Ab Initio Studies on Disubstituted *closo*-Icosahedral Heteroboranes, $X_2B_{10}H_{10}$ (X = CH, SiH, N, P, and Sb)☆

Eluvathingal D. Jemmis*[a], Boggavarapu Kiran[a], and Dewitt Coffey, Jr.*[b]

School of Chemistry, University of Hyderabad[a],
Hyderabad 500 046, India
E-Mail: edjsc@uohyd.ernet.in

Department of Chemistry, San Diego State University[b],
San Diego, California 92182-0328, USA
E-Mail: dcoffey@sciences.sdsu.edu

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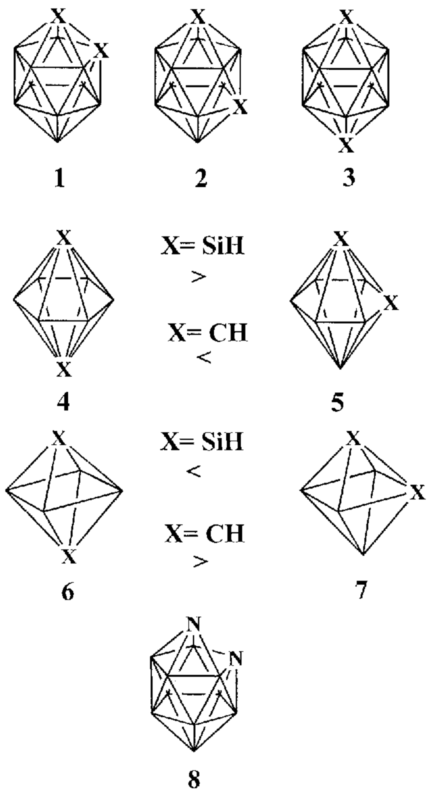
Ab initio theoretical studies on $X_2B_{10}H_{10}$ (X = CH, SiH, N, P and Sb) have been done for all the three possible isomers. Unlike lower-vertex heteroboranes, all the hetero derivatives have shown similar trends n the relative stabilities, the 1,12-isomer being more stable followed by 1,7- and 1,2-isomers, except for N and Sb. No conventional 1,2-isomer for N could be found. Instead, a new *nido* isomer which is 18.1 kcal/mol higher in energy than the most stable isomer has been loctaed. Any hetero group substitution to icosahedral $B_{12}H_{12}^{2-}$ is found to be thermodynamically destabilizing. However, the Nucleus Independent Chemical Shift criterion shows that all compounds, except for **8**, have similar aromaticity.

Polyhedral boranes have been a fascinating area of research for many years. The icosahedral $B_{12}H_{12}^{2-}$ is one of the earliest known stable dianions[1]. Several recent developments have added a renewed interest in the chemistry of boranes. New icosahedral monoanions have been synthesized and used as weakly nucleophilic units to stabilize naked cations[2]. The neutral analogs of $B_{12}H_{12}^{2-}$ such as carboranes have also provided exciting new chemistry. Following the similarity of benzene and *o*-carborane[3], an equivalent of benzyne (1,2-dehydrobenzene), 1,2-$C_2B_{10}H_{10}$ has been synthesized[4]. Properties of 1,2-$C_2B_{10}H_{10}$ are comparable to those of benzyne[5]. Other heterosubstituted icosahedral boranes have been targets of synthesis. A disila analog of *o*-carborane, 1,2-$(SiMe)_2B_{10}H_{10}$, has been obtained recently[6]. The dianions $XB_{11}H_{11}^{2-}$ and the monoanions $CH_3XB_{11}H_{11}^{1-}$ (X = Si, Ge, and Sn) are also known[7]. Several neutral derivatives of 1,2-$X_2B_{10}H_{10}$ and 1,2-$XYB_{10}H_{10}$ (X and Y = P, As, Sb, and Pb), $CH_3SiSnB_{10}H_{10}$, and $CH_3SiSbB_{10}H_{10}$ have been synthesized[8]. Incorporation of nitrogen as a heterovertex in the boron polyhedral cage is not common. So far only one icosahedral azaborane, 1-$NB_{11}H_{12}$, has yielded to synthesis[9].

More than one hetero group substitution in the icosahedral skeleton brings in the interesting question of isomer stabilities. For disubstituted icosahedral systems the three possible isomers are *ortho* (1,2-), **1**, *meta* (1,7-), **2**, and *para* (1,12-), **3**, prefixes following the system used in the 2-dimensionally aromatic benzene derivatives. The distinction to be noted here is that in the *ortho*, *meta*, and *para* benzenes, the carbon skeleton is intact. The *ortho*, *meta*, and *para* nomenclature in the icosahedral boranes refer to the replacement of the BH atoms with other hetero atoms. The most studied disubstituted boranes are the carboranes. The three isomers of $C_2B_{10}H_{12}$ have been known for a long time and are well characterized structurally. Thermal isomerization and equilibrium studies involving the three species are known. The 1,2-isomer, **1CH** (structure **1** with X = CH, unlabeled vertices refer to BH) is the least stable one and isomerizes to the next stable *meta* isomer, **2CH**, at 500°C. This in turn goes to the most stable 1,12-isomer above 615°C[10]. Theoretical studies at various levels have confirmed these relative energies[11]. The disilaborane, 1,2-$Si_2B_{10}H_{12}$ is much more reactive, the only known derivative $(SiMe)_2B_{10}H_{10}$ decomposes above 230°C. The *ortho* isomer of $P_2B_{10}H_{10}$ is also known but requires temperatures in the range of 560−590°C for conversion to the 1,7-isomer[12].

Several strategies have been suggested to explain the relative stabilities of the positional isomers of the dihetero boranes all of which adhere to the same electron count. The most dominant hetero substituent in borane chemistry has been carbon and hence these rules have been based predominantly on carboranes. Early on Williams suggested that the isomer with the more electronegative atoms as far as possible will be more favourable[13]. While this was found to be successful for many carboranes, there were ambiguities for other heterosubstituted boranes. Gimarc's topological charge stabilization model suggested that the electronegative atoms tend to occupy the places of maximum charge density calculated for the parent borane[14]. Though this model has done well in several inorganic ring systems and carbonates it failed to predict the relative stabilities of lower-vertex heteroboranes[15]. One of us suggested a cri-



terion based on the orbital compatibility which matches the diffuse nature of the orbitals of the hetero groups vis-à-vis the skeletal rings[16]. This is successful in predicting the relative stabilities of several hetero substituted lower-vertex boranes. Especially important were the correct predictions that the order of the relative of stabilities of 5-, 6-, and 7-vertex *closo* boranes will be reversed on going to the corresponding silaboranes[17].

Is the concept of orbital compatibility applicable to higher-vertex boranes as well? What is in store for other substituents such as N, P, and Sb. In the present study the structures and relative stabilities of *closo*-$X_2B_{10}H_{10}$ (X = CH, SiH, P, N, and Sb) are examined by ab initio methods. Another point of interest is the aromaticity of *closo* boranes. Despite the difficulty in quantifying aromaticity, several attempts have been made in that direction. Of all the criteria in use, methods based on magnetic properties, in particular Nucleus Independent Chemical Shift (NICS) introduced by Schleyer and co-workers has been shown to be very useful[18]. NICS has been used in the present study to estimate the relative aromaticity of various heteroboranes.

Method of Calculation

Hartree-Fock calculations using 6-31G* basis set has been used for all the structures considered except for isomers of Sb where the LANL1DZ basis set is employed. Frequency calculations are done on all the isomers to ascertain the nature of the stationary points except for the isomers of $Sb_2B_{10}H_{10}$. All the isomers reported correspond to minima on the potential energy surface. Single point MP2 calculations were done on HF geometries. In the discussion MP2 relative energies are used unless otherwise specified. All the calculations were performed by the Gaussian94 series of programs[19].

Results and Discussion

Table 1 gives the relative energies of the *closo* hetero-icosahedral systems, $X_2B_{10}H_{10}$ (X = N, CH, SiH, P and Sb). In agreement with the earlier theoretical and experimental studies, the 1,12-isomer of $C_2B_{10}H_{12}$ is more stable followed by the 1,7- and 1,2-isomers. The C−C bond length in **1CH** is 1.609 Å (1.624 Å, X-ray) which is longer than the normal $Csp^3{-}Csp^3$ distance of 1.540 Å. This bond length is intermediate between the C−C bond lengths of **7CH** (1.538 Å) and **5CH** (1.628 Å). The demand of an icosahedral skeleton cannot be met by the regular C−C bond length, which is smaller than the normal B−B bond. This causes unusual strain in the 1,2-isomer resulting in stretching the C−C bond. This is also reflected in the Wiberg Bond Index (WBI) 0.752 of C−C bond in **1CH**. However, the stretched C−C bond is not very reactive. Numerous derivatives of 1,2-$C_2B_{10}H_{12}$ are known to be very stable and to participate in reactions without the rupture of the C−C bond. In general, both 1,7- and 1,12-isomers differ by only a small amount of energy due to the structural similarity between them.

Table 1. Total energies (a.u.) and relative energies (kcal/mol) (ZPE-corrected) (MP2 values in parenthesis) of disubstituted icosahedral heteroboranes $X_2B_{10}H_{10}$

	HF/6-31G*	MP2//HF	ZPE(NIMAG)	RE
1BH	−303.28332	−304.44372	100.10 (0)	–
8[a]	−361.54432	−362.80956	97.44 (0)	18.0 (23.0)
2N	−361.57306	−362.84330	100.30 (0)	0.0 (1.8)
3N	−361.57188	−362.84621	100.25 (0)	0.8 (0.0)
1CH	−329.62084	−330.83000	117.54 (0)	20.3 (22.8)
2CH	−329.64938	−330.85539	117.83 (0)	2.4 (4.2)
3CH	−329.64938	−330.86116	117.91 (0)	0.0 (0.0)
1P	−934.17726	−935.36600	96.21 (0)	10.1 (8.4)
2P	−934.18963	−935.37608	96.38 (0)	2.3 (2.1)
3P	−934.19336	−935.39935	96.45 (0)	0.0 (0.0)
1SiH	−831.69385	−832.82773	106.12 (0)	4.2 (3.6)
2SiH	−831.69858	−832.83203	106.13 (0)	1.2 (0.9)
3SiH	−831.70048	−832.83349	106.16 (0)	0.0 (0.0)
1Sb	−263.04968	–	–	0.0
2Sb	−263.04587	–	–	1.8
3Sb	−263.04869	–	–	0.6

[a] **1N** collapses to **8**.

The reversal of trends observed on going from C to Si in the lower-vertex (5, 6, and 7) boranes is not seen with the icosahedral skeleton. The relative energies of $Si_2B_{10}H_{12}$ fall in a narrow range (Table 1) but the trends are similar to those of carboranes. This is not contrary to the overlap matching criteria. The highly symmetric icosahedral skeleton provides the same five-membered ring when any vertex is removed. Substitution of one hetero atom in the rigid skeleton does not change this picture substantially. The Si−Si bond length (2.308 Å, X-ray[6]) in **1SiH** is reproduced at the present theoretical level. This bond length is slightly shorter than the normal Si−Si bond length, 2.348 Å, and longer than the Si−Si bond length in **7SiH** (2.106 Å) and

5SiH (2.228 Å). This compressed Si−Si distance is not an indication of the strength of the bond, as the WBI is only 0.508, reflecting the participation of the Si−Si σ bond in the skeletal multicentre bonding. In contrast to the C−C stretching in **1CH**, the Si atoms are forced to be closer by the rigid icosahedral framework in **1SiH**. However, **1SiH** is thermally less stable than **1CH**; at 500°C **1CH** rearranges to **2CH** but above 230°C **1SiMe** decomposes. Despite the similarity between **1CH** and **1SiH**, they differ substantially in the charge distribution. Consistent with the electronegativity differences, there is a polarization of the negative charge on the carbon atoms in **1CH**, while the positive charge is localized at the silicon atoms in **1SiH**. This difference in charge distribution is reflected in their reactivity towards electrophiles and nucleophiles. The dimethyl derivative of **1SiH** is attacked by nucleophilic bases resulting in the loss of a MeSi vertex, whereas in **1CH** a B atom adjacent to the two C atoms reacts with the nucleophiles[6]. The remaining two isomers, **2SiH** and **3SiH**, have not been synthesized. Our theoretical results indicate that both the isomers are very close in energy and should be amenable to synthesis.

Similar trends in the relative stabilities continue for group-15 elements as well. The 1,12-isomer of $P_2B_{10}H_{10}$ is the most stable one followed by the 1,7- and 1,2-isomers. However, the energy difference between **1P** and **3P** is half of what is found for the corresponding carboranes (Table 1). The P−P bond length in **1P** of 2.293 Å, compares well with the X-ray value of 2.284 Å[12]. This length is slightly longer than the normal P−P bond length of 2.258 Å; while the corresponding bond length in 1,2-$P_2B_4H_4$ is 2.222 Å. The WBI of P−P bond in **1P** is 0.5081.

One interesting aspect concerning the X−X internuclear distances in 1,2-disubstituted hetero boranes is that these increase or decrease in length from their standard values to accommodate the boron skeleton. The C−C intermolecular distance in **1CH** is elongated compared to the normal C−C distance due to the very small size of the CH group vis-à-vis BH. The size of the orbitals of the P is close to that of the BH, and there is only a slight elongation in the P−P distance in **1P**. On the other hand, the SiH group is slightly larger than the BH group. Consequently, there is a compression of the Si−Si internuclear distance in **1SiH**. These size differences are also reflected in the relative stabilities of the isomers. As the difference between the size of the hetero group vis-à-vis BH decreases, the relative stabilities of the isomers also decrease. The dramatic effect of the size difference of the hetero atom can be seen with nitrogen as substituent in the icosahedral skeleton.

Unlike **1P**, we could not locate a stationary point corresponding to the conventional 1,2-isomer of $N_2B_{10}H_{10}$. The C−C distance in **1CH** is calculated to be 1.609 Å (1.624 Å from X-ray). This is already too short in comparison to the B−B distance (1.795 Å) expected for the icosahedral skeleton. The N−N distance in **1N**, expected to be much shorter, is not able to withstand the strain of the icosahedral skeleton. Despite the electron count appropriate for a *closo* arrangement, the N−N distance in **1N** on optimization is stretched to 2.453 Å, with practically no bonding interaction (WBI = 0.036). This is not comparable to the *nido* structure of the B_4N_2 skeleton[20]. Structure **8** is 18.1 kcal/mol higher in energy than the 1,7-isomer. At the HF/6-31G* level of theory the 1,7-isomer is more stable than the 1,12-isomer. Single point calculations at the MP2/6-31G*//HF/6-31G* level indicate that the 1,7-isomer is lower in energy than the 1,12-isomer. Obviously, these two isomers are very close in energy.

When the X group is too diffuse compared to BH, as in $Sb_2B_{10}H_{10}$, all the isomers are found to be of equal energy (Table 1). The 1,2-isomer is slightly more stable than the 1,12-isomer. The 1,7-isomer is the least stable one. Unlike lower-vertex heteroboranes, the icosahedral cage absorbs differences between the various hetero groups until the difference becomes too large as in the case of nitrogen and antimony.

Bonding in $X_2B_{10}H_{10}$ Systems

Icosahedral $B_{12}H_{12}^{2-}$ is exceptionally stable. A three-dimensional network comprising of icosahedral B_{12} can be seen as a part of the stable form of elemental boron[21]. It has been argued that BH is perfectly suited as a "cap" to the B_5 plane of icosahedral skeleton[22]. Let us consider the nature of the p orbitals in any of the B_5 rings in the skeleton. The geometry of the icosahedron does not permit the B−H hydrogen atoms to lie in the B_5 plane. They are bent by an angle of 26.6° towards the "cap". This bending rehybridizes the p orbitals of the B_5 plane and orient them towards the cap. This is absent in either $B_6H_6^{2-}$ or $B_7H_7^{2-}$, where the p orbitals are perpendicular to B_4 and B_5 planes, respectively. Thus, the effective diffuse nature of the B_5 plane in an icosahedron is intermediate between B_4 and B_5 rings, which favours the BH group to fit exactly with the ring. This is one of the reasons attributed for the extraordinary stability of $B_{12}H_{12}^{2-}$. Thus, any other cap which is different from B−H should destabilize the icosahedral cage. The extent of destabilization again depends on how much the size of the hetero group differs from B−H. This can be understood from the following equation (1).

$$B_{12}H_{12}^{2-} + 2\,XH_3 \rightarrow 1{,}12\text{-}X_2B_{10}H_{10} + 2\,BH_4^- \qquad (1)$$

X	**CH**	**SiH**	**P**	**N**
Δ*E* [kcal/mol]	**56.67**	**64.57**	**34.94**	**94.10**

Clearly, all the hetero caps are destabilizing, two, N and SiH, being the worst; the smallest and the largest in relation to BH. This is because the orbitals of N are too small and those SiH too large to effectively cap B_5 ring of the icosahedron. This is to be contrasted with the similar kind of equations for $B_6H_6^{2-}$ and $B_7H_7^{2-}$ [eq. (2) and (3)].

$$B_6H_6^{2-} + 2\,XH_3 \rightarrow 1{,}6\text{-}X_2B_4H_4 + 2\,BH_4^- \qquad (2)$$

X	**CH**	**SiH**	**P**
Δ*E* [kcal/mol]	**−36.67**	**−11.11**	**−72.45**

$$B_7H_7^{2-} + 2\,XH_3 \rightarrow 1{,}7\text{-}X_2B_5H_5 + 2\,BH_4^- \qquad (3)$$

X	**CH**	**SiH**	**P**
Δ*E* [kcal/mol]	**41.72**	**−20.40**	**−37.67**

For the octahedron, substitution by hetero groups is exothermic, more so for phosphorus. Pentagonal-bipyramidal substitution by carbon is endothermic, because CH is too small to cap a five-membered ring, but is exothermic for substitution by silicon and phosphorus (eq. 3). Both 1,6-$N_2B_4H_4$ and 1,7-$N_2B_5H_5$ are higher order stationary points for nitrogen; therefore were not considered. The conclusion from the above equations is that any substitution in the icosahedra skeleton is destabilizing and the reverse is true for the octahedron.

Recent developments in the area of magnetic resonance led to new methods to quantify aromaticity[23]. One such cirteria is Nucleus Independent Chemical Shift (NICS). It is defined as the negative of the absolute magnetic shielding computed at the geometrical centre of the ring[18]. Thus, aromatic rings have negative NICS values (diatropic) and antiaromatic compounds have positive values (paratropic). The advantage of NICS is that, unlike several other criteria, no reference compounds need to be considered. The calculated NICS values of various molecules are given in Table 2. Surprisingly, NICS values are similar for all of the isomers except **1N**. This is expected because **1N** has a *nido* structure and hence delocalization will be less. Thus, aromaticity is not affected by the hetero atom substitution but we have seen that hetero substitution is destabilizing thermodynamically. There is a growing body of evidence to support the fact that the thermodynamic stability need to be associated with aromaticity; strain and other factors also influence thermodynamic stabilities. The geometry of hetero-substituted icosahedral systems tend to adjust so as to retain maximum delocalization possible.

Table 2. NICS (Nucleus Independent Chemical Shifts) of various isomers[a]

Isomer	1,2	1,7	1,12
BH	- 34.27		
N	- 9.19	- 31.79	- 35.21
CH	- 34.18	- 34.16	- 35.37
P	- 32.17	- 31.09	- 29.66
SiH	- 34.26	- 34.56	- 34.21

[a] The NICS values were calculated by placing the ghost atom at the origin; the coordinates were taken from the Gaussian 94 standard orientation for the corresponding molecule.

In conclusion, the high symmetry of $B_{12}H_{12}^{2-}$ favours no substitution. Any heteroatom substitution is destabilizing. It appears that the hetero group substitution does not affect the aromaticity and the geometries tend to adjust to retain maximum delocalization. The finer differences observed in lower-vertex boranes for C, Si, and other elements are found to be absent in the $X_2B_{10}H_{10}$ systems.

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