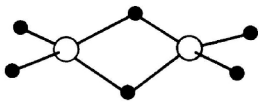
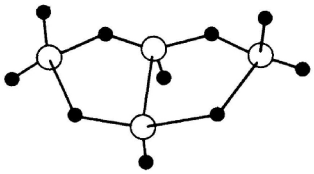
Boranes

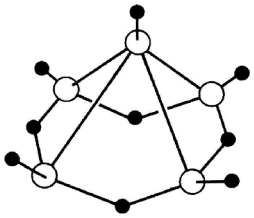
- ✔ Boranes have structures and bonding that frequently cannot be adequately described by Lewis conventions.
- ✔ The simplest borane, BH_3, does not exist as a stable species, although it may be a transient species in the reactions producing higher boranes.
- ✔ The simplest stable borane is B_2H_6.
- ✔ Many higher boranes exist with complex cage-like structures.



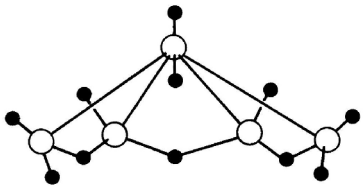
B_2H_6
Diborane (6) ($\mathbf{D}_{2h}$)



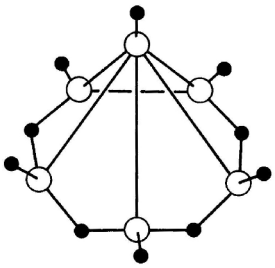
B_4H_{10}
Tetraborane (10) ($\mathbf{C}_{2v}$)



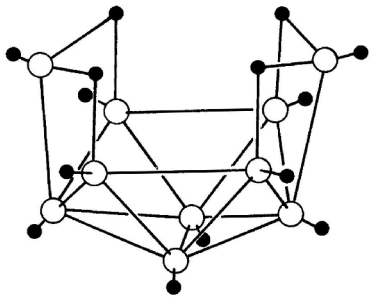
B_5H_9
Pentaborane (9) ($\mathbf{C}_{4v}$)



B_5H_{11}
Pentaborane (11) ($\mathbf{C}_s$)



B_6H_{10}
Hexaborane (10) ($\mathbf{C}_s$)



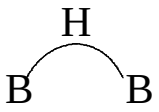
$B_{10}H_{14}$
Decaborane (14) ($\mathbf{C}_{2v}$)

Bonding Types in Boranes

✔ Bonds in boranes consist of types that can and cannot be described by conventional Lewis concepts.

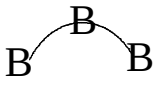
✔ In the "semitopological" description of Lipscomb[1] five distinct bonding types are identified, only two of which conform to Lewis concepts:

B—H terminal 2-center-2-electron BH bond (2c-2e)

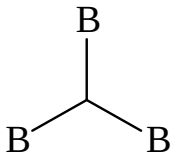


3-center-2-electron H-bridge bond (3c-2e)

B—B 2-center-2-electron BB bond (2c-2e)

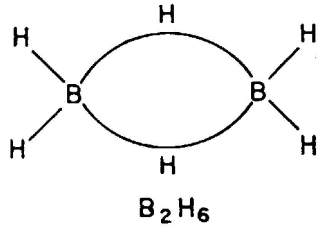


open 3-center-2-electron B-bridge bond (3c-2e)



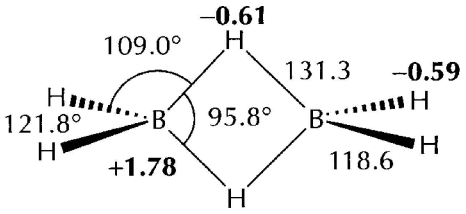
closed 3-center-2-electron B-bond (3c-2e)

✔ Diborane has four 2c-2e B–H bonds and two 3c-2e B–H–B bridge bonds, represented in semitopological notation as follows:

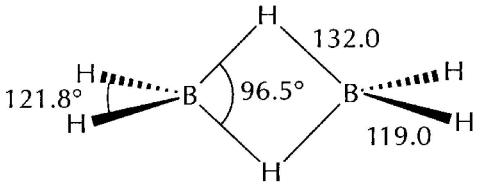


[1]W. N. Lipsom, *Inorg. Chem.* **1964**, *3*, 1683.

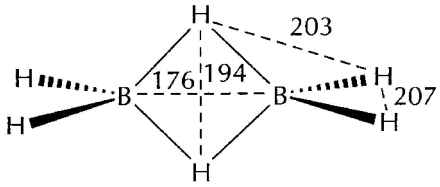
Diborane Structure



Calculated



Observed



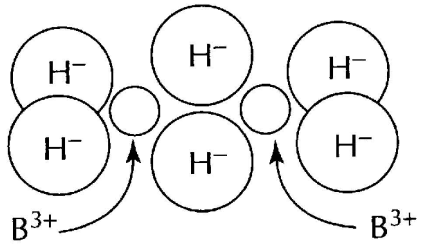
Calculated Distances

- ✔ H···H ligand distances are close to those calculated for BH_4^- (202 pm) and BH_3 (203 pm).
- ✔ Bridging H···H distance is short, suggesting that attraction between negatively charged bridging hydrogens and two positively charged borons causes the two hydrogens' electron densities to be compressed.
- ✔ Compression of bridging hydrogens allows terminal hydrogens to move apart, similar to C_2H_4, giving ∠H–B–H of 121.8°.

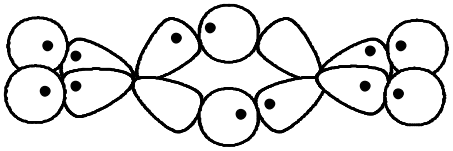
Bonding Models of B_2H_6

✔ With only 12 valence electrons, rather than 16 needed for complete 2c-2e bonding, diborane is an example of an electron deficient compound.

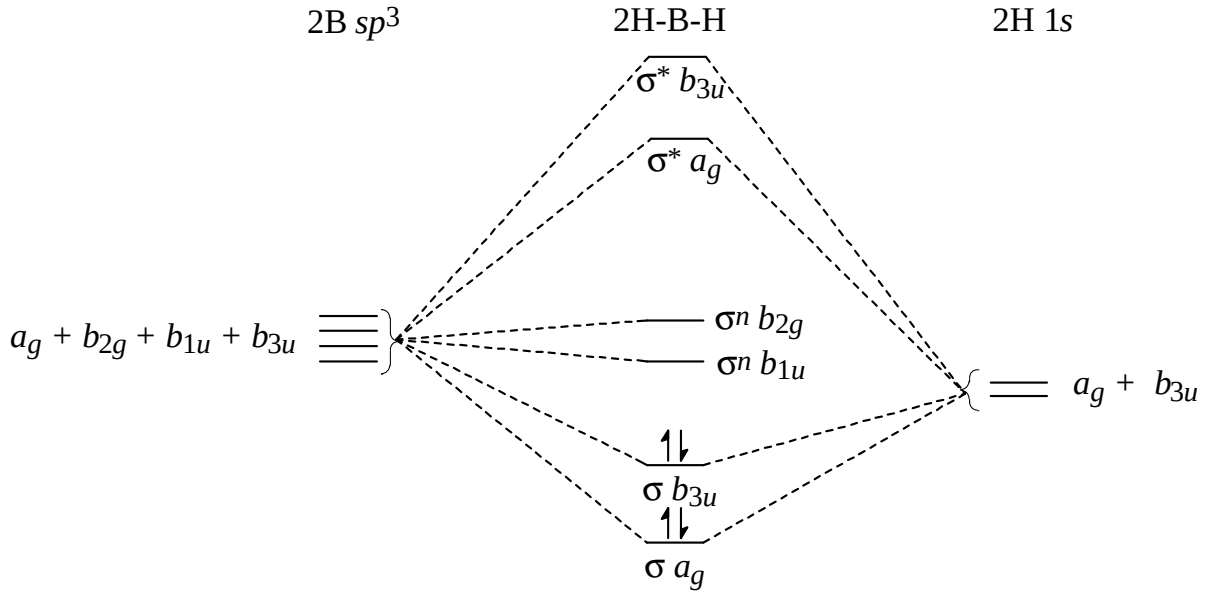
✔ Given the large atomic charges (B, +1.78; H, –0.60±0.01), B_2H_6 is approximately tetrahedrally arranged H^- ions around two B^{3+} cations.



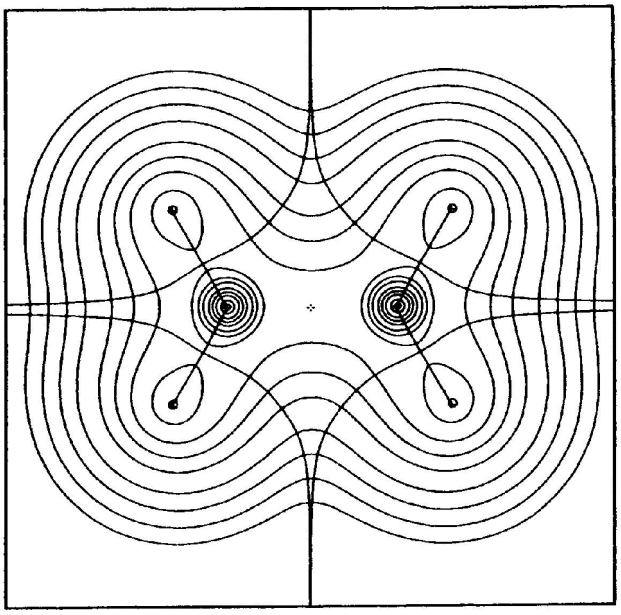
✔ Using sp^3 hydridized B, the bridge bonds are represented as 3c-2e.



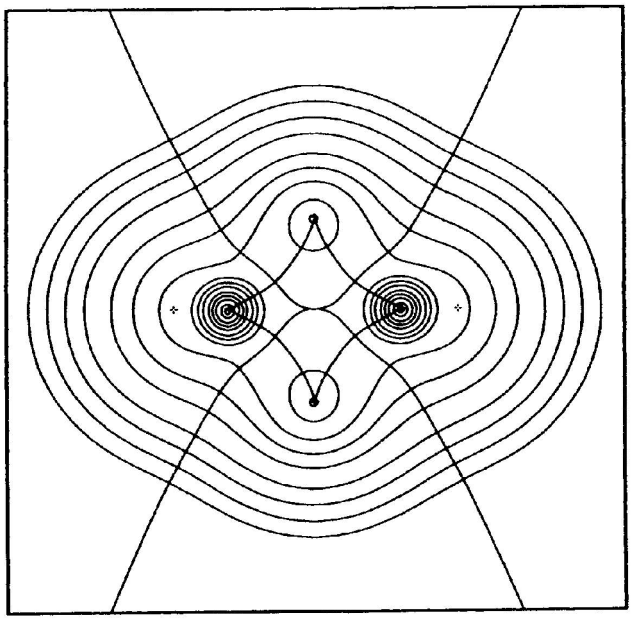
✔ From this, the two bridge bonds can be represented by the following MO scheme:



AIM Model of B_2H_6



Contour map in B_2H_4 plane



Contour map in H–B–H bridge plane

- ✔ Bond paths exist for terminal B–H 2c-2e bonds
- ✔ No bond path exists between boron atoms
- ✔ Bond paths exist between each boron and the two bridging hydrogen atoms, but they do not correspond to two 2c-2e bonds.
- ✔ Electron density across the B–H–B bridge corresponds to one electron pair, consistent with the 3c-2e model.
- ✔ AIM analysis of higher boranes similarly shows bond paths between all adjacent atoms, but all bonds cannot be considered conventional Lewis 2c-2e type.