

## 6.10: Boron Compounds with Nitrogen Donors

The “B-N” unit is isoelectronic (3 + 5 valence electrons) to the “C-C” unit (4 + 4 valence electrons). The two moieties are also isolobal, and as such there are many of the compound types formed by carbon have analogous derivatives in the chemistry of boron-nitrogen.

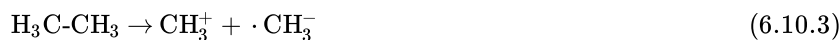
### Lewis acid-base addition compounds

Boron compounds,  $BX_3$ , are strong Lewis acids and as such form stable addition compounds with Lewis bases, in particular those with nitrogen donor ligands.



In principle these Lewis acid-base complexes should be similar to their isolobal hydrocarbon analogs, however, whereas the dipole in ethane is zero (by symmetry) the dipole in  $H_3NBH_3$  is 5.2 D as a consequence of the difference in the Pauling electronegativities (i.e., B = 2.04 and N = 3.04). It is this dipole that generally differentiates the B-N compounds from their C-C analogs.

Homolytic cleavage of the C-C bond in ethane will yield two neutral methyl radicals, (6.7.2). In contrast, heterolytic cleavage will result in the formation of two charged species, (6.7.3). Thus, the products either have a net spin, (6.7.2), or a net charge, (6.7.3). By contrast, cleavage of the B-N bond in  $H_3N-BH_3$  either yields products with both spin and charge, (6.7.5), or neither, (6.7.4). Heterolytic cleavage of the B-N bond yields neutral compounds, (6.7.4), while homolytic cleavage results in the formation of radical ions, (6.7.5).



The difference in bond strength between  $H_3N-BH_3$  and ethane is reflected in the difference in bond lengths (Table 6.10.1).

Table 6.10.1: A comparison of bonding in  $H_3E-E'H_3$ .

Compound	Bond length (Å)	Bond strength (kcal/mol)
$H_3C-CH_3$	1.533	89
$H_3N-BH_3$	1.658	31

### Aminoboranes

The group  $R'_2N-BR_2$  is isoelectronic and isolobal to the olefin sub-unit  $R'_2C=CR_2$ , and there is even appreciable  $\pi$ -bonding character (Figure 6.10.1). A measure of the multiple bond character can be seen from a comparison of the calculated B-N bond in  $H_2NBN_2$  (1.391 Å) as compared to a typical olefin (1.33 Å). It is interesting that a consideration of the possible resonance form (Figure 6.10.1) suggest the dipole in the  $\sigma$ -bond is in the opposite direction of that of the  $\pi$ -bond.

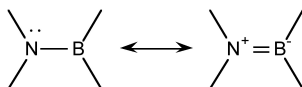


Figure 6.10.1: Resonance forms for  $X_2N-BX'_2$ .

Unlike olefins, borazines oligomerize to form dimers and trimers (Figure 6.10.2) in the absence of significant steric hindrance. Analogous structures are also observed for the other Group 13-15 homologs ( $R_2AlNR'_2$ ,  $R_2GaPR'_2$ , etc.).

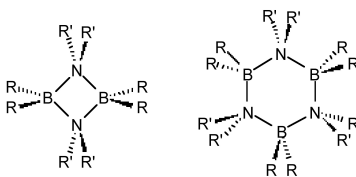
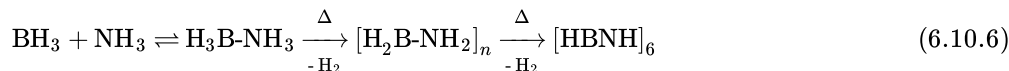


Figure 6.10.2: Typical structures of aminoboranes.

## Borazines

The condensation of boron hydride with ammonia results in the formation of a benzene analog: borazine, (6.7.6). Substituted derivatives are formed by the reaction with primary amines.



Despite the cyclic structure (Figure 6.10.3), borazine is not a true analog of benzene. Despite all the B-N bond distances being equal (1.44 Å) consistent with a delocalized structure, the difference in electronegativity of boron and nitrogen (2.04 and 3.04, respectively) results in a polarization of the bonds (i.e.,  $\text{B}^{\delta+}\text{-N}^{\delta-}$ ) and hence a limit to the delocalization. The molecular orbitals of the  $\pi$ -system in borazine are lumpy in appearance (Figure 6.10.4 a) compared to benzene (Figure 6.10.4 b). This uneven distribution makes borazine prone to addition reactions, making it as a molecule less stable than benzene.

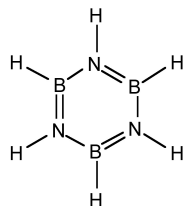


Figure 6.10.3: Structure of borazine, the inorganic analog to benzene.

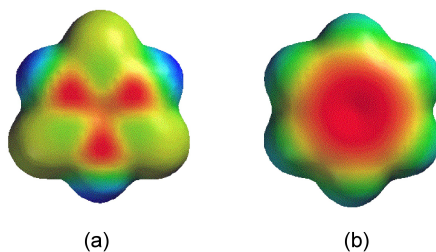


Figure 6.10.4: Probability distributions for the  $\pi$ -bond orbitals in (a) borazine and (b) benzene.

### Iminoboranes: analogs of acetylene

Iminoboranes,  $\text{RB=NR}'$ , are analogs of alkynes, but like aminoboranes are only isolated as monomers with sterically hindered substituents. In the absence of sufficient steric bulk oligomerization occurs, forming substituted benzene analogs.

### Boron nitrides: analogs of elemental carbon

The fusion of borax,  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4]$  with ammonium chloride ( $\text{NH}_4\text{Cl}$ ) results in the formation of hexagonal boron nitride (h-BN). Although h-BN has a planar, layered structure consisting of six-membered rings similar to graphite (Figure 6.10.5), it is a white solid. The difference in color is symptomatic of the more localized bonding in BN than in graphite.

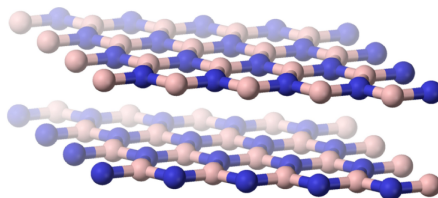


Figure 6.10.5: Structure of h-BN.

As is found for its carbon analog, hexagonal boron nitride (h-BN or  $\alpha$ -BN) is converted at high temperatures (600 – 2000 °C) and pressures (50 – 200 kbar) to a cubic phase (c-BN or  $\beta$ -BN). In a similar manner to diamond, cubic-BN is very hard being actually able to cut diamond, and as a consequence its main use is as an industrial grinding agent. The cubic form has the sphalerite crystal structure (Figure 6.10.6). Finally, a wurtzite form of boron nitride (w-BN) is known that has similar structure as lonsdaleite, rare hexagonal polymorph of carbon. Table 6.10.2 shows a comparison of the properties of the hexagonal and cubic phases of BN with their carbon analogs.

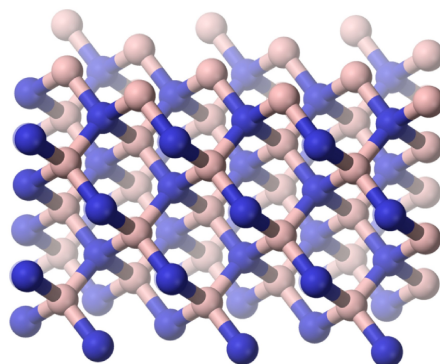


Figure 6.10.6: Structure of c-BN.

Table 6.10.2: Comparison of structural and physical properties of carbon and boron nitride analogs.

Phase	Carbon	Boron nitride
Cubic	Colorless, hard, mp = 3550 °C. C-C = 1.514 Å	Colorless, hard, B-N = 1.56 Å
Hexagonal	Black solid, planar layers, conductor, mp = 3652 – 3697 °C (sublimes), C-C = 1.415 Å	White solid, planar layers, semiconductor (Eg = 5.2 eV), mp = 2973 °C (sublimes), B-N = 1.45 Å

The partly ionic structure of BN layers in h-BN reduces covalency and electrical conductivity, whereas the interlayer interaction increases resulting in higher hardness of h-BN relative to graphite.

### Bibliography

- K. M. Bissett and T. M. Gilbert, *Organometallics*, 2004, **23**, 850.
- P. Paetzold, *Adv. Inorg. Chem.*, 1987, **31**, 123.
- L. R. Thorne, R. D. Suenram, and F. J. Lovas, *J. Chem. Phys.*, 1983, **78**, 167.

6.10: Boron Compounds with Nitrogen Donors is shared under a CC BY 1.0 license and was authored, remixed, and/or curated by LibreTexts.