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INORGANIC CHAINS, RINGS, CAGES AND CLUSTERS I—

RINGS — The most important ring system of organic chemistry is the benzene ring, either as a seperate entity or as in polynuclear hydrocarbons such as naphthalene, anthracene and phenanthrene. Inorganic chemistry has two analogues of benzene i.e borazines and tricyclic cyclophosphazene compounds.

BORAZINES — Alfred stock was the first chemist who studied compound such as the B boranes, Silanes and other non-metal compounds and he perfected vacuum line techniques for the handling of air and moisture sensitive compounds Stake synthesized borazine by heating the adduct of diborane and ammonia.

$$3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_2][BH_4]$$

Heat

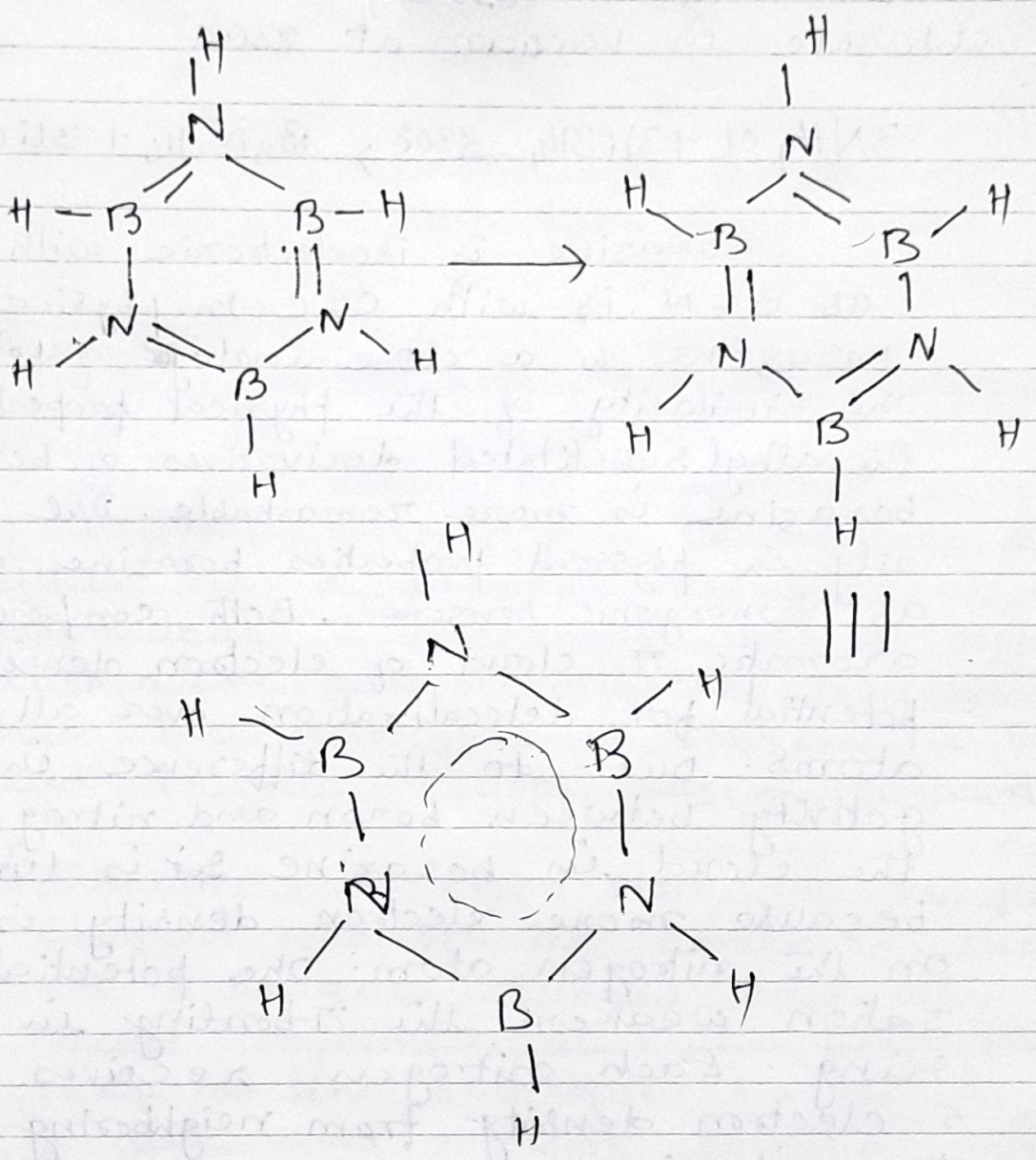
$$2B_3N_3H_6 + 12H_2$$

Borazine also synthsized by heating a mixture lithium borohydride and ammonium chloride in vacuum at 230°C.

$$3NH_4Cl + 3LiBH_4 \xrightarrow{230^\circ C} B_3N_3H_6 + 3LiCl + 9H_2$$

Borazine is isoelectronic with Benzene as B=N is with C=C. In physical properties borazine is a close analogue of benzene. The similarity of the physical properties of the alkyl substituted derivatives of benzene and borazine is more remaskable. Due to similarity in physical properties borazine is known as "inorganic benzene". Both compounds have aromatic π cloud of electron density with potential for delocalization over all the ring atoms. Due to the difference in electronegativity between boron and nitrogen, the cloud in borazine ~~is~~ is lumpy, because more electron density is localized on the nitrogen atom. The potential localization weakens the π-bonding in the ring. Each nitrogen receives more σ-electron density from neighboring boron than it gives away as a π-donor. The net effect is that the charge density of nitrogen increases. In addition nitrogen retains its basicity and boron its acidity. Polar species such as HCl can therefore attack the double bond between nitrogen and boron. Thus in contrast to benzene

borazines readily undergoes addition reaction -



Electronic structure of Borazine -

X-ray crystallography has shown that boron and nitrogen atoms in borazine are arranged alternately in a planar hexagonal ring. Electron diffraction photographs of ~~benz~~ borazine

and benzene are very similar and confirm that benzene borazine has a benzene like configuration. The bonding in borazine has been the single bonded triaminotriborine ring in which double bonds are present due to the participation of the lone pairs on nitrogen in the boron-nitrogen bonds. This results in a formal negative charge on the boron and formal positive charge on the nitrogen atom. The resonance hybrid is based on the similarity which exist between borazine and benzene. In borazine the B-N bond length is 0.144nm which is very close to the value in benzene for C-C 1.42nm.