P₃N₃). *Sci. Adv.* **6**, eaba6934 (2020). doi:10.1126/sciadv.aba6934.

Chapter 2: Synthesis, characterization, and reactivity of a neutral and aromatic B₄N₂ inorganic benzene

2.1 Introduction

Aromaticity is one of the most significant fundamental concepts in many fields of chemistry, and six-membered aromatic scaffolds, as represented by benzene (C₆H₆), are ubiquitous in a multitude of organic compounds and natural products.¹⁻⁷ To modulate the intrinsic electronic nature of aromatic molecules, partial incorporation of heteroatoms into the benzene scaffold, giving rise to hybrid organic/inorganic benzene, represents a widely used strategy in modern inorganic chemistry.⁸⁻¹⁷ In sharp contrast, only a handful isolable examples of carbon-free purely inorganic benzenes have been described so far (Figure 2.1.1). In 1926, Stock et al. reported the first isolation of borazine (B₃N₃H₆),¹⁸ which possesses a planar six-membered ring associated with a 6 π electron system. While the physical properties of borazine were found to be similar to those of benzene, its aromaticity is still under debate.¹⁹⁻²⁴ After that, the “heavy” borazine derivatives have been reported (Figure 2.1.1 a), but again, the nature of its aromaticity still remains unclear.²⁵⁻²⁹ Boroxines (B₃O₃R₃)^{30,31} and its heavier analogues (B₃S₃R₃ and B₃Se₃R₃)^{32,33} formally bear the 6 π electron system over the six-membered ring, making them isoelectronic to benzene, but it is recognized nowadays that they possess only little aromaticity (Figure 2.1.1 b). Cyclophosphazenes (N₃P₃R₆) and triars- and triphosphatrisilabenzenes (Si₃As₃R₆, Si₃P₃R₆) are also considered as a relevant class of molecules with electron delocalization (Figure 2.1.1 c).^{34,35} Despite their potential applications,³⁶⁻⁴² to the best of our knowledge, only a small number of inorganic benzenes exhibiting a pronounced aromatic nature have been confirmed to date.⁴³⁻⁴⁵

Figure 2.1.1. Structure motifs of the reported examples of inorganic benzenes containing a) group 13/15, b) group 13/16 and c) group 14/15 and 15/15.

2.2 Objectives

We reasoned that the “Boron-rich” B_4N_2 system containing two B–B bonds and four B–N units, would be less polarized than the extant B_3N_3 borazine system containing six B–N units. Consequently, the pronounced aromatic nature could be expected (Figure 2.2.1).

Figure 2.2.1. Structure motif of neutral B_4N_2 benzene derivative.

2.3 Results and Discussions

A diazatetraborinane derivative (**1**) was obtained from the deprotonation of 1,2-bis(anilide)-1,2-bis-(dimethylamido)diborane with two equivalents of *n*-butyllithium, followed by treatment with bis(dimethylamido)diborondichloride (Scheme 2.3.1). Subsequent reaction of **1** with four equivalents of boron trichloride (BCl₃) in dichloromethane (DCM) afforded the corresponding chlorinated B₄N₂ heterocycle (**2**) in 56% yield. In the presence of trimethyl phosphine (PMe₃), reduction of **2** with excess potassium graphite (KC₈) in benzene at room temperature proceeded smoothly and led a dark blue solution. After workup, single crystals of product **3** were obtained in 81% yield. In the ¹¹B NMR spectrum of **3**, a broad signal for the boron atoms attached to PMe₃ group appeared at $\delta = 20.8$ ppm and a broad peak for the boron atoms with chlorine substituent was observed at $\delta = 38.6$ ppm. Both signals shifted downfield compared with those of the precursor **2** ($\delta = 48.8$ ppm). The ³¹P NMR spectrum shows a broad singlet at $\delta = -24.4$ ppm.

The solid-state structure of **3** was determined by a single-crystal X-ray diffraction study (Figure 2.3.1), revealing that **3** adopts a C₂-symmetry and the B₄N₂ six-membered ring is completely planar with the sum of the internal bond angles of 720°. The central B₄N₂ ring and the mesityl rings are nearly perpendicular to each other (the torsion angle: B1–N1–C1–C6 = 85.3°). All boron atoms display trigonal-planar geometry (the sum of bond angles: B1 = 360.0° and B2 = 360.0°), which are characteristic for *sp*² hybridization. The B–B bond length of **3** [1.622(6) Å] is in the range between the typical boron–boron single and double bonds,⁴⁶⁻⁵⁰ and shorter compared to that of **1** [1.725(4)–1.727(4) Å] and **2** [1.718(2) Å]. The B–N bond lengths [N1–B1: 1.432(5) Å, N1–B2: 1.464(5) Å] are within the typical boron–nitrogen single and double bonds length, and comparable to those in the reported azaborine and diazadiborinine.⁵¹⁻

⁵⁵ These metric parameters indicate the delocalization of 6 electrons over the central B₄N₂ ring.

In the UV-vis absorption spectrum, the maximum absorption band at a wavelength of 607 nm

was observed (Figure 2.5.21). The cyclic voltammogram (CV) of **3** shows an irreversible oxidation wave at $E_{\text{OX}}^1 = -1.45$ V (Figure 2.5.25), indicating the electron-rich nature of **3**.⁵⁵

Scheme 2.3.1. Synthesis of **3** (Mes = 2,4,6-trimethylphenyl).

Figure 2.3.1. Solid-state structure of **3** (hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

To gain insight into the electronic structure of **3**, DFT calculation involving geometry optimization, natural bond orbital (NBO) analysis, and natural population analysis was carried out at the B3LYP/6-311G level of theory. The HOMO comprises delocalized π -type orbitals over the B-B units, whereas the B-N π -bonding orbitals are found in the HOMO-7 as well as

the HOMO-10 with some contribution from the lone pairs of the chlorine atoms (Figure 2.3.2). In the HOMO-12, the bonding orbital is delocalized over the entire B₄N₂ six-membered ring. NBO analysis gave Wiberg bond index (WBI) value of 1.25 for the B-B moieties, indicating the multiple bond nature. The WBI values for the boron-nitrogen bonds are 0.94 for B1-N1 and 0.95 for B2-N1, respectively. The compositions of B-N π bonds in **3** (B1 (18%)–N1 (82%) and of B2 (21%)–N1 (79%)) are less polarized than that of borazine (B (12%)–N (88%)).⁵⁶

In order to assess the aromatic nature of **3**, we have further performed theoretical studies. The calculated nucleus-independent chemical-shift (NICS) values of **3** [NICS(0) = -3.93, NICS(1) = -4.59] are less negative than those of benzene [NICS(0) = -7.16, NICS(1) = -10.65], but more negative than those of borazine [NICS(0) = -2.23, NICS(1) = -3.37]. Natural resonance theory (NRT) analysis⁵⁷⁻⁵⁹ revealed the considerable delocalization of π -electrons over the B₄N₂ ring (Figure 2.3.3 a). Among whole resonance structures, two covalent (Kekulé) structures (**3a** and **3a'**) show the largest weights (27.5%). The resonance weights of the structures with a lone pair on the B atom with PMe₃ (**3b** and **3b'**) and those with a lone pair on the Cl-substituted B atom (**3c** and **3c'**) are 11.1% and 8.2%, respectively. The ionicity of B-N bonds of **3** (61.4% and 57.7%) is comparable to that of borazine (62.5%).⁶⁰ Delocalization of π -electrons in **3** was further evaluated by the anisotropy of the current-induced density (ACID) analysis (Figure 2.3.3 b),^{61,62} and the clockwise current density vectors plotted on the ACID isosurface confirms the distinct diatropic ring current effect over the B₄N₂ six-membered ring. These computational outcomes indicate the genuine aromatic nature for the 6 π system of **3**.

Figure 2.3.2. Selected key molecular orbitals of **3**.

Figure 2.3.3. (a) Resonance structures of **3** and their NRT weights (%) (mesityl groups on the N atoms are omitted for clarity, $P = \text{PMe}_3$). (b) ACID plot of **3** at an isosurface value of 0.02.

Under inert atmosphere, compound **3** is stable at room temperature, both in the solid state and in solutions, but gradually decomposes upon heating at 60 °C in a benzene or THF solution. Subsequently, we briefly investigated the reactivity of **3** towards unsaturated bonds (Scheme 2.3.2). Treatment of **3** with a stoichiometric amount of diphenylacetylene in benzene at room temperature instantaneously led to a colourless solution, and after workup compound **4** was gained in 82% yield. **4** was characterized by standard spectroscopic, analytical and crystallographic methods. In the ^{11}B NMR spectrum, a set of new broad peaks was detected at 45.7 ppm for the Cl-bound boron atoms and -9.18 ppm for the tetracoordinate boron atoms. The solid-state structure of **4** exhibits the bicyclo[2.2.2] framework involving the B=N double bonds (B1–N1: 1.394(3) Å and B4–N2: 1.381(3) Å).^{63,64} The phosphine-bounded boron atoms (B2 and B3) are attached to the central carbon atoms of diphenylacetylene, confirming that a [4+2] cycloaddition reaction took place between **3** and PhCCPh. We also observed a similar cycloaddition reaction between **3** and CO₂. Thus, when CO₂ gas was introduced into a benzene solution of **3** at 1 bar, the solution colour promptly turned to yellow, which displayed broad singlets at 50.9 ppm for the tricoordinate boron atoms and at 0.49 ppm and -12.4 ppm for the tetracoordinate boron atoms in the ^{11}B NMR spectrum. After workup, compound **5** was isolated as a pale-yellow solid in 87% yield. A ^{13}C -labelling study with $^{13}\text{CO}_2$ afforded **5**- ^{13}C (93% yield), and the ^{13}C NMR spectrum of which showed a broad singlet at 196.8 ppm for the bound CO₂ unit. X-ray diffractometry confirmed the bicyclo[2.2.2] structure of **5** bearing two phosphine-coordinated boron atoms (B2 and B3) at the bridgehead. The solid-state IR spectrum of **5** exhibited characteristic C=O vibration at 1622 cm⁻¹ (Figure 2.5.24). The boron-centered reactivity of **3** is reminiscent of that of diazadiborinines which also undergo the formal [4+2] cycloaddition reactions with unsaturated molecules.^[14c,d,f,g] To the best of our knowledge, formation of **4** and **5** represents the first example of alkyne and CO₂ activation by inorganic benzene under the ambient conditions.

Scheme 2.3.2. Formation of **4** and **5** by the reactions of **3** with diphenylacetylene and CO₂ (¹³CO₂).

More than ninety years after the discovery of borazine, a neutral B,N-based inorganic benzene derivative **3** featuring the B₄N₂ ring system has joined into a class of 6 π -Hückel molecules. A joint experimental and computational study indicates the moderate but pronounced aromatic nature of **3**. A preliminary reactivity study showed that compound **3** readily undergoes a [4+2] cycloaddition reaction with unsaturated molecules such as diphenylacetylene and CO₂. The further investigation of the reactivity of **3** is currently being carried out in our laboratory.

2.4 Summary

In conclusion, we have developed a novel inorganic benzene derivative based on the B_4N_2 core, and its spectroscopic properties as well as the solid-state structure have been revealed. The aromaticity of **3** was evaluated computationally, which suggested **3** exhibits less aromatic than benzene but more aromatic than borazine. We also investigated the reactions of **3** with diphenylacetylene and carbon dioxide, which afforded the respective [2.2.2] bicyclic products via a formal [4+2] cycloaddition.

2.5 Experimental Sections

1. Synthesis of compounds 1-5

General procedure: All reactions were performed under an atmosphere of argon or nitrogen by using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH₂. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. ¹H, ¹³C{¹H}, ¹¹B NMR spectra were obtained with a Bruker Avance 300MHz spectrometer, and a Bruker AVIII 400MHz BBFO spectrometer at 298 K. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. In the ¹³C NMR spectra of compounds **4** and **5**, presumable owing to the coupling with boron atoms, signals for the carbon atoms directly bonding to boron atoms could not be observed. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with an OpticMelt Stanford Research System. UV-Vis absorption spectra were carried out with Cary 300 UV-Vis spectrometer. Cyclic voltammetry (CV) was performed on a Biologic SP-50 electrochemical analyzer in anhydrous THF containing recrystallized tetra-*n*-butylammoniumhexafluorophosphate (TBAPF₆, 0.1M) as supporting electrolyte at 298 K under an inert atmosphere of argon. A conventional three electrode cell was used with a glassy carbon electrode as the auxiliary electrode, silver/silver nitrate as the reference electrode, and a platinum wire as the working electrode. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker ALPHA-Transmittance FT-IR Spectrometer. (MesNH)(NMe₂)B–B(NMe₂)(NHMes)⁶⁵ and (NMe₂)ClB–BCl(NMe₂)⁶⁶ were prepared following the literature procedures.

Synthesis of 1

ⁿBuLi (8.30 mL, 2.0M) in cyclohexane was added dropwise to a hexane solution (30 mL) of diborane(4) (MesNH)(NMe₂)B-B(NMe₂)(NHMe₂) (3.03 g, 8.02 mmol) at -30 °C, then small amount of THF (2 mL) was added dropwise at -30 °C. The mixture was then stirred for 4 hours at room temperature. After the completion of reaction, all the solvent was removed in vacuum and lithium salt was collected by filtration and washed by hexane (3×10 mL). After that, the mixture of the lithium salt (1.00 g, 1.87 mmol) and (NMe₂)ClB-BCl(NMe₂) (330 mg, 1.83 mmol) in toluene (20 mL) was heated 55 °C over 2 days. All the solvent was removed in vacuum and the residue was extracted with hexane. After removal of hexane, the pure product was obtained by recrystallization in toluene at room temperature (300 mg, 34%).

¹H NMR (C₆D₆, 400 MHz, 298 K): δ 6.90 (s, 4H, ArH), 2.83 (s, 12H, N(CH₃)₂), 2.37 (s, 12H, N(CH₃)₂), 2.24 (s, 6H, CH₃), 2.15 (s, 12H, CH₃); ¹¹B NMR (C₆D₆, 128 MHz, 298 K): δ 38.4 (br, B-N(CH₃)₂); ¹³C{¹H} NMR (C₆D₆, 100 MHz, 298 K): δ 147.7 (C-Ar), 133.8 (C-Ar), 131.7 (C-Ar), 129.1 (CH-Ar), 44.6 (N(CH₃)₂), 38.2 (Ar-CH₃), 21.0 (Ar-CH₃). M.p.: 137.9 °C (dec.); HRMS (ESI): *m/z* calcd for C₂₆H₄₇B₄N₆: 487.4234. [(*M*+*H*)]⁺; found: 487.4251.

Synthesis of 2

To a DCM solution (10 mL) of **1** (100 mg, 0.21 mmol), BCl₃ (0.84 mL, 1.0 M) in DCM was added dropwise at -78 °C. The mixture was then stirred overnight at room temperature. All the solvent was removed in vacuum and the residue was extracted with hexane. After removal of hexane, the desired product was obtained as a white solid (52 mg, 56%). ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 6.79 (s, 4H, ArH), 2.11 (s, 6H, CH₃), 1.93 (s, 12H, CH₃); ¹¹B NMR (128 MHz, C₆D₆, 298 K): δ 48.8 (br, B-Cl); ¹³C{¹H} NMR (C₆D₆, 100 MHz, 298 K): δ 139.7 (C-Ar), 136.4 (C-Ar), 131.5 (C-Ar), 129.7 (CH-Ar), 20.9 (Ar-CH₃), 18.7 (Ar-CH₃). M.p.: 222.3 °C-

223.0 °C; HRMS (ESI): m/z calcd for $C_{18}H_{23}B_4N_2^{35}Cl_3^{37}Cl$: 453.0958. $[(M+H)]^+$; found: 453.0969.

Synthesis of **3**

To a benzene (1 mL) solution of **2** (19.8 mg, 0.044 mmol) and PMe_3 (12 μ L, 0.12 mmol), KC_8 (32 mg, 0.24 mmol) was added at room temperature. The mixture was stirred for 5 minutes and the dark blue solution was separated by filtration. After removal of the solvent, the residue was dried under vacuum to afford **3** as the blue powder (19.0 mg, 81%). 1H NMR (C_6D_6 , 300 MHz, 298 K): δ 6.88 (s, 4H, ArH), 2.38 (s, 12H, CH_3), 2.21 (s, 6H, CH_3), 0.90 (d, J = 11.3 Hz, 18H, $P(CH_3)_3$); ^{11}B NMR (C_6D_6 , 128 MHz, 298 K): δ 38.6 (br, $B-Cl$), 20.8 (br, $B-P(CH_3)_3$); $^{13}C\{^1H\}$ NMR (C_6D_6 , 100 MHz, 298 K): δ 149.3 ($C-Ar$), 133.7 ($C-Ar$), 133.5 ($C-Ar$), 128.8 ($CH-Ar$), 21.1 (Ar- CH_3), 18.9 (Ar- CH_3), 13.9 ($P(CH_3)_3$), 13.5 ($P(CH_3)_3$); ^{31}P NMR (C_6D_6 , 161 MHz, 298 K): δ -24.4 ($P(CH_3)_3$). M.p.: 128.3 °C (dec.); UV-Vis (in toluene): 607 nm; FT-IR (solid, cm^{-1}): 2906, 1473; 1364; 1306; 1254; 1209; 1160; 1090; 1021; 940; 846; 797; 748; 674; HRMS (ESI): m/z calcd for $C_{24}H_{41}^{10}B_2^{11}B_2N_2P_2^{37}Cl_2$: 535.2508. $[(M+H)]^+$; found: 535.2514.

Synthesis of **4**

Diphenylacetylene (6.4 mg, 0.036 mmol) was added to a hexane (1.0 ml) solution of **3** (19.0 mg, 0.036 mmol), and the reaction mixture stirred for 15 min at room temperature. After removal of the solvent, the residue was washed with hexane and dried under vacuum to afford **4** as the white powder (20.8 mg, 82%). 1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.21 (br, 2H, ArH), 6.98 (br, 4H, ArH), 6.92 (s, 2H, ArH), 6.83-6.80 (m, 2H + 2H, ArH), 6.72 (br, 2H, ArH), 2.47 (s, 6H, CH_3), 2.27 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 0.90 (d, J = 10.8 Hz, 18H, $P(CH_3)_3$); ^{11}B NMR ($CDCl_3$, 96 MHz, 298 K): δ 45.7 (br, $B-Cl$), -9.18 (br, $B-C$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 298 K): δ 149.7, 146.6, 135.6, 135.0, 133.4, 130.4, 128.4, 127.3, 126.7, 123.8, 21.1

(Ar-CH₃), 20.8 (Ar-CH₃), 19.9 (Ar-CH₃), 12.0 (P(CH₃)₃), 11.6 (P(CH₃)₃); ³¹P NMR (CDCl₃, 161 MHz, 298 K): δ -14.9 (P(CH₃)₃); M.p.: 210.4 °C (dec.); FT-IR (solid, cm⁻¹): 2912, 1592; HRMS (ESI): m/z calcd for C₃₈H₅₁B₄N₂P₂Cl₂: 711.3277. [(M+H)]⁺; found: 711.3278.

Synthesis of **5**

A benzene (1.0 ml) solution of **3** (19.0 mg, 0.036 mmol) was degassed using a freeze–pump–thaw method, and then CO₂ (1bar) was introduced into the schlenk tube, and the reaction mixture stirred for 5 min at room temperature. After removal of the solvent, the residue was dried under vacuum to afford **5** as a pale yellow powder (17.8 mg, 87%).

¹H NMR (C₆D₆, 400 MHz, 298 K): δ 6.80 (s, 1H, ArH), 6.79 (s, 1H, ArH), 6.77 (s, 1H, ArH), 6.76 (s, 1H, ArH), 2.40 (s, 3H, CH₃), 2.38 (s, 9H, CH₃), 2.13 (s, 6H, CH₃), 1.03 (d, J = 11.6 Hz, 9H, P(CH₃)₃), 0.73 (d, J = 11.6 Hz, 9H, P(CH₃)₃); ¹¹B NMR (C₆D₆, 128 MHz, 298 K): δ 50.9 (br, B–Cl), 0.49 (br, B–O), -12.4 (br, B–C); ¹³C{¹H} NMR (C₆D₆, 100 MHz, 298 K): δ 145.32 (C-Ar), 145.29 (C-Ar), 135.2 (C-Ar), 135.0 (C-Ar), 134.9 (C-Ar), 134.4 (C-Ar), 134.0 (C-Ar), 133.9 (C-Ar), 129.1 (CH-Ar), 129.07 (CH-Ar), 128.9 (CH-Ar), 128.8 (CH-Ar), 20.99 (Ar-CH₃), 20.96 (Ar-CH₃), 20.03 (Ar-CH₃), 19.96 (Ar-CH₃), 19.8 (Ar-CH₃), 19.7 (Ar-CH₃), 9.54 (P(CH₃)₃), 9.13 (P(CH₃)₃), 7.87 (P(CH₃)₃), 7.50 (P(CH₃)₃); ³¹P NMR (C₆D₆, 161 MHz, 298 K): δ -13.7 (P(CH₃)₃), -19.3 (P(CH₃)₃). M.p.: 233.8 °C (dec.); FT-IR (solid, cm⁻¹): 1622; HRMS (ESI): m/z calcd for C₂₄H₄₁¹⁰B¹¹B₃N₂P₂O₂³⁵Cl³⁷Cl: 578.2339. [(M+H)]⁺; found: 578.2405.

Synthesis of **5**-¹³CO₂

By following the same procedure utilized for the synthesis of **5**, the reaction employing ¹³CO₂ afforded **5**-¹³C (23.5 mg, 93%). ¹¹B NMR (C₆D₆, 128 MHz, 298 K): δ 49.3 (br, B–Cl), 0.34 (br, B–O), -12.1 (br, B–C); ¹³C{¹H}c NMR (C₆D₆, 100 MHz, 298 K): δ **196.8 (C=O)**, 145.3

(C-Ar), 135.2 (C-Ar), 135.0 (C-Ar), 134.9 (C-Ar), 134.4 (C-Ar), 134.0 (C-Ar), 133.9 (C-Ar), 129.10 (CH-Ar), 129.07 (CH-Ar), 128.9 (CH-Ar), 128.8 (CH-Ar), 20.99 (Ar-CH₃), 20.96 (Ar-CH₃), 20.03 (Ar-CH₃), 19.96 (Ar-CH₃), 19.8 (Ar-CH₃), 19.7 (Ar-CH₃), 9.54 (P(CH₃)₃), 9.14 (P(CH₃)₃), 7.88 (P(CH₃)₃), 7.50 (P(CH₃)₃). M.p.: 239.1 °C (dec.); HRMS (ESI): m/z calcd for ¹²C₂₄¹³CH₄₁B₄N₂P₂³⁵Cl₂: 578.2426. [(*M*+*H*)]⁺; found: 578.2419.

2. NMR Spectra of 1-5

Figure 2.5.1. ^1H NMR spectrum of **1** (C_6D_6).

Figure 2.5.2. ^{11}B NMR spectrum of **1** (C_6D_6).

Figure 2.5.3. ^{13}C NMR spectrum of **1** (C_6D_6).

Figure 2.5.4. ^1H NMR spectrum of **2** (C_6D_6).

Figure 2.5.5. ^{11}B NMR spectrum of **2** (C_6D_6).

Figure 2.5.6. ^{13}C NMR spectrum of **2** (C_6D_6).

Figure 2.5.7. ¹H NMR spectrum of **3** (C₆D₆; Because **3** is extremely air- and moisture-sensitive, despite many attempts, satisfactory clean NMR spectrum even using single crystals could not be obtained).

Figure 2.5.8. ¹¹B NMR spectrum of **3** (C₆D₆).

Figure 2.5.9. ¹³C NMR spectrum of **3** (C₆D₆).

Figure 2.5.10. ³¹P NMR spectrum of **3** (C₆D₆).

Figure 2.5.11. ¹H NMR spectrum of **4** (CDCl₃).

Figure 2.5.12. ¹¹B NMR spectrum of **4** (CDCl₃).

Figure 2.5.13. ^{13}C NMR spectrum of **4** (CDCl_3).

Figure 2.5.14. ^{31}P NMR spectrum of **4** (CDCl_3).

Figure 2.5.15. ¹H NMR spectrum of **5** (C₆D₆).

Figure 2.5.16. ¹¹B NMR spectrum of **5** (C₆D₆).

Figure 2.5.17. ¹³C NMR spectrum of **5** (C₆D₆).

Figure 2.5.18. ³¹P NMR spectrum of **5** (C₆D₆).

Figure 2.5.19. ^{11}B NMR spectrum of $5\text{-}^{13}\text{CO}_2$ (C_6D_6).

Figure 2.5.20. ^{13}C NMR spectrum of $5\text{-}^{13}\text{CO}_2$ (C_6D_6).

3. UV-Vis spectroscopy of 3

Figure 2.5.21. Experimental (black line) and calculated (red line) UV-Vis absorption spectra of 3.

4. FT-IR spectroscopy of 3-5

Figure 2.5.22. FT-IR spectrum of 3.

Figure 2.5.23. FT-IR spectrum of 4.

Figure 2.5.24. FT-IR spectrum of **5**.

5. Cyclic voltammogram of **3**

Figure 2.5.25. Cyclic voltammogram of **3** in THF/0.1 M [ⁿBu₄N][PF₆] at room temperature. Scan rate: 200 mVs⁻¹.

6. Crystal structural parameters of 1-5

X-ray data collection and structural refinement. Intensity data for compounds **1-5** was collected using a Bruker APEX II diffractometer, and a Bruker X8 CCD Diffractometer. The structure was solved by direct phase determination (SHELX-2014) and refined for all data by full-matrix least squares methods on F^2 .⁶⁷ All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC: 1969148-1969152 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 2.5.1. Crystallographic data for **1-5**.

Compounds	1	2	3	4	5
Formula	C ₂₆ H ₄₆ B ₄ N ₆	C ₁₈ H ₂₂ B ₄ Cl ₄ N ₂	C ₂₄ H ₄₀ B ₄ Cl ₂ N ₂ P ₂	C ₃₈ H ₅₀ B ₄ Cl ₂ N ₂ P ₂	C ₂₅ H ₄₀ B ₄ Cl ₂ N ₂ O ₂ P ₂
Fw	485.93	451.41	532.66	710.88	576.67
Cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P 1 21/c 1	P 1 21/c 1	P 1 21/n 1	P 1 21/n 2	P 1 21/c 1
Size (mm ³)	0.240 x 0.260 x 0.300	0.040 x 0.220 x 0.260	0.080 x 0.100 x 0.120	0.100 x 0.100 x 0.200	0.080 x 0.080 x 0.100
T, K	100(2)	100(2)	100(2)	100(2) K	100(2) K
a, Å	14.1091(7)	11.4876(6)	7.0447(6)	15.7933(3)	14.4607(7)
b, Å	13.8079(6)	11.8856(8)	12.9508(9)	15.0952(4)	15.3808(8)
c, Å	15.0760(8)	8.2149(6)	16.4862(15)	17.8064(4)	14.0667(6)
a, deg	90	90	90	90	90
b, deg	93.4548(19)	91.589(4)	97.110(6)	114.0553(11)	106.328(3)
g, deg	90	90	90	90	90
V, Å ³	2931.7(2)	1121.21(13)	1492.5(2)	3876.42(16)	3002.5(3)
Z	4	2	2	4	4
d_{calcd} g·cm ⁻³	1.101	1.337	1.185	1.218	1.276
m, mm ⁻¹	0.064	0.535	0.341	0.28	0.349

Refl collected	6481	13564	8040	26621	18680
T_{max}/T_{min}	0.9850/0.9810	0.9790/0.8730	0.9730/0.9600	0.9730/0.9460	0.9730/0.9660
N _{measd}	6481	3930	3038	8341	5319
[R _{int}]	0.0787	0.0489	0.0768	0.0541	0.1011
R [I>2sigma(I)]	0.073	0.0397	0.0563	0.0423	0.0547
R _w [I>2sigma(I)]	0.1792	0.0846	0.1293	0.113	0.1298
GOF	1.045	1.016	0.836	0.855	0.88
Largest diff. peak/hole[e·Å ⁻³]	0.412/-0.299	0.501/-0.294	0.393/-0.362	0.382/0.311	0.370/-0.385

Figure 2.5.26. Solid structures of **1** (hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability. Selected bond length (Å): B1–B2 1.725(4), B1–N1 1.471(4), B1–N3 1.428(4), B2–N2 1.474(4), B2–N4 1.419(4), B3–N2 1.478(4), B3–B4 1.727(4), B3–N5 1.419(4), B4–N1 1.485(4), B4–N6 1.408(4), N1–C1 1.431(3), N2–C14 1.434(3).

Figure 2.5.27. Solid structures of **2** (hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability. Selected bond length (Å): B1–B2 1.718(2), B1–N1 1.424(2), B1–Cl1 1.7606(17), B2–Cl2 1.7659(17), B2–N1 1.424(2), N1–C1 1.4641(17).

Figure 2.5.28. Solid structures of **3** (hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability. Selected bond length (Å) and angles (°): B1–B2 1.622(6), B1–N1 1.432(5), B1–Cl1 1.860(4), B2–P1 1.917(4), B2–N1 1.464(5), N1–C1 1.451(5), B1–N1–B2 120.0(3), N1–B1–B2 121.4(3), N1–B1–Cl1 115.1(3), B2–B1–Cl1 123.5(3), N1–B2–B1 118.6(3), N1–B2–P1 123.9(3), B1–B2–P1 117.5(3).

Figure 2.5.29. Solid structures of **4** (hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability. Selected bond length (Å): B1–B2 1.721(3), B3–B4 1.730(3), B1–N1 1.394(3), B2–N2 1.594(3), B3–N1 1.597(3), B4–N2 1.381(3), B1–Cl1 1.827(3), B2–P1 1.957(2), B3–P2 1.952(2), B4–Cl2 1.831(2), B2–C25 1.646(3), B3–C32 1.641(3), C25–C32 1.357(3), N1–C1 1.438(3), N2–C10 1.442(2).

Figure 2.5.30. Solid structures of **5** (hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability. Selected bond length (Å): B1–B2 1.742(6), B3–B4 1.721(6), B1–N1 1.391(6), B2–N2 1.581(6), B3–N1 1.570(6), B4–N2 1.395(6), B1–Cl1 1.814(5), B2–P1 1.961(5), B3–P2 1.966(5), B4–Cl2 1.807(5), B2–C25 1.619(6), B3–O1 1.529(6), C25–O1 1.357(5), C25–O2 1.235(5).

7. Computational Details

Density functional theory calculations were performed using the Gaussian 09 software package.⁶⁸ Geometry optimization calculations, frequency calculations and Natural bond order (NBO) analysis were done at the B3LYP/6-311G level of theory.

NBO/NRT and ACID calculation were performed with the Gaussian 16 program package.⁶⁹ NBO/NRT analyses were performed with NBO 6.0 software.⁷⁰ The ACID calculation was performed at the B3LYP/6-311G level. For this calculation, the mesityl group and methyl groups were replaced with hydrogen atoms.

Table 2.5.2. Energies of **3**, C₆H₆, B₃N₃H₆, diphenylacetylene, CO₂, 3', 4', 4'-isomer, 5', 5'-isomer, TS1, and TS2 obtained by DFT calculations (atom, x-, y-, z-positions in Å).

3:

Zero-point correction=	0.612142 (Hartree/Particle)
Thermal correction to Energy=	0.655337
Thermal correction to Enthalpy=	0.656281
Thermal correction to Gibbs Free Energy=	0.534119
Sum of electronic and zero-point Energies=	-2750.278233
Sum of electronic and thermal Energies=	-2750.235038
Sum of electronic and thermal Enthalpies=	-2750.234094
Sum of electronic and thermal Free Energies=	-2750.356256

Cl	1.42836202	-3.09551693	-0.00218608
P	s	2.74018261	-0.00004602

C	-3.64465302	0.5973844	-1.22406878
C	-3.64598433	0.59551974	1.22349566

N	1.52590225	-0.22877347	-0.00032699
C	2.96324979	-0.46778513	0.00070295
C	3.64424976	-0.59714078	1.22443127
C	3.64637477	-0.59574177	-1.22313504
C	5.74234379	-0.92078095	0.00217951
C	5.02954145	-0.81194361	1.20107794
H	5.55712302	-0.91114485	2.14279914
C	2.90247464	-0.55101663	2.53985078
H	2.21635126	0.29582329	2.59441682
H	3.59908628	-0.49009186	3.37669321
H	2.29789901	-1.45192598	2.66917807
C	4.00395417	2.62820966	-0.0030697
H	4.34341841	2.09713851	-0.88651066
H	4.34641159	2.0885688	0.8739897
H	4.40698962	3.63994448	0.00099967
C	5.03070225	-0.81023996	-1.19843014
H	5.55939192	-0.90815916	-2.13985014
C	2.90542357	-0.54785696	-2.53896231
H	2.222349	0.30142051	-2.59448873
H	2.29761372	-1.44660869	-2.66793693
H	3.60269837	-0.48994804	-3.3754536
C	1.78951078	3.85423397	1.48172838
H	2.33048811	4.79306113	1.37027733
H	2.11900332	3.34343806	2.38356734
H	0.72184317	4.04060267	1.53982577
B	0.61342155	-1.34622171	-0.00079388
B	0.97720966	1.12070561	-0.00007167
C	7.23123986	-1.19097386	0.00038203
H	7.43862506	-2.25798685	-0.12440526
H	7.69479691	-0.87661362	0.93671286
H	7.73313543	-0.666252	-0.81496054
Cl	-1.42834351	3.09553233	0.00207204
P	-2.12786397	-2.74017287	-0.00059538
N	-1.52590948	0.22878074	-0.00001555
C	-2.96325585	0.46780712	-0.00057957

C	-5.74235168	0.92078257	-0.00108477
C	-5.02992558	0.81218086	-1.20023664
H	-5.5578063	0.91154139	-2.14177594
C	-2.90328584	0.55139675	-2.5397218
H	-2.21750525	-0.29569737	-2.59475912
H	-3.6001701	0.49098944	-3.37637382
H	-2.29839624	1.45210446	-2.66895775
C	-4.00396289	-2.62816606	0.00137832
H	-4.34396542	-2.09573556	0.88378936
H	-4.34587745	-2.08986431	-0.87671891
H	-4.40701002	-3.6398999	-0.00144856
C	-5.03033523	0.80999528	1.19927233
H	-5.55872675	0.90773182	2.14087479
C	-2.90462596	0.54729594	2.53907723
H	-2.22281112	-0.30299114	2.59487644
H	-2.29540584	1.44518238	2.66733985
H	-3.60169871	0.4908852	3.37583437
C	-1.78893738	-3.85452211	-1.48200195
H	-2.32998685	-4.79330984	-1.37056224
H	-2.11809182	-3.34390114	-2.38406362
H	-0.72125995	-4.04093355	-1.53967736
B	-0.61341475	1.34623367	0.00035528
B	-0.97721058	-1.12069146	-0.00045335
C	-7.23122351	1.1910963	0.00117722
H	-7.4384027	2.25852773	0.12272137
H	-7.69567931	0.87380203	-0.93372783
H	-7.73240332	0.66903103	0.81864581
C	1.78593913	3.8565659	-1.47924398
H	2.11318679	3.34705696	-2.38263329
H	0.71820827	4.04329159	-1.53457135
H	2.32743133	4.79508269	-1.3676889
C	-1.78650861	-3.85632989	1.47890895
H	-0.71895757	-4.04429215	1.53367975
H	-2.11254987	-3.34604876	2.38229378
H	-2.32920553	-4.79423352	1.3680575

C₆H₆:

Zero-point correction=	0.101039 (Hartree/Particle)
Thermal correction to Energy=	0.105357
Thermal correction to Enthalpy=	0.106301
Thermal correction to Gibbs Free Energy=	0.073604
Sum of electronic and zero-point Energies=	-232.147087
Sum of electronic and thermal Energies=	-232.142769
Sum of electronic and thermal Enthalpies=	-232.141825
Sum of electronic and thermal Free Energies=	-232.174521

C	-1.354934	-0.345309	0
C	-0.378306	-1.34606	0.000082
C	0.976495	-1.000751	-0.000072
C	1.354907	0.345427	0.000011
C	0.378419	1.346026	0.000069
C	-0.976581	1.000668	-0.000065

H	-2.403532	-0.612683	-0.000065
H	-0.671281	-2.387805	0.000089
H	1.732386	-1.77513	-0.000149
H	2.403568	0.612531	0.000017
H	0.671145	2.387837	0.000017
H	-1.732282	1.775241	-0.000055

B₃N₃H₆:

Zero-point correction=	0.094379 (Hartree/Particle)
Thermal correction to Energy=	0.099379
Thermal correction to Enthalpy=	0.100324
Thermal correction to Gibbs Free Energy=	0.066389
Sum of electronic and zero-point Energies=	-242.591516
Sum of electronic and thermal Energies=	-242.586516

Sum of electronic and thermal Enthalpies= -242.585572

Sum of electronic and thermal Free Energies= -242.619506

H	0.73558799	-2.84177713	0.00045
H	4.47772499	-0.68162913	0.000634
H	0.73544399	1.47900287	-0.002631
B	2.68039099	0.52679987	-0.001199
H	3.27000584	1.54893194	-0.00180792
B	2.68050699	-1.88946013	0

H	3.27071424	-2.91125042	0
B	0.58796499	-0.68148413	-0.000682
H	-0.59203496	-0.68167868	-0.00041639
N	3.37804499	-0.68170913	0
N	1.28556599	0.52672187	-0.001678
N	1.28534699	-1.88946013	0

Diphenylacetylene:

Zero-point correction= 0.192873 (Hartree/Particle)

Thermal correction to Energy= 0.202743

Thermal correction to Enthalpy= 0.203687

Thermal correction to Gibbs Free Energy= 0.156013

Sum of electronic and zero-point Energies= -539.264012

Sum of electronic and thermal Energies= -539.254141

Sum of electronic and thermal Enthalpies= -539.253197

Sum of electronic and thermal Free Energies= -539.300871

C	-0.606728	0.000009	-0.000005
C	0.606728	-0.000001	-0.000012
C	2.037047	0.000004	-0.000012
C	2.755935	-0.858068	-0.857285
C	2.755927	0.858069	0.857279
C	4.149931	-0.85521	-0.854417
H	2.211643	-1.518914	-1.517521
C	4.149919	0.855208	0.85443
H	2.211623	1.518911	1.51751

H	5.933628	0.000002	0.000016
C	-2.037047	-0.000002	-0.000005
C	-2.755926	-0.858105	0.857244
C	-2.755937	0.858108	-0.857245
C	-4.149921	-0.855249	0.854389
H	-2.211625	-1.518965	1.51746
C	-4.149928	0.855243	-0.854383
H	-2.211639	1.518977	-1.517454
C	-4.85184	-0.000006	0.000006

C	4.85184	0	0.000007
H	4.687883	-1.51933	-1.517919
H	4.687869	1.519325	1.517937

H	-4.687867	-1.51939	1.517876
H	-4.687887	1.519383	-1.517861
H	-5.933628	-0.000006	0.000008

CO₂:

Zero-point correction=	0.010606 (Hartree/Particle)
Thermal correction to Energy=	0.013332
Thermal correction to Enthalpy=	0.014276
Thermal correction to Gibbs Free Energy=	-0.010175
Sum of electronic and zero-point Energies=	-188.546627
Sum of electronic and thermal Energies=	-188.5439
Sum of electronic and thermal Enthalpies=	-188.542956
Sum of electronic and thermal Free Energies=	-188.567408

C	0	0	0
O	0	0	1.185084
O	0	0	-1.185084

3':

Zero-point correction=	0.342095 (Hartree/Particle)
Thermal correction to Energy=	0.368114
Thermal correction to Enthalpy=	0.369059
Thermal correction to Gibbs Free Energy=	0.285524
Sum of electronic and zero-point Energies=	-2131.173857
Sum of electronic and thermal Energies=	-2131.147837
Sum of electronic and thermal Enthalpies=	-2131.146893
Sum of electronic and thermal Free Energies=	-2131.230428

Cl	1.603524	3.011397	0.000477
N	-0.72296	1.362614	-0.000679
B	0.717361	1.294303	-0.000114
B	-1.48336	0.120131	-0.000334
Cl	-1.603502	-3.01144	-0.000633
N	0.722961	-1.362645	0.000192
B	-0.717362	-1.294335	-0.000133
B	1.483358	-0.120159	0.000217
C	-1.363485	2.704443	-0.001695
H	-1.062456	3.272812	0.877014
H	-1.059102	3.272948	-0.879124
H	-2.444686	2.624124	-0.003915
C	1.363476	-2.704479	0.000359
H	1.059603	-3.273351	0.877729
H	1.061922	-3.272473	-0.878411
H	2.444678	-2.624176	0.001912
P	-3.46848	0.240414	0.000218
P	3.468478	-0.240396	0.000084
C	-4.257163	1.117892	1.484172
H	-3.904561	2.142518	1.556397
H	-5.341784	1.108761	1.384049

H	-3.965757	0.580461	2.383448
C	-4.258688	1.114259	-1.485143
H	-5.343223	1.105118	-1.38416
H	-3.906388	2.138809	-1.559928
H	-3.967801	0.574825	-2.383388
C	-4.401819	-1.385564	0.002892
H	-4.138417	-1.965464	-0.874725
H	-4.136482	-1.963462	0.881253
H	-5.467848	-1.161407	0.00381
C	4.258306	-1.11552	1.484859
H	3.906094	-2.14017	1.5587
H	5.342866	-1.10618	1.384108
H	3.967218	-0.576921	2.383538
C	4.257584	-1.116545	-1.484463
H	5.34218	-1.107586	-1.384098
H	3.90492	-2.14108	-1.557649
H	3.966378	-0.578277	-2.383305
C	4.401754	1.385619	-0.0006
H	4.136963	1.964398	-0.878546
H	4.137757	1.964617	0.877435
H	5.467793	1.161508	-0.001064

4':

Zero-point correction=	0.536939 (Hartree/Particle)
Thermal correction to Energy=	0.574384
Thermal correction to Enthalpy=	0.575328
Thermal correction to Gibbs Free Energy=	0.467997
Sum of electronic and zero-point Energies=	-2670.506642
Sum of electronic and thermal Energies=	-2670.469196
Sum of electronic and thermal Enthalpies=	-2670.468252

Sum of electronic and thermal Free Energies=

-2670.575584

B	-0.71754	-1.697865	1.286532
B	-1.31616	-0.944563	-0.145119
B	1.316349	-0.944458	0.144991
B	0.717793	-1.698224	-1.286409
C	-4.108663	-0.08989	1.308666
H	-5.188492	-0.231108	1.314855
H	-3.874086	0.967507	1.233381
H	-3.679379	-0.493902	2.220067
C	-4.088627	-2.72999	0.00132
H	-3.611932	-3.227704	0.839714
H	-3.904743	-3.294354	-0.908685
H	-5.161833	-2.66324	0.174048
C	-4.37549	-0.292418	-1.603555
H	-5.436652	-0.416117	-1.390878
H	-4.127544	-0.81796	-2.521193
H	-4.14674	0.762857	-1.715289
C	4.108659	-0.089621	-1.308773
H	5.188486	-0.230847	-1.315231
H	3.874136	0.967793	-1.233439
H	3.679159	-0.493626	-2.220066
C	4.375323	-0.291231	1.603555
H	4.127561	-0.816719	2.521292
H	4.146012	0.763935	1.715091
H	5.43656	-0.414449	1.39098
C	4.089312	-2.729451	-0.000543
H	3.612993	-3.227484	-0.838964
H	3.90518	-3.293591	0.909552
H	5.162565	-2.662554	-0.172901
C	-0.678208	0.572667	-0.057365
C	-1.4754	1.836009	-0.088572
C	-2.015964	2.317275	-1.297255
H	-1.823297	1.768199	-2.210517
C	-2.759792	3.499755	-1.339557

H	-3.14878	3.856773	-2.285131
C	-2.989945	4.229152	-0.169147
H	-3.564217	5.145697	-0.200504
C	-2.45879	3.769397	1.038958
H	-2.619585	4.332246	1.949773
C	-1.709303	2.590051	1.077304
H	-1.292142	2.245352	2.014
C	0.678361	0.572741	0.05702
C	1.475255	1.836267	0.088313
C	1.709311	2.590239	-1.077572
H	1.292565	2.245303	-2.014368
C	2.45842	3.769826	-1.039116
H	2.619342	4.332616	-1.949946
C	2.989022	4.229889	0.169111
H	3.56298	5.146628	0.200557
C	2.75872	3.50055	1.339529
H	3.14729	3.857798	2.285188
C	2.015287	2.317829	1.297118
H	1.822517	1.76877	2.210366
Cl	-1.738081	-2.439324	2.726411
Cl	1.738456	-2.439861	-2.726128
N	0.664495	-1.706374	1.377735
N	-0.664233	-1.706711	-1.377704
P	-3.379117	-0.995204	-0.164615
P	3.379358	-0.994796	0.164705
C	1.450931	-2.24202	2.492357
H	0.798446	-2.712163	3.224282
H	2.163722	-2.999699	2.156409
H	2.00528	-1.448822	3.004629
C	-1.450603	-2.241349	-2.492833
H	-2.164625	-2.998071	-2.157377
H	-2.003464	-1.447405	-3.005558
H	-0.798216	-2.712429	-3.224251

4'-isomer:

Zero-point correction=	0.536658 (Hartree/Particle)
Thermal correction to Energy=	0.574027
Thermal correction to Enthalpy=	0.574971
Thermal correction to Gibbs Free Energy=	0.467692
Sum of electronic and zero-point Energies=	-2670.482236
Sum of electronic and thermal Energies=	-2670.444867
Sum of electronic and thermal Enthalpies=	-2670.443923
Sum of electronic and thermal Free Energies=	-2670.551202

B	1.31965	1.423591	0.655307
B	1.004084	0.69175	-0.862178
B	-1.003685	0.692254	0.862234
B	-1.318889	1.424232	-0.655227
C	0.535701	-0.815976	-0.425768
C	1.260774	-2.05123	-0.836003
C	1.468633	-2.366922	-2.192866
H	1.100275	-1.69176	-2.951655
C	2.14262	-3.529629	-2.569707
H	2.282519	-3.750715	-3.620611
C	2.643095	-4.402934	-1.599517
H	3.169428	-5.302441	-1.892518
C	2.457608	-4.101474	-0.247615
H	2.83744	-4.770955	0.51441
C	1.774632	-2.942641	0.126761
H	1.620459	-2.722728	1.174623
C	-0.536022	-0.815725	0.425887

H	-0.695443	2.747171	2.909855
C	-0.132853	2.042719	-2.855538
H	0.697029	2.747231	-2.909321
H	0.059986	1.267905	-3.599634
H	-1.046244	2.570764	-3.122453
P	3.184909	1.969208	1.162066
P	-3.183942	1.970549	-1.162167
Cl	2.553224	0.740663	-2.142836
Cl	-2.552856	0.742023	2.142831
C	-3.862695	3.288519	-0.013119
H	-4.915706	3.459867	-0.229229
H	-3.739785	2.940761	1.008217
H	-3.303205	4.210489	-0.15628
C	-4.30523	0.481061	-0.954155
H	-4.015717	-0.282407	-1.672406
H	-4.177567	0.091008	0.050863
H	-5.340285	0.774239	-1.120222

C	-1.261748	-2.050609	0.836085
C	-1.775964	-2.941785	-0.126707
H	-1.621511	-2.722022	-1.174558
C	-2.459607	-4.100236	0.247639
H	-2.839703	-4.76955	-0.514401
C	-2.645424	-4.401533	1.599531
H	-3.172282	-5.30074	1.892506
C	-2.144605	-3.528453	2.569744
H	-2.284754	-3.749418	3.620641
C	-1.469949	-2.366124	2.192932
H	-1.101323	-1.691122	2.951739
N	0.238021	1.466792	1.509028
N	-0.237237	1.466943	-1.508962
C	0.13403	2.042196	2.855799
H	-0.059192	1.267235	3.599642
H	1.047747	2.569617	3.122842

C	-3.630632	2.609509	-2.880766
H	-3.14177	3.562506	-3.065323
H	-3.316616	1.891219	-3.633395
H	-4.710398	2.741904	-2.935779
C	4.305688	0.479283	0.954371
H	4.018359	-0.282384	1.675413
H	4.175292	0.086827	-0.049353
H	5.341205	0.772941	1.116692
C	3.632026	2.608426	2.880465
H	3.143293	3.561512	3.064918
H	3.318082	1.890323	3.633299
H	4.711819	2.740697	2.935242
C	3.863921	3.28675	0.012692
H	3.30445	4.208796	0.155432
H	4.916898	3.458112	0.228958
H	3.741185	2.938668	-1.008555

5':

Zero-point correction=	0.355695 (Hartree/Particle)
Thermal correction to Energy=	0.384356
Thermal correction to Enthalpy=	0.3853
Thermal correction to Gibbs Free Energy=	0.298435
Sum of electronic and zero-point Energies=	-2319.807673
Sum of electronic and thermal Energies=	-2319.779012
Sum of electronic and thermal Enthalpies=	-2319.778068
Sum of electronic and thermal Free Energies=	-2319.864933

B	0.690842	-1.24967	-0.719541
B	1.243093	0.176286	0.077935

H	-3.581863	2.096423	0.962736
H	-4.697857	1.140411	1.973046

B	-1.32859	-0.163611	0.051642
B	-0.811033	1.278093	-0.698859
C	0.591482	0.038086	1.557066
Cl	1.760676	-2.554507	-1.577874
Cl	-1.908003	2.577836	-1.53143
N	-0.69497	-1.365649	-0.720721
N	0.567444	1.414026	-0.656519
O	-0.779114	-0.127144	1.487488
O	1.163548	0.020868	2.666272
P	3.232583	0.273665	0.394154
P	-3.289927	-0.299376	0.539357
C	-1.498547	-2.378869	-1.413218
H	-0.853161	-3.093857	-1.91854
H	-2.126649	-2.934706	-0.710548
H	-2.145517	-1.920864	-2.16774
C	1.358295	2.491964	-1.260388
H	1.991682	2.114271	-2.069094
H	0.700332	3.249486	-1.681275
H	1.997442	2.980561	-0.519923
C	-3.686149	1.206113	1.577266
H	-2.962975	1.245014	2.387083

C	-4.564604	-0.310612	-0.833129
H	-4.368205	0.532729	-1.490803
H	-4.487871	-1.233571	-1.401813
H	-5.565319	-0.224292	-0.414148
C	-3.678697	-1.754944	1.656393
H	-3.667817	-2.678766	1.083604
H	-2.900864	-1.795311	2.414622
H	-4.652642	-1.62719	2.125062
C	3.799214	1.666397	1.51756
H	3.18781	1.614631	2.414436
H	4.85045	1.536874	1.769221
H	3.657334	2.62739	1.030191
C	3.781571	-1.275368	1.29084
H	3.564854	-2.142453	0.67355
H	4.849026	-1.222186	1.497948
H	3.216594	-1.32927	2.216712
C	4.328917	0.358665	-1.125986
H	4.193434	1.310784	-1.631893
H	5.371623	0.249858	-0.832412
H	4.051634	-0.449408	-1.798223

5'-isomer:

Zero-point correction=	0.355658 (Hartree/Particle)
Thermal correction to Energy=	0.384138
Thermal correction to Enthalpy=	0.385082
Thermal correction to Gibbs Free Energy=	0.29838
Sum of electronic and zero-point Energies=	-2319.762091
Sum of electronic and thermal Energies=	-2319.733612
Sum of electronic and thermal Enthalpies=	-2319.732668
Sum of electronic and thermal Free Energies=	-2319.81937

B	-1.384316	0.36239	-0.252848
B	-0.757462	-1.095765	0.412327
B	0.784394	1.026881	0.604144
B	1.498147	-0.321359	-0.174945
C	-0.496871	-0.597697	1.93728
N	-0.526635	1.441762	-0.20124
N	0.658025	-1.410319	-0.25042
O	0.37057	0.505742	1.94555
O	-0.99977	-0.991186	2.995004
C	-0.725251	2.822665	-0.66359
H	-1.631299	2.905508	-1.261456
H	-0.78467	3.510798	0.180419
H	0.116761	3.141507	-1.277856
C	0.935148	-2.766178	-0.749765
H	0.226252	-3.040745	-1.530635
H	1.941386	-2.825136	-1.159209
H	0.832146	-3.499592	0.049875
P	3.453496	-0.341573	-0.603086
P	-3.342986	0.490621	-0.668949
Cl	-1.93765	-2.671511	0.333557
Cl	1.929103	2.605178	0.923638
C	-4.156069	2.107255	-1.194879
H	-3.778749	2.417507	-2.165826

H	-5.232322	1.953685	-1.258393
H	-3.944791	2.879816	-0.460717
C	-3.889652	-0.735605	-1.976793
H	-3.449774	-0.460396	-2.933039
H	-3.541825	-1.72186	-1.685086
H	-4.975092	-0.727307	-2.056433
C	-4.243739	0.029093	0.911989
H	-3.834279	-0.904032	1.287354
H	-4.074795	0.809943	1.650045
H	-5.308949	-0.073322	0.713822
C	4.393734	-0.065438	0.996363
H	5.453773	0.062595	0.785771
H	3.992633	0.820752	1.479673
H	4.243964	-0.924314	1.646389
C	4.326579	-1.809419	-1.402686
H	4.242603	-2.68305	-0.7619
H	3.879448	-2.026507	-2.369436
H	5.378513	-1.561934	-1.538206
C	3.894308	1.100652	-1.716638
H	3.441656	0.950036	-2.694363
H	3.500486	2.007605	-1.267314
H	4.975487	1.171125	-1.819168

TS1:

Zero-point correction=	0.534824 (Hartree/Particle)
Thermal correction to Energy=	0.57264
Thermal correction to Enthalpy=	0.573584
Thermal correction to Gibbs Free Energy=	0.46504
Sum of electronic and zero-point Energies=	-2670.422951
Sum of electronic and thermal Energies=	-2670.385134
Sum of electronic and thermal Enthalpies=	-2670.38419
Sum of electronic and thermal Free Energies=	-2670.492735

Cl	-2.085187	-1.494631	-2.67561
N	0.508239	-1.513911	-1.477651
B	-0.889788	-1.414928	-1.173393
B	1.413492	-1.313118	-0.358807
Cl	2.085096	-1.49459	2.675682
N	-0.50831	-1.513853	1.4777
B	0.88972	-1.414902	1.173439
B	-1.413558	-1.313052	0.358853
C	0.977516	-1.650042	-2.875094
H	0.233748	-2.161902	-3.476285
H	1.156888	-0.671718	-3.327842
H	1.894068	-2.23605	-2.918766
C	-0.977553	-1.649895	2.875164
H	-0.233965	-2.16213	3.476265
H	-1.156465	-0.671528	3.328006
H	-1.894357	-2.2355	2.918856
C	0.614991	1.209541	0.117261
C	-0.614853	1.209544	-0.117396
C	1.820347	1.968482	0.321412
C	2.401842	2.105306	1.603889
C	2.432101	2.656198	-0.755494
C	3.536871	2.893815	1.794956
H	1.956123	1.583054	2.437959
C	3.571151	3.436472	-0.555874
H	1.982377	2.590517	-1.737703
C	4.134443	3.560419	0.719194
H	3.955913	2.987898	2.788901
H	4.01025	3.963233	-1.394289
H	5.014058	4.171239	0.872681
C	-1.820219	1.968484	-0.321498
C	-2.401772	2.105232	-1.60396

H	-1.95609	1.582937	-2.438024
C	-3.570957	3.436555	0.555774
H	-1.982145	2.590676	1.7376
C	-4.134323	3.560405	-0.71927
H	-3.955887	2.987731	-2.788951
H	-4.010004	3.963391	1.394171
H	-5.013947	4.171213	-0.872753
P	3.390029	-1.339413	-0.76143
P	-3.390092	-1.339269	0.761466
C	4.029717	-3.089236	-1.073257
H	5.102857	-3.065013	-1.257413
H	3.82091	-3.688297	-0.190118
H	3.520116	-3.528394	-1.927236
C	4.533144	-0.717444	0.58689
H	4.486677	-1.380437	1.44228
H	5.544228	-0.683225	0.183477
H	4.222715	0.275193	0.897351
C	4.011198	-0.361068	-2.24939
H	3.581424	-0.734563	-3.17188
H	3.735643	0.681058	-2.11189
H	5.095996	-0.444656	-2.290516
C	-4.011256	-0.36049	2.24912
H	-3.580977	-0.733257	3.171667
H	-3.736244	0.681685	2.110917
H	-5.095998	-0.444599	2.290667
C	-4.533234	-0.717721	-0.587025
H	-4.222656	0.274696	-0.898061
H	-4.487022	-1.381178	-1.442073
H	-5.544258	-0.683101	-0.18349
C	-4.029801	-3.089006	1.073768
H	-5.102949	-3.064714	1.257867

C	-2.431903	2.656283	0.755403
C	-3.536805	2.893723	-1.795016

H	-3.820964	-3.688321	0.190809
H	-3.520252	-3.527937	1.927894

TS2:

Zero-point correction=	0.353087 (Hartree/Particle)
Thermal correction to Energy=	0.382697
Thermal correction to Enthalpy=	0.383641
Thermal correction to Gibbs Free Energy=	0.292589
Sum of electronic and zero-point Energies=	-2319.727681
Sum of electronic and thermal Energies=	-2319.698072
Sum of electronic and thermal Enthalpies=	-2319.697127
Sum of electronic and thermal Free Energies=	-2319.788179

Cl	-1.787556	2.759981	-0.741476
N	0.716859	1.347511	-0.641104
B	-0.715382	1.161037	-0.521155
B	1.54506	0.180912	-0.510052
Cl	2.02259	-2.88007	-0.41803
N	-0.511612	-1.492976	-0.338458
B	0.899584	-1.301505	-0.423596
B	-1.35699	-0.293802	-0.3176
C	1.269977	2.703185	-0.892154
H	1.310453	3.287412	0.029296
H	2.263613	2.632462	-1.322597
H	0.638657	3.239849	-1.593937
C	-1.111504	-2.849778	-0.274738
H	-0.339414	-3.609908	-0.268116

H	5.338085	1.82363	0.498975
H	4.408354	2.520337	-0.839827
H	3.765958	2.586941	0.811371
C	3.873976	-0.531866	1.505961
H	3.272191	-0.055016	2.275544
H	3.588247	-1.575982	1.432888
H	4.933839	-0.445026	1.740076
C	-4.091361	0.022173	-1.993269
H	-3.773162	-0.717491	-2.724443
H	-5.178684	0.041015	-1.930659
H	-3.716768	0.999407	-2.284723
C	-4.2377	-2.019757	0.117558
H	-5.309912	-1.832254	0.088469
H	-3.989684	-2.80145	-0.593212

H	-1.706847	-2.962143	0.630705	H	-3.958013	-2.337055	1.118644
H	-1.747686	-3.024406	-1.144005	C	-4.186384	0.79321	0.860348
P	3.504482	0.314853	-0.133369	H	-3.853229	0.582916	1.871387
P	-3.34752	-0.411861	-0.313753	H	-3.895228	1.803974	0.59799
C	4.625482	-0.53758	-1.38157	H	-5.265741	0.67557	0.776218
H	4.576435	0.001773	-2.324851	C	-0.64895	0.436033	2.594636
H	5.650403	-0.549296	-1.013672	O	-1.775291	0.52586	2.989618
H	4.268825	-1.552375	-1.527433	O	0.536507	0.350884	2.50781
C	4.336708	1.990188	0.105537				

Table 2.5.3. Wiberg bond index among B atoms in **3**.

	B1–B2#	B1–N1	B2–N1
3	1.2478	0.9357	0.9453

Table 2.5.4. Selected data of Natural Bond Orbital Analysis of **3**.

NATURAL BOND ORBITAL ANALYSIS:

(Occupancy) Bond orbital/ Coefficients/ Hybrids

```

7. (1.80628) BD ( 1) N 3 - B 28
( 81.51%) 0.9028* N 3 s( 0.00%)p 1.00(100.00%)
-0.0000 -0.0003 -0.0000 -0.0000 -0.0003
0.0000 -0.0000 -0.0002 -0.0000 0.0000
0.9999 0.0128 -0.0030
( 18.49%) 0.4300* B 28 s( 0.00%)p 1.00(100.00%)
-0.0000 -0.0001 0.0000 0.0000 -0.0001
-0.0000 0.0000 -0.0006 0.0000 -0.0000
0.9997 0.0244 0.0087

46. (1.81740) BD ( 1) N 36 - B 62
( 79.01%) 0.8889* N 36 s( 0.26%)p99.99( 99.74%)
0.0000 -0.0505 0.0001 -0.0000 -0.0308
0.0004 -0.0002 0.0140 0.0000 0.0001
0.9980 0.0178 -0.0031
( 20.99%) 0.4581* B 62 s( 0.09%)p99.99( 99.91%)
0.0002 -0.0308 -0.0013 -0.0000 0.0209
0.0002 0.0002 -0.0483 -0.0038 -0.0004
0.9978 0.0261 0.0029

519. (0.38625) BD*( 1) N 3 - B 28
( 18.49%) 0.4300* N 3 s( 0.00%)p 1.00(100.00%)
0.0000 0.0003 0.0000 0.0000 0.0003
-0.0000 0.0000 0.0002 0.0000 -0.0000
-0.9999 -0.0128 0.0030
( 81.51%) -0.9028* B 28 s( 0.00%)p 1.00(100.00%)
0.0000 0.0001 -0.0000 -0.0000 0.0001
0.0000 -0.0000 0.0006 -0.0000 0.0000
-0.9997 -0.0244 -0.0087

558. (0.51153) BD*( 1) N 36 - B 62
( 20.99%) 0.4581* N 36 s( 0.26%)p99.99( 99.74%)
-0.0000 0.0505 -0.0001 0.0000 0.0308
-0.0004 0.0002 -0.0140 -0.0000 -0.0001
-0.9980 -0.0178 0.0031
( 79.01%) -0.8889* B 62 s( 0.09%)p99.99( 99.91%)
-0.0002 0.0308 0.0013 0.0000 -0.0209
-0.0002 -0.0002 0.0483 0.0038 0.0004
-0.9978 -0.0261 -0.0029

```


NATURAL BOND ORBITAL ANALYSIS:

7.	(1.81873)	BD (2) B	4 - N 11						
	(12.08%)	0.3476* B	4 s (	0.00%)	p 1.00	(100.00%)			
				0.0000	0.0000	0.0000	0.0000	0.0004	
				0.0000	0.0000	0.0001	0.0000	0.0000	
				0.9988	-0.0398	0.0273			
	(87.92%)	0.9376* N	11 s (	0.00%)	p 1.00	(100.00%)			
				0.0000	0.0000	0.0000	0.0000	0.0001	
				0.0000	0.0000	0.0003	0.0000	0.0000	
				1.0000	0.0040	-0.0010			
10.	(1.81880)	BD (2) B	6 - N 10						
	(12.09%)	0.3476* B	6 s (	0.00%)	p 1.00	(100.00%)			
				0.0000	0.0001	0.0000	0.0000	-0.0003	
				0.0000	0.0000	-0.0005	0.0000	0.0000	
				0.9988	-0.0398	0.0273			
	(87.91%)	0.9376* N	10 s (	0.00%)	p 1.00	(100.00%)			
				0.0000	0.0000	0.0000	0.0000	0.0001	
				0.0000	0.0000	-0.0002	0.0000	0.0000	
				1.0000	0.0040	-0.0010			
15.	(1.81873)	BD (2) B	8 - N 12						
	(12.08%)	0.3476* B	8 s (	0.00%)	p 1.00	(100.00%)			
				0.0000	0.0001	0.0000	0.0000	-0.0002	
				0.0000	0.0000	0.0003	0.0000	0.0000	
				0.9988	-0.0398	0.0273			
	(87.92%)	0.9376* N	12 s (	0.00%)	p 1.00	(100.00%)			
				0.0000	0.0000	0.0000	0.0000	-0.0004	
				0.0000	0.0000	0.0001	0.0000	0.0000	
				1.0000	0.0040	-0.0010			
88.	(0.18100)	BD* (2) B	4 - N 11						
	(87.92%)	0.9376* B	4 s (	0.00%)	p 1.00	(100.00%)			
				0.0000	0.0000	0.0000	0.0000	0.0004	
				0.0000	0.0000	0.0001	0.0000	0.0000	
				0.9988	-0.0398	0.0273			
	(12.08%)	-0.3476* N	11 s (	0.00%)	p 1.00	(100.00%)			
				0.0000	0.0000	0.0000	0.0000	0.0001	
				0.0000	0.0000	0.0003	0.0000	0.0000	
				1.0000	0.0040	-0.0010			
91.	(0.18106)	BD* (2) B	6 - N 10						
	(87.91%)	0.9376* B	6 s (	0.00%)	p 1.00	(100.00%)			
				0.0000	0.0001	0.0000	0.0000	-0.0003	
				0.0000	0.0000	-0.0005	0.0000	0.0000	
				0.9988	-0.0398	0.0273			
	(12.09%)	-0.3476* N	10 s (	0.00%)	p 1.00	(100.00%)			
				0.0000	0.0000	0.0000	0.0000	0.0001	
				0.0000	0.0000	-0.0002	0.0000	0.0000	
				1.0000	0.0040	-0.0010			
96.	(0.18107)	BD* (2) B	8 - N 12						
	(87.92%)	0.9376* B	8 s (	0.00%)	p 1.00	(100.00%)			
				0.0000	0.0001	0.0000	0.0000	-0.0002	
				0.0000	0.0000	0.0003	0.0000	0.0000	
				0.9988	-0.0398	0.0273			
	(12.08%)	-0.3476* N	12 s (	0.00%)	p 1.00	(100.00%)			
				0.0000	0.0000	0.0000	0.0000	-0.0004	
				0.0000	0.0000	0.0001	0.0000	0.0000	
				1.0000	0.0040	-0.0010			

	B1-B2	B3-B4	B1-N1	B2-N2	B3-N1	B4-N2
total	1.3311	1.3312	1.4983	1.4396	1.4396	1.4982
covalent	1.2378	1.2378	0.5789	0.6088	0.6088	0.5789
ionic	0.0933	0.0933	0.9194	0.8308	0.8308	0.9194
% ionic	7.0	7.0	61.4	57.7	57.7	61.4

Table 2.5.7. NRT bond orders and bond ionic characters in B₃N₃H₆.

	B4-N10	B6-N12	B8-N11	B4-N11	B6-N10	B8-N12
total	1.8139	1.8138	1.8139	1.093	1.0931	1.0931
covalent	0.6808	0.6808	0.6809	0.5003	0.5003	0.5004
ionic	1.1331	1.133	1.1331	0.5926	0.5928	0.5927
% ionic	62.5	62.5	62.5	54.2	54.2	54.2

Table 2.5.8. The NPA charges of **3**.

Natural Population

Atom	No	Natural Charge	Core	Valence	Rydberg	Total
Cl	1	-0.34164	9.99976	7.33763	0.00426	17.34164
P	2	1.1011	9.99793	3.89009	0.01088	13.8989
N	3	-0.88765	1.99921	5.88248	0.00595	7.88765
C	4	0.16295	1.99870	3.82088	0.01747	5.83705
C	5	-0.00733	1.99889	3.9962	0.01224	6.00733
C	6	-0.00683	1.99889	3.99573	0.0122	6.00683
C	7	-0.00652	1.99901	3.99595	0.01157	6.00652
C	8	-0.22179	1.99895	4.20979	0.01305	6.22179
H	9	0.19743	0.00000	0.79934	0.00323	0.80257
C	10	-0.59188	1.99925	4.58703	0.0056	6.59188
H	11	0.21304	0.00000	0.78557	0.0014	0.78696
H	12	0.19692	0.00000	0.80173	0.00134	0.80308
H	13	0.22533	0.00000	0.77306	0.0016	0.77467
C	14	-0.84885	1.99926	4.84297	0.00663	6.84885
H	15	0.24101	0.00000	0.75757	0.00143	0.75899
H	16	0.24134	0.00000	0.75722	0.00144	0.75866

H	17	0.21777	0.00000	0.78088	0.00135	0.78223
C	18	-0.22144	1.99895	4.20936	0.01313	6.22144
H	19	0.1974	0.00000	0.79943	0.00317	0.8026
C	20	-0.59189	1.99925	4.58703	0.0056	6.59189
H	21	0.2129	0.00000	0.7857	0.0014	0.7871
H	22	0.22543	0.00000	0.77297	0.0016	0.77457
H	23	0.19692	0.00000	0.80173	0.00134	0.80308
C	24	-0.84567	1.99925	4.83938	0.00704	6.84567
H	25	0.21433	0.00000	0.78415	0.00152	0.78567
H	26	0.22531	0.00000	0.77359	0.0011	0.77469
H	27	0.25259	0.00000	0.7463	0.0011	0.74741
B	28	0.38696	1.99776	2.59547	0.0198	4.61304
B	29	-0.01086	1.99798	2.99674	0.01615	5.01086
C	30	-0.58665	1.99925	4.58142	0.00598	6.58665
H	31	0.20992	0.00000	0.78851	0.00158	0.79008
H	32	0.20138	0.00000	0.79722	0.0014	0.79862
H	33	0.20236	0.00000	0.79621	0.00143	0.79764
Cl	34	-0.34163	9.99976	7.33762	0.00426	17.34163
P	35	1.10109	9.99793	3.8901	0.01088	13.89891
N	36	-0.88765	1.99921	5.88248	0.00595	7.88765
C	37	0.16296	1.99870	3.82087	0.01747	5.83704
C	38	-0.0073	1.99889	3.99618	0.01224	6.0073
C	39	-0.00685	1.99889	3.99575	0.0122	6.00685
C	40	-0.00652	1.99901	3.99595	0.01157	6.00652
C	41	-0.22177	1.99895	4.20977	0.01305	6.22177
H	42	0.19742	0.00000	0.79935	0.00323	0.80258
C	43	-0.59187	1.99925	4.58703	0.0056	6.59187
H	44	0.21302	0.00000	0.78558	0.0014	0.78698
H	45	0.19692	0.00000	0.80173	0.00134	0.80308
H	46	0.22534	0.00000	0.77306	0.0016	0.77466
C	47	-0.84885	1.99926	4.84297	0.00663	6.84885
H	48	0.24106	0.00000	0.75751	0.00143	0.75894
H	49	0.2413	0.00000	0.75727	0.00143	0.7587
H	50	0.21777	0.00000	0.78088	0.00135	0.78223
C	51	-0.22146	1.99895	4.20938	0.01313	6.22146
H	52	0.1974	0.00000	0.79943	0.00317	0.8026
C	53	-0.59185	1.99925	4.587	0.0056	6.59185
H	54	0.21286	0.00000	0.78574	0.0014	0.78714
H	55	0.22544	0.00000	0.77296	0.0016	0.77456
H	56	0.19693	0.00000	0.80173	0.00134	0.80307
C	57	-0.84567	1.99925	4.83938	0.00704	6.84567

H	58	0.21434	0.00000	0.78414	0.00152	0.78566
H	59	0.22531	0.00000	0.77359	0.0011	0.77469
H	60	0.2526	0.00000	0.74629	0.0011	0.7474
B	61	0.38694	1.99776	2.5955	0.0198	4.61306
B	62	-0.01081	1.99798	2.99668	0.01615	5.01081
C	63	-0.58665	1.99925	4.58142	0.00598	6.58665
H	64	0.20992	0.00000	0.7885	0.00158	0.79008
H	65	0.20139	0.00000	0.79721	0.0014	0.79861
H	66	0.20234	0.00000	0.79623	0.00143	0.79766
C	67	-0.84567	1.99925	4.83937	0.00704	6.84567
H	68	0.22526	0.00000	0.77364	0.00111	0.77474
H	69	0.25265	0.00000	0.74625	0.0011	0.74735
H	70	0.21433	0.00000	0.78415	0.00152	0.78567
C	71	-0.84568	1.99925	4.83938	0.00704	6.84568
H	72	0.25264	0.00000	0.74626	0.0011	0.74736
H	73	0.22528	0.00000	0.77361	0.00111	0.77472
H	74	0.21433	0.00000	0.78415	0.00152	0.78567
=====		=====	=====	=====	=====	=====
* Total *		0.00000	99.96309	181.6254	0.4115	282.00000

Figure 2.5.31. Free energy profile (kcal·mol⁻¹) for the formation of 4' and 5' by the reactions of the model compound 3' with diphenylacetylene and CO₂. Products 4' and 5' are thermodynamically more stable compared with the corresponding isomers 4'-isomer and 5'-isomer.

2.6 References

- 1 M. Faraday. On new compounds of carbon and hydrogen, and on certain other products obtained during the decomposition of oil by heat. *Phil. Trans. R. Soc. Lond.* **115**, 440-466 (1825). doi: 10.1098/rstl.1825.0022.
- 2 A. Kekulé. Sur la constitution des substances aromatiques. *Bull. Soc. Chim. Fr.* **3**, 98-110 (1865).
- 3 W. A. L. van Otterlo, C. B. de Koning. Metathesis in the Synthesis of Aromatic Compounds. *Chem. Rev.* **109**, 3743-3782 (2009). doi:10.1021/cr900178p.
- 4 G. Domínguez, J. Pérez-Castells. Recent advances in [2+2+2] cycloaddition reactions. *Chem. Soc. Rev.* **40**, 3430-3444 (2011). doi:10.1039/C1CS15029D.
- 5 T. R. Hoye, B. Baire, D. Niu, P. H. Willoughby, B. P. Woods. The hexadehydro-Diels-Alder reaction. *Nature* **490**, 208-212 (2012). doi:10.1038/nature11518.
- 6 R. D. Taylor, M. MacCoss, A. D. G. Lawson. Rings in Drugs. *J. Med. Chem.* **57**, 5845-5859 (2014). doi:10.1021/jm4017625.
- 7 S. Suzuki, Y. Segawa, K. Itami, J. Yamaguchi. Synthesis and characterization of hexaarylbenzenes with five or six different substituents enabled by programmed synthesis. *Nat. Chem.* **7**, 227-233 (2015). doi:10.1038/nchem.2174.
- 8 A. J. Ashe. The Group 5 heterobenzenes. *Acc. Chem. Res.* **11**, 153-157 (1978). doi:10.1021/ar50124a005.
- 9 A. P. Sadimenko. in *Adv. Heterocycl. Chem.* Vol. 89 (ed Alan R. Katritzky) 125-157 (Academic Press, 2005).
- 10 V. Y. Lee, A. Sekiguchi. Aromaticity of Group 14 Organometallics: Experimental Aspects. *Angew. Chem. Int. Ed.* **46**, 6596-6620 (2007). doi:10.1002/anie.200604869.
- 11 V. Y. Lee, A. Sekiguchi. Cyclic polyenes of heavy group 14 elements: new generation ligands for transition-metal complexes. *Chem. Soc. Rev.* **37**, 1652-1665 (2008). doi:10.1039/B800580J.

- 12 Z. Liu, T. B. Marder. B-N versus C-C: how similar are they? *Angew. Chem. Int. Ed. Engl.* **47**, 242-244 (2008). doi:10.1002/anie.200703535.
- 13 A. J. Ashe. Aromatic Borataheterocycles: Surrogates for Cyclopentadienyl in Transition-Metal Complexes. *Organometallics* **28**, 4236-4248 (2009). doi:10.1021/om900308e.
- 14 M. J. D. Bosdet, W. E. Piers. B-N as a C-C substitute in aromatic systems. *Can. J. Chem.* **87**, 8-29 (2009). doi:10.1139/v08-110.
- 15 G. Bélanger-Chabot, H. Braunschweig, D. K. Roy. Recent Developments in Azaborinine Chemistry. *Eur. J. Inorg. Chem.* **2017**, 4353-4368 (2017). doi:10.1002/ejic.201700562.
- 16 R. Kinjo, B. Su. Construction of Boron-Containing Aromatic Heterocycles. *Synthesis* **49**, 2985-3034 (2017). doi:10.1055/s-0036-1588832.
- 17 B. J. Frogley, L. J. Wright. Recent Advances in Metallaaromatic Chemistry. *Chem. Eur. J.* **24**, 2025-2038 (2018). doi:10.1002/chem.201704888.
- 18 A. Stock, E. Pohland. Borwasserstoffe, IX.: B₃N₃H₆. *Ber. Dtsch. Chem. Ges.* **59**, 2215-2223 (1926). doi:10.1002/cber.19260590907.
- 19 D. L. Cooper, S. C. Wright, J. Gerratt, P. A. Hyams, M. Raimondi. The electronic structure of heteroaromatic molecules. Part 3. A comparison of benzene, borazine, and boroxine. *J. Chem. Soc., Perkin Trans. 2*, 719-724 (1989). doi:10.1039/P29890000719.
- 20 P. W. Fowler, E. Steiner. Ring Currents and Aromaticity of Monocyclic π -Electron Systems C₆H₆, B₃N₃H₆, B₃O₃H₃, C₃N₃H₃, C₅H₅⁻, C₇H₇⁺, C₃N₃F₃, C₆H₃F₃, and C₆F₆. *J. Phys. Chem. A* **101**, 1409-1413 (1997). doi:10.1021/jp9637946.
- 21 D. Benker, T. M. Klapötke, G. Kuhn, J. Li, C. Müller. An ab initio valence bond (VB) calculation of the π delocalization energy in borazine, B₃N₃H₆. *Heteroat. Chem* **16**, 311-315 (2005). doi:10.1002/hc.20095.

- 22 I. Fernandez, G. Frenking. Direct estimate of conjugation and aromaticity in cyclic compounds with the EDA method. *Faraday Discuss.* **135**, 403-421; discussion 489-506 (2007). doi:10.1039/b606835a.
- 23 R. Islas, E. Chamorro, J. Robles, T. Heine, J. C. Santos, G. Merino. Borazine: to be or not to be aromatic. *Struct. Chem.* **18**, 833-839 (2007). doi:10.1007/s11224-007-9229-z.
- 24 J. J. Torres-Vega, A. Vásquez-Espinal, J. Caballero, M. L. Valenzuela, L. Alvarez-Thon, E. Osorio, W. Tiznado. Minimizing the risk of reporting false aromaticity and antiaromaticity in inorganic heterocycles following magnetic criteria. *Inorg. Chem.* **53**, 3579-3585 (2014). doi:10.1021/ic4030684.
- 25 H. V. R. Dias, P. P. Power. Synthesis and X - Ray Structure of (2,4,6 - Me₃C₆H₂BPC₆H₁₁)₃: A Boron-Phosphorus Analogue of Borazine. *Angew. Chem. Int. Ed. Engl.* **26**, 1270-1271 (1987). doi:10.1002/anie.198712701.
- 26 K. M. Waggoner, H. Hope, P. P. Power. Synthesis and Structure of [MeAlN(2,6- iPr₂C₆H₃)]₃: An Aluminum-Nitrogen Analogue of Borazine. *Angew Chem. Int. Ed. Engl.* **27**, 1699-1700 (1988). doi:10.1002/anie.198816991.
- 27 H. V. R. Dias, P. P. Power. Boron-phosphorus analogs of benzene and cyclobutadiene. Synthesis and characterization of the boraphosphabenzenes (RBPR')₃ (R = Mes, Ph; R' = Ph, Mes, C₆H₁₁, tert-Bu) and the diphosphadiboretane (thexylBPMe)₂. *J. Am. Chem. Soc.* **111**, 144-148 (1989). doi:10.1021/ja00183a025.
- 28 P. P. Power. The synthesis, characterization and some properties of new quasi-aromatic main group ring systems. *J. Organomet. Chem.* **400**, 49-69 (1990). doi: 10.1016/0022-328X(90)83005-5.
- 29 K. M. Waggoner, P. P. Power. Reactions of trimethylaluminum or trimethylgallium with bulky primary amines: structural characterization of the thermolysis products. *J. Am. Chem. Soc.* **113**, 3385-3393 (1991). doi:10.1021/ja00009a025.

- 30 C. R. Kinney, D. F. Pontz. The Structure of the Organoboron Oxides. *J. Am. Chem. Soc.* **58**, 197-197 (1936). doi:10.1021/ja01293a005.
- 31 H. R. Snyder, J. A. Kuck, J. R. Johnson. Organoboron Compounds, and the Study of Reaction Mechanisms. Primary Aliphatic Boronic Acids1. *J. Am. Chem. Soc.* **60**, 105-111 (1938). doi:10.1021/ja01268a033.
- 32 M. Schmidt, E. Kiewert. Notizen: Zur Kenntnis des ersten Vertreters eines „Borselenol“-Systems / Triphenylboroselenol — The First Representative of the “Boroselenol”-System. *Z. Naturforsch. B Chem. Sci.* **26**, 613-613 (1971). doi:10.1515/znb-1971-0623.
- 33 W. Schwarz, H. D. Hausen, J. Hess, J. Mandt, W. Schmelzer, B. Krebs. Trimere Metathioborsäure (HSBS)3. *Acta Crystallogr. B* **29**, 2029-2031 (1973). doi:doi:10.1107/S0567740873006035.
- 34 H. R. Allcock. *Phosphorus-nitrogen Compounds*. (Academic Press, 1972).
- 35 A. E. Seitz, M. Eckhardt, A. Erlebach, E. V. Peresypkina, M. Sierka, M. Scheer. Pnictogen–Silicon Analogues of Benzene. *J. Am. Chem. Soc.* **138**, 10433-10436 (2016). doi:10.1021/jacs.6b07389.
- 36 D. B. Davies, T. A. Clayton, R. E. Eaton, R. A. Shaw, A. Egan, M. B. Hursthouse, G. D. Sykara, I. Porwolik-Czomperlik, M. Siwy, K. Brandt. Chiral Configurations of Cyclophosphazenes. *J. Am. Chem. Soc.* **122**, 12447-12457 (2000). doi:10.1021/ja0028469.
- 37 A. P. Côté, A. I. Benin, N. W. Ockwig, M. O’Keeffe, A. J. Matzger, O. M. Yaghi. Porous, Crystalline, Covalent Organic Frameworks. *Science* **310**, 1166-1170 (2005).
- 38 V. Chandrasekhar, P. Thilagar, B. Murugesu Pandian. Cyclophosphazene-based multi-site coordination ligands. *Coord. Chem. Rev.* **251**, 1045-1074 (2007). doi:10.1016/j.ccr.2006.07.005.

- 39 A. L. Korich, P. M. Iovine. Boroxine chemistry and applications: A perspective. *Dalton Trans.* **39**, 1423-1431 (2010). doi:10.1039/B917043J.
- 40 L. Xu, B.-J. Li, Z.-H. Wu, X.-Y. Lu, B.-T. Guan, B.-Q. Wang, K.-Q. Zhao, Z.-J. Shi. Nickel-Catalyzed Efficient and Practical Suzuki–Miyaura Coupling of Alkenyl and Aryl Carbamates with Aryl Boroxines. *Org. Lett.* **12**, 884-887 (2010). doi:10.1021/ol9029534.
- 41 J. Jiménez, A. Laguna, E. Gascón, J. A. Sanz, J. L. Serrano, J. Barberá, L. Oriol. New Liquid Crystalline Materials Based on Two Generations of Dendronised Cyclophosphazenes. *Chem.: Eur. J.* **18**, 16801-16814 (2012). doi:10.1002/chem.201202748.
- 42 Y. Tokunaga. Boroxine Chemistry: From Fundamental Studies to Applications in Supramolecular and Synthetic Organic Chemistry. *Heterocycles* **87**, 991-1021 (2013). doi:10.3987/rev-13-767.
- 43 R. A. Bartlett, P. P. Power. Synthesis and structural characterization of the cyclic species [GeN(2,6-iso-Pr₂C₆H₃)]₃: the first "germanazene". *J. Am. Chem. Soc.* **112**, 3660-3662 (1990). doi:10.1021/ja00165a062.
- 44 H. Hope, D. C. Pestana, P. P. Power. Synthesis and Structure of the Novel Ga₃P₃ Ring Compound [(2,4,6-Ph₃C₆H₂)GaP(cyclo-C₆H₁₁)]₃. *Angew. Chem. Int. Ed.* **30**, 691-693 (1991). doi:10.1002/anie.199106911.
- 45 R. J. Wehmschulte, P. P. Power. Reactions of (H₂AlMes*)₂ (Mes* = 2,4,6-(t-Bu)₃C₆H₂) with H₂EAr (E = N, P, or As; Ar = aryl): Characterization of the Ring Compounds (Mes*AlNPh)₂ and (Mes*AlEPh)₃ (E = P or As). *J. Am. Chem. Soc.* **118**, 791-797 (1996). doi:10.1021/ja952021c.

- 46 B. Su, K. Ota, K. Xu, H. Hirao, R. Kinjo. Zwitterionic Inorganic Benzene Valence Isomer with sigma-Bonding between Two pi-Orbitals. *J. Am. Chem. Soc.* **140**, 11921-11925 (2018). doi:10.1021/jacs.8b08025.
- 47 A. Moezzi, M. M. Olmstead, P. P. Power. Boron-boron double bonding in the species [B₂R₄]²⁻: synthesis and structure of [{(Et₂O)Li}₂{Mes₂BB(Mes)Ph}], a diborane(4) dianion analog of a substituted ethylene. *J. Am. Chem. Soc.* **114**, 2715-2717 (1992). doi:10.1021/ja00033a054.
- 48 X. Xie, M. F. Haddow, S. M. Mansell, N. C. Norman, C. A. Russell. New polycyclic borazine species. *Chem. Commun.* **47**, 3748-3750 (2011). doi:10.1039/C1CC10196J.
- 49 S. R. Wang, M. Arrowsmith, J. Böhnke, H. Braunschweig, T. Dellermann, R. D. Dewhurst, H. Kelch, I. Krummenacher, J. D. Mattock, J. H. Müssig, T. Thiess, A. Vargas, J. Zhang. Engineering a Small HOMO–LUMO Gap and Intramolecular C–H Borylation by Diborene/Anthracene Orbital Intercalation. *Angew. Chem. Int. Ed.* **56**, 8009-8013 (2017). doi:10.1002/anie.201704063.
- 50 W. Lu, R. Kinjo. Coordination of Asymmetric Diborenes towards Cationic Coinage Metals (Au, Ag, Cu). *Chem. Eur. J.* **24**, 15656-15662 (2018). doi:10.1002/chem.201803139.
- 51 E. R. Abbey, L. N. Zakharov, S.-Y. Liu. Crystal Clear Structural Evidence for Electron Delocalization in 1,2-Dihydro-1,2-azaborines. *J. Am. Chem. Soc.* **130**, 7250-7252 (2008). doi:10.1021/ja8024966.
- 52 H. Braunschweig, K. Geetharani, J. O. C. Jimenez-Halla, M. Schäfer. Direct Synthetic Route to Functionalized 1,2-Azaborinines. *Angew. Chem. Int. Ed.* **53**, 3500-3504 (2014). doi:10.1002/anie.201309707.

- 53 D. Wu, L. Kong, Y. Li, R. Ganguly, R. Kinjo. 1,3,2,5-Diazadiborinine featuring nucleophilic and electrophilic boron centres. *Nat. Commun.* **6**, 7340 (2015). doi:10.1038/ncomms8340.
- 54 B. Wang, Y. Li, R. Ganguly, H. Hirao, R. Kinjo. Ambiphilic boron in 1,4,2,5-diazadiborinine. *Nat. Commun.* **7**, 11871 (2016). doi:10.1038/ncomms11871.
- 55 B. Wang, R. Kinjo. Boron-based stepwise dioxygen activation with 1,4,2,5-diazadiborinine. *Chem. Sci.* **10**, 2088-2092 (2019). doi:10.1039/c8sc04624g.
- 56 J. T. Nelson, W. J. Pietro. Natural bond orbital (NBO) analysis of substituent effects in borazine derivatives. *Inorg. Chem.* **28**, 544-548 (1989).
- 57 E. D. Glendening, J. K. Badenhoop, F. Weinhold. Natural resonance theory: III. Chemical applications. *J. Comput. Chem.* **19**, 628-646 (1998). doi:10.1002/(SICI)1096-987X(19980430)19:6<628::AID-JCC5>3.0.CO;2-T.
- 58 E. D. Glendening, F. Weinhold. Natural resonance theory: I. General formalism. *J. Comput. Chem.* **19**, 593-609 (1998). doi:10.1002/(SICI)1096-987X(19980430)19:6<593::AID-JCC3>3.0.CO;2-M.
- 59 E. D. Glendening, F. Weinhold. Natural resonance theory: II. Natural bond order and valency. *J. Comput. Chem.* **19**, 610-627 (1998). doi:10.1002/(SICI)1096-987X(19980430)19:6<610::AID-JCC4>3.0.CO;2-U.
- 60 M. Zhang, Z.-M. Su, L.-K. Yan, Y.-Q. Qiu, G.-H. Chen, R.-S. Wang. Theoretical interpretation of different nanotube morphologies among Group III (B, Al, Ga) nitrides. *Chem. Phys. Lett.* **408**, 145-149 (2005). doi:10.1016/j.cplett.2005.04.025.
- 61 R. Herges, D. Geuenich. Delocalization of Electrons in Molecules. *J. Phys. Chem. A* **105**, 3214-3220 (2001). doi:10.1021/jp0034426.

- 62 D. Geuenich, K. Hess, F. Köhler, R. Herges. Anisotropy of the Induced Current Density (ACID), a General Method To Quantify and Visualize Electronic Delocalization. *Chem. Rev.* **105**, 3758-3772 (2005). doi:10.1021/cr0300901.
- 63 N. Arnold, H. Braunschweig, R. D. Dewhurst, F. Hupp, K. Radacki, A. Trumpp. Desymmetrizing Electron-Deficient Diboranes(4): Diverse Products and Their Reactivity. *Chem. Eur. J.* **22**, 13927-13934 (2016). doi:10.1002/chem.201602805.
- 64 Y. Katsuma, L. Wu, Z. Lin, S. Akiyama, M. Yamashita. Reactivity of Highly Lewis-Acidic Diborane(4) toward C≡N and N=N Bonds: Uncatalyzed Addition and N=N Bond-Cleavage Reactions. *Angew. Chem. Int. Ed.* **58**, 317-321 (2019). doi:10.1002/anie.201812692.
- 65 E. Fırıncı, H. Can Söyleyici, E. Giziroğlu, E. Temel, O. Büyükgüngör, Y. Şahin. Synthesis and characterization of new air stable primary amido substituted diborane(4) derivatives. *Polyhedron* **29**, 1465-1468 (2010). doi: 10.1016/j.poly.2010.01.031.
- 66 J. T. Patton, S. G. Feng, K. A. Abboud. Chelating Diamide Group IV Metal Olefin Polymerization Catalysts. *Organometallics* **20**, 3399-3405 (2001). doi:10.1021/om010101l.
- 67 G. Sheldrick. A short history of SHELX. *Acta Crystallographica Section A* **64**, 112-122 (2008). doi:doi:10.1107/S0108767307043930.
- 68 Gaussian 09, Rev. B.01 (Wallingford, CT, 2010).
- 69 Gaussian 16 Rev. C.01 (Gaussian, Inc., Wallingford, CT, 2016).
- 70 E. D. Glendening, C. R. Landis, F. Weinhold. NBO 6.0: Natural bond orbital analysis program. *J. Comput. Chem.* **34**, 1429-1437 (2013). doi:10.1002/jcc.23266.

Chapter 3: Synthesis, characterization, and reactivity of a Dewar-type of isomer of B₄N₂ inorganic benzene

3.1 Introduction

3.1.1 Dewar type inorganic benzene isomer containing group 13/15 elements

Dewar type isomers of borazine (RBNR')₃ have been explored in the early 1980s. The general synthetic method of Dewar borazine is oligomerization of iminoboranes. The Paetzold group published a pioneering example of Dewar borazine in 1984.¹ Thermal isomerization of iminoboranes with tert-butyl and isopropyl group provided the corresponding Dewar borazine **III-BN1** in 72% yield (Scheme 3.1.1). The authors mentioned that the formation of **III-BN1** is initiated by the dimerization of iminoborane, followed by [4+2] cycloaddition with another iminoborane. In 1986, the Nöth and Storch group also isolated **III-BN1** by the reaction of tert-butyl bis(trimethylstannyl)amine tBuN(SnMe₃)₂ with dichloroisopropylborane (iPrBCl₂).² The central bond distance between the two tetracoordinate bridgehead atoms (B1 and N1) is 1.752(5) Å, which is an extra-long single bond. The two B-N double bonds between the tricoordinate atoms (B2-N3 and B3-N2) are 1.364(6) Å and 1.384(6) Å, respectively. The other four B-N bonds (1.548(5) Å – 1.564(5) Å) are in the typical B-N single bond length. The holding angle of two square planes is 114.6(3)°.

Scheme 3.1.1. Formation of **III-BN1**.

In 1984, the Paetzold group also reported the thermal isomerization of iminonborane with the n-butyl group on B atoms, which generated borazine **I-BN4** through a Dewar borazine **III-BN2** as an intermediate (Scheme 3.1.2).³ In 1985, the Eleter group reported the formation of a Dewar borazine **III-BN3** from borazine.⁴ The substitution reaction of borazine $(\text{FBNiPr})_3$ with tBuLi , afforded the tBu-substituted Dewar borazine **III-BN3** (Scheme 3.1.3). Employment of the bulky substituent results in the formation of Dewar borazine, which is thermally more favorable than the corresponding borazine.

Scheme 3.1.2. Formation of **III-BN2** as the intermediate.

Scheme 3.1.3. Synthesis of **III-BN3**.

In 1991, the Paetzold group reported the second example of a structurally characterized Dewar borazine **III-BN4** by the reaction of an iminoborane (tBuNBPh) and its dimer (tBuNBPh)₂ (Scheme 3.1.4).⁵ The structural parameter of **III-BN4** is similar to those of **II-BN1**. **III-BN4** has the long central B1-N1 bond (174.1(4) Å) as well as two B-N double bonds (1.370(4) – 1.376(4) Å). The holding angle of two square planes is 117.0(2)°.

Scheme 3.1.4. Synthesis of **III-BN4**.

In 1995, the Paetzold group reported the Dewar borazine **III-BN5** as an intermediate in the reaction of tri-tert-butyl azadiboriridine (tBuN(BtBu)₂) with trimethylsilylazide (TMSN₃) (Scheme 3.1.5).⁶ **III-BN5** undergoes 1,3-sigmatropic silyl migration to furnish its isomer.

Scheme 3.1.5. Formation of **III-BN5** as an intermediate.

In 2004, the same group published the mixture of Dewar borazines **III-BN6/III-BN6'** derived from a mixture of methyl(1-methylcycloheptyl)iminoboranes, which were generated by the gas-phase thermolysis of the corresponding azidoborane (Scheme 3.1.6).⁷ The structure of the Dewar borazines **III-BN6/III-BN6'** is proposed only by the ^{11}B NMR signal observed at $\delta = 30.8$ ppm.

Scheme 3.1.6. Formation of a mixture of **III-BN6/III-BN6'**.

The thermal conversion of Dewar borazines has also been investigated and revealed that the conversion of **III-BN1**, **III-BN3**, and **III-BN4** into the corresponding dimer (RBNR')₂ proceeded at 160 - 300 °C (Scheme 3.1.7).^{1,4,5}

Scheme 3.1.7. Thermal conversion of **III-BN1**, **III-BN3**, and **III-BN4**.

The reported ¹¹B NMR chemical shifts of Dewar borazines at room temperature appear around $\delta = 30$ ppm, which are not in line with the value expected from the structure. Low temperature ¹¹B NMR measurements of **III-BN3** or **III-BN6/III-BN6'** revealed that two peaks correspond to the expected Dewar borazine structure ($\delta = 35.9$ ppm and 13.1 ppm or $\delta = 22.6$ ppm and 33.4 ppm, respectively).^{4,7} Paetzold and co-workers suggested a fluxional process between the three possible equivalent structures of Dewar borazine in a CDCl₃ solution at room temperature (Scheme 3.1.8), with the corresponding borazine as the transition state.

Scheme 3.1.8. A fluxional rearrangement of Dewar borazine in a solution.

The Paetzold group performed the mechanistic study on the formation of Dewar borazines from iminoborane.⁸ They discovered the size of the substituents on both boron and nitrogen atoms provides a great impact on the selectivity of the resulting cyclic structure. As shown in Figure 3.1.9, the oligomerization of iminoboranes may yield mainly five different types of products (BN)_n. With sterically less hindered ligands (e.g. R, R' = Me), the

trimerization of iminoboranes occurs to give rise to borazines, whereas with the sterically demanding substituents (e.g. R = iPr, R' = tBu) the formation of Dewar borazines is more favorable. Employment of the more bulky substituents on both B and N atoms (e.g. R, R' = tBu) leads to the formation of dimers.

Figure 3.1.9. Products by oligomerization of iminoboranes (RBNR').

3.1.2 Dewar type inorganic benzene isomer containing group 14 elements

It has been reported that hexasila- and hexagerma-Dewar benzenes can be synthesized by photoisomerization of the corresponding prismanes. The group of Sekiguchi and Sakurai reported the generation of hexasila-Dewar benzene **III-Si1** upon irradiation of **II-Si1** with a light of 360-380 nm wavelength in solution (3-Methylpyridine or 2-MeTHF) at $-50\text{ }^{\circ}\text{C}$ or in a glass matrix at $-196\text{ }^{\circ}\text{C}$ (Scheme 3.1.10).⁹⁻¹¹ The UV-vis spectrum of **III-Si1** shows absorption bands at 335 nm, 455 nm, and 500 nm. Excitation of the bands with wavelengths longer than 460 nm resulted in the immediate regeneration of **II-Si1**, which was confirmed by the original absorption at 241 nm. **III-Si1** is thermally stable at $-150\text{ }^{\circ}\text{C}$, however, it gradually reverts to the **II-Si1**.

Scheme 3.1.10. Formation of hexasila Dewar benzene **III-Si1**.

The same group reported that upon irradiation of UV light to hexagermaprismane **II-Ge2** at low temperature new absorption bands appeared at 342 nm, 446 nm, and 560 nm corresponding to hexagerma-Dewar benzene **III-Ge1** (Scheme 3.1.11).⁹⁻¹¹ Excitation of these bands with $\lambda > 460$ nm light led to the regeneration of the original absorption due to **II-Ge2**. Hexagerma Dewar benzene **III-Ge1** is gradually reverted to the prismane **II-Ge1** above – 160 °C.

Scheme 3.1.11. Preparation of hexagerma Dewar benzene **III-Ge1**.

3.1.3 Dewar type inorganic benzene isomer containing group 15/15 elements

In 2020, Zhu, and Eckhardt reported the Dewar benzene type isomer of cyclotriphosphazene (PN)₃ **III-PN1** in the gas phase upon sublimation via photoionization reflection time-of-flight mass spectrometry (Scheme 3.1.12).¹²

Scheme 3.1.12. Preparation of Dewar benzene isomer of cyclotriphosphazene **III-PN1**.

3.2 Objectives

Although several inorganic Dewar benzene derivatives have been synthesized and investigated, the chemistry in this field is still in its infancy. In particular, the extant B,N-derivatives are limited to the B_3N_3 type featuring a B-N σ bond and no other examples have been described thus far. Considering not only the fundamental curiosity but the potential application, for instance, as the synthetic building blocks, the investigation of other derivatives are highly desired from both experimental and theoretical points of view, which prompted us to design a novel inorganic Dewar benzene based on the B_4N_2 scaffold. We aimed the synthesis and characterization of the B_4N_2 Dewar benzene featuring a B-B σ -bond between diagonal boron atoms, as well as, the examination of the reactivity.

3.3 Results and Dsicussions

Reaction of **1** with two equivalents of boron trichloride (BCl_3) over 2 days led to the formation of dichloro B_4N_2 derivative **2** in 65% yield (Scheme 3.3.1). **2** was also formed by disproportionation of **1** with tetrachloro-substituted B_4N_2 . The ^{11}B NMR spectrum of **2** displays a set of new broad peaks at 47.2 ppm for Cl-bound boron atoms, and 34.1 ppm for the NMe_2 -bound boron atoms. The reduction of **2** with excess potassium graphite (KC_8) in the presence of three equivalents of trimethyl phosphine (PMe_3) in benzene/thf mixture led to the desired B_4N_2 Dewar benzene **3** in 51% yield. In the ^{11}B NMR spectrum, the broad singlets appear at 33.9 ppm for the tricoordinate boron atoms and at -19.8 ppm for the tetracoordinate boron atoms. The ^{31}P NMR spectrum shows a broad doublet at -23.4 ppm, indicating the presence of PMe_3 groups coordinating to the boron center.

Scheme 3.3.1. Synthesis of **3** (Mes = 2,4,6-trimethylphenyl).

The crystalline structure of **3** (Figure 3.3.1) was solved in the P212121 space group. The central $\text{B2-B2\#}$ bond length between the four-coordinate bridgehead B atoms is $1.802(3)$ Å, which is an extra-long single bond but still in the range of the reported ($\text{sp}^3\text{-sp}^3$) B-B bond lengths. The B1-B2 bond length ($1.748(2)$ Å) is in the typical B-B single bond length. The two B-N bond lengths ($\text{B1-N1} = 1.4346(19)$ Å, $\text{B2-N1} = 1.558(2)$ Å) are consistent with the typical B-N

double bond and single bond, respectively. All the tricoordinate boron and nitrogen atoms are in trigonal planar environments ($\Sigma B1 = 360.0^\circ$, $\Sigma N1 = 359.4^\circ$, $\Sigma N2 = 359.8^\circ$). The B1-N2 bond and pendant substituents lie within a single plane. Each four-membered B_3N ring is completely planar (sum of the interior angles of B1-B2-B2-#N1 = 360°), and the holding angle of two square planes (B1-B2-N1) is $121.94(11)^\circ$.

Figure 3.3.1. Solid-state structures of **3** (Top view (1), Side view (2). H atoms are omitted.). Thermal ellipsoids (50%).

In the UV/Vis absorption spectrum, an absorption band [$\lambda_{\text{max}} = 322 \text{ nm}$] was observed (Figure 3.5.14). The CV and DPV of **3** shows a reversible reduction wave at $E_{\text{ox}} = -1.6 \text{ eV}$, and an irreversible oxidation wave at $E_{\text{ox}} = +1.0 \text{ eV}$, respectively (Figure 3.5.16).

DFT and QTAIM calculations of **3** were carried out using the B3LYP/6-311G level of theory and the Multiwfn program. The crystal structure of **3** is well reproduced by the optimized structure.

Figure 3.3.2 illustrates that the HOMO of **3** mainly corresponds to the central B-B σ -bond. According to CMO analysis, the electron density of HOMO of **3** primary delivers from B2-#B2 (31.5%), two of B1-B2 (ave. 15.6%), and two of LP(1)N1 (ave. 8.6%) NBOs. The endocyclic B=N π -bonding interaction is represented by the HOMO-8. Note that in the case of C₆-Dewar benzene the MO corresponding to the skeletal C=C double bonds is located higher in energy than the MO of the central C-C σ bond.¹³

Figure 3.3.2. HOMO of **3** (H atoms are omitted.).

NBO electron occupancies of the B1-B2 and B2-#B2 σ -bonding orbitals in **3** are 1.89 and 1.79. WBI values of 0.86 (B1-B2), and 0.73 (B2-#B2) indicate the single bond character of the B-B bond (Table 3.5.5). WBI analysis shows a multiple bond character of B1-N1 (0.95). An AIM analysis confirmed the existence of a BCP between the B2 and #B2 atoms (Figure 3.5.25).

While the thermal and photochemical skeletal isomerization are commonly observed for benzene and valence isomers, upon heating at 60 °C in benzene **3** readily decomposed to end up with a complex mixture concomitant with the slow release of free PMe₃.

It has been reported that the cycloaddition of alkynes or alkenes with B-B unsaturated bonds proceeds without any catalysts, which is owing to the significantly high-lying HOMO of the

B-B multiply bonded species relative to those of carbon analogue. Because **3** possesses the high-lying B-B σ -bond as confirmed in the HOMO (Figure 3.3.2), next we investigated its reactivity towards unsaturated bonds.

Reaction of **3** with ethylene gas proceeded slowly at room temperature, which was monitored by in situ ^1H , ^{11}B , and ^{31}P NMR spectroscopy. After one hour, the ^{11}B NMR spectrum of the reaction mixture shows two new signals at 39.2 and -10.4 ppm beside the signal for unreacted **3** (at 47.2 and 34.1 ppm), indicating the presence of tetracoordinate boron atoms. In the ^{31}P NMR spectrum, one broad signal appeared at -16.1 ppm, indicative of the presence of the B- PMe_3 moiety. These signals are consistent with previously reported [2.2.2]bicyclo compound (Chapter 2, Scheme 2.3.2) from the reaction of B_4N_2 benzene with diphenylacetylene. Therefore, we tentatively assigned these new peaks to the [2.2.2]bicyclo intermediate **4-int** (Scheme 3.3.2). The isolation of **4-int** was not achieved due to its thermal instability. Upon removal of the solvent and ethylene gas, **4-int** decomposes to unidentified complex mixture. After few more hours, the new signals appeared in ^1H and ^{31}P NMR, with the release of free PMe_3 . This reaction completed over one week at room temperature or $60\text{ }^\circ\text{C}$ for two days, affording a sole product **4**. In the ^{11}B NMR spectrum, a set of new broad peaks was detected at 60 ppm for the central boron atoms and at 30 ppm for the NMe_2 group bounded boron atoms.

Scheme 3.3.2. Reactions of **3**.

Based on a XRD analysis, the nearly planar B₄N₄ framework of **4** features a completely BN substituted (3*Z*,5*Z*)-1,3,5,7-Octatetraene framework (Figure 3.5.20). The central B-B bond length [1.716(5) Å] is significantly shortens compared to that of **3** [1.802(3) Å], and in the range of typical (sp²-sp²) B-B single bond lengths. The B-N bond lengths in the B₄C₄N₂ ring [1.431(3) - 1.491(3) Å] fall between those for the reported B-N single and double bond. Note that, there are somewhat bond alternation of the B₄N₄ chain (Table 3.5.2). The B-C bond lengths [1.570(3) - 1.594(3) Å] are consistent with B-C single bonds. All the boron and nitrogen atoms are in trigonal planar environments. The Me₂N substituents are aligned approximately in parallel to the B-N-B planes (interplane torsion angle: 177.14°). Each mesityl ring on the N atom is nearly perpendicular to the BNB plane (torsion angle: B1-N1-C3-C8 = 100.83°). These geometrical parameters indicate the π conjugation system of the B₄N₄ moiety.

The presence of a π-conjugation of **4** is supported by DFT calculations. There are four occupied π-type orbitals delocalized on the B₄N₄ chain, being similar to those of the calculated carbon system **4-C** (Fig 4.5.23). The BN-doped organic π-conjugation systems, such as PAHs, have been widely developed due to the isoelectronic relationship between the B-N and C=C bonds.¹⁴⁻

¹⁸ However, the number of reported aliphatic polyenes with a completely BN-substituted backbone have been unexplored. This is presumably due to the limitation of the synthetic access.

Based on the formation of **4**, we thought that **3** can be a building block for the BN-containing polyenes. With this in mind, we next tried the reaction of **3** with phenylacetylene. Heating of the benzene solution of **3** with two equivalents of phenylacetylene at 60 °C over 2 days led to a complex mixture. By recrystallization from ether solution, compound **5** was obtained (Scheme 3.3.3). The ¹¹B NMR spectrum shows a set of new broad peaks at 48.8 ppm and 37.0 ppm, that were assigned to the central boron atoms and the NMe₂ group bounded boron atoms. Monitoring the reaction by ¹H and ¹¹B NMR spectroscopy did not allow for the clear observation of the corresponding bicyclo-intermediate. The attempt of 1:1 reaction of **3** with phenylacetylene gave the mixture of **3** and **5**.

(b)

• naphthalene dication

• 2,6-naphthoquinodimethane

Scheme 3.3.3. Formation of **5** by the reactions of **3** with phenylacetylene.

An XRD study (Figure 3.5.21) confirmed the [4.4.0]bicyclic structure of **5** with the conjugated B-B and B-N bonds [B-B: 1.700(5) Å, B-N: 1.419(4) – 1.495(5) Å], trigonal planar B and N

atoms [Σ B: 360.0° , Σ N: $259.5 - 360.0^\circ$], as well as, the planar arrangement of the NMe_2 groups. The B-C bonds [$1.569(5) - 1.578(5)$ Å] of **5** are consistent with the B-C single bonds in **4** [$1.570(3) - 1.594(3)$ Å]. The endocyclic C-C bond lengths [$1.348(4) - 1.358(4)$ Å] are in the typical range for a C=C double bond. The phenyl ring on C and the olefin part are somewhat coplanar, which suggests the presence of π -delocalisation over the styrene moieties. Surprisingly, **5** has a twisted geometry around the central B-B bond (averaged twist angle τ of **4**: 0.37° , **5**: 30.5°). and DFT calculations revealed that the presence of partial π conjugation of $(\text{BN})_4$ moiety in **5**.

These geometrical parameters indicate the presence of π conjugation across the B_4N_4 moiety, and less conjugation between the B_4N_4 and C=C moieties. Based on the bond alternation and its pattern, we concluded that **5** represents a BN doped analogue of naphthalene dication or 2,6-naphthoquinodimethane (Figure 3.3.3). The naphthalene core calculated on these carbon analogues exhibits a planar geometry with a perfect bond alternation (Figure 3.5.24). It is envisaged that the distorted structure of **5** could be the result from the bulky substituents (NMe_2 , Ph, Mes).

To better understanding the reaction mechanism between **3** and unsaturated molecules, we computationally investigated the plausible reaction pathway for the reaction with ethylene (Figure 3.5.26). The mechanism for the formation of **4** presumably involves the generation of bicyclic compound **4-int** as a transient intermediate. **4-int** then undergoes a rapid skeletal isomerization. Following similar ethylene insertion and subsequent skeletal isomerization may give **5**. The optimization of all possible intermediates indicate that these steps are energetically favourable (Fig 3.5.26 a). In the first step, a transition state (corresponding to C-B bond formation and B-B bond cleavage) could be identified with the associated activation energy ($46.5 \text{ kcal}\cdot\text{mol}^{-1}$), yielding **Int1**. Next step is a skeletal isomerization concomitant with the release of one PMe_3 to give ring-fused **Int2**. Surprisingly, the relative energy of one PMe_3 -

adduct **Int2** is more stable by 4.1 kcal mol⁻¹ compared to that of two PMe₃-adduct **Int3**, which structure was proposed from the symmetric signals in ¹H NMR. The migration of ethylene from **Int2** or **Int3**, followed by the addition of ethylene resulted in the formation of **4**.

3.4 Summary

In summary, a hitherto unknown B₄N₂-type Dewar benzene **3** featuring a B-B bond was successfully developed. The extra-long B-B σ -bond exhibits unique reactivity towards unsaturated C-C bonds, which allowed constructing the fused B₄C₄N₂ ring. Spectroscopic and DFT studies proposed that the reaction of **3** with ethylene proceeds through the formal [2+2] cycloaddition between the B-B σ -bond of **3** and the C-C π -bond of ethylene.

3.5 Experimental Sections

1. Synthesis of compounds 2-5 and their spectral data

Synthesis of 2.

To a DCM solution (6 mL) of **1** (300 mg, 0.62 mmol), BCl₃ (1.24 mL, 1.0 M) in DCM was added dropwise at –78 °C. The mixture was then stirred over two days at room temperature. All the solvent was removed in vacuum and the residue was extracted with hexane. After removal of hexane, the desired product was obtained as a white solid (220 mg, 65%). ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 6.83 (s, 4H, ArH), 2.90 (s, 6H, CH₃), 2.28 (s, 12H, CH₃) 2.15 (s, 6H, CH₃), 2.10 (s, 6H, CH₃); ¹¹B NMR (128 MHz, C₆D₆, 298 K): δ 47.2 (br, B–Cl), 34.1 (br, B–NMe₂); ¹³C{¹H} NMR (C₆D₆, 100 MHz, 298 K): δ 142.7 (C–Ar), 134.6 (C–Ar), 133.1 (C–Ar), 129.5 (CH–Ar), 43.7 (N–CH₃), 38.2 (N–CH₃), 21.0 (Ar–CH₃), 20.1 (Ar–CH₃). M.p.: 164.3 °C – 165.4 °C; HRMS (ESI) m/z: Calcd for C₂₂H₃₅B₄N₄Cl₂ 469.2611; Found 469.2600. Anal. Calc. for C₂₂H₃₄B₄N₄Cl₂: C 56.38%, H 7.31%, N 11.95%; found: C 56.28%, H 7.90%, N 11.96%.

Synthesis of 3.

To a benzene (5 mL) solution of **2** (100 mg, 0.20 mmol) and PMe₃ (62.5 μL, 0.61 mmol), KC₈ (110 mg, 0.81 mmol) was added at room temperature. The mixture was stirred for 2 days and the yellow solution was separated by filtration. After removal of the solvent, the residue was dried under vacuum to afford **3** as the yellow powder (57.3 mg, 51%). ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 7.03 (s, 2H, ArH), 6.99 (s, 2H, ArH), 2.79 (s, 6H, N–CH₃), 2.73 (s, 6H, CH₃), 2.53 (s, 6H, N–CH₃), 2.42 (s, 6H, CH₃), 2.31 (s, 6H, CH₃), 0.94 (d, J = 7.8 Hz, 18H, P–(CH₃)₃); ¹¹B NMR (128 MHz, C₆D₆, 298 K): δ 33.9 (br, B–NMe₂), –19.8 (br, B–PMe₃); ¹³C{¹H} NMR

(C₆D₆, 100 MHz, 298 K): δ 150.7(C-Ar), 136.1 (C-Ar), 133.1 (C-Ar), 130.1 (C-Ar), 129.5 (CH-Ar), 127.9 (CH-Ar), 42.8 (N-CH₃), 36.1 (N-CH₃), 21.2 (Ar-CH₃), 20.3 (Ar-CH₃), 19.5 (Ar-CH₃), 15.3 (P-(CH₃)₃), 15.0 (P-(CH₃)₃); ³¹P NMR (C₆D₆, 161 MHz, 298 K): δ -23.4 (P-(CH₃)₃). M.p.: 147.5 °C (dec.); UV-Vis (in toluene): 322 nm; HRMS (ESI) m/z: Calcd for C₂₈H₅₃B₄N₄P₂ 551.4125; Found 551.4118. Anal. Calc. for C₂₈H₅₂B₄N₄P₂: C 61.15%, H 9.53%, N 11.26%; found: C 61.43%, H 9.32%, N 10.16%.

Synthesis of 4.

A benzene (0.6 ml) solution of **3** (20.3 mg, 0.037 mmol) was degassed using a freeze–pump–thaw method, and then ethylene gas (1bar) was introduced into the schlenk tube, and the reaction mixture kept over 1 week at room temperature. After removal of the solvent, the residue was dried under vacuum. Recrystallization from benzene/hexane yielded the targeted compound as the coloueless crystals (10.5 mg, 63%). ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 6.86 (s, 4H, ArH), 2.50 (br, 6H, N-CH₃), 2.20 (s, 6H, CH₃), 2.11 (s, 12H, CH₃), 2.06 (br, 6H, N-CH₃), 1.43 (t, J = 8.0 Hz, 4H, CH₂), 1.02 (t, J = 8.0 Hz, 4H, CH₂); ¹¹B NMR (128 MHz, C₆D₆, 298 K): δ 58.9 (br, B–B), 36.4 (br, B-NMe₂); ¹³C{¹H} NMR (C₆D₆, 100 MHz, 298 K): δ 146.3 (C-Ar), 133.3 (C-Ar), 132.9 (C-Ar), 129.2 (CH-Ar), 41.5 (N-CH₃), 38.7 (N-CH₃), 21.0 (Ar-CH₃), 19.6 (Ar-CH₃). M.p.: 214.3 °C – 214.8 °C; HRMS (ESI) m/z: Calcd for C₂₆H₄₃B₄N₄ 455.3860; Found 455.3867. Anal. Calc. for C₂₆H₄₂B₄N₄: C 68.80%, H 9.33%, N 12.34%; found: C 68.64%, H 9.28%, N 12.07%.

1. Scheme

2. ^1H NMR

3. ^{11}B , ^{31}P NMR

S8722658
F:\spms\wcb\ProfKinjo\Oct20\KEI\201010_170-2-1; 75+C2H4; 11B

11B 3+C₂H₂, rt 1h

31P 3+C₂H₂, rt 1h

Scheme 3.5.1. The reaction between **3** and ethylene.

Synthesis of 5.

Phenylacetylene (4.1 mg, 0.073 mmol) was added to a benzene (0.6 ml) solution of **3** (20.0 mg, 0.036 mmol), and the reaction mixture kept over 3 days at room temperature. After removal of the solvent, the residue was dried under vacuum to obtain white solids (55%, ^1H NMR). ^1H NMR (C_6D_6 , 400 MHz, 298 K): δ 7.37 (s, 2H, CH), 6.99 (m, 4H, Ar-CH), 6.93 (m, 6H, Ar-CH), 6.40 (s, 4H, Ar-CH), 2.70 (6H, N-CH₃), 2.17 (s, 6H, CH₃), 2.06 (s, 12H, CH₃), 1.99 (br, 6H, N-CH₃); ^{11}B NMR (128 MHz, C_6D_6 , 298 K): δ 48.8 (br, B-B), 37.0 (br, B-NMe₂); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz, 298 K): δ 146.4 (C-Ar), 145.0 (C-Ar), 133.4 (C-Ar), 132.97 (C-Ar), 128.9 (CH-Ar), 127.1 (CH-Ar), 126.6 (CH-Ar), 124.9 (CH-Ar), 41.3 (N-CH₃), 38.9 (N-CH₃), 20.7 (Ar-CH₃), 20.0 (Ar-CH₃). M.p.: 211.2 °C – 211.9 °C; HRMS (ESI) m/z : Calcd for $[(\text{M}+\text{H})]^+$ $\text{C}_{50}\text{H}_{54}\text{B}_4\text{N}_4$: 755.4799; Found: 755.4827.

Figure 3.5.1. ^1H NMR spectrum of **2** (C_6D_6).

Figure 3.5.2. ^{11}B NMR spectrum of **2** (C_6D_6).

Figure 3.5.3. $^{13}\text{C}\{^1\text{H}\}$ and $^{13}\text{C}(\text{DEPT } 135)$ NMR spectra of **2** (C_6D_6).

F:\spms\cbo\ProfKinjo\Aug20\KEI\200805; 75 crystal; c6d6; 1H
ECA 400

Figure 3.5.4. ^1H NMR spectrum of **3** (C_6D_6).

ECA 400

Figure 3.5.5. ¹¹B NMR spectrum of **3** (C₆D₆).

Figure 3.5.6. ¹³C{¹H} and ¹³C(DEPT 135) NMR spectra of **3** (C₆D₆).

ECA 400

Figure 3.5.7. ³¹P NMR spectrum of **3** (C₆D₆).

201114 exp170-10 crystal nmr c6d6

BBFO2 400

Figure 3.5.8. ¹H NMR spectrum of **4** (C₆D₆).

Figure 3.5.9. ^{11}B NMR spectrum of **4** (C_6D_6).

Figure 3.5.10. $^{13}\text{C}\{^1\text{H}\}$ and $^{13}\text{C}(\text{DEPT } 135)$ NMR spectra of **4** (C_6D_6).

Figure 3.5.11. ^1H NMR spectrum of **5** (C_6D_6).

Figure 3.5.12. ^{11}B NMR spectrum of **5** (C_6D_6).

Figure 3.5.13. $^{13}\text{C}\{^1\text{H}\}$ and $^{13}\text{C}(\text{DEPT } 135)$ NMR spectra of **5** (C_6D_6).

Figure 3.5.14. UV-vis spectra of **3** in hexane.

Figure 3.5.15. Solid-state IR spectrum of **3**.

2. Cyclic voltammograms of 3 and 4

Figure 3.5.16. (a) CV [range: -2 to 0 eV, scan rate: 100 mVs⁻¹], (b) CV [range: 0 to +2 eV, scan rate: 20 mVs⁻¹], and (c) DPV [range: 0.7 to 1.4 eV, scan rate: 100 mVs⁻¹] of **3** in THF/0.1 M [ⁿBu₄N][PF₆] at room temperature.

Figure 3.4.17. (a) CV [range: -2 to 0 eV, scan rate: 20 mVs⁻¹], and (b) CV [range: -1 to +2 eV, scan rate: 20 mVs⁻¹] of **5** in THF/0.1 M [ⁿBu₄N][PF₆] at room temperature.

3. Crystal structural parameters for 2, 3, 4, and 5

Table 3.5.1. Summary of Data Collection and Structure Refinement for 2, 3, 4, and 5.

Compounds	2	3	4	5
Formula	C ₂₂ H ₃₄ B ₄ Cl ₂ N ₄	C ₂₈ H ₅₂ B ₄ N ₄ P ₂	C ₂₆ H ₄₂ B ₄ N ₄	C ₃₈ H ₄₆ B ₄ N ₄
Fw	468.67	549.91	453.87	602.03
Cryst syst	triclinic	orthorhombic	orthorhombic	monoclinic
Space group	P -1	P b c n	P b c n	P 1 21/n 1
Size (mm ³)	0.050 x 0.150 x 0.150	0.220 x 0.260 x 0.280	0.200 x 0.220 x 0.280	0.020 x 0.200 x 0.220
T, K	100(2)	100(2)	100(2)	100(2)
a, Å	8.4003(3)	10.5705(3)	13.7125(10)	14.395(4)
b, Å	10.5122(3)	16.2488(6)	12.2608(8)	19.421(7)
c, Å	15.1602(5)	19.3932(5)	15.5161(13)	24.941(9)
a, deg	80.0295(15)	90	90	90
b, deg	77.7219(15)	90	90	92.173(7)
g, deg	88.7292(15)	90	90	90
V, Å ³	1288.20(7)	3330.94(18)	2608.7(3)	6968.(4)
Z	2	4	4	8
<i>d</i> _{calcd} g·cm ⁻³	1.208	1.097	1.156	1.148
m, mm ⁻¹	0.269	0.154	0.066	0.066
Refl collected	38935	29958	10299	44792
<i>T</i> _{max} / <i>T</i> _{min}	0.9870/0.9610	0.9670/0.9580	0.9870/0.9820	0.9990/0.9860
N _{measd}	8219	6063	2308	11435
[R _{int}]	0.0646	0.0726	0.0410	0.1287
<i>R</i> [I>2sigma(I)]	0.0432	0.0543	0.0546	0.0734
<i>R</i> _w [I>2sigma(I)]	0.0971	0.1172	0.1440	0.1665
GOF	1.03	1.029	1.235	0.967
Largest peak/hole[e·Å ⁻³] diff.	0.467/-0.285	0.405/-0.347	0.447/-0.457	0.320/-0.312

Figure 3.5.18. Solid structures of **2**. Thermal ellipsoids (50%). Selected bond length (Å) and angles (°): B1–B2 1.725(2), B1–N1 1.4096(17), B2–N2 1.4904(18), B2–N3 1.394(2), B3–N1 1.5027(18), B3–N4 1.3915(17), B4–B3 1.711(2).

Figure 3.5.19. Solid structures of **3**. Thermal ellipsoids (50%). Selected bond length (Å) and angles (°): B1–B2 1.748(2), B1–N1 1.4346(19), B1–N2 1.429(2), B2–B2 1.802(3), B2–N1 1.558(2), B2–P1 1.9008(16), N2–B1–N1 126.54(13), N2–B1–B2 136.24(12), N1–B1–B2 97.22(11), N1–B2–B1 121.94(11), N1–B2–B2 90.71(12), B1–B2–B2 76.97(11), N1–B2–P1 118.17(10), B1–B2–P1 115.05(10), B2–B2–P1 124.75(5), C1–N1–B1 137.04(13), C1–N1–B2 127.27(11), B1–N1–B2 95.10(11), B1–N2–C10 125.07(12), B1–N2–C11 122.42(13), C10–N2–C11 112.31(12).

Figure 3.5.20. Solid structures of **4**. Thermal ellipsoids (50%). Selected bond length (Å) and angles (°):

B1–N2 1.414(3), B1–N1 1.494(3), B1–C1 1.594(3), B2–N1 1.431(3), B2–C2 1.570(3), B2–B2 1.716(5), C1–C2 1.548(3), N2–B1–N1 123.55(19), N2–B1–C1 120.10(19), N1–B1–C1 116.29(18), N1–B2–C2 123.12(19), N1–B2–B2 120.2(2), C2–B2–B2 116.7(2), B2–N1–C3 117.53(17), B2–N1–B1 120.39(18), C3–N1–B1 122.03(17), B1–N2–C12 121.81(18), B1–N2–C13 129.71(18), C12–N2–C13 108.41(17).

Figure 3.5.21. Solid structures of **5**. Thermal ellipsoids (50%). Selected bond length (Å): B1–N1 1.409(5), B1–N2 1.482(5), B1–C93 1.578(5), B2–N3 1.419(4), B2–C17 1.572(5), B2–B3 1.700(5), B3–N2 1.430(5), B3–C15 1.570(5), B4–N4 1.405(5), B4–N3 1.495(5), B4–C78 1.569(5), B5–N5 1.408(5), B5–N6 1.488(5), B5–C23 1.578(5), B6–N6 1.427(4), B6–C25 1.569(5), B6–B7 1.705(5), B7–N7 1.426(5), B7–C32 1.569(5), B8–N8 1.412(5), B8–N7 1.486(5), B8–C41 1.565(5).

Table 3.5.2. Selected bond lengths of **4** and **5** (Å).

	N1–B1	B1–N2	N2–B2	B2–B3	B3–N3	N3–B4	B4–N4
5	1.414(3)	1.494(3)	1.431(3)	1.716(5)	1.431(3)	1.494(3)	1.414(3)

6	1.409(5)	1.482(5)	1.430(5)	1.700(5)	1.419(4)	1.495(5)	1.405(5)
	1.408(5)	1.488(5)	1.427(4)	1.705(5)	1.426(5)	1.486(5)	1.412(5)

4. Computational Details

Table 3.5.2. Energies of **3**, **4**, and **5** (atom, x-, y-, z-positions in Å).

3

Zero-point correction=	0.773304
Thermal correction to Energy=	0.823233
Thermal correction to Enthalpy=	0.824177
Thermal correction to Gibbs Free Energy=	0.686164
Sum of electronic and zero-point Energies=	-2098.748034
Sum of electronic and thermal Energies=	-2098.698105
Sum of electronic and thermal Enthalpies=	-2098.697161
Sum of electronic and thermal Free Energies=	-2098.835175

B	-0.49735780	-0.25135056	-1.51685316
B	-0.70860093	0.57017692	0.54260728
C	-2.87532232	-0.70495450	-0.40402390
C	-4.00038881	-0.00441279	-0.90086514
C	-5.29090691	-0.51351896	-0.68267823
H	-6.14177202	0.03936841	-1.06726342
C	-5.50881639	-1.71091545	0.00095005
C	-4.38353156	-2.41946803	0.44435532
H	-4.52206909	-3.37118160	0.94628144
C	-3.08104417	-1.94890314	0.24866755
C	-1.90596703	-2.79713752	0.67155522
H	-1.35731064	-3.16110292	-0.20140812
H	-2.23926076	-3.66500854	1.24288263
H	-1.19253129	-2.23612145	1.27152983
C	-6.90640896	-2.23218885	0.25573659
H	-7.20071814	-2.09715332	1.30119367
H	-6.98167686	-3.29974336	0.03595950
H	-7.64197952	-1.71304007	-0.36071841
C	-3.83973900	1.25694630	-1.72050543
H	-4.55462699	2.02735145	-1.41853704
H	-4.01674807	1.05697161	-2.78222559
H	-2.82866534	1.64542489	-1.63142642
C	-1.72117950	-1.54338798	-3.38436035
H	-2.57371064	-1.46416382	-2.71840086
H	-1.52935044	-2.60812176	-3.56865731
H	-1.99002442	-1.08868825	-4.34678686
C	0.62665794	-0.98805844	-3.67208196
H	1.48946134	-0.55323637	-3.17471169
H	0.46693627	-0.47297789	-4.63020703
H	0.86246788	-2.03471671	-3.90293519
C	-0.37872779	2.84703128	2.74818064

B	0.50618997	-0.24191342	1.52247581
B	0.70953424	0.57419350	-0.53929222
C	2.88028601	-0.69689210	0.40263536
C	4.01180624	0.01016058	0.87435175
C	5.29904275	-0.50616752	0.65282929
H	6.15491556	0.05168572	1.01878094
C	5.50735369	-1.71658443	-0.01010645
C	4.37595618	-2.43066108	-0.42883268
H	4.50739205	-3.39179785	-0.91442712
C	3.07671679	-1.95336383	-0.22898899
C	1.89546525	-2.80535379	-0.62649312
H	1.34746638	-3.14441409	0.25674591
H	2.22224907	-3.68887238	-1.17721830
H	1.18335430	-2.25549701	-1.23851254
C	6.90101850	-2.24635592	-0.26876812
H	7.18448451	-2.13356831	-1.31983237
H	6.97629327	-3.30934682	-0.02783093
H	7.64418497	-1.71639116	0.32908806
C	3.86364494	1.28810113	1.67058599
H	4.54222620	2.06767695	1.31268235
H	4.10200651	1.11959025	2.72557515
H	2.84012436	1.65048683	1.62394418
C	1.74966335	-1.50046965	3.39973728
H	2.60046012	-1.41437560	2.73247062
H	1.57324941	-2.56627529	3.59294008
H	2.01262795	-1.03395928	4.35813595
C	-0.60388709	-0.97121926	3.68802813
H	-1.47316197	-0.55099613	3.18944845
H	-0.44692758	-0.44505137	4.64057632
H	-0.82701302	-2.01815927	3.92988503
C	0.35886182	2.83977137	-2.75300740

H	0.55452434	3.15957868	2.28676413	H	-0.57974213	3.14116256	-2.29503247
H	-0.16207868	2.05867307	3.46341500	H	0.15449523	2.04743750	-3.46749381
H	-0.84099080	3.69321155	3.25400126	H	0.81174195	3.69088886	-3.25904823
C	-2.03134977	3.73857867	0.48074965	C	1.99477227	3.75794723	-0.48531204
H	-2.37380374	4.49898294	1.18225548	H	2.33945681	4.51663548	-1.18758227
H	-2.83298635	3.50043915	-0.21269395	H	2.79003687	3.53009804	0.21874344
H	-1.17846689	4.11689502	-0.07625315	H	1.13260573	4.13325875	0.05932675
C	-3.13318812	1.86278689	2.39324392	C	3.12264407	1.88707102	-2.39015285
H	-2.94963448	1.12099995	3.16554579	H	2.94705577	1.14203805	-3.16122476
H	-3.88720608	1.47704252	1.71109426	H	3.87955826	1.50946145	-1.70672787
H	-3.48198690	2.78858828	2.84999088	H	3.46314171	2.81522697	-2.84835248
N	-1.56274845	-0.15554955	-0.54196957	N	1.56941778	-0.14412804	0.54508398
N	-0.54407516	-0.88745943	-2.80274340	N	0.56292603	-0.86572976	2.81403273
P	-1.53214110	2.16690480	1.42634672	P	1.51706530	2.17703079	-1.42646967

4

Zero-point correction=	0.658681
Thermal correction to Energy=	0.696434
Thermal correction to Enthalpy=	0.697378
Thermal correction to Gibbs Free Energy=	0.586432
Sum of electronic and zero-point Energies=	-1334.043885
Sum of electronic and thermal Energies=	-1334.006132
Sum of electronic and thermal Enthalpies=	-1334.005187
Sum of electronic and thermal Free Energies=	-1334.116134

N	1.9318020	0.5329290	0.0783860	N	-1.9317550	-0.5329050	-0.0782350
N	2.8517020	2.8979560	0.4397080	N	-2.8516720	-2.8978490	-0.4397650
C	3.7444860	-0.8248170	1.0978470	C	-3.7443150	0.8249630	-1.0977560
C	3.2434800	-0.0959250	-0.0017510	C	-3.2434560	0.0959090	0.0018020
C	5.7603220	-1.3680850	-0.1824590	C	-5.7603740	1.3679490	0.1823180
C	5.2366510	-0.6466940	-1.2594180	C	-5.2368530	0.6463930	1.2592380
H	5.8073480	-0.5779640	-2.1784940	H	-5.8076970	0.5774860	2.1782090
C	4.9968080	-1.4414510	0.9886690	C	-4.9966730	1.4415380	-0.9886760
H	5.3830580	-1.9910150	1.8396270	H	-5.3828020	1.9912380	-1.8396010
C	3.9880010	-0.0119350	-1.1942410	C	-3.9881700	0.0116880	1.1941540
C	3.4653350	0.7442500	-2.3945290	C	-3.4656790	-0.7446920	2.3943960
H	2.4547400	0.4267220	-2.6578280	H	-2.4551210	-0.4272130	2.6578900
H	4.1074660	0.5834750	-3.2608270	H	-4.1079340	-0.5840540	3.2606280
H	3.4215050	1.8195710	-2.2048390	H	-3.4218290	-1.8199850	2.2045410
C	0.8718790	-1.8691630	-0.3716550	C	-0.8718370	1.8691830	0.3718560
H	0.8259300	-1.9700110	-1.4696570	H	-0.8258430	1.9700370	1.4698550
H	1.8078740	-2.3551610	-0.0828090	H	-1.8078410	2.3551800	0.0830400
C	7.0957400	-2.0715420	-0.2867830	C	-7.0958340	2.0713420	0.2865390
H	7.7396680	-1.5961530	-1.0283070	H	-7.7397820	1.5959390	1.0280360
H	6.9721290	-3.1173170	-0.5846310	H	-6.9722960	3.1171320	0.5843640
H	7.6250790	-2.0672380	0.6678720	H	-7.6251160	2.0669840	-0.6681480
C	2.9630920	-0.9306210	2.3880610	C	-2.9627010	0.9310460	-2.3878150
H	2.5931600	0.0417370	2.7189250	H	-2.5925970	-0.0412200	-2.7187580
H	3.5839970	-1.3484040	3.1811400	H	-3.5835110	1.3488760	-3.1809450
H	2.0888160	-1.5769270	2.2773590	H	-2.0885200	1.5774370	-2.2768600
C	2.7943960	4.3433550	0.1550960	C	-2.7944960	-4.3432790	-0.1552880
H	2.6951170	4.9300030	1.0755230	H	-2.6952710	-4.9298470	-1.0757720
H	1.9685700	4.5883250	-0.5028310	H	-1.9686920	-4.5883870	0.5026140

H	3.7198450	4.6554040	-0.3391960	H	-3.7199730	-4.6552930	0.3389750
C	4.1276790	2.5715730	1.0995480	C	-4.1276160	-2.5712660	-1.0995660
H	4.3111980	3.2948670	1.9007110	H	-4.3111830	-3.2944160	-1.9008500
H	4.9699990	2.6225650	0.4016620	H	-4.9699480	-2.6222990	-0.4016990
H	4.1110730	1.5837080	1.5369470	H	-4.1109200	-1.5833280	-1.5368040
C	-0.3472570	-2.6286120	0.2344440	C	0.3472780	2.6286200	-0.2342920
H	-0.2374120	-2.6321670	1.3301390	H	0.2373880	2.6321890	-1.3299820
H	-0.2845190	-3.6768070	-0.0649450	H	0.2845650	3.6768160	0.0651060
B	0.7822700	-0.3274670	-0.0628290	B	-0.7822310	0.3274870	0.0630510
B	1.7754740	2.0134290	0.1325720	B	-1.7754250	-2.0134000	-0.1324890

5

Zero-point correction=	0.775674
Thermal correction to Energy=	0.821968
Thermal correction to Enthalpy=	0.822913
Thermal correction to Gibbs Free Energy=	0.692985
Sum of electronic and zero-point Energies=	-1793.58031
Sum of electronic and thermal Energies=	-1793.534015
Sum of electronic and thermal Enthalpies=	-1793.533071
Sum of electronic and thermal Free Energies=	-1793.662998

N	1.68039645	-0.98044609	-0.40279920	H	-3.64349441	-1.00952799	-3.24557793
N	1.51302017	-3.26911280	-1.56626086	H	-2.55980394	-1.64891821	-2.01102649
N	-1.68031629	0.98058259	-0.40256851	C	2.70205600	-3.15543027	-2.42832282
N	-1.51306675	3.26924663	-1.56598299	H	3.10965667	-2.15586277	-2.41876259
C	3.89490562	-1.61003282	0.49728871	H	2.43144993	-3.41115149	-3.45756140
C	-3.12852536	0.86906322	-0.42742365	H	3.48646569	-3.84793118	-2.10578482
C	2.50015994	1.94511100	1.17281239	C	3.96352596	1.59008207	3.09405978
C	-5.94745432	0.65288755	-0.43334437	H	4.22337436	1.01144016	3.97113707
C	-2.70216679	3.15546997	-2.42794126	C	-3.24297437	2.52816770	1.50656093
H	-3.10969452	2.15587031	-2.41832147	H	-3.94976774	2.80090416	2.29072474
H	-2.43166670	3.41118719	-3.45720831	H	-2.89126031	3.45397964	1.04281422
H	-3.48659786	3.84792120	-2.10534867	H	-2.37569172	2.06203093	1.97520267
C	2.87400180	1.20714253	2.31129563	C	4.37216571	3.45085261	1.61309276
H	2.29215764	0.33922080	2.59203234	H	4.95702416	4.31668855	1.32946614
C	-5.28914676	1.48670489	0.47619588	C	-4.37225990	-3.45078216	1.61247835
H	-5.87181965	2.04974938	1.19633355	H	-4.95708152	-4.31660807	1.32874523
C	5.16699870	0.05623931	-1.35103693	C	3.24297131	-2.52839642	1.50601810
H	5.65465642	0.69649706	-2.07720622	H	2.37575941	-2.06224102	1.97477293
C	0.39675572	2.53255727	0.01128949	H	3.94976835	-2.80134155	2.29010587
H	0.66234758	3.56244847	0.24735740	H	2.89113217	-3.45409319	1.04213490
C	-3.76862768	0.03271775	-1.36733095	C	7.45221603	-0.50258054	-0.40715420
C	1.28155446	1.57075502	0.39968173	H	7.94010173	-1.41752838	-0.06645045
C	3.76876090	-0.03265396	-1.36758842	H	7.75551757	0.30089486	0.27102833
C	3.12861111	-0.86899352	-0.42770299	H	7.84693426	-0.26015403	-1.39537760
C	5.94756466	-0.65314059	-0.43375561	C	-0.87232929	4.57882115	-1.78262653
C	-3.27492951	-3.07202150	0.83714754	H	-0.01522696	4.72033089	-1.13707146
H	-3.02328389	-3.64180305	-0.04788639	H	-1.58789105	5.38433353	-1.58918812
C	5.28921180	-1.48698921	0.47572299	H	-0.53740465	4.67361440	-2.82080688
H	5.87185897	-2.05018858	1.19576044	C	0.87217349	-4.57864462	-1.78281563
C	-5.16685443	-0.05633115	-1.35072263	H	1.58768917	-5.38420579	-1.58941083
H	-5.65447502	-0.69659561	-2.07691120	H	0.53715025	-4.67344160	-2.82096387
C	-1.28145356	-1.57067188	0.39957963	H	0.01511344	-4.72005753	-1.13717675

C	3.27496713	3.07208849	0.83757764	B	-0.98318003	2.27063208	-0.70382151
H	3.02345882	3.64188285	-0.04748700	B	0.98321591	-2.27047447	-0.70408222
C	-3.89485157	1.60989796	0.49770928	C	-4.71933178	-2.71406932	2.74791516
C	-2.50015940	-1.94506367	1.17253260	H	-5.56791321	-3.00822066	3.35154713
C	-0.39666767	-2.53244730	0.01110266	C	2.99225980	0.73204943	-2.41606625
H	-0.66231492	-3.56237412	0.24696592	H	2.56008405	1.64910579	-2.01123749
C	4.71905280	2.71413633	2.74858323	H	2.16319930	0.14390534	-2.81305334
H	5.56752681	3.00829449	3.35236294	H	3.64370261	1.00964174	-3.24581012
C	-2.87420021	-1.20708269	2.31094256	B	-0.84090378	-0.11747825	-0.02006719
H	-2.29241133	-0.33915112	2.59176736	C	-7.45208712	0.50215159	-0.40667969
C	-3.96386176	-1.59001576	3.09351894	H	-7.75525658	-0.30149860	0.27135484
H	-4.22386304	-1.01136721	3.97054656	H	-7.84684091	0.25988542	-1.39492859
C	-2.99206948	-0.73189265	-2.41583458	H	-7.94005358	1.41697384	-0.06575548
H	-2.16306583	-0.14366469	-2.81281486	B	0.84101650	0.11758033	-0.02009077

Figure 3.5.22. Selected MO of **3**.

Figure 3.5.23. Selected MO of **4** and **4-C**

4

4-C

Figure 3.5.24. Selected MO of **6** and **6-C**

5

5-C

Table 3.5.3. CMO NBO Analysis of Canonical Molecular Orbitals of **3**

CMO: NBO Analysis of Canonical Molecular Orbitals

Leading (> 5%) NBO Contributions to Molecular Orbitals

```
=====
```

MO 149 (occ): orbital energy = -0.13327 a.u.

-0.562*[57]: BD (1) B 2- B47

0.396*[56]: BD (1) B 2- B46

0.393*[53]: BD (1) B 1- B47

0.293*[47]: LP (1) N43(lp)

0.292*[49]: LP (1) N88(lp)

```
=====
```

Table 3.5.4. Selected data of Natural Bond Orbital Analysis of **3**.

NATURAL BOND ORBITAL ANALYSIS:

(Occupancy) Bond orbital/ Coefficients/ Hybrids

```
=====
```

57. (1.78936) BD (1) B 2- B 47

(50.02%) 0.7072* B 2 s(21.67%)p 3.62(78.33%)

0.0000 0.4655 -0.0008 0.0026 0.6390

-0.0143 0.0011 0.3176 0.0030 0.0007

-0.5231 0.0145 -0.0027

(49.98%) 0.7070* B 47 s(21.67%)p 3.61(78.33%)

0.0000 0.4655 -0.0008 0.0026 -0.6413

0.0143 -0.0012 0.3130 0.0033 0.0006

0.5231 -0.0146 0.0027

```
=====
```

Table 3.5.5. Wiberg bond index among B₄N₂ skeleton in **3**.

		1	2	43	46	47	88
		B	B	N	B	B	N
1	B		0.8172	0.0248	0.0021	0.0116	0.8901
2	B	0.8172		0.9791	0.0205	0.0026	0.0044
43	N	0.0248	0.9791		0.9543	0.0073	0.0032
46	B	0.0021	0.0205	0.9543		0.9026	0.0146
47	B	0.0116	0.0026	0.0073	0.9026		1.0057
88	N	0.8901	0.0044	0.0032	0.0146	1.0057

Figure 3.5.25. The topology of the Laplacian distribution of the charge density in the six-membered B₄N₂ ring of **3** with bond critical points (blue dots).

Figure 3.5.26. Free energy profile (kcal·mol⁻¹) for the (a) proposal intermediates to form **4** and (b) reaction of model compound **3'** (replace Mes with Ph) with ethylene to form **Int3** at the B3LYP/6-31G(d) level of theory.

3.6 References

- 1 P. Paetzold, C. Vonplotho, G. Schmid, R. Boese. 1,3,5-Tri-tert-butyl-2,4,6-triisopropyl-3,5-diaza-1-azonia-2,6-dibora-4-borata[2.2.0]bicyclohexan, der erste Vertreter der Dewarborazine. *Z. Naturforsch. B* **39**, 1069-1075 (1984). doi:10.1515/znb-1984-0814.
- 2 T. Franz, E. Hanecker, H. Noth, W. Stocker, W. Storch, G. Winter. Beiträge zur Chemie des Bors, 167. Zur Synthese von Diazadiboretidinen, Borazinen und Octahydrotetrazatetraborocinen durch Stannazan-Spaltung. *Chem. Ber. Recl.* **119**, 900-916 (1986). doi:10.1002/cber.19861190314.
- 3 K. Delpy, H. U. Meier, P. Paetzold, C. Vonplotho. Die Cyclodimerisierung der Alkyl(tert-butylimino)borane. *Z. Naturforsch. B* **39**, 1696-1701 (1984). doi:10.1515/znb-1984-1213
- 4 H. A. Steuer, A. Meller, G. Elter. B-t-butyl-borazine und -diazadiboretidine. *J. Organomet. Chem.* **295**, 1-6 (1985). doi:10.1016/0022-328x(85)88065-7.
- 5 P. Paetzold, J. Kiesgen, K. Krahe, H. U. Meier, R. Boese. Ringerweiterungs- und -verengungsreaktionen bei BN-Vier- und -Sechsringen. *Z. Naturforsch. B* **46**, 853-860 (1991).
- 6 S. Luckert, E. Eversheim, M. Müller, B. Redenz-Stormanns, U. Englert, P. Paetzold. Tri-tert-butylazadiboriridin: Ringerweiterung mit Isonitrilen, α -Bromlithioalkanen und Aziden. *Chem. Ber.* **128**, 1029-1035 (1995). doi:10.1002/cber.19951281011.
- 7 P. P. J. Münster, E. Schröder, H. Schwan, T. von Bennisen-Mackiewicz. Cyclic iminoboranes: Analogues of cycloalkynes. *Z. Anorg. Allg. Chem.* **630**, 2641-2651 (2004). doi:10.1002/zaac.200400334.
- 8 P. Paetzold. Iminoboranes. *Adv. Inorg. Chem.* **31**, 123-170 (1987). doi:10.1016/s0898-8838(08)60223-8.

- 9 A. Sekiguchi, T. Yatabe, C. Kabuto, H. Sakurai. Chemistry of organosilicon compounds. 303. The missing hexasilaprismane: synthesis, x-ray analysis and photochemical reactions. *J. Am. Chem. Soc.* **115**, 5853-5854 (1993). doi:10.1021/ja00066a075.
- 10 A. Sekiguchi, T. Yatabe, S. Doi, H. Sakurai. Cage Compounds of Si and Ge: Synthesis and Structures. *Phosphorus, Sulfur Relat. Elem.* **93**, 193-196 (1994). doi:10.1080/10426509408021814.
- 11 A. Sekiguchi, H. Sakurai. in *Adv. Organomet. Chem.* Vol. 37 (eds F. Gordon, A. Stone, & Robert West) 1-38 (Academic Press, 1995).
- 12 C. Zhu, A. K. Eckhardt, A. Bergantini, S. K. Singh, P. R. Schreiner, R. I. Kaiser. The elusive cyclotriphosphazene molecule and its Dewar benzene-type valence isomer (P₃N₃). *Sci. Adv.* **6**, eaba6934 (2020). doi:10.1126/sciadv.aba6934.
- 13 M. Tsuda, S. Oikawa, K. Kimura. Potential-energy surfaces in the lower excited states of benzene $\rightleftharpoons$ Dewar-benzene isomerization process. *Int. J. Quantum Chem.* **18**, 157-164 (1980). doi: 10.1002/qua.560180122.
- 14 X.-Y. Wang, J.-Y. Wang, J. Pei. BN Heterosuperbenzenes: Synthesis and Properties. *Chem. Eur. J.* **21**, 3528-3539 (2015). doi:10.1002/chem.201405627.
- 15 S. Nakatsuka, N. Yasuda, T. Hatakeyama. Four-Step Synthesis of B₂N₂-Embedded Corannulene. *J. Am. Chem. Soc.* **140**, 13562-13565 (2018). doi:10.1021/jacs.8b08197.
- 16 A. Abengózar, P. García-García, D. Sucunza, D. Sampedro, A. Pérez-Redondo, J. J. Vaquero. Synthesis, Functionalization, and Optical Properties of 1,2-Dihydro-1-aza-2-boraphenanthrene and Several Highly Fluorescent Derivatives. *Org. Lett.* **21**, 2550-2554 (2019). doi:10.1021/acs.orglett.9b00448.

- 17 T. Kaehler, M. Bolte, H.-W. Lerner, M. Wagner. Introducing Perylene as a New Member to the Azaborine Family. *Angew. Chem. Int. Ed.* **58**, 11379-11384 (2019). doi:10.1002/anie.201905823.
- 18 H. Lu, T. Nakamuro, K. Yamashita, H. Yanagisawa, O. Nureki, M. Kikkawa, H. Gao, J. Tian, R. Shang, E. Nakamura. B/N-Doped p-Arylenevinylene Chromophores: Synthesis, Properties, and Microcrystal Electron Crystallographic Study. *J. Am. Chem. Soc.* (2020). doi:10.1021/jacs.0c10337.

Chapter 4: Synthesis, characterization, and reactivity of a zwitterionic valence isomer of B₄N₂ inorganic benzene

4.1 Introduction

Among many proposed valence isomers of benzene (CR)₆, prismane, Dewar-benzene, and benzvalene, have been isolated and structurally characterized to date. Likewise, several inorganic benzene valence isomers have been developed thus far. Significantly, by reflecting unique electronic and bonding nature of heteroatoms, it has been demonstrated that valence isomers which have never been reported in all-carbon systems, are synthetically accessible. Thus, employment of heteroatoms as the skeletal scaffold may be the efficient strategy to expand the chemistry relevant to benzene valence isomers, and allow developing unusual structural architectures

4.1.1 “Unexpected” benzene valence isomer containing Group 14 elements

In 2010, the group of Rzepa and Scheschkewitz reported a tricyclic aromatic isomer of hexasilabenzene.¹ Reduction of a trichlorocyclotrisilane precursor with three equivalents of lithium naphthalenide (Li/Np) led to the hexasilabenzene isomer Si₆Tip₆ **V-Si1** in 52% yield (Scheme 4.1.1, **A**). In 2012, the same group reported the alternative synthetic pathway to **V-Si1** by employing Cp*Si⁺ as a stoichiometric source of silicon.² Reaction of the Cp*Si⁺ salt with two equivalents of the lithium disilenide (Tip₂Si=SiTipLi(dms)₂) afforded a mixture of **V-Si1** and tetrasilabutadiene Si₄Tip₆ as the main products (Scheme 4.1.1, **B**). Meanwhile, the reaction of Cp*Si⁺ salt with one equivalent of Tip₂Si=SiTipLi(dms)₂ gave a cyclotrisilene (Tip₃Si₃Cp*), reduction of which with one equivalent of Li/Np afforded **V-Si1** in 50% yield (Scheme 4.1.1, **C**). Surprisingly, **V-Si1** is stable to air for hours in the solid-state and for minutes even in a solution without detectable changes.

Scheme 4.1.1. Synthetic route of **V-Si1**.

The solid-state structure of **V-Si1** exhibits a tricyclic chair-like structure with a central rhomboid Si₄ ring. The six silicon atoms are in three different oxidation states, +**II** (SiTip₂), +**I** (SiTip), and 0 (Si). The bond length of Si1–Si3 is only slightly longer than Si1–Si3', both being at the shorter end of typical Si–Si single bonds. Theoretical analysis reveals that the six mobile electrons are delocalized over the central four-membered ring leading to the π -, σ - and non-bonding interaction, which can be described by the resonance forms **A** and **B** (Scheme 4.1.2).

Scheme 4.1.2. Resonance forms for **V-Si1**.

Compound **V-Si1** undergoes thermal or photochemical valence isomerization to give **V-Si2** in 58% yield (Scheme 4.1.3).³ The solid-state structure of **V-Si2** represents the global minimum of the Si₆H₆ potential energy surface. The distance of 2.7076(8) Å between the unsubstituted bridgehead silicon atoms Si1–Si5 is significantly longer than the other Si–Si single bond lengths (2.3536(6) - 2.3819(5) Å). The theoretical calculation revealed that there is no interstitial bond between Si1–Si5, while it is presented in the carbon analogue of propellane.⁴

Scheme 4.1.3. Synthesis of **V-Si2** by the isomerization of **V-Si1**.

Treatment of **V-Si2** with bromine (Br₂) or iodine (I₂) at room temperature afforded the 1,5-dihalogenated derivatives (Scheme 4.1.4). While the reaction of **V-Si2** with excess iodine at 110°C gave hexaiodocyclopentasilane (Tip₃Si₅I₆) in 28 % yield.⁵

Scheme 4.1.4. Reactions of **V-Si2**.

While the reactions of **V-Si1** with elemental chlorine (Cl_2) and Br_2 gave a complex mixture, the halogenation of **V-Si1** with BiCl_3 afforded a mixture of multiple products (Scheme 4.1.5).

Scheme 4.1.5. Reaction of **V-Si1** with BiCl_3 .

Recently, functionalization of the Si_2 , Si_4 and Si_6 atoms in **V-Si2** has been developed.⁶⁻¹⁰ In 2014, the Wesemann group isolated the isostructural tin analogue $\text{Sn}_6(\text{Tip})_6$. The reaction of TipSnH_3 with a carbene proceeded at -40°C , and after workup crystals of **V-Sn1** were gained in 15% yield (Scheme 4.1.6).¹¹

Scheme 4.1.6. Preparation of **V-Sn1**.

Heteronuclear isomers $\text{E}_2\text{Si}_4(\text{Tip})_6$ ($\text{E} = \text{Ge}, \text{Sn}$) were also reported by the group of Berger and Scheschkewitz.¹² The reaction of a lithium disilenide with GeCl_2 -dioxane and subsequent reduction with one equivalent of Li/Np resulted in the formation of the digermatetrasilane-analogue **V-SiGe1** (Scheme 4.1.7). In contrast to **V-Si1**, **V-SiGe1** slowly rearranges to the propellane-type global minimum isomer **V-SiGe2** in solution even at room temperature, and the conversion completes after 12 hours at 65°C .

Scheme 4.1.7. Synthesis of **V-SiGe1** and rearrangement to **V-SiGe2**.

In the case of $\text{E} = \text{Sn}$, the propellane-type species **V-SiSn2** was directly obtained, suggesting that **V-SiSn1** may be generated as the transient intermediate (Scheme 4.1.8).

Scheme 4.1.8. Synthesis of **V-SiSn2** through **V-SiSn1**.

4.1.2 “Unexpected” benzene valence isomer containing Group 14/15 elements

In 2019, Scheschkewitz and co-workers reported the synthesis of two Si_4P_2 isomers.¹³ Dimerization of the Si_2P three-membered ring precursor by heating in the presence of Lewis acid BPh_3 , gave a mixture of **V-SiP1** (58%) and **V-SiP2** (14%) (Scheme 4.1.9). **V-SiP1** and **V-SiP2** correspond to the global minimum isomer (**V-Si2**) and a chair-like conformation (**V-Si1**) of hexasilabenzene, respectively. **V-SiP1** possesses a typical single P-P bond (2.243(1) Å), while the Si-P (2.281(1) – 2.300(1) Å) and Si-Si bonds (2.354(1) – 2.462(1) Å) are slightly longer than the corresponding typical single bonds. **V-SiP2** features a centrosymmetric diamond-shaped Si_2P_2 moiety with two short Si-P (2.2372(4) Å) and two long Si-P bonds (2.3210(4) Å).

Scheme 4.1.9 Formation of Si_4P_2 isomers **V-SiP1** and **V-SiP2**.

4.2 Objectives

Interestingly, the calculated natural resonance theory (NRT) weight values for benzene suggest a slight admixture of ionic canonical forms in the electronic structure.¹⁴ The ionic character of benzene allows one to envision a number of zwitterionic valence isomers. For example, based on ionic resonance form **I'**, it may be postulated that zwitterionic valence isomer **VI** (Figure 4.2.1 A) could be formed via a four-center two-electron¹⁵⁻¹⁷ bonding interaction between two odd-electron π -orbitals (Figure 4.2.1 B).¹⁸⁻²¹ Thus far, however, such possible zwitterionic valence isomers have not yet been observed, either experimentally or computationally. Given that B and N are isolobal to cationic and anionic CH fragments, respectively, the incorporation of these elements in the framework of benzene may furnish inorganic analogues of the proposed zwitterionic valence isomers of benzene. Herein, we report the synthesis of diazatetraborinane **1** and its chemical reduction. The latter afforded the first valence isomer derivative of diazatetraborabenzene that is relevant to the envisioned zwitterionic benzene valence isomer **VI**.

Figure 4.2.1. (A) Zwitterionic valence isomer **VI** is formed from the ionic resonance form **I'** of benzene. (B) Four-center two-electron bonding interaction via σ -type overlap of two π -orbitals in **I'**.

4.3 Results and Discussions

A neutral diazatetraborinane derivative featuring a six-membered B₄N₂ heterocycle (**1**) was obtained from the deprotonation of 1,2-bis(anilide)-1,2-bis-(dimethylamido)diborane with two equivalents of *n*-butyllithium, followed by treatment with bis(dimethylamido)diborondichloride (Figure 4.3.1).

Figure 4.3.1. Synthesis of diazatetraborinane **1** and its chemical reduction reactions. Reduction of **1** with potassium graphite (KC₈), followed by addition of one and two equivalents of 18-crown-6 ether (18C6) afforded **2** and **3**, respectively. When the reaction mixture is not immediately treated with crown ether after the reduction of **1**, **4** is formed.

Tetrahydrofuran (THF) was added to a solid mixture of **1** and five equivalents of potassium graphite (KC₈) at room temperature, which immediately afforded a dark purple solution. After filtration, a stoichiometric amount of 18-crown-6 ether (18C6) was added to the solution, which resulted in an immediate color change from dark purple to dark blue. By slow

diffusion of hexane into the blue solution at $-26\text{ }^{\circ}\text{C}$, single crystals of dianionic product **2** were obtained in 68% yield. The ^1H NMR spectrum of **2** shows only a broad singlet at 2.21 ppm, which corresponds to the protons of NMe_2 . In the ^{11}B NMR spectrum, a broad signal at 12.9 ppm was observed, which is upfield-shifted relative to that of **1** (39.5 ppm), and thus indicative of an increase in the electron density on the boron centers. A single-crystal X-ray diffraction analysis confirmed the ionic nature of **2**, in which two potassium cations are trapped by 18C6, whereas the C_2 -symmetric dianionic fragment contains two six-membered B_4N_2 units that interact with one potassium ion each. Both potassium atoms are bridged by a molecule of THF (Figure 4.3.2).

Figure 4.3.2. Solid-state structures of **1** (top left), the dianionic part of **2** (top right), **3** (bottom left), and **4** (bottom right) (hydrogen atoms, solvent molecules, and the counterion in **2** are omitted for clarity). All ellipsoids are shown at 50% probability.

Each B₄N₂ ring exhibits a distorted boat shape, whereby both N atoms are bent toward the coordinating potassium atom (sum of the bond angles around the N atoms: $\Sigma N1 = 360.0^\circ$; $\Sigma N2 = 359.0^\circ$). The N atoms of the NMe₂ groups at the B2 and B4 atoms display a pyramidal geometry ($\Sigma N4 = 345.9^\circ$; $\Sigma N6 = 345.0^\circ$), whereas those at the B1 and B3 atoms retain a planar geometry. The distance between the K1 and K2 atoms (3.660 Å) is well within the sum of the van der Waals radii of two potassium atoms (5.6 Å). The B1–B4 and B2–B3 bonds are not parallel to each other; i.e., they include a torsion angle of 27.2°. The B1–B4 (1.700(9) Å) and B2–B3 (1.673(9) Å) bond distances are shorter than those in **1** (1.732(3) Å and 1.717(3) Å, respectively) but slightly longer than the reported B–B bond distances of diborane radical anions (1.636(7)–1.661(5) Å).^{22–26} The distances between these boron atoms, i.e., B1–B2 (2.201 Å), B1–B3 (3.038 Å), B2–B4 (2.330 Å), and B3–B4 (2.176 Å), are longer than typical B–B single bonds (1.72 Å). However, density functional theory (DFT) calculations performed on **2** at the M06-2X/6-31G(d) level of theory indicated bonding interactions between these four B atoms. The highest occupied molecular orbital (HOMO) and the HOMO–1 correspond to σ -type bonding orbitals formed between two π (B–B) orbitals in the six-membered B₄N₂ rings (Figure 4.3.3 A). Thus, the four B atoms in each B₄N₂ ring share two electrons, which is consistent with the results of a natural population analysis (NPA), suggesting that the B atoms in **2** are less positively charged (B1: 0.63; B2: 0.48; B3: 0.51; B4: 0.47) than those in **1** (B1: 0.71; B2: 0.79). A natural bond orbital (NBO) analysis yielded the following Wiberg bond index (WBI) values: B1–B2 (0.17), B1–B3 (0.06) B1–B4 (1.02), B2–B3 (1.06), B2–B4 (0.34), and B3–B4 (0.23), which confirm that the bonding interaction between the B2 and B4 atoms is stronger than that between the B1 and B3 atoms. Indeed, an atoms-in-molecules (AIM) analysis revealed the existence of a bond critical point between the B2 and B4 atoms (Figure 4.3.3 B). In the solid state, **2** is stable for several days at room temperature, while it decomposes into an unidentified mixture after 6 hours in solution.

Figure 4.3.3. (A) Plots of the HOMO (left) and HOMO-1 (right) of **2**. (B) The topology of the Laplacian distribution of the charge density in the six-membered B₄N₂ ring of **2** with bond critical points (blue dots). (C) Plot of the SOMO of **3-D**.

To prevent the potassium atoms from interacting with the six-membered B₄N₂ rings, two equivalents of 18C6 were added immediately after the reduction reaction. The reduction of **1** with KC₈ (5 equiv.) in THF, followed by treatment with 18C6 (2 equiv.), afforded a dark blue solution, which is NMR silent even at low temperature (−60 °C). Slow diffusion of hexane into this THF solution afforded dark needle-shaped crystals of **3** in 63% yield. We found that **3** could also be prepared by adding 18C6 to a THF solution of **2**. An X-ray diffraction analysis at 103 K revealed the involvement of an anionic B₄N₂ unit and two potassium atoms that are coordinated by 18C6 and two molecules of THF in the unit cell (Figure 4.3.2). The shortest distance between the B₄N₂ anion and the [K(18C6)(THF)₂]⁺ counterions is greater than 3.0 Å, indicating weak interactions. The boat-shaped geometry of the B₄N₂ ring of **3**, as well as its

structural parameters, is similar to those of **2**, suggesting that the four B atoms in **3** share electrons, as seen in **2**. The paramagnetic nature of **3** was confirmed by means of electron paramagnetic resonance (EPR) spectroscopy and SQUID magnetic measurements. The EPR spectrum of **3** shows a broad unresolved resonance both in THF solution ($g = 2.00476$; $-90 \sim 20$ °C) and in the solid state ($g = 2.00484$; $-150 \sim 20$ °C) (Figure 4.5.13). The observed temperature dependence of both the EPR spectrum of the THF solution and the magnetic susceptibility for the crystalline sample of **3** fits well with the Bleaney–Bowers equation,²⁷ from which a singlet ground state was estimated with the single-triplet gaps ($2J$) of -419.15 cm^{-1} (-1.2 $\text{kcal}\cdot\text{mol}^{-1}$) by the EPR measurements (Figure 4.5.13) and -647.08 cm^{-1} (-3.7 $\text{kcal}\cdot\text{mol}^{-1}$) by the SQUID magnetic measurements (Figure 4.5.14), respectively. This observation agrees reasonably well with the DFT results, which show that the singlet ground state 3-S is by 7.8 $\text{kcal}\cdot\text{mol}^{-1}$ more stable than the triplet state. Significantly, the most stable triplet state consists of a doublet state of **3** (**3-D**) and a neutral potassium atom $[\text{K}(\text{18C6})(\text{THF})_2]$ rather than a triplet state of **3** (**3-T**). Such alkali metal-doped radical ion pairs of the type $\text{M}_2^{+\bullet}\text{A}^{\bullet-}$ (M = alkali metal; A = organic molecule) are considered to be prospective molecular materials with large nonlinear optical (NLO) responses.²⁸ A comparison of the calculated and experimental geometric parameters for **3** suggests that, even at 103 K, **3** should be best described as a thermally populated triplet state.²⁹⁻³⁹ Indeed, a triplet was still detected experimentally even at 103 K by the SQUID measurements. These results indicate the significant role of K^+ . While the localization of two negative charges in the $(\text{N}_2\text{B}_4)^{2-}$ core must be essentially disfavored, such electronic state is allowed if there is a potassium cation in close proximity, because a K^+ cation stabilizes the negative charges and thus the closed-shell singlet state **2**. Without K^+ , the electrons will get delocalized in a wider range to gain greater stabilization, which may lead to the triplet state **3**. The singly occupied molecular orbital (SOMO) of **3-D** corresponds to the σ -type bonding orbital formed between two $\pi(\text{B-B})$ orbitals

(Figure 4.3.3 C), confirming that the four B atoms in the B₄N₂ ring share one electron. An NBO analysis yielded WBI values between those boron atoms of B1–B2 (0.11), B1–B3 (0.03), B2–B4 (0.18), and B3–B4 (0.11). The spin density is mainly localized on the two B atoms (B1: 0.09; B2: 0.31; B3: 0.08; B4: 0.31). The synthesis and isolation of **3-D** via independent control reactions have not been successful thus far.

When crown ether was not added immediately after the reduction of **1**, the dark purple solution gradually turned into a colorless solution, indicative of thermal isomerization (Figure 4.5.19–4.5.21). After work-up, i.e., treatment with two equivalents of 12C4, single crystals of **4** were obtained in 71% yield, and an X-ray diffraction study revealed the dianionic tetraborane structure of **4**. Compound **4** represents a rare example of long-chain homocatenated tetraboranes.⁴⁰ It seems quite likely that **4** was formed via a ring-opening reaction coupled with an electron-precise B–B bond formation^{41,42} from an in-situ-generated dianionic intermediate (Figure 4.5.22). This notion is consistent with the results of the NBO and AIM analyses of **2**, which show bonding interactions among the four B atoms, especially between the B2 and B4 atoms.

4.4 Summary

In conclusion, we have demonstrated that a diazatetraborabenzene analogue **2** of a hypothetical zwitterionic valence isomer of benzene can be synthesized by simple reduction of diazatetraborinane **1** with KC_8 followed by the addition of 2 eq 18-crown-6 ether. X-ray analysis and DFT calculation disclose that two electrons are delocalized over the four boron atoms in the six-membered B_4N_2 ring with exhibiting a σ -bonding interaction between two B-B π -orbitals, which is further supported by the generation of the long-chain homocatenated tetraborane **4**. Treatment of **1** with twice amount of 18-crown-6 ether for **2** leads to the formation of a paramagnetic potassium-doped radical ion pair **3** that exhibits a thermally populated triplet character. These results in their entirety show that this method represents a useful strategy for the construction of benzene valence isomers that are not accessible via conventional hydrocarbon systems, indicating that this method may potentially lead to a variety of molecules with unique bonding.

4.5 Experimental Sections

4.5.1 Synthesis of compounds 1-4 and their spectral data

Materials and Methods

General considerations: All reactions were performed under an atmosphere of argon or nitrogen by using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH_2 . Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{11}B NMR spectra were obtained with a Bruker AVIII 400MHz BBFO1 spectrometer at 298 K or the low temperature. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Coupling constants J are given in Hz. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with a OpticMelt Stanford Research System. UV-Vis absorption spectra were carried out with Cary 300 UV-Vis spectrometer. Cyclic voltammetry (CV) was performed on a Biologic SP-50 electrochemical analyzer in anhydrous THF containing recrystallized tetra-*n*-butylammoniumhexafluorophosphate (TBAPF_6 , 0.1M) as supporting electrolyte at 298 K under an inert atmosphere of argon. A conventional three electrode cell was used with a glassy carbon electrode as the auxiliary electrode, silver/silver nitrate as the reference electrode, and a platinum wire as the working electrode. Continuous wave X-band electron paramagnetic resonance (EPR) spectra were recorded on a Bruker ELEXSYS E500 EPR spectrometer and a JEOL (FA200) spectrometer. Magnetic measurements were performed using a Quantum Design MPMS XL SQUID magnetometer in the temperature range 1.8 – 300 K with field up to 7 T.

Synthesis of diborane(4) (PhNH)(NMe₂)B–B(NMe₂)(NHPh)

The diborane(4) (PhNH)(NMe₂)B–B(NMe₂)(NHPh) was prepared following the reported synthetic procedure with little modification. A diethyl ether solution (20 mL) of (NMe₂)ClB–BCl(NMe₂) (4.92 g, 27.2 mmol) was added dropwise to a solution of PhNHLi (5.40 g, 54.5 mmol) in diethyl ether (30 mL) at –78 °C. Then, the mixture was stirred overnight at room temperature. All the solvent was removed in vacuum and the residue was extracted with hexane. After removal of hexane, the desired product was obtained as a white solid (6.75 g, 84.4 %). ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 7.13 (t, *J* = 7.3 Hz, 4H, Ph), 7.02 (d, *J* = 7.5 Hz, 4H, Ph), 6.80 (t, *J* = 7.3 Hz, 2H, Ph), 4.97 (s, 2H, NH), 2.61 (s, 6H, N–CH₃), 2.34 (s, 6H, N–CH₃); ¹³C{¹H} NMR (C₆D₆, 100 MHz, 298 K): δ 147.0 (Ph), 129.4 (Ph), 120.2 (Ph), 118.1 (Ph), 41.8 (N–CH₃), 35.6 (N–CH₃); ¹¹B NMR (128.3 MHz, C₆D₆, 298 K): δ 33.90 (s, B–N(CH₃)₂); M.p.: 88 °C; HRMS (ESI): *m/z* calcd for C₁₆H₂₅B₂N₄: 295.2265. [(*M*+*H*)]⁺; found: 295.2268.

Synthesis of 1

ⁿBuLi (1.65 mL, 2.5M) in hexane was added dropwise to a hexane solution (25 mL) of diborane(4) (PhNH)(NMe₂)B–B(NMe₂)(NHPh) (0.605 g, 2.06 mmol) at –78 °C. The mixture was then allowed to stir overnight at room temperature. After the completion of reaction, all the resulting lithium salt was collected by filtration and washed by hexane (3×10 mL). After that, the lithium salt was dissolved in small amount THF (8 mL) and then slowly added to a toluene solution of (NMe₂)ClB–BCl(NMe₂) (0.365 g, 2.02 mmol) at room temperature. The mixture was stirred for two days and then all the solvents were removed to afford a sticky solid. The solid was first washed by hexane (3×10 mL) and then extracted with hot toluene (20 mL). Removal of all the solvent resulted in the desired product as white solid (0.146 g, 18%). Colorless single crystals suitable for X-ray diffraction studies were grown by evaporation of a

dichloromethane solution at room temperature. ^1H NMR (C_6D_6 , 400 MHz, 298 K): δ 7.22 (t, J = 6.9 Hz, 4H, Ph), 7.05 (d, J = 7.8 Hz, 4H, Ph), 6.92 (t, J = 7.3 Hz, 2H, Ph), 2.77 (s, 12H, N- CH_3), 2.21 (s, 12H, N- CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz, 298 K): δ 151.3 (Ph), 129.1 (Ph), 126.8 (Ph), 121.4 (Ph), 43.7 (N- CH_3), 40.0 (N- CH_3); ^{11}B NMR (128.3 MHz, C_6D_6): δ 39.49 (br, B-N(CH_3)₂); M.p.: 236 °C (dec.); HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{35}\text{B}_4\text{N}_6$: 403.3295. $[(M+H)]^+$; found: 403.3311.

Synthesis of 2

THF (0.5 mL) was added to the mixture of **1** (10 mg, 0.024 mmol) and KC_8 (16.8 mg, 0.12 mmol) at room temperature in the small vial. The mixture was stirred for 5 minutes and the dark purple solution was separated by filtration. After that, a small amount of THF (0.1 ml) of 18-crown-6 ether (6.35 mg, 0.024 mmol) was added to the purple solution quickly. During this process, the solution changed to dark blue. Recrystallization by slow diffusion of hexane to the solution at -20 °C over two days afforded the targeted compound as the dark crystals (15.1 mg, 68%). ^1H NMR (THF-d_8 , 400 MHz, 233 K): δ 6.63 (t, J = 7.3 Hz, 8H, Ph), 6.03 (d, J = 8.0 Hz, 8H, Ph), 5.58 (t, J = 6.8 Hz, 4H, Ph), 3.56 (s, 48H, crown ether), 2.21 (br, 48H, N- CH_3), the signals for coordinating THF molecules are overlapped with these of free THF solvents. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-d_8 , 100 MHz, 233 K): δ 148.7 (Ph), 128.5 (Ph), 112.6 (Ph), 105.6 (Ph), 70.9 (crown ether), 43.3 (N- CH_3), the signals for coordinating THF molecules are overlapped with these of free THF solvents. ^{11}B NMR (128.3 MHz, THF-d_8 , 233 K): δ 12.86 (br, B-N(CH_3)₂); M.p.: 84 °C (dec.); HRMS (ESI): m/z calcd for $\text{C}_{40}\text{H}_{72}\text{B}_4\text{KN}_6\text{O}_8$: 847.5421. $[(M-K_2\cdot\text{THF})/2]^-$; found: 847.5411.

Synthesis of 3

THF (0.5 mL) was added to the mixture of **1** (10 mg, 0.024 mmol) and KC_8 (16.8 mg, 0.12 mmol) at room temperature in the small vial. The mixture was stirred for 5 minutes and the dark purple solution was separated by filtration. After that, a small amount of THF (0.1 ml) of 18-crown-6 ether (12.7 mg, 0.048 mmol) was added to the purple solution quickly. During this process, the solution changed to dark blue. Recrystallization by slow diffusion of hexane to the solution at $-20\text{ }^\circ\text{C}$ over two days afforded the targeted compound as the dark crystals (19.6 mg, 63%). M.p.: $69\text{ }^\circ\text{C}$ (dec.); HRMS (ESI): m/z calcd for $\text{C}_{40}\text{H}_{72}\text{B}_4\text{KN}_6\text{O}_8$: 847.5421. $[\text{M}-\text{K}(\text{18C6})(\text{THF})_2]^-$; found: 847.5445.

Synthesis of **4**

THF (1 mL) was added to the mixture of **1** (20 mg, 0.048 mmol) and KC_8 (33.6 mg, 0.24 mmol) at room temperature in the small vial. The mixture was stirred for 5 minutes and the dark purple solution was separated by filtration and then kept at room temperature overnight. The solution changed to nearly colorless and a THF (0.2 ml) solution of 12-crown-4 ether (16.9 mg, 0.096 mmol) was added. Recrystallization by slow diffusion of hexane to the solution at $-20\text{ }^\circ\text{C}$ over two days afforded the targeted compound as the colorless crystals (28.4 mg, 71%). Crystals suitable for X-ray diffraction studies were grown by slow diffusion of hexane to a dimethoxyethane solution of **4** at $-20\text{ }^\circ\text{C}$. ^1H NMR (THF- d_8 , 400 MHz, 213 K): δ 6.62 (t, $J = 7.5\text{ Hz}$, 4H, Ph), 6.04 (d, $J = 7.7\text{ Hz}$, 4H, Ph), 5.71 (t, $J = 6.9\text{ Hz}$, 2H, Ph), 3.51 (s, 32H, crown ether), 2.97 (s, 6H, $\text{N}-\text{CH}_3$), 2.95 (s, 6H, $\text{N}-\text{CH}_3$), 2.71 (s, 6H, $\text{N}-\text{CH}_3$), 2.43 (s, 6H, $\text{N}-\text{CH}_3$), the signals for coordinating THF molecules are overlapped with these of free THF solvents; $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 100 MHz, 298 K): δ 161.1 (Ph), 129.0 (Ph), 120.1 (Ph), 107.4 (Ph), 70.8 (crown ether), 46.6 ($\text{N}-\text{CH}_3$), 46.4 ($\text{N}-\text{CH}_3$), the signals for coordinating THF molecules are overlapped with these of free THF solvents; ^{11}B NMR (128.3 MHz, THF- d_8 , 298 K): δ

65.84 (br, BB_2B), 36.63 (br, PhNB); M.p.: 83 °C (dec.); HRMS (ESI): m/z calcd for $C_{28}H_{50}B_4KN_6O_4$: 617.3903. $[M-K\bullet I2C4]^-$; found: 617.3929.

Figure 4.5.1 ¹H NMR spectrum of diborane(4) (C₆D₆).

Figure 4.5.2 ¹³C{¹H} NMR spectrum of diborane(4) (C₆D₆).

Figure 4.5.3 ^{11}B NMR spectrum of diborane(4) (C_6D_6).

Figure 4.5.4 ^1H NMR spectrum of **1** (C_6D_6).

Figure 4.5.5 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** (C_6D_6).

Figure 4.5.6 ^{11}B NMR spectrum of **1** (C_6D_6).

Figure 4.5.7 ^1H NMR spectrum of **2** (THF-d_8).

Figure 4.5.8 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** (THF-d_8).

Figure 4.5.9 ^{11}B NMR spectrum of **2** (THF-d_8).

Figure 4.5.10 ^1H NMR spectrum of **4** (THF-d_8).

Figure 4.5.11 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** (THF-d_8).

Figure 4.5.12 ^{11}B NMR spectrum of **4** (THF-d_8).

Figure 4.5.13 EPR spectra of **3** in THF solution at room temperature ($g = 2.00476$) (a) and from 0 °C to -90 °C (b). The dependence of natural logarithm of integral intensity (I) multiplied by temperature (T) vs. reverse temperature ($1/T$) (c). EPR spectra of **3** in the solid-state at room temperature ($g = 2.00484$) (d), and from 0 °C to -150 °C (e).

Figure 4.5.14 χ_m - T plot (left) and $\chi_m T$ - T plot (right) for the solid sample of **3** in the SQUID measurement. The red solid curve is the best fit using Bleaney-Bowers equation with $g = 2.00$.

(a)

(b)

(c)

Figure 4.5.15 UV-visible spectra of **2** (a), **3** (b) and **4** (c) in THF.

Figure 4.5.16 Cyclic voltammograms of **1** in THF/0.1 M [$n\text{Bu}_4\text{N}$][PF_6] at room temperature.

$E_p^{\text{red}} = -1.47 \text{ V}$, $E_p^{\text{ox}} = -1.11 \text{ V}$. Scan rate: 200 mVs^{-1} .

Figure 4.5.17 ^1H NMR spectrum of the mixture of **1**, KC_8 and 18-crown-6 ether (1:1:1) in THF-d_8 . No signals for **1** was observed.

Figure 4.5.18 ^1H NMR spectrum of the mixture of **3** and **1** (1:1) in THF-d_8 . No signals for **1** was observed.

Figure 4.5.19 ^1H NMR spectrum of the reaction mixture of **1** with KC_8 (5 eq) in THF-d_8 .

Figure 4.5.20 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture of **1** with KC_8 (5 eq) in THF-d_8 .

Figure 4.5.21 ^{11}B NMR spectrum of the reaction mixture of **1** with KC_8 (5 eq) in THF-d_8 .

Figure 4.5.22 Proposed mechanism for the formation of **4**.

4.5.2 Crystal structure parameters

X-ray data collection and structural refinement. Intensity data for compounds **1-4** was collected using a Bruker APEX II diffractometer. The structure was solved by direct phase determination (SHELX-2013) and refined for all data by full-matrix least squares methods on F_2^{S3} . All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC: 1845324-1845327 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 4.5.1 Crystallographic data for **1-4**.

Compounds	1	2 •(THF) ₄	3 •(THF) ₁	4 •(C ₆ H ₁₄) ₁
Formula	C ₂₀ H ₃₄ B ₄ N ₆	C ₁₀₀ H ₁₈₈ B ₈ K ₄ N ₁₂ O ₂₁	C ₆₄ H ₁₂₂ B ₄ K ₂ N ₆ O ₁₇	C ₄₂ H ₈₀ B ₄ K ₂ N ₆ O ₈
Fw	401.77	2137.49	1369.11	918.56
Cryst syst	monoclinic	triclinic	monoclinic	monoclinic
Space group	C 1 2/c 1	P -1	P 1 21 1	P 1 21 1
Size (mm ³)	0.120 x 0.240 x 0.320	0.140 x 0.220 x 0.320	0.140 x 0.220 x 0.300	0.100 x 0.220 x 0.320
T, K	100(2)	103(2)	103(2)	100(2)
a, Å	16.6605(6)	16.2795(4)	11.4106(2)	10.4493(3)

<i>b</i> , Å	12.2075(3)	17.1593(4)	26.1750(6)	17.1573(5)
<i>c</i> , Å	11.3131(4)	22.3276(6)	13.0678(3)	14.9166(5)
□, deg	90	90.0344(18)	90	90
□, deg	95.0619(13)	90.0987(17)	101.5162(14)	106.7915(12)
□, deg	90	106.2799(17)	90	90
<i>V</i> , Å ³	2291.92(13)	5987.0(3)	3824.42(14)	2560.25(14)
<i>Z</i>	4	2	2	12
<i>d</i> _{calcd} g·cm ⁻³	1.164	1.186	1.189	1.192
□, mm ⁻¹	0.069	1.854	1.621	0.237
Refl collected	26894	70951	18908	49409
<i>T</i> _{max} / <i>T</i> _{min}	0.9920/0.9780	0.7810/0.5880	0.8050/0.6420	0.9770/0.9280
<i>N</i> _{measd}	3970	20409	11556	16238
[<i>R</i> _{int}]	0.0816	0.1411	0.0708	0.0768
<i>R</i> [<i>I</i> >2σ(<i>I</i>)]	0.0630	0.0864	0.0665	0.0607
<i>R</i> _w [<i>I</i> >2σ(<i>I</i>)]	0.1221	0.2104	0.1570	0.1216
GOF	1.093	1.045	1.006	1.037
Largest diff. peak/hole[e·Å ⁻³]	0.460/-0.264	1.167/-0.556	0.815/-0.590	0.714 /-0.677

4.5.3 Computational Details

All calculations were performed using the Gaussian 09 software package^{S4}. Geometry optimization calculations were done at the M06-2X/6-31G(d) level of theory (M06-2X/B1) in the gas phase^{S5-S7}. Frequency calculations were also performed at the same level, which yielded free-energy correction (*G*_{corr}) values. Subsequently, single-point energy calculations were performed at the M06-2X(SCRF)/6-311G(d,p) level of theory (M06-2X/B2)^{S8,S9}. The solvent effect of THF was taken into consideration using the IEFPCM-SCRF model as implemented in Gaussian 09^{S10}. Relative free energies were calculated using B2 energies and *G*_{corr}. AIM analysis was performed with Multiwfn software^{S11}.

Table 4.5.2 Energies of **1**, **2**, [K(18C6)(THF)₂], **3-D**, **3** (singlet), and **3** (triplet) obtained by DFT calculations.

	E[M06-2X/B1] (a.u.)	G _{corr} (a.u.)	E[M06-2X(SCRf)/B2//M06-2X/B1] (a.u.)	ΔG (kcal/mol)
1	-1210.226735	0.497693	-1210.559987	
2	-3852.593928	1.112819	-3853.564180	
[K(18C6)(THF) ₂]	-1987.184651	0.553684	-1987.652100	
3-D	-3197.459577	1.075665	-3198.262927	
3 (singlet) ^a	-5184.651328	1.647148	-5185.939476	0.0
3 (triplet) ^b	-5184.667061	1.652290	-5185.932113	7.8

^a: **3-S** in complex with a positively charged [K(18C6)(THF)₂]⁺; ^b: **3-D** in complex with a neutral potassium atom [K(18C6)(THF)₂].

Figure 4.5.23 B₄N₂ moieties in **2**, **3** (singlet), and **3** (triplet).

Table 4.5.3 Key B-B distances in B₄N₂ moieties in **2**, **3** (singlet), and **3** (triplet).

	2	3 (singlet)	3 (triplet)
B1-B2 (Å)	2.18	2.12	2.24
B1-B3 (Å)	3.02	3.01	3.04
B1-B4 (Å)	1.68	1.66	1.70
B2-B3 (Å)	1.67	1.69	1.71

B2-B4 (Å)	2.26	2.28	2.41
B3-B4 (Å)	2.13	2.19	2.25

Table 4.5.4 Wiberg bond index among B atoms in **2**, **3** (singlet), and **3** (triplet).

	2	3 (singlet)	3 (triplet)
B1-B2	0.1715	0.2567	0.1123
B1-B3	0.0598	0.0572	0.0303
B1-B4	1.0083	1.0918	0.9548
B2-B3	1.0619	1.0118	0.9524
B2-B4	0.3409	0.3403	0.1802
B3-B4	0.2312	0.1537	0.1077

Figure 4.5.24 The topology of the Laplacian distribution of charge density in the B₄N₂ six-membered ring of **3** (singlet) and **3** (triplet) with bond critical points (blue dots).

Table 4.5.5 NPA charges for B atoms in **1**, **2**, **3** (singlet), and **3** (triplet).

	1	2	3 (singlet)	3 (triplet)
B1	0.70745	0.63230	0.50941	0.65604
B2	0.78695	0.47582	0.43070	0.61850
B3	0.70688	0.51112	0.65636	0.65834
B4	0.78658	0.46568	0.47900	0.62123

Table 4.5.6 NPA charges for **1**, **2**, **3** (singlet), and **3** (triplet).

====**1**====

B	0.70745	C	-0.19733	H	0.18787	H	0.21766	H	0.20918	H	0.20319
B	0.78695	H	0.20959	C	-0.34573	C	-0.19738	H	0.18787	H	0.18156
B	0.70688	C	-0.26926	H	0.20251	H	0.20962	C	-0.34947	H	0.18384
B	0.78658	H	0.21787	H	0.17793	C	-0.25403	H	0.18577	N	-0.99816
C	0.19626	C	-0.34931	H	0.18321	H	0.21050	H	0.20865	N	-0.99840
C	-0.25519	H	0.18571	C	-0.35292	C	-0.19832	H	0.18367	N	-0.73740
H	0.22171	H	0.20867	H	0.20294	H	0.21011	C	-0.34588	N	-0.73577
C	-0.19813	H	0.18360	H	0.18165	C	-0.25438	H	0.20267	N	-0.73698
H	0.21007	C	-0.36005	H	0.18402	H	0.22156	H	0.17781	N	-0.73590
C	-0.25429	H	0.18583	C	0.19618	C	-0.36014	H	0.18337		
H	0.21044	H	0.20917	C	-0.26878	H	0.18589	C	-0.35280		

====2=====

B	0.63230	H	0.20517	H	0.16610	H	0.22898	H	0.16279	H	0.20703
B	0.47582	H	0.16568	H	0.19208	C	-0.34691	C	-0.35223	H	0.21508
B	0.51112	H	0.16279	H	0.14985	H	0.16062	H	0.16612	C	-0.42298
B	0.46568	C	-0.35217	C	0.19735	H	0.20982	H	0.19109	H	0.20614
B	0.50974	H	0.16619	C	-0.31218	H	0.15676	H	0.14805	H	0.21495
B	0.46748	H	0.19099	H	0.22871	C	-0.35032	C	-0.34918	C	-0.02415
B	0.63385	H	0.14729	C	-0.20924	H	0.15727	H	0.14725	H	0.17619
B	0.47432	C	-0.34848	H	0.21356	H	0.20292	H	0.20083	H	0.21818
C	0.18494	H	0.14987	C	-0.34715	H	0.16338	H	0.15955	K	0.65862
C	-0.30499	H	0.20109	H	0.21860	C	-0.35378	C	0.18452	K	0.65972
H	0.21946	H	0.15976	C	-0.21551	H	0.16621	C	-0.30485	N	-0.96282
C	-0.20421	C	-0.34701	H	0.22339	H	0.19189	H	0.21957	N	-0.93231
H	0.20410	H	0.16054	C	-0.29881	H	0.14942	C	-0.20451	N	-0.76316
C	-0.31458	H	0.21044	H	0.22695	C	-0.34767	H	0.20416	N	-0.78871
H	0.20445	H	0.15667	C	0.19742	H	0.15117	C	-0.31438	N	-0.75386
C	-0.19507	C	-0.35032	C	-0.29912	H	0.19736	H	0.20448	N	-0.78673
H	0.20245	H	0.15716	H	0.22620	H	0.16116	C	-0.19476	N	-0.93283
C	-0.30417	H	0.20313	C	-0.21507	C	-0.35559	H	0.20256	N	-0.96325
H	0.22939	H	0.16330	H	0.22353	H	0.21246	C	-0.30505	N	-0.75462
C	-0.35592	C	-0.34823	C	-0.34687	H	0.16226	H	0.22983	N	-0.78666
H	0.21273	H	0.14906	H	0.21859	H	0.16665	C	-0.02462	N	-0.76383
H	0.16256	H	0.19681	C	-0.20841	C	-0.35280	H	0.17692	N	-0.78859
H	0.16646	H	0.16071	H	0.21350	H	0.20530	H	0.21908	O	-0.64058
C	-0.35263	C	-0.35376	C	-0.31251	H	0.16568	C	-0.42320		

====3 (singlet)=====

B	0.50941	C	-0.20646	C	-0.03005	C	-0.04062	H	0.22552	H	0.18439
B	0.43070	H	0.19766	H	0.19556	H	0.17567	H	0.20364	C	-0.03244
B	0.65636	C	-0.33333	H	0.17582	H	0.19290	C	-0.42725	H	0.17654
B	0.47900	H	0.20133	O	-0.61047	C	-0.05857	H	0.22178	H	0.18220

C	0.20363	C	-0.21930	C	-0.02901	H	0.23049	H	0.21208	C	-0.03507
C	-0.30535	H	0.19750	H	0.17234	H	0.18167	C	-0.01881	H	0.18050
H	0.21678	C	-0.29736	H	0.20746	C	-0.07103	H	0.17136	H	0.17680
C	-0.22992	H	0.21313	C	-0.41642	H	0.18804	H	0.18435	C	-0.03576
H	0.19676	C	-0.35077	H	0.21626	H	0.23850	C	-0.03440	H	0.17863
C	-0.37453	H	0.16404	H	0.20075	C	-0.03641	H	0.18757	H	0.18642
H	0.20035	H	0.19198	C	-0.42126	H	0.17985	H	0.17657	K	0.52680
C	-0.22340	H	0.14745	H	0.20763	H	0.17657	C	-0.03629	K	0.49579
H	0.19875	C	-0.34800	H	0.20581	C	-0.03034	H	0.19145	N	-0.90844
C	-0.33491	H	0.14527	C	-0.02140	H	0.17501	H	0.17616	N	-0.95049
H	0.22075	H	0.20126	H	0.19212	H	0.17182	C	-0.03470	N	-0.78274
C	-0.34973	H	0.15758	H	0.16115	C	-0.03425	H	0.17795	N	-0.76403
H	0.14869	C	-0.34668	C	-0.03527	H	0.17220	H	0.18827	N	-0.78821
H	0.19799	H	0.21162	H	0.18557	H	0.18872	C	-0.03300	N	-0.76166
H	0.15820	H	0.15396	H	0.17227	C	-0.02731	H	0.18114	O	-0.59480
C	-0.37275	H	0.15584	C	-0.03571	H	0.17505	H	0.17498	O	-0.59326
H	0.16582	C	-0.36356	H	0.18749	H	0.18467	C	-0.03415	O	-0.59603
H	0.19492	H	0.20270	H	0.17265	C	-0.42815	H	0.17367	O	-0.60321
H	0.14999	H	0.16038	C	-0.03528	H	0.20797	H	0.18473	O	-0.62004
C	-0.35086	H	0.15307	H	0.17378	H	0.22098	C	-0.04112	O	-0.60294
H	0.21221	O	-0.61184	H	0.18639	C	-0.41353	H	0.18275	O	-0.60601
H	0.15986	C	-0.03317	C	-0.03294	H	0.20425	H	0.19215	O	-0.62249
H	0.16109	H	0.17613	H	0.17606	H	0.21849	C	-0.07028	O	-0.59594
C	-0.35397	H	0.19678	H	0.17535	C	-0.02891	H	0.23484	O	-0.59602
H	0.20574	C	-0.41535	C	-0.03202	H	0.20064	H	0.17759	O	-0.60148
H	0.16246	H	0.19990	H	0.17593	H	0.16307	C	-0.04603	O	-0.61257
H	0.16282	H	0.21177	H	0.17707	C	-0.01974	H	0.19656	O	-0.60784
C	0.21449	C	-0.42134	C	-0.03063	H	0.17334	H	0.18328	O	-0.59837
C	-0.30919	H	0.20557	H	0.17397	H	0.18545	C	-0.03302		
H	0.22214	H	0.20851	H	0.17580	C	-0.42635	H	0.17497		

====3 (triplet)====

B	0.65604	C	-0.20323	C	-0.01418	C	-0.04831	H	0.21251	H	0.17645
B	0.61850	H	0.20468	H	0.17897	H	0.17661	H	0.19582	C	-0.03640
B	0.65834	C	-0.29578	H	0.17063	H	0.20746	C	-0.42576	H	0.17639
B	0.62123	H	0.20657	O	-0.62360	C	-0.04929	H	0.21230	H	0.17877
C	0.20315	C	-0.21312	C	-0.02492	H	0.21093	H	0.20992	C	-0.03592
C	-0.27003	H	0.20649	H	0.18246	H	0.17399	C	-0.02217	H	0.17783
H	0.21621	C	-0.28157	H	0.18491	C	-0.05552	H	0.16554	H	0.17219
C	-0.22779	H	0.21872	C	-0.42505	H	0.19151	H	0.18535	C	-0.03224
H	0.20872	C	-0.35451	H	0.21779	H	0.20905	C	-0.03488	H	0.17275
C	-0.30145	H	0.17644	H	0.20132	C	-0.03073	H	0.19156	H	0.18565
H	0.21765	H	0.19827	C	-0.42094	H	0.17394	H	0.16911	K	0.48321
C	-0.22308	H	0.16191	H	0.21577	H	0.18199	C	-0.03601	K	-0.14692
H	0.20739	C	-0.34931	H	0.21468	C	-0.03061	H	0.18762	N	-0.97852

C	-0.29829	H	0.15869	C	-0.02603	H	0.17769	H	0.17002	N	-0.97649
H	0.22257	H	0.20315	H	0.16171	H	0.17194	C	-0.03391	N	-0.77906
C	-0.34911	H	0.17118	H	0.19837	C	-0.03464	H	0.17156	N	-0.75176
H	0.15815	C	-0.34984	C	-0.03481	H	0.17321	H	0.18390	N	-0.77984
H	0.20270	H	0.20983	H	0.18748	H	0.19051	C	-0.03601	N	-0.75720
H	0.17135	H	0.16905	H	0.17295	C	-0.02376	H	0.17347	O	-0.59655
C	-0.35612	H	0.16987	C	-0.03524	H	0.17491	H	0.18367	O	-0.59877
H	0.17667	C	-0.35805	H	0.18944	H	0.17865	C	-0.04112	O	-0.59718
H	0.19813	H	0.20358	H	0.17327	C	-0.42420	H	0.18921	O	-0.61160
H	0.16164	H	0.17093	C	-0.03423	H	0.19553	H	0.17444	O	-0.61290
C	-0.34915	H	0.17392	H	0.17534	H	0.20711	C	-0.04144	O	-0.60484
H	0.20892	O	-0.62292	H	0.18797	C	-0.44553	H	0.16702	O	-0.62659
H	0.16880	C	-0.03161	C	-0.03271	H	0.20548	H	0.19265	O	-0.61920
H	0.17172	H	0.17495	H	0.17932	H	0.21294	C	-0.04319	O	-0.59585
C	-0.35283	H	0.18908	H	0.17298	C	-0.03031	H	0.19204	O	-0.59449
H	0.20431	C	-0.43746	C	-0.03409	H	0.18985	H	0.16807	O	-0.59963
H	0.17129	H	0.19959	H	0.17417	H	0.16000	C	-0.04716	O	-0.59652
H	0.17311	H	0.22659	H	0.17948	C	-0.01586	H	0.17570	O	-0.59843
C	0.21007	C	-0.42345	C	-0.04193	H	0.17299	H	0.19853	O	-0.59465
C	-0.29532	H	0.21488	H	0.18669	H	0.18317	C	-0.03865		
H	0.22248	H	0.20172	H	0.17797	C	-0.41772	H	0.18447		

Table 4.5.7. XYZ coordinates of optimized geometries.

====1====

B	5.575512	16.207237	3.274891	C	7.275330	17.622053	-0.359928
B	7.667731	15.916922	4.381223	H	6.607260	18.386151	0.023199
B	8.613201	16.340861	2.989533	C	7.406156	17.456522	-1.735672
B	6.547000	17.436886	2.529688	H	6.848384	18.109762	-2.400777
C	6.153500	13.890768	4.244889	C	8.233919	16.469992	-2.260476
C	5.282089	13.167085	3.411258	H	8.337454	16.346906	-3.333521
H	4.763625	13.690923	2.614975	C	8.911605	15.628654	-1.379890
C	5.106786	11.799695	3.573393	H	9.540029	14.830700	-1.765237
H	4.424814	11.272065	2.912477	C	8.779777	15.780898	-0.006632
C	5.809428	11.099791	4.552892	H	9.278186	15.091815	0.667483
H	5.671722	10.030517	4.675147	C	7.207064	19.829561	2.047831
C	6.704546	11.796834	5.356858	H	6.743704	20.411839	1.239508
H	7.278971	11.270857	6.114149	H	8.111274	19.353997	1.665729
C	6.878352	13.169587	5.208530	H	7.482070	20.529512	2.847718
H	7.594384	13.686344	5.838935	C	5.133855	19.403232	3.211907
C	9.176288	16.948080	6.110781	H	5.451469	20.139108	3.962286
H	8.914329	17.854479	6.672017	H	4.556269	18.623286	3.709331
H	9.743535	17.236965	5.225321	H	4.487658	19.921728	2.489851
H	9.813232	16.328440	6.757104	C	3.422389	16.859458	2.135900
C	7.079862	15.990279	6.837560	H	4.107581	17.446484	1.519589
H	7.530287	15.299182	7.563185	H	2.673673	17.535319	2.575654
H	6.143355	15.562160	6.477769	H	2.888612	16.159489	1.477735
H	6.864601	16.930737	7.361406	C	3.287121	15.378228	4.031306
C	10.753551	15.280963	3.798177	H	3.850998	14.977492	4.874759
H	10.074222	14.837232	4.530042	H	2.808186	14.536622	3.510433
H	11.548614	15.820799	4.333749	H	2.490470	16.028793	4.418216
H	11.229140	14.463827	3.237778	N	6.360025	15.268779	4.055742

C	10.885749	16.803776	1.934743	N	7.817923	16.929091	1.928219
H	10.336772	17.573213	1.390116	N	7.972945	16.237263	5.718443
H	11.295307	16.094038	1.201726	N	10.023939	16.160449	2.907050
H	11.732384	17.277134	2.451010	N	6.293935	18.822145	2.560410
C	7.979041	16.801345	0.537024	N	4.156811	16.144650	3.160489

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B	9.145836	0.720504	4.037524	H	12.133117	5.513544	8.593763
B	9.394993	-0.301348	5.94226	C	12.467174	9.178117	9.076426
B	8.813477	0.822727	7.039025	H	11.905347	8.803808	9.952495
B	7.979694	1.260198	5.126134	H	11.768168	9.668837	8.393099
B	12.83221	7.798686	6.984871	H	13.173375	9.940515	9.455305
B	13.829574	7.244981	5.182309	C	14.14039	7.461288	9.182448
B	12.765421	7.720715	3.966065	H	14.961712	8.155763	9.446344
B	12.349602	8.852421	5.778012	H	14.575458	6.622303	8.636448
C	11.614826	0.027473	4.613338	H	13.727839	7.073851	10.131398
C	12.312404	0.670167	3.550817	C	16.113126	7.016838	6.223964
H	11.730252	1.23216	2.823637	H	17.179162	6.925602	5.96288
C	13.694041	0.597443	3.450088	H	15.807997	6.090328	6.718479
H	14.189411	1.111947	2.62831	H	16.024957	7.843655	6.961896
C	14.455321	-0.109412	4.387323	C	15.872014	8.389446	4.327041
H	15.536243	-0.162208	4.300329	H	15.988631	9.272841	4.988282
C	13.787407	-0.729873	5.446353	H	15.208619	8.689925	3.513617
H	14.358221	-1.272324	6.198144	H	16.865528	8.159116	3.905886
C	12.405058	-0.671291	5.57087	C	14.092859	7.137157	1.888502
H	11.888038	-1.169016	6.388001	H	14.589619	6.488079	2.616067
C	8.01005	1.186353	1.821907	H	14.848058	7.832788	1.479739
H	7.444667	1.864442	2.468318	H	13.736503	6.524599	1.041966
H	7.297856	0.468717	1.375658	C	12.357438	8.785998	1.667487
H	8.444749	1.761787	0.985602	H	11.569857	9.310907	2.211401
C	9.752641	-0.47011	1.846365	H	11.904145	8.301488	0.784347
H	10.487254	-0.961903	2.486808	H	13.073977	9.539475	1.291513
H	10.283652	-0.032311	0.982292	C	12.248456	11.082748	4.625727
H	9.070598	-1.244486	1.449415	H	12.255728	12.165828	4.824371
C	9.599916	-2.603175	4.949785	H	11.282527	10.828302	4.180032
H	9.575897	-3.670527	5.219735	H	13.036215	10.883187	3.865747
H	10.602848	-2.372364	4.579513	C	13.654246	10.853333	6.502568
H	8.886425	-2.462219	4.107652	H	14.527228	10.862183	5.817881
C	8.023182	-2.257977	6.666974	H	13.923999	10.220956	7.3498
H	7.222698	-2.330602	5.902322	H	13.505825	11.885827	6.861806
H	7.668062	-1.563805	7.430347	C	10.255858	8.437961	4.281244
H	8.139626	-3.25741	7.119275	C	9.652063	7.7392	3.196928
C	8.988114	-0.437254	9.226941	H	10.293282	7.139101	2.554641
H	9.476331	-0.016644	10.125769	C	8.28483	7.804828	2.971889
H	9.738748	-0.967188	8.633737	H	7.861286	7.247808	2.13763
H	8.246531	-1.175629	9.585161	C	7.446222	8.557981	3.801345
C	7.324837	1.289139	9.09242	H	6.377252	8.604026	3.617548
H	6.477881	0.61419	9.323197	C	8.02057	9.234219	4.880558
H	6.947159	2.097082	8.463147	H	7.387679	9.815216	5.549283
H	7.65819	1.728234	10.050034	C	9.386807	9.185335	5.127669
C	6.022279	0.050821	4.170485	H	9.832687	9.726555	5.959154
H	5.868175	-0.794924	4.872069	C	12.175879	4.321572	3.196936
H	6.747454	-0.285383	3.426676	H	12.738503	3.388346	3.333838
H	5.060205	0.241309	3.66521	H	12.757904	5.159193	3.597605
C	5.613178	1.538827	5.947946	C	11.748707	4.524104	1.746819
H	4.573739	1.603593	5.589908	H	11.601989	5.594419	1.557105
H	5.870148	2.497768	6.407001	H	12.494407	4.146509	1.041267
H	5.639055	0.761642	6.742299	C	10.416824	3.770174	1.692882
C	8.303879	3.368632	6.662188	H	10.57858	2.690083	1.59208
C	8.839674	3.909698	7.874697	H	9.761906	4.097692	0.88016
H	9.350959	3.232747	8.557585	C	9.821561	4.069475	3.063957

C	8.647338	5.244074	8.214378	H	9.249858	5.006978	3.06703
H	9.054757	5.609745	9.155508	H	9.19407	3.258313	3.448558
C	7.963663	6.125968	7.366761	K	11.177644	2.485156	6.023149
H	7.829503	7.170267	7.629352	K	10.542277	6.083467	5.888353
C	7.493918	5.629722	6.138366	N	10.282541	0.166737	4.783884
H	7.00756	6.310047	5.441538	N	8.436338	2.072615	6.339083
C	7.663612	4.299891	5.782903	N	9.031575	0.527551	2.594891
H	7.262007	3.913199	4.848682	N	9.265876	-1.789958	6.095541
C	13.354476	5.237653	6.821395	N	8.390471	0.594538	8.424236
C	14.06934	4.24368	6.079332	N	6.501527	1.231823	4.851868
H	14.563616	4.559257	5.162826	N	13.261759	6.507985	6.397075
C	14.189338	2.942088	6.543642	N	11.567321	8.310409	4.576367
H	14.735968	2.21282	5.94848	N	13.13409	8.108199	8.386517
C	13.595148	2.536551	7.750832	N	15.325395	7.256108	5.038126
H	13.688941	1.512411	8.097175	N	13.006081	7.831545	2.530124
C	12.843242	3.480073	8.463411	N	12.467583	10.348181	5.849541
H	12.341245	3.184911	9.383372	O	10.949271	4.224173	3.948768
C	12.699871	4.787381	8.012827				

====[K(18C6)(THF)₂]====

C	3.990056	9.415846	10.925592	H	5.188434	12.670256	11.584752
H	3.69739	9.203364	11.961435	C	5.349994	14.313076	9.596137
H	4.518944	10.378033	10.904688	H	5.764199	13.328394	9.325112
C	4.8389	8.30581	10.299374	H	6.144753	14.918285	10.061896
H	4.661389	7.347126	10.797648	C	4.846088	15.009554	8.356415
H	5.907615	8.535925	10.357745	H	4.482996	16.020095	8.603643
C	4.32398	8.274272	8.858911	H	5.668385	15.099458	7.629973
H	4.794265	9.074128	8.271752	C	3.276376	14.743389	6.616768
H	4.489083	7.318642	8.354149	H	4.082848	15.135141	5.978313
C	2.851136	8.597307	9.05035	H	2.570436	15.564222	6.826446
H	2.389481	9.066905	8.171721	C	2.597988	13.620045	5.874203
H	2.272965	7.70179	9.327297	H	2.232172	13.988437	4.901944
C	1.587291	15.575577	9.980932	H	3.333619	12.819792	5.699509
H	2.357302	15.529275	9.203034	C	0.932361	12.006454	5.993308
H	2.04052	15.979982	10.890635	H	1.672575	11.195355	5.900228
C	0.362153	16.344936	9.49831	H	0.592299	12.289539	4.984116
H	0.622793	17.212721	8.887085	C	-0.249149	11.527722	6.795866
H	-0.238368	16.685503	10.349155	H	-0.945265	12.364074	6.97496
C	-0.379374	15.250085	8.728799	H	-0.782233	10.748688	6.229391
H	-1.442244	15.457638	8.580984	C	-0.847081	10.535639	8.828825
H	0.087844	15.087844	7.750893	H	-1.356728	9.693334	8.336399
C	-0.13338	14.031293	9.615795	H	-1.584758	11.337759	8.992923
H	-0.904871	13.919209	10.389496	C	-0.282545	10.089158	10.154473
H	-0.077126	13.099152	9.048096	H	-1.104204	9.697249	10.776167
C	0.754068	10.9044	12.079842	H	0.462033	9.295501	10.012565
H	1.441498	10.048145	12.057672	K	2.590743	12.15422	9.193748
H	-0.109551	10.651945	12.716452	O	2.810068	9.543981	10.12186
C	1.448773	12.117245	12.645379	O	1.128347	14.250476	10.25676
H	0.827186	13.00934	12.478768	O	0.313998	11.204074	10.774555
H	1.594154	11.979614	13.729085	O	2.69618	12.280881	12.009894
C	3.397983	13.382499	12.538502	O	4.260401	14.155872	10.480834
H	3.669108	13.18734	13.588421	O	3.803073	14.232517	7.816711
H	2.765844	14.282903	12.502153	O	1.515331	13.121089	6.638323
C	4.645627	13.618693	11.724263	O	0.20822	11.009341	8.024458
H	5.308565	14.321507	12.25446				

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B	7.448905	16.921303	3.114043	H	3.390672	9.941922	4.084999
B	8.832257	16.879134	2.110711	C	5.148775	9.128434	3.063342
B	7.057282	16.776013	0.734995	H	4.922137	8.503388	2.197968
B	5.951506	15.974022	1.752111	H	5.331375	10.161244	2.717424
C	6.311314	14.783324	4.037805	O	9.682977	8.973352	-0.175713
C	5.553051	13.612007	3.788069	C	10.115034	10.25628	-0.633801
H	5.127622	13.475649	2.797744	H	9.228894	10.843417	-0.877244
C	5.348629	12.666964	4.780379	H	10.730399	10.128887	-1.536586
H	4.739267	11.793452	4.553985	C	10.949241	10.820498	0.526757
C	5.904248	12.818185	6.056748	H	10.327177	11.443205	1.176889
H	5.727736	12.081753	6.83578	H	11.768936	11.446023	0.170652
C	6.671671	13.956091	6.31071	C	11.436483	9.550508	1.269871
H	7.11332	14.101414	7.293689	H	12.525597	9.484199	1.32723
C	6.881738	14.917591	5.32905	H	11.052226	9.530435	2.296715
H	7.468512	15.807815	5.54243	C	10.831968	8.405491	0.44005
C	7.604805	19.333687	3.743864	H	11.537471	8.072449	-0.336222
H	6.898272	19.906339	3.115919	H	10.504109	7.544815	1.026912
H	8.549442	19.275935	3.200975	C	7.317933	6.804802	0.333242
H	7.760897	19.901713	4.672388	H	8.28682	6.843739	-0.185114
C	5.77438	18.063175	4.599266	H	6.645604	6.134425	-0.225306
H	5.755167	18.777106	5.433468	C	7.500018	6.274425	1.733474
H	5.469213	17.08694	4.982353	H	6.580908	6.436641	2.314767
H	5.02039	18.392801	3.859262	H	7.713218	5.194966	1.6949
C	10.535762	17.780107	3.742904	C	8.780983	6.515659	3.670651
H	9.742608	17.515123	4.446871	H	9.023573	5.441422	3.682829
H	10.75714	18.853648	3.855667	H	7.868774	6.680231	4.262247
H	11.450339	17.2307	4.016826	C	9.925844	7.295057	4.26888
C	11.071308	17.875973	1.394349	H	10.171786	6.877359	5.257294
H	10.663385	17.714161	0.395144	H	10.819182	7.213691	3.628975
H	12.02532	17.329728	1.470779	C	10.467229	9.430718	5.095061
H	11.298513	18.947668	1.505437	H	11.41541	9.48332	4.538758
C	9.179372	15.592377	-0.129839	H	10.667904	8.989942	6.083218
C	8.575061	15.273877	-1.371181	C	9.880897	10.810085	5.262225
H	7.609963	15.718465	-1.603328	H	8.93184	10.746711	5.818345
C	9.183955	14.397351	-2.260072	H	10.574201	11.434467	5.84704
H	8.684561	14.165754	-3.198044	C	9.053067	12.650092	4.087889
C	10.423476	13.821818	-1.973581	H	9.678646	13.316398	4.699339
H	10.903091	13.151651	-2.680441	H	8.069445	12.555365	4.565575
C	11.051718	14.166989	-0.772888	C	8.901681	13.222788	2.708208
H	12.032257	13.757839	-0.538827	H	8.512214	14.247603	2.769926
C	10.451132	15.029734	0.133107	H	9.87233	13.255942	2.19142
H	10.933379	15.258467	1.079297	C	7.666969	12.967847	0.739206
C	7.770641	18.595943	-0.844407	H	8.54124	12.950618	0.070739
H	7.367467	19.154966	-1.699439	H	7.351853	14.011432	0.871628
H	8.56163	17.937933	-1.211471	C	6.530783	12.191528	0.134235
H	8.226474	19.327641	-0.151237	H	5.643394	12.232845	0.784235
C	5.559611	18.659845	0.06052	H	6.275832	12.636768	-0.839026
H	5.830911	19.547474	0.661062	C	5.999059	10.049514	-0.700913
H	4.815954	18.098321	0.628497	H	5.767993	10.474732	-1.689525
H	5.101137	19.016898	-0.873048	H	5.062152	9.99517	-0.123519
C	4.040898	15.703071	0.121304	C	6.585709	8.66988	-0.871506
H	4.850792	15.897953	-0.586551	H	5.905681	8.048907	-1.475307
H	3.255894	16.460957	-0.032003	H	7.557471	8.737232	-1.379548
H	3.592326	14.723241	-0.114564	K	8.256524	9.727991	2.135029
C	3.523798	15.594223	2.471135	N	6.533235	15.717598	3.06856
H	3.943957	15.72765	3.469203	N	8.502316	16.332444	0.79859
H	3.030025	14.608739	2.435349	N	7.098826	18.004739	4.017
H	2.742983	16.356363	2.321468	N	10.117727	17.458868	2.397665
O	6.332816	8.617254	3.669241	N	6.719437	17.834632	-0.202125
C	6.374559	9.216095	4.963234	N	4.556517	15.72847	1.469924
H	6.716227	10.260576	4.877728	O	6.758346	8.096296	0.408919
H	7.094286	8.656976	5.564648	O	8.576621	6.953625	2.346692
C	4.927615	9.1637	5.474695	O	9.530407	8.641417	4.390746

H	4.762988	8.268475	6.079287	O	9.664759	11.363754	3.989861
H	4.68791	10.0339	6.090172	O	8.000503	12.394833	1.990559
C	4.088273	9.10574	4.174283	O	6.944622	10.844584	-0.031145
H	3.507961	8.181018	4.130566				

====**3 (singlet)**====

B	5.425083	15.095552	2.782123	H	12.297829	11.209021	4.391051
B	6.999421	15.740457	4.044703	C	9.891723	12.096768	3.72159
B	8.218787	16.195379	2.967173	H	10.520391	12.793682	4.295404
B	6.279102	16.247827	1.943241	H	9.203242	11.588675	4.411845
C	6.267782	13.251303	4.423104	C	9.116365	12.861365	2.687526
C	5.410726	12.166771	4.021665	H	8.563539	13.680441	3.166719
H	4.735349	12.342189	3.187201	H	9.805857	13.297397	1.949176
C	5.431606	10.95118	4.677434	C	7.432969	12.650452	1.08587
H	4.752174	10.166251	4.339683	H	8.061624	12.98936	0.249303
C	6.285678	10.708882	5.772871	H	6.951751	13.528713	1.537301
H	6.259037	9.766788	6.312325	C	6.381334	11.708126	0.578381
C	7.131755	11.757549	6.177688	H	5.771623	11.32787	1.41089
H	7.807057	11.602029	7.020214	H	5.732953	12.244389	-0.130193
C	7.127094	12.992638	5.54823	C	6.132703	9.727859	-0.670962
H	7.766603	13.806094	5.887694	H	5.51531	10.240497	-1.425433
C	6.997928	17.816561	5.413478	H	5.457308	9.289218	0.082327
H	6.122458	18.350404	4.991346	C	6.938932	8.639475	-1.333055
H	7.861214	18.094966	4.806666	H	6.275398	7.973663	-1.907451
H	7.15348	18.185209	6.440388	H	7.676214	9.087104	-2.014571
C	5.584502	16.061417	6.077361	C	2.512962	11.146322	11.70139
H	5.557109	16.520268	7.082087	H	2.549272	10.696045	12.701451
H	5.48284	14.977804	6.186699	H	2.883355	12.175134	11.776672
H	4.690906	16.430386	5.520849	C	3.274492	10.285327	10.664485
C	10.063579	16.901074	4.544259	H	3.726683	9.414807	11.14658
H	9.453831	16.301187	5.226027	H	4.061327	10.84304	10.152523
H	10.159442	17.916595	4.965979	C	2.174952	9.865734	9.673554
H	11.081842	16.475538	4.505425	H	2.147319	10.563492	8.828731
C	10.115324	17.775617	2.297937	H	2.309084	8.854302	9.283217
H	9.570818	17.782112	1.351346	C	0.908653	10.033267	10.503612
H	11.153559	17.45857	2.098367	H	0.008439	10.201036	9.908632
H	10.160098	18.810605	2.677297	H	0.755267	9.178847	11.180258
C	8.278177	15.624454	0.416813	C	2.396596	16.448004	8.495821
C	7.45061	15.471933	-0.730445	H	3.151754	15.649801	8.494709
H	6.403433	15.750752	-0.640881	H	2.802866	17.298888	9.051467
C	7.959775	14.967111	-1.917909	C	1.949086	16.802509	7.080336
H	7.292397	14.854515	-2.77031	H	2.74956	16.67913	6.347143
C	9.307495	14.615236	-2.045002	H	1.595591	17.837939	7.037325
H	9.701248	14.246382	-2.987935	C	0.780566	15.836203	6.875862
C	10.143478	14.80592	-0.937875	H	0.099354	16.14156	6.077969
H	11.205317	14.572769	-1.01258	H	1.154288	14.828856	6.64772
C	9.654431	15.302578	0.260616	C	0.135803	15.864583	8.256989
H	10.313113	15.425845	1.116114	H	-0.524568	16.734842	8.373028
C	6.585484	18.491948	0.839943	H	-0.438086	14.964073	8.50842
H	6.017469	19.268693	0.306346	C	-0.73815	14.051448	12.199894
H	7.295423	18.051119	0.1348	H	-0.399952	13.160305	12.748733
H	7.168	19.0014	1.636284	H	-1.702656	14.381644	12.614683
C	4.639966	18.123388	2.134427	C	0.283236	15.152088	12.344822
H	5.050782	18.811249	2.901338	H	0.079463	15.949311	11.614953
H	4.052108	17.373221	2.666569	H	0.227959	15.574337	13.359979
H	3.967561	18.712881	1.48991	C	2.578431	15.58471	12.199586
C	3.146519	15.260891	1.662714	H	2.553174	16.080918	13.182075
H	3.789139	15.638287	0.863022	H	2.431556	16.340329	11.414676
H	2.416318	16.052063	1.914083	C	3.908347	14.896649	12.013829
H	2.564126	14.40161	1.282132	H	4.72649	15.617918	12.156622
C	3.196059	14.524582	3.940028	H	4.019162	14.092443	12.75861

H	3.868507	14.187664	4.732195	C	5.122673	13.659125	10.404964
H	2.475595	13.710193	3.724794	H	5.117901	12.687079	10.922686
H	2.600489	15.376026	4.336953	H	6.00515	14.223068	10.739772
O	8.20775	7.680099	3.028157	C	5.184645	13.492742	8.906833
C	8.575455	8.032331	4.359164	H	5.21803	14.487774	8.441001
H	8.492346	9.124153	4.493691	H	6.091788	12.952964	8.60418
H	9.610786	7.721356	4.51294	C	3.875864	12.940732	7.062019
C	7.541926	7.315443	5.228284	H	4.828283	12.768039	6.550545
H	7.854342	6.282028	5.405213	H	3.541145	13.967854	6.842101
H	7.406663	7.806468	6.193932	C	2.857632	11.963774	6.552463
C	6.270592	7.357272	4.348165	H	2.818819	12.035809	5.45812
H	5.813733	6.367936	4.266212	H	3.14033	10.937551	6.83051
H	5.524309	8.045854	4.74997	C	0.543206	11.495133	6.648635
C	6.791945	7.854393	2.983702	H	0.658024	10.463078	7.017926
H	6.420993	7.301067	2.11829	H	0.534029	11.470062	5.549043
H	6.558977	8.923831	2.853515	C	-0.756067	12.081186	7.147415
O	9.995555	9.822581	-1.168174	H	-0.890972	13.097524	6.746104
C	9.934585	11.242644	-1.346468	H	-1.597212	11.458163	6.808754
H	10.081298	11.756903	-0.380361	C	-1.950692	12.494178	9.129082
H	8.941917	11.498322	-1.71808	H	-2.706877	11.718919	8.933883
C	11.086502	11.534661	-2.302673	H	-2.304826	13.440023	8.691159
H	11.420926	12.570812	-2.241768	C	-1.765912	12.66824	10.616849
H	10.769668	11.334073	-3.33022	H	-2.744444	12.875716	11.077515
C	12.162424	10.5219	-1.858054	H	-1.354585	11.753274	11.067061
H	12.648396	10.044651	-2.712045	K	9.134909	9.562614	1.366108
H	12.940425	11.00405	-1.260208	K	1.596343	13.357574	9.626776
C	11.371319	9.5043	-1.00533	N	6.275856	14.420602	3.786198
H	11.508065	8.460238	-1.297831	N	7.744212	15.988874	1.60266
H	11.648897	9.593856	0.060175	N	6.809451	16.380679	5.397818
C	8.393658	6.874437	-0.872061	N	9.450002	16.91081	3.240956
H	9.123687	7.290925	-1.582147	N	5.688912	17.490128	1.369444
H	7.75495	6.152905	-1.406656	N	3.961453	14.885652	2.787512
C	9.121999	6.171578	0.24611	O	7.606515	7.905208	-0.326338
H	8.428157	5.963755	1.074363	O	10.170745	7.001373	0.694844
H	9.531327	5.217794	-0.122983	O	11.402051	8.481551	2.730653
C	10.89959	6.401581	1.739223	O	10.714518	11.132972	3.063747
H	11.339532	5.449979	1.40018	O	8.229543	11.964565	2.043209
H	10.236447	6.201361	2.593551	O	7.029514	10.621479	-0.072907
C	11.999486	7.346347	2.152928	O	1.153666	11.215016	11.26101
H	12.662696	6.850153	2.878763	O	1.223893	15.966565	9.182859
H	12.599483	7.630082	1.274041	O	-0.885097	13.747687	10.827965
C	12.341339	9.429093	3.192347	O	1.564834	14.605298	12.119345
H	12.877529	9.879189	2.342701	O	3.937038	14.36959	10.708935
H	13.077194	8.946999	3.85422	O	4.030274	12.794422	8.471984
C	11.586679	10.491446	3.952492	O	1.594131	12.3015	7.117701
H	11.025479	10.020626	4.776263	O	-0.712665	12.126526	8.560283

====3 (triplet)=====

B	5.983297	16.10112	1.805366	H	10.114383	11.595133	6.102465
B	7.62455	17.089712	2.957051	C	9.147075	12.772154	4.032552
B	8.909906	16.918137	1.845396	H	9.92899	13.399588	4.485983
B	7.013936	16.797238	0.643827	H	8.210469	12.934775	4.571239
C	6.537317	15.049156	4.120109	C	8.964225	13.148184	2.588614
C	5.772642	13.860355	4.007805	H	8.748395	14.225612	2.518808
H	5.279021	13.651984	3.061223	H	9.876477	12.942892	2.00524
C	5.688635	12.965727	5.063885	C	7.44424	12.921732	0.825281
H	5.098158	12.05634	4.955891	H	8.27687	12.953412	0.108879
C	6.34602	13.198525	6.275841	H	7.06219	13.944363	0.958543
H	6.24534	12.486613	7.093375	C	6.365904	12.024021	0.27991
C	7.124951	14.350454	6.390415	H	5.49308	11.990003	0.951584
H	7.674159	14.541001	7.312155	H	6.044844	12.41344	-0.696941

C	7.221755	15.264282	5.344133	C	6.205041	9.874359	-0.714446
H	7.827907	16.162081	5.442001	H	6.130275	10.311446	-1.72162
C	7.908781	19.531632	3.389533	H	5.18458	9.702764	-0.335349
H	7.173063	20.066577	2.76101	C	6.957545	8.567659	-0.779423
H	8.812278	19.400438	2.791727	H	6.472388	7.891902	-1.501403
H	8.141581	20.173414	4.251557	H	7.993094	8.751625	-1.097967
C	6.129242	18.392409	4.497513	C	4.266203	9.377486	10.418627
H	6.206268	19.15634	5.283083	H	4.058598	9.177857	11.476197
H	5.826242	17.45157	4.964656	H	4.759011	10.357205	10.337202
H	5.325349	18.705459	3.803735	C	5.109203	8.298629	9.739598
C	10.784559	17.847644	3.258473	H	4.956017	7.321054	10.207984
H	10.041465	17.67974	4.04218	H	6.177169	8.543898	9.77496
H	11.070516	18.911765	3.270389	C	4.55198	8.320052	8.315618
H	11.689293	17.267183	3.499059	H	4.984562	9.173244	7.772351
C	11.123042	17.742951	0.87393	H	4.735985	7.398573	7.75266
H	10.625008	17.530253	-0.073513	C	3.074443	8.581118	8.564396
H	12.050885	17.149879	0.916194	H	2.572896	9.098399	7.734266
H	11.413588	18.80498	0.88141	H	2.534653	7.646493	8.783897
C	9.001795	15.469164	-0.320534	C	1.523243	15.350334	10.229287
C	8.286065	15.115106	-1.490456	H	2.193238	15.33251	9.362197
H	7.323041	15.587736	-1.668633	H	2.082757	15.713055	11.095783
C	8.787517	14.172754	-2.379474	C	0.257342	16.138528	9.916841
H	8.206512	13.918381	-3.262885	H	0.45671	17.040889	9.333556
C	10.022242	13.559275	-2.16214	H	-0.258265	16.424092	10.840477
H	10.418468	12.837944	-2.870022	C	-0.54738	15.082505	9.157192
C	10.754317	13.925177	-1.028497	H	-1.620001	15.288059	9.115804
H	11.730598	13.478627	-0.851843	H	-0.163171	14.985672	8.135288
C	10.262999	14.856484	-0.123547	C	-0.218507	13.816875	9.949731
H	10.826075	15.10605	0.77188	H	-0.92668	13.651425	10.77299
C	7.623832	18.484308	-1.119343	H	-0.19863	12.919037	9.328463
H	7.161414	18.974064	-1.987	C	0.960998	10.387804	11.836237
H	8.378619	17.785021	-1.48579	H	1.689896	9.582478	11.678107
H	8.137628	19.266675	-0.529462	H	0.131965	10.005836	12.454155
C	5.498905	18.663704	-0.041448	C	1.611746	11.549963	12.543127
H	5.832202	19.589069	0.463709	H	0.937832	12.419091	12.520395
H	4.79807	18.16181	0.62813	H	1.804767	11.276304	13.593049
H	4.967506	18.95859	-0.958128	C	3.462648	12.957155	12.533436
C	3.941907	15.753224	0.355337	H	3.763446	12.672672	13.554469
H	4.690262	15.911325	-0.425337	H	2.771321	13.811264	12.593606
H	3.138225	16.495435	0.222523	C	4.679342	13.361489	11.737633
H	3.488509	14.757511	0.214954	H	5.292901	14.056527	12.333232
C	3.624581	15.766984	2.741454	H	5.290678	12.475623	11.50271
H	4.126448	15.970933	3.690228	C	5.300491	14.411325	9.72457
H	3.160592	14.766821	2.804992	H	5.839818	13.537045	9.326273
H	2.810348	16.498609	2.616469	H	6.006958	15.038525	10.291392
O	5.902192	8.488246	3.551097	C	4.706882	15.210127	8.591278
C	5.619004	8.925315	4.885203	H	4.179897	16.093556	8.988413
H	6.052308	9.921863	5.06315	H	5.503458	15.551528	7.917428
H	6.091922	8.223576	5.578273	C	3.327248	14.95385	6.712082
C	4.100672	8.967858	4.969463	H	4.170591	15.288612	6.086245
H	3.698672	7.962304	5.139511	H	2.685652	15.821177	6.94461
H	3.748413	9.635753	5.764833	C	2.564684	13.910615	5.938714
C	3.734181	9.483795	3.574358	H	2.203458	14.351806	4.996581
H	2.738659	9.172526	3.248248	H	3.242699	13.080949	5.702164
H	3.762415	10.580218	3.568318	C	0.80881	12.404263	5.967806
C	4.846717	8.912572	2.681113	H	1.522319	11.600149	5.718567
H	4.526768	8.041924	2.098891	H	0.400013	12.81379	5.030201
H	5.234088	9.660352	1.97508	C	-0.313707	11.821005	6.78681
O	9.890559	9.196824	0.519391	H	-0.976505	12.620843	7.156488
C	10.22092	10.544446	0.127468	H	-0.908982	11.148276	6.149912
H	9.486548	11.219386	0.579009	C	-0.751788	10.431099	8.621255
H	10.137815	10.63785	-0.959686	H	-1.234591	9.652807	8.010283
C	11.633014	10.814544	0.656669	H	-1.527209	11.141351	8.951019
H	11.760588	11.854235	0.965787	C	-0.096425	9.807271	9.829417
H	12.385361	10.588361	-0.106763	H	-0.86226	9.266692	10.409408

C	11.735704	9.820513	1.817142	H	0.682913	9.096031	9.526663
H	12.764672	9.584241	2.099855	K	8.038575	9.711959	2.459746
H	11.206121	10.215334	2.693599	K	2.609873	12.156599	9.106059
C	10.986623	8.627845	1.236191	N	6.668467	15.924027	3.080567
H	11.629586	8.06087	0.545983	N	8.441195	16.299658	0.609662
H	10.5738	7.938149	1.978416	N	7.395525	18.245435	3.812654
C	7.62331	6.754399	0.53837	N	10.237619	17.456429	1.979776
H	8.669012	6.885423	0.22183	N	6.619613	17.797084	-0.335401
H	7.134926	6.042349	-0.145949	N	4.565574	15.864715	1.65286
C	7.573014	6.21059	1.944888	O	6.949271	7.991288	0.509847
H	6.550628	6.30127	2.339227	O	8.463966	6.948646	2.753607
H	7.862705	5.148137	1.942896	O	9.045614	8.717934	4.826525
C	8.393578	6.553391	4.104654	O	9.513595	11.397209	4.131005
H	8.632438	5.482245	4.202862	O	7.885509	12.393711	2.062886
H	7.379366	6.724735	4.488868	O	6.921095	10.726221	0.14191
C	9.39727	7.356827	4.894264	O	3.023883	9.440143	9.70504
H	9.39923	7.012516	5.940003	O	1.086989	14.015618	10.504225
H	10.407158	7.204317	4.480471	O	0.46539	10.843205	10.597942
C	9.937897	9.538076	5.553701	O	2.824668	11.870986	11.899402
H	10.952807	9.448873	5.135042	O	4.238815	13.989386	10.557749
H	9.966546	9.223697	6.60791	O	3.807321	14.374092	7.901893
C	9.464197	10.966663	5.474116	O	1.466656	13.418798	6.694882
H	8.438078	11.048065	5.865012	O	0.233467	11.103681	7.870815

4.6 References

- 1 K. Abersfelder, A. J. P. White, H. S. Rzepa, D. Scheschkewitz. A Tricyclic Aromatic Isomer of Hexasilabenzene. *Science* **327**, 564-566 (2010). doi:10.1126/science.1181771.
- 2 K. Leszczyńska, K. Abersfelder, M. Majumdar, B. Neumann, H.-G. Stammler, H. S. Rzepa, P. Jutzi, D. Scheschkewitz. The Cp*Si⁺ cation as a stoichiometric source of silicon. *Chem. Commun.* **48**, 7820-7822 (2012). doi:10.1039/C2CC33911K.
- 3 K. Abersfelder, A. J. P. White, R. J. F. Berger, H. S. Rzepa, D. Scheschkewitz. A Stable Derivative of the Global Minimum on the Si₆H₆ Potential Energy Surface. *Angew. Chem. Int. Ed.* **50**, 7936-7939 (2011). doi:10.1002/anie.201102623.
- 4 D. Kratzert, D. Leusser, J. J. Holstein, B. Dittrich, K. Abersfelder, D. Scheschkewitz, D. Stalke. An Experimental Charge Density Study of Two Isomers of Hexasilabenzene. *Angew. Chem. Int. Ed.* **52**, 4478-4482 (2013). doi:10.1002/anie.201209906.
- 5 K. Abersfelder, A. Russell, H. S. Rzepa, A. J. P. White, P. R. Haycock, D. Scheschkewitz. Contraction and Expansion of the Silicon Scaffold of Stable Si₆R₆ Isomers. *J. Am. Chem. Soc.* **134**, 16008-16016 (2012). doi:10.1021/ja307344f.
- 6 Y. Heider, D. Scheschkewitz. Stable unsaturated silicon clusters (siliconoids). *Dalton Trans.* **47**, 7104-7112 (2018). doi:10.1039/C8DT01009A.
- 7 A. Rammo, D. Scheschkewitz. Functional Disilenes in Synthesis. *Chem. Eur. J.* **24**, 6866-6885 (2018). doi:10.1002/chem.201704090.
- 8 Y. Heider, N. E. Poitiers, P. Willmes, K. I. Leszczyńska, V. Huch, D. Scheschkewitz. Site-selective functionalization of Si₆R₆ siliconoids. *Chem. Sci.* **10**, 4523-4530 (2019). doi:1.

- 9 Y. Heider, P. Willmes, V. Huch, M. Zimmer, D. Scheschkewitz. Boron and Phosphorus Containing Heterosiliconoids: Stable p- and n-Doped Unsaturated Silicon Clusters. *J. Am. Chem. Soc.* **141**, 19498-19504 (2019). doi:10.1021/jacs.9b11181.
- 10 L. Klemmer, V. Huch, A. Jana, D. Scheschkewitz. An anionic heterosiliconoid with two germanium vertices. *Chem. Commun.* **55**, 10100-10103 (2019). doi:10.1039/C9CC04576G.
- 11 C. P. Sindlinger, L. Wesemann. Hydrogen abstraction from organotin di- and trihydrides by N-heterocyclic carbenes: a new method for the preparation of NHC adducts to tin(II) species and observation of an isomer of a hexastannabenzene derivative [R₆Sn₆]. *Chem. Sci.* **5**, 2739-2746 (2014). doi:10.1039/c4sc00365a.
- 12 A. Jana, V. Huch, M. Repisky, R. J. F. Berger, D. Scheschkewitz. Disputational and Global- Minimum Isomers of Heavier 1,4-Dimetallatetrasilabenzenes of Group 14. *Angew. Chem. Int. Ed.* **53**, 3514-3518 (2014). doi:10.1002/anie.201310475.
- 13 Y. Heider, P. Willmes, D. Mühlhausen, L. Klemmer, M. Zimmer, V. Huch, D. Scheschkewitz. A Three-Membered Cyclic Phosphasilene. *Angew. Chem. Int. Ed.* **58**, 1939-1944 (2019). doi:10.1002/anie.201811944.
- 14 W. P. Oziminski, T. M. Krygowski. Natural bond orbital (NBO) analysis of the angular group induced bond alternation (AGIBA) substituent effect. *J. Phys. Org. Chem.* **23**, 551-556 (2010). doi:10.1002/poc.1647.
- 15 K. Hofmann, M. H. Prosenc, B. R. Albert. A new 4c–2e bond in B₆H₇[–]. *Chem. Commun.*, 3097-3099 (2007). doi:10.1039/B704944G.
- 16 J. S. Miller, J. J. Novoa. Four-Center Carbon–Carbon Bonding. *Acc. Chem. Res.* **40**, 189-196 (2007). doi:10.1021/ar068175m.
- 17 A. Nova, H.-W. Suh, T. J. Schmeier, L. M. Guard, O. Eisenstein, N. Hazari, F. Maseras. An Unusual Example of Hypervalent Silicon: A Five-Coordinate Silyl Group Bridging

- Two Palladium or Nickel Centers through a Nonsymmetrical Four-Center Two-Electron Bond. *Angew. Chem. Int. Ed.* **53**, 1103-1108 (2014). doi: 10.1002/anie.201307618.
- 18 Y. Canac, D. Bourissou, A. Baceiredo, H. Gornitzka, W. W. Schoeller, G. Bertrand. Isolation of a Benzene Valence Isomer with One-Electron Phosphorus-Phosphorus Bonds. *Science* **279**, 2080 (1998). doi:10.1126/science.279.5359.2080.
- 19 S. Brownridge, I. Krossing, J. Passmore, H. D. B. Jenkins, H. K. Roobottom. Recent advances in the understanding of the syntheses, structures, bonding and energetics of the homopolyatomic cations of Groups 16 and 17. *Coord. Chem. Rev.* **197**, 397-481 (2000). doi: 10.1016/S0010-8545(00)00230-7.
- 20 T. Kato, H. Gornitzka, W. W. Schoeller, A. Baceiredo, G. Bertrand. Dimerization of a Cyclo-1 σ 4,3 σ 2,4 σ 2-Triphosphapentadienyl Radical: Evidence for Phosphorus–Phosphorus Odd-Electron Bonds. *Angew. Chem. Int. Ed.* **44**, 5497-5500 (2005). doi: 10.1002/anie.200501369.
- 21 R. Gleiter, G. Haberhauer. Electron-rich two-, three- and four-center bonds between chalcogens – New prospects for old molecules. *Coord. Chem. Rev.* **344**, 263-298 (2017). doi: 10.1016/j.ccr.2017.03.003.
- 22 H. Klusik, A. Berndt. A Boron-Boron One-Electron π -Bond. *Angew. Chem. Int. Ed.* **20**, 870-871 (1981). doi: 10.1002/anie.198108701.
- 23 W. J. Grigsby, P. P. Power. Comparison of B–B π -bonding in singly reduced and neutral diborane (4) derivatives: isolation and structure of [$\text{Li}(\text{Et}_2\text{O})_2$]{ $\text{MeO}(\text{mes})\text{BB}(\text{mes})\text{OMe}$ }. *Chem. Commun.*, 2235-2236 (1996). doi:10.1039/CC9960002235.

- 24 W. J. Grigsby, P. Power. One-Electron Reductions of Organodiborane(4) Compounds: Singly Reduced Anions and Rearrangement Reactions. *Chem. Eur. J.* **3**, 368-375 (1997). doi: 10.1002/chem.19970030308.
- 25 H. Asakawa, K.-H. Lee, K. Furukawa, Z. Lin, M. Yamashita. Lowering the Reduction Potential of a Boron Compound by Means of the Substituent Effect of the Boryl Group: One-Electron Reduction of an Unsymmetrical Diborane(4). *Chem. Eur. J.* **21**, 4267-4271 (2015). doi: 10.1002/chem.201406609.
- 26 Y. Su, R. Kinjo. Boron-containing radical species. *Coord. Chem. Rev.* **352**, 346-378 (2017). doi:10.1016/j.ccr.2017.09.019.
- 27 B. Bleaney, K. D. Bowers. Anomalous paramagnetism of copper acetate. *Proc. R. Soc. A* **214**, 451-465 (1952). doi:10.1098/rspa.1952.0181.
- 28 Z.-J. Li, F.-F. Wang, Z.-R. Li, H.-L. Xu, X.-R. Huang, D. Wu, W. Chen, G.-T. Yu, F. L. Gu, Y. Aoki. Large static first and second hyperpolarizabilities dominated by excess electron transition for radical ion pair salts $M_2^+ + TCNQ^-$ ($M = Li, Na, K$). *Phys. Chem. Chem. Phys.* **11**, 402-408 (2009). doi:10.1039/B809161G.
- 29 M. Abe. Diradicals. *Chem. Rev.* **113**, 7011-7088 (2013). doi:10.1021/cr400056a.
- 30 T. Kubo. Recent Progress in Quinoidal Singlet Biradical Molecules. *Chem. Lett.* **44**, 111-122 (2014). doi:10.1246/cl.140997.
- 31 M. Nakano. *Excitation Energies and Properties of Open-Shell Singlet Molecules: Applications to a New Class of Molecules for Nonlinear Optics and Singlet Fission*. (Springer, 2014).
- 32 Z. Sun, Z. Zeng, J. Wu. Zethrenes, Extended p-Quinodimethanes, and Periacenes with a Singlet Biradical Ground State. *Acc. Chem. Res.* **47**, 2582-2591 (2014). doi:10.1021/ar5001692.

- 33 A. Kostenko, B. Tumanskii, M. Karni, S. Inoue, M. Ichinohe, A. Sekiguchi, Y. Apeloig. Observation of a Thermally Accessible Triplet State Resulting from Rotation around a Main-Group π Bond. *Angew. Chem. Int. Ed.* **54**, 12144-12148 (2015). doi:10.1002/anie.201506291.
- 34 Z. Zeng, X. Shi, C. Chi, J. T. López Navarrete, J. Casado, J. Wu. Pro-aromatic and anti-aromatic π -conjugated molecules: an irresistible wish to be diradicals. *Chem. Soc. Rev.* **44**, 6578-6596 (2015). doi:10.1039/C5CS00051C.
- 35 G. E. Rudebusch, J. L. Zafra, K. Jorner, K. Fukuda, J. L. Marshall, I. Arrechea-Marcos, G. L. Espejo, R. Ponce Ortiz, C. J. Gómez-García, L. N. Zakharov, M. Nakano, H. Ottosson, J. Casado, M. M. Haley. Diindeno-fusion of an anthracene as a design strategy for stable organic biradicals. *Nat. Chem.* **8**, 753-759 (2016). doi:10.1038/nchem.2518.
- 36 Y. Su, X. Wang, L. Wang, Z. Zhang, X. Wang, Y. Song, P. P. Power. Thermally controlling the singlet–triplet energy gap of a diradical in the solid state. *Chem. Sci.* **7**, 6514-6518 (2016). doi:10.1039/C6SC01825D.
- 37 C. Wentrup, M. J. Regimbald-Krnel, D. Müller, P. Comba. A Thermally Populated, Perpendicularly Twisted Alkene Triplet Diradical. *Angew. Chem. Int. Ed.* **55**, 14600-14605 (2016). doi:10.1002/anie.201607415.
- 38 A. Kostenko, B. Tumanskii, Y. Kobayashi, M. Nakamoto, A. Sekiguchi, Y. Apeloig. Spectroscopic Observation of the Triplet Diradical State of a Cyclobutadiene. *Angew. Chem. Int. Ed.* **56**, 10183-10187 (2017). doi:10.1002/anie.201705228.
- 39 T. Y. Gopalakrishna, W. Zeng, X. Lu, J. Wu. From open-shell singlet diradicaloids to polyradicaloids. *Chem. Commun.* **54**, 2186-2199 (2018). doi:10.1039/C7CC09949E.

- 40 H. Braunschweig, Q. Ye, A. Vargas, R. D. Dewhurst, K. Radacki, A. Damme. Controlled homocatenation of boron on a transition metal. *Nat. Chem.* **4**, 563-567 (2012). doi:10.1038/nchem.1379.
- 41 H. Braunschweig, R. D. Dewhurst, S. Mozo. Building Electron-Precise Boron–Boron Single Bonds: Imposing Monogamy on a Promiscuous Element. *ChemCatChem* **7**, 1630-1638 (2015). doi: 10.1002/cctc.201500219.
- 42 M. Arrowsmith, H. Braunschweig, T. E. Stennett. Formation and Reactivity of Electron-Precise B–B Single and Multiple Bonds. *Angew. Chem. Int. Ed.* **56**, 96-115 (2017). doi: 10.1002/anie.201610072.

Chapter 5: Evaluation of the aromaticity of B₄N₂ benzene analogues by theoretical calculations

5.1 Introduction

Since the discovery of the cyclic feature of benzene (CH)₆ **1** in 1865, “aromaticity” has represented one of the most significant fundamental concepts in modern chemistry arsenal.¹⁻³ Nowadays, its implication is not limited to the molecules obeying the $[4n + 2]$ Hückel rule, but extended to those satisfying various criteria—structural, electronic, magnetic and energetic indices can be employed to assess the aromatic nature of a molecule comprehensively. It is well known that benzene **1**, an archetypal aromatic molecule, displays the planar geometry, cyclic delocalization of 6 π electrons, peculiar magnetic property and extra thermodynamic stability.^{4,5}

Synthetically, incorporation of isolobal heteroatom units into the benzene scaffold is one of the useful strategies to modify the intrinsic electronic property of aromaticity without significant change of the geometric feature. Indeed, a variety of inorganic benzenes have been developed thus far,⁶ most of which are mainly based on the (XY)₃ system, such as borazine (HBNH)₃ **2**, boroxines (RBO)₃ and phosphazenes (R₂PN)₃.⁷⁻¹⁰ The six-membered ring aromatics based on heavier elements have little been described.¹¹⁻¹⁵

Theoretically, the aromaticity of inorganic benzenes has been evaluated using computational methods such as nucleus-independent chemical shift (NICS), aromatic stabilization energies (ASE) and electron localization function (ELF) analyses.¹⁶⁻²⁶ In 1991, Fink and Richards reported the calculated ASE values of the (XY)₃ ring systems (X = BR, AlR; Y = NR, PR),¹⁶ and revealed that the ASE values increase in order AlN < BN < BP < CC. In 1997, the group of Schleyer estimated the NICS values of the (XY)₃ rings (X = BH, AlH, CH; Y = NH, PH, O, S), as well as, the E₆ rings (E = SiH, GeH, N, P).¹⁷ The NICS values of the

(XY)₃ systems are found to be less negative than that of benzene whereas the E₆ systems are comparable to benzene. In 1998, Jemmis et al. systematically evaluated the aromaticity of the (XY)₃ molecules (X = BH, AlH, GaH, PH₂; Y = NH, PH, AsH, N, O, S, Se) using ASE, magnetic susceptibility exaltation (MSE), and NICS analyses. As a result, they concluded that judicious use of all criteria is needed in gauging aromaticity of those systems.¹⁸ In 2005, Jenneskens and coworkers reported the electronic structure of the (XY)₃ (X = BH, AlH; Y = NH, PH, O, S) and E₆ (E = SiH, GeH, N, P) systems by using Valence bond (VB) theory and ring-current maps. The authors unveiled that in general, the heteronuclear systems (XY)₃ show localization of the lone pair of electrons on the electronegative atoms, and Kekulé-like structures do not contribute.¹⁹ In 2010, Phukan and Silvi et al. calculated the NICS, ASE, and ELF values for the substituted (XY)₃ systems (X = BR, AlR; Y = NH, PH, AsH, O, S, Se). The results clarified the substituent effect—the bulky electronegative substituents (R) on B or Al atoms dramatically increases the stability and aromaticity.²⁰ Recently, Alvarez-Thon and Tiznado examined the (XYH)₃ systems (X = C–Pb, Y = N–Bi) by magnetically induced current density (MICD) and the zz component of NICS, and revealed that most of them are aromatic except for (XNH)₃ (X = Si–Pb).²¹

The extant theoretical study on the aromaticity of inorganic benzenes mainly focuses on the above-mentioned (XY)₃ and E₆ systems, because those types of analogues have been isolated to date. Recently, we have reported the synthesis of a neutral B₄N₂-based benzene analogue, namely 1,4-diaza-2,3,5,6-tetraborinine derivative **3**,²⁷ being the first examples of the Lewis base-stabilized X₄Y₂ system.⁶ Preliminary theoretical investigations including NICS, natural bond orbital (NBO), and anisotropy of the current-induced density (ACID) analysis suggested the pronounced aromatic nature of **3** (Scheme 5.1.1). By contrast, the dianionic B₄N₂ ring system **4**: [(Ph-N)₂(Me₂N-B)₄]²⁻ is found to furnish a non-aromatic twisted structure despite its 6π-electron configuration isoelectronic with **3**.²⁸

Scheme 5.1.1. The list of the molecules discussed in this article (Mes = 2,4,6-Me₃C₆H₂).

5.2 Objectives

With the isolable neutral and dianionic B₄N₂ derivatives in hand, we wondered (i) how the aromatic nature of the B₄N₂ ring systems differs from the reported (XY)₃ systems, and (ii) whether the charge of molecules affects the aromaticity or not. Here, we have investigated the aromaticity of 1,4-diaza-2,3,5,6-tetraborinine derivatives, B₄N₂ analogues of benzene, by using modern computational aromaticity descriptors involving structure, molecular orbital, electron density, magnetic shielding, and energetics.²⁹ For purpose of comparison, reference molecules—benzene (CH)₆ **1**, and borazine (HBNH)₃ **2** have also been examined (Scheme 5.1.1). The substituent effect on the aromaticity in benzene as well as in borazine has been reported.^{30–36} According to those prior studies, while the aromaticity of benzene resists substituent influences, that of borazine is significantly affected by the nature of substituents. In borazine, generally the electron-donating group (EDG) on B decreases the aromaticity, although electron-withdrawing group (EWG) on B and both EDG and EWG on N lead to the

pronounced aromaticity. Therefore, we employed model compound **3'**, and a dianionic $B_4N_2H_6$ derivative **4'** (Scheme 5.1.1). To evaluate the aromatic nature, five criteria including the harmonic oscillator model of aromaticity (HOMA), ELF, *para*-delocalization index (PDI), NICS, and ASE have been assessed.¹⁶⁻²⁰ Moreover, we have carried out ACID analysis to visualize the ring current.

5.3 Results and Discussions

Figure 5.3.1 displays the optimized structures and selected bond lengths of benzene (**1**), borazine (**2**), and three B_4N_2 systems (**3**, **3'**, and **4'**). All molecular geometries were fully optimized as closed-shell species and characterized as energy minima by the absence of imaginary vibrational frequencies. The central six-membered ring in compounds **1**, **2**, **3** and **3'** exhibits a planar geometry. Notably, dianionic **4'** also bears a planar B_4N_2 ring, which is in stark contrast to the twisted ring framework experimentally observed for **4**, implying the impact of substituents at the B and N atoms on the skeletal geometry.^{30,32-36} The selected π -type molecular orbitals (π -MOs) of **3'** and **4'** are summarized in Figure 5.3.2. Three explicit π -MOs are seen in **3'** and **4'**, which are similar to those of benzene **1** and borazine **2**. While **1** and **2** have two degenerated highest occupied molecular orbitals (HOMOs), the B_4N_2 systems (**3**, **3'**, **4'**) possess non-degenerate π -MOs.²⁷ In the π -MOs of **3**, some contributions from 3p-orbitals of the substituents (Cl and PMe_3) are found. To assess the essential nature of the six-membered skeleton without consideration of the significant electronic perturbation from the substituent, **3** is omitted from NICS π and ELF π calculation (*vide infra*).

Figure 5.3.1. Optimized structures and selected bond lengths (in Å) of **1**, **2**, **3**, **3'** and **4'**.

Firstly, a structural criterion is evaluated using the HOMA index, which is based on the equalization of the bond lengths and symmetry.³⁷⁻³⁹ The calculated HOMA values, resonance energy (EN), and bond length alternation (GEO) are summarized in Table 5.3.1 (for the details of bond number, see Table 5.5.2).^{40,41} It should be noted that the HOMA index reflects only the geometrical features and does not consider the polarization effect on electronic distribution. Besides, HOMA values may depend on the choice of reference bond lengths and normalization constant. The reported constants of B-B and B-N bond are calculated in different way.^{42,43}

The HOMA values increase in the order **4'** < **3'** < **3** < **1** $\approx$ **2**, from 0.288 for **4'** up to 1.000 for **2**. There is little bond alternation in **1** and **2**, in line with their essential D_{6h} and D_{3h} symmetries. For the B_4N_2 systems (**3**, **3'**, **4'**), both EN and GEO values are larger than those for benzene **1** and borazine **2**. Particular diagnostic is that the HOMA value of **4'** is mainly dominated by EN term (0.428) rather than GEO term (0.284), indicating elongation of the skeletal bonds. The bond numbers of **3** [1.143 (B-B), 1.444-1.513 (B-N)], and **3'** [1.101 (B-B), 1.504-1.561 (B-N)] indicate partial bond alternation in **3** and **3'**, which results in the large GEO values. The average bond numbers of **3** [1.367] and **3'** [1.388] are smaller than that of benzene

1 [1.533] and borazine **2** [1.582], which leads to the increased EN values of **3** and **3'**. The bond numbers of **4'** show B-B single bond [0.950] and B-N multiple bond [1.437] characters, suggesting that the π electrons are relatively localized on each B-N-B unit. The average of the bond number of **4'** [1.275] is smaller than other systems, in agreement with the relatively large EN value.

Figure 5.3.2. Plots of the π molecular orbitals of **3'** and **4'** (in eV).

Secondly, as an electronic criterion, the ELF and PDI values have been computed.⁴⁴⁻⁴⁹ The calculated average ELF values together with its σ - and π -contributions and PDI values are listed in Table 5.3.1,⁵⁰⁻⁵² and the ELF isosurfaces at the bifurcation points of the σ and π systems are depicted in Figure 5.3.3.⁵² The ELF_{ave} values increase in the order **2** < **3'** < **4'** < **1**, from 0.56 for **2** to 0.81 for **1**, and the ELF_{π} values are found to be larger than the ELF_{σ} values for all molecules. The ELF_{π} values greater than 0.70 indicate that all molecules may have some aromatic character.⁵³ Benzene **1** shows the high ELF_{π} value of 0.91, in line with the pronounced aromatic nature. Borazine **2** presents an ELF_{π} value of 0.72 lower than that of benzene **1**, implying the less aromatic character. In contrast to highly symmetric benzene **1** (D_{6h}) and borazine **2** (D_{3h}), the B_4N_2 systems with the lower symmetry exhibit several distinguishable ELF_{π} values. For the neutral B_4N_2 system **3'**, the separations at the $(\text{H}_3\text{P})\text{B-N}$ bonds, HB-N

bonds, and B-B bonds occur at the ELF_π values of 0.68, 0.82, and 0.94, respectively. The dianionic B_4N_2 system **4'** shows the first separation at the B-N bonds with a relatively high ELF_π value of 0.75 and the B-B bonds are split at a significantly higher ELF_π value of 0.92. The average ELF_π values of 0.81 for **3'** and 0.81 for **4'** are between those of benzene **1** (0.91) and borazine **2** (0.72), indicating moderate delocalization of π -electrons in those B_4N_2 systems.

The ELF_σ values of inorganic benzenes [**2** (0.40), **3'** (0.47), **4'** (0.50)] are much smaller than that of benzene **1** (0.70), reflecting the difference of electronegativity between B and N atoms. The PDI values increase in the order **2** (0.041) < **3** (0.068) < **3'** (0.078) < **1** (0.105) < **4** (0.118), suggesting the moderate aromaticity of **3** and **3'**, which is in agreement with the ELF_π values. However, the PDI value of **4** greater than that of benzene **1**, as inconsistent with those ELF_π values, points out that the PDI measures might not be suitable for the evaluation of the relative aromaticity among the differently charged molecules, as well as, compounds consisting of different skeletal atoms.^{54,55} The calculated ring critical point properties of compounds **1**, **2**, **3**, **3'**, **4'** are summarized in Table 5.5.4.

<p>1</p>	σ	$ELF_{\sigma}(C5-C6) = 0.70$		
	π	$ELF_{\pi} = 0.91$
<p>2</p>	σ	$ELF_{\sigma}(N4-B5) = 0.40$		
	π	$ELF_{\pi} = 0.72$
<p>3'</p>	σ	$ELF_{\sigma}(B2-N3) = 0.46$	$ELF_{\sigma}(B1-N6) = 0.52$	$ELF_{\sigma}(B1-B2) = 0.62$
	π	$ELF_{\pi}(B2-N3) = 0.68$	$ELF_{\pi}(B1-N6) = 0.82$	$ELF_{\pi}(B1-B2) = 0.93$
<p>4'</p>	σ	$ELF_{\sigma}(B1-N6) = 0.49$	$ELF_{\sigma}(B1-B2) = 0.59$	
	π	$ELF_{\pi}(B1-N6) = 0.75$	$ELF_{\pi}(B1-B2) = 0.92$	

Figure 5.3.3. The ELF isosurfaces at the bifurcation points of the σ and π systems of **1**, **2**, **3'**, and **4'**.

Thirdly, as a magnetic criterion, a series of NICS values have been estimated (Table 5.3.2).⁵⁶⁻⁶¹ Isotropic NICS can be represented by the anisotropic components: $\text{NICS} = (\text{NICS}_{xx} + \text{NICS}_{yy} + \text{NICS}_{zz})/3 = \text{NICS}_{\text{in-plane}} + \text{NICS}_{\text{out-of-plane}}$, in which $(\text{NICS}_{xx} + \text{NICS}_{yy})/3 = (\text{NICS}_{\text{in-plane}})$ and $(\text{NICS}_{zz})/3 = \text{NICS}_{\text{out-of-plane}}$. Free of in-plane component NICS (FiPC-NICS) indicates the NICS value at a point above the molecular ring with zero of $\text{NICS}_{\text{in-plane}}$. Figure 5.3.4(a) presents the NICS-profiles of the full- NICS_{zz} and σ - and π -electron contribution to the NICS_{zz} for **3'** and **4'**, from the center of the six-membered ring and above up to 5.00 Å, and Figure 5.3.4(b) shows FiPC-NICS plot, respectively.

While the $\text{NICS}_{zz}(0)$ values of **1** (−14.48), **3** (−3.36), **3'** (−3.75), and **4'** (−5.49) are negative, borazine **2** shows the highly positive $\text{NICS}_{zz}(0)$ values of 11.98, which is due to the significantly positive $\text{NICS}_{\sigma zz}(0)$ contribution.⁵⁹ It has been demonstrated that $\text{NICS}_{\pi zz}$ in addition to $\text{NICS}_{zz}(1)$ could be the most reliable aromaticity indexes, with statistically good correlation with aromatic stabilization energies.^{57,62} The NICS_{zz} values of **3** [$\text{NICS}_{zz}(1) = -12.32$], **3'** [$\text{NICS}_{zz}(1) = -15.18$, $\text{NICS}_{\pi zz}(0) = -19.73$, $\text{NICS}_{\pi zz}(1) = -16.54$] and **4'** [$\text{NICS}_{zz}(1) = -15.42$, $\text{NICS}_{\pi zz}(0) = -20.73$, $\text{NICS}_{\pi zz}(1) = -17.02$] lie in between those of benzene **1** [$\text{NICS}_{zz}(1) = -29.25$, $\text{NICS}_{\pi zz}(0) = -35.78$, $\text{NICS}_{\pi zz}(1) = -29.07$] and borazine **2** [$\text{NICS}_{zz}(1) = -5.17$, $\text{NICS}_{\pi zz}(0) = -7.89$, $\text{NICS}_{\pi zz}(1) = -5.88$].

The NICS_{zz} profiles of **3'** and **4'** (Figure 5.3.4a) confirm that the $\text{NICS}_{\sigma zz}$ values are significantly positive near the ring center [$\text{NICS}_{\sigma zz}(0) = 15.98$ (**3'**), 15.25 (**4'**)], and they decrease as being apart from the ring and become negative around at 1 Å. On the other hand, the $\text{NICS}_{\pi zz}$ values are significantly negative at the molecular center, and gradually become less negative as being away from the ring. The greatly negative $\text{NICS}_{\pi zz}$ contribution over the $\text{NICS}_{\sigma zz}$ component leads to the overall negative NICS_{zz} value. A similar trend of the NICS_{zz} profile is found for benzene.⁵⁹ The FiPC-NICS value corresponds to the interception on the vertical axis ($\text{NICS}_{\text{out-of-plane}}$) in Figure 5.3.4b. The FiPC-NICS values of −4.03 for **3** and −3.85

for **3'**, appear to be between those of benzene **1** (−9.07) and borazine **2** (−2.34), supporting the moderate aromatic character of **3** and **3'**. The shape of FiPC-NICS plots of **3** and **3'** is similar to that of **1** but different from that of **2**. The positive NICS_{out-of-plane} values are observed near the ring center of **2**, which is due to the pronounced σ -contribution but marginal π -contribution in the region.⁵⁹ The significant deviation of the FiPC-NICS plot of **4'** from others can be rationalized by the largely positive NICS_{xx} values, and therefore, the FiPC-NICS value of **4'** could not be gained.

ACID plot of **4'** is shown in Figure 5.3.5 (For the plots of **1**, **2**, **3'**, see Figure 5.5.1). While the clear clockwise current-density vectors are confirmed on the ACID isosurface of benzene **1**, borazine **2** shows the imperceptible ring current consisting of the three localized circulations on the nitrogen atoms, which is consistent with previous studies.²⁴ The clockwise current-density vectors on the ACID isosurface also observed in **3**.²⁷ Despite somehow weak vectors, an explicit diatropic ring current is seen over the B₄N₂ ring of **4'** with the pronounced stopover at the B-H moieties.

Finally, an energetic criterion is evaluated using the ASE method (Table 5.3.3). The ASE values computed by the reactions (a)–(d) (Scheme 5.3.2, Table 5.5.5)^{58,63} decrease in the order **1** (33.4 kcal mol^{−1}) > **3'** (23.8 kcal mol^{−1}) > **4'** (11.0 kcal mol^{−1}) > **2** (10.1 kcal mol^{−1}). Based on the ASE values, it can be estimated that inorganic benzene analogues **2**, **3'**, **4'** present 30%, 71% and 33% of aromaticity in comparison to benzene, respectively. Note that the significantly smaller ASE value of **4'** compared with that of **3'** is not in line with those NICS _{π_{zz} (0)} values [**3'** = −19.73; **4'** = −20.73], indicating that magnetic and energetic criteria are not in good correlation with each other when comparing the differently charged molecules.⁵⁷

Table 5.3.1. Calculated HOMA, bifurcation values of ELF functions and PDI (electrons) values.

	HOMA	EN	GEO	ELF _{ave}	ELF _π	ELF _σ	PDI
1: (CH) ₆	0.990	0.010	0.000	0.81	0.91	0.70	0.105
2: (HBNH) ₃	1.000	0.000	0.000	0.56	0.72	0.40	0.041
3: [(MesN)(BCl)(BPM ₃)] ₂	0.698	0.189	0.113	-	-	-	0.068
3': [(HN)(BH)(BPH ₃)] ₂	0.654	0.163	0.183	0.64	0.81	0.47	0.078
4': [(HN) ₂ (BH) ₄] ²⁻	0.288	0.428	0.284	0.66	0.81	0.50	0.118

Table 5.3.2. Calculated NICS values (ppm).

Distance (Å)	NICS _{zz}		NICS _{πzz}		FiPC
	0	1	0	1	
1: (CH) ₆	-14.48	-29.25	-35.78	-29.07	-9.07
2: (HBNH) ₃	11.98	-5.17	-7.89	-5.88	-2.34
3: [(MesN)(BCl)(BPM ₃)] ₂	-3.36	-12.32	-	-	-4.03
3': [(HN)(BH)(BPH ₃)] ₂	-3.75	-15.18	-19.73	-16.54	-3.85
4': [(HN) ₂ (BH) ₄] ²⁻	-5.49	-15.42	-20.73	-17.02	-

Figure 5.3.4. (a) Dissected NICS_{zz} (ppm) vs. distance (Å) of **3'** and **4'**. (b) Plots of the NICS_{in-plane} vs NICS_{out-of-plane} of **1**, **2**, **3**, **3'** and **4'**, to identify the FiPC-NICS.

Figure 5.3.5. ACID plot of the selected π orbitals of **4'**, at an isosurface value of 0.03.

Table 5.3.3. Calculated ASE values (kcal mol⁻¹).

	ASE
1: (CH) ₆	33.4 (100)
2: (HBNH) ₃	10.1 (30)
3: [(MesN)(BCl)(BPMes)] ₂	-
3': [(HN)(BH)(BPH ₃)] ₂	23.8 (71)
4': [(HN) ₂ (BH) ₄] ²⁻	11.0 (33)

Scheme 5.3.1. Homodesmotic reaction schemes used to estimate the aromatic stabilization energy (ASE).

5.4 Summary

In conclusion, we have assessed the aromatics-relevant indices of B_4N_2 -based inorganic benzene analogues together with benzene and borazine, with the aid of HOMA, ELF, PDI, NICS, ACID and ASE methods. It has been demonstrated that the aromaticity of the neutral B_4N_2 systems **3** and **3'** clearly differs from that of borazine **2** of the $(XY)_3$ system. The major parameters (ELF, PDI, $NICS_{zz}$, and ASE) other than HOMA suggest that the neutral B_4N_2 systems **3** and **3'** are less aromatic than benzene and more aromatic than borazine **2**. While ELF_π , PDI and $NICS_{\pi zz}$ values propose the pronounced aromatic nature of the dianionic B_4N_2 system **4'**, the ASE result estimates the aromaticity of **4'** to be smaller than that of **3'** and similar to borazine **2**. Moreover, the FiPC-NICS plot of **4'** is different from those observed for the aromatic molecules.⁵⁸ Besides, ACID plot of **4'** shows that in addition to the ring current over the six-membered ring, localized currents in the RB-BH fragment significantly contributes to magnetic anisotropy. These data indicate that even with the same B_4N_2 -skeletal framework of 6π -system, the index value of each criterion varies depending on the overall charge of the B_4N_2 systems,^{32,33,36} giving rise to the different aromatic nature.^{64,65} This study paves a way for the further design and development of aromatic inorganic benzenes.

5.5 Experimental Sections

Computational Methods

All density functional theory calculations have been performed using the Gaussian 16 program package at the B3LYP/6-311+G(d,p) level,⁶⁶ which is widely employed for the estimation of aromaticity of monocyclic heterobenzenes and inorganic benzenes.^{17,67-69} Note that when the basis sets as 6-311+G(2df,2pd) and 6-311+G(3df,3pd) in the optimization and NICS calculations for dianionic **4'** were employed, almost no significant improvement was observed (Table 5.5.2). We used the NBO method in the current NBO 7.0 version of the general NBO analysis program.⁷⁰ PDI, ELF, and atoms in molecules (AIM) studies were generated with the Multiwfn 3.6 program.⁷¹

Methodology

1. HOMA

The HOMA scheme for *N*-membered cyclic hydrocarbon compound is defined as shown in eq 1:

$$\text{HOMA} = 1 - \frac{\alpha}{N} \sum_i (R_{\text{opt}} - R_i)^2 \quad (1)$$

In the equation, α is an empirical constant chosen to give a value of HOMA = 0 for a nonaromatic system and HOMA = 1 for aromatic system with all bonds equal to an optimal bond length (R_{opt}), N is the number of bonds taken into summation, R_i is an individual bond length and i represents the type of the bond. Krygowski and co-workers have proposed the extended HOMA scheme for heterocyclic compounds.

$$\text{HOMA} = 1 - \left[257.7(1.388 - r_{\text{av}})^2 + \frac{257.7}{N} \sum_i (r_{\text{av}} - r_i)^2 \right] \quad (2)$$

$$= 1 - \text{EN} - \text{GEO} \quad (3)$$

where r_{av} and r_i are an average of C-C bond lengths and individual C-C bond lengths, respectively. To apply this scheme to the heterocyclic compounds, the Pauling concept of bond number n was introduced:

$$R(1) - R(n) = c \ln(n) \quad (4)$$

$$n = \exp \frac{R(1)-R(n)}{c} \quad (5)$$

where $R(n)$ and $R(1)$ are the bond lengths whose bond numbers are n and 1, respectively. From reference value of $R(1)$ and $R(2)$, we can estimate the constant c for X-Y bond by using Eq.(5). The $R(1)$, $R(2)$, and c values for CC, BB, and BN bonds listed in Table, have been recommended and were used herein for HOMA calculations. Using the bond number n , the X-Y bond length can be converted into the virtual C-C bond length (r_i) as

$$r_i = 1.467 - 0.1702 \ln(n) \quad (6)$$

Now we can evaluate HOMA value of various heterocyclic compounds by using Eq. (2).

Table. The $R(1)$, $R(2)$, and c values for CC, BB, and BN bonds.

	$R(1)$	$R(2)$	c
CC	1.467	1.349	0.1702
BB	1.647	1.526	0.1751
BN	1.564	1.363	0.2900

2. ELF

The electron localization function (ELF), introduced by Becke and Edgencombe, can be used to analyse the electronic localization and characteristics of a chemical bond. The value of ELF at which two basins merge is called a bifurcation value. The ring-closure bifurcation value is the value of ELF at which all basins in the ring merge to form one continuous cyclic basin. A separation of the ELF values into its σ and π components (namely, ELF_{σ} and ELF_{π}) was

proposed as new aromaticity scales. Both ELF_σ and ELF_π are defined as the ELF values at the relative bifurcation points that is the (3, -1) critical points (CPs) of the ELF basin that only contribute from different molecular orbitals (π -orbitals or σ -orbitals). Aromatic molecules should hold at least the following two properties: (i) the maximal difference between the bifurcation values, ELF_π should be small, and (ii) the ELF_π should be above a certain threshold (0.64–0.70).⁵³ In this study, the aromaticity of the heterocyclic inorganic benzenes were also considered by averaged ELF_σ and ELF_π .⁷²

3. PDI

The *para*-delocalization index (PDI), proposed by Sola and co-workers is derived from Bader's Atoms in Molecules (AIM) theory.⁷³ This index is defined as the average of three electron delocalization index (DIs) of *para*-related atoms in a given six-membered ring.⁷⁴⁻⁷⁶ The higher PDI values, the more aromatic system is.

4. NICS

The computation of nucleus independent chemical shifts (NICSs): $\text{NICS}(1)_{zz}$, $\text{NICS}(0)_{\pi zz}$, and FiPC-NICS was used. Significantly negative (shielded) NICS values indicate a diatropic ring current and aromaticity, while positive (deshielded) values denote a paratropic ring current and antiaromaticity. The group of Pino-Rios and Tiznado remarked evaluating the s- and p-electron contributions to the out-of-plane components of NICS is the most adequate assessment for the quantitative analysis. The Tiznado and co-workers proposed a free of in-plane component NICS (FiPC-NICS) to assess aromaticity, identifying the point along the axis perpendicular to the molecular plane where the in-plane component of NICS becomes zero. It also allows visualizing the relation between the in-plane and out-of-plane components of NICS. The plots of these correlations provide curves whose shapes seem to be characteristics for

aromatic, nonaromatic and antiaromatic systems. We also used the anisotropy of the current-induced density (ACID) to visualize ring current over the studied rings.

5. ASE

ASE has been evaluated using different isodesmic and homodesmotic (Scheme 5.3.1) reactions. The isodesmic reaction have been proposed for inorganic analogues. On the other hand, the Tiznado and co-workers proposed the homodesmotic reaction to avoid sp^3 hybridization of boron atom, which is expected to generate strain in the B–H bonds.^{58,63} Here, we can evaluate ASE value of model compounds.

Table 5.5.1. Optimized structure of **1**, **2**, **3**, **3'**, and **4'** obtained by DFT calculations (atom, x-, y-, z-positions in Å).

1:

C	-1.337282	-0.394667	0.000002
C	-0.326732	-1.355449	0.000062
C	1.010416	-0.960785	-0.000056
C	1.337249	0.394786	0.000007
C	0.326849	1.355419	0.000057
C	-1.010499	0.960699	-0.000052

H	-2.377180	-0.701703	-0.000061
H	-0.581008	-2.409500	0.000080
H	1.796302	-1.707800	-0.000122
H	2.377220	0.701555	0.000021
H	0.580872	2.409526	-0.000001
H	-1.796207	1.707909	-0.000038

2:

B	1.107098	0.939067	-0.000001
B	0.259706	-1.428296	-0.000013
B	-1.366800	0.489237	0.000011
N	-0.252105	1.386574	-0.000012
N	1.326878	-0.474967	0.000009
N	-1.074774	-0.911613	-0.000001

H	-1.844157	-1.564238	-0.000002
H	0.472832	-2.600706	-0.000006
H	2.276761	-0.814952	0.000017
H	2.015871	1.709846	0.000017
H	-0.432620	2.379185	-0.000016
H	-2.488699	0.890870	0.000036

3:

Cl	1.443887	3.034615	-0.000316
P	2.074707	-2.734296	0.000166
N	1.525743	0.220088	0.000007
C	2.953580	0.448090	-0.000027
C	3.638188	0.571637	-1.219821
C	3.638169	0.572060	1.219728
C	5.732364	0.886061	-0.000087
C	5.020150	0.780271	-1.195624
H	5.550417	0.870728	-2.139647
C	2.903183	0.523746	-2.536999
H	2.197125	-0.309114	-2.582505
H	3.604289	0.437479	-3.369896
H	2.318105	1.437564	-2.680231
C	3.908169	-2.642620	0.000389
H	4.265469	-2.111609	0.881626
H	4.265653	-2.112009	-0.881021

C	-3.638197	-0.571850	1.219737
C	-3.638059	-0.571683	-1.219810
C	-5.732329	-0.885878	-0.000180
C	-5.020175	-0.780408	1.195411
H	-5.550500	-0.871028	2.139386
C	-2.903300	-0.524195	2.536985
H	-2.196713	0.308218	2.582382
H	-3.604438	-0.437315	3.369793
H	-2.318847	-1.438375	2.680472
C	-3.908216	2.642231	0.000284
H	-4.265620	2.111933	-0.881348
H	-4.265465	2.110847	0.881316
H	-4.307606	3.659656	0.000939
C	-5.020035	-0.780233	-1.195683
H	-5.550249	-0.870728	-2.139733
C	-2.902985	-0.524017	-2.536961

H	4.307449	-3.660086	0.000652
C	5.020140	0.780681	1.195472
H	5.550400	0.871437	2.139471
C	2.903176	0.524628	2.536930
H	2.196737	-0.307899	2.582534
H	2.318535	1.438741	2.680091
H	3.604265	0.438131	3.369818
C	1.724883	-3.809655	-1.450930
H	2.247077	-4.765681	-1.356419
H	2.061385	-3.301556	-2.356273
H	0.651368	-3.980820	-1.518282
B	0.629450	1.352049	-0.000034
B	0.979599	-1.131259	0.000067
C	7.219589	1.150633	-0.000134
H	7.426659	2.226599	-0.000696
H	7.701455	0.726021	-0.884352
H	7.701337	0.726960	0.884596
Cl	-1.443771	-3.034662	-0.000005
P	-2.074758	2.734156	0.000116
N	-1.525674	-0.220099	0.000097
C	-2.953514	-0.448089	0.000018

H	-2.196528	0.308505	-2.582381
H	-2.318335	-1.438104	-2.680251
H	-3.604023	-0.437366	-3.369876
C	-1.724780	3.809562	1.451123
H	-2.247057	4.765543	1.356634
H	-2.061119	3.301476	2.356536
H	-0.651272	3.980801	1.518344
B	-0.629391	-1.352063	0.000127
B	-0.979510	1.131238	0.000079
C	-7.219566	-1.150377	-0.000302
H	-7.426689	-2.226332	-0.001189
H	-7.701290	-0.726944	0.884555
H	-7.701414	-0.725477	-0.884394
C	1.724473	-3.809670	1.451143
H	2.060694	-3.301588	2.356599
H	0.650940	-3.980847	1.518169
H	2.246703	-4.765689	1.356763
C	-1.725060	3.809602	-1.450963
H	-0.651575	3.980992	-1.518244
H	-2.061382	3.301429	-2.356334
H	-2.247458	4.765523	-1.356501

3':

B	-0.689367	1.398504	-0.000123
B	1.446781	0.045569	-0.000050
B	0.689367	-1.398409	-0.000154
B	-1.446782	-0.045466	-0.000042
P	-3.356866	0.025883	0.000128
H	-4.135502	-0.515849	1.065419
H	-3.784547	1.362637	0.000207
H	-4.135919	-0.515770	-1.064910
P	3.356865	-0.025968	0.000032

H	3.784315	-1.362794	-0.000001
H	4.135799	0.515637	-1.065110
H	4.135801	0.515571	1.065210
H	-1.172566	2.499066	0.000112
H	1.172597	-2.498958	-0.000283
N	0.753049	1.301630	-0.000028
N	-0.753042	-1.301537	-0.000127
H	-1.267176	-2.175714	-0.000174
H	1.267175	2.175811	0.000067

4':

N	1.476540	0.000000	0.000002
B	0.828160	-1.306783	-0.010984
B	0.828162	1.306782	0.011048
N	-1.476540	0.000002	-0.000019
B	-0.828153	1.306794	0.011677
B	-0.828155	-1.306793	-0.011660

H	2.492346	-0.000002	-0.000031
H	1.592312	-2.268909	0.032669
H	-1.592339	-2.268979	0.031682
H	-2.492368	0.000001	-0.000040
H	-1.592334	2.268976	-0.031805
H	1.592315	2.268900	-0.032763

Table 5.5.2. Calculated NICS values (ppm) of 4' at different level.

Distance (Å)	NICS		NICS _{zz}		NICS _{πzz}	
	0	1	0	1	0	1
6-311g+(d,p)	7.70	2.33	-5.68	-15.42	-20.73	-17.02
6-311g+(2df,2pd)	8.07	1.79	-6.71	-16.38	-21.41	-17.93
6-311g+(3df,3dp)	7.79	1.34	-4.94	-14.75	-19.96	-16.00

Table 5.5.3. Calculated HOMA values of studied molecules.

	Type	Bond length	bond number
1	C-C	1.39439	1.532
	C-C	1.39418	1.534
	C-C	1.39441	1.532
	C-C	1.39417	1.534
	C-C	1.39438	1.532
	C-C	1.39420	1.534
2	B-N	1.43101	1.582
	B-N	1.43098	1.582
	B-N	1.43101	1.582
	B-N	1.43096	1.582
	B-N	1.43100	1.582
	B-N	1.43098	1.582
3	B-B	1.62407	1.143
	B-B	1.62404	1.143

	B-N	1.45754	1.444
	B-N	1.44384	1.513
	B-N	1.45753	1.444
	B-N	1.44384	1.513
3'	B-B	1.63056	1.101
	B-B	1.63057	1.101
	B-N	1.43492	1.561
	B-N	1.44566	1.504
	B-N	1.43491	1.561
	B-N	1.44567	1.504
4'	B-B	1.65632	0.950
	B-B	1.65632	0.950
	B-N	1.45885	1.437
	B-N	1.45885	1.437
	B-N	1.45883	1.437
	B-N	1.45883	1.437

Table 5.5.4. Properties of electron density at ring critical point of **1-4'**.

	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$H(r_c)$	λ_1	λ_2	λ_3	ε
1	0.0215	0.1614	0.0326	0.0078	-0.0168	0.0891	0.0891	-1.1886
2	0.0197	0.1195	0.0251	0.0047	-0.0140	0.0668	0.0668	-1.2100
3	0.0171	0.0785	0.0171	0.0025	-0.0108	0.0346	0.0546	-1.3104
3'	0.0172	0.0850	0.0184	0.0029	-0.0113	0.0417	0.0546	-1.2708
4'	0.0156	0.0821	0.0174	0.0031	-0.0096	0.0453	0.0464	-1.2110

Table 5.5.5. Raw energy data for RSE calculation of (a).

(a)	Zero-point correction	Thermal correction to Energy	Thermal correction to Enthalpy	Thermal correction to Gibbs Free Energy	Sum of electronic and zero-point Energies	Sum of electronic and thermal Energies	Sum of electronic and thermal Enthalpies	Sum of electronic and thermal Free Energies
1	0.100153	0.104553	0.105497	0.072688	-232.211089	-232.206689	-232.205745	-232.238554
1a	0.14558	0.151103	0.152048	0.116929	-234.567577	-234.562053	-234.561109	-234.596227
1b	0.121786	0.126971	0.127916	0.093549	-233.362089	-233.356904	-233.35596	-233.390326
Cy	0.169491	0.175223	0.176168	0.141737	-235.775335	-235.769602	-235.768658	-235.803089
RSE [au]								0.053168
RSE [kcal mol ⁻¹]								33.36292

Table 5.5.6. Raw energy data for RSE calculation of (b).

(b)	Zero-point correction	Thermal correction to Energy	Thermal correction to Enthalpy	Thermal correction to Gibbs Free Energy	Sum of electronic and zero-point Energies	Sum of electronic and thermal Energies	Sum of electronic and thermal Enthalpies	Sum of electronic and thermal Free Energies
2	0.093176	0.098388	0.099333	0.065051	-242.655345	-242.650133	-242.649189	-242.68347
2a	0.14289	0.148729	0.149673	0.113981	-238.02607	-238.020231	-238.019287	-238.054979
2b	0.11703	0.122837	0.123781	0.088211	-240.314275	-240.308469	-240.307524	-240.343095
Cy	0.169491	0.175223	0.176168	0.141737	-235.775335	-235.769602	-235.768658	-235.803089
RSE [au]								0.016033
RSE [kcal mol ⁻¹]								10.0607075

Table 5.5.7. Raw energy data for RSE calculation of (c).

(c)	Zero-point correction	Thermal correction to Energy	Thermal correction to Enthalpy	Thermal correction to Gibbs Free Energy	Sum of electronic and zero-point Energies	Sum of electronic and thermal Energies	Sum of electronic and thermal Enthalpies	Sum of electronic and thermal Free Energies
3'	0.123163	0.133732	0.134676	0.087362	-897.661346	-897.650776	-897.649832	-897.697147
3'a	0.162639	0.171086	0.17203	0.129642	-580.344718	-580.336271	-580.335326	-580.377715
3'b	0.14289	0.148729	0.149673	0.113981	-238.02607	-238.020231	-238.019287	-238.054979
3'c	0.151726	0.160224	0.161169	0.119034	-550.613642	-550.605144	-550.6042	-550.646334
3'd	0.125097	0.133662	0.134606	0.092361	-552.891209	-552.882645	-552.881701	-552.923945
3'e	0.146388	0.157479	0.158423	0.109679	-895.368798	-895.357707	-895.356763	-895.405507
3'f	0.137604	0.145877	0.146821	0.104905	-582.572987	-582.564714	-582.56377	-582.605686
Cy	0.169491	0.175223	0.176168	0.141737	-235.775335	-235.769602	-235.768658	-235.803089
RSE [au]								0.037948
RSE [kcal mol ⁻¹]								23.81237

Table 5.5.8. Raw energy data for RSE calculation of (d).

(d)	Zero-point correction	Thermal correction to Energy	Thermal correction to Enthalpy	Thermal correction to Gibbs Free Energy	Sum of electronic and zero-point Energies	Sum of electronic and thermal Energies	Sum of electronic and thermal Enthalpies	Sum of electronic and thermal Free Energies
4'	0.081778	0.087475	0.08842	0.053433	-212.502999	-212.497301	-212.496357	-212.531343
4'a	0.14289	0.148729	0.149673	0.113981	-238.02607	-238.020231	-238.019287	-238.054979
4'b	0.130619	0.137045	0.137989	0.101362	-207.915235	-207.908809	-207.907865	-207.944492
4'c	0.106233	0.112401	0.113345	0.077334	-210.215626	-210.209458	-210.208514	-210.244525
4'd	0.117573	0.123267	0.124211	0.088945	-240.247536	-240.241842	-240.240897	-240.276163
Cy	0.169491	0.175223	0.176168	0.141737	-235.775335	-235.769602	-235.768658	-235.803089
RSE [au]								0.017491
RSE [kcal mol ⁻¹]								10.9756025

(1)

(2)

(3')

(4')

Figure 5.5.1. ACID plot of selected π orbitals at an isosurface value of 0.03.

5.6 References

- 1 P. R. v. Schleyer, J. Haijun. What is aromaticity? *Pure Appl. Chem.* **68**, 209-218 (1996). doi: 10.1351/pac199668020209.
- 2 P. v. R. Schleyer. Introduction: Aromaticity. *Chem. Rev.* **101**, 1115-1118 (2001). doi:10.1021/cr0103221.
- 3 A. T. Balaban, P. v. R. Schleyer, H. S. Rzepa. Crocker, Not Armit and Robinson, Begat the Six Aromatic Electrons. *Chem. Rev.* **105**, 3436-3447 (2005). doi:10.1021/cr0300946.
- 4 M. Faraday. On new compounds of carbon and hydrogen, and on certain other products obtained during the decomposition of oil by heat. *Phil. Trans. R. Soc. Lond.* **115**, 440-466 (1825). doi: 10.1098/rstl.1825.0022.
- 5 A. Kekulé. Sur la constitution des substances aromatiques. *Bull. Soc. Chim. Fr.* **3**, 98–110 (1865).
- 6 K. Ota, R. Kinjo. Inorganic Benzene Valence Isomers. *Chem. Asian J.* **15**, 2558-2574 (2020). doi:10.1002/asia.202000535.
- 7 A. Stock, E. Pohland. Borwasserstoffe, IX.: B₃N₃H₆. *Ber. Dtsch. Chem. Ges.* **59**, 2215-2223 (1926). doi:10.1002/cber.19260590907.
- 8 H. R. Allcock. Recent advances in phosphazene (phosphonitrilic) chemistry. *Chem. Rev.* **72**, 315-356 (1972). doi:10.1021/cr60278a002.
- 9 A. L. Korich, P. M. Iovine. Boroxine chemistry and applications: A perspective. *Dalton Trans.* **39**, 1423-1431 (2010). doi:10.1039/B917043J.
- 10 Y. Tokunaga. Boroxine Chemistry: From Fundamental Studies to Applications in Supramolecular and Synthetic Organic Chemistry. *Heterocycles* **87**, 991-1021 (2013). doi:10.3987/rev-13-767.

- 11 E. W. David. Organo-phosphorus-boron compound and method of making same. United States patent US3035095A (1962).
- 12 H. V. R. Dias, P. P. Power. Synthesis and X - Ray Structure of (2,4,6 - Me₃C₆H₂BPC₆H₁₁)₃: A Boron-Phosphorus Analogue of Borazine. *Angew. Chem. Int. Ed. Engl.* **26**, 1270-1271 (1987). doi:10.1002/anie.198712701.
- 13 H. V. R. Dias, P. P. Power. Boron-phosphorus analogs of benzene and cyclobutadiene. Synthesis and characterization of the boraphosphabenzenes (RBPR')₃ (R = Mes, Ph; R' = Ph, Mes, C₆H₁₁, tert-Bu) and the diphosphadiboretane (thexylBPMes)₂. *J. Am. Chem. Soc.* **111**, 144-148 (1989). doi:10.1021/ja00183a025.
- 14 P. P. Power. The synthesis, characterization and some properties of new quasi-aromatic main group ring systems. *J. Organomet. Chem.* **400**, 49-69 (1990). doi: 10.1016/0022-328X(90)83005-5.
- 15 A. E. Seitz, M. Eckhardt, A. Erlebach, E. V. Peresypkina, M. Sierka, M. Scheer. Pnictogen–Silicon Analogues of Benzene. *J. Am. Chem. Soc.* **138**, 10433-10436 (2016). doi:10.1021/jacs.6b07389.
- 16 W. H. Fink, J. C. Richards. Relative aromaticity in heteropolar inorganic analogs of benzene. *J. Am. Chem. Soc.* **113**, 3393-3398 (1991). doi:10.1021/ja00009a026.
- 17 P. v. R. Schleyer, H. Jiao, N. J. R. v. E. Hommes, V. G. Malkin, O. L. Malkina. An Evaluation of the Aromaticity of Inorganic Rings: Refined Evidence from Magnetic Properties. *J. Am. Chem. Soc.* **119**, 12669-12670 (1997). doi:10.1021/ja9719135.
- 18 E. D. Jemmis, B. Kiran. Aromaticity in X₃Y₃H₆ (X = B, Al, Ga; Y = N, P, As), X₃Z₃H₃ (Z = O, S, Se), and Phosphazenes. Theoretical Study of the Structures, Energetics, and Magnetic Properties. *Inorg. Chem.* **37**, 2110-2116 (1998). doi:10.1021/ic970737y.

- 19 J. J. Engelberts, R. W. A. Havenith, J. H. van Lenthe, L. W. Jenneskens, P. W. Fowler. The Electronic Structure of Inorganic Benzenes: Valence Bond and Ring-Current Descriptions. *Inorg. Chem.* **44**, 5266-5272 (2005). doi:10.1021/ic050017o.
- 20 A. K. Phukan, A. K. Guha, B. Silvi. Is delocalization a prerequisite for stability of ring systems? A case study of some inorganic rings. *Dalton Trans.* **39**, 4126-4137 (2010). doi:10.1039/B920161K.
- 21 R. Pino-Rios, A. Vásquez-Espinal, L. Alvarez-Thon, W. Tiznado. Relativistic effects on the aromaticity of E3M3H3 (E = C-Pb; M = N-Bi) benzene analogues. *Phys. Chem. Chem. Phys.* **22**, 22973-22978 (2020). doi:10.1039/d0cp04446f.
- 22 P. W. Fowler, E. Steiner. Ring Currents and Aromaticity of Monocyclic π -Electron Systems C6H6, B3N3H6, B3O3H3, C3N3H3, C5H5-, C7H7+, C3N3F3, C6H3F3, and C6F6. *J. Phys. Chem. A* **101**, 1409-1413 (1997). doi:10.1021/jp9637946.
- 23 A. Y. Timoshkin, G. Frenking. "True" Inorganic Heterocycles: Structures and Stability of Group 13–15 Analogues of Benzene and Their Dimers. *Inorg. Chem.* **42**, 60-69 (2003). doi:10.1021/ic020361a.
- 24 R. Islas, E. Chamorro, J. Robles, T. Heine, J. C. Santos, G. Merino. Borazine: to be or not to be aromatic. *Struct. Chem.* **18**, 833-839 (2007). doi:10.1007/s11224-007-9229-z.
- 25 R. Ghiasi. Theoretical study of the properties of fluoroborathiin and fluoroboroxine. *J. Mol. Struct. (Theochem)* **853**, 77-81 (2008). doi: 10.1016/j.theochem.2007.12.007.
- 26 S. Pelloni, G. Monaco, P. Lazzeretti, R. Zanasi. Beyond NICS: estimation of the magnetotropy of inorganic unsaturated planar rings. *Phys. Chem. Chem. Phys.* **13**, 20666-20672 (2011). doi:10.1039/C1CP21952A.
- 27 K. Ota, R. Kinjo. A Neutral and Aromatic Boron-Rich Inorganic Benzene. *Angew. Chem. Int. Ed.* **59**, 6572-6575 (2020). doi:10.1002/anie.201915790.

- 28 B. Su, K. Ota, K. Xu, H. Hirao, R. Kinjo. Zwitterionic Inorganic Benzene Valence Isomer with sigma-Bonding between Two pi-Orbitals. *J. Am. Chem. Soc.* **140**, 11921-11925 (2018). doi:10.1021/jacs.8b08025.
- 29 M. Solà. Why Aromaticity Is a Suspicious Concept? Why? *Front. Chem.* **5** (2017). doi:10.3389/fchem.2017.00022.
- 30 J. T. Nelson, W. J. Pietro. Natural bond orbital (NBO) analysis of substituent effects in borazine derivatives. *Inorg. Chem.* **28**, 544-548 (1989).
- 31 T. M. Krygowski, K. Ejsmont, B. T. Stepień, M. K. Cyrański, J. Poater, M. Solà. Relation between the Substituent Effect and Aromaticity. *J. Org. Chem.* **69**, 6634-6640 (2004). doi:10.1021/jo0492113.
- 32 R. Miao, G. Yang, C. Zhao, J. Hong, L. Zhu. Substituent effect on molecular geometry and aromaticity of symmetric B-trisubstituted borazine. *J. Mol. Struct. THEOCHEM* **728**, 197-202 (2005). doi: 10.1016/j.theochem.2005.05.020.
- 33 M. Baranac-Stojanović, M. Stojanović. Substituent effects on cyclic electron delocalization in symmetric B- and N-trisubstituted borazine derivatives. *RSC Adv.* **3**, 24108-24117 (2013). doi:10.1039/C3RA44189J.
- 34 A. K. Srivastava, S. K. Pandey, N. Misra. The aromaticity and electronic properties of monosubstituted benzene, borazine and diazadiborine rings: an ab initio MP2 study. *Theor. Chem. Acc.* **135**, 158 (2016). doi:10.1007/s00214-016-1918-5.
- 35 A. K. Srivastava, S. K. Pandey, N. Misra. Stability versus aromaticity in mono-hydroxylated borazine, 1,2-azaborine and 1,3,2,4-diazadiborine. *Mol. Phys.* **114**, 1763-1770 (2016). doi:10.1080/00268976.2016.1145749.
- 36 W. A. Rabanal-León, W. Tiznado, L. Alvarez-Thon. Relativistic effects on the ring current strengths of the substituted borazine: B₃N₃H₆ (X=H, F, Cl, Br, I, At). *Int. J. Quantum Chem* **119**, e25859 (2019). doi:10.1002/qua.25859.

- 37 A. Julg, P. François. Recherches sur la géométrie de quelques hydrocarbures non-alternants: son influence sur les énergies de transition, une nouvelle définition de l'aromaticité. *Theor. Chim. Acta* **8**, 249-259 (1967). doi:10.1007/BF00527311.
- 38 J. Kruszewski, T. M. Krygowski. Definition of aromaticity basing on the harmonic oscillator model. *Tetrahedron Lett.* **13**, 3839-3842 (1972). doi: 10.1016/S0040-4039(01)94175-9.
- 39 T. M. Krygowski. Crystallographic studies of inter- and intramolecular interactions reflected in aromatic character of π -electron systems. *J. Chem. Inf. Comput. Sci.* **33**, 70-78 (1993). doi:10.1021/ci00011a011.
- 40 T. M. Krygowski, M. Cyrański. Separation of the energetic and geometric contributions to the aromaticity. Part IV. A general model for the π -electron systems. *Tetrahedron* **52**, 10255-10264 (1996). doi: 10.1016/0040-4020(96)00560-1.
- 41 T. M. Krygowski, M. Cyrański. Separation of the energetic and geometric contributions to the aromaticity of π -electron carbocyclics. *Tetrahedron* **52**, 1713-1722 (1996). doi: 10.1016/0040-4020(95)01007-6.
- 42 I. D. Madura, T. M. Krygowski, M. K. Cyrański. Structural aspects of the aromaticity of cyclic π -electron systems with BN bonds. *Tetrahedron* **54**, 14913-14918 (1998). doi: 10.1016/S0040-4020(98)00933-8.
- 43 K. K. Zborowski, I. Alkorta, J. Elguero, L. M. Proniewicz. HOMA parameters for the boron–boron bond: How the introduction of a BB bond influences the aromaticity of selected hydrocarbons. *Struct. Chem.* **24**, 543-548 (2013). doi:10.1007/s11224-012-0109-9.
- 44 A. D. Becke, K. E. Edgecombe. A simple measure of electron localization in atomic and molecular systems. *J. Chem. Phys.* **92**, 5397-5403 (1990). doi:10.1063/1.458517.

- 45 A. Savin, A. D. Becke, J. Flad, R. Nesper, H. Preuss, H. G. von Schnering. A New Look at Electron Localization. *Angew. Chem. Int. Ed.* **30**, 409-412 (1991). doi:10.1002/anie.199104091.
- 46 B. Silvi, A. Savin. Classification of chemical bonds based on topological analysis of electron localization functions. *Nature* **371**, 683-686 (1994). doi:10.1038/371683a0.
- 47 A. Savin, R. Nesper, S. Wengert, T. F. Fässler. ELF: The Electron Localization Function. *Angew. Chem. Int. Ed.* **36**, 1808-1832 (1997). doi:10.1002/anie.199718081.
- 48 J. Poater, X. Fradera, M. Duran, M. Solà. The Delocalization Index as an Electronic Aromaticity Criterion: Application to a Series of Planar Polycyclic Aromatic Hydrocarbons. *Chem. Eur. J.* **9**, 400-406 (2003). doi:10.1002/chem.200390041.
- 49 F. Feixas, E. Matito, J. Poater, M. Solà. Quantifying aromaticity with electron delocalisation measures. *Chem. Soc. Rev.* **44**, 6434-6451 (2015). doi:10.1039/C5CS00066A.
- 50 J. C. Santos, W. Tiznado, R. Contreras, P. Fuentealba. Sigma-pi separation of the electron localization function and aromaticity. *J. Chem. Phys.* **120**, 1670-1673 (2004). doi:10.1063/1.1635799.
- 51 J. C. Santos, J. Andres, A. Aizman, P. Fuentealba. An Aromaticity Scale Based on the Topological Analysis of the Electron Localization Function Including σ and π Contributions. *J. Chem. Theory Comput.* **1**, 83-86 (2005). doi:10.1021/ct0499276.
- 52 J. Pilmé. Electron localization function from density components. *J. Comput. Chem.* **38**, 204-210 (2017). doi: 10.1002/jcc.24672.
- 53 M. Solà. *Aromaticity*. (2017).
- 54 P. Bultinck. Critical analysis of the local aromaticity concept in polyaromatic hydrocarbons. *Faraday Discuss.* **135**, 347-365 (2007). doi:10.1039/B609640A.

- 55 F. Feixas, E. Matito, J. Poater, M. Solà. On the performance of some aromaticity indices: A critical assessment using a test set. *J. Comput. Chem.* **29**, 1543-1554 (2008). doi:10.1002/jcc.20914.
- 56 Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer. Nucleus-Independent Chemical Shifts (NICS) as an Aromaticity Criterion. *Chem. Rev.* **105**, 3842-3888 (2005). doi:10.1021/cr030088+.
- 57 H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer. Which NICS Aromaticity Index for Planar π Rings Is Best? *Org. Lett.* **8**, 863-866 (2006). doi:10.1021/ol0529546.
- 58 J. J. Torres-Vega, A. Vásquez-Espinal, J. Caballero, M. L. Valenzuela, L. Alvarez-Thon, E. Osorio, W. Tiznado. Minimizing the risk of reporting false aromaticity and antiaromaticity in inorganic heterocycles following magnetic criteria. *Inorg. Chem.* **53**, 3579-3585 (2014). doi:10.1021/ic4030684.
- 59 R. Báez-Grez, L. Ruiz, R. Pino-Rios, W. Tiznado. Which NICS method is most consistent with ring current analysis? Assessment in simple monocycles. *RSC Adv.* **8**, 13446-13453 (2018). doi:10.1039/C8RA01263F.
- 60 A. Stanger. NICS – Past and Present. *Eur. J. Org. Chem.* **2020**, 3120-3127 (2020). doi:10.1002/ejoc.201901829.
- 61 R. Gershoni-Poranne, A. Stanger. Magnetic criteria of aromaticity. *Chem. Soc. Rev.* **44**, 6597-6615 (2015). doi:10.1039/C5CS00114E.
- 62 R. Báez-Grez, W. A. Rabanal-León, L. Alvarez-Thon, L. Ruiz, W. Tiznado, R. Pino-Rios. Aromaticity in heterocyclic analogues of benzene: Dissected NICS and current density analysis. *J. Phys. Org. Chem.* **32**, e3823 (2019). doi:10.1002/poc.3823.

- 63 E. Osorio, J. K. Olson, W. Tiznado, A. I. Boldyrev. Analysis of Why Boron Avoids sp² Hybridization and Classical Structures in the BnHn+2 Series. *Chem. Eur. J.* **18**, 9677-9681 (2012). doi:10.1002/chem.201200506.
- 64 P. C. Parambil, R. Hoffmann. Alkyl Isosteres. *J. Am. Chem. Soc.* **140**, 12844-12852 (2018). doi:10.1021/jacs.8b06141.
- 65 P. C. Parambil, S. S. R. R. Perumal. Lewis Base/Acid Coordination Stabilizes Planar 6π Aromatic Si6/P6. *Organometallics* **39**, 2951-2955 (2020). doi:10.1021/acs.organomet.0c00449.
- 66 Gaussian 16 Rev. C.01 (Wallingford, CT, 2016).
- 67 M. Baranac-Stojanović. Aromaticity and Stability of Azaborines. *Chem. Eur. J.* **20**, 16558-16565 (2014). doi:10.1002/chem.201402851.
- 68 M. Stojanović, M. Baranac-Stojanović. Aromaticity of Diazaborines and Their Protonated Forms. *J. Org. Chem.* **81**, 197-205 (2016). doi:10.1021/acs.joc.5b02499.
- 69 R. A. Iwaki, T. Udagawa. Effect of heteroatoms on aromaticity analyzed by geometric, magnetic, and electronic criteria. *Chem. Phys. Lett.* **745**, 137271 (2020). doi: 10.1016/j.cplett.2020.137271.
- 70 NBO 7.0. (Theoretical Chemistry Institute, University of Wisconsin, Madison, 2018).
- 71 T. Lu, F. Chen. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **33**, 580-592 (2012). doi:10.1002/jcc.22885.
- 72 B. Hou, P. Yi, Z. Wang, S. Zhang, J. Zhao, R. L. Mancera, Y. Cheng, Z. Zuo. Assignment of aromaticity of the classic heterobenzenes by three aromatic criteria. *Comput. Theor. Chem.* **1046**, 20-24 (2014). doi: 10.1016/j.comptc.2014.07.012.
- 73 R. F. W. Bader. A quantum theory of molecular structure and its applications. *Chem. Rev.* **91**, 893-928 (1991). doi:10.1021/cr00005a013.

- 74 R. F. W. Bader, M. E. Stephens. Spatial localization of the electronic pair and number distributions in molecules. *J. Am. Chem. Soc.* **97**, 7391-7399 (1975). doi:10.1021/ja00859a001.
- 75 X. Fradera, M. A. Austen, R. F. W. Bader. The Lewis Model and Beyond. *J. Phys. Chem. A* **103**, 304-314 (1999). doi:10.1021/jp983362q.
- 76 X. Fradera, J. Poater, S. Simon, M. Duran, M. Solà. Electron-pairing analysis from localization and delocalization indices in the framework of the atoms-in-molecules theory. *Theor. Chem. Acc.* **108**, 214-224 (2002). doi:10.1007/s00214-002-0375-5.