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The unification of lipscomb numbers- the scramble for the octet rule by boranes

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ABSTRACT

Applying the concept of octet rule and the Kiremire equation to a given hydrocarbon molecular formula , suitable structures of isomers can be constructed. In this paper, it is shown that the Kiremire equation can be applied to both the neutral and ionic boranes. The equation is related to the Lipscomb symbols by K = s +2t +y. In this way, the Kiremire equation may be considered to complement the Lipscomb's numbers utilized in the construction of valence bond molecular structures of a given boron hydride. The relationship is also a clear testimony that despite the electron deficiency, the borane clusters constitute themselves in such a way as to attain the octet rule around the boron atoms.

Key words: Lipscomb numbers, scarmble, octet rule, boran.

INTRODUCTION

Since the discovery of the first boron hydride, B_2H_6 by Stock, and the subsequent hundreds of others, the structure and bonding of boranes continue to be of great interest to many chemists. This is because boranes are electron deficient and hence the conventional two electrons and two atoms (A-B) model could not be utilized to explain the bonding in such molecules. Many chemical species containing the atoms of the second and third rows of the periodic table do obey the OCTET RULE.

The Kiremire Formula

Recently a simple equation (hereto referred to as the Kiremire equation) that could be used to derive the number of skeletal bonds for molecules that obey the octet or eighteen electron rule was developed[1]. The Kiremire eq. is given by

$$K^{Ú} = (E-V)/2 ;$$

where K = the total number of skeletal bonds, E = the total number of electrons of all the isolated atoms each of which is assumed to obey the octet rule, and V= the total number of valence electrons in the system of the chemical species in question. The formula is readily utilized to derive resonance structures or canonical forms of any given molecular formula of chemical species that obey the octet rule from simple to complex ones.

Examples:

C_2H_6

Each of the carbon atoms will obey the octet rule. Hence E= 2 x 8 =16 and V =2x4+ 1x6 =

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*K , E, and V symbol has been used in this paper rather than B, X, and Y used in reference 1 to avoid confusion with B, x and y the symbol for boranes.

Therefore K = (E-V)/2 = (16-14)/2 = 1. This means that there is only one C—C skeletal bond in C_2H_6. By adding the H atoms to this skeletal bond in such a way that each of the C atoms obey the octet rule we get the expected molecular geometry shown in figure 1.

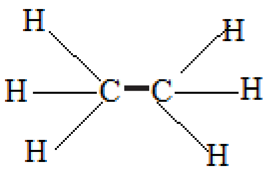


Fig. -1: C_2H_6 geometry

C_2H_4

C_2H_4 ; K= (E-V)/2, E =2x8 =16, V=2x4+4 = 12. Hence,K = (16-12)/2 =2.

This means that C_2H_4 is held by 2 skeletal bonds (C=C). We then add the H atoms to the skeletal system to ensure that each of the C-atoms obey the octet rule. The final geometry is given in figure 2.

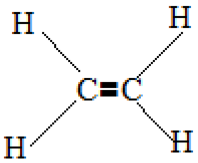


Fig. - 2: C_2H_4 geometry

C_2H_2

C_2H_2 ; K= (E-V)/2, E=2x8 = 16,
V =2x4+2 =10, K =(E-V)/2 =(16-10)/2 =3.
Hence, C_2H_2 is held by 3 skeletal bonds (**C≡C).**

This gives us the expected C_2H_2 geometry shown in figure 3.

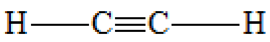


Fig. - 3: C_2H_2 geometry

C_6H_6

C_6H_6 ; E = 6x8 =48, V =6x4+6 = 24+6 =30,
K =(48-30)/2 = 9.

Thus, C_6H_6 is held by 9 skeletal bonds. This is consistent with the selected isomers shown in figures 4 and 5.

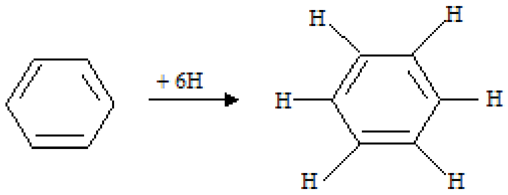


Fig. - 4: C_6H_6 isomer

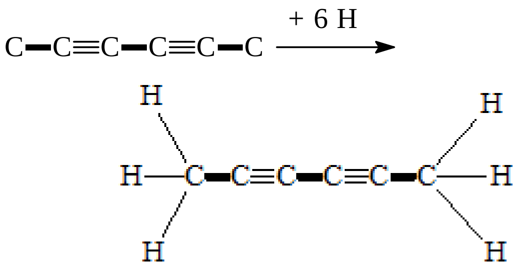


Fig. - 5: C_6H_6 isomer

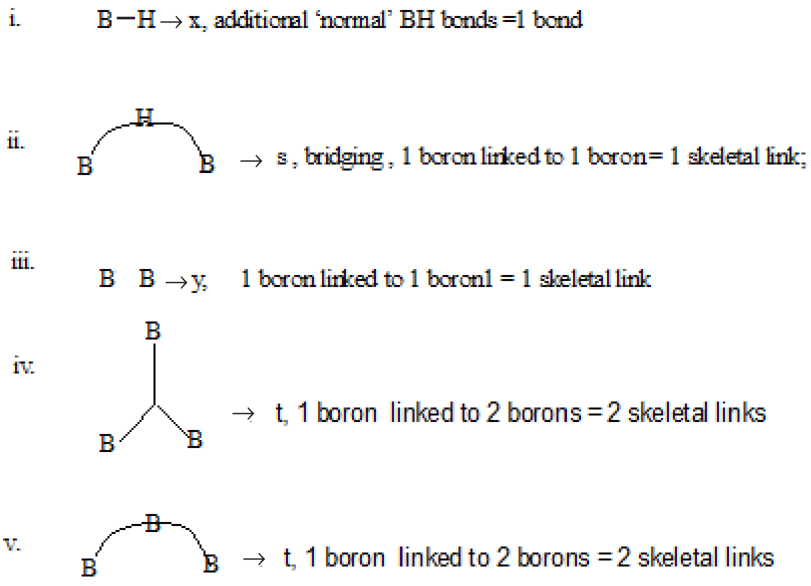
By using single, double and triple bonds for the skeleton C atoms and then adding the single C-H bonds, we get a chemical structure (or one of the isomers if the chemical species has more than one possible geometries) that obeys the octet rule.

The Kiremire Formula and Boranes (Boron Hydrides)

Boranes

Whereas the Kiremire equation can be applied to the hydrocarbons to facilitate the sketching of molecular structures easily, in the case of boranes it has to work in conjunction with the Lipscomb equations and numbers. The formula has been found to be so versatile that it is readily applicable to the formulae of the neutral and ionic boranes. Furthermore, it beautifully unifies the Lipscomb symbols s, t and y which rationalize the skeletal bonds of boranes by the relationship K= (E –V)/2 = s +2t +y.

A neutral borane may be expressed by a general formula B_pH_{p+q}. The bonding is regarded to consist of BH fragments linked by the following bonds as defined by Lipscomb[2-3]. These are shown in scheme 1.



Scheme-1: Types of bonds found in in boranes

The skeletal links are related to the molecular formula of boranes by the following Lipscomb's equations:

i. $s + x = q$
ii. $s + t = q$
iii. $p = t + y + q/2$

Let us consider a number of Boranes for illustration:

B_2H_6

$K = (E - V)/2$, Assuming each boron atom will obey the octet rule, $E = 2 \times 8 = 16$ and $V = 2 \times 3 + 6 = 12$. $K = (16-12)/2 = 2$. This means that there are two skeletal links binding the two boron atoms. B_2H_6 can be written as B_2H_{2+4}. Applying Lipscomb's equations for B_2H_6 , p=2, q=4, q/2 =2

$$s+x = q = 4 \quad \text{.......i.}$$
$$s+t = p = 2 \quad \text{..........ii.}$$
$$p= t+ y +q/2$$
$$2 = t+y +2$$
$$t+y = 0 \quad \text{...........iii.}$$

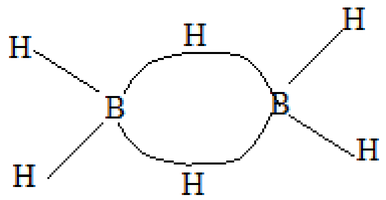
Selected possible solutions are given in Table -1.

Table - 1: Lipscomb numbers for B_2H_6

s	t	y	x	Comment
0	2	-2	4	Reject
1	1	-1	3	Reject
2	0	0	2	Accept
3	-1	1	1	Reject

Hence the acceptable (styx) numbers are (2002). In this paper, the styx values will be referred to as Lipscomb numbers.

The structure of B_2H_6 consistent with the Lipscomb numbers[2-6] is given in figure 6.



2002

Fig. - 6: B_2H_6 geometry

The number of skeletal links K = 2 corresponds to the bridging BHB bonds =2 = s.

B_4H_{10}

Consider B_4H_{10} . K= (E-V)/2, E = 4x8 =32, E = 4x3+10 = 22.
K = (32-22)/2 =5. $B_4H_{10} = B_4H_{4+6}$; p =4, q =6, q/2 =3.

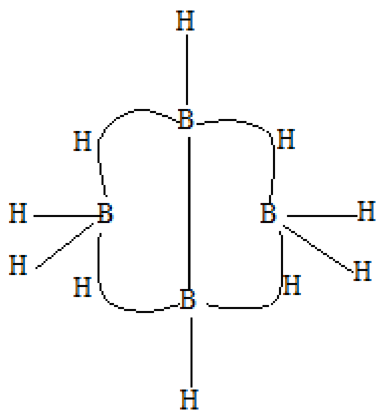
s+x = q =6
s+t = p =4
t+y = p-q/2 =4-3 =1

The selected possible solutions are given in table 2..

Table - 2: Lipscomb numbers for B_4H_{10}

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

Taking Lipscomb's set of numbers styx = 4012, the geometry shown in figure 7 can be drawn.



4012

Fig. - 7: B_4H_{10} isomer

In the case of this geometry, K =5 = 4+1 = s + y, where s= the sum of all bridging bonds (BHB), and y = sum of BB bonds. Since t represents a boron atom linked to two others, its intrinsic value is 2. Thus for the Lipscomb set of numbers styx = 3103,

K = s+2t +y = 3+2x1+0 = 5. Indeed as the more examples to follow will illustrate, the general relationship between K and Lipscomb symbols s, t and y can be generalized into the following unifying Kiremire equation.

$$\boxed{K = (E - V)/2 = s+2t+y}$$

K = total number of skeletal bonds in the borane cluster, s = total number of the bridging H bonds, t = is total number of three centered boron bobds (BBB), and y = is the total two centered boron bonds (BB). The above equation focuses on the skeletal bonds and not the additional H bonds (x). It should be noted that the Kiremire equation satisfies the sty values for both rejected and accepted Lipscomb numbers. The rejected sets are those whose one of the numbers is negative and hence has no physical significance.

B_5H_9

Let us consider $B_5H_9 = B_5H_{5+4}$, p=5,q=4, q/2 =2
K = (E-V)/2, E = 5x8 =40, V = 5x3 +9 = 24. Hence K =(40-24)/2 = 8.
s+x = q =4 ; s+t = p =5; t+y = p –q/2 =5-3 =3
The selected solutions are given in table 3.

Table-3: Lipscomb numbers for B_5H_9

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

Testing for K-values for the sets,
Set 3, K = s+2t+y = 2 +2x3+0 =8
Set 4, K = 3+2x2+1 =8
Set 5, K = 4+2x1+2 = 8

Taking one set of Lipscomb numbers 4120, suitable isomers of B_5H_9 can be drawn. These are given in figure 8.

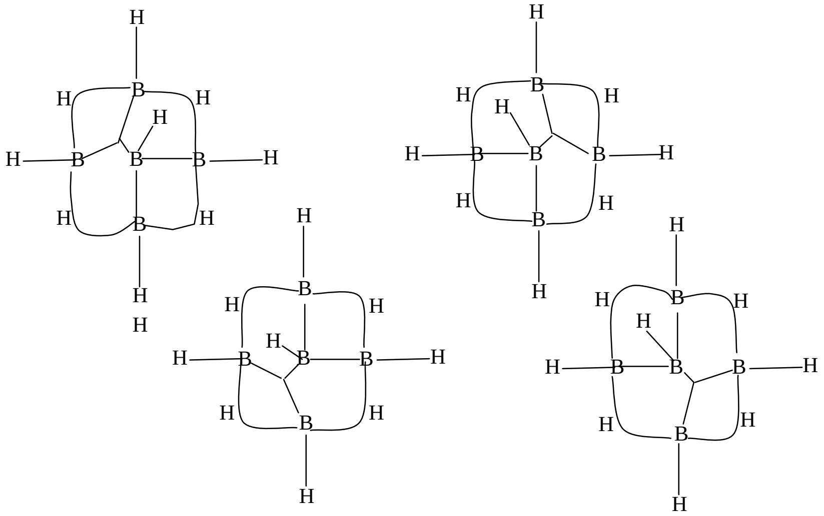


Fig. - 8: B_5H_9 Isomers

$B_{10}H_{14}$

Let us take a more complex cluster $B_{10}H_{14} = B_{10}H_{10+4}$, p =10, q = 4.

K = (E-V)/2 , E = 10x8 =80, V = 10x3+14 = 44, K = (80 – 44)/2 = 18. This means that there will be 18 skeletal bonds that hold the $B_{10}H_{14}$ cluster together. s+x = q = 4, s+t = p = 10, t+y = p –q/2 = 10-2 =8

Again testing the Kiremire equation on the accepted sets we get:
Set 3, K = s+2t+y = 2+2x8 +0 = 18
Set 4, K = 3+2x7+1 = 18
Set 5, K = 4+2x6+2 = 18

A sketch of one isomer for the Lipscomb numbers 4620 is shown in figure 9.

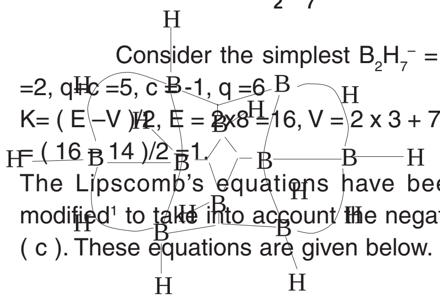


Fig. - 9: $B_{10}H_{14}$ Isomer for 4620 Lipscomb numbers

Negatively charged boranes

The Kiremire formula also applies to the negatively charged boranes.

$B_2H_7^-$

Consider the simplest $B_2H_7^- = B_2H_{2+5}^-$, p =2, q+c =5, c = -1, q =6
K= (E –V)/2, E = 2x8 =16, V = 2 x 3 + 7 +1 = 14, K = (16 – 14)/2 =1.

The Lipscomb's equations have been slightly modified[1] to take into account the negative charge (c). These equations are given below.

s+x = q+c ,s+t = p+c, p = t+y +q/2 +c

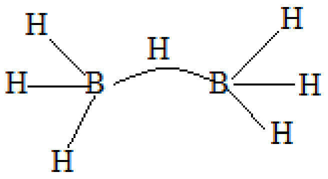
Applying these to $B_2H_7^-$ system we get
s+x = q+c = 5 , s+t = p+c = 2-1 =1, t+y = p –(q/2+c) = 2-(6/2-1) =2-(2) = 0

The selected solutions are given in table-4.

Table - 4: Lipscomb numbers for $B_2H_7^-$

s	t	y	x	Comment	Set
0	1	-1	5	x	1
1	0	0	4	√	2
2	-1	1	3	x	3

The valence bond structure consistent with the Lipscomb numbers 1004 is shown Fig.-10.



1004

Fig. - 10 $B_2H_7^-$ geometry

K = s +2t + y = 1+2x0+0 =1 for set 2.

$B_3H_8^-$

Another good example is $B_3H_8^- = B_3H_{3+5}^-$. In this case, p =3, q+c = 5, c = -1, q = 6. Hence,

s +x = q + c = 5, s+t = p+c = 3-1 = 2, t+y = p-(q/2+c) = 3 – (6/2 -1) = 3 – (2) = 1
The selected solutions are given in table 5.

Table - 5: Lipscomb numbers for $B_3H_8^-$

s	t	y	x	Comment	Set
0	2	-1	5	x	1
1	1	0	4	√	2
2	0	1	3	√	3
3	-1	3	2	s%	4

The isomers consistent with the Lipscomb sets of numbers 1104 and 2013 are shown in

K = (E-V)/2 , E = 3x8 =24, V =3x3+8+1 = 18, K = (24 -18)/2 = 3.
K = s + 2t +y = 1+ 2x1 + 0 =3 (for 110), K = 2+2x0 +1 =3 (for 201)

$B_4H_7^-$.

Let us consider a slightly more complex cluster $B_4H_7^-$.

$B_4H_7^- = B_4H_{4+3}^- = B_pH_{p+q+c}^-$, p = 4, q+c = 3, c = -1, q =4.

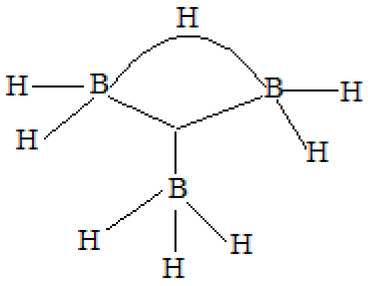
s + x = q+c = 3
s+t = p+c = 4 -1 =3
t+y = p – (q/2+c) = 4 – (2-1) = 3

The selected solutions are given in table 6.

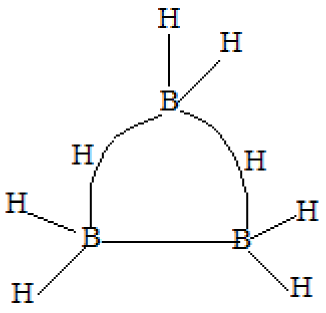
Table - 6: Lipscomb numbers for $B_4H_7^-$

s	t	y	x	Comment	Set
0	3	0	3	√	1
1	2	1	2	√	2
2	1	2	1	√	3
3	0	3	2	√	4
4	-1	4	3	x	5

The selected isomers for the accepted Lipscomb numbers are shown in figure 12.



1104



2013

$B_3H_8^-$ Isomers

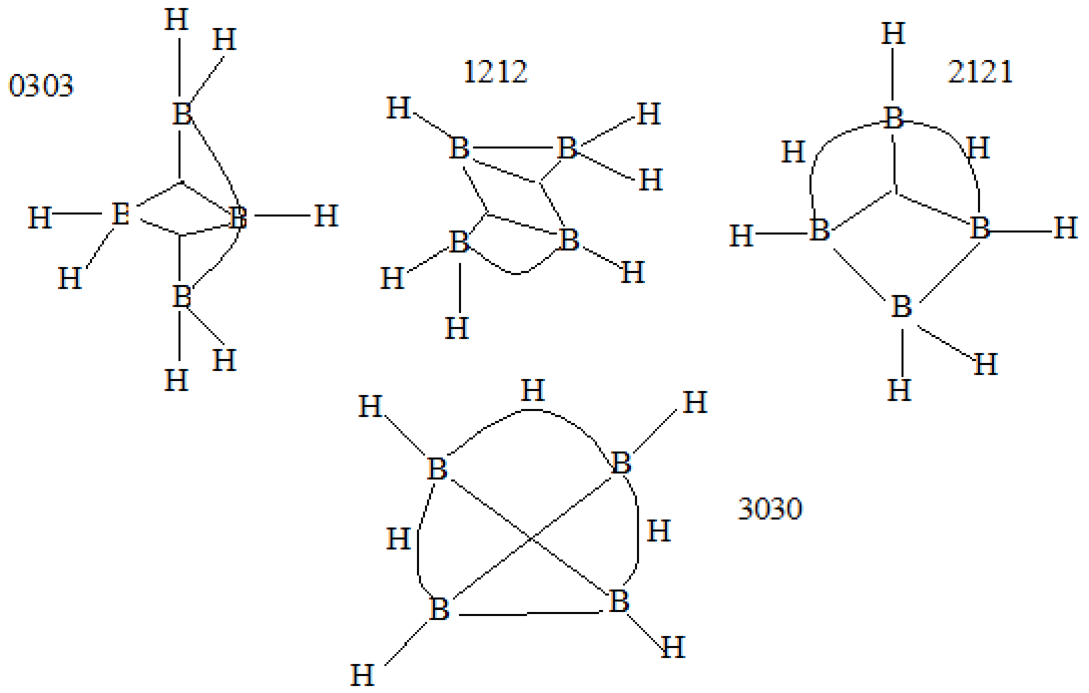


Fig. - 12: Isomers of B_5H_9

K = (E-V)/2 , E = 4x8 =32, V = 4x3+7+1 = 20,
K = (32 – 20)/2 = 6.

K = s + 2t + y = 0 + 2x3 + 0 = 6 (for 030) ,
K = 1+2x2 +1 = 6 (121), K = 2+2x1 +2 = 6,
K = 3+2x0+3 = 6 (303).

$B_6H_6^{2-}$

Let us take one more illustration with $B_6H_6^{2-}$ cluster. For this ion, K = (E-V)/2,E = 6x8 = 48, V= 6x3 + 6 + 2 = 26, K = (48 – 26)/2 = 11. This means the cluster will be held together by 11 linkages. Also $B_6H_6^{2-}$ cluster belongs to the general form $B_pH_{p+q+c}^{2-}$.

Hence, p = 6, q+c = 0, c = -2, and q = 2. Applying the modified Lipscomb's equations we get,

s+x = q+c = 0, s+t = p+c = 6 – 2 = 4,
t+y = p-(q/2 + c) = 6 – (2/2-2) = 7.

The possible solutions are given in Table - 7 below.

Table - 7: Lipscomb numbers for $B_6H_6^{2-}$

s	t	y	x	Comment	Set
0	**4**	**3**	**0**	√	1
1	3	4	-1	x	2
2	2	5	-2	x	3

Two possible isomers for the accepted Lipscomb numbers is given in figures 13 and 14.

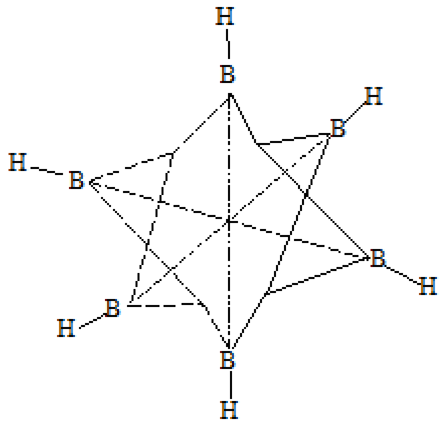


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Fig. - 13: One of $B_6H_6^-$ isomers

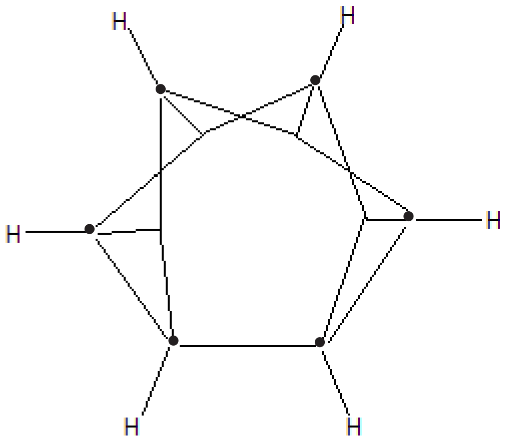

Fig. - 14: One of the $B_6H_6^{2-}$ Isomers

The three BB bonds are represented by the dashed diagonals. The four BBB bonds are the dashed linked lines on the edges.

K = s + 2t + y = 0 + 2x4 + 3 =11.

$B_9H_{12}^-$

Let us consider a more complex example, $B_9H_{12}^-$.

K = (E – V) /2 = (72-40)/2 = 16. This means that the cluster is held by 16 links to the boron atoms. The cluster $B_9H_{12}^- = B_9H_{9+3}^-$. p = 9, q+c = 3, c = -1, and q = 4. Hence, Lipscomb's equations will be:

s + x = q+c = 3, s + t = p+c = 9-1 = 8, and t+y = p-(q/2 +c) = 9-(4/2 -1) =8.

The possible solutions are given in table 8.

Table - 8: Lipscomb numbers for $B_9H_{12}^-$

s	t	y	x	comment
0	8	0	3	√
1	7	1	2	√
2	6	2	1	√
3	5	3	0	√

A sketch of one possible isomer corresponding to the Lipscomb numbers (2621) is given in figure 15.

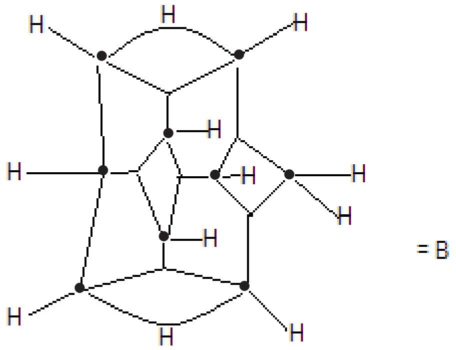

Fig. - 15: $B_9H_{12}^-$ isomer, 2621

K = s + 2t + y = 2 +2x6 +2 =16 for the 2621 Lipscomb numbers.

$B_{10}H_{16}^{2-}$

The final example to iluustrate the link between the Lipscomb symbols and the Kiremire equation is $B_{10}H_{16}^{2-}$. K = (E –V)/2 = (80-48)/ 2 = 16.

$B_{10}H_{10+6}^{2-}$, p =10, q = 8, c = -2. Hence, the Lipscomb equations become:

s + x = 6, s + t = 8, t + y = 8. The possible solutions are given in table 9.

Table - 9: Lipscomb numbers for $B_{10}H_{16}^{2-}$

s	t	y	x	comment
0	8	0	6	√
1	7	1	5	√
2	6	2	4	√
3	5	3	3	√
4	4	4	2	√
5	3	5	1	√
6	2	6	0	√

One of the possible isomers corresponding to the Lipscomb numbers 0806 is sketched in figure 16.

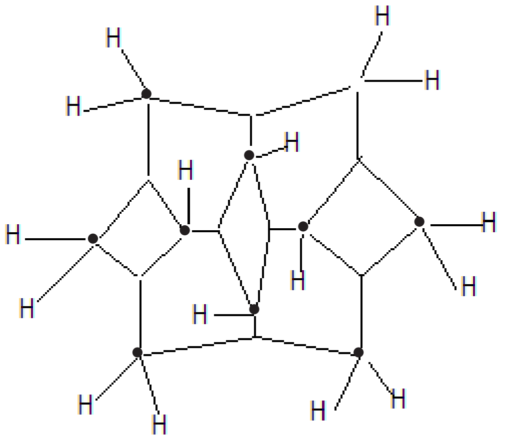

Fig. - 16: One of the isomers of $B_{10}H_{16}^{2-}$, 0806

K = s + 2t + y = 0 + 2 x 8 + 0 = 16.

Conclusion

The boron atoms in the neutral and ionic boranes scramble to obey the octet rule. Thus, each of the boron atoms is linked to its neighbouring atoms by four bonds each of which may be regarded to contribute two electrons giving a total of eight electrons around the boron atom. In so doing, they utilize the bridged linkages [BHB and BBB (closed and open)] as well as the conventional bonds (BB and BH). The Kiremire equation that may be used to determine the total number of skeletal bonds in simple and complex cluster molecules and ions that obey the octet rule has been found to unify the Lipscomb symbols s, t and y through K =s +2t +y relationship. In this way, the Kiremire equation complements the Lipscomb equations.

REFERENCES

1. Kiremire, E M R., *Orient. J. Chem*., **22**(1), 29 (2006).
2. Douglas B, McDaniel D., Alexander J., " *Concepts and Models of Inorganic Chemistry",* 3rd Edition,
3. John Wiley & Sons, Inc., New York (1994).
4. Lipscomb W N, *Proceedings of the National Academy of Sciences*, **47,** 1791 (1961).
5. Greewood N N and Earnshaw A., "*Chemistry of the Elements*", 2nd Edition, Butterworth Heinemann, Oxford, (1998).
6. Lagowski J J, " *Modern Inorganic Chemistry",* Marcel Dekker, Inc., New York, (1973).
7. Cotton F A, Wilkinson G, " *Advanced Inorganic Chemistry*", 4th Edition, John Wiley & Sons, New York (1980).