Polyhedral Boranes and Elemental Boron: Direct Structural Relations and Diverse Electronic Requirements

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Abstract: Details of the electronic and structural connections between macropolyhedral boranes and elemental boron are reported. The nature of electron deficiency in the β-rhombohedral polymorph of boron is analyzed by using a molecular fragments approach with boranes as model systems. The $B_{57}H_{36}$ molecule constructed from such an approach has three more electrons than mandated by the electron-counting rules (Balakrishnarajan, M. M.; Jemmis, E. D. *J. Am. Chem. Soc*. **2000**, *122*, 456. Jemmis, E. D.; Balakrishnarajan, M. M.; Pancharatna, P. D. *J. Am Chem. Soc*. **2001**, *123*, 4313−4323.) devised for macropolyhedral boranes. This is also confirmed by electronic structure calculations at the extended Hückel and B3LYP/6-31G* levels. The aromaticity of this $B_{57}H_{36}{}^{3+}$ molecule is on par with the most stable $B_{12}H_{12}{}^{2-}$ itself, as revealed by nuclear independent chemical shift calculations. The B_{57} skeleton can be made electron precise by adopting a *nido* arrangement by eliminating an atom from the *closo* skeleton, so that three valence electrons will be removed. The exact site of elimination, governed by thermodynamic factors, necessitates the removal of a boron atom from any of the six symmetrically equivalent B[13] sites in the unit cell. This leads to partial occupancies, which causes disorder in packing, as revealed by X-ray structure studies. The rest of the boron atoms are distributed in icosahedral B_{12} fragments, whose two-electron deficiency is satisfied by the capping of extra atoms, distributed statistically in the interstitial sites. These results show that the three-dimensional network of the idealized β-rhombohedral unit cell is not stable, unlike the electron-precise carbon polymorphs such as diamond and graphite. Thus, disorder in the form of partial occupancies, interstitial atoms, alien atoms, etc., is necessary for electron sufficiency and hence for the stability of this polymorphic form. Through these ingenious steps, all components of the unit cell attain electron sufficiency, which explains the high thermodynamic stability of the polymorph. The connection established between boranes and elemental boron in terms of their structure and distribution of electrons has important implications in understanding the structure of boron-rich solids and new strategies to utilize their diverse and technologically important properties.

Introduction

Boron exists in a wide variety of complex isomorphic forms. Approximately 16 allotropes have been reported so far,[1] and many of them have widely varying crystal structures with well-defined holes and often have more than 50 atoms per unit cell. Due to the high melting point and corrosiveness of the liquid boron, the phase diagram of boron is largely unknown.[2] Only three pure boron phases, α-rhombohedral B_{12}, β-rhombohedral B_{105}, and tetragonal B_{192}, are known experimentally, with others being contaminated by various impurities.[3]

The thermodynamically most stable allotropic form, the β-rhombohedral polymorph, has very unusual properties.[2,4] It has very low volatility, with a dramatically high melting point (~2450 °C). It is stronger than steel, harder than corundum, and at the same time lighter than aluminum. On the modified Mohr's scale, it has a hardness value of 11, compared to the values 15 for diamond and 14 for boron nitride. β-Rhombohedral boron also acts as a p-type semiconductor and can be made an n-type by doping with elements such as iron.[5,6] These remarkable physical properties and the chemical inertness of β-rhombohedral boron presage a diverse range of industrial applications.[4] The high hardness and melting point make this polymorph an ideal starting point in the development of new materials to withstand extreme velocities, high temperatures, and intense pressures.[7] They are mainly employed in heat-resistant alloys, in devices in rocket building, and as an abrasive in cutting and polishing materials.[8a] Filaments of boron have considerable tensile and flexural strength. Their dimensional response to stress is entirely elastic, with no discernible dislocation movements.[8b] Isotopic boron is used in the protective coating of the walls of the nuclear reactor and as control rods

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for neutron capture and shielding.[8c] Boriding extends the lifetime of tools, and there is immense also hope that high-temperature semiconductor devices (~1800 °C) can be generated by suitable doping.[5,6] Boron is also superior to diamond and cubic boron nitride in terms of its ease of preparation and its density.[9] Due to the diverse range of applications, several theoretical and experimental studies were conducted to exploit the structural features responsible for its remarkable properties. Boron's experimentally reported ideal unit cell is found to be electron deficient by theoretical studies. A clear understanding of the structural features and electronic requirements of this polymorph will provide useful insights about the prerequisites for B_{12}-based clusters in general and β-rhombohedral boron in particular.

It is worthwhile to analyze the bonding and electronic structure of a covalent solid in relation to the dominant covalent compounds of the element. Nowhere is it as well illustrated as in the compounds of carbon and its polymorphs. The structural similarity between saturated hydrocarbons and diamond is obvious as the construction of sp^3 hybridization extends naturally to diamond. Similarly, the relationship between benzene, benzenoid hydrocarbons, and graphite is tangible through planar sp^2 hybridization of carbon. The same principles also govern the structure of fullerenes. Huckel's $4n + 2$ rule that governs the π-delocalized structure has been an early guide in the development of condensed aromatics. Direct comparison of boron to carbon through sp, sp^2, and sp^3 is possible in some metal borides. Equivalent to the linear polycarbyne C_n is $(B^-)_n$, which is experimentally observed as stacks of $(B^-)_n$ and $(Li^+)_n$.[10] Similarly, the graphite structure resulting from the polycondensation of benzene is reproduced by MgB_2, where each carbon is replaced by B^- and for every two B^- units there is an Mg^{2+} intercalating.[11] With weakly bound electrons, these anionic sheets have just now been characterized as superconducting at ~40 K.[11b] The chemistry of sp^3-hybridized tetrahedral carbon is reproduced by monomeric structures such as BH_4^- and BH_3-CO. A diamond-like arrangement of B^- is impractical because of charge accumulation. Polycondensation based on polyhedral boranes that are the equivalents of aromatic hydrocarbons is necessary to get to the structure of elemental boron. In many ways, macropolyhedral boranes[12] are equivalent for condensed polycyclic hydrocarbons. Despite the existence of several macropolyhedral boranes[12] and metalloboranes, there had been no generally applicable electron-counting scheme to systematic development. We have recently delineated an electron-counting scheme[13,14] for macropolyhedral boranes, so the stage is set to explore the relationship between polyhedral boranes and polymorphs of elemental boron, which are also covalent solids.

Icosahedral $B_{12}H_{12}^{2-}$ adopts the perfect symmetry of icosahedron,[15] is found to be the most stable among the various polyhedral boranes synthesized so far, and is the equivalent of benzene in polyhedral borane chemistry.[16] The three-dimensional aromaticity of the highly symmetrical structure[17] and perfect matching of the geometric requirements from overlap[18] criteria and from the solid geometry of icosahedron[15] account for this extra stability. Hence, it is natural that the icosahedral B_{12} appears as the dominant structural pattern ubiquitously present in all boron polymorphs and many boron-rich solids.[1,4,7] But, unlike benzene and graphite, the construction of boron polymorphs from the B_{12} unit poses several difficulties. The 5-fold rotational symmetry of the icosahedra is incompatible with lattice periodicity. Besides, unlike methane and benzene, which are neutral building blocks of diamond and graphite, $B_{12}H_{12}$ requires an additional two electrons.[16] Thus, a B_{12}-based covalent network will accumulate negative charge. Consequently, the stability of all boron polymorphs and B_{12}-based solids depends on the extent to which and the mechanism by which electron sufficiency is achieved in the lattice.[16] The wide variety of physicochemical properties exhibited by boron and boron-rich solids are a direct consequence of these electronic structure details.

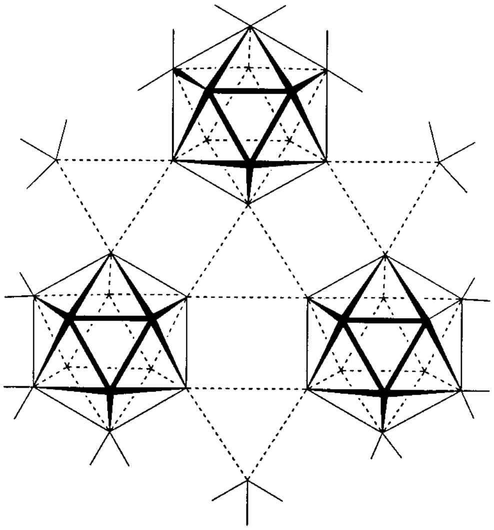

Figure 1. Structure of α-rhombohedral boron viewed through the C_3 axis, showing 3c-2e bonds. The triangular boron atoms above and below form 2c-2e bonds with other B_{12} units.

The principles by which the icosahedral B_{12} skeleton and other boron clusters are put together to form the polymorphs of boron are rather involved in view of the complexity of the unit cells encountered. Among the many polymorphs, the α-rhombohedral boron[4] is the only polymorph in which the connection to $B_{12}H_{12}^{2-}$ is obvious due to its ingenious structure (Figure 1). Here, the B_{12} itself forms the unit cell, and six boron atoms of the icosahedron that lie in the opposite faces form exohedral two-center, two-electron (2c-2e) bonds with neighboring icosahedra along the lattice directions. The remaining six boron atoms bind with adjacent B_{12} units in electron-saving three-center, two-electron (3c-2e) bonds, leaving two electrons $(6 - (6 \times 2)/3)$ for the skeletal binding, so that the structure is electron sufficient. The thermodynamic stability of this polymorph is greatly reduced due to the presence of these weak 3c-2e bonds.

Theoretical studies[19] on the idealized β-rhombohedral boron unit cell have shown that the experimentally reported structure[20] is electron deficient. Several conflicting views about its bonding

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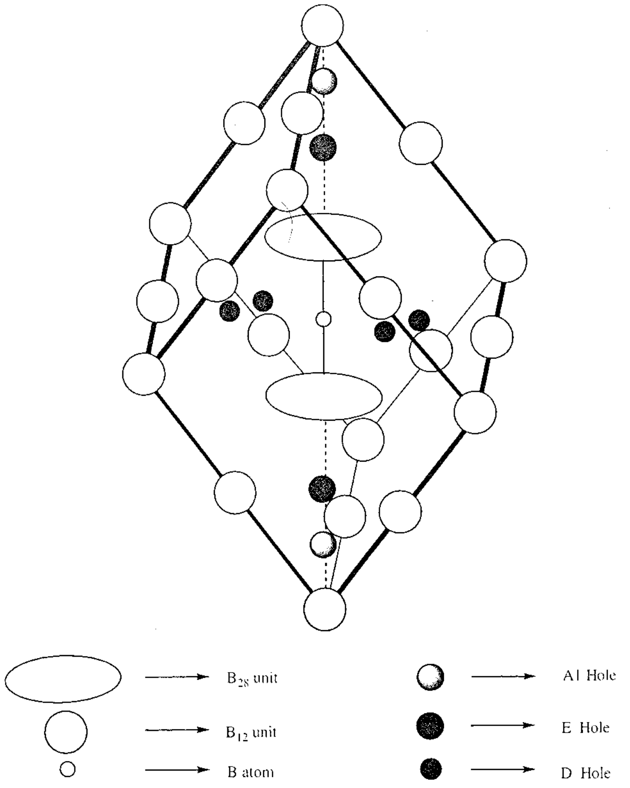

Figure 2. Structure of the ideal β-rhombohedral boron unit cell, depicting the B_{12} units at the vertex and edge centers leaving the $B_{28}-B-B_{28}$ unit along the main body diagonal.

prevail in the literature.[6,21] The difficulty is amplified by the disorder in the crystal due to interstitial atoms and partial occupancies.[22,23] The present investigation is the first systematic attempt to explain the structural motifs responsible for its phenomenal stability. We approach this problem of estimating the electron deficiency in the β-rhombohedral skeleton by conducting an in-depth inquiry into the structural patterns of its ideal unit cell using MO theory. We analyze the known crystal structure to determine the various fragments of the polymorph and to arrive at the appropriate electronic requirements. In the final section, we explain how the disorder in the unit cell, such as partial occupancies and "impurities" in the interstitial sites, is necessary to expiate the electron requirements.

The Structure of β-Rhombohedral Boron

This section provides an abstract characterization of the β-rhombohedral polymorph of elemental boron and generates stable molecular fragments by pruning the 2c-2e bonds whose fusion produces the original skeleton. The β-rhombohedral polymorph has 105 atoms in its idealized unit cell, which falls in the space group $R\bar{3}m$ with the lattice constants $a = 10.145$ Å, $\alpha = 65.28°$.[20] The 105 atoms can be separated as $B_{84} + B_{10}-B-B_{10}$ in an intricate arrangement. The different sites of the atoms are partially depicted in Figures 2 and 3. The numbering scheme for the boron atoms in Figure 3 is the same as that used earlier in the X-ray report.[22] The B_{84} cluster (the three soccer balls of Figure 3) can be viewed as a truncated icosahedron, formed by a central B_{12} unit (B[5] and B[6]), linked to 12 staggered half-icosahedral B_6 units in the directions of its six quasi-5-fold axes ($B_{12}@B_{12}@B_{60}$). Six of these B_6 units (2B-[1], 2B[2], B[9], and B[7]) are juxtaposed with similar B_{84} units in the rhombohedral directions to complete six additional B_{12} units. The remaining six equatorial B_6 units (2B[3], 2B[4], B[10], and B[8]) are linked to six different B_{10} units (3B[11], 3B[12], 3B[13], and B[14]) with C_{3v} symmetry, to acquire nearly icosahedral arrangement. Each of these B_{10} units completes three icosahedra by connecting three B_6 units from three different B_{84} neighbors. These three icosahedra share the central atom B[14] of B_{10}. Six atoms of B_{10} (3B[11] and 3B[12]) are posited in such a way that each pair of B_{12} units shares two of these atoms. One each of the remaining three atoms of the B_{10} belongs exclusively to each of the three B_{12} units (B[13]). In addition, a unique atom B[15] links these three atoms to a similar set of three atoms of an adjacent B_{10} unit. B[15] is the only atom that is not a part of any icosahedral arrangement in the whole unit cell. Thus, 104 atoms of this 105-atom unit cell are involved in the polyhedral network, scattered in 13 perceivable icosahedral or nearly icosahedral B_{12} frameworks.

The whole system can be viewed as a giant molecule bound by covalent bonds just as in diamond. It is to be noted that this structure is very open, as the space filling is only 36%. Three major types of holes exist (Figure 2).[24] Four similar holes (D) of smaller size surround the unique boron atom, which links two B_{10} units. Two distinct holes comparatively larger in size are located along the major symmetry axis of the $B_{10}-B-B_{10}$ skeleton, one inside the B_{84} unit (A1) and the other outside (E). All these holes are frequently occupied by boron itself or by alien atoms, which makes preparation of the pure sample impossible. The larger holes can accommodate even transition metal atoms without forging any major change in the structure.[25]

To assess the electronic requirements, the β-rhombohedral unit cell of 105 atoms can be pruned at the points of external 2c-2e bonds saturating the dangling valences with hydrogen atoms. The resulting fragments consist of one central B_{12} unit, six half-icosahedral units, and a giant B_{57} fragment. The B_{12} at the center (B_{12a}) of the B_{84} unit has almost equal B−B distances and hence requires two electrons. The six half-icosahedral units (2B[1], 2B[2], B[9], and B[7]) are an integral part of B_{12} units that are shared between B_{84} units and hence require one electron each. Hence, apart from the requirements of the B_{57} unit, the system requires eight electrons for electron sufficiency.

The electronic requirement of the B_{57} unit is difficult to assign by chemical intuition.[26] Its skeleton consists of two B_{28} units linked together by a central boron atom. Each B_{28} unit has three B_{12} units, in which each B_{12} unit shares a boron triangle with the other two. The geometry of the B_{28} unit obtrudes the central capping atoms as much as 0.5 Å into the icosahedron, which distorts the icosahedral geometry considerably. The B_{57} unit cannot be pruned further without breaking the polyhedral bonds, as the 2c-2e bonds are completely absent. Here, we employ our recently introduced *mno* rule[14] for macropolyhedral boranes to assess its electronic requirements. Computations based on

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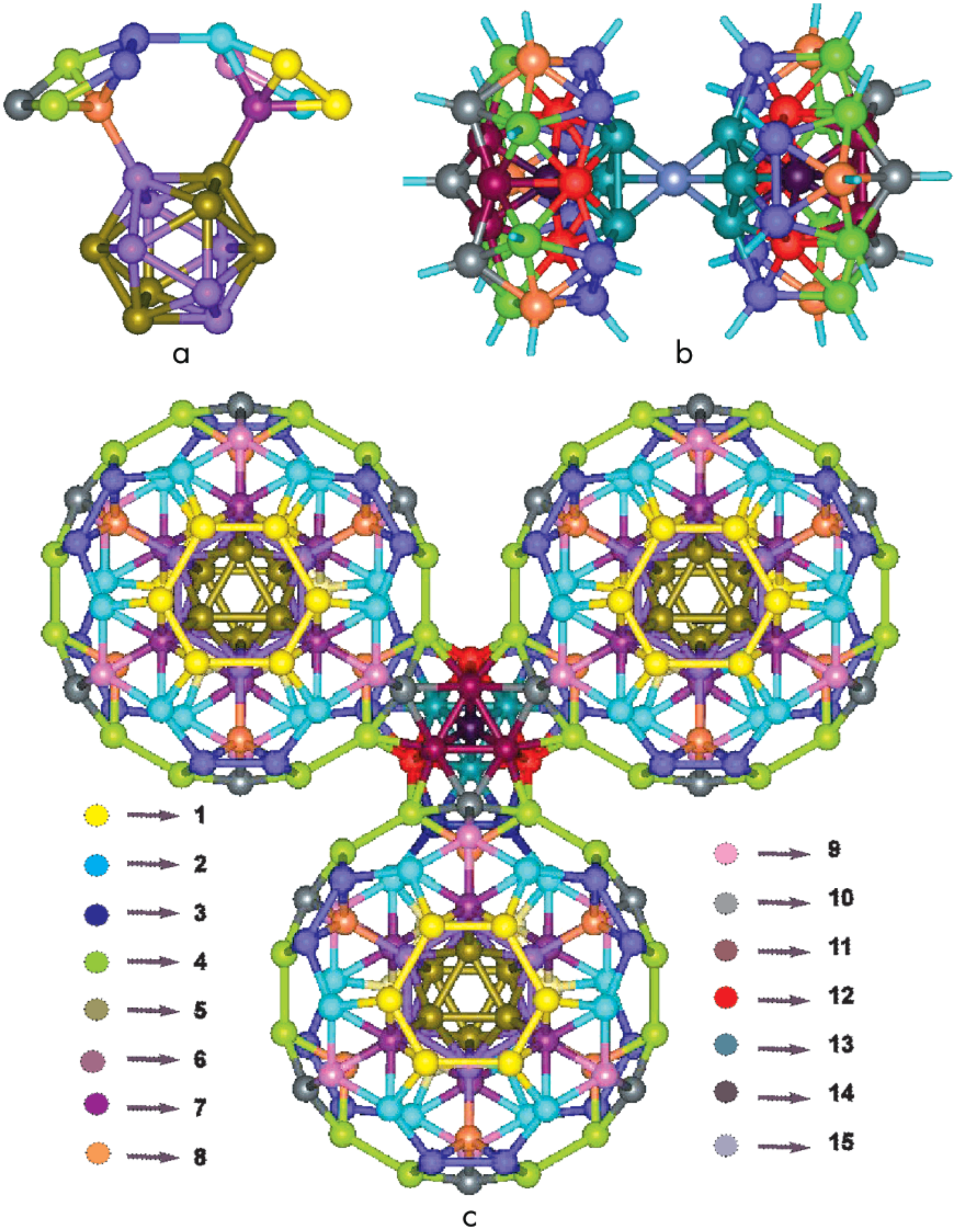

Figure 3. Description of the crystal structure of β-rhombohedral boron, starting from the smaller fragments. (a) Construction of the B_{84} unit, starting with the inner B_{12} icosahedron. Each vertex of this inner B_{12} is connected to a pentagonal pyramidal B_6 unit, leading to B_{84} cluster (B_{12}@B_{12}@B_{60} arrangement). The two unique B_6 units are shown. (b) Each B_{84} has six B_{84} units and six B_{10} units around it. One B_{10} unit and three B_{84} units are shown here. Each pentagonal pyramid unit attached to the central B_{10} achieves a nearly icosahedral arrangement, which is shown in the middle. (c) The B_{28} unit referred to in (b) is connected to another B_{28} unit through a single boron atom bridge ($B_{28}-B-B_{28}$). The bonds that are directed out correspond to the B−H bonds of the associated $B_{57}H_{36}$ molecule obtained from this fragment.

molecular orbital theory are performed to confirm the electronic requirements of this unit precisely and to assess its stability, which is the subject of the next section.

Bonding in the B_{57} Unit

The electronic requirement of the B_{57} unit can be easily deduced by making a direct connection of macropolyhedral boranes to β-rhombohedral boron. The dangling orbitals that are remnants of the σ bonds can be saturated with hydrogens to give the molecular formula $B_{57}H_{36}$ (Figure 3c). According to the *mno* rule,[14] polycondensed polyhedral boranes require $m + n + o$ skeletal electron pairs for stability, where m is the number of polyhedra, n is the number of vertices, and o is the number of single-vertex-sharing connections. For $B_{57}H_{36}$, $m = 8$, $n = 57$, and $o = 1$, so that 66 electron pairs are required. The number available is 67.5 [36(from 36 BH) + (21 × 3)/2 (from 21 B)]. Obviously, there are three electrons more than necessary in the B_{57} fragment. The results are contrary to the popular notion that polyhedral boranes are always electron deficient and anionic.[26] Extended Hückel calculations[27] on $B_{57}H_{36}$ (Figure 3c) with structural parameters of $B_{57}H_{36}$ obtained from X-ray data and standard B−H distances help to confirm this electron count. This molecule is of D_{3d} symmetry and there is a large difference (3.22 eV) between the HOMO and LUMO if we consider $B_{57}H_{36}$ as a trication. No such significant splitting exists anywhere else in the frontier range. The structure is optimized using AM1 and PM3 semiempirical methods[28] and found to be a minimum in the potential energy surface (HOMO−LUMO gaps 7.84 and 6.43 eV, respectively). The molecule was also optimized[28] keeping D_{3d} symmetry constraints at the B3LYP/6-31G* level,[29] which is known to give bond lengths with an accuracy of 0.005 Å for the borane family. The B−B bond lengths in the optimized geometry are within the reasonable range for the *closo*-borane family.[31] In addition, there exists good correspondence between the X-ray-determined values of the B_{57} skeleton of the β-rhombohedral boron and the bond lengths calculated for $B_{57}H_{36}^{3+}$ (variation within 0.006 Å).[23] The longest bond length (1.991 Å) is found between the boron atoms forming the triangle that connects the central boron atom, which is very close to the X-ray value of 1.98 Å. Though the difference in exohedral substitution may alter the bond lengths, these bonds are formed between boron atoms with no exohedral substituents.

The requirement of a +3 charge for $B_{57}H_{36}$ can be further confirmed by removing the central boron atom (B[15]) and individually assessing the electronic requirements of the B_{28} unit by saturating the three dangling bonds with hydrogen atoms. This results in the borane $B_{28}H_{21}$ with C_{3v} symmetry. Application of the *mno* rule ($m = 3$, $n = 28$, and $o = 0$) gives 31 skeletal bonding molecular orbitals for this borane. The 21 B−H groups give 42 electrons, and the seven shared boron atoms give 21 electrons for polyhedral bonding, making a total of 63 electrons. Since 62 electrons are sufficient to fill up the bonding molecular orbitals, this molecule should exist as a positive charged species. The +1 charge of this molecule was confirmed by extended Hückel calculations. The geometry of a $B_{28}H_{21}^{+}$ molecule of C_{3v} symmetry was optimized at the B3LYP/6-31G* level and was characterized as a minimum by frequency calculations. All the bond lengths fell well within the range typical of the borane family (1.952−1.729 Å) and agreed with the experimental data, except for the breaking of the triangular face (B[13]) that has been hydrogenated.

The electronic requirement of the giant $H_{18}B_{28}{-}B{-}B_{28}H_{18}$ molecule can also be obtained by bringing two B_{28} units ($B_{28}H_{21}$ without the three hydrogens at the triangular face) and a boron atom together. Removal of six hydrogen atoms from the two $B_{28}H_{21}^{+}$ species generates six valence orbitals, each with an electron. Four of the six symmetry-adapted linear combinations of these orbitals interact with the four atomic orbitals of the central boron atom. Only four stabilized molecular orbitals result from these, so that eight electrons can be accommodated.[31] However, there are nine electrons available, six from the two $B_{28}H_{18}^{+}$ species and three from the central boron atom. It is therefore necessary to have an additional positive charge for $B_{57}H_{36}$, making a total charge of +3.

The stabilities of polyhedral boranes are also reflected in the magnetic properties. Nucleus independent chemical shift (NICS) calculations[30] were carried out (B3LYP/6-31G* level) by positing a ghost atom at the centroid of a B_{12} unit to estimate the amount of aromatic stabilization. The NICS value for $B_{28}H_{21}^{+}$ is −17.98, which indicates that these boranes are appreciably aromatic and comparable to the NICS value of −23.14 computed for the experimentally reported[33] condensed system $B_{20}H_{16}$. We also estimated the aromaticity of the giant $B_{57}H_{36}$ molecule using NICS calculations. The NICS value of −33.3 that we calculate for the aromaticity of condensed B_{12} units in $B_{57}H_{36}$ is on par with the value of −35.7 found for $B_{12}H_{12}^{2-}$, a system acknowledged to be highly aromatic and the most stable.[32]

Consistent results from all of these MO computations lead to the conclusion that the $B_{57}H_{36}$ polyhedral skeleton demands a +3 charge for stability. Hence, this provides a counterbalancing effect by partially offsetting the electron deficiency of other individual B_{12} units in the idealized unit cell. If this charge is taken into account, the electron deficiency of the unit cell is reduced to just five electrons. These results also account for the five-electron deficiency estimated by the earlier band structure calculations[19] made on the idealized unit cell. The idealized unit cell, with its 10 icosahedral or nearly icosahedral units, is anticipated to require a minimum of 20 electrons for stability. The reduction in electron deficiency from 20 to 5 can be primarily attributed to the polycondensed icosahedra of the B_{57} fragment. But the lack of metal-like character associated with the electron deficiency and high thermodynamic stability suggests that the initially reported ideal crystal structure is improbable. Nature circumvents this five-electron deficiency by means of partial occupancies and implanting additional atoms in the interstitial sites, which can be best understood, once again, by inquiring into the nature of bonding in boranes.

Electronic Effects of Disorder

The idealized unit cell and the fragments discussed above are based on the first experimental X-ray structure study,[20] which tacitly assumed the disorder in the crystal, such as partial occupancies and interstitial atoms, was due to errors in the preparation and inaccuracy of the X-ray data. However, the idealized structure with 105 atoms in the unit cell is impossible to prepare due to the presence of interstitial atoms termed “boron impurities” and partial occupancies in boron. X-ray studies are also complicated by the presence of carbon, which is the major impurity in β-rhombohedral boron, as it is difficult to distinguish a few carbon atoms in a boron cluster. However, the most recent X-ray report[23] on the structure of β-rhombohedral boron in three different samples reveals five more partially occupied boron sites where the carbon concentration is estimated to be less than 0.2 atom for the 320-atom hexagonal unit cell. This study also

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shows the existence of six partially occupied sites. Here we show that this disorder is innate to the crystal in order to alleviate electronic requirements of various fragments and is not necessarily due to errors in the experiment. It should, however, be emphasized that there is room for improvement in the structural analysis. We also show that the extent and nature of this disorder can be best understood again by using the knowledge of bonding acquired from the chemistry of boranes.

In polyhedral boranes chemistry, it is generally accepted that for an *n*-vertex borane, when the vertices are equally spaced on the surface of a sphere (i.e., *closo*), the number of skeletal bonding molecular orbitals required is just one more than the number of boron atoms in the cluster.[8a] Thus, for an icosahedral cluster, $n + 1$ skeletal electron pairs are required. More importantly, this requirement is not altered, even if this *closo*-borane has defects, by removing some vertices to form *nido*,*arachno* structures or by the presence of additional capping vertices. The former is ubiquitously known as Wade's rule,[34] whereas the latter attribute is known as the capping principle.[35] Though the capping group will normally have exo bonds in borane chemistry, our recent results based on theoretical calculations show that even isolated atoms such as boron, beryllium, etc., without any exohedral substitution, can cap a deltahedral face of polyhedral boranes without altering the electronic requirements, functioning merely as electron donors for polyhedral bonding.[36] These concepts are true even in the case of macropolyhedral systems, where there are more than one polyhedral unit condensed. These rules suggest that there are several possible ways to make the various fragments of the β-rhombohedral units electron precise. The only way for the individual B_{12} units to obtain the required two additional electrons is to acquire capping vertices that can be easily accommodated in the interstitial holes. The B_{57} fragment can solve the problem of having three extra electrons by shedding one of its vertices to become a *nido* skeleton. Since the boron atoms with exopolyhedral 2c-2e-bonds cannot be removed without disturbing the framework, the expulsion of a vertex should originate from one of the boron atoms in the B_{10} unit. There are four such positions, B[11], B[12], B[13], and B[14], from which boron could be removed. The borane structure $B_{56}H_{36}$ that is left behind still requires the same 66 electron pairs. The actual electron count is also 66 $(36 + (20 \times 3)/2)$. Frontier orbital energies from the extended Hückel calculations using the geometry obtained at the B3LYP/6-31G* level for each of these isomers of $B_{56}H_{36}$ support the formulation as neutral. Among these isomers, the one where one boron atom is absent from the B[13] position is found to be the most stable, and others are higher in energy than the structure without B[13] by 18.0 (B[11]), 42.4 (B[12]), and 20.8 (B[14]) kcal/mol, respectively. But do these computational results agree with the experiments?

The partial occupancies of the framework sites as well as the interstitial sites support this analysis. Of the 15 distinct framework sites reported earlier,[20] the site B[13] is found to be partially occupied, as expected.[22,23] As there are six equivalent B[13] positions, the absence of a single B[13] atom in β-B_{105} translates to an occupancy of $100 \times 5/6 = 83.33\%$. The observed occupancies of the B[13] site in the three samples are 77.7%, 74.5%, and 73.0%.[23] This is considerably lower than the anticipated value of 83.3%. The exact percent occupancy of B[13] depends on many factors, but the most important one is the number and extent of occupancy of interstitial atoms. The β-rhombohedral boron structure has at least five interstitial atoms, B[16]−B[20], with partial occupancies ranging from 2.5% to 28.4%. Of these, B[17], a site near the D hole, is within bonding distance to B[15] and B [13], which are involved in the capping. This has an occupancy range of 3.2−9.7% in various samples.[23] It is as if the system has overcorrected the excess electron by removing more than one boron atom and then tried to restore it by bridging with an additional site of low occupancy. This idea is reinforced by the fact that the percent occupancies of B[13] (77.7%, 74.5%, 73.0%) and B[17] (3.2%, 8.5%, 9.7%) sites for the three well-studied elemental boron samples total 80.9%, 83.0%, and 82.7%, respectively. This is, indeed, not far from the 83.33% estimated above on the basis of the structure. As mentioned earlier, there are many causes for uncertainties in the experimentally reported occupancy data. However, the general trends are clear.

There are four other partially occupied sites in addition to the B[17] discussed above:[23] B[16] (25.8−28.4% occupancy), B[18] (5.8−7.4%), B[19] (7.0−7.2%), and B[20] (0.25%). These atoms provide the extra electrons required for the individual B_{12} units by deltahedral capping. Of these, B[16] with the highest occupancy is positioned near the "A" hole within bonding distance of pairs of B[1], B[5], and B[7], the atoms belonging to the four electron-deficient icosahedra. Among the other partially occupied holes, B[20] is also within bonding distance of the central icosahedra. B[18] and B[19] are almost at the periphery of the B_{84} ball, within bonding distance of it. The partial occupancies of these atoms add up to 38.8%, 44.0%, and 47.8% in the three different samples. This translates to 7, 8, and 8.6 electrons, not far from the 8 electrons necessary. Thus, the ideal unit cell does not represent 105 atoms. At the B_{57} fragment, one B is missing, so that three extra electrons are removed. At the same time, the interstitial B atoms, $8/3 = 2.66$ of them, provide eight electrons so that the unit cell has $(105 - 1 + 2.66) = 106.66$ atoms.

It is important to notice that the electron deficiency has been and can be compensated by an array of different elements occupying the interstitial sites. However, excess electrons in B_{57} mandate the partial occupancy of B[13]. For example, eight lithium atoms are needed to fill the β-rhombohedral boron structure with electrons.[37] The Li atoms are in the D (18h, 6-fold symmetry) and E (6c, 2-fold symmetry) holes with complete occupancies, so that eight electrons are provided. No further lithium is taken up by the structure in the rhombohedral geometry. Once the structure is electron sufficient, the extraneous B(17−20) disappears. However, the excess electrons of the B_{57} unit remain as evidenced by the partial occupancy of B[13] of 0.64. Even with the perfect electron count, the icosahedra in $B_{57}H_{36}{}^{3+}$ must be distorted, as the symmetry is less than I_h. This is also true of the icosahedra in the element. While the extent of distortion may be controlled by the electron occupancy, the distortion away from the ideal icosahedron is built into the system by the lower symmetry. The variation in the properties of the boron and borides therefore should arise from the partial occupancies as well as extra atoms in the interstitial holes. The occupancies of alien atoms in several β-rhombohedral boron structure-based compounds can be understood in a similar way.

Conclusion

The five-electron deficiency of an ideal β-rhombohedral boron unit cell discovered earlier by band structure calculations can

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be systematically understood by drawing parallels between boron-rich solids and polyhedral borane chemistry. This approach clearly reveals that the condensed polyhedral unit B_{57} is found to have three electrons more than required for its bonding. This reasoning also reveals that the partial occupancies of the framework atoms and the presence of interstitial atoms are necessary for the stable growth of the β-rhombohedral unit cell to satisfy the varying electronic requirements. The current results open up a new way of counting electrons and explaining and arriving at an innumerable combination of atoms and ions that can be used to control the properties of β-B_{105} structures through planned doping for the electron-rich and electron-deficient parts. We should gain a better understanding of the increased size of the unit cell, the variation of the oxidation state of the doped metals as a function of its concentration, the optimum concentration of dopants for highest hardness, the change of p- to n-type conductivity with increasing dopant concentrations, and many other characteristics of β-B_{105}-related solids from the molecular connection established here. This study also points to new directions in molecular chemistry. For example, the B_{10} unit of B_{57} suggests a possible encapsulated structure $X@B_{12}H_{12}$ species.[36] Recognition of these facts should benefit the solid-state and the molecular worlds. The quest for β-B_{105}-based structures and their diverse and intriguing properties of technological importance can proceed better with the molecular connection. Many examples of similar interconnections between compounds of an element and its polymorphs must exist and are worth pursuing. This study also suggests the necessity to take a close look at vacancies and extra occupancies in solids before ignoring them as structural defects: these may be required by the electronic structure.

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