

# CHAPTER 10

## Metal Clusters:

### ❖ Structure and Bonding in Higher Boranes

Boron hydrides or simply boranes are a class of compounds that have the generic formula  $B_xH_y$ . Though the boron does not react with hydrogen directly to form any of the boron hydrides, yet many of these compounds can easily be synthesized under special reaction conditions. However, because of the high affinity of boron for oxygen, these compounds readily oxidize on contact with air (lighter boranes even explode); and therefore, do not occur in nature. This class is derived from the borane ( $BH_3$ ) itself, which exists only as a transient intermediate and dimerizes to form diborane ( $B_2H_6$ ) immediately. The higher boranes are all consisted of boron clusters that are actually polyhedral in nature. Besides the neutral boranes, a large number of anionic boron hydrides also exist. The general formula for single-cluster boron hydrides is  $B_nH_n^{2-}$ ,  $B_nH_{n+4}$ ,  $B_nH_{n+6}$ ,  $B_nH_{n+8}$  and  $B_nH_{n+10}$  ( $n$  is the number of boron atoms) for closo-, nido-, arachno-, hypho- and klado- type, respectively. There also exists a series of substituted neutral hypercloso-boranes that have the theoretical formulae of  $B_nH_n$ .

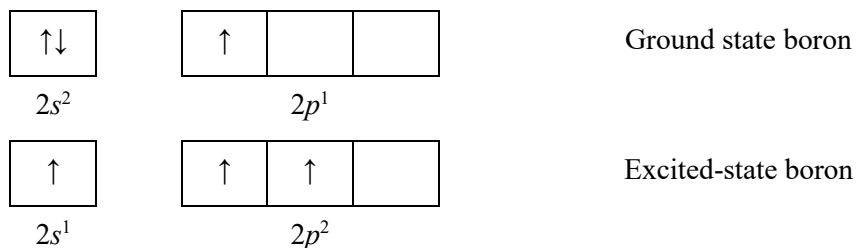
The naming of neutral boranes is done with a Greek prefix showing the number of boron atoms and the number of hydrogen atoms in brackets. In the naming of anions, the hydrogen count is specified first followed by the boron count and the overall charge in the bracket in the last. Furthermore, the prefix closo-nido- etc. can also be added. For example:

Formula	$B_5H_9$	$B_4H_{10}$	$B_6H_6^{2-}$
Name (IUPAC)	Pentaborane(9)	Tetraborane(10)	hexahydrido-hexaborate(2-)
Type	Nido-	Arachno-	Closo-

Understandably many of the compounds have abbreviated common names. The prefix like closo-, nido are actually related to geometry and the number of framework electrons of a particular cluster. Now because the boron hydrides are electron-deficient compounds, the structure and bonding in higher boranes can be understood only after rationalizing the 3-center-2-electron bond involved.

#### ➤ Valence Bond Treatment of Three-Centre Two-Electron Bond

The simplest example of boron hydride containing 3-center-2-electron bond is diborane; and therefore, the first orbital based approach we can use to study the diborane structure is valence bond theory. The  $B_2H_6$  or diborane can be considered as a dimeric unit of two  $BH_3$  molecules. Now, as all the three half-filled  $sp^3$  hybrid orbitals of boron are already used to bind hydrogens, the dimerization seems to be impossible. However, the valence bond theory still suggests a mode of dimerization through  $sp^3$ -hybridization. The electronic configuration of boron in its ground state and excited state are:



The mixing of one  $s$  and three  $p$  orbitals generate four  $sp^3$  hybrid orbitals; three half-filled and one empty. Each boron atom in the diborane structure can use two of its  $sp^3$  hybrid orbitals half-filled to bind two hydrogen atoms (terminal-H). The remaining two hybrid orbitals (one half-filled and one empty) are then used to bind bridging-H atoms as given below.

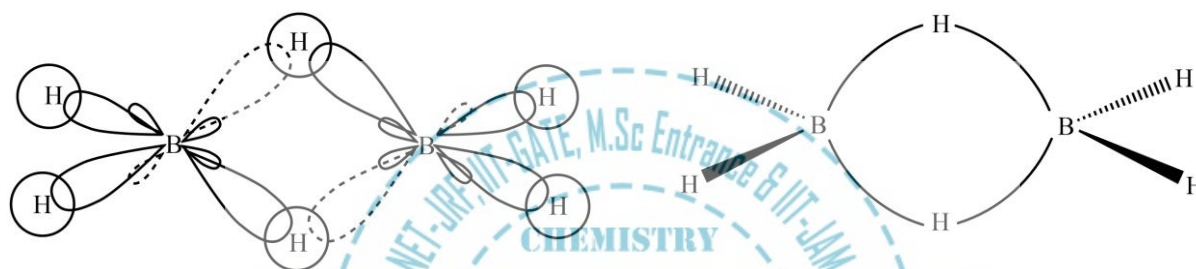
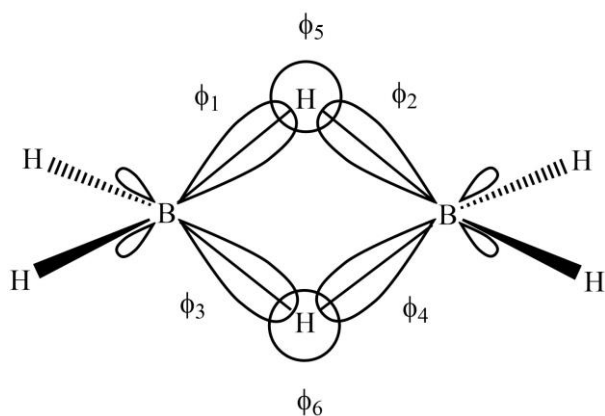


Figure 1. The (a) orbital overlap of hybrid atomic orbital of boron with hydrogens and (b) the resulting banana-shaped 3-center-2-electron bond.

It can be clearly seen that the valence electron in each bridging hydrogen must get delocalize over all three atoms (B–H–B) to bond to both of the B atoms simultaneously. This is pretty much contradictory for the valence bond theory, which likes to bound the valence electrons into regions of space that are localized between two participating nuclei only. Additionally, the molecular geometry of diborane cannot be explained using valence shell electron pair repulsion (VSEPR) theory as far as bridging hydrogens are concerned. According to VSEPR model, two bonds around each bridging hydrogen should be linear i.e. the B–H–B bond angle should be equal  $180^\circ$  with straight-line coordination around.

#### ➤ **Molecular Orbital Treatment of Three-Centre Two-Electron Bond**

The rationalization of the 3-centre-2-electron bond is much more convincing from the molecular orbital approach, which considers the delocalization of electron density in bonding as a common phenomenon. Now because we only want to understand the nature of bonding involved in B–H–B bridges, we need to focus on just the part of the molecule. Before the formation of molecular orbitals, we need to identify the basis function required. Owing to the partial success of the valence bond theory in the rationalization of the 3-center-2-electron bond, we can make the use of four equivalent  $sp^3$  hybrid orbitals and two  $s$  orbitals of hydrogen atoms to construct the symmetry adapted linear combinations (SALCs) of atomic orbitals.

Figure 2. Basis functions for the B–H–B portion in B<sub>2</sub>H<sub>6</sub>.

The reducible representation based upon four hybrid orbitals of borons and two 1s orbitals hydrogens in the B–H–B portion of diborane can be given as:

Table 1. The reducible representation based upon four hybrid orbitals of borons and two 1s orbitals hydrogens in the B–H–B portion of diborane.

$D_{2h}$	$E$	$C_2^z$	$C_2^y$	$C_2^x$	$i$	$\sigma_{xy}$	$\sigma_{xz}$	$\sigma_{yz}$	Irreducible components
$\Gamma_H$	2	0	0	2	0	2	2	0	$a_{1g} + b_{3u}$
$\Gamma_B$	4	0	0	0	0	4	0	0	$a_{1g} + b_{1g} + b_{2u} + b_{3u}$

The mathematical forms of the six normalized SALCs can be deduced through the projection operator theorem and are given by the equations (1) to (6) as:

$$\psi_{a_{1g}}(H) = \frac{1}{\sqrt{2}}(\phi_5 + \phi_6) \quad (1)$$

$$\psi_{b_{3u}}(H) = \frac{1}{\sqrt{2}}(\phi_5 - \phi_6) \quad (2)$$

$$\psi_{a_{1g}}(B) = \frac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4) \quad (3)$$

$$\psi_{b_{1g}}(B) = \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4) \quad (4)$$

$$\psi_{b_{2u}}(\text{B}) = \frac{1}{2}(\phi_1 - \phi_2 - \phi_3 + \phi_4) \quad (5)$$

$$\psi_{b_{3u}}(\text{B}) = \frac{1}{2}(\phi_1 + \phi_2 - \phi_3 - \phi_4) \quad (6)$$

The single-electron wave functions and corresponding molecular orbital shapes for B–H–B portion of diborane are shown in Figure 3. For simplicity, only the largest lobes of the four  $sp^3$  hybrid orbitals are depicted. Nevertheless, the smaller lobes on the opposite side also have a good possibility to overlap, which makes the energies two nonbonding molecular orbitals unequal. The mixing of two SALCs of  $a_{1g}$  symmetry generates two molecular orbitals; one bonding and other antibonding shown by  $a_{1g}$  and  $a_{1g}^*$ , respectively. Similarly, the mixing of two SALCs of  $b_{3u}$  symmetry yields two molecular orbitals of  $b_{3u}$  and  $b_{3u}^*$  symmetry.

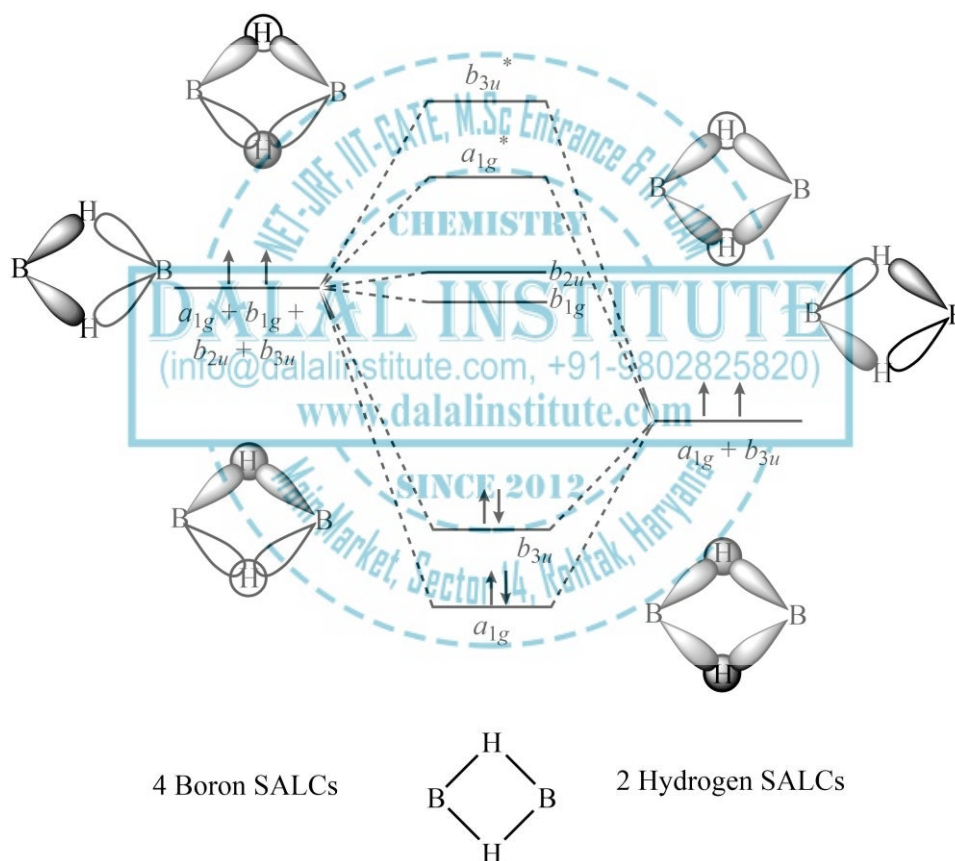


Figure 3. Partial one-electron molecular orbital energy level diagram for the B–H–B part of  $\text{B}_2\text{H}_6$ .

The shapes of molecular orbital with  $a_{1g}$  and  $b_{3u}$  symmetry evidently show that the electron density present in them is actually delocalized over all three nuclei involved in B–H–B unit of diborane. A certain amount of direct B–B bonding in diborane is also present which helps to stabilize the molecule geometry; which is attributed to small-sized H-groups.

➤ **Classification of Bonds Present in Higher Boranes**

The explanation of overall bonding in higher boranes needs the calculation of electrons involved in the skeletal structure of  $B_n$  cluster and these electrons are generally referred as the “framework electrons”. Moreover, the B–H–B bridges are considered as part of the  $B_n$  framework while the terminal B–H are discarded. Though the electrons involved in the framework construction of  $B_n$  cluster are very much delocalized, yet the localized 3-centre 2-electron and 2-centre 2-electron orbital approach can be used to explain the main features of the boranes. Each B atom uses one electron in the normal 2-center-2-electron terminal B–H bond and the remaining two electrons are used in  $B_n$  framework. The structure of higher boranes may or may not have all of the following kinds of bonds i.e. they may possess few or all types.

**1. Terminal B–H bond:** This is a normal 2-center-2-electron covalent bond and is generally shown as B–H.



**2. Direct B–B bond:** This is a 2-center-2-electron bond and is able to connect two boron atoms. These bonds are generally represented as B–B.



**3. Bridging or open B–H–B bond:** This is a 3-center-2-electron bond and is able to connect two boron and one hydrogen atoms. These bonds are generally represented as B–H–B.



**4. Closed B–B–B bond:** This is a 3-center-2-electron bond and is able to connect three boron atoms that are at the corners of an equilateral triangle. These bonds are generally represented as B–B–B.



**5. Open bridging B–B–B bond:** This is a 3-center-2-electron bond and is able to connect three boron atoms to form a B–H–B like bridge found in diborane. These bonds are represented as B–B–B.



➤ **Geometry Prediction in Higher Boranes Using Lipscomb's Model Involving STYX Numbers**

The main initial approach to understand the structures of boranes and related species was Lipscomb's topological model involving STYX numbers and rules. W. N. Lipscomb was an American chemist who developed a method to find the key combinations of bonding profile that are actually possible for a specific boron hydride formula. Each boron atom in neutral boranes or hydroborate anions has at least one H attached by a normal 2-center-2-electron sigma bond; therefore, it can be assumed that one B–H bond is present per boron atom. Besides, Lipscomb also proposed that every other bond present in the cluster must belong to any of the following categories.

- i) 3-centre-2-electrons B–H–B bond, labeled as “S”.
- ii) Closed, open, or a mixture of both 3-centre 2-electrons B–B–B bond, labeled as “T”.
- iii) 2-center-2-electrons B–B bond, labeled as “Y”.
- iv) 2-center-2-electrons B–H terminal bond (simply no. of BH<sub>2</sub> groups), labeled as “X”.

The structure prediction of borane clusters using the Lipscomb model involves the three major components which are discussed in detail below.

**1. The relationship between STYX code and valence electrons:** The correlation between the boranes formula and the number and types of bonds in the cluster is given by simple equations of balance. These equations relate all kinds of sigma bonds to the number of valence electrons available.

i) *Three centers orbital balance:* The electron deficiency in a borane cluster can be removed only if one 3-center-2-electron bond is created by each boron atom. Thus, the sum of the number of 3-centre 2-electron B–H–B bonds and the number of 3-centre 2-electron B–B–B bonds must be equal the number of B–H units ( $n$ ).

$$n = S + T \quad (7)$$

ii) *The hydrogen balance:* Supposing that one terminal hydrogen is attached to each boron atom, the number of hydrogen atoms leftover ( $m$ ), must be distributed among bridges and additional B–H terminal bonds.

$$m = S + X \quad (8)$$

iii) *The electron balance:* Now, if each BH unit contributes one pair of electrons to the skeleton and each of the extra hydrogens gives one electron; the number of electron pairs contributed by additional hydrogens must be calculated by halving their number. All of these electron pairs must be participating in bonding; and therefore, the total number of bond pairs can be given as:

$$n + (m/2) = S + T + Y + X \quad (9)$$

From equation (7) and (8) we get

$$Y = \frac{1}{2}(S - X) \quad (10)$$

**2. The calculation of various STYX possibilities:** After knowing the correlation between various kinds of bonds with framework electron pairs in boron hydrides, we need to follow the following steps to write various STYX possibilities.

- Write down the general formula of given borane cluster in form like  $B_nH_{n+m}$  to fix the value of  $n$  and  $m$ .
- Calculate the number of B–H–B bridges which are represented by  $S$ . The value of  $S$  must lie within the range of  $m/2$  to  $m$ . In other words, the value of  $S$  must satisfy the following condition.

$$\frac{m}{2} \leq S \leq m \quad (11)$$

The validation of the higher limit comes from the fact that  $m$  represents the total additional hydrogens out of which some are present in B–H–B bond and some are present in B–H terminal bond. Therefore, if all the additional hydrogens are present in B–H–B bond, the value of “ $S$ ” at its maximum can just be equal to  $m$ . The validation of the lower limit can be derived equation (8) and equation (9) as:

$$n + (m/2) = (m - X) + T + Y + X \quad (12)$$

$$n = \left(\frac{m}{2}\right) + T + Y \quad (13)$$

From equation (7), we get

$$S + T = \left(\frac{m}{2}\right) + T + Y \quad (14)$$

$$S = \left(\frac{m}{2}\right) + Y \quad (15)$$

Thus, the value of  $S$  is always equal to or greater than  $m/2$ .

iii) For different values of  $S$  obtained in 2<sup>nd</sup> step, we have to calculate the equally possible solutions for the values of  $T$ ,  $Y$  and  $X$ .

iv) There are many sets of STYX numbers for a given borane cluster and thus many possible topologies.

**3. The shortlisting of STYX codes using empirical rules:** In order to select the correct STYX code among several possibilities, empirical rules have been developed which follow as:

- The STYX number sets with negative value are not considered as they have no physical meaning.
- All boranes have at least a 2-fold symmetry, so it is assumed that any new hydride probably would have at least one plane, center, or two-fold axis of symmetry. Low symmetry seems to activate the center of reactivity.
- Only one terminal hydrogen and no bridging hydrogen may be attached to boron that is bound to five neighboring borons. This restricts B–H–B bridges and  $BH_2$  groups to the open edges of boron frameworks.
- If a boron atom is bound to four other boron, it will probably not make use of more than one B–H–B bridge.
- A boron atom that is bound to only two other boron atoms will be involved in at least one B–H–B bridge.

The whole concept can be exemplified using the diborane structure. The general formula for diborane can be written in the form of  $B_2H_{2+4}$ ; which gives the values of  $n$  and  $m$  as 2 and 4, respectively. From equation (11), we get

$$\frac{4}{2} \leq S \leq 4 \quad (16)$$

The possible values of  $S = 2, 3, 4$ . By using  $S = 2$  in equation (7), we get

$$2 = 2 + T \quad (17)$$

$$T = 0 \quad (18)$$

Similarly, putting  $S = 2$  in equation (8), we get

$$4 = 2 + X \quad (19)$$

$$X = 2 \quad (20)$$

Now putting the values of  $T$  and  $X$  from equation (18) and equation (20) in equation (9), we get

$$2 + (4/2) = 2 + 0 + Y + 2 \quad (21)$$

$$Y = 0 \quad (22)$$

Similarly, by taking the value of  $S$  as 3 and 4, one can get two another set of possible STYX numbers as tabulated as given below.

Table 2. Three possible sets of STYX numbers for  $B_2H_6$ .

Number of B–H–B bonds (S)	Number of B–B–B bonds (T)	Number of B–B bonds (Y)	Number of BH <sub>2</sub> groups (X)
2	0	0	2
3	-1	1	1
4	-2	2	0

It can clearly be seen that out of three sets of STYX numbers, only the first one is physically reasonable since the latter two involve negative values. Besides, this also confirmed by the experimental geometrical structure of the diborane that the STYX number of 2002 is, of course, seems to be correct; because there are two B–H–B bridges, no three-center B–B–B bonds or two-center B–B bonds and two B–H terminal bonds in addition to those already considered i.e. two BH<sub>2</sub> groups. A similar procedure can be applied to find out the topological structures of other borane clusters like  $B_4H_{10}$ ,  $B_5H_9$ ,  $B_{10}H_{14}$ .



➤ **Structure and Bonding Profile of Some Typical Higher Borane Clusters**

As we have already discussed the fundamentals of structure and bonding in higher borane systems, now we will implement those ideas to explain some typical examples.

**1. Tetraborane-10 ( $B_4H_{10}$ ):** The bonding in  $B_4H_{10}$  can easily be explained by drawing the plane projections of its three-dimensional structure as shown below.

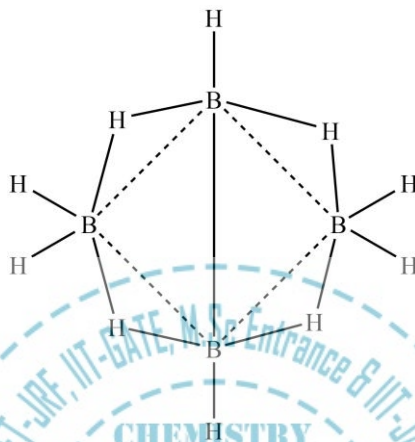


Figure 4. Planar view for the structure of  $B_4H_{10}$ .

It can be clearly seen that there are four B–H–B bridges, no closed or bridging B–B–B unit, one B–B bond and two terminal  $BH_2$  groups. Hence, the overall STYX code for  $B_4H_{10}$  molecule is 4012. Now considering the electron requirement of various kinds of bonds present, the individual contribution of boron and hydrogen atoms can easily be tabulated.

Table 3. Nature and number of bonds (along with electrons required) present in  $B_4H_{10}$ .

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 4 B atoms	Contribution from 10 H atoms
B–H–B	4	8	4	4
B–B–B	0	0	0	0
B–B	1	2	2	0
B–H	6	12	6	6

Hence, four 3-centre 2-electron and seven 2-centre 2-electron bonds require a total  $4 \times 2 + 7 \times 2 = 22$  electrons. Four boron atoms have 12 valence electrons while 10 electrons are actually contributed by ten hydrogen groups that participating in both types of bonds.

**2. Pentaborane-9 ( $B_5H_9$ ):** The pentaborane-9 (commonly called pentaborane) is an inorganic compound with the formula  $B_5H_9$ , and is different from pentaborane-11 ( $B_5H_{11}$ ). It is one of the most common cluster hydrides of boron, though it is a highly reactive compound. Owing to its high reactivity toward oxygen, it was once evaluated as rocket or jet fuel. Like many of the smaller boron hydrides, pentaborane is colorless, diamagnetic, and volatile. The bonding in  $B_5H_9$  can easily be explained by drawing the plane projections of its three-dimensional structure as shown below.

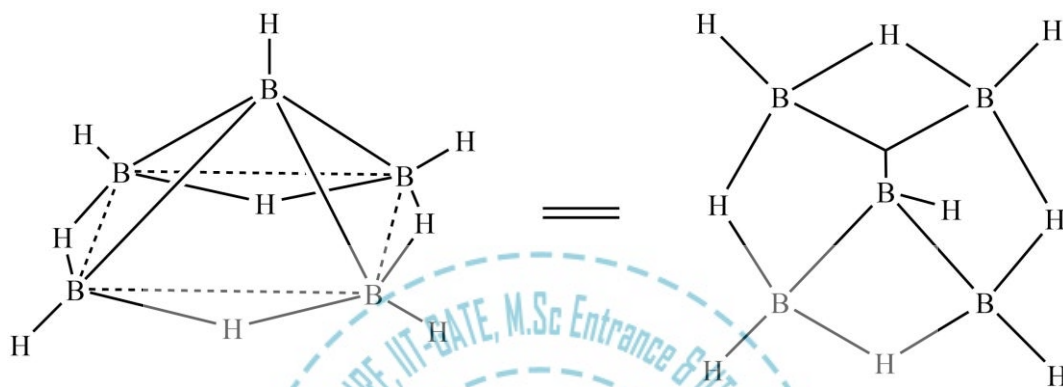


Figure 5. Structure of  $B_5H_9$ .

Its structure is that of five atoms of boron arranged in a square pyramid. Each boron has a terminal hydride ligand and four hydrides span the edges of the base of the pyramid. It can be clearly seen that there are four B–H–B bridges, one closed or triply bridged B–B–B unit, two B–B bond and no terminal  $BH_2$  groups. Hence, the overall STYX code  $B_5H_9$  molecule is 4120. Now considering the electron requirement of various kinds of bonds present, the individual contribution of boron and hydrogen atoms can easily be tabulated.

Table 4. Nature and number of bonds (along with electrons required) present in  $B_5H_9$ .

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 5 B atoms	Contribution from 9 H atoms
B–H–B	4	8	4	4
B–B–B	1	2	2	0
B–B	2	4	4	0
B–H	5	10	5	5

Hence, five 3-centre 2-electron and seven 2-centre 2-electron bonds require a total  $5 \times 2 + 7 \times 2 = 24$  electrons. Five boron atoms have 15 valence electrons while 9 electrons are actually contributed by nine hydrogen groups that are participating in both types of bonds.

**3. Pentaborane-11 ( $B_5H_{11}$ ):** The pentaborane-11 is a compound with the general formula  $B_5H_{11}$ . It is a colorless liquid at room temperature with a boiling point of  $63^\circ\text{C}$ . The bonding in  $B_5H_{11}$  can easily be explained by drawing the plane projections of its three-dimensional structure as shown below.

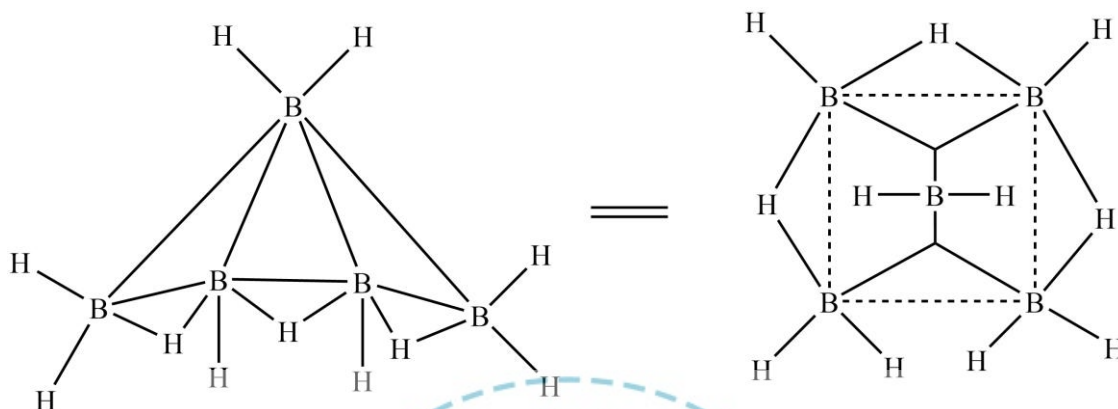


Figure 6. Structure of  $B_5H_{11}$ .

The pentaborane-11 is having unsymmetrical square-pyramidal and five boron atoms are present at the five corners of a square pyramid, just like in the case  $B_5H_9$  molecule. Three out of five boron atoms have a terminal hydride ligand while two adjacent boron has two hydride group each, and four hydrides span the edges of the base of the pyramid. It can be clearly seen that there are three B–H–B bridges, two closed or triply bridged B–B–B unit, zero B–B bond and three-terminal  $BH_2$  groups. Hence, the overall STYX code  $B_5H_{11}$  molecule is 3203. Now considering the electron requirement of various kinds of bonds present, the individual contribution of boron and hydrogen atoms can easily be tabulated.

Table 5. Nature and number of bonds (along with electrons required) present in  $B_5H_{11}$ .

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 5 B atoms	Contribution from 11 H atoms
B–H–B	3	6	3	3
B–B–B	2	4	4	0
B–B	0	0	0	0
B–H	8	16	8	8

Hence, five 3-centre 2-electron and eight 2-centre 2-electron bonds require a total  $5 \times 2 + 8 \times 2 = 26$  electrons. Five boron atoms have 15 valence electrons while 11 electrons are actually contributed by eleven hydrogen groups that are participating in both types of bonds.

**4. Hexaborane-10 ( $B_6H_{10}$ ):** The bonding in  $B_6H_{10}$  can easily be explained by drawing the plane projections of its three-dimensional structure as shown below.

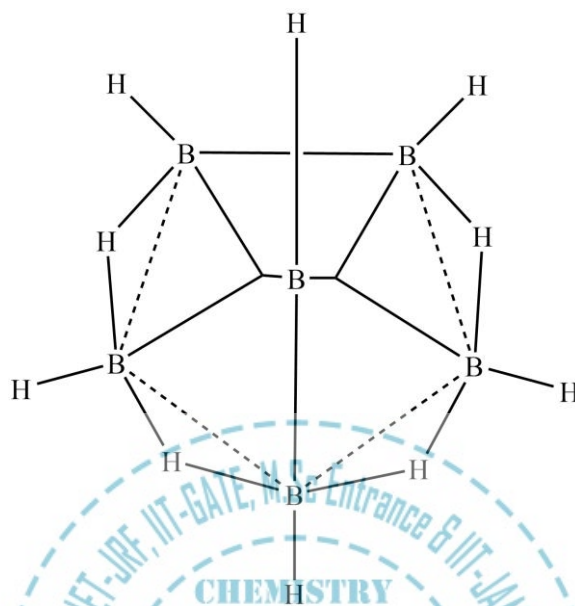


Figure 7. Structure of  $B_6H_{10}$ .

It can be clearly seen that there are four B–H–B bridges, two closed or triply bridged B–B–B unit, two B–B bond and no terminal  $BH_2$  groups. Hence, the overall STYX code  $B_6H_{10}$  molecule is 4220. Now considering the electron requirement of various kinds of bonds present, the individual contribution of boron and hydrogen atoms can easily be tabulated.

Table 6. Nature and number of bonds (along with electrons required) present in  $B_6H_{10}$ .

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 6 B atoms	Contribution from 10 H atoms
B–H–B	4	8	4	4
B–B–B	2	4	4	0
B–B	2	4	4	0
B–H	6	12	6	6

Hence, six 3-centre 2-electron and eight 2-centre 2-electron bonds require a total  $6 \times 2 + 8 \times 2 = 28$  electrons. Six boron atoms have 18 valence electrons while 10 electrons are actually contributed by ten hydrogen groups that are participating in both types of bonds.

**5. Decaborane-14 ( $B_{10}H_{14}$ ):** The bonding in  $B_{10}H_{14}$  can easily be explained by drawing the plane projections of its three-dimensional structure as shown below.



Figure 8. Structure of  $B_{10}H_{14}$ .

In decaborane, the  $B_{10}$  framework resembles an incomplete octadecahedron. Each boron has one radial hydride, and four boron atoms near the open part of the cluster feature extra hydrides. It can be clearly seen that there are four B–H–B bridges, six B–B–B unit (four B–B–B triple bridge bonds and two B–B–B bent bridge), two B–B bond and zero terminal  $BH_2$  groups. Hence, the overall STYX code  $B_{10}H_{14}$  molecule is 4620. Now considering the electron requirement of various kinds of bonds present, the individual contribution of boron and hydrogen atoms can easily be tabulated.

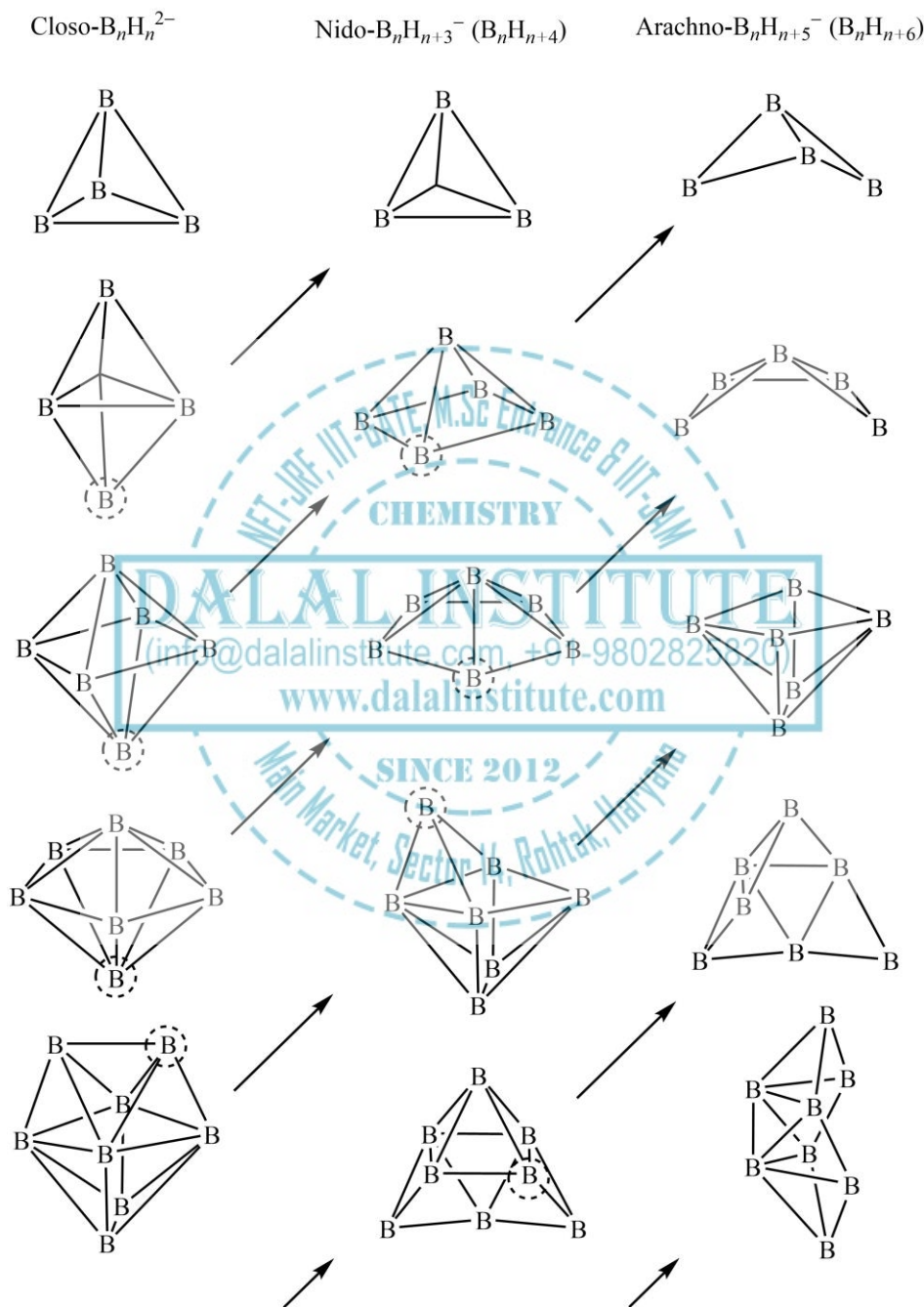
Table 7. Nature and number of bonds (along with electrons required) present in  $B_{10}H_{14}$ .

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 10 B atoms	Contribution from 14 H atoms
B–H–B	4	8	4	4
B–B–B	6	12	12	0
B–B	2	4	4	0
B–H	10	20	10	10

Hence, ten 3-centre 2-electron and twelve 2-centre 2-electron bonds require a total  $10 \times 2 + 12 \times 2 = 44$  electrons. Ten boron atoms have 30 valence electrons while 14 electrons are actually contributed by fourteen hydrogen groups which are participating in both types of bonds.

➤ **Structural Relationship Between Closo, Nido and Arachno Boranes**

The structural relationship between closo, nido and arachno boranes is shown by the diagonal connecting species having the same number of skeletal electron pairs. Hydrogen atoms are omitted for clarity.



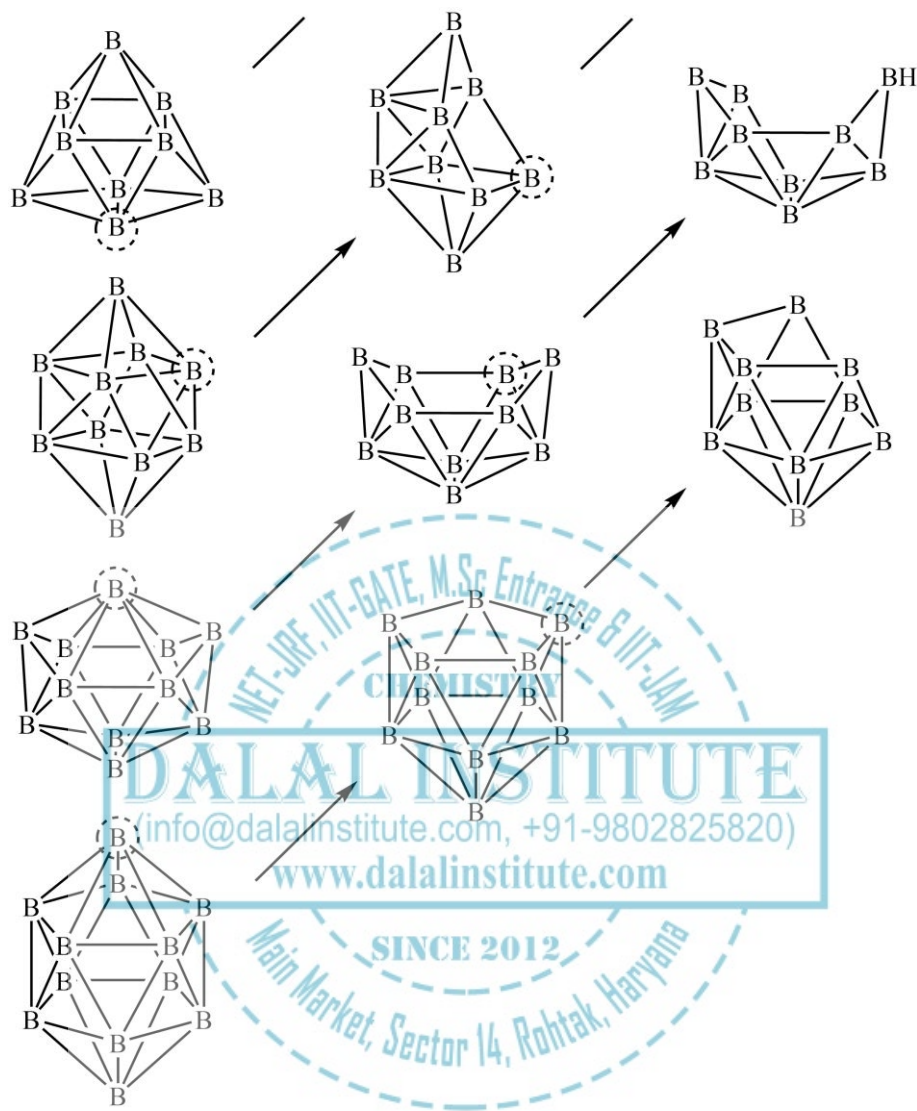


Figure 9. The structural relationship between closo, nido, and arachno boranes; the diagonal lines connect species that have the same number of skeletal electron pairs (SEP).

The structural relationships shown above explain various geometrical aspects of borane clusters; and provides a somewhat conceptual way to think about these systems. For instance, the structure of dodecahydro-closo-dodecaborate anion ( $B_{12}H_{12}^{2-}$ ) is a regular icosahedron. Similarly, the structure of nido- $B_{10}H_{14}$  can easily be obtained just by removing a six-degree vertex from closo-decaborate ( $B_{10}H_{10}^{2-}$ ) anion. The removal of one B–H unit and the addition of two H atoms converts nido- $B_5H_9$  into a butterfly-shaped arachno- $B_4H_{10}$  borane. Nevertheless, it should also be noted that the interconversion of these structures may or may not be possible chemically; and the same statement can be made for their chemical formula.

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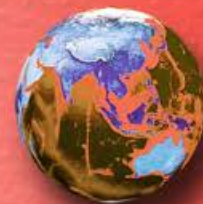
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# A TEXTBOOK OF INORGANIC CHEMISTRY

**Volume I**

**MANDEEP DALAL**



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