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# Conjuncto Closo Boranes and Relationships to Dual Structures

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Conceptual placement of new vertices (atoms) in the faces of a polyhedral molecule leads to a dual (reciprocal) polyhedral molecule which is related to the first by the Descartes−Euler equation,[1] $P + F = C + 2$. Here, $P$ is the number of vertices (points), $F$ is the number of faces, and $C$ is the number of edges ("curves"). Examples, from the closo boranes[2,3] and carbon fullerenes, are $B_{12}H_{12}^{2-}$ and $C_{20}$ or ($C_{20}H_{20}$) or a proposed[4] $B_{32}H_{32}$ borane or ion (Figure 1) and $C_{60}$[5,6] (or $C_{60}H_{60}$). Following an earlier suggestion of single nearly spherical polyhedra relating boranes to fullerenes,[7] we now extend this relationship to some less spherical multicage structures of closo conjuncto boranes in which boron atoms are shared between the polyhedra.

Of course, polyhedra or polyhedral fragments are known to join to make a larger molecule in a multitude of ways.[8−11] In this initial study we explore icosahedral fragments containing shared boron atoms, although the ideas are more generally applicable to other fragments.

Examples are a $B_{22}$ polyhedron which has $D_{5h}$ symmetry (Figure 2), a $B_{30}$ polyhedron of $D_{3h}$ symmetry (Figure 3), and a $B_{36}$ polyhedron of $T_d$ symmetry. The relationship of these polyhedra to the dual (reciprocal) fullerenes is shown in Table 1. Except for $B_{12}H_{12}^{2-}$, the charges on the boron species have not yet been predicted. Moreover, the number of hydrogen atoms ($a$, $b$, $c$) on the other three boranes is not yet specified because that number is less than the number of boron atoms when the polyhedral surface is nearly flat in certain regions of the molecule.

For example, in $B_{20}H_{16}$ the four shared boron atoms between the two $B_{12}$ units have no hydrogens.[12] The $C_{35}$ and $C_{47}$ species (Table 1) have structures which have been suggested for $Zr_{13}C_{22}$ and $Zr_{18}C_{29}$, respectively.[13] However, the $C_{56}$ species is not the same as the $Zr_{22}C_{35}$ proposal, which corresponds to a $C_{57}$ species in which there is an internal bond. While this $Zr_{22}C_{35}$

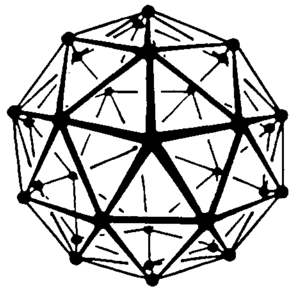

**Figure 1.** Proposal[4] for a $B_{32}H_{32}$ molecule or ion of icosahedral symmetry.

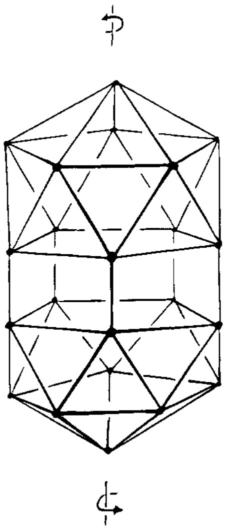

**Figure 2.** In this $B_{22}$ polyhedron ($D_{5h}$) each vertex is connected to five other vertices. The dual is a 35-vertex polyhedron in which five vertices are shared between two $C_{20}$ units, a structure proposed[13] for $Zr_{13}C_{22}$.

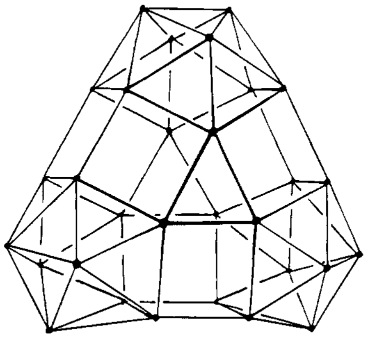

**Figure 3.** This $B_{30}$ polyhedron ($D_{3h}$) is the dual of a $C_{47}$ fullerene in which $C_{20}$ units share three faces, a structure proposed for $Zr_{18}C_{29}$.

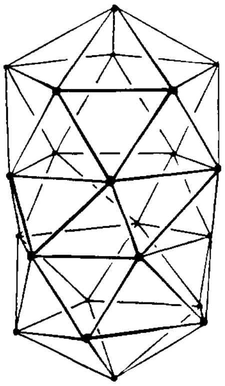

**Figure 4.** Twist-collapse of the $B_{22}$ polyhedron to a $D_{5d}$ structure having 40 triangular faces. The dual structure ia a candidate for a $C_{40}$ species of $D_{5d}$ symmetry.

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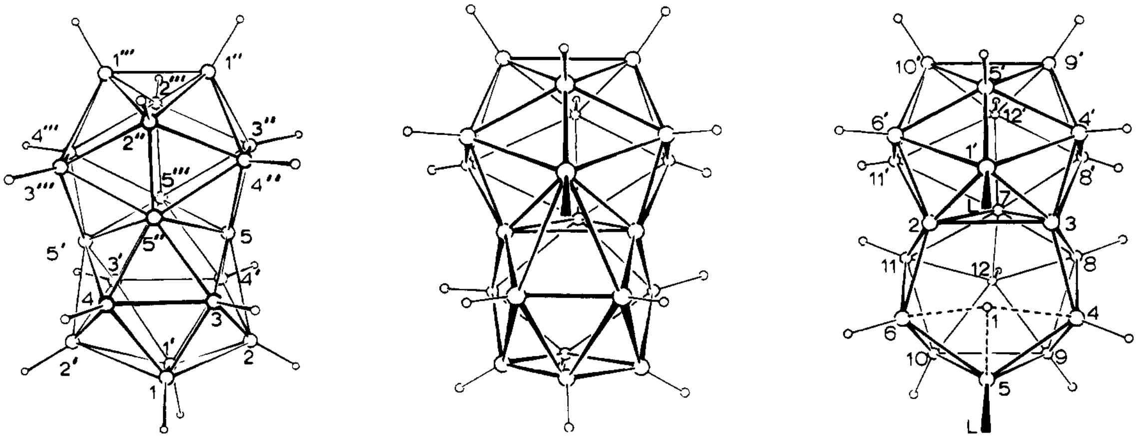

**Figure 5.** Left: $B_{20}H_{16}$ showing four shared boron atoms. Center: Putative intermediate in rearrangement of the lower part of the molecule. Right: The $B_{20}H_{16}L_2$ molecule, where L is a ligand such as acetonitrile.

**Table 1.** Multicage Polycarbon Species and Boron Analogues

| carbon species | *P* | *F* | *C* | sym | boron species | *P* | *F* |
|---|---|---|---|---|---|---|---|
| $C_{20}$ | 20 | 12 | 30 | $I_h$ | $B_{12}H_{12}^{2-}$ | 12 | 20 |
| $C_{35}$ | 35 | 22 | 55 | $D_{5h}$ | $B_{22}H_a$ | 22 | 35 |
| $C_{47}$ | 47 | 30 | 75 | $D_{3h}$ | $B_{30}H_b$ | 30 | 47 |
| $C_{56}$ | 56 | 36 | 90 | $T_d$ | $B_{36}H_c$ | 36 | 56 |

proposal is a reasonable structure, there is no simple dual. We conjecture that this dual relationship fails when internal bonds occur.

Closo borane structures which have square faces are expected to be unstable with respect to distortions of the DSD (diamond–square–diamond) type.[14] The result of this distortion in the $B_{22}$ structure, shown in Figure 4, has 40 triangular faces. The dual-related closo fullerene is a $C_{40}$. Similar distortions are conceivable for the $B_{30}$ polyhedron of Figure 3 to imply a dual, $C_{56}$. A similar distortion of the $B_{36}$ polyhedron from $T_d$ to $T$ symmetry yields 68 triangular faces and suggests a dual, $C_{68}$.

These collapsed structures present another problem because the BH units in the collapsed region have boron atoms joined to six adjacent boron atoms. This feature is present in $C_2B_9H_{11}$,[15,16] which is isoelectronic with fluxional[17] $B_{11}H_{11}^{2-}$. Boron atoms without attached hydrogen atoms occur at 6 or higher coordination in the junctures of many conjuncto boranes, the first of which was $B_{18}H_{22}$.[18] However, further transformation may be found to more stable structures involving a decrease in the number of shared atoms. An early example[8] is the transformation of $B_{20}H_{16}$ by bases such as acetonitrile (L) to a ligated $B_{20}H_{16}L_2$ (Figure 5). This process may occur through a local cuboctahedral intermediate (Figure 5, middle), and it yields the nido product in which one vertex is missing (Figure 5, right).

Perhaps the most promising method of synthesis involves the oxidative coupling reactions starting from single metal or small clusters of metal ions bound to nido borane or nido carborane species, a reaction elaborated by Grimes and co-workers.[19–21] These reactions could also be investigated for coupling of nido clusters which are different from one another.

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