

Analogies between Boron and Carbon

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ABSTRACT

The structural connections between the compounds of boron and carbon are extended using the *mno* rule beyond the borane–carbocation continuum, the lithium boride–polycarbyne analogy, and the magnesium boride (MgB₂)–graphite equivalence to β -rhombohedral boron and fullerenes. The structural similarity of the pentagonal pyramidal C₆H₆²⁺ and MgB₄ is established. An interesting electronic structural relationship between the B₈₄ fragment of the β -rhombohedral boron and the fulleride anion, C₆₀¹²⁻, is derived by replacing the 12 pentagonal pyramidal B₆⁴⁻ units by isoelectronic C₅⁻ units and removing the central B₁₂ from the electron-deficient B₈₄ unit. This relationship is well supported by the experimental realization of C₆₀M₁₂ (M = Li, K) and C₄₈N₁₂.

Introduction

Though they are neighbors in the periodic table, boron and carbon differ dramatically. Carbon forms the backbone of life. Boron is not essential to support life except in trace amounts for some plants. When boron finds a medicinal application, as in boron neutron capture therapy (BNCT), the healing process actually involves killing malignant cells by the high-energy ⁴He²⁺ and ⁷Li³⁺ ions formed by the decomposition of the ¹⁰B nucleus by thermal neutron absorption.¹ Carbon is a key player in much of modern material science: fullerenes and nanotubes are in the foreground. Yet the bonding in carbon is elegantly simple, making it into high school textbooks. In contrast, the structure and bonding of boron, boranes, and boron-rich solids present extreme complexity. Nevertheless, many similarities exist between the chemistry of

carbon and boron. This Account adds novel relationships of consequence in this area.

Familiar two-dimensional aromatic compounds such as C₃H₃⁺, C₅H₅⁻, and C₆H₆ are governed by Hückel's (4*n* + 2) π electron rule, where *n* is zero or any integer. At a simple level, the (4*n* + 2) π electron rule is applicable to condensed systems: benzene, naphthalene, and anthracene have 6, 10, and 14 π electrons (*n* = 1, 2, and 3), respectively. Polycondensation in two dimensions leads to graphite. Similar direct relationships between compounds of boron and elemental boron do not exist. The boranes, hydrocarbon equivalents, are well known for their electron deficiency and multicenter bonding, and are characterized by deltahedral structures, B_{*n*}H_{*n*}²⁻ (*n* = 5–12), which are aromatic.² In this connection, a deltahedron is a polyhedron in which all faces are triangles. The deltahedral borane structures with all vertices intact are called *closo* structures; *nido* and *arachno* borane structures are more open, with one and two missing vertices, respectively. Wade's (*n* + 1) skeletal electron pair rule, which explains the electronic requirements for *closo*-deltahedral boranes, is the boron equivalent of Hückel's rule of organic chemistry. Here *n* is the number of vertices. Thus, the icosahedral B₁₂H₁₂ has two negative charges.³ Wade's (*n* + 1) skeletal electron pair rule is applicable only to monopolyhedral boranes. We have recently extended Wade's rule to explain the electronic requirements of condensed polyhedral boranes.⁴ The (4*n* + 2) π electron rule is a special case of our new rule called the *mno* rule. Despite their complexity, structural connections between boranes and elemental boron continue to emerge.⁵ While the familiar benzene-to-graphite connection appears to be far removed from the relationship between icosahedral boranes and elemental boron, there are several analogies that are discernible. This Account attempts to bring out many similarities not noticed earlier.

Obvious Connections

The isoelectronic relationships between the two sets CH₃⁺, CH₄, CH₅⁺, CH₆²⁺, CH₇³⁺ and BH₃, BH₄⁻, BH₅, BH₆⁺, BH₇²⁺ are obvious.^{6,7} Equally obvious, but of rather recent origin, is the connection between C and B⁻ in extended binary structures. The adjacent stacks of boron and lithium synthesized by Nesper are indeed structurally reminiscent of polycarbyne: the crystal structure shows a linear borynide chain (B⁻)_{*n*}, isoelectronic to polycarbyne.⁸ While the extent of charge transfer can be debated, the connection to sp-hybridized carbon is obvious in this one-dimensional structure. The graphite equivalent of boron was forgotten in the literature⁹ until Akimitsu brought it into the limelight in 2001: the structure of the superconductor MgB₂ provides a close analogy to the graphite structure.¹⁰ The graphite-like boron sheets (B⁻), alternating with a similar sheet of magnesium (Mg²⁺) with hexagons twice as large, establish the link (Figure 1, 1). Indeed, the discovery of superconductivity of MgB₂ has brought renewed interest in boron-rich metal borides.

Eluvathingal D. Jemmis (PhD, Princeton; PDF, Cornell), joined the School of Chemistry, University of Hyderabad, in 1980 as a lecturer. He is currently Professor and Dean of the School and Professor-in-Charge of the newly established Centre for Modelling Simulation and Design of the University. Jemmis was a Visiting Fellow at the Research School of Chemistry, Australian National University, Canberra (1991), and a Visiting Professor at the Centre for Computational Quantum Chemistry of the University of Georgia, Athens (2000). Jemmis is a Fellow of the Indian Academy of Sciences, Bangalore, and the Indian National Science Academy, New Delhi, and is currently a member of editorial advisory board of *Journal of Computational Chemistry* and an honorary Professor at JNCASR, Bangalore. His research interests are in applied theoretical chemistry, especially organometallics, clusters, and aromaticity with an emphasis on finding common threads between problems in different areas, for example, between organic and organometallic chemistry, among the chemistry of main group elements, between polymorphs of elements and their compounds, and so on. Recent work by his group led to an extension of the Wades rules with implications in many areas, some of which are presented here (<http://202.41.85.161/~jemmis/>).

Elambalassery G. Jayasree obtained her M.Sc. from Calicut University, Kerala, and is pursuing her Ph.D. under the supervision of Prof. Jemmis at the University of Hyderabad. Her current research involves exploring the electronic structure and stability of polyhedral boranes with intriguing structural patterns and bonding.

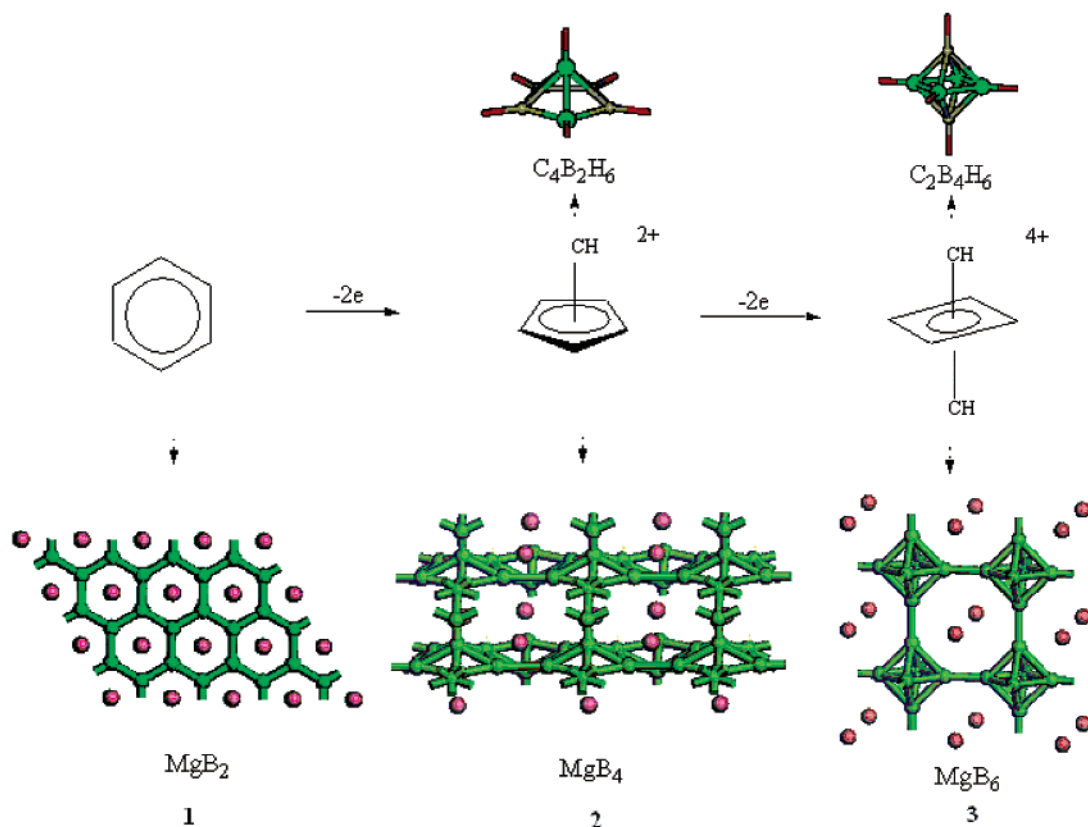


FIGURE 1. Structural similarities between hydrocarbons and the magnesium borides. (1) Benzene and MgB_2 . The diagram indicates the projection of a graphite-like boron sheet and a magnesium sheet into one plane. There is one magnesium on each B_6 hexagon. (2) Pentagonal pyramidal $\text{C}_6\text{H}_6^{2+}$, $\text{C}_4\text{B}_2\text{H}_6$, and MgB_4 obtained by edge-sharing of pentagonal pyramidal B_6 units. (3) Octahedral $\text{C}_6\text{H}_6^{4+}$, $\text{C}_2\text{B}_4\text{H}_6$, and MgB_6 .

Moving beyond Two Dimensions

Diamondoid structures are difficult for boron, as it is not easy to find a metal ion of the appropriate charge and size to fill the holes in a B^- diamond lattice. A diamond-like structure of a metal boride has not been reported, yet three-dimensional structures are not foreign to boron: they form the mainstay of its chemistry and physics.² The large family of three-dimensional polyhedral structures represented by $\text{B}_n\text{H}_n^{2-}$ and $\text{C}_2\text{B}_{n-2}\text{H}_n$ is well known.^{2,11} Several connections between polyhedral boranes and carbocations are recognized (Figure 1).¹²

Schematically, we can remove electrons from benzene and get $\text{C}_6\text{H}_6^{2+}$ (Figure 1). While there are several structures that may be envisaged for the dication, the one that relates to boron most easily is the pyramidal structure.¹³ This also satisfies Wade's rule for *nido* structures (polyhedron with one missing vertex).³ Replacement of one or more carbons by B^- results in C_5BH_6^+ ,¹⁴ $\text{C}_4\text{B}_2\text{H}_6$,¹⁵ and B_6H_{10} ($\text{B}_6\text{H}_6^{4-}$ with four bridging hydrogens to neutralize the charge),¹⁶ all known experimentally with pentagonal pyramidal structure. When another pair of electrons is taken away we have $\text{C}_6\text{H}_6^{4+}$, unrealistic in view of the high charge. Replacing four carbons by four B^- and the neutral $\text{C}_2\text{B}_4\text{H}_6$ gives an octahedral structure;¹⁷ an all-boron octahedron has two negative charges ($\text{B}_6\text{H}_6^{2-}$), compensated by an accompanying cation.¹⁸ A similar procedure of removing electrons and arriving at three-dimensional structures can be applied to the cyclopentadienyl anion

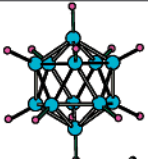
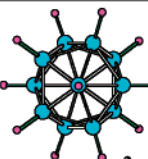
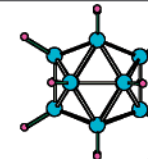
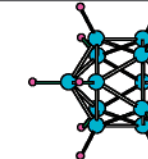
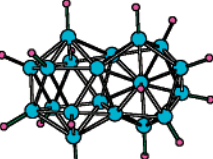
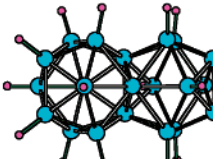
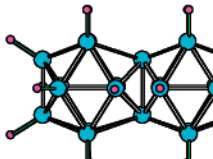
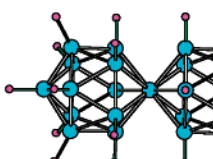
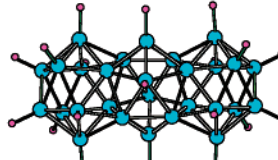
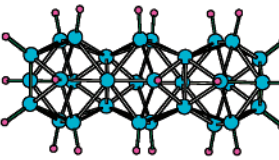
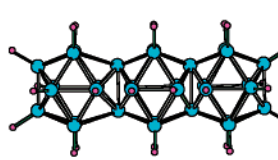
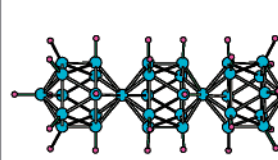
as well. Removal of two electrons from C_5H_5^- leads to square pyramidal C_5H_5^+ ;¹⁹ isoelectronic and isostructural B_5H_9 ²⁰ is known with four bridging hydrogens. Removal of another electron pair leads to $\text{C}_5\text{H}_5^{3+}$; the *closo*- $\text{B}_5\text{H}_5^{2-}$ is theoretically predicted to have a *closo*-trigonal bipyramidal structure, and its neutral analogue, isostructural $\text{C}_2\text{B}_3\text{H}_5$, is well known.¹²

We saw the relationship between benzene and the periodic two-dimensional sheet structure of MgB_2 (Figure 1). A three-dimensional structure is easily seen for the B_6^{2-} octahedra, where each B atom bonds to another B atom of the adjacent B_6 unit by a two-center, two-electron (2c-2e) bond. Divalent metal ions in the interstitial space of this $(\text{B}_6^{2-})_n$ solid make a neutral MB_6 network. Molecular structures with an empirical formula of MB_6 are well known with divalent metals such as Ca, Sr, and Ba; the crystal structure consists of an octahedral B_6 unit surrounded by eight metal atoms at each corner of the cubic unit cell.²¹ It is only a question of time until MgB_6 is also studied structurally.

Condensation Modes for Polyhedral Boranes

While $\text{B}_6\text{H}_6^{2-}$ could condense to give periodic structures through 2c-2e bonds, the electronic requirement for condensation of pentagonal pyramidal $\text{B}_5\text{H}_6^{4-}$ or $\text{C}_4\text{B}_2\text{H}_6$ is less obvious. In general, condensation between polyhedral borane cages can occur through sharing of one,

Chart 1. Application of the *mno* Rule: Variation of Charge as a Function of Increasing Condensation of Polyhedra with One-, Two-, Three-, and Four-Atom Sharing^a

	Type of Condensation			
	4-Vertex sharing ($B_{8m+4}H_{4m+8}^{2m-4}$)	Face sharing ($B_{9m+3}H_{6m+6}^{m-3}$)	Edge sharing ($B_{10m+2}H_{8m+4}^{-2}$)	Single vertex sharing ($B_{11m+1}H_{10m+2}^{-3m+1}$)
$m=1$	 $B_{12}H_{12}^{-2}$	 $B_{12}H_{12}^{-2}$	 $B_{12}H_{12}^{-2}$	 $B_{12}H_{12}^{-2}$
$m=2$	 $B_{20}H_{16}^0$	 $B_{21}H_{18}^{-1}$	 $B_{22}H_{20}^{-2}$	 $B_{23}H_{22}^{-5}$
$m=3$	 $B_{28}H_{20}^{+2}$	 $B_{30}H_{24}^0$	 $B_{32}H_{28}^{-2}$	 $B_{34}H_{32}^{-8}$
$m=4$	$B_{36}H_{24}^{+2}$	$B_{39}H_{30}^{+1}$	$B_{42}H_{36}^{-2}$	$B_{45}H_{42}^{-11}$
Increment in Charge	+2	+1	0	-3
Known examples	<i>closo</i> - $B_{20}H_{16}$ ²¹	<i>nido</i> - $B_{20}H_{16}(\text{NCCH}_3)_2$ ^{22a} <i>nido</i> - $S_2B_{16}H_{16}$ ^{22b}	<i>nido</i> - $B_{22}H_{22}^{-2}$; ^{23a} <i>bisnido</i> - $B_{18}H_{20}^{-2}$ ^{23b}	<i>closo</i> - $[(B_{11}H_{11})_2Cu]^{-3}$ ²⁴

^a The only sharing that does not change (neither increases nor decreases) charge is edge-sharing. This is involved in the polycondensation of benzenoid aromatics to graphite. Experimentally known examples of each condensation are also listed.

two, three, or four vertices. The electronic requirements of these condensation pathways are important in many ways; for example, this could help in understanding the structure of elemental boron.^{5d} We have formulated an electron counting rule, the *mno* rule for this purpose; according to this, the number of electron pairs needed for a stable condensed polyhedral structure is given by the sum of the number of cages (*m*), the number of vertices (*n*), and the number of single vertex shared atoms (*o*).⁴ This is demonstrated in Chart 1 using the icosahedral skeleton.

(i) *Four-vertex sharing*. Condensation of two icosahedral $B_{12}H_{12}^{2-}$ sharing four vertices leads to $B_{20}H_{16}$. According to the *mno* rule, 22 electron pairs ($m = 2$, $n = 20$, $o = 0$) are needed by this structure (Chart 1).²² Sixteen BH vertices provide one electron pair each, and the 4 shared boron atoms give 3 valence electrons each, making the structure neutral. The structure of $B_{20}H_{16}$ has been well known for many years.²² Further condensation by four-vertex sharing leads to a structure $B_{28}H_{20}$, with the *mno* count of 31 ($m = 3$, $n = 28$, $o = 0$). Twenty BH vertices and 8 shared boron atoms contribute 32 electron pairs,

making the structure electron excess by 2 units. This structure is not known. The *mno* rule leads to the homologous series with the molecular formula $B_{8m+4}H_{4m+8}^{2m-4}$. Thus, each condensation involving the sharing of four vertices reduces the charge by two units.

(ii) *Face or three-vertex sharing*. For the condensed product $B_{21}H_{18}$, formed by the face sharing of two icosahedra, the *mno* rule demands 23 electron pairs ($m = 2$, $n = 21$, $o = 0$). The structure has 18 electron pairs from 18 BH vertices, and 4.5 electron pairs from the three shared boron atoms. Thus, $B_{21}H_{18}$ should have unit negative charge. Further condensation leads to the neutral $B_{30}H_{24}$ ($m = 3$, $n = 30$, $o = 0$). Face condensation thus leads to a homologous series with the molecular formula $B_{9m+3}H_{6m+6}^{m-3}$. The decrease of charge by one unit with each condensation is to be contrasted to the decrease of two charges by the four-vertex shared condensation. Though these face-sharing *closo* structures are not experimentally characterized, the face sharing is observed in boron-rich solids.^{23,24} There are several examples of condensed *nido* boranes sharing triangular faces.²⁵ These follow the *mno* rule.

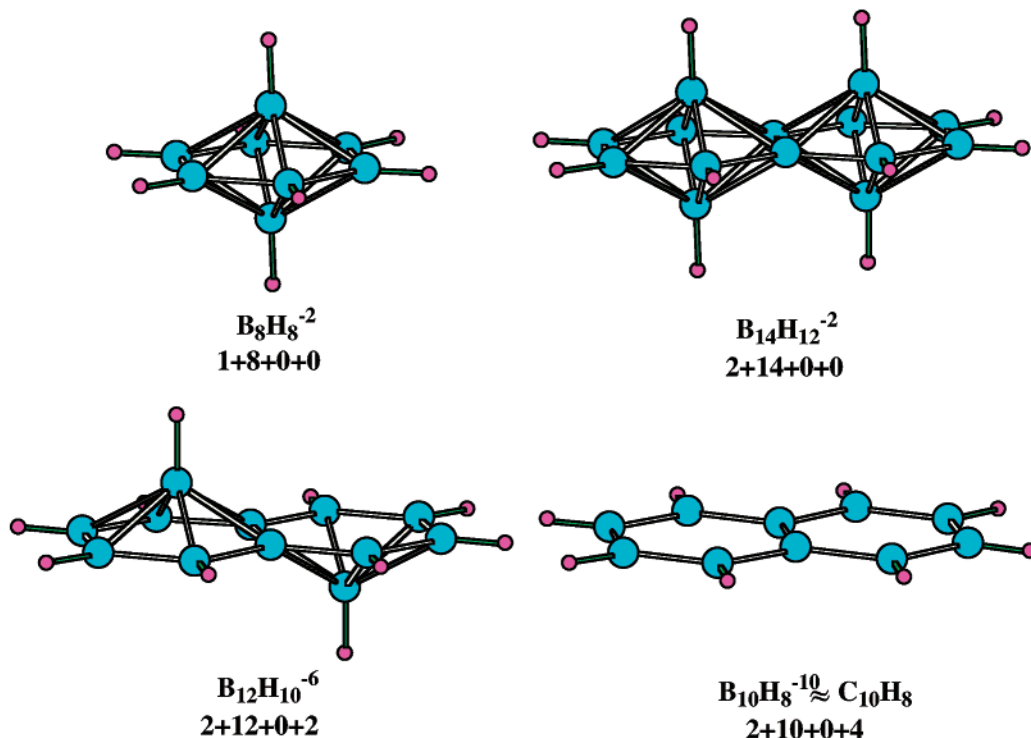


FIGURE 2. The relationship between Hückel aromatic naphthalene and hypothetical hexagonal boranes shows that Hückel's rule is a special case of the *mno* rule. The electron counting according to the *mno* rule is also indicated below each structure. For *closo*- $\text{B}_8\text{H}_8^{2-}$, $m = 1$, $n = 8$, $o = 0$, and p (number of missing vertices) = 0; for *closo*- $\text{B}_{14}\text{H}_{12}^{2-}$, $m = 2$, $n = 14$, $o = 0$, and $p = 0$; for *bisnido*- $\text{B}_{12}\text{H}_{10}^{6-}$, $m = 2$, $n = 12$, $o = 0$, and $p = 2$; and for *bisarachno*- $\text{B}_{10}\text{H}_8^{10-}$, $m = 2$, $n = 10$, $o = 0$, and $p = 4$.

(iii) *Edge-sharing condensation* (the *mno* rule and the Hückel rule). The edge-sharing $\text{B}_{22}\text{H}_{20}$ ($m = 2$, $n = 22$, $o = 0$) and $\text{B}_{32}\text{H}_{28}$ ($m = 3$, $n = 32$, $o = 0$) are found to have $2-$ charges. The molecular formula of the homologous series, $\text{B}_{10m+2}\text{H}_{8m+4}^{2-}$, shows that edge-sharing of *closo* structures does not change the charge. Icosahedral *closo* structures of this kind are not known owing to the nonbonding interaction between the adjacent atoms of fused cages. However, many edge-sharing *nido* systems have been synthesized.²⁶ Edge-sharing *bisarachno* systems lead to the equivalence of the *mno* rule and Hückel's $(4n + 2)$ π electron rule. This is demonstrated by the hypothetical hexagonal bipyramidal molecule, $\text{B}_8\text{H}_8^{2-}$ (D_{6h}), and by the edge-sharing condensed system $\text{B}_{14}\text{H}_{12}^{2-}$ ($m = 2$, $n = 14$, $o = 0$) (Figure 2). Removal of two vertices from $\text{B}_{14}\text{H}_{12}^{2-}$ leads to a *bisnido* structure, $\text{B}_{12}\text{H}_{10}$, with a $6-$ charge (Figure 2). The *bisarachno* structure, with a $10-$ charge, obtained by the removal of two more vertices, is isoelectronic to naphthalene, C_{10}H_8 . The difference between the electron counts comes from the skeletal σ -bonds, which are left out in the Hückel rule. Thus, Hückel's $(4n + 2)$ rule is a special case of the *mno* rule for edge-sharing *bisarachno* systems. If the number of C-C σ electrons is added to the number of $(4n + 2)$ π electrons, we get the number of electrons demanded by the *mno* rule.

(iv) *Single vertex sharing*. The single-vertex-sharing system $\text{B}_{23}\text{H}_{22}$ ($m = 2$, $n = 23$, $o = 1$) requires $5-$ charges for the skeletal bonding, and further condensation increases this requirement to $8-$, as in $\text{B}_{34}\text{H}_{32}$ ($m = 3$, $n = 34$, $o = 0$). The molecular formula of this homologous

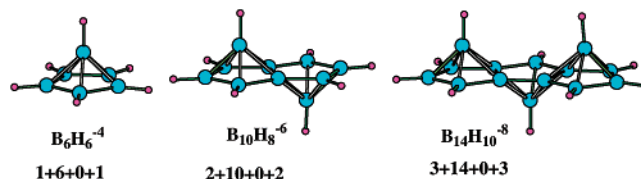


FIGURE 3. Edge-shared products of pentagonal pyramid $\text{B}_6\text{H}_6^{4-}$. The difference of B_4^{2-} between the two consecutive fused products is obvious. The electron counting according to the *mno* rule is also indicated.

series is $\text{B}_{11m+1}\text{H}_{10m+2}^{(-3m+1)}$. Such single-vertex-sharing systems are known with heavier elements at the shared position; an all-boron sandwiched structure is unrealistic due to the high charges.²⁷ In addition, a larger atom at the shared position ensures minimal steric interactions between the ring atoms on either side of it.

Thus, the charge requirement for condensation depends on the number of shared vertices (Chart 1). The *mno* rule also helps to find the combinations of condensations that retain the charge during polycondensation, such as three face sharings for every single atom sharing, etc. It is also important to note that such condensations are possible in principle between combinations of different polyhedra.

Armed with these rules, we return to $\text{B}_6\text{H}_6^{4-}$ (C_{5v}) and its polycondensation. By the *mno* rule, an edge-shared *bisnido* polyhedral borane B_{10}H_8 should have a charge of $6-$ ($m = 2$, $n = 10$, $o = 0$, p (no. of missing vertices) = 2) (Figure 3). A second condensation leads to $\text{B}_{14}\text{H}_{10}^{8-}$. Thus, condensation of each pentagonal pyramid results in the addition of a B_4 unit and an increase of $2-$ charges. An

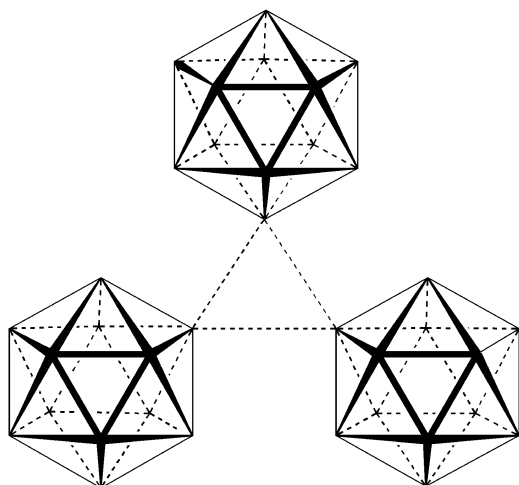


FIGURE 4. Structure of the α -rhombohedral boron. Six vertices lying close to the plane of the paper form the 3c-2e bonds among the icosahedral B_{12} 's, as shown, and the remaining vertices form a 2c-2e bond with the B_{12} above and below.

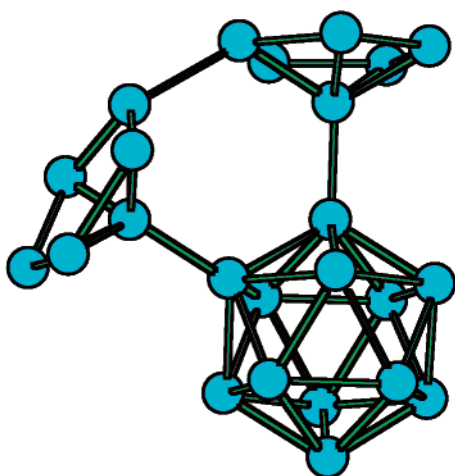


FIGURE 5. Fragment of B_{84} which shows the construction of B_{84} . Each vertex of B_{12} is connected to one pentagonal pyramidal B_6 unit, thus leading to the formation of a B_{84} unit.

analysis of this process also suggests the structure of MgB_4 .²⁸ The chains of pentagonal pyramidal units are connected to each other by removing the hydrogen atoms

of the remaining BH bonds and forming 2c-2e B-B bonds to complete the three-dimensional structure of MgB_4 ! Thus, we find the relationship between the three organic-based structures and metal borides in terms of MgB_2 -, MgB_4 -, and MgB_6 -based structures (Figure 1). The superconducting MgB_2 has distinct σ and π frameworks. It will be intriguing to see the changes when the structure is varied to a pentagonal pyramid, as in MgB_4 , or an octahedron, as in MgB_6 .

Fullerene (C_{60}) and β -Rhombohedral Boron

Icosahedral $B_{12}H_{12}^{2-}$ is the most stable among the polyhedral borane anions,²⁹ and so it is natural for nature to construct elemental boron from B_{12} icosahedra. The options available to satisfy the electron count are surprisingly numerous and contribute to the variety of structures available to elemental boron. Here, boron is far more versatile than carbon. The simplest, though not thermodynamically most stable, form of boron has a unit cell of icosahedral B_{12} , where six boron atoms form 2c-2e bonds with the neighboring B_{12} units. The remaining six boron atoms form the electron-saving 3c-2e bonds (Figure 4).^{5b,30} This saves two electrons ($1/3 \times 6 = 2$) per icosahedron, so that Wade's rule for the individual B_{12} unit is satisfied.

Three-center, two-electron bonds are not the strongest. The structure of the most stable polymorph, β -rhombohedral boron, starts out in the most natural way by building 12 icosahedra around an icosahedron. However, there are many problems with this perfect packing, as it cannot lead to three-dimensional periodicity.²³ (Incidentally, 12 B_{12} around a B_{12} is indeed a part of boron chemistry, but to sustain this arrangement requires electron donors in the form of metals, as in YB_{66} .³¹) The 12 outer icosahedra are not completed in β -boron; only the pentagonal pyramidal half is retained (Figure 5), so that a B_{84} unit is generated ($B_{12}@B_{12}@B_{60}$, Figure 6).⁵

We will come to the close similarity of the outer B_{60} surface of B_{84} to C_{60} shortly.⁵ Let us consider the way β -boron is built. When two of these B_{84} units come together, two half-icosahedra form a new icosahedron (Figure 7). The size of B_{84} restricts the total number of

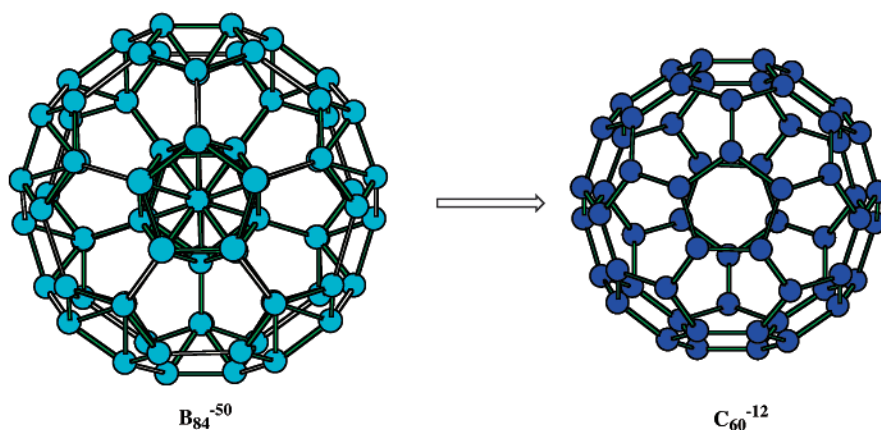


FIGURE 6. The B_{84} fragment of β -rhombohedral boron and fullerene are related structurally and electronically. The replacement of 12 pentagonal pyramidal B_6^{4-} by 12 C_5^- and removal of the inner B_{12} unit of the B_{84} leads to the fulleride anion, C_{60}^{12-} .

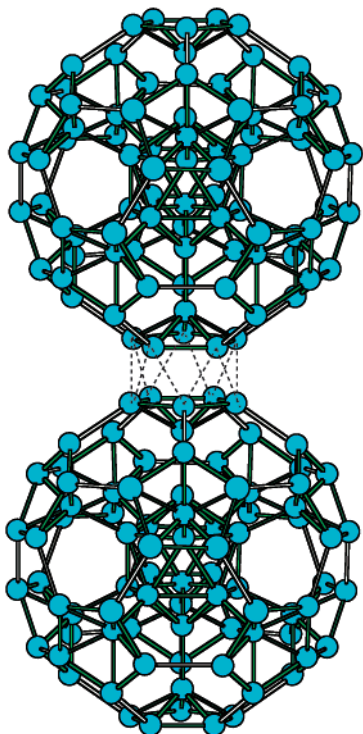


FIGURE 7. Arrangement of two B_{84} units in the β -rhombohedral boron. The six pentagonal pyramidal B_6 units on the surface of B_{84} complete the icosahedral framework, with similar B_6 units on other B_{84} units, as shown.

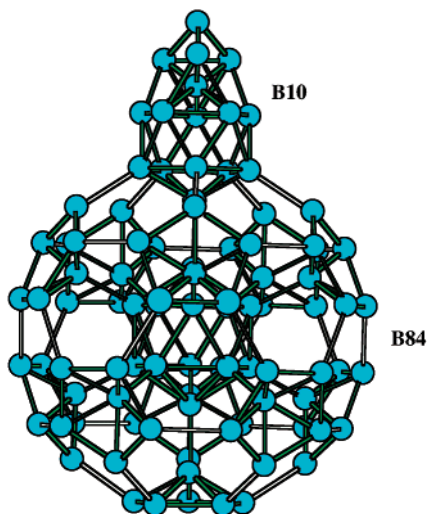


FIGURE 8. The six B_6 units on the B_{84} surface form an icosahedron with B_6 units of the B_{10} fragments.

units that can come around any one B_{84} in this fashion to six. Nature finds a way to generate icosahedra out of the remaining six half-icosahedra of B_{84} by adding a B_{10} unit which, by its unusual symmetry, provides three half-icosahedra (Figure 8). Three B_{84} units can be brought around this B_{10} unit. Two of these giant $(B_{84})_3B_{10}$ units are connected to each other by a single boron atom.

Removing the symmetry-related atoms, one gets the unit cell $84 + 10 + 10 + 1 = 105$. This also generates a new structural type that can be separated by breaking 2c-2e bonds, the B_{57} unit $B_{28}-B-B_{28}$ (Figure 9). The electron requirement for this large structure is worked out using

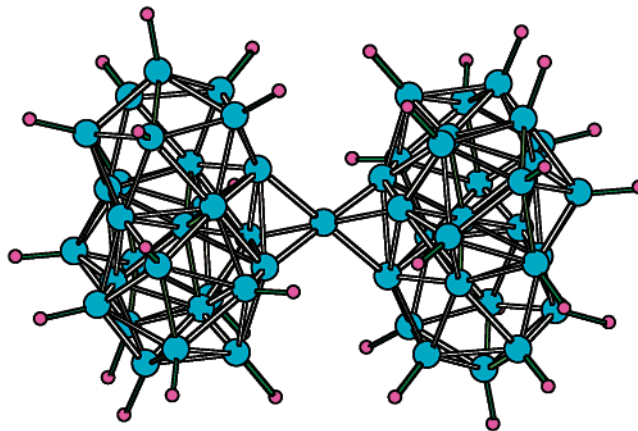


FIGURE 9. B_{57} unit in the β -rhombohedral boron. It consists of two B_{28} units which are connected through one boron atom. Each B_{28} unit has three icosahedral B_{12} 's, with each B_{12} sharing a face with the other two B_{12} 's.

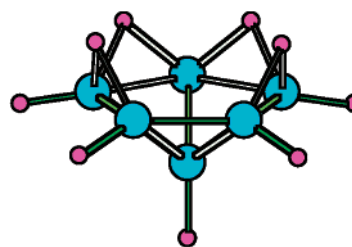


FIGURE 10. Structure of the well-known B_6H_{10} . The charge of $B_6H_6^{4-}$ is compensated by four bridging hydrogens.

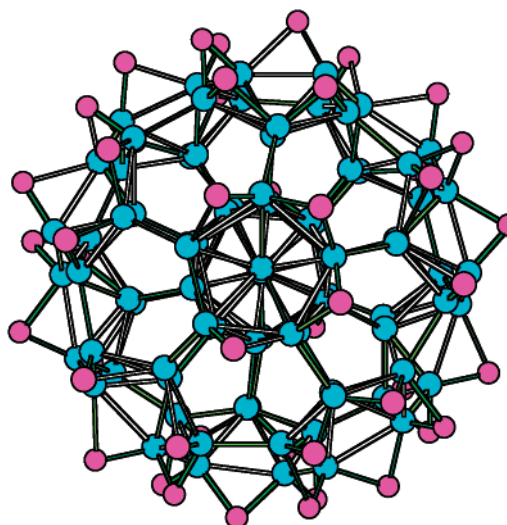


FIGURE 11. Structure of $B_{84}H_{50}$. The electron deficiency of B_{84} is compensated by adding 50 bridging hydrogens.

the *mno* rule by adding hydrogens to the dangling valencies.^{5d} According to this, the B_{57} unit has three extra electrons and should have a 3+ charge (the *mno* count of the $B_{57}H_{36}$ molecule is $8 + 57 + 1 = 66$; 36 electron pairs are obtained from BH vertices, and 31.5 electron pairs are provided by the remaining boron vertices, making the molecule in excess of 3 electrons), which is confirmed computationally as well.^{5d} The remaining B_{48} unit (out of the B_{105}) has four icosahedral B_{12} units and must have 8- charge. Thus, the unit cell, B_{105} , will be deficient by 5 ($= 8 - 3$) electrons. An early band structure

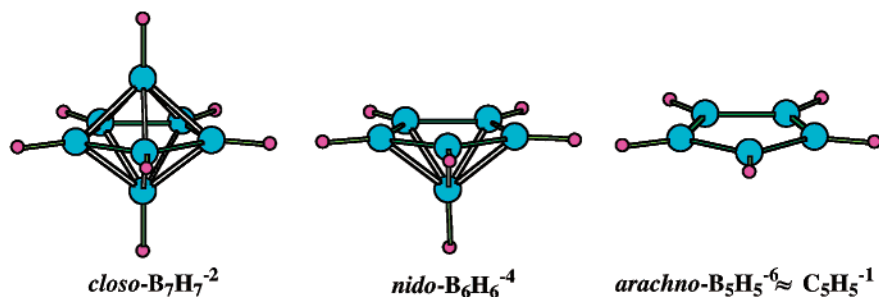


FIGURE 12. The isoelectronic equivalence of *arachno*-B₅H₅⁶⁻, derived from the *closo*-B₇H₇²⁻ by removing two vertices, with C₅H₅⁻ is shown.

calculation by Bullet confirmed this deficiency in the B₁₀₅ structure.³² However, the properties of elemental boron do not support this. More recent X-ray studies indicate that the unit cell is B_{106.66} and there are 20 symmetry-equivalent atomic positions in the unit cell, of which 6 are partially occupied.²⁴ Among these, one has six-fold symmetry and a partial occupancy of about 5/6 and belongs to the B₅₇ part. This missing boron atom, with its three valence electrons, takes care of the 3+ charge. The unit cell still requires eight electrons; these are provided by the extra occupancy of 2.66 (106.66 – 104) boron atoms in the many holes inside B₈₄ (2.66 × 3 ≈ 8). Counterions can also impart neutrality to the structure. Lithium boride (LiB₁₃), with β -rhombohedral structure, is known experimentally.³³ Here the deficiency of electrons is taken care of by lithium atoms (Li₈B₁₀₄). This points to the possibility of MgB₂₆ with a β -rhombohedral structure, thus adding one more candidate to the list of magnesium borides discussed earlier.

Since the discovery of fullerenes, chemists have been fascinated by the endohedral chemistry possible by encapsulating large atoms inside the vacant cavity (stuffing). Were the B₈₄ (B₁₂@B₇₂) (Figure 6) unit electron sufficient, it would be a remarkably stable stuffed boron fullerene similar to the endohedral fullerenes with 24 boron atoms inside borafullerene (B₆₀). The electron deficiency of B₈₄ can be easily calculated. The 12 pentagonal pyramidal B₆ units in B₈₄ require four electrons each (a la C₄B₂H₆), totaling 48 electrons. An additional two electrons are required for the central B₁₂. Thus, a B₈₄⁵⁰⁻ should be appropriate! Therefore, we could anticipate a stable isoelectronic Si₅₀B₃₄ with 50 Si atoms and 10B atoms on the fullerene-like surface.³⁴ The molecular species B₆H₆⁴⁻ (C_{5v}) could compensate the charge by replacing 4B⁻ by 4C;¹⁵ an additional way that nature has found is to protonate four times, as in B₆H₁₀ (Figure 10).¹⁶ An analogous B₈₄H₄₈²⁻ species, where each of the 12 five-membered B₅ rings is quadruply protonated, must be electron sufficient.³⁵ We have carried out PM3 calculations³⁶ on B₈₄H₅₀ structures obtained by adding two bridging hydrogen atoms to the B₈₄H₄₈²⁻ isomer with D_{3d} symmetry. (There are 1256602779 isomers possible for B₈₄H₅₀, including geometrical and optical isomers, the number obtained from the enumeration of isomers reported for C₆₀H₅₀.³⁷) The calculations showed this isomer of neutral B₈₄H₅₀ to be a minimum on the potential energy surface (Figure 11).

A more direct connection between fullerenes and β -boron is available through the *arachno* formulation of

polyhedral boranes. Removal of the axial BH group from the *nido* pentagonal pyramidal B₆H₆⁴⁻ leads to the *arachno* planar B₅H₅⁶⁻ (Figure 12). This is isoelectronic with the aromatic cyclopentadienyl anion C₅H₅⁻. If the central B₁₂ of the B₈₄ is removed and the 12 pentagonal pyramidal B₆ units are replaced by 12 C₅⁻ units, what remains is C₆₀¹²⁻ (Figure 6). This has already been generated from C₆₀ as C₆₀Li₁₂ and C₆₀K₁₂.³⁸ There is also experimental evidence for the stable neutral structure C₄₈N₁₂.³⁹ While there may be other structures that are lower in energy, the one with a nitrogen in each of the five-membered rings should be a good possibility. Once such a relation is established, it is possible to reverse the argument. It should be possible to design polyhedral boranes and even elemental boron polymorphs based on other fullerenes with the right electron count, even though individual stabilities will depend on many factors. Thus, even the fullerenes are not so far away from boron after all.

Obviously, the relationships between carbon and boron are manifold. The isoelectronic equivalence of carbon by B⁻ on one hand and the relationship between C₆₀¹²⁻ and B₈₄ on the other indicate that these neighboring elements share a lot in common; nature is yet to unveil many secrets in this area.

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References

- (1) Hawthorne, M. F. The role of chemistry in the development of boron neutron capture therapy of cancer. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 950–984.
- (2) (a) Lipscomb, W. N. *Boron Hydrides*; Benjamin: New York, 1963. (b) Lipscomb, W. N. Borides and Boranes. *J. Less-Common Met.* **1981**, *82*, 1–20.
- (3) (a) Wade, K. The structural significance of the number of skeletal bonding electron-pairs in carboranes, the higher boranes and borane anions, and various transition metal carbonyl cluster compounds. *Chem. Commun.* **1971**, 792–793. (b) Wade, K. Structural and Bonding Patterns in Cluster Chemistry. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–16.
- (4) (a) Jemmis, E. D.; Balakrishnarajan, M. M.; Pancharatna, P. D. A unifying electron counting rule for macropolyhedral boranes, metallaboranes and metallocenes. *J. Am. Chem. Soc.* **2001**, *123*, 4313–4323. (b) Jemmis, E. D.; Balakrishnarajan, M. M.; Pancharatna, P. D. Electronic requirements for macropolyhedral boranes. *Chem. Rev.* **2002**, *102*, 93–144.

- (5) (a) Buschbeck, K. C. Boron compounds: Elemental boron and boron carbides. *Gmelin Handbook of Inorganic Chemistry*; Springer: Berlin, 1981; Vol. XIII, Suppl. 2. (b) Wells, A. F. *Structural Inorganic Chemistry*; Oxford University Press: Oxford, 1975. (c) King, R. B. Three-dimensional aromaticity in polyhedral boranes and related molecules. *Chem. Rev.* **2001**, *101*, 1119–1152. (d) Jemmis, E. D.; Balakrishnarajan, M. M. Polyhedral boranes and elemental boron: direct structural relations and diverse electronic requirements. *J. Am. Chem. Soc.* **2001**, *123*, 4324–4330.
- (6) (a) Pople, J. A.; Lathan, W. A.; Hehre, W. J. Molecular orbital theory of the electronic structure of organic compounds. VI. Geometries and energies of small hydrocarbons. *J. Am. Chem. Soc.* **1971**, *93*, 808–815. (b) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. Molecular orbital theory of the electronic structure of organic molecules. 40. Structure and energies of C1–C3 carbocations, including effects of electron correlation. *J. Am. Chem. Soc.* **1981**, *103*, 5649–5657. (c) Kaldor, A.; Porter, R. F. Infrared spectra of the pyrolysis products of borane carbonyl in an argon matrix. *J. Am. Chem. Soc.* **1971**, *93*, 2140–2145.
- (7) (a) Olah, G. A.; Westerman, P. W.; Mo, Y. K.; Klopman, G. Electrostatic reactions at single bonds. VII. Hydrogen–Deuterium exchange accompanying protolysis (Deuterolysis) of the borohydride and aluminium hydride anions with anhydrous strong acids. The intermediacy of pentahydroboron (BH₅) and pentahydroaluminum (AlH₅) and their structural relationship with the methonium ion (CH₅⁺). *J. Am. Chem. Soc.* **1972**, *94*, 7859–7862. (b) Rasul, G. A.; Olah, G. A. Hexa-, Hepta- and Octacoordinate boronium ions: BH₆⁺, BH₇²⁺ and BH₈³⁺. *Inorg. Chem.* **1997**, *36*, 1278–1281. (c) DePu, C. H.; Gareyev, R.; Hankin, J.; Davico, G. E.; Damrauer, R. Formation of BH₆⁺ in the gas phase. *J. Am. Chem. Soc.* **1997**, *119*, 427–428. (d) Olah, G. A.; Rasul, G. Triprotonated methane, CH₇³⁺: The parent heptacoordinate carbonium ion. *J. Am. Chem. Soc.* **1996**, *118*, 8503–8504.
- (8) Worle, M.; Nesper, R. Infinite, linear, unbranched boronide chains in LiB_x–Isoelectronic to polyynes and polycumulene. *Angew. Chem., Int. Ed.* **2000**, *39*, 2349–2353.
- (9) Jones, M. E.; Marsh, R. E. The preparation and structure of magnesium boride, MgB₂. *J. Am. Chem. Soc.* **1954**, *76*, 1434–1436.
- (10) Nagamatsu, J.; Nakagawa, N.; Muranaka, T.; Zenitani, Y.; Akimitsu, J. Superconductivity at 39 K in magnesium boride. *Nature* **2001**, *410*, 63–64.
- (11) (a) Aihara, J.-I. Three-dimensional aromaticity of polyhedral boranes. *J. Am. Chem. Soc.* **1978**, *100*, 3339–3342. (b) King, R. B.; Rouvray, D. H. Chemical applications of group theory and topology. 7. A graph-theoretical interpretation of the bonding topology in polyhedral boranes, carboranes, and metal clusters. *J. Am. Chem. Soc.* **1977**, *99*, 7834–7840. (c) Shapiro, I.; Good, C. D.; Williams, R. E. The carborane series: B_nC₂H_{n+2}. I. B₃C₂H₅. *J. Am. Chem. Soc.* **1962**, *84*, 3837–3840.
- (12) *The Borane, Carborane, Carbocation Continuum*; Casanova, J., Ed.; John Wiley: New York, 1998.
- (13) (a) Hogeveen, H.; Kwant, P. W. (CCH₃)₆²⁺, an Unusual dication. *J. Am. Chem. Soc.* **1974**, *96*, 2208–2214. (b) Hogeveen, H.; Kwant, P. W. Pyramidal mono- and dications: bridge between organic and organometallic chemistry. *Acc. Chem. Res.* **1975**, *8*, 413–420.
- (14) (a) Jutzi, P.; Seufert, A. Synthesis and dynamic behavior of pentamethyl cyclopentadienyl boranes. *Angew. Chem., Int. Ed.* **1977**, *16*, 41–42. (b) Brown, H. C.; Ravindran, N. The reaction of alkynes with dichloroborane ethyl etherate in the presence of boron trichloride. A simple, general synthesis of alkenyl dichloroboranes. *J. Organomet. Chem.* **1978**, *61*, C5–C7. (c) Jutzi, P.; Seufert, A.; Buchner, W. 1-Halogen-2,3,4,5,6-pentamethyl-2,3,4,5,6-pentacarba-nido-hexaboran(6)-Kationer, ein neuer nido-carbaboran-Typ. *Chem. Ber.* **1979**, *112*, 2488–2493. (d) Jutzi, P.; Dohmeier, C.; Koppe, R.; Robl, C.; Schnockel, H. Crystal structure of [Cp⁺BBR]⁻[AlBr₄]. *J. Org. Met. Chem.* **1995**, *487*, 127–130.
- (15) (a) Binger, P. Darstellung alkylierter tetracarbahexaborane(6), eine neue klasse stabilisierter organoborane. *Tetrahedron Lett.* **1966**, *7*, 2675–2680. (b) Onak, T. P.; Wong, G. F. Preparation of the pentagonal pyramidal carborane, 2,3,4,5-tetracarba-nido-hexaborane(6). *J. Am. Chem. Soc.* **1970**, *92*, 5226–5226. (c) Miller, V. R.; Grimes, R. N. Carborane formation in alkyne-borane gas-phase systems. V. Conversion of two-carbon to four-carbon carboranes via alkyne insertion. Nuclear magnetic resonance studies of tetra carba-nido-hexaboranes. *Inorg. Chem.* **1972**, *11*, 862–865. (d) Pasinski, J. P.; Beudet, R. Microwave spectrum, structure and dipole moment of 2,3,4,5-tetracarbahexaborane(6). *J. Chem. Phys.* **1974**, *61*, 683–691. (e) Herberhold, M.; Bertholdt, U.; Milius, W.; Glockle, A.; Wrackmeyer, B. Combining carboranes with transition metal clusters: Synthesis and X-ray structure analysis of a 1,2,3,4,5-pentamethyl-2,3,4,5-tetracarba-nido-hexaborane(6) derivative. *Chem. Commun.* **1996**, 1219–1220.
- (16) (a) Hirschfeld, F. L.; Eriks, K.; Dickerson, R. E.; Lippert, E. L., Jr.; Lipscomb, W. N. Molecular and crystal structure of B₈H₁₀. *J. Chem. Phys.* **1958**, *28*, 56–61. (b) Stock, A. *Hydrides of Boron and Silicon*; Cornell University Press: Ithaca, NY, 1957; pp 74–79.
- (17) Shapiro, I.; Keilin, B.; Williams, R. E.; Good, C. D. The Carborane series: B_nC₂H_{n+2}. II. The two isomers of B₄C₂H₆. *J. Am. Chem. Soc.* **1963**, *85*, 3167–3171.
- (18) Schaeffer, R.; Johnson, Q.; Smith, G. S. The crystal and molecular structure of Tetramethyl Ammonium Hexahydrohexaborate. *Inorg. Chem.* **1965**, *4*, 917–918.
- (19) (a) William, R. E. Carboranes and boranes; Polyhedra and polyhedral fragments. *Inorg. Chem.* **1971**, *10*, 210–214. (b) Masamune, S.; Sakai, M.; Ona, H. Nature of the (CH)₅⁺ species. I. Solvolysis of 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pent-3-yl benzoate. *J. Am. Chem. Soc.* **1972**, *94*, 8955–8956.
- (20) (a) Dulmage, W. J.; Lipscomb, W. N. The molecular structure of pentaborane. *J. Am. Chem. Soc.* **1951**, *73*, 3539–3539. (b) Hedberg, K.; Jones, M. E.; Schomaker, V. On the structure of stable pentaborane. *J. Am. Chem. Soc.* **1951**, *73*, 3538–3539.
- (21) Blum, P.; Bertaut, F. Contribution à l'Étude des Borures à Teneur Élevée en Bore. *Acta Crystallogr.* **1954**, *7*, 81–86.
- (22) (a) Miller, H. C.; Muetterties, E. L. A new boron hydride, B₂₀H₁₆. *J. Am. Chem. Soc.* **1963**, *85*, 3506–3506. (b) Dobrott, D. R.; Friedman, L. B.; Lipscomb, W. N. Molecular and Crystal Structure of B₂₀H₁₆. *J. Chem. Phys.* **1964**, *40*, 866–872. (c) Miller, N. E.; Forstener, J. A.; Muetterties, E. L. Chemistry of boranes. XXI Icosaborane-16. *Inorg. Chem.* **1964**, *3*, 1690–1694.
- (23) (a) Hoard, J. L.; Sullenger, D. B.; Kennard, C. H. L.; Hughes, R. E. The structure analysis of β-rhombohedral boron. *J. Solid State Chem.* **1970**, *1*, 268–277.
- (24) (a) Slack, G. A.; Hejna, C. I.; Garbaskar, M. F.; Kasper, J. S. The crystal structure and density of β-rhombohedral boron. *J. Solid State Chem.* **1988**, *76*, 52–63. (b) Slack, G. A.; Hejna, C. I.; Garbaskar, M. F.; Kasper, J. S. X-ray study of transition metal dopants in β-Boron. *J. Solid State Chem.* **1988**, *76*, 64–86.
- (25) (a) Enemark, J. H.; Friedman, H.; Lipscomb, W. N. The molecular and crystal structure of B₂₀H₁₆(NCCH₃)₂. CH₃CN. *Inorg. Chem.* **1966**, *5*, 2165–2173. (b) Jelinek, T.; Kennedy, J. D.; Stibr, B. Macropolyhedral borane containing cluster chemistry. Cluster fusion to give the novel nido-nido eighteen vertex dithiooctadecaborane (anti)-[9,9'-S₂B₁₆H₁₆]. *J. Chem. Soc., Chem. Commun.* **1994**, 1415–1416.
- (26) (a) Pitochelli, A. R.; Hawthorne, M. F.; The preparation of a new boron hydride B₁₈H₂₂. *J. Am. Chem. Soc.* **1962**, *84*, 3218–3218. (b) Hosmane, N. S.; Franken, A.; Zhang, G.; Srivastava, R. R.; Smith, R. Y.; Spielvogel, F. Synthesis and crystal structure of a novel fused polyhedral borane dianion, [B₂₂H₂₂]²⁻: Potential precursor for use in boron neutron capture therapy (BNCT) of cancer. *Main Group Met. Chem.* **1988**, *21*, 319–324.
- (27) Kester, J. G.; Keller, D.; Huffmann, J. C.; Benefiel, M. A.; Geiger, W. E.; Atwood, C.; Siedle, A. R.; Korba, G. A.; Todd, L. J. Synthesis and properties of copper and nickel complexes of the general formula (B₁₁H₁₁)₂Mⁿ⁺. Crystal structure of [(n-Bu)₄N]₃[Cu(B₁₁H₁₁)₂]. *Inorg. Chem.* **1994**, *33*, 5438–5442.
- (28) Naslain, R.; Guette, R.; Barret, M. *J. Solid State Chem.* **1973**, *8*, 68–85.
- (29) (a) Jemmis, E. D. Overlap control and stability of polyhedral molecules: Closo-carboranes. *J. Am. Chem. Soc.* **1982**, *104*, 7017–7020. (b) Jemmis, E. D.; Pavankumar, P. N. V. Stability of polyhedral borane anions and carboranes. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1984**, *93*, 479–489. (c) Porterfield, W. W.; Jones, M. E.; Gill, W. R.; Wade, K. Extended Hückel MO studies of boranes. 1. Relative stabilities of closo-B_nH_n and -B_nH_n²⁻. *Inorg. Chem.* **1990**, *29*, 2914–2919. (d) Jemmis, E. D.; Balakrishnarajan, M. M. The ubiquitous icosahedral B₁₂ in boron chemistry. *Bull. Mater. Sci.* **1999**, *22*, 863–867.
- (30) Emin, D.; Aselage, J.; Beckel, C. L.; Howard, I. A.; Wood, C. *Boron Rich Solids: AIP Conference Proceedings 231*; American Institute of Physics: New York, 1994.
- (31) Richards, S. M.; Kaspar, J. S. The crystal structure of YB₆₆. *Acta Crystallogr.* **1969**, *B25*, 237–251.
- (32) Bullet, D. W. Structure and bonding in crystalline boron and B₁₂C₃. *J. Phys. C* **1982**, *15*, 415–426.
- (33) Kobayashi, M.; Higashi, I.; Matsuda, H.; Kimura, K. Rietveld Analysis of LiB₁₃ with β-Rhombohedral Boron Structure. *J. Alloys Compd.* **1995**, *221*, 120–124.
- (34) (a) Jemmis, E. D.; Kiran, B. A covalent way to stuff fullerenes. *Curr. Science.* **1994**, *66*, 766–767. (b) Jemmis, E. D.; Kiran, B. Elemental boron route to stuffed fullerenes. In *Computational Chemistry: Reviews of Current Trends*, Vol. 1; Leszczynski, J., Ed.; World Scientific: Singapore, 1996; p 175.

- (35) Yao, H.-J.; Hu, C.-H.; Sun, J.; Jin, R.-S.; Zheng, P.-J.; Bould, J.; Greatrex, R.; Kennedy, J. D.; Ormsby, D. L.; Thornton-Pett, M. Isolation and structure of $[(PPh_3)_3(PPh_2)_2Pd_4B_{20}H_{16}]$. A possible prognostic for new globular borane-based cluster architectures. *Collect. Czech. Chem. Commun.* **1999**, *64*, 927–937.
- (36) (a) Stewart, J. J. P. Optimization of parameters for semi-empirical methods I—method. *J. Comput. Chem.* **1989**, *10*, 209–220. (b) Stewart, J. J. P. Optimization of parameters for semi-empirical methods II—applications. *J. Comput. Chem.* **1989**, *10*, 221–264.
- (37) Balasubramanian, K. Enumeration of isomers of polysubstituted C_{60} and application to NMR. *Chem. Phys. Lett.* **1991**, *182*, 257–262.
- (38) (a) Martin, T. P.; Malinowski, N.; Zimmermann, U.; Näher, U.; Schaber, H. Metal coated fullerene molecules and clusters. *J. Chem. Phys.* **1993**, *99*, 4210–4212. (b) Cristofolini, L.; Ricco, M.; De Renzi, R. Li Doping of fullerene: $Li_{12}C_{60}$. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Ed.; The Electrochemical Society Inc.: Pennington, NJ, 1998; Vol. 6, pp 667–676.
- (39) (a) Hultman, L.; Stafström, S.; Czigány, Z.; Neidhardt, J.; Hellgren, N.; Brunell, I. F.; Suenaga, K.; Colliex, C. Cross-linked nano-onions of Carbon Nitride in the solid phase: Existence of a novel $C_{48}N_{12}$ Aza-Fullerene. *Phys. Rev. Lett.* **2001**, *87*, 225503–225700. (b) Manaa, M. R.; Sprehn, D. W.; Ichord, H. A. Prediction of extended aromaticity for a novel $C_{48}N_{12}$ azafullerene structure. *J. Am. Chem. Soc.* **2002**, *124*, 13990–13991. (c) Aromaticity provides bucky stability. *Chem. Eng. News.* **2002**, *80* (48), 30.

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