

Bond Order and Bond Length in Closo Polyhedral Boranes

The number of edges in the *closo* deltahedra far exceeds the number of framework or skeletal electron pairs available for cluster bonding. Indeed the ratio of framework bonding electron pairs to the number of bonds (edges) is as follows:

$$\frac{n+1}{3n-6}$$

Because of this, the B–B bond order at a given edge of a deltahedron is always less than one, and diminishes with an increasing number of vertices.

It is observed experimentally that B–B edge distances in the *closo* deltahedra vary over quite a large range (from about 1.6 to 2.0 Å), suggesting in turn that the degree of delocalization (3D aromaticity) is quite variable in this series of compounds. To address this issue, Wade proposed a “fractional bond order”. In this formalism, each boron atom has $(n+1)/n$ electron pairs available for sharing with its neighbors. If boron r shares its $(n+1)/n$ electron pairs with x_r neighboring boron atoms, then boron r shares $(n+1)/nx_r$ electron pairs with each neighbor. Two adjacent vertices r and s share f_{rs} pairs of electrons as follows:

$$f_{rs} = \frac{(n+1)}{nx_r} + \frac{(n+1)}{nx_s} = \frac{(n+1)}{n} \left(\frac{x_r+x_s}{x_r x_s} \right)$$

A value of $f_{rs} = 1.0$ would mean that the bond order is one, and that the boron atoms r and s share a full electron pair along their connecting edge. Because these compounds are electron deficient, Wade’s fractional bond order is much less than one, but it does vary in a way that correlates with the observed B–B edge distances.

Here is an example: $(\text{BH})_{12}^{2-}$ has all 5-connected vertices and all identical edges, so calculation of Wade’s fractional bond order amounts to:

$$f_{rs} = \frac{13}{12} \frac{10}{25} = 0.433$$

A more revealing example is for the case of $(\text{BH})_{10}^{2-}$. Here the two vertices lying on the C_4 axis are four-connected, while the other eight vertices are five-connected. Therefore, we have present both the (4,5) and the (5,5) types of edges. For the (4,5) case, $f_{rs} = 0.495$, while for the (5,5) case f_{rs} works out to a smaller value, 0.440. The higher fractional bond order for the (4,5) case corresponds to a shorter B–B distance of 1.73 Å, while the lower fractional bond order value for the (5,5) case corresponds to a longer B–B edge distance of either 1.83 or 1.86 Å (there are two different types of (5,5) edges in the structure that are not related by symmetry).

A limitation of Wade’s fractional bond order formalism is the assumption that the $n+1$ electron pairs for skeletal bonding are spread out evenly over the n vertices, as this is only strictly the case when all vertices are symmetry equivalent. However, this accounting for the available number of electron pairs with consideration of the number of two-center interactions gives a nice “back of the envelope” starting point for understanding bond distance variations, and for anticipating the results of high-level molecular orbital calculations used for accurate bond order predictions.

From Nido to Arachno Boranes

There is a steady progression of structures as one goes from a *closo* parent structure to successively more open *nido* and on to *arachno* boranes by the process of vertex subtraction. One such series is from *closo* $(\text{BH})_6^{2-}$ to *nido* $(\text{BH})_5\text{H}_4$ (pentaborane-9), and on to *arachno* $(\text{BH})_4\text{H}_6$ (tetraborane-10). Note that in the first vertex subtraction from the *closo* parent, the deleted vertex is removed

together with the 2- charge, so the isoelectronic replacement is to bring in four neutral hydrogen atoms. The *nido* structure so obtained has $n + 2$ framework bonding electrons, the same number as in the parent *closo* deltahedron. In the second vertex subtraction that gives rise to B_4H_{10} , there is no longer a 2- charge to be taken away with the vertex, so the isoelectronic replacement is just with a pair of neutral hydrogen atoms.

Tetraborane(10) is a toxic liquid with boiling point 18 °C, and it ignites spontaneously upon contact with air.

Carborane Isomers

Another very interesting way to effect isoelectronic substitution by way of modifying a *closo* borane structure is to replace one or more $(BH)^{n-}$ vertices with isoelectronic moieties. For example, consider replacement of a single $(BH)^{1-}$ unit of $B_{12}H_{12}^{2-}$ with an isoelectronic C-H fragment. This results in the “carborane” having the formula $CB_{11}H_{12}^-$. On the other hand, double substitution along those lines leads to very interesting *neutral* carborane species, such as the one that results from combination of acetylene with $B_{10}H_{10}^{2-}$ upon two-electron oxidation: $C_2B_{10}H_{12}$. The carborane $C_2B_{10}H_{12}$ has three isomers, named *ortho*, *para*, and *meta*, by analogy with substituted benzene isomers.

Elemental Boron

Different modifications of crystalline, elemental boron have in common the presence of B_{12} icosahedra very similar in structure to that found in the molecular ion, $B_{12}H_{12}^{2-}$. These modifications of the element can be thought of as arising by the polymerization of B_{12} icosahedra in a way that staples in inter-icosahedral B-B bonds to replace the missing B-H bonds present in $B_{12}H_{12}^{2-}$.

This is nicely in analogy to the presence in crystalline carbon (diamond) of C_{10} cages structurally identical to that found in the tetrahedral adamantane molecule, $C_{10}H_{16}$.