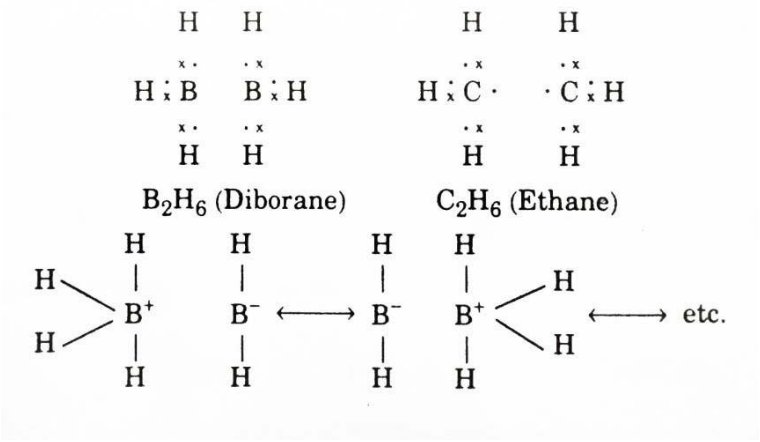
Structure and Bonding of Boranes

Structure of Diborane

The structure of the diborane is of great interest. The diborane is an electron deficient compound i.e. there are not enough valency electrons to form the expected number of covalent bonds. The following structures were proposed for diborane:

The ethane like structure of diborane and the ionic form :



These structures have lack of experimental support, hence treated as incorrect one. $B_2H_4^{2-}$ anion is isoelectronic with ethylene C_2H_4 but these two are not isostructural. Because this ion has a cloud of electron density above and below the B-H plane as in C_2H_4· The neutral B_2H_6 molecule could then be formally produced by embedding a proton in the electromc cloud above and below the plane of $B_2H_4^{2-}$ ion. Although this structure was not accepted but this bonding model is currently accepted as the three centre-two electron 3c-2e bond. Recent work on electron diffraction and spectral studies support the hydrogen bridge structure in which one hydrogen atom form a bridge between two boron atoms, while the terminal hydrogen atoms form normal covalent bonds with boron atoms. This structure may be represented as below:

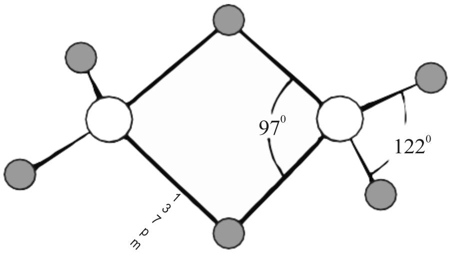


Figure : Hydrogen bridged structure of diborane molecule.

In this structure four hydrogen atoms (two each on the left and right hand side) are known as terminal hydrogens (H_t) and two other hydrogen atoms are known as bridging hydrogens (H_b). The two boron atoms and four terminal hydrogen atoms lie in the same plane while two bridging hydrogen atoms lie in a plane perpendicular to this plane. Different parameters are as given below :

The bond lengths between B-H_t, B-Hand B-B are 1.19 Å, 1.37 Å and 1.77 Å respectively, B-H_b is longer than B-H_t due to electron deficiency. Bond angles $\angle H_tBH_t$, $\angle BH_bB$ and $\angle H_bBH_b$ are 122°,100° and 97° respectively.

The above bridge structure is supported by the followingfacts :

(i) Electron diffraction measurements confirm that four terminal hydrogen atoms are coplanar and two bridge hydrogen atoms occupy the place above and below the plane.

(ii) Vibrational spectral (Raman and infrared) studies show two intense bands at 2102 cm-1 and 2523 cm-1 for B-H bonds. This indicates that all the B-H bonds are not identical.

(iii) Nuclear magnetic resonance studies show three main regions of absorption which are due to boron atoms, terminal hydrogen atoms and bridge hydrogen atoms. These studies again support the presence of bridging structure.

(iv) The specific heat of diborane is found to be 54.4 kJ while for ethane it is 12.5 kJ. This indicates that there is hindrance of rotation in diborane molecule that is due to bridge structure. Because bridge structure is considered it should be 21-63 kJ.

(v) Diborane on methylation gives $B_2H_2(CH_3)_4$ indicating that four hydrogen atoms are of different nature than the rest two hydrogen atoms i.e. bridge hydrogen atoms.

Nature of Bonding in Hydrogen-Bridge: Structure of Diborane

The hydrogen bridge formation is now well established. The orbital theory explains its formation, in which boron atoms show sp^3 hybridisation.

Because three electrons are available hence out of four sp3 hybrid orbitals, one sp3 hybrid orbital i empty. There is one s-orbital of hydrogen atom. Now two sp3 hybrid orbitals of one boron atom overlap with two s-orbitals of two hydrogen atoms and form sp3_ s bonds with hydrogen atoms which are known

as terminal hydrogen atoms in the diborane. This third hydrogen atom form bond with one sp3 hybrid orbital of the first boron atom and one sp3 hybrid orbital of the second boron atom which is empty hybrid orbital. Such type of overlapping cause of banana type bond as shown below :

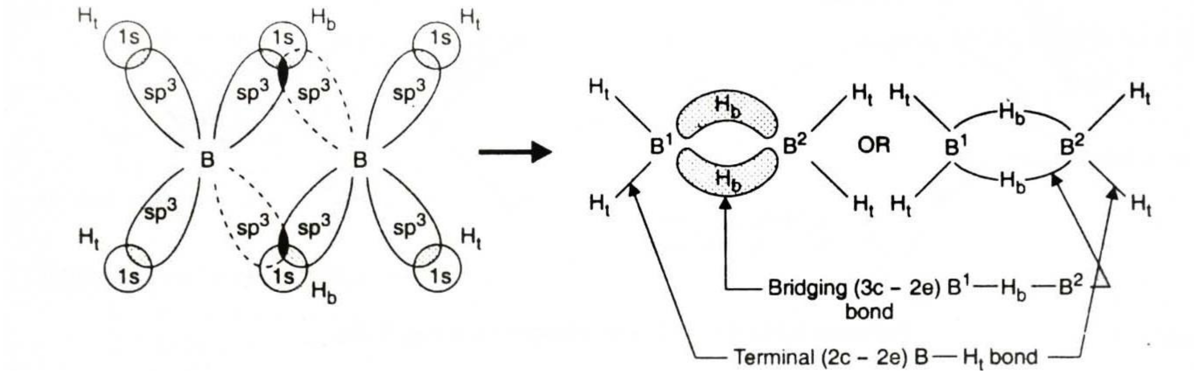


Figure : Fromation of two bridging 3c-2e in B^1-H_b-B^2 and four rterminal 2c-2e in B-H_t bonds in diborane molecule.

The above idea gives a riew concept of the three centre- bond formation; in which the three nuclei are bonded by two electrons hence also known as 3c-2e i.e. three centres-two electrons while terminal hydrogen atoms form usual bond i.e. 2c-2e (two centres-two electrons) bond. Hence diborane may also be represented as shown alongside.

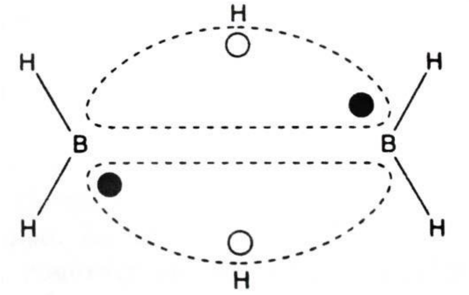


Figure : Diborane

In this figure dark circular spot (•) represents an electron originally on boron atom and empty spot (°) represents an electron originally on a hydrogen atom. Hence each loop links two boron atoms and one hydrogen atom.

Types of Bonds Found in Higher Boranes

Higher boranes may contain few or all of the following types of bonds :

i) Terminal (2c-2e) B-H bond : This is a normal covalent bond formed by overlapping of singly filled sp3 -hybrid orbital of boron atom and singly filled Is-orbital of hydrogen atom.

ii) Direct (2c-2e) B-B bond : This is a normal covalent bond formed by overlapping of singl filled sp3-hybrid orbitals of two boron atoms.

iii) Bridging or Open (3c-2e) B-H-B bond: This type of bond is formed by overlapping of two sp3-hybrid orbitals of two boron atoms (one singly filled and other empty) and Is-orbital of hydrogen atom.

iv) Triply bridged or closed (3c-2e) B-B-B bond: This type of bond is formed by overlapping of three sp3-hybrid orbitals of three boron atoms. Out of these one sp3-hybrid orbital is empty. Thus each boron atom contributes 2/3 electrons for the formation of this bond.

Structure and Bonding in Some Higher Boranes

The structure and bonding of some common boranes are given here.

I) Tetraborane-10 (B_4H_{10}) : In this molecule four B-atoms form slightly distorted octahedral geometry. In this molecule there are (i) four bridging (3c-2e) B-H-B bonds viz. B1-H-B3, B3-H-B2, B2-H-B4 and B4-H-B1; (ii) one direct (2c-2e) B-B bond (Bl-B2) and (iii) six terminal (2c-2e) B-H bonds viz Bl-H, B2-H, B3- H, B3-H B4-H and B4-H bonds.

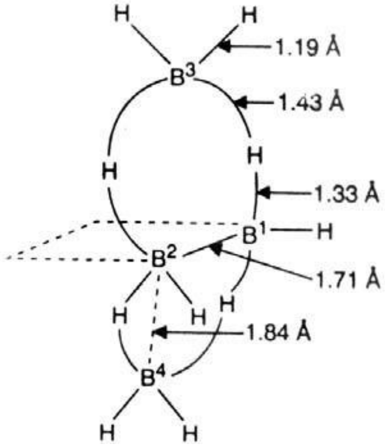


Figure : Structure of Tetraborane-10 (B_4H_{10})

II) Pentaborane-9 (B_5H_9) : In this molecule five B-atoms are situated at five corners of a square pyramida. Four B-atoms (B1,B2, B3 and B4) are at the base and fifth B-atom (B5) is at the apex of the pyramid. All these B-atoms form five terminal (2c-2e) B-H bonds. The basal B-atoms are bonded each other by four bridging (3c-2e) B-H-B bonds. The apex B-atom is bonded tothe two B-atoms (B1 and B4) by two (2c-2e) B-B bonds. There is one closed (3c-2e) B-B-B bond also viz. B5-B3-B2 bond. Thus this molecule possesses all the four types of bonds discus d above.

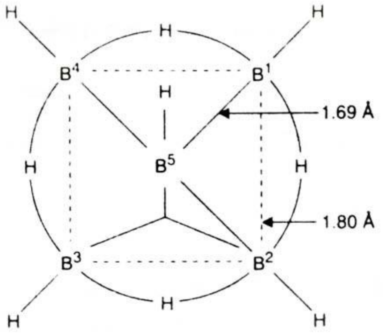


Figure : Structure of Pentaborane-9 (B_5H_9)

III) Pentaborane-11 (B_5H_{11}): In thi molecule five B-atoms are situated at five corners of an asymmetrical square pyramidal. Four B-atoms (B1, B2, B3 and B4) are at the base and fifth B-atom (B5) is at the apex of the pyramid, which form two closed (3c-2e) B-B-B bonds viz B1-B4-B5 and B2-B3-B5. Two basal B-atoms (B2, B3) and"apical B-atom (B5) each are linked with two H-atoms by two terminal B-H bonds while the remaining Bl and B4 atoms are linked with one H-atom by one terminal B-H bond. Thus there are eight terminal (2c-2e) B-H bonds in this molecule. Except it there are three bridging (3c-2e) B-H-B bonds viz Bl-H-B4, B4-H-B3 and Bl-H-B2 bonds.

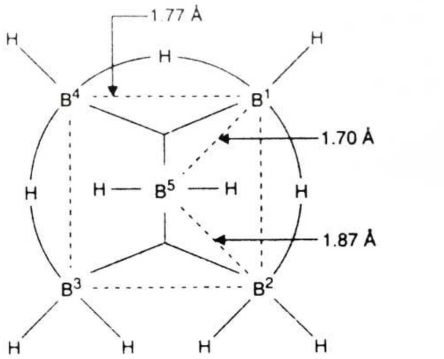
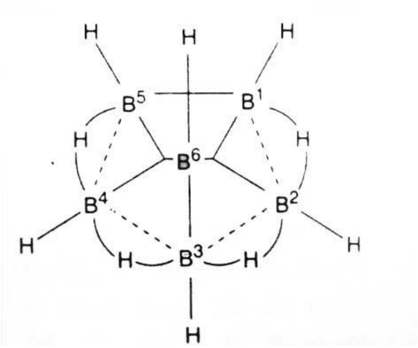


Figure : Structure of Pentaborane-11 (B_5H_{11})

IV) Hexaborane-l0 (B_6H_{10}) : In this molecule six B-atoms are situated at the corners of a pentagonal pyramid. Five B-atoms are at the base of the pyramid and sixth B-atom (B6) is at the apex. The basal and apical B-atoms each are linked with six H-atoms by six terminal (2c-2e) B-H bonds. There are (our bridging (3c-2e) B-H-B bonds viz B1-H-B2, B2-H-B3, B3-H-B4



and B4-H-B5. Except it there are two (2c-2e) B-B bonds viz B1-B5 and B3-B6, and two closed (3c-2e) B-B-B bonds viz B1-B2-B6 and B4-B5-B6 bonds also present in the molecule.

Figure : Structure of Hexaborane-l0 (B_6H_{10})

v) Decaborane-14 ($B_{10}H_{14}$) : As revealed by X-ray analysis, in $B_{10}H_{14}$ molecule the B-

atoms are arranged in two pentagonal pyramids with an edge common to both the pentagonal pyramids. This molecule consist (our bridging (3c-2e) B-H-B bonds (viz B5-H-B6, B6-H-B7, B8-H-B9 and B9-H-B10) in the open face. There are ten terminal (2c-2e) B-H bonds. In addition to these there are four (2c-2e) B-B bonds (viz B2-B5, B2-B7, B4-B8 and B4-B8) and four closed (3c-2e) B-B-B bonds viz Bl-B2-B3, Bl-B3-B4, Bl-B5-Bl0 and B3-B7-B8 bonds).

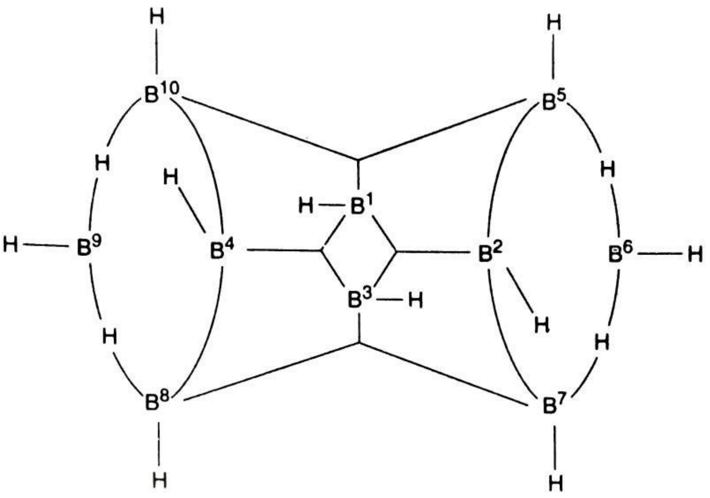
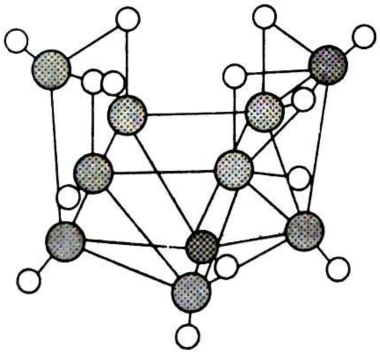


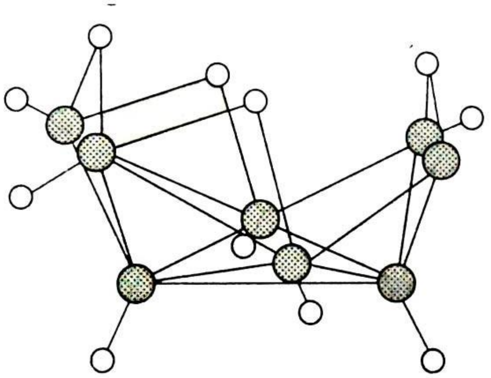
Figure : Structure of Decaborane-14 ($B_{10}H_{14}$)

The structures of B_8H_{12}, B_9H_{15}, $B_{10}H_{14}$, $B_{10}H_{16}$, $B_{18}H_{22}$,$B_{20}H_{16}$,$B_{10}H_{10}^{2-}$ and B H $^{2-}$ are also given below.

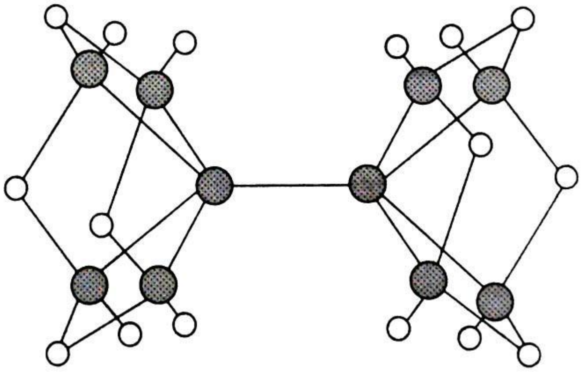
12 12



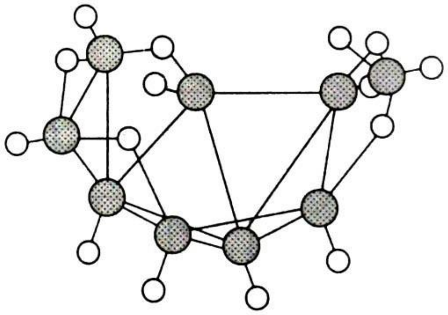
Decaborane-14 ($B_{10}H_{14}$)



Octaborane-12 (B_8H_{12})



Decaborane-16 ($B_{10}H_{16}$)



Nonaborane-15 (B_9H_{15})

10.5 Metalloborane

Borane-clusters, in which metals are present are know as 'Metalloboranes'. Many metalloboranes have been prepared. In some cases metal atom is attached with the borohydride ion through hydrogen bridge. The most common and important metalloborane group is one in which direct metal boron bond is present.

An important example of main group element metallocarborane is closo $[B_{11}H_{11}AlCH_3]^{2-}$. It is prepared by the action of trim ethyl aluminium $[Al(CH_3)_3]_2$ with $Na_2[B_{11}H_{13}]$:

$$Al_2(CH_3)_6 + 2[B_{11}H_{13}]^{2-} \xrightarrow{\Delta} 2[B_{11}H_{11}AlCH_3]^{2-} + 4CH_4$$

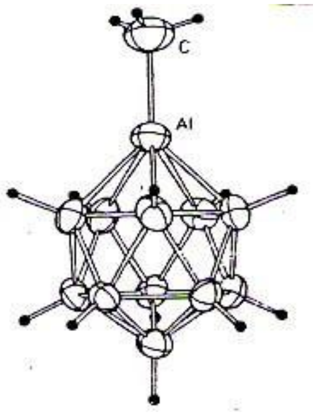


Figure: Closo $[B_{11}H_{11}AlCH_3]^{2-}$