Unknowns in the chemistry of boron

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Structural links between benzenoid aromatics and graphite as well as saturated hydrocarbons and diamond are seen in high school text books. A similar understanding is only beginning to emerge in the chemistry of boron. Unlike benzenoid aromatics where the condensation is usually by edge-sharing, there are several ways of condensing polyhedral boranes. These include edge-sharing, triangular face sharing, four atom sharing and a single atom sharing. An electron counting *mno* rule similar to the Hückel $4n + 2$ π electron counting rule will be presented for mono and condensed polyhedral boranes. Application of this rule shows that the structural details of β-rhombohedral boron, such as the vacancies and extra occupancies in the unit cell are a consequence of the electronic requirements rather than defects in the structure. While this is the beginning of a general understanding, there is a long way to go before the quantitative details emerge in this area, along with the synthesis and chemistry of a variety of condensed boranes. These ideas also provide a relationship between boron and fullerenes. Further, designing stable boron-rich candidates for physiological applications and materials for use in extreme conditions are areas that are waiting to be explored.

Keywords: Benzoid aromatics, elemental boron, macropolyhedral boranes, *mno* electron counting rule.

Introduction

AFTER 150 years of the periodic table one would imagine that the basic chemistry surrounding each element is fully characterized. While this is true of several elements there are many elements whose chemistry is only beginning to take shape. Carbon is an element whose basic chemistry is largely known. Organic and bio-chemistry is the mainstay for life and the basic principle of the structure, synthesis and reaction here are well characterized. Similarly, the bonding principles available for explaining the chemistry of carbon compounds have also provided a link to the allotropes of carbon. The tetrahedral sp^3 hybridization has brought the connection between saturated hydrocarbons and the structure of diamond. Trigonal sp^2 hybridization has brought the structural connection between graphite and benzenoid aromatics. The fullerenes, nano-

tubes and graphene are an extension of the saga of the sp^2 hybridization of carbon (Figure 1). The adjacent element, boron, has not developed to the same extent and we would highlight the recent developments in the chemistry of boron and the unknown world of boron in this article. There are still many mysteries that we would like to know in this area.

With one electron less than carbon which is the embodiment of electron precise chemistry, boron has been termed as electron deficient. The electron deficient boron compounds do not fit into the conventional wisdom of the two centre two electron ($2c–2e$) localized chemical bonding[1]. However, the structural chemistry relating to electron deficiency is already seen in cationic carbon compounds and often these are treated as exceptions. But the electron deficient boron compounds can only be explained by delocalized multicentre bonding, the kind that brings in an extension of the Lewis $2c–2e$ bond so prevalent in carbon chemistry[2]. However, the concept is not so unknown even in carbon chemistry. Delocalization of electrons has been the norm in sp^2 carbon compounds and the related allotrope graphite[3]. Over the years the multicentre bonding has been successfully employed to explain the structure, bonding and reactivity of electron deficient boron compounds[4]. While the chemistry of boron can be described without recourse to carbon, the familiarity of carbon chemistry helps to bring out the contrast. So we often compare the chemistry of the two elements[5].

Boranes and elemental boron

The bonding of the smaller compounds such as B_2H_6, higher boranes and polyhedral boranes is studied well[4,6]. The connection between the compounds of boron and its allotropes has been exclusive. Figure 2 indicates the effect of bringing in electron deficiency to the compounds of carbon and the gradual variations that uses the structural principles of boron and its chemistry in relation with carbon[7–9].

What is commonly known about the multicentre picture of bonding in boranes and relationship to small organic molecules is shown in Figure 2. A correlation diagram between the molecular orbitals of benzenoid aromatics and the corresponding pyramidal and polyhedral structures is the beginning point in this exercise (the part of Figure 2 enclosed in a square). While this is the molecular end of the picture, the solid state or the elemental end has the equivalent of the benzenoid aromatics, the pyramidal cation
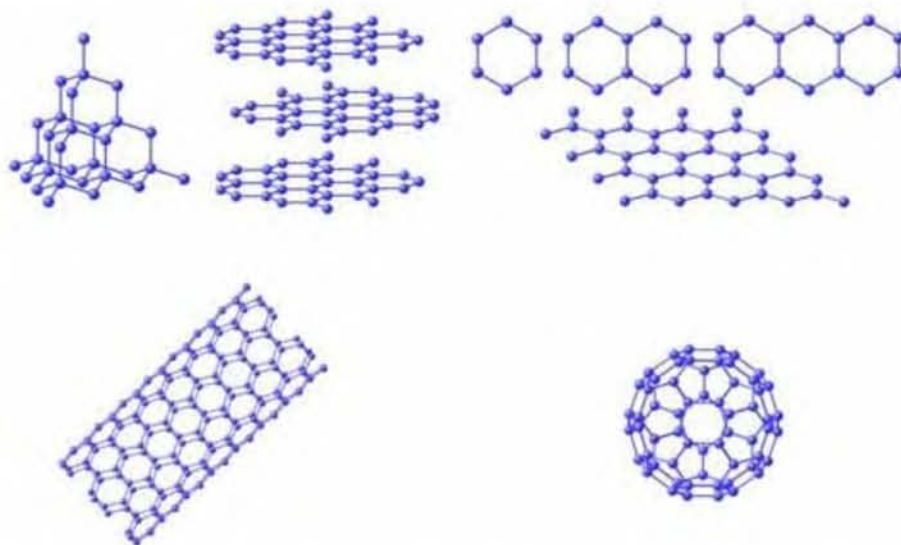
Figure 1. The common allotropes of carbon with its rich structural chemistry: diamond, graphite, graphene, nanotube and fullerene.
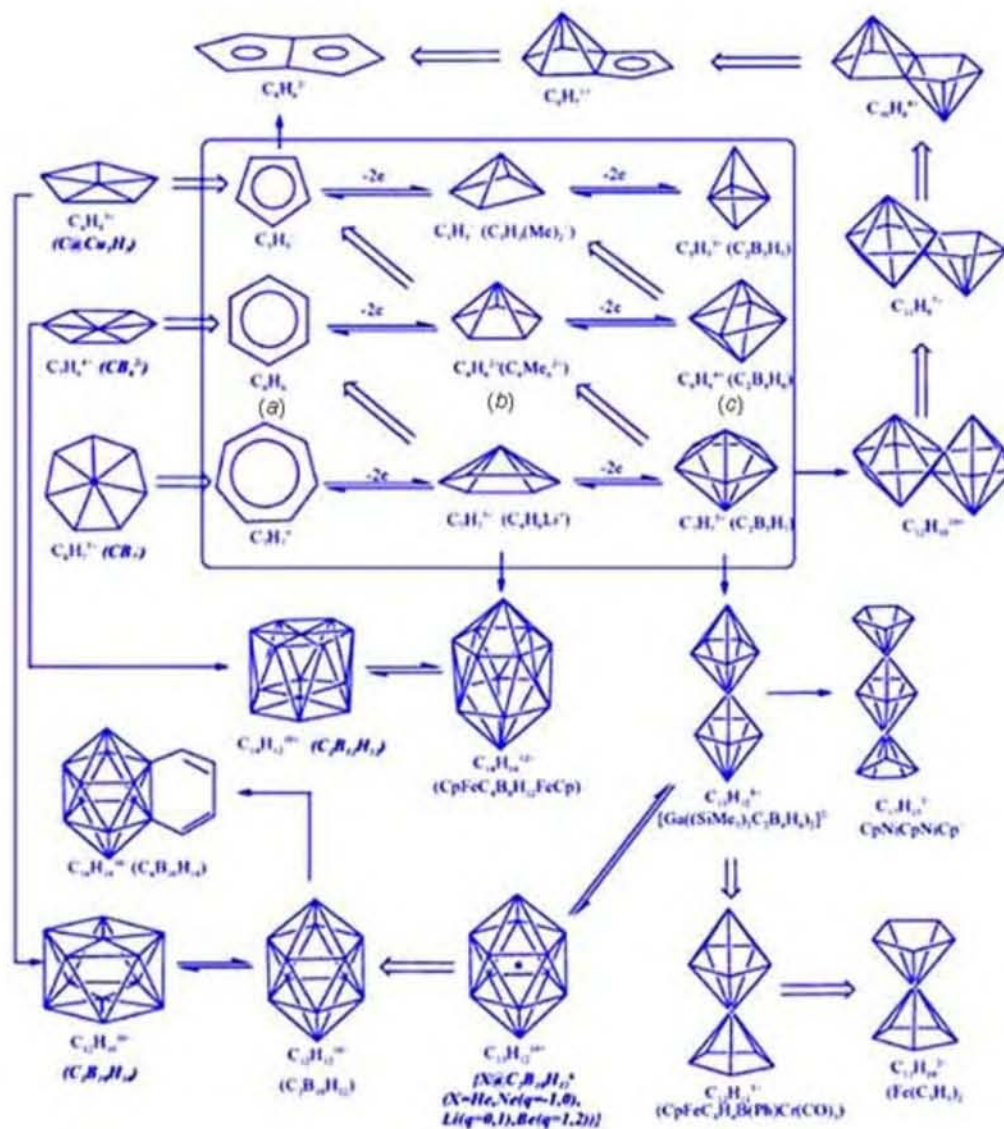
Figure 2. Structural variation as a function of electrons: a connection between carbon and its analogous electron deficient boron compounds.

and the octahedral cation all represented by the equivalent boron metal combinations. Coming back to the Figure 2, it is easy to go from benzene to the pentagonal pyramidal cation to the octahedron and move from the Hückel $4n + 2$ π electron rule to the Wade's polyhedral skeletal electron pair counting rules[10,11]. If the starting aromatic organic system has a different size, we would lead to three dimensional aromatic structures which are different[12]. For example, the same exercise with the tropylium cation ($C_7H_7^+$) leads to a hexagonal pyramid and a pentagonal bipyramid. Just as the stability of the benzenoid compounds has been explained by the aromatic $4n + 2$ π electron rule, the mono-deltahedral boron compounds have been explained by Wade–Mingos polyhedral skeletal electron pair counting rules. This has led to a whole series of polyhedral boranes as shown in Figure 3, com-
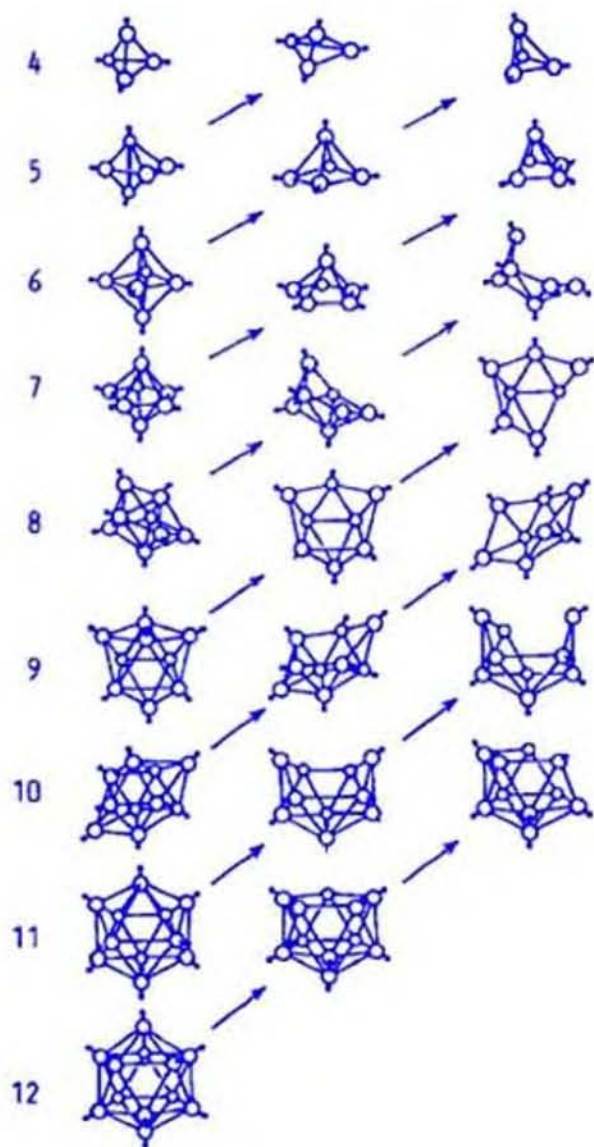
monly known as Rudolph diagram[13]. Novel applications continue to emerge.

The concept of condensation that gave naphthalene from benzene takes on a whole new meaning when applied to the structure of polyhedral boranes. Here, we could have a condensation similar to edge sharing seen in benzenoid aromatics. Further, we could have a triangular face sharing and there is also the possibility of a four vertex sharing between polyhedra and indeed a connection that could be possible through a single vertex sharing. Such condensed polyhedral boron compounds stability can be gauged by the *mno* skeletal electron counting rule[14–17].

While all of these are perhaps not possible for every polyhedron, the rules that govern these are important in bringing a relationship between the compounds of boron and allotropes of elemental boron[18–20]. It is necessary at this stage and to have a glimpse of the thermodynamically most stable allotrope of elemental boron, β-rhombohedral boron. The idealized unit cell of β-rhombohedral boron has 105 atoms in the unit cell (B_{105})[21–23]. A good description, which is chemically meaningful, can be obtained by dividing the three-dimensional structures into fragments that are familiar[18–20]. From the Wade's rule we know that the polyhedral boranes require $n + 1$ skeletal electron pairs. This is found to be true experimentally and all computational methods also reproduce these results. From the criterion of optimization of overlap in orbitals we also understand that the most stable polyhedral borane anion is $B_{12}H_{12}^{-2}$ (ref. 7). In this scenario the likely starting point for the structure of β-rhombohedral boron is a $B_{12}H_{12}^{-2}$ icosahedron. This is not surprising in comparison to benzene which is structurally the starting point for the construction of graphite. The structure of β-rhombohedral boron begins with an icosahedral B_{12} unit. In principle one B_{12} icosahedra coming out of each boron atom of central icosahedron, $B_{12}@12B_{12}$ would be the ideal situation (Figure 4). However, this does not form a periodic solid.

What nature does instead is to begin with B_{12} icosahedron and then connect each vertex to a pentagonal pyramid like of which found in Figure 2 b. The electronic requirement for the pentagonal pyramid is well understood. With 12 pentagonal pyramids surrounding the B_{12}
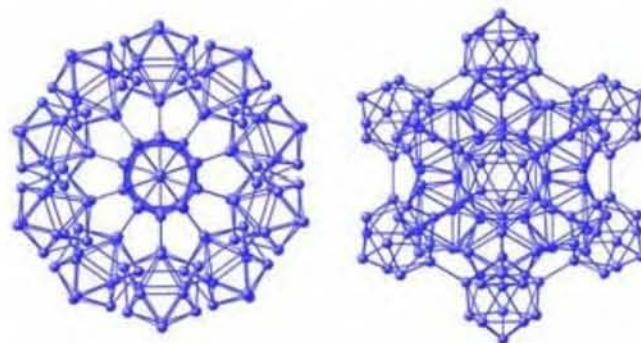

Figure 3. Rudolph diagram, connecting *closo-*, *nido-* and *arachno*-boranes by systematical expulsion of vertices of polyhedra.

Figure 4. Icosahedral B_{156} ($B_{12}@12B_{12}$) along C_5 and C_3 axis of inner B_{12} unit.

icosahedra, it is easy to visualize the building block. There are 12 five-membered rings connected to each vertex of an icosahedral B_{12} unit via 12 boron atoms. Obviously, this has icosahedral symmetry. From a structural point of view, the outer surface is the same as carbon fullerene, C_{60} (ref. 24). The difference is the following. Below each 5 membered ring there is one atom so that these are pentagonal pyramids and right in the middle there is the starting B_{12} unit. The resulting B_{84}, which could be described as $B_{12}@B_{12}@B_{60}$, is the dominant building block of β-rhombohedral boron (Figure 5).

The way in which the B_{84} is put together is the story of the β-rhombohedral boron. Given that icosahedral B_{12} is the most stable arrangement for boron, the attempt of nature should be to bring as many icosahedral B_{12} as possible. If two B_{84} units are brought together so that the two pentagonal pyramidal units come close to each other in the appropriate symmetry we would have generated an additional icosahedra. The large size of the B_{84} structure allows only six of these to be brought around one structure.

However, there are additional six pentagonal pyramidal units on the surface of each B_{84}. This requires additional boron atoms to assume an icosahedral arrangement. This is done by bringing a B_{10} unit of C_{3v} point group. This unit has three five membered rings viewed from three sides. The central atom present in this B_{10} unit together with the five membered rings provides three pentagonal pyramidal units even though some of the atoms are shared. It is possible to bring three B_{84} units around each of the B_{10} unit (Figure 6), so that the six vacant pentagonal pyramidal units of B_{84} will bind to the pentagonal pyramids of B_{10} units completing the icosahedral arrangement for each of these. This way six pentagonal pyramidal units of one B_{84} becomes a part of three icosahedra. Further, a B_{10} unit of this sort surrounded by three B_{84} units is connected to another one of the same kind through a single boron atom. This boron atom bridges the triangular face of a B_{10} unit with the triangular face of another B_{10} unit. This completes the total requirement of the formation of the icosahedral network in β-rhombohedral boron.
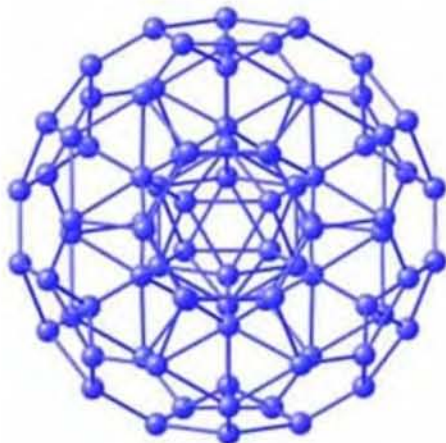
Let us now look at the electronic requirements of different parts of the unit cell. The electronic requirements of the icosahedral units generated need an additional two electrons. The shape of these condensed polyhedral structures is shown independently, in Figure 6. There are 57 condensed boron atoms (B_{57}) involved in bridging the B_{84} units via a boron atom. In this the atom count is easy. We have to connect one B_{10} unit with 3 pentagonal pyramids, i.e. $3 \times 6 = 18$, $18 + 10 = 28$. The 28 atom unit (B_{28}) is connected to another B_{28} unit through a single bridging boron atom, which leads to B_{57} (B_{28}–B–B_{28}). Just as naphthalene can be cut out of a graphite sheet and the dangling valencies are saturated by hydrogen, the B_{57} unit can be cut out of boron and hydrogens can be added so that we get $B_{57}H_{36}$ ($B_{28}H_{18}$–B–$B_{28}H_{18}$) as shown in Figure 7. The electronic requirement of $B_{57}H_{36}^{+3}$ condensed
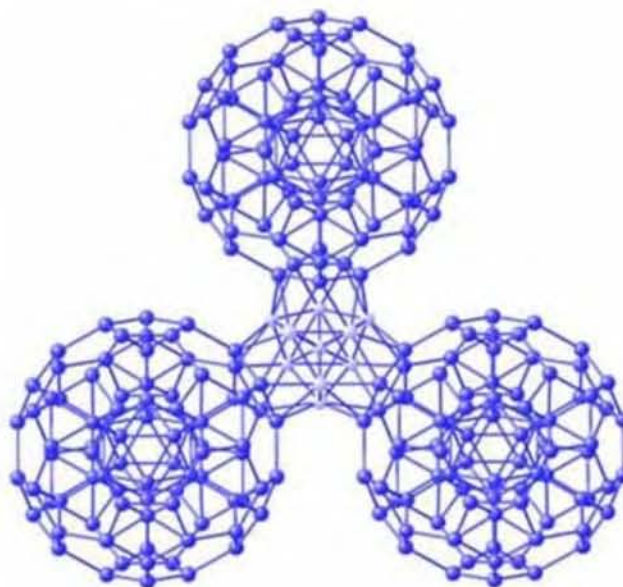

Figure 6. $B_{10}(3B_{84})$, where the three icosahedral B_{84} units are connected via a B_{10} unit shown in pale blue.

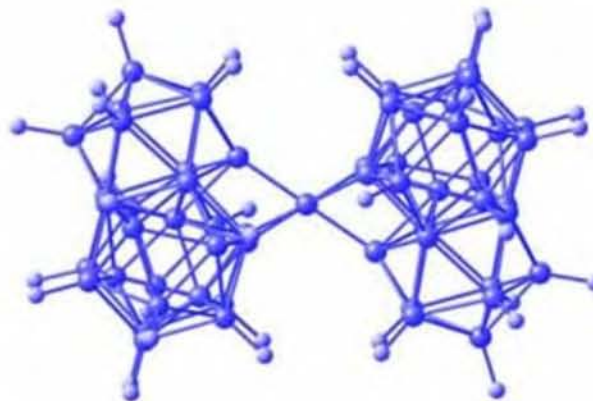**Figure 5.** Icosahedral B_{84} ($B_{12}@B_{12}@B_{60}$) along C_3 axis.

Figure 7. $B_{57}H_{36}^{+3}$, where two B_{28} units are connected via a boron atom and the dangling valences are saturated by hydrogen atoms.

macropolyhedral boron structure is not so obvious. We had looked at this problem from a general point of view[18]. Just as benzene is condensed to form naphthalene and other higher benzenoid aromatics, it is possible to envisage the condensation of polyhedral boranes. In the case of benzene, obvious condensation possibilities are only edge sharing. The Hückel's $4n + 2$ π electron rule justifies the formation of benzenoid aromatics. The situation is more complex in the condensation of polyhedral boranes. For example, icosahedral B_{12} can have in addition to edge sharing, triangular face sharing, four atoms sharing and a single atom sharing[16]. The electronic requirements for these processes were not known. It appeared as though we should be able to analyse the electronic structure of a series of condensed polyhedral boranes and arrive at such an understanding[14–16]. We have looked at the various possibilities starting with an icosahedral borane $B_{12}H_{12}^{-2}$.

After several electronic structure calculations it was possible to arrive at an electron counting rule, which explains the requirement of condensation of polyhedral boranes. It is clear from the beginning, that the electron counting rules should reduce to the Wade's $n + 1$ skeleton electron counting rule for polyhedral boranes where only one polyhedron is considered. The variable n is the number of vertices and has to be a part of the electron counting rule. The number of polyhedra should be another obvious variable in this process. We have introduced the variable m to indicate this by replacing '1' by m in $n + 1$. When there is only one polyhedron $m = 1$ and we get the Wade's rule. It is also necessary to see that when we restrict the condensation to edge sharing in polyhedra that is the condensation in two dimensions, the electron counting

rule should reduce to the Hückel $4n + 2$ π electron rule. We proposed a new electron counting rule, the *mno* rule, which satisfies these criteria[14–16]. The structures $B_{20}H_{16}$ and $B_{21}H_{18}^{-1}$ demonstrate the application of this rule. Let us apply the *mno* rule to $B_{20}H_{16}$. According to the *mno* rule, $B_{20}H_{16}$ has two polyhedra ($m = 2$), 20 vertices ($n = 20$) and zero single vertex sharing ($o = 0$) which implies $B_{20}H_{16}$ needs 22 ($m + n + o$) skeletal electron pairs to have a stable structure. In $B_{20}H_{16}$, there are 16 BH groups each providing an electron pair, the four bridging boron atoms provide six electron pairs, making a total of 22 ($16 + 6$) electron pairs (Figure 8). Indeed, $B_{20}H_{16}$ does not require any extra electrons unlike the *closo*-monopolyhedral boranes. $B_{20}H_{16}$ was synthesized 45 years ago as a neutral polyhedral structure[25,26]. Similarly, if we apply the *mno* rule to $B_{21}H_{18}^{-1}$, it turns out that, it needs an electron to have a stable structure (Figure 8). This was synthesized only last year[27]. Obviously, the chemistry of condensed polyhedral boranes is only beginning.

Let us now come back to the β-rhombohedral boron allotrope. Employing the *mno* rule to the β-rhombohedral boron allotrope, which is fragmented as four B_{12} icosahedra and a B_{57} unit ($48 + 57 = 105$), turns out to be a five electron deficient. This can be calculated by considering the four B_{12} and a B_{57} unit as boranes, four $B_{12}H_{12}$ units and a $B_{57}H_{36}$ unit. Each $B_{12}H_{12}$ needs two additional electrons and three electron should be taken away from
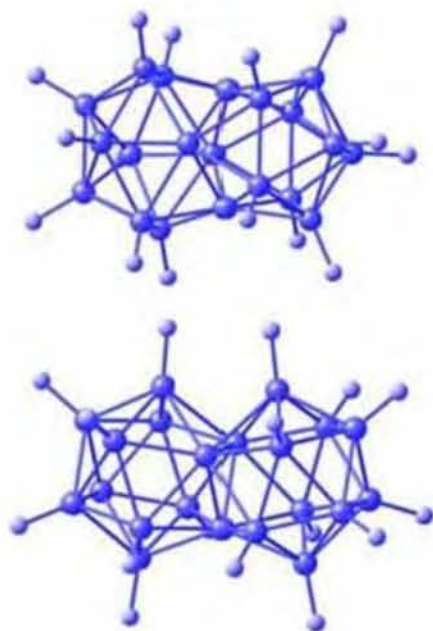

Figure 8. $B_{20}H_{16}$ and $B_{21}H_{18}^{-1}$ are four-atom and three-atom shared experimental macropolyhedral boranes.
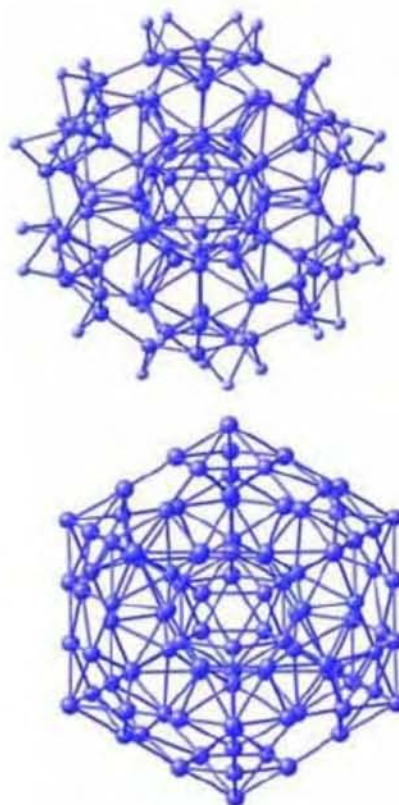

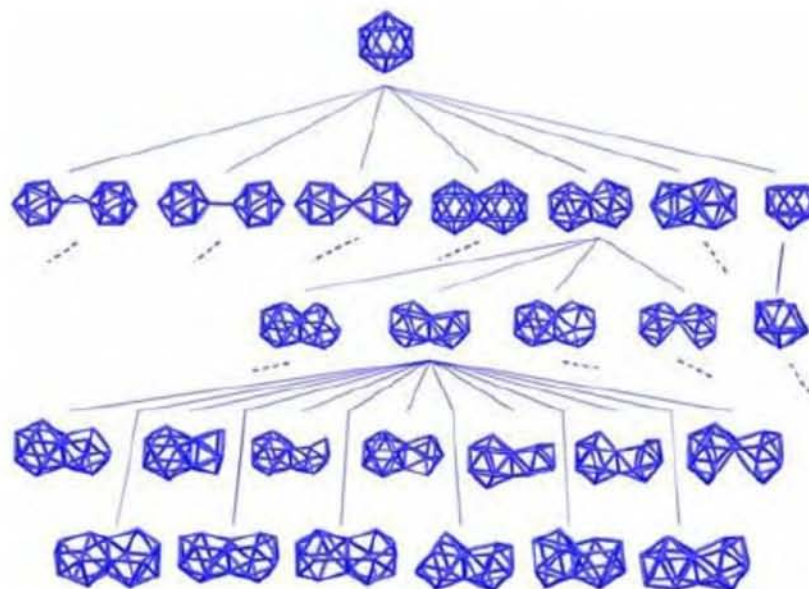**Figure 9.** $B_{84}H_{50}$ and B_{102} are shown along C_3 axis.

Figure 10. Demonstration of the diversity of condensed polyhedral boranes.

$B_{57}H_{36}$ ($m = 8$, $n = 57$, $o = 1$). Therefore β-rhombohedral boron allotrope is an electron deficient by five electrons[18]. This five electron deficiency of β-rhombohedral boron has also been verified by the band structure calculations[19,28]. According to this β-rhombohedral boron must be metallic, which contradicts the experimental results that it is a semiconductor.

However, the well refined X-ray structural analysis of β-rhombohedral boron shows that the unit cell is not so ideal with 105 boron atoms, it has on the average an additional 1.66 boron atoms, leading to a unit cell $B_{106.66}$ (ref. 23). The additional 1.66 fractional boron atoms correspond to five electrons which essentially corroborate the *mno* electron counting rule.

Detailed analysis of the occupancy of the atoms of the idealized structure as well as the placement of additional 1.66 boron atoms provided better understanding. In the B_{57} unit (Figure 7) the six boron atoms that are bonded with the central unique boron atom are fractionally occupied. Statistically, approximately one boron atom is missing among the six positions. So the B_{57} unit is in reality only B_{56}. This provides an ingenious example where nature prevents charge separation. The B_{57} unit has three extra electrons and must be positively charged. Expulsion of one boron removes three electrons so that the resulting B_{56} unit can be neutral. This can be visualized as the β-rhombohedral boron, $B_{106.66} = B_{104} + B_{2.66}$. The $B_{2.66}$ translates into eight valence electrons which accounts for the stability of four B_{12} units. Thus the $B_{106.66}$ is an electron sufficient solid.

These take us back to the stability of the building blocks of graphite. Benzene, naphthalene, anthracene and similar fragments cut-off from graphite have a chemistry of their own. These are obtained by saturating the dangling valencies and putting in the right number of electrons. In principle it must be possible to do the same exercise with the building block B_{84}. How do we arrive at the electronic structure requirement of the B_{84} units? We have to go back to the Wade's rule in attempting this. The central B_{12} requires two electrons according to the $n + 1$ skeletal electron counting rule. The pentagonal pyramids are reminiscent of the $B_6H_6^{-4}$ or the $C_4B_2H_6$ or the B_6H_{10} structures of Figure 2 *b*. This demands therefore that each of the pentagonal pyramids of B_{84} requires four additional electrons. These could be given by four bridging hydrogens. There are 12 such five membered rings; we require 48 electrons in addition to the two electrons required for the central B_{12}. The $48 + 2 = 50$ electrons could indeed be provided by 50 hydrogens. Thus, it may sound $B_{84}H_{50}$ should be a respectable molecule[5]. On the other hand with the same electron counting principle stuffed fullerene-like elemental boron would be possible. The required 50 electrons can be provided by placing additional 16.66 boron atoms in the voids presented in B_{84}. As the fractional boron atom is not computable easily, a close electron requirement can be brought into the B_{84} cluster by adding additional boron atoms. This leads to stable B_{100}, B_{101} and B_{102} fullerene-like boron clusters[29]. The electron sufficient $B_{84}H_{50}$ and fullerene-like boron clusters need not form an extended solid and can have its own independent existence (Figure 9).

Future perspective

The complete quantitative understanding of the origin of vacancies and partial occupancies in β-rhombohedral boron is yet to evolve. One way to understand this is from first principles molecular dynamics (FPMD) simulation which is quite a complex process. However the current day computing facilities would help solve this problem

eventually. There have been some recent attempts of FPMD on β-rhombohedral boron, the results are yet to commence[30]. On the other hand, the recent synthesis of macropolyhedral borane, $B_{21}H_{18}^{-1}$ analogue has taken 45 years after the first synthesis of $B_{20}H_{16}$ (ref. 27). Several proposed macropolyhedral boranes have to go a long way for their real existence (Figure 10). If just B_{12} can lead to this amazing series, imagine starting with each structure of the Rudolph diagram (Figure 3). We believe in the near future many of them can be made.

These electron counting rules not only help to understand the structure and stability, they are further useful in designing novel molecular candidates for physiological applications, catalysis, and materials for specific electrical and mechanical properties. For example, the carboranes are already in use for boron neutron capture therapy (BNCT) of cancer. In order to have a more successful BNCT reagent, one would look for bio-compatible boron cluster carriers towards the target tumour[31]. Boranes as bioisosteres (for example, carborane-based analogues of non-steroidal anti-inflammatory drugs, and boranophosphate) are in progress in many laboratories to achieve better drug compatibility[32]. On the other hand, it is just beginning to help to design and improve the electrical conductivity and mechanical strength of boron-rich borides[19]. It is also possible to design carbon analogous of boron materials such as fullerenes, nanotubes and graphene. The recent proposal of fullerene-like boron clusters, boron nanotubes and one atom thick boron layers are evidences for the use of an understanding of the structure and bonding using electron counting rules. Chemistry of boron, boranes, macropolyhedral boranes, elemental boron and boron-rich solids form an unknown continent to be explored and understood. Only the initial rules of the game have appeared.

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