DFT study of Si/Ge conjugated systems

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DFT STUDY OF Si/Ge CONJUGATED SYSTEMS

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fulfilment of the requirement for the degree of

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For my husband....

The happiness of my life

*"The important thing in science is not so much to obtain new facts
as to discover new ways of thinking about them."*

William Bragg

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Abstract

Though significant efforts have been extended to improve material/material design, the organic luminescent molecule containing π -conjugated aromatic system opens a new avenue for understanding the molecular modelling strategies. The molecular electronics components largely depend on π -conjugation as for charge transportation. An n - π conjugated small molecule, formamide was primarily studied within density functional theory (DFT) framework to investigate the Si/Ge substitution effect on its inherent geometric and electronic properties. The nature of hydrogen bond in these types of molecules both at ground state and at low-lying states was also extensively explored based on electronegativity as a part of investigation of π -conjugated system. Several π -conjugated systems including Si/Ge heteroatoms were then investigated substantially to get deep insight into their geometric and electronic properties, as for example, planarity, dihedral angles, potential energy surface, aromaticity, stability, hyperconjugation, and so on. It enables someone to modify the structure or composition in search of more active molecules. We continued our DFT studies along with TD-DFT (Time-dependent density functional theory) on π -conjugated cyclic structures to know how heteroatoms (like Si, S or N) within conjugated backbone and extension of π -conjugation length by incorporation of donor/acceptor fragments under different architectures influence electron delocalization and bring change into their inherent electronic and optical properties. This detailed study is expected to be helpful for effective design of molecular systems for optoelectronic applications.

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List of abbreviations

BCP	Bond critical point
BLW	Block localization wave function
CCSD	Coupled-cluster singles and doubles
CIS	Configuration interaction singles
DFT	Density functional theory
H-bond	Hydrogen bond
HOMO	Highest molecular orbital
LOL	Localized orbital locator
LP	Lone-pair orbital
LUMO	Lowest unoccupied molecular orbital
MCBI	Multicentre bond index
MP2	Second-order Møller–Plesset perturbation theory
NBO	Natural bond orbital
NEDA	Natural energy decomposition analysis
NICS	Nuclear independent chemical shifts
NLMO	Natural localized molecular orbital
NPA	Natural Population Analysis
NSA	Natural Steric Analysis
NTO	Natural Transition orbital
PDMS	Polydimethylsiloxane
PES	Potential energy surface
QTAIM	Quantum theory of atoms in molecules
RE	Resonance Energy
SONO	Singly occupied natural orbitals
TD-DFT	Time-dependent density functional theory
TS	Transition state
WBI	Wiberg Bond Index
ZPE	Zero-point energies

Chapter 1

Introduction

According to J.H. Burroughes et al. conjugated polymers are organic semiconductors as they can act as a promising substitute of Si counterparts due to their high electronic efficiency with delocalized π -molecular orbitals along the polymer chain.¹ In case of pentacene used as FET (field-effect-transistor) has the hole mobility of $5.5 \text{ cm}^2/\text{V.s}$ which is even more than that of amorphous silicon.² The widely used n-type materials are suffered from serious difficulties such as design of electron deficient materials, scare solubility, processabilities, instability in air. However the conjugated organic polymers mostly act as p-type materials though nature of aromatic moieties can determine either n-type or p-type of semiconductor.³ Compared to ionic organic dyes OLED (organic light-emitting diode) which have been intensively studied recently, the organic luminescent molecule containing π -conjugated aromatic system is a novel type of promising material in this field.^{4, 5} Photoluminescence organic molecules appeal fascination of researchers by their unique electronic and photonic properties, especially their high quantum luminescence efficiency and for versatility, high non-linearity and flexibility in tuning their optical properties. Their fascinating properties open new avenues for more and more potential applications and widen the scope for molecular sensors, switches, non-linear optical materials, FET, photoluminescence and electroluminescence.⁶⁻¹¹ Organic conjugated molecules as well as polymers have benefit over inorganic luminescence molecules due to their easy colour tuning.¹²

Figure 1.1 Potential applications of organic semiconductor.

The origin of term “Photonic Molecule” is analogous to chemical molecule because the optical resonance is coupled in photonic molecule like the atomic orbitals in a chemical molecule. Generally, emission and absorption of photons due to the molecular orbital transitions occur in the range of UV and visible spectrum. Only the molecules with small band gap (1.75 to 3.1 eV or 200-800 nm)¹³ can emit or absorb photon owing to orbital excitations in the visible region. Only $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions contribute to emission in the visible range (400-800 nm) (see the below Figure 1.2).

Figure 1.2 Energy associated with the excitations of orbitals.

In a π -conjugated molecule, single and double bonds alternate that increase the delocalization of electrons. Thus, addition of more and more conjugated double bonds to the system results in more and more interacting molecular orbitals (see the Figure 1.3) which leads to the decrease in band gap which is determined by the energy gap between HOMO (highest molecular orbital) and LUMO (lowest unoccupied molecular orbital). The decrease in band gap refers to the absorption and emission with longer wavelength of light. As soon as the absorption peak reaches to visible region, the molecule becomes coloured with the complementary colour of reflected or scattered light according to Woodward-Fieser rules. For

an example, generally the organic luminescence conjugated molecules have the absorption peak around at 500 nm, thus they emit NIR (near infra-red) colour.

Figure 1.3 Addition of more and more conjugated double bonds leads more interacting molecular orbitals.

High mobility semiconductor molecules possess small band gap energy, large bandwidth, small ionization potential and large π -conjugation length. Considering the energy levels, there is hardly difference in inorganic semiconductor and π -conjugated polymer as both of their electrons arranged not at discrete levels, rather in mostly valence bands i.e., the highest occupied band (HOMO in case of single molecule) and conductive band i.e., the lowest or partially occupied band (LUMO for single molecule). In case of π -conjugated polymers, these bands are generated with the increase of π -interactions in the polymer chain. As more and more π -interactions with neighbouring molecules lead to hybridization of electronic energy levels which ultimately constitute these three dimensional band structures like inorganic semiconductor.¹⁴ Organic π -conjugated polymers with the band gap of 1.75 to 3.1 eV show good conductivity and photoluminescence properties¹³ as reduced band gap results a good overlap between the absorption and emission spectra through the increased number of absorbed photons.

Small band gap of conjugated polymers can be achieved by varying the electronic nature like extending the π -conjugation length, introducing donor acceptor units and minimizing bond-length alternations along polymer chains.¹⁴⁻¹⁸ In addition, it is also crucial how the donor and acceptor units are linked under different chemical archetypes. Extended π -conjugation length

means longer distance for charges to be transferred i.e. increase of π -electron delocalization. It has experimentally and theoretically been shown that extending conjugation length of organic conjugated molecules can lead to tremendous increase in photonic adsorption and emission cross-sections.^{19, 20} In 1931, Goppert-Mayer introduced the concept of multi-photon absorption cross-sections. Multi-photon absorption means the simultaneous absorption of two or three photons by a molecule or atom to reach excited state from ground state. It is found that one-, two-, and three- photon absorption cross-section increases with the exponent of 1.3, 2.6 and 5.6, respectively with the enhancement of the π -conjugation length. π -Conjugated organic molecule has triggered the research on these multi-photon absorption cross-section field as they enrich the photo science by their contribution in optical power limiting^{21, 22}, frequency up-converted lasing²³, 3-D optical data storage²⁴, 3-D micro-fabrication²⁵, 3-D fluorescence imaging^{26, 27} and photodynamic therapy²⁸. They are also seemed to be promising for bio-medical applications.

Figure 1.4 Conductive polymer with heteroatom.

Band gap energy can also be engineered through the insertion of the heteroatom into the aromatic molecules as it significantly changes the molecular polarity. Thus, heteroatomic polycyclic aromatic molecules can serve as fundamental skeleton for functional organic photonic materials. For an example, generally acenes suffer serious disadvantages like instability and insolubility which can be overcome by introducing S or N atom into acene that tune the solid-state structure and electronic properties as well. Figure 1.4 shows some of heteroatomic polycyclic molecules with good conductivity. Si and Ge can be effective

substituent of C in ring structure as they belong to the same group in periodic table. They have the potential like delocalized π -systems with the carbon backbone that is the main reason of fascinating properties in polyacetylene, fullerene and carbon nanotubes. Insertion of Si atom into π -conjugation framework also changes molecular conformation, bond strengths, electronic properties, as well as photochemical properties. In 2005, Masae Takahashi and Yoshiyuki Kawazoe proposed that acyclic silicon (Si) oligomer and D_{6h} silicon (Si) benzene have the electrons delocalized on sp^2 silicon backbone like that of π -system of carbon and the latter one has high NICS (Nucleus independent chemical shift) value. In 2012, Miriam Karni and Yitzhak Apeloig elaborately explained the geometries and electronic properties of N-heterocyclic silylenes and phosphorus ylide substituted silylenes. They concluded that both have high resonance energies and thermodynamic stability and thus isolable, though latter one ($R'=Ph$) act as better σ -donor due to its high energy of lone pair orbital on Si.²⁹

Comparing to the pure C analogues, Si substitution can effectively tune the excitation energies at excited states and alter optoelectronic properties. It can shift the fluorescent spectra further into the visible region in many cases due to the reduction of $\pi \rightarrow \pi^*$ energy gaps as a result of an enhancement of $\sigma^* \rightarrow \pi^*$ interaction.^{30, 31} In 1967, Atwell group and later in 1981, O'Brien and Breeden synthesized anion, dianions and tetra anions of silole derivatives.^{32, 33} Silole is a silicon analogue of cyclopentadiene though its electronic nature is quite different from its parent molecule. It shows high electron affinity due to its exceptionally low-lying LUMO which originates from $\sigma^* - \pi^*$ conjugation in the silole ring. Yamaguchi and Tamao synthesized a series of silole derivatives and developed new silole based π -conjugated systems since 1994.³⁰ They reported attractive photophysical properties

of those systems and remarked as efficient materials for organic electroluminescent devices. Though various photoluminescence molecules as well as polymer are designed and also synthesized, it still remains a challenge to design molecules with balance charge transport in emission levels which can reduce the hole current. For bio-medical application, emission needs to be centred at 1100-1300 nm which is semi-transparent windows for living organism and at 1350-1550 nm for telecommunication windows. Both ranges are still far away from the emission from designed or synthesized π -conjugated organic photoluminescence molecule. This limitation prompts us to explore the unique nature of Si/Ge substituted π -conjugated systems in designing new molecules to enhance their performance as photoluminescence materials.

The goals of the present work are

1. To study Si/Ge π -conjugated systems from various theoretical points of view to explore their unique electronic properties.
2. To study substitution effect by Si-substituted cyclic structure and other heterocyclic compounds on tuning the electronic and photophysical properties of conjugated polymer backbone.
3. To design low band gap material with different cyclic structures including Si and other heteroatoms as donor units under different donor-acceptor architectures considering attractive applications in optoelectronics field.

In this dissertation, theoretical background and the computational method used are presented in Chapter 2 with literature review in Chapter 3. A detailed study on formamides, n - π conjugated small molecules and their Si/Ge analogs is carried out in Chapter 4 where the change in geometries, electronic properties, conjugation, internal rotation barrier, stability, bonding and even existing hydrogen bond nature of several formamide derivatives from its parent molecule is extensively discussed. To get deeper insight into Si/Ge based structures, a series of π -conjugated Si/Ge heterocyclic molecules are substantially studied in Chapter 5. In this context several methods are considered. The influences of facile modifications on the HOMO-LUMO band gap and other photophysical properties of conjugated polymer system through incorporation of several donors under different architectures have been presented in Chapter 6. Finally, our findings and remarks are summarized in Chapter 7.

Chapter 2

Theory and Computational Details

This chapter is dedicated to a brief description of the quantum-chemical methods within which our calculations were performed. In this work, the electronic structure calculations were carried out using both *ab initio*³⁴⁻³⁶ and density functional theory (DFT) techniques.^{37, 38} with the help of Gaussian 03³⁹ and 09⁴⁰ packages. Frequency analysis was performed where minima structures are of concern and correction of the relative energies is necessary through evaluating of zero-point energies (ZPEs). All the calculations in the subsequent chapters were performed mostly with B3LYP (Becke's three-parameter hybrid function⁴¹ with the nonlocal correlation of Lee-Yang-Parr⁴² and VWN3⁴³ local correlation) methods along with different basis sets. To account for the relativistic effect on atoms other than H to Kr (Krypton) elements in the periodic table, as for example, tin (Sn) and tellurium (Te) atoms, an augmented LanL2DZ(d,p) basis set^{44, 45} which include the p, d polarization functions was adopted in the calculations. The theory of DFT, MP2 (Second-order Møller-Plesset perturbation), CCSD (Coupled-cluster singles and doubles), CIS (configuration interaction singles) and TDDFT (time-dependent DFT) methods are briefly presented in following sections including an overview of QTAIM (quantum theory of atoms in molecules), NEDA (natural energy decomposition analysis), BLW (block localization wave function), NBO (Natural bond orbital) and few other important terms used in our works. Anyone wish to know about these quantum-chemical methods in detail can find in the following references.^{36, 38, 46-61}

2.1 Density Functional Theory (DFT)

The density functional theory (DFT) is derived from the theorem of Hohenberg and Kohn⁴⁶ which states that the ground-state molecular energy, wave function, and other molecular properties of a molecule can be determined by the ground-state electron probability density $\rho_0(x, y, z)$.⁴⁷

The electron density³⁸ is as follows –

$$\rho(\vec{r}) = N \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 ds_1 d\vec{x}_2 \dots d\vec{x}_N \quad 2.1$$

Where, $\rho(\vec{r})$ is the probability of finding any of the N electrons within the volume element $d\vec{r}_1$ and $\rho(\vec{r})$ is probability.

The complete ground state energy is defined as –

$$E_0[\rho_0] = T[\rho_0] + E_{ee}[\rho_0] + E_{Ne}[\rho_0] \quad 2.2$$

$E_{Ne}[\rho_0]$ is the potential energy due to the nuclei-electron attraction which is dependent on the actual system and the combination of other two independent terms is known as Hohenberg-Kohn functional.³⁸ HK functional is the sum of the kinetic energy and the electron-electron repulsion operator with the ground state wave function Ψ connected with the density ρ .³⁸ The HK functional is the goal of density functional theory albeit it fails to provide solution for E_0 . In case of Kohn-Sham (KS) theory, its exchange-correlation potential is unknown. However, with few approximations like local density approximation (LDA), generalized gradient approximation (GGA), etc. it is able to give practical solution for E_0 . The reader can refer to the references³⁶⁻³⁸ for details on DFT.

2.2 Second-order Møller–Plesset perturbation theory (MP2)

It is one of the quantum chemistry post-Hartree-Fock (HF) ab initio methods that improve Hartree-Fock wavefunction by considering electron correlation effects. When this improvement is made up to second order, it is called second-order Møller–Plesset (MP2) perturbation theory.⁴⁷ This perturbation theory is a special case of Rayleigh–Schrödinger perturbation theory. If the molecular energy is taken as $E^{(0)} + E^{(1)} + E^{(2)} = E_{HF} + E^{(2)}$, the calculation is designated as MP2.^{47, 48} The detailed information can be found in the following references.^{36,38,47,48}

2.3 The Coupled-cluster singles and doubles (CCSD) method

In 1958, Coester and Kummel introduced the Coupled-cluster (CC) method. It becomes one of the most prevalent methods in quantum chemistry now-a-days that considers electronic correlations for a systems of interacting particles.^{47, 49} The fundamental of CC theory is

$$\psi = e^{\hat{T}} \phi_0 \quad 2.3$$

Where, Ψ is the exact non-relativistic ground-state molecular electronic wave function, Φ_0 is the normalized ground-state HF wave function and the operator $e^{\hat{T}}$ is defined as follows–

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \dots = \sum_{k=0}^{\infty} \frac{\hat{T}^k}{k!} \quad 2.4$$

$\hat{T}$ is the cluster operator which is given by –

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n \quad 2.5$$

Where n is the number of electrons in the molecule and the operators $\hat{T}_1, \hat{T}_2, \dots$ are one particle, two particle, ... excitation operators, respectively. When CC includes both single and double excitation operators, it is called CCSD. Additional information can be found in any standard computational chemistry book.^{36,38}

2.4 Configuration Interaction Singles (CIS)

Configuration interaction (CI)⁵⁰⁻⁵⁴ is a post-Hartree-Fock linear variational method. Configuration mathematically refers to the linear combination of Slater determinants for wave functions whereas interaction means the mixing of different electronic states (configurations). CI is actually expressed as a linear combination of configuration state functions (CSF) built from spin orbitals. When the CI space is occupied with every possible CSF, it is called “full CI”. Configuration interaction singles (CIS) restricts CI space to Hartree-Fock self-consistent-field for single substitution of orbital only; i.e., one spin orbital is swapped with virtual orbital of the Hartree-Fock determinant. Thus, the CIS excitation state cannot well correlate with the ground state. But CIS is still broadly applicable method for describing electron correlation, as it needs comparatively less computational resources.

2.5 Time-Dependent Density Functional Theory (TDDFT)

TDDFT^{55, 56} can be called an extension of density functional theory (DFT) as it extends the basic idea of ground state DFT to deal with time-dependent phenomena. It is formalized from the Runge-Gross (RG) theorem⁵⁷ and the time-dependent Hohenberg-Kohn (HK) theorem⁵⁸ and there is no general minimization principle in time-dependent quantum mechanics. It deals with time-dependent density to investigate the properties and dynamics of many-body systems in the presence of time-dependent potentials, such as electric or magnetic fields. The most popular application of TDDFT is in the calculation of the energies of excited states, frequency-dependent response properties, and photo absorption spectra of isolated systems. The details on this method are available in the following references.^{36-38,55-56}

2.6 Quantum Theory of Atoms in Molecules (QTAIM)

Quantum theory of atoms in molecules (QTAIM)^{59, 60} provides a quantum mechanical description of an atom in a molecule. It can naturally define and describe a molecular structure based on topology of electron density. It reveals the molecular structure through network of gradient paths of electron density connecting the stationary points. Each of these stationary points are QTAIM atoms defined as proper open system that able to share energy and localized electron density in three dimensional space. They are bounded by surface having zero flux in the gradient vector field of electron density and chemical bonds are defined with the presence of bond path connecting two stationary points of electron density and its associated virial path.⁶¹ QTAIM calculates certain physical properties of a system by dividing the space into atomic volumes having single nucleus or local attractor of electron density. This model is broadly accepted for a wide range of applications due to its ability to describe certain factors which was hardly handled by other methods before.

The post HF methods, such as MP2 or CCSD can calculate the properties of small molecules (up to 40 electrons) with sufficient accuracy but for the many electrons models, significant error can be introduced due to computational expense of full realistic-inclusive models. The computational accuracy of post HF methods: HF < MP2 ~ MP3 ~ CCD < CISD < CCSD < MP4 < CCSD(T).^{36,38} Larger molecules can be computationally tractable by DFT

which is the expression of total one-electron density rather than the wavefunction. Thus, it can very accurately calculate the properties of the molecules at the little computational expense.³⁶⁻³⁸ TDDFT is the extension of DFT which deals with the time-dependent density to calculate the properties and dynamics of many body systems.^{55,56} On the other hand, QTAIM models demonstrates the chemically useful concepts such as atoms in molecules, functional groups, bonding etc. that are related to the topology of the observable charge density distribution measured from a quantum mechanical wavefunction.^{59,60}

2.7 Potential Energy Surface (PES)

Potential energy surface represents how the energy of a molecular system changes with the small change in bond length, bond angle or dihedral angle.⁶² It is defined by the certain number of independent coordinates which can be obtained by subtracting six from three times of the number of nuclei (N) in the molecule. The electronic energy is a function of these coordinate which ultimately generates the potential energy surface for the molecule.⁴⁷ The minima and saddle points on the potential energy surface indicate the minimum structures and transition states respectively. Different minima may obtain which indicates the different conformations or structural isomers.

2.8 Basis Set Superposition Error (BSSE)

In quantum chemistry, calculations of molecular properties include errors due to using finite basis sets. This error is known as Basis Set Superposition Error (BSSE). Assume a system where A and B react and yield the product AB. The equation which determines the interaction energy is given bellow-

$$E_{\text{interaction}} = E(\text{AB}) - E(\text{A}) - E(\text{B}) \quad 2.6$$

According to this equation, while using finite basis sets for A, B and AB the interaction energy will be underestimated due to basis set superposition error. The reason is that when basis sets using for the A and B fragments, their molecular orbitals can be expanded only through the space created by those individual basis sets only whereas in case of AB, basis sets overlap i.e., molecular orbitals will expand through the space formed by both basis sets

and ultimately they compensate the incompleteness of the basis functions themselves. If α and β are the basis sets using for A and B fragments, the equation 2.6 becomes –

$$E_{\text{interaction}} = E_{AB}^{\alpha\cup\beta}(AB) - E_A^{\alpha}(A) - E_B^{\beta}(B) \quad 2.7$$

Where, $E_X^Y(Z)$ defines the energy of Z using the Y basis set in X geometry. So, energy calculated for AB will be treated better than each of the monomers, thus, calculated energies for A, B will be overestimated due to the finite basis set and an error will be associated with the calculated interaction energy using the equation 2.6 which is called BSSE. Usually, this is a positive term and offers a significant corrections in case of weakly bonded molecules, such as H-bonded complex. So, we can write the equation 2.7 as–

$$\delta E_{A,B}^{\text{BSSE}} = E_A^{\alpha}(A) - E_A^{\alpha\cup\beta}(A) + E_B^{\beta}(B) - E_B^{\alpha\cup\beta}(B) \quad 2.8$$

Then the corrected interaction energy will be as bellow–

$$E_{\text{corrected interaction}} = E_{\text{interaction}} + \delta E_{A,B}^{\text{BSSE}} \quad 2.9$$

Putting the value from the equation 2.9, the corrected interaction energy will be–

$$E_{\text{corrected interaction}} = E_{AB}^{\alpha\cup\beta}(AB) - E_A^{\alpha\cup\beta}(A) - E_B^{\alpha\cup\beta}(B) \quad 2.10$$

To eliminate the BSSE, an obvious solution is using infinite or large basis set which is not feasible most of the cases. An alternative solution is to apply counterpoise method.

2.9 Counterpoise Method (CP)

Counter poise method is a posterior approach introduced by Boys and Bernardi to eliminate the error introduced by BSSE.^{63, 64} In this method, all calculations are re-performed using the mixed basis sets using the ghost orbitals.

$$\delta E^{\text{BSSE}}(A,B) = \begin{array}{c} \text{A} \\ \text{E}^{\alpha}(A) \end{array} - \begin{array}{c} \text{B} \quad \text{A} \\ \text{E}^{\alpha\cup\beta}(A) \end{array} + \begin{array}{c} \text{B} \\ \text{E}^{\beta}(B) \end{array} - \begin{array}{c} \text{B} \quad \text{A} \\ \text{E}^{\alpha\cup\beta}(B) \end{array}$$

It means that in the procedure of energy calculation for A, the basis functions for B are placed

on its centre which is considered having no electrons and nuclear charge. Then the orbital is called ghost orbital and the atom B is considered as ghost atom as well. Finally, the counterpoise energy is added to the interaction energy estimated with finite basis sets like the equation 2.9 to get the correct interaction energy.

$$E_{\text{interaction}}^{\text{CP}}(\text{AB}) = E_{\text{AB}}^{\alpha\beta}(\text{AB}) + \delta E_{\text{AB}}^{\text{BSSE}} \quad 2.11$$

2.10 Natural Bond Orbital (NBO)

Natural bond orbitals can be said as estimated localized orbitals having highest electron density in atoms or in bonds as the orbital details such as polarization coefficients, atomic hybrid compositions are chosen mathematically. NBO is one of the intermediate steps in between the transformation from atomic orbitals to canonical molecular orbitals (AOs→NAOs→NHOs→NBOs→NLMOs→MOs).⁶⁵⁻⁶⁸

The optimal condensation of occupancies in natural localized orbitals leads to division into two types of molecular orbitals with highest and lowest electron occupancies. The NBOs with highest electron density are called bonding NBOs which provide most accurate possible natural Lewis structure and similarly the lowest unoccupied NBOs are called anti-bonding orbital which is of “non-Lewis structure” types. Both types of NBOs fill the total NBO valence span. If c_A , c_B are the respective polarization coefficients for A, B and h_A , h_B are natural hybrid orbitals on atom A, B form the bonding NBO orbital and σ_{AB} and anti-bonding NBO σ_{AB}^* in the following way–

$$\sigma_{AB} = c_A h_A + c_B h_B \quad 2.12$$

$$\sigma_{AB}^* = c_A h_A - c_B h_B \quad 2.13$$

c_A , c_B are chosen in such a way that they can vary from covalent ($c_A = c_B$) to ionic ($c_A \gg c_B$). The donor and acceptor NBOs interactions ($\sigma_{AB} \rightarrow \sigma_{AB}^*$) defines the stabilization energy in a molecule. According to the 2nd order perturbation theory, the stabilization energy for $\sigma_i \rightarrow \sigma_j^*$ interaction is as follows–

$$\Delta E_{i \rightarrow j}^{(2)} = -2 \frac{\langle \sigma_i | \hat{F} | \sigma_j^* \rangle^2}{\epsilon_{j^*} - \epsilon_i} \quad 2.14$$

Where, $\hat{F}$ is the Fock operator and $\varepsilon_i = \langle \sigma_i | \hat{F} | \sigma_i \rangle$ and $\varepsilon_j^* = \langle \sigma_j^* | \hat{F} | \sigma_j^* \rangle$ are the donor and acceptor orbital energies, respectively.

2.11 Steric Analysis

Steric effect^{69, 70} is one of the most pronounced terms especially in case of chemical reaction, molecular structure and its dynamics, but still it remains a controversial topic. According to the DFT based energy partitioning scheme, steric analysis can be presented as–

$$E_s[\rho] \equiv E[\rho] - E_e[\rho] - E_q[\rho] \quad 2.15$$

Where, $E[\rho]$ is total electronic energy density functional of an atom and molecular system. $E_e[\rho]$ and $E_q[\rho]$ represent electrostatic and quantum effect, respectively. So, steric contribution can be defined as the total energy of state without considering the contribution of electrostatic and quantum effect. It is repulsive terms and does not depend on other terms.

2.12 Natural Energy Decomposition Analysis (NEDA)

NEDA is an energy partitioning scheme introduced by Eric D. Glendening and Andrew Streitwieser in 1994. The partitioning of self-consistent field energies is essential to get an idea about the nature of molecular interactions and also to build the empirical potentials for molecular simulation.⁷¹ The familiar Kitaura and Morokuma (KM) method has been widely used for more than two decades which is susceptible to serious violation of Pauli Exclusion Principle. According to KM methods, SCF interaction is partitioned into five components: electrostatic (ES) associated with permanent dipoles, polarization (PL) for interaction of induced dipoles, charge transfer (CT) due to delocalization of electron density from occupied orbitals into vacant orbitals, exchange (EX) arisen from anti-symmetry of the wave function and lastly coupling term (MIX) to balance the difference between the total interaction energy and the sum of the above mentioned four terms. But violation of Pauli Exclusion Principle by the ES and PL components of KM scheme, NEDA energy decomposition scheme was proposed using NBO approach as its basis. It divides the SCF interaction fields into only three components: Electrostatic (ES), Charge transfer (CT) and Deformation (DEF)

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components. The interaction energy is normally defined in terms of wavefunction of complex and each fragment as–

$$\Delta E = E(\bar{\Psi}_{AB}) - E(\bar{\Psi}_A) - E(\bar{\Psi}_B) \quad 2.16$$

According to NEDA,

$$CT = E(\bar{\Psi}_{AB}) - E(\bar{\Psi}_{AB}^{loc}) = E(\bar{\Psi}_{AB}) - A(\bar{\Psi}_A^{def}, \bar{\Psi}_B^{def}) \quad 2.17$$

Where, $\bar{\Psi}_A^{def}$ and $\bar{\Psi}_B^{def}$ are localized, mutually orthogonal wave functions and $\bar{\Psi}_{AB}^{loc}$ is the anti-symmetric product of these two.

$$ES = E(\bar{\Psi}_{AB}^{loc}) - E(\bar{\Psi}_A^{def}) - E(\bar{\Psi}_B^{def}) \quad 2.18$$

and

$$DEF = E(\bar{\Psi}_A^{def}) - E(\bar{\Psi}_A) + E(\bar{\Psi}_B^{def}) - E(\bar{\Psi}_B) \quad 2.19$$

Finally the NEDA, decomposition scheme becomes–

$$\Delta E = CT + ES + DEF + BSSE \quad 2.20$$

Scheme 2.1 NEDA

The scheme2.1 shows the schematic representation of NEDA for AB complex. At first each fragment A and B distort a little bit to keep their wave functions orthogonal at equilibrium separation. This deformation stage is destabilizing which rises to repulsive DEF components. Then, these two distorted fragments approach to each other by classical electrostatic interaction and inter-fragment exchange effect which leads to ES components. Lastly, CT component stabilizes AB complex by delocalization of fragment wave function over the whole complex.⁷¹

2.13 Block localization Wave Function (BLW)

BLW method⁷²⁻⁷⁹ offers a convenient and cost effective means to study the localized, valence bond like, electronic structures. To do that, it probes the delocalization nature of molecular orbitals in HF level of theory. The localized orbitals which are derived from unitary transformation of canonical orbitals cannot be said localized straightforwardly as they have both the orthogonalization and delocalization tails. In BLW, both are avoided by restricting the expansion space of molecular orbitals as they have the contribution in delocalization of electron and so, no longer be appropriate for describing the diabatic potential energy surfaces. If we make subgroups for all electrons and basis functions $\chi_{a\mu}$, $\mu = 1, 2, 3, \dots, m_a$ for individual unique form of Lewis structures and consider each subgroup is a closed shell, we can write the total number of primitive basis functions, M and total number of electrons, N as–

$$M = \sum_{a=1}^k m_a \quad \text{and} \quad N = \sum_{a=1}^k n_a \quad 2.21$$

Where, a represents the a^{th} subgroup and m_a , n_a are the basis functions and electrons, respectively. The molecular orbitals belonging in a subgroup can be expressed in a linear combination of primitive basis functions.

Using block localized orbitals in KS-DFT procedure, the BLW method has been extended to the DFT level also. This method involves several steps like, calculation of DFT energy from the DFT Fock matrix, constructing effective Fock and overlap matrix for each subgroup/block, forming the new coefficient and density matrix by solving generalized secular equations, following the all above mentioned steps if not converge.

Chapter 3

Literature Review

3.1 Introduction

There is a rapidly growing interest in the realm of silicon (Si) and germanium (Ge) chemistry due to their unparalleled properties and for their diverse applications. Especially Si is ubiquitously present in microelectronics as semiconducting material. Despite of huge research, still the surface chemistry of Si and Ge is not fully understood.^{80, 81} Their photophysical properties are markedly different from their carbon analogues and this generates immense interest in optoelectronics field.³⁰

A π -conjugated molecule shows good multi photon absorption properties if it possesses small band gap. The movement of hole and π -electron through the repeated units generates the conducting properties in π -conjugated organic molecules. Over inorganic semiconductors, organic semiconductor molecules have some advantages like low cost, easy fabrication, mechanical flexibility, easy colour tuning and so on. Based on aromatic precursor, different classes of photonic molecules are formed such as pyrrole, benzene, aniline, thiophene based photonic molecules. π -Conjugated molecules or polymer and fused ring system can be used as precursor also. There are also a huge number of synthesized polymers with different type of alkyl chains. The fascinating reactions of Si and Ge with different organic molecules are of contemporary research interest due to their incredible diversity.⁸⁰ In this chapter, we provide a brief review on both experimental and theoretical works covering the electronic and optical properties of Si/Ge based compounds including their π -conjugated heterocyclic systems.

3.2 Historical Background

That was 1949, when one of the most important and potential polymers, polydimethylsiloxane $[\text{CH}_3[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Si}(\text{CH}_3)_3]$ (PDMS) (see Figure 3.1) as solid was synthesized which is afterwards used as SiC ceramic precursors, photoresist materials and photo initiator for vinyl polymerization.⁸² The delocalization of σ -electrons along Si backbones induces special characteristics like intense near-UV absorptions, electroluminescence, photoluminescence and semiconducting properties in polysilanes. Most of the cases, for applications, polysilanes were grafted with alkyl-aryl chains, siloxane or methoxy units to increase the molecular weight as high molecular weight helps uniform thin film formation. Broad interest is drawn to polysilanes because of its application for LED due to its 30% quantum efficiency of photoluminescence with sufficient hole mobility of $10^{-4} \text{ cm}^2/\text{V.s.}$ ⁸²

Figure 3.1 The chemical structures of polydimethylsiloxane (PDMS) and Polysilanes.

Five-member cyclic structure of silole (see Figure 3.2) then attracted the attention due to its comparative lower LUMO level than those of cyclopentadiene and of other heterocyclopentadienes, like pyrrole, furan or thiophene. In 1959, Braye and Hubel first synthesized 1,1,2,3,4,5-hexaphenylsilole and extensively studied their reactivity and properties.^{83, 84} Later, Atwell group synthesized 1,1-dimethyl-2,5-diphenyl- and 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene radical anions and dianions in 1967 and in 1981, O'Brien and Breeden synthesized tetraanion of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene.^{32, 33} The aromaticity of anion and cation of silole derivatives triggered immense research on this field. Since then chemistry of silole has been developed significantly. The inherent σ - π conjugation in siloles that comes from the interaction between σ -orbital of two exocyclic σ -bond on Si atom and π -orbital of butadiene lowers their LUMO level.⁸⁵ This low-lying LUMO level induces unique photo-electronic properties in silole and

makes a very promising molecule for electroluminescence devices and fluorescent chemosensor for explosives and organic solvent vapours.^{85, 86}

Figure 3.2 The chemical structures of siloles.

The elusive nature of disilenes and other doubly bonded compounds of heavier group-14 elements has stimulated a large scale of research works both experimental and theoretical studies to explore their various aspects, especially for their exceptional reactivity and promising application as novel reagents for organic synthesis.⁸⁷ The earliest successful attempt to isolate thermally stable compounds having Si=Si double bond (disilene) was claimed by Robert Westin 1981.⁸⁸ In the same year, Brook and co-workers successfully synthesized first stable silene having Si=C bond.⁸⁹ Subsequently, Trinquier and Malrieu theoretically studied the conjugation between Si=Si and Si=C π -bonds in 1- silabutadiene and 2- silabutadiene.⁹⁰ They concluded that 2-silabutadiene is more stable than 1-sila butadiene by 6 kcal/mol due to both larger π -conjugation and σ -substitution.⁹⁰ However, this was totally opposed by Farnandez et al. The authors suggested that polarization of π -bond in Si=C is the reason for higher π -conjugation energy in trans 1-silabutadiene (24.8 kcal/mol) over trans 2-silabutadiene (12 kcal/mol).⁹¹ The first stable cyclic disilene i.e. tetra-silacyclobutene was isolated by Kira et al. in 1996.⁹² They reported that the bond length of Si=Si is 2.174Å and the longest Si-Si bond length is 2.450Å. They remarked that the steric repulsion could be the reason of this unusual longer bond length. He also found with X-ray crystallography that the four-member ring is not planar and it adopts trans-bent structure with 13.2° bend angle around Si-Si double bond.⁹² In 1997 Weidenbruch and co-workers synthesized the first stable tetra-silabuta 1, 3-diene. This crystalline molecule possesses C_2 symmetry with 51° SiSiSiSi dihedral angle, 2.175Å Si=Si and 2.321Å Si-Si bond lengths. They remarked that the conjugation between two double bonds exists even in solution.

Allenes are more reactive than most of other alkenes. Former is considered as useful building blocks of organometallic chemistry.^{93, 94} Heavier groups 14 analogues of allene possess rich chemical properties and have fascinating applications in different domains. After West et al. successfully synthesized 1-silaallene in 1993⁹⁵, heavier group 14 analogues of allene, silaallenes^{95, 96}, germaallenes^{97, 98} and tristannaallene⁹⁹, have attracted much attention from experimental and theoretical chemists. In 2005, Kira et al. synthesized the first trimetalaallene containing Ge=Si double bonds: 1,3-digermasilaallene¹⁰⁰ (see Figure 3.3, 1). It has a C_2 axis through the central atom with two Ge=Si double bond of length 2.269 Å and the distance between the two terminal Ge atoms is 4.039 Å. In the same year, they synthesized another heteronuclear trimetalaallene, 2-germadisilaallene¹⁰¹ (see Figure 3.3, 2). The Ge=Si double bond length in it is 2.237 Å, the distance between two terminal Si atoms is 4.093 Å and the $\angle\text{SiGeSi}$ bond angle is 132.4° .

Figure 3.3 Structures of synthesized germasilaallenes **1** and **2**.

In contrast to normal allene ($\text{H}_2\text{C}=\text{C}=\text{CH}_2$) having linear skeleton, the synthesized heavy allenes are bent at central metal atom and pyramided at terminal metal atoms, e.g., 1-silaallene and 1-germaallene are bent with an angle of 173.5° ⁹⁵ and 159.2° ,¹⁰² respectively, and trisilaallene and trigermaallene have remarkably bend structures with a bond angle of 136.5° ¹⁰³ and 122.6° ¹⁰⁰ respectively. Apeloig et al.¹⁰⁴ found that although the highly bend trimetalallenes are similar to the corresponding cyclic trisilacyclopylidene in geometry; the nature of their chemical bonding is different. The origin of highly bend skeleton of trimetalallenes was described by Kira et al.¹⁰⁵ and Frenking et al.¹⁰⁶ Very recently Sarmah et al.¹⁰⁷ also studied similar compounds as Frenking et al.¹⁰⁶ for Si(0) and Ge(0) compounds stabilized by different silylenes and germylenes.

3.3 Theoretical and experimental works on Si/Ge based π -conjugated system

Significant attempts were expended to synthesize stable silenes. From then, the molecules having C and Si were considered as “elusive”. Successful isolation of silene as crystalline has been triggered for several research works both theoretically and experimentally to investigate their structures and electronic properties. Including heteroatom into a π -conjugated organic molecule changes the molecular polarity as well as photo-electronic properties. As a result, the excitation energy lowers resulting in large multi-photon absorption cross-section. For decades, heteroatom effect on electronic and structural parameters as well as photonic properties is being studied. In this section, a very brief description on Si/Ge based conjugated molecules is provided.

From NICS (nuclear independent chemical shifts) study in 1996, it was found that among various 4-heterosubstituted (CH_2 , O, S, PH, NH, BH, AlH, CH^- , SiH^- , SiH^+) triafulvenes, 4-sila triafulvene is quite unique due to intrinsically polarized Si^+-C^- (see Figure 3.4).¹⁰⁸

Figure 3.4 Plot of NICS (ppm) as a function of the aromatic stabilization energies (kcal/mol) for 5-membered ring heterocyclic, $\text{C}_4\text{H}_4\text{X}$ adapted from ref. 108.

Due to unusual high thermodynamic and kinetic stability, the below three molecules were undergone a serious research (see Figure 3.5). In 1997, the following five systems were studied mainly based on NICS by which cyclic conjugation was measured.¹⁰⁹

Figure 3.5 Structures of Si-substituted five member rings.

Their finding was that the silenes were strongly shielded (**1**. -11.9; **2**. -7.0; **5**.-10.5 ppm) when the ghost atom was placed in the centre of ring to measure the contribution of nearby σ -bonds. Still they possess appreciable amount of the ring current (though significantly less than that of benzene) if the ghost atom has been placed 2.0 Å above the ring. NICS(2) values for **1-5** are -2.7, -0.6,-2.9, -0.7 and -2.6 ppm, respectively where for benzene is -5.3ppm.¹⁰⁹

Figure 3.6 Investigation of 3- and 5-membered rings of 4-silatriafulvene systems (**6- 14**).

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In figure 3.6, it is observed that there is an appreciable change in structures depending on the position of Si atoms insertion into 3- or 5-membered rings.¹¹⁰ According to the aromaticity indices (in terms of ΣCC , NICS and bird index), the sequence is for 3-membered ring: **8** > **7** > **6** and for 5-membered ring: **14** > **10**, **11** > **9**, **12** > **8** > **6**, **13**. The barrier to planarity of **12** and **13** is smaller than that of **6** and it is also found that aromaticity of the planar form increases when the barrier height becomes larger. **14** has a unique structure for what it has highest aromaticity from its similar structure like **6**, **12** or **13**. In planar form, it is assumed that two π -systems have interaction. Naturally, when they are forced to be perpendicular to each other, it also can be assumed there is no interaction. Surprisingly, during twisting of Si-C of **14**, charge shifts from 3- to 5-membered rings intensifies aromaticity in both of the rings. In case of **10** and **11**, AlH_2 and SiH_3 substituents make an appreciable reduction of planarization barrier whereas **9** is found to be planar at its stable conformer and thus, its planar ground state has the lower aromaticity compare to **10** and **11**.¹¹⁰

Table 3.1 Calculated energy at MP2/6-311G* for silylene, silene and silane derivatives in a.u.

	1	2	3	4	5	6
a	-476.72283	-476.77208	-476.79896	-476.84345		
b	-476.74337	-476.75805	-476.76541	-476.77781	-476.78149	-476.79399
c	-476.72590	-476.73564	-476.77968	-476.80035		

Comparative study on terms of stability and aromaticity of silylenes, silenes and silanes derivatives (see in Table 3.1) was carried out theoretically by Tamaz Veszpremi et al.¹¹¹ They found that silylene derivatives are most aromatic and they concluded that aromaticity is not only the factor to interpret the stability of cyclic isomers. Geometry studies at MP2/6-311G*

revealed that heteroatom insertion, their relative position and shortening of bond length after introducing heteroatom, all have the influence on stabilization of ring structures. For diazasilole rings, favourable position for N atom is at alpha position from Si atom with imidazole form rather than pyrrole structure (nearest position of two N atoms is unfavourable). Table 3.1 shows that **a4**, **a3** are the most stable isomers, probably due to the stabilizing effect arisen from the interaction of neighbour N with Si atoms. The difference between N–H and Si–H bond strength might be the reason of comparatively high stability of group **a**.

It is established that the aromaticity associates with the stabilization which results in shortening of bond strength. The sum of the peripheral bond lengths ($\sum r$) and bond separation energies (ΔE_{des}) from isodesmic reactions were calculated (see in Table3.2) to get an idea about delocalization.¹¹¹ Isodesmic reaction scheme is as follows–

According to Table 3.2, silenes (**b**) are more stable than silylene (**a**) and silanes(**c**) though the aromaticity of **a** is more pronounced.¹¹¹

Table 3.2 Calculated bond length index and isodesmic reaction energies

		1	2	3	4	5	6
a	$\sum r$	7.745	7.725	7.709	7.661		
	ΔE_{des}		40.880		27.210		
b	$\sum r$	7.609	7.580	7.581	7.542	7.578	7.577
	ΔE_{des}	53.560	49.320	47.420	43.370	45.050	35.540
c	$\sum r$	7.817	7.769	7.708	7.669		
	ΔE_{des}	18.980	10.720	15.100	12.980		

It was believed that imidazole derivatives, electron deficient carbene can be stabilized by the attachment of a heteroatom to its divalent centre. But in 2006, a stable 3-membered highly strained ring was synthesized which proved its stability without any heteroatom.¹¹²

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Figure 3.7 Chemical structures of carbene and its silicon and germanium analogues.

Stabilizing effect among neighbouring N atoms and carbene centre makes **18**, the most stable isomer of all as shown in Figure 3.7.¹¹³ Generally, substituents effect, delocalization and aromaticity are the main three factors that influence the stability of carbenes. The isodesmic equations are used to measure net stabilization including π -electrons donation by N atoms, electrons delocalization and ring strain energies in carbene and its silicon and germanium analogues which are presented in Table 3.3.¹¹³

Table 3.3 Calculated energies for carbene and its silicon and germanium analogues

Ref.		ΔE (kcal/mol)					
		15	16	17	18	19	20
	ΔE_{stab}	42.98	46.74	00.00	21.48	35.80	56.61
	ΔE_{strain}	-64.51		-25.44			
	ΔE_{subs}	27.75		95.39			
	ΔE_{ring}	97.17		49.41			
		21	22	23	24	25	26
	ΔE_{stab}	53.52	47.75	00.00	31.06	43.66	80.80
	ΔE_{strain}	-38.73		-7.47			
	ΔE_{subs}	0.68		37.28			
	ΔE_{ring}	72.34		35.19			
		27	28	29	30	31	32
	ΔE_{stab}	48.69	47.42	00.00	25.58	41.47	75.10
	ΔE_{strain}	-38.04					
	ΔE_{subs}	2.01					
	ΔE_{ring}	67.51					

From Table 3.3, it is clear that stabilization energies fall from carbene to its germanium analogues which indicate the weaker π -conjugation and aromaticity in later two. Trends are similar among all the isomers for these three groups. Though 3-membered rings are less stable than their 5-membered rings by 43-54 kcal/mole, they are considerably stable kinetically. For all the cases, the divalent structures become most stable.¹¹³

Figure 3.8 Activation energy as a function of HUMO-LUMO gap (right) in **1-10** (X= Si or Ge; left) at B3LYP/6-311+G**, the graph taken from ref. 114.

Yong Wang investigated the H₂ splitting reaction with silylene (X=Si) or germynes (X=Ge) as this reaction correlates to the HOMO-LUMO or the singlet-triplet gaps.¹¹⁴ The activation energy for silylene and germayne is 4.82 and 14.68 kcal/mol respectively. HOMOs of silylene and germayne act as electron donor while H₂ acts as electron acceptor. They performed the same calculation for the N-heterocyclic silenes and germynes and obtained the HOMO-LUMO gap. From above graph (see Figure 3.8), it is found that 2- and 3-halo-substituted silylenes and germynes can have better performance.¹¹⁴

In 2009, a 4-membered Si-ring, 2,3-diphenyl-4-neopentyl-1-silacyclo-but-2-enes (**1-R**) had been synthesized from 1,1-dichlorosilacyclobutene (**1-Cl**) by Duanchao Yan et al. (see Figure 3.9).¹¹⁵ Depending on the substituents, synthesized **1-R** can have 8-23% fluorescence quantum efficiency in solid form. Thus, the derivatives of **1-R** can be expected to have the potentiality of chromophores for condensed-phase luminescence applications.¹¹⁵

Figure 3.9 Synthesis of a series of **1-R** molecules from **1-Cl**, adapted from ref. 115.

Maximum absorption wave length is 287.9 nm with 0.33 oscillator strength for **1-ph** (R= phenyl) in ethanol (EtOH) solution while it red shifted to 294.0 nm as nano-aggregates in water-EtOH solution. In solid states, it has higher value than the above two cases. For **1-Et** (R= ethyl) derivatives, **1-R** emits fluorescence in blue-green region with 21.0% quantum efficiency in their solid states. The authors also suggested that the optical properties of **1-R** can be well tuned by crystal engineering like using bulkier substituents for their enhanced performance.¹¹⁵

Figure 3.10 Synthesis of novel monomeric chlorosilylene, adapted from ref. 116.

In 2006, a stable monomeric chlorosilylene was synthesized and characterized by Oswald and co-workers.¹¹⁶ It is claimed to be the first stable system at room temperature with Si–Cl bond and expected for potential use as functionalized silylene in metathesis reaction. According to the reaction mentioned in Figure 3.10, it was isolated as solid crystal and afterwards, it was characterized as stable system in solution as diethyl ether, toluene and in an inert atmosphere at room temperature.¹¹⁶

Figure 3.11 Contour plots for two molecular orbitals represents phase of wavefunction, taken from ref. 116.

The amidinate ligand bonded to Si centre leads a trigonal pyramidal geometry with the sum of the bond angle 260.73° at Si.¹¹⁶ The bonding situation among the four member ring is quite unique. C–N bond is formed with their hybrids orbitals whereas Si–N bond is formed from predominant interactions between s orbital of Si and p orbital of N. The dominant p character of the orbitals is involved in Si–Cl bond due to overlapping of p orbitals of both Si and Cl and thus, the systems is strongly delocalized (see Figure 3.11).¹¹⁶

Figure 3.12 Chemical structure of didehydro-1, 3-silapiperazine (a) and its structural conformers (b and D).

First stable six-member ring germylene¹¹⁷ was isolated in 2006 by C. van Wüllen and co-workers. In the same year, the isolation of a new type of N-heterocyclic silylene, didehydro-1,3-silapiperazine derivative (**a** in Figure 3.12)¹¹⁸ was also reported. Subsequently, **a** and its structural conformers (**b**) and (**D**) were theoretically studied by Kinga Nyiri and Tamas Veszpremi to get insight into the electronic structure and the stability of **a**.¹¹⁹ They calculated relative energy of **a** with respect to **b** (3.40 kcal/mole) at B3LYP/cc-pVTZ level. It indicates to the fact that **b** is more stable structure than **a**. NICS values of **a**, **b** and **D** are 3.9, -8.6 and -10.3 referring that **D** gains more aromaticity from its structure and the aromaticity makes it the most stable structure among all.

Figure 3.13 shows the Kohn-Sham orbital-correlation diagram of **b** and **D**, formation from their parent molecules. **D** and **b** include an ethylene and butadiene units and so, there must have an additional π -orbital in **b**. But this additional orbital has almost same energy, -7.56 eV compared to the ethylene π -orbital. So, the conjugation between the two double bond of butadiene has no effect on the structure. They are diminished and the endocyclic double bond is combined to the π -system and C=C bond acts just like a weakly conjugated vinyl group.¹¹⁹

Figure 3.13 MO correlation diagram of **b** and **D**, adapted from ref.119.

In 2010, another important six-member ring, amidinato supported 1,4-disilanenene had been synthesized (see Figure 3.14) which has interestingly planar structure with six π -electrons.¹²⁰ The four-member amidinato rings are just perpendicular to six-member ring having a Si-Si bond length of 1.8Å which is less than standard single bond length (1.86Å - 1.93Å) but longer than that of double bond(1.76Å). Its nucleus independent chemical shift (NICS) at 1Å above the ring centre is -3.64 which refers to its aromatic nature.

Figure 3.14 Preparation of amidinato supported 1,4-disilabenzene, adapted from ref. 120.

Another Si-Ge based four-member ring; an amidinate-stabilized germatrisilacyclobutadiene was synthesized in 2012 by C.-W. So et al. (see Figure 3.15)¹²¹ They have ylide structures with central puckered Si₃Ge four-member rings. The authors remarked that both structures in Figure 3.15 are not antiaromatic and are stabilized by amidinate ligands and strong delocalization of central four-member ring.¹²¹

Figure 3.15 Chemical structure of amidinate-stabilized germatrisilacyclobutadiene.

3.4 Theoretical design of molecular photonics materials

One of the astounding inventions of Albert Einstein is to define the photo electronic effect. According to him, a photon when gaining the energy more than a particular threshold frequency corresponding to the ionization energy of a certain atom can ionize that atom. Without this threshold energy, an atom may be ionized, explained theoretically by Maria Goppert Mayer in 1931.¹²² She explained that an atom may absorb more than one photons simultaneously that allow an electron transition to a state which is unreachable with single photon absorption and it was verified experimentally after thirty years of invention of laser. Generally absorption of single photon leads a grounds state s-electron to move to p-state, again absorption of a photon just after the first one may lead to transition to another s- or d-state and simultaneous interaction of third photon with atom may ionize that atom.

Multi-photon absorption is a non-linear optical (NLO) process as its quadratic dependency on light intensity. It can be defined as a simultaneous process of absorption of two or three photons via one or two virtual states (see Figure 3.16) in such a way that the sum of photon energies with identical or different frequency are equal to the energy that switch one atom or molecule from ground state to higher energy electronic state. In nature, multi-photon absorption process is strongly correlated to the excited states. It strongly influences the intrinsic electronic structures parameter, i.e., band gap of conjugated organic molecules.

Figure 3.16 Multi-photon absorption processes via one or two virtual states.

On the aim of reducing band gap, inserting heteroatom, extending π -bond length, introducing donor-acceptor groups, polarization of ground state and molecular dimensionality can be good ways to increase delocalization of π -electrons which leads to increase of multi-photon absorption-emission cross section. There are some other factors for higher multi-photon absorption cross section like vibronic coupling, aggregation, etc.

3.4.1 Effect of donor-acceptor substitution into π -conjugated system

Donor-acceptor substitutions greatly influence the multi-photon absorption properties of π -conjugated molecules by intensifying the charge mobility. Increased charge transfer rate leads to large transition dipole moments and low excitation energies which ultimately result in large multi-photon absorption cross section.¹¹

Scheme 3.1

In **3** and **4**, additional CF_3 functional groups are introduced which act as stronger electron withdrawing groups. As a result, transition dipole moment is increased from intermediate states and allowed to go to excited states (see dipole moment given in Table 3.4). We see that the enhancement of 2PA cross section is more articulate than that of 3PA cross-section with the increase of the strength of donor-acceptors.

Table 3.4 Excitation energies, dipole moments, 2- and 3-PA cross-section for molecules 1-4 at INDO/MRDCI level of theory.¹¹

Molecules	1	2	3	4
E_{ge} (eV)	2.64	2.58	2.55	2.49
E_{ge}' (eV)	3.11	3.02	3.01	2.90
μ_{ge} (D)	13.5	15.5	13.9	15.7
μ_{ge}' (D)	10.1	12.2	12.9	14.1
3-state σ_2 (GM)	793.0	1454.0	1384.0	1996.0
Convverged σ_2 (GM)	773.0	1334.0	1310.0	1881.0
Expt σ_2 (GM)	2400.0	4200.0	3600.0	5000.0

The substituent's effect on electronic structures and properties, on intramolecular proton transfer of the substituted derivatives at ground and excited states, on absorption and on fluorescence–phosphorescence spectra can be explained in terms of ionization potential (IP) and electron affinity (EA).¹²³ These two parameters are very important for property analysis of organic dyes used in organic light-emitting diode (OLED). The materials using as OLED should have small IP and large EA.

$$IP = E(M^+) - E(M^0) \text{ and } EA = E(M^0) - E(M^-)$$

Where, $E(M^0)$, $E(M^+)$ and $E(M^-)$ refer to the total energy of neutral, catatonic and anionic form of molecule and its substituted derivatives. Consider a molecule, 2-(2-hydroxyphenyl)-5-phenyl-1,3,4-oxadiazole (HOXD) with its enol and keto form (see Figure 3.17). Substituent can be considered with Hammett σ_{para} constant (δp) which is varied from -0.37 (OH) to 0.66 (CN) along strong electron donor to strong electron acceptor.¹²³

Figure 3.17 Enol & keto forms of 2-(2-hydroxyphenyl)-5-phenyl-1,3,4-oxadiazole (HOXD).

Different electron donating or withdrawing groups for HOXD changes the electronic structures and properties for its derivatives. From Figure 3.18, it is clear that IP and EA both increase with the ability of electron withdrawing groups and EA is more appropriate as its slope is higher. Electron withdrawing group is more favourable for decrease of IP and EA. There is a linear relationship of IP and EA with δ_p which means substituent effect can be qualitatively analysed. HOXD remains at enol form at ground state, and upon photo excitation process, HOXD reaches its enol to keto form at excited state. Then by fluorescence emission it returns to its ground state. Finally, the proton moves back to ground state in thermal processes.¹²³

Figure 3.18 IP and EA vs δ_p for HOXD at B3LYP/6-31+G(d,p) at left and absorption(λ_{abs}), fluorescence(λ_{fl}) and phosphorescence(λ_{ph}) vs δ_p at TD-B3LYP/6-31+G(d,p) at right, taken from ref. 123.

Substituent effect on fluorescence wavelength is much stronger than that of absorption and phosphorescence spectra (see Figure 3.18; right). All are linearly increasing with the growing ability of electron withdrawing groups. Slope for all three are positive indicating that the high electron withdrawing ability of substituent increases the bathochromic shift.¹²³

Figure 3.19 Near-infrared chromophores **5 a, b** and **6 a, b**.

In 2009, Min Luo et al. successfully designed and synthesized an organic polymer (**5** and **6**, see Figure 3.19) which has quite good conducting properties.¹²⁴ Before fusing thiadiazole units into **5a,b** or **6a,b** (where Ar = ph), they have the band gap of 3.30 and 3.20 eV, after fusing, they become 2.30 and 2.20 eV respectively. The optical and electrochemical properties of **5** and **6** is as follows -

Table 3.5 Optical and electrochemical properties with band gap of chromophores¹²⁴

Polymer	$\lambda_{\text{max}}^{\text{abs}}$	$\lambda_{\text{max}}^{\text{abs}}$	$\lambda_{\text{max}}^{\text{abs}}$	$\lambda_{\text{max}}^{\text{PL}}$	Stokes shift	$\Delta E_{\text{HOMO-LUMO}}$	Band gap	
	nm ^a	nm ^b	nm ^c	nm ^a			E ^d	E ^e _{opt}
5a	932,665	971,685	1035,713	1250	318	4.97	0.97	1.01
5b	1003	1040,702	1054,711	1290	287	5.15	0.71	0.97
6a	746	772	798	1035	279	5.00	1.27	1.40
6b	844	864	856	1100	256	5.08	1.22	1.24

^ameasured in toluene, ^bmeasured as a film, ^cmeasured with PCBM doped film, ^dfrom electrochemical data, E(HOMO)=- (E_{ox}+4.44)eV, E(LUMO)=- (E_{red}+4.44)eV, ^eOptical band gap(op)=1240/ $\lambda_{\text{abs}}^{\text{onset}}$ eV

3.4.2 Effect of extending π -conjugated length under different architectures of polymer backbones

Scheme 3.2

Longer π -conjugation length causes π -electrons to be more delocalized and the delocalized electron cloud in a conjugated molecule lowers the excitation energies.¹¹ This ultimately results in larger multi-photon absorption cross-section. It can be easily proved by comparing two molecules to each other. Molecules **2** and **4** are designed by an addition of one heterocycle-vinylene unit with the structure of **1** and **2**, respectively (see Scheme 3.2).

Table 3.6 Excitation energies, dipole moments, 2- and 3-PA cross-section for molecules **1-4** at INDO/MRDCI level of theory.

Molecules	1	2	3	4
E_{ge} (eV)	3.41	3.08	3.37	3.04
E_{ge}' (eV)	5.20	4.73	4.94	4.42
μ_{ge} (D)	11.30	13.60	10.20	12.20
μ_{ge}' (D)	19.10	23.60	20.20	22.80
σ_2 (GM)	9471	22453	6104	10031

From Table 3.6, it is clear that how π -conjugation length influences the multi-photon absorption properties. 2PA cross-section is highly enhanced from **1** to **2** and **3** to **4**. The root

cause will be the detuning energies and larger transition dipole moment due to extend π -conjugation length. There is a power law dependence of multi-photon absorption properties on π -conjugation length with exponent of 2.6 for 2PA and 5.6 for 3PA respectively.¹¹ Two phenylene-vinylene groups were added on each side of the fluorenyl ring of **5**, **6**, **7** in order to extend the conjugation length in **5'**, **6'** and **7'** respectively (see Scheme 3.3). Each end of the chain, either electron donor (N,N-diphenylamino) or electron acceptor (benzothiazole) or both are attached to constitute a chain in a form of A- π - π - π -A (**5'**), D- π - π - π -D (**6'**) and D- π - π - π -A (**7'**).¹⁹

Scheme 3.3

For **5'**, **6'** and **7'**, a strong linear absorption in the spectral range from 300 to 500 nm was observed (See absorption peak in Figure 3.20 left) and no liners absorption after 500 nm was found for any of these three molecules. 3PA cross-section of **5**, **6** and **7** is highly enhanced in case of **5'**, **6'** and **7'**. The three-photon absorption cross-section for **5** and **5'**, **6** and **6'**, **7** and **7'** is 335 and 511 cm⁶s²/photon², 82 and 145 cm⁶s²/photon² and 37 and 245 cm⁶s²/photon² respectively.¹⁹ It can be calculated with the following rule–

$$\sigma_3 = \frac{\alpha_3}{N_A d_0 10^{-3}} \left(\frac{hc}{\lambda} \right)^2$$

Where, α_3 , N_A , d_0 and (hc/λ) are 3PA coefficient, Avogadro's number, concentration of solution used and energy of the incident photons, respectively. So, it can be said that 3PA cross section is enhanced by a factor of 1.6, 1.8 and 6.6 corresponding to **5'**, **6'** and **7'**. The

fluorescence spectra are moved to longer wavelength for molecules with extended π -conjugation length. Figure 3.20 (right) shows the maximum emission intensity for **5'**, **6'** and **7'** is at 489, 502 and 596 nm with 1230, 1280 and 1260 nm excitation wavelength, respectively. In case of **5**, **6** and **7**, the excitation wavelengths are 1095, 1110 and 1200 nm, respectively.¹⁹

Figure 3.20 Absorption-emission (left) and fluorescence (right) spectra of **5'**, **6'** and **7'**, taken from ref. 19.

The increase of the π -conjugation length means the increase of the distance between the π -electron donor and acceptor i.e., the length of movement for π -electrons. Increase conjugation leads less the distance over which electron charge induced and transferred. Increased π -delocalization thus increases dipole moment and as a result, the excitation energy becomes lower and the optoelectronic properties in molecules get influenced and enhanced.¹⁹

3.5 Recently synthesized Si-based photomaterial and their optical performance

Conjugated polymers possess electronically delocalized backbones that develop semiconducting nature into them. Their optical and electronic properties can be controlled and tailored for a wide range of applications through structural modification and molecular engineering; such as choice of repeat unit, planarization of skeleton, incorporation of heteroatoms, different architectures of polymer backbones and so on. Si-based molecules have the special characteristic due to its sigma conjugation, which is the main reason of their conductivity.¹²⁵ In this section, we have focused on Si-based molecules used in molecular engineering to enhance the performance of polymers for various applications.

The high electron accepting properties of silole³⁰ can be explored by introducing it as building unit of π -conjugated systems with unique electronic properties. Because of its $\sigma^*-\pi^*$ conjugation from interactions between energetically comparable exocyclic σ^* orbital of silole and π^* orbital of butadiene moiety, silole has comparably very low-lying LUMO level than its carbon analogue. It ultimately lowers the band gap of materials without having any effect on open circuit voltage (V_{OC}).¹²⁶ In 2009, Y. Yang et al. synthesized a series of dithieno[3,2-b:2',3'-d]silole-containing polymers (**PSiDTBT12**, see Figure 3.21) by Stille coupling reaction.¹²⁷

Figure 3.21 Chemical structure of dithieno[3,2-b:2',3'-d]silole, **PSiDTBT12**.

They reported that their synthesized silole containing polymer (**PSiDTBT12**) with long alkyl side chain exhibited a high power conversion efficiency of 3.43% which is even higher to that of well-known class of low band gap photovoltaic materials, poly[(9,9-dialkylfluorene)-2,7-diyl-*alt*-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl] (**PFDTBT**) and its derivatives (efficiency 2-3%).¹²⁸ They also claimed that silole unit was the reason of

superior performance of their synthesized polymer after being compared with their counterparts having no silole units.¹²⁷

In 2012, G. C. Bazan groups systemically synthesized a series of pyridal-[2,1,3]thiadiazole (**PT**) based π -conjugated materials and altered molecular framework by using different substituting groups (**R**) on dithieno(3,2-b;2',3'-d)silole and different donor units (**D**) as well (see Figure 3.22) to evaluate structure-property relationship.¹²⁹ They remarked that substituents on silole unit do not have much influence on π -delocalized framework. Thus, the optical properties remain same irrespective of **R** (= hexyl, 2-ethylhexyl and dodecyl) on Si. However, for 2-ethylhexyl substituent, in solid state, the absorption band is broader and incorporation of it makes the material more soluble and more thermally stable than with other two. Thus, 2-ethylhexyl group will be more appropriate choice considering practical purposes.¹²⁹

Figure 3.22 Investigation of pyridalthiadiazole based chromophores with different donor units and different alkyl groups on silole unit.

The change of central aromatic core brings significant change in the electrochemical and optical properties of π -conjugated materials. Comparing the optoelectronic properties, benzodithiophene (**BDT**), dithienosilole (**DTS**) and cyclopentadithiophene (**CDT**) are more favourable for photovoltaic applications due to their enhanced performance. The absorption

spectra are blue-shifted for **BDT** whereas those of **DTS** and **CDT** are similar and red shifted in solution. In solid state, **DTS** exhibits red shifted solid state absorptions compared to that of **CDT** that indicates the higher degree of crystallinity in **DTS** in solid state.¹²⁹

Figure 3.23 Molecular structure of 5,5'-bis{(4-(7-hexylthiophen-2-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine}-3;3'-di-2-ethylhexylsilylene-2;2'-bithiophene, **DTS(PTTh₂)₂**.

At the very beginning of 2012, Y. Sun et al. synthesized a dithienosilole based small molecular solar cell, 5,5'-bis{(4-(7-hexylthiophen-2-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine}-3;3'-di-2-ethylhexylsilylene-2;2'-bithiophene, **DTS(PTTh₂)₂** which was solution processed and exhibits the highest efficiency (6.7%) till then.¹³⁰ The molecular structure of **DTS(PTTh₂)₂** is shown in Figure 3.23. Its optical bandgap is approximately 1.5 eV with the HOMO and LUMO level at -5.2 and -3.6 eV, respectively. The dithienosilole unit leads to strong intramolecular charge transfer due to its inherent electronic properties through the conjugated backbones and four coordinated Si atom allows long alkyl side chain to cause high solubility in organic solution. **DTS(PTTh₂)₂** exhibits broad absorption at 600-800 nm in both solution and thin films with hole mobility of $\approx 0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in field effect configuration. The small molecules bulk heterojunction (BHJ) based on the ratio of 7:3 of **DTS(PTTh₂)₂** : **PC₇₀BM**, shows its highest power conversion efficiency of 6.7% with 0.78 V of open circuit voltage (V_{OC}), 14.4 mAcm^{-2} of short circuit current (J_{sc}) and 59.3% of fill factor.¹³⁰

Figure 3.24 Molecular structure of **DTS (PTTh₂)₂** and its extended structures.

X. Liu et al. studied the influence of extending π -conjugation length (see Figure 3.24) of chromophore, **DTS(PTTh₂)₂** on its optoelectronic properties based on relevant applications.¹³¹ They remarked that through extending π -conjugation length, high thermal stability can be achieved into field effect transistor configuration and incorporation of **PC₆₁BM** in solar cell devices, more than 6.0% of power efficiency can be attainable. With the increase of molecular size, a systematic enhancement of their optical features and hole mobility is observed.¹³¹

T.S. van der Poll and co-workers synthesized and characterized a narrow bandgap semiconductor, 7,7'-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole), **p-DTS(FBTTh₂)₂** which has a CF group as an inert electron-withdrawing functionality, in place of N in pyridal[2,1,3]thiadiazole (PT) of **p-DTS(PTTh₂)₂** (see Figure 3.25).¹³² Authors suggested this molecule, **p-DTS(FBTTh₂)₂** for having more favourable optical properties with enhanced stability than its **p-DTS(PTTh₂)₂** counterpart.¹³²

Figure 3.25 Molecular structures of **p-DTS (PTTh₂)₂** and **p-DTS (FBTTh₂)₂**.

G. C. Bazan groups experimentally investigated on **p-DTS(FBTTh₂)₂** molecule and reported that within optimizing condition through solvent additive or thermal annealing, a system consisting of **p-DTS(FBTTh₂)₂** and PC₇₁BM, can achieve more than 90.0% internal quantum efficiency with high fill factor as **p-DTS(FBTTh₂)₂** molecule has the ability to tune the nanoscale morphology.¹³³

Chapter 4

Internal Rotation Barriers and Hydrogen Bonds in Formamides and Their Complexes

Prior to design a photonic molecule, it is necessary to gain knowledge about π -conjugated system and be familiar with molecular modeling as well as different computational theories and methods to explore their electronic and photonic properties. Formamide is an $n-\pi$ conjugated system having interesting bonding properties. It can be a good choice in order to study electronic properties, conjugation strength and delocalization effect with inserting heteroatom such as Si, Ge and Sn into system. Their role as donor and acceptor during bonding with solvent (water) and Lewis acid-base (HF, NH_3) has been also studied here to gain a deep insight into the nature of hydrogen bonds existing in their complexes.

Formamide has been reported to have relatively higher internal rotational barrier and stronger hydrogen bonds (H-bond) with other molecules as both donor and acceptor. In the past, the higher internal rotational barrier of formamide is always attributed to the stronger electronic delocalization.¹³⁴⁻¹³⁶ In 2003, Mo et al. reported the origin of formamide and its derivatives HCYNH_2 ($\text{Y}=\text{O}$, NH , CH_2 , S and Se) rotational barrier by decomposing it into various components such as resonance conjugation energy, σ -framework steric effects, hyperconjugation energy, and pyramidization energy.¹³⁷ In 2008, Wang et al. reported their findings on the cooperative effect between H-bond and resonance effect for formamide and

water based on ab initio calculation and natural resonance theory (NRT).¹³⁸ Thus, it is crucial to quantitatively evaluate the strength of delocalization and correlate various conjugations with the internal rotation barrier.^{139, 140} Currently, the delocalization strength can be quantitatively estimated by stabilization energies using the Energy Decomposition Analysis (EDA)¹⁴¹, the Natural Bond Orbital (NBO) analysis¹⁴² and the Block Localized Wave function (BLW) method.⁷⁷ The NBO theory is able to quantify the conjugation independent of a reference system.¹⁴³

For H-bonded complex, the NBO method had also proposed a decomposition scheme, varying from the classical Morokuma and Kitaura (KM) partition¹⁴⁴, based on the optimal orthonormal set of localized orbitals. To deeply explore the nature of H-bond and evaluate its strength, wavefunction-based analyses like natural energy decomposition analysis (NEDA)^{71, 145}, block-localized wavefunction energy decomposition analysis (BLW-ED)^{73, 77} and quantum theory of atoms in molecules (QTAIM)^{59, 146-151} are also very efficient tools. Recent reports¹⁵² indicate that the strength of hydrogen bond can be strengthened or weakened in their low-lying electronically excited states. These changes are responsible for many observed photophysical processes and photochemical reactions^{152, 153} and can also facilitate the photo induced electron transfer,¹⁵⁴ charge carrier transfer,¹⁵⁵ intramolecular charge transfer.¹⁵⁶ Thus, for formamide complexes, the influence of the electronic excitation on the intermolecular hydrogen bonding is an important area of study.¹⁴³

In this chapter, we provide a systematic theoretical study of electronic structure, internal rotational barrier of the heavier group-14 analogue of formamide **2-4** and H-bond strength and its nature. For reference, formamide **1** was also studied. The trend of conjugation strength in formamide and its heavier group-14 analogue **1-4** are compared using the perturbation stabilization energies and their origin was discussed based on the natural bond orbital (NBO) analysis. The factors that govern internal rotation barrier heights are analyzed based on correlating the rotational barrier with the $n\text{-}\pi^*$, $n\text{-}\sigma^*$ conjugation and steric effect. In the last section of this chapter covers a detailed investigation of H-bond nature and its strength in heavier formamide complexes (XYHNH_2 ; $\text{X} = \text{C, Si, Ge, Sn}$ and $\text{Y} = \text{O, S, Se, Te}$ with the help of QTAIM, NBO, NEDA and BLW-ED).¹⁴³

4.1 Computational Methods

Comparisons of the optimized geometric parameters for formamide and its heavier group-14 analogues **1-4** among various theoretical methods and experimental measurement are listed in Table A1 (see Appendix A). A careful comparison between different theoretical methods by Wang etc. reveals that the MP2/cc-pVTZ calculation can give the geometry close to the experimental structure¹⁵⁷ and reliable H-bond stable energies and the B3LYP structure is also in good agreement with the experimental and higher level (CCSD/aug-cc-pVTZ) theoretical structures.^{137, 143}

However, MP2 calculations for heavier group-14 analogue of formamide are not always able to obtain the planar structure confirmed by CCSD calculations. Thus, all the calculations in the following discussion were performed by the B3LYP (Becke's three-parameter hybrid function⁴¹ with the nonlocal correlation of Lee-Yang-Parr⁴² and VWN3¹⁵⁸ local correlation). The B3LYP/6-311+G(d,p) method generates slight deviations (0.004 – 0.021 Å) for X-N bond (X=C, Si, Ge) from CCSD theoretical structures while the B3LYP calculation augmented with the cc-pVTZ basis set^{43, 159-162} give deviations between 0.000 – 0.016 Å. Thus, the optimization and internal rotation of formamide, sila-formamide and germa-formamide were carried out at the level of B3LYP/cc-pVTZ. To account for the relativistic effect on the tin (Sn) and Tellurium (Te) atoms, one augmented LanL2DZ basis set,^{44, 45} which include the p, d polarization functions and is denoted as LanL2DZ(d,p)), is adopted in the calculation. The NBO analysis was used to characterize the charge delocalization of formamide and its heavier group-14 analogues **1-4** and explore the H-bond nature of formamide complexes. The Natural Population Analysis (NPA),^{65, 68, 163} the Natural Resonance Analysis (NRT)¹⁶⁴⁻¹⁶⁶ and the Steric Analysis (SA)^{69, 70, 167} and WBI calculation¹⁶⁸ were carried out also.

The H-bond dissociation energies were calculated based on Equation 4.1:

$$\Delta E_{\text{H-bond}} = E_{\text{complex}} - E_{\text{formamide}} - E_{\text{ZH}} + \Delta E_{\text{BSSE}} + \Delta E_{\text{ZPE}} \dots \dots \dots 4.1$$

where $\Delta E_{\text{H-bond}}$ is the dissociation energy for formamide complexes; $\Delta E_{\text{complex}}$, $\Delta E_{\text{formamide}}$, ΔE_{ZH} (=F, OH, NH₂) are the interaction energies for complexes, formamide (NH₂XHY; X=C, Si, Ge, Sn and Y=O, S, Se, Te) monomers and ZH (Z=F, OH, NH₂) monomers respectively;

ΔE_{ZPE} is the zero-point energy correction and lastly, ΔE_{BSSE} is the basis set superposition error.¹⁴³

NEDA is an energy decomposition scheme using NBO approach to estimate the nature of molecular interactions.

$$\Delta E_{\text{NEDA}} = \Delta E_{\text{EL}} + \Delta E_{\text{CT}} + \Delta E_{\text{Core}} \dots \dots \dots 4.2$$

Here, ΔE_{NEDA} refers to the H-bond energy (BSSE has been automatically incorporated in it) by NEDA analysis at the same B3LYP/aug-cc-pVTZ level. ΔE_{EL} represents the sum of polarization, self-energy and electrostatic energy between two distorted fragments, ΔE_{CT} is the component which stabilizes the complex by charge delocalization. The last term, ΔE_{Core} is attributed to the sum of inter-fragment exchange effect and deformation penalty (subtracting the self-energy (SE) term).¹⁴³

In BLW-ED analysis, the SCF convergence field is divided based on three physically meaningful contributions (without considering deformation energy): Heitler-London energy (ΔE_{HL}) which includes electrostatic energy and exchange repulsion; polarization (ΔE_{POL}) and charge transfer energy (ΔE_{CT}) with BSSE.

$$\Delta E_{\text{BLW}} = \Delta E_{\text{HL}} + \Delta E_{\text{CT}} + \Delta E_{\text{POL}} + \text{BSSE} \dots \dots \dots 4.3$$

4.2 Structure and conjugation of formamide's heavy analogue of group 14.

Similar to formamide **1**, heavier group-14 analogue of formamide also prefer to be planar: their D_{OXNH_2} dihedral angles are essentially 180° at the present calculation level (see Table 4.1). The C-N bond of formamide at the B3LYP/cc-pVTZ level is substantially shorter than at the corresponding $\text{CH}_3\text{-NH}_2$ molecule by $0.108 \text{ \AA}$. Wang reported that the apparent shortening of C-N bond is not mainly due to the hybridization difference from sp^2 to sp^3 and the C-N bond at formamide has the double bond character.¹³⁸ After X atom ($\text{X} = \text{Si, Ge and Sn}$) substitution, the shortening of X-N bond ($\text{X} = \text{Si, Ge and Sn}$) relative to the standard single X-N bond for $\text{XH}_3\text{-NH}_2$ is relatively smaller compared to the C-N bond for formamide: the reductions of X-N bond at sila-, germa- and stanna-formamide are only 0.046 , 0.075 and $0.055 \text{ \AA}$, respectively, which imply that there is still partial double bond character for the X-N

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bonds, but considerably weaker than formamide. It is interesting to note that the shortening of Ge-N bond is more than Si-N and Sn-N bonds. In contrast, the X=O bond length for heavier group-14 analogues is essentially identical with the X=O double bond at corresponding heavier ketones $\text{XH}_2=\text{O}$ and the C=O bond length at formamide is slightly longer than ketone $\text{CH}_2=\text{O}$ by 0.010 Å.¹⁴³

Scheme 4.1 Formamide and its heavier group-14 analogues, **1-4**¹⁴³

Table 4.1 Optimized geometric parameters^a for formamide and its heavy analogue of group 14 (NH_2XOH , $\text{X}=\text{C, Si, Ge}$)¹⁴³ at the B3LYP levels augmented with cc-pVTZ basis set (for NH_2SnOH with the basis set LanL2dz(d,p).^{b, c}

Species	$R_{\text{X-N}}$	$R_{\text{X=O}}$	$R_{\text{X-H3}}$	$R_{\text{N-H2}}$	$R_{\text{O-H1}}$	$R_{\text{O-H3}}$	A_{NXO}	A_{H1NX}	A_{H2NX}	D_{OXXH2}
CHONH ₂	1.357	1.209	1.105	1.004	2.548	2.033	125.0	119.4	121.3	179.7
SiHONH ₂	1.686	1.525	1.478	1.007	3.169	2.679	126.7	123.1	123.3	180.0
GeHONH ₂	1.792	1.640	1.536	1.006	3.278	2.864	123.8	122.0	123.3	180.0
SnHONH ₂	1.965	1.797	1.713	1.017	3.586	3.205	123.8	123.7	124.2	180.0

^aBond lengths and distance between two atoms (R) are given in angstrom, bond angles(A) and dihedral angles(D) are in degrees. ^bC-N, Si-N, Ge-N and Sn-N single bond lengths in $\text{XH}_3\text{-NH}_2$ ($\text{X}=\text{C, Si, Ge, Sn}$) molecules are 1.465, 1.732, 1.854 and 2.020 Å, respectively; C-O, Si-O, Ge-O and Sn-O single bond lengths in $\text{XH}_3\text{-OH}$ molecules are 1.421, 1.661, 1.792 and 1.947 Å, respectively; C=N, Si=N, Ge=N and Sn=N double bond lengths in $\text{XH}_2=\text{NH}$ molecules are 1.263, 1.603, 1.711 and 1.882 Å, respectively; C=O, Si=O, Ge=O and Sn=O double bond lengths in $\text{XH}_2=\text{O}$ molecules are 1.199, 1.526, 1.639 and 1.796 Å, respectively (at B3LYP/cc-pVTZ or /LanL2dz(d,p) level).^cFor the LanL2dz(d,p) basis set, see Ref.37.

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We use the Wiberg bond index (WBI) value to estimate the n - π conjugation effect for the heavier group-14 analogues of formamide. Although the WBI value of X-N (X=Si, Ge and Sn) bond is lesser than C-N bond due to weaker electronegativity of X, they are still greater than corresponding standard single X-N (X=Si, Ge and Sn) bond by 0.05, 0.04 and 0.02, respectively. It indicates that there is electron delocalization in heavier group-14 analogues of formamide and the n - π conjugation in heavier group-14 analogue is weaker than that of in formamide. Correspondingly, the extend of Ge-N bond shortening from the standard single Ge-N bond is more than Si-N bond, in agreement with higher WBI of 0.84 for Ge-N compared to Si-N (WBI=0.82, see Table 4.2).¹⁴³

Table 4.2 NPA charges, Wiberg bond index (WBI) and the weights of resonance I and II in formamide and its heavier analogue of the group 14 (NH_2XOH , X= Si, Ge, Sn)¹⁴³ at the B3LYP/cc-pVTZ level^a.

species	NPA					WBI ^b			resonance weight ^c	
	O	X	N	H ₂	H ₃	O=X	X-N	N-H ₂	I	II
formamide 1	-0.59	0.52	-0.79	0.38	0.09	1.74	1.22	0.84	62.9	29.4
silafornamide 2	-1.13	1.86	-1.28	0.40	-0.25	1.35	0.82	0.83	81.7	7.8
germaformamide 3	-1.04	1.69	-1.24	0.39	-0.20	1.39	0.84	0.84	80.2	7.9
stannaformamide 4	-1.20	2.11	-1.40	0.40	-0.33	1.19	0.68	0.83	83.6	6.2

^aAtom numbering is given in Figure 1. ^bThe Wiberg bond indexes between O and H₁ atom are zero for formamide and heavy group-14 analogues **1-4**. ^cThe weights (at %) of resonance I and II come from the NRT analysis (NBO 5.0).

The electronic structure of $\text{O}=\text{XH}-\text{NH}_2$ localized Lewis structure is adjusted because of $n_{\text{N}}-\pi_{\text{X}=\text{O}}$ conjugation and $n_{\text{O}}\rightarrow\sigma_{\text{X}-\text{N}}^*$ hyperconjugation. The conjugation strength of heavy formamides can be compared on the basis of the perturbative correction to the zero-order natural Lewis-structure wave functions. NBO analysis shows that the lone-pair of p electrons on N atom delocalizes into vacant $\pi_{\text{X}=\text{O}}^*$ anti-bonding orbitals (see Figure 4.1(left)) so that heavier group-14 formamide are stabilized and a charge distribution of $\text{O}^--\text{XH}=\text{N}^+\text{H}_2$ type is induced. Comparing to the strong n - π conjugation in formamide (the second order perturbation stabilization energy $\Delta E(n_{\text{N}}\rightarrow\pi_{\text{C}=\text{O}}^*) = 61.90$ kcal/mol), the n - π conjugation of

heavier group-14 formamide is weak: 22.75 (Si), 23.79 (Ge) and 17.41(Sn) kcal/mol, respectively.¹⁴²

Figure 4.1 NBO contour figures for the donor-acceptor interaction of formamide and its heavy analogue of group 14 **1 - 4**: $n_N \rightarrow \pi_{X=O}^*$ delocalization (left); $n_O \rightarrow \sigma_{X-N}^*$ delocalization (middle) and $n_O \rightarrow \sigma_{X-H3}^*$ (right) delocalization.¹⁴³

In the NBO analysis, except for the second order perturbation energies, the $n_N \rightarrow \pi_{X=O}$ conjugation strength can also be described by charge transfer from p_N to $\pi_{X=O}^*$ orbital. The charge transfers from p_N to $\pi_{X=O}^*$ for sila-, germa- and stanna-formamide are 0.14 (Si), 0.14 (Ge) and 0.12 (Sn), respectively, which are considerably smaller than formamide (0.25). These indicate a weakening of $n \rightarrow \pi$ conjugation in heavier group-14 analogues of formamide and imply that they become easier to rotate internally along the X-N single bond. Similar second order perturbation stable energies and charge transfers between silaformamide and germaformamide indicate that the $n \rightarrow \pi$ conjugations in between silaformamide and germaformamide have similar contribution to their planar structures and internal rotational barrier.¹⁴²

In the second-order correction of NBO analysis, the variations of the Fock matrix element $\langle \pi_b | \hat{F} | \pi_b^* \rangle$ have quite stronger effect on the magnitude of the second order perturbation stabilization energy although it always gives a smaller number.⁶⁶ Its value reflects the overlapping strength between the low-lying lone-pair orbital of N and higher-energy unoccupied $\pi_{X=O}^*$ orbital. As carbon in formamide is substituted by the heavier group-14 element, the Fock matrix element $\langle \pi_b | \hat{F} | \pi_b^* \rangle$ drastically declines from 0.119 (C) to 0.076 (Si), 0.070 (Ge) and 0.058 (Sn) (see Table 4.3). The variation at the Fock matrix element

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from C to heavier atoms reveals a small overlap between lone-pair orbital of N and unoccupied $\pi^*_{X=O}$ orbital for the heavier group-14 analogues of formamide. It appears that the smaller overlap induces a weak delocalization in the heavier group-14 analogue of formamide. In addition, there are barely any difference of the Fock matrix element $\langle \pi_b | \hat{F} | \pi_b^* \rangle$ between silaformamide **2** and germaformamide **3** (see Table 4.3), which correspond to their similar $n \rightarrow \pi$ conjugation.¹⁴²

Table 4.3 NBO second order perturbation stabilization energies (in kcal/mol) of $n\text{-}\pi^*$ conjugation involving $\pi_{O=X}$ bond and p_N orbital ($\Delta E_{N\text{-}OX}(n \rightarrow \pi^*)$), $n\text{-}\sigma^*$ hyperconjugation involving n_O and σ^*_{X-N} and involving n_O and $\sigma^*_{X-H_2}$ bond.¹⁴²

species	second order perturbation energies			Fock matrix element	
	$\Delta E_{N\text{-}OX}(n \rightarrow \pi^*)$	$\Delta E_{O\text{-}XN}(n\text{-}\sigma^*)$	$\Delta E_{O\text{-}XH}(n\text{-}\sigma^*)$	p_N and π_{OX}^*	p_O and π_{XN}^*
formamide 1	61.90	25.02	24.01	0.119	0.120
silaformamide 2	22.75	14.91	14.15	0.076	0.080
germaformamide 3	23.79	13.67	14.00	0.070	0.068
stannaformamide 4	17.41	5.83	8.73	0.058	0.051

The NBO analysis reveals the $n_O \rightarrow \sigma^*_{X-N}$ donor-acceptor interaction (second order perturbation stabilization energy $\Delta E_{n_O \rightarrow \sigma^*_{X-N}} = 25.02, 14.91, 13.67$ and 5.83 kcal/mol for formamide, sila-, germa-, stanna-formamide, respectively), which partially offsets the $O^- \text{--} XH=N^+H_2$ ($X=C, Si, Ge$ and Sn) dipolar state by the donor-acceptor interaction from the lone-pair electron on O atom to vacant σ^*_{X-N} anti-bonding orbitals (see Table 4.3 and Figure 4.1(middle)). The result is consistent with the charge flow direction on the basis of electron density difference (EDD) map that electrons transfer from the C-O bond to the amino group.¹³⁷ However, the $n_O\text{-}\sigma^*_{C-N}$ hyperconjugation does not increase the internal rotational barrier because of cylindrical symmetry for the σ^*_{C-N} orbital.¹⁴²

The weights of two predominant resonance structures (Scheme 4.2) from the quantitative NRT analysis are listed in Table 4.2. The comparison between NBO and NRT analysis shows that the vicinal $n_N \rightarrow \pi_{C=O}$ conjugation is a proper tool for estimating trends in resonances: consistently with the inverse trend of $n \rightarrow \pi$ conjugation going down the group 14 column, resonance I increase from formamide (62.9%) to sila-formamide (81.7%); resonance I of sila-

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formamide and germa- formamide are similar (there is a small gap of 1.5% at resonance I, see Table 4.2). Thus, the NBO analysis, using nature orbital figure, is a good complement to the NRT analysis, which focuses on charge changes. However, it must be noted that the $n \rightarrow \pi$ conjugative energies from NBO analysis can't be used for estimating absolute resonance stabilization energies since the electronic structure of the Lewis structure at NBO analysis is not relaxed. Our previous researches show that NBO conjugation stable energies are in average twice larger than other methods.^{139, 140, 143}

Scheme 4.2 Two predominant resonance structures of compound, 1-4.¹⁴²

4.3 The internal rotational barriers and the governing factors

We defined the internal rotational angle (θ) around the X-N single bond as the torsion angle between the carbonyl group and nitrogen lone-pair orbital (see scheme 4.3). The internal rotational PESs, $E(\theta)$, were obtained by performing clockwise rotations around the X-N single bond and start with the planar molecular structure with $\theta = -90.0^\circ$ (see scheme 4.3). The geometries of conformers have been optimized at a set of selected θ values ranging from -90.0° to 180.0° , then to 90.0° and lastly back to -90.0° (see Figure 4.2), which were kept constant, while all other geometric parameters were fully optimized.¹⁴² To show concisely the pyramiding of nitrogen atom when amino group rotate out of the original molecular plane, we define the sum of the bond angles around N atom as $\Sigma\alpha$, $\Sigma\alpha = \angle XNH_1 + \angle XNH_2 + \angle H_1NH_2$.

During the internal rotation, the structure of formamide and its heavier group-14 analogues 1-4 at the dihedral angle of $-\theta$ is the mirror image of their rotamer at a dihedral angle of θ , the partial PES at a range from $\theta = -90^\circ$ to 90° (or from $\theta = 90^\circ$ to -90°) is symmetrical at $\theta = 180^\circ$ (or 0°), respectively. Since the steric energetic difference between amino and carbonyl group is small, rotamer A ($\theta = 90^\circ - \alpha$) have similar potential energetics with rotamer B ($\theta =$

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$90^\circ + \alpha$) (see Scheme 4.4) so that the whole PES is almost symmetrical at $\theta = 90^\circ$ (see Figure 4.2). Based on the highly symmetrical PES, we explore the electronic structure and internal rotation barriers for formamide and heavier analogues by focusing on the rotational range from -90° to 180° .¹⁴²

Scheme 4.3 Internal rotational angle (θ) around the X–N single bond¹⁴²

Along the internal rotational PESs for formamide and heavier group-14 analogues **1-4**, there exist only one type of stable conformer for $\theta = -90^\circ$ or 90° , that is, their planar structure. The internal rotational TSs for formamide and heavier group-14 analogues **1-4** are located at the rotational angle of 0.0° and 180.0° (for pertinent optimized geometric parameters for TSs, see Appendix A).¹⁴²

Scheme 4.4 Conformations of rotamer A ($\theta = 90^\circ - \alpha$) and rotamer B ($\theta = 90^\circ + \alpha$)¹⁴²

The potential energetics (including the zero-point-correction) for their TSs relative to their plane minima, i.e., the internal rotation barriers, are calculated to be 18.19, 11.61, 9.01 and 7.56 kcal/mol for C, Si, Ge and Sn at the B3LYP/cc-pVTZ level, respectively (see Table 4.4). The same trend was observed when the barriers are computed using CCSD(T)/aug-cc-pVTZ, namely, 15.73, 11.73, 9.45 and 7.50 kcal/mol for C, Si, Ge and Sn, respectively (see Table 4.4).¹⁴²

Figure 4.2 Internal rotation potential energy curves for formamide and heavy group-14 analogues **1-4** at the CCSD(T)/aug-cc-pVTZ (in blue, for Sn, the Lanl08d basis set) and B3LYP/cc-pVTZ (in grey, for Sn, the LanL2dz(d,p) basis set) level.¹⁴²

The C=O double bond of amide group in the formamide group **1-4** remain stable during the internal rotation. When amino group rotate out of the molecular plane, the value of $\Sigma\alpha$ will decrease gradually (see Appendix A, Figure A2). It indicates that the pyramid degree of amino group will be enhanced and the nitrogen atom will not adopt the sp^2 hybridization. The change in hybridization from sp^2 for the stable planar structure to the sp^3 for TS comes from the weakening of $n-\pi$ delocalization with reduced overlapping between n and π orbitals. The elongation of N-X bond along the internal rotation from -90.0° to 180.0° , for example, the N-Si bond for silaformamide change from 1.686 Å of planar structure to 1.723 Å of TS (see Table 4.1), confirms the weakening of $n-\pi$ delocalization.¹⁴²

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Table 4.4 Occupancy charge in the $\pi_{X=O}^*$, σ_{X-O}^* and $\sigma_{X-H_2}^*$ orbitals, the conjugation stabilization energies ($\Delta E_{N \rightarrow X=O}$ ($n \rightarrow \pi^*$), $\Delta E_{N \rightarrow XN}$ ($n \rightarrow \sigma^*$) and $\Delta E_{O \rightarrow XH_2}$ ($n \rightarrow \sigma^*$)) for stable planar structure and TSs of formamide and its heavy group-14 analogue **1-4**,¹⁴² the relative steric repulsion energies for TS to the planar structure and their internal rotation barriers at the CCSD(T)/aug-cc-pVTZ//B3LYP/cc-pVTZ)^{a, b}.

formamide	occupancy of TS			stabilization energies of TSs			relative steric repulsion (ΔE_{steric})	sum of energy (ΔE_{sum})	rotational barrier
	$\pi_{X=O}^*$	σ_{X-O}^*	$\sigma_{X-H_3}^*$	ΔE_{N-XO} ($n \rightarrow \pi^*$)	ΔE_{N-XO} ($n \rightarrow \sigma^*$)	ΔE_{N-XH_2} ($n \rightarrow \sigma^*$)			
formamide 1	0.043 (0.245) ^c	0.023 (0.006) ^c	0.070 (0.070) ^c	0.00 (61.90) ^d	10.24 (0.00) ^d	3.37 (0.00) ^d	-3.19 ^e	45.1 ^f	15.73, 18.10 ^{g, h}
silafornamide 2	0.018 (0.138)	0.065 (0.019)	0.072 (0.071)	0.00 (22.75)	10.34 (0.00)	4.93 (0.00)	5.42	12.9	11.73, 11.61
germaformamide 3	0.017 (0.145)	0.080 (0.043)	0.080 (0.078)	0.00 (23.79)	6.71 (0.00)	2.96 (0.00)	-6.81	7.31	9.45, 9.01
stannaformamide 4	0.008 (0.115)	0.071 (0.039)	0.069 (0.066)	0.00 (17.41)	4.02 (0.00)	3.08 (0.00)	-4.29	6.02	7.50, 7.56

^aFor Sn, the basis set is the LanL08d and LanL2dz(d,p) basis set. ^bThe NBO occupancy charges in coulomb. ΔE in kcal/mol. ^cThe relative energetic value is the difference between the sum of $\Delta E_{N-OX}(n \rightarrow \pi^*)$ and $\Delta E_{N-OX}(n \rightarrow \sigma^*)$ conjugation stabilization energies at stable planar structure and at TS. ^dThe NBO occupancy charges of $\pi_{X=O}^*$, σ_{X-O}^* and $\sigma_{X-H_2}^*$ for stable planar structure. ^eThe difference of total steric exchange energies between at stable planar structure and at TS. ^fThe sum of the energetic difference of conjugational, hyperconjugational stable energies and steric repulsion energies between at stable planar structure and at TS, $\Delta E_{sum} = \Delta E_{N-XO}(n \rightarrow \pi^*) - \Delta E_{N-XO}(n \rightarrow \sigma^*) - \Delta E_{N-XH_2}(n \rightarrow \sigma^*) + \Delta E_{steric}$. ^gThe barrier height of internal rotation around X-N bond at the level of CCSD(T)/aug-cc-pVTZ and B3LYP/cc-pVTZ, respectively. ^hThe barrier height of internal rotation of formamide at the MP2/6-31+G(d) level and from the G2 theory are 17.2, 16.0 kcal/mol, respectively.¹³⁷

We also estimated the trend of $n-\pi^*$ conjugative strength based on its NBO perturbation stabilization energies. The $n-\pi^*$ conjugative stabilization energies for **1-4** decrease with the rotation from planar structure to TS and are equal to zero at their TSs (see Table 4.4). Thus, the $n-\pi^*$ delocalization will vanish in their TSs. However, the N-X single bond lengths in TSs of **1-3** (1.442, 1.723 and 1.853 Å, for **1-3**, respectively) are still shorter than in isolated molecules NH_2-XH_3 (1.465, 1.732 and 1.854 Å). The single X-N bond for the formamide

group should be longer than in isolated molecules $\text{NH}_2\text{-XH}_3$ since the amide group weakens the electron density at X. The phenomenon indicates that there is still other delocalization effect along the N-X single bond in the TS structures.¹⁴²

Figure 4.3 NBO contour figure: (a) $n_{\text{N}}\text{-}\sigma_{\text{X-O}}^*$ delocalization and (b) $n_{\text{N}}\text{-}\sigma_{\text{X-H3}}^*$ delocalization at TSs of internal rotation around X-N bond, the contour plane is chosen along the formamide plane.¹⁴²

The NBO analysis shows that there are two gradually increasing $n\text{-}\sigma^*$ hyper conjugations from p lone-pair orbital of N to $\sigma_{\text{O-X}}^*$ and $\sigma_{\text{X-H3}}^*$ along the internal rotation from -90.0° to 180.0° (see Figure 4.3 and Table A2 in Appendix A), which will reduce the heights of internal rotations. The sum of NBO second order perturbation energies of two $n\text{-}\sigma^*$ hyper-conjugation in rotational TS for the formamide group **1-4** are 13.61, 15.27, 9.67 and 7.20 kcal/mol, for $\text{X} = \text{C}, \text{Si}, \text{Ge}$ and Sn , respectively. Thus, it is not appropriate to use the internal rotational barrier to evaluate the $n\text{-}\pi$ electronic delocalization strength, even for formamide. Comparing the differences between $n\text{-}\pi$ conjugation (61.90 kcal/mol) and the $n\text{-}\sigma^*$ hyper-conjugation (13.61 kcal/mol) in formamide, these differences for the heavier group-14 analogues of formamide become lesser: the differences for **2-4** are 7.48, 14.12 and 10.21 kcal/mol, respectively. Thus, the $n_{\text{N}}\text{-}\pi_{\text{O=X}}$ conjugation in heavier group-14 analogues of formamide is not the only governing factor for their rotational barrier.¹⁴²

Since the $n_{\text{N}}\text{-}\pi_{\text{O=X}}$ conjugation in both silaformamide **2** and germaformamide **3** (22.75 and 23.79 kcal/mol for **2** and **3**) are similar and silaformamide **2** has stronger $n_{\text{N}}\text{-}\sigma_{\text{X-O}}^*$ and $n_{\text{N}}\text{-}\sigma_{\text{X-H}}^*$ stabilization energy (15.27 kcal/mol) for the TS of internal rotation compared to

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germaformamide **3** (9.67 kcal/mol), the rotational barrier of **2** should be lower than **3**, which is contradictory to the actual rotational barrier. Our NBO steric analysis shows stronger steric congestion at the internal rotation TS of silaformamide **2** compared to formamide and germaformamide: the differences of steric exchange energies between TS and planar rotamer for **1-3** are -3.19, 5.42 and -6.81 kcal/mol, respectively (see Table 4.4). It is the stronger steric congestion that increases the rotational barrier of silaformamide **2** so that the internal rotational barrier of formamide and its heavier group-14 analogues decreases down the group 14 column. This demonstrates that for heavy group-14 formamide the steric effect stabilization becomes an important factor in determining the barrier of internal rotation.¹⁴²

Figure 4.4 Correlation between the internal rotation barrier and the difference between the sum of the $n\text{-}\pi$ conjugative, $n_{\text{N}}\text{-}\sigma_{\text{X-O}}^*$ and $n_{\text{N}}\text{-}\sigma_{\text{X-H3}}^*$ hyper-conjugative stabilization energies and steric repulsion energies in the planar structure and the TS of formamide and heavy group-14 analogues **1-4**.¹⁴²

The sum of energetic difference of conjugational, hyperconjugational stabilization energies and steric repulsion energies between planar structure and TS (ΔE_{sum}) of formamide and its heavier group-14 analogues **1-4** and their internal rotational barriers have the same trend: a reasonably good linear correlation coefficient ($y=0.25x + 7.15$, $R^2=0.94$) was found (see Figure 4.4). It is obvious that heavier analogues of formamide, $n\rightarrow\pi^*$ delocalization stable energy is not the predominant factor that dictates the internal rotational barrier around X-N bond, although it is still more important factor, and the $n\rightarrow\sigma^*$ hyperconjugation and steric

effect also considerably contribute to the overall rotational barrier. The NBO analysis reveals the effect factors of internal rotation barriers for formamide and its heavier analogues and provides insight into and understanding of the differences in their electronic structure. However, the NBO energetic difference between stable planar structure and internal rotation TS can't evaluate exactly the internal rotation barrier height. For example, the sum energetic difference of formamide (45.1 kcal/mol) is larger than the respective barrier (18.10 kcal/mol) at the same B3LYP level. The gap still comes from the factor that the NBO second perturbation energies were overestimated to some extent.¹⁴²

4.4 H-bond of group-14 heavier analogues of formamide

We explore the two types of H-bond complex of heavier group-14 analogues of formamide as H-bond donor and H-bond acceptor with water, denoted as FXO-H₂O and FXH-H₂O (X= C, Si, Ge and Sn) complex, respectively. Quantum mechanical calculations and the NEDA analysis were used to analyze the complexes. With weaker electronegativity for heavier X atoms (X=Si, Ge and Sn) and the stronger donor-acceptor interaction from O lone-pair orbital to σ^*_{X-H3} orbital (the second order perturbation stabilization energy $\Delta E(n_O \rightarrow \pi_{X-H3}^*) = 14.15$, 14.00 and 8.73 kcal/mol for sila-, germa- and stanna-formamide, respectively, see Table 4.3 and Figure 4.1(right)), the NPA charge density at H₃ (from -0.25 to -0.33, see Table 4.2) of heavier group-14 analogues of formamide is higher than other amino group H atom (about 0.40, see Table 4.2). Thus, H₂ atom of amino group is selected as the target atom of H-bond acceptor at FXH-H₂O since it is easier to accept the charge transfer of water than H₃.¹⁴²

4.4.1 H-bond of FXO-H₂O complex

Pertinent geometries for FXO-H₂O complexes of formamide and their heavier analogue are displayed in Figure 4.5. The O(water)-H(Formamide) distance of formamide's and its heavier group-14 analogues' complexes show a trend of contraction when X moves down the group 14 column: the O₁-H₄ distance from 1 to 4 are 1.891, 1.845, 1.839 and 1.797 Å for C, Si, Ge and Sn respectively, which implies a trend of stronger H-bond stability for formamide and its heavier group-14 analogue 2-4. The calculated H-bond dissociation energies (ΔE_{H-diss}) agree with the increasing trend of H-bond stability: the ΔE_{H-diss} for 1 - 4 are -3.12, -5.46, -5.76 and -

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7.03 kcal/mol, respectively (the $\Delta E_{\text{H-diss}}$ of formamide at MP2/aug-ccp-pVTZ level equal to -3.30 kcal/mol).¹³⁷ Thus, the FXO-H₂O complexes of heavier group-14 analogues of formamide have stronger H-bond than formamide.¹⁴²

Figure 4.5 The optimized geometries of FXO-H₂O (X = C, Si, Ge and Sn) complexes, including the bond length in angstroms and the dihedral angles in degrees at the B3LYP/aug-cc-pVTZ level.¹⁴²

In general, for free binary H-bonded complexes, for example, A-H $\cdots$ B, the donor atom B and A-H bond should be collinear in order to maximize the overlap between the orbitals. However, the O₂-H₄ $\cdots$ O₁ bond angle for formamide **1** is reduced to 160.4°. The WBI index of 0.002 between O₂(water) and H₃(formamide) for the FCO-H₂O complex reveals a slight interaction between O₂(water) and H₃(formamide), which is weaker than the O₂-H₄ $\cdots$ O₁ H-bond (WBI=0.033). The NBO analysis also indicates a weak n $\rightarrow$ σ^* donor-acceptor interaction from n orbital at O₂(water) into σ^* orbital of H₃-C(formamide) with the second order perturbation energy of 1.58 kcal/mol. The strain from the weak interaction between O₂(water) and H₃(formamide) distorted the linear H-bond geometry of FCO-H₂O complex. The O₂(water)-H₃(formamide) distance at FXO-H₂O complex of heavier group-14 analogues (from 3.441 to 3.996 Å, see Figure 4.5) is longer than formamide (2.945 Å, see Figure 4.5) because of longer X=O bond. The WBI indexes for O₂-H₃ for group-14 heavier analogue of formamide are essentially zero (WBI=0.0001~0.0004, see Table 4.2). These data indicate that there is essentially no strain between O₂(water) and H₃(formamide) for the FXO-H₂O complexes of heavier group-14 analogues.¹⁴²

Table 4.5 H-bond dissociation energies $\Delta E_{\text{H-diss}}$, H-bond length $R_{\text{O}_2\text{H}_4\cdots\text{O}_1}$ for FXO-H₂O (X=C, Si, Ge and Sn) complex and the NBO analysis (the net intermolecular charge transfer $\Delta Q_{\text{O}_1\rightarrow\text{H}_4}$, and the $n_{\text{O}}\rightarrow\sigma^*_{\text{HO}}$ second order perturbation stabilization energies (kcal/mol), the WBI between O₂ and H₃ atoms) at the B3LYP/aug-cc-pVTZ level and the NEDA analysis (the NEDA H-bond energies and its components: the charge transfer (CT), electrical (EL) and net repulsive CORE term, in kcal/mol) at the B3LYP/6-31G(d,p) level^{a, 143}

species	$\Delta E_{\text{H-diss}}$	$R_{\text{O}_1\cdots\text{H}_4}$	$\Delta Q_{\text{O}_1\rightarrow\text{H}_4}$	WBI _{O₂-H₃}	Q_{O_1}	$\Delta E(n_{\text{O}}\rightarrow\sigma^*_{\text{H}_4\text{-O}_2})$	ΔE_{CT}	ΔE_{EL}	ΔE_{CORE}	$\Delta E_{\text{H-bond}}$
formamide 1	-3.12 ^b	1.891	0.021 (0.021) ^c	0.002	-0.627	-(7.35+ 1.59 ^d)	-14.68 (-15.37) ^e	-15.08	24.12	-5.64 ^f
silformamide 2	-5.46	1.845	0.022 (0.022)	0.000	-1.194	-(6.85+ 3.69)	-16.92 (-19.27)	-17.35	27.05	-7.22
germaformamide 3	-5.76	1.839	0.025 (0.026)	0.000	-1.092	-(9.52+ 2.16)	-19.77 (-20.73)	-19.34	31.14	-7.97
stannaformamide 4	-7.03	1.797	0.029 (0.032)	0.000	-1.267	-(13.65+ 1.98)	-36.07 (-37.60)	-26.61	52.61	-10.07

^aThe optimization and dissociation energies at the B3LYP/aug-cc-pVTZ level. ^bThe H-bond dissociation energies $\Delta E_{\text{H-diss}}$ is 3.30 kcal/mol at MP2/aug-cc-pVTZ level, see reference 6. ^cThe electron density at unfilled $\sigma^*_{\text{H}_4\text{-O}_2}$ antibonding orbital. ^dThe no-align n orbital of O(Formamide) donate into $\sigma^*_{\text{H-O}}$ of water (see Figure 4.6(b)). ^eThe sum of $n_{\text{O}}\rightarrow\sigma^*_{\text{HO}}$ second order perturbation stabilization energies at the B3LYP/6-31G(d,p) level. ^fThe H-bond energies from Morokuma-Kitaura EDA analysis at RHF level is -6.82 kcal/mol and its ES, exchange repulsion (EX) and CT contribution are -10.66, 7.66 and -2.59 kcal/mol.

We explore the nature of H-bond and evaluate the strength of “net H-bond” energies on the basis of the NBO theory. Mainly, there are two theories for H-bond formation: the partial covalence emphasizing the resonance contribution represented as $\text{B}\cdots\text{H}-\text{A} \leftrightarrow \text{B}-\text{H}^+\cdots\text{A}^-$ and a classical electrostatic attraction. The NBO analysis gives a clear orbital figure of resonance contribution: the charge transfer (CT) of “ionic resonance” origins in that electron density from the lone pair n_{B} of B: delocalizes into the unfilled σ_{AH}^* antibonding orbital of H-A, that is, a two-electron intermolecular $n_{\text{B}}\rightarrow\sigma_{\text{AH}}^*$ donor-acceptor interaction, and the CT strength can be evaluated by the perturbative stabilization energetics of $n_{\text{B}}\rightarrow\sigma_{\text{AH}}^*$ interaction and the value of intermolecular CT.¹⁴²

Table 4.5 summarizes the NPA charge on O₁ and unfilled $\sigma^*_{\text{H}_4\text{-O}_2}$ anti-bonding orbital, the net intermolecular CT $\Delta Q_{\text{O}_1\rightarrow\text{H}_4}$ and the $n_{\text{O}_1}\rightarrow\sigma^*_{\text{H}_4\text{O}_2}$ second order perturbation stabilization energies. The NPA analysis shows that for the FXO-H₂O complex, the CT from formamide

and its heavier group-14 analogues to water is almost identical with electron density at unfilled $\sigma^*_{\text{O}_2\text{H}_4}$ anti-bonding orbital (see Table 4.5). It indicates that the CT between monomers at H-bond complex is essentially the $n \rightarrow \sigma^*$ donor-acceptor interaction. Since two lone-pair electronic orbital at O_1 (formamide) and water molecule is coplanar and O_1 (formamide) adopts the sp^2 hybridization, the $\sigma^*_{\text{O}_2\text{H}_4}$ anti-bonding orbital does not only overlap with the aligning n-orbital (for example, for formamide and silaformamide, the whole p character and the PNBO overlapping integral $S_{n \rightarrow \sigma^*} = 0.031$ and 0.038 , see Figure 3(a)), but also overlap with another n-orbital, deviating from $\text{O}_1 \cdots \text{H}_4\text{-O}_2$ direction, with the $\text{sp}^{0.63}$ and $\text{sp}^{0.59}$ hybridization, whose PNBO overlapping integral ($S_{n \rightarrow \sigma^*}$) are 0.009 and 0.015 at sila- and germaformamide complex, respectively (see Figure 4.6(b)).¹⁴²

Figure 4.6 NBO contour figure of donor-acceptor interaction forming O_1 (Formamide) $\cdots \text{H}_4$ (H_2O) hydrogen bond at FXO- H_2O complex. The contour plane is chosen along the formamide plane (with estimated second-order stabilization energies in parenthesis).¹⁴²

Thus, in contrast from the normal $n \rightarrow \sigma^*$ interaction of H-bond, the CT of the donor-acceptor interaction for FXO- H_2O complex arise from two n lone-pair orbitals. The NBO perturbation analysis indicates that the stable energetic of n_{O_1} aligning orbitals delocalization into unfilled $\sigma^*_{\text{O}_2\text{H}_4}$ anti-bonding orbital are 7.35, 6.85, 9.52 and 13.65 kcal/mol at FXO- H_2O for C, Si, Ge and Sn respectively; and the second n_{O_1} orbitals delocalize into unfilled $\sigma^*_{\text{H}_4\text{-O}}$ anti-bonding orbital of H_2O concurrently with 1.59, 3.69, 2.16 and 1.98 kcal/mol, for C, Si, Ge and Sn respectively. For the FSiO- H_2O complex, the stronger delocalization from the second n_{O_1} orbitals into the $\sigma^*_{\text{H}_4\text{-O}_2}$ orbital (3.69 kcal/mol), larger than FCO- H_2O (1.59

kcal/mol) and FGeO-H₂O (2.16 kcal/mol) complexes stabilized the water at the location away from sila-formamide, i.e., $\sigma^*_{\text{H4-O2}}$ orbital deviating from the p orbital direction (see Figure 4.6). With the increasing electron density at O₁ (from -0.63 to -1.27 e) for heavier group-14 analogues of formamide, the CT are strengthened, following the order: formamide (8.94 kcal/mol) < silaformamide (10.54 kcal/mol) < germaformamide (11.68 kcal/mol) < stannalformamide (15.63 cal/mol), which indicates stronger CT contribution to H-bond for heavier group-14 analogue of formamide compared to formamide. Although the NBO analysis provides a clear H-bond resonance figure and quantity the CT strength, it cannot estimate the electrostatic contribution and steric repulsion contributor on the basis of an energetic criterion. As such, we used the natural energy decomposition analysis (NEDA)¹⁶⁹ to explore how other factors affect the H-bond stability for the heavier group-14 analogues of formamide.¹⁴²

The NEDA analysis, performed at the B3LYP/6-31(d,p) level for the present study, divides the H-bond stabilization energetics into electrical-type (EL), core-type (CORE) and charge transfer-type (CT) contributions (see Table 4.5), which correspond with Coulson's partition on contributions to H-bond energies,¹⁷⁰ and also includes the basis set superposition (BSSE) correction:

$$\Delta E_{\text{NEDA}} = \text{EL} + \text{CORE} + \text{CT}$$

According to NEDA analysis, the CT contribution (ΔE_{CT}) comes from $n_{\text{O1}} \rightarrow \sigma^*_{\text{H4O2}}$ donor-acceptor interaction (since the NEDA analysis is sensitive to the basis set, it is higher than the $\Delta E(n_{\text{O1}} \rightarrow \sigma^*_{\text{H4-O2}})$ from the NBO analysis at the B3LYP/aug-cc-pVTZ level.).¹⁶⁹ The EL term, being a sum of electrostatic (ES), polarization (POL) and exchange (EX) contributions, and CORE term, attributed to the sum between the deformation (DEF) penalty and exchange (EX) (subtracting the self-energy (ST)), represent the total electrical attraction and the net repulsion, respectively (for detailed NEDA analysis, see Appendix A). The NEDA analysis indicates that the net H-bond stabilization energies for formamide and its heavier group-14 analogue **1-4** follow the trend (at kcal/mol) 5.64 (C) < 7.22 (Si) < 7.97 (Ge) < 10.07 (Sn). Figures 4.7 and 4.8 present the correlation between the NEDA H-bond stabilization energies ($\Delta E_{\text{H-bond}}$) and dissociation energies ($\Delta E_{\text{H-diss}}$), H-bond length ($R_{\text{O2H4} \cdots \text{O1}}$). There is a good linear correlation between the NEDA H-bond stabilization energies and dissociation energies

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($y = 0.85x + 1.22$, with linearly dependent coefficient of $R^2 = 0.88$; see Figure 4.7), H-bond length ($y = 0.02x + 2.00$, with linearly dependent coefficient of $R^2 = 0.97$; see Figure 4.8), indicating that the strength of H-bond at formamide and its heavier group-14 analogues can be fairly evaluated by the NEDA H-bond stabilization energies ($\Delta E_{\text{H-bond}}$).¹⁴²

Figure 4.7 Correlation between the NEDA H-bond stable energies ($\Delta E_{\text{H-bond}}$, at kcal/mol) and dissociation energies ($\Delta E_{\text{H-diss}}$, at kcal/mol) for FXO-H₂O complex.¹⁴²

Figure 4.8 Correlation between the NEDA H-bond stable energies ($\Delta E_{\text{H-bond}}$, at kcal/mol) and H-bond length ($R_{\text{O}_2\text{H}_4 \cdots \text{O}_1}$, at Å) for FXO-H₂O complex.¹⁴²

The NEDA analysis indicates that the CT and EL contribution to the H-bond stabilization energy gradually increase at the same time and the POL term remains stable when heavier elements substitute C. The CT and ES terms are the largest individual contributors to binding. In particular, CT attraction plays an important role to binding, which is stronger than the EL contribution (see Table 4.5). The stronger CT and EL contribution for heavier analogues of formamide **2-4** lead to shorter H-bond length compared to formamide, which will lead to stronger steric repulsion. However, the stronger attractions from CT and EL for heavier analogues of formamide are greater than the increasing CORE repulsions with heavier X, thus, resulting in more stable H-bond complexes for the heavier analogues of formamide.¹⁴²

Although the NEDA stabilization energy is a powerful tool to estimate the strength of H-bond (a parallel Morokuma-Kitaura EDA analysis for formamide indicates similar stabilization energy of 6.82 kcal/mol, see footnote 'f' of Table 4.5), they are higher than the calculated H-bond dissociation energies by one and a half times. Thus, it cannot be used to estimate absolute H-bond stabilization energies. In addition, we cannot change the conclusion on the electrostatic nature of H-bond although the CT contributions to the H-bond stabilization energy for FXO-H₂O complexes are always slightly higher than the EL contribution. Although the quantum calculation showed that the CT is an important factor dictating the H-bond formation,¹⁷¹ the energy partition is only an arbitrary definition. Contrary to the weak CT contribution for Morokuma-Kitaura EDA partitioning since CT interaction is largely absorbed into "EL + EX" terms, for example, only 1.45 kcal/mol for formamide, the CT contribution from NEDA analysis seems over estimated (15.37 kcal/mol), but the excess is offset by the CORE contribution. In any case, the arbitrary definition does not affect the NEDA analysis to compare the same type of contribution to H-bond for a series of compounds by dissecting the H-bond.¹⁴²

4.4.2 H-bond of FXH-OH₂ complex

The H-bond dissociation energies $\Delta E_{\text{H-diss}}$, H-bond length $R_{\text{NH}_2\cdots\text{O}_2(\text{water})}$, NBO analysis and NEDA analysis are given in Table 4.6. Pertinent geometries for the FXH-OH₂ complexes of formamide and their heavier group-14 analogues are displayed in Figure 4.9. The FXH-OH₂ complexes (X = C, Si, Ge and Sn) form a near-aligning N-H₂⋯O₂ geometry. The NBO analysis shows that the entire CT from water to the formamide and its heavier group-14

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analogues **1-4** comes wholly from the aligning hybridization orbital of O_2 (water) and there is no overlapping between the second lone-pair orbital of O_2 (water) and $\sigma_{H_2N}^*$ orbital (formamide) for the FXH- OH_2 complexes (see Figure 4.10). It is because water and formamide for the FXH- OH_2 complexes are not coplanar and O_2 (water) adopt the sp^3 hybridization, in contrast to the FXO- H_2O complexes. The CTs of FXH- OH_2 complexes are also weaker than the corresponding FXO- H_2O complexes, for example, the intermolecular charge transfer $\Delta Q_{O_2 \rightarrow H_2}$ for FXH- OH_2 complexes, about 0.12 electron, is less than the intermolecular charge transfer $\Delta Q_{O_1 \rightarrow H_4}$ for FXO- H_2O complexes, from 0.21 to 0.32 electron, and the $n_{O_1} \rightarrow \sigma_{HN}^*$ perturbation stabilization energies of FXH- OH_2 complexes at the range of 3.26 to 5.29 kcal/mol are lower than FXO- H_2O complexes with a range from 8.94 to 15.63 kcal/mol (see Table 4.5 and 4.6).¹⁴²

Figure 4.9 Optimized geometries of FXH- OH_2 (X = C, Si, Ge and Sn) complexes, the bond length at Å and the bond angles in degrees at the B3LYP/aug-cc-pVTZ level.¹⁴²

NRT analysis indicates that the ionic property for heavier group-14 analogue is identical with formamide (see Table 4.6). Not surprisingly, NEDA analysis indicates that the ΔE_{CT} (from -9.32 to -11.84 kcal/mol) and ΔE_{EL} (from -9.02 to -10.41 kcal/mol) values for heavier analogues of group 14 are similar to those of formamide (-10.22 and -10.91 kcal/mol). The FXH- OH_2 complexes of heavier group-14 analogues have similar repulsion (ΔE_{CORE} being from -14.57 to -16.21 kcal/mol) to formamide (-15.94 kcal/mol). Thus, the FXH- OH_2 complexes (X=C, Si, Ge and Sn) have similar H-bond stability (see Table 4.6).¹⁴²

Table 4.6 H-bond dissociation energies $\Delta E_{\text{H-diss}}$, H-bond length $R_{\text{NH}_2\cdots\text{O}_2(\text{water})}$, ionic property for N-H bond for FXH-OH₂ (X=C, Si, Ge and Sn) complex and the NBO analysis (the net intermolecular charge transfer $\Delta Q_{\text{O}_2\rightarrow\text{H}_2}$, the $n_{\text{O}}\rightarrow\sigma^*_{\text{H}_2\text{-N}}$ second order perturbation stabilization energies (kcal/mol) and the ionic property between N and H₂ atoms) at the B3LYP/aug-cc-pVTZ level and the NEDA analysis (the NEDA H-bond energies and its components: the charge transfer (CT), electrical (EL) and net repulsive CORE term, in kcal/mol) at the B3LYP/6-31G(d,p) level^{a, 142}

species	$\Delta E_{\text{H-diss}}$	$R_{\text{O}_2\cdots\text{H}_2}$	$\Delta Q_{\text{O}_2\rightarrow\text{H}_2}$	$i_{\text{N-H}_2}$	$\Delta E(n_{\text{O}}\rightarrow\sigma^*_{\text{H}_2\text{-N}})$	ΔE_{CT}	ΔE_{EL}	ΔE_{CORE}	$\Delta E_{\text{H-bond}}$
formamide 1	-3.19 ^b	2.037	0.013 (0.017) ^c	0.42	-5.29	-10.22 (10.92) ^d	-10.91	15.94	-5.18 ^e
silafornamide 2	-3.24	2.046	0.012 (0.013)	0.44	-4.38	-9.88 (10.39)	-10.41	15.32	-4.98
germaformamide 3	-2.83	2.068	0.011 (0.013)	0.43	-3.96	-9.32 (9.79)	-9.89	14.57	-4.64
stannaformamide 4	-2.56	2.107	0.011 (0.010)	0.42	-3.26	-11.84 (11.50)	-9.02	16.21	-4.63

^aThe optimization and dissociation energies at the B3LYP/aug-cc-pVTZ level. ^bThe H-bond dissociation energies $\Delta E_{\text{H-diss}}$ is 2.22 kcal/mol at MP2/aug-cc-pVTZ level, see reference 6. ^cThe electron density at unfilled $\sigma^*_{\text{H}_2\text{-N}}$ antibonding orbital. ^dThen $n_{\text{O}}\rightarrow\sigma^*_{\text{H}_2\text{-N}}$ second order perturbation stabilization energies at the B3LYP/6-31G(d,p) level. ^eThe H-bond energies from Morokuma-Kitaura EDA analysis at RHF level is -5.80 kcal/mol and its ES, exchange repulsion (EX) and CT contribution are -7.81, 4.13 and -1.45 kcal/mol.

Figure 4.10 NBO contour figure of donor-acceptor interaction forming O₇(H₂O)⋯H₂(Formamide) hydrogen bond at FXH-OH₂ complex, The contour plane is chosen along the formamide plane.¹⁴²

4.4.3 H-bond of group-14 heavier analogues of formamide at electronically excited states

At the lowest-lying electronically excited states, the triplet and S_1 excited state, formamide and its heavier analogues adopt a different mode of H-bond with H_2O . Formamide and heavier analogues no longer prefer the planar structure at excited-state H-bond complexes: they are calculated to be pyramided at O and N at the DFT (the triplet) and CIS (S_1 excited state) level (see Figure 4.11). The sum of bond angle around N ($\Sigma\theta$) is with the range of $335.2^\circ\sim 349.1^\circ$ at the first two low-lying electronically excited states and, for heavier formamide, O is more distorted ($\Sigma\theta_O=310.0^\circ\sim 336.8^\circ$) than formamide ($\Sigma\theta_O=341.0^\circ$ and 350.0°). The pyramids of O and N elements at the same direction make formamide and heavier analogues to form two H-bonds with water at the same time (see Figure 4.11). Thus, formamide and its heavier analogues have a double H-bonding mode with H_2O except stanna-formamide-water complex at S_1 excited state.¹⁴²

Figure 4.11 Optimized geometries of formamide (heavy analogues) - H_2O complexes at (a) their triplet and (b) S_1 excited state (the bond length at Å and the bond angle at degree).¹⁴²

Through formamide and its heavier analogues have formed two H-bonds with water at the same time as donor and acceptor respectively, the excited-state H-bonds between them become weakened at the triplet and S_1 excited state. NBO analysis indicates that H-bond donor-acceptor interaction at low-lying excited states is considerably weaker than the ground state: the sum of NBO stabilization energies of two H-bonds at excited states are rather less than the single H-bond stabilization energy at the ground state (see Table 4.5, 4.6 and 4.7).

When excited to the higher S_1 electronic state, there are weaker H-bond attractions between formamide (heavier analogues) and water than the triplet. For heavy formamide, there are minimal H-bond interactions at their S_1 excited state.¹⁴²

Table 4.7 NBO stable energies of donor-acceptor interaction in double H-bonds of formamide and heavier analogues-water complex (at kcal/mol) and the adiabatic excitation energies (at eV) at two lowest-lying electronically excited states, triplet state and S_1 excited state, calculated at the TD-DFT level.¹⁴²

	formamide-water			silaformamide-water		
	$\Delta E(n_O \rightarrow \sigma^*_{H2-N})$	$\Delta E(n_O \rightarrow \sigma^*_{H4-O2})$	$\Delta E_{excited}$	$\Delta E(n_O \rightarrow \sigma^*_{H2-N})$	$\Delta E(n_O \rightarrow \sigma^*_{H4-O2})$	$\Delta E_{excited}$
the triplet	-0.94	-0.28	3.90	-1.11	-1.71	2.92
S_1 excited state	-1.06	-0.00	4.43	-0.54	-0.08	3.46
	germaformamide-water			stannaformamide-water		
	$\Delta E(n_O \rightarrow \sigma^*_{H2-N})$	$\Delta E(n_O \rightarrow \sigma^*_{H4-O2})$	$\Delta E_{excited}$	$\Delta E(n_O \rightarrow \sigma^*_{H2-N})$	$\Delta E(n_O \rightarrow \sigma^*_{H4-O2})$	$\Delta E_{excited}$
the triplet	-1.53	-0.75	2.16	-1.15	-3.70	1.69
S_1 excited state	-0.18	-0.00	2.93	-0.00	-0.00	2.62

4.5 H-bond of group-16 heavier analogues of formamide

In scheme-4.5, optimized geometries of different formamide-complexes (**1**→Formamide, **2**→S-Formamide, **2**→Se-Formamide and **4**→Te-Formamide) are shown. Those formamide-complexes are divided into three classes, **A**, **B** and **C**, based on the monomer with which formamide form complexes. **A** class includes formamide-HF complexes and **B** and **C** classes are hydrated and ammoniated formamide complexes. Formamides **A1-A4** act as “donor” while forming complexes with HF. Interestingly, except for **B1** and **C1**, both formamide-H₂O (**B2-B4**) and formamide-NH₃ complexes (**C2-C4**) appear to have five member ring structures unlike formamide-HF complexes. It implies that formamides and monomers play dual role as both a donor and an acceptor at the same time, which results in the ring structures. These structures and their energetic results are in agreement with both experimental and theoretical data.^{172, 173} The dissociation energies were calculated by equation 4.1 at the B3LYP level. It is found that formamide-HF complexes (**A**) are more stable than their corresponding cyclic or non-cyclic structure of **B** and **C** by 24.01 and 43.87 kcal/mol (considering only the energy of

complexes, see Appendix A, Table A5), respectively.¹⁷⁴

Scheme 4.5 Formamide complexes under investigation.

4.5.1 Geometric analysis of group-16 heavier analogues of formamide complexes.

Dissociation energy of formamide complexes and the optimized H-bond length along with other important geometric parameters are tabulated (See Appendix A, Table A6). The positive values of each parameter in Table A6 indicate the increase of that parameter for complexes compared to their monomer structures at the same level. Compare to $\text{CH}_3\text{-NH}_2$ molecule, formamide has shorter C–N bond length which was investigated in our previous work.^{143, 175} Further shortening of C–N bond taking place here as a consequence of H-bond formation between formamides and H_4Z ($\text{Z}=\text{F}, \text{OH}, \text{NH}_2$) molecules. More specifically, contraction of C–N due to $n_{\text{N}} \rightarrow \pi^*_{\text{CY}}$ (which is also cause for the elongation of CY bond length) is more significant in complexes of class **A** than class **B** or **C**. Interestingly, with the declination of the strength of $\text{Y} \cdots \text{H}_4$ bond in complexes (for class **A** and **B**), the shortening of C–N bond is getting lesser (from 0.014 to 0.004 Å) and for class **C** complexes, it remains unchanged

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(0.003 Å) where $Y \cdots H_4$ bond becomes very weak. As expected, according to the difference in electronegativity between C and Y atom, the C–Y bond distance elongates (by 0.005–0.012 Å) from C to Te. It is found that H-bond length ($Y \cdots H_4$) also increases both from group A to C and from 1 to 4 attributed to the consecutively weaker $n_Y \rightarrow \sigma^*_{H_4Z}$ interactions between H-bond acceptor (Y) and H-bond donor (H_4-Z). It also gives rise to an increase in the bond length of H_4-F , H_4-O_2 and H_4-N_2 by 0.022–0.030 Å, 0.008–0.011 Å and 0.003–0.004 Å respectively from their isolated optimized structures at the same B3LYP level. Contracted bond distance ($Y \cdots H_4/Z \cdots H_3$) refers to stronger H-bond in formamide complexes which is supported by their progressively higher value of dissociation energies (See Appendix A, Table A6). The dissociation energies ($|\Delta E_{Diss}|$) increase in this order: **C1**<**C2**<**C4**<**C3**<**B4**<**B3**<**B2**<**B1**<**A4**<**A3**<**A2**<**A1**.¹⁷⁴

It is observed that the C–H₃ bond length in formamide complexes (**C1**, **B1-B2** & **A1-A3**) shrinks about 0.001 ~ 0.006 Å. It can be considered as a combined effect of $Y \cdots H_4$ bond formation with negligible interaction between formamide H₃ and H-bond acceptor Z atoms. Generally as H-bond donor (in cyclic formamide complexes) C–H₃ bond length is expected to be elongated; surprisingly it only occurs in **C3** (0.001 Å) and **C4** (0.002 Å). Nevertheless, the difference of bond length between formamide monomers and their respective complexes, Δr_{C-H_3} , appeared to be a better indicator of the H-bond strength with ZH₄ than Δr_{Y-H_4} . Its higher negative values indicate stronger H-bond in Y and H₄ atoms. In contrast, its higher positive values point to weaker $Y \cdots H_4$ bond and comparatively stronger $Z \cdots H_3$ bond. Though it is difficult to find out the quantitative contribution of each H-bond to total dissociation energy in case of complexes with bi-functional H-bonds, the above results suggest that major contribution in dissociation energies, comes from $Y \cdots H_4$ bond formation for classes A and B. But for class C complexes, the contribution from $Z \cdots H_3$ bond becomes also significant. The strength of $Z \cdots H_3$ gradually increases from **C2** and it becomes the highest in **C4** where there is very weak interaction between Y and H₄ atoms. Figure 4.12 (a) shows a linear correlation between $r_{Y \cdots H_4}$ and their corresponding dissociation energies in both cyclic and non-cyclic formamide complexes where the slope of C is only negative unlike classes A and B.¹⁷⁴

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Figure 4.12 (a) Correlation between dissociation energy (kcal/mol) and H-bond length, $Y\cdots H_4$ (Å) (b) Correlation between $\angle Y\cdots H_4Z$ and H-bond length, $Y\cdots H_4$ (Å) for all formamide complexes.¹⁷⁴

There is also a good correlation ($R^2=0.98$) found between $Y\cdots H_4$ bond length and the bending angle between H-bond donor and acceptor ($\angle Y\cdots H_4Z$) in Figure 4.12(b). It appears that $Y\cdots H_4$ is the dominating H-bond in formamide complexes. The bond angle $\angle Y\cdots H_4Z$ in complexes of **A** indicates less deviation from co-linearity (than B/C complexes) where stronger $Y\cdots H_4$ bond exists and no bond formation between H_3 and Z atoms. It makes sense

as linear bonding ensures maximum overlap between donor-acceptor orbitals thus results in stronger H-bond. But in **B** and **C** complexes, there is considerable bending of H-bond which could be the reason for their cyclic structures with bi-functional H-bonds. It is to be noted that $\angle \text{CH}_3 \cdots \text{Z}$ is getting higher with the decrease of angle $\angle \text{Y} \cdots \text{H}_4\text{Z}$. Both incidents suggest that $\text{Z} \cdots \text{H}_3$ bond is formed because of the strain from $\text{Y} \cdots \text{H}_4$ and it is consistent with graph $\angle \text{CH}_3 \cdots \text{Z}$ versus $\angle \text{Y} \cdots \text{H}_4\text{Z}$ where $R^2=0.99$ (See Appendix A, Figure A4). Further discussion on the nature of H-bond is presented in later sections.¹⁷⁴

4.5.2 QTAIM analysis

It is a topological analysis based on quantum theory of atom in molecules, a good representation of bonding interactions. It confirms the possibility of H-bond formation and also examines their nature. It is evident that the electron density at bond critical point (BCP) is a good measure of H-bond strength which is the fundamental step for AIM (Atoms in

Figure 4.13 Molecular graphs for formamide complexes (**A1-A4**, **B1-B4**, **C1-C4**) and monomers (formamide **1-4**, HF, H₂O and NH₃). Large circles corresponds to nuclear critical point (3,-3) attributed to nuclei and small green/blue circles on bond path correspond bond critical points(3,-1) whereas red small circles correspond to ring critical points (3,1). Electron density values (a.u.) are mentioned above the BCPs and also the ellipticity values at C–N and at C=Y are indicated in parenthesis.¹⁷⁴

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molecules) calculation. BCP indicates the minimal values of electron density along the bond path between two atoms and it is evidenced that H-bond forms when the value of electron density at BCP falls typically in the range of 0.002 to 0.040 au.¹⁷⁶⁻¹⁷⁸ Based on this criterion, QTAIM analysis confirms the existence of single H-bond in formamide complexes except **B2-B4** and **C2-C4** (Figure 4.13) with a wide range of electron density (highest: 0.051au on O···H₄ of **A1** and lowest: 0.006 au Te···H₄ of **C4**; see Table 4.8). It can be a useful indicator for H-bond strength.¹⁷⁴

Table 4.8 AIM parameters for formamide complexes.¹⁷⁴

Complexes	Hydrogen bond, Y···H ₄				Hydrogen bond, Z···H ₃			
	$\nabla^2\rho_{b1}$	$-V_{b1}$	G_{b1}	H_{b1}	$\nabla^2\rho_{b2}$	$-V_{b2}$	G_{b2}	H_{b2}
A1	0.154	0.051	0.045	-0.006	-	-	-	-
A2	0.056	0.021	0.018	-0.003	-	-	-	-
A3	0.047	0.016	0.014	-0.002	-	-	-	-
A4	0.028	0.013	0.010	-0.003	-	-	-	-
B1	0.100	0.021	0.023	0.002	-	-	-	-
B2	0.043	0.009	0.010	0.001	0.033	0.005	0.007	0.002
B3	0.036	0.007	0.008	0.001	0.032	0.005	0.006	0.001
B4	0.024	0.006	0.006	0.000	0.035	0.005	0.007	0.002
C1	0.050	0.009	0.011	0.002	-	-	-	-
C2	0.024	0.004	0.005	0.001	0.032	0.005	0.007	0.002
C3	0.020	0.003	0.004	0.001	0.035	0.006	0.007	0.001
C4	0.014	0.002	0.003	0.001	0.038	0.006	0.008	0.002

Due to H-bond formation, the electron density at CN and CY bonds in formamides is redistributed by the change of ellipticity values (and also $\Delta\rho$ values). From **A** to **C**, the values of $|\Delta\rho|$ on Y···H₄ bond decreases by almost 50% whereas this rate is very minimal from **2** to **4** (**1-2**, it is about 40%). A good correlation ($R^2=0.96$; Figure. 4.14(a)) is found between electron density at BCP and H-bond strength as a function of bond length Y···H₄. The decreasing value of ρ at CY bond in all formamide complexes describes lengthening/weakening of that bonds due to charge shift to $n_N\rightarrow\pi^*_{CY}$. Like BCP, density at ring critical point (RCP) depicts the structural stability of the ring structure due to the coexistence of more than one H-bond.¹⁷⁴

Figure 4.14 (a) Correlation of ρ_{BCP} (a.u.) with H-bond length, $\text{Y}\cdots\text{H}_A$ (Å) and (b) Correlation between $\log \nabla^2 \rho_{\text{BCP}}$ (a.u.) with H-bond length, $\text{Y}\cdots\text{H}_A$ (Å) for formamide complexes.¹⁷⁴

Laplacian of electron density ($\nabla^2 \rho$) derived from hessian matrix of ρ , is another important topological parameter which characterize H-bond nature into electrostatic or covalent. Koch and Popelier determined its range from 0.024 to 0.139 au for moderate strength of H-bond.¹⁷⁶⁻¹⁷⁸ Considering this range, both **A1** and **C4** fall outside of the range. The virial theorem in

QTAIM framework explains the nature of H-bond more precisely by introducing two more terms: G_b and V_b as kinetic and potential energy density at BCP. The relation among them is as follows:

$$\frac{1}{4} \nabla^2 \rho_b = G_b + (G_b + V_b) = G_b + H_b,$$

Where H_b is total electronic energy density and G_b is always positive whereas V_b is always negative. In general, when G_b is prevailing, H_b and $\nabla^2 \rho_b$ both become positive pointing to the depletion of electronic charge along the bond.

It is generally experienced in close shell interactions like electrostatic bonding. But when V_b is dominating, it immediately turns H_b negative whereas $\nabla^2 \rho_b$ still remains positive until $|V_b|$ is greater than twice of G_b . Negative value of $\nabla^2 \rho_b$ refers to the accumulation of electronic charge which is encountered in covalent bond. The intermediate situation ($H_b < 0 < \nabla^2 \rho_b$) is defined as partially electrostatic and partially covalent. H-bonds ($Y \cdots H_4$) in **A** complexes are of this category i.e. partially electrostatic and partially covalent in nature. In the same way, H-bonds in **B** and **C** are electrostatic in nature with decreasing strength from **1** to **4**. It indicates that covalent nature strengthens the H-bonds. In our studied complexes, electrostatic character becomes more conspicuous in weaker H-bond. It is to be noted that $\nabla^2 \rho_b$ is a more sensible parameter than ρ_b and has better correlation with $Y \cdots H_4$ ($R^2=0.99$; Figure 4.14(b)).¹⁷⁴

4.5.3 NBO analysis

NBO analysis is an effective tool to define the H-bond through charge delocalization based on donor-acceptor orbital interactions. It reveals that $Y \cdots H_4$ and $Z \cdots H_3$ take place due to electron transfer from almost filled lone pair (LP) orbitals of Y (=C, S, Se, Te) atom to unfilled antibonding orbital of H_4Z ($n_Y \rightarrow \sigma^*_{H_4Z}$) and again LP orbitals of Z to antibonding orbital of $\sigma^*_{H_3C}$ ($n_Z \rightarrow \sigma^*_{H_3C}$) respectively. Though there are several interactions taking place between different donor and acceptor orbitals of both formamides and small molecules (ZH_4), NBO shows that highly electron occupied lone pair orbital of Y in formamides and Z in small molecules are major channels for electron transfer which initiates electron flows between two fragments.¹⁷⁴

Table 4.9 The 2nd order perturbation energies from NBO analysis in formamide complexes at the level of B3LYP/aug-cc-pvtz.¹⁷⁴

species	HF-complex(kcal/mol)				H ₂ O-complex(kcal/mol)				NH ₃ -complex(kcal/mol)			
	ΔE	ΔE	ΔE	ΔE_t	ΔE	ΔE	ΔE	ΔE_t	ΔE	ΔE	ΔE	ΔE_t
	($n_{Y1} \rightarrow$	($n_{Y2} \rightarrow$	($n_F \rightarrow$		($n_{Y1} \rightarrow$	($n_{Y2} \rightarrow$	($n_{O2} \rightarrow$		($n_{Y1} \rightarrow$	($n_{Y2} \rightarrow$	($n_{N2} \rightarrow$	
	σ^*_{H4-F}	σ^*_{H4-F}	σ^*_{H3-C}		σ^*_{H4-O2}	σ^*_{H4-O2}	σ^*_{H3-C}		σ^*_{H4-N2}	σ^*_{H4-N2}	σ^*_{H3-C}	
formamide	5.76	21.64	0.00	27.40	1.67	7.50	0.03	9.20	0.25	2.32	0.43	3.00
S-formamide	1.05	19.83	0.04	20.92	0.12	5.57	0.25	5.94	0.00	1.33	1.43	2.76
Se-formamide	0.64	17.55	0.03	18.22	0.04	4.88	0.31	5.23	0.00	1.08	1.73	2.81
Te-formamide	0.53	14.92	0.01	15.46	0.05	3.53	0.33	3.91	0.00	0.77	1.85	2.62

Decrease of occupancy in n_Y is found from **C** to **A** complexes which indicates the increment in electron outflow from LP orbitals of Y atoms (see Appendix A, Table A7). It correlates with their gradually elongated C–Y bond length and also with shortening of $Y \cdots H_4$ bond. Latter is ensured by maximum orbital overlap between n_Y and σ^*_{H4Z} . It also corresponds with their increasing stabilization energies for $n_Y \rightarrow \sigma^*_{H4Z}$ from second order perturbation analysis (see Table 4.9). For any class, reduction of occupancy in n_Y from **4** to **1** (Y=Te to O) is associated with more charge flow towards σ^*_{H4Z} . In the same manner, almost fully occupied n_F and n_{O2} orbitals and poor occupancy in σ^*_{H3-C} show their (HF and H₂O) poor ability as H-bond acceptor for these complexes. On the other hand, comparatively less electron occupancy in n_N of NH₃ (from Y=O to Te) appeared as a result of more electron outflow towards σ^*_{H3-C} is the indication to its better performance as H-bond acceptor. Their increasing second order perturbation energies (0.43 to 1.85 kcal/mol) for electron flow directed to $n_{N2} \rightarrow \sigma^*_{H3C}$ can also explain the ascending trend of dissociation energy from **C1** to **C4** where there is weak to no $Y \cdots H_4$ bond exists.¹⁷⁴

From the donor-acceptor orbital interactions, it is found that its s character more concentrates in $n_{Y1/Y2}$ lone pair orbitals of Y in **A** rather than **B** or **C** complexes (see Appendix A). According to Bent's rule¹⁷⁹, this implies more polarized nature of C^+-Y^- bond in **A** complexes which increases their capacity as Lewis base for H-bond formation with H₄Z. But LP of N atom in NH₃ shows more P character on going from **C1** to **C4** in bonding with H₃ describing its enhanced affinity towards bond formation with more positively charged

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H₃as H-bond donor. It is also noted that for class **A**, both the LP orbitals (Y₁/Y₂) of Y effectively overlap with acceptor orbital σ^*_{H4F} making nearly aligning H-bond (see figure 4). Because of its linear geometry, the distance between n_F and σ^*_{H3C} becomes too large to form a second H-bond. In case of **B/C** complexes, comparatively weak Y...H₄ bond attributed to smaller electronegative difference between C & Y and the overlap with only one n_Y orbital (except **B1**) is compensated with their decreased H-bonding angle.¹⁷⁴ And it becomes favourable for weak interaction between n_Z and $\sigma^*_{\text{H3-Cto}}$ to form a five-member ring structure.

Figure 4.15 NBO contour figures for the donor-acceptor interaction (a) $n_Y-\sigma_{\text{H4F}}^*$ delocalization for **A1-14**; (b) $n_Y-\sigma_{\text{H4O}}^*$ and $n_O-\sigma_{\text{H3C}}^*$ delocalization for **B1-B4**; (c) $n_Y-\sigma_{\text{H4N}}^*$ and $n_N-\sigma_{\text{H3C}}^*$ delocalization for **C1-C4**.¹⁷⁴

4.5.4 H-bond strength by BLW-ED and NEDA analysis and correlation among different methods

With the help of energy decomposition analyses, the total interaction energy can be divided into several meaningful quantities such as deformation, electrostatic, exchange repulsion, polarization, charge transfer etc. Each of the components has a particular role in the formation of the H-bonds, albeit the nature of H-bond can be determined by a quantitative comparison among them i.e. the “net effect” of all interacting energy components. Nevertheless, it is difficult to quantify their contributions separately for each of two H-bonds existing in the same complex. Table 4.10 presents the energy components of the interaction

Table 4.10 Different energy components from NEDA analysis and BLW-ED analysis in formamide complexes.¹⁷⁴

Energy components	HF-complex(kcal/mol)				H ₂ O-complex(kcal/mol)				NH ₃ -complex(kcal/mol)			
	A1	A2	A3	A4	B1	B2	B3	B4	C1	C2	C3	C4
ΔE_{HL}	-0.77	0.10	-0.11	-0.02	-1.58	-1.08	-1.09	-1.13	-1.39	-1.21	-1.24	-1.22
$\Delta E'_{CT}$	-5.33	-5.36	-5.04	-5.41	-2.26	-2.30	-2.23	-2.10	-1.07	-1.28	-1.31	-1.25
$\Delta E'_{POL}$	-5.78	-3.71	-3.28	-2.08	-2.14	-1.44	-1.34	-1.06	-0.87	-0.88	-0.94	-0.95
ΔE_{BLW}	-11.89	-8.97	-8.43	-7.51	-5.98	-4.81	-4.66	-4.29	-3.33	-3.38	-3.49	-3.42
ΔE_{EL}	-20.93	-13.01	-12.24	-8.71	-12.81	-10.24	-10.44	-8.83	-8.32	-8.55	-9.17	-8.80
$(\Delta E_{ES};$	(-10.97; (-8.53; (-8.38; (-7.69;				(-19.43; (-13.28; (-12.30; (-10.50;				(-6.41; (-6.66; (-7.04; (-7.04;			
$\Delta E_{POL})$	- 3.75) -3.42) -4.14) -2.34)				-3.13) 0.66) 0.25) 3.74)				-3.86) -3.79) -1.77) -1.87)			
ΔE_{CT}	-27.99 -23.35 -21.08 -19.04				-11.60 -9.81 -9.22 -7.64				-5.45 -5.86 -6.02 -5.60			
ΔE_{CR}	37.88 29.35 26.79 22.3				19.04 16.11 15.73 12.78				10.76 11.35 11.85 10.95			
ΔE_{NEDA}	-11.04 -7.01 -6.52 -5.45				-5.37 -3.93 -3.94 -3.69				-3.02 -3.06 -3.34 -3.45			

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energies for all complexes stabilized by H-bond(s). At first, block localized wavefunction (BLW-ED) approach^{77, 79} based on the combined concepts of valence bond (VB) theory and molecular orbital (MO) theory is used to decompose the total energy step by step into the major three components: Heitler-London, polarization and charge transfer energy. Deformation energy is not considered here due to using of the monomer geometries in complex. Heitler-London energy is obtained by probing the fixed electron density into each unchanged monomer geometries in complex illustrating the net effect from coulomb attractive and Pauli exchange repulsive interactions. Smaller value of ΔE_{HL} indicates that electrostatic energy in complex is appreciably offset by the positive value of exchange repulsion energy. Nevertheless, comparatively higher values of ΔE_{HL} (36~42%) in **C** complexes explicitly express about the electrostatic nature of H-bond in them (figure 5a). In addition to this, about 26~28% contribution originates from reorganization of electron densities in individual fragments termed as polarization energy which enhances the electrostatic interactions. The sum of electrostatic and polarization energies are very often termed as “purely electrostatic part” by Morokuma¹⁸⁰, which is comparable to the electrical component of NEDA analysis, an efficient and robust tool to explore H-bonding. Both ΔE_{ES} and ΔE_{POL} are defined for electron densities within monomer geometries having no overlap between them but they help to direct the two fragments with more favourable orientation for H-bond formation.¹⁷⁴

NEDA analysis based on Weinhold's natural bond orbitals approach^{67, 181, 182} is also carried out to compare the results within different schemes and also compute electrostatic term separately which is included in the Heitler-London exchange energy by the BLW-ED analysis. Energy components of NEDA analysis are also presented in (Table 4.10, Figure 4.16 (b)) but only the stabilization energy component is discussed here. According to NEDA results, electrical (ΔE_{EL}) contribution in **C** complexes is about 60% in which electrostatic (ΔE_{ES}) components is dominating with respect to the charge transfer amount. So, NEDA result is in complete agreement with the BLW-ED analysis carried out for **C** complexes. Analyzing the NBO data for **C2** to **C4**, the average ratio of charge transfer (attributed to $n \rightarrow \sigma^*$) for $Y \cdots H_4$ and $Z \cdots H_3$ H-bond is 1:1.70. But, it does not necessarily mean the higher electrical contribution in $Y \cdots H_4$ in spite of having their overall electrostatic nature of H-bonds. Rather electrostatic nature is qualitatively more profound in $Z \cdots H_3$ than in $Y \cdots H_4$

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(Table 4.9). So, electrostatic and charge transfer terms both are comparatively higher in $Z \cdots H_3$ than in $Y \cdots H_4$ of **C** complexes. Overall, the energy cost for charge transfer between two fragments strengthens the H-bond a little bit more with their slightly lower (higher) contribution than ΔE_{HL} (polarization) component.¹⁷⁴

Figure 4.16 (a) Contribution of BLW-ED energy components (heitle-London, polarization and charge transfer terms) to the total interaction energy (kcal/mol) of formamide complexes; (b) Contribution of NEDA energy components (electrostatic, polarization and charge transfer terms) to the total interaction energy (kcal/mol) of formamide complexes.¹⁷⁴

A higher influence of charge transfer to the interaction energy with respect to the electrostatic or polarization component (by both NEDA and BLW-ED analyses) is observed in **B** complexes though the combined effect from electrostatic energy and polarization give them electrostatic nature over the charge transfer effect. The percentage of contribution by polarization is quite different from BLW-ED to NEDA but it does not influence our conclusion about H-bond nature in **B** complexes. From **B2** to **B4** the ratio of charge transfer ($n_Y \rightarrow \sigma^*_{H4Z}$ to $n_Z \rightarrow \sigma^*_{H3C}$) attributed to the formation of $Y \cdots H_4$ and $Z \cdots H_3$ H-bond varies like 23:1, 16:1 and 11:1. It means that the influence of charge transfer on $Y \cdots H_4$ bond decreases from **B2** to **B4** for which the covalent character of that bond reduces and it is consistent with increasing H-bond length ($Y \cdots H_4$).¹⁷⁴

When formamides react with Lewis acid like HF to form **A** complexes, charge transfer component is found to make a significant contribution (60~70%) to the interaction energy, even more than the electrical contribution (sum of electrostatic and polarization). It is reflected on their covalence nature of H-bond with shorter bond length and it is consistent with QTAIM analysis. In NEDA framework, we can note that for **A2** and **A4**, polarization energy is destabilizing which should be considered quantitatively rather than qualitatively. It is due to the self-energy (SE) terms for formamide and HF. Compare to this the BLW-ED data is quite reasonable with the positive value of Heitler-London energy. It is indicative of an increase of exchange repulsive energy over electrostatic energy in the fragments. All these observations on H-bond formation in formamide complexes highlight the fundamental significance of CT as its relative magnitude ultimately decides the nature and strength of H-bond in these complexes.¹⁷⁴

H-bond strength in each formamide complexes calculated by BLW-ED and NEDA methods has good linear relation with the dissociation energy. We have also put the second order stabilization energy of H-bond by NBO analysis on the same plot. It is found that both BLW-ED and NEDA methods can well describe H-bond strength in these systems and latter can evaluate H-bond strength more accurately in weaker H-bond system like formamide-NH₃ complex (Figure. 4.17). Thus, we have extended the NEDA analysis to the excited states of formamide complex which will be discussed in next section.¹⁷⁴

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Figure 4.17 Correlation between evaluated H-bond strength in formamide complexes by different methods (NEDA, BLW and NBO) with dissociation energies of formamide complexes.¹⁷⁴

4.5.5 Formamide-water complexes (B1-B4) at their low-lying excited states

We analyzed only formamide-H₂O (**B1-B4**) system to understand the nature and electronic properties of H-bonded formamide complexes at their low-lying excited states (T₁, T₂ and S₁) and also the effect of electronegativity at Y in forming H-bond. Replacing Y= O by S, Se or Te, the heavier atoms with less electronegativity; the conjugation between $n_Y \rightarrow \pi^*_{CN}$ at all three states, gets stronger reflecting in the increased double bond character of CN bond. It appears that heavier atoms cause large electron density irrespective of their decreasing trend of electronegativity. But it can be explained by their larger polarizability with the increased atom size and can be said that like at their ground states (S₀) polarizability can also plays an important role at their low lying excited electronic states. Theoretical optimization with CIS (configuration interaction singles) method leads to different bond formation between formamide with water molecules at their low-lying triplets (T₁ and T₂) and singlet excited states (S₁). Interestingly, they become pyramided both at C and N of formamide at electronically excited states ($\Sigma\theta_N=335.2\sim357.9^\circ$; $\Sigma\theta_C=340.5\sim359.5^\circ$) and form weaker to stronger H-bond (H₁⋯O₂ or H₂⋯O₂ and sometimes Y⋯H₄) from T₁ to T₂ and S₁ compared to those of at the ground state of formamide-H₂O complex. It signifies the fact, how changes in structure at excited states influences the intermolecular charge transfer and thus the nature of H-bond.¹⁷⁴

At T₁ state, H-bond is formed in order for $n_Y \rightarrow \sigma^*_{O_2H_4}$ and $n_{O_2} \rightarrow \sigma^*_{NH_1}$ interactions while both the H-bonds formed at the same side of C–N bond (with Y and H₁ of formamide). Along O to Te; towards less electronegativity atoms (Y), H-bond (Y⋯H₄) is getting weaker which results in the strengthening of other H-bond (H₁⋯O₂). The important parameters of H-bond formation at excited states are listed in Table 4.11. Interestingly T₂ state is the lower lying electronically excited state than S₁ state for formamide and its complexes. It is also found that at T₂, H-bond is formed in **B3** and **B4** at the different side of C–N bond (with H₂ of formamide) and this pattern of H-bond (in **B1-B4**) remains same at S₁ state also. Thus, except **B1**, both at T₂ and S₁ excited states, **B2-B3** have almost no interactions in between Y (formamide) and H₄ (water) which leads them to possess single H-bond, H₁/H₂⋯O₂ resulting from $n_{O_2} \rightarrow \sigma^*_{N_1H_1/H_2}$ interactions. Unlikely H₁/H₂⋯O₂ bond in **B2-B3**, H-bond in **B1** is much deviated from linearity in order to undergo the influence of charge transfer from $\pi_{CY} \rightarrow \sigma^*_{O_2H_4}$ at S₁. These structural changes are consistent with resonance structures from earlier studies⁷⁶,

^{137, 183-186} and an indication of increased ionic contribution. The different nature of H-bonding in **B1** can be explained with NTO (The natural transition orbital) analysis.¹⁷⁴

Table 4.11 The important parameters of H-bond formed in Formamide-H₂O complexes (**B1**-**B4**) at their low-lying excited states (T₁, T₂ and S₁).¹⁷⁴

Complexes	ΔE_{rel}	$r_{\text{C-N}}$	$r_{\text{C-Y}}$	$r_{\text{H1/H2...O2}}$	$r_{\text{Y...H4}}$	$\angle_{\text{Y...H4O2}}$	$\angle_{\text{N-H1...O2}}$	$\Sigma\theta_{\text{N}}$	$\Sigma\theta_{\text{C}}$
B1 _(T1)	3.87	1.430	1.323	2.085	2.075	141.3	146.8	342.4	340.9
B2 _(T1)	2.62	1.393	1.759	2.059	2.572	137.5	156.2	353.7	346.3
B3 _(T1)	2.27	1.378	1.934	2.052	2.681	138.6	156.3	357.9	344.1
B4 _(T1)	1.81	1.374	2.143	2.083	2.866	140.4	153.7	355.9	343.2
B1 _(T2)	4.21	1.398	1.393	2.345	4.534	73.7	174.7	341.3	340.5
B2 _(T2)	2.67	1.393	1.726	2.291	3.724	105.2	180.0	346.7	352.4
B3 _(T2)	2.43	1.398	1.824	2.322	5.371	71.6	174.1	343.0	351.3
B4 _(T2)	1.74	1.413	2.027	2.344	6.467	60.6	176.5	336.4	347.8
B1 _(S1)	4.43	1.427	1.263	2.358	2.524	125.8	142.4	335.2	350.0
B2 _(S1)	3.30	1.406	1.656	2.305	5.317	74.7	176.4	338.4	359.5
B3 _(S1)	2.84	1.390	1.814	2.276	5.697	66.9	173.1	344.2	356.3
B4 _(S1)	2.29	1.377	2.032	2.237	6.414	55.8	173.4	346.2	350.8

Figure 4.18 describes the low-lying electronic transition in a very convenient way with the term of “hole-particle excitation”. Figure 4.18 represents the NTO orbitals of formamides (**B1**-**B4**) describing the S₀→T₁, S₀→T₂ and S₀→S₁ transitions where λ denotes the fractional contribution of holes and particles in their respective occupied and unoccupied spaces. From TDDFT calculations it is found that the holes and particles both maintain the delocalized nature while it decreases from **B1** to **B4** in the S₁ state. It shows how the electronegativity of Y plays significant role in charge transfer like transitions. It is of interest that HOMO-1→LUMO is mainly responsible for S₀→T₁ transition (though for **B1**, the main contribution comes from HOMO-1→LUMO+1) whereas S₀→T₂ and S₀→S₁ transitions are predominantly HOMO→LUMO transition (only for **B1**:HOMO-2→LUMO+1 at S₀→T₂ and HOMO-1→LUMO+1 contributes at S₀→S₁) though there are some secondary/minor contributions from lower HOMOs to LUMO. It is clearly found that in all these excitation states, H-bond strength depends on the extent of delocalized or localized nature of electron

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density over its formamide skeleton mainly which is due to the charge transfer like transition through hole-particle excitation among the natural transition orbitals.¹⁷⁴

Figure 4.18 Pictorial representation of natural transition orbitals (NTO) of B1-B4 in formamide-H₂O complex describing the S₀→T₁, S₀→T₂ and S₀→S₁ transitions calculated with TDDFT/aug-cc-pVTZ (LANL08d for Te).¹⁷⁴

Figure 4.19 Correlation between evaluated relative H-bond strength in formamide-H₂O complexes by NEDA methods with their relative electronic energies (kcal/mol).¹⁷⁴

We have carried out NEDA analysis on optimized structures of formamide-H₂O complexes in their excited states as it provides good results in their ground states also. After plotting the extent of H-bond strength by NEDA analysis against the relative electronic energy of corresponding formamide complexes, a good correlation is found with $R^2 = 0.83 \sim 1.00$ (see Figure 4.19). NEDA result shows that at T₁ state, H-bond in all formamide complexes is getting weaker. But at T₂ and S₁, they become slightly stronger or similar as that of at ground state except **B1**. The H₁/H₂...O₂ bond is more dominating in excited state unlike the ground state due to deformed structures.¹⁷⁴

4.6 Conclusions

The current DFT calculations and NBO analysis on the heavier group-14 analogue of formamide, including silaformamide **2**, germaformamide **3** and stannaformamide **4**, contributed fundamental understanding to their electron structures, the nature and strength of H-bond and the origin of internal rotational barrier.¹⁷⁴ The n- π conjugation strengths of heavier group-14 analogues of formamide do not always show the downward trend as X atom moves down the group 14 column. The n- π conjugation for heavier analogues of the second or third row, silaformamide and germaformamide, are of similar magnitude by NBO perturbation analysis. The weaker delocalization in heavier group-14 analogue than formamide is attributed to the smaller overlap between lone-pair orbital of nitrogen and π orbital of X=O bond.¹⁷⁴

At the level of CCSD(T)/aug-cc-pVTZ, the rotational barriers of formamide and heavier group-14 analogues **1-4** show a gradually reducing trend: formamide (15.73 kcal/mol) > silaformamide (11.73 kcal/mol) > germaformamide (9.45 kcal/mol) > stannaformamide (7.50 kcal/mol). In contrast to formamide, the $n \rightarrow \pi_{X=O}$ conjugation of heavier group-14 analogue is not the only factor that dictates the internal rotational barrier, the $n_N \rightarrow \sigma_{X-O}^*$ hyperconjugation at TS and steric effect also contribute to the overall rotational barrier. A reasonably good linear correlation is observed between the internal rotational barriers and the sum of the energetic difference of conjugational, hyperconjugational stabilization energies and steric repulsion energies between the planar structure and TS, indicating that there are many cooperative factors determining the internal rotation barrier.¹⁷⁴

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NBO and NEDA analyses have been carried out to study the strength and nature of H-bond of formamide and its heavier group-14 analogues with water as donor and acceptor (including two lowest electronically excited states). From the point of $n_B \rightarrow \sigma_{AH}^*$ CT interaction, FXO-H₂O and FXH-OH₂ complexes have different CT trend. For the FXO-H₂O complexes, the CT from non-aligning lone-pair orbital of heavier analogues of formamide into the unfilled σ_{OH}^* anti-bonding orbital of H₂O induce the deviation of O-H bond in the direction of n_O orbital, which give a maximal cooperative CT. The heavier group-14 analogues of formamide prefer being H-bond acceptors to form FXO-H₂O complexes compare to being H-bond donors to form FXH-OH₂ complexes. The FXO-H₂O complexes with the higher-row X atoms have larger H-bond stabilization energies and the FXH-OH₂ complexes have similar H-bond stability. NEDA analysis indicates that the higher H-bond stability of FXO-H₂O complexes come from the stronger CT and electrostatic attraction. At the triplet and S_1 excited state, formamide and its heavier analogues become pyramided at O and N atoms and tend to adopt double H-bonds with H₂O as donor and acceptor at the same time. Weaker H-bond attraction can be expected when the H-bond complex has been excited to higher excited states.¹⁷⁴

When the donor of H-bond complex is Lewis acid like HF, heavier group-16 analogues of formamide only act as proton acceptor and form acyclic structure almost with linear alignment. However, the dual behavior of group-16 analogues of formamide as proton donor and acceptor in the H-bonded complex with H₂O and NH₃ prefers to form cyclic structure. QTAIM analysis shows that the electron density at BCP can shed light into the H-bond nature. The electron density at BCP of single H-bond is always more than the sum of electron density at BCPs of bi-functional H-bonds, for example, ρ at Y...H₄ of A2 is 0.032 a.u. whereas ρ_{sum} at Y...H₄ and H₃...Z of B2 and C2 is 0.024 and 0.019 a.u. respectively. It refers that the acyclic structure with single H-bond stabilizes the complexes more than the cyclic structure formed by bi-functional H-bonds. Especially the electron density at BCP of H-bond can well describe the H-bond strength in formamide complexes. NBO analysis indicates that the charge transfer from $n \rightarrow \sigma^*$ donor-acceptor interaction plays an important role in stabilizing the H-bond complex: the second order perturbation stabilization energy for $n \rightarrow \sigma^*$ donor-acceptor interaction are higher. Both NEDA and BLW-ED methods explain this fact by partitioning the H-bond stabilization energies into different physical components. The NEDA and BLW-ED bond energy of H-bond have good correlation with the dissociation energies. It indicates

that the NEDA and BLW-ED stabilization energy of H-bond can correctly evaluate the strength of H-bond. In any cases, H-bond whether it is purely electrostatic or partially covalent increases the charge mobility i.e. redistribution of electron cloud takes place which adds extra stabilization to the systems compared to the simple van der Waals molecular interaction.¹⁷⁴

The study at the electronically excited states (T_1 , S_1 and T_2) of formamide- H_2O complexes elucidates how changes in excited states structure influence the intermolecular charge transfer and thus the bond pattern for H-bond. It is found that NEDA is also capable to evaluate H-bond strength at excited state.¹⁷⁴

Chapter 5

Theoretical Studies on Germasilaallenes and their isomers

In this chapter, we study a series of germasilaallenes; Si/Ge based acyclic and cyclic systems and vigorously investigate their structures and electronic properties within density functional theory (DFT) framework. The study aims to elucidate some interesting phenomenon of germasilaallenes, such as their bent structures, stability and the low ring-opening barrier. We also investigate their bond-stretch cyclic isomers to explore their elusive nature.

Heavier groups 14 analogues of allene possess rich chemical properties and are very useful building blocks of organometallic chemistry.^{93, 94, 187} Since 1993, the first successful attempt of synthesizing 1-silaallene by West et al.,⁹⁵ heavier group 14 analogues of allene, silaallenes^{95, 96}, germaallenes^{97, 98} and tristannaallene⁹⁹, have attracted much attention from experimental and theoretical chemists. In 2005, Kira et al. synthesized the first trimetalaallene containing Ge=Si double bonds: 1,3-digermasilaallene **1** (see Scheme 5.1).¹⁰⁰ X-ray crystallographic analysis on 1,3-digermasilaallene **1** showed that similar to trisilaallene³ and trigermaallene,¹⁰⁰ the most stable structure of 1,3-digermasilaallene **1** is not linear but bent at central Si atom with bond angle of 125.7°. The 1,3-digermasilaallene **1** has a C₂ axis through the central atom with two Ge=Si double bond of the same length (2.269 Å) and the distance between the two terminal Ge atoms is 4.039 Å. In the same year, Kira et al. synthesized another heteronuclear trimetalaallene, 2-germadisilaallene **2**¹⁰¹ (see Scheme 5.1). The Ge=Si double bond length in the most stable isomer of 2-germadisilaallene **2** is 2.237 Å, the distance between two terminal Si atoms is 4.093 Å and the ∠SiGeSi bond angle is 132.4°.

A number of theoretical studies found that the parent trisilaallene and trigermaallene are highly bent at the central atom, e.g., the $\angle\text{SiSiSi}$ bond angle of trisilaallene is 70.4° at the B3LYP/6-311G(2d,p) level¹⁰⁴ and $\angle\text{GeGeGe}$ of trigermaallene is $\angle\text{GeGeGe} = 72.9^\circ$ at the B3LYP/6-311+G(d,p) level,¹⁸⁸ respectively.

Scheme 5.1 Structures of synthesized germasilaallenes **1** and **2**.

Although trimetalallenes had been extensively studied, some interesting phenomena are still not understood. For example, the reason behind the facts: why there are no slightly-bend isomer (within the range of a bond angle from 180° to 100°) for trimetalallenes while stable slightly-bend conformer of mono- and di- heavier allenes have been observed; why their cyclic isomers are actually bond-stretch isomers¹⁸⁹⁻¹⁹¹ and have low ring-opening barriers along the bending potential energy surface (PES). In the present study, we aim to explain the disappearance of slightly-bend isomers of trimetalallenes and the appearance of “bond-stretch” isomers and try to find the factors stabilize trimetalallenes.¹⁹²

In the current work we provide a theoretical study of four germasilaallenes (1,3-digermasilaallene **3**, 1,2-digermasilaallene **4**, 2-germadisilaallene **6** and 1-germadisilaallene **8** (see Scheme 5.2). Based on DFT calculations and NBO analysis, we discuss the bond-stretch phenomenon of cyclic isomers of germasilaallenes and the low ring-opening barrier. We will explore the reason why slightly-bend conformers of trimetalallenes vanish by comparing their bending PES with corresponding dimetalallene’s bending PES. We try to elucidate the factors to stabilize germadisilaallene within NBO framework. The recent

synthesis of 2-silaallene and 2-germaallene derivatives $[(\text{PPh}_2\text{S})_2\text{C}=\text{Si}=\text{C}(\text{PPh}_2\text{S})_2]$ and $[(\text{PPh}_2\text{S})_2\text{C}=\text{Ge}=\text{C}(\text{PPh}_2\text{S})_2]$ ¹⁹³ have also motivated us to search for one new type of linear trimetalallenes.¹⁹²

Scheme 5.2 Trimetalallenes and definition of geometric parameters, α and $\Sigma\theta$.¹⁹²

5.1 Computational methods

For the ease of discussing our results, we defined the central bond angle of all germasilaallenes, $\text{M}^1\text{M}^2\text{M}^3$ ($\text{M}=\text{Ge}, \text{Si}, \text{C}$), as α and the sum of bond angles ($\theta_1 + \theta_2 + \theta_3$) around terminal atoms as $\Sigma\theta$ (see Scheme 5.2). The detailed bending PESs of four trimetalallenes were obtained by decreasing the bond angle α from 180.0° to 45.0° with the step size of 15.0° . For the optimization of selected points along the bending PES, the bond angle α was kept constant while the other parameters were optimized. All the stationary points were fully optimized and frequency analysis was performed to ensure that the structure is a minimum and also to evaluate the zero-point energies (ZPEs) for correcting the relative energies. All the stationary points were fully optimized and frequency analysis was performed to ensure that the structure is a minimum and also to evaluate the zero-point energies (ZPEs) for correcting the relative energies.

The Natural Bond Orbital (NBO) analysis⁶⁶ and Wiberg Bond Index (WBI)¹⁶⁸ were used to characterize the bond pattern. The Natural Population Analysis (NPA)^{65, 181}, Natural Steric Analysis (NSA)^{69, 166} and WBI calculation were performed with NBO 5.0 package¹⁹⁴. The

topological analysis of the electron densities according to Bader's quantum theory of atoms in molecules (AIM)^{59, 147, 151} was performed to evaluate the bond property using AIM2000 package.¹⁹⁵ The multicentre bond index¹⁹⁶ was computed using Multiwfn 3.0 software¹⁹⁷, which used the Gaussian-09 formatted wfn files.¹⁹²

5.2 The bending PESs of germasilaallenes and minima

The bending PESs of four germasilaallene compounds are illustrated in Figure 5.1. Similar to trisilaallene and trigermaallene,^{104, 188} linear conformers of four germasilaallenes are not stable. Full geometry optimization except the bond angle ($\alpha = 180^\circ$) indicates that linear conformers of 1,3-digermasilaallene **3** (C_2) (see Figure 5.2) and 1,2-digermasilaallene **4** (C_1) are transition states on the bending PES with one imaginary frequency, which are lower in energetic than their linear allenic structure (D_{2d} and C_{2v} symmetry, see Figure 5.2) by 1.90 and 3.57 kcal/mol, respectively.¹⁹²

Figure 5.1 Bending PESs of 1,3-digermasilaallene **3**, 1,2-digermasilaallene **4**, 2-germadisilaallene **6** and 1-germadisilaallene **8** at the level of B3LYP/6-311+G(d,p).¹⁹²

Although the terminal atoms are pyramided (for **3** and **4**, $\Sigma\theta$ around Ge terminal atom are 305.1° and 287.4° , respectively; for **4**, $\Sigma\theta$ around Si terminal atom is 329.1°), the WBI indices of bond (for **3**, $\text{WBI}_{\text{Ge-Si}} = 1.61$; for **4**, $\text{WBI}_{\text{Ge-Ge}}$ and $\text{WBI}_{\text{Ge-Si}} = 1.71$ and 1.44 , respectively) indicate that they remain as double bonds. NBO analysis indicates that their π orbitals are mainly formed from the p orbitals of Ge and Si, e.g., for 1,2-digermasilaallene **4** (C_1), $\pi_{\text{Ge-Si}}$ NBO orbital come from $s^{0.13}p^{6.60}$ hybrid on Ge and $s^{0.02}p^{41.46}$ hybrid on Si (see Figure 5.3).¹⁹²

Figure 5.2 Optimized geometry of linear isomers of 1,3-digermasilaallene **3** (C_2) and 1-germadisilaallene **8** (C_s) and their linear isomers of allenic structure (D_{2d} and C_{2v} symmetry) at the level of B3LYP/6-311+G(d,p).¹⁹²

Full geometry optimization shows that linear conformers of 2-germadisilaallene **6** (D_{2d}) and 1-germadisilaallene **8** (C_1) are the second-order saddle point with two imaginary frequencies on the bending PES. The terminal Si on **6** and **8** are almost planar (with the HSiSiH dihedral angle of 176.7° , see Figure 5.2) and NBO analysis indicates that there are two perpendicular double bonds along the molecule's skeleton (their WBI bond index ranged from 1.94~1.97 see Figure 5.3).¹⁹²

The bending PESs of 1,2-digermasilaallene **4** and 2-germadisilaallene **6** are similar to those reported for trisilaallene **9**^{104, 198} and trigermaallene **10**^{97, 188}: there are two minima along the PES skeletons. For 1,2-digermasilaallene **4**, two minima are located at bond angle α of 70.1° (highly-bend isomer) and 54.7° (cyclic isomer, referred as **5**, see Figure 5.1); and for 2-

germadisilaallene, they appear at bond angle α of 67.4° (highly-bend isomer) and 54.0° (cyclic isomer, referred as **7**, see Figure 5.1). The relative energies of highly-bend isomer and cyclic isomers with respect to linear structure are given in Table 5.1.¹⁹²

Figure 5.3 Two NBO π orbitals of linear conformers of (a) 1,3-digermasilaallene **3** and (b) 1-germadisilaallene **8**.¹⁹²

Table 5.1 Relative energies (in kcal/mol) of highly-bend isomer, transition states and their cyclic isomers with respect to linear structure of germasilaallenes and trisilaallene, trigermaallene along their respective bending PESs.¹⁹²

Molecules	Highly-bend isomer	TS	Cyclic isomer
$\text{H}_2\text{Ge}_1=\text{Si}=\text{Ge}_2\text{H}_2$, 3	-23.94	-	-
$\text{H}_2\text{Ge}_1=\text{Ge}_2=\text{SiH}_2$, 4	-24.08	-20.56	-20.76
$\text{H}_2\text{Si}_1=\text{Ge}=\text{Si}_2\text{H}_2$, 6	-24.98	-23.59	-24.15
$\text{H}_2\text{Si}_1=\text{Si}_2=\text{GeH}_2$, 8	-23.40	-	-
$\text{H}_2\text{Si}=\text{Si}=\text{SiH}_2$, 9	-20.70	-16.63	-16.67
$\text{H}_2\text{Ge}=\text{Ge}=\text{GeH}_2$, 10	-15.75	-9.57	-9.63

The cyclic isomer of 1,2-digermasilaallene, **5** and 2-germadisilaallene, **7** ($\alpha \approx 55^\circ$, see Figure 5.4), with C_s and C_{2v} symmetry respectively, have GeH₂-SiH₂ and SiH₂-SiH₂ distance of 2.348 Å and 2.296 Å, which are shorter than regular Ge-Si and Si-Si single bond of 2.405 Å and 2.349 Å in digermasilacyclopropane and germadisilacyclopropane are respectively. Topological analysis of the electron densities is carried out to confirm the covalent bond between terminal atoms.¹⁹²

Figure 5.4 Optimized highly-bend and cyclic isomer of germasilaallenes at the level of B3LYP/6-311+G(d,p).¹⁹²

In Bader's theory, the presence of "bond critical point", i.e., the electron distribution goes through a saddle point in the inter-nuclear region, always ensures bonding between atoms. The electron density (ρ) at (3, -1) bond critical point (BCP) between M¹ and M³ atoms of cyclic isomer of 1,2-digermasilaallene (**5**) and 2-germadisilaallene(**7**) is similar to that of corresponding single bonds in cyclodigermasilane and cyclogermadisilane e.g., for cyclic isomer of 1,2-digermasilaallene (**5**), the ρ (0.0394) at (3, -1) BCP between Ge and Si is almost identical with Ge-Si bond in cyclodigermasilane (0.0384, see Table 5.2).¹⁹²

These results indicate that these are single bonds for cyclic isomer of 1,2-digermasilaallene (**5**) and 2-germadisilaallene(**7**). The WBI index (see Table 5.2) of M^1-M^2 and M^2-M^3 bonds in cyclic isomer of 1,2-digermasilaallene (**5**) and 2-germadisilaallene (**7**) confirms that these are typical single bonds. Thus, the cyclic isomer of 1,2-digermasilaallene (**5**) and 2-germadisilaallene (**7**) should be cyclic digermasilacyclopropylidene and germadisilacyclo-propylidene, respectively as compared to other conformers of four germasilaallenes.¹⁹²

Table 5.2 Electron density (ρ) at (3, -1) BCP point, bond length (L , at Å), Wiberg bond index (WBI) between terminal atoms and NBO occupancy for highly-bend trimetalaallene **4**, **6** and their corresponding cyclic isomer **5**, **7**.¹⁹²

Molecules		$L(M^1-M^3)$	ρ	WBI ^a	Occupancy
1,2-digermasilaallene					
$H_2M^1=M^2=M^3H_2$	Highly-bend 4	2.601	0.0304	0.68	-
	cyclic structure 5	2.348	0.0394	1.02	1.98
2-germadisilaallene					
$H_2M^1-M^2H_2-M^3H_2$	Highly-bend 6	2.601	0.0179	0.68	-
	cyclic structure 7	2.296	0.0913	1.03	1.98
	GeH ₂ GeH ₂ SiH ₂	2.405	0.0384	0.97	1.96
	SiH ₂ GeH ₂ SiH ₂	2.349	0.0497	0.98	1.96

^aThe WBI orders of Ge-Si and Si-Si bonds in germasilane and disilane are 0.97 and 0.98, respectively. For highly-bend and cyclic isomer (**5**) of 1,2-digermasilaallene, the WBI orders of M^1-M^2 bond are 1.26 and 0.94 and of M^2-M^3 bond are 1.28 and 0.95; for highly-bend and cyclic isomer (**7**) of 2-germadisilaallene, the WBI orders of M^1-M^2 or M^2-M^3 bond are 1.28 and 0.95.

5.3 Cyclic isomers of germasilaallenes

It is interesting to note that there are no cyclic minima of 1,3-digermasilaallene **3** and 1-germadisilaallene **8** on their bending PES skeletons, which is in contrast to other trimetalallenes. Here, we will first discuss the reason for the instability of cyclic isomer of compound **3** and **8** and then will explore the “bond-stretch” structure on the bending PES of other trimetalallenes.¹⁰⁴

In the vicinity of their highly-bend isomers, we compare the bending PES of germasilaallene with the PES of the corresponding cyclic structures, which is forced to cyclic C_{2v}/C_s arrangement. We have obtained the detailed bending PESs of 1,3-digermasilaallene **3** and 1,2-digermasilaallene **4** by using very small step size of 1.0° (see Figure 5.5).¹⁹²

Figure 5.5 Detailed bending PESs of (a) 1,3-digermasilaallene **3** and (b) 1,2-digermasilaallene **4** at the level of B3LYP/6-311+G(d,p). The red solid lines are the bending PESs of cyclic isomers of 1,3-digermasilaallene and 1,2-digermasilaallene forced to cyclic C_{2v} and C_s arrangements; and the black dash dotted lines are the bending PESs of 1,3-digermasilaallene and 1,2-digermasilaallene.¹⁹²

Figure 5.5 shows that the bond-stretch phenomenon of germasilaallene comes from the crossing between the bending PES of germasilaallene and of the cyclic structures. The minimum along the bending PES of cyclic structures of 1,3-digermasilaallene **3** is located

slightly above the corresponding point of the bending PES of 1,3-digermasilaallene (black dash dotted line in Figure 5.5a) when close to $\alpha = 57.0^\circ$. Frequency calculation indicates that the minimum along the bending PES of cyclic structures of 1,3-digermasilaallene has one imaginary frequency. This suggests that the 1,3-digermasilaallene **3** has no cyclic isomer. In contrast, minimum along the bending PES of cyclic structures of 1,2-digermasilaallene **4** at $\alpha = 54.7^\circ$ is slightly more stable than the corresponding 1,2-digermasilaallene (see Figure 5.5b). The point where the bending PESs of 1,2-digermasilaallene **4** and the PES of its cyclic structure cross each other forms the transition state (TS) between the highly-bend isomer of 1,2-digermasilaallene **4** and cyclic isomer **5**. We have found similar phenomenon for 2-germadisilaallene **6** and 1-germadisilaallene **8** (see Appendix B).¹⁹²

We correlate the stability of cyclic isomer of 1,3-digermasilaallene and 1-germadisilaallene with their ring strain. The strain energy of cyclic isomer of germasilaallenes is calculated according to the isodesmic reaction (see eq. 1). The calculated strain energies of cyclic isomer of germasilaallenes are listed in Table 5.3. To compare with other trimetallallene, we also calculate the strain energy of cyclic isomer of trisilaallene **9** and trigermaallene **10**.¹⁹²

Table 5.3 Calculated strain energy (kcal/mol) and barrier height (kcal/mol) of cyclic conformers of germasilaallenes, trisilaallene and trigermaallene at the level of B3LYP/6-311+G(d,p).¹⁹²

	H ₂ Ge=Si=GeH ₂	H ₂ Si=Si=GeH ₂	H ₂ Ge=Ge=SiH ₂	H ₂ Si=Ge=SiH ₂	H ₂ Si=Si=SiH ₂	H ₂ Ge=Ge=GeH ₂
Strain	28.12	28.57	26.97	26.16	27.19	27.14
Ring-opening barrier	-	-	0.20	0.56	0.04	0.06

According to eq. 5.1, the cyclic isomer of 1,3-digermasilaallene and 1-germadisilaallene have higher strain energy (28.12 and 28.57 kcal/mol, respectively) as compared to cyclic isomer of 1,2-digermasilaallene and 2-germadisilaallene (26.97 and 26.16 kcal/mol,

respectively). Natural Steric Analysis (NSA) supports the trend of strain effect from the isodesmic reaction, e.g., total natural localized molecular orbital (NLMO) steric exchange energy from the pair wise sum for cyclic isomer of 1,3-digermasilaallene is higher than the cyclic isomer of 1,2-digermasilaallene by 1.71 kcal/mol. The isodesmic reaction indicates that the cyclic isomer of trisilaallene and trigermaallene have medium ring strain (27.19 and 27.14 kcal/mol) among trimetallallenes. Thus the higher strain energy destabilizes the cyclic isomer of 1,3-digermasilaallene and 1-germadisilaallene and leads to the disappearance of cyclic isomers on their bending PESs.¹⁹²

The presence of ring-opening barrier of cyclic isomers of germasilaallene and trisilaallene, trigermaallene helps to clarify for the appearance of cyclic isomers of 1,2-digermasilaallene **5**, 2-germadisilaallene **7** and trisilaallene, trigermaallene. In their bending PESs, compounds **5** and **7** are unstable kinetically and can easily be transformed to their more stable highly-bend isomers because of their quite lower ring-opening barrier (0.20 and 0.56 kcal/mol at the level of B3LYP/6-311+G(d,p), see Figure 5.1(a)). The ring-opening process of the cyclic isomer of trisilaallene and trigermaallene has lower barrier of 0.04 and 0.06 kcal/mol respectively. Their high strain energies destabilize the cyclic isomer of trisilaallene and trigermaallene and thus lead to essentially zero ring-opening barrier.¹⁹²

Examination of Table 5.3 shows that the degree of ring strain of cyclic isomer of Si and Ge allenes follows the order $8 \approx 3 > 9 \approx 10 > 4 \approx 6$. The strain strengths (y) for cyclic isomers of compound **4**, **6**, **9** and **10** have a good linear correlation with ring-opening barrier (x), ($y = -0.50x + 13.67$, with linearly dependent coefficient of $R^2 = 0.99$; see Figure 5.6). Thus, the ring tension is highly correlated to ring-opening barrier. It is also reasonable to predict that the appearance of cyclic isomers of 1,2-digermasilaallene **5**, 2-germadisilaallene **7** and trisilaallene, trigermaallene is due to weaker strain energy.¹⁹²

Figure 5.6 Correlation between the calculated strain energies and the barrier height of ring-opening process of 1,2-digermasilaallene **4** and 2-germadisilaallene **6**, trisilaallene **9** and trigermaallene **10**.¹⁹²

5.4 Electronic structures and stability of highly-bend isomer of germasilaallenes

The optimized structures of four germasilaallene deviate significantly from their crystal structures,^{100, 101} E.g., the crystal structure for 1,3-digermasilaallene and 1,2-digermasilaallene have a considerably larger $\text{M}^1\text{M}^2\text{M}^3$ bond angle (125.7° and 132.4°) as compared to the DFT-optimized highly-bend geometry (67.4° and 75.0°). The difference comes from the stronger steric interaction of the bulky substituents attached to the terminal Ge atoms in the crystal structure. For example, optimization with bulkier *t*-Bu groups will lead to bond angle α of 110.3° and 112.7° (at the B3LYP/6-311+G(d,p) level, see Figure 5.7) respectively for compound **3** and **4**.¹⁹²

The electronic structures of highly-bend isomer of germasilaallenes **3**, **4**, **6**, and **8** show that these compounds with bond angle α ranging from 67.4° to 75.0° belong to germasilaallenes instead of germasilacyclopropylidene. Although the highly-bend isomer of **3**, **4**, **6**, and **8** adopt more acute bond angle α , smaller WBI values between terminal atoms of

3, **4**, **6** and **8** (0.55, 0.68, 0.68 and 0.60, respectively; similar to highly-bend isomer of trisilaallene **9** and trigermaallene **10**, WBI = 0.65 and 0.56) imply that there is only partial bonding interaction between M^1 and M^3 . NBO analysis shows that the partial bond between the two terminal atoms in highly-bend isomer comes from the partial overlapping of their p orbitals: their overlap matrices in the PNBO basis (S_{PNBO}) are 0.41, 0.39, 0.51 and 0.68, respectively. In fact, the two p orbitals rotate in the opposite direction to have partially head-to-head interaction (see Figure 5.7a).¹⁹² In contrast to the sp^2 hybridization on the terminal atoms, the central M^2 atom does not adopt the sp^2 hybridization: its two p orbitals interact with the two terminal atoms by σ bonding, one valence orbital belongs to s orbital with a lone-pair electron (close to 2.00) and the another valence orbital belongs to the pure p orbital which is perpendicular to the ring plane (see Figure 5.7b).^{9,17}

Figure 5.7 NBO orbital figures of highly-bend isomer of 1,3-digermasilaallene **3**: (a) p-p overlapping interaction between terminal Ge atoms; (b) p-p donor-acceptor interaction from two terminal Ge to the central Si.¹⁹²

The stability of highly-bend isomers of **3**, **4**, **6** and **8** comes mainly from p-p donor-acceptor interaction from the terminal to central atom. To evaluate the stabilization of $p_{M1} \rightarrow p_{M2}$ (or $p_{M3} \rightarrow p_{M2}$) donor-acceptor interaction, we have performed the NBO deletion (DEL) calculation for the interactions involving singly occupied natural orbitals (SONO, pure p property at M^1 or M^3) as donors and empty nature orbital (p property at M^2) as acceptor. In

other words, this deletion calculation deactivates $p_{M1} \rightarrow p_{M2}$ (or $p_{M3} \rightarrow p_{M2}$) donor-acceptor interaction along the germasilaallenic rings. The NBO DEL energies show that the stabilization energy from p-p donor-acceptor interaction are at the range of 82.43~108.17 kcal/mol (see Table 5.4), which are close to those of highly-bend isomer of trisilaallene **9** and trimermaallene **10** (102.22 and 101.30 kcal/mol). Since NBO DEL energies in highly-bend isomer of 1,3-digermasilaallene **3** (108.17 kcal/mol) is higher than highly-bend isomer of 2-germadisilaallene **6** (82.43 kcal/mol), the $p_{Ge} \rightarrow p_{Si}$ interaction should have stronger donor-acceptor effect than $p_{Si} \rightarrow p_{Ge}$ interaction.¹⁹²

NPA analysis^{65, 181} shows that there is charge transfer from p_{M1} or p_{M3} to p_{M2} : the p_{M2} orbital has partial electrons and the p_{M1} (p_{M3}) orbital is not pure SONO, e.g., for highly-bend isomer of 1,2-digermasilaallene **4**, the NPA occupancy of p orbitals of central and terminal atoms are 0.45 and 0.78 (see Appendix B), respectively. The strong p-p delocalization strengthen the bonding between terminal atoms (M^1 and M^3) and central M^2 so that their bonding is intermediate between double and single bond: the WBI bond index between terminal atoms (M^1 or M^3) and central M^2 ranges from 1.26~1.36 (the WBI of normal Ge-Ge, Ge-Si and Si-Si single bonds range from 0.96~0.98, the WBI of normal double bonds range from 1.73~1.90).¹⁹²

Table 5.4 Overlapping matrix element (S_{PNBO}) between p orbitals of M^1 and M^3 , the WBI bond index among M^1 , M^2 and M^3 , the stabilization energies of $M^1 \rightarrow M^2$ donor-acceptor effect (ΔE_{DA} , at kcal/mol) and M^1 - M^3 partial overlapping in highly-bend isomers of germasilaallenes (ΔE_{PO} , at kcal/mol) from NBO DEL analysis at the B3LYP/6-311+G(d,p) level.¹⁹²

Compound	$S_{PM1-PM3}$	WBI_{M1-M3}	WBI_{M2-M1}	WBI_{M2-M3}	ΔE_{DA}	ΔE_{PO}
$H_2Ge_1=Si=Ge_2H_2$, 3	0.41	0.56	1.33	1.33	108.17	24.40
$H_2Ge_1=Ge_2=SiH_2$, 4	0.39	0.68	1.26	1.28	93.04	43.75
$H_2Si_1=Ge=Si_2H_2$, 6	0.51	0.68	1.28	1.28	82.43	61.73
$H_2Si_1=Si_2=GeH_2$, 8	0.68	0.60	1.36	1.29	103.68	36.24
$H_2Si=Si=SiH_2$, 9	0.48	0.65	1.33	1.33	102.22	47.85
$H_2Ge=Ge=GeH_2$, 10	0.42	0.56	1.30	1.30	101.30	29.14

The stability of highly-bend isomer of **3**, **4**, **6** and **8** not only comes from $p_{M1}(p_{M3}) \rightarrow p_{M2}$ donor-acceptor interaction, but also from p-p partial orbital overlapping between terminal atoms. To evaluate the stabilization effect of the p-p partial orbital overlapping, we have also performed the NBO DEL calculation to the p-p orbital overlapping between terminal atoms. The deletion calculation shows that the NBO DEL energies of the p-p partial orbital overlapping are in the range of 24.40 ~ 61.73 kcal/mol.¹⁹²

For highly-bend isomer of **3**, **4** and **8**, the NBO DEL energies of the p-p partial orbital overlapping between M^1 and M^3 are 24.40, 43.75 and 36.24 kcal/mol (see Table 5.4), which are 22.6%, 47.0% and 35.0% that of their corresponding p-p donor-acceptor interaction from terminal to central atoms. Similar to highly-bend isomer of trisilaallene **9** and trigermaallene **10**, the stability of the $p_{M1}(p_{M3}) \rightarrow p_{M2}$ donor-acceptor interaction is stronger than the p-p partial overlapping between terminal atoms. However, in highly-bend isomer of **6**, the stabilization effect of p-p partial orbital overlapping becomes close to the strength of $p_{M1}(p_{M3}) \rightarrow p_{M2}$ donor-acceptor interaction: the NBO DEL energy from the p-p partial orbital overlapping in highly-bend isomer of **6** has increased to 61.73 kcal/mol, which is 74.9% of the stabilization energy for its p-p donor-acceptor interaction. Thus, for highly-bend isomer of **6**, p-p partial orbital overlapping between terminal atoms is also responsible for its stability.¹⁹²

Although there are strong $p_{M1}(p_{M3}) \rightarrow p_{M2}$ donor-acceptor and p-p partial overlapping effect to stabilize the highly-bend isomers of germasilaallenes, they are still not able to compensate for the bonding effect of M^1-M^3 σ single bond at its corresponding cyclic isomers. For example, the sum of the NBO DEL energies of the $p_{Ge1} \rightarrow p_{Ge2}$ and $p_{Si} \rightarrow p_{Ge2}$ donor-acceptor and the $p_{Ge1}-p_{Si}$ partial orbital overlapping effect for highly-bend isomer of 1,2-digermasilaallene **4** (136.79 kcal/mol) is lesser than the NBO DEL energies of Ge-Si single bond on its cyclic isomer **5** (322.88 kcal/mol). By comparison, we have learnt that the strengths of other bond of highly-bent isomers are comparable to cyclic isomers and at the same time the strain effect is not the main factor to dictate the relative stability of two isomers (see below). Therefore, there is the further reason to stabilize the highly-bend isomers of germasilaallenes.¹⁹²

We have noticed that there are two electrons dissected into three p orbitals perpendicular or partially perpendicular to the $M^1M^2M^3$ ring in highly-bent isomers, which meets the $4n+2$

Huckel rule. The localized orbital locator (LOL) analysis shows that the region of partial overlapping bond between terminal atoms has lower LOL value (the lower LOL value shown by the blue and the higher LOL value shown by the yellow in Figure 5.8 for highly-bend isomer of **3**.¹⁹²

Figure 5.8 The shaded surface map with projection of localized orbital locator (LOL) on highly-bend isomer of 1,3-digermasilaallene **3**. The chosen plane is at 0.50 bohr below GeSiGe ring plane. The region of partially overlapping $p_{\text{Ge}}-p_{\text{Ge}}$ bond is pointed out by red arrow.¹⁹²

It means that electrons at partially overlapping $p_{\text{Ge}}-p_{\text{Ge}}$ bond are easy to delocalize to other regions. NICS calculation indicates that germasilaallenes can form the aromatic rings e.g., the higher NICS(0) value (-23.70) and NICS(1) value (-20.06, down; -10.62, up, based on the plane of Figure 5.4) of highly-bend isomer of 1,2-digermasilaallene **4** show that there should be strong aromatic shielding along the $M^1M^2M^3$ ring. NBO NICS calculation further indicates that NICS(1, down) is mainly attributed to two p orbitals of terminal Ge and Si (the sum of $\text{NICS}_{\pi} = -7.95$) except for the contribution from Ge-Si and Ge-Ge σ bonds (the sum of $\text{NICS}_{\sigma} = -11.51$) and the NICS(1, up) is similar to NICS(1, down), which has the sum of $\text{NICS}_{\pi} = -9.10$ mainly from two p orbitals of terminal Ge and Si. In contrast, for its corresponding cyclic isomer (germasilacyclopropylidenes), NMR calculation indicates the

NICS(1) value is only 0.19. Thus, the presence of aromaticity in the ring should also be accounted for the stability of the highly-bend isomer. NBO DEL calculation only determines the energetic of the individual p-p donor-acceptor and p-p partial orbital overlapping interaction by deleting certain NBO orbital and specific NBO donor-acceptor interaction. Thus, its stabilization energy does not account for the aromatic delocalization contribution. During the bending process (see below), we find that the formation and enhancement of aromatic ring current is an important stabilization factor to highly-bend isomer of trimetallallenes in contrast to mono- and di-metallallenes. Thus, the higher stability of highly-bend isomers as compared to their cyclic isomers is due to a combination of their p-p donor-acceptor, and p-p partial orbital overlapping interaction and the aromatic delocalization.¹⁹²

Although the cyclic isomers are more highly bent than highly-bend isomers of germasilaallenes; highly-bend germasilaallenes have slightly higher strain interaction than their respective cyclic isomers e.g., in highly-bend isomer of 1,2-digermasilaallene **4**, the NLMO steric exchange energy (143.55 kcal/mol) is higher than their corresponding cyclic isomers **5** (110.08 kcal/mol). The steric interaction mainly comes from the interaction between the p orbital of terminal Ge and other bonds and lone-pair orbitals, e.g., Ge (central)-Si σ bond (20.40 kcal/mol), 2s(Si) (10.73 kcal/mol) and lone-pair orbital (LP, s character, at central Ge) (6.10 kcal/mol). Since the steric interaction is quite less than the other NBO stabilization energies between highly-bend and cyclic isomers, e.g., the difference of the second-order perturbation stabilization energies of donor-acceptor effect (272.29 kcal/mol), the steric interaction is not the determining factor of their relative stability.¹⁹²

5.5 Reason for vanishing slightly-bend conformers of germasilaallenes

In contrast to mono- and di-metalallenes, stable slightly-bend conformers have disappeared on the bending PESs of trimetallallenes.^{7,17} To understand this interesting phenomenon in trimetallallenes, we study the specialty of the geometry and electronic structure of their bending conformers by comparing with similar dimetallallenes, whose one terminal Ge or Si had been substituted by C. We choose 1,3-digermasilaallene **3** and 1-germa-2-silaallene **11** as reference for the comparison (the bending PESs of four corresponding dimetallallenes see Appendix B).¹⁹²

Figure 5.9 The comparison between the bending PES of trimetalallene (1,3-digermasilaallene**3**) and dimetalallene (1-germa-2-silaallene**11**) at the B3LYP level and the bending PES of 1,3-digermasilaallene**3** at the CCSD level.¹⁹²

The bending PESs of 1,3-digermasilaallene **3** and 1-germa-2-silaallene **11** are plotted in Fig. 9. The bending PES of 1-germa-2-silaallene **11** shows that 1-germa-2-silaallene **11** has a relatively flat PES between $180.0^\circ \sim 97.7^\circ$ with one minima at $\angle\text{GeSiC} = 139.9^\circ$, which is more stable than its linear structure by 3.98 kcal/mol. In contrast, for the bending PES of 1,3-digermasilaallene **3**, its potential energy decreases gradually from 180° to 75° and there is no minimum along the part of PES and only a tilted step between $120.0^\circ \sim 105.0^\circ$ (see Figure 5.9). CCSD calculation also agrees the result that there is no minimum for 1,3-digermasilaallene (red dot line, see Figure 5.9). With bending from 180.0° to 97.7° , the energetic gap between 1,3-digermasilaallene **3** and 1-germa-2-silaallene **11** becomes larger and one maximum appears as the transition state of the 1-germa-2-silaallene's bending **11** ($\alpha = 97.7^\circ$). 1,3-digermasilaallene **3** and 1-germa-2-silaallene **11** drop sharply to their highly-bend isomer and cyclic isomer after bond angle $\alpha = 97.7^\circ$, respectively. The difference in PES skeletons between 1,3-digermasilaallene **3** and 1-germa-2-silaallene **11** imply us that

there is a bending barrier to stabilize the slightly-bend minimum of 1-germa-2-silaallene **11** while there are no such feature for 1,3-digermasilaallene **3**.¹⁹²

After investigating the geometry and bond order of bending conformers (α ranging from 180° – 97.7°), we found that the bending process of 1,3-germasilaallene **3** could be divided into two stages, which had different electronic structures. Before the tilted step ($120.0^\circ \sim 105.0^\circ$) of bending PES, two terminal atoms of 1,3-digermasilaallene **3** are pyramided (lower than 360° , see Figure 5.9 and Table 5.5). WBI bond index and NBO analysis indicate that 1,3-digermasilaallene **3** continue to adopt two $\pi_{\text{Ge-Si}}$ bond along the skeleton (see Table 5.5), similar to its linear conformer (see Figure 5.3). With increase in bending, the conformer becomes more stable through π orbital delocalization, mainly $\pi_{\text{Ge2-Si}} \rightarrow \pi^*_{\text{Si-Ge1}}$ and $\sigma_{\text{Ge2-Si}} \rightarrow \pi^*_{\text{Si-Ge1}}$ donor-acceptor effect (see Figure 5.10). For example, for 1,3-digermasilaallene **3**, the sum of second order perturbation energies of π orbital delocalization effect at bond angle $\alpha = 120.0^\circ$ (26.92 kcal/mol) is more than at bond angle $\alpha = 135.0^\circ$ (22.50 kcal/mol). In contrast, for 1-germa-2-silaallene **11**, similar geometry and bonding type (see Table 5.5) are observed. For the $\pi_{\text{Ge-Si}}$ and $\pi_{\text{Si-C}}$ orbitals of 1-germa-2-silaallene **11**, there is hardly any $\pi \rightarrow \pi^*$ delocalization effect observed. Thus, the potential energies of 1,3-digermasilaallene **3** are decreasing gradually from 180° to 120° while the potential for 1-germa-2-silaallene **11** is rather flat.¹⁹²

After the slightly-tilted step, two terminal Ge atoms of 1,3-digermasilaallene **3** adopt the sp^2 hybridization and is no longer pyramided (the sum of bond angles around them being 360.0° , see Table 5.5). NPA analysis shows that the conformers have now adopted similar electronic structure as its highly-bend isomer (see Table 5.5): two electrons are dissected into three p orbitals perpendicular to the $M^1M^2M^3$ ring. NMR calculation indicates that the ring current arises from the three-member ring structure of 1,3-germasilaallene **3** and the aromaticity of germasilaallenic rings become stronger with deeper bending. For example, when the Ge-Si-Ge bond angle decreases from 105.0° to 90.0° , the NICS(1) value of germasilaallenic ring will increase from 14.61 to 16.75 and at the same time the gap between HOMO and LUMO also increases from 54.60 kcal/mol to 62.66 kcal/mol. We further perform the analysis of multicentre bond index (MCBI) to measure the extent of aromaticity of germasilaallenic rings. The MCBI values of aromaticity of 1,3-germasilaallene **3** at bond angle $\alpha = 105.0^\circ$ and 90.0° are 0.31 and 0.34. It means that the extent of aromaticity of

germasilaallenic ring increases with deeply bending. As the bending proceed from 105.0° to 90.0°, the stabilization energy from p-p overlapping increases slightly (from 0.17 kcal/mol to 0.96 kcal/mol). In contrast, the p-p donor-acceptor interaction decreases from 144.29 kcal/mol to 129.00 kcal/mol. Thus, we conclude that it is the increased aromaticity of germasilaallene that stabilizes its highly-bend isomer of 1,3-digermasilaallene **3** after bond angle $\alpha = 105.0^\circ$ and the gradually dropping curve vanishes the bending barrier to stabilize a slightly-bend minimum.¹⁹²

Table 5.5 Sum of bond angles around two terminal atoms, WBI bond index and NPA orbital in 1,3-digermasilaallene ($\text{H}_2\text{Ge}=\text{Si}=\text{GeH}_2$) **3** and 1-germa-2-silaallene ($\text{H}_2\text{Ge}=\text{Si}=\text{CH}_2$) **11** at bond angle $\alpha = 120.0^\circ, 105^\circ, 90^\circ$ and 75° at the B3LYP/6-311+G(d,p) level.¹⁹²

$\text{H}_2\text{Ge}_1=\text{Si}=\text{Ge}_2\text{H}_2$					$\text{H}_2\text{Ge}=\text{Si}=\text{CH}_2$				
	135.0°	120.0°	105.0°	90.0°		135.0°	120.0°	105.0°	90.0°
$\Sigma\theta_{\text{Ge}1}$	339.3	344.8	360.0	360.0	$\Sigma\theta_{\text{Ge}}$	320.1	330.1	334.0	338.3
$\Sigma\theta_{\text{Ge}2}$	339.3	344.8	360.0	360.0	$\Sigma\theta_{\text{C}}$	360.0	360.0	358.6	360.0
WBI					WBI				
Ge ₁ -Si	1.72	1.67	1.44	1.41	Ge-Si	1.51	1.45	1.34	1.09
Si-Ge ₂	1.72	1.67	1.44	1.41	Si-C	1.74	1.74	1.63	1.41
Ge ₁ -Ge ₂	0.10	0.14	0.36	0.42	Ge-C	0.05	0.06	0.19	0.40
Occupancy					Occupancy				
p _{Ge1} ($\pi_{\text{Ge}1-\text{Si}}$)	(1.90)	(1.87)	0.58	0.62	p _{Ge} ($\pi_{\text{Ge}-\text{Si}}$)	(1.84)	(1.83)	(1.81)	0.49
p _{Si} ($\pi_{\text{Si}-\text{Ge}2}$)	(1.90)	(1.87)	0.84	0.77	$\pi_{\text{Si}-\text{C}}$	1.98	1.98	1.91	1.62
p _{Ge2}	-	-	0.58	0.62	-	-	-	-	-

However, the geometry and electronic structure of conformers of 1-germa-2-silaallene **11** do not change fundamentally and the steric effect of 1-germa-2-silaallene **11** becomes stronger with deeper bending. A bending barrier appears at bond angle $\alpha = 97.7^\circ$ and it stabilizes a slightly-bend minimum along its PES.¹⁹²

Figure 5.10 (a) The π - π^* donor-acceptor interaction at bond angle $\alpha = 120^\circ$ conformer of 1,3-digermasilaallene **3**. (b) Three p orbitals of Ge₁, Si, Ge₂, perpendicular to the ring plane, at bond angle $\alpha = 105^\circ$ conformer of 1,3-digermasilaallene **3**.¹⁹²

5.6 New slightly bend isomers

Theoretical calculations show that the σ -donor, π -acceptor substituents can lead to the linear structure of germasilaallenes and the steric effect of bulky substituents has similar effect.¹⁹⁹ We find that the donor-acceptor effect from substituents to central atoms can also stabilize the slightly-linear germasilaallenes structure: the substitution of germasilaallenes **3**, **4**, **6** and **8** with one $-\text{PMe}_2\text{S}$ group at each terminal atom can stabilize a slightly-bend geometry with bond angle α from 132.0° to 140.6° (see Figure 5.11 and Appendix B).¹⁹²

Figure 5.11 The optimized $\text{H}(\text{PMe}_2\text{S})\text{Si}=\text{Ge}=\text{Si}(\text{PMe}_2\text{S})\text{H}$ **12** at the level of B3LYP/6-311+G(d,p) and the donor-acceptor interaction from S to central Ge.¹⁹²

For example, DFT calculations show that $[(\text{H}(\text{PMe}_2\text{S})\text{Si}=\text{Ge}=\text{SiH}(\text{PMe}_2\text{S}))]$ **12**, adopts bond angle α of 140.1° and Si-Ge bond length of $2.491 \text{ \AA}$. NBO analysis shows that there is a lone pair orbital (NBO occupancy = 1.90) on each terminal Si atom, which have more s character ($\text{sp}^{0.42}$ hybrid) than the pure p orbital like highly-bend isomer of 2-germadisilaallene **6**, and two Si-Ge occupied σ orbital, comprised of an $\text{sp}^{10.60}$ hybrid orbital on Si and $\text{sp}^{1.83}$ hybrid orbital on Ge. WBI bond index shows that the Si-Ge bonds is a single bond (WBI=0.89). The NRT bond order of 0.95 further supports the conclusion of single bond between Si and Ge. NRT analysis also indicates that there is a covalent component of 0.68 and ionic component of 0.27 and thus its character is mainly covalent. The WBI bond index shows that the P-Si and P-S bonds are single bonds (WBI, P-Si: 0.78; P-S: 1.05, respectively). Thus, one electron of LP orbital of terminal Si should be from the central Ge.¹⁹²

It is interesting that NPA analysis indicates that central Ge is only slightly positive charged: the NPA charge of Ge is 0.28. In fact, it is because each S element donates one of its three LPs to two empty orbitals of central Ge so that there is no formation of the $\text{Si}^--\text{Ge}^{2+}-\text{Si}^-$ ylidic skeleton. The central Ge adopts the sp^2 hybridization and has two orbitals ($\text{sp}^{2.43}$, p) to accept the electrons from the LP orbital of two S. As a result, there are two LPs remaining on two S atoms ($\text{sp}^{0.37}$ and p) and the central Ge become slightly positive charged.¹⁹²

5.7 Conclusions

The heavy trimetalallene is a group of intriguing compounds, which have interesting isomers with unusual bonding. Their cyclic isomers, germasilacyclopropylidene, are sensitive to the strain energies. The slightly higher ring strain on cyclic structure of 1,3-digermasilaallenes **3** and 1-germadisilaallene **8** can destabilize their cyclic isomers. 1,2-digermasilaallene **4** and 2-germadisilaallene **6** are less strained and the crossing between the bending PES of cyclic isomer and highly-bend isomer of germasilaallene resulted a low ring-opening barrier and a shallow cyclic minimum along their PES.¹⁹²

DFT calculations and NBO analysis on germasilaallenes indicate that the p-p donor-acceptor interactions from terminal to central atom, partial p-p orbital overlapping between terminal atoms and the aromaticity along the ring plane stabilize the highly-bent isomers

more than their respective cyclic isomers. In contrast to cyclic isomer of trisilaallene and trigermaallene, where p-p donor-acceptor interactions from terminal to central atom is stronger than partial p-p orbital overlapping between the terminal atoms, p-p partial orbital overlapping in highly-bend isomer of 2-germadisilaallene **6** become close to p-p donor-acceptor interactions, where NBO DEL stabilization energy of partial p-p orbital overlapping is 74.8% of NBO DEL stabilization energy of the p→p donor-acceptor interaction due to the weak p_{Si}→p_{Ge} donor-acceptor interaction.¹⁹²

NBO analysis shows that there is a change in bonding nature along bending process of germasilaallenes. For 1,3-digermasilaallenes **3**, when $\alpha > 120^\circ$, strong π orbital delocalization effect stabilizes the bend conformer and when $\alpha < 120^\circ$, aromaticity stabilizes the deep-bend structure. Thus, the potential energy of germasilaallenes gradually decreases along the bending PES so that there is no bending barrier to stabilize the slightly-bend isomer. In contrast, the bonding mode of slightly-bend conformers of mono-, di-metallallene remains the same: they pyramided at its terminal atoms and adopts two π bonds. Since there is hardly any π - π delocalization and aromaticity along the ring plane, the increased steric interaction leads to a bending maximum to stabilize one slightly-bend minimum along the bending PES.¹⁹²

DFT calculations indicate that strong electron donor interaction from substituents to central atom, for example, two PMe₂S: substituents → Ge or Si at [H(PMe₂S)M¹M²M³(PMe₂S)H], can make trimetalallene to adopt slightly-bend structures with α ranging from 132.0° to 140.6°. The strong donor effect forces the central atoms to transfer its electrons into terminal atoms and form two LP orbitals on the terminal atoms. The central atoms then adopt sp² hybridization to allow it to receive electrons from substituents to stabilize the slightly bend structure, in contrast to germasilaallenes.¹⁹²

Chapter 6

DFT Study and Molecular Design of Low Band Gap Oligomers

We systematically study triazole-based monomers as acceptor moieties on the basis of DFT and TD-DFT calculation and investigate how to tune their electronic and optical properties. We also study how the changes to the chemical structure of donor-acceptor (DA) oligomers influence the intrinsic geometric, electronic, and optical properties. Four donor units with bridging atom C, N, Si and P are considered to be coupled with acceptors units to tailor and to enhance their electronic and optical properties. Additionally, we attempt to explore [2D-A]_n architecture with an additional donor unit linked to DA conjugated backbone to manifest the improvement of their optical behavior and they are expected to be good candidates for optoelectronics applications.

As organic semiconductors, π -conjugated molecules have their intrigue potential in optical fields such as organic light emitting diodes (OLED), field effect transistors, photovoltaic cells, optical power limiting,^{21, 22} frequency up-converted lasing, 3-D optical data storage,²⁰⁰ 3-D micro-fabrication,²⁵ 3-D fluorescence imaging^{27, 201} and photodynamic therapy²⁸. They trigger immense research in this field due to their versatility, flexibilities and optoelectronic property tuning abilities: a great number of π -conjugated molecules/polymers with exciting electronic and optical properties have been synthesized for decades. This process is on-going though it still remains a challenge to design low band gap (LBG) materials with higher optical efficiency especially for photovoltaic applications. The LBG materials, which have wide absorption range and also red or near IR region absorption of solar spectrum, will be highly

efficient for large photon harvesting.²⁰²⁻²⁰⁹ π -Conjugated compounds with lower HOMO (the highest occupied molecular orbital)-LUMO (the lowest unoccupied molecular orbital) gap are among the most important building block of LBG polymer since they have possessed large intrinsic conductivities and enriched absorption properties.

Though many monomers have been synthesized, benzothiadiazole (BT), benzobisthiadiazole (BBT) and thiadiazoloquinoxaline (TQ, see scheme 6.1) have still attracted intense attention due to their preferable charge transfer properties and optical absorption characteristics in the visible and near IR region.²¹⁰⁻²¹² The low-energetic level of LUMO orbital makes them better π -electron acceptor and thus they are commonly used as acceptor units of LBG material. In 2011, Grimsdale and co-workers successfully synthesized the triazole analogue of BT, chalcogena-diazolobenzotriazoles, (**XBTa**; X=S,Se) and the triazole analogue of TQ, [1,2,3]triazolo[3,4-g]quinoxaline, (**TaQ**) compounds²¹² and the next year, the same group synthesized another triazolo analogue, benzo[1,2-d;4,5-d']bitriazole (**BBTa**), by one pot synthesis process.²¹⁰ These triazole analogues have a further advantage at high solubility and enhanced stability compared to their thiadiazole counterparts. This criterion makes them very promising in the field of solution processable organic electronics.^{210, 212} It prompts us to perform further theoretical investigation, which will provide a molecular level understanding of the promising properties. Based on the theoretical analysis on XBTa, BBTa and TaQ, we will further develop some novel LBG oligomers with better nature by adding different types of substituent group to XBTa, BBTa and TaQ.²¹³

Scheme 6.1 Chemical structures of BT, BBT and TQ.

Chapter 6-Low band gap oligomers

For polymers, these factors influence their HOMO-LUMO gaps including geometry alteration, resonance structure, presence of heteroatom, intermolecular coupling.^{17, 214-219} It has been proven theoretically and experimentally that an appropriate matching between donor and acceptor groups and proper substitutions on donor/acceptor fragment can afford a fine tune over the HOMO and LUMO levels and further over their optical properties.^{220, 221} The lower HOMO-LUMO gap ensures the greater intermolecular charge mobility.²²² In this work, we have chosen different donor units (**Y1-Y4**, see scheme 6.2) to efficiently design DA oligomers. Additionally we have designed D-D-A (2DA; D=**Y4**, A=**BBTa**, **SeBTa** and **TaQ**) oligomer to enhance their promising properties to make it more suitable for applications, such as solar cell.²¹³

Scheme 6.2 Acceptors monomers and DA oligomers linkage with the donor units.

In the present work, based on a systematic study of electronic properties and absorption-

emission spectra of triazole based acceptor units, we have investigated the change in structures and photophysical properties of the new type of acceptor, XBTA, BBTA and TAQ (see scheme 6.2). Then, we have studied the optoelectronic properties of DA oligomers after coupling of the promising donor units (Y1-Y4) with the acceptor moieties both at their ground state and at low-lying excited state within DFT and TD-DFT frameworks. These advanced computational tools are used to get a reliable structure-property relationship as a function of acceptor units that were differently synthesized or theoretically investigated under various levels of theory and basis sets. This study carried out at same theoretical level with same basis set can able to effectively compare different acceptor/donor fragments under DA architecture and thus be helpful as a good reference work for further research in this area of LBG DA polymer.²¹³

6.1 Computational methods

All the calculations on monomers and DA oligomers were performed using ab initio and density functional theory (DFT)^{37, 58} techniques. Based on previous calculations,^{175, 202, 204} we had used B3LYP (Becke's three-parameter hybrid function²²³ with the non-local correlation of Lee-Yang-Parr^{224, 225}) method with the Pople 6-31G(d,p) basis set. Time-dependent density functional theory (TD-DFT)⁵⁶ at the level of B3LYP/6-31G(d,p) has been used to gain insight into the optical progress and calculate the electronic excited energies. On the basis of the B3LYP calculation at the DFT geometry of the ground state, we obtained the vertical excitation energy and simulated absorption spectra of acceptor and oligomers. Based on the B3LYP calculation at the TD-DFT optimized geometry for S₁ electronic state of acceptor monomers and oligomers, we simulated emissionspectra. All the calculations were carried out using Gaussian 09 suite of programs.⁴⁰

The Natural Bond Orbital (NBO)¹⁴² analysis and Wiberg Bond Index (WBI)¹⁶⁸ were used to characterize the local bond pattern. NBO analysis and WBI calculation were performed with NBO 5.0 package¹⁹⁴. Additionally, the band gap of polymer has been estimated from the graphical analysis with linear extrapolation method, which is successfully employed for several polymers²²⁶⁻²²⁸. Natural transition orbitals (NTO) have been also generated to explain the hole-electron transition at excited state of trimers.

6.2 Optimized geometries and electronic properties of isolated acceptor fragments

To use monomers having quinoidal characteristics in the conjugated backbone is the simple design principle of preparing low band gap polymer.²²⁹ In order to reduce the computational resources, the long alkyl side chain in synthesized monomers has been replaced by a methyl group since there is no significant influence of the solubilizing alkyl chain on HOMO-LUMO energies or other optoelectronic properties.^{230, 231} DFT calculations show that when two thienyl groups fused to central ring structures of parent acceptors (BBT, XBT and TQ), these new monomers, **BBTa**, **XBTa** (X=S, Se) and **TaQ**, can offer better quinoid character and have also more stable structure.^{232, 233} To reduce the computational resources and focus on the central quinoidal ring, new acceptors have replaced a long alkyl side chain, attached to N elements, by a methyl group (see Scheme 6.1).²¹³

The optimized structures of central quinoid of **BBTa**, **XBTa** and **TaQ** at the B3LYP/6-31G(d,p) level are slightly different from their synthesized parents. For acceptor monomers, important geometric parameters were given in Table 6.1. DFT calculations indicate that other acceptor monomers except **BBTa16** have almost a planar structure, i.e. two thienyl planes are parallel to the central quinoidal plane. For **BBTa16**, one thienyl plane, at the same side of methyl group, has a torsional angle of 55.5° along the quinoidal backbone. It is obvious that the torsion of thienyl group out of the quinoidal backbone plane comes from the steric effect of methyl group. The torsion breaks the π -conjugation between thienyl and quinoidal group, whose conjugative stabilization energies is 22.27 kcal/mol, so that there is a longer bridge bond length (r_{b2}) than another bridge bond length (r_{b1}) by 0.016 Å (see Table 6.1). Additionally, the steric effect of bulky groups fused to quinoxaline ring of **TaQ**, for example, biphenyl or bithiophene rings, reduces the π -conjugation between thienyl and quinoidal group and two planes is slightly tilted about 5.7° ~ 8.4° (see Table 6.1). The conjugative stabilization energies between thienyl and quinoidal group will accordingly be lower than three planar acceptor monomers, **BBTa26**, **SBTa** and **SeBTa**, by 1.00-1.51 kcal/mol for **TaQ1** and 0.85-1.36 kcal/mol for **TaQ2**. For three planar acceptor monomers, **BBTa26**, **SBTa** and **SeBTa**, shorter bridge bond lengths (1.448 ~ 1.449 Å, C-C and C=C bond length at ethane and ethene being 1.531 and 1.330 Å) and higher WBI bond index (1.14 - 1.16) imply that they have the property of partial double bond. The partial double bond is the indication of better conjugation and thus increased delocalization. Thus, there is stronger electronic

delocalization across the skeleton from better conjugation between thienyl and quinoidal group at **BBTa26**, **SBTa** and **SeBTa** acceptors. To obtain potential photoelectric acceptors with the stronger electronic delocalization, we should control the orientation of side chain and select the short branched.²¹³

Table 6.1 The bond lengths^a (r, in Å) of bridge bonds and the torsion angles (Φ , in degree) between two thienyl groups and quinoidal backbone for acceptor monomers (**BBTa**, **SBTa** and **TaQ**) at the B3LYP/6-31G(d,p) level.²¹³

Parameters	BBTa26	BBTa16	SBTa	SeBTa	TaQ1	TaQ2
$r_{b1}(r_{b2})$	1.449	1.466	1.448	1.448	1.455	1.454
	(1.448)	(1.450)	(1.448)	(1.448)	(1.455)	(1.454)
$\Phi_1(\Phi_2)$	0.0	55.5 (0.0)	0.0	0.0	6.1 (5.7)	8.4 (7.7)
WBI	1.14 (1.14) ^b	1.06 (1.14)	1.15 (1.15)	1.16 (1.16)	1.14 (1.14)	1.14 (1.14)

^a C-C bond length of H₃C-CH₃ and H₂C=CH₂ Calculated at the same computation level are 1.531 and 1.330 Å, respectively. ^b WBI bond index at the bracket being the right bridge bond, see scheme 6.2.

Another design concern is the presence of heteroatom (here, S or Se) in acceptors. These heteroatoms stabilize the acceptors by increasing the possibilities of intermolecular van der Waals and electrostatic interaction for a particular configuration.²⁰² Above all, these heteroatoms can reduce HOMO-LUMO gap significantly by stabilization of their LUMO energies (-3.00 and -3.00 eV, see Table 6.2), for example, **SBTa**, **SeBTa** have lower HOMO-LUMO gap than **BBTa26** by 0.41, 0.61 eV. The effect of heteroatom mainly comes from the enhancement of conjugation along the molecular plane by adjusting local conjugated structure -C=C-N=S(Se)-, which had been include in LUMO orbital. NBO analysis indicates that the conjugative stabilization energies of -C=C-and -N=S(Se)- at **SBTa**, **SeBTa** (59.74 and 71.29 Kcal/mol) is higher than of -C=C-and -N=N- at **BBTa26** (45.49 Kcal/mol).²¹³

Table 6.2 HOMO and LUMO level (in eV) of acceptor monomers calculated at the B3LYP/6-31G(d,p) level and the comparison between computational and experimentally derived HOMO-LUMO gap (in eV).²¹³

Energy	BBTa26	BBTa16	SBTa	SeBTa	TaQ1	TaQ2
E _{LUMO}	-2.40	-2.25	-3.00	-3.08	-2.56	-2.61
E _{HOMO}	-4.73	-5.17	-4.92	-4.82	-4.80	-4.75
E _{H-L}	2.33(2.28) ^a	2.91(2.75) ^a	1.91(1.77) ^a	1.75(1.58) ^a	2.24(2.01) ^a	2.13(1.88) ^a
E _{g (exp)} ^b	2.21 ²¹²	2.55 ²¹²	1.80 ²¹⁰	1.60 ²¹⁰	1.95 ²¹⁰	1.86 ²¹⁰

^aHOMO-LUMO gap in parenthesis come from the TDDFT B3LYP calculation. ^bThe experimentally derived HOMO-LUMO gap are estimated from absorption maxima²¹² or absorption onset²¹⁰, see ref. 212 and 210.

DFT calculation indicate that for different acceptor monomer, the level of HOMO orbital lie in the limited range of -4.73 ~ -5.17 eV where the energy range of LUMO is significantly large, from -2.25 to -3.08 eV. The LUMO energies for the monomers suggest that their electron accepting ability follows **BBTa16<BBTa26<TaQ1<TaQ2<SBTa <SeBTa**. MO analysis indicates that two fused thiophene rings mainly affect the HOMO orbitals of acceptor: in Figure 6.1, HOMO orbitals are delocalized over acceptor and thiophene rings whereas LUMO orbitals are mainly localized on acceptor fragments.²¹³

Figure 6.1 Frontier orbitals of acceptor monomers.²¹³

The further calculation shows that the HOMO of isolated acceptor fragments and thiophene rings are close at energetic level and there is a large gap between their LUMO orbitals. Thus, HOMO orbitals between isolated acceptor fragment and thiophene groups are easy to combine. The long bithienyl and biphenyl rings at **TaQ1** and **TaQ2** can slightly stabilize the LUMO and then reduce HOMO-LUMO gap by the weak delocalization between them.²¹³

6.3 Absorption spectra of monomers

The vertical excitation energies (E_{ex}), vertical absorption wavelength (λ) of monomers, oscillator strength (f) and the orbital contribution to the electronic excitation calculated at the TD-DFT level was given in Table 6.3. The excitation (transition) energies, compared to HOMO-LUMO gaps, are determined from B3LYP wavefunction of frontier orbitals and also from experimental band gaps (see Table 6.3). TDDFT excitation energies are slightly higher than the experimentally determined optical band gaps (in case of XB Ta molecules, it underestimates). Vertical absorption wavelengths have a good agreement with experimental data (see the footnote of Table 6.3). **SeBTa** and **SBTa** have lower energy absorption compared to other monomers. It looks that those compounds with heteroatom are a type of potential acceptor, which reduce frontier orbital gap since heteroatom enhances the conjugation along the monomer skeleton. The absorption spectra of **SeBTa** and **SBTa** comprised of two peaks having energy splitting on order of 1.63~1.71 eV (see Figure 6.2(a)). The first red shifted absorption bands are all attributed to the almost 100% contribution of HOMO→LUMO transition. The magnitude of the optical gaps is similar to the electron excitation energy for HOMO→LUMO transition at $S_0 \rightarrow S_1$ excited state. Calculated data shows that experimentally found second peak in absorption spectra is due to the transition of electron from mainly HOMO to LUMO+1 orbitals that essentially points to the contribution of heteroatom S/Se in acceptor moieties. Interestingly, only for **BBTa26** and **BBTa16**, the oscillator strengths due to HOMO→LUMO transition are the strongest (>0.50) one amongst their own absorption bands whereas for others, different orbital contributions were found for the strongest oscillator strength. Higher oscillator strength means enhanced spatial overlap between ground state and excited state wave functions.²⁰² For **TaQ** molecules, the absorption spectra are quite different from other as their consequent absorption bands are nearly

Table 6.3 Experimental vertical absorption wavelength (λ_{exp}) and calculated vertical excitation energies (E_{ex}), maximum wavelength (λ), oscillator strength (f) and main orbital configuration in acceptor monomers at TD-DFT B3LYP/6-31G(d,p) level.

Acceptor	$\lambda_{\text{exp}}^{\text{a}}$ (nm)	λ (nm)	E_{ex} (eV)	Oscillator strength, f	Main transition configuration ^b		
BBTa26	535	542	2.28	0.5008	HOMO	→ LUMO	(100%)
	502	323	3.83	0.1206	HOMO-4	→ LUMO	(44%)
	311	300	4.12	0.3208	HOMO-4	→ LUMO	(43%)
		297	4.17	0.2315	HOMO-5	→ LUMO	(85%)
BBTa16	450	450	2.75	0.5082	HOMO	→ LUMO	(99%)
		259	4.78	0.1667	HOMO	→ LUMO+3	(81%)
SBTa	618	702	1.77	0.2733	HOMO	→ LUMO	(100%)
		365	3.40	0.2666	HOMO	→ LUMO+	(92%)
	337	312	3.96	0.2811	HOMO-5	→ LUMO	(66%)
		311	3.98	0.3556	HOMO	→ LUMO+	(62%)
SeBTa	700	785	1.58	0.2151	HOMO	→ LUMO	(100%)
	363	377	3.29	0.2757	HOMO	→ LUMO+	(92%)
	322	331	3.74	0.2620	HOMO-5	→ LUMO	(92%)
		315	3.92	0.4065	HOMO	→ LUMO+	(88%)
TaQ1	597 ^s	617	2.01	0.2112	HOMO	→ LUMO	(98%)
	553	488	2.54	0.2759	HOMO -1	→ LUMO	(97%)
	440	392	3.16	0.1144	HOMO	→ LUMO+	(66%)
	365	363	3.41	0.2806	HOMO	→ LUMO+	(90%)
	308	347	3.56	0.1062	HOMO-7	→ LUMO	(57%)
TaQ2	626	659	1.88	0.1070	HOMO	→ LUMO	(99%)
	516	567	2.19	0.2021	HOMO-1	→ LUMO	(83%)
		499	2.48	0.4440	HOMO	→ LUMO+	(83%)
		477	2.60	0.1061	HOMO-2	→ LUMO	(93%)
	428 ^s	437	2.83	0.5772	HOMO -1	→ LUMO+	(95%)
	377	397	3.12	0.4020	HOMO	→ LUMO+	(89%)
	340	373	3.32	0.1502	HOMO-2	→ LUMO+	(75%)

^a See ref 212 and 210. ^b percentage of contribution mentioned in brackets.

degenerated (separated by only small amount of energy due to symmetry problem). It causes the exhibition of one broad peak near at 450 nm for **TaQ1** and at 475 nm for **TaQ2** instead of several discrete absorption bands with small splitting energies ($<0.62\text{ eV}$ for **TaQ1** and $<0.32\text{ eV}$ for **TaQ2**). The small difference between the absorption peaks of **TaQ1** and **TaQ2** suggest specific difference in contribution of attached biphenyl and bithienyl groups. The strongest absorption of **TaQ1** is mainly corresponds to $\text{HOMO} \rightarrow \text{LUMO}+2$ transitions which are quite higher in energy ($\sim 1.40\text{ eV}$) than their $\text{HOMO} \rightarrow \text{LUMO}$ transitions. For **TaQ2**, the strongest absorptions take place due to the electron transitions from the initial state predominately contributed by the HOMO and HOMO-1 to the final state contributed by the LUMO+1. Besides HOMO and LUMO of **TaQ1** and **TaQ2**, the contribution from other electronic transitions explicitly points to their strong electron delocalization in two biphenyl and bithienyl groups that are fused with **TaQ** core.²¹³

Figure 6.2 Simulated Gaussian type absorption and emission spectra for monomers.²¹³

6.4 Electronic properties at low-lying excited state and emission spectra of monomers

The emission spectra based on optimized excited state geometries are presented in Figure 6.2(b). Broader range (red shifted about to 78~188 nm) of fluorescence spectra of all monomers and higher oscillator strength indicate the larger overlapping between the ground state (S_0) and S_1 excited state wave functions. It should come from the increased quinoid character in S_1 excited states.²³⁴ That results into the enhanced rigidity of molecular skeleton upon excitation along with reduced bridge bond length (by $0.021\sim 0.033\text{ \AA}$) and coplanar

geometry except **BBTa16** ($\Phi_1 = 26.8^\circ$, $\Phi_2 = 1.6^\circ$), **TaQ1** ($\Phi_1 = 2.3^\circ$, $\Phi_2 = 2.2^\circ$) and **TaQ2** ($\Phi_1 = 1.1^\circ$, $\Phi_2 = 0.9^\circ$). Larger bathochromic shift occurs in **SBTa** (156 nm) and **SeBTa** (188 nm) suggesting larger rearrangement upon photo excitation. Maximum emission wavelengths are all assigned for $S_0 \rightarrow S_1$ transition contributed by HOMO $\rightarrow$ LUMO electronic transition. However, besides **BBTa**, strong emissions with higher oscillator strength take place due to the electronic transitions other than HOMO $\rightarrow$ LUMO that is coincident with those in absorption. In **SBTa** and **SeBTa**, highest emission peak near at 350–400 nm, comprises of electronic transitions predominantly from HOMO $\rightarrow$ LUMO+1 and HOMO $\rightarrow$ LUMO+2. It is to be noted that LUMO+1 are highly localized on thiophene rings and S–N/Se–N skeleton whereas LUMO+2 are localized mainly on thiophene rings and triazole rings. The stronger emissions of **TaQ** molecules are due to transition between several frontier orbitals, which extensively shows the contribution from their fused biphenyl and bithienyl rings, as expected. The larger bathochromic shift in **TaQ2** compared to that of in **TaQ1** indicates the efficiency of bithienyl groups over biphenyl groups.²¹³

6.5 Geometries and electronic properties of DA oligomers at ground state

Recent material design have reached an agreement that it is the efficient way to afford narrow band gap material to incorporate electron-rich and electron-deficient moieties into the polymer chain.²³⁵⁻²³⁷ Proper choice of electron-rich (donor) unit can essentially tune the optoelectronic properties of polymer for their various applications. In this study, four donor units with bridging atom C, N, Si and P, cyclopenta[2,1-b:3,4-b']dithiophene (**Y1**), dithieno[3,2-b:2',3'-d]pyrrole (**Y2**), dithieno[3,2-b:2',3'-d]silole (**Y3**) and dithieno[3,2-b:2',3'-d]phospholes (**Y4**) (see scheme 6.2), are chosen to be coupled with model monomers (acceptors) with the intention of manipulating the HOMO-LUMO level within DA architecture and also manifesting the improvement of their optical behaviour. The theoretically HOMO energies of isolated donor are in the range of -5.09 to -5.91 eV at B3LYP/6-31G(d,p) level. Since HOMO and LUMO orbitals of donor **Y4** are more stable than at other donors, donor **Y4** show the advantage as organic electronics (n-type semiconductor material). Different from the stronger delocalization from lone pair orbital of N to thiophene rings in donor **Y2**, there is not $n(P) \rightarrow \pi(\text{thiophene})$ delocalization in donor **Y4**

since lone pair of P form a covalent bond by entering the empty orbital of B. It results in the electron deficiency of P so that higher degree of π -conjugation occurs after fused with bithiophene. The stronger π -conjugation induces the planar structure of **DA** oligomer and efficiently stabilizes its HOMO at -5.91 eV. LUMO of **Y4** is also highly stabilized (-1.86 eV) by an exceptional $\sigma^*-\pi^*$ ($\sigma-\pi$ exo-endocyclic hyperconjugation) orbital interaction.²³⁸ In **Y3**, there is $\sigma^*-\pi^*$ conjugation between two exocyclic Si-C σ^* bond and endocyclic C=C π^* bond, which reduce its LUMO to -1.29 eV. The π electron donating effect of N in **Y2** causes higher elevation of its HOMO energy (-5.09 eV) than that of **Y1** or **Y3**.²¹³

Figure 6.3 shows that the attached donor groups (**Y1-Y4**) contribute to lower the HOMO-LUMO gap of DA oligomers. Incorporation of donor units predominantly destabilizes the HOMOs of DA oligomers. On the other hand, the energies of LUMO in isolated donor and acceptor fragments significantly differ (by 0.39~2.52 eV) and they are mainly localized over the acceptor moieties (see Figure 6.3). This mismatch causes less influence on LUMO energies of DA oligomers as expected. Among all oligomers, HOMOs in DA oligomers of **Y2** are more destabilized on the basis of the same of respective acceptors under investigations. It highlights the contribution from higher HOMO level (closer to HOMOs of isolated acceptors) of **Y2**. Due to larger mismatch between LUMOs of **Y2** and acceptors units, **Y2A** oligomers have higher LUMOs than other DAs. Even in **Y2-SBTa** and **Y2-SeBTa**, LUMOs are elevated by 0.03 and 0.04 eV than their respective acceptor LUMOs. Though LUMOs are energetically less stabilized (0.05~0.07 eV) or slightly lifted in **Y2A** oligomers, they have the lowest HOMO-LUMO gap (1.42 to 2.30 eV) of all other studied oligomers as the extent of change in LUMO energies is less than that of HOMO energies. The mixing of HOMO or LUMO wave functions in DA oligomers also depends on torsion angles along the donor-acceptor bridge skeleton. It is found from the values of Φ_1 and Φ_2 that DA architecture reduces the deviation from coplanarity. This reduction in torsion angles impacts the electronic structures of oligomers through improving the wave function delocalization.²⁰² Due to similar torsion angles along the conjugation backbone and LUMO (HOMO) energies in **Y1A** and **Y3A** oligomers, they have similar HOMO-LUMO gap. However, slightly better match of HOMO energies between isolated **Y1** and acceptor units results into lower HOMO-LUMO gap in **Y1A** oligomers (1.43 to 2.30 eV) compared to **Y3A** oligomers (1.46 to 2.34 eV).²¹³

Interestingly, introduction of donor unit **Y4** increases the torsion angle in oligomers unlike of others and a better match is found for LUMO energies between isolated donor and acceptor fragments instead of their HOMO energies. As a result, the LUMO orbitals of **Y4A** oligomers are highly stabilized (-2.56 to -3.24 eV) whereas the HOMO energies (-4.69 to -5.01 eV) of oligomers are more approximate to that of their respective isolated acceptor units.

Figure 6.3 Frontier orbitals and their HOMO-LUMO energies for oligomers.²¹³

Figure 6.3 also shows comparatively more delocalized LUMOs for **Y4A** oligomers. Though LUMOs are stabilized, **Y4A** oligomers have the highest HOMO-LUMO gaps as

there is very less effect on HOMOs. These properties of **Y4A** oligomers can make them efficient for solar cell application.^{239, 240} The higher HOMO-LUMO gap as a combined effect of stabilized LUMO and lower HOMO level under DA architecture can play a significant role on increasing the open-circuit voltage of the solar cell.²¹³ Even their lower LUMO-LUMO offset, (especially for **Y4-BBTa26** and **Y4-BBTa16** where LUMO-LUMO offset is 0.54 and 0.39 eV respectively) helps to increase the device efficiency.^{241, 242}

6.6 Absorption spectra of DA oligomers

TDDFT calculation has been performed to gain insight into the electron excitation of DA oligomers. Simulated absorption spectra for all DA series of oligomers are presented in Figure 6.4 (for the detailed absorption spectra, see Appendix C). From this Figure 6.4, it is easily observed that the absorption spectra of oligomers get stronger and red-shifted with the enhancement of degree of conjugation on DA oligomer backbone than that of monomers. The first excitation $S_0 \rightarrow S_1$ in DA oligomers corresponds exclusively to the electron excitation from HOMO to LUMO. And this electronic transition causes the absorption maxima for **Y-BBTa26** and **Y-BBTa16** oligomers irrespective of different donor units. Absorption takes place towards longer wavelength in the DA oligomers with lower HOMO-LUMO gap, i.e. **Y4A** < **Y3A** < **Y1A** < **Y2A**. But incorporation with the same donor unit, stronger acceptors have the absorption band at longer wavelength.²¹³

The first absorption peaks for **Y1A** oligomers take place within 577~935 nm, whereas for **Y2A**, they are slightly move towards longer wavelength (577~941 nm). Compared to them, **Y3A** and especially **Y4A** oligomers have blue-shifted absorption peaks at 569~924 nm and 546~885 nm, respectively. All **Y-BBTa** oligomers have single absorption peak with the highest oscillator strength in their absorption band for $S_0 \rightarrow S_1$ electronic transition contributed by HOMO $\rightarrow$ LUMO. **Y-BBTa16** oligomers have the absorption peaks at 546~577 nm which are at the shortest absorption wavelengths compared to other absorption bands. **Y-BBTa26** have slightly red-shifted absorption peaks (~20 nm) at 628~658 nm whereas **Y-TaQ1** and **Y-TaQ2** have larger red shifted peaks (>147 nm and >182 nm) at 693~759 nm and at 728~810 nm, respectively. However, the strongest absorption peaks are found for **Y-TaQ1** and **Y-TaQ2** oligomers at 421~486 nm and at 457~470 nm, respectively contributed by several

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orbital transitions (mainly by HOMO→LUMO+1 and HOMO→LUMO+2) other than HOMO→LUMO. The small shift between **Y-BBTa26** and **Y-BBTa16** suggests the limited influence of attached methyl side chain.²¹³

Figure 6.4 Simulated Gaussian type of absorption-fluorescence spectra for copolymers.²¹³

The optical advantage of modelling with bithienyl groups over biphenyl groups for **TaQ** molecules is evident from the difference between their absorption maxima as well as the oscillator strengths. Among all, **SeBTa** with any of donor (**Y1-Y4**) have broader absorption band upto 2000 nm with the highest red shifted peak at 935(**Y1-SeBTa**), 941(**Y2-SeBTa**), 924(**Y3-SeBTa**), 885(**Y4-SeBTa**) nm due to $S_0 \rightarrow S_1$ electronic transition. They exhibit the shoulder peaks with the highest oscillator strength in their absorption bands at 471(**Y1-SeBTa**), 485(**Y3-SeBTa**), 498(**Y4-SeBTa**) nm due to mainly $S_0 \rightarrow S_3$ transitions and at 453(**Y2-SeBTa**) nm due to $S_0 \rightarrow S_4$ electronic transition. **Y-SBTa** oligomers have the similar absorption profiles but blue shifted (~ 87 nm) peaks compared to that of **Y-SeBTa**. It accounts for having more electron rich, Se atom on acceptor moiety. The strongest absorptions for both **Y-SBTa** and **Y-SeBTa** take place due to the molecular orbital transition of HOMO $\rightarrow$ LUMO+1. Their LUMO+1 orbital is localized on donor unit and N-S/Se of acceptor units (see Appendix C) that indicates the contribution of S/Se heteroatoms in acceptor moieties.²¹³

All of DA oligomers exhibit a wide range of light absorption spectra in visible and IR regions that suggests that these oligomers can be a very good candidate in optoelectronic field, especially for organic solar cell applications where the broad absorption near IR will ensure greater match with solar spectrum, thus higher absorption efficiency.²¹³

6.7 Geometries at excited state and emission spectra of DA oligomers

TDDFT calculation indicates that large rearrangement occurs in all DA oligomers upon photo excitation (see Appendix C). The bridge bond lengths are reduced to a great extent at the excited states compared to that of ground states. It implies that there is better conjugation between donor and acceptor groups in the S_1 excited states. Moreover, they have a strong coplanar tendency in all series at S_1 excited state, thus the geometries of **Y-BBTa**, **Y-TaQ1** and **Y-TaQ2** are greatly influenced by excitation.²¹³

The emission spectra of DA oligomers based on the optimized structure of S_1 excited-state are presented in Figure 6.4. The maximum emission wavelengths are all assigned to $\pi \rightarrow \pi^*$ character arising from HOMO $\rightarrow$ LUMO transition. Emission spectra look similar

to absorption spectra besides their broadened emission region upto 2500 nm with higher oscillator strengths. The lowest stokes shift (60~133 nm) is found for **Y2D** oligomers whereas the largest stokes shift (81~174 nm) takes place for **Y4D** oligomers.²¹³

Like absorption spectra, emission spectra exhibit large red shifts from **Y-BBTa16** to **Y-SeBTa** by 457 nm in **Y1D**, 464 nm in **Y2D**, 454 nm in **Y3D** and 432 nm in **Y4D** oligomers. **Y-BBTa26** and **Y-BBTa16** have stronger oscillator strengths than others contributed by HOMO→LUMO electronic transition. **Y-SBTa** and **Y-SeBTa** have also stronger oscillator strength but for their shoulder peaks near at ~500nm contributed by HOMO→LUMO+1 electronic transition. That is coincident with absorption spectra.²¹³

Though **Y-TaQ1** oligomers have shorter absorption wavelength than **Y-TaQ2**, they have stronger emission peak (at ~850 nm) for HOMO→LUMO electronic transition. From Figure 6.4, it is clearly visible that the second emission peaks for **Y-TaQ2** are very stronger than those of **Y-TaQ1** due to electronic transitions other than HOMO→LUMO. It is to be noted that for the secondary emission peaks of **Y1-TaQ1**, **Y4-TaQ1**, **Y2-TaQ2** and **Y3-TaQ2** occur due to the major contribution of the electronic transition of molecular orbitals that are different from those of absorption. It indicates the large rearrangement of **Y-TaQ1/2** upon excitation (see Table 6.4).²¹³

All the DA oligomers have the emission peaks near at 500 nm though **Y-SBTa**, **Y-SeBTa**, **Y-TaQ1** and **Y-TaQ2** have also emission peaks in the near IR and IR region. Their emission characteristics are very attractive for the use as photo detectors, photovoltaic cells and other photoelectronic devices. The radiative lifetime has been determined for spontaneous emission by using the following simple working formula²⁴³:

$$\tau = \frac{1.5003}{f^*(E_{flu})^2}$$

where, f is the oscillator strength at excited state and ΔE_{flu} is the excitation energy in cm^{-1} .

Table 6.4 Simulated emission spectra of DA oligomers at TD-B3LYP/6-31g(d,p) level.²¹³

DA oligomers	Electronic Transition	E _{ex} (eV)	λ (nm)	Oscillator strength, f	Main transition configuration and their contribution			Radiative life, τ(ns)	
Y1-BBTa26	S ₁ → S ₀	1.71	726	1.0197	HOMO	→	LUMO	1.00	7.75
Y1-BBT16	S ₁ → S ₀	1.94	640	1.2429	HOMO	→	LUMO	1.00	4.94
Y1-SBTa	S ₁ → S ₀	1.27	975	0.5271	HOMO	→	LUMO	1.00	27.06
	S ₃ → S ₀	2.55	486	1.0432	HOMO	→	LUMO+1	0.91	
Y1-SeBTa	S ₁ → S ₀	1.13	1097	0.4073	HOMO	→	LUMO	1.00	44.33
	S ₃ → S ₀	2.48	500	1.1133	HOMO	→	LUMO+1	0.92	
Y1-TaQ1	S ₁ → S ₀	1.42	871	0.5213	HOMO	→	LUMO	1.00	21.83
	S ₄ → S ₀	2.55	486	0.4596	HOMO	→	LUMO+1	0.69	
Y1-TaQ2	S ₁ → S ₀	1.33	930	0.3654	HOMO	→	LUMO	1.00	35.51
	S ₆ → S ₀	2.52	491	0.8357	HOMO	→	LUMO+2	0.43	
Y2-BBTa26	S ₁ → S ₀	1.71	725	0.9747	HOMO	→	LUMO	1.00	8.09
Y2-BBT16	S ₁ → S ₀	1.95	637	1.1691	HOMO	→	LUMO	1.00	5.21
Y2-SBTa	S ₁ → S ₀	1.27	977	0.5190	HOMO	→	LUMO	1.00	27.59
	S ₄ → S ₀	2.66	466	1.1011	HOMO	→	LUMO+1	0.92	
Y2-SeBTa	S ₁ → S ₀	1.13	1101	0.4017	HOMO	→	LUMO	1.03	45.27
	S ₄ → S ₀	2.57	481	1.1341	HOMO	→	LUMO+1	0.93	
Y2-TaQ1	S ₁ → S ₀	1.41	876	0.5000	HOMO	→	LUMO	1.00	23.03
	S ₇ → S ₀	2.78	446	0.7397	HOMO	→	LUMO+2	0.75	
Y2-TaQ2	S ₁ → S ₀	1.31	943	0.3433	HOMO	→	LUMO	1.00	38.86
	S ₇ → S ₀	2.56	484	0.6936	HOMO-4	→	LUMO	0.48	
Y3-BBTa26	S ₁ → S ₀	1.72	721	1.0497	HOMO	→	LUMO	1.00	7.43
Y3-BBT16	S ₁ → S ₀	1.94	637	1.2962	HOMO	→	LUMO	1.00	4.70
Y3-SBTa	S ₁ → S ₀	1.28	969	0.5251	HOMO	→	LUMO	1.00	26.83
	S ₃ → S ₀	1.47	502	0.8947	HOMO	→	LUMO+1	0.91	
Y3-SeBTa	S ₁ → S ₀	1.14	1091	0.4040	HOMO	→	LUMO	1.00	44.20
	S ₃ → S ₀	2.40	515	0.9796	HOMO	→	LUMO+1	0.92	
Y3-TaQ1	S ₁ → S ₀	1.43	865	0.5196	HOMO	→	LUMO	1.00	21.60
	S ₄ → S ₀	1.51	493	0.3919	HOMO	→	LUMO+1	0.47	
Y3-TaQ2	S ₁ → S ₀	1.34	924	0.3658	HOMO	→	LUMO	1.00	35.02
	S ₆ → S ₀	2.50	496	0.6830	HOMO-3	→	LUMO	0.56	
Y4-BBTa26	S ₁ → S ₀	1.75	707	1.1165	HOMO	→	LUMO	1.00	6.72
Y4-BBT16	S ₁ → S ₀	1.98	627	1.4116	HOMO	→	LUMO	1.00	4.18
Y4-SBTa	S ₁ → S ₀	1.32	941	0.5173	HOMO	→	LUMO	1.00	25.68
	S ₃ → S ₀	2.41	515	0.7805	HOMO	→	LUMO+1	0.79	
Y4-SeBTa	S ₁ → S ₀	1.17	1059	0.3926	HOMO	→	LUMO	1.00	42.86
	S ₃ → S ₀	2.34	528	0.8848	HOMO	→	LUMO+1	0.85	
Y4-TaQ1	S ₁ → S ₀	1.49	830	0.5346	HOMO	→	LUMO	1.00	19.33
	S ₄ → S ₀	2.46	503	0.4259	HOMO-2	→	LUMO	0.39	
Y4-TaQ2	S ₁ → S ₀	1.42	872	0.3791	HOMO	→	LUMO	0.99	30.09
	S ₅ → S ₀	2.35	526	0.4539	HOMO-3	→	LUMO	0.41	

From Table 6.4, it is observed that **Y4A** oligomers have comparatively shorter radiative life of all. It indicates the advantage of using **Y4** as donor unit for DA polymers as it increases their light-emitting efficiency. Carbazole, the famous host material, has the radiative life >30 ns.²⁴⁴ Particularly, **Y-SeBTa** and **Y-TaQ2** having the radiative life more than 30 ns can be expected as good host material as their longer radiative life facilitates the electron and energy transfer to attack active species. The short radiative life of remaining DA oligomers enhances their luminescence properties and thus, can be good candidates for light-emitting materials.²¹³

6.8 Electronic and photophysical properties of 2D-A copolymers at ground state and low-lying excited state

It becomes a great challenge to design a material with narrow band gap, especially for solar cell applications with no compromise with either the open circuit voltage (V_{oc}) or the efficiency of devices. The increase of open circuit voltage (V_{oc}) which can be considered as the difference between HOMO of donor and LUMO of acceptor, facilitates higher power conversion though narrow band gap (<2 eV) ensures maximum photon harvest from solar spectrum.²⁰⁷ Again reduced LUMO(donor)-LUMO(acceptor) offset increases device efficiency but results in loss of V_{oc} . Then, material with high V_{oc} and low LUMO-LUMO offset can be the efficient and promising one for solar cell. By lowering the LUMO of donor, LUMO-LUMO offset can be reduced whereas V_{oc} remains same. But if the HOMO and LUMO of donor are lowered simultaneously or lifted the LUMO of acceptor, both high V_{oc} and low LUMO-LUMO offset can be obtainable.²⁰⁷

We have found that **Y4** has slightly lifted the HOMO but greatly stabilized the LUMO of **Y4A** oligomers. It prompts us to add another **Y4** unit to **Y4A** (**A**= **BBTa26**, **SeBTa**, **TaQ2**; taking more promising one from three different groups of acceptors) to maximize its possibilities under 2DA architecture for the solar cell application.²¹³

Table 6.5 Frontier orbitals and absorption spectra of 2DA trimer (n=3) determined at B3LYP and TD-DFT respectively with 6-31g(d,p) basis sets.²¹³

2DA (n=3)	HOMO- LUMO gap (eV) ^a	Electronic Transition	E _{ex} (eV) ^b	λ (nm)	Oscillator strength, f	Main transition configuration and their contribution
2Y4-BBTa26	1.58 (1.37) ^c	S ₀ → S ₁	1.36	912	6.1716	HOMO → LUMO 0.80
		S ₀ → S ₄	1.67	744	0.5997	HOMO-1 → LUMO+1 0.70
2Y4-SeBTa	1.17(1.01)	S ₀ → S ₁	1.00	1237	3.9145	HOMO → LUMO 0.89
		S ₀ → S ₅	1.24	998	0.2787	HOMO → LUMO+2 0.78
2Y4-TaQ2	1.55(1.36)	S ₀ → S ₁	1.31	945	4.2466	HOMO → LUMO 0.62
		S ₀ → S ₅	1.60	774	0.2453	HOMO → LUMO+2 0.60

^a At the B3LYP level. ^b At the TDDFT B3LYP level. ^c band gap of 2DA from the intercept of graph.,see Appendix C.

The geometries of **2Y4-BBTa26**, **2Y4-SeBTa** and **2Y4-TaQ2** (repeating 3 units) are optimized as a representation of full polymer systems (the bridge bond length and torsion angles of optimized structures for single unit of oligomers, see Appendix C). Addition of another donor unit tends to planarize the oligomer backbone for **2Y4-BBTa26** and **2Y4-SeBTa**. However, the structure of **2Y4-TaQ2** is slightly more twisted than that of **Y4-TaQ2** due to increased steric hindrance between H-atoms of bulky bithienyl groups and alkyl group attached to **Y4**. There is little change in bridge bond length as an indication of extended delocalization.²¹³

Though there is a small lift of HOMO level (0.03eV), LUMO level is appreciably lowered (0.06 ~ 0.11eV) by the addition of another **Y4** unit. The effect is more significant from n=2 to 3 where the lift of HOMO level is limited within ~0.09 to ~0.12 eV but the lowering of LUMO is within range of (0.15~0.22 eV) and (0.18~ 0.17 eV). For trimer, the LUMO and HOMO levels are at -3.05~ -3.48 eV and at -4.60~ -4.65 eV, respectively. With the help of extrapolation procedure, the band gaps of polymers are roughly estimated from the linear relationship between their HOMO-LUMO gap and the inverse number of repeat units (see Appendix C) and the band gaps are found to be within the range of 1.01~ 1.37eV (see Table 6.5). All these electronic configurations are well suited for the solar cell application. The structure of **2Y4-SeBTa** trimer is relatively linear with the dihedral angle ~4⁰ between thiophene of acceptor and next donor unit. It is a bit higher in **2Y4-BBTa**(~8⁰) and **2Y4-**

TaQ2 ($\sim 13^0$). Figure 6.5 shows a regular zigzag pattern for all three trimers. It is considered a key feature behind distinct film-forming properties and enhanced performance of solar cell.^{245,}

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Figure 6.5 Pictorial representation of the natural transitional orbitals (NTO) determined with TD-DFT/6-31g(d,p) describing the electronic transition of $S_0 \rightarrow S_1$, λ is the fraction of hole-electron contribution at the excited states.²¹³

Figure 6.5 is a pictorial representation of natural transition orbitals (NTO) that describe the electronic transition $S_0 \rightarrow S_1$ through hole-particle excitations. The fraction (λ) of hole-particle pair contributions for $S_0 \rightarrow S_1$ is also shown. For **2Y4-BBTa26**, both hole and electron NTO are well delocalized over the entire conjugated backbone for which it has the highest oscillator strength (see Table 6.5) of all three. For **2Y4-SeBTa** and **2Y4-TaQ2**, hole NTO is delocalized across donor unit to acceptor unit where electron NTO has the electron density mainly on acceptor unit. It represents their partial charge-transfer like nature. It is to be noted that the hole-electron resides the same spatial extent of the trimers which ensures their large spatial overlap between hole and electron NTO and thus, large transition dipole moments for trimers. This is the reason of their high oscillator strength. TDDFT analysis for absorption spectra (see Table 6.5) shows that absorption take place in IR region contributed mainly HOMO $\rightarrow$ LUMO orbital transition for $S_0 \rightarrow S_1$. All their absorption spectra are similar characterized by a strong dominating absorption peak at 912 ~1237 nm with low energy transition and a secondary weak absorption peak at 744 ~998 nm with comparatively high energy transition.²¹³

6.9 CONCLUSION

A comprehensive investigation on triazole based **BBTa**, **XBTa** and **TaQ** monomers (as acceptor) and their DA oligomer has been performed based on the DFT calculation. From the present study, it is found that heteroatom effect of **XBTa** (X=S,Se) monomer has largely enhanced its electronic and photophysical properties as acceptors by exceptionally stabilized LUMO. When they are fused to biphenyl/ bithienyl ring, the type of acceptor can modify its electronic properties for better performance through enhanced delocalization. Stabilized LUMO of acceptor fragment can efficiently lower the HOMO-LUMO gap of material and again destabilized LUMO of acceptor effectively reduces the LUMO-LUMO effect of solar cell (also increases V_{oc}).

Under DA architecture, electronic and photophysical properties of monomers have been greatly enhanced. Different donor units can fine tune their optical properties. Among four donors, **Y4** is the most effective donor unit for application like solar cell since after incorporation of **Y4**, the LUMO of DA oligomers is largely stabilized albeit it slightly lifts

the HOMO level. The TD-DFT calculation on electronic properties of trimers under D-D-A backbone indicates that 2DA oligomers have essentially stabilized HOMO at the range of -4.60 to -4.65 eV, which results V_{oc} more than 1.01 eV. These are quite attractive properties for using them as solar cell material. The NTO of trimer explains their nature of partial charge transfer through hole-electron transition and shows the reason of their higher oscillator strength of absorption peak. The study shows that all the oligomers absorb photon in the red and near IR region and have emission in IR region with boarder emission band. The stronger oscillator strength suggests that they are good candidates for optoelectronic properties.²¹³

Chapter 7

Summary

π -Conjugated systems are considered as the organic semiconductors and offersome extra advantages over the inorganic semiconductors. Their flexibility in designing molecular devices and tunability of optical properties and overall easy and less expensive synthesizing process make them attractive to the researchers worldwide. It prompts us to study with the conjugated systems with the intention of exploring the different methods to tailor/enhance their properties. Before molecular engineering, it is essential to know about the systems and their electronic and optical properties. A theoretical study on heavier group-14 substituting effect on the electronic property of formamide, internal rotational barrier and strong hydrogen bond with water and other solvents helps to know how to altering the properties essentially and to what extent the changes influence their performances. For heavier group-14 analogues of formamide (XHONH_2 , $\text{X}=\text{Si}$, Ge and Sn), the $n_{\text{N}}-\pi_{\text{X}=\text{O}}$ conjugation strength does not always reduce as X becomes heavier, for example, silaformamide and germaformamide have similar strength of delocalization. The barrier heights of internal rotation become gradually low from C to Sn , formamide (15.73 kcal/mol) > silaformamide (11.73 kcal/mol) > germaformamide (9.45 kcal/mol) > stannalformamide (7.50 kcal/mol) at the CCSD(T)/aug-cc-pVTZ//B3LYP/cc-pVTZ level. NBO analysis indicates that the barrier does not only come from the $n_{\text{N}} \rightarrow \pi^*_{\text{XO}}$ conjugation and for heavier analogues of formamide the $n_{\text{N}} \rightarrow \sigma^*_{\text{XO}}$ hyperconjugation effect and steric effect considerably contribute to the overall rotational barrier. Heavier formamide prefer being H-bond donorsto form $\text{FXO}-\text{H}_2\text{O}$ complexes to

being H-bond acceptors to form FXH-OH₂ complexes. The NEDA analysis indicates that H-bond energies of FXO-H₂O complexes increase as moving down to group 14 due to concurrently stronger charge transfer and electrostatic attraction and for the FXH-OH₂ complexes H-bond strengths are similar. The model of charge transfers from FXO to H₂O differs from that at FXH-OH₂ complexes, which are contributed not only by aligning lone pair orbital of O but also by another lone pair orbital. At two lowest-lying excited states (the triplet and *S*₁ excited states), formamide and its group-14 heavier analogues form double H-bonds with H₂O molecule at the same time.

Further investigation was carried out on formamide molecules for its group 16 analogues. The nature of hydrogen bond for formamide and its heavy complexes (CYHNH₂⋯ZH; Y=O, S, Se, Te; Z=F, HO, NH₂) was performed on the basis of DFT B3LYP calculations and the quantum chemistry analysis. Except for the CYHNH₂⋯NH₃ complexes, the substitution of O atom at formamide with less electronegative atoms (S, Se & Te) is found to weaken the hydrogen bond (H-bond). This substitution results in cyclic structure of hydrated and ammoniated formamide complexes by the formation of bi-functional H-bonds (Y⋯H₄Z; Z⋯H₃C). NBO analysis indicates that the H-bond is weakened due to less charge transfer from lone pair orbital of H-bond acceptor to antibonding orbital of H-bond donor. QTAIM (The Quantum Theory of Atoms in Molecules) analysis reveals that the acyclic structure with single H-bond stabilizes the complexes more than the cyclic structure formed by bi-functional H-bonds. NEDA and BLW-ED analyses show that the H-bond stabilization energies of NEDA and BLW-ED have good correlation with the dissociation energy of formamide complexes and charge transfer (CT) from donor to acceptor atom plays an important role in H-bonding. We have also studied the low-lying electronic excited states (*T*₁, *T*₂ and *S*₁) for CYHNH₂⋯H₂O complexes to explore the nature of H-bond on the basis of electronegativity and found that hydrogen bond is highly influenced at the excited states with the changed charge transfer characteristic.

Our investigation was then extended to Si/Ge based systems (germasilaallenes) from their linear to cyclic conformations through highly bent structures. This study mainly focused on the uniqueness of Si/Ge based systems as well as their mysterious nature. Systematic density functional theory (DFT) calculations and natural bond orbital (NBO) analyses were carried out to understand the reason behind the disappearance of linear and slightly-bend isomer of

germasilaallenes and the bond-stretch phenomenon of their cyclic isomer, unusual electronic properties of highly-bend isomers of gerasilaallenes. Our results show that in contrast to trisilaallene and trigermaallene; 1,3-digermasilaallene and 1-germadisilaallene do not have stable cyclic isomers, due to increased ring strains. DFT calculations and NBO analyses indicate that the stability of highly-bend isomers of gerasilaallenes arise from three parts: p(terminal)→p(central) donor-acceptor interaction, p(terminal)-p(terminal) partial overlapping and the aromatic delocalization along the ring. Different from mono- and digermasilaallene, DFT and CCSD calculations indicate that there is no stable minimum along the first half, from 180° to 90.0°, of the potential energy surface of trigermasilaallene. For trigermasilaallene, for bending angle $\alpha > 120.0^\circ$, π - π^* orbital delocalization effect dominates the stability and when $\alpha < 120.0^\circ$, aromatic delocalization of the conformer becomes the main factor. With the bending angle lighter, the stable energy becomes larger. Thus, the gerasilaallenes gradually become more stable along the bending PES from 180° to 90.0° and no barrier stabilizes the slightly-bend isomer. Stability of these types of system becomes the main concern in many applications. DFT calculations indicate that strong donor effect from substituents attached to terminal Si (Ge) to central Si (Ge) can stabilize the slightly-bend isomer of gerasilaallenes.

We have explored the fascinating properties of Si based molecules as donor for conjugated polymer and compared their performances with those of other similar donor units under donor-acceptor (DA) skeleton. We have extensively studied the isolated acceptors and donor units and incorporated the donors with the acceptors under different DA architectures. Heteroatom in acceptor fragments plays an important role in lowering the HOMO-LUMO gap of DA conjugated systems as well as increasing the solubility. The planar conjugated backbone is always expected for better electron delocalization. Though the large aryl bulky groups fused to the acceptor segment deviate the polymer skeleton from coplanarity to some extent (due to increased steric hindrance), they are found to take part in enhancing the optical behavior of conjugated polymer.

It is observed that the properties of donors as well as different DA architectures influence and enhance the performance of polymer to a great extent. The choice of donor unit is very important to design low band gap material. Using different donor units can well tune their optical properties. It still remains a great challenge to design low band gap material with high

optical efficiency. Si-based donors have comparatively more stabilized HOMO and LUMO level compared to their C counterpart, which is a very essential property in designing photonic molecules for optoelectronic applications, especially for photovoltaic cells. Highly stabilized HOMO level of donor unit generally increases the open circuit voltage which enhanced the power conversion from photon absorption. Comparatively shorter radiative life of Si and P based donor-acceptor oligomer indicates their better performances as light-emitting materials. Due to enhanced charge transfer characteristic and larger spatial overlapping from D-A to 2D-A architecture, the absorption spectra for oligomers broaden and red-shifted with stronger oscillator strength.

Our designed all DA oligomers are found to be absorbed photon in the red and near IR region and have emission in IR region with broader emission band and stronger oscillator strength. It suggests that they are good candidates for optoelectronic properties and thus, worthy of our investigation.

Appendix A

Supplementary Material for Internal Rotation Barriers and Hydrogen Bonds in Formamides and Their Complexes

Figure A1. There is a linear correlation between the internal rotational barriers and the sum of the energetic difference of conjugational, hyperconjugational stabilization energies and steric repulsion energies between the planar structure and TS.

Appendix A

A1. The geometries for stable plane structures and internal rotational TSs optimized at the B3LYP/cc-pVTZ (or LanL2dz) level and the total energies of formamide and heavier analogue of the group 14 (All energies below including the zero-point correction energy (ZPE)).

1) Formamide 1, E= -169.920277 hartree.

O	0.00090100	-0.01336500	0.00255500
C	0.00232300	-0.00001500	1.21189800
N	1.11443900	-0.00288700	1.98957900
H	-0.92574000	0.01542400	1.81141700
H	2.02171600	-0.01347900	1.55413500
H	1.05106200	0.01360000	2.99116900

2) Silaformamide 2, E= -421.362853 hartree.

O	1.45565100	-0.44007300	0.00014200
Si	0.14750200	0.34362200	-0.00021300
N	-1.41132400	-0.29816600	0.00007200
H	0.00952500	1.81473400	0.00105500
H	-1.59804000	-1.28788200	0.00020200
H	-2.24244500	0.27019000	0.00008500

3) Germaformamide 3, E= -2208.877332 hartree.

O	1.46867800	-0.65850700	-0.00001900
Ge	0.10173000	0.24734000	-0.00000100
N	-1.55201400	-0.44364500	0.00002100
H	-0.03899600	1.77645400	0.00017300
H	-1.71576700	-1.43649300	0.00020200
H	-2.38593500	0.11874700	-0.00033800

4) Stannaformamide 4, E= -134.712931 hartree.

O	-1.60022000	0.79053000	-0.00222100
Sn	-0.08209100	-0.19523800	0.00367200
N	1.75489900	0.54740700	-0.07165900
H	0.14679800	-1.89384500	-0.04597800
H	1.92730300	1.52857000	0.15951400
H	2.54789900	-0.02892500	0.22223800

Appendix A

A2. The optimized geometric parameters of the transition state of internal rotation along Y-N single bond for formamide and its heavy analogue of group 14 at the B3LYP level augmented with the basis set of cc-pVTZ (Y=C, Si and Ge) and Lanl2dz(d,p) (Y=Sn) and the total energies including the zero-point correction energy.

1) Internal rotation TS of formamide 1, E= -169.892227 hartree.

O	-1.16288500	-0.30745300	0.00001100
C	-0.20189500	0.40734800	-0.00001500
N	1.17210700	-0.03002200	-0.00002100
H	-0.30017400	1.50456500	-0.00002600
H	1.30494900	-0.63930600	0.80509500
H	1.30492700	-0.63956700	-0.80492000

2) Internal rotation TS of silaformamide 2, E= -421.345652 hartree.

O	1.43750800	-0.48721000	0.00003600
Si	0.15843700	0.34472500	-0.00008000
N	-1.47943300	-0.19008200	-0.00000800
H	0.19199400	1.82033100	0.00032400
H	-1.77746100	-0.70931400	-0.81717500
H	-1.77669600	-0.70892000	0.81773600

3) Internal rotation TS of germaformamide 3, E= -2208.863437 hartree.

O	-1.44343300	-0.70861100	-0.00000100
Ge	-0.11076200	0.24834200	-0.00000500
N	1.65223800	-0.32084600	0.00001200
H	-0.14446700	1.78438500	0.00008600
H	1.83521300	-0.90829800	0.80918000
H	1.83542700	-0.90820600	-0.80916600

4) Internal rotation TS of stannaformamide 4, E= -135.118180 hartree.

O	1.56049300	0.83969200	0.00026700
Sn	0.08963200	-0.19524300	-0.00010600
N	-1.84445000	0.41776400	-0.00004100
H	0.03484700	-1.90816800	0.00144800
H	-2.04425500	1.01300000	0.81060900
H	-2.04500400	1.01541100	-0.80862700

Appendix A

A3. The geometries of optimized for FXH-H₂O and FXO-H₂O (X= C, Si, Ge and Sn) complex at the B3LYP level augmented with the basis set of aug-cc-pVTZ (X=C, Si and Ge) and Lanl08d (Y=Sn) and the total energies including the zero-point correction energy.

1) FXO-H₂O complex of formamide, E= -246.375114 hartree.

O	2.38263400	-0.14870600	0.00008500
C	1.18446300	-0.34631200	-0.00008900
N	0.23171400	0.61264300	-0.00004200
H	0.75546100	-1.36386400	-0.00030900
H	0.51540300	1.57842900	0.00015100
H	-0.75122700	0.38119200	-0.00018300
O	-2.72929700	-0.10554100	0.00000400
H	-3.23710400	-0.38640700	0.76726600
H	-3.23800900	-0.38600100	-0.76680500

2) FXO-H₂O complex of silaformamide, E= -497.818681 hartree.

O	-2.54514900	0.04990300	0.00012400
Si	-1.05941600	-0.30805700	0.00007100
N	0.24007300	0.75754000	-0.00034800
H	-0.51458300	-1.68128800	0.00030200
H	0.11970300	1.75758800	-0.00060300
H	1.20805300	0.45873400	-0.00029100
O	3.15996100	-0.15523600	0.00009900
H	3.70897800	-0.34379100	-0.76691200
H	3.71066800	-0.33856200	0.76716500

3) FXO-H₂O complex of germaformamide, E= -2285.33246 hartree.

O	2.32614400	0.24083100	0.00003700
Ge	0.74865000	-0.22484500	-0.00000800
N	-0.63245000	0.90961700	-0.00001800
H	0.19427000	-1.65632700	-0.00004000
H	-0.49185100	1.90602200	-0.00001100
H	-1.59791500	0.60824600	-0.00005900
O	-3.50913100	-0.18032100	0.00001000
H	-4.08506600	-0.25713000	0.76671300
H	-4.08519600	-0.25716400	-0.76659200

4) FXO-H₂O complex of stannaformamide, E= -211.612466 hartree.

O	2.30402700	0.38333600	-0.00019400
Sn	0.60655900	-0.17962600	0.00002900
N	-0.94449600	1.00254900	0.00007800
H	-0.02691500	-1.76654000	0.00040200
H	-0.86316300	2.00584400	-0.00017100
H	-1.90225600	0.67860600	-0.00004100
O	-3.81942000	-0.19555300	-0.00015800
H	-4.39991800	-0.22752600	0.76634000
H	-4.40105200	-0.22919500	-0.76572200

5) FXH-H₂O complex of formamide, E= -246.376448 hartree.

O	-0.07034900	0.81235900	-0.00328500
C	-0.74305600	-0.20315000	0.01097100
N	-2.09194400	-0.22309700	-0.00087200
H	-0.28997900	-1.20542400	0.03584900
H	-2.60342400	0.64378800	-0.02601900
H	-2.59806500	-1.09013700	0.00916600
O	2.51890000	-0.32170700	-0.02552700
H	3.26782600	0.24864700	0.16430300
H	1.73717100	0.25849000	-0.01252200

6) FXH-H₂O complex of silaformamide, E= -497.82228 hartree.

O	-0.40915200	-0.70904800	-0.00028500
Si	0.74945600	0.28957600	0.00009300
N	2.38119100	-0.11580100	0.00012600
H	0.63199000	1.75785100	0.00061300
H	2.71420900	-1.06677700	-0.00039400
H	3.11800700	0.57086000	0.00000000
O	-3.06099400	0.23132500	-0.00055500
H	-3.68517400	-0.49844400	0.00500000
H	-2.17857800	-0.18515700	-0.00068800

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7) FXH-H₂O complex of germaformamide, E= -2285.337143 hartree.

O	-0.64032600	1.03291200	-0.00159700
Ge	0.46347300	-0.19092700	0.00212000
N	2.22270200	0.12503400	-0.00264900
H	0.21965200	-1.70019500	0.01071200
H	2.59757600	1.05930100	-0.00983700
H	2.91513600	-0.60480100	-0.00232800
O	-3.09919500	-0.29485600	-0.01464400
H	-3.87363800	0.26302900	0.09089300
H	-2.33260500	0.31263900	-0.00882800

8) FXH-H₂O complex of stannaformamide, E= -211.620015 hartree.

O	-0.81127300	1.25467400	0.01777200
Sn	0.31053500	-0.14416700	0.01744400
N	2.24159100	0.13228000	-0.05897300
H	0.08066300	-1.82409100	0.08450300
H	2.66557200	1.04431200	-0.10999600
H	2.92222400	-0.60918000	-0.06811400
O	-3.01887700	-0.34176400	-0.09663500
H	-3.84188100	-0.05566800	0.30679400
H	-2.40328500	0.42372000	-0.04165700

A4. The optimized geometries of FXO-H₂O (X= C, Si, Ge and Sn) complex at their triplet state with B3LYP/aug-cc-pvtz basis set (X=C, Si and Ge) and B3LYP/Lanl08d (X=Sn) and the total energies.

1) FXO-H₂O complex of formamide, E= -246.3024981 hartree.

O	-0.62236500	-1.06408100	-0.34991600
C	-1.24219100	-0.19558500	0.42462600
N	-0.82596300	1.07284300	-0.10761900
H	-1.23010100	-0.30824700	1.50615400
H	-1.07436600	1.18555900	-1.08325200
H	0.15492900	1.31020000	0.05154500
O	2.01650500	0.11103300	0.03311500
H	2.81476400	-0.27048800	0.40832900
H	1.41654200	-0.62903100	-0.14279100

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2) FXO-H₂O complex of silaformamide, E= -497.7767367 hartree.

O	-0.22341600	-1.12907300	-0.52908400
Si	-1.27488100	-0.14213800	0.23912300
N	-0.35196300	1.30722400	-0.21464700
H	-1.27687800	-0.26088300	1.73244700
H	-0.39955800	1.60958300	-1.17938500
H	0.60688900	1.37226100	0.12598700
O	2.31279400	0.02916500	0.15180700
H	3.00753300	-0.44572300	0.61519200
H	1.65905900	-0.63661500	-0.12121800

3) FXO-H₂O complex of germaformamide, E=-2285.317135 hartree.

O	0.26688400	-1.12743800	-0.58682600
Ge	-0.96635900	-0.07634200	0.10968100
N	0.14671300	1.42370400	-0.23435300
H	-1.09587000	-0.23998700	1.66293900
H	0.16891700	1.71628300	-1.20458600
H	1.10558000	1.30443700	0.09685700
O	2.76522900	-0.01625700	0.19909300
H	3.36948600	-0.49867100	0.76929400
H	2.09147700	-0.65547000	-0.09197400

4) FXO-H₂O complex of stannaformamide, E= -211.6154967 hartree.

O	0.68534900	-1.39057900	-0.05083900
Sn	-0.77425200	-0.05983600	-0.03463100
N	0.37185900	1.60239500	0.08833600
H	-1.54399600	-0.35920900	1.50359800
H	0.08848000	2.42452600	-0.42896600
H	1.35901100	1.41815000	-0.08788900
O	3.06689300	0.04812000	0.10058300
H	3.76604500	-0.29308200	-0.46367400
H	2.42213200	-0.67564700	0.19218500

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A5. The optimized geometries of FXO-H₂O (X= C, Si, Ge and Sn) complex at their excited state with CIS/aug-cc-pvtz basis set (X=C, Si and Ge) and CIS/Lanl08d (X=Sn) and the total energies.

1) FXO-H₂O complex of formamide, E= -246.283152 hartree.

O	-0.74696300	-1.08238300	-0.31262400
C	-1.30222100	-0.17308100	0.36513900
N	-0.85658000	1.10604700	-0.08361400
H	-1.52023500	-0.31720600	1.40708500
H	-1.13503700	1.29240200	-1.02368800
H	0.13475700	1.24103100	0.00521800
O	2.18825400	0.07722600	0.03993300
H	1.74489200	-0.73418200	-0.14388900
H	3.05468700	-0.14463000	0.33127000

2) FXO-H₂O complex of silaformamide, E= -497.7567611 hartree.

O	-0.38752900	-1.28990800	-0.50475600
Si	-1.18292200	-0.12562400	0.28700500
N	-0.50539900	1.36131600	-0.24424700
H	-1.00243900	-0.27512100	1.74556000
H	-0.74217800	1.70523100	-1.14745000
H	0.44725000	1.56755400	-0.02086700
O	2.41435500	0.06178200	0.11809000
H	1.93654600	-0.68207100	-0.21145000
H	3.24492000	-0.26106700	0.41918800

3) FXO-H₂O complex of germaformamide, E= -2285.333032hartree.

O	0.00840600	-1.39014600	-0.63664800
Ge	-0.85859800	-0.07564700	0.18280300
N	-0.18523900	1.51390400	-0.38180300
H	-0.53268800	-0.17575900	1.68729400
H	-0.27276000	1.72532900	-1.35068000
H	0.72650900	1.75700900	-0.05493200
O	2.83555100	0.06784000	0.16776800
H	2.43048900	-0.69374500	-0.21212200
H	3.66860400	-0.21102500	0.50439300

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4) FXO-H₂O complex of stannaformamide, E= -211.5813708 hartree.

O	-0.80321300	-1.13096600	0.79563400
Sn	0.67081000	-0.20649600	-0.12655000
N	0.73604800	1.68437000	0.37176700
H	0.30599300	-0.14528600	-1.80406800
H	0.85795000	1.98651700	1.31045400
H	0.30087500	2.39172300	-0.17615700
O	-3.32859400	0.42727900	-0.24336700
H	-2.87283600	-0.23155100	0.25301300
H	-4.23036000	0.16228200	-0.27624800

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TABLE A1. Optimized geometric parameters^a for formamide and its heavy analogue of group 14 (NH₂XOH, X=C, Si, Ge) at the B3LYP and MP2 levels augmented with 6-311+G(d,p) and cc-pVTZ basis set, the CCSD/aug-cc-pVTZ (for NH₂SnOH with the basis set Lanl2dz, and Lanl2dz(d,p) and aug-cc-pVTZ(N, O and H)+Lanl08d (Sn)).^{a,b}

Species	Level of theory	R_{X-N}	$R_{X=O}$	R_{X-H}	R_{N-H_2}	R_{O-H_1}	R_{O-H_2}	A_{NXO}	A_{H_1NX}	A_{H_2NX}	D_{OHNH_2}
CHONH ₂	B3LYP/6-311+G(d,p)	1.361	1.212	1.106	1.007	2.553	2.034	124.9	119.4	121.4	179.8
	B3LYP/cc-pVTZ	1.357	1.209	1.105	1.004	2.548	2.033	125.0	119.4	121.3	179.7
	MP2/6-311+G(d,p)	1.369	1.216	1.105	1.007	2.537	2.039	124.7	117.4	119.3	165.7
	MP2/cc-pVTZ	1.358	1.215	1.100	1.001	2.546	2.035	124.9	119.2	121.1	179.7
	CCSD/aug-cc-pVTZ	1.357	1.209	1.100	1.001	2.541	2.027	124.7	119.4	121.1	180.0
	Experimental	1.352	1.219	1.105	1.002	2.530	2.041	125.0	118.5	120.8	180.0
SiHONH ₂	B3LYP/6-311+G(d,p)	1.688	1.529	1.477	1.010	3.177	2.678	126.7	123.1	123.4	180.0
	B3LYP/cc-pVTZ	1.686	1.525	1.478	1.007	3.169	2.679	126.7	123.1	123.3	180.0
	MP2/6-311+G(d,p)	1.687	1.534	1.468	1.009	3.197	2.677	127.3	123.5	123.0	179.9
	MP2/cc-pVTZ	1.685	1.533	1.473	1.005	3.188	2.684	127.2	123.3	122.8	179.9
	CCSD/6-311+G(2df,p)	1.683	1.524	1.474	1.005	3.164	2.674	126.6	123.2	123.1	179.9
GeHONH ₂	B3LYP/6-311+G(d,p)	1.797	1.649	1.534	1.009	3.290	2.870	123.9	122.0	123.3	180.0
	B3LYP/cc-pVTZ	1.792	1.640	1.536	1.006	3.278	2.864	123.8	122.0	123.3	180.0
	MP2/6-311+G(d,p)	1.797	1.657	1.530	1.009	3.328	2.871	124.8	122.8	122.7	180.0
	MP2/cc-pVTZ	1.779	1.640	1.519	1.005	3.281	2.845	124.4	122.3	123.2	180.0
	CCSD/aug-cc-pVTZ	1.776	1.634	1.520	1.004	3.252	2.841	123.4	122.2	123.7	180.0
SnHONH ₂	B3LYP/LanL2dz	1.955	1.829	1.716	1.016	3.598	3.232	124.2	123.1	123.8	180.0
	B3LYP/LanL2dz(d,p)	1.965	1.797	1.713	1.017	3.586	3.205	123.8	123.7	124.2	180.0
	MP2/LanL2dz	1.968	1.828	1.713	1.021	3.630	3.209	124.8	123.3	123.5	180.0
	MP2/LanL2dz(d,p)	1.983	1.810	1.715	1.023	3.608	3.203	125.0	120.5	119.7	161.1
	CCSD/aug-cc-pVTZ	1.947	1.782	1.703	1.005	3.568	3.168	124.6	123.5	124.3	180.0
	+LanL08dc										

^a Bond lengths(R) and distance between two atoms(d) are given in Å, bond angles(A) and dihedral angles(D) are in degrees. ^bC-N, Si-N, Ge-N and Sn-N single bond lengths in XH₃-NH₂ (X=C, Si, Ge, Sn) molecules are 1.465, 1.732, 1.854 and 2.020 Å, respectively; C-O, Si-O, Ge-O and Sn-O single bond lengths in XH₃-OH molecules are 1.421, 1.661, 1.792 and 1.947 Å, respectively; C=N, Si=N, Ge=N and Sn=N double bond lengths in XH₂=NH molecules are 1.263, 1.603, 1.711 and 1.882 Å, respectively; C=O, Si=O, Ge=O and Sn=O double bond lengths in XH₂=O molecules are 1.199, 1.526, 1.639 and 1.796 Å, respectively (at B3LYP/cc-pVTZ or /LanL2dz(d,p) level).^cFor the LanL08d basis set, see Reference 37.

Figure A2. The sum of the bond angles around terminal N atom ($\Sigma\alpha$) along the internal rotation PES at a range from -90.0° to 180.0°.

Figure A3. The relative N-X bond length to the single bond (angstrom) along the internal rotation PES at a range from -90.0° to 180.0°.

TABLE A2. The NBO second order perturbation stabilization energies (in kcal/mol) of n- π^* conjugation involving $\pi_{O=X}$ bond and p_N orbital ($\Delta E_{N-OX}(n \rightarrow \pi^*)$), the n- σ^* hyperconjugation involving n_N and σ^*_{X-O} and involving n_N and σ^*_{X-H3} bond at a set of selected dihedral angles (θ) values ranging from -90.0° to 180.0°.

Dihedral Angle(θ)	formamide 1				silaformamide 2				germaformamide 3				stannaformamide 4			
	ΔE_{N-OX}	ΔE_{N-OX}	ΔE_{N-OX}	ΔE_{O-XHB}	ΔE_{N-OX}	ΔE_{N-OX}	ΔE_{N-OX}	ΔE_{O-XHB}	ΔE_{N-OX}	ΔE_{N-OX}	ΔE_{N-OX}	ΔE_{O-XHB}	ΔE_{N-OX}	ΔE_{N-OX}	ΔE_{N-OX}	ΔE_{O-XHB}
	(n- π^*)	(n- π^*)	(n- π^*)	(n- σ^*)	(n- π^*)	(n- π^*)	(n- π^*)	(n- σ^*)	(n- π^*)	(n- π^*)	(n- π^*)	(n- σ^*)	(n- π^*)	(n- π^*)	(n- π^*)	(n- σ^*)
-90	62.57	0.00	0.00	62.57	22.76	0.00	0.00	0.00	22.76	22.92	0.00	0.00	22.92	16.68	0.00	0.00
-105	19.47	6.79	0.00	26.26	15.31	1.50	0.00	0.00	16.81	20.71	0.00	0.00	20.71	16.27	0.00	0.00
-120	11.84	11.15	1.10	24.09	10.57	3.35	0.94	0.83	14.86	12.41	1.24	0.83	14.48	14.86	0.00	0.00
-135	7.86	10.93	1.97	20.76	3.06	9.68	2.15	1.52	14.89	1.03	9.70	1.52	12.25	8.65	1.00	1.53
-150	3.54	10.67	2.75	16.96	1.84	10.59	3.89	2.30	16.32	0.00	8.23	2.30	10.53	4.81	2.29	2.09
-165	0.84	10.40	3.29	14.53	0.00	10.53	4.90	2.76	15.43	0.00	7.15	2.76	9.91	1.41	3.53	2.48
180	0.00	10.25	3.45	13.70	0.00	10.33	5.20	2.95	15.53	0.00	6.72	2.95	9.67	0.00	4.04	2.63

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TABLE A3. The detailed components for NEDA analysis (the electrostatic, polarization, exchange and deformation term) and the PNBO overlap integrals for attractive $n_O-\sigma^*_{H-O}$ ($S_{p-\sigma^*}$) for FXO-H₂O (X=C, Si, Ge and Sn) complex.

species	ΔE_{ES}	ΔE_{POL}	ΔE_{EX}	ΔE_{DEF-NH_2XHO}	ΔE_{DEF-H_2O}	$S_{p-\sigma^*}$
formamide 1	-11.91	-6.32	-2.23	18.09	11.40	0.23
silafornamide 2	-13.99	-6.74	-2.06	21.47	11.01	0.24
germaformamide 3	-15.95	-7.65	-2.36	24.05	13.28	0.29
stannaformamide 4	-23.14	-6.72	2.45	40.53	17.78	0.33

TABLE A4. The detailed components for NEDA analysis (the electrostatic, polarization, exchange and deformation term) and the PNBO overlap integrals for attractive $n_O-\sigma^*_{H-O}$ ($S_{p-\sigma^*}$) for FXH-H₂O (X=C, Si, Ge and Sn) complex.

species	ΔE_{ES}	ΔE_{POL}	ΔE_{EX}	ΔE_{DEF-NH_2XHO}	ΔE_{DEF-H_2O}	$S_{p-\sigma^*}$
formamide 1	-8.57	-4.66	-1.47	4.34	15.40	0.23
silafornamide 2	-8.26	-4.31	-1.40	3.87	14.99	0.23
germaformamide 3	-7.79	-4.19	-1.35	3.72	14.29	0.22
stannaformamide 4	-7.49	2.92	0.87	2.99	15.47	0.20

A6. The geometries of optimized for formamide complexes, $\text{CYH}\text{NH}_2\text{--Z}\text{H}$ at the B3LYP level augmented with the basis set of cc-pVTZ (for $\text{Y}=\text{C}$, Si and Ge) and Lanl2dz(d,p) (for $\text{Y}=\text{Sn}$) and the total energies including the zero-point correction energy.

1) Formamide complex **A1**, $E = -270.419746\text{hartree}$.

O	0.00000000	0.66713200	0.00000000
C	-0.70983100	-0.32818600	0.00000000
N	-2.05229100	-0.29143500	0.00000000
H	-0.29087000	-1.34354200	0.00000000
H	-2.52706200	0.59691700	0.00000000
H	-2.59469200	-1.13643200	0.00000000
H	1.59587300	0.34563200	0.00000000
F	2.49353100	0.02328100	0.00000000

2) Formamide complex **A2**, $E = -593.376018\text{hartree}$.

S	-0.86967600	-0.49802200	0.00000000
C	0.00000000	0.90522900	0.00000000
N	-0.50943800	2.13653800	0.00000000
H	1.08710800	0.88177400	0.00000000
H	-1.50847600	2.27027600	0.00000000
H	0.08482800	2.94800200	0.00000000
H	0.96123700	-1.61255400	0.00000000
F	1.87290900	-1.87847600	0.00000000

3) Formamide complex **A3**, $E = -2596.778627\text{hartree}$.

Se	0.00000000	0.77978300	0.00000000
C	-0.81600300	-0.82567300	0.00000000
N	-2.12750400	-1.03396500	0.00000000
H	-0.22162300	-1.73392900	0.00000000
H	-2.76585400	-0.25347100	0.00000000
H	-2.51150100	-1.96454400	0.00000000
H	1.95617500	-0.40400900	0.00000000
F	2.59237200	-1.10721100	0.00000000

4) Formamide complex **A4**, $E = -203.193832$ hartree.

Te	0.00000000	0.67450100	0.00000000
C	-0.88558700	-1.12629500	0.00000000
N	-2.18818500	-1.37558000	0.00000000
H	-0.26981100	-2.01944000	0.00000000
H	-2.85462000	-0.61867500	0.00000000
H	-2.54636800	-2.31715700	0.00000000
H	2.09588900	-0.70996600	0.00000000
F	2.68952500	-1.44688500	0.00000000

5) Formamide complex **B1**, $E = -246.376358$ hartree.

O	-0.78972000	-0.14839300	0.00000000
C	0.00000000	0.77895000	0.00000000
N	-0.35456800	2.08071900	0.00000000
H	1.08892200	0.62163300	0.00000000
H	-1.32959700	2.33186900	0.00000000
H	0.33835900	2.80723900	0.00000000
O	0.98388800	-2.35401200	0.00000000
H	0.60541900	-3.23661500	0.00000000
H	0.22552700	-1.74361900	0.00000000

6) Formamide complex **B2**, $E = -569.334666$ hartree.

S	-1.06843300	-0.44632600	0.00000000
C	0.00000000	0.80977400	0.00000000
N	-0.31928600	2.10602800	0.00000000
H	1.07217600	0.62575200	0.00000000
H	-1.28720600	2.38648300	0.00000000
H	0.39042200	2.81862300	0.00000000
O	1.98842800	-1.73764500	0.00000000
H	2.23043200	-2.66744800	0.00000000
H	1.01668600	-1.72187500	0.00000000

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7) Formamide complex **B3**, $E = -2572.737675$ hartree.

Se	0.00000000	0.89322300	0.00000000
C	-0.75749100	-0.73957400	0.00000000
N	-2.06279600	-0.99298600	0.00000000
H	-0.13215300	-1.62730500	0.00000000
H	-2.72547300	-0.23321200	0.00000000
H	-2.41426000	-1.93625500	0.00000000
O	2.36197100	-1.61660300	0.00000000
H	3.32069100	-1.55160000	0.00000000
H	2.03994400	-0.70003600	0.00000000

8) Formamide complex **B4**, $E = -179.153488$ hartree.

Te	0.00000000	0.77966700	0.00000000
C	-0.77199300	-1.07276200	0.00000000
N	-2.05903300	-1.39629000	0.00000000
H	-0.10390400	-1.92786700	0.00000000
H	-2.76616000	-0.67733900	0.00000000
H	-2.36193200	-2.35705300	0.00000000
O	2.35205900	-2.02618500	0.00000000
H	3.31146500	-2.08311400	0.00000000
H	2.14925500	-1.07723100	0.00000000

9) Formamide complex **C1**, $E = -226.482693$ hartree.

O	1.01506400	0.08233200	0.00000000
C	0.00000000	0.75185600	0.00000000
N	-0.02351600	2.10527700	0.00000000
H	-1.00150800	0.29489600	0.00000000
H	0.84209800	2.61915100	0.00000000
H	-0.89207600	2.60866200	0.00000000
N	-0.78186600	-2.47842200	0.00000000
H	-0.74915100	-3.08126700	0.81368700
H	0.06695300	-1.91795500	0.00000000
H	-0.74915100	-3.08126700	-0.81368700

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10) Formamide complex **C2**, $E = -549.44236$ hartree.

S	1.25227500	-0.31107100	0.00000000
C	0.00000000	0.76074000	0.00000000
N	0.11338600	2.09267200	0.00000000
H	-1.02918400	0.40455000	0.00000000
H	1.02629600	2.51932100	0.00000000
H	-0.69892900	2.68554500	0.00000000
N	-2.04501600	-1.87699500	0.00000000
H	-2.39050900	-2.37029500	0.81475100
H	-1.03216200	-1.96587000	0.00000000
H	-2.39050900	-2.37029500	-0.81475100

11) Formamide complex **C3**, $E = -2552.845646$ hartree.

Se	0.74387500	-0.65319100	0.00000000
C	0.00000000	0.98529600	0.00000000
N	0.66196600	2.14004500	0.00000000
H	-1.08288500	1.08466800	0.00000000
H	1.67017000	2.14466900	0.00000000
H	0.17681100	3.02200900	0.00000000
N	-3.03978600	-0.38501000	0.00000000
H	-3.59281800	-0.62312900	0.81491100
H	-2.22546800	-0.99361100	0.00000000
H	-3.59281800	-0.62312900	-0.81491100

12) Formamide complex **C4**, $E = -159.26181$ hartree.

Te	0.00000000	0.85572700	0.00000000
C	-0.74769300	-1.00645300	0.00000000
N	-2.03236500	-1.34209600	0.00000000
H	-0.06441800	-1.85207800	0.00000000
H	-2.74587800	-0.62934000	0.00000000
H	-2.32551000	-2.30589700	0.00000000
N	2.27893300	-2.46587000	0.00000000
H	2.79086000	-2.78287400	0.81502100
H	2.31427400	-1.45023700	0.00000000
H	2.79086000	-2.78287400	-0.81502100

Table A5. A comparison of energy in formamide complexes and their dissociation energies calculated at B3LYP/aug-cc-pvtz level.

species	HF-complex(kcal/mol)		H ₂ O-complex(kcal/mol)		NH ₃ -complex(kcal/mol)	
	$\Delta E_{\text{Complex}}$	ΔE_{Diss}	$\Delta E_{\text{Complex}}$	ΔE_{Diss}	$\Delta E_{\text{Complex}}$	ΔE_{Diss}
formamide	-270.48 (-270.02) ^a	-8.66	-246.45 (-246.01)	-3.93	-226.56 (-226.15)	-1.83
S-formamide	-593.43 (-592.61)	-6.66	-569.40 (-568.60)	-3.22	-549.52 (-548.74)	-1.93
Se-formamide	-2596.83 (-2594.99)	-6.38	-2572.80 (-2570.98)	-3.18	-2552.93 (-2551.12)	-2.09
Te-formamide	-203.25 (-202.85)	-5.77	-179.22 (-178.84)	-2.96	-159.34 (-158.98)	-2.07

^a Complex energy at CCSD(T)/aug-cc-pvtz level using B3LYP optimized geometries.

Table A6. Geometric parameters of formamide complexes and of formamide, hydrofluoric acid, water and ammonia monomers at the level of B3LYP/aug-cc-pvtz

Complexes	ΔE_{Diss}	$\Delta r_{\text{N1-H1}}$	$\Delta r_{\text{C-N1}}$	$\Delta r_{\text{C-Y}}$	$\Delta r_{\text{C-H3}}$	$\Delta r_{\text{H4-Z}}$	$r_{\text{Y...H4}}$	$r_{\text{H3...Z}}$	$\angle_{\text{Y...H4-Z}}$	$\angle_{\text{C-H3...Z}}$
A1	-8.66	0.000	-0.014	0.012	-0.006	0.030	1.628	3.102	171.6	86.3
A2	-6.66	0.000	-0.007	0.009	-0.002	0.026	2.143	2.870	164.9	107.1
A3	-6.38	0.000	-0.006	0.008	-0.001	0.024	2.286	2.883	163.3	110.6
A4	-5.77	0.000	-0.005	0.006	0.000	0.022	2.512	3.014	162.3	113.6
B1	-3.93	0.000	-0.008	0.007	-0.004	0.011	1.891	2.978	161.3	96.2
B2	-3.22	0.000	-0.005	0.007	-0.001	0.010	2.444	2.535	149.5	120.9
B3	-3.18	0.000	-0.004	0.007	0.000	0.009	2.588	2.494	147.3	124.9
B4	-2.96	0.000	-0.004	0.006	0.000	0.008	2.840	2.458	142.9	130.3
C1	-1.83	0.000	-0.003	0.005	-0.003	0.004	2.214	2.782	148.8	110.0
C2	-1.93	0.000	-0.003	0.006	0.000	0.004	2.821	2.497	139.1	133.1
C3	-2.09	0.000	-0.003	0.006	0.001	0.004	2.989	2.447	136.7	137.8
C4	-2.07	0.001	-0.003	0.006	0.002	0.003	3.267	2.422	132.9	143.6

Table A7. Hybridization and occupancy in particulars NBOs of formamide complexes at the level of B3LYP/aug-cc-pvtz

Complex	Hybridization of molecular orbitals					Occupancies in molecular orbitals				
	n_{Y1}^a	n_{Y2}^b	n_Z^c	$\sigma^*_{H4-Z}^d$	$\sigma^*_{H3-C}^e$	n_{Y1}	n_{Y2}	n_Z	σ^*_{H4-Z}	σ^*_{H3-C}
A1	$sp^{0.67}$	$sp^{41.50}$	$sp^{99.99}$	$sp^{2.88}$	$sp^{2.11}$	1.971	1.844	1.998	0.055	0.061
A2	$sp^{0.26}$	$sp^{40.11}$	$sp^{99.99}$	$sp^{2.99}$	$sp^{2.28}$	1.986	1.848	1.997	0.065	0.042
A3	$sp^{0.19}$	$sp^{41.27}$	$sp^{99.99}$	$sp^{3.05}$	$sp^{2.22}$	1.989	1.861	1.997	0.062	0.035
A4	$sp^{0.15}$	$sp^{35.43}$	$sp^{99.99}$	$sp^{3.09}$	$sp^{2.25}$	1.990	1.874	1.997	0.058	0.029
B1	$sp^{0.63}$	$sp^{99.99}$	$sp^{0.99}$	$sp^{2.77}$	$sp^{2.12}$	1.980	1.854	1.998	0.022	0.066
B2	$sp^{0.24}$	$sp^{99.99}$	$sp^{0.97}$	$sp^{2.88}$	$sp^{2.27}$	1.988	1.882	1.997	0.021	0.044
B3	$sp^{0.17}$	$sp^{99.99}$	$sp^{0.96}$	$sp^{2.91}$	$sp^{2.20}$	1.990	1.897	1.997	0.020	0.036
B4	$sp^{0.13}$	$sp^{99.99}$	$sp^{0.95}$	$sp^{2.96}$	$sp^{2.21}$	1.991	1.913	1.997	0.015	0.030
C1	$sp^{0.63}$	$sp^{99.99}$	$sp^{3.61}$	$sp^{2.66}$	$sp^{2.11}$	1.984	1.858	1.992	0.007	0.069
C2	$sp^{0.23}$	$sp^{99.99}$	$sp^{3.55}$	$sp^{2.73}$	$sp^{2.23}$	1.989	1.895	1.989	0.006	0.048
C3	$sp^{0.17}$	$sp^{99.99}$	$sp^{3.53}$	$sp^{2.75}$	$sp^{2.15}$	1.990	1.910	1.988	0.005	0.040
C4	$sp^{0.13}$	$sp^{99.99}$	$sp^{3.50}$	$sp^{2.77}$	$sp^{2.15}$	1.991	1.924	1.988	0.004	0.034

^{a,b}Hybridization of n_{Y1} and n_{Y2} orbitals in NH_2CYH where $Y=C, S, Se$ and Te are $sp^{0.64}, sp^{0.23}, sp^{0.16}, sp^{0.12}$ and $p, sp^{99.99}, sp^{99.99}, sp^{99.99}$ respectively. ^{c,d} Hybridization of n_X orbitals in NH_3 is $sp^{3.48}$ and same of σ^*_{H4-Z} in HF, H_2O and NH_3 is $sp^{3.24}, sp^{3.85}$ and $sp^{2.86}$ respectively. ^eHybridization of σ^*_{H3-C} orbitals in NH_2CYH where $Y=C, S, Se$ and Te is $sp^{2.17}, sp^{2.35}, sp^{2.28}, sp^{2.30}$ respectively at B3LYP/cc-pvtz level of theory.

Table A8. NPA analysis of formamide complexes at the level of B3LYP/aug-cc-pvtz

species	HF-complex(kcal/mol)						H ₂ O-complex(kcal/mol)						NH ₃ -complex(kcal/mol)							
	N ₁	C	H ₃	Y	H ₄	F	N ₁	C	H ₃	Y	H ₄	O ₂	H ₅	N ₁	C	H ₃	Y	H ₄	N ₂	H ₅
formamide	-0.77	0.53	0.13	-0.63	0.56	-0.61	-0.78	0.53	0.12	-0.63	0.46	-0.97	0.49	-0.79	0.52	0.12	-0.62	0.38	-1.08	0.35
S-formamide	-0.72	-0.06	0.20	-0.15	0.54	-0.60	-0.73	-0.06	0.20	-0.17	0.48	-0.96	0.46	-0.73	-0.07	0.20	-0.18	0.37	-1.08	0.35
Se-formamide	-0.72	-0.10	0.20	-0.11	0.54	-0.60	-0.72	-0.11	0.20	-0.14	0.48	-0.96	0.47	-0.73	-0.11	0.21	-0.15	0.37	-1.08	0.35
Te-formamide	-0.72	-0.23	0.20	-0.02	0.54	-0.60	-0.72	-0.23	0.20	-0.02	0.48	-0.96	0.47	-0.73	-0.23	0.21	-0.03	0.37	-1.08	0.36

Figure A4. Correlation between $\angle \text{Y} \cdots \text{H}_4\text{Z}$ and $\angle \text{CH}_3 \cdots \text{Z}$ for all formamide complexes

Figure A5. Contribution of energy components (Electrical, Charge transfer and core repulsion term) of NEDA analysis to the interaction energy for formamide complexes.

Figure A6. H-bond formation in Formamide-H₂O complexes (B1-B4) at their triplet (T₁ and T₂) states and singlet state (S₁).

Appendix B

Supplementary Material for theoretical studies on germasilaallenes and their isomers

Figure B1. Detailed bending PESs of (a) 2-germasilaallene **6** and (b) 1-germadisilaallene **8** at the level of B3LYP/6-311+G(d,p). The red solid lines are the bending PES of cyclic isomers of 2-germasilaallene and 1-germadisilaallene forced to cyclic C_{2v} and C_s arrangements and the black dotted lines are bending PES of 2-germasilaallene and 1-germadisilaallene.

Appendix B

B1. The optimized Cartesian coordinates and total energies of the minima and cyclic isomers of germsilaallenes 3-16 at the level of B3LYP/6-311+G(d,p).

1) $\text{GeH}_2=\text{Si}=\text{GeH}_2$, **3**

Minimum, $E=-4445.853269$ hartree, (including the zero-point-correction energy)

Si	0.009135	1.565103	0.000000
Ge	0.009135	-0.279445	1.414188
Ge	0.009135	-0.279445	-1.414188
H	-0.970286	-0.316950	2.613350
H	0.614035	-1.696514	1.284061
H	-0.970286	-0.316950	-2.613350
H	0.614035	-1.696514	-1.284061

2) $\text{GeH}_2=\text{Ge}=\text{SiH}_2$, **4**

Minimum, $E=-4445.871872$ hartree, (including ZPE)

Ge	0.982778	-0.792894	-0.026479
Ge	-1.300907	-0.048743	-0.001217
Si	0.906130	1.545604	0.011857
H	-2.243031	-0.672982	1.057893
H	-2.063152	1.137930	-0.633354
H	1.742514	2.289936	0.997709
H	0.057992	2.539051	-0.701970

3) $\text{GeH}_2=\text{Ge}=\text{SiH}_2$, **5**

Cyclic isomer, $E=-4445.866971$ hartree, (including ZPE)

Ge	-0.833145	-1.167745	0.000000
Si	1.594669	-0.448001	0.000000
Ge	0.000000	1.275916	0.000000
H	-0.215923	2.103026	1.274941
H	-0.215923	2.103026	-1.274941
H	2.383556	-0.697766	1.234389
H	2.383556	-0.697766	-1.234389

4) $\text{SiH}_2=\text{Ge}=\text{SiH}_2$, **6**Minimum, $E=-2658.364127$ hartree, (including ZPE)

Ge	-0.006938	-1.019344	0.000000
Si	-0.006938	0.932645	1.300679
Si	-0.006938	0.932645	-1.300679
H	1.002625	1.057899	2.389846
H	-0.794475	2.194571	1.260661
H	1.002625	1.057899	-2.389846
H	-0.794475	2.194571	-1.260661

5) $\text{SiH}_2=\text{Ge}=\text{SiH}_2$, **7**Cyclic, $E=-2658.363856$ hartree, (including ZPE)

Ge	0.000000	0.000000	1.132129
Si	0.000000	1.165387	-1.082907
Si	0.000000	-1.165387	-1.082907
H	-1.237606	1.886896	-1.476683
H	1.237606	1.886896	-1.476683
H	-1.237606	-1.886896	-1.476683
H	1.237606	-1.886896	-1.476683

6) $\text{SiH}_2=\text{Si}=\text{GeH}_2$, **8**Minimum, $E=-2658.345868$ hartree, (including ZPE)

Si	0.700264	1.378482	-0.064411
Si	1.627216	-0.686339	0.012535
Ge	-1.036589	-0.164240	0.000234
H	2.751678	-0.955011	0.954148
H	1.265490	-1.973570	-0.642044
H	-2.192132	0.070002	1.002373
H	-1.238885	-1.575742	-0.595684

7) $\text{GeH}_2=\text{Si}=\text{CH}_2$, **9**Minimum, $E=-2406.919512$ hartree, (including ZPE)

Si	-0.294017	-1.197242	0.000000
Ge	0.000000	1.108735	0.000000
C	0.634459	-2.633509	0.000000
H	-0.794280	1.661568	1.221561
H	-0.794280	1.661568	-1.221561
H	0.177988	-3.618550	0.000000
H	1.720061	-2.621675	0.000000

8) $\text{GeH}_2=\text{Si}=\text{CH}_2$, **10**Highly bent isomer, $E=-2406.925866$ hartree, (including ZPE)

Si	-1.514423	-0.576088	-0.045965
Ge	0.815538	-0.098077	-0.014652
C	-1.005788	1.168469	0.073873
H	1.627337	0.931782	-0.824358
H	1.535661	-0.324807	1.337178
H	-0.557008	1.801039	-0.691604
H	-1.466556	1.784859	0.847931

9) $\text{GeH}_2=\text{Ge}=\text{CH}_2$, **11**Minimum, $E=-4194.429881$ hartree, (including ZPE)

Ge	0.000000	0.945818	0.000000
Ge	0.260734	-1.420000	0.000000
C	-1.241808	2.226918	0.000000
H	1.189400	-1.727134	1.217166
H	1.189400	-1.727134	-1.217166
H	-0.971476	3.277149	0.000000
H	-2.299948	1.989422	0.000000

10) $\text{GeH}_2=\text{Ge}=\text{CH}_2$, **12**Cyclic isomer, $E=-4194.447155$ hartree, (including ZPE)

Ge	0.380486	-1.264033	0.000000
Ge	0.000000	1.196773	0.000000
C	-1.381215	-0.206444	0.000000
H	0.044608	2.036454	1.281851
H	0.044608	2.036454	-1.281851
H	-1.988745	-0.340950	0.895421
H	-1.988745	-0.340950	-0.895421

11) $\text{SiH}_2=\text{Ge}=\text{CH}_2$, **13**Minimum, $E=-2406.918613$ hartree, (including ZPE)

Ge	0.000000	0.472005	0.000000
Si	0.662359	-1.726933	0.000000
C	-1.434152	1.530877	0.000000
H	1.553949	-1.921522	1.187148
H	1.553949	-1.921522	-1.187148
H	-1.337781	2.609760	0.000000
H	-2.438229	1.120914	0.000000

12) $\text{SiH}_2=\text{Ge}=\text{CH}_2$, **14**Cyclic isomer, $E=-2406.954133$ hartree, (including ZPE)

Ge	0.000000	0.949430	0.000000
Si	0.598437	-1.411578	0.000000
C	-1.154378	-0.776056	0.000000
H	1.046235	-2.098883	1.236007
H	1.046235	-2.098883	-1.236007
H	-1.772160	-0.882782	0.892898
H	-1.772160	-0.882782	-0.892898

13) $\text{SiH}_2=\text{Ge}=\text{SiH}_2$, **15**Minimum, $E=-619.409018$ hartree, (including ZPE)

Si	0.000000	0.696869	0.000000
Si	0.657970	-1.450964	0.000000
C	-1.414501	1.659349	0.000000
H	1.530061	-1.683878	1.192397
H	1.530061	-1.683878	-1.192397
H	-1.375656	2.743846	0.000000
H	-2.409040	1.225141	0.000000

14) $\text{SiH}_2=\text{Si}=\text{CH}_2$, **16**Cyclic isomer, $E=-619.432219$ hartree, (including ZPE)

Si	0.711533	-1.130863	0.000000
Si	0.000000	1.119088	0.000000
C	-1.093460	-0.403766	0.000000
H	-0.016491	1.931724	1.239293
H	-0.016491	1.931724	-1.239293
H	-1.683863	-0.638003	0.889161
H	-1.683863	-0.638003	-0.889161

B2. TS of germasilaallenes (3-16) at the B3LYP/6-311+G(d,p) level and the total energies (including the zero-point-correction energy)

1) $\text{GeH}_2=\text{Ge}=\text{SiH}_2$, **TS (4-5)** $E=-4445.867027$ hartree, (including ZPE)

Ge	-1.343336	-0.419967	0.014757
Ge	1.206030	-0.408914	-0.008967
Si	0.016768	1.654979	-0.030692
H	1.853824	-1.145595	-1.191547
H	2.098861	-0.450056	1.238863
H	-0.139345	2.686937	-1.088888
H	0.345727	2.263204	1.285974

2) $\text{SiH}_2=\text{Ge}=\text{SiH}_2$, TS (6-7) $E=-2658.362594$ hartree, (including ZPE)

Ge	-1.108522	-0.000004	0.019479
Si	1.042421	-1.181411	-0.028406
Si	1.042413	1.181416	-0.028410
H	1.298120	-2.178164	-1.100736
H	1.844458	-1.478579	1.186758
H	1.298077	2.178207	-1.100713
H	1.844388	1.478601	1.186791

3) $\text{GeH}_2=\text{Si}=\text{CH}_2$, TS (9-10) $E=-2406.912548$ hartree, (including ZPE)

Si	-1.249734	-0.754540	-0.000780
Ge	0.985115	0.083412	-0.040017
C	-2.085631	0.799314	0.014795
H	2.042341	-0.906269	0.539637
H	1.310460	1.419337	0.699915
H	-3.030726	0.913494	0.547309
H	-1.835703	1.671931	-0.584180

4) $\text{GeH}_2=\text{Ge}=\text{CH}_2$, TS (11-12) $E=-4194.425132$ hartree, (including ZPE)

Ge	-1.030990	-0.458944	0.003121
Ge	1.355197	0.107148	-0.040205
C	-1.743811	1.247870	0.010873
H	2.288142	-1.060136	0.412601
H	1.884963	1.307973	0.808153
H	-2.704655	1.441863	0.486433
H	-1.380212	2.080574	-0.585758

5) $\text{SiH}_2=\text{Ge}=\text{CH}_2$, TS (13-14) $E=-2406.912913$ hartree, (including ZPE)

Ge	-0.545636	-0.462915	0.000332
Si	1.718664	0.247900	-0.070535
C	-1.351916	1.208276	0.011754
H	2.714145	-0.794412	0.336740
H	2.161145	1.480030	0.660616
H	-2.311155	1.350982	0.508307
H	-1.053586	2.056424	-0.599308

6) $\text{SiH}_2=\text{Si}=\text{CH}_2$, TS (15-16) $E=-619.400796$ hartree, (including ZPE)

Si	-0.711662	-0.752711	-0.006756
Si	1.395135	0.187674	-0.069297
C	-1.620855	0.766303	0.015103
H	2.489831	-0.694763	0.442827
H	1.654519	1.521976	0.561042
H	-2.559096	0.840336	0.566421
H	-1.428740	1.645150	-0.596166

B3. The optimized Cartesian coordinates and total energies of
 $\text{H}(\text{PMe}_2\text{S})\text{M}_1=\text{M}_2=\text{M}_3\text{H}(\text{PMe}_2\text{S})$ (17-20) at the level of B3LYP/6-311+G(d,p).

1) $\text{H}(\text{PMe}_2\text{S})\text{Ge}=\text{Si}=\text{GeH}(\text{PMe}_2\text{S})$, 17

Minimum, $E=-6083.571396$ hartree, (including the zero-point-correction energy)

S	1.653883	-0.827476	-0.942167
S	-1.653883	0.827476	-0.942167
P	-0.801790	2.727712	-0.600988
P	0.801790	-2.727712	-0.600988
C	0.000000	3.287311	-2.158954
H	0.441326	4.274590	-1.999506
H	0.791769	2.585087	-2.419126
H	-0.727094	3.335752	-2.972910
C	-2.199303	3.904131	-0.391155
H	-1.799115	4.910919	-0.245322
H	-2.854489	3.895683	-1.265020
H	-2.771533	3.621612	0.492784
C	0.000000	-3.287311	-2.158954
H	-0.441326	-4.274590	-1.999506
H	-0.791769	-2.585087	-2.419126
H	0.727094	-3.335752	-2.972910
C	2.199303	-3.904131	-0.391155
H	2.771533	-3.621612	0.492784
H	1.799115	-4.910919	-0.245322
H	2.854489	-3.895683	-1.265020
Ge	0.567189	2.229242	1.393014
H	-1.877076	-2.396877	0.503575
H	1.877076	2.396877	0.503575
Ge	-0.567189	-2.229242	1.393014
Si	0.000000	0.000000	0.388460

2) $\text{H(PMe}_2\text{S)Ge=Ge=SiH(PMe}_2\text{S)}$, **18**Minimum, $E=-6083.565972$ hartree, (including ZPE)

S	1.539313	0.094493	1.557919
S	-0.907593	1.455225	-1.060459
P	-2.552954	0.785437	0.059814
P	3.049021	0.297649	0.114782
C	-2.709686	1.839318	1.558992
H	-3.571507	1.507918	2.143997
H	-1.809108	1.729763	2.162956
H	-2.834416	2.887876	1.278745
C	-4.064921	1.187942	-0.906396
H	-4.947587	0.884896	-0.337136
H	-4.117550	2.258163	-1.118215
H	-4.044217	0.635493	-1.846144
C	3.313082	2.087106	-0.217850
H	4.092001	2.202136	-0.975948
H	2.385361	2.518616	-0.593286
H	3.609501	2.604233	0.697722
C	4.628586	-0.229886	0.891367
H	4.554974	-1.282617	1.164972
H	5.442402	-0.107421	0.171827
H	4.837910	0.363784	1.783719
Ge	-2.069552	-1.622868	0.335608
Ge	0.190417	-0.565054	-0.326379
Si	2.260770	-1.089141	-1.619259
H	2.148442	0.084404	-2.581145
H	-1.815564	-1.374434	1.887254

3) $\text{H}(\text{PMe}_2\text{S})\text{Si}=\text{Ge}=\text{SiH}(\text{PMe}_2\text{S}), \mathbf{19}$ Minimum, $E=-4296.046157$ hartree, (including ZPE)

S	1.431230	-1.285242	-0.668290
S	-1.431230	1.285242	-0.668290
P	0.000000	2.789522	-0.367947
P	0.000000	-2.789522	-0.367947
C	1.022592	2.947182	-1.887951
H	1.777902	3.722549	-1.736391
H	1.521933	1.997175	-2.077881
H	0.395086	3.205094	-2.744186
C	-0.893949	4.391991	-0.281557
H	-0.170537	5.201969	-0.156702
H	-1.476841	4.559848	-1.189631
H	-1.561331	4.379131	0.580434
C	-1.022592	-2.947182	-1.887951
H	-1.777902	-3.722549	-1.736391
H	-1.521933	-1.997175	-2.077881
H	-0.395086	-3.205094	-2.744186
C	0.893949	-4.391991	-0.281557
H	1.561331	-4.379131	0.580434
H	0.170537	-5.201969	-0.156702
H	1.476841	-4.559848	-1.189631
H	-2.368333	-1.905199	0.944229
H	2.368333	1.905199	0.944229
Si	-1.029903	-2.102891	1.640005
Si	1.029903	2.102891	1.640005
Ge	0.000000	0.000000	0.790559

4) $\text{H(PMe}_2\text{S)Si=Si=GeH(PMe}_2\text{S)}$, **20**Minimum, $E=-4296.052373$ hartree, (including ZPE)

S	0.876302	1.441648	0.957245
S	-1.510589	0.007436	-1.482415
P	-3.044337	0.217165	-0.052431
P	2.550775	0.673437	-0.072319
C	-3.398352	2.008134	0.167362
H	-4.178159	2.129053	0.923709
H	-2.492203	2.506284	0.511540
H	-3.725497	2.455418	-0.774019
C	-4.585496	-0.439927	-0.805341
H	-5.406379	-0.326651	-0.092289
H	-4.828633	0.090349	-1.728546
H	-4.449420	-1.500263	-1.018963
C	2.789896	1.664049	-1.603483
H	3.657493	1.279735	-2.146138
H	1.906166	1.559045	-2.232528
H	2.943481	2.718421	-1.362333
C	4.028882	1.084581	0.940765
H	3.951209	0.579088	1.903631
H	4.924500	0.726863	0.426027
H	4.107517	2.161964	1.102160
H	1.710931	-1.542086	-1.783935
H	-2.048443	0.190995	2.619231
Si	-2.107621	-1.026549	1.709303
Si	-0.204968	-0.464222	0.327129
Ge	1.901442	-1.706338	-0.211858

Appendix B

Table B1. NPA occupancies of p orbitals, perpendicular to their ring planes, at M¹, M² and M³ (M=Si and Ge) and NBO second order perturbation stabilization energy (at kcal/mol) of p(terminal)→p(central) donor-acceptor effect for highly-bend isomers of 1,3-digermasilaallene **3**, 1,2-digermasilaallene **4**, 2-germadisilaallene **6**, 1-germadisilaalle **8**, silaallene **9** and germaallene **10**.

H ₂ Ge=Si=GeH ₂ , 3	p _{M1} Occ.	p _{M2} Occ	p _{M3} Occ	H ₂ Ge=Ge=SiH ₂ , 4	p _{M1} Occ.	p _{M2} Occ	p _{M3} Occ
	0.71	0.59	0.71		0.73	0.52	0.73
	ΔE p _{M1} →p _{M2}	ΔE p _{M3} →p _{M2}			ΔE p _{M1} →p _{M2}	ΔE p _{M3} →p _{M2}	
	203.49	203.49			133.83	138.46	
H ₂ Si=Ge=SiH ₂ , 6	p _{M1} Occ.	p _{M2} Occ	p _{M3} Occ	H ₂ Si=Si=GeH ₂ , 8	p _{M1} Occ.	p _{M2} Occ	p _{M3} Occ
	0.78	0.45	0.78		0.75	0.54	0.72
	ΔE p _{M1} →p _{M2}	ΔE p _{M3} →p _{M2}			ΔE p _{M1} →p _{M2}	ΔE p _{M3} →p _{M2}	
	112.77	112.77			167.99	160.22	
H ₂ Si=Si=SiH ₂ , 9	p _{M1} Occ.	p _{M2} Occ	p _{M3} Occ	H ₂ Ge=Ge=GeH ₂ , 10	p _{M1} Occ.	p _{M2} Occ	p _{M3} Occ
	0.76	0.49	0.76		0.71	0.58	0.71
	ΔE p _{M1} →p _{M2}	ΔE p _{M3} →p _{M2}			ΔE p _{M1} →p _{M2}	ΔE p _{M3} →p _{M2}	
	124.00	124.00			209.04	209.04	

Table B2. NPA occupancies of M¹, M² and M³ (M=Si and Ge) at (PMe₂S)Ge=Si=Ge(PMe₂S)H, H(PMe₂S)Ge=Ge=Si(PMe₂S)H,H(PMe₂S)Si=Ge=Si(PMe₂S)H and H(PMe₂S)Si=Si=Ge(PMe₂S)H.

HRGe=Si=GeRH	M ₁ Occ.	M ₂ Occ	M ₃ Occ	HRGe=Ge=SiRH	M ₁ Occ.	M ₂ Occ	M ₃ Occ
	0.03	0.25	0.03		0.07	0.27	0.04
HRSi=Ge=SiRH	M ₁ Occ.	M ₂ Occ	M ₃ Occ	HRGe=Si=SiRH	M ₁ Occ.	M ₂ Occ	M ₃ Occ
	0.05	0.28	0.05		0.01	0.26	0.03

Figure B2. The Bending PESs of four dimetalallenes at the B3LYP/6-311+G(d,p)level.8.

Figure B3. The optimized $\text{H(PMe}_2\text{S)Ge=Si=Ge(PMe}_2\text{S)H}$, $\text{H(PMe}_2\text{S)Ge=Ge=Si(PMe}_2\text{S)H}$, $\text{H(PMe}_2\text{S)Si=Ge=Si(PMe}_2\text{S)H}$ and $\text{H(PMe}_2\text{S)Si=Si=Ge(PMe}_2\text{S)H}$ at the B3LYP/6-311+G(d,p)level.

Appendix C

Supplementary Material for DFT Study and Molecular Design of Low Band Gap Oligomers

Figure C1. Molecular design of donor acceptor oligomers

Table C1. Simulated absorption spectra of substituted monomers at TD-B3LYP/6-31g(d,p)level.

Monomers	Electronic Transition	E _{ex} (eV)	λ (nm)	Oscillator strength, <i>f</i>	Main transition configuration and their contribution			
BBTa26/X1	S ₀ → S ₁	2.96	418	0.3132	HOMO	→	LUMO;	0.99
BBT16/X1	S ₀ → S ₁	3.29	376	0.3067	HOMO	→	LUMO;	0.98
SBTa/X1	S ₀ → S ₁	2.48	499	0.1876	HOMO	→	LUMO;	0.99
SeBTa/X1	S ₀ → S ₁	2.28	544	0.1502	HOMO	→	LUMO;	0.99
TaQ1/X1	S ₀ → S ₁	2.57	481	0.3293	HOMO	→	LUMO;	0.99
TaQ2/X1	S ₀ → S ₁	2.27	545	0.3681	HOMO	→	LUMO;	0.98
BBTa26/X2	S ₀ → S ₁	2.55	485	0.4237	HOMO	→	LUMO;	1.00
BBT16/X2	S ₀ → S ₁	2.79	443	0.4689	HOMO	→	LUMO;	0.99
SBTa/X2	S ₀ → S ₁	2.07	598	0.2477	HOMO	→	LUMO;	0.99
SeBTa/X2	S ₀ → S ₁	1.87	662	0.1944	HOMO	→	LUMO;	1.00
TaQ1/X2	S ₀ → S ₁	2.33	531	0.1186	HOMO	→	LUMO;	0.97
TaQ2/X2	S ₀ → S ₁	2.15	576	0.0217	HOMO	→	LUMO;	0.98
BBTa26/X3	S ₀ → S ₁	2.16	573	0.2727	HOMO	→	LUMO;	0.98
BBT16/X3	S ₀ → S ₁	2.60	477	0.2107	HOMO	→	LUMO;	0.96
SBTa/X3	S ₀ → S ₁	1.41	877	0.1567	HOMO	→	LUMO;	1.00
SeBTa/X3	S ₀ → S ₁	1.22	1080	0.1217	HOMO	→	LUMO;	1.00
TaQ1/X3	S ₀ → S ₁	1.79	692	0.1181	HOMO	→	LUMO;	0.99
TaQ2/X3	S ₀ → S ₁	1.82	680	0.0603	HOMO	→	LUMO;	0.99
BBTa26/X4	S ₀ → S ₁	1.18	1050	0.2062	HOMO	→	LUMO;	1.00
BBT16/X4	S ₀ → S ₁	2.68	462	0.1913	HOMO	→	LUMO;	0.93
SBTa/X4	S ₀ → S ₁	0.61	3113	0.0234	HOMO	→	LUMO;	1.00
SeBTa/X4	S ₀ → S ₁	0.40	3113	0.0234	HOMO	→	LUMO;	1.00
TaQ1/X4	S ₀ → S ₁	1.96	633	0.0518	HOMO	→	LUMO;	0.96
TaQ2/X4	S ₀ → S ₁	1.83	678	0.0253	HOMO	→	LUMO;	0.97

Table C2. Simulated absorption spectra of DA oligomers at TD-B3LYP/6-31g(d,p)level.

DA oligomers	Electronic Transition	E _{ex} (eV)	λ (nm)	Oscillator strength, <i>f</i>	Main transition configuration and their contribution		
Y1-BBTa26	S ₀ → S ₁	1.89	656	1.0653	HOMO	→ LUMO;	1.00
Y1-BBT16	S ₀ → S ₁	2.15	577	1.1764	HOMO	→ LUMO;	1.00
Y1-SBTa	S ₀ → S ₁	1.46	848	0.6280	HOMO	→ LUMO;	1.00
	S ₀ → S ₃	2.70	459	0.9407	HOMO	→ LUMO+1;	0.93
Y1-SeBTa	S ₀ → S ₁	1.33	935	0.5166	HOMO	→ LUMO;	1.00
	S ₀ → S ₃	2.63	471	1.0142	HOMO	→ LUMO+1;	0.93
Y1-TaQ1	S ₀ → S ₁	1.65	752	0.5740	HOMO	→ LUMO;	0.99
	S ₀ → S ₆	2.94	421	0.4058	HOMO	→ LUMO+2;	0.89
Y1-TaQ2	S ₀ → S ₁	1.56	796	0.4009	HOMO	→ LUMO;	0.99
	S ₀ → S ₆	2.68	463	0.9342	HOMO	→ LUMO+2;	0.76
Y2-BBTa26	S ₀ → S ₁	1.88	658	1.0257	HOMO	→ LUMO;	1.00
Y2-BBT16	S ₀ → S ₁	2.15	577	1.1281	HOMO	→ LUMO;	1.00
Y2-SBTa	S ₀ → S ₁	1.45	853	0.6199	HOMO	→ LUMO;	1.00
	S ₀ → S ₄	2.81	441	1.0428	HOMO	→ LUMO+1;	0.93
Y2-SeBTa	S ₀ → S ₁	1.32	941	0.5119	HOMO	→ LUMO;	1.00
	S ₀ → S ₄	2.73	453	1.0894	HOMO	→ LUMO+1;	0.94
Y2-TaQ1	S ₀ → S ₁	1.63	759	0.5570	HOMO	→ LUMO;	0.99
	S ₀ → S ₇	2.94	421	0.6581	HOMO	→ LUMO+2;	0.84
Y2-TaQ2	S ₀ → S ₁	1.53	810	0.3860	HOMO	→ LUMO;	0.99
	S ₀ → S ₇	2.71	457	0.8230	HOMO	→ LUMO+2;	0.73
Y3-BBTa26	S ₀ → S ₁	1.91	648	1.0940	HOMO	→ LUMO;	1.00
Y3-BBT16	S ₀ → S ₁	2.18	569	1.2116	HOMO	→ LUMO;	1.00
Y3-SBTa	S ₀ → S ₁	1.48	837	0.6278	HOMO	→ LUMO;	1.00
	S ₀ → S ₃	2.62	472	0.7725	HOMO	→ LUMO+1;	0.92
Y3-SeBTa	S ₀ → S ₁	1.34	924	0.5134	HOMO	→ LUMO;	1.02
	S ₀ → S ₃	2.56	485	0.8550	HOMO	→ LUMO+1;	0.93
Y3-TaQ1	S ₀ → S ₁	1.67	742	0.5825	HOMO	→ LUMO;	0.99
	S ₀ → S ₄	2.67	463	0.4269	HOMO	→ LUMO+1;	0.69
Y3-TaQ2	S ₀ → S ₁	1.58	786	0.4024	HOMO	→ LUMO;	0.99
	S ₀ → S ₆	2.64	470	0.9059	HOMO	→ LUMO+2;	0.70
Y4-BBTa26	S ₀ → S ₁	1.97	628	1.1800	HOMO	→ LUMO;	1.00
Y4-BBT16	S ₀ → S ₁	2.27	546	1.2993	HOMO	→ LUMO;	1.00
Y4-SBTa	S ₀ → S ₁	1.55	798	0.6315	HOMO	→ LUMO;	1.00
	S ₀ → S ₃	2.56	484	0.6144	HOMO	→ LUMO+1;	0.81
Y4-SeBTa	S ₀ → S ₁	1.40	885	0.5010	HOMO	→ LUMO;	1.00
	S ₀ → S ₃	2.49	498	0.7246	HOMO	→ LUMO+1;	0.87
Y4-TaQ1	S ₀ → S ₁	1.79	693	0.5851	HOMO	→ LUMO;	0.99
	S ₀ → S ₄	2.63	471	0.3337	HOMO-3	→ LUMO;	0.47
Y4-TaQ2	S ₀ → S ₁	1.70	728	0.3824	HOMO	→ LUMO;	0.98
	S ₀ → S ₆	2.66	466	0.3569	HOMO-3	→ LUMO;	0.45

Table C3. Bridge bond length (*r* in Å), torsion angles (Φ in deg) along the conjugated backbones of 2DA oligomers and their frontier orbitals determined at B3LYP/6-31g(d,p) level of theory.

2DA (n=1)	<i>r</i> _{b1} (Å)	<i>r</i> _{b2} (Å)	<i>r</i> _{b3} (Å)	Φ_1 (deg)	Φ_2 (deg)	Φ_3 (deg)	Φ_4 (deg) ^a	HOMO (eV)	LUMO (eV)
2Y4-BBTa26	1.447	1.442	1.439	0.0	0.1	10.4	10.6	-2.78	-4.75
2Y4-SeBTa	1.446	1.440	1.438	0.1	0.1	3.2	11.0	-3.30	-4.79
2Y4-TaQ2	1.453	1.449	1.440	8.3	3.1	15.3	12.0	-2.83	-4.72

^aTorsion angles between two attached donor groups.

Table C4. Bridge bond length (*r* in Å) and torsion angles (Φ in deg) along the conjugated backbones of DA oligomers optimized at B3LYP/6-31g(d,p) level of theory.

DA oligomers	Y1						Y2					
	<i>r</i> _{b1}	<i>r</i> _{b2}	<i>r</i> _{b3}	Φ_1	Φ_2	Φ_3	<i>r</i> _{b1}	<i>r</i> _{b2}	<i>r</i> _{b3}	Φ_1	Φ_2	Φ_3
BBTa26	1.447	1.441	1.439	0.0	0.0	0.0	1.447	1.441	1.439	0.0	0.0	0.0
BBTa16	1.466	1.443	1.440	55.1	0.1	1.4	1.466	1.443	1.440	55.2	0.0	3.0
SBTa	1.447	1.439	1.437	0.0	0.0	0.0	1.447	1.439	1.437	0.0	0.0	0.0
SeBTa	1.447	1.438	1.436	0.0	0.0	0.0	1.447	1.438	1.437	0.0	0.0	0.0
TaQ1	1.454	1.447	1.439	4.8	4.5	9.2	1.454	1.447	1.439	5.0	4.0	10.3
TaQ2	1.454	1.447	1.439	6.7	2.7	10.1	1.454	1.447	1.439	5.8	1.2	9.8
	Y3						Y4					
	<i>r</i> _{b1}	<i>r</i> _{b2}	<i>r</i> _{b3}	Φ_1	Φ_2	Φ_3	<i>r</i> _{b1}	<i>r</i> _{b2}	<i>r</i> _{b3}	Φ_1	Φ_2	Φ_3
BBTa26	1.447	1.442	1.440	0.0	0.0	0.0	1.447	1.442	1.440	0.1	0.5	3.3
BBTa16	1.466	1.444	1.441	55.1	0.1	1.4	1.466	1.446	1.442	54.9	0.1	11.5
SBTa	1.447	1.440	1.438	0.0	0.0	0.0	1.446	1.441	1.440	0.2	0.1	3.1
SeBTa	1.447	1.439	1.438	0.0	0.0	0.0	1.446	1.441	1.439	0.2	0.2	0.3
TaQ1	1.454	1.448	1.440	4.7	4.3	5.8	1.454	1.450	1.442	4.8	6.3	19.8
TaQ2	1.454	1.447	1.440	7.1	2.3	6.3	1.453	1.450	1.441	7.6	2.6	16.4

Appendix C

Table C5. Bridge bond length (*r* in Å) and torsion angles (Φ in deg) along the conjugated backbones of DA oligomers optimized at TD-B3LYP/6-31g(d,p) level of theory.

DA oligomers	Y1						Y2					
	<i>r</i> _{b1}	<i>r</i> _{b2}	<i>r</i> _{b3}	Φ_1	Φ_2	Φ_3	<i>r</i> _{b1}	<i>r</i> _{b2}	<i>r</i> _{b3}	Φ_1	Φ_2	Φ_3
BBTa26	1.433	1.428	1.422	0.0	0.0	0.0	1.433	1.430	1.424	0.0	0.0	0.0
BBTa16	1.448	1.434	1.421	38.0	0.7	0.2	1.449	1.438	1.424	37.9	0.7	0.1
SBTa	1.431	1.431	1.427	0.0	0.0	0.0	1.431	1.432	1.429	0.0	0.0	0.0
SeBTa	1.430	1.427	1.427	0.0	0.0	0.0	1.430	1.428	1.429	0.0	0.0	0.0
TaQ1	1.439	1.439	1.424	2.2	2.6	1.7	1.440	1.441	1.426	2.2	3.1	4.0
TaQ2	1.440	1.434	1.423	0.2	0.4	1.5	1.440	1.436	1.425	0.0	0.6	2.6
	Y3						Y4					
	<i>r</i> _{b1}	<i>r</i> _{b2}	<i>r</i> _{b3}	Φ_1	Φ_2	Φ_3	<i>r</i> _{b1}	<i>r</i> _{b2}	<i>r</i> _{b3}	Φ_1	Φ_2	Φ_3
BBTa26	1.433	1.427	1.422	0.0	0.0	0.0	1.431	1.420	1.419	0.1	0.2	0.1
BBTa16	1.448	1.432	1.420	37.8	0.7	0.1	1.446	1.421	1.415	36.9	0.9	1.5
SBTa	1.431	1.430	1.428	0.0	0.0	0.0	1.429	1.425	1.426	0.1	0.1	1.8
SeBTa	1.429	1.427	1.428	0.0	0.0	0.0	1.429	1.424	1.428	0.0	0.0	1.4
TaQ1	1.439	1.437	1.424	2.3	3.0	3.7	1.437	1.430	1.423	1.9	3.2	8.9
TaQ2	1.439	1.433	1.424	0.1	0.8	2.0	1.423	1.425	1.423	0.1	0.5	2.8

Figure C1. HOMO (left hand side), HOMO-1 (middle) and LUMO (right-hand side) orbitals of isolated donor units (Y1-Y4).

Figure C2. LUMO+1 frontier orbital for Y-XBTa (Y= Y1, Y2, Y3, Y4; X=S, Se) oligomers

Figure C3. The correlation between the HOMO-LUMO gap (eV) and inverse number of repeat units calculated at the B3LYP/6-31g(d,p) level of theory.

List of Publications

Journal Publications

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