Polyhedral Boranes and Wade's Rules

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Outline

Polyhedral Boranes

An Important Class of Electron-Deficient Borane Compounds

Hydroborane Clusters

1. Electron-deficient species possess fewer valence electrons than are required for a localized bonding scheme
2. In a cluster atoms form a cage-like structure
3. There are a great number of known neutral and anionic hydroborane clusters
4. These structures are often described as being polyhedral or deltahedral
5. A deltahedron is a polyhedron that possesses only triangular faces, e.g., an octahedron

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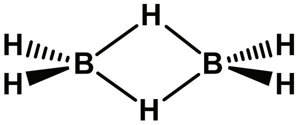
B_2H_6
The Simplest Hydroborane



- This is an electron-deficient compound held together by two 3c-2e bonds.
- Higher boranes are prepared by pyrolysis of B_2H_6 in the vapor phase.

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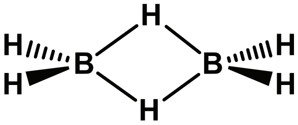

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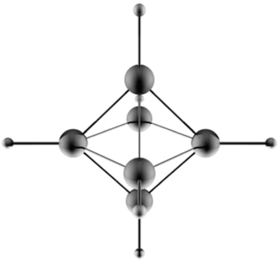
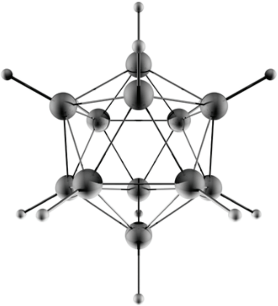
$[B_6H_6]^{2-}$ and $[B_{12}H_{12}]^{2-}$

Selected Examples of Polyhedral Boranes





- What are the point groups of these two anions?

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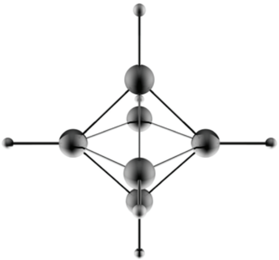

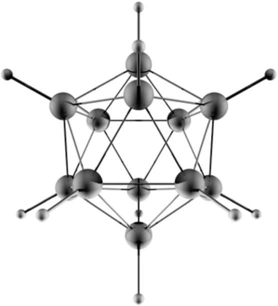

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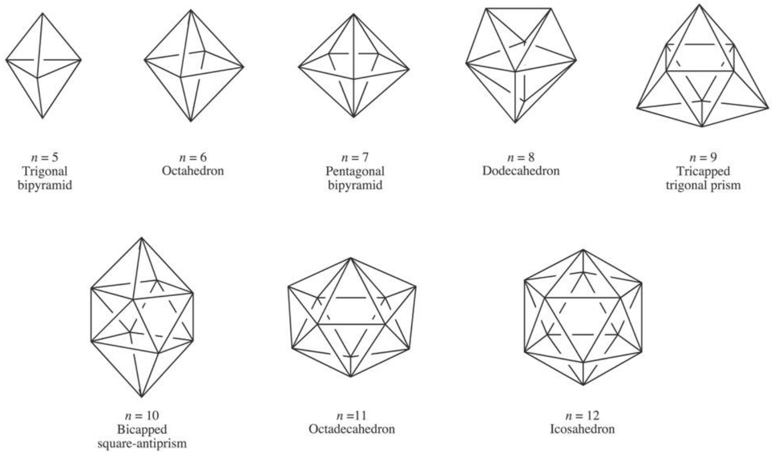
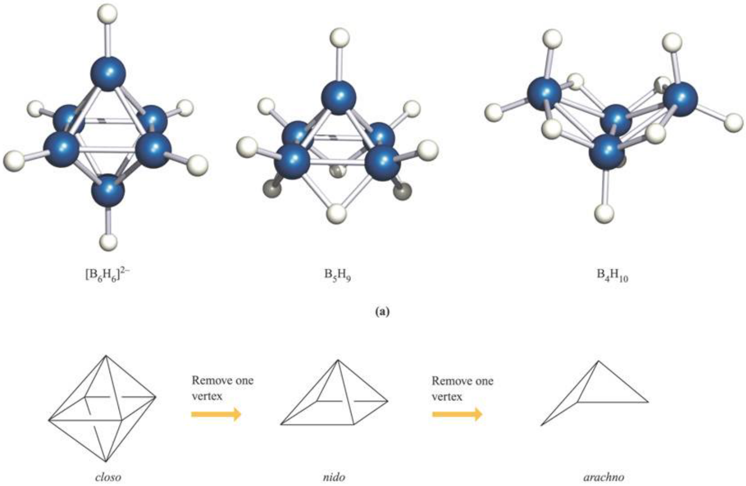
Deltahedral Cages With Five to Twelve Vertices
Can Be Used to Rationalize Borane Cluster Structures



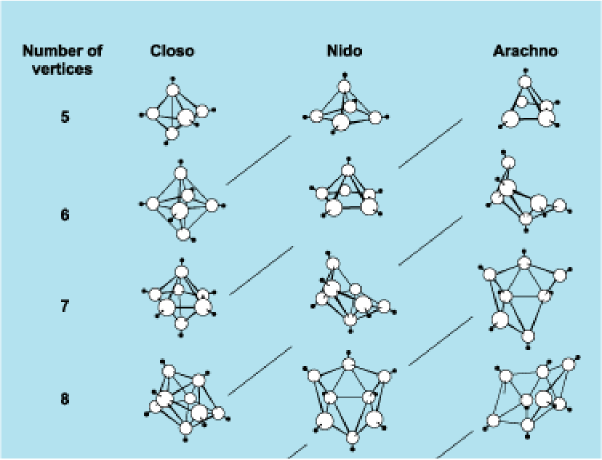
Naming Polyhedral Boranes

Closo, *Nido*, *Arachno*...



Families of Polyhedral Boranes

The *Closo* Structures Are The Parent Structures



Wade's Rules

A Classification Scheme For Polyhedral Borane Clusters

- Classification of structural types can often be done more conveniently on the basis of valence electron counts.
- Most classification schemes are based on a set of rules formulated by Prof. Kenneth Wade, FRS, in 1971.

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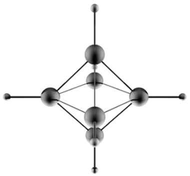
Wade's Rules

A Classification Scheme For Polyhedral Borane Clusters

- In a *closo* polyhedral borane structure:
- The number of pairs of framework bonding electrons is determined by subtracting one B-H bonding pair per boron.
- The n+1 remaining framework electron pairs may be used in boron-boron bonding or in bonds between boron and other hydrogen atoms.

Example: $[B_6H_6]^{2-}$

Understanding Wade's Rules



- Number of valence electrons = 6(3) + 6(1) + 2 = 26 or 13 pairs of electrons.
- Six pairs of electrons are involved in bonding to terminal hydrogens (one per boron).
- Therefore seven (n + 1) pairs of electrons are involved in framework bonding, where n = number of boron atoms in cluster.

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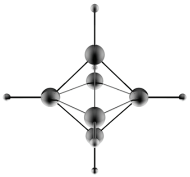

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Tabular Summary of Wade's Rules

Classification and Electron Count of Boron Hydrides

Type	Formula	Skeletal Electron Pairs
Closo	$[B_nH_n]^{2-}$	$n + 1$
Nido	B_nH_{n+4}	$n + 2$
Arachno	B_nH_{n+6}	$n + 3$
Hypho	B_nH_{n+8}	$n + 4$
Klado	B_nH_{n+10}	$n + 5$

- *Closo* comes from the Greek for cage, *Nido* the Latin for nest, *Arachno* the Greek for spider, *Hypho* the Greek for net, and *Klado* the Greek for branch.

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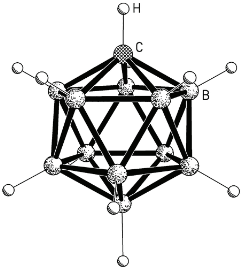
Examples

Understanding Wade's Rules

- Classify the following polyhedral boranes according to their valence electron count:
- B_5H_9
- B_4H_{10}
- $[B_2H_7]^-$

Heteroboranes

Inclusion of Other Atoms in the Hydroborane Cage



- Many derivatives of boranes containing other main group atoms are also known.
- These heteroboranes may be classified by formally converting the heteroatom to a BH_x group having the same number of valence electrons.

Heteroboranes

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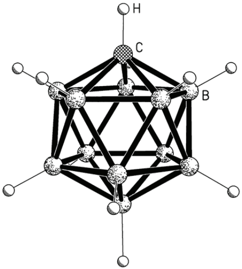

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Considering Other Atoms in the Context of Wade's Rules

Classification of Heteroborane Clusters

Heteroatom	Replace With
C, Si, Ge, Sn	BH
N, P, As	BH_2
S, Se	BH_3

- These represent the most common main group heteroatoms incorporated into hydroborane clusters.

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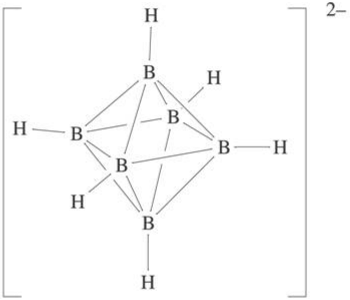
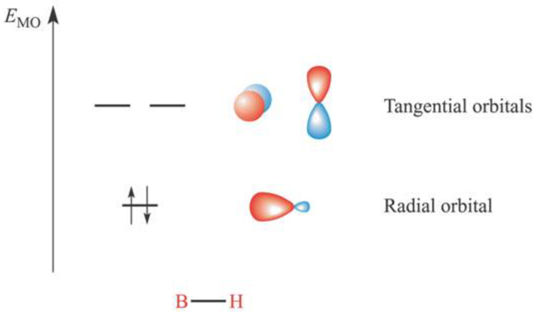
Understanding Wade's Rules

- Classify the following polyhedral heteroboranes according to their valence electron count:
- $C_2B_7H_{13}$
- SB_9H_{11}
- $CPB_{10}H_{11}$

Bonding in $[B_6H_6]^{2-}$

Frontier Orbitals for Each BH Unit





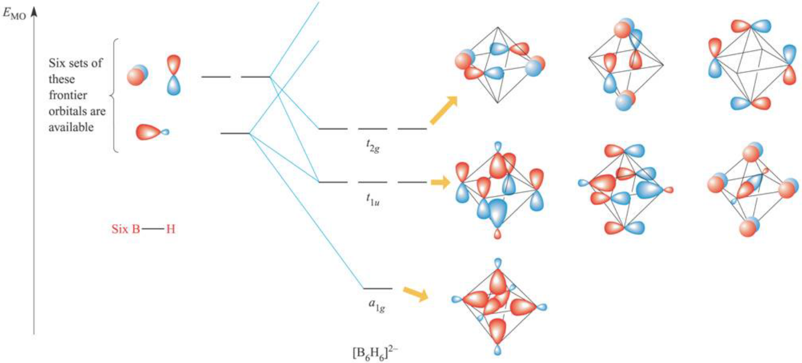
Bonding in $[B_6H_6]^{2-}$

Frontier Orbitals for Each BH Unit

- Choose z-axis to point to center of polyhedron
- Consider *s* and p_z to form two sp hybrid orbitals: one bonds to H 1*s* and the other points into center of cluster.
- The p_x and p_y orbitals on boron are unhybridized and are called tangential orbitals.
- The six hybrids not used in bonding to hydrogen and the unhybridized 2*p* orbitals of the borons remain to participate in bonding with the B_6 core.

Bonding in $[B_6H_6]^{2-}$

Radial and Tangential Bonding Molecular Orbitals



Bonding in $[B_6H_6]^{2-}$

Radial and Tangential Bonding Molecular Orbitals

- When the six B-H units come together, a total of 18 (6 x 3) atomic orbtials combine to from 18 molecular orbitals.
- There are seven orbitals with net bonding character delocalized over the skeleton.
- All of the bonding orbitals are filled (n + 1 framework bonding pairs), so seven pairs of electrons are used to hold the cluster together. The bonding cannot be interpreted using a localized electron model.
- There is a considerable energy gap between the bonding MOs and the remaining largely antibonding MOs, contributing to the stability of the cluster.

Bonding in $[B_6H_6]^{2-}$

Full Molecular Orbital Diagram