

The influence of the octet rule on the carborane cluster structures

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ABSTRACT

The concept of deriving the structures of isomers of boranes using Kiremire's and Lipscomb's equations has been extended to the derivation of the structures of carboranes. The carbon atom is considered to be isoelectronic to the boron atom plus one electron. Just like the boranes, the carboranes also obey the relationship $K = s + 2t + y$. A good number of carborane clusters both neutral and ionic are given as illustrative examples.

Key words: Octet rule, Carborane cluster structures.

INTRODUCTION

Unlike the hydrocarbons, sketching molecular structures of borane and carboranes isomers present considerable difficulty to many students at both undergraduate and graduate levels. In a paper presented earlier, it was shown that boranes obey the Kiremire's equation¹ whose basis is the octet rule as well as the Lipscomb's equations. Many conventional textbooks²⁻⁹ have scanty or no information concerning how the geometries of the boranes and carboranes are derived. The common carboranes fall into the following categories, the neutral types such as $C_2B_{n-2}H_n$ ($n = 5-12$), $C_2B_nH_{n+2}$ ($n = 3-10$) and a large number of anions⁶. The aim of this paper is popularize the teaching of the derivation of the carborane structures. The illustrative examples are hereby presented.

$C_2B_3H_5$

Consider $C_2B_3H_5$ cluster. Applying Kiremire's equation¹ to determine the number of skeletal linkages, we get $K = (E - V)/2 = [5 \times 8 - (4 \times 2 + 3 \times 3 + 5)]/2 = 9$. This means that $K = s + 2t + y = 9$. Isoelectronically, $C \equiv B + e^-$. Hence, $C_2B_3H_5 \equiv (B + e^-)_2 B_3H_5 \equiv B_5H_5^{2-}$. Thus, $C_2B_3H_5$ can be treated as if it is a negatively charged borane and apply the appropriate Lipscomb's equations.

Comparing $B_5H_5^{2-}$ with $B_pH_{p+q+c}^{2-}$, $p=5$, $q+c=0$, $c=-2$, $q-2=0$, and $q=2$. Therefore the Lipscomb equations will be: $s+x=0$, $s+t=3$, and $t+y=6$. Following the procedure presented in earlier work^{*}, the solution to the equation is (0330). One of the isomers consistent with the Lipscomb numbers is shown in figure 1.

$K = s + 2t + y = 0 + 2 \times 3 + 3 = 9$ as deduced by $K = (E - V)/2$ calculation above.

$C_2B_4H_8$

This cluster is handled in the same way as in $C_2B_3H_5$ case.

$K = (E - V)/2$, $E = 6 \times 8 = 48$, $V = 4 \times 2 + 3 \times 4 + 8 = 28$, $K = (48 - 28)/2 = 10$.

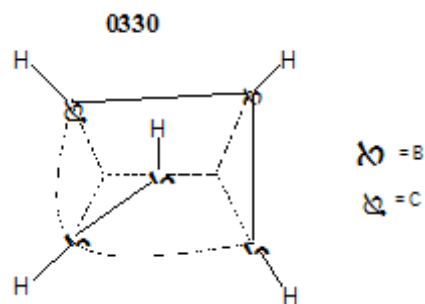


Fig. -1: One of the possible isomers of $C_2B_3H_5 \equiv B_5H_5^{2-}$

Table - 1: The possible solutions for $C_2B_4H_8$

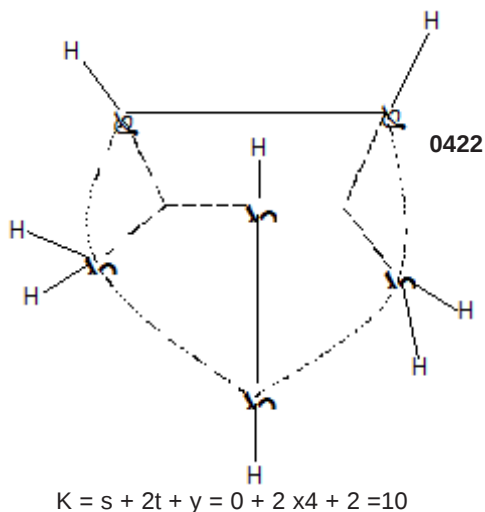
s	t	y	x
0	4	2	2
1	3	3	1
2	2	4	0

This means that the cluster is held by 10 skeletal linkages. Furthermore, $C_2B_4H_8 \equiv C_6H_8^{2-}$. Comparing this with $B_pH_{p+q+c}^{2-}$, $p = 6$, $q + c = 2$, $c = -2$, $q = 4$.

Hence, the appropriate Lipscomb's equations are:

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

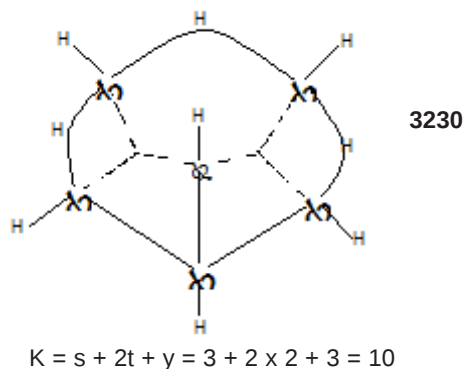
The possible solutions are given in Table 1. One of the possible isomers is given in Fig.- 2.

**Fig. -2: One of the possible isomers of $C_2B_4H_8$** **Table - 2: The possible solutions for CB_5H_9**

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

 CB_5H_9

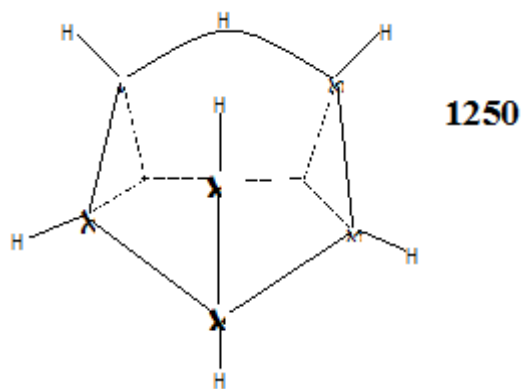
The cluster linkages in this molecule are given by $K = (E - V)/2 = [48 - (4 + 15 + 9)]/2 = 10$. The cluster $CB_5H_9 = B_6H_9^{3-}$. In this case, $p = 6$, $c = -1$, $q + c = 3$, $q = 4$. Lipscomb's equations will be: $s + x = 3$, $s + t = 5$, $t + y = 5$. The solutions are given in table 2. The geometry of one of the possible isomers is given in Fig. 3.

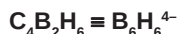
**Fig. -3: One of the possible isomers of CB_5H_9** **$C_3B_3H_7 = B_6H_7^{3-}$**

In $C_3B_3H_7$ molecule, the cluster linkages will be given by $K = (E - V)/2 = [6 \times 8 - (3 \times 4 + 3 \times 3 + 7)]/2 = (48 - 28)/2 = 10$. By equating $B_6H_7^{3-}$ to $B_pH_{p+q+c}^{3-}$, $p = 6$, $q + c = 1$, $c = -1$, $q = 4$. The corresponding Lipscomb's equations will be as follows:

$$s + x = q + c = 1, s + t = p + c = 6 - 3 = 3, t + y = p - (q/2 + c) = 6 - (4/2 - 3) = 7.$$

The possible solutions of the equations are (0341) and (1250). One of the possible isomers of the Lipscomb numbers (1250) is shown in Fig. 4.

**Fig - 4: Possible isomer for $C_3B_3H_7$**



Looking at the isoelectronic equivalence of $C_4B_2H_6$ with $B_6H_6^{4-}$, it is tempting to compare $C_4B_2H_6$ with the C_6H_6 in terms of skeletal linkages consistent with the octet rule. Applying the Kiremire formula $K = (E - V)/2$ for C_6H_6 , we get $K = (48 - 30)/2 = 9$. This gives us the usual benzene framework shown in Fig. 5.

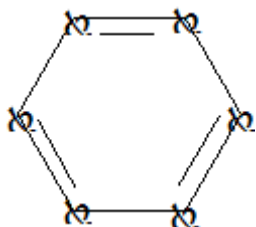
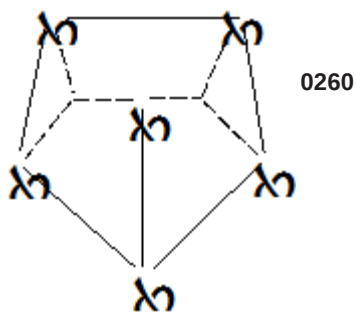


Fig - 5: An isomer of C_6H_6 , H atoms ignored

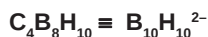
On the other hand in the case of $C_4B_2H_6$, K value = $(E - V)/2 = [48 - (4 \times 4 + 2 \times 3 + 6)]/2 = (48 - 28)/2 = 10$. Setting up the Lipscomb equations we get, $s + x = 0$, $s + t = 2$, $t + y = 8$. This has one possible solution of positive Lipscomb numbers of (0260). One of the plausible skeletal framework is shown in Fig. - 6.



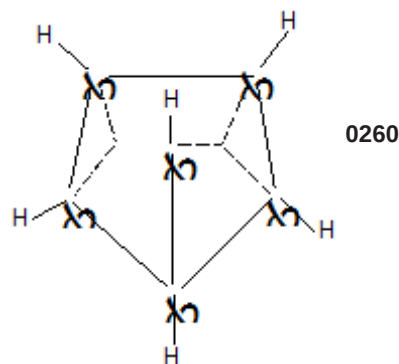
$$K = s + 2t + y = 0 + 2 \times 2 + 6 = 10$$

Fig -6: Skeletal framework of one of the isomers of $C_4B_2H_6$

When we include the hydrogen atoms to complete the octet rule, we get Fig. -7.



It is interesting to compare the skeletal linkages of $C_{10}H_{10}$ with those of $C_2B_8H_{10}$. The K value for $C_{10}H_{10}$ is $(80 - 50)/2 = 15$. This gives one of the skeletal isomers shown in Fig. - 8.



$$K = s + 2t + y = 0 + 2 \times 2 + 6 = 10$$

Fig. -7: Skeletal framework of one of the isomers of $C_4B_2H_6$

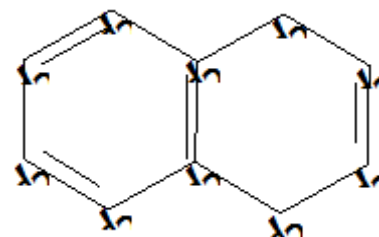
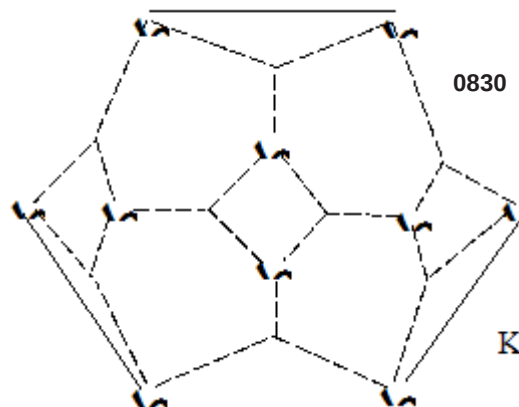


Fig. -8: One of the possible isomers of $C_{10}H_{10}$

In the case of $C_2B_8H_{10}$, the K value is 19. Setting up the Lipscomb's equations for the cluster we get,

$$s + x = 0, s + t = 8 \text{ and } t + y = 11.$$

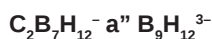
The possible 'positive' solution is 0830. This gives us a sketch structure of one of the isomers shown in Fig. -9.



$$K = s + 2t + y = 0 + 2 \times 8 + 3 = 19$$

Fig. -9: The skeletal framework of $C_2B_8H_{10}$

The negatively charged carboranes



These are treated in the same manner as the uncharged one. Let us consider the example of $\text{C}_2\text{B}_7\text{H}_{12}^-$. K value = 15. The derived Lipscomb equations are :

$$s + x = 3, s + t = 6, t + y = 9.$$

The 'positive' solutions are given in table 3.

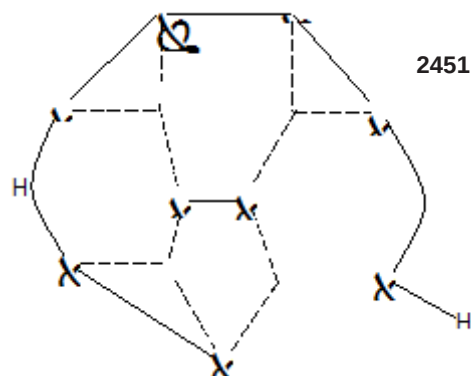
Table - 3: The possible solutions of $\text{C}_2\text{B}_7\text{H}_{12}$

s	t	y	x
0	6	3	3
1	5	4	2
2	4	5	1
3	3	6	10

CONCLUSION

Although the boranes and carboranes are electron deficient, their structures are centered on the fulfilment of the octet rule and thus attain stability. They do this through utilization of both the conventional two atom-two electron centered bonds

The skeletal sketch of one of the isomers corresponding to the Lipscomb set of numbers (2451) is given in Fig. 10.



$$K = s + 2t + y = 2 + 2 \times 4 + 5 = 15$$

Fig. -10: The skeletal framework of $\text{C}_2\text{B}_7\text{H}_{12}^-$

and the unique three atom-two electron centered bonds. The Kiremire equation complements the Lipscomb's equations in constructing the borane and carborane valence bond cluster structures. This article is aimed at popularizing the teaching of boranes and carborane clusters at both undergraduate and postgraduate levels.

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