Polyhedral Boranes

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Orbital Compatibility in the Condensation of Polyhedral Boranes**

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The Wade $n+1$ rule[1] and the *mno* rule[2] describe the electronic requirements for the stability of polyhedral boranes (e.g., **1**) and macropolyhedral boranes (e.g., **2** and **3**), respectively (see Figure 1). Though useful in explaining and designing structures, electron-counting rules provide a yes or no answer; not all molecules having the stipulated numbers of electrons are equally stable. It is desirable to have a qualitative understanding, wherever possible, of the factors that control the relative stability of a family of molecules. We formulated the concept of compatibility of orbitals to explain the relative stability of polyhedral boranes, carboranes, and metallaboranes.[3] Herein we demonstrate that similar concepts can be used to determine the best combination of polyhedra for the formation of condensed macropolyhedral boranes.

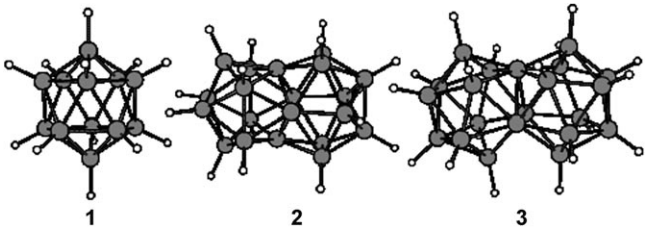

Figure 1. Structures of $B_{12}H_{12}^{2-}$ (**1**), four-shared-atom $B_{20}H_{16}$ (**2**), and three-shared-atom $B_{21}H_{18}^{1-}$ (**3**).

There is intense current interest in macropolyhedral boranes for application in boron neutron capture therapy,[4] pharmaceuticals,[5] nanotechnology,[6] and materials science.[7] A variety of homonuclear and heteronuclear macropolyhedral structures are known with varying architectural patterns.[8] Several computational studies have been performed to find the thermodynamic preference of structural patterns in macropolyhedral boranes.[2,9] However, the question why the numbers turn out the way they do was not answered. Herein we investigate the factors that contribute to the preference of a polyhedron with a given number of vertices for another polyhedron with a particular number of vertices in forming condensed polyhedral boranes.

We began our analysis with three-shared-atom *closo*–*closo* macropolyhedra. The geometries of all structures were optimized by using the Gaussian 03 suite of programs[10] with the hybrid HF-DFT methods B3LYP/6-31G* and BP86/6-311+G*.[11]

Let us consider the formation of a macropolyhedron with three shared atoms. Hydrogen atoms of the three B–H bonds of one polyhedron must be removed to free the exohedral hybrid orbitals for condensation with another polyhedron. The spread of orbital combinations arising from the three orbitals is larger for a smaller polyhedron (Figure 2a vs. b). A measure of this spread can be inferred from the X-B-H angle, where X is the centroid of the triangular B_3 face (Figure 2c). The X-B-H angle for *n*-vertex *closo* polyhedra with $n=5$–12 (Table 1) shows that $B_5H_5^{2-}$ has the largest angle of bending (151.9) and $B_{12}H_{12}^{2-}$ the smallest (127.3). This implies that the smaller the cluster the larger the effective diffuseness and spread of the fragment orbitals pointing outwards from the cluster. Therefore, the small cluster fragment is better poised to interact with a large cluster, whereas a large cluster with less diffuse fragment orbitals prefers to condense with a small

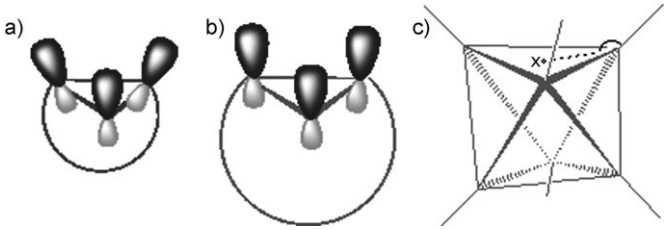

Figure 2. a), b) Schematic representation of the B–H bond orbitals of small and large polyhedra, respectively. c) Definition of the X-B-H angle.

Table 1: X-B-H angle of $B_nH_n^{2-}$ polyhedra with $n=5$–12 taken as the average of the three X-B-H angles of the face.

Structure	X-B-H [°]
$B_5H_5^{2-}$	151.9
$B_6H_6^{2-}$	144.7
$B_7H_7^{2-}$	140.7
$B_8H_8^{2-}$	137.8, 137.0
$B_9H_9^{2-}$	132.6, 134.2, 135.5
$B_{10}H_{10}^{2-}$	128.7, 134.8
$B_{11}H_{11}^{2-}$	122.4, 127.7, 129.3, 129.9,131.0, 133.9
$B_{12}H_{12}^{2-}$	127.3

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cluster (Figure 3). Structural details of π complexes of tricarbonyl metal clusters were explained by Hoffmann et al. in 1976 using a similar argument.[3e]

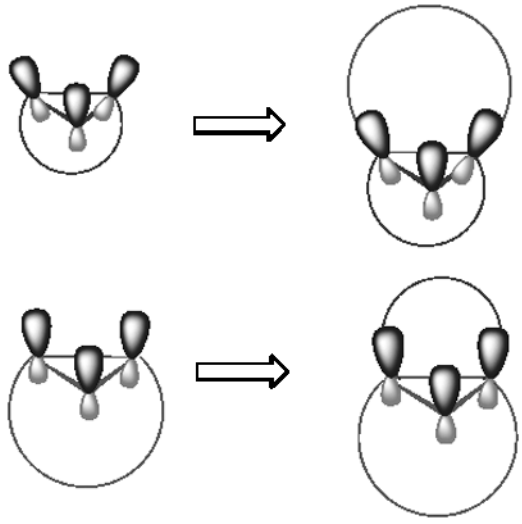

Figure 3. Schematic representation of orbital compatibility for the condensation of a small polyhedron with a large polyhedron.

A detailed quantitative analysis of the diverse condensation processes and a comparison of the stabilities of the macropolyhedral structures confirm this hypothesis. Consider the formation of $B_{21}H_{18}^-$ (**3**) from two $B_{12}H_{12}^{2-}$ polyhedra [Eq. (1)]. This equation and several others involving $B_nH_n^{2-}$

$$B_{12}H_{12}^{2-} + B_{12}H_{12}^{2-} \rightarrow B_{21}H_{18}^- + B_3H_3^{3-} \quad (1)$$

are used to estimate the stability of the resulting macropolyhedral structure, but they artificially favor the side of the equation with larger $B_nH_n^{2-}$ due to the higher stability of larger anions (Table 1 in the Supporting Information). The isodesmic Equation (2) estimates the energetics of condensation most convincingly.

$$closo(n_1) - closo(n_1) + closo(n_2) - closo(n_2) \rightarrow 2\,\mathrm{closo}(n_1) - closo(n_2) \quad (2)$$

The reaction energies of isodesmic Equation (2), listed in Table 2, clearly show the preference of a small cluster to condense with a large cluster. Where many isomers are possible, only the energy associated with the most stable fusion is quoted. These are plotted against the difference in the number of vertices of the individual polyhedra of the macropolyhedral structure in Figure 4. The reaction energy increases with increasing difference in the number of vertices. Formation of *closo*(12)–*closo*(6) is more exothermic (−68.8 kcal mol^{-1}) than any other combination with a 12-vertex cluster. The 12-vertex polyhedron ($B_{12}H_{12}^{2-}$) is the most stable of the single polyhedra considered herein, and among the small polyhedra the 6-vertex polyhedron ($B_6H_6^{2-}$) has the highest stability.[12] The reaction energies reveal that the best fragment for condensation with 5-, 6-, and 7-vertex clusters is a 12-vertex cluster, whereas for 9-, 10-, 11-, and 12-vertex clusters the 6-vertex cluster is best suited.

Table 2: Reaction energies ΔH [kcal mol^{-1}] of Equation (2) calculated at the B3LYP/6-31G* level for the same triangular faces wherever possible.

n_1 \ n_2	5	6	7	8	9	10	11	12
5	0	–	–	–	–	–	–	–
6	−8.6	0	–	–	–	–	–	–
7	1.2	−7.1	0	–	–	–	–	–
8	−17.8	−1.8	7.7	0	–	–	–	–
9	−18.7	−23.8	6.9	7.9	0	–	–	–
10	−31.6	−55.3	−17.6	−5.9	0.9	0	–	–
11	−26.7	−33.6	−10.5	−2.9	8.3	−2.5	0	–
12	−50.5	−68.8	−36.3	−13.1	−21.2	−17.7	3.1	0

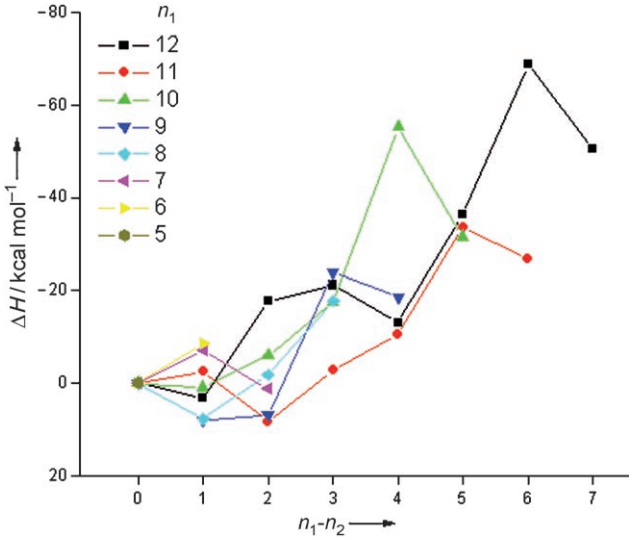

Figure 4. Reaction energy of Equation (2) versus difference in the number of vertices.

For an 8-vertex polyhedron the reaction energies for condensation with 5- and 12-vertex clusters are similar (−17.8 and −13.1 kcal mol^{-1}). The reaction energies for condensation of any n_1-vertex cluster with clusters having $n_2 = n_1 \pm 1$ vertices of less than −10 kcal mol^{-1} (−8.6, −7.1, 7.7, 7.9, 0.9, −2.5, 3.1 kcal mol^{-1} for *closo*(5)–*closo*(6), *closo*(6)–*closo*(7), *closo*(7)–*closo*(8), *closo*(8)–*closo*(9), *closo*(9)–*closo*(10), *closo*(10)–*closo*(11), and *closo*(12)–*closo*(11), respectively) indicate mismatched fragment orbitals of the individual clusters and hence suboptimal overlap.

We compared the energy of the different macropolyhedral structures formed by condensation of a given polyhedron through different triangular faces with that of a *closo* 12-vertex cluster with an X-B-H angle of 127.3°. Calculations show that *closo*(9)–*closo*(12) is more stable when it is condensed through a triangular face with an average X-B-H angle of 135.5° rather than through one having an X-B-H angle of 132.6° (Table 3). This is valid for the isomers of other macropolyhedral structures, too. Thus when the difference in the X-B-H angle of two polyhedra is large, they are more

Table 3: Relative energies of macropolyhedra formed by condensation with *closo*(12) through different types of triangular faces of polyhedra *closo*(*n*) with $n = 8$–11.

Structure[a]	X-B-H [°]	Relative energy [kcal mol^{-1}]	
		B3LYP/6-31G*	BP86/6-311+G*
closo(8)–*closo*(12)	137.8	0.0	0.0
closo(8)–*closo*(12)	137.0	8.4	6.1
closo(9)–*closo*(12)	135.5	0.0	0.0
closo(9)–*closo*(12)	134.2	2.9	2.3
closo(9)–*closo*(12)	132.6	24.4	20.9
closo(10)–*closo*(12)	134.8	0.0	0.0
closo(10)–*closo*(12)	128.7	3.3	2.6
closo(11)–*closo*(12)	133.9	0.0	0.0
closo(11)–*closo*(12)	122.4	12.2	14.5
closo(11)–*closo*(12)	127.7	24.3	23.5

[a] Structures which are minima in the potential-energy surface are considered.

compatible for orbital overlap to form the condensed structure.

Relative energies of isomeric macropolyhedral structures depend on the stability of individual clusters and orbital compatibility. Since a large polyhedron prefers a small polyhedron as partner for condensation, the macropolyhedral structures will be more stable when the difference in the number of vertices between individual polyhedra is large and thus allows optimum overlap of the fragment orbitals. Relative energies of macropolyhedral structures are given in Table 4. In most cases, the energetics follows the difference in the number of vertices of the individual clusters ($\Delta k = n_1 - n_2$) of the macropolyhedra. For example *closo*(12)–*closo*(10) is 19.4 kcal mol^{-1} more stable than *closo*(11)–*closo*(11). The stability order of *closo*(12)–*closo*(7) > *closo*(11)–*closo*(8) > *closo*(10)–*closo*(9) and *closo*(12)–*closo*(6) > *closo*(11)–*closo*(7) > *closo*(10)–*closo*(8) > *closo*(9)–*closo*(9) shows the role of orbital compatibility in determining the stability of macropolyhedral structural patterns. However, when the energy difference is very small (e.g., *closo*(7)–*closo*(6) vs. *closo*(8)–*closo*(5)), factors such as steric interactions also become important. Since $B_{21}H_{18}^{1-}$, a combination of two $B_{12}H_{12}^{2-}$ units by triangular-face sharing, was already synthesized last year, we can be optimistic about the synthesis of many condensation products which are even more exothermic.

Table 4: Relative energies for isomeric macropolyhedral structures *closo*(n_1)–*closo*(n_2). Only the most stable isomer of an n_1–n_2 combination is considered.

Structure		Δk	Relative energy [kcal mol^{-1}]	
n_1	n_2		B3LYP/6-31G*	BP86/6-311+G*
12	10	2	0.0	0.0
11	11	0	19.4	17.8
12	9	3	0.0	0.0
11	10	1	27.7	24.7
12	8	4	0.0	0.0
10	10	0	35.2	29.9
11	9	2	45.6	42.3
12	7	5	0.0	0.0
11	8	3	51.8	49.7
10	9	1	52.2	47.3
12	6	6	0.0	0.0
11	7	4	53.3	49.7
10	8	2	58.1	54.8
9	9	0	63.5	60.4
12	5	7	0.0	0.0
11	6	5	25.8	24.6
10	7	3	33.5	29.2
9	8	1	51.3	50.2
10	6	4	0.0	0.0
11	5	6	11.0	9.6
8	8	0	25.6	25.0
9	7	2	26.7	27.9
9	6	3	0.0	0.6
10	5	5	0.6	0.0
8	7	1	8.8	9.8
7	7	0	0.0	0.0
9	5	4	7.1	4.2
8	6	2	8.5	7.8
7	6	1	0.0	0.0
8	5	3	4.1	2.9
6	6	0	0.0	0.0
7	5	2	0.7	0.1

Herein we have considered only the three-shared-atom *closo*(n_1)–*closo*(n_2) structural patterns, for which the results show a preference of a large polyhedron for a small polyhedron in condensations. We anticipate that this will be true in general with any macropolyhedra involving *nido* and *arachno* patterns. The contributions of orbital compatibility to the stability will vary with each macropolyhedral borane. These details, as well as the condensation involving *nido* and *arachno* arrangements, will be published elsewhere.

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