Styx Numbers and Rules of Boron Hydrides

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Boron hydrides are a class of **electron deficient** compounds that have unusual bonding behavior and form **cages** and **clusters**. The electron deficient BH_3 is the simplest boron hydride which exists as a dimer B_2H_6 (diborane). The structure of B_2H_6 contains **bridging** B-H-B (or BHB) bonds; quite different to those of carbon hydrides.

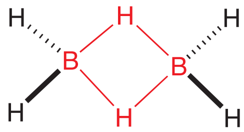


Figure 1: Molecular structure of B_2H_6

The three main types of boron hydrides are (i) ***closo***, (ii) ***nido*** and ***arachno*** with the general formulae, $B_nH_n^{2-}$, B_nH_{n+4} and B_nH_{n+6}, respectively. The American chemist W. N. Lipscomb developed a method using **styx numbers** and **rules** to predict **structures** of boron hydrides. The letters s, t, y and x stand for types of bonds in boron hydrides.

Types of Bonds

First, we identify the **five** types of bonds that exist in a boron hydride.

1. Terminal B-H bond (BH_t)

This is a normal 2-centre-2-electron (2c-2e) bond. It is assumed in a simple boron hydride; each B atom has got a terminal hydrogen (**H_t**).

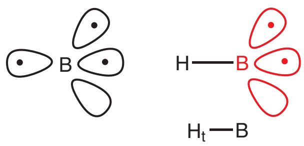
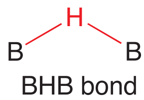


Figure 2: *sp*^{3}-hybridised-B and H_t-B bond

Thus, each H_tB unit uses 3 orbitals and 2e for cluster formation.

2. Bridging B-H-B bond (BHB)

It is a 3-centre-2-electron (3c-2e) bridging BHB bond. It is labelled as "s".



3. Closed or open B-B-B bond

This is a 3-centre-2-electron bond. It is labelled as "t". Boron atoms in a B_3 unit are arranged at the corners of a triangle in a closed structure. Other B_3 units are open bridges.

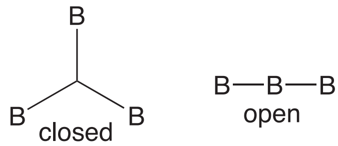


Figure 3: Closed and open B3 units

4. Direct B-B bond

This is a 2-centre-2-electron bond. It is labelled as "y".

5. BH_2 group

This boron atom has another B-H bond in addition to H_t. It is labelled as "x".

Let us take the simplest neutral borane B_2H_6.

Just look at the molecular structure of B_2H_6 (Figure 1). It has two B-H-B bonds, two BH_2 groups and **no** BBB and BB bonds; that means (s = 2, t = 0, y = 0, x = 2). Thus, the set of styx numbers of B_2H_6 is (**2,0,0,2**) or (**2002**).

Why do we need styx numbers?

If we know the molecular structure, we know, how to determine the styx numbers. But what is important is to determine the set/s of styx number/s of an **unknown** compound, and then use this information to **determine the topological structure/s** of the new borane.

Relationships between styx codes

Let us find out relationships of p and q with styx codes and valence electrons for a general binary borane $(BH)_pH_q \Rightarrow B_pH_{p+q}$.

3-Centre balance

We know each boron atom donates 3 orbitals and 2e for cluster formation. Each boron atom should form one 3-centre bond in order to achieve the octet. Thus, the sum of 3c-2e BHB bonds and BBB bonds must be equal the number of boron atoms (p).

$$\mathbf{p = s + t} \qquad [1]$$

H balance

The sum of BH_2 groups and the BHB bonds equal the number of additional hydrogen atoms (q) present in the borane.

$$\mathbf{q = s + x} \qquad [2]$$

Electron balance

Each boron atom donates 2e for the cluster formation. The number of electrons given by boron atoms (p) = 2p

Each additional H donates one electron. The number of electrons donated by additional hydrogens = q

∴ Total number of electrons donated to the cluster framework = 2p + q

(Note that H_t-B bonds do not contribute for the cluster formation)

Total number of bonds (**electron pairs**) =

$$\mathbf{p + q/2 = s + t + y + x} \qquad [3]$$

Using equations [1], [2], [3] we can obtain

$$\mathbf{y = ½ (s-x)} \qquad [4]$$

Other Hints: $s \geq 0, y \geq 0, x \geq 0, t \geq 0$

and $q/2 \leq s \leq q$

Let us use above mentioned relationships to determine the sets of styx numbers of some of the simple boranes; B_3H_9, B_4H_{10}.

Steps to be followed

Step 1: Write the general formula of the given borane in terms of $\mathbf{(BH)_pH_q}$ so that values of p and q can be found. For diborane $B_2H_6 = (BH)_2H_4$; p = 2 and q = 4.

Step 2: Then calculate the number of B-H-B bridges which are represented by **s**. s can have values between q/2 to q (*i.e.*, s must satisfy the condition, $q/2 \leq s \leq q$).

Step 3: Find the values (**t**, **y** and **x**) for different values of **s** obtained in step 2. Now, include these values in a Table; it shows possible sets of styx numbers. Note that sets with negative numbers are excluded.

Step 4: You can now draw the topological structures for each set of styx numbers.

Let us find the topological structures of *arachno*-B_3H_9.

***arachno*-Triborane(9) $\mathbf{B_3H_9}$**

$B_3H_9 = (BH)_3H_6$, thus, p = 3   q = 6;

$q/2 \leq s \leq q$; $3 \leq s \leq 6$; i.e.,   s = 3, 4, 5, 6

Let us determine the styx numbers (see Table 1).

Table 1: Sets of styx numbers of B_3H_9

s	t	y	x
3	0	0	3
4	-1	1	2
5	-2	2	1
6	-3	3	0

The sets with negative values are excluded, thus, the set of styx numbers is (3,0,0,3).

Accordingly, B_3H_9 contains only three BHB bonds and three BH_2 groups; BBB and BB bonds are not present. The topological structure can be drawn as shown in Figure 4.

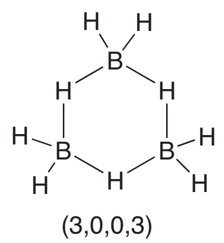


Figure 4: Topological structure of B_3H_9

***arachno*-Tetraborane(10) $\mathbf{B_4H_{10}}$**

$B_4H_{10} = (BH)_4H_6$, thus, p = 4   q = 6;

$q/2 \leq s \leq q$; $3 \leq s \leq 6$;   i.e.,   s = 3, 4, 5, 6

Let us determine the sets of styx numbers (see Table 2).

Table 2: Sets of styx numbers of B_4H_{10}

s	t	y	x
3	1	0	3
4	0	1	2
5	-1	2	1
6	-2	3	0

The possible sets of styx numbers are (3103) and (4012). The corresponding topologies are shown in Figure 5.

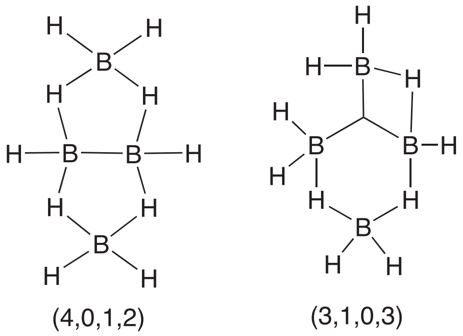


Figure 5: Possible topologies for B_4H_{10}

The topological structure (4012) is favoured as it is symmetrical. The topological structure (3103) is excluded as it is not symmetrical.

Empirical rules

The following empirical rules have been developed to select/choose the best topological structure among several possibilities.

(a) The sets of styx numbers with negative value are not included as they have no physical significance.

(b) Almost all known boron hydrides have at least a two-fold symmetry. It is assumed that any new hydride probably would have at least one plane, center, or two-fold axis of symmetry. The preferred structure is the one with the highest symmetry.

(c) Only one terminal hydrogen and no bridging hydrogen is attached to a boron that is bound to five neighboring boron atoms. This restricts B-H-B bridges and BH_2 groups to the open edges of boron frameworks. Normally, the maximum connectivity is 6.

(d) Every pair of boron atoms which are geometric neighbours must be connected by a BB, BHB or BBB bond.

(e) Every B atom must use four orbitals and achieve its octet.

(f) No two boron atoms may be bonded together by **both** two-centre and three-centre bonds (see Figure 6).

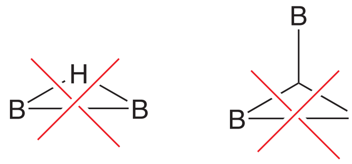


Figure 6: Examples for B atoms having both 2c and 3c bonds

***nido*-Triborane(7) B_3H_7**

B_3H_7 can be arranged as $(BH)_3H_4$.

$p = 3 \quad q = 4; \; q/_2 \leq s \leq q; \quad 2 \leq s \leq 4;$

s = 2, 3, 4.

Let us determine the sets of styx numbers (see Table 3).

Table 3: Sets of styx numbers of B_3H_7

s	t	y	x
2	1	0	2
3	0	1	1
4	-1	2	0

(2102) and (3011) are the possible sets of styx numbers. Two possible topologies are shown in Figure 7. The topology corresponding to (2102) is the most favoured. The topology corresponding to (3011) violates the empirical rule (f).

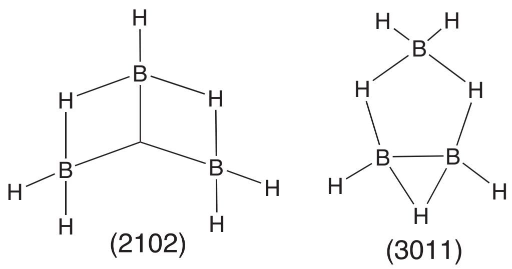


Figure 7: Possible topologies for B_3H_7

***nido*-Pentaborane(9) B_5H_9**

B_5H_9 can be arranged as $(BH)_5H_4$

$p = 5 \quad q = 4; \; q/_2 \leq s \leq q \quad ; 2 \leq s \leq 4;$

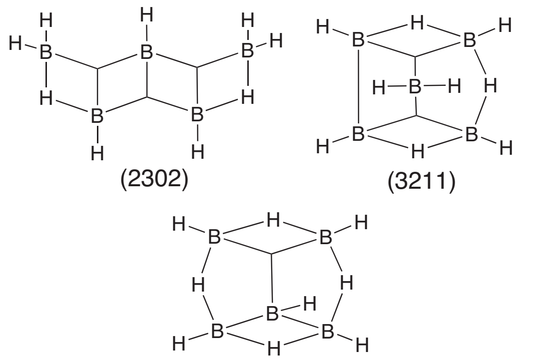
s = 2,3,4.

Let us determine the sets of styx numbers (see Table 4).

Table 4: Sets of styx numbers of B_5H_9

s	t	y	x
2	3	0	2
3	2	1	1
4	1	2	0

Three sets of styx numbers are possible. They are (2302), (3211) and (4120). The most favoured set of styx numbers is (4120), see Figure 8 for topologies.

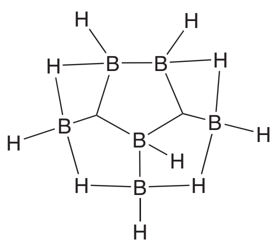


(2302) (3211) (4120)

Figure 8: Topological structures of B_5H_9

nido-Hexaborane(10) B_6H_{10}

The most preferred set of styx numbers of B_6H_{10} is (4220) and its topology is given in Figure 9.

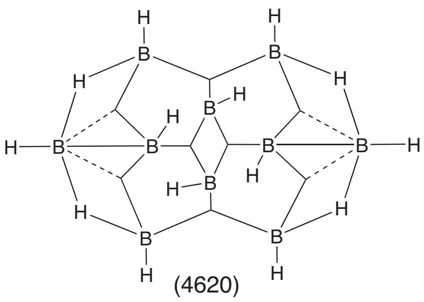


(4220)

Figure 9: Most preferred topology for B_6H_{10}

nido-Decaborane(14) $B_{10}H_{14}$

The most preferred set of styx numbers of $B_{10}H_{14}$ is (4620) and its topology is given in Figure 10. Note that $B_{10}H_{14}$ generates a total of 24 possible sets of styx numbers.



(4620)

Figure 10: Most preferred topology of $B_{10}H_{14}$

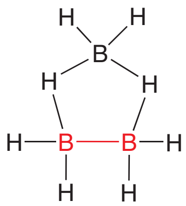
styx Numbers of borate ions

How can we determine the sets of styx numbers of a borate ion? Let us consider the simple borate ion, $[B_3H_8]^-$ formed by the deprotonation of neutral borane, B_3H_9.

Octahydridotriborate(-1) $[B_3H_8]^-$

One way to determine the set of styx numbers of $[B_3H_8]^-$ is to find out the styx numbers of the neutral borane B_3H_9. Protonation of $[[B_3H_8]^-$ gives B_3H_9.

The set of styx numbers of B_3H_9 is (3003), see Table 1 and Figure 4. Now remove one B-H-B and form a B-B bond. Thus, the set of styx numbers of $[B_3H_8]^-$ is (2013). The topological structure of $[B_3H_8]^-$ is shown in Figure 11.



(2013)

Figure 11: Topological structure of $[B_3H_8]^-$

styx Numbers of *closo*-borates

Boron hydrides with the general formulae, $\mathbf{B_nH_n^{2-}}$ are classified as *closo*-borates. The sets of styx numbers of *closo*-borates are summarised in Table 5.

Table 5: Sets of styx numbers of closo-borates with the formula $B_nH_n^{2-}$.

closo-borate	styx numbers
$B_5H_5^{2-}$	(0330)
$B_6H_6^{2-}$	(0430)
$B_7H_7^{2-}$	(0530)
$B_8H_8^{2-}$	(0630)
$B_9H_9^{2-}$	(0730)
$B_{10}H_{10}^{2-}$	(0830)
$B_{11}H_{11}^{2-}$	(0930)
$B_{12}H_{12}^{2-}$	(0,10,3,0)

The relationships of p and q with s, t, y and x of a borate with the general formula $[\mathbf{B_pH_{p+q-1}}]^-$ are given below.

$$\mathbf{s + x = q-1}$$

$$\mathbf{s + t = p-1}$$

$$\mathbf{t + y = p + 1 - q/2}$$