Ab Initio Predictions on Novel Stuffed Polyhedral Boranes

Eluvathingal D. Jemmis* and Musiri M. Balakrishnarajan

School of Chemistry, University of Hyderabad
Hyderabad 500 046, India

Despite the great advances made in the chemistry of polyhedral *closo*-boranes,[1,2] these are never seriously thought of as large enough to enclose an atom inside.[3−6] The most stable polymorph of elemental boron provides the closest example of an encapsulated arrangement.[7] We present here the results of theoretical studies that strongly suggest that a rich endohedral chemistry is awaiting to be unfolded for $B_{12}H_{12}{}^{2-}$ and higher boranes. This strategy could be particularly employed in stabilizing higher *closo*-boranes that are otherwise less stable.[3−6]

The B1−B12 distance of 3.36 Å in $B_{12}H_{12}{}^{2-}$ allows as much as 1.68 Å to the bond between the central and peripheral atoms,[8] even in the absence of any relaxation in the B_{12} shell (Figure 1a). This is approximately 0.1 Å short in comparison to standard multicentered B−B bonding distance. Hence, introducing a central atom of size comparable to boron will impart steric strain, making the cage to expand. However, introducing a central atom with a set of 2s and 2p orbitals (a_g and t_{1u}) will stabilize the corresponding set of orbitals of $B_{12}H_{12}{}^{-2}$, provided no additional valence electrons are added (Figure 2). Encapsulating ions such as Li^+, Be^{2+}, B^{3+}, C^{3+} Mg^{2+}, Al^{3+}, and Zn^{2+} should achieve this goal. Accordingly, $C@B_{12}H_{12}{}^{2+}$, $B@B_{12}H_{12}{}^+$, $Be@B_{12}H_{12}$, $Li@B_{12}H_{12}{}^-$, $Mg@B_{12}H_{12}$, $Al@B_{12}H_{12}{}^+$, $Zn@B_{12}H_{12}$ are considered as possible cases (Figure 1a). We also study $X@B_{14}H_{14}{}^n$ (Figure 1b) to find out the extent of stabilization of higher boranes by endohedral binding. With these goals in mind $X@B_{12}H_{12}{}^n$ (**1−7**) and $X@B_{14}H_{14}{}^n$ (**8−12**) are optimized at the hybrid HF-DFT level B3LYP/6-31G*.[10,11] All calculations were performed with symmetry constraints using Gaussian 94 package.[12] Vibrational frequencies are calculated to ascertain the nature of the stationary points. The corresponding exohedral isomers are also computed to assess the amount of strain involved in encapsulation. For this purpose, structures with X outside the B3 triangle is optimized
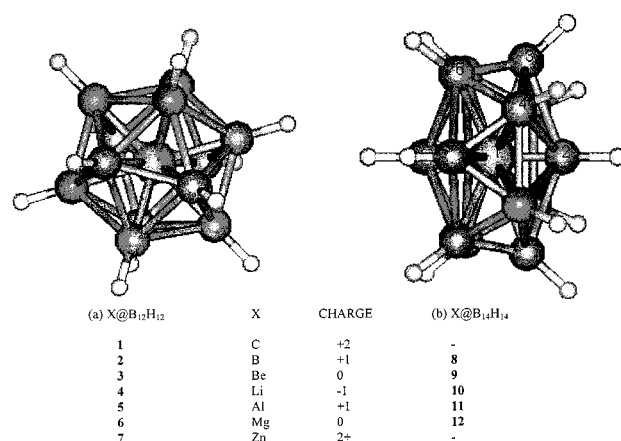

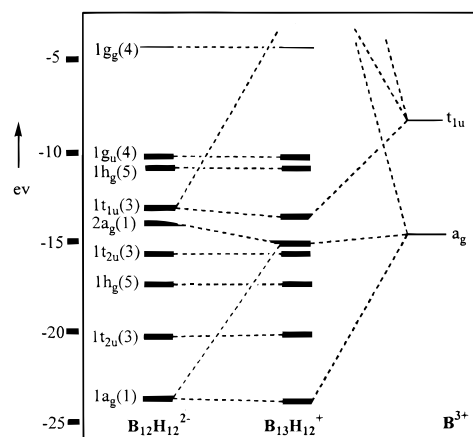**Figure 1.** Schematic structures and the actual molecular formulas of (a) $X@B_{12}H_{12}$ and (b) $X@B_{14}H_{14}$.

(a) $X@B_{12}H_{12}$	X	CHARGE	(b) $X@B_{14}H_{14}$
1	C	+2	-
2	B	+1	8
3	Be	0	9
4	Li	-1	10
5	Al	+1	11
6	Mg	0	12
7	Zn	2+	-

Figure 2. Schematic diagram for the interaction of $B_{12}H_{12}{}^{2-}$ with B^{3+} constructed using extended Huckel theory.[9] The occupied levels are shown as thick lines.

at the same level of theory. Here, the substituent is placed just outside the center of the triangular face. Selected geometric parameters, zero point energies, lowest frequencies, and the strain energies due to stuffing in comparison to their exohedral counterparts are given in Tables 1–3.

All the endohedral structures of B_{12} cage except **1** and **7** are calculated to be minima at the B3LYP/6-31G* level (Table 1) with large HOMO−LUMO gaps. These structures are fairly rigid, the lowest frequencies being in the range 200−425 cm^{-1}. The peripheral B−B bonds are stretched from 1.787 Å in $B_{12}H_{12}{}^{-2}$ to 1.859 Å in $B@B_{12}H_{12}{}^+$. The central boron to peripheral boron radial bond distance is shorter (1.768 Å). The B−B bonding distances of all these systems are well within the range observed in boranes[1] and elemental boron.[7] The B−H bond lengths of stuffed systems with respect to $B_{12}H_{12}{}^{2-}$ are systematically shortened indicating an increased *s* character of the bond. In general the stability of the endohedral system is enhanced when the stuffed atom has low electronegativity and small size. For example, with the high electronegativity of carbon, $C@B_{12}H_{12}{}^{2+}$ is not a minimum. Similarly, the large size of Zn makes $Zn@B_{12}H_{12}$ not a minimum.

The immediate alternative with which these endohedral species may be compared is the corresponding exohedral structures. The energy difference between the exohedral and endohedral structures, termed as strain energy (E^c) in Table 3 indicates that the exohedral species are energetically more favorable by varying

* Author for correspondence. Fax: 91-40-301-2460. E-mail: jemmis@ uohyd.ernet.in.

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Table 1. Bond Lengths, Zero Point Energies and Lowest Vibrational Frequencies at B3LYP/6-31G* Level for $B_{12}H_{12}^{2-}$ and the Stuffed Systems 1−5

no.	doped molecule	ZPE (min freq.) kcal/mol (cm^{-1})	bond lengths (Å)		
			radial B−B	skeletal B−B	B−H
	$B_{12}H_{12}^{-2}$	104.9 (520)	1.700	1.787	1.208
1	$C@B_{12}H_{12}^{2+}$	90.3 (−563)	1.767	1.858	1.192
2	$B@B_{12}H_{12}^{+}$	100.8 (214)	1.768	1.859	1.180
3	$Be@B_{12}H_{12}$	105.7 (409)	1.779	1.870	1.180
4	$Li@B_{12}H_{12}^{-}$	106.8 (414)	1.779	1.870	1.190
5	$Al@B_{12}H_{12}^{+}$	98.6 (231)	1.910	2.000	1.175
6	$Mg@B_{12}H_{12}$	99.5 (235)	1.923	2.020	1.180
7	$Zn@B_{12}H_{12}$	91.0 (−177)	1.936	2.036	1.180

Table 2. Bond Lengths, Zero Point Energies and Lowest Vibrational Frequencies at B3LYP/6-31G* Level for $B_{14}H_{14}^{2-}$ and the Stuffed Systems 8−12

no.	doped molecule	ZPE (min. freq.) kcal/mol (cm^{1-})	bond lengths (Å)				
			1−2	1−3	2−3	3−4	4−5
	$B_{14}H_{14}^{2-}$	122.5 (337)	1.581		1.927	1.744	1.769
8	$B@B_{14}H_{14}^{+}$	117.0 (−362)	1.633	1.983	2.047	1.841	1.756
9	$Be@B_{14}H_{14}$	122.0 (221)	1.738	1.952	2.038	1.952	1.799
10	$Li@B_{14}H_{14}^{-}$	123.9 (268)	1.754	1.950	2.035	1.786	1.816
11	$Al@B_{14}H_{14}^{+}$	117.0 (−174)	1.902	2.036	2.178	1.875	1.861
12	$Mg@B_{14}H_{14}$	118.2 (−210)	1.923	2.045	2.191	1.882	1.873

Table 3. Interaction Energies with the Central Ions (E^a and E^b) and Their Strain Energies E^c and E^d (the Difference between Exohedral and Endohedral Structures) in kcal/mol·Total Energies (au) Are Given in Supporting Information

ion	E^a $X@B_{12}H_{12}^n$	E^b $X@B_{14}H_{14}^n$	E^c $X@B_{12}H_{12}^n$	E^d $X@B_{14}H_{14}^n$
C^{4+}	−2923.9	−2808.4	153.7	
B^{3+}	−1413.6	−1396.4	60.6	
Be^{2+}	−584.2	−584.9	58.3	46.4
Li^{+}	−99.6	−125.3	115.9	82.8
Al^{3+}	−848.0	−900.9	157.1	
Mg^{2+}	−232.0	−308.3	263.3	
Zn^{2+}	−569.0		266.0	

amounts. The lowest difference is obtained with B and Be as the encapsulating elements. Calculations including electron correlation at the MP2/6-31G* level reduces the strain energies for $B@B_{12}H_{12}^+$ and $Be@B_{12}H_{12}$ from 60.6 and 58.3 kcal/mol (Table 3) to 38.3 and 48.5 kcal/mol respectively. While the endohedral structures are less favorable, such unfavorable energetics does not preclude their synthesis. For example, prismane is approximately 130 kcal/mol less stable than benzene and yet yielded to the experimentalist.

Unlike the icosahedral $B_{12}H_{12}^{2-}$ that is structurally homeomorphic to a sphere, $B_{14}H_{14}^{2-}$ (D_{6d}) is more like an ellipsoid, whose radius across the minor axis is less than the radius of $B_{12}H_{12}^{2-}$. Hence, the interaction of the central ion with the skeletal atoms is not alike. Besides, the central atom is required to exhibit even higher coordination. Hence, in contrast to structures 2−6, only two systems $Be@B_{14}H_{14}$ and $Li@B_{14}H_{14}^-$ are minima in the case of $B_{14}H_{14}^{2-}$ (Table 2). The strain energies of stuffing with respect to the exohedral isomers are also comparatively less than the B_{12} cage indicating that the higher boranes of $n > 14$ will benefit much from stuffing (Table 3).

Estimation of the interaction of $B_{12}H_{12}^{2-}$ with the encapsulating atoms or ion is obviously exothermic due to the neutralization of charge involved. However, the difference in the exo-thermicity between $B_{12}H_{12}^{-2}$ and $B_{14}H_{14}^{-2}$ is revealing (Table 3). The interaction of the small ion B^{3+} with the former is more exothermic than with the latter. On the other hand, the interaction of larger Li^+ with $B_{14}H_{14}^{-2}$ is more exothermic than with $B_{12}H_{12}^{-2}$ (Table 3, E^a and E^b).

These are better seen in the polyhedron exchange reactions, given in eq 1.

$$X@B_{12}H_{12} + B_{14}H_{14}^{-2} \rightarrow X@B_{14}H_{14} + B_{12}H_{12}^{-2} \quad (1)$$
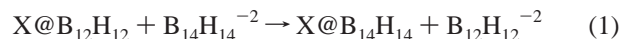
$$\Delta E \text{ (kcal/mol)} = 17.2 \text{ (X = B}^+\text{)}; -0.9 \text{ (Be)}; -25.7 \text{ (Li}^-\text{)};$$
$$-52.9 \text{ (Al}^+\text{)}; -76.3 \text{ (Mg)}$$

The preference of a smaller encapsulating atom for $B_{12}H_{12}^{2-}$ is clearly demonstrated here. Thus, the stability of $B_{14}H_{14}^{-2}$ in relation to $B_{12}H_{12}^{-2}$ is increased by encapsulation with Li. These are to be considered in the background of the inherently higher stability of (∼30 kcal/mol) of $B_{12}H_{12}^{-2}$.[3,7] The extra stability of the polyhedral dianions is avoided in the near isodesmic exchange equation (2). These again indicate the preference of the larger ion for the larger polyhedron.

$$X@B_{12}H_{12} + Y@B_{14}H_{14} \rightarrow X@B_{14}H_{14} + Y@B_{12}H_{12} \quad (2)$$
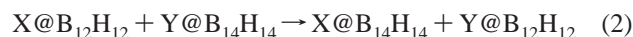
$$\Delta E \text{ (kcal/mol)} = 42.9 \text{ (X = B}^+, \text{Y = Li}^-\text{)}; 18.0 \text{ (B}^+, \text{Be)};$$
$$70.1 \text{ (B}^+, \text{Al}^+\text{)}; 93.5 \text{ (B}^+, \text{Mg)}; 24.9 \text{ (Be, Li}^-\text{)};$$
$$52.1 \text{ (Be, Al}^+\text{)}; 75.5 \text{ (Be, Mg)}; 27.2 \text{ (Li}^-, \text{Al}^+\text{)};$$
$$50.6 \text{ (Li}^-, \text{Mg)}; 23.4 \text{ (Al}^+, \text{Mg)}$$

In each case, the larger central ion prefers the larger polyhedron by substantial magnitudes. Stuffed icosahedral systems are well characterized in metallic elements such as aluminum[13−15] but the highest coordination for boron experimentally reported so far is nine, which occurs in its β-rhombohedral polymorph.[7] Isolated B13 clusters prefer nonicosahedral sheetlike geometries.[16,17]

If our calculations are any indication, the chemistry of higher polyhedral boranes will find a match in these charged and neutral stuffed boranes proposed here. These compounds should have a diverse chemistry of their own, one which is very different from that of $B_nH_n^{2-}$. Extension of these ideas, to other icosahedral and larger clusters is straightforward.[14] While there seems to be no immediate conventional synthetic routes for these stuffed systems, the strategies adopted for $X@C_{60}$ compounds and large Al clusters come obviously to mind.[14,18−21] Stuffing in combination with polycondensation of boranes can lead to the design and synthesis of novel stuffed borane nanotubes.[22] The ingenuity of the experimentalists knows no bounds.

Supporting Information Available: Listing of total energies and Cartesian coordinates of structures 1−12 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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