

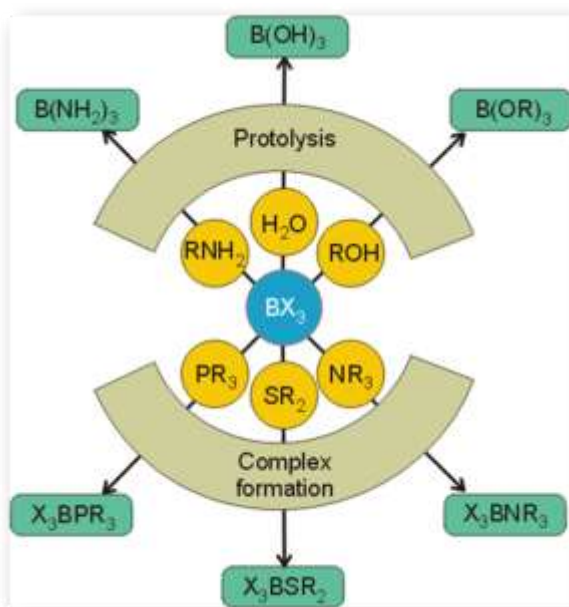
BORON CHEMISTRY

Electronic Configuration of B

GROUND STATE: $1s^2 2s^2 2p^1$

EXCITED STATE: $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0$

SINCE $2p_z$ IS VACANT IN BORON COMPOUNDS, IT CAN BEHAVE AS LEWIS ACID



Hydrides of Boron are called BORANES

BORANES are of five classes:

1. *Closo-boranes* [cage] : B_nH_{n+2}
2. *Nido-boranes* [Nest] : B_nH_{n+4} , B_2H_6
3. *Arachno-boranes* [Spider-web] : B_nH_{n+6}
4. *Hypho-boranes* [net] : B_nH_{n+8}
5. *Conjuncto-boranes* [joined together] : B_nH_m

DIBORANE (B_2H_6)

PREPARATIONS:

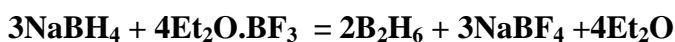
1. Action of iodine on sodium borohydride in diglyme solvent [(MeOCH₂CH₂)₂O]



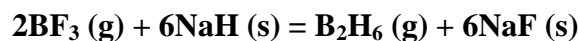
2. Reduction of sodium borohydride with 85% H₃PO₄



3. Addition of BF₃ ether adduct to sodium borohydride (NaBH₄) in diglyme at room temperature. This method is particularly useful when B₂H₆ is required as a reaction intermediate without the need of isolation or purification.

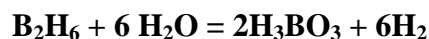


4. Reduction of BF₃ gas by solid NaBH₄ at 180°C gives diborane. To prevent pyrolysis diborane is to be trapped out as soon as it is formed.



Property:

1. Diborane is a highly toxic, diamagnetic, colourless gas. Rapidly decomposed by water (H₃BO₃ + H₂).

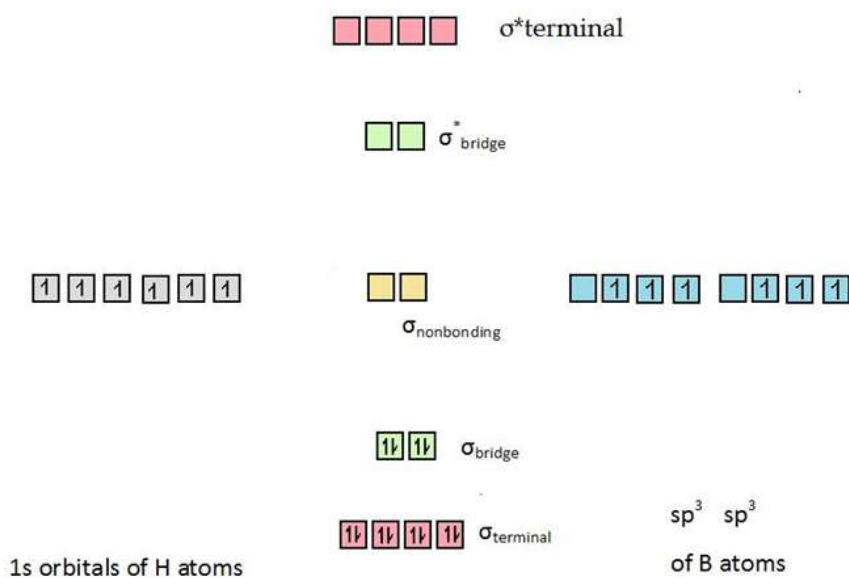
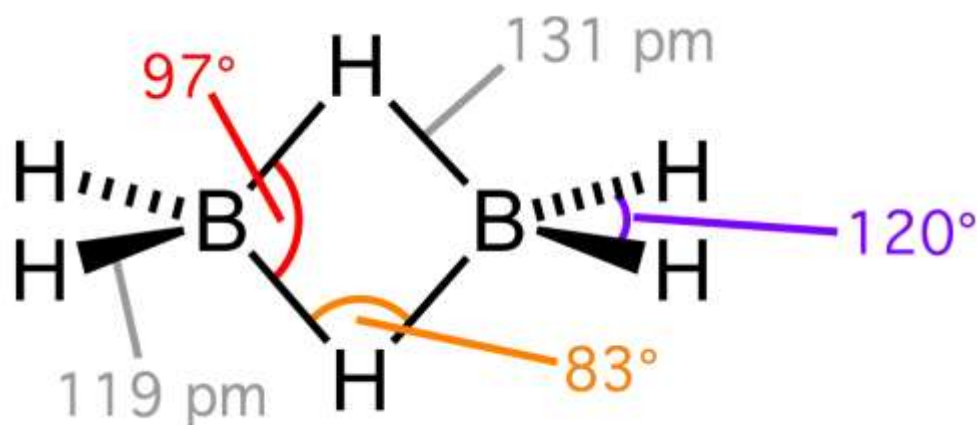


2. Its mixture with air or oxygen are inflammable and explosive.



THE HYDROLYTIC BEHAVIOUR DESCRIBES DIBORANES LEWIS ACIDITY

STRUCTURE OF B₂H₆



Molecular orbital description starts with 4 roughly sp^3 hybrid orbitals on each boron and the 1s atomic orbitals of the hydrogen atoms. 2 orbitals on each boron now overlap with 1s atomic orbitals of two hydrogen atoms to give the terminal boron hydrogen bonds (2c-2e bonds). This corresponds to 4 bonding and 4 antibonding MOs.

We are now left with 2 hybrid atomic orbitals and one valence electron on each boron atom in the BH_2 units. If the 2 BH_2 units are brought close, keeping all the

boron and hydrogen atoms in a plane, the unused hybrid orbitals on the 2 boron atoms will point to each other in an approximately perpendicular plane. 2 hydrogen atoms can now overlap suitably with these orbitals forming 2 sets of B-H-B bridge bonds.

Reactions of B₂H₆

1. B₂H₆ + 6MeOH = 2B(OMe)₃ + 6H₂
2. B₂H₆ + 3Cl₂ = 2BCl₃ + 6HCl
3. B₂H₆ + 2Me₃N = 2H₃B←NMe₃
4. 2B₂H₆ + 2Na = NaBH₄ + NaB₃H₈
5. B₂H₆ + 2LiH = 2LiBH₄

REACTION WITH AMMONIA



At very high temperature: The product is (BN)_x

BORON-NITROGEN COMPOUNDS

Two factors have contributed to the special interest:

1. B-N Unit is isoelectronic with C-C
2. With respect to size and electronegativity C being the mean of B & N

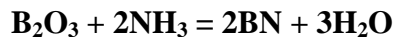
	B	C	N
Valence electrons	3	4	5
Cov radius(pm)	88	77	70
Electronegativity	2.0	2.5	3.0

The repetition of much organic chemistry by replacing pair of C atoms with the B-N grouping has led to many new compounds.

BORON NITRIDE (BN)_x

LABORATORY SCALE PREPARATION:

By fusion of borax with ammonium chloride.

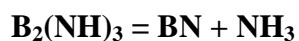
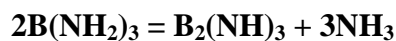


INDUSTRIAL SCALE PREPARATION:

Fusion of urea with boric acid in an atmosphere of ammonia at 500 - 950°C.

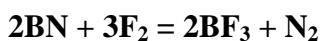
BY THERMAL DECOMPOSITION OF BORON AMIDES:

Boron amide is obtained by reacting boron trichloride with ammonia

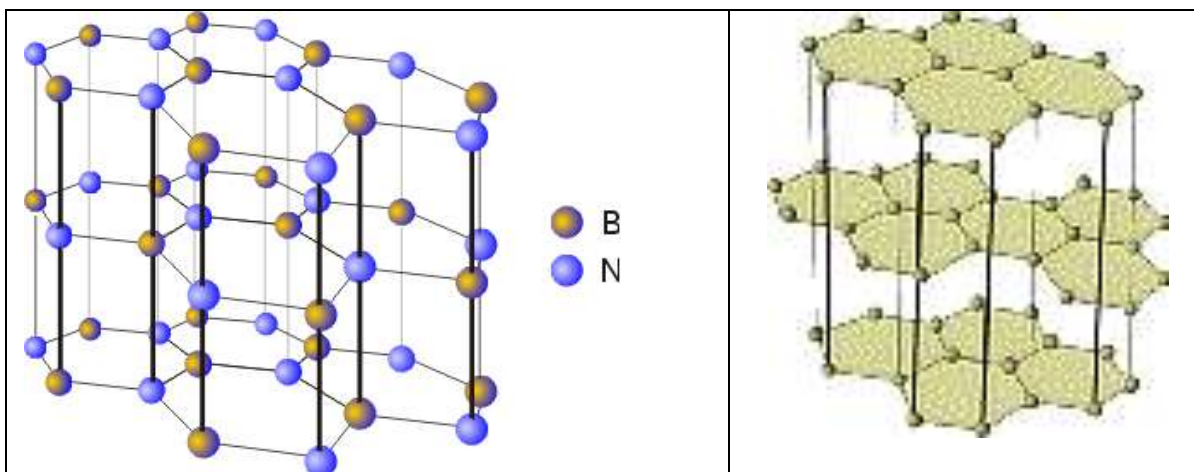


STRUCTURE OF BORON NITRIDE:

1. A simple layer structure.
2. Layers are packed directly on top of each other so that B atom in one layer is located over an nitrogen atom in the next layer at a distance of 333 pm.
3. Within each layer B-N is 145 pm (144 pm in borazine)
4. Boron nitride is colourless and good insulator.
5. Resistant to most reagents (fluorine convert it to BF_3 & N_2)

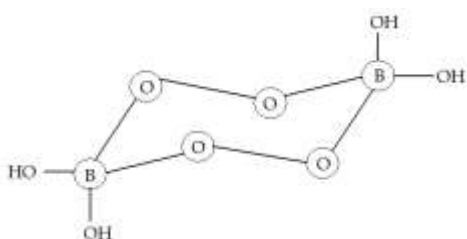


6. Boron nitride melts under pressure at 3000°C



DATA IN pm	INTER-LAYER SPACING	INTRA- LAYER SPACIN G	⁻³ d/ g cm
BN	333	144.6	2.29
Graphit e	335	142	2.255

PEROXOBORATES



$[(\text{OH})_2\text{B}(\text{O}_2)_2\text{B}(\text{OH})_2]^{2-}$, Sodium peroxodiborate, commonly known as ‘perborate’. It is prepared by the action of H_2O_2 or Na_2O_2 on borax solution or electrolysis of borax solution with Pt-gauze anode in presence of a little Na_2CO_3

USE: Used as brightner in detergents as produce hydrogen peroxide in solution. In solution the anion first hydrolyzes to $[\text{B}(\text{OH})_3\text{OOH}]^-$ and then $[\text{B}(\text{OH})_4]^-$, liberating H_2O_2 .

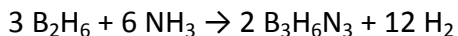


Borazine

Borazine is an inorganic compound composed of the elements boron, nitrogen and hydrogen. In this cyclic compound three hydroborane (BH) units and three amino units (NH) alternate. The compound was synthesised in 1926 by the chemists Alfred Stock and Pohland by a reaction of diborane with ammonia.^[1] The structure is isoelectronic and isostructural with benzene and for this reason borazine is called **inorganic benzene** by a proposal of Nils Wiberg and the compound also goes by the name of **borazol** from the German name for benzene which is benzol.

Synthesis

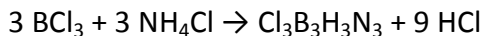
Borazine is synthesized from diborane and ammonia in a 1:2 ratio at 250 - 300 °C with a conversion of 50%.



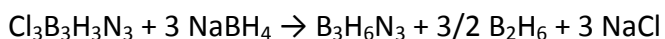
An alternative more efficient route begins with lithium borohydride and ammonium chloride with improved chemical yield:



In a two-step process to borazine, boron trichloride is first converted to trichloroborazine:



The B-Cl bonds are subsequently converted to B-H bonds:



Properties

Borazine is a colourless liquid with an aromatic smell. In water it decomposes to boric acid, ammonia, and hydrogen. Borazine, with a standard enthalpy change of formation ΔH_f of -531 kJ/mol, is thermally very stable.

Structure

Borazine is isostructural with benzene and bond lengths are identical just as in benzene. The distance between boron and nitrogen in the ring is 0.1436 nm, the carbon carbon bond in benzene has a length of 0.1397 nm. The boron nitrogen bond is between that of the boron nitrogen single bond with 0.151 nm and the boron nitrogen double bond which is 0.131 nm. This suggests partial delocalisation of nitrogen lone pair electrons.

Mesomers

The electronegativity of boron (2.04 on the Pauling scale) compared to that of nitrogen (3.04) and also the electron deficiency on the boron atom and the lone pair on nitrogen favor alternative mesomer structures for borazine.

Boron is the Lewis acid and nitrogen is the Lewis base.

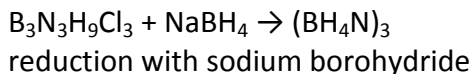
Reactions

Borazine is more reactive than benzene. It reacts with hydrogen chloride in an addition reaction. If borazine were truly aromatic like benzene this reaction would not occur without a Lewis acid catalyst.

Polyborazylene



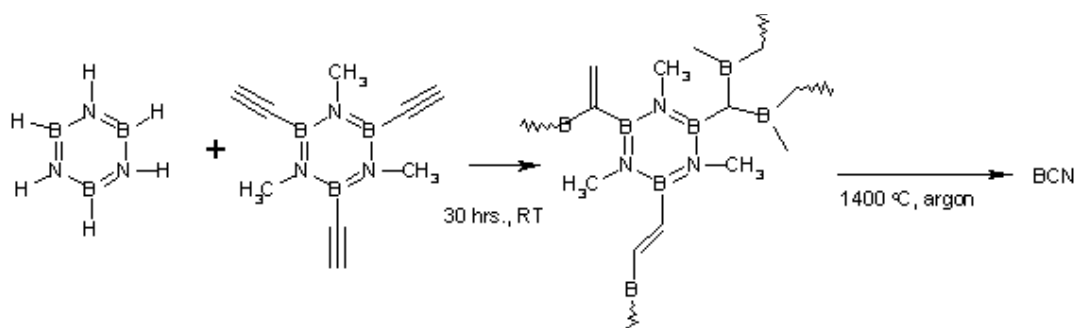
Addition reaction of borazine with hydrogen chloride



The addition reaction with bromine takes place without catalyst. Borazines interact with nucleophilic attack at boron and electrophilic attack at nitrogen. Heating borazine at 70 °C expulses hydrogen with formation of a **borazinyl polymer** or **polyborazylene** in which the monomer units are coupled in a para fashion by new boron - nitrogen bonds.

Applications

Borazine and borazine derivatives are potential precursors to boron nitride ceramics. Boron nitride can be prepared by heating polyborazylene to 1000 °C. Borazines are also starting materials for other potential ceramics such as **boron carbonitrides**:



Borazine can also be used as a precursor to grow boron nitride thin films on surfaces, such as the nanomesh structure which is formed on rhodium.

