Boron, Borides and Boranes

Eluvathingal D. Jemmis
School of Chemistry
University of Hyderabad
Hyderabad 500046
India
E-mail: jemmis@uohyd.ernet.in

Abstract

A new electron-counting rule has been devised to explain the electronic requirements of condensed polyhedral boranes and the many possible products created by merging boranes and metallocenes together into macromolecules. This *mno* Rule helps to find the missing links between polyhedral boranes and complex allotropes of boron, similar to the structural and bonding connections between benzene, condensed aromatics, and graphite. In addition, the *mno* rule explains the electronic requirements of β-rhombohedral boron, its structural defects, and structural variations in several metal borides and boron-rich solids.

1.0 Introduction

Unlike carbon, whose polymorphs diamond and graphite have direct structural links to saturated hydrocarbons and benzenoid aromatics respectively,
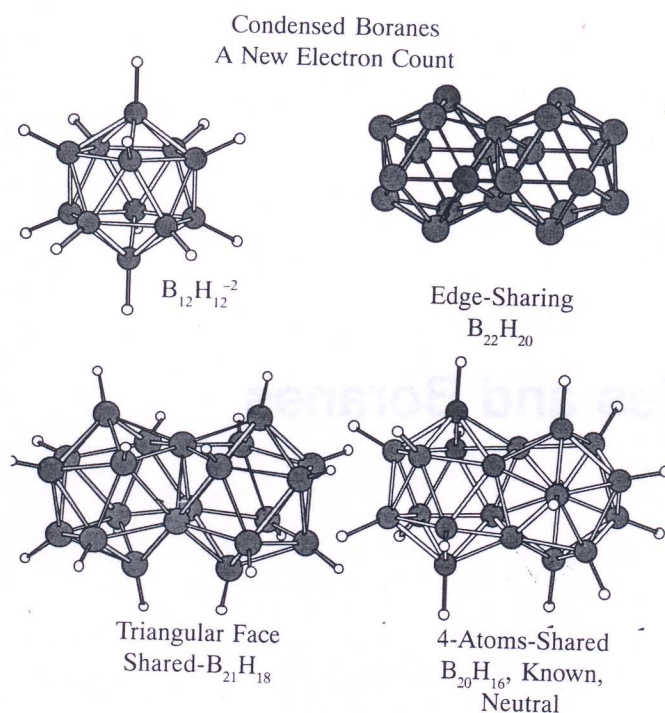
Condensed Boranes
A New Electron Count

$B_{12}H_{12}^{-2}$

Edge-Sharing
$B_{22}H_{20}$

Triangular Face
Shared-$B_{21}H_{18}$

4-Atoms-Shared
$B_{20}H_{16}$, Known,
Neutral

Fig. 1:   An icosahedral $B_{12}H_{12}{}^{2-}$ and the various condensations possible with two icosahedral units to form macropolyhedral boranes. The number of shared boron atoms ranges from two to four, with the last being an experimental reality among the condensed systems.

connection between boranes and elemental boron is largely unknown. The three-dimensional equivalent of the Hückel $4n + 2\pi$ Electron Rule and the tetrahedral sp^3 hybridisation are not available for boron. A new Electron Counting Rule is introduced here to find the electronic requirements of polycondensation of polyhedral boranes. This also establishes the missing links between poly-condensed polyhedral boranes and elemental boron.

2.0 Wades Rule

Polyhedral boranes, $B_nH_n^{-2}$ are supreme examples of compounds that exhibit most of the characteristics of aromaticity of hydrocarbons. Wade introduced the n + 1 Skeletal Electron Pair Rule to account for the *closo, nido* and *arachno* structures of boranes. According to this rule, n + 1 skeletal electron pairs are required for stability of a *closo*-borane where *n* is the number of vertices of a closed polyhedron. With each B-H group contributing two electrons, an additional two negative charge is required for stability, as is found in all *closo*-polyhedral boranes. The neutral carboranes, $C_2B_{n-2}H_n$, where the

two charges are compensated by two carbon atoms have generated much chemistry of its own.

3.0 mno Rule

Unlike planar aromatic systems, there are several modes of condensation possible with the polyhedral boranes (Figure 1). Let us consider icosahedral $B_{12}H_{12}^{-2}$ as an example. Edge sharing is similar to that of benzene giving naphthalene. This leads to the $B_{22}H_{20}$ skeleton with severe crowding of hydrogens. It is possible to share a triangular face between two icosahedra; resulting $B_{21}H_{18}$ is less crowded. This structure is not yet known experimentally. There is an experimentally characterised structure corresponding to the condensed product arising from sharing of four boron atoms starting from two icosahedral boranes. This $B_{20}H_{16}$ structure is neutral and any new electron-counting Rule should take into account of this structure. In addition it should explain the many *nido* and *arachno* condensed structures available in the literature. The first step here is to increase one variable in the n + 1 electron pair rule. Replacing 1 in n + 1 by a variable m does this. The n + m Rule falls back to the

$$[Fe(C_2B_9H_{11})_2]^{-2}$$
m = 2, n = 23, o = 1

$$Ge(C_2R_2B_4H_4)_2$$
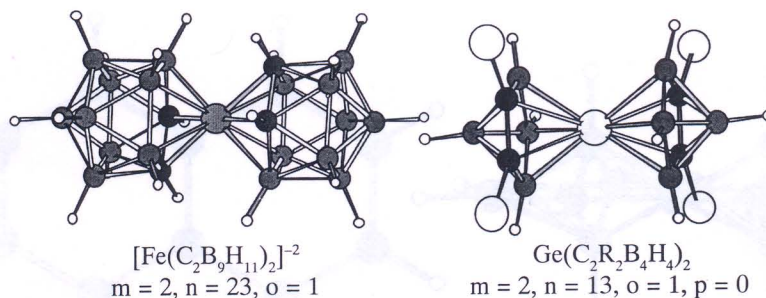m = 2, n = 13, o = 1, p = 0

Fig. 2:   Application of *mno* Rule on experimentally known single vertex shared sandwich complexes. The central atom is always a heteroatom bigger in size than boron to avoid the proximity of neighbouring units.

n+1 Rule if m is taken as the number of polyhedra, which is unity in the Wades Rule. Application of the n + m Rule to $B_{20}H_{16}$ is simple. Here m = 2 and n = 20. Therefore there should be 22 skeletal electron pairs. There are 16 BH groups, each contributing an electron pair. The four bridging boron atoms together have 12 valence electrons, or six electron pairs. Thus there are 22 electron pairs available in $B_{20}H_{16}$ so that the molecule is neutral.

The structure is known for over 40 years and, unlike all known *closo*-boranes of the time, is neutral. Similarly we can calculate the electronic requirements of $B_{22}H_{20}$ and $B_{21}H_{18}$ using the n + m rule.[1] Obviously $B_{22}H_{20}$ should have −2 charge and $B_{21}H_{18}$, −1 charge. The correctness of these electron-counting rules is established from electronic structure calculations.

It should be possible to incorporate single atom-sharing condensation also in the electron counting scheme. Such bridging is usually not seen with boron atoms, except in the structure of β–rhombohedral boron. But there are several examples with larger atoms at the bridging positions. Since the bridging atom has an orbital pointing to the centroid of each polyhedron, an additional stable MO is available in these systems, which require one more variable to be added to the n + m rule. This is verified by electronic structure calculations on a series of such experimental structures. We have therefore added another variable o and rearranged the letters to have the *mno* Rule, where *m* represents the number of polyhedra, *n* the number of vertices and *o* the number of single atom bridging (Figure 2).[2] For example, the $Fe(C_2B_9H_{11})_2$ requires 2 + 23 + 1 electron pairs for stability. The total number of electron pairs available is 18 from $(BH)_{18}$, 6 from $(CH)_4$, one from the Fe(II), requiring the −2 charge to satisfy the electron count.

4.0 Relation between mno Rule and Huckel 4n + 2 Rule

How does the *mno* Rule relate to the Hückel 4n + 2 Rule? Let us consider the hypothetical borane $B_{14}H_{12}$ generated by the condensation of two hexagonal bipyramidal structures B_8H_8 sharing an edge. The electron count required according to the *mno* Rule is 2 + 14 electron pairs. The molecular formula provides 12 electron pairs from 12BH groups and 3 from the two bridging boron atoms. Thus the structure requires −2 charges. If the four capping BH groups are removed, we get a bis-*arachno* system, the planar $B_{10}H_8$.

The *mno* Rule leads to 2 + 10 + 4 = 16 electron pairs. The 8 BH provides 8 and the 2 boron atoms provide 3 electron pairs. Thus we need additional 16–11 = 5 electron pairs. This leads to a charge of −10 for $B_{10}H_8$. The corresponding carbon equivalent is, not surprisingly, naphthalene (Figure 3). If one adds the C–C σ bonding electrons to the 4n + 2π electrons of naphthalene, the Hückel Rule becomes a part of the *mno* Rule. Obviously such planar arrangements can be obtained only from one of the many possible condensation pathways available for polyhedral boranes, namely the edge sharing. Thus the 4n + 2 Rule of Hückel for planar aromatics is a subset of the *mno* Rule.

5.0 mno Rule and β-Rhombohedral Boron

Armed with these electron-counting rules let us get to the structure of β-rhombohedral boron. The idealized structure of the β-rhombohedral boron has 105 atoms in the unit cell.[3] Eighty four of them form a part of the
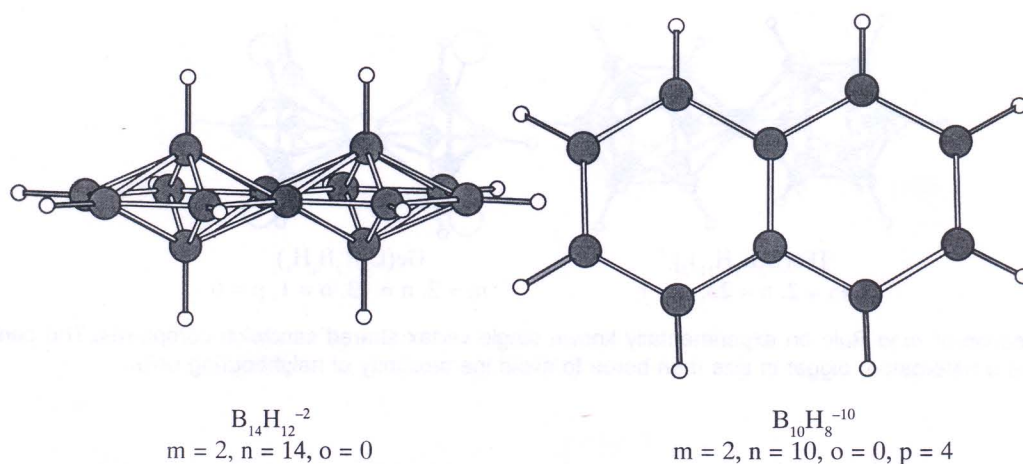
$$B_{14}H_{12}^{-2}$$
m = 2, n = 14, o = 0

$$B_{10}H_8^{-10}$$
m = 2, n = 10, o = 0, p = 4

Fig. 3:   The relation between *mno* Rule and Huckel's Rule is illustrated taking the polyhedral and planar analogues of an edge shared borane. $B_{10}H_8^{-10}$ is isoelectronic to naphthalene which shows the continuum of 3D and 2D aromatic systems and hence the generalisation of the *mno* Rule.
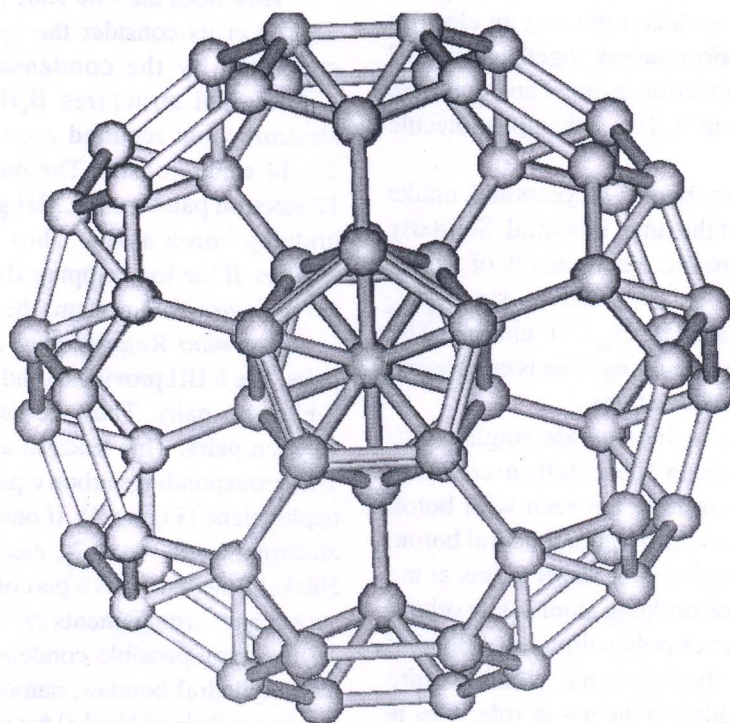

Fig. 4:   The structure of B84 constructed by attaching 12 pentagonal pyramidal units around B12.

spheroidal structure which can be best described as B12@B12@B60 (Figure 4). The structure begins with a B12 icosahedron. A pentagonal pyramidal group is attached to each of these boron atoms. The 12 five membered rings of the pentagonal pyramids form the outer B60 skeleton similar to C60 in this B84 structure. When two such B84 units come close to each other, yet another icosahedral B12 unit emerges. However around
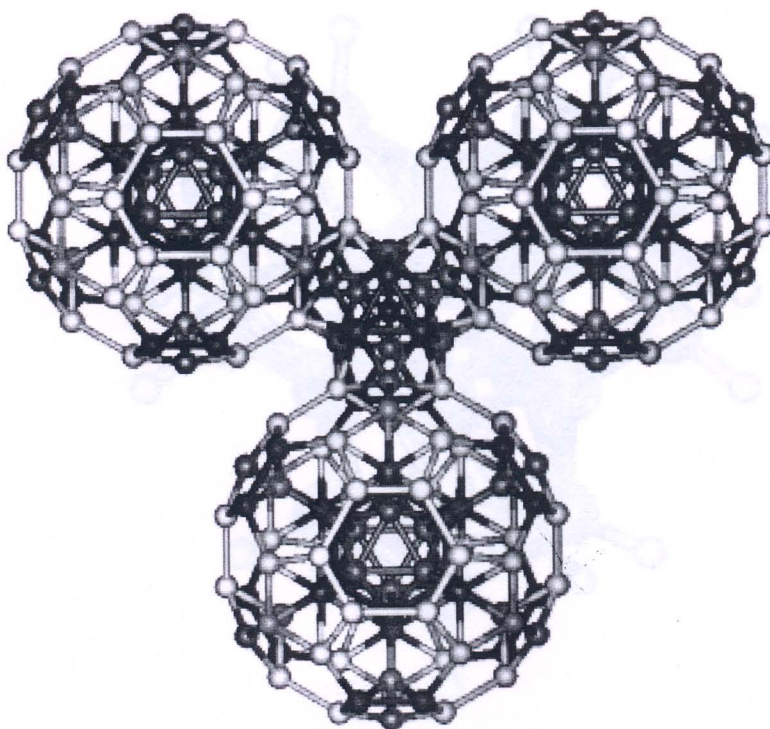
Fig. 5: Each B84 has six B84 units and six B10 units around it. One B10 unit and three B84 units are shown here. Each pentagonal pyramid unit attached to the central B10 achieves a nearly icosahedral arrangement, which is shown in the middle.

on B84 unit of the β-rhombohedral boron only six B84 units can be brought. The remaining six five-membered rings of the B84 unit also form an icosahedral arrangement using the 21 atoms left in the unit cell (Figure 5).

These B21 units are arranged as two B10 units connected by one boron atom (B10-B-B10). The B10 unit has three pentagonal faces each of which provide the equivalent of a pentagonal pyramidal arrangement to a different B84. In the process the B10 units have added three B6 units out of B84 to itself so that these can be separately represented as B28 (Figure 6). Two of these units are attached through the single atom completing the B10-B-B10 (B21) part of the unit cell.

We had provided an overlap and symmetry-based explanation for the unusual preference of icosahedron for boranes, in comparison to all known $B_nH_n^{-2}$.[4] However, as mentioned above, the construction of the β-rhombohedral boron by assembling B12 units is not straightforward. If these building blocks were stand-alone B12 units, each such unit requires two additional electrons, which is not possible for neutral elemental boron. Obviously new strategies have to be found for

the condensation of the icosahedral B12 units. The B105 atoms of the unit cell had been divided into 4 B12 units and the B28-B-B28 units. The latter may be disconnected from the solid by breaking 36 B-B bonds, much the same way a naphthalene frame may be cut out from graphite. The dangling valencies can be saturated to give $B_{57}H_{36}$ (Figure 7) just as naphthalene; $C_{10}H_8$ is obtained from C10 fragment of graphite.

Application of the *mno* Rule shows that there has to be 66 electron pairs ($m = 8$, $n = 57$, $o = 1$) to make the $B_{57}H_{36}$. The number of electron pairs available is 67.5 (36 from 36 BH, 31.5 from B21). Thus $B_{57}H_{36}$ must have +3 charge, contrary to the expectations of electron deficiency. Calculations indicate that $B_{57}H_{36}^{+3}$ has all characteristics of a highly delocalized aromatic system.[5] The B48 part which is made up of B12 units is truly electron deficient. The two negative charge of the stable $B_{12}H_{12}^{-2}$ implies that the B48 part needs 8 electrons. In an idealized structure three out of these eight could be obtained from the B57 part. Thus the B105 unit cell of β-rhombohedral boron is deficient by 5 electrons. This electron count is in tune with the band structure calculations carried out by Bullet as early as 1982. The
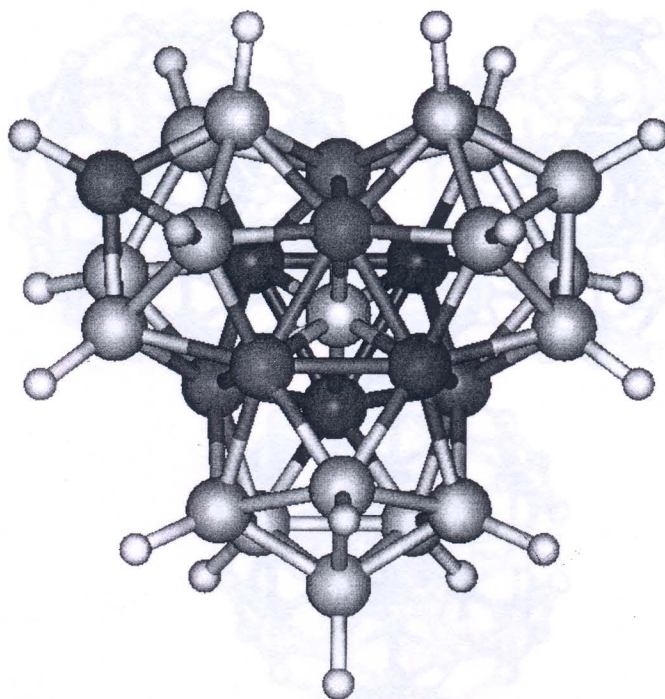
Fig. 6: A B10 unit along with the three pentagonal pyramidal B6 units taken from three B84 structures to give B28. The dangling valencies are satisfied by B-H bonds.
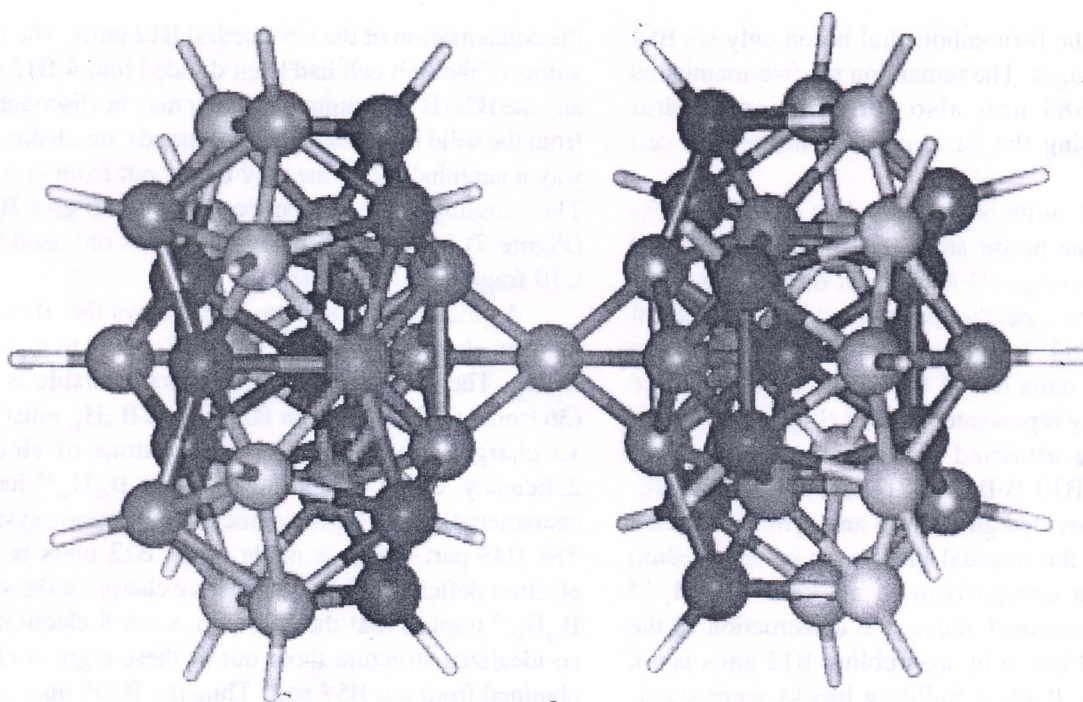

Fig. 7: The B28 unit connected to another B28 unit through a single boron atom bridge (B28-B-B28). The bonds that are directed out correspond to the B-H bonds of the associated $B_{57}H_{36}$ molecule obtained from this fragment.
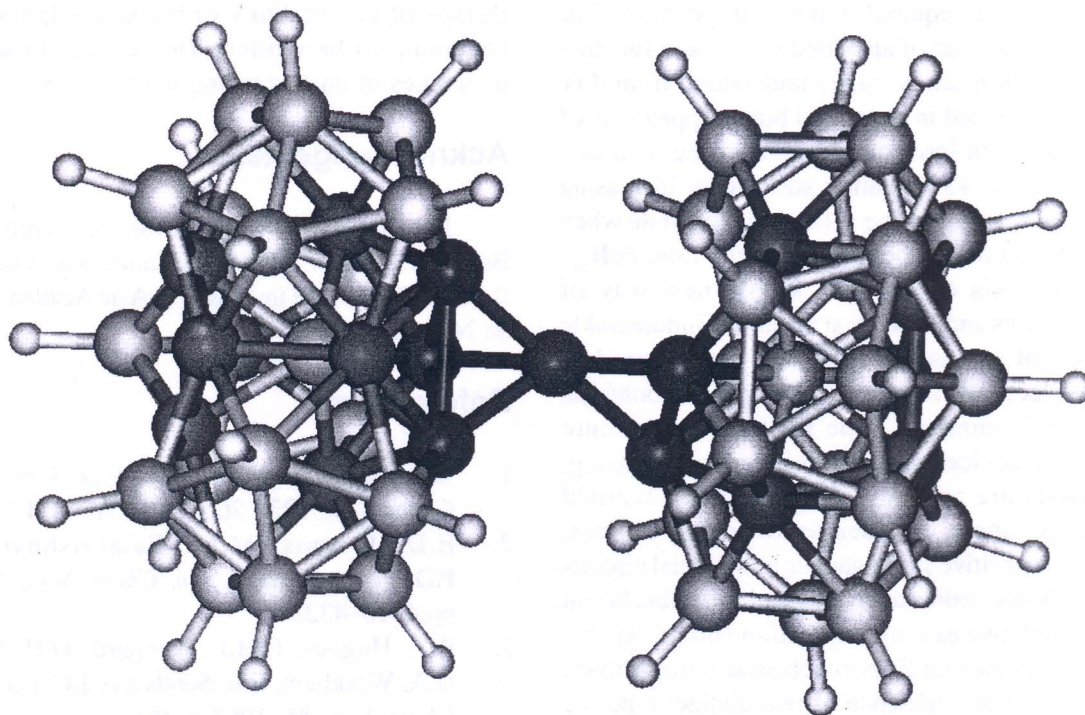
Fig. 8:   The B56 structure with the partial occupancy demanded by the electron count and observed in the β-rhombohedral structure.

properties of elemental boron do not however fit with this description of the electronic structure. Nature finds an ingenious way to salvage the situation, taking lessons from boranes again.

The *nido*, *arachno*, and *hypo* boranes are polyhedral boranes which have one, two, and three missing vertices, but which require the same number of skeletal bonding electrons. For example, $C_2B_9H_{13}$ is a stable icosahedral structure where one vertex is missing, but has the same number of skeletal bonding electrons.[6] The easiest way of alleviating the excess electrons in the B57 region is to knock off an atom so that three valence electrons are decreased. Figure 8 shows the B56 structure where a boron atom is deleted, with least disturbance to the structure.

The $B_{56}H_{36}$ structure that is left behind requires 66 electron pairs ($8 + 56 + 1 + 1$, the last one to account for a *nido* corner that is generated). The actual electron count is also $66(36 + (20 \times 3)/2)$. More recent experiments have located these partial occupancies.[7,8] As there are 6 equivalent positions that may be vacant in B56 (Figure 8), this translates to an occupancy of $100 \times 5/6 = 83.33\%$. This estimate based on the fragment analysis is higher than the experimental value of 74.5% by only 8.83%. There are several reasons for this discrepancy. The

experimental value ranges from 77.7 to 73.0% depending on the method of preparation. The experimental structure has at least five extra interstitial atoms with partial occupancies ranging from 2.5–28.4%. One of these with a partial occupancy of 9.7% is close to the central atom of the B28-B-B28 unit. It is as if the system has overcorrected by removing more than one boron atom from the B57 skeleton and then tried to put back the atoms by bridging with a site of low occupancy.

Just as excess of electrons is removed by partial occupancy, electron deficiency is remedied by bringing in extra atoms at the interstitial holes, which are very large in the idealized skeleton, B105. X-Ray structure shows that there are five additional partially occupied sites within and around B84, adding up to 2.66 boron atoms. This corresponds to eight valence electrons. This is almost identical to the electron deficiency. This level of correspondence is fortuitous in view of the many uncertainties involved. Different experimental samples differ more than this magnitude. Available experiments strongly support this picture of electron deficiency and electron excess. The requirement of eight electrons is most directly provided by adding Li atoms as found in $B_{13}Li$.[9] It is easy to see how other metal atoms can be

used to provide the required number of electrons. The variable oxidation state of an added metal, as a function of its concentration can be easily understood from this. For example Fe doped in elemental boron appears in +3 oxidation state with low concentration of Fe, and in a mixture of +2 and +3 oxidation states with increasing concentration of Fe, reaching a +2 oxidation state when the concentration of Fe corresponds to the ratio FeB_{26}.

This analysis opens up a whole new way of counting electrons and arriving at an almost innumerable combination of atoms and ions that can be used to balance the electronic requirements of β-rhombohedral boron. There is immense hope for high temperature semiconductor devices (~1800°C) by suitable doping. Boron crystals are seriously considered for thermal resistor development, for thermo switching devices, temperature insensitive strain gauges and special circuits and devices. Boron scores over diamond and cubic boron nitride in the relative ease of preparation and its density. Any doping schemes on β-rhombohedral boron should take into account the existence of two distinct types of sub-units in its unit cell. The connection between boranes and boron solids, established here, opens a new reasoning in this field.

The methodology adopted here of relating the electronic structure of well-defined family of compounds of an element to the structure of its polymorph is obviously amenable to extension. Especially important is the realisation that small variations in partial occupancies are not accidental or to be ignored, but are to be traced to the electronic structural requirements.

The process of finding the mode of understanding to connect boranes to the β-rhombohedral boron also brings about several structural possibilities for novel boranes. The nature of B57 has prompted the series of stuffed boranes.[10] The family of YB_{66} structures have led to the unusual possibility of a benzyne equivalent $B_{12}H_{10}$ structure.[11] The larger polyhedral structures that are possible with polycondensation should help in designing better candidates for boron neutron capture therapy of cancer. Story of boron and boranes is only beginning to be written. The process brings in new modalities of understanding in chemistry.

Acknowledgements

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