Notes

Isomer Preferences in 5-, 6-, and 7-Vertex Monoheteroboranes—A Theoretical Study

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closo-Carboranes form one of the most widely studied class of compounds among polyhedral boranes with heteroatom substitution in the boron cage.[1] Other members in this series include the *closo*-aza-[2] and *closo*-phosphaboranes.[3] Many of these compounds have two heteroatoms of the same kind apart from boron, occupying the vertices of the polyhedral cage. Recently, synthesis of *closo*-boranes with only one heteroatom incorporated in the polyhedral boron cage has evoked considerable interest.[1b,4] These are mainly based on 10 and 12 vertex cages with B_9H_9NH,[5] B_9H_9S,[6] $B_{11}H_{11}NH$,[7] $B_{11}H_{11}PR$,[8] and $B_{11}H_{11}S$[9] as representative examples. There has been no report on the synthesis of small vertex mono-substituted *closo*-boranes, nor could we find any theoretical studies in the literature. In this note, we present the theoretical study on a series of *n*-vertex heterosubstituted *closo*-boranes (n = 5–7) with NH, S, and PH as the heterovertex, isoelectronic to $B_nH_n^{2-}$.

Lower vertex *closo*-boranes have a bipyramidal structure. Perturbation of the cage by a heteroatom leads to two possible positional isomers in trigonal bipyramid and pentagonal bipyramid forms. Three qualitative approaches have been proposed in the literature which predict the relative stabilities of the positional isomers in polyhedral boranes. The first is due to Williams,[10] which suggests that electronegative atoms prefer sites of lower coordination in order to have minimum electron sharing. This empirical rule was specifically developed to rationalize the positional isomers of *closo*-carboranes. Accordingly, the 1,5-isomer is predicted to be favored among the positional isomers of *closo*-$C_2B_3H_5$ as is found experimentally.[1] The rule of topological charge stabilization by Gimarc[11] proved to be a versatile tool in predicting the relative stabilities of *closo*-heteroboranes.[11b] It suggests that a more electronegative atom prefers the site of maximum electron density. This is determined by topology for an isoelectronic homonuclear reference framework. The rule was successful in predicting the positional isomers of *closo*-carboranes and agreed well with that observed experimentally.[1,11b] The compatibility of orbitals in overlap and the six interstitial electron rule for three dimensional delocalization proposed by Jemmis and Schleyer[12] was another alternative used to predict the relative preferences of various positional isomers in a polyhedral skeleton.

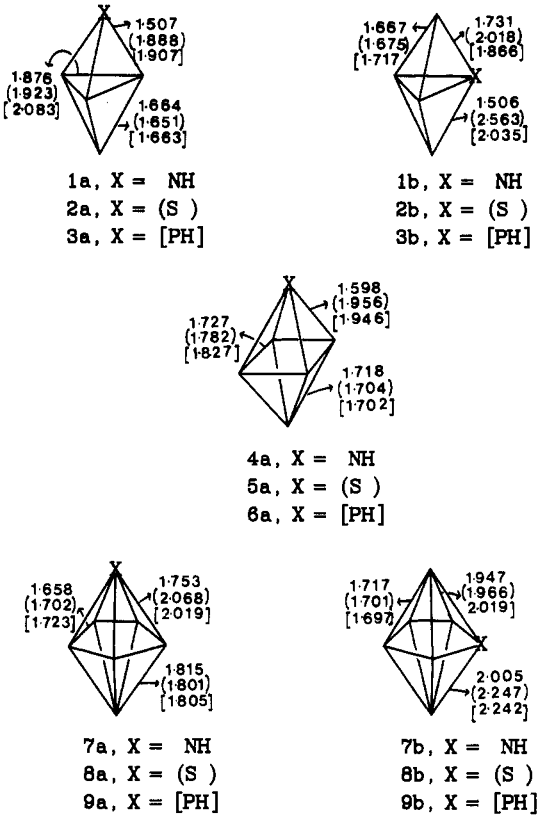

Figure 1. Important geometric parameters for **1–9**.

In the present study, we predict the relative stabilities based on the above qualitative models for heterovertex closo boranes and confirm them by using ab initio molecular orbital theory. The geometries of **1–9** (Figure 1) were optimized initially using the HF/6-31G* basis[13] within the given symmetry restriction.

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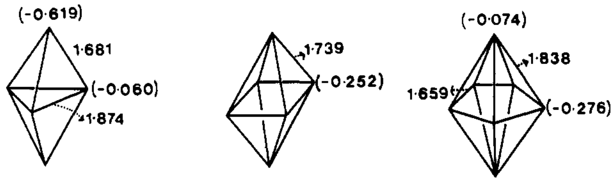
Table 1. Total (hartree), Relative (kcal/mol), and Zero Point Energies (ZPE; kcal/mol) of **1–9** (Number of Imaginary Frequencies (NIM) in Parentheses)

	total energy		relative energy			
no. (sym)	HF/6-31G*	MP2/6-31G* [a]	HF/6-31G*	MP2/6-31G*	ZPE (NIM)	θ,[b] deg
1a (C_{3v})	−156.08214	−156.53811	0.00	0.00	45.6 (0)	12.0
1b (C_{2v})	−155.97882	−156.52524	62.14	5.39	42.6 (2)	
2a (C_{3v})	−498.54793	−499.05629	0.00	0.00	34.9 (0)	4.2
2b (C_{2v})	−498.33525	−498.84329	128.64	128.84	29.6 (1)	
3a (C_{3v})	−442.26097	−442.74616	0.00	0.00	39.5 (0)	0.1
3b (C_{2v})	−442.23268	−442.73168	16.52	7.86	38.1 (2)	
4a (C_{4v})	−181.34785	−181.98667			55.4 (0)	14.7
5a (C_{4v})	−523.83664	−524.45065			45.0 (0)	6.8
6a (C_{4v})	−467.57271	−468.17313			50.1 (0)	2.4
7a (C_{5v})	−206.53780	−207.27822	57.23	50.49	62.8 (0)	16.8
7b (C_{2v})	−206.63114	−207.36081	0.00	0.00	64.3 (0)	
8a (C_{5v})	−549.06849	−549.77747	17.03	18.21	53.6 (0)	8.3
8b (C_{2v})	−549.09623	−549.80707	0.00	0.00	53.9 (0)	
9a (C_{5v})	−492.83938	−493.53733	0.74	0.11	59.6 (0)	3.4
9b (C_{2v})	−492.84009	−493.53703	0.00	0.00	59.3 (0)	
NH_3 (C_{3v})	−56.18436	−56.35689			23.2 (0)	
SH_2 (C_{2v})	−398.66732	−398.79849			10.3 (0)	
PH_3 (C_{3v})	−342.44796	−342.39113			16.4 (0)	
H_2 ($D_{\infty h}$)	−1.12683	−1.14410			6.6 (0)	
B_4H_4 (T_d)	−100.92570	−101.29196			32.6 (0)	

[a] MP2(FULL)/6-31G*//HF/6-31G* level of calculation. [b] Out-of-plane bending of the ring hydrogens are toward the heterovertex.

Chart 1. Bond Distances and Natural Charges (in Parentheses) Obtained at the HF/6-31G* Level for $B_nH_n^{2-}$ (n = 5–7)



Analytical second derivatives were evaluated at the same level of theory to characterize the nature of the stationary point. A single point MP2(FULL)/6-31G* calculation[14] was performed on the HF/6-31G* optimized geometries to estimate the effect of electron correlation. Table 1 gives the total and relative energies along with their zero-point energies and some important geometric parameters used in the discussion. Energy comparisons, wherever made, are at the MP2/6-31G* level of theory (including a zero point energy correction scaled by a factor of 0.89).

Results and Discussion

The rule of topological charge stabilization requires a uniform reference framework to emphasize the charge differences between vertices in a polyhedral cage.[11] Accordingly, $B_nH_n^{2-}$ (n = 5–7) serves as the reference framework. The natural charges on each vertex, calculated using the NBO analysis of Reed,[15] provides a measure of the electron concentration or depletion in that site.[16] Such a pattern obtained for the 5–7-vertex boranes are shown in Chart 1. For a 5-vertex cage, the electrons are concentrated on the apical position. Hence, more electronegative atoms should prefer this position. **1a–3a** with NH, S, and PH as caps are found to be minima, while **1b–3b** with the heteroatoms in the ring are characterized to be higher order stationary points (Table 1). For a 6-vertex cage, all the sites are equivalent due to the octahedral symmetry. Hence, only one isomer is possible. **4a–6a**, the representative examples for the octahedral arrangement, are characterized to be minima (Table 1). In contrast to the 5-vertex cage, the electrons in the 7-vertex cage are concentrated on the equatorial position (Chart 1). Hence isomers **7b–9b** with the heteroatom in the ring should be favored compared to **7a–9a**, where they occupy the apical position. This is indeed reflected in their relative energies (Table 1).

While the relative stabilities of the isomers are characterized fully, the bonding pattern in these molecules can be understood using the six interstitial electron rule and the ring–cap orbital overlap match.[12] The cage can be viewed as being formally constructed from a n-membered ring (n = 3–5) capped on either side, leading to a bipyramidal arrangement. A -BH unit acting as a cap donates two electrons while the heteroatoms (NH, S, and PH) in the apical position contributes four electrons toward the cage bonding. On the other hand, if the heteroatoms are present in the ring they provide only two electrons to the interstitial electron count. Thus, all the molecules provide six electrons for three dimensional delocalization and hence the bonding in these systems are similar to that observed in other *closo*-boranes and carboranes.

The equatorial B–B bond distances in **1a**, **4a**, and **7a** (X = NH; Figure 1) are close to that observed in $B_nH_n^{2-}$ (n = 5–7; Chart 1). On the other hand, it is slightly longer when X = PH or S. This is due to the difference in the covalent radii of X which elongates the B–B bond distance of the ring to accommodate the B–X bond. This is further evident from the marginal change in the B–B distance involving the equatorial and the apical boron atoms (Figure 1).

The hydrogens in the planar ring of **1a–9a** are bent towards the apex (θ) containing the heteroatom (Table 1), while in disubstituted heteroboranes they are forced to be in the plane of the ring by symmetry.[1–4] This out-of-plane bending of the ring substituents rehybridizes the π orbitals of the ring to maximize the ring–cap orbital overlap. NH with more contracted p-orbitals has the maximum out-of-plane bending (**1a**, **4a**, **7a**—Table 1), while PH with more diffuse orbitals (**3a**, **6a**, **9a**) has minimum bending.[17] **2a**, **5a**, and **8a**, with S as the cap, lie in between them (Table 1).

For a given cap the out-of-plane bending of the ring hydrogens increases (Table 1). This indicates that a smaller ring prefers a cap with less diffuse orbitals, while a larger ring may prefer caps with still more diffuse orbitals. The relative preferences of various heteroboranes for a particular cap combination can also

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(17) Atomic radii or the optimized exponents in a basis set indicate the expected trend of the diffuse nature of orbitals.

be estimated from the following reaction. The exothermicity of the reaction (in kcal/mol) validates the above argument further. An NH cap prefers a three-membered borocycle, and a PH cap, a five-membered borocycle.

$$\underset{\mathbf{3a}}{B_4H_4PH} + \underset{\mathbf{7a}}{B_6H_6NH} \rightarrow \underset{\mathbf{1a}}{B_4H_4NH} + \underset{\mathbf{9a}}{B_6H_6PH} \quad -29.5$$

Another means of estimating the preference of various heterosubstituted cages is the following reaction. The large exothermicities of the reactions (in kcal/mol) indicate the strongtendency for the formation of *closo*-heteroboranes in comparison to tetraborane(4).

$$B_4H_4 + NH_3 \rightarrow B_4H_4NH + H_2 \quad \Delta H = -24.1$$

$$B_4H_4 + SH_2 \rightarrow B_4H_4S + H_2 \quad \Delta H = -70.2$$

$$B_4H_4 + PH_3 \rightarrow B_4H_4PH + H_2 \quad \Delta H = -132.6$$

In conclusion, a simple perturbative approach and ring–cap orbital overlap match proves to be a versatile tool in predicting the preferences of various positional isomers of heteroboranes and provides qualitative information about their bonding. In a trigonal bipyramidal arrangement, the heteroatoms prefer only the apical position, and in the pentagonal bipyramidal arrangement, it occupies the equatorial position. These structures are promising synthetic targets as interesting as the higher vertex monoheteroboranes already synthesized.

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