

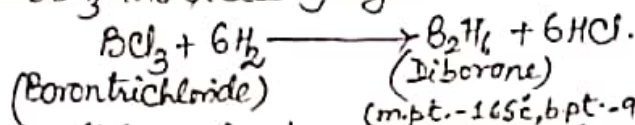
⇒ Boranes:

Boron forms a number of hydrides of types: B_nH_{n+4} & B_nH_{n+6} , where $n = 2, 5, 6 \text{ \& } 10$. These are called boranes by analogy with alkanes (saturated hydrocarbons, C_nH_{2n+2}). The important hydride of boron/borane is diborane (B_2H_6).

* Preparation: 1. It is prepared by the action of lithium hydride (LiH) and boron trifluoride (BF_3). $BF_3 + 6LiH \longrightarrow B_2H_6 + 6LiBF_4$

(Diborane)

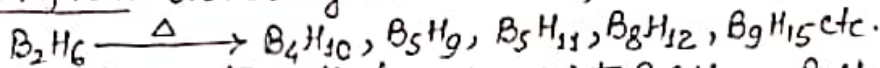
2. It may also be prepared by passing silent electric discharge through a mixture of BCl_3 or BBr_3 and excess hydrogen.



(m.p. $-145^\circ C$, b.p. $-92.5^\circ C$)

* Properties: 1. It is a colourless gas, stable at lower temperature and easily liquified. It has a disagreeable odour and causes headache. It is ^{spontaneously} inflammable in air.

2. Action of heat: On heating it at $100-250^\circ C$, a number of other boranes obtained.



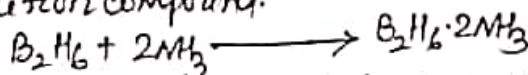
On red hot temperature, it decomposes into B & H_2 . $B_2H_6 \xrightarrow[\text{temp.}]{\text{Red hot}} 2B + 3H_2 \uparrow$

3. Reaction with water: It is hydrolysed by water into orthoboric acid (H_3BO_3) & H_2 .

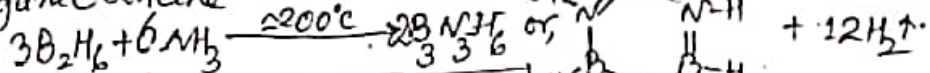


4. Reaction with HCl: It reacts with hydrogen chloride gas to form chlorodiborane. $B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2 \uparrow$

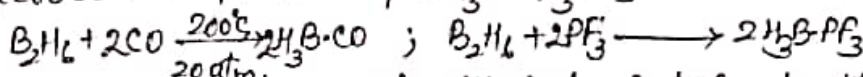
5. Reaction with ammonia: (i) At low temperature, it reacts with ammonia (NH_3) to form an addition compound.



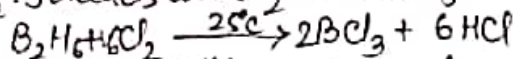
(ii) At higher temperature ($\approx 200^\circ C$), it forms a volatile compound borazole, called inorganic benzene.



6. Reaction with CO & PF_3 : It reacts with CO & PF_3 at $200^\circ C$ & 20 atm pressure to form $H_3B \cdot CO$ & $H_3B \cdot PF_3$.



7. Reaction with Cl_2 : It reacts with Cl_2 at $25^\circ C$ to form boron trichloride & HCl.



8. Reaction with alkyl/alkoxy lithium: It reacts with alkyl lithium (RLi) or alkoxy lithium ($LiOR$) to form lithium borohydride ($LiBH_4$). $3RLi + B_2H_6 \longrightarrow 4LiBH_4 + BR_3$

* Uses: 1. As reducing agent in organic synthesis. 2. In polymerization catalysis. 3. In formation of high energy fuels & propellants.

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

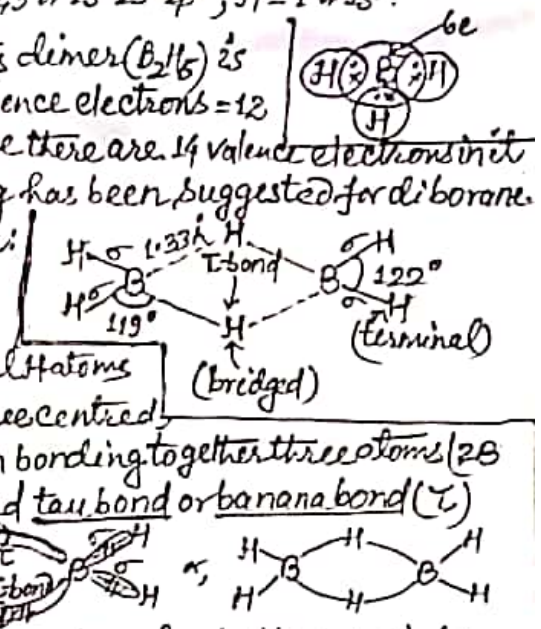
BH_3 is an electron deficient molecule and its dimer (B_2H_6) is also an electron deficient molecule. Total no. of valence electrons = 12

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:

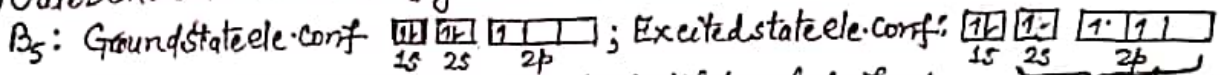
- (a) Terminal hydrogen (4)
- (b) Bridged hydrogen (2)

(i) The bonding between each boron and the terminal H atoms are σ -type (linear), 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



Each B-atom is assumed to have 4 sp^3 hybrid orbitals, out of which three have unpaired single electron while one sp^3 hybrid orbital of B is vacant. The two sp^3 hybrid orbitals of 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:

