Boranes?

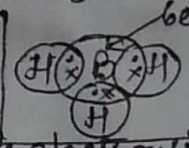
Hydrides of boron(B_5) are collectively known as **Boranes**. There are two series of boranes having general formulae B_nH_{n+4} and B_nH_{n+6} (where n = number of B-atoms).

(i) B_nH_{n+4} type boranes: B_2H_6 (Diborane-6), B_4H_8 (Tetraborane-8), B_5H_9 (Pentaborane-9) etc.

(ii) B_nH_{n+6} type boranes: B_4H_{10} (Tetraborane-10), B_5H_{11} (Pentaborane-11), B_6H_{10} (Hexaborane-10) etc.

B_2H_6 & B_4H_{10} are known as **boroethane** & **borobutane** as they resemble to C_2H_6 (ethane) & C_4H_{10} (butane) in molecular formula. Boranes are very important in recent time as they are used as rocket fuel and in supersonic bomber.

⇒ **Structure & Bonding in Boranes:** (1) **Diborane(B_2H_6):** Diborane(B_2H_6) is dimer of BH_3 (boron hydride). $2BH_3 \rightleftharpoons B_2H_6$. B_5: 2,3 or $1s^2 2s^2 2p^1$; H = 1 or $1s^1$.



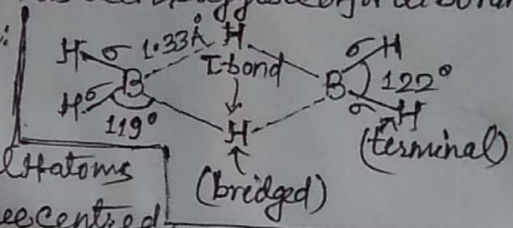
BH_3 is an electron deficient molecule and its dimer(B_2H_6) is also an electron deficient molecule. Total no. of valence electrons = 12.

Its structure does not resemble to C_2H_6 because there are 14 valence electrons in it. A bridge structure with multicentre bonding has been suggested for diborane.

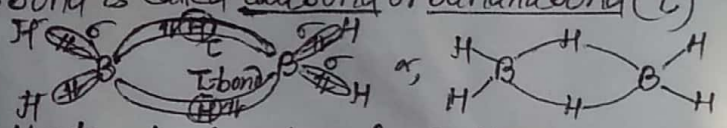
There are two types of hydrogen in this structure:

(a) Terminal hydrogen (4)

(b) Bridged hydrogen (2)



(i) The bonding between each boron and the terminal H-atoms are σ-type (colinear), but each B-H-B bonding is a three centred two electrons bond, i.e. two electrons are involved in bonding together three atoms (2B & H). This two electrons three centred bond is called **tau bond** or **banana bond** (τ) and may be represented as follows:

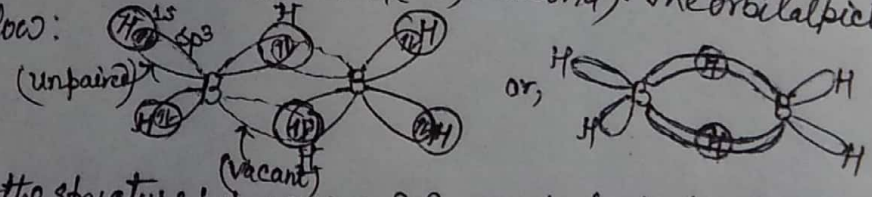


(ii) The two BH_2 groups which involved the terminal H-atoms lie in the remaining two H-atoms lie in a perpendicular planes, one above the plane and another below the plane.

(iii) Outer shell electronic configuration of boron atom is

B_5: Ground state ele. conf. 1s | 2s | 2p ; Excited state ele. conf.: 1s | 2s | 2p (sp³ hybridisation)

Each B-atom is assumed to have 4 sp^3 hybrid orbitals, out of which three (sp^3 hybrid orbitals) have unpaired or single electron while one sp^3 hybrid orbital of B is vacant. The two sp^3 hybrid orbitals of each B-atom overlap with 1s orbital of the two H-atoms forming two B-H bonds. Out of the two sp^3 hybrid orbitals left, one contains an unpaired electron while the other is empty or vacant. The hybrid orbital(sp^3) to one B-atom and the empty sp^3 hybrid orbital belonging to the other B atom overlap simultaneously with the 1s orbital of H-atom on both sides resulting three centred two electron bond (i.e; tau bond). The orbital picture of diborane(B_2H_6) shown below:



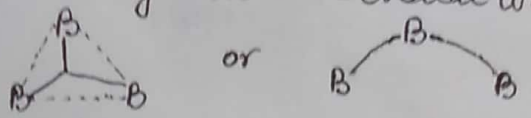
* **Experimental evidences for the structure:** (i) NMR and Raman spectra indicate that two H-atoms in B_2H_6 are different from that of C_2H_6 (ethane).

(ii) Electron diffraction studies show that the bridging H-atom lie in a plane perpendicular to the two BH_2 planes containing terminal H-atoms.
(iii) Specific heat measurements points the hindered rotation of one of these BH_2 groups about the other. This is due to intervening bridging H-atoms in a perpendicular plane.
(iv) Chemical reaction such as methylation of diborane also indicate that two H-atoms in B_2H_6 are of different type.

(2) Structure of higher boranes:

Diborane provides basis of two types of bond found in higher boranes.
(a) Three centred bond: These are B-H-B bonds which are tau or banana bond.
(b) Sigma (σ) bond: These are terminal B-H bonds

Besides the above two types of bonds, two other type of bonds are important in higher boranes. They are
(c) B-B bond: These are two centred two electrons bond, which is best illustrated by boranes substitutes (X_aB-BX_a).
(d) B-B-B bond: These are three centred bonds which may be formed by the overlap of three orbitals from three corners of an equilateral trigonal of boron atoms like the three centred B-H-B bonds. Three molecular orbitals will results of which only the lowest energy or bonding molecular orbital will be occupied by two pairs of electrons.



For example,

Structure of Tetra-borane-10 (B_4H_{10}):

The structure of tetraborane molecule has been deduced from X-ray diffraction studies. It has the following bonds:
(a) There are four B-H-B bonds (tau or banana).
(b) There are six B-H bonds (σ), which are terminal bonds.
(c) There is only one B-B-B bond, three centred like B-H-B bond.

The boron atoms lie at the corners of two triangles like together. The structure of tetraborane (B_4H_{10}) as shown below: