Closo Polyhedral Boranes

Polyhedral boranes of the designation *closo* have the general formula $(BH)_n^{2-}$. The shapes of these molecules are also referred to as "deltahedra" because all the faces of the polyhedron are triangles. Specific examples of closo deltahedra mentioned in class are as follows: $(BH)_6^{2-}$ belonging to the point group O_h, $(BH)_7^{2-}$ belonging to the point group D_{5h}, and $(BH)_{12}^{2-}$ belonging to the point group I_h.

Electronic Structure of Closo Polyhedral Borane Anions

Wade's rules have to do with the fact that there are $n + 1$ pairs of framework or cluster bonding electrons in the closo anions, where n is the number of B–H vertices. This designation assumes that the terminal B–H bonds are two-center two-electron localized bonds, while the boron-boron bonding in the cluster framework involves overlap of boron valence atomic orbitals, and the filling of the resulting delocalized MOs with the n electron pairs, plus one more electron pair coming from the -2 charge on the cluster dianion. The separate treatment of terminal B–H bonds is a simplification. A complete MO treatment of any of these molecules will allow for mixing of any linear combinations that belong to a given irreducible representation of the point group.

This separate consideration of terminal B–H bonds and cluster framework MOs is convenient and brings a focus on the cluster bonding; for the high-symmetry deltahedra, the cluster bonding MOs resemble atomic orbitals, such that the clusters can be thought of as pseudo-atoms, or super-atoms, in terms of their electronic structure. For example, the seven cluster bonding MOs of $(BH)_6^{2-}$ have the symmetry of s, p_x, p_y, p_z, d_{xy}, d_{xz}, and d_{yz}.

The electronic structure of the *closo* polyhedral boranes has been referred to as 3D-aromatic because of the delocalization in three dimensions, analogous to the 2D delocalization of the π electrons in benzene. Associated with this 3D-delocalized electronic structure is thermodynamic stability, and this can be maintained in more open structures obtained by isoelectronic replacement.

Nido Boranes

There are a great many known molecules composed only of boron and hydrogen. Those referred to as *nido* are derived conceptually from a parent *closo* deltahedron by the removal of a single BH^{2-} vertex, and replacement of that vertex by four hydrogen atoms. It is important to note that this is an isoelectronic replacement. For example, pentaborane-9 (nine is the number of hydrogens) has the formula $(BH)_5H_4$ and belongs to the point group C_{4v}. It is the *nido* borane derived from *closo* $(BH)_6^{2-}$ by subtraction of a single BH^{2-} vertex, and replacement of that vertex by four *bridging* hydrogen atoms. Pentaborane-9 thus has $n + 2 = 7$ pairs of cluster bonding electrons, the same number as in *closo* $(BH)_6^{2-}$. The bridging hydrogens in pentaborane-9 bridge between pairs of boron atoms around the base of the molecule, at the location of the subtracted vertex.

Neutral compounds composed only of boron and hydrogen have attracted interest due to their high energy content on a mass basis. Pentaborane-9 burns with a characteristic green flame, and has been termed the "Green Dragon". In contrast to hydrocarbons, many such boranes burn spontaneously in air, and so must be manipulated carefully in an inert atmosphere.