Boranes

Boranes are compounds composed solely of boron and hydrogen (and sometimes a cation) and may be neutral or anionic.

History: The chemistry of the boranes was first studied systematically by Alfred Stock and his research group beginning in 1912 and continuing for almost 25 years. His initial work involved the reaction of acids with magnesium boride, although better routes have been developed since then. Because these compounds are exceedingly air-sensitive (they instantaneously burn in air) he developed the glass vacuum line and techniques for using it. As much of the inorganic chemistry done today involves oxygen and moisture sensitive compounds this development permitted advances in a wide range of fields beyond boranes. Another giant in the field of boranes is W.N. Lipscomb of Harvard Univ. whose work on the theory of bonding within boranes (*vide infra*) led to his being awarded the Nobel Prize in Chemistry in 1976. Furthermore, H.C. Brown (Purdue) shared the 1979 Nobel prize for synthetic work in organic chemistry utilizing boranes.

Nomenclature: Boranes are named as follows:

a) The Latin prefixes mono-, di-, tri-, etc. are used before "borane" to indicate the number of boron atoms in the compound.
b) Immediately following the "e" in "borane" the number of hydrogen atoms is placed in parentheses using Arabic numerals.

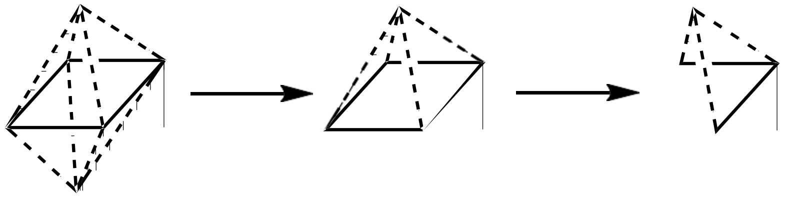
Example: B_5H_{11} is pentaborane(11).

Structure: Boranes fall into 6 structure categories, the 3 most important of which are:

a) *closo* - $B_nH_n^{2-}$ b) *nido* - B_nH_{n+4} c) *arachno* - B_nH_{n+6}

These are prefixes that can be given to the borane designation above. However they are not necessary because each structure type has only one general formula, thus the formula gives the structure.

The boron atoms will form a shape by occupying vertices on a polyhedron (e.g. for 4 B atoms the polyhedron can be a tetrahedron), whether or not the boron atoms are actually bound to each other. This arrangement is frequently called a "cage." *Closo*- refers to the most symmetrical possible arrangement, a closed polyhedron (e.g. 6 B atoms form an octahedron, see figure below). *Nido*- comes from the next higher *closo*- polyhedron with the most highly connected boron vertex removed (e.g. for 5 B atoms, an octahedron less any one vertex to yield a square pyramid). *Arachno*- comes form the next higher *nido*- structure with the most highly connected boron vertex on the open face removed (e.g. for 4 B atoms, a square pyramid less any basal vertex to yield a butterfly structure). The words *closo*-, *nido*-, and *arachno*- are derived from words meaning "closed" (Greek), "nest" (Latin), and "spider's web" (Greek). A large number of examples are shown on p. 799 of Huheey, Keiter, and Keiter.



closo
octahedral

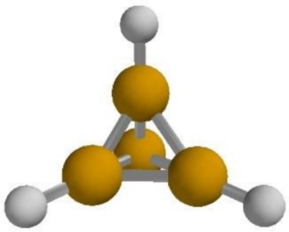
nido
square pyramid

arachno
butterfly

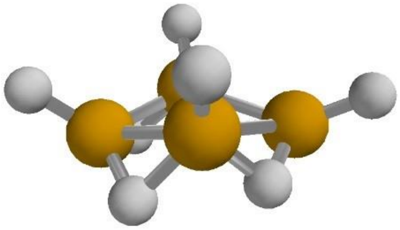
Examples: $B_4H_4^{2-}$ is *closo* and the 4 B's lie on the 4 vertices of a tetrahedron.

B_4H_8 is *nido* and the 4 B's lie on 2 equatorial and 2 axial positions of a trigonal bipyramid.

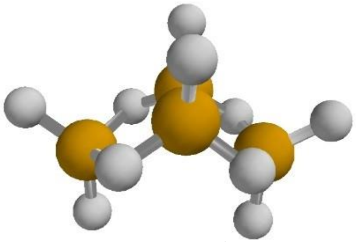
B_4H_{10} is *arachno* and the 4 B's lie on an octahedron with adjacent vertices removed (one edge).



$B_4H_4^{2-}$



$B_4H_8^{\dagger}$



$B_4H_{10}^{\ddagger}$

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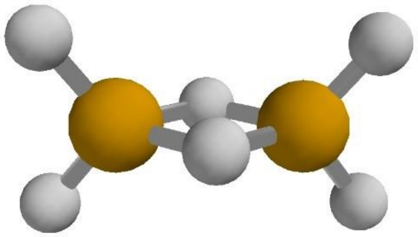
Diborane

The simplest of the boranes is diborane(6) or B_2H_6. It is the only stable borane with 2 boron atoms and is frequently just called diborane.

Diborane can be conveniently prepared by the reaction:

$$3\ NaBH_{4\,(s)} + 4\ BF_3{\bullet}OEt_{2\,(\ell)} \longrightarrow 3\ NaBF_{4\,(s)} + 2\ B_2H_{6\,(g)} + 4\ Et_2O_{(\ell)}$$

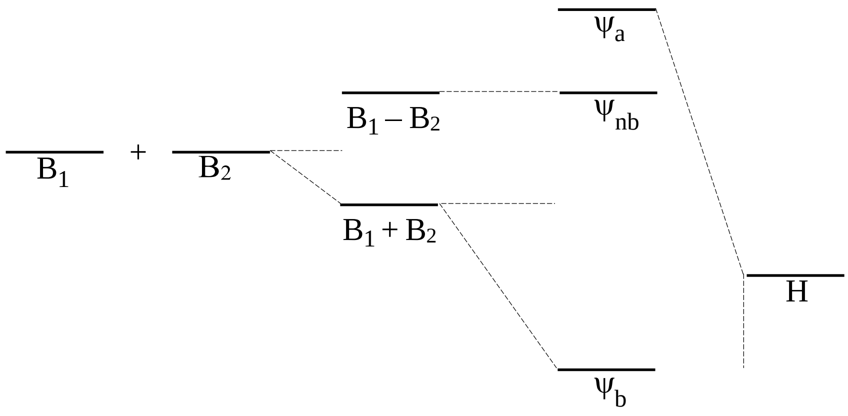
Diborane, like most boranes, is very air-sensitive.
Diborane has the structure:



where each boron is pseudo-tetrahedral.

The terminal hydrogens are each bound to the boron atoms with a standard 2-electron bond. The bridging bonds are unusual in that there do not appear to be enough electrons to form a bond between the two boron atoms and the bridging hydrogen. (Recall the standard definition of a covalent bond is a shared pair of electrons between two atoms.) The bridging hydrogens bind through a 3-center 2-electron bond. This bonding arrangement can be explained in terms of MO theory.

In this bonding arrangement there are 2 boron sp^3 hybrids overlapping 1 hydrogen 1*s* orbital.



$\psi_b = \frac{1}{2}\psi_{B1} + \frac{1}{2}\phi_{B2} + \frac{1}{\sqrt{2}}\phi_H$

$\psi_{nb} = \frac{1}{2}\phi_{B1} - \frac{1}{2}\phi_{B2}$

$\psi_a = \frac{1}{2}\phi_{B1} + \frac{1}{2}\phi_{B2} - \frac{1}{\sqrt{2}}\phi_H$

Reactions of Diborane

Diborane, like all boranes, is thermodynamically unstable with respect to its component elements. They owe their existence to kinetic factors. That is, in an anaerobic, anhydrous environment, no pathway for decomposition exists with an accessible energy barrier at room temperature.

1) $B_2H_6 \rightleftharpoons 2\ BH_3$ $K_{eq} \approx 10^{-5}$, $\Delta H = 150$ kJ/mol
2) $B_2H_6 + 3\ O_2 \longrightarrow B_2O_3 + 3\ H_2O$ $\Delta H = 2050$ kJ/mol (115 kcal/mol)
   Note: This is a very exothermic reaction, $\Delta H \cong 2100$ kJ/mol compared with $\Delta H \cong 1000$ kJ/mol for burning ethane. This reaction also begins on contact with oxygen, as is the case for all boranes.
3) $B_2H_6 + 6\ H_2O \longrightarrow 2\ B(OH)_3 + 3\ H_2$ (boric acid)
4) $B_2H_6 + 6\ ROH \longrightarrow 2\ B(OR)_3 + 3\ H_2$ (a borate ester)
5) $B_2H_6 + 6\ H_2C{=}CH_2 \longrightarrow 2\ BEt_3$
6) $B_2H_6 + 2\ MH \xrightarrow{\text{ether}} 2\ M[BH_4]$ (M = Li or Na)
7) $B_2H_6 + 2\ NR_3 \longrightarrow 2\ R_3N{\bullet}BH_3$ (R = alkyl)
8) $B_2H_6 + 2\ NH_3 \longrightarrow [BH_2(NH_3)_2][BH_4]$
9) $Me_2O{\bullet}BH_3 + NH_3 \longrightarrow H_3N{\bullet}BH_3 + Me_2O$

The last 3 reactions illustrate an interesting feature of diborane chemistry. Soft Lewis bases induce symmetrical cleavage of diborane (Figure 1), while hard Lewis bases induce asymmetrical cleavage (Figure 2).

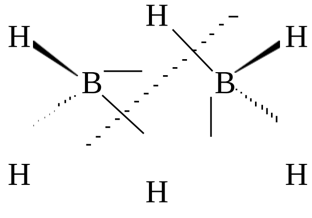


Figure 1

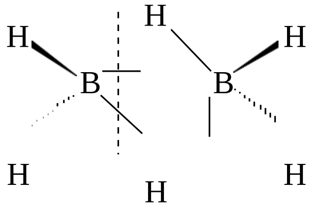


Figure 2

Higher Boranes

Higher boranes are usually formed by pyrolysis of diborane or other boranes followed by separating the product mixture. The air sensitivity of boranes decreases with increasing size.

There are also several systematic methods to produce particular higher boranes.

1) $B_2H_6 + NaBH_4 \longrightarrow B_5H_8$
$\longrightarrow B_6H_6^{2-}$ increasing temperature and
$\longrightarrow B_{12}H_{12}^{2-}$ increasing $B_2H_6/NaBH_4$ ratio

2) $B_5H_9 + KH \longrightarrow B_5H_8^- + H_2$
$B_5H_8^- + R_2O{\bullet}BH_3 \longrightarrow B_6H_{11}^- \xrightarrow{H^+} B_5H_{12} + H_2$

3) $B_4H_{10} + KH \longrightarrow B_4H_9^- + H_2$
$B_4H_9^- + BH_3 \longrightarrow B_5H_{12}^- \xrightarrow{H^+} B_5H_{11} + H_2$

4) $B_{10}H_{14} + NR_3 \longrightarrow B_{10}H_{10}^{2-} + 2\ HRN_3^+$

Cluster Valence Electron Theory

This is a second method for determining the geometry of a cluster. It is more comprehensive than the structure rules given on the first page and works for all boranes, as well as related carboranes.

To use this method, the total number of valence electrons used in cluster binding must be determined. There are 3 valence electrons for each boron atom, 1 valence electron for each hydrogen atom, and the total charge on the complex must be added in.

The structure is determined according to the following equations:

closo - $4n + 2$ valence electrons
nido - $4n + 4$ valence electrons n = number of boron atoms in the cluster
arachno - $4n + 6$ valence electrons

Example: $B_4H_4^{2-}$: $(4 \times 3e^-) + (4 \times 1e^-) + 2e^- = 18$ valence electrons
$4n = 4 \times 4 = 16$ and $18 - 16 = 2 \Rightarrow$ a *closo*- structure, this is also predicted for this molecule from the structure rules on p. 1