

The ubiquitous icosahedral B_{12} in boron chemistry

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Abstract. Though boranes exhibit a wide variety of polyhedral structures, all the three polymorphs of elemental boron essentially contain icosahedral B_{12} units as the predominant building block in their unit cell. Theoretical and experimental studies on boranes show that the icosahedral arrangement leads to most stable boranes and borane anions. This paper attempts to explain the phenomenal stability associated with the icosahedral B_{12} structure. Using fragment molecular orbital theory, the remarkable stability of $B_{12}H_{12}^{2-}$ among *closo* boranes are explained. The preferential selection icosahedral B_{12} unit by elemental boron is explained by improvising a contrived B84 sub-unit of the β -rhombohedral, the most stable polymorph. This also leads to a novel covalent way of stuffing fullerenes with icosahedral symmetry.

Keywords. Boron; polyhedral *closo* borane dianions; icosahedral B_{12} ; β -rhombohedral polymorph; orbital compatibility.

1. Introduction

The chemistry of boron formed a vast discipline by itself and helped to alter the concept of structure and bonding radically (Lipscomb 1963). Starting from the famous three-centre two-electron bond, many of the structural features exhibited by boron compounds (most significantly, its hydrides) have extended bonding to multiple centres and aromaticity to three dimensions (Muetterties 1975).

It is tempting to compare boron and boranes to their neighbours in the periodic table viz. carbon and hydrocarbons. Despite the enormous variety and sophistication of organic chemistry, most of the carbon structures can be explained by sp^3 , sp^2 and sp hybridization at carbon. This also extends to the polymorphs of elemental carbon which forms covalent solids. Diamond, graphite and carbyne correspond to sp^3 , sp^2 and sp hybridization, respectively. The fullerenes, new polymorphs of carbon (Kroto *et al* 1985), can also be explained based on sp^2 hybridized carbon array with slight distortion. Is it possible to generate a similar parallel between the structural motifs of compounds of boron and its polymorphs? Obviously no easily transferable description can be obtained from the compounds of boron. Boranes alone present a variety of polyhedral structures represented by the dianions $B_nH_n^{2-}$, $n = 5-12$ and various structural fragments derived from them. Representative compounds are given in figure 1. Despite this wide variety of polyhedra available for boranes, polymorphs of elemental boron are based mostly on the icosahedral B_{12} units. An explanation for this preference is given in this paper.

Elemental boron exists in three different polymorphic forms (Wells 1979). The thermodynamically most stable β -rhombohedral form has 105 boron atoms in its unit cell. The next stable α -rhombohedral form has 12 boron atoms. The meta stable α -tetragonal form has fifty boron atoms in its unit cell. The icosahedral B_{12} unit is the primary building block in all of these polymorphic forms. The most stable polymorph has maximum number of boron atoms forming a part of B_{12} icosahedra. Obviously there is something unique about the icosahedron for boron. Here we explore the origin of this preference.

Let us analyze the role of icosahedron in the compounds of boron. Amongst the borane anions of figure 1, the icosahedral $B_{12}H_{12}^{2-}$ is known to be more favourable than all others. An approximate relative energy ordering of anions is $B_{12}H_{12}^{2-} > B_6H_6^{2-} > B_7H_7^{2-} > B_{10}H_{10}^{2-} > B_9H_9^{2-}$, $B_8H_8^{2-} > B_{11}H_{11}^{2-} > B_5H_5^{2-}$ (Schleyer 1998). It is natural to search for an equivalent of the connection between hybridization and carbon-polymorphs, for boron through the stability of polyhedral borane anions.

We have included in figure 1 the bicapped hexagonal antiprism structure of $B_{14}H_{14}^{2-}$. This structure is conspicuous by its absence in the chemistry of borane anions (Jemmis 1982). Another related observation concerns the relative stability of *closo* carboranes, the neutral analogs of polyhedral borane anions. For example, the trans isomer 1,5-*closo*- $C_2B_3H_5$ is more favourable than 1,2-*closo*- $C_2B_3H_5$ (Grimes 1970). Similarly 1,6-*closo* $C_2B_4H_6$ is more favourable than 1,2-*closo*- $C_2B_4H_6$. On the other hand, the trans structure 1,7-*closo*- $C_2B_5H_7$ is the least stable isomer; 2,4-*closo*- $C_2B_5H_7$ is known to be most stable experimentally. An explanation for these relative energies, which naturally leads to the extra stability of $B_{12}H_{12}^{2-}$ is developed based on a qualitative electron

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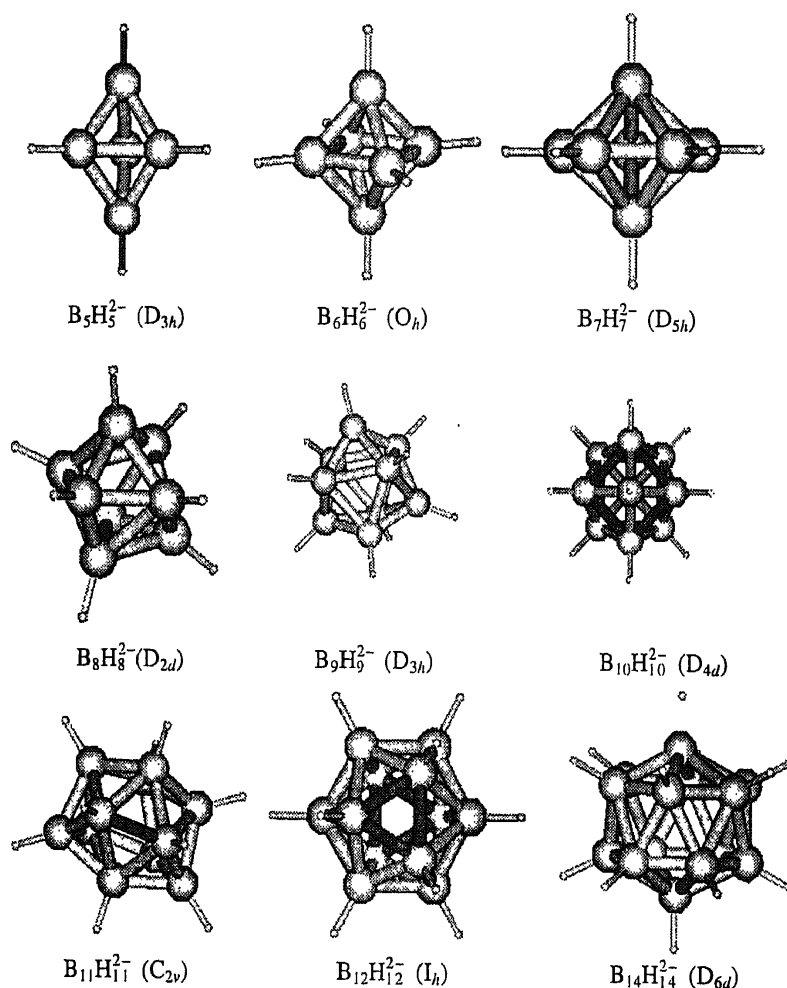


Figure 1. The structure of close-polyhedral borane anions, $B_nH_n^{2-}$, $n = 5-12$. The unknown $B_{14}H_{14}^{2-}$ is also shown.

counting model and the orbital compatibility in overlap.

2. The $4n + 2$ interstitial electron rule

closo-Boranes can be viewed as a combination of rings and caps. The overall stability of the system can then be deduced by a $(4n + 2)$ pi-electron rule (Jemmis 1982). This is actually a generalization of Huckel's $4n + 2$ rule applied in the domain of polycyclic aromatic hydrocarbons. As an illustration let us consider the $B_7H_7^{2-}$ which can be schematically constructed from the interaction of a five borocycle and two B-H caps from both sides perpendicular to the plane of the ring (figure 2). We take all B-H bonds and the B-B bonds in the B_5H_5 ring to have two centre two electron bonds. Hence all the three valence electrons in the boron will be exhausted. Now, each B-H group in the capping position has three electrons left. This will interact with the empty p orbitals of boron in the borocyclic ring. Hence all boranes with

$B_nH_n^{2-}$ satisfies the $4n + 2$ rule. $B_6H_6^{2-}$ is second in the order of stability of boranes with O_h symmetry (figure 1). This can be viewed as a square B_4H_4 with two caps as in the case of $B_7H_7^{2-}$. Counting of interstitial electrons can be done in a similar fashion. One interesting feature of $B_6H_6^{2-}$ is its high symmetry. Due to the presence of three C_4 axis, any two trans B-H groups can be considered as caps. This symmetrical equivalence accounts for its increased stability. This $4n + 2$ rule is equivalent to the rules developed by Williams and Wade (Williams 1998; Fox and Wade 1998).

A similar electron count may be established for more complex polyhedra. For example, the icosahedral $B_{12}H_{12}^{2-}$ may be conceptually put together from two pentagonal pyramidal B_6H_6 units. Pyramidal B_6H_6 does not have independent existence because of the lack of $4n + 2$ electrons. B_5H_5 ring has no electrons to contribute to ring cap binding. The B-H cap has only two valence electrons. (Additional four electrons can be obtained by adding four hydrogens as indeed found in the pyramidal B_6H_{10}). Two B_6H_6 pentagonal pyramidal units can be brought together

to give icosahedral $B_{12}H_{12}$. The -2 negative charge of the molecule makes the six electrons (2 each formally from the two caps and two from the negative charge). It is to be immediately noticed that there is no unique way to divide the icosahedron into two pentagonal pyramids. Any two B–H groups at opposite ends may be taken as capping groups in this analysis. A similar interaction diagram can be constructed for pyramidal molecules so that the $4n + 2$ -electron rule can be applied for them. For example $B_5H_5^{-4}$ (C_{4v}) and $B_6H_6^{-4}$ (C_{5v}) follow this electron count.

3. Orbital compatibility and stability of *closo* boranes

All the pyramidal and bi-pyramidal boron B_nH_n compounds obey $4n + 2$ interstitial electron rule and have three dimensional aromaticity. Obviously all compounds with six delocalized electrons cannot have the same stability. We find that a convenient geometric parameter to gauge the stability, can be obtained from the study of pyramidal molecules. Let us take hypothetical six-electron molecules such as $B_5H_5^{-4}$ (C_{4v}) and $B_6H_6^{-4}$ (C_{5v}). Theoretical studies show that the B–H bonds of the B_4H_4 ring in $B_5H_5^{-4}$ is almost in the plane of the B_4 ring (Jemmis and Pavan Kumar 1984). From a schematic point of view this could be represented as a perfect matching of the B_4H_4 orbitals with those of the B–H orbitals (figure 3a). On the other hand the orbitals of the B–H cap does not overlap optimally with the orbitals of a planar B_5H_5 ring (figure 3b). The overlap can be increased by bending the B–H bonds of the ring towards the cap thereby redirecting the pi orbitals towards the cap (figure 3c). This is calculated to be as much as 17° (Jemmis and Pavan Kumar 1984). When two capping orbitals interact with a ring, the ring B–H bonds remain in the plane by

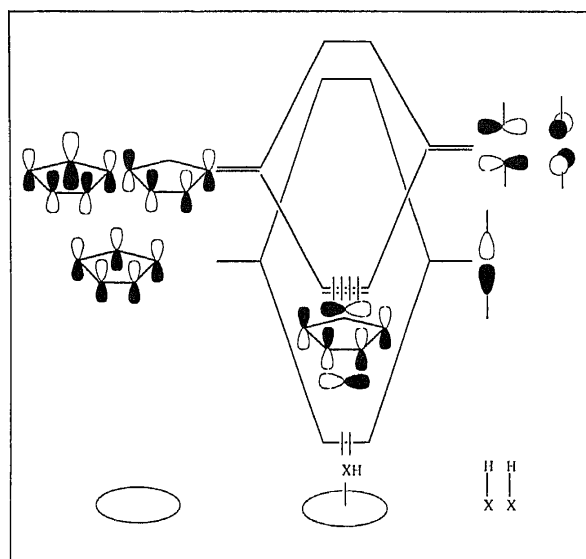
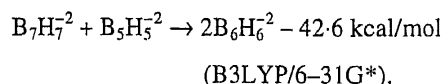


Figure 2. The schematic interaction diagram between the orbitals of B_5H_5 ring and two B–H caps leading to $B_7H_7^{-2}$ (D_{5h}).

symmetry. This still leaves optimal orbital interactions for the octahedron (figure 3d). However, for the pentagonal bipyramid, the situation is less than satisfactory. The overlaps with both the caps are less than ideal. It is as if the ring is too large or the orbitals of the B–H cap is too contracted (figure 3e). It is then not surprising that $B_7H_7^{-2}$ is not very stable comparatively. The unusual stability of $B_6H_6^{-2}$ over $B_7H_7^{-2}$ and $B_5H_5^{-2}$ can be seen by the exothermicity of the following reaction (Schleyer 1998):



These ideas could explain the absence of a hexagonal bipyramidal $B_8H_8^{-2}$. The two B–H caps will have negligible overlap with the rings. The relative stabilities of *closo*-carboranes also stem from similar arguments (Jemmis 1982; Jemmis *et al* 1992).

It is still not clear why the $B_{12}H_{12}^{-2}$, which is made up of two pentagonal pyramids, is unusually stable. Let us look at the geometry of the icosahedron. Each B–H bond makes an angle of 26.6° with the B_5 ring which contains it (figure 4). The pentagonal pyramidal $B_6H_6^{-4}$ has a corresponding angle of 17° . B_6H_{10} with four bridging hydrogens is the neutral analog. The terminal B–H bonds of the B_5 ring here are bent towards the B–H cap by an angle of 25° , close to the 26.6° dictated by the icosahedral symmetry (Jemmis and Kiran 1996). Thus the compatibility of overlap and the dictates of icosahedral symmetry coincides to make $B_{12}H_{12}^{-2}$ the most favourable borane anion. The elemental boron adapts this polyhedron for the various polymorphs.

4. A polyhedral construct of elemental boron

Let us now look at the way elemental boron is constructed using B_{12} units. Ideally one should begin the structure

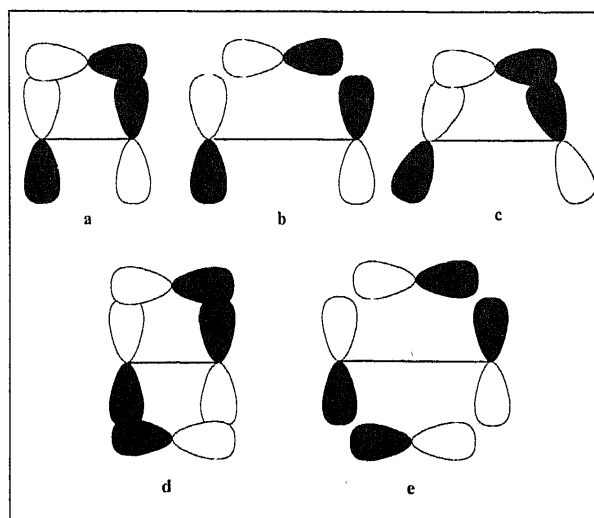


Figure 3. Schematic diagrams indicating the overlap compatibility between ring and cap orbitals.

around a B_{12} icosahedron with each boron connected to another B_{12} icosahedron. Unfortunately, the available space does not permit this. Instead the B_{12} structure begins with 12 half icosahedra each attached to a boron atom. The structure corresponding to one such attachment is given in figure 5a. Together this leads to 12 five-membered rings at the outer surface (figure 5b). These five-membered rings are connected to each other by B–B sigma bonds, thus forming a B_{60} unit akin to C_{60} . The B_{84} structure obtained so far can be described as $B_{12}@B_{12}@B_{60}$. If this structure is electron sufficient we would have obtained the B_{84} molecule. Since this is not so, the B_{84} units form the elemental boron structure in the following fashion. Six B_{84} units surround a given B_{84} unit symmetrically so that B_5 faces of the adjacent B_{84} units come together generating new B_{12} units (figure 5c). This would still leave six five-membered rings free on each B_{84} unit.

In the formation of the unit cell these six five-membered rings acquire resemblance of a B_{12} in the following fashion. Three such units arrange around a B_{10} unit so that each one gets to complete the B_{12} structure albeit by sharing some vertices (figures 6a, b). Thus the most stable polymorph with the unit cell of 105 atoms have each boron atom a part of either a regular icosahedron or a shared-vertex icosahedron.

We conclude this article by suggesting a way to make the B_{84} unit electron sufficient so that a molecule with this topology of $X_{12}@X_{12}@X_{60}$ can be made stable. The electron counting that is required for this purpose is arrived at in the following way. Let us begin with the

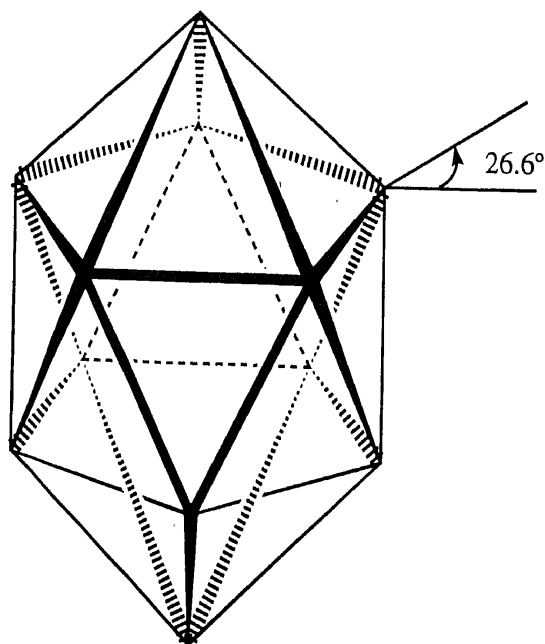


Figure 4. The geometric detail of icosahedron showing the angle B–H makes to the B_5 plane.

central B_{12} . This requires two additional electrons, so that it becomes isoelectronic to $B_{12}H_{12}^{-2}$. The 12 half icosahedra are also electron deficient. These require 4 electrons each to be electron sufficient as seen earlier. Thus the B_{84} unit with a charge of $50 - (2 + 48)$ will be electron sufficient. Obviously this high charge is unrealistic. One way of getting around the problem is to replace 50 boron atoms by 50 carbon atoms. Thus $C_2B_{10}@B_{12}@C_{48}B_{12}$ would satisfy the electron count. However this does not satisfy the space requirement. The $C_{48}B_{12}$ unit is too small to include the $C_2B_{10}@B_{12}$ unit inside. One approach at

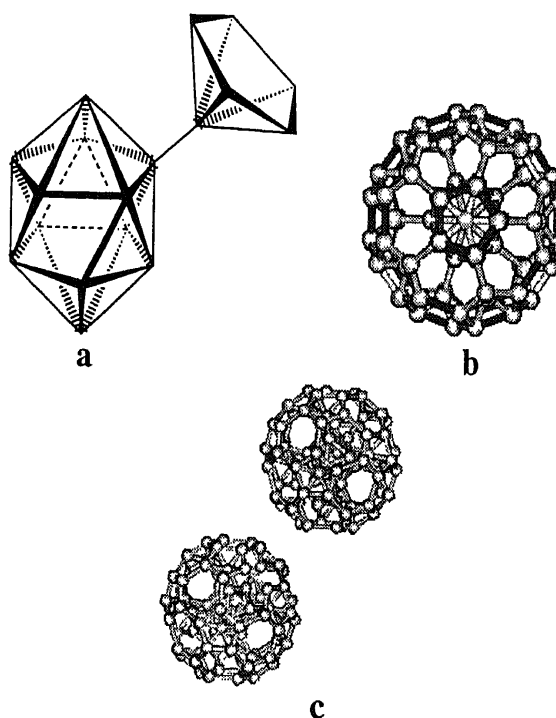


Figure 5. The structure of central B_{12} link to half icosahedra, B_{84} icosahedra and shared icosahedral bridge between two B_{84} units.

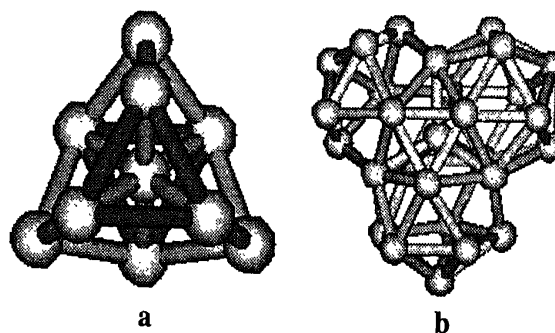


Figure 6. The structural details of the B_{10} unit that provides pentagonal pyramidal arrangements to three B_{84} structures. (a) Structure of B_{10} and (b) structure of B_{28} resulting from the addition of three pentagonal pyramidal B_6 units from three $B_{84}(I_h)$ to the three pentagonal faces of B_{10} .

this stage is to replace the 48 carbons of the outside ring by 48 silicon atoms so that the space requirement will be met. Studies in this direction are in progress.

5. Conclusions

The compatibility of ring and cap orbitals and the geometry of icosahedron leads to preferences of icosahedron for boron and boranes. The most stable polymorph of elemental boron i.e. β -rhombohedral has all boron atoms (except one) forming a part of independent icosahedra or icosahedra that share vertices. It is possible to envisage an electron count that would make $X_{12}@X_{12}@X_{60}$ electron sufficient.

Acknowledgements

We thank the Department of Science and Technology and the Council of Scientific and Industrial Research, New Delhi, for supporting this research. A research associateship of CSIR to one of the authors (MMB) is gratefully acknowledged.

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