An Introduction to Boranes

- For undergraduate students, boranes means only diborane which is not true.
- Boranes means electron deficient molecules but probably that is not true.
- Boranes are a class of compounds comprising of several hundreds of compounds ranging from simple to polyhedral to macro polyhedral types having intriguing structures.
Boron is an element with atomic no. 5 having two isotopes $^5\text{B}^{10}$ (20%) and $^5\text{B}^{11}$ (80%).

It occupies group XIII and is a p-block element.

- Boranes are binary compounds of boron and hydrogen and are the fourth most extensive group of hydrides after the Carbon, Phosphorous and Silicon hydrides.
- $\text{BH}_3$ is the simplest of all the boranes but non-existent.
- $\text{B}_2\text{H}_6$ is the dimer of $\text{BH}_3$ and is the most primitive among the existing boranes.
- Boranes are not found in the nature. These are always synthesised in the laboratory.
- Very first synthesis was carried out in 19th century by protolysis of metal borides.
  
  $2\text{Mg}_3\text{B}_2 + 12\text{HCl} \rightarrow 6\text{MgCl}_2 + \text{mixture of boranes}$

- But neither correctly analysed nor identified.
The first systematic study of boranes was performed by Alfred Stock during the year 1912-1936.

He used Schlenk line technique for the synthesis of boranes in a systematic way.

He studied nature, stoichiometry and reactivity of boranes in a systematic way.

\[3 \text{NaBH}_4 + 4 \text{BF}_3 \rightarrow 3 \text{NaBF}_4 + \text{mixture of boranes}\]

\[\text{BCl}_3 + 3 \text{H}_2 \rightarrow \text{mixture of boranes} + 3 \text{HCl}\]

\[\text{BH}_4^- + \text{BX}_3 \rightarrow \text{mixture of boranes} + \text{HBX}_3^-\]

\((X = \text{Cl, Br})\)

Structure and bonding of boranes were tried to be understood in terms of octet theory of Kossel, Langmuir and Lewis.

How to have the 7th bond in diborane

Hence, di borane was not fitted in the octet theory and was labelled as an electron deficient molecule.
But there was neither theoretical basis nor any experimental confirmation for this structure.

In 1940 H.C. Longuet Higgins proposed the theoretical consideration for Banana Bond i.e. 2 electron-3 center bond (2e-3c bond).

In the octet theory of bonding a chemical bond means 2 electron-2 centre bond (2e-2c bond).

W. Dielthy postulated bridged structure for diborane in 1921.
Linear and triangular ways of overlap for a triatomic system -

- The bridging B-H-B bonds in diborane having 2 electrons only should overlap in a triangular fashion rather than a linear one, as it is clear from the following illustration:

![Diagram showing linear and triangular overlap]

The structure of B₂H₆ was elucidated in 1957 by K. Hedberg and V. Schomaker by X-ray crystallography and was found to be postulated as early as 1921 by W. Dilthey.

K. Hedberg

V. Schomaker

Bridged structure of diborane
Thus, the concept of 2e-3c bond was added in the classical 2e-2c concept of bond for the proper understanding of structure and bonding of boranes.

In higher boranes like $\text{B}_6\text{H}_6^2^-$, $\text{B}_5\text{H}_5$, $\text{B}_6\text{H}_{10}$ there are more than 2 boron atoms. Hence, we may have 2e-3c along with 2e-2c types of bonds among boron atoms also on the similar line of boron and hydrogen atoms.

The higher boranes (where no. of boron atoms are four or more than four) adopt deltahedral structure i.e. a polyhedral structure where the faces are triangular.
Complex and cluster are antithesis to each other.
Let us try to understand the pattern of bonding in a higher borane viz. $\text{B}_6\text{H}_6^{2-}$

- The total number of orbitals over here is: $4 \times 6 + 1 \times 6 = 30$ ao’s, Hence 30 mo’s should be formed.

- Out of this $2 \times 6 = 12$ orbitals are used for peripheral B-H bonds. Remaining 18 orbitals are used for the cluster bonding as shown.

- Out of these 18, $n+1$ i.e. $6+1 = 7$ are bonding molecular orbitals while, $18 - 7 = 11$ anti bonding molecular orbitals.

![Diagram of B$_6$H$_6^{2-}$ anion]
How many bmos and abmos will be there in $B_7H_7^{2-}$ and $B_{12}H_{12}^{2-}$?

In $B_7H_7^{2-}$:
- Total no. of orbitals = $4 \times 7 + 1 \times 7 = 35$ ao’s
- Out of this $2 \times 7 = 14$ orbitals for the peripheral bonding i.e. for B-H bonds and remaining 21 orbitals for cluster core bonding.
- Out of this 21, $n+1$ i.e. $7+1=8$ orbitals as bmo and remaining 13 as abmo.
- Total no. of electrons; $3 \times 7 + 7 \times 1 + 2 = 30$; $2 \times 7 = 14$ for B-H bonds remaining $30-14=16$ (8 pairs)

Similarly in $B_{12}H_{12}^{2-}$:
- $4 \times 12 + 1 \times 12 = 60$ orbitals.
- Out of this $2 \times 12 = 24$ for B-H bonds while 36 for cluster core bonding.
- Out of this 12+1=13 as bmos while 23 abmos.
- Total no. of electrons=$3 \times 12+12 \times 1+2=50$; $12 \times 2=24$ for B-H bonds and remaining $26$ (13 pairs)

Thus one thing is clear that due to adoption of triangular way of overlap less no. of bmos are to be filled in boranes. Hence, they are able to cope-up their so called electron deficiency.

**Polyhedral Skeleton Electron Pair Theory (PSEPT)**

K. Wade along with his co-workers developed a generalization known as Polyhedral skeleton electron pair theory (PSEPT) to rationalize internal structural rearrangement of a closed deltahedral borane cluster (closo) into nido, arachno and hypho clusters in terms of electron pairs used for their cluster core bonding.

**Cluster core:** The deltahedral borane structure without B-H bonds.

The general formulae of closo, nido, arachno and hypho boranes are as follows:

$$B_n^3H_{3n+2}^-, B_n^3H_{3n+4}^-, B_n^3H_{3n+6}^-, B_n^3H_{3n+8}^-$$

(Where, $n=$ no. of Boron atoms)

The important point to be remembered over here is that the closo boranes are never found in their neutral form but always in their di-anion form i.e. $B_n^3H_{3n+2}^-$. 

![Keneth Wade](image.png)

*The [B₆H₆]²⁻ anion*
- The PSEPT states that when a p-block element forms a deltahedral cluster using its hybrid orbitals by the mixing of its s and p orbitals then (n+1) electron pairs are required for its cluster core bondings in its closo, nido, arachno and hypho forms with no, one, two, and three vertices missing respectively.

<table>
<thead>
<tr>
<th>Cluster core</th>
<th>Electron pairs</th>
</tr>
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<tbody>
<tr>
<td>7x2 + 2 = 16/2</td>
<td>8</td>
</tr>
<tr>
<td>6x2 + 4x1 = 16/2</td>
<td>8</td>
</tr>
<tr>
<td>5x2 + 6x1 = 16/2</td>
<td>8</td>
</tr>
<tr>
<td>4x2 + 8x1 = 16/2</td>
<td>8</td>
</tr>
</tbody>
</table>

- Similarly, 

<table>
<thead>
<tr>
<th>Closo</th>
<th>Nido</th>
<th>Arachno</th>
<th>Hypho</th>
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<tr>
<td>( \text{B}<em>7 \text{H}</em>{12} )</td>
<td>( \text{B}<em>6 \text{H}</em>{10} )</td>
<td>( \text{B}<em>5 \text{H}</em>{11} )</td>
<td>( \text{B}<em>4 \text{H}</em>{12} )</td>
</tr>
</tbody>
</table>

- All have 7 pairs it means \( \text{B}_7 \text{H}_{12} \) i.e. closo having all the vertices (6) intact hence, n+1 pairs i.e. 6+1=7 pairs, \( \text{B}_6 \text{H}_{10} \) is nido (1 vertex missing), \( \text{B}_5 \text{H}_{11} \) is arachno (2 vertices missing) and \( \text{B}_4 \text{H}_{12} \) is hypho (3 vertices missing).

- The above situation is analogous to VSEPR prediction for \( \text{CH}_4 \), \( \text{NH}_3 \) and \( \text{H}_2\text{O} \).
During 1950s William N. Lipscomb developed a useful bonding model (styx) for boranes.

This model was based on the results of X-ray structural analysis for a variety of boranes and on theoretical considerations developed by H.C. Longuet-Higgins.

Lipscomb received the Nobel prize in 1976 for his great contributions towards structure and bonding in boranes.

Salient features of styx model: (i) There are a total of following 5 types of bonds in the borane chemistry: B-H(2e-2c), BHB(2e-3c), B-B(2e-2c), BBB(2e-3c) open type and closed types.

Here are the following impossible and possible combinations of above bonds:

- A line formula known as semitopological structure for a particular borane can be drawn by having a judicious combination of appropriate bond types from the above list. A particular line formula can be represented by a set of styx no. where,

  \[ s = \text{total no. of BHB three centred bond} \]
  \[ t = \text{total no. of BBB three centred bond} \]
  \[ y = \text{total no. of BB two centered bond} \]
  \[ x = \text{total no. of BH}_2 \text{ units} \]
Styx no. for a particular borane can be derived by solving following three simultaneous equations set by Lipscomb:

- Hydrogen balance equation: \( s + x = q \) -----------(i)
- Orbital balance equation: \( s + t = p \) -----------(ii)
- Electron balance equation: \( s + t + y + x = p + q \)------(iii)

Put \( s + x = q \) from (i) into (iii) then \( t + y = p - q/2 \) -----------(iii) rearranged

Let’s work out styx no. for \( \text{B}_2\text{H}_9 \)

\( \text{B}_2\text{H}_9 \) rearranged in the form of \( \text{B}p\text{H}p+q : \text{B}_2\text{H}_9 4 \)

Hence, \( s + x = 4 \)--------(i)
\( s + t = 5 \)--------(ii)
\( t + y = 3 \)--------(iii)

For, \( s = 0, t=5, y=-2, x=4 \) Discarded
\( s = 1, t=4, y=-1, x=3 \) Discarded
\( s = 2, t=3, y=0, x=2 \)
\( s = 3, t=2, y=1, x=1 \)
\( s = 4, t=1, y=2, x=0 \)
\( s = 5, t=0, y=3, x=-1 \) Discarded

Finally, We have three valid styx sets: 2302, 3211, 4120
Nomenclature of Boranes; Neutral and anionic forms:

- **Neutral forms:**
  The no. of boron atoms is indicated by a Greek prefix attached to the root word “borane” and the no. of hydrogen atoms is indicated by an Arabic numeral added to the word in parenthesis.

  **For e.g.** \( \text{B}_2\text{H}_6 \) Diborane(6), \( \text{B}_5\text{H}_9 \) Pentaborane(9), \( \text{B}_6\text{H}_{10} \) Hexaborane(10), \( \text{B}_8\text{H}_{12} \) Octaborane(12), \( \text{B}_{10}\text{H}_{14} \) Decaborane(14), \( \text{B}_{14}\text{H}_{18} \) Tetradecaborane(18)

- **Anionic forms:** The anionic boron hydrides are named as hydrido borates and the charge is indicated in the parenthesis.

  **For e.g.** \( \text{B}_3\text{H}_8^- \) Octahydridoborate(1-), \( \text{B}_9\text{H}_{6}^{2-} \) Hexahydridohexaborate(2-), \( \text{B}_{12}\text{H}_{12}^{2-} \) Dodecahydridododecaborate(2-)
Types of Boranes

- **Lower boranes**: No. of boron atoms 1-3, e.g. $\text{BH}_3$, $\text{B}_2\text{H}_6$.
- **Higher boranes**: No. of boron atoms 4-12, e.g. $\text{B}_4\text{H}_{10}$, $\text{B}_5\text{H}_{11}$, $\text{B}_6\text{H}_{10}$, $\text{B}_{12}\text{H}_{12}^2$ etc. These adopt polyhedral particularly deltahedral structure.
- **Gigantic boranes**: No. of boron atoms more than 12, e.g. $\text{B}_{13}\text{H}_{19}$, $\text{B}_{14}\text{H}_{18}$, $\text{B}_{15}\text{H}_{23}$, $\text{B}_{18}\text{H}_{22}$, $\text{B}_{20}\text{H}_{26}$. These adopt macro polyhedral structure.

**Physical states**: A very wide window

- The diborane and tetraborane are colour less gases.
- The penta to nona boranes are colourless liquids.
- The larger ones starting with deca boranes are either colourless or yellow solids.
- The lower boranes are unstable to heat(pyrophoric) and water(undergoes hydrolysis). The resulting solution in water is acidic.
- In sharp contrast to the neutral hydrides the $\text{B}_n\text{H}_n^{2-}$ dianions(closo boranes) particularly $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{12}\text{H}_{12}^{2-}$ are far more stable, thermally and hydrolytically. Their salts can be heated to several hundred degree celsius without decomposition. At the same time they are highly soluble in water and form stable aqueous solutions.

<table>
<thead>
<tr>
<th>Boranes</th>
<th>M.P. / B.P.</th>
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<tbody>
<tr>
<td>$\text{B}_2\text{H}_6$</td>
<td>$-164.85 \degree\text{C} / -92.49 \degree\text{C}$</td>
</tr>
<tr>
<td>$\text{B}_5\text{H}_9$</td>
<td>$-46.74 \degree\text{C} / 60.10 \degree\text{C}$</td>
</tr>
<tr>
<td>$\text{B}<em>{10}\text{H}</em>{10}^{2-}$</td>
<td>$-62.3 \degree\text{C} / 108 \degree\text{C}$</td>
</tr>
<tr>
<td>$\text{B}<em>{10}\text{H}</em>{14}$</td>
<td>$99.7 \degree\text{C} / 213 \degree\text{C}$</td>
</tr>
<tr>
<td>$\text{B}<em>{12}\text{H}</em>{16}$</td>
<td>$64.66 \degree\text{C}$</td>
</tr>
</tbody>
</table>
Importance of Boranes:

- Study of Boranes enriched the Chemistry in terms of theory and experiment both. The concept of 2e-3c(banana) bond was mooted out and got established in the field of chemistry.

- The same is very useful in understanding the bonding and structures of not only boranes but also of those molecules which were considered to be electron deficient in classical sense.

- At the same time the discovery of Schlenk line technique by Alfred Stock is very useful for the synthesis of not only boranes but to all those molecules which are air and water sensitive as well as low melting.

- A very important reagent for reducing a large no. of oxygen containing groups like aldehyde, ketone, ester, lactone, carboxylic acid as well as addition reactions on unsaturated hydrocarbons (alkenes and alkynes, hydroboration). H. C. Brown was pioneer in this field and got Nobel prize in 1979.

M.F Hawthorne synthesized a no. of metalloboranes and metallocarboranes and tested them as a potential candidate towards development of drug delivery system.
**Borospherene** (the boron analogue of fullerene) and their metal complexes have got a no. of applications. Recently their lanthanide complexes have been synthesized and subjected for their material applications.

Due to their pyrophoric nature boranes particularly the lower ones were used as rocket fuels. Nowadays, the ammonia adducts of boranes and their corresponding modified forms are being used in the development of fuel cells.
THANK YOU