Polyhedral Boranes and Wade’s Rules

Dr. Heather A. Spinney

Massachusetts Institute of Technology

February 17, 2009
Outline

1. Polyhedral Boranes
2. Wade’s Rules
3. Heteroboranes
4. Molecular Orbital Picture
Electron-deficient species possess fewer valence electrons than are required for a localized bonding scheme.

In a cluster atoms form a cage-like structure.

There are a great number of known neutral and anionic hydroborane clusters.

These structures are often described as being polyhedral or deltahedral.

A deltahedron is a polyhedron that possesses only triangular faces, e.g., an octahedron.
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.
Electron-deficient species possess fewer valence electrons than are required for a localized bonding scheme.

In a cluster atoms form a cage-like structure.

There are a great number of known neutral and anionic hydroborane clusters.

These structures are often described as being polyhedral or deltahedral.

A deltahedron is a polyhedron that possesses only triangular faces, e.g., an octahedron.
### 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 deltalhedral.
5. A deltahedron is a polyhedron that possesses only triangular faces, e.g., an octahedron.
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.
\(B_2H_6\)

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.
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.
What are the point groups of these two anions?
What are the point groups of these two anions?
Deltahedral Cages With Five to Twelve Vertices
Can Be Used to Rationalize Borane Cluster Structures

- $n = 5$
  - Trigonal bipyramid
- $n = 6$
  - Octahedron
- $n = 7$
  - Pentagonal bipyramid
- $n = 8$
  - Dodecahedron
- $n = 9$
  - Tricapped trigonal prism
- $n = 10$
  - Bicapped square-antiprism
- $n = 11$
  - Octadecahedron
- $n = 12$
  - Icosahedron
Naming Polyhedral Boranes

*Closo, Nido, Arachno...*

(a) 

\[
[B_6H_9]^{2-}
\]

\[
B_2H_9
\]

\[
B_4H_{10}
\]
Families of Polyhedral Boranes

The Closo Structures Are The Parent Structures

<table>
<thead>
<tr>
<th>Number of vertices</th>
<th>Closo</th>
<th>Nido</th>
<th>Arachno</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td><img src="image1" alt="Closo 5-vertex" /></td>
<td><img src="image2" alt="Nido 5-vertex" /></td>
<td><img src="image3" alt="Arachno 5-vertex" /></td>
</tr>
<tr>
<td>6</td>
<td><img src="image4" alt="Closo 6-vertex" /></td>
<td><img src="image5" alt="Nido 6-vertex" /></td>
<td><img src="image6" alt="Arachno 6-vertex" /></td>
</tr>
<tr>
<td>7</td>
<td><img src="image7" alt="Closo 7-vertex" /></td>
<td><img src="image8" alt="Nido 7-vertex" /></td>
<td><img src="image9" alt="Arachno 7-vertex" /></td>
</tr>
<tr>
<td>8</td>
<td><img src="image10" alt="Closo 8-vertex" /></td>
<td><img src="image11" alt="Nido 8-vertex" /></td>
<td><img src="image12" alt="Arachno 8-vertex" /></td>
</tr>
</tbody>
</table>
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.
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.
In a \textit{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.
Example: $[\text{B}_6\text{H}_6]^{2-}$

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 $n = \text{number of boron atoms in cluster}$. 
### Tabular Summary of Wade’s Rules
**Classification and Electron Count of Boron Hydrides**

<table>
<thead>
<tr>
<th>Type</th>
<th>Formula</th>
<th>Skeletal Electron Pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closo</td>
<td>$[\text{B}_n\text{H}_n]^{2-}$</td>
<td>$n + 1$</td>
</tr>
<tr>
<td>Nido</td>
<td>$\text{B}<em>n\text{H}</em>{n+4}$</td>
<td>$n + 2$</td>
</tr>
<tr>
<td>Arachno</td>
<td>$\text{B}<em>n\text{H}</em>{n+6}$</td>
<td>$n + 3$</td>
</tr>
<tr>
<td>Hypho</td>
<td>$\text{B}<em>n\text{H}</em>{n+8}$</td>
<td>$n + 4$</td>
</tr>
<tr>
<td>Klado</td>
<td>$\text{B}<em>n\text{H}</em>{n+10}$</td>
<td>$n + 5$</td>
</tr>
</tbody>
</table>

*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.
### Tabular Summary of Wade’s Rules
Classification and Electron Count of Boron Hydrides

<table>
<thead>
<tr>
<th>Type</th>
<th>Formula</th>
<th>Skeletal Electron Pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closo</td>
<td>([B_nH_n]^{2-})</td>
<td>(n + 1)</td>
</tr>
<tr>
<td>Nido</td>
<td>(B_nH_{n+4})</td>
<td>(n + 2)</td>
</tr>
<tr>
<td>Arachno</td>
<td>(B_nH_{n+6})</td>
<td>(n + 3)</td>
</tr>
<tr>
<td>Hypho</td>
<td>(B_nH_{n+8})</td>
<td>(n + 4)</td>
</tr>
<tr>
<td>Klado</td>
<td>(B_nH_{n+10})</td>
<td>(n + 5)</td>
</tr>
</tbody>
</table>

- **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.
Classify the following polyhedral boranes according to their valence electron count:

- $B_5H_9$
- $B_4H_{10}$
- $[B_2H_7]^{-}$
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.
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.
### Considering Other Atoms in the Context of Wade’s Rules

#### Classification of Heteroborane Clusters

<table>
<thead>
<tr>
<th>Heteroatom</th>
<th>Replace With</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, Si, Ge, Sn</td>
<td>BH</td>
</tr>
<tr>
<td>N, P, As</td>
<td>BH$_2$</td>
</tr>
<tr>
<td>S, Se</td>
<td>BH$_3$</td>
</tr>
</tbody>
</table>

These represent the most common main group heteroatoms incorporated into hydroborane clusters.
Considering Other Atoms in the Context of Wade’s Rules

Classification of Heteroborane Clusters

<table>
<thead>
<tr>
<th>Heteroatom</th>
<th>Replace With</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, Si, Ge, Sn</td>
<td>BH</td>
</tr>
<tr>
<td>N, P, As</td>
<td>BH₂</td>
</tr>
<tr>
<td>S, Se</td>
<td>BH₃</td>
</tr>
</tbody>
</table>

These represent the most common main group heteroatoms incorporated into hydroborane clusters.
Examples
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 1s 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 2p 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

Six sets of these frontier orbitals are available.

- \(t_{2g}\)
- \(t_{1u}\)
- \(a_{1g}\)

\([B_6H_6]^{2-}\)
Bonding in $[B_6H_6]^{2-}$
Radial and Tangential Bonding Molecular Orbitals

- When the six B-H units come together, a total of 18 ($6 \times 3$) atomic orbitals combine to form 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

Energy

HOMO

LUMO

$t_{1u}$

$e_g$

$t_{2g}$

$t_{2u}$

$a_{1g}$

$5.03$ Lecture $6$ Polyhedral Boranes and Wade’s Rules