Stability of polyhedral borane anions and carboranes

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Abstract. Polyhedral borane anions and carboranes that can be constructed formally from the interaction of rings and caps will be stable with six interstitial electrons. Interstitial electron count is obtained by summing the number of π electrons of the ring and the electrons of the caps involved in ring cap binding. Thus $B_7H_7^{-2}$ (D_{5h}) has 6 interstitial electrons (none from the B_5H_5 ring, two each from the two BH caps and two negative charge). MNDO calculations on isoelectronic pyramidal molecules $B_6H_6^{-4}$ (C_{5v}), $B_5H_5CH^{-3}$ (C_{5v}), $B_5H_5^{-4}$ (C_{4v}), $B_4H_4CH^{-3}$ (C_{4v}), $B_4H_4^{-4}$ (T_d) and $B_3H_3CH^{-3}$ (C_{3v}) suggests a criterion based on the out-of-plane bendings of the ring B–H bonds to select the best combination of borocycles and BH or CH caps. Three-membered borocycle prefers CH cap, five-membered borocycle prefers BH cap. The preference of four-membered ring for BH or CH cap is not as pronounced. The extra stability of $B_{12}H_{12}^{-2}$ arises from the geometry of the icosahedron. The relative stabilities of *nido* and *closo* carboranes follow from these rules.

Keywords. Polyhedral borane anion; carboranes; overlap matching.

1. Introduction

Great strides in chemistry are made often with the help of electron counting rules. For example the Huckel $4n + 2$ rule for planar conjugated π systems (Huckel 1931), the 18 electron rule in transition metal complexes (Purcell and Kotz 1977), the Wades rule in polyhedral molecules (Wade 1976) and the Woodward-Hoffmann rules for pericyclic reactions (Woodward and Hoffmann 1971) have all helped in organizing facts and in predicting new chemistry. Yet all molecules and all reactions obeying a particular rule are not equally favourable. Can one develop a qualitative criterion to decide the relative stabilities among a set of molecules obeying a given rule? Of course one can calculate the energy of every molecule and reaction if reliable theoretical methods exist and are accessible. The resulting relative energies even if correct do not provide an explanation for the observed relative stabilities. On the other hand a qualitative explanation almost always increases ones understanding and helps in predicting the stability of the yet to be synthesized molecules of the same set. Such an attempt has been very successful in the application of the conservation of orbital symmetry and in its simpler alternative, frontier orbital theory (Fukui 1971; Fleming 1976). We present here a qualitative criterion to explain and to predict the relative stabilities and structural details of polyhedral borane anions and carboranes that obey Wades rule. Specific questions we would like to ask are (i) what are the causes for the instability of $B_5H_5^{-2}$ and $B_7H_7^{-2}$ relative to $B_6H_6^{-2}$ and $B_{12}H_{12}^{-2}$ and (ii) what controls the stabilities of carborane isomers.

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2. Electron counting rules for polyhedral boranes

Even though the concept of 3c–2e bond and 'styx' formalism developed by Lipscomb is the oldest approach, the polyhedral skeletal electron pair theory of Wade is the most popular method of electron counting in polyhedral boranes (Lipscomb 1963; Wade 1976). We first give a brief description of the Wades approach and the six interstitial electron rule (Jemmis and Schleyer 1982). The latter provides a qualitative criterion that can be applied to polyhedral molecules.

2.1 Skeletal electron pair theory (Wades rules)

According to this theory n B–H groups with $n + 1$ skeletal electron pairs favour a closed polyhedral structure. Some of the commonly observed polyhedra in boron chemistry are shown in figure 1. Each B–H group in polyhedral boranes is considered to donate two electrons for polyhedral binding. The remaining one-valence electron of boron atom is used in the B–H bond. The rule further states that an increase of two electrons, i.e. n BH groups with $n + 2$ skeletal electron pairs, lead to a nido arrangement of BH groups. Nido clusters are obtained by removal of one vertex from a closo structure. Addition of yet another electron pair ($n + 3$ skeletal electron pairs) changes the cluster to an arachno type obtained by removing two vertices from a closo structure.

Let us consider the example of $(BH)_6$. The dianion $B_6H_6^{-2}$ has $6 + 1$ skeletal electron pairs and hence should have the closo structure 2 (figure 1). Experimentally $B_6H_6^{-2}$ is found to be a stable species having octahedral symmetry (Schaeffer et al 1965). The neutral isoelectronic carborane $C_2B_4H_6$ also has the closo structure (Grimes 1970). $B_6H_6^{-4}$ with 8 $(6 + 2)$ skeletal electron pairs should favour a nido structure. This tetra anion is unfavourable due to the large negative charge. The corresponding neutral carborane, $C_4B_2H_6$, has a nido structure 9 obtained by removing one axial group from a pentagonal bipyramid 4 (Groszek et al 1971; Franz et al 1972; Onak and Wong 1970). If
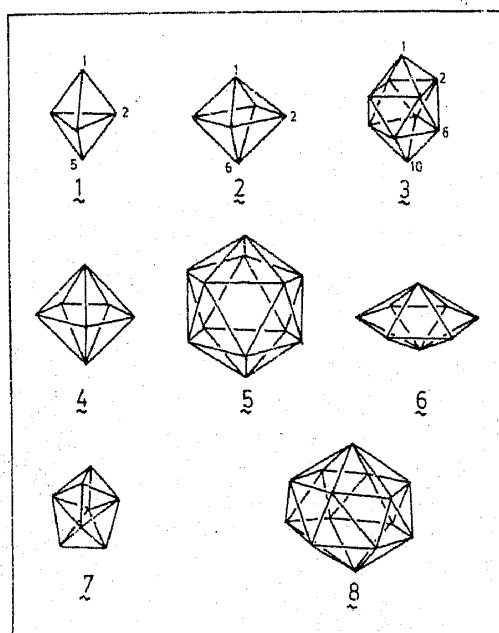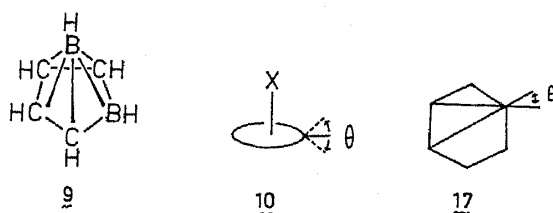

Figure 1.   Some of the polyhedra found commonly among borane and carborane structures.

two more electrons are added we get $B_6H_6^{-6}$ which should adapt an *arachno* structure expected from the $n+3$ skeletal electron pairs. Benzene, the neutral all carbon isoelectronic analog, certainly has an *arachno* structure obtained from a hexagonal bipyramid by removing two vertices. The $n+3$ skeletal electron pairs in benzene are distributed as follows: six in the six conventional C–C σ-bonds and three in the three delocalized π molecular orbitals. The latter three are the familiar delocalized π MOs of benzene giving rise to the $4n+2$ rule ($n=1$). Here begins the link between the Wades rule and the six-interstitial electron rule that we discuss below.

2.2 Six-interstitial electron rule

In the planar structure benzene the π delocalization is the major cause for unusual stability or aromaticity. The C–C σ bonds are neglected in the electron count. This electron counting rule may be extended to three-dimensional systems as follows. Let us divide the polyhedral molecules conceptually into rings and caps. Thus 9 may be divided into a five-membered C_4BH_5 ring and a BH cap. If two electrons are assigned to the C–C and C–B σ bonds of the ring there are 4 π electrons available in the ring. The BH group contributes 2 electrons to the ring cap binding. Thus there are six electrons available to bind the ring and the cap. What is even more interesting is that three delocalized π-type molecular orbitals are always obtained from the interaction of rings and caps. A qualitative interaction diagram (figure 2) indicates the stabilization involved. A similar diagram will be obtained for the interaction of one ring with two caps (Jemmis 1982). Since the electrons involved cannot be called π electrons, the descriptive term 'interstitial electrons' was suggested (Collins and Schleyer 1977). This concept of six-interstitial electron rule has been previously suggested and differs from the Wades rule in the following way. If a polyhedral molecule is divided into rings and caps the electrons corresponding to the ring σ bonds are removed from the skeletal electron pair count so that the favourable structure will have six interstitial electrons. Even though the six-interstitial electron rule has several advantages we concentrate on the handle it provides in deciding the best ring-cap combinations to form polyhedral molecules.

3.1 Six-interstitial electron rule and ring-cap matching

The interaction diagram in figure 2 points to three molecular orbitals that mainly determine the strength of the interaction between the ring and the cap. The lower the energy of these MOs the more stable the molecule becomes. What are the factors that determine the strength of this interaction? From perturbation theory we can anticipate two major factors—the overlap between the two interacting molecular orbitals and their energy difference (Heilbronner and Bock 1968). It is convenient if a criterion can be obtained to judge the energy and the overlap from the study of a set of molecules.
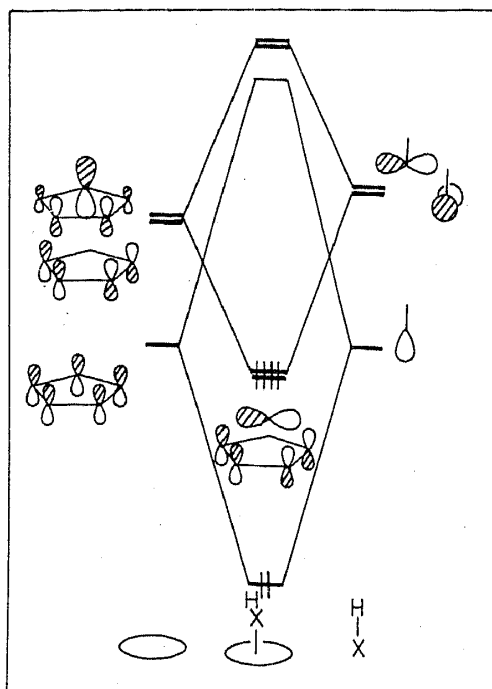
Figure 2. Schematic diagram showing the interaction of the ring and the cap orbitals. Only the lowest three π orbitals of a five-membered ring and the three frontier orbitals of an X–H group (X = B,C) are given. When the pyramidal molecule does not possess C_{5v} symmetry (*e.g.* 9) no orbitals will be degenerate. The six interstitial electrons occupy the three-stable delocalized levels given in the middle of the diagram.

3.2 Overlap matching

During a study of pyramidal molecules, 10, involving carbocyclic rings and caps from the elements of the first row it was seen that the ring-cap binding may be increased by the out-of-plane bending of the ring C–H bonds towards or away from the cap (Jemmis and Schleyer 1982). Walsh diagrams for the out-of-plane bendings indicated that the energy gain on bending comes mostly from the degenerate MOs indicated in figure 2. Since there was a gradation in the optimum out-of-plane bending with increasing ring size for a given cap and with cap having different diffuse orbitals for a given ring, the following explanation was suggested. The ring C–H out-of-plane bending is an attempt to increase the ring-cap overlap by rehybridization of the ring π orbitals. If the orbitals of the cap is too diffuse or the ring size is too small the C–H bonds are bent away from the cap so that the ring-cap overlap increases (figure 3a). The ring C–H bonds are bent towards the cap in the reverse situation (figure 3c). The magnitude of out-of-plane
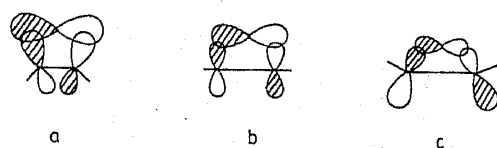

a   b   c

Figure 3. Ring B–H out-of-plane bending and increase of overlap in pyramidal molecules. (a) Small ring and cap with diffuse orbitals—B–H bonds bent away from the cap. (b) Optimum situation. (c) Large ring and cap with contracted orbitals—B–H bonds bent towards the cap.
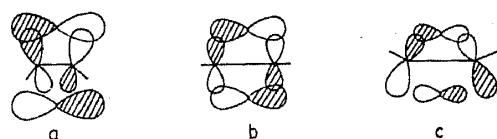
Figure 4. Ring-cap matching in bipyramidal systems. (a) Too small a ring, caps with diffuse orbitals. (b) Ideal combination (c) Too large a ring, caps with contracted orbitals.

bendings to increase the overlap cannot be very large as this weakens the ring C–H. The extent of out-of-plane bendings can be used as a criterion for ring-cap matching. Ideal ring cap combinations will have no out-of-plane ring hydrogen bending (figure 3b).

The out-of-plane bendings can be reproduced by any molecular orbital method that takes into account of overlap, starting with extended Huckel theory (Hoffmann 1963; Hoffmann and Lipscomb 1962). It is interesting to note here that the extended Huckel theory was developed initially to the study of polyhedral boranes and carboranes. However the problems of the type we discuss were not asked till now. When there are two caps, one from each face of a ring, whatever advantage available from ring out-of-plane bendings are lost because the stabilization gained on one face will be cancelled by the decreased interaction on the opposite face (figure 4). Even though the qualitative interaction diagram as well as the explanations for ring out-of-plane bendings remain the same for borocycles and carbocycles interacting with caps the exact magnitudes for borocycles will be different. These are estimated using MNDO calculations on pyramidal systems having six interstitial electrons (Dewar and Thiel 1977; Thiel 1980).

3.2a *MNDO calculations on pyramidal molecules.* Geometry optimizations were carried out on the anions 11–16 using the MNDO method with the symmetry restriction of C_{nv} for all structures (Thiel 1980). The results are shown in table 1. $B_4H_4^{-4}$ optimizes to T_d symmetry as anticipated. The θ column in the table gives the optimum out-of-plane bendings of the ring B–H bonds. Neither BH nor CH prefers to interact with the B_5H_5 ring but BH which has more diffuse orbitals has a smaller value of θ. Therefore given a choice between the BH and the CH groups B_5H_5 should prefer the BH group. The preference for B_4H_4 ring is less clear cut, both CH and BH caps give a planar arrangement of the ring. The B_3H_3 ring favours CH group as the cap with near zero B–H out-of-plane bendings. The out-of-plane bendings in $B_4H_4^{-4}$ is decided by symmetry—the expected tetrahedral geometry is indeed preferred by this ion. We shall mention here the uncertainties involved in applying the criterion of out-of-plane bendings to polyhedral molecules. The B–H ring out-of-plane bendings calculated here strictly applies to these specific molecules. A different isoelectronic system will have different ring B–B lengths and ring centre-cap distance which also affects the ring out-of-plane bendings. The extra charge present in the ions calculated here may mask the correct 'size' of the orbitals involved. A finer detail is missing in the interpretation based solely on the overlap matching. What are the energies of the ring and cap orbitals involved in these interaction? We compare these in the next section.

3.2b *The energy criterion.* The division of a polyhedral molecule into rings and caps is an artificial process, carried out only to understand the electronic structure of the parent molecule. The fragments themselves need not have independent existence. It is therefore difficult to find the energy levels of the fragments from experiments. It is not easy to obtain these from calculations. The most difficult problem is to decide on the

Table 1. Optimized geometries (Distances in A, Angles in degrees) and heats of formation (kcal/mol) of C_{nv} molecules 11–16 using MNDO method. X–H, the cap = BH or CH.

Molecule	a^a	b^a	B–B	B–H	X–H	X–B	θ^b	ΔH_f
$B_5H_5BH^{-4}$ (C_{5v}) 11	1·397	1·158	1·642	1·232	1·202	1·815	−17·4	580·2
$B_5H_5CH^{-3}$ (C_{5v}) 12	1·387	1·056	1·630	1·203	1·107	1·743	−22·3	276·7
$B_4H_4BH^{-4}$ (C_{4v}) 13	1·171	1·320	1·656	1·237	1·194	1·765	0·0	712·2
$B_4H_4CH^{-3}$ (C_{4v}) 14	1·154	1·242	1·632	1·201	1·094	1·696	0·0	361·0
$B_3H_3BH^{-4}$ (T_d) 15	0·973	1·379	1·687	1·220	1·220	1·687	19·5	866·3
$B_3H_3CH^{-3}$ (C_{3v}) 16	0·956	1·297	1·657	1·195	1·090	1·611	2·4	454·1

^{a} Ring centre-ring boron distance = a, ring center – Cap distance = b.
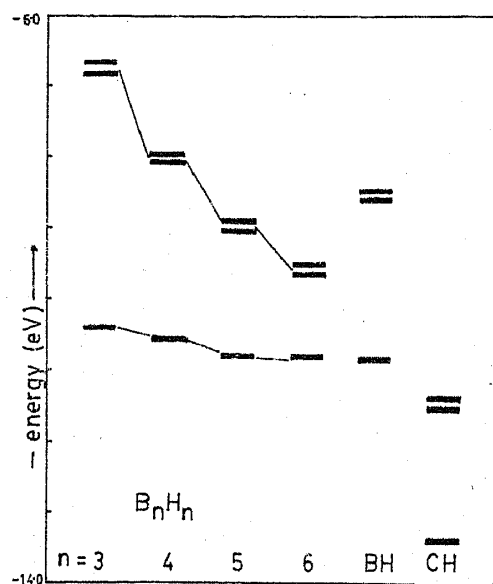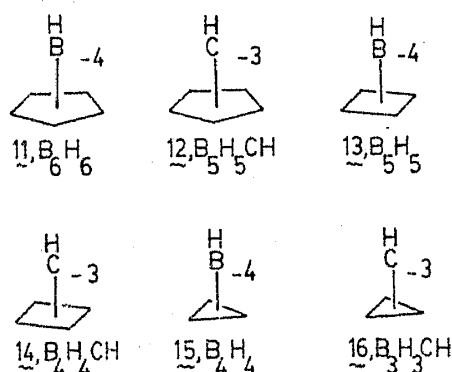^{b} Positive value indicates that ring hydrogens are bent away from the cap, see 10.

Figure 5. The energies of the lowest three π MOs of B_nH_n ring ($n = 3$–6) plotted with the frontier orbital energies of BH and CH groups, obtained from extended Huckel calculations.
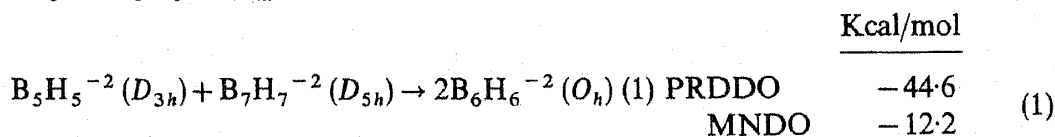
charges in the fragments. $B_5H_5CH^{-3}$ (C_{5v}) may be divided into $B_5H_5^{-6}$ and CH^{+3}, or any other charge separated combination. In any SCF method the molecular charge changes the energy levels. Therefore we have studied the relative energies of the fragment molecular orbitals using extended Huckel calculations (Hoffmann 1963). Since electron repulsion is totally neglected the energy levels will be independent of the occupancy of electrons. We calculated the ring and cap orbital energies using constant geometries and parameters given in the appendix. Despite the assumptions involved the extended Huckel method is found to reproduce structural details that depend mostly on overlap. Thus the out-of-plane bending angle θ of table 1 may be obtained with only a minor lateral shift by optimization of θ using standard geometries with the extended Huckel theory. Figure 5 shows the energy of the π MOs of $(BH)_n$ ring ($n = 3, 4, 5, 6$) and the frontier orbitals of BH and CH caps. It is clear that the energy considerations alone would favour the interaction of boron rings with the BH cap independent of the ring size. The ring π orbitals remains substantially higher in energy than that of the CH group orbitals.

4. Relative stabilities of $B_nH_n^{-2}$, $n = 5, 6, 7$ and 12

Among the polyhedral borane anions $B_6H_6^{-2}$ and $B_{12}H_{12}^{-2}$ stand out in stability (Muetterties 1975). In contrast $B_5H_5^{-2}$ and $B_7H_7^{-2}$ are not stable. Though prepared in solution the high reactivity of $B_7H_7^{-2}$ has prevented the detailed study of its structure (Klanberg *et al* 1967). Available experiments suggest a D_{5h} structure in solution. All attempts to make $B_5H_5^{-2}$ have been unsuccessful. Theoretical calculations of varying sophistication have confirmed these results (Dixon *et al* 1977). These are unusual observations especially because the corresponding neutral carboranes $C_2B_{n-2}H_n$ are all well known. Molecular size is not the determining point as $B_6H_6^{-2}$ is more stable than $B_7H_7^{-2}$.

$\underset{\sim}{11}, B_6H_6 \qquad \underset{\sim}{12}, B_5H_5CH \qquad \underset{\sim}{13}, B_5H_5$

$\underset{\sim}{14}, B_4H_4CH \qquad \underset{\sim}{15}, B_4H_4 \qquad \underset{\sim}{16}, B_3H_3CH$

As shown earlier we can conceptually construct these molecules step by step by the interaction of rings and cap. For example the interaction of a five-membered B_5H_5 ring with one BH cap gives the pyramidal B_6H_6 (11 C_{5v}). A second cap from the opposite side completes the pentagonal bipyramid, B_7H_7 (D_{5h}). Since the interaction of rings and caps always lead to three low lying three-dimensionally delocalized molecular orbitals six interstitial electrons are needed for ring-cap binding. $B_6H_6^{-4}$ (11, C_{5v}), $B_5H_5^{-2}$ (1, D_{3h}), $B_6H_6^{-2}$ (2, O_h) and $B_7H_7^{-2}$ (4, D_{5h}) satisfy the six-electron rule. What then makes $B_6H_6^{-2}$ (O_h) more stable than $B_5H_5^{-2}$ (D_{3h}) and $B_7H_7^{-2}$ (D_{5h})? Let us look at the criterion for ring cap matching developed in the earlier sections. The pyramidal arrangements obtained from these *closo* structures are 11, 13 and 15. The optimum out-of-plane ring B–H bendings for 11, 13, 15 using the MNDO method (table 1) shows that 11 and 15 has to change from the optimum out-of-plane bendings considerably in going to the corresponding *closo* structures. The differences in the resulting ring cap overlaps are shown schematically in figure 6. $B_5H_5^{-4}$ (13, C_{4v}) requires minimum change in the process of forming the *closo* structure $B_6H_6^{-2}$ (O_h). $B_5H_5^{-2}$ (D_{3h}) and $B_7H_7^{-2}$ (D_{5h}) have diminished ring cap interactions because the ring B–H out-of-plane bendings of $19.5°$ in $B_4H_4^{-4}$ (15) and of $17.4°$ in $B_6H_6^{-4}$ (11) have to be brought to $0°$. The extra stability of $B_6H_6^{-2}$ (O_h) is also seen in the exothermicity of equation (1).

$$\begin{array}{lll} & & \text{Kcal/mol} \\ B_5H_5^{-2} (D_{3h}) + B_7H_7^{-2} (D_{5h}) \to 2B_6H_6^{-2} (O_h) \ (1) & \text{PRDDO} & -44.6 \\ & \text{MNDO} & -12.2 \end{array} \qquad (1)$$

The heat of reactions given are by PRDDO (Dixon *et al* 1977) and by MNDO (Dewar and McKee 1978) methods.

Why should then the icosahedral $B_{12}H_{12}^{-2}$ that may be divided into two pyramidal
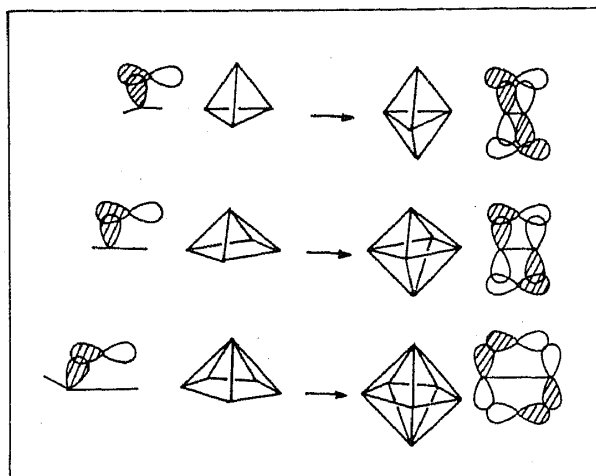
Figure 6. Pictorial representation of the changes of pyramidal systems in going to bipyramidal arrangements. Three and five-membered boron rings experience maximum change. There is minimum geometrical change needed in going from the square pyramid to the octahedron.

B_6H_6 (C_{5v}) units be unusually stable? The answer lies in the property of the icosahedron, one of the platonic solids (5). The geometry of the icosahedron dictates the ring B–H out of plane bendings in $B_{12}H_{12}^{-2}$ to be 22·6° as shown in the two-dimensional projection 17. This is only a few degrees higher than the out-of-plane bendings calculated for 11 (table 1). Two such pentagonal pyramidal units can be combined to give icosahedral $B_{12}H_{12}^{-2}$ with minimum change in the geometry of the individual fragments so that $B_{12}H_{12}^{-2}$ is very stable.

5. Ring-cap matching and relative stability of closo-carboranes

closo-Carboranes are neutral polyhedral molecules obtained by replacing two boron atoms from $B_nH_n^{-2}$ by two carbon atoms. The gross electronic structure of *closo*-carboranes is similar to that of *closo*-borane anions but there are number of isomers possible for a given molecular formula due to the presence of two different XH groups. Thus the problem of stability of carboranes are two-fold—the stability of a set of isomers of a given molecular formula and the relative stability of carboranes based on different closed polyhedra. The former question has been discussed in detail previously (Jemmis 1982). Only a brief account is given here.

With two CH groups several positional isomers are possible for each polyhedron. The number of selected polyhedra from figure 1 and the number of isomers possible (given in parenthesis as number of CH positions according to the accepted numbering of the polyhedra) are 1 (1, 2; 1, 3; 2, 3), 2 (1, 2 and 1, 6), 3 (1, 2; 1, 6; 1, 10; 2, 3; 2, 4; 2, 6; 2, 8; and 1, 10), 4 (1, 2; 1, 7; 2, 3; and 2, 4), 5 (1, 2; 1, 7 and 1, 12). Some of these isomers are not known experimentally. The concept of ring-cap matching based on the out-of-plane bendings of 11–16 (table 1) can be applied to the *closo* carboranes. Following the arguments developed in § 4 we can distinguish the various isomers as having either CH or BH groups interacting with three, four or five membered rings. With three-membered rings C–H groups will be the ideal caps because in the *closo* structure the B_3H_3 ring will be planar. Experimentally $1,5$-$C_2B_3H_5$ is found to be the most stable

$C_2B_3H_5$ isomer (Onak 1982). With five-membered ring neither B–H nor C–H is especially good, but the ring B–H out-of-plane bending is larger for 12 than for 11 so that BH forms a better cap than CH for a five membered ring. Accordingly 2,3- and 2,4-$C_2B_5H_7$ are more stable than 1,7-$C_2B_5H_7$. In fact all attempts to prepare 1,7-$C_2B_5H_7$ have been unsuccessful so far. It is also possible to infer that 2,3- and 2,4-$C_2B_5H_7$ will be more favourable compared to $B_7H_7^{-2}$ for the following reason. The five-membered ring $C_2B_3H_5$ involved in the former two molecules will be smaller in size than the B_5H_5 ring of $B_7H_7^{-2}$ due to shorter B–C and C–C bond length as opposed to B–B bond length. The unusual stability of the icosahedral carboranes $C_2B_{10}H_{12}$ also follows from this. The out-of-plane B–H bending in 12 is almost identical to the 22·6° dictated by an ideal icosahedron. Experimentally the 1,12-$C_2B_{10}H_{12}$ is the most stable polyhedral carborane. Since every vertex in the icosahedron is equivalent, clear-cut predictions about their isomer stabilities cannot be made based on the ring-cap matching criterion alone.

With four-membered rings the preference of B–H or C–H as cap is not very clear; the rings in 13 and 14 are nearly planar. Therefore we can anticipate a small energy difference between the 1,2-$C_2B_4H_6$ and 1,6-$C_2B_4H_6$. Various theoretical calculations give a difference in energy of approximately 15 Kcal/mol (Dixon *et al* 1977; Dewar and McKee 1980). Experimentally the 1,2-isomer on heating is known to isomerize to the 1,6-isomer (Onak *et al* 1964).

Do the various dicarbacarboranes parallel the relative stabilities found in $B_nH_n^{-2}$. Our qualitative analysis shows that there are important changes brought to the stabilities of various polyhedral arrangements by the substitution of two B–H groups by two C–H groups. $B_5H_5^{-2}$ (D_{3h}), for example, has not been prepared while the corresponding 1,5-$C_2B_3H_5$ is a stable molecule. This can be attributed to the less diffuse orbitals of the C–H cap needed for the three membered B_3H_3 ring. $B_7H_7^{-2}$ (D_{5h}) is a very reactive species, but the corresponding carborane 2,4-$C_2B_5H_7$ is very stable. Here the B–H capping groups are not replaced. The C–H groups form part of the ring. This reduces the size of the five membered ring (B_5H_5 vs $C_2B_3H_5$) so that there is better matching between the ring and the cap. The readers may note that substitution of BH group by CH group need not always be stabilizing. The 1,7-$C_2B_5H_7$ (D_{5h}) is expected to be less stable than $B_7H_7^{-2}$ (D_{5h}). The B–H caps do not have sufficiently diffuse orbitals to have optimum interaction with five-membered B_5H_5 ring. The replacement of these caps by C–H groups having still contracted orbitals should reduce the ring-cap interaction. Further 1,7-$C_2B_5H_7$ has not been synthesized.

6. Relative stabilities of nido-carboranes

The concept of the compatibility of orbitals of the rings and caps can be applied to predict the stable isomers of nido carboranes. Let us consider a series of *nido* structures based on pentagonal pyramid- $C_5BH_6^+$, $C_4B_2H_6$, $C_3B_3H_7$, $C_2B_4H_8$ and CB_5H_9. They have six interstitial electrons if the hydrogens present in addition to the six X–H groups are counted as bridging the B–B bonds. Each of these has a choice of a BH or a CH group to be made as the cap. Experimentally a BH group is present as the cap in all of them (Onak 1982). This has been attributed to the hypothesis that carbon prefers a position of lower coordination (Williams 1976). The concept of optimization of overlap by the ring-cap matching provides a theoretical explanation for this preference. The

overlap of orbitals of a B–H cap and of a five-membered ring is more favourable than that between a CH cap and a five membered ring. Similar arguments can be used for nidoboranes based on four membered rings. The preferences here are not very distinct for BH and CH as the out-of-plane ring B–H bendings in 13 and 14 are nearly zero.

7. Conclusions

Polyhedral borane anions and carboranes that obey the Wades rule or the six-interstitial electron rule are not equally stable. The relative stabilities of polyhedral borane anions $B_nH_n^{-2}$ can be understood from a ring cap matching criterion. MNDO calculations on $B_6H_6^{-4}$ (11, C_{5v}), $B_5H_5^{-4}$ (13, C_{4v}) and $B_4H_4^{-4}$ (15, T_d) shows that the B–H bonds of the B_nH_n ring are bent towards the capping BH group in 11 and away from it in 15. The B_4H_4 ring in $B_5H_5^{-4}$ (C_{4v}) is planar. These optimum out-of-plane bendings necessary for maximum ring-cap interaction will be maintained only in $B_6H_6^{-2}$ (O_h) and not in $B_5H_5^{-2}$ (D_{3h}) and $B_7H_7^{-2}$ (D_{5h}). Experimentally $B_6H_6^{-2}$ is found to be more stable than $B_5H_5^{-2}$ and $B_7H_7^{-2}$. The extra stability of $B_{12}H_{12}^{-2}$ arises from the geometry of the icosahedron which accommodates two pentagonal pyramid B_6H_6 (C_{5v}) units with minimum changes in the ring B–H out-of-plane bendings. The same criterion can be used to explain the relative stabilities of a set of isomers of carboranes of given molecular formula. $1,5\text{-}C_2B_3H_5$ (D_{3h}) obtained by replacing the two BH caps in $B_5H_5^{-2}$ (D_{3h}) is very stable because of the more contracted orbitals of the CH group. Similarly $2,4\text{-}C_2B_5H_7$ (C_s) is very stable in a pentagonal bipyramidal geometry compared to $B_7H_7^{-2}$ (D_{5h}). The two C–H groups in the ring reduces the ring size so that B–H caps can have better ring-cap interaction. These concepts can be extended to metalloboranes, metallocarboranes and H-bridged boranes. These results will be published elsewhere.

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Appendix

Extended Huckel calculations were carried out using the following set of Hii's (eV) and exponents: B(2s − 15·2, 2p − 8·5, ζ 1·300); C(2s − 21·4, 2p − 11·4, ζ 1·625); H (1s − 13·6, ζ 1·300). Fixed B–B (1·77 A) and B–H (1·15 A) distances were used for B_nH_n rings.

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