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Electronic Requirements of Polycondensed Polyhedral Boranes

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The unusually high stability of $B_{12}H_{12}^{2-}$ (**1**, I_h) and the existence of condensed B_{12} units in the stable polymorphs of boron[1,2] have resulted in the renewed interest in macropolyhedral boron clusters.[3−7] As these new generation structures are beyond the scope of the earlier Williams−Wade formalism,[8] synthesis is largely exploratory.[7] In an effort to understand the intriguing rules that govern the condensation of boranes, a systematic theoretical investigation of condensed borane systems (Figure 1) is conducted. This reveals the following: (1) the condensation of polyhedral boranes leads to the overall reduction in the electron deficiency of the system and (2) it is impossible to extend the conventional fusion to infinity,[5] due to the accumulation of positive charge. This also reveals a new electron counting rule that governs the electronic requirements of these polycondensed systems.

Almost 30 years ago, both Lipscomb[4] and Muetterties[5,6] reported the synthesis of a neutral polyhedral borane, which is composed of two condensed icosahedral structures sharing four boron atoms. In recent years $B_{20}H_{16}$ has become a convenient entry point for the synthesis of macropolyhedral borane systems.[9] However, the need for a theoretical electron counting rule is being badly felt. We begin with a statement, which helps in estimating the electronic requirements of a polycondensed polyhedral borane. *The overall electronic requirement of a polycondensed polyhedral system is the sum of the electronic requirements of the individual polyhedral fragments.* This rule is similar to the one derived by Mingos[10] to explain the condensation of polyhedral fragments of transition metal complexes. However, Mingos' rule relies heavily on the "18 electron rule" of the transition metals and its equivalent "octet rule" for main group elements is not valid for boron clusters.

We rationalize the structure of many condensed polyhedral borane systems reported earlier and verify the correctness of the intuitive assignment of charges to some of these systems.[11] Further, this rule also explains the formation of several condensed systems reported experimentally, whose electronic structures are yet to be resolved.[4,6]

Though several different approaches are available to evaluate the electronic requirements of polyhedral borane anions,[8,12] there is a general agreement that a stable closo polyhedral borane with n vertexes requires $n + 1$ electron pairs to bind the skeleton. For nido, arachno, and hypo structures, the required number of electron pair is $n + 2$, $n + 3$, $n + 4$, respectively. For a polycondensed *closo*-borane, the required electron pairs can be calculated as $n + m$ where m represents the number of polyhedral borane units in the system.

Let us consider the structures obtained by sharing 4 and 3 vertexes, respectively. Structure **2** (Figure 1), $B_{20}H_{16}$ (D_{2d}), requires 20 + 2 ($n = 20$, $m = 2$) skeletal electron pairs for stability. The total number of electron pairs available is also 22 (one electron pair from each of the 16 B−H groups and 6 electron pairs from the four shared boron atoms), so that **2** is neutral in accordance with the experimental finding. Structure **3** ($B_{21}H_{18}$), obtained by sharing three vertexes between two icosahedra, has 21 vertexes and two polyhedral units. So the number of skeletal electron pairs required is 23 (i.e., 21 + 2). The total number available is only 22.5 (18 from the B−H group and 4.5 from the three shared boron atoms). Thus **3** requires a negative charge, so that $B_{21}H_{18}^{-}$ is the stable species as predicted earlier.[11]

Condensation of another unit to **2** by sharing four vertexes leads to $B_{28}H_{20}$ (**4**) with D_{2h} symmetry. By the $n + m$ rule, it requires 31 electron pairs (28 + 3). $B_{28}H_{20}$ has 32 electron pairs. Thus the dication $B_{28}H_{20}^{2+}$ should be the stable species. Extension of **3** in a similar fashion leads to $B_{30}H_{24}$ (**5**). The $n + m$ electron pair rule gives 36 electron pairs for **5**. The molecular formula provides the same number so that **5** should be neutral as was intuitively expected by Lipscomb.[11] The next higher member in the series **1**, **3**, **5** is $B_{39}H_{30}^{+}$. This homologous series can be represented by the molecular formula $B_{9x+12}\ H_{6x+12}^{x-2}$ ($x = 0$, 1, 2, ...). Obviously the positive charge increases quickly so that higher members will be unfavorable without appropriate substitutions such as Be in the place of B. Similarly, the series **1**, **2**, **4** has the molecular formula $B_{8x+12}H_{4x+12}^{2x-2}$ ($p = 0$, 1, 2, ...). Here the charge increases by two with unit increase in m, so that the higher members will be unfavorable. Condensation of more than two polyhedra brings in isomerism akin to that of anthracene and phenanthrene. For example, **6** (C_{2v}) and **7** (C_2) are isomers of **5** (D_{3h}).

A variety of mixing and matching is possible in polycondensed polyhedral boranes. Structure **2** can be condensed with icosahedral $B_{12}H_{12}^{2-}$ by sharing three vertexes to give $B_{29}H_{22}^{+}$ (**8**). Obviously, several isomers are possible. It is not necessary to limit the condensation among identical polyhedra. For example, condensation of an octahedron with an icosahedron by sharing three vertexes leads to $B_{15}H_{12}^{-}$ (**9**). Condensation with another icosahedral B_{12} symmetrically leads to the neutral $B_{24}H_{18}$ (**10**). The possibilities are endless. Among these structures $B_{20}H_{16}$ (**2**) has been known for a long time.[4,5] The B_{21} skeleton of **3** is shown to be a part of the tetragonal boron polymorph.[2]

The $n + m$ electron count can be extended to include common polyhedral fragments such as the nido, arachno, and hypo variety by adding the appropriate number of electron pairs. Thus, the condensation of one nido and one closo polyhedron requires $n + m + 1$ electron pairs. For example, $B_{20}H_{16}$ (**2**) is found to add with bases to form stable molecules of the type $B_{20}H_{16}L_2$, viz., $B_{20}H_{16}(NCCH_3)_2$, $B_{20}H_{16}(S(CH_3)_2)_2$, $B_{20}H_{16}(N(CH_3)_3)_2$, $B_{20}H_{16}(P(C_6H_5)_3)_2$, and $B_{20}H_{16}(OC_2H_5)_2)_2$, without any release of hy-

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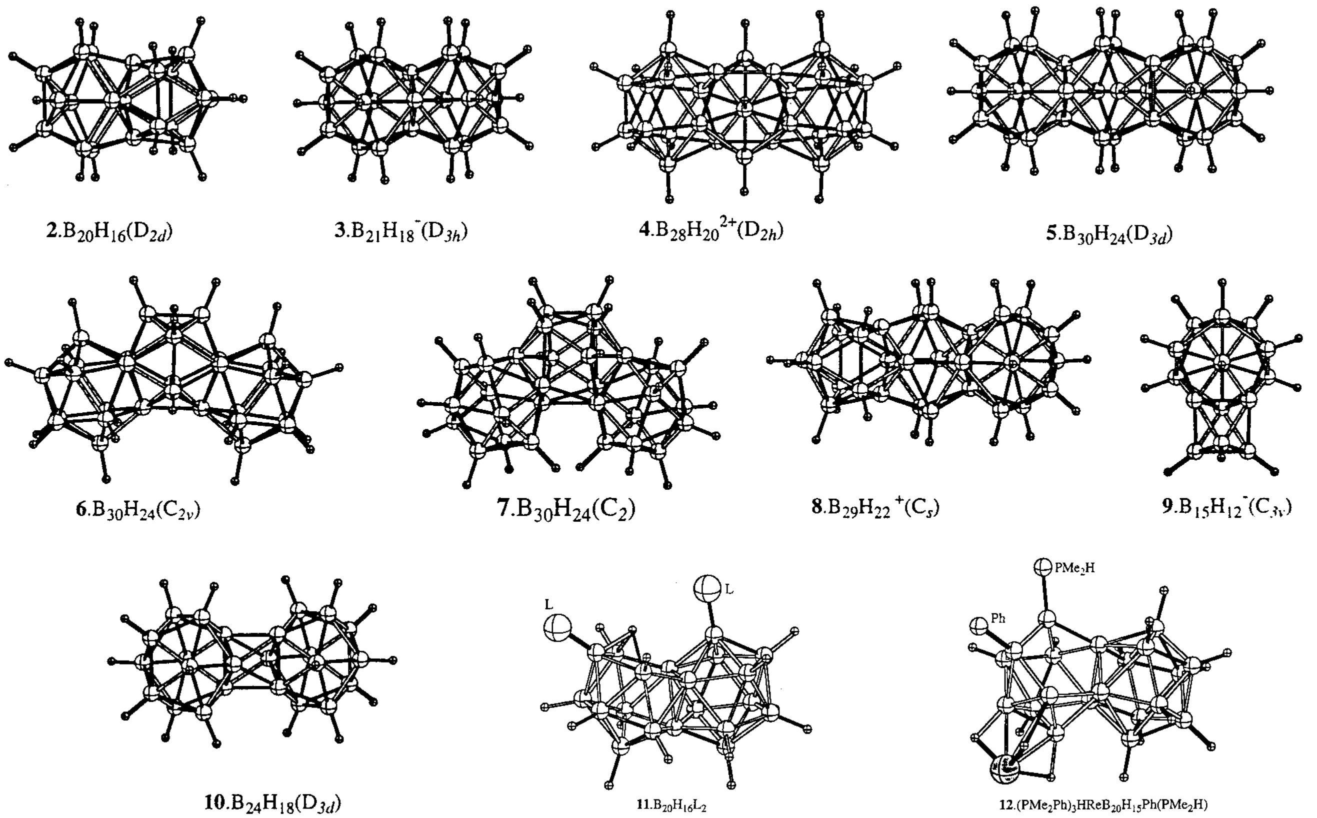

Figure 1. Structure (B3LYP/6-31G*) of the condensed polyhedral boranes (**2**−**12**) considered in this study.

drogen.[6,11] The structure of $B_{20}H_{16}(CH_3CN)_2$ has been characterized experimentally (**11**, Figure 1).[11] This structure can be formally derived from **3** by removing a B−H vertex. With the condensation of a closo and a nido fragment the skeleton represented by **11** requires 23 ($n = 20$, $m = 2$ and one for nido) electron pairs. In $B_{20}H_{16}(CH_3CN)_2$, the 15 B−H groups provide 15 electron pairs. Three shared borons provide 4.5 lone pairs. Since the lone pair on the nitrogen is involved in the $N^+ \rightarrow B^-$ dative bond, these two boron atoms have an extra electron for skeletal bonding. This adds up to 22.5 electron pairs. The remaining one electron is obtained from the bridging hydrogen. Since the primary motif for these reactions is to form the *nido*-$B_{20}H_{16}L_2$ skeleton with the L having its own lone pair for the B−L bond, all the other unresolved structures should be similar though the position of L-substitution may differ.

$B_{20}H_{16}$ reacts with water to form a strong acidic solution forming a product of unknown structure with the characteristics of a diprotic acid.[6] The molecular structure is not resolved but the composition is found to be $[B_{20}H_{16}(OH)_2]^{2-}\cdot 2[H_3O]^+$. The electron count rule helps to visualize the structure of this compound. The polyhedral skeleton may remain the same as that of **11** but here, the nature of the O−B bond requires one electron from boron, similar to that of the *exo*-B−H bond. This makes the skeleton electron deficient and hence requires two more electrons to attain stability. Other adducts such as $[B_{20}H_{16}(OH)_2]^{2-}[N(CH_3)_4]^{2+}$ and $[Cs^+]_2[B_{20}H_{16}(OC_2H_5)_2]^{2-}$ can be deduced in a similar way.

Even heteroboranes can be analyzed in a similar manner. For example, the electronic requirements of the recently reported metalloborane[9] $[(PMe_2Ph)_3HReB_{20}H_{15}Ph(PHMe_2)]$ given in Figure 1 (**12**) can be understood in this way. The number of skeletal electron pairs required by the rule remains 23, the same as that of **11**. The 15 B−H groups and one B−Ph in **12** give 16 electron pairs. The $Me_2HP \rightarrow B$ vertex contributes 1.5 electron pairs. The three shared borons contribute 4.5 electron pairs, making a total of 22 electron pairs so far. The remaining two electrons are obtained by an equally ingenious transition metal bridge. $Re(PMe_3)_3H$ requires 4 electrons to satisfy the 18 electron rule. This is achieved by accepting two B−H bond pairs as ligands, so that two 3c−2e bridges involving Re, B, and H are formed. This would however leave the B_{20} skeleton without its share of two electrons. Re becomes more generous by sharing an additional B−H bond so that the extra electrons can be put to the boron skeleton.

Just about all methods used in justifying the $n + 1$ electron pair rule of polyhedral boranes can be used in the $n + m$ electron count rule as well.[4,8] An easy way to check the validity the electron count, however, is by performing an extended Huckel calculation,[14] looking for the number of electrons that provide a closed shell species with large HOMO-LUMO separation. All structures considered here satisfy this criterion. Needless to say, electron counts are only indicators. Especially, crowding of *exo*-hydrogens could bring instability from steric interactions. Quantitative studies are required for details of energetics and structure (see Supporting Information). In summary, this skeletal electron pair rule provides the necessary theoretical guidance in the experimental exploration of the polycondensed polyhedral borane family.

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Supporting Information Available: Listing of total energy and Cartesian coordinates of **1**−**10** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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