

| | |
|----------------------------|---|
| Subject | Chemistry |
| Paper No and Title | 11. Inorganic Chemistry –III (Metal π-Complexes and Metal Clusters) |
| Module No and Title | Module20. STYX rules and structure of higher boranes |
| Module Tag | CHE_P11_M20 |

| | | |
|--|---|---|
| Principal Investigator | | Co- Principal Investigator and Technical Coordinator |
| Prof A.K.Bakhshi Sir Shankar Lal Professor, Department of Chemistry University of Delhi | | Dr Vimal Rarh Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi <i>Specialised in : e-Learning and Educational Technologies</i> |
| Paper Coordinator | Content Writer | Reviewer |
| Prof. Ranjit K. Verma Professor Department Of chemistry Magadh University, Bodh Gaya, Bihar | Dr.(Mrs.) Neeraj Sharma Professor, Deptt. of Chemistry, Himachal Pradesh University | Prof. B. S. Garg Professor emeritus Dept. of Chemistry University of Delhi |
| Anchor Institute : SGTB Khalsa College, University of Delhi | | |

TABLE OF CONTENTS

1. Learning Outcomes
2. Introduction
3. STYX rules
 - 3.1 What is styx rule/Number
 - 3.2 styx Rules (steps for writing styx number)
4. Structure of higher boranes
 - 4.1 Wade's rules
 - 4.2 Application of Wade's rules in determining the structure of higher boranes
5. Summary



1. Learning Outcomes

After studying this module, you will be able to learn

- How to assign styx code for a given borane
- Different types of bonds which exist in boranes
- Wade's rules and its application
- Different structures of boranes

2. Introduction

The boranes and carboranes are electron-deficient compounds with interesting molecular geometries and characteristic bonding features.

3. Styx Rules

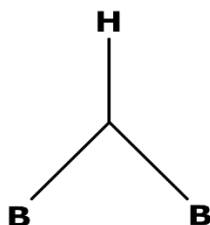
3.1 What is styx Rule/ Number?

The styx number is used to understand the types of bonds in boranes. W.N. Lipscomb developed a method for determining what combinations of bonding features (types of bonds) are possible for a specific formula of boron hydride. The each boron in neutral boron hydrides, hydroborate anions and carboranes cations each boron has at least one H (or, other substituent) attached by a normal two electron sigma bond (2c-2e). It can be assumed that one B-H bond is present per boron atom.

Lipscomb proposed that in addition to this, any of the following

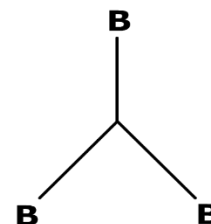
- Three center-two electrons (3c-2e) B-H-B bond (labeled as- s)
- Closed and / or open three center-two electrons (3c-2e) B-B-B bond (labeled as- t)
- Two center-two electrons (2c-2e) B-B bond (labeled as-y)
- Two center-two electrons (2c-2e) B-H_{terminal} bond (labeled as- x) (simply no. of BH₂ groups)

Type → (a) **BHB (3c-2e)**



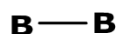
Number → **s**

(b) BBB (3c-2e)



t

Type → (c) **BB (2c-2e)**



Number → **y**

(d) Extra B-H (2c-2e)



x

could be present. The four kinds of bonding features are given by the symbols s, t, y, and x, which together constitute the styx code. The B-B-B bond may be open or closed but subsequent theoretical studies have shown that open B-B-B bonds need not to be considered. The three-center bonds are necessary to account for boron hydride bonding because each B-H unit at a polyhedral vertex can supply three orbitals but two electrons only to the framework. This is because one B-H bond uses one electron and one orbital of the B-atom, leaving three orbitals and two electrons for skeletal bonding (framework). For example, in B_2H_6 there are 12 valence shell electrons (one boron has $2s^2 2p^1$ and hydrogen has $1s^1$) and 14 valence orbitals (one boron has 4 valence orbitals and one hydrogen has one valence orbital); therefore, two, three-center (3c-2e) BHB bridges are formed in addition to two extra two-center (2c-2e) B-H bonds. In another example B_6H_{10} has 28 valence electrons and 34 valence orbitals. Its 14 pairs can be accommodated in eight two-center (2c-2e) bonds (B-H and B-B) and six three-center bonds (BHB and BBB). So it is clear that one three-center bond is formed per boron atom as in B_2H_6 , two boron atoms having two three-center (3c-2e) BHB bonds. Similarly in B_6H_{10} , six boron atoms have total six three-center (3c-2e) bonds which are localized. Utilizing the concept of localized, three-center BHB and BBB bonds, in addition to two-center BB and additional BH bonds, it is possible to describe the topology of the boron hydrides.

The relationship between the formula of the boranes and the number and kinds of bonds in the molecule is described by simple equations of balance that relate the number of valence electrons to the different types of sigma bonds that can form

- (i) Three centre orbital balance.

$$p = s + t$$

eq. (1)

The electron deficiency in a boron hydride is eliminated if one three-center bond is formed per boron atom. Therefore the sum of the number of three-center BHB bonds (labeled as s) and number of three-center BBB bonds (labeled as t) must equal the number of B-H units (p).

- (ii) Hydrogen balance

$$q = s + x$$

eq. (2)

Assuming that each boron has at least one "terminal" hydrogen attached to it and the remaining hydrogen atoms, q, must be divided between bridges (s) and additional B-H terminal bonds (x).

- (iii) Electron balance

No. of electron pairs = No. of bonds

$$p + (q/2) = s + t + y + x$$

eq. (3)

or simply by calculations using equation from (1) and (2) we have

$$y = 1/2(s-x)$$

eq. (4)

This rule arises from the fact that each of the p (BH) groups can contribute two electrons or one pair to the skeleton and each of the additional q hydrogens can contribute one electron or half of a pair. All of these electron pairs must then be used in bonding, the total number of bond pairs being $s + t + y + x$.

3.2 Steps for writing styx number (STYX rules)

Step 1 : Write the general formula of given borane in terms of $(BH)_pH_q$, so that value of p and q can be fixed. As in case of diborane $B_2H_6 = (BH)_2H_4$, $p=2$ and $q=4$

Step 2: Then calculate the no. of B-H-B bridges which are represented by s.

s must have value in a range from $q/2$ to q or the value of s must satisfy the condition $q/2 \leq s \leq q$.

- (a) The statement that $s \leq q$ is true because q 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(x) as additional one which are also explained by equation as

$$q = s + x$$

Thus it is clear that no. of B-H-B bonds (value of s) cannot exceed the number of total additional hydrogens (i.e. q)

- (b) The statement that $s \geq q/2$ is derived as

Since $p + (q/2) = (q - x) + t + y + x$, then $p = t + y + (q/2)$.

From eq.(1), $(s + t) = t + y + (q/2)$ so $y = s - (q/2)$ and $s = (q/2) + y$, so that s is greater than $q/2$.

So we have different possible value of s which satisfy the condition $q/2 \leq s \leq q$.

Step 3 : For different value of s obtained in step 2, we have to calculate the equally possible solutions for the values of t, y and x (collectively called styx numbers).

Step 4 : There are usually several styx numbers for a given boron hydride and therefore several possible topologies.

Empirical Rules

In order to choose among several possibilities, empirical rules have been developed and are given as follows:

- The sets of styx no. with negative value are not included as they have no physical significance.
- All known boron hydrides have at least a two-fold symmetry, so it is assumed that any new hydride probably would have at least one plane, centre, or two-fold axis of symmetry. Low symmetry appears to provide centre of reactivity.
- Only one terminal hydrogen and no bridging hydrogen, may be attached to a 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 is bound to four other boron atoms, it will probably not make use of more than one BHB bridge.
- A boron atom that is bound to only two other boron atoms will be involved in at least one BHB bridge.

For example consider the simplest possible case, diborane $B_2H_6 = (BH)_2H_4$

Step 1. Diborane can be represented as $B_2H_6 = (BH)_2H_4$, so $p = 2$ and $q = 4$

Step 2. Here $q = 4$ and $q/2 = 2$, so that $2 \leq s \leq 4$,

The possible values of $s = 2, 3, 4$

Step 3. From equation (1) $t = p - s$ and $t = 2 - 2$ giving $t = 0$, and from equation (2) $x = q - s$ and $x = 4 - 2$ (by taking the value of $s = 2$), then $x = 2$.

After having knowing the value of ($s=2$) and ($x=2$) one can calculate the value of y from equation (4) $y = \frac{1}{2}(s-x)$ as y comes out to be zero. So by considering the value of $s = 2$, the first possible set of styx numbers is $styx = 2002$. Similarly, by taking value of $s = 3$ and 4 one will get two another set of possible styx numbers as described in table 1.

Table 1 Possible three sets of styx numbers for diborane

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

Only the first of these three solutions is physically reasonable, since the latter two involve negative values. From our knowledge of the diborane structure (Fig.1), the styx number 2002 is of course seen to be correct; that is, there are two BHB bridges ($=s$), no three center BBB bonds ($=t$) or two-center BB bonds ($=y$) and two B-H terminal bonds in addition to those already assumed.

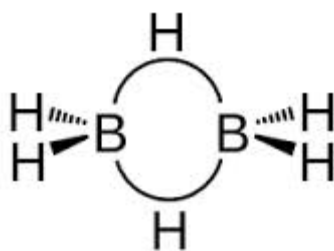


Figure 1. Structure of diborane (B_2H_6) with styx no. = 2002

Table 2 The styx codes of some closo boranes

| | Boranes | | | | | | | |
|---|---------------|---------------|---------------|---------------|---------------|---------------------|---------------------|---------------------|
| | $B_5H_5^{2-}$ | $B_6H_6^{2-}$ | $B_7H_7^{2-}$ | $B_8H_8^{2-}$ | $B_9H_9^{2-}$ | $B_{10}H_{10}^{2-}$ | $B_{11}H_{11}^{2-}$ | $B_{12}H_{12}^{2-}$ |
| S | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| T | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Y | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| X | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

Table 3 The styx codes of some nido

| boranes | Boranes | | | | | | |
|---------|-------------------------------|-------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|---------------------------------|
| | B ₄ H ₈ | B ₅ H ₉ | B ₆ H ₁₀ | B ₇ H ₁₁ | B ₈ H ₁₂ | B ₉ H ₁₃ | B ₁₀ H ₁₄ |
| S | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| T | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
| Y | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| X | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

4. Structure of higher boranes

Boranes fall into five structural categories

1. *Closo*-boranes, B_nH_n²⁻: n vertices of n concerned polyhedron are occupied by boron atoms.
2. *Nido*-boranes, B_nH_{n+4}: one vertex is missing from parent closo borane.
3. *Arachno*-boranes, B_nH_{n+6}: two vertices are missing from parent closo borane.
4. *Hypho*-boranes, B_nH_{n+8}: three vertices are missing from parent closo borane.
5. *Conjuncto*-boranes (from Latin: join together): conjuncto boranes are formed by joining two or more preceding types.

Illustrations

1. Closo boranes B_nH_n²⁻; e.g. in hexahydrohexaborate (2-), B₆H₆²⁻ has regular octahedron structure. Six boron atoms occupy the six corners of regular polyhedron. It has closed symmetrical structure.

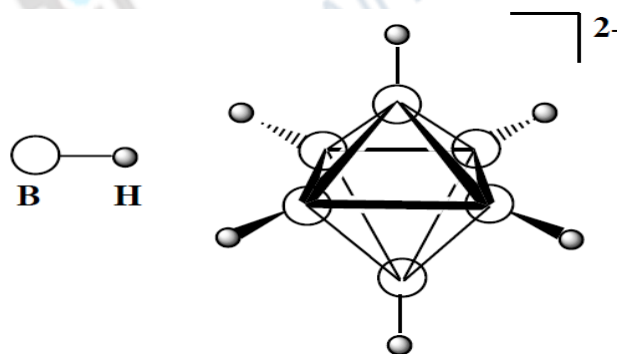


Figure2. Structure of B₆H₆²⁻ (all vertices are occupied).

2. *Nido*-boranes (B_nH_{n+4}): e.g. in pentaborane(9) ,B₅H₉ only five vertices(n-1) are occupied by boron atoms of regular ,six cornered octahedron (with n vertices).

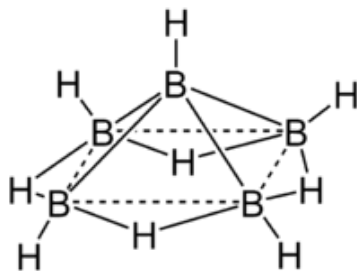


Figure 3. Structure of B₅H₉(one vertex is missing).

3. *Arachno*-boranes (B_nH_{n+6}): e.g. in tetraborane(10) ,B₄H₁₀ only four vertices are occupied by boron atoms

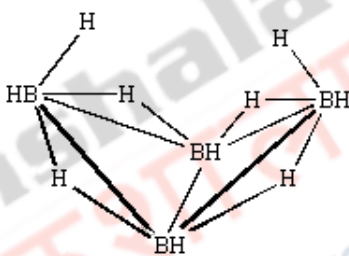


Figure 4. Structure of B₄H₁₀(two vertices are missing).

Some important cage structures with regular geometry are shown below in fig. 5

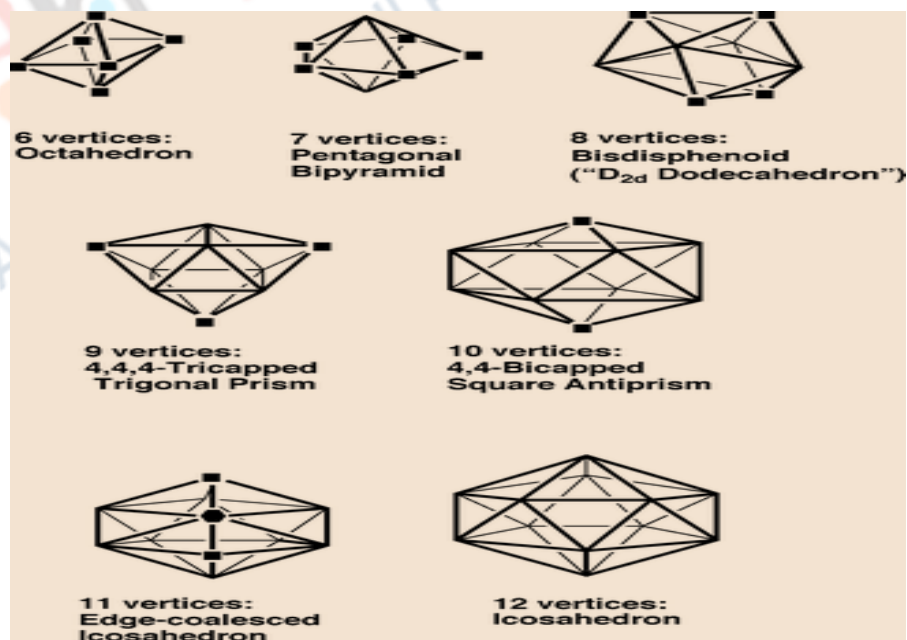


Figure 5. Cage structures

4.1 WADE-MINGO RULES (polyhedral skeleton electron pair theory)

In order to rationalize the structure of boranes and their derivatives, a scheme of skeletal electron counting was developed to which the following rules are applicable:

Step-1 : First, the number of skeletal electrons are calculated as sum of the following contributions.

- Each B-H bond contributes 2 electrons.
- Each C-H bond contributes 3 electrons.
- Each additional hydrogen contributes 1 electron.
- Finally the anionic charge on the cluster is to be added to above contributions.

i.e. skeletal electron count = 2(B-H) + 3(C-H) + 1(additional H) + anionic charge on cluster

Step-2 : Calculate the number of pairs of electrons

$$\text{no. of electron pairs} = \frac{\text{skeletal electron count}}{2}$$

Step-3 : Let the number of vertices (no. of B and C atoms) is given by 'n'. Then by comparing the number of electron pairs with no. of vertices(n) , the cluster's structure can be identified as follows

| No. of electron pairs | Type of borane |
|-----------------------|----------------|
| n+1 | Closo |
| n+2 | Nido |
| n+3 | Arachno |
| n+4 | Hypo |

4.2 Application of Wade's rule in determining the structure of higher boranes

A) Consider $B_7H_7^{2-}$, Heptahydroheptaborate(2-)

Step-1 :Skeletal electron count = 2(B-H) + 3(C-H) + 1(additional H) + anionic charge on cluster
 $= 2(7) + 0 + 0 + 2$
 $= 16$

Step-2 :

$$\text{No. of electron pairs} = \frac{\text{skeletal electron count}}{2} = \frac{16}{2} = 8$$

Step-3 : The no. of vertices = n= 7

No. of electron pairs = 8 , which corresponds to n+1.

Hence it is closo borane (no vertex is missing)

As no vertex is missing ,the cage structure should contain n = 7 vertices and is pentagonal bipyramidal.

B) Consider B_6H_{10} – Hexaborane (10)

Step-1 :Skeletal electron count = 2(B-H) + 3(C-H) + 1(additional H) + anionic charge on cluster
 $= 2(6) + 0 + 4 + 0$
 $= 16$

Step-2 :

$$\text{No. of electron pairs} = \frac{\text{skeletal electron count}}{2} = \frac{16}{2} = 8$$

Step-3 : The no. of vertices = $n = 6$

No. of electron pairs = 8, which corresponds to $n+2$.

Hence it is nido borane (one vertex is missing)

As only one vertex is missing, the parent cage must contain $n+1 = 7$ vertices. Hence, the structure of B_6H_{10} must be pentagonal bypramidal with one vertex missing (we can call it as pentagonal pyramid with six vertices)

C) Consider B_5H_{11} – Pentaborane (11)

Step-1 : Skeletal electron count = $2(B-H) + 3(C-H) + 1(\text{additional H}) + \text{anionic charge on cluster}$
 $= 2(5) + 0 + 6 + 0$
 $= 16$

Step-2 :

$$\text{No. of electron pairs} = \frac{\text{skeletal electron count}}{2} = \frac{16}{2} = 8$$

Step-3 : The no. of vertices = $n = 5$

No. of electron pairs = 8, which corresponds to $n+3$.

Hence, it is arachno borane (two vertices are missing)

As two vertices are missing, the parent cage must contain $n+3=7$ vertices. Hence, the cage structure of B_5H_{11} must be pentagonal bypramidal with two missing vertices :

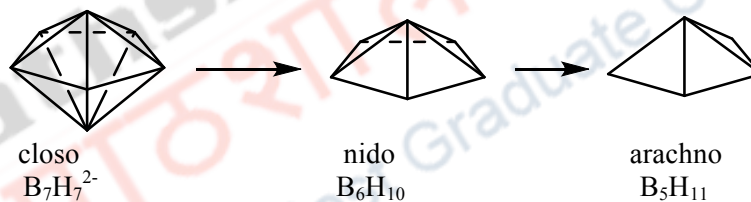


Figure.6 Structural shape of boron atoms is shown only. Line may or may not represent the actual bonds between them.

5. Summary

- The styx number is used to understand the types of bonds in boranes.
- The symbols s, t, y, and x which together constitute styx code correspond to
 - s= no. of 3c-2e B-H-B, bridge bonds
 - t= no. of 3c-2e B-B-B bonds
 - y= no. of 3c-2e B-B bonds
 - x=no. of terminal hydrogen atoms (simply no. of BH₂ groups)
- Boranes are classified structurally into five categories viz. closo, nido, arachno, hypo and conjuncto boranes
- *Closo*-boranes (B_nH_n²⁻) n vertices of n concerned polyhedron are occupied by boron atoms
- *Nido*-boranes (B_nH_{n+4}): one vertex is missing from parent closo borane
- *Arachno*-boranes (B_nH_{n+6}): two vertices are missing from parent closo borane
- *Hypho*-boranes (B_nH_{n+8}): three vertices are missing from parent closo borane
- *Conjuncto*-boranes : conjuncto boranes are formed by joining two or more preceding types