Quantum Chemical Studies of 6-Vertex *hypercloso*-Heteroboranes

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MASTER THESIS WORK

We hereby recommend that the dissertation prepared under our supervision by: Aslam Hayat, NUST201464697MRCMS64015STitled: Quantum Chemical Studies of 6-Vertex *hypercloso*-Heteroboranes be accepted in partial fulfillment of the requirements for the award of MS Computational Science and Engineering degree with (____________Grade).

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Declaration

I hereby declare that this thesis report entitled **"Quantum Chemicals Studies of 6-Vertex *hypercloso*-Heteroboranes"** written and submitted by me in partial fulfillment of the requirement for the degree of master of Science in computational science and engineering is my original research work. It is not plagiarized and the conclusion drawn is truly validated by me. I really acknowledge the efforts, the contributions, suggestions of my supervisor, my colleagues, my GEC members and previously published literature which is duly referenced.

I further declare that this work is submitted here first time. This is not submitted before to any other university for the award of any other degree or course.

Aslam Hayat

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Dedicated to my parents

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I would like to thank my supervisor Dr. Farooq Ahmad Kiani (Associate Professor RCMS) whose office was always open whenever I needed help or reported any question about my research project/thesis writing. He always encouraged me in this project.

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Thank you all,

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ABSTRACT

Boron hydride clusters have always fascinated chemists because of their electron-deficient chemistry, aesthetically pleasing three dimensional cluster shapes and because of numerous applications. Boron hydride clusters have several cluster types i.e. *hypercloso*-, *closo*- *nido*-, *arachno*- and *hypho*- clusters. There has been recent interest in determining the structure of the thermodynamically most stable 6-vertex-*hypercloso*-carboranes. In this thesis computational quantum mechanical studies have been extended to 6-vertex *hypercloso*-$X_2B_4H_4$ (X = C, Si, Ge) clusters. The computations are carried out using DFT for these *hypercloso*-heteroboranes of carbon, silicon and germanium at the B3LYP/LANL2DZ+ZPE level of theory. A large number $X_2B_4H_4$ (X = C, Si, Ge) isomers were optimized. The optimization results of *hypercloso* silaboranes ($Si_2B_4H_4$) and germaboranes ($Ge_2B_4H_4$) indicate that unlike carboranes ($C_2B_4H_4$), the thermodynamically most stable sila- and germaborane structures constitute themselves in cluster shape (and not planar form). The reason behind this structural transition in the cluster shape upon heteroatom replacement is the degree of electron-localization (electronegativity) of the heteroatom. When less electronegative silicon and germanium atoms are placed in the 6-vertex *hypercloso*-heteroborane structures, the thermodynamically most stable structure adapts cluster shape. This is because more electronegative carbon heteroatom has strong destabilizing effect on the cluster shape in the electron deficient environment of *hypercloso*-$C_2B_4H_4$ cluster, whereas less electronegativity of silicon and germanium atoms can be tolerated in the *hypercloso*-cluster. The results are completely consistent with previous work on 12-vertex *closo*-heteroboranes.

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Introduction

1 Introduction

Boron chemistry and the compounds of boron are well known from ancient time for their use in hard glass materials and glazes.[1] Boron is not an abundant element. It occurs in traces in most of the soil and is essential in very small amount for growth of plants.

Boron hydrides clusters are important compounds in inorganic chemistry, which fascinated chemists due to their cluster shapes, bonding behavior and their broad range of applications. Boron hydride clusters are polyhedral or deltahedral clusters. They have three-dimensional cage-like-structures. There are some other non-cluster inorganic compounds of boron like polyboric acids, sodium borates, sodium tetraborates and metaborates. Polyboric acids for instance, have many applications in cosmetic, soap, textile, paints and medicines.

The boron hydride clusters exist in gas phase as individual species. Boron hydrides clusters show catenation like carbon. The shapes of cluster also define the aromatic behavior of borane clusters as delocalization of electrons cloud in the cluster. These boron hydrides compounds are called boranes. Boranes are the compounds containing boron and hydrogen and are neutral or anionic species.

There is much utilization of boron hydrides clusters, for instance, they are utilized as hard materials like heat-resistant glasses, tennis rackets, p-type semiconductor, and drug-delivery tools and antitumor agents.[2]

Boron is a p-block element having one 2s orbital and three valence 2p-orbitals. There is only one electron in p-orbital. The element boron has some similarity with carbon. Both carbon and boron have partially filled p-orbitals. Both carbon and boron form hydrides compounds. But the hydrides cluster chemistry of boron is very interesting and versatile.[3]

In 1912, the neutral boron hydride compounds such as like B_2H_6, B_4H_{10}, B_5H_9 were identified by Alfred Stock.[4] These compounds have different physicals and chemicals properties. Some compounds are volatile in nature and some are solid like $B_{10}H_{14}$ and other are gases. Initially chemical bonding in boron hydride cluster was not clear and it was difficult to explain the bonding in boron hydrides cluster according to traditional valence bond theory. For several decades, these compounds were not well understood and were studied in academic point of view. But in 1940 and onward, the boron hydride chemistry has created special interest. This was partially because of their potential use as rocket fuel in comparison with hydrocarbons. Groups of scientist worked on boron hydride chemistry and investigated many clusters of boranes and their derivative. Millions of dollars were spent to investigate the boron hydride clusters for fuel effectiveness by United State and Soviet Union.

Boron hydride clusters form multicenter bonding. For example, the 3c-2e bonds formed between bridging hydrogen and two boron atoms is shown in Figure 1.1. This type of bridging in boron hydrides molecules was first time investigated by Dilthy in 1921.[5] This concept of 3centre-2electron (3c-2e) is given by W.N Lipcomb (Harvard Univ.) which led to his being awarded the Nobel Prize in Chemistry in 1976.[6a-b]

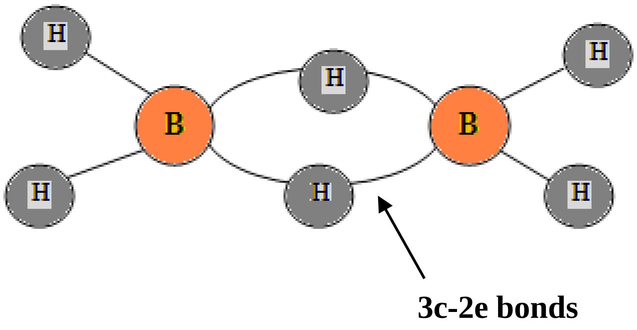


Figure 1.1: ***The structure of B2H6. Two bridged hydrogen atoms form 3c-2e bonds***

The structure B_2H_6 (Figure 1.1) is the simplest diboranes structure. Diboranes like most boranes are air sensitive. Terminal hydrogen and boron bond is 2e standard covalent bond (sharing two electrons between two atoms).

Experimental techniques like IR, electron diffraction techniques and X-ray analysis of boron hydride clusters confirm the presence of 3c-2e bonding that involves one bridging hydrogen atom between two boron atoms, thus confirming the electron deficient nature of boron hydride clusters. Because of this electron deficient nature, the BH_3 units rapidly dimerize to form a B_2H_6 molecule and complete the octet. In B_2H_6 there is 3c-2e hydrogen bridging between BHB, so one electron pair is delocalized over three atoms. As the 3c-2e bonding involves three atoms and their three atomic orbital as a result of hybridization three molecular orbital are generated i.e. a bonding molecular orbital, a non-bonding molecular orbital and an antibonding molecular orbital as shown in Figure 1.2.

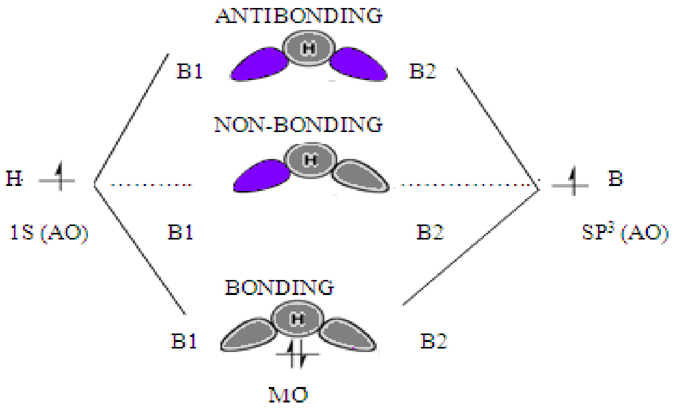


Figure 1.2. ***The molecular orbital description of B_2H_6. Two electrons go to lower energy bonding molecular orbital. The non-bonding and antibonding lying at higher energy level.***

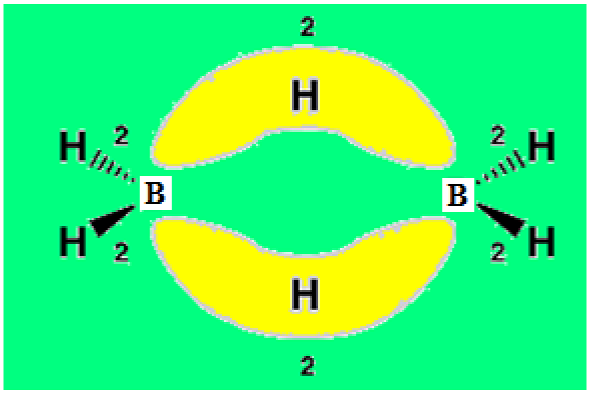
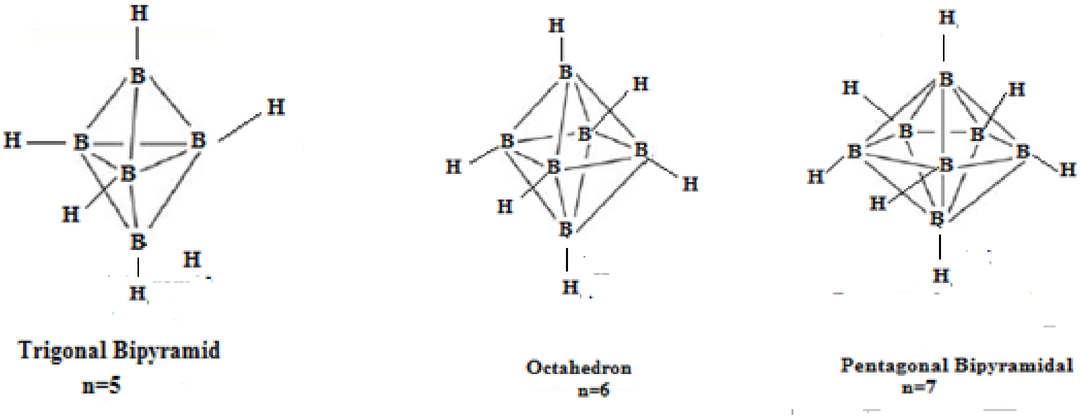


Figure 1.3: ***Delocalized electron cloud in 3c-2e bonds (B2H6). Thus each boron completes its octet due to this 3c-2e bonding.***

The bonding molecular orbital is at lower energy so two electrons of (3c-2e) go to this low energy molecular orbital and delocalize on three atoms these three atoms share three hybrid orbital. This delocalization of electron pair gives aromatic character to boron hydrides cluster. While the antibonding molecular orbitals remain empty. This bridging in boron is very interesting. Due to this bridging, boron hydride clusters have many cluster shapes in three dimensional framework. Like trigonal bipyrmidal, octahedral, pentagonal bipyramidal and so on as shown in Figure 1.4.



Trigonal Bipyramid
n=5

Octahedron
n=6

Pentagonal Bipyramidal
n=7

Figure 1.4. ***Polyhedral three dimensional clusters of closo-*** B_nH_{n2}***- (n=5, 6, 7)***

The octahedral shape in boron was first investigated by Allard in 1932 and by Pauling & Weinbaum in 1934.[7][8]

After this investigation boron hydride chemistry became a branch of inorganic chemistry having polyhedral and deltahedral structures. Work of M. Dev.Robert and Longuet-Higgin identified a closed structure of $[B_6H_6]^{2-}$.[9][10] They also studied B_{12} icosahedral structure of boron hydride[8]They indicated that the $B_{12}H_{12}$ boron hydrides cluster is stable in dianion structural form like $[B_{12}H_{12}]^{2-}$. They investigated a series of such structures with the general formula $[B_nH_n]^{2-}$. Later on work of M. Dev.Robert and Longuet-Higgin was confirmed by X-ray analysis and experiments in1960.[11] They experimentally confirmed the Longuet-Higgin concept when $[B_{12}H_{12}]^{2-}$ was synthesized as side product by the reaction of 2-iododecaborane and trimethylamine in refluxing with benzene. The deltahedral structures of $[B_6H_6]^{2-}$, $[B_9H_9]^{2-}$, $[B_8H_8]^{2-}$ were also reported by F. Klangberg.[12][13] The structures, bonding and no of skeletal electron count of boron hydrides clusters are described by some theoretical principals put forward by different scientist. There is a large list of scientists who have contributed in the formulation of these rules. These scientists include Dickerson, Lipscomb, Williams, Wade, Jemmis, Schleyer and Mingos.[14][15][16][17][18] In 1971 R.E Williams described boron hydrides clusters and put forward the concept of clusters types. He classified cluster into *closo-*, *nido-* *arachno*-clusters.[16] The words *closo*-, *nido*-, and *arachno*- are derived from words meaning "closed" (Greek), "nest" (Latin), and "spider's web" (Greek). The relationship between *closo-* *nido*- and *arachno*- clusters is shown in Figure 1.5.

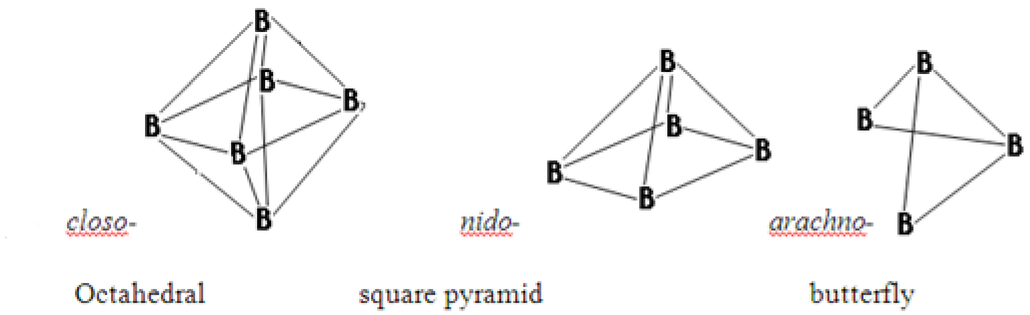


Figure 1.5. ***The 6-vertex closo-, 5 vertex nido-, and 4 vertex arachno- clusters.***

All these types *closo*-, *nido*- and *arachno*-boron hydride clusters have deltahedral geometry. The general formula of *closo*-type clusters is $[B_nH_n]^{2-}$ or B_nH_{n+2}. The *nido*-cluster is obtained from this *closo*-cluster by the removal of one highly connected vertex. The *nido*- clusters have a general formula B_nH_{n+4}. Similarly the *arachno*-cluster is obtained by further removing one highly connected vertex from open face and the resulting cluster is called *arachno*-cluster general a formula is B_nH_{n+6}.

In 1971, Wade put forward rules for boron hydrides clusters.[17] These rules are called Wade's rules. According to these rules, all types of boron hydrides clusters, i.e. c*loso*- *nido*- *arachno*- and *hypho*-clusters have same skeletal electron pair count. These skeletal electron pair counts remain same but the cluster shape change from *closo*- to *hypho*-clusters. Generally represented with (2n+2) SEP (skeletal electron pairs) and n is number of boron atoms in cluster.

12 vertex *closo*-	11 vertex *nido*-	10 vertex *archno*-	9 vertex *hypho*-
13 (n+1) SEP	13 (n+2) SEP	13 (n+3) SEP	13 (n+4) SEP

Gellespie also has a contribution to boron hydrides cluster.[19] According to his concept there is 2n skeletal electron pair remain localized on each vertex of polyhedral cluster where as the (2e) delocalized over the whole cluster. Boron hydrides cluster show aromatic behavior due to delocalization of 2 electrons on the polyhedron.

The boron hydrides clusters have many interactions with other p-block elements like carbon, silicon, nitrogen, phosphorus. Similarly these clusters are also involved in coordination with transition metal complexes. So boron has covalent and chemical bonding with itself and other electron donor species. These bonding patterns result in many nano-scale structures of boron. The reactions of boron with magnesium and lithium are also reported, where (MgB_2) is the building block. Salt of $Li_6B_6H_6$ has similarity with benzene. Boron also form compounds with chlorine. Low energy planar and non-planar isomer of $[B_6H_6]^{-2}$ boron has many applications with transition metals.[20]

As the aromatic character is present in boron hydrides cluster due to delocalization of electron cloud so they have many aromatic properties just like benzene i.e. the structure of icosahedron $[B_{12}H_{12}]^{2-}$ anion having aromatic character. This cluster show the many nucleophilic substitution reaction.[21] Thus the halogenations of *closo*-dodecaborane anion with HX gives different derivatives of fluorine, chlorine, iodine having various substitution position at 12 vertex icosahedrons (X = 1, 2, 3,….. 12). The substitution also depends upon the molar ratio of reagent and reaction temperature. Thus the *floro-, chloro-, iodo-* substituted cluster are obtained.

Similarly the carbonyl derivatives are obtained by the reaction of $[B_{12}H_{12}]^{-2}$ anion with carbon monoxide. Product of this substitution is mono and disubstituted derivative of $[B_{12}H_{11}CO]^{-1}$, $[B_{12}H_{10}(CO)_2]^{2-}$ and also $[1,7\text{-}B_{12}H_{10}(CO)_2]^{2-}$. Similarly, the icosahedron $[B_{12}H_{12}]^{2-}$ anion gives the derivative with nitrogen, phosphorus, arsenic and sulpher by substitution reaction.

1.1. The *hypercloso*-clusters, incorporation of hetero atom and stabilities trends in cluster

The *hypercloso* boron hydrides clusters have general formula B_nH_n i.e. B_6H_6, $B_{12}H_{12}$.The hetero atom like Carbon, incorporated into *hypercloso* cluster. When carbon atom is incorporated into B_6H_6 new structure is CB_5H_5. Similarly when two carbon atoms inserted into B_6H_6, hypercloso-$C_2B_4H_4$ is obtained. When *hypercloso*-$C_2B_4H_4$ computationally studied the results are quite surprising that the thermodynamically most stable cluster shape is not closed but planar.[22] All known boron hydride compounds have regular cluster shapes. The *hypercloso*- clusters also previously known to have cluster shape. The hetero atoms incorporation changes the shape of clusters. As the boron hydrides cluster are electron deficient molecules and the *hypercloso* cluster is obtained from the *closo* cluster by further removing of two electrons. The heteroatom like carbon is much more electronegative as compared to the boron atom. When carbon atom is incorporated in *hypercloso*-clusters, it withdraws electrons from the rest of the cluster. This causes the disfavoring effect on the stability of the *hypercloso*-cluster form. Therefore the cluster shape become less stable and the corresponding planar form gets more thermodynamic stability.

1.2. Aims and objectives

a) The main objective of this study is to find out the effect of electronegativity of heteroatom placement on the *hyopercloso*-$X_2B_4H_4$ (X = C, Si, Ge) clusters. It was also investigated that how does the heteroatom substitution results in the structural transition in the 6-vertex *hypercloso*-heteroborane clusters.

b) To find out the geometries of the thermodynamically most stable *hyopercloso*-$X_2B_4H_4$ (X = C, Si, Ge) isomer. For this purpose it was necessary to compute a large number of possible isomers. This also included the re-optimization of 150 $C_2B_4H_4$ isomers using basis set B3lyp/LANL2DZ method. Previous work by Ding. et. al.[22] was done using at CCSD(T) aug-cc-pvtz//B3lyp/aug-cc-pvtz level of theory. However, the aug-cc-pvtz basis set is not available for silicon and germanium atoms. To compare the results of 6-vertex *hypercloso*-$C_2B_4H_4$[22] with those of *hypercloso*-$Si_2B_4H_4$ and *hypercloso*-$Ge_2B_4H_4$, it was necessary to optimize all structures at the same basis set. We opted the LANL2DZ basis set, which is available for all type of heteroborane clusters.

c) The shape of heteroborane clusters is very important. It is known that the *closo*-carboranes with the deltahedral spherical cluster shape have perfect structural complementarity with the enzyme active sites. This structural complementarity results in high affinity of the carborane based inhibitors with the active site of enzymes. All other deltahedral forms (e.g., *nido*-, *arachno*-, and *hypho*-shapes) are not perfect cluster shapes. The purpose of the thesis was to identify closed-shape *hypercloso*-$X_2B_4H_4$ isomers, which can also have structural complementarity with the enzyme active sites.

d) To verify the hypothesis that the less electronegative heteroatoms when incorporated in 6-vertex *hypercloso*-cluster favor the cluster shape.

Chapter 2

Literature Review

2 Literature Review

In literature a lot of work has been reported on boron hydride cluster chemistry. Various theoretical models on boron hydride cluster are put forward i.e. William’s rule, Wade’s rule, Mingo’s rule and Jemmis rule for macropolyhedral.[14][15][16][17][18] Different geometric parameters are studied computationally as well experimentally. Similarly there is enormous experimental work on boron hydride clusters. Thermodynamically most stable cluster was identified using computational methods. Different physical and chemical characteristics are confirmed experimentally as well computationally.

A number of scientist computationally studied boron hydrides cluster using quantum chemical methods. Quantum chemical calculations are much effective and accurate in optimizing different geometric parameters of molecules like bond energies, bond length, dihedrals, relative energies, molecular shapes and three dimensional structures of boron hydride cluster.[23] The quantum chemical calculations also applicable on other field of chemistry like organic chemistry, physical chemistry , biology and to study reaction mechanisms, transition states etc. Computationally neutral, anionic, cationic and substituted boron hydrides cluster are studied using ab-initio and density function methods.[24]

The Clusters of boranes, carboranes, metlaboranes, azaboranes and other heteroatom boron hydride clusters have been studied qualitatively as well as quantitatively by a number of scientist at different level of theories and basis set.[25] Previous qualitative and quantitative studies on boron hydride cluster help us to understand bonding in cluster, shape of cluster and stability.[26] Carborane clusters are the cluster containing one, two or three carbon atoms and metlaboranes are the cluster containing metal atoms and also the heteroboranes contain main group elements like N/P/Si/Ge/Pb and Sn. Different structural features and energy penalties are calculated in *closo*-, *nido*-, *arachno*- clusters and substituted derivative.[27]

The first *closo* heteroatom cluster discovered is *closo*-1,2-dicarbadodicaborane 1, 2- $[C_2B_{10}H_{10}]^{2-}$. This heteroatom cluster is very important for further development of carborane and other heteroatom chemistry of boron hydride cluster. When heteroatoms are incorporated in the cluster the shape of cluster is change and cage is rearranged to next most stable position.[28]

The Boron hydride 11-vertex *nido* and 12-vertex *closo*-clusters are very important for theoretical studies of heteroatom placement.[29] Different structural features or increments system have been studied. The 11-vertex *nido* has more structural features[30] as compared to 12-vertex *closo* cluster like $[B_{10}H_{10}]^{2-}$ and $[B_{10}H_{10}]^{2-}$ anion. These *closo* cluster anions have analogous properties with aromatic hydrocarbons. Like aromatic hydrocarbons *closo* cluster have very important ortho- meta- para- position. Stability of ortho- meta- para- position clusters are quite different for different heteroatom and also the size of atom and electronic cloud play a vital role in stability of cluster.[31]

2.1 Structural transition and π electron delocalization in boron hydride clusters

The boron hydride dihydrogenated clusters like H_2B_n- (n=7-12) i.e. H_2B_8 - . In such type of boron hydride clusters structural transition also observed. Most of the dihydrogenated clusters form planar or ladder like elongated structures and electron cloud is delocalized over the whole structure. Due to this delocalization of electron the clusters look like olefins similar to butadiene and 1, 3, 5-hexatrienes. Such clusters are called polyboroenes with conjugated π bonds.[32]

Similarly recent theoretical studies reported that there are some heteroboranes hydride clusters like $B_3S_2H_3^-$ and $B_3S_2H_3$ which are planar and thermodynamically stable.[33] The cluster of $B_3S_2H_3^-$ and $B_3S_2H_3$ are perfectly planar and featured like five membered ring. The delocalization of π electron in these clusters similar to cyclopentadiene (C_5H_5).

2.2 The 12-vertex *closo*-heteroboranes

In 12-vertex *closo* borane the heteroatoms are incorporated and different qualitative and quantitative rules are applicable to explain the *closo* 12-vertex heteroboranes. The12-vertex *closo* borane anion is explained by qualitative rules put forward by William and Wade.[16][17]

In 12-vertex *closo* borane anion has symmetry and the entire vertices are equal for incoming heteroatom. Due to incorporation of heteroatom 12-vertex *closo*-cluster structural features are changed. The 12-vertex *closo* heteroborane structural features are identified by quantitative rules.[34][35]

In 12-vertex *closo* cluster when heteroatom is incorporated we obtained three isomers 1, 2-ortho substituted 1, 7-meta substituted and 1,12-para substituted. All these isomers have different energy penalties with respect to position and chemical properties of heteroatom.

2.3 Periodic trends and the energy penalties for 12-vertex *closo*-cluster

The thermodynamic stability of dihetero dodecaborane 12-vertex *closo* cluster depends upon position of heteroatom in the cluster like at position (1, 2 or 1, 7 or 1, 12). Normally when heteroatoms are placed at ortho position (1, 2) cluster become less stable in case of carborane, it rearrange itself to para position (1, 12). Thus the energy difference of ortho and meta isomers is calculated with respect to para position. Similarly energy penalties are also affected by periodic trends in heteroatom.[36] see Figure 2.1.

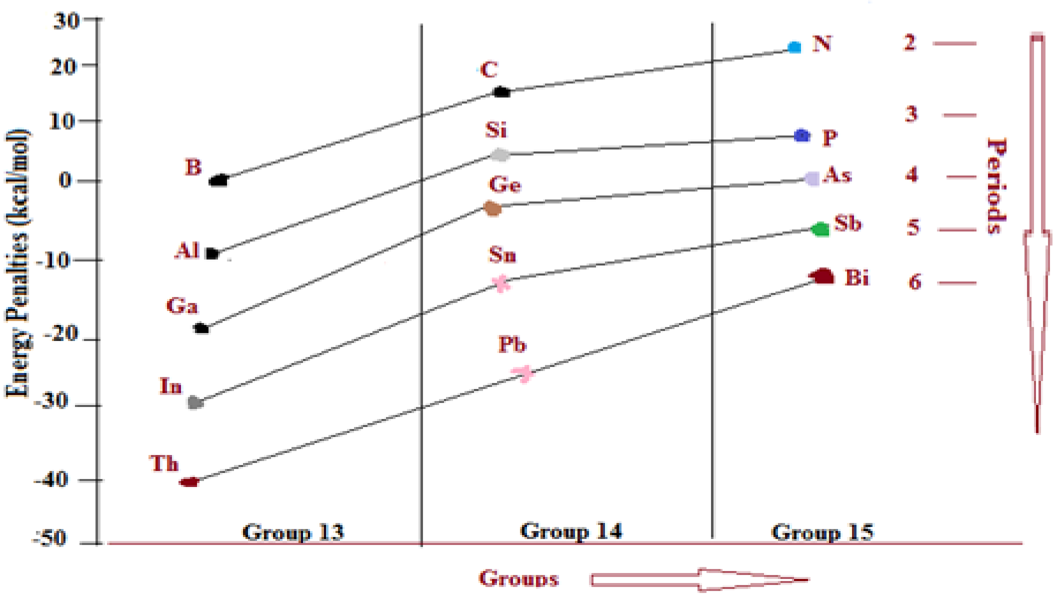


Figure 2.1. ***The Periodic trends in 12 vertex closo cluster. As the electronegativity increases along the group the energy penalties (kcal/mol) increase. The figure shows that down the group electronegativity decreases so that the energy penalties (kcal/mol) also decrease.***

When move along the period the energy penalties increases and the ortho (1, 2) diheterododecaboranes isomer becomes more unstable but the trend is reverse down the group. Down the group ortho (1, 2) and meta (1, 7) diheterododecaborane isomers get more stabilities then to para (1, 12) isomer. Similarly when more electronegative atoms present at adjacent position the energy penalties of ortho 1, 2-diheterododecaboranes drastically change and the shape of 12-vertex *closo* cluster converted to four membered open face. Thus the energy penalties changes with change in electronegativity value of heteroatom. Small size more electronegative heteroatom disfavoring the stability of cluster. But when large size less electronegative heteroatom is incorporated in 12-vetrex cluster the ortho isomer is preferred or heteroatoms like to remain at adjacent or ortho position. In 12-vertex *closo*-cluster there are less structural features as compared to open face *nido*-boron hydride cluster.[36]

2.4 The 11-Vertex *nido*- cluster and energy penalties

The 11-vertex *nido* is obtained by removal of one highly connected vertex of 12-vertex *closo*-cluster.[37] Energy penalties for exo-substituted heteroborane for 12-vertex *closo* boron hydride and 11-vertex *nido*-cluster are different. This is because in open face *nido*-cluster the structural features of heteroatoms are different from the structural features in the middle ring and apex. As in the case of carbon two adjacent carbon atoms have same energy penalties for both *closo* and *nido* but all other hetero atom energy penalties are different for *closo* isomer and *nido* isomer. A large number of structural features are possible in 11-vertex *nido* cluster due to open face. Thus the structural increment features are different for different heteroatom and structural features are much more versatile in 11-vertex *nido* boron hydrides cluster. Similarly connectivity of heteroatom, position in cluster, size of atom and electronegativity are key factors when comparing stability order either in 12-vertex *closo* cluster or 11-vertex *nido* cluster.[38]

2.5 The 12-vertex closo- Cyclopentadienyl metala borane clusters and metals effects

Transition metal have very important role in 12-vertex *closo* cluster. The transition metals have an ortho, meta, and para directing effect on incoming hetero atom.[39] As in 12-vertex *closo* cyclopentadienyl metalaheteroboranes small size more electronegative hetero atom mostly like to connect at non adjacent position.[40] When two heteroatoms are present at ortho-position the effect is disfavoring on the cluster and it is rearranged to meta or para position. The case is reverse for large sized less electronegative atom and the transition metal. Structural features for 12-vertex *closo* cluster in case of metal heteroatom are different as compared to main group element. In 12-vertex didodecametlaborane the ortho and meta isomer of 12-vertex didodecametlaborane are more stable then para isomer of 12-vertex didodecametalaborane. Thus structural features are quantitatively calculated and the energy penalties are determined for *nido*- and *closo* clusters with incorporation and connectivity of heteroatom.[41]

2.6 Macropolyhedral boranes

The single cluster of boron hydrides are well understood and explain by a no of scientist and a number of rules governed by these single clusters are known but macropolyhedral boranes cluster are at investigational stage.[42][43]

The macropolyhederal cluster derived from single cluster by (a) combining either (2e-2c) or (3c-2e) bond or (b) by sharing two, three or four vertices.[44][45] Only a little theoretical work was conducted on macropolyhedralboranes. Jemmis formulate a rule called mno rule to describe skeletal electron count in macropolyhedralboranes clusters.[46] Thermodynamically most stable structure in macroployhedral is difficult to identify because a large number of possibilities are there in macroployhederal. In most cases (H_nB_{n+n}) two *nido* units join by two vertices to give macroployhedral boranes. Macroployhedral boranes stability depends upon the open face hydrogen atom and also on the cluster nature (anionic or neutral).[47]

2.7 The *hypercloso* boron hydrides cluster

The *hypercloso* boron hydrides clusters are obtained from *closo* cluster. The general formula for *hypercloso* boron hydrides cluster is B_nH_n e.g. H_6B_5 or $H_{12}B_{12}$. The *hypercloso* clusters are different from the rest of the *closo*- *nido*- *arachno*- *hypho*- and *klado* clusters.[48][49] The *nido* cluster is obtained from *closo* by removing highly connected vertex and similarly *arachno* is obtained from *nido*- cluster by removing one highly connected vertex from open face of *nido* cluster and same procedure for *hypho*- and *klado*. But all these cluster have remain the same number of SEP (skeletal electron pairs) by Wade,s rule.[17] The *hypercloso* cluster on the other hand are obtained from *closo* cluster by removing one electron pair from the cluster but the cluster shape remains same.

Research Gap:

2.8 Heteroatom effect on *hypercloso*-cluster, energy penalties and stabilities

As the heteroatom play a vital role in cluster stability and quantitatively structural feature identification in the cluster of 12-vetrex *closo* and 11-vertex *nido* clusters.[37][38] Similarly in *hypercloso* cluster the heteroatoms have effect on cluster shape and stability[22]. Although *hypercloso*-clusters are the least studied cluster of boranes, especially the effect of heteroatomic placement on 6-vertex *hypercloso*-clusters.

2.9 The 6-vertex *hypercloso* heteroborane cluster $C_2H_4B_4$ and work of Hoffman.[50]

Hoffmann and coworkers studied all possible *hypercloso* $C_2B_4H_4$ isomers formed from the dimerization of two monomer $C(BH)_2$ units. Two $C(BH)_2$ units dimerize in a way similar to the (2+2) cycloaddition in carbene. Hoffmann and coworkers optimized 12 isomers obtained by this dimerization or cycloaddition. Some are higher energy and but the most thermodynamically $C_2B_4H_4$ dimer is an octahedral (1, 6 didehydrocarborane). Two carbon hetero atoms are incorporated and this structure is in closed form and also thermodynamically most stable. All these12 isomers optimized using quantum chemicals method at DFT. Hoffmann and coworkers[50] also optimized $Al(BH)_2$ units as the aluminum is also electron deficient molecules. When two $C(BH)_2$ units dimerize it give 1,6-dicarborane but when two $Al(BH)_2$ units dimerize the most stable structure is not (1,6 dialaborane) octahedral. It is a planar structure. So the work by Hoffmann showed that upon hetero atom (carbon) addition in *hypercloso*-B_6H_6 octahedral cluster the cluster shape is retained in the heteroatomic cluster of $C_2H_4B_4$ as shown in Figure 2.2

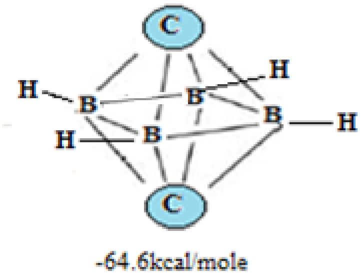


Figure 2.2. *The hypercloso 6-vertex heteroborane cluster C2H4B4 octahedral in shape thermodynamically most stable structure.*

2.10 Extensive conformational search on the potential energy surface of the 6-vertex ***hypercloso***- $C_2B_4H_4$ cluster[22]

The heteroatom carborane cluster $C_2H_4B_4$ was studied by Ding and coworkers. They have thoroughly searched and studied 1282 isomers of mixed carbon-bororn hydrogenated *hypercloso* clusters $C_2H_4B_4$. It is worth mentioning that according to the isolable principle the BH group is isoelectronic with carbon so two BH vertex replace with two carbon atom. Thus through extensive search they observed anomaly that global minima of $C_2H_4B_4$ is ribbon like isomer shown in Figure 2.3

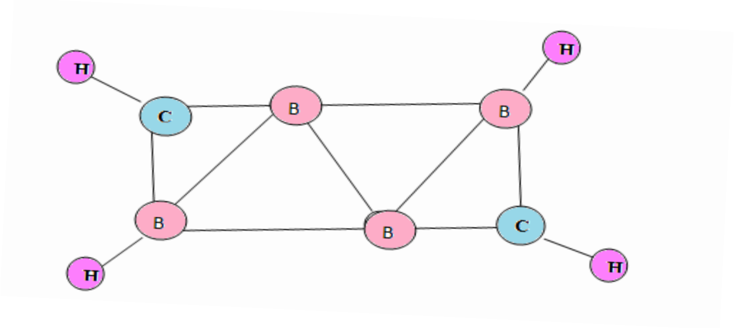


Figure 2.3. *The hypercloso 6-vertex heteroborane cluster $C_2H_4B_4$ ribbon like rectangular planar in shape thermodynamically most stable structure. This structure is different from the of octahedral hypercloso cluster that was exhibited in results of Hoffmann and coworkers*[50] *as shown in Figure 2.2.*

2.11 Research questions

1. Is this change in shape from the regular cluster shape to the planar form an artifact of the heteroatom placement?
2. What is the effect of the type of heteroatom on the relative stabilities of *hypercloso*-$X_2B_4H_4$ (X = C, Si, Ge)?
3. Is the more electronegative heteroatom like carbon change the shape of the *hypercloso*- $X_2B_4H_4$ clusters?
4. Can cluster shape be retained when less electronegative heteroatoms like (Si, Ge, Sn, Pb.) etc. are incorporated in *hypercloso* 6-vertex cluster because all known boron hydride compounds have the regular cluster shapes
5. The *hypercloso*-clusters are also previously known to have closed-shape

2.12 Formulation of research hypothesis

All known boron hydride compounds have the regular cluster shapes. The *hypercloso*-clusters are also previously known to have closed-shape. The boron hydride clusters are already electron deficient. The *hypercloso*-cluster is obtained from the *closo*-cluster by further removing two electrons. The carbon atom is much more electronegative as compared to the boron atom. When carbon atom is incorporated in *hypercloso*-clusters, it withdraws electrons from the rest of the cluster and the electron density imbalance on the cluster. This causes the disfavoring effect on the stability of the *hypercloso*-cluster form. Therefore the cluster shape become less stable and the corresponding planar form gets more thermodynamic stability. It expected that placement of a less electronegative atom like silicon or germanium in *hypercloso* 6-vertex $C_2B_4H_4$ in place of carbon the sila- and germaboranes will be closed shape structure and thermodynamically most stable.

2.13 General Applications of boron hydride cluster:

The polyhedral boron hydrides clusters are very simple inorganic compounds only consisting of boron and hydrogen atom with some incorporation of heteroatom i.e. carbon, silicon, germanium etc. But they have wide range of applications in everyday science. Two things are very important for application point of view. First is the cluster shape and second the cluster itself.[51] Before discussing interesting applications of this emerging branch of chemistry here are some facts about boron hydrides chemistry.

This branch of chemistry get much attention in early 1900 when Alfred Stock discovered some cluster[52] and opened a new door of structural chemistry. In applications point of view many students and teachers consider it a static science and clusters appear bizarre and have no interest. Literature guide sometime most novel compounds take long time for identifying their useful applications to society and researchers. Like benzene today is one of the most useful industrial chemical. But it was considered just a lab chemical for three quarter of its discovery in 1825. The boron hydrides clusters have many applications [53a-d] i.e. icosahedral $[B_{12}H_{12}]^{2-}$ anion is water soluble but when a heteroatom cesium is incorporated its properties totally change and a rigid heat resistant cluster is obtained which bear heat upto 810 C^0 without decomposition.

2.13.1 Boron hydride clusters and their use in medicines

Medicinally boron clusters get novelty. Medicinally and pharmacologically clusters shapes are very important due to two main properties of cluster. First the clusters have low chemical reactivity not easily breakdown in biological systems and second their hydrophobic nature. Their use in boron-neutron capture therapy is very important. A teteracarbonyl porphyrin having very good boron neutron capture therapy (BNCT) applications.[54a-b] Similarly many other heteroboranes clusters substituted for BNCT agents are under investigational process like polyamine clusters, glycosides, carbohydrates, nucleosides as well as liposomes.[55] To date clinical BNCT trails approved by U.S. Food and drug administration for treatment of glioblastoma multiforme (GBM), for this purpose three boron clusters[56] i.e. 4-dihydroxyborylphenylalanine and derivative of $[B_{12}H_{12}]2-$ and the salt like $Na_2(B_{10}H_{10})$ are selected. Similarly BNCS (boron neutron capture synovectomy) also used to treat arthritis.[57] BNCS more localized and minimum tissues damage.[58] Carboranes containing one or two metal atoms have significant anticancer activity also effective against breast cancer and certain glioma[59] i.e. MC_3B_7 and MC_2B_4 clusters have cytotoxic effect on common tumor cell type [60] like L-1210 lymphoid leukemia, $Tmolt_3$ leukemia, murine P388 lymphocytic growth, Sk-2 melanoma, HeLa-S^3 human uterine carcinoma, and lung bronchogenic MB-9812.

2.13.2 Boron hydride cluster and metal extraction:

Boron hydirde clusters having hydrophobic as well as hydrophilic nature are very useful in solubility point of view. Neutral boron are soluble in organic solvent while the anionic polyhedral dissolved in water. Many metals like alkali metals, alkaline earth metals, lanthanides cations etc. are extracted [61] i.e. $Co(1,2\text{-}C_2B_9H_{11})^-$ and their derivatives are very important in extraction of metals and metals ions.

2.13.3 Host-guest recognition of anion

Host-guest phenomenon is well known in crown ether.[62] A group of scientist have synthesized heteroborane cluster like $Hg(C_2B_{10}H_{10})$ type mercurocarborands which has anticrown type activity. These anticrown cluster trapped different ions like chloride ions.[63]

2.13.4 Boron clusters have noncoordinating property

Many heteroboron hydride clusters and their derivatives have very weak coordination to cations[64] i.e. icosahedral $[CB_{11}H_{12}]^-$ ion and the halogenated derivatives.

2.13.5 Nonlinear optic materials (NLO)

There is another very important application of boron cluster in the study of non-linear optical materials (NLO). These materials have the ability to change the electromagnetic field into a new field with different properties such as frequency and pulse.[65] The NLO are very useful materials in advance technology like data storage devices, retrieval, and communications. Synthetic and theoretical studies shown that the incorporation of heteroatom having electron withdrawing effect on cluster like cluster of carboranes or any other more electronegative atom increase hyperpolarizability and it is good for NLO materials. i.e. $B_{10}H_{10}$, $[B_{12}H_{12}]^{2-}$, $[CB_{11}H_{12}]^-$ and $C_2B_{10}H_{10}$ isomers[66][67] and 1,2-$C_2B_{10}H_{10}$ P-carborane.

2.13.6 Boron clusters and Homogeneous Catalysis

This is anther most important application of boron clusters. In many reactions boron hydride clusters are very important catalyst i.e. 1, 2, 3-$H(Ph_3P)Rh(C_2B_9H_{11})$ used as catalyst in hydrogenation, hydroformylation of alkenes and alkynes.[68]

2.13.7 Boron cluster in liquid crystal

This is also important application of three dimensional cages like geometry of polyhedral boranes in daily life. Liquid crystals are very important in electro-optical devices.[69]

Chapter 3

Methodology

3 Methodology details

Computational methodology for geometric optimization of molecules, fragments of molecules, clusters, macromolecules, anion, cations and neutral species of inorganic, organic or biological class plays critical part in computational chemistry. This allows the study of different aspects of chemistry, e.g., reaction mechanisms and determination of molecular properties. Computationally we explore the molecules through the use of computer when the laboratory investigations are impractical or impossible. Computational methods are broadly categorized as molecular mechanics and quantum mechanics. The quantum mechanical methods are subdivided into the following categories, i.e., *ab-initio*, desnity functional theory and semiemprical methods. These methods allow calculating the potential energy surface (PES) of the system under investigation. Computational methodology is also helpful in calculating the physical and chemicals properties (such as electronic charge, dipole movement, heat of formation) of known and unknown compounds.

The ab-initio and semiemperical are wave function based method while the DFT is determined the electron density of the molecule. DFT is a highly accurate method which also has a good balance between accuracy and computational cost. The wave functions based *ab-initio* methods become much more complicated when the number of electron increases in the system. DFT methods is also very well implemented in many popular computational program package like Gaussian, hyperchem and Spartan. Thus DFT methods have significant advantages such as computational accuracy and reasonable computing time.

DFT is very well robust with B3LYP functional. It is hybrid functional and explains the electrons correlation. B3LYP is Becke’s 3 parameterized functional together with the Lee Yang and Parr correlation functional . B3LYP is faster than previous Hartree-Fock methods.

The basis set LANL2DZ called as Los Alamos National Laboratory basis set developed by Hay and Wadt[70] is used to study quantum chemistry of transitional metals complexes and cluster compounds containing heavier atoms.

The software package G09 (Gausssian 09) is very important computational chemistry program that can be run on any 32 bit or 64 bit computer. G09 is very important to get the useful information about the molecules or compounds like geometries optimizations, HOMO/LOMO , dipole movement, bond agles, IR, UV spectra and many more applications.

Geometric optimization of 150 *hypercloso*–$C_2B_4H_4$ carboranes, 150 *hypercloso*-$Si_2B_4H_4$ silaboranes and 150 *hypercloso*-$Ge_2B_4H_4$ germaboranes were carried out. The work consisted of finding their lowest energy structure, frequency calculations, zero point vibrational energy correction and single point energies at B3LYP/LANL2DZ.[70][71] The basis set LANL2DZ is well tested for the 2nd and 3rd row of element. The energies reported in Table 1, 2 and 3 are the relative energies with respect to the most stable isomer.

The structures of all isomers of the *hypercloso* boron hydrides clusters containing carbon, silicon and germanium heteroatoms were optimized. All calculations were obtained using Gaussian 09 suite[72] of package. Different structural characteristics were identified as well as the effect of heteroatom electronegativity on cluster shapes *hypercloso* clusters was studied.Methoodology is also explained in a flow chart shown in Figure

Methodology Work flow

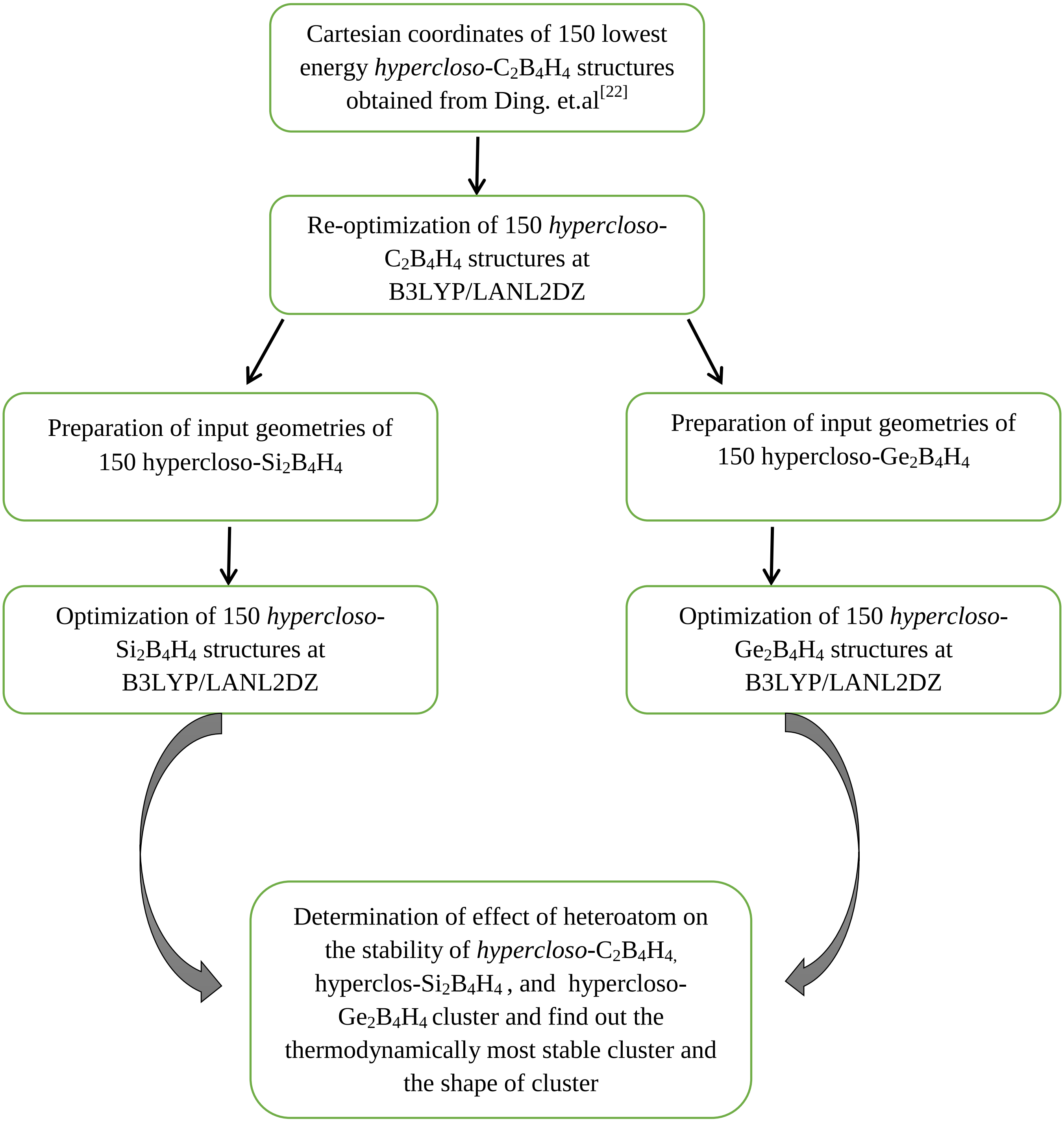


Figure 3.1. ***The Flow chart diagram of the computational methodology***

Chapter 4

Results

4 Results

4.1 Optimization of $X_2B_4H_4$ cluster (X = C, Si, Ge)

To determine the effect of heteroatom substitution on the structure of 6-vertex *hypercloso*-$X_2B_4H_4$ (X = C, Si, Ge) a large number of isomeric $C_2B_4H_4$, $Si_2B_4H_4$, and $Ge_2B_4H_4$ structures were computed. It was previously reported by Hoffman and coworkers[50] that the thermodynamically most stable $C_2B_4H_4$ isomer is a regular octahedral. Later on Ding and coworkers performed an extensive search of the hypercloso-$C_2B_4H_4$ clusters and found that the global minima for the $C_2B_4H_4$ cluster is not cluster shape but is rather planar.[22]

To investigate whether this transition from cluster shape to the planar shape is an artifact of the carbon atom substitution in $C_2B_4H_4$ cluster the $Si_2B_4H_4$ and $Ge_2B_4H_4$ cluster were computed.

4.2 Starting geometries

The starting geometries were taken from the $C_2B_4H_4$ reported by Ding et.al. [22] However instead of computing all 1282 $C_2B_4H_4$ isomers only 150 thermodynamically favorable isomers were selected. Listed in table 1.

4.3 The need for re-optimization of $C_2B_4H_4$ clusters

However to compare the results of $C_2B_4H_4$ with the results obtained from $Si_2B_4H_4$ and $Ge_2B_4H_4$ it was necessary to re-optimize *hypercloso*-$C_2B_4H_4$ structures using B3LYP/LANL2DZ basis set. For this purpose all 150 geometries obtained from Ding et.al[22] were re-optimized.

The basis set B3LYP/aug.cc-pvtz-CCSD(T) level used by Ding et.al[22] is available for carbon and boron atoms but this basis set is not suitable for silicon and germanium atom. To address this problem basis set LANL2DZ was used which is available for all the elements involved in current study i.e. boron, carbon, silicon and germanium.

4.4 Rearrangement of different starting geometries to similar/same structures

During the course of optimization it is possible that different starting geometries end up in similar structures. This depends on several factors such as the type of basis sets used the shape of the potentials energy surface and the type of the density functional used.

In this thesis each of the starting 150 $C_2B_4H_4$ geometries taken from Ding et.al[22] were subjected to geometry optimization. However in many cases the different starting geometries results in same final structures on the potential energy surface. In all these cases only one final structure is reported to avoid multiple entries.

4.5 The starting geometries of $Si_2B_4H_4$ and $Ge_2B_4H_4$

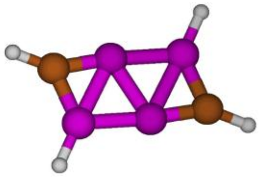
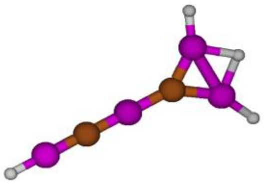
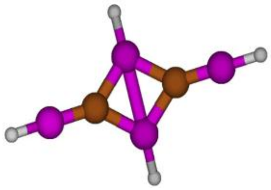
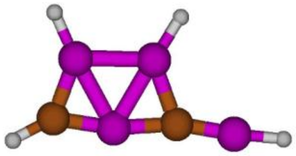
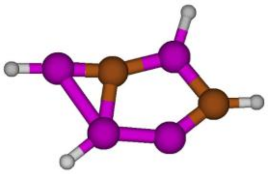
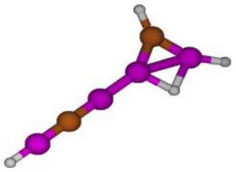
The starting geometries of $Si_2B_4H_4$ and $Ge_2B_4H_4$ were obtained by editing the input coordinates provided by Ding et.al[22] for *hypercloso*-$C_2B_4H_4$. The carbon was replaced either with silicon or germanium to obtain the starting geometries of $Si_2B_4H_4$ and $Ge_2B_4H_4$ structures.

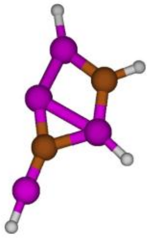
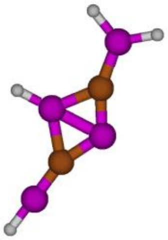
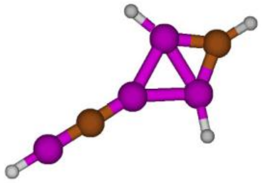
4.6 Re-optimization results of the *hypercloso* $C_2B_4H_4$ isomers

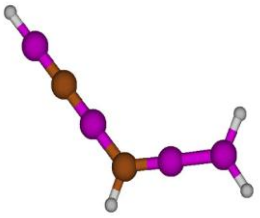
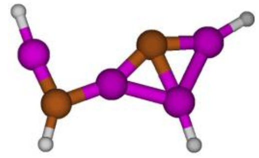
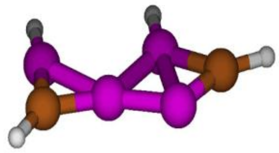
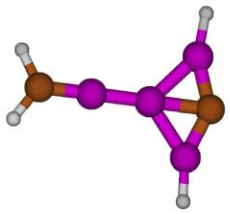
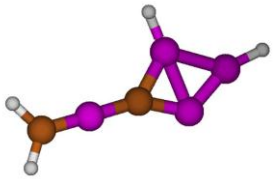
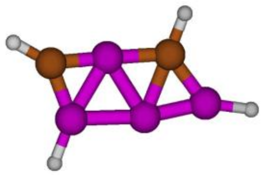
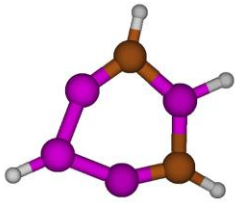
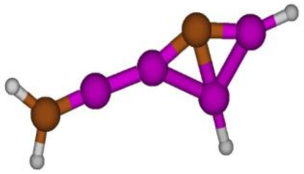
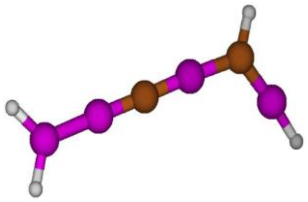
The 150 different isomers of *hypercloso*-$C_2B_4H_4$ obtained from Ding et.al[22] were re-optimized using basis set B3LYP/LANL2DZ+ZPE level. From these 150 structures the 30 structures of low energy lying with 30.0 kcal/mol shown in Figure 4.1. It is evident in Figure 4.1 that the structure 01 which is planar and most stable structure is the lowest energy structure (0.0 kcal/mol). In the structure 01 two carbon atom are at maximum distance from each other and present at opposite edge of the rectangular ribbon like structure. Two hydrogen atom form terminal bonding with carbon and two with boron in this structure.

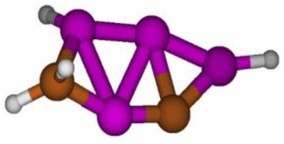
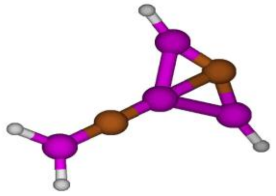
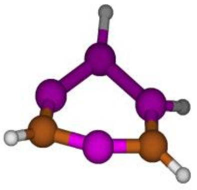
All structures (structure 01 through 30) shown in Figure 4.1 are *hypercloso* structures of $C_2B_4H_4$. They have great preference to arranged in planar pattern. [22] The results of re-optimized structures are quite similar with the work conducted by Ding and coworkers.[22] Structure 01 is rectangular type structure having two carbon atoms positioned at edge of rectangle. This is due that the carbon is more electronegative than boron and likes to form 2c-2e bonding while boron prefers to form delocalized bonding. In structure 02 and 06 the axial hydrogen has side bridging with boron. Structure 26 in Figure 4.1 is quite similar to 01 and is rectangular planar but it is 28.1 kcal/mol higher in energy as compared to 01. This is because in structure 26 the more electronegative carbon atoms are closer to each other. Similarly structure 15 is also rectangular planar and also have close resemblance with 01 but is higher in energy. In this structure again the two heteroatoms are close to each other and are lying on similar side of the rectangle. Due to repulsion between two more electronegative heteroatoms this is at higher energy level as compared to 01. Structure 02 is the second most stable structure in the selected 30 isomers. The structure 02 is triangular type planar structure with side chain attached with carbon and also side hydrogen bridging with boron atoms. There is little bit strain in triangular shape as compared to rectangular planar shape where the delocalization of electrons is on more space.

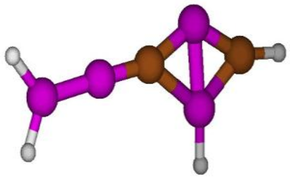
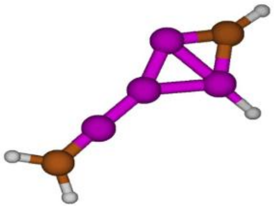
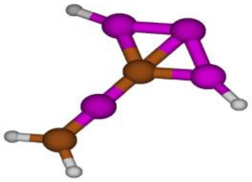
There are some similarities in structures 02 and 06. Both have a side hydrogen bridging and triangle is sandwiched with side bridging and a side chain. But structure 06 is 14.6kcal/mol higher in energy as compared to structure 02. The structure 02 is planar but structure 06 is little bent to bridging side. The structures 10 and 18 having no triangular formation just L shaped bent structure. There are some planar ring type structures like 16, 21, 27, 28 and 30 but are higher in energy. Thus the planar structure 01 is different from the parent octahedral B_6H_6 *hypercloso*-structure which is in cluster shape. This change in shape from cluster to planar is caused by isoelectronic replacement of BH with carbon atom and the carbon electronegativity is higher as compared to boron atom. The relative energies of all optimized *hypercloso*-carboranes are listed in Figure 4.1.1.

01  **0.0 kcal/mol**	**02**  **1.7 kcal/mol**	**03**  **4.8 kcal/mol**
04  **8.5 kcal/mol**	**05**  **11.4 kcal/mol**	**06**  **14.6 kcal/mol**

07  **15.9 kcal/mol**	**08**  **16.5 kcal/mol**	**09**  **17.5 kcal/mol**

10  **17.9 kcal/mol**	**11**  **18.1 kcal/mol**	**12**  **18.3 kcal/mol**
13  **18.7kcal/mol**	**14**  **20.0 kcal/mol**	**15**  **20.2 kcal/mol**
16  **21.7 kcal/mol**	**17**  **22.3 kcal/mol**	**18**  **23.0 kcal/mol**

19  **23.8 kcal/mol**	**20**  **24.6 kcal/mol**	**21**  **24.7 kcal/mol**

22  **24.8 kcal/mol**	**23**  **27.2 kcal/mol**	**24**  **27.5 kcal/mol**

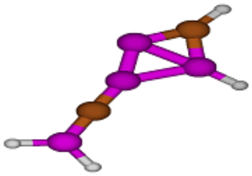
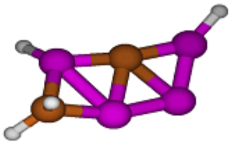
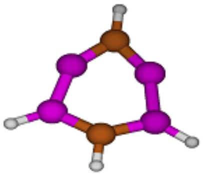
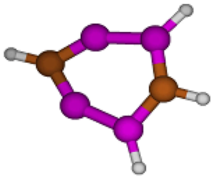
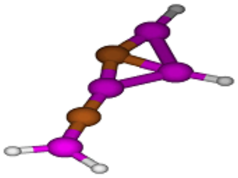
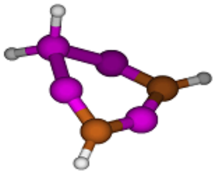
25  **27.9kcal/mol**	**26**  **28.1 kcal/mol**	**27**  **28.3 kcal/mol**
28  **28.6kcal/mol**	**29**  **28.7 kcal/mol**	**30**  **29.7kcal/mol**

Figure 4.1. ***The 30 thermodynamically stable $C_2B_4H_4$ isomers in the ascending order of relative energies.***

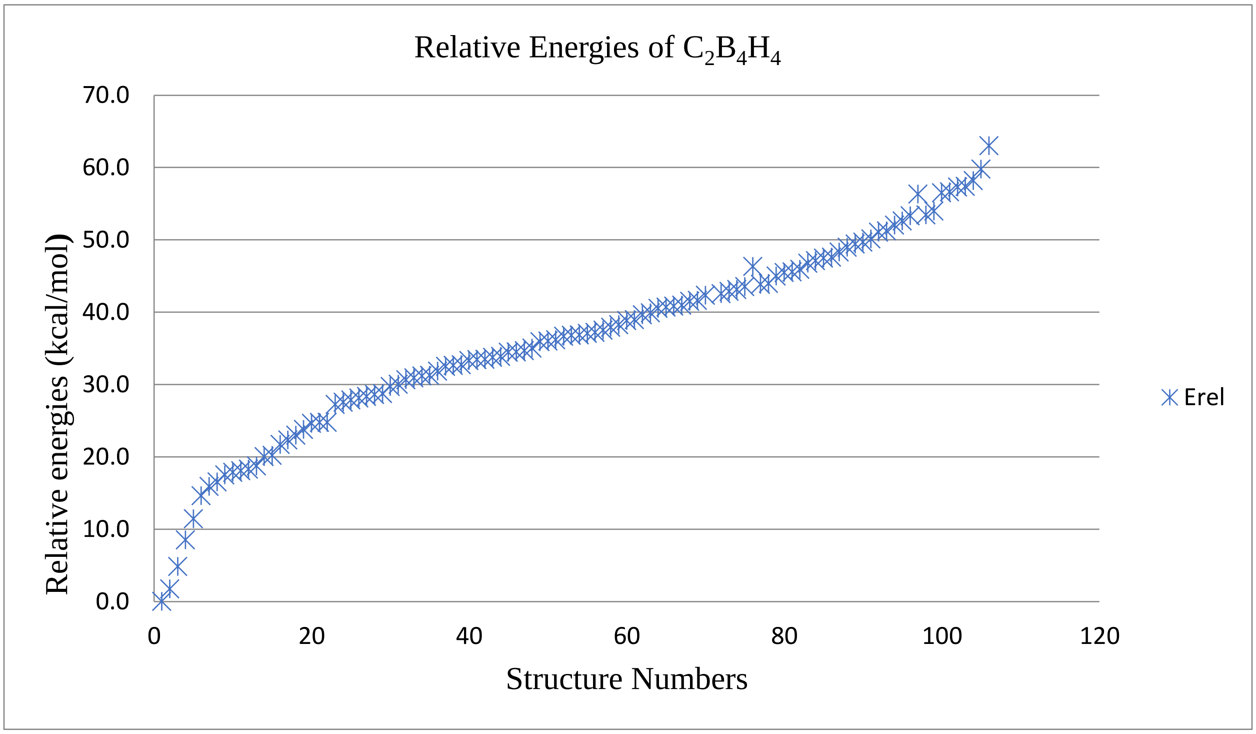


Figure 4.1.1 *Relative Energies Of Carboranes ($C_2B_4H_4$) Structures*

4.7 Optimization of the *hypercloso* $Si_2B_4H_4$ isomers

The *hypercloso* heteratomic $Si_2B_4H_4$ structures are shown in Figure 4.2. All these isomers are optimized at B3LYP/LANL2DZ+ZPE level. The relative energies of all these 30 isomers are listed in Figure 4.2. in ascending order.

Structure 01 is the most stable structure amongst all these 30 isomers. This structure has two silicon atoms present at position 1 and 6. Terminal hydrogen form exo-substituted bonding with four boron atoms. Each silicon atom has four connectivity but two boron have three and other two boron have four connectivity.

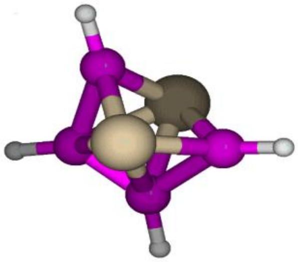
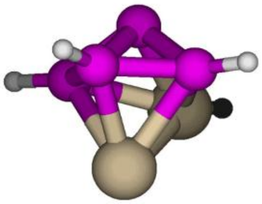
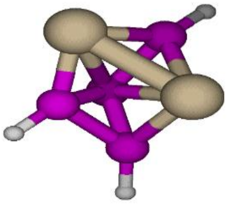
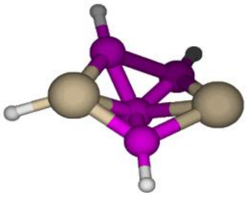
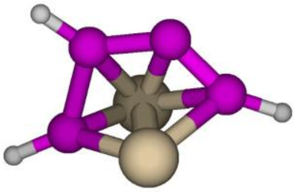
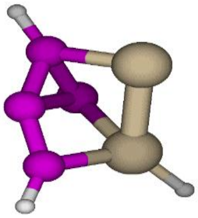
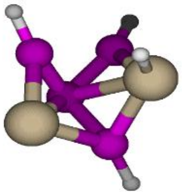
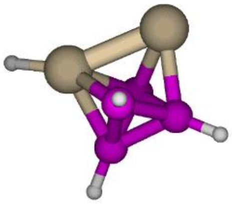
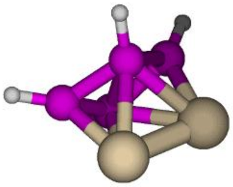
Structure 02 is compact octahedral geometry. But it is higher in energy than 01 by 4.8kcal/mol. This is because the two silicon hetero atom are adjacent to each other but in structure 01 the heteroatom are at opposite position(1,6) but in 02 the two heteroatoms are (1,2) position. One terminal hydrogen atom is bonded to silicon atom. This is also a disfavoring factor in heteroatom chemistry. Each atom in this structure has four connectivity similar to parent *hypercloso* structure B_6H_6.

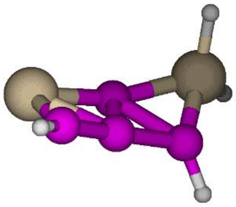
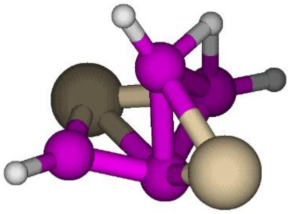
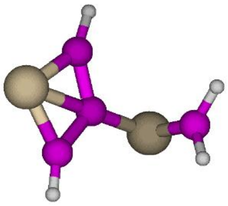
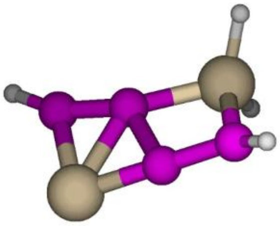
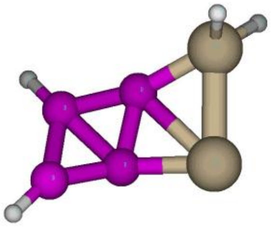
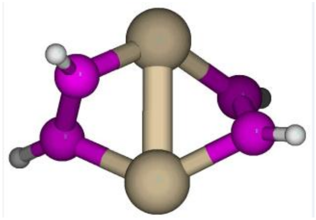
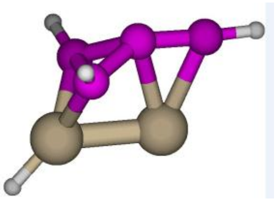
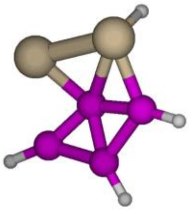
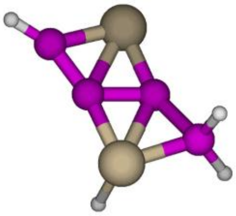
In structure 03 two silicon atoms are interconnected with each other or at adjacent position like in structure 02 but in this structure the octahedral shape is distorted. The two silicon atoms in structure 04 are separated and the energy is 11.2 kcal/mol higher as compared to structure 01. It is an umbrella shape structure. The structure 05, 06 have distorted cluster. They have two silicon atoms adjacent to each other. Similarly structure 07 is open face structure with 14.6 kcal/mol relative energy.

The structure 08 and 02 has some similarity. Both structures have two silicon atoms at adjacent (1, 2) positions in a regular octahedral geometry. In structure 08 one connectivity between silicon and boron atom is missing.

It is interesting to note that in all the 30 structures the cluster shape distort when relative energies increases. The structures with higher relative energies prefer to arrange in open shape rectangular type geometries as we look at structure 10, 13, 14, 18, 22, and 26. They have relative energies of 19.1kcal/mol, 19.8kcal/mol, 20.5kcal/mol, 23.3kcal/mol, 24.8kcal/mol with respect to to structure 01. In all these structures the cluster shapes is completely vanished. Similarly other respective distorted structures like 11, 16, 17, 21, and 27 have higher relative energies.

The most stable or lower energy structures follow the parent of *hypercloso* cluster shape octahedral geometries. As the size of silicon atom is bigger as compared to carbon atom but still the emerging thermodynamically stable heteroboranes are in cluster shapes. The relative energies of *hypercloso*-$Si_2B_4H_4$ structures optimized in our study are shown in Figure 4.2.1.

01  **0.0 kcal/mol**	**02**  **4.8 kcal/mol**	**03**  **5.0 kcal/mol**
04  **11.2 kcal/mol**	**05**  **12.3 kcal/mol**	**06**  **13.5 kcal/mol**
07  **14.6 kcal/mol**	**08**  **14.8 kcal/mol**	**09**  **15.4 kcal/mol**

10  **16.3 kcal/mol**	**11**  **17.9 kcal/mol**	**12**  **18.7 kcal/mol**
13  **19.1 kcal/mol**	**14**  **19.8 kcal/mol**	**15**  **20.0 kcal/mol**
16  **20.2 kcal/mol**	**17**  **20.3 kcal/mol**	**18**  **20.5 kcal/mol**

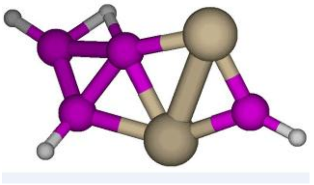
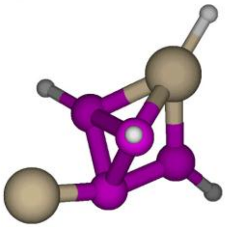
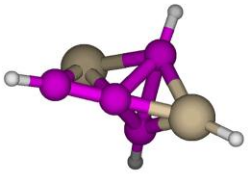
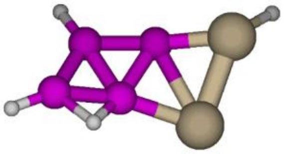
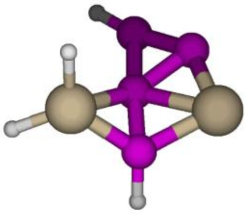
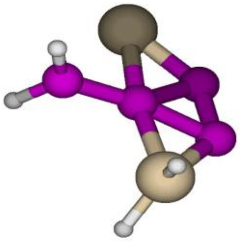
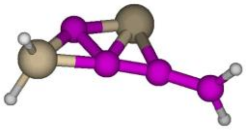
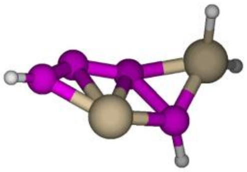
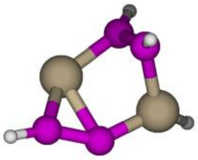
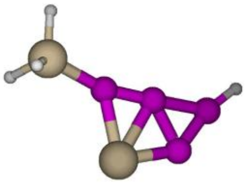
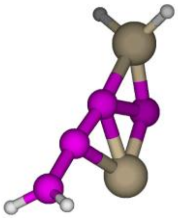
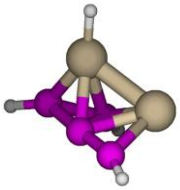
19  **21.1 kcal/mol**	**20**  **22.2 kcal/mol**	**21**  **23.1kcal/mol**
22  **21.1 kcal/mol**	**23**  **22.2 kcal/mol**	**24**  **23.1 kcal/mol**
25  **24.7 kcal/mol**	**26**  **24.8 kcal/mol**	**27**  **25.2 kcal/mol**
28  **25.4 kcal/mol**	**29**  **25.5 kcal/mol**	**30**  **25.8 kcal/mol**

Figure 4.2 ***The 30 thermodynamically stable $Si_2B_4H_4$ isomers in the ascending order of relative energies***.

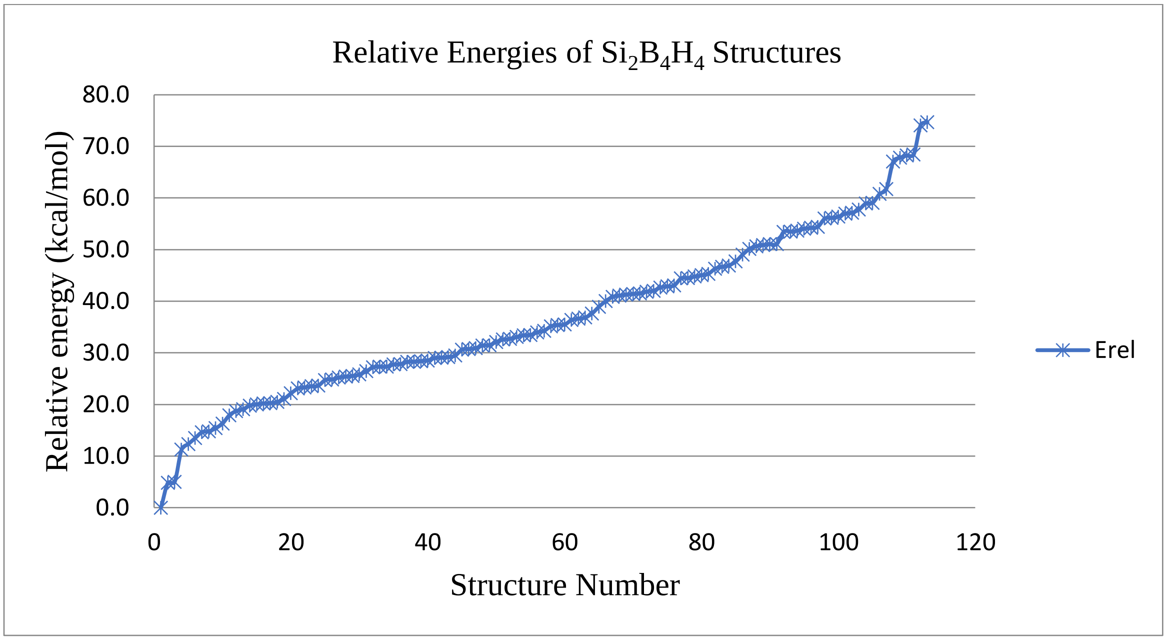


Figure 4.2.1 ***Relative Energies Of silaboranes ($Si_2B_4H_4$) Structures***

4.8 Optimization of the *hypercloso* $Ge_2B_4H_4$ Isomers

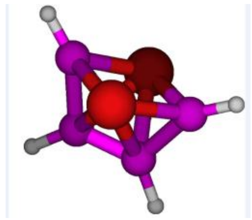
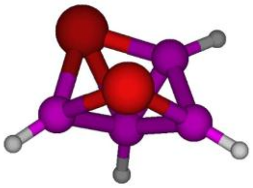
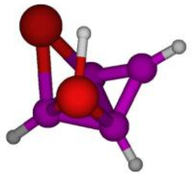
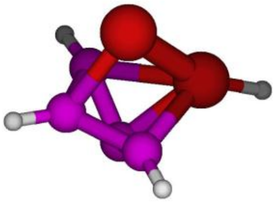
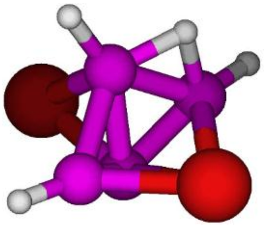
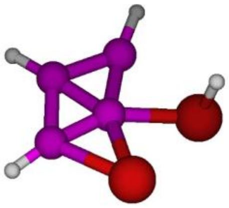
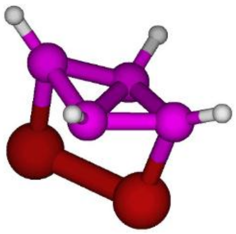
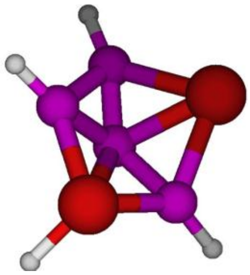
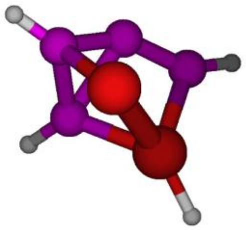
There are 150 *hypercloso* heteroboranes structures of Germanium studied and the 30 lower energy structures are presented in Figure 4.3. Global minima structure 01 is in cluster shape, two Germanium atoms are at maximum distance having less strain or repulsion forces, four terminally bonded hydrogen atoms with four boron atoms and two Germanium atoms are at (1,6) positions with four connectivities like *hypercloso* B_6H_6 octahedral cluster. But in structure 01 all atoms do not have equal connectivity as two boron with four connectivity and other two with three connectivity.

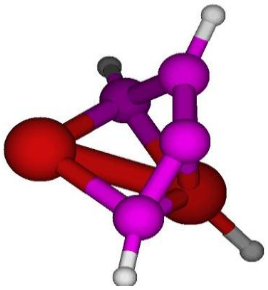
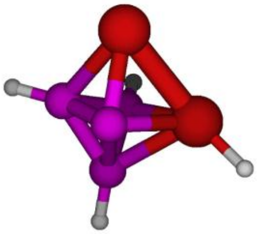
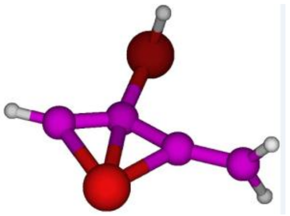
Similarly in the structures 02,03,04,05 cluster shape persist but the octahedral geometry change. In structure 02 which is 4.5 kcal/mol higher relative to global minima. In structure 02 the two

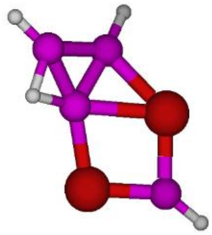
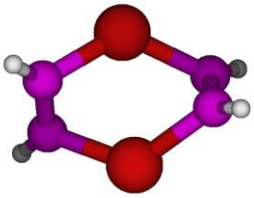
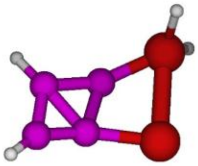
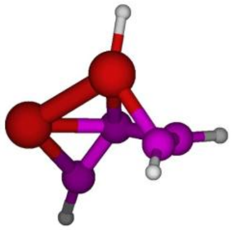
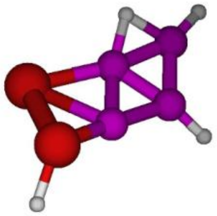
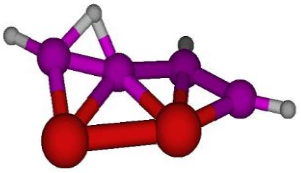
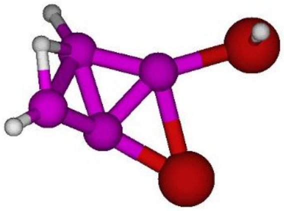
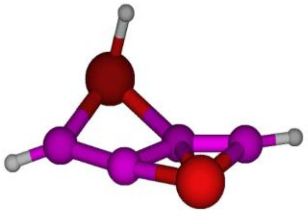
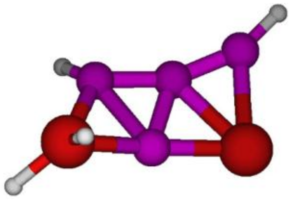
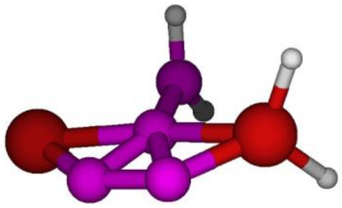
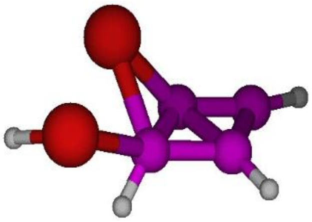
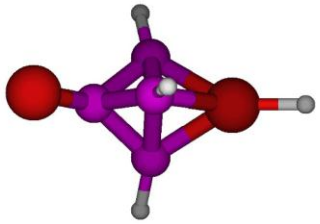
Germanium atoms are located at opposite corners but the connectivity varies one has three and the other has just two connectivity. Thus this is different to octahedral geometry where four connectivity per atom.

In structure 03 each Germanium atom has two connectivity and the structure 04 shows different connectivity. One terminal hydrogen atom is bonded with Germanium in both 03 & 04 structures.

The relative energies of all computed $Ge_2B_4H_4$ isomers are listed in Figure 4.3.1.

1  **0.0 kcal/mol**	02  **4.5 kcal/mol**	03  **7.2 kcal/mol**
04  **9.0 kcal/mol**	05  **11.6 kcal/mol**	06  **11.8 kcal/mol**
07  **14.0 kcal/mol**	08  **16.1 kcal/mol**	09  **16.2 kcal/mol**

10	11	12
		
16.5 k cal/mol	**17.1 k cal/mol**	**17.5 k cal/mol**

13  **22.4 kcal/mol**	14  **23.6 kcal/mol**	15  **25.0 kcal/mol**
16  **25.5 kcal/mol**	17  **25.7 kcal/mol**	18  **26.6 kcal/mol**
19  **28.8 kcal/mol**	20  **29.3 kcal/mol**	21  **29.7 kcal/mol**
22  **30.2 kcal/mol**	23  **30.3 kcal/mol**	24  **30.4 kcal/mol**

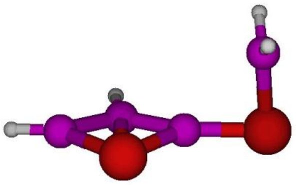
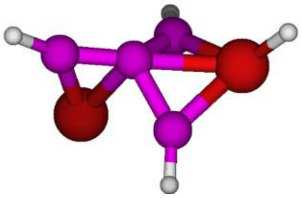
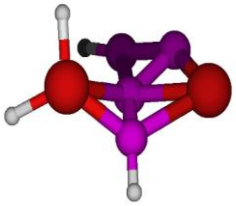
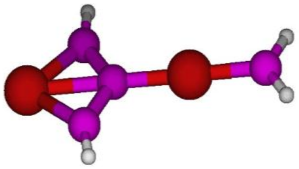
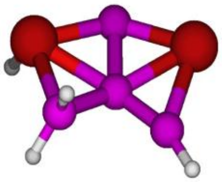
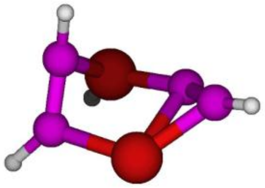
25  **30.8 k cal/mol**	26  **31.3 k cal/mol**	27  **31.9 k cal/mol**
28  **33.8 k cal/mol**	29  **34.2 k cal/mol**	30  **34.5 k cal/mol**

Figure 4.3 ***The 30 thermodynamically stable $Ge_2B_4H_4$ isomers in the ascending order of relative energies.***

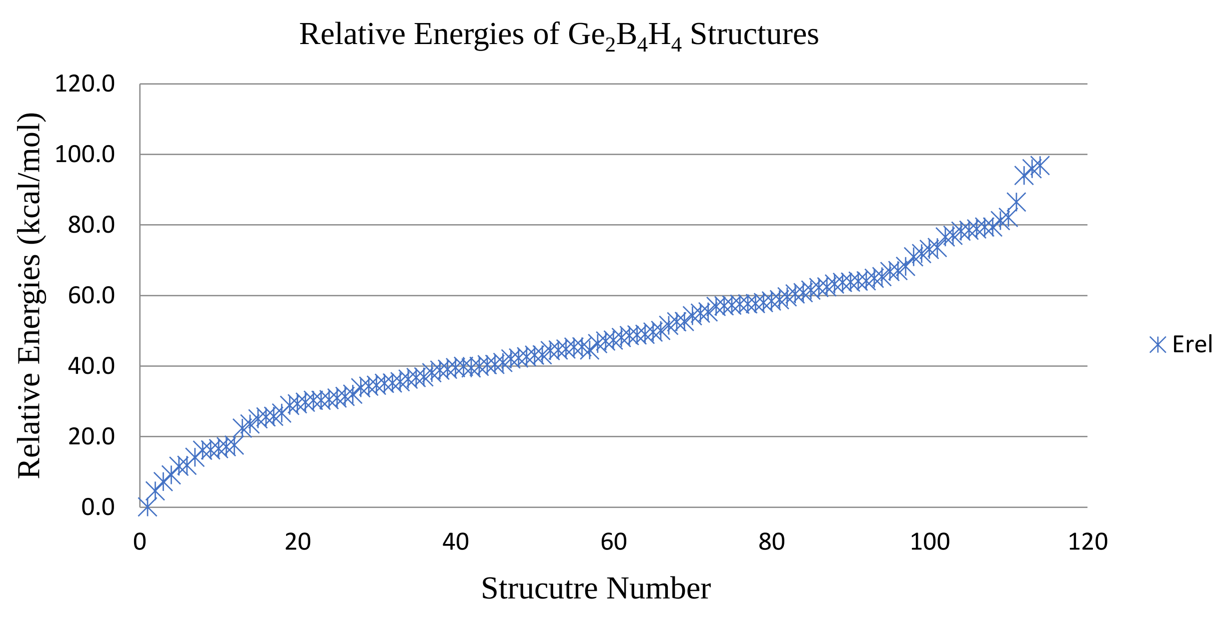


Figure 4.3.1 ***Relative Energies Of germaboranes ($Ge_2B_4H_4$) Structures***.

4.9 Novelty of work

Previous theoretical works on boron hydrides cluster have resulted in a large number of qualitative and quantitative rules. These rules have been established by Wade, Williames, Jemmis, Schelayer and Hofmann.[14][15][16][17][18] These all theoretical works deal with the relationship between boron hydrides classes (wade’s rule), the rules for heteroatom placement(Williams’ rule), the electron counting rules (Jemmis’ rule) and relationship between skeletal electron count and macropolyhedrla structures (Kiani-Hofmann rule)

This is the very first study that established that the type of heteroatom present in a *hypercloso*-cluster can significantly introduce structural transition from closed cluster (common in boron hydride chemistry) to planar forms (rare in boron hydride chemistry).

Chapter 5

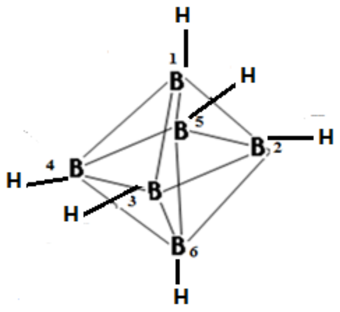
Discussion

5 Discussion

Boron hydrides chemistry is a versatile field of chemistry being very attractive to both theoretical as well as experimental chemists. It is a chemistry of clusters and polyhedral structures. Boron hydrides cluster consist of two atoms boron and hydrogen. But the other cluster containing heteroatoms are also well known and the presence of heteroatom in cluster is very objective question for computational chemists.

Boron hydrides are mostly known in cluster shapes. There are different types of clusters like *closo-*, *nido-*, *arachno-*, *klado-*, etc. If we look at the boron hydrides chemistry and studies carried out in this field we can find a large number of scientist and chemists who have played a very vital role in investigating cluster rules, cluster shapes, nomenclature of clusters, properties and application of boron hydrides chemistry. These are polyhedral clusters like deltahedrals, octahedrals , trigoanl bipyramidal, trigonal and square planar etc.

There is another class of boron hydrides cluster called *hypercloso* clusters obtained from *closo* cluster by removing a pair of electron. For example *hypercloso*-B_6H_6 is obtained by removing two electrons from closo $[B_6H_6]^{-2}$.This is an octahedral shape cluster. All six hydrogen are terminally bonded with six borons by covalent bond. The numbering in this octahedral structure is as in Figure 5.1.



Closo **Octahedral Strucutre**

Figure 5.1. ***Octahedral structure of closo boranes hydride cluster***

A hetero atom is inserted at any of the six positions of this octahedron. When carbon is substituted at any position a BH group is replaced with carbon. When two carbon atoms inserted then two BH,s are replaced and the resulting structure is $C_2B_4H_4$. This is very important heteroborane cluster a lot of study is carried out computationally on this cluster and different findings were observed by different scientist.

Hoffmann and co-workers[50] studied different isomeric form of $C_2B_4H_4$ and the concept behind the studies is BH_3 electron deficient molecules which immediately dimerize to B_2H_6 planar structure. Using this concept C(BH)2 units dimerized and different isomers obtained by Hoffmann and optimized computationally and thermodynamically stable dimer is identified. This dimer is in cluster shape of octahedral structure.

Boranes hydrides octahedral *hypercloso* B_6H_6 structure is incorporated with carbon as a heteroatom and 1282 isomers are computationally studied by Ding et.al.[22] and fond out thermodynamically stable rectangular ribbon like planar structure. This is *hypercloso* $C_2B_4H_4$ hetero boranes structure.

We selected 150 most stable isomers and geometries of all these 150 structures of $C_2B_4H_4$ are re-optimized using basis set B3LYP/LANL2DZ+ZPE level. The results of all these 150 isomers have very good agreement with Ding work[22] and the most stable structure is rectangular ribbon like planar shape. All the atoms are in one plane. The 30 low lying energy structures are selected and represented in Figure 4.1. All these 30 structures have preference to arrange in planar form.

In the case of $Si_2B_4H_4$ silicon atom is less electronegative as compared to carbon and carbon is more electronegative than boron. All these 150 *hypercloso* structures of $Si_2B_4H_4$ are computationally optimized using B3LY/LANL2DZ+ZPE level. Most stable isomer of $Si_2B_4H_4$ is identified which is in cluster shape. The 30 structures of having lowest energies are represented and mostly is in cluster shape. But as energy increases the cluster shape distorted.

The geometries of 150 *hypercloso*-$Ge_2B_4H_4$ were also optimized using the same basis set B3LYP/LANL2DZ+ZPE level. Different geometric parameters were studied and the most stable structure was identified which is also a cluster shape.

The results of all these optimizations of 150 $Si_2B_4H_4$ structures and 150 $Ge_2B_4H_4$ structures are validate our hypothesis that the most stable structure is in cluster shape when heteroatoms are less electronegative. All known boron hydrides compounds have the regular cluster shapes. In case of *hypercloso* $C_2B_4H_4$ an anomaly is observed that the thermodynamically most stable *hypercloso* $C_2B_4H_4$ is in planar form. Our results confirm that the change in shape from regular cluster shape to planar form is artifact of heteroatom or the more electronegative atom than boron like carbon change the shape of *hypercloso* octahedral cluster. The boron hydrides clusters are already electron deficient and *hypercloso* cluster B_6H_6 is obtained from the closo cluster by further removing electron pair. The carbon atom is more electronegative as compared to boron atom. When carbon is incorporated in *hypercloso* cluster B_6H_6 it withdraws the electron cloud to itself due this electronegativity. This cause the disfavoring effect on the stability of the *hypercloso* cluster shape. Therefore the cluster shape becomes less stable and corresponding planar form get more thermodynamic stability.

Thus we placed less electronegative element as compared to carbon like Silicon and Germanium from the similar group. As we move in period the electronegativity increases while it decreases down the group. Our results of optimization we concluded that the more electronegative atom have disfavoring effect and higher energy penalties. When inserted less electronegative atom in the cluster of 6-vertex *hypercloso* B_6H_6 then the cluster shape retain and the cluster get thermodynamic stability. Therefore we concluded by substituting silicon and Germanium the most stable structures are in cluster shapes and the electronegativity is main factor to change the shape.

Chapter 6

Conclusion

6 Conclusion

A large number of possible isomeric *hypercloso*-$X_2B_4H_4$ (X = C, Si, Ge) structures were computed at B3LYP/LANL2DZ level of theory to find out the thermodynamically most stable isomer. The thermodynamically most stable isomer of the *hypercloso*-$C_2B_4H_4$ is a planar structure, whereas the thermodynamically most stable *hypercloso*-$Si_2B_4H_4$ and *hypercloso*-$Ge_2B_4H_4$ structures adapt the cluster shape. Apparently this appears to be an anomaly; however, the work conducted in this thesis has shown that the transition from the cluster shape to the planar form in $C_2B_4H_4$ is because of the more electronegative carbon heteroatom. The *hypercloso*-clusters are highly electron deficient clusters. They are obtained by the removal of one electron pair from the already electron deficient *closo*-clusters. When carbon atoms are inserted in the *hypercloso*-cluster, they localize the electron density on carbon vertices, which is a highly disfavoring situation for the *hypercloso*-$C_2B_4H_4$ cluster. Because of this disfavoring situation, the *hypercloso*-$C_2B_4H_4$ molecule is unable to sustain the cluster shape, and rearranges to a planar form in the thermodynamically most stable structure.

On the other hand, when silicon and germanium atoms are substituted, the thermodynamically most stable *hypercloso*-$Si_2B_4H_4$ and *hypercloso*-$Ge_2B_4H_4$ structures retain the cluster configuration. This is because silicon and germanium atoms are less electronegative: They cause less degree of electron localization, and consequently cluster shape is retained.

This is an important study of one of its own kind in boron hydride chemistry, in which it is shown that the type of heteroatom can affect the shape of the boron hydride clusters. This study is consistent with previous work on boron hydride clusters in which it was shown that more electronegative heteroatoms tend to be disfavoring for the 11-vertx *nido*- and 12-vertex *closo*-clusters.

Chapter 7

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Chapter 8

Appendixes

8 Appendixes

LIST OF TABLES

Table 1: Relative energies of the 6-vertex *hypercloso*-$C_2B_4H_4$

Sr.No	E_{opt} (Hartree)	E_{opt} (kcal mol^{-1})	ZPE(kcal mol^{-}1)	E_{opt}+ZPE	E_{rel}
1	-177.9096284	-111640.0709	39.73417	-111600.3367	0.0
2	-177.9044365	-111636.8129	38.20231	-111598.6106	1.7
3	-177.9044365	-111636.8129	38.20233	-111598.6106	1.7
4	-177.8983027	-111632.9639	37.4412	-111595.5227	4.8
5	-177.8983027	-111632.9639	37.4412	-111595.5227	4.8
6	-177.8983027	-111632.9639	37.44121	-111595.5227	4.8
7	-177.8936213	-111630.0263	38.20963	-111591.8167	8.5
8	-177.8936241	-111630.0281	38.20974	-111591.8183	8.5
9	-177.8936213	-111630.0263	38.20965	-111591.8167	8.5
10	-177.8898779	-111627.6773	38.78318	-111588.8941	11.4
11	-177.8898759	-111627.676	38.78126	-111588.8948	11.4
12	-177.8898779	-111627.6773	38.78322	-111588.8941	11.4
13	-177.8846634	-111624.4051	38.66665	-111585.7385	14.6
14	-177.8846639	-111624.4054	38.66855	-111585.7369	14.6
15	-177.8820594	-111622.7711	38.3522	-111584.4189	15.9
16	-177.8820594	-111622.7711	38.35223	-111584.4189	15.9
17	-177.882062	-111622.7727	38.35399	-111584.4187	15.9
18	-177.8796429	-111621.2547	37.42997	-111583.8247	16.5
19	-177.8796429	-111621.2547	37.43	-111583.8247	16.5
20	-177.8796391	-111621.2523	37.42708	-111583.8253	16.5
21	-177.8796429	-111621.2547	37.42995	-111583.8248	16.5
22	-177.8796429	-111621.2547	37.42994	-111583.8248	16.5
23	-177.8788527	-111620.7589	37.91176	-111582.8471	17.5
24	-177.8774748	-111619.8942	37.41445	-111582.4798	17.9
25	-177.8774471	-111619.8768	37.63114	-111582.2457	18.1
26	-177.8797591	-111621.3276	39.28001	-111582.0476	18.3
27	-177.8797603	-111621.3284	39.27703	-111582.0514	18.3
28	-177.8777396	-111620.0604	38.45567	-111581.6047	18.7
29	-177.8761631	-111619.0711	38.77108	-111580.3	20.0
30	-177.8762935	-111619.1529	39.0151	-111580.1378	20.2
31	-177.8743256	-111617.9181	39.29475	-111578.6233	21.7
32	-177.8714491	-111616.113	38.08311	-111578.0299	22.3
33	-177.8714524	-111616.1151	38.08623	-111578.0289	22.3
34	-177.8689497	-111614.5446	37.21197	-111577.3327	23.0

35	-177.8718298	-111616.3519	39.81751	-111576.5344	23.8
36	-177.8652031	-111612.1936	36.47535	-111575.7182	24.6
37	-177.8689191	-111614.5254	38.92623	-111575.5992	24.7
38	-177.8689191	-111614.5254	38.92621	-111575.5992	24.7
39	-177.8689191	-111614.5254	38.92623	-111575.5992	24.7
40	-177.8672487	-111613.4772	37.89905	-111575.5782	24.8
41	-177.8666025	-111613.0717	39.95873	-111573.113	27.2
42	-177.8660728	-111612.7393	39.61935	-111573.12	27.2
43	-177.8660671	-111612.7358	39.61271	-111573.1231	27.2
44	-177.8660671	-111612.7358	39.61271	-111573.1231	27.2
45	-177.8642999	-111611.6268	38.83143	-111572.7954	27.5
46	-177.8623	-111610.3719	37.88986	-111572.482	27.9
47	-177.8622982	-111610.3707	37.88841	-111572.4823	27.9
48	-177.8651773	-111612.1774	39.96586	-111572.2115	28.1
49	-177.8623977	-111610.4332	38.44323	-111571.99	28.3
50	-177.8627473	-111610.6526	38.9434	-111571.7092	28.6
51	-177.8627473	-111610.6526	38.94349	-111571.7091	28.6
52	-177.8582313	-111607.8187	36.21599	-111571.6027	28.7
53	-177.8607743	-111609.4145	38.81492	-111570.5996	29.7
54	-177.8607743	-111609.4145	38.81491	-111570.5996	29.7
55	-177.8608635	-111609.4705	39.15855	-111570.3119	30.0
56	-177.8608635	-111609.4705	39.15852	-111570.3119	30.0
57	-177.8579584	-111607.6475	37.94483	-111569.7026	30.6
58	-177.8579532	-111607.6442	37.93922	-111569.705	30.6
59	-177.8595631	-111608.6544	38.87343	-111569.781	30.6
60	-177.8563775	-111606.6554	37.23952	-111569.4159	30.9
61	-177.8570113	-111607.0532	37.91231	-111569.1409	31.2
62	-177.8570132	-111607.0544	37.91154	-111569.1428	31.2
63	-177.8604247	-111609.1951	40.11163	-111569.0835	31.3
64	-177.8584796	-111607.9745	39.49656	-111568.478	31.9
65	-177.8546963	-111605.6005	37.77088	-111567.8296	32.5
66	-177.8546963	-111605.6005	37.77085	-111567.8296	32.5
67	-177.8558232	-111606.3076	38.60081	-111567.7068	32.6
68	-177.8545113	-111605.4844	37.8658	-111567.6186	32.7
69	-177.8552316	-111605.9364	38.89814	-111567.0382	33.3
70	-177.8578463	-111607.5771	40.68024	-111566.8969	33.4
71	-177.8527494	-111604.3788	37.50717	-111566.8716	33.5
72	-177.8558686	-111606.3361	39.72493	-111566.6112	33.7
73	-177.8569231	-111606.9978	40.36223	-111566.6356	33.7
74	-177.8558686	-111606.3361	39.72492	-111566.6112	33.7
75	-177.8539082	-111605.1059	38.64088	-111566.4651	33.9
76	-177.855039	-111605.8155	39.91558	-111565.8999	34.4

77	-177.8534928	-111604.8453	39.02085	-111565.8244	34.5
78	-177.8541147	-111605.2355	39.57893	-111565.6566	34.7
79	-177.8542594	-111605.3263	40.02022	-111565.3061	35.0
80	-177.8528764	-111604.4585	40.01736	-111564.4411	35.9
81	-177.8480562	-111601.4337	37.1055	-111564.3282	36.0
82	-177.849272	-111602.1967	38.04737	-111564.1493	36.2
83	-177.8493078	-111602.2191	38.04145	-111564.1777	36.2
84	-177.8564473	-111606.6992	43.00624	-111563.693	36.6
85	-177.8520907	-111603.9654	40.41708	-111563.5484	36.8
86	-177.8499224	-111602.6048	39.11847	-111563.4863	36.9
87	-177.8457709	-111599.9997	36.73743	-111563.2623	37.1
88	-177.8489217	-111601.9769	38.85445	-111563.1224	37.2
89	-177.8489217	-111601.9769	38.85444	-111563.1224	37.2
90	-177.8489217	-111601.9769	38.85447	-111563.1224	37.2
91	-177.8463039	-111600.3342	37.49012	-111562.844	37.5
92	-177.8463039	-111600.3342	37.49006	-111562.8441	37.5
93	-177.8503241	-111602.8569	40.43416	-111562.4227	37.9
94	-177.8469234	-111600.7229	38.32465	-111562.3983	37.9
95	-177.8463588	-111600.3686	38.31196	-111562.0567	38.3
96	-177.8463646	-111600.3723	38.31941	-111562.0528	38.3
97	-177.8467048	-111600.5857	39.06319	-111561.5225	38.8
98	-177.8462452	-111600.2973	38.94443	-111561.3529	39.0
99	-177.8482324	-111601.5443	40.85354	-111560.6908	39.6
100	-177.8443781	-111599.1257	38.69357	-111560.4321	39.9
101	-177.840893	-111596.9388	37.12777	-111559.811	40.5
102	-177.8441367	-111598.9742	39.33972	-111559.6345	40.7
103	-177.844449	-111599.1702	39.66313	-111559.5071	40.8
104	-177.8491335	-111602.1098	42.72266	-111559.3871	40.9
105	-177.8433829	-111598.5012	39.66493	-111558.8363	41.5
106	-177.8444553	-111599.1741	40.45867	-111558.7155	41.6
107	-177.8429732	-111598.2441	40.21976	-111558.0244	42.3
108	-177.8429732	-111598.2441	40.21978	-111558.0243	42.3
109	-177.8361608	-111593.9693	36.2048	-111557.7645	42.6
110	-177.8361649	-111593.9718	36.20897	-111557.7629	42.6
111	-177.8429121	-111598.2058	40.75132	-111557.4545	42.9
112	-177.8401525	-111596.4741	39.28055	-111557.1935	43.1
113	-177.8375672	-111594.8518	38.02501	-111556.8268	43.5
114	-177.8375672	-111594.8518	38.02504	-111556.8268	43.5
115	-177.8401499	-111596.4725	39.5977	-111556.8748	43.5
116	-177.8381301	-111595.205	38.36427	-111556.8407	43.5
117	-177.831432	-111591.0019	36.98039	-111554.0215	46.3
118	-177.8396211	-111596.1406	39.64035	-111556.5003	43.8

119	-177.8396237	-111596.1423	39.64457	-111556.4977	43.8
120	-177.839264	-111595.9166	39.54551	-111556.371	44.0
121	-177.8351704	-111593.3478	38.01664	-111555.3311	45.0
122	-177.8340947	-111592.6728	37.79068	-111554.8821	45.5
123	-177.8340947	-111592.6728	37.79074	-111554.882	45.5
124	-177.8338196	-111592.5001	37.71559	-111554.7845	45.6
125	-177.8392149	-111595.8857	41.44956	-111554.4362	45.9
126	-177.8392149	-111595.8857	41.44955	-111554.4362	45.9
127	-177.8348976	-111593.1766	39.58168	-111553.5949	46.7
128	-177.8324581	-111591.6458	38.40423	-111553.2416	47.1
129	-177.8309317	-111590.688	37.82195	-111552.866	47.5
130	-177.8329416	-111591.9492	39.23196	-111552.7172	47.6
131	-177.8334079	-111592.2418	40.20869	-111552.0331	48.3
132	-177.828207	-111588.9782	36.89944	-111552.0787	48.3
133	-177.8312615	-111590.8949	39.56325	-111551.3317	49.0
134	-177.8260389	-111587.6177	36.27032	-111551.3474	49.0
135	-177.8261882	-111587.7114	36.78959	-111550.9218	49.4
136	-177.8300604	-111590.1412	39.49043	-111550.6508	49.7
137	-177.8298617	-111590.0165	39.79735	-111550.2192	50.1
138	-177.8246722	-111586.7601	37.4802	-111549.2799	51.1
139	-177.8246722	-111586.7601	37.48028	-111549.2798	51.1
140	-177.8250233	-111586.9804	37.86574	-111549.1146	51.2
141	-177.8265907	-111587.9639	39.65448	-111548.3095	52.0
142	-177.8242766	-111586.5118	38.78944	-111547.7224	52.6
143	-177.8242829	-111586.5158	38.79961	-111547.7162	52.6
144	-177.8226576	-111585.4959	38.49023	-111547.0056	53.3
145	-177.8169702	-111581.927	37.89375	-111544.0332	56.3
146	-177.8243736	-111586.5727	39.69193	-111546.8807	53.5
147	-177.8211693	-111584.5619	38.21828	-111546.3437	54.0
148	-177.8200139	-111583.8369	40.0148	-111543.8221	56.5
149	-177.8145902	-111580.4335	36.74746	-111543.686	56.7
150	-177.8145902	-111580.4335	36.7475	-111543.686	56.7
151	-177.8163863	-111581.5606	38.51154	-111543.049	57.3
152	-177.8180696	-111582.6169	39.65256	-111542.9643	57.4
153	-177.8139164	-111580.0107	37.84406	-111542.1666	58.2
154	-177.812173	-111578.9167	38.34152	-111540.5752	59.8
155	-177.8066561	-111575.4548	38.10441	-111537.3504	63.0
156	-177.8066561	-111575.4548	38.1044	-111537.3504	63.0

CHAPTER 8 Appendixes

Table 2: Relative energies of the 6-vertex *hypercloso*-$Si_2B_4H_4$

Sr.No	**E_{opt} (Hartree)**	**E_{opt} (kcal mol^{-1})**	**ZPE(kcal mol^{-1})**	**E_{opt}+ZPE**	**E_{rel}**
1	-109.4462161	-68678.59506	32.79349	-68645.80157	0.0
2	-109.4380531	-68673.4727	32.47212	-68641.00058	4.8
3	-109.4378808	-68673.36458	32.55061	-68640.81397	5.0
4	-109.4378808	-68673.36458	32.55045	-68640.81413	5.0
5	-109.4276824	-68666.96498	32.40216	-68634.56282	11.2
6	-109.425547	-68665.625	32.16318	-68633.46182	12.3
7	-109.4229079	-68663.96894	31.66198	-68632.30696	13.5
8	-109.4229079	-68663.96894	31.66202	-68632.30692	13.5
9	-109.4209616	-68662.74761	31.58141	-68631.1662	14.6
10	-109.4213661	-68663.00144	31.97293	-68631.02851	14.8
11	-109.4213661	-68663.00144	31.97323	-68631.02821	14.8
12	-109.4204077	-68662.40004	32.014	-68630.38604	15.4
13	-109.4176047	-68660.64113	31.15224	-68629.48889	16.3
14	-109.4173349	-68660.47182	32.59511	-68627.87671	17.9
15	-109.4146038	-68658.75803	31.68181	-68627.07622	18.7
16	-109.4132415	-68657.90317	31.18596	-68626.71721	19.1
17	-109.4115332	-68656.8312	30.82656	-68626.00464	19.8
18	-109.412706	-68657.56714	31.55322	-68626.01392	19.8
19	-109.4131302	-68657.83333	32.04741	-68625.78592	20.0
20	-109.4120706	-68657.16842	31.55325	-68625.61517	20.2
21	-109.4116221	-68656.88698	31.3421	-68625.54488	20.3
22	-109.4116751	-68656.92024	31.60939	-68625.31085	20.5
23	-109.4116751	-68656.92024	31.60944	-68625.3108	20.5
24	-109.4124538	-68657.40888	32.68604	-68624.72284	21.1
25	-109.4107328	-68656.32894	31.64814	-68624.6808	21.1
26	-109.4124538	-68657.40888	32.68628	-68624.7226	21.1
27	-109.408956	-68655.21398	31.56428	-68623.6497	22.2
28	-109.4068331	-68653.88184	31.15733	-68622.72451	23.1
29	-109.407541	-68654.32605	31.8335	-68622.49255	23.3
30	-109.4067618	-68653.8371	31.54659	-68622.29051	23.5
31	-109.4068127	-68653.86904	31.71527	-68622.15377	23.6
32	-109.4038834	-68652.03087	30.9701	-68621.06077	24.7
33	-109.4031522	-68651.57204	30.50583	-68621.06621	24.7
34	-109.4038834	-68652.03087	30.97001	-68621.06086	24.7
35	-109.404294	-68652.28853	31.32393	-68620.9646	24.8
36	-109.4038934	-68652.03715	31.43695	-68620.6002	25.2
37	-109.4020307	-68650.86828	30.46245	-68620.40583	25.4
38	-109.4027265	-68651.30491	31.01413	-68620.29078	25.5
39	-109.4022295	-68650.99303	30.99513	-68619.9979	25.8

40	-109.4025818	-68651.21411	31.83706	-68619.37705	26.4
41	-109.4028278	-68651.36847	31.99322	-68619.37525	26.4
42	-109.4028278	-68651.36847	31.99331	-68619.37516	26.4
43	-109.4025818	-68651.21411	31.83708	-68619.37703	26.4
44	-109.4007682	-68650.07605	31.47073	-68618.60532	27.2
45	-109.399904	-68649.53376	31.04386	-68618.4899	27.3
46	-109.399904	-68649.53376	31.04384	-68618.48992	27.3
47	-109.4000849	-68649.64728	31.58565	-68618.06163	27.7
48	-109.4003379	-68649.80604	31.83063	-68617.97541	27.8
49	-109.397582	-68648.07668	30.49765	-68617.57903	28.2
50	-109.3990331	-68648.98726	31.46704	-68617.52022	28.3
51	-109.3981245	-68648.4171	31.01651	-68617.40059	28.4
52	-109.3981245	-68648.4171	31.01654	-68617.40056	28.4
53	-109.3976715	-68648.13284	30.77422	-68617.35862	28.4
54	-109.3977327	-68648.17125	30.89883	-68617.27242	28.5
55	-109.3985896	-68648.70896	31.88183	-68616.82713	29.0
56	-109.3973848	-68647.95294	31.21123	-68616.74171	29.1
57	-109.3964993	-68647.39728	30.77615	-68616.62113	29.2
58	-109.397412	-68647.97	31.63806	-68616.33194	29.5
59	-109.3947099	-68646.27441	31.10251	-68615.1719	30.6
60	-109.3940145	-68645.83804	30.75619	-68615.08185	30.7
61	-109.3930568	-68645.23707	30.34536	-68614.89171	30.9
62	-109.3920796	-68644.62387	30.23188	-68614.39199	31.4
63	-109.3920827	-68644.62582	30.23089	-68614.39493	31.4
64	-109.3928405	-68645.10134	30.79799	-68614.30335	31.5
65	-109.3919789	-68644.56068	30.86855	-68613.69213	32.1
66	-109.391432	-68644.21749	30.98233	-68613.23516	32.6
67	-109.3907735	-68643.80428	30.7076	-68613.09668	32.7
68	-109.3907735	-68643.80428	30.70762	-68613.09666	32.7
69	-109.3915692	-68644.30359	31.55752	-68612.74607	33.1
70	-109.3897072	-68643.13517	30.72126	-68612.41391	33.4
71	-109.3890041	-68642.69396	30.32178	-68612.37218	33.4
72	-109.3890813	-68642.74241	30.41114	-68612.33127	33.5
73	-109.3879216	-68642.01468	30.18436	-68611.83032	34.0
74	-109.3879216	-68642.01468	30.18446	-68611.83022	34.0
75	-109.3873231	-68641.63912	30.12965	-68611.50947	34.3
76	-109.38677	-68641.29204	30.62433	-68610.66771	35.1
77	-109.3862344	-68640.95595	30.54627	-68610.40968	35.4
78	-109.3862344	-68640.95595	30.54629	-68610.40966	35.4
79	-109.3875769	-68641.79838	31.47998	-68610.3184	35.5
80	-109.3851859	-68640.298	30.83713	-68609.46087	36.3
81	-109.3839571	-68639.52692	30.0272	-68609.49972	36.3

82	-109.3844822	-68639.85643	30.67965	-68609.17678	36.6
83	-109.3844822	-68639.85643	30.67969	-68609.17674	36.6
84	-109.3840846	-68639.60693	30.6412	-68608.96573	36.8
85	-109.3840846	-68639.60693	30.64116	-68608.96577	36.8
86	-109.3834164	-68639.18763	31.01431	-68608.17332	37.6
87	-109.3819785	-68638.28533	31.40623	-68606.8791	38.9
88	-109.3793307	-68636.62381	30.85184	-68605.77197	40.0
89	-109.37687	-68635.07969	30.10809	-68604.9716	40.8
90	-109.3782508	-68635.94616	31.22835	-68604.71781	41.1
91	-109.3770191	-68635.17326	30.64591	-68604.52735	41.3
92	-109.3763764	-68634.76995	30.38733	-68604.38262	41.4
93	-109.3763007	-68634.72245	30.34279	-68604.37966	41.4
94	-109.3763007	-68634.72245	30.34279	-68604.37966	41.4
95	-109.3770154	-68635.17093	30.86723	-68604.3037	41.5
96	-109.3759404	-68634.49636	30.54439	-68603.95197	41.8
97	-109.3760281	-68634.55139	30.57341	-68603.97798	41.8
98	-109.3760249	-68634.54938	30.57841	-68603.97097	41.8
99	-109.3752723	-68634.07712	30.31557	-68603.76155	42.0
100	-109.3746772	-68633.70369	30.55678	-68603.14691	42.7
101	-109.3738297	-68633.17188	30.11412	-68603.05776	42.7
102	-109.3728305	-68632.54487	29.60626	-68602.93861	42.9
103	-109.3737692	-68633.13391	30.38546	-68602.74845	43.1
104	-109.3722629	-68632.18869	30.80255	-68601.38614	44.4
105	-109.3717344	-68631.85705	30.51892	-68601.33813	44.5
106	-109.3710507	-68631.42802	30.40113	-68601.02689	44.8
107	-109.3716024	-68631.77422	30.98608	-68600.78814	45.0
108	-109.3716042	-68631.77535	30.98934	-68600.78601	45.0
109	-109.3702483	-68630.92451	30.43402	-68600.49049	45.3
110	-109.3702483	-68630.92451	30.43398	-68600.49053	45.3
111	-109.3702483	-68630.92451	30.43395	-68600.49056	45.3
112	-109.3690554	-68630.17595	30.69991	-68599.47604	46.3
113	-109.3688012	-68630.01644	30.52525	-68599.49119	46.3
114	-109.368811	-68630.02259	30.52877	-68599.49382	46.3
115	-109.368811	-68630.02259	30.52884	-68599.49375	46.3
116	-109.368811	-68630.02259	30.52884	-68599.49375	46.3
117	-109.3674968	-68629.19792	30.04493	-68599.15299	46.6
118	-109.3674502	-68629.16868	30.29375	-68598.87493	46.9
119	-109.367088	-68628.94139	30.79068	-68598.15071	47.7
120	-109.3662179	-68628.39539	30.288	-68598.10739	47.7
121	-109.3647154	-68627.45256	30.67643	-68596.77613	49.0
122	-109.3609919	-68625.11603	29.45254	-68595.66349	50.1
123	-109.3599354	-68624.45306	29.30397	-68595.14909	50.7

124	-109.3599354	-68624.45306	29.30397	-68595.14909	50.7
125	-109.361884	-68625.67583	30.75127	-68594.92456	50.9
126	-109.3610085	-68625.12644	30.35961	-68594.76683	51.0
127	-109.3629207	-68626.32637	31.63208	-68594.69429	51.1
128	-109.3615252	-68625.45068	30.72922	-68594.72146	51.1
129	-109.3550399	-68621.38109	29.02353	-68592.35756	53.4
130	-109.3569671	-68622.59042	30.26017	-68592.33025	53.5
131	-109.3562564	-68622.14445	29.98839	-68592.15606	53.6
132	-109.3548915	-68621.28797	29.5443	-68591.74367	54.1
133	-109.3554284	-68621.62488	30.0123	-68591.61258	54.2
134	-109.3574501	-68622.89351	31.25124	-68591.64227	54.2
135	-109.3569927	-68622.60649	31.22267	-68591.38382	54.4
136	-109.3529425	-68620.06495	30.25897	-68589.80598	56.0
137	-109.35316	-68620.20143	30.51695	-68589.68448	56.1
138	-109.3531585	-68620.20049	30.52273	-68589.67776	56.1
139	-109.3530219	-68620.11477	30.67772	-68589.43705	56.4
140	-109.3532319	-68620.24655	30.8505	-68589.39605	56.4
141	-109.3507046	-68618.66064	29.81806	-68588.84258	57.0
142	-109.3500879	-68618.27366	29.60477	-68588.66889	57.1
143	-109.3512498	-68619.00276	30.952	-68588.05076	57.8
144	-109.3496179	-68617.97873	29.94702	-68588.03171	57.8
145	-109.3493144	-68617.78828	30.90498	-68586.8833	58.9
146	-109.3487897	-68617.45902	30.69649	-68586.76253	59.0
147	-109.3487964	-68617.46323	30.70538	-68586.75785	59.0
148	-109.3450654	-68615.12199	30.08362	-68585.03837	60.8
149	-109.3428254	-68613.71637	29.64434	-68584.07203	61.7
150	-109.3428254	-68613.71637	29.64445	-68584.07192	61.7
151	-109.3358971	-68609.36879	30.61003	-68578.75876	67.0
152	-109.3358971	-68609.36879	30.61012	-68578.75867	67.0
153	-109.3321454	-68607.01456	28.99649	-68578.01807	67.8
154	-109.3324796	-68607.22427	29.62419	-68577.60008	68.2
155	-109.334669	-68608.59814	31.20952	-68577.38862	68.4
156	-109.3250412	-68602.5566	30.83153	-68571.72507	74.1
157	-109.3242999	-68602.09143	30.94326	-68571.14817	74.7

Table 3: Relative energies of the 6-vertex *hypercloso*-$Ge_2B_4H_4$

Sr.No	**E_{opt} (Hartree)**	**E_{opt} (kcal mol^{-1})**	**ZPE(kcal mol^{-1})**	**E_{opt}+ZPE**	**E_{rel}**
1	-109.2550648	-68558.64571	31.44188	-68527.20383	0.0
2	-109.247555	-68553.93324	31.25289	-68522.68035	4.5
3	-109.247555	-68553.93324	31.25289	-68522.68035	4.5
4	-109.2418512	-68550.35405	30.33149	-68520.02256	7.2
5	-109.2418512	-68550.35405	30.33142	-68520.02263	7.2
6	-109.2398183	-68549.07838	30.92424	-68518.15414	9.0
7	-109.2370467	-68547.33917	31.71035	-68515.62882	11.6
8	-109.2370467	-68547.33917	31.71021	-68515.62896	11.6
9	-109.2342241	-68545.56796	30.17157	-68515.39639	11.8
10	-109.2314556	-68543.8307	30.66217	-68513.16853	14.0
11	-109.2284634	-68541.95307	30.81775	-68511.13532	16.1
12	-109.2284634	-68541.95307	30.81774	-68511.13533	16.1
13	-109.2275989	-68541.41059	30.38179	-68511.0288	16.2
14	-109.2275989	-68541.41059	30.38179	-68511.0288	16.2
15	-109.2277625	-68541.51325	30.84145	-68510.6718	16.5
16	-109.2267901	-68540.90306	30.75578	-68510.14728	17.1
17	-109.2267901	-68540.90306	30.75578	-68510.14728	17.1
18	-109.2241687	-68539.2581	29.55462	-68509.70348	17.5
19	-109.2241687	-68539.2581	29.55462	-68509.70348	17.5
20	-109.219648	-68536.42132	31.57335	-68504.84797	22.4
21	-109.219648	-68536.42132	31.57335	-68504.84797	22.4
22	-109.2168805	-68534.68468	31.03464	-68503.65004	23.6
23	-109.21213	-68531.7037	29.5183	-68502.1854	25.0
24	-109.213292	-68532.43286	30.23681	-68502.19605	25.0
25	-109.213292	-68532.43286	30.2368	-68502.19606	25.0
26	-109.2125115	-68531.94309	30.28583	-68501.65726	25.5
27	-109.2127311	-68532.08089	30.52996	-68501.55093	25.7
28	-109.2111727	-68531.10298	30.48696	-68500.61602	26.6
29	-109.2074548	-68528.76996	30.37756	-68498.3924	28.8
30	-109.2057551	-68527.70338	29.76162	-68497.94176	29.3
31	-109.2047169	-68527.0519	29.5049	-68497.547	29.7
32	-109.2050339	-68527.25082	30.2733	-68496.97752	30.2
33	-109.2035939	-68526.34721	29.42063	-68496.92658	30.3
34	-109.2050278	-68527.24699	30.43465	-68496.81234	30.4
35	-109.203575	-68526.33535	29.97106	-68496.36429	30.8
36	-109.2028569	-68525.88473	29.96993	-68495.9148	31.3
37	-109.2027051	-68525.78948	29.89913	-68495.89035	31.3
38	-109.2017125	-68525.16661	29.89324	-68495.27337	31.9
39	-109.2001627	-68524.1941	30.74061	-68493.45349	33.8
40	-109.2001627	-68524.1941	30.74061	-68493.45349	33.8
41	-109.1989108	-68523.40852	30.43711	-68492.97141	34.2
42	-109.1989108	-68523.40852	30.43711	-68492.97141	34.2

43	-109.1980076	-68522.84175	30.13597	-68492.70578	34.5
44	-109.1965059	-68521.89942	29.69962	-68492.1998	35.0
45	-109.1958682	-68521.49925	29.41283	-68492.08642	35.1
46	-109.1958682	-68521.49925	29.41284	-68492.08641	35.1
47	-109.1958682	-68521.49925	29.41282	-68492.08643	35.1
48	-109.1944439	-68520.60549	28.87708	-68491.72841	35.5
49	-109.1932199	-68519.83742	28.87516	-68490.96226	36.2
50	-109.1947764	-68520.81414	30.24643	-68490.56771	36.6
51	-109.1938661	-68520.24292	29.93282	-68490.3101	36.9
52	-109.191815	-68518.95583	28.6169	-68490.33893	36.9
53	-109.1925195	-68519.39791	30.24306	-68489.15485	38.0
54	-109.1925195	-68519.39791	30.24317	-68489.15474	38.0
55	-109.1899216	-68517.7677	29.31042	-68488.45728	38.7
56	-109.1899216	-68517.7677	29.31042	-68488.45728	38.7
57	-109.1911988	-68518.56916	30.41466	-68488.1545	39.0
58	-109.1893584	-68517.41429	29.74608	-68487.66821	39.5
59	-109.1874119	-68516.19284	28.81074	-68487.3821	39.8
60	-109.1902237	-68517.95727	30.11805	-68487.83922	39.4
61	-109.1874119	-68516.19284	28.81077	-68487.38207	39.8
62	-109.1888051	-68517.06709	30.17773	-68486.88936	40.3
63	-109.186443	-68515.58485	28.79297	-68486.79188	40.4
64	-109.1861292	-68515.38793	29.15501	-68486.23292	41.0
65	-109.1836833	-68513.85311	28.6855	-68485.16761	42.0
66	-109.1836833	-68513.85311	28.68549	-68485.16762	42.0
67	-109.1836833	-68513.85311	28.6855	-68485.16761	42.0
68	-109.1836833	-68513.85311	28.6855	-68485.16761	42.0
69	-109.1848595	-68514.59118	29.3427	-68485.24848	42.0
70	-109.1841893	-68514.17063	29.20617	-68484.96446	42.2
71	-109.1841893	-68514.17063	29.20616	-68484.96447	42.2
72	-109.1829455	-68513.39013	28.80579	-68484.58434	42.6
73	-109.1819437	-68512.76149	28.5715	-68484.18999	43.0
74	-109.1825354	-68513.13279	29.03435	-68484.09844	43.1
75	-109.1814538	-68512.45407	29.55063	-68482.90344	44.3
76	-109.1795643	-68511.26839	28.52877	-68482.73962	44.5
77	-109.1808647	-68512.08441	29.67089	-68482.41352	44.8
78	-109.1784516	-68510.57016	28.66173	-68481.90843	45.3
79	-109.1784494	-68510.56878	28.6592	-68481.90958	45.3
80	-109.1788664	-68510.83045	29.00464	-68481.82581	45.4
81	-109.1795643	-68511.26839	28.5288	-68482.73959	44.5
82	-109.1770747	-68509.70614	28.76249	-68480.94365	46.3
83	-109.175673	-68508.82656	28.67021	-68480.15635	47.0
84	-109.176091	-68509.08886	29.15031	-68479.93855	47.3
85	-109.174236	-68507.92483	28.71869	-68479.20614	48.0
86	-109.1739906	-68507.77084	29.09111	-68478.67973	48.5
87	-109.1737243	-68507.60374	29.17808	-68478.42566	48.8

88	-109.1729665	-68507.12821	28.85041	-68478.2778	48.9
89	-109.1728009	-68507.02429	29.3725	-68477.65179	49.6
90	-109.1710297	-68505.91285	28.70701	-68477.20584	50.0
91	-109.1698426	-68505.16793	29.43361	-68475.73432	51.5
92	-109.1666198	-68503.14559	28.37987	-68474.76572	52.4
93	-109.1683783	-68504.24907	29.62631	-68474.62276	52.6
94	-109.1672353	-68503.53182	28.89365	-68474.63817	52.6
95	-109.1672353	-68503.53182	28.89365	-68474.63817	52.6
96	-109.1683798	-68504.25001	29.62564	-68474.62437	52.6
97	-109.1636513	-68501.28283	28.28541	-68472.99742	54.2
98	-109.1632609	-68501.03785	28.76856	-68472.26929	54.9
99	-109.1628163	-68500.75886	28.80598	-68471.95288	55.3
100	-109.161355	-68499.84188	29.49924	-68470.34264	56.9
101	-109.1594693	-68498.65858	28.49458	-68470.164	57.0
102	-109.1594693	-68498.65858	28.49458	-68470.164	57.0
103	-109.1595433	-68498.70502	28.67297	-68470.03205	57.2
104	-109.160346	-68499.20872	29.43541	-68469.77331	57.4
105	-109.1591073	-68498.43142	28.70311	-68469.72831	57.5
106	-109.1596406	-68498.76607	29.0703	-68469.69577	57.5
107	-109.1588287	-68498.2566	28.73295	-68469.52365	57.7
108	-109.1588287	-68498.2566	28.73295	-68469.52365	57.7
109	-109.1584951	-68498.04726	28.73703	-68469.31023	57.9
110	-109.1581668	-68497.84125	28.99757	-68468.84368	58.4
111	-109.1581668	-68497.84125	28.99758	-68468.84367	58.4
112	-109.1570317	-68497.12896	28.62882	-68468.50014	58.7
113	-109.1565287	-68496.81332	29.11549	-68467.69783	59.5
114	-109.1543433	-68495.44196	28.59235	-68466.84961	60.4
115	-109.1536365	-68494.99844	28.54765	-68466.45079	60.8
116	-109.1523832	-68494.21198	28.50333	-68465.70865	61.5
117	-109.1523971	-68494.2207	29.1883	-68465.0324	62.2
118	-109.151706	-68493.78703	28.99093	-68464.7961	62.4
119	-109.1507305	-68493.1749	29.1602	-68464.0147	63.2
120	-109.1507305	-68493.1749	29.1602	-68464.0147	63.2
121	-109.1480865	-68491.51576	27.94503	-68463.57073	63.6
122	-109.1486755	-68491.88536	28.43405	-68463.45131	63.8
123	-109.1495022	-68492.40413	29.22081	-68463.18332	64.0
124	-109.1503762	-68492.95257	29.88155	-68463.07102	64.1
125	-109.1471628	-68490.93613	28.51561	-68462.42052	64.8
126	-109.1471628	-68490.93613	28.51561	-68462.42052	64.8
127	-109.1478182	-68491.3474	29.45194	-68461.89546	65.3
128	-109.1463977	-68490.45602	30.01654	-68460.43948	66.8
129	-109.1442047	-68489.07989	28.85468	-68460.22521	67.0
130	-109.140489	-68486.74825	27.72645	-68459.0218	68.2
131	-109.140489	-68486.74825	27.72645	-68459.0218	68.2
132	-109.1383832	-68485.42684	29.12036	-68456.30648	70.9

133	-109.136492	-68484.24009	28.80776	-68455.43233	71.8
134	-109.1336213	-68482.4387	28.23433	-68454.20437	73.0
135	-109.1336213	-68482.4387	28.23433	-68454.20437	73.0
136	-109.1317847	-68481.28622	27.54367	-68453.74255	73.5
137	-109.1317847	-68481.28622	27.54365	-68453.74257	73.5
138	-109.1319415	-68481.38461	27.67678	-68453.70783	73.5
139	-109.1282816	-68479.08799	28.43755	-68450.65044	76.6
140	-109.1287788	-68479.39998	29.20228	-68450.1977	77.0
141	-109.128634	-68479.30912	29.06673	-68450.24239	77.0
142	-109.1259499	-68477.62482	28.56918	-68449.05564	78.1
143	-109.1259055	-68477.59696	28.85694	-68448.74002	78.5
144	-109.1243149	-68476.59884	28.1496	-68448.44924	78.8
145	-109.124851	-68476.93525	29.07903	-68447.85622	79.3
146	-109.1247304	-68476.85957	29.00581	-68447.85376	79.4
147	-109.1196678	-68473.68274	27.64722	-68446.03552	81.2
148	-109.1186906	-68473.06954	27.9183	-68445.15124	82.1
149	-109.1122711	-68469.04124	28.25133	-68440.78991	86.4
150	-109.1122711	-68469.04124	28.25133	-68440.78991	86.4
151	-109.1024569	-68462.88273	29.64611	-68433.23662	94.0
152	-109.0988303	-68460.607	29.23075	-68431.37625	95.8
153	-109.0975569	-68459.80793	29.3464	-68430.46153	96.7