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Aromaticity, Orbital Size and Relative Stability of Closocarboranes

by E. D. JEMMIS

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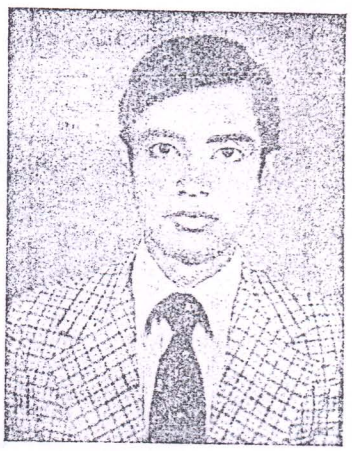

The electronic structure of benzene, the prototype of aromatic systems, is well known. The three delocalized bonding π molecular orbitals are occupied by six electrons. Let us see what happens when electrons are removed from benzene (Fig. 1). $C_6H_6^{+2}$, the dication of benzene, is not

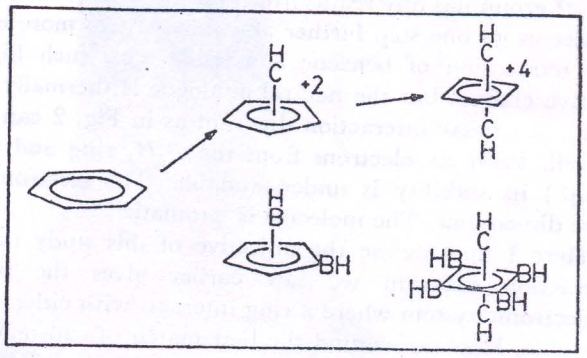

Fig. 1. Structure of $C_6H_6^{+2}$, $C_6H_6^{+4}$ and their neutral isoelectronic analogs.

observed in solution but several of its derivatives have been prepared (Hogeveen and Kwant, 1975). ^{13}C nmr studies indicate the C_{5v} symmetry of the cation. Corresponding neutral molecule obtained by replacing two carbon atoms by two boron atoms is well known (Franz *et. al.* 1972). The electronic structure of this pyramidal system can be easily understood from an orbital interaction diagram where the frontier orbitals of C_5H_5 group interact with those of the *CH* group to give three stabilized *MOs* (Fig. 2).

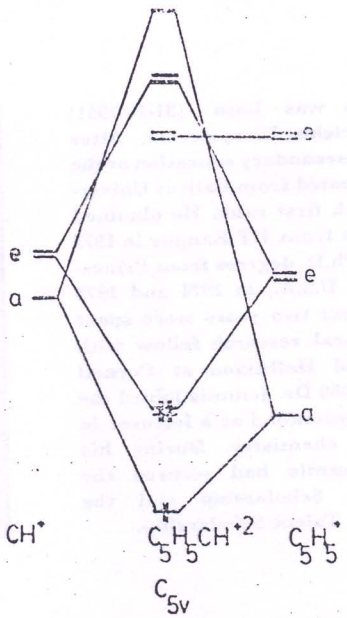

Fig. 2. Interaction diagram between the frontier orbitals of CH^+ (left) and of $C_5H_5^+$ (right) leading to the frontier orbitals of $C_6H_6^{+2}$ (C_{nv}, middle).

As the total number of electrons is six (four π electrons from $C_6H_6^+$ and two electrons from the CH^+—the division of charges here is arbitrary, only the $C_6H_6^{+2}$ group has any reality) the system should be stable.

Let us go one step further and remove two more electrons from C_6H_6. The tetracation of benzene is terrible with such high concentration of positive charge, but the neutral analogue is thermally very stable (Grimes, 1970). A similar interaction diagram as in Fig. 2 can be constructed here as well. With six electrons from the B_4H_4 ring and three each from *CH* groups) its stability is understandable. The electrons are delocalized in three dimensions. The molecule is 'aromatic'.

Here I may define the objective of this study more specifically. The interaction diagram we saw earlier gives the impression that any isoclectronic system where a ring interacts with either one or two caps may be stable. How do we find the best match of caps and rings to give stable arrangements. We shall consider a series of pyramidal molecules where the

ring hydrogens are free to move towards or away from the cap. Such out-of-plane bendings provide a criterion to make appropriate ring-cap combinations for pyramidal or in general polyhedral structures represented schematically in Fig. 3. In bicapped rings positional isomerism is possible (see the positions of *X* and *Y* in Fig 3). The best known examples are in the carborane

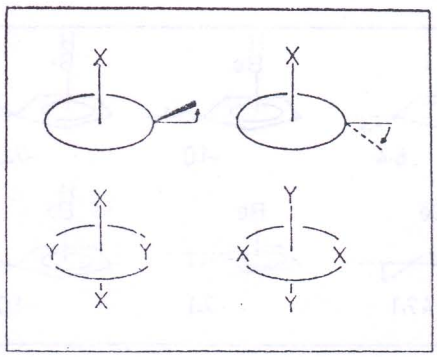

Fig. 3. Schamatic representation of mono and biscapped systems showing out-of-plane bending of the ring atoms and isomerism.

family where relative stabilities of isomers have been determined experimentally as well as theoretically, but no consistent explanation is available. Criterion of ring cap matching will be used to explain and predict relative stabilities of molecules.

We chose to study a series of isoelectronic pyramidal systems to obtain an idea of the out of plane bendings of the ring hydrogens. This leads us to the criterion we are looking for. Study of the following isoelectronic pyramidal systems (Fig. 4) using *ab initio* SCF MO theory with a minimal

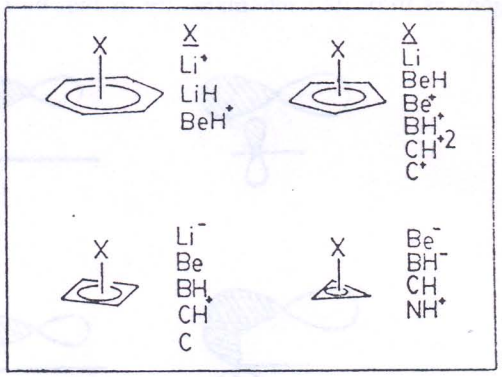

Fig. 4. Isoelectronic pyramidal structures (C_{nv}) studied theoretically.

Gaussian basis (STO-3*G*) showed that the ring hydrogens indeed bend towards or away from the cap depending on the ring size and the cap. More interestingly the direction and the rough magnitude of bending can

be reproduced using just about any MO method starting from the Extended Huckel approach. Let us see some of the results in greater detail. The top row in Fig. 5 shows the pattern of out-of-plane bending for a five membered ring with various caps. There is a gradation in going from Li to C. A similar gradation in ring hydrogen bending can be seen with ring size (lower row in Fig. 5) where the cap has been Be or BeH with appropriate charges.

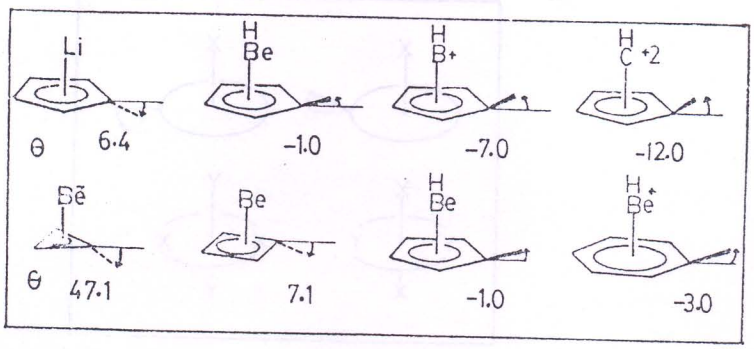

Fig. 5. Calculated variation of the out-of-plane bendings for Be (BeH) cap with 3, 4, 5 and 6 membered ring (bottom row) and for five membered ring with Li, BeH, BH, and CH caps (top tow).

Obviously the two parameters are (a) the ring size (b) the type of atom. Walsh diagrams for the bending of the ring hydrogens in several of these pyramidal molecules traced the bendings to the degenerate pair of orbitals that we saw as stabilized ones in the interaction diagram (Fig. 2). These orbitals result from a bonding combination of the degenerate π orbitals of the ring and the p orbitals of the cap. When the overlap between these sets of orbitals is not optimum either due to a large ring or due to the size of the orbital, the situation may be improved by out-of-plane bending of ring hydrogens as indicated schematically in Fig. 6. The rehybridization of the

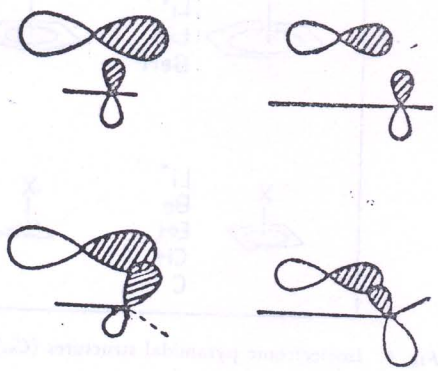

Fig. 6. Schematic representation of the consequences of out-of-plane bending of ring hydrogens in ring cap overlap. The poor overlap in the top two is improved in the bottom two.

the ring π orbitals will also decrease the binding of the hydrogens to the ring. The observed geometry will be a compromise between these factors. Bonding should be optimum when there is maximum overlap without any bending at all. Thus each ring will have an optimum cap and each cap an optimum ring.

Fig 7 gives a stable of out of plane bendings. Any row or column here shows the anticipated gradation: column corresponds to the change in the cap while row corresponds to the change in ring size. The preference of a ring for a specific cap and viceversa may be expressed quantitatively as reaction energies as in Figure 8. These are estimated using energies from a minimal basis calculation with complete geometry optimization within C_{nv} point group. Similar numbers are obtained from other methods tried. The large exothermicity of these reactions shows, despite the approximations involved, the validity of the order of preference for ring cap combinations. From table (Fig. 7) one can find that the favourable ring-cap combinations

Out-of-Plane Bending, θ°

CAP	RING			
	C_3H_3	C_4H_4	C_5H_5	C_6H_6
Li		17.2	6.4	2.5
Be	47.1	7.1	—0.9	—3.1
B	31.8	—1.2	—8.1	
C	19.5	—5.4	—11.7	
N	10.1			

Fig. 7. Table of ring out-of-plane bendings for the isoelectronic systems calculated using a minimal STO-3G basis set. All geometrical parameters were optimized within C_{nv} point group. +ve values indicate that the ring CH bonds are bent away from the cap.

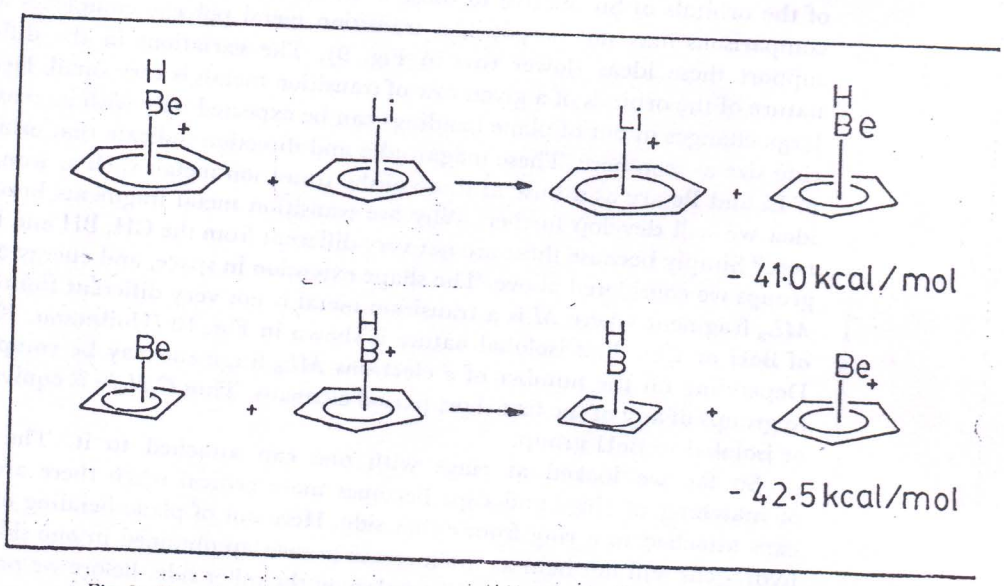

Fig. 8. Reaction energies showing the preference of a cap with diffuse orbitals for a larger ring (STO-3G energies).

have smaller out of plane bending of ring hydrogens. Let us see how these ideas compare to experiments. Fig. 9 gives some neutron, electron and

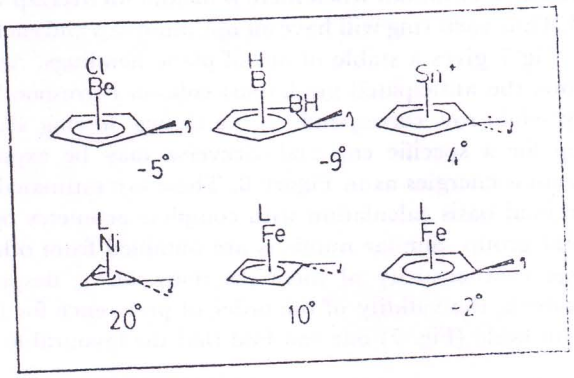

Fig. 9. Comparison of calculated out-of-plane bendings to observed values. Except in the molecules with BeCl and BH as caps, the rings were permethylated.

X-ray diffraction results taken from literature. Cyclopentadienyl beryllium chloride has been studied by low temperature X-ray diffraction (Goddard, 1979). The ring *C-H* bonds bend towards chlorine. The effect of a change in cap is evident. The difference in out of plane bending is not large, but one has to make allowance for the larger bond lengths in the ring (*C-C* vs *B-C*). The tin derivative is studied by X-ray crystallography (Kohl and Jutzi, 1981). The out of plane bending shows the expected diffuse nature of the orbitals of Sn relative to those of Be and boron. Even though direct comparisons may not be possible, transition metal polyene complexes also support these ideas (lower row in Fig. 9). The variations in the diffuse nature of the orbitals of a given row of transition metals is very small. Hence large changes in out of plane bendings can be expected only with increasing ring size as seen here. These magnitudes and direction indicate that orbitals of Li and Be are as diffuse as those of the transition metals such as iron, an idea we will develop further. Why are transition metal fragments brought here? Simply because these are not very different from the CH, BH and BeH groups we considered above. The shape extension in space, and energy of an ML_3 fragment where M is a transition metal is not very different from that of BeH or CH. This isolobal nature is shown in Fig. 10 (Hoffmann, 1981). Depending on the number of d electrons ML_3 fragment may be compared to groups of any of the first short period elements. Thus C_5H_5Fe is equivalent or isolobal to BeH group.

So far we looked at rings with one cap attached to it. The idea of matching of rings and caps becomes more critical when there are two caps attached to a ring from either side. Here out of plane bending of ring hydrogens will not help as the increase in overlap obtained in one side will be cancelled by the decrease in overlap on the other side. Before we proceed any further let us look at a family of compounds having the pattern of a ring

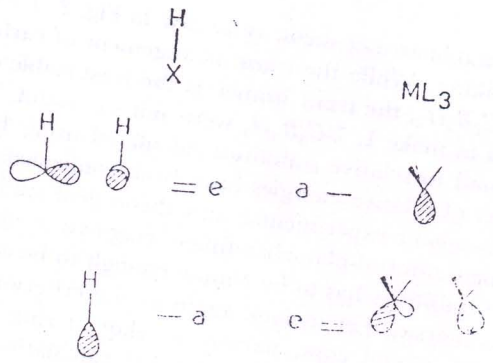

Fig. 10. Isolobal character of XH(X=first row atom) and ML_3 (M=transition metal) fragments. Thus BeH is isolobal to C_5H_5Fe or $Mn(CO)_3$ and CH^+ is isolobal to $Fe(CO_3)$.

with two caps attached from either side. The closocarboranes shown in Figure 11 form an excellent set of examples. The electronic structure of these molecules have been studied in detail but no consistent explanation has been offered for the relative isomer stabilities. They all have the six electrons

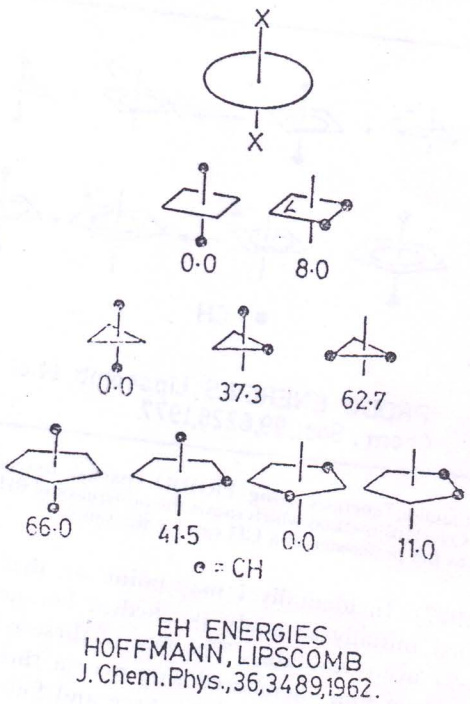

Fig. 11. Selected list of closocarboranes with relative energies. The values given are obtained by Extended Huckel Method, the first ones tried on these systems. Similar numbers were obtained experimentally and by numerous other theoretical methods.

needed to give a stable arrangement as we saw in Fig. 2. The relative isomer stabilities are striking. While the trans arrangement of carbons is favoured in $C_2B_4H_6$ and $C_2B_3H_5$, the trans isomer is the least stable one for $C_2B_5H_7$. In fact attempts to make 1, 7-$C_2B_5H_7$ were not successful. The numbers in Fig. 11 correspond to relative stabilities calculated using Extended Huckel Theory. This set of relative energies have been confirmed with only minor changes by subsequent experimental and theoretical studies. As we noted earlier regarding the out-of-plane bending of ring hydrogens, the explanation for the relative stabilities has to be simple enough to be a part of Extended Huckel approximation. Let us look again at the criterion for selecting the best match of rings and caps, namely overlap of ring and cap orbitals. Overlap is the only thing went in the *EH* calculations without drast c assumptions. Fig. 7 shows that if allowance is made for the longer bonds in carboranes compared to the all-carbon ring analogs of the table (*B-B*> *B—C*>*C—C*), the best overlap match for *BH* cap with borocycles will be in the order of ring size 5>4>>3≈6. Similarly for *CH* it will be 4≈3> 5>>6. Correctness of our judgement here is reinforced by the explanations it provides. But a more direct check of this may be obtained from the following reactions (Fig. 12) calculated using PRDDO energies (Dixon

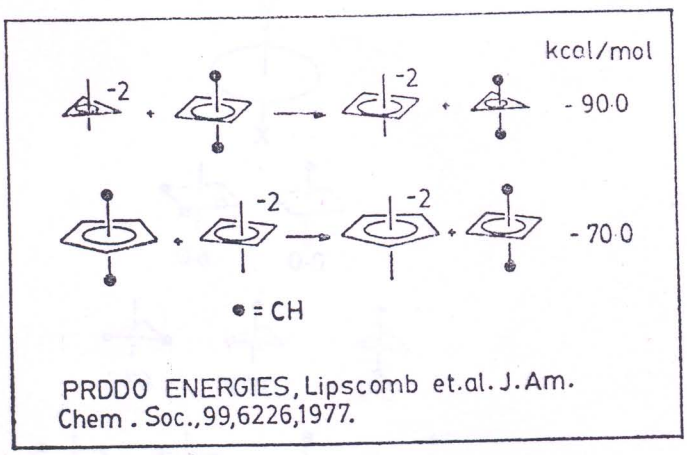

Fig. 12. Reaction energies using PRDDO (partial Retention of Diatomic Differential Overlap) method which shows the preference of BH cap for a larger ring compared to the preference of a CH cap for the same.

et. al. 1977). Incidentally I may point out that even though PRDDO was developed initially to study polyhedral boranes, such isodesmic reactions has never been evaluated. The first of these reactions indicates that a *BH* cap prefers a four membered ring over a three membered ring. In other words, given a choice between three and four membered rings *CH* would prefer the three membered ring while boron would prefer the four membered ring. The cap having a more diffuse orbital prefers a larger ring. The second equation compares in a similar way the preference of *BH* cap for a

five membered ring relative to a four membered ring. With this background let us look at the carboranes shown in figure 11. The axial or trans positions above and below a three membered ring will be more suitable for carbon than for boron cap and hence 1, 5—$C_2B_3H_5$ is more stable. Between 1, 6—$C_2B_4H_6$ and 1, 2—$C_2B_4H_6$ a similar preference is maintained but by a diminised magnitude. The relative stabilities have been explained by postulating that carbon prefers to be on the opposite sides of the molecule, leading to zero dipole moment. According to this argument 1, 7—$C_2B_5H_7$ must be the most stable isomer, but experimental and theoretical studies indicate that 2, 4 and 2, 3—$C_2B_5H_7$ are more stable. Concept of overlap-matching explains the observed stabilities. *BH* group will be a better cap than *CH* on a five membered ring so that 1, 7—$C_2B_5H_7$ is the least stable isomer.

Let us see why borane and carborane polyhedra based on six membered rings are unknown. Carbon or even boron does not have atomic orbitals diffuse enough to have sufficient overlap with the π type orbitals of a six membered boron ring. How can the situation be improved? Capping groups need more diffuse orbitals for better overlap. As we move to the left of the periodic table atomic orbitals become more diffuse. BeH or Li will be better caps to fit on a six membered ring. In order to keep the polyhedral systems isoelectronic, either electrons have to be added or boron atoms have to be replaced by carbon atoms. Alternatively transition metal fragments having the right number of frontier orbitals and electrons may be used as caps. As possible candidates we suggest the following (Fig. 13). Already a derivative of the dicobalt complex has been made (Maxwell *et al.*, 1977, Evans and Hawthorne, 1974).

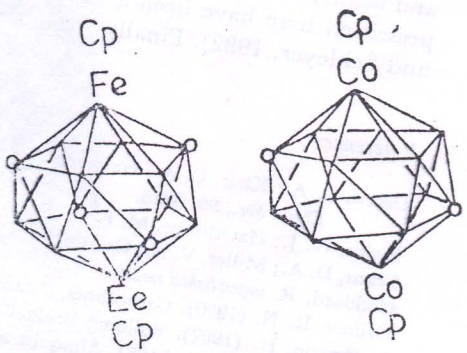

Fig. 13. Candidates for carboranes based on six membered rings.

What happens when the caps are not identical? The ring hydrogens may then bend out of the plane of the ring profitably. An interesting application of this will be stabilisation of an unusual coordination of nitrogen as in Fig. 14. If *NH* and BeH are selected as the caps the ring hydrogens can bend such that the bonding to both the caps will be increased. Ring hydrogens

will be bent away from the cap having more diffuse orbitals, rehybridizing the π orbitals as indicated schematically in figure 14. The atoms in the ring will have to be chosen so that it is isoelectronic to the closocarboranes. An acceptable ring will be a four membered ring, CB_3H_4.

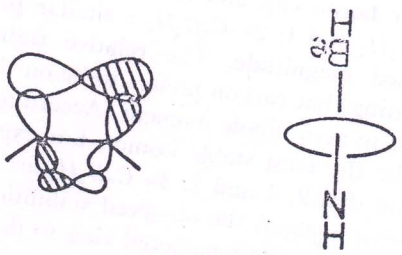

Fig. 14. The mismatch of the orbitals of the ring and cap can be used to advantage if the two caps are not identical as shown here.

We shall conclude by mentioning a mechanistic possibility arising out of these concepts in organic chemistry. The 1, 2-hydrogen shift of vinyl cations is found to be very fast, most probably passing through the least motion pathway. In cyclic vinyl cations such 1, 2-hydrogen shifts may not take this path; in the transition state (or intermediate: still there is a controversy that the bridged form may be the most stable arrangement in parent vinyl cation) the proton may prefer to attach itself to the unchanged orbital if θ is sufficiently large. Preliminary calculations show this to be true and experimental attempts to prove this will be rewarding (Sarma, 1982).

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