by both theory and experiment. Topological charge stabilization is a useful generalizing principle for understanding the relative stabilities of individual molecules within structural classes.

Predictions of Relative Stabilities among Series of Carborane Isomers by the Criterion of Topological Charge Stabilization

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Abstract: We have used topological charge stabilization considerations to predict the qualitative ordering of stabilities of positional isomers among the various classes of *closo*-carboranes, C$_2$B$_{n-2}$H$_n$, $5 \leq n \leq 12$. The rule of topological charge stabilization states that the positions of heteroatoms in a structure are related to the distribution of atomic charges that are determined by connectivity or topology for an isoelectronic, isostructural, homoatomic reference system. For charges we used Mulliken net atomic populations calculated from extended Hückel wave functions. The order of stabilities we predict agrees perfectly with what can be deduced from experimental data and matches reasonably well with the results of detailed calculations.

The *rule of topological charge stabilization* states that heteroatoms prefer to be located at sites that conform to the pattern of relative electron densities determined by connectivity or topology in an isoelectronic, isostructural, homoatomic system that we call the *uniform reference frame*.[1] An example from planar conjugated molecules is the series of thienothiophene positional isomers (**1–4**). For these structures the pentalene dianion (**5**) serves as
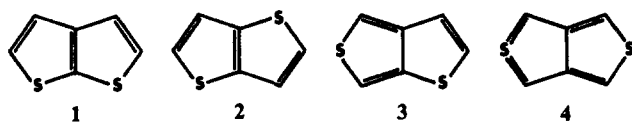
the uniform reference frame. Charge densities shown in **5** are π electron charge densities from simple Hückel calculations.
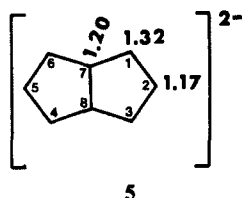
The largest charge densities in **5** are at equivalent positions 1, 3, 4, and 6. Therefore, placement of electronegative heteroatoms at these positions would be favored. It follows, then, that structures **1** and **2** would be expected to be the most stable isomers. **3** somewhat less so, and **4** the least stable, an ordering that agrees with the known reactivities and calculated resonance energies of the thienothiophenes.[1]

Although the relative thermodynamic stabilities of positional isomers are surely determined by relative total energies of the individual molecules, the rule of topological charge stabilization, focusing on a single common homoatomic reference structure, can

point out what is right or wrong with a particular heteroatomic structure, and it allows one to order quickly the relative stabilities of a group of heteroatomic positional isomers. Simple first-order perturbation theory relates charge density distributions to total energy differences.[2]

The concept of topological charge stabilization was introduced as early as 1950 when Longuet-Higgins, Rector, and Platt[3] pointed out that the locations of nitrogens in porphine are those corresponding to positions of high π charge densities in the corresponding isoelectronic hydrocarbon. Meutterties and Hoffmann accounted for the structure of PCl$_3$F$_2$, with axial fluorines and equatorial chlorines, as a result of charge distributions established by topology in PF$_5$.[4,5] Gimarc[6] and Burdett[7] have discussed the arrangement of heteroatoms in linear and bent triatomic molecules and ions. Burdett mentioned charge densities calculated for a homoatomic reference structure as the basis for explaining the different positions taken by elements from groups VA (15)[55] and VIA (16)[55] in S$_4$N$_4$ and P$_4$S$_4$.[8] Gimarc has surveyed the structures of a large collection of planar conjugated systems.[1] Finally, Gimarc and Ott have used the rule of topological charge stabilization to rationalize the structures and properties of a group of cage-type molecules related to adamantane.[2,9] Only in these most

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recent works has the concept been used to systematize information about the structures and relative stabilities of large classes of related molecules.

For charge patterns in 3-dimensional structures we have used Mulliken net atomic populations calculated from extended Hückel wave functions.[10] Although these values are admittedly quantitatively poor, their use here is acceptable because we seek qualitative conclusions. To simplify the interpretation of charges we have introduced *normalized charges* that sum to zero even for ions.[2]

Carboranes

In this paper we show how the rule of topological charge stabilization can be used to predict the relative stabilities of the positional isomers of the well-known *closo*-carboranes, $C_2B_{n-2}H_n$, where $5 \leq n \leq 12$. The structures of these molecules are closed polyhedra with triangular faces, carbon and boron atoms occupying cage vertices and each bearing an *exo*-hydrogen. The coordination number or number of bonds issuing from each cage vertex, but not counting the bond to the *exo*-hydrogen, ranges from 4 to 6.

After predicting the order of stabilities of carborane positional isomers, we compare those predictions with experimental evidence for relative stabilities, with predictions based on empirical valence rules and with stability orders obtained from total molecular energies calculated with various levels of molecular orbital theory. Several other methods have previously been used to explain the relative stabilities of these compounds. In the 1960s, as new carboranes were prepared and their structures elucidated, Williams and co-workers developed a set of valence rules to rationalize the structures of these compounds.[11-13] The most important of these empirical valence rules are (a) carbon atoms prefer locations in which they form the fewest numbers of bonds and (b) the two carbon atoms prefer to be as far apart as possible. Rule a seems to take precedence over rule b. These rules can be rationalized from traditional valence concepts. Carbon is more electronegative than boron. More electronegative elements tend to form fewer bonds with less electronegative atoms in order to do less electron sharing, suggesting rule a. Since like charges repel, the carbon atoms minimize repulsions by being as far apart as possible, giving rise to rule b. A somewhat weaker expression of rule b says that, consistent with rule a, carbon atoms take up positions so as to maximize the number of C–B bonds. More recently Jemmis has proposed a "six-electron rule" and ring cap matching to explain the relative stabilities of carborane positional isomers.[14]

Williams' valence rules are empirically based topological rules that were developed specifically to rationalize the observed structures of the *closo*-carboranes. The rule of topological charge stabilization is more general in that it can be used to account for or predict the relative stabilities of isomers of structural classes of any sort, planar rings, chains, complexes or cages that contain atoms of any element, as well as the entire series of *closo*-carboranes.

To use the rule of topological charge stabilization, reference frames are required that simulate the structures of the *closo*-boron hydrides, $B_nH_n^{2-}$, $5 \leq n \leq 12$, which are the homoatomic analogues of the carboranes. The hydrogen atoms of the *closo*-boron hydrides and carboranes involve simple two-center, two-electron bonding. When these *exo* hydrogens are included in extended Hückel calculations, the electron charge is more evenly distributed over the entire structure than for an otherwise bare main-atom frame. To emphasize charge differences and to simplify the calculations we have omitted the hydrogens from the references frames and used carbons rather than borons to construct the homoatomic model. The resulting bare carbon frames are isoelectronic with the *closo*-boron hydrides and the corresponding carboranes. For example, C_5^{2-} serves as the uniform reference

frame from which to model charge distributions in $B_5H_5^{2-}$ and to base conclusions concerning the relative stabilities of $C_2B_3H_5$ positional isomers.

Except for $B_8H_8^{2-}$, $B_9H_9^{2-}$, and $B_{11}H_{11}^{2-}$, the structures of the *closo*-boron hydrides are reasonably well represented by polyhedra with uniform edges, or in chemical terms, bonds of equal length. In our calculations we took these equivalent bonds to have the length of a normal carbon–carbon single bond, 1.54 Å. The structures of $B_8H_8^{2-}$, $B_9H_9^{2-}$, and $B_{11}H_{11}^{2-}$ do not permit all bond distances to be equal, and for these reference frames we took distances related to the actual structures of the boron hydrides as determined by X-ray diffraction studies.[15-17] The scheme for numbering atoms in the accompanying diagrams follows IUPAC recommendations.[18]

$B_5H_5^{2-}$ **and** $C_2B_3H_5$. The simplest *closo*-carborane $C_2B_3H_5$ has a trigonal-bipyramidal structure. The corresponding boron hydride $B_5H_5^{2-}$ has never been prepared. The uniform reference frame (6) for the trigonal-bipyramidal structure shows the normalized charges to be negative at the apical positions and positive at the equatorial sites. Topological charge stabilization says that electronegative heteroatoms, the carbons in $C_2B_3H_5$, prefer to be at
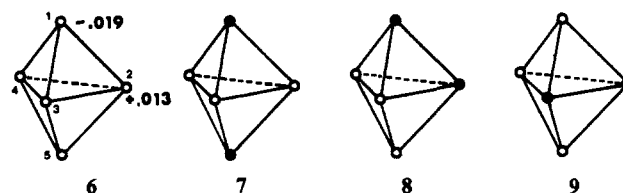
sites where electron density is already greatest in the uniform reference frame. Therefore, the three possible isomeric carboranes should follow the decreasing order of stability: $1,5$-$C_2B_3H_5$ (7) $> 1,2$- (8) $> 2,3$- (9). The $1,5$-isomer shows a perfect match between the negative charges in the reference frame and the location of the more electronegative heteroatoms. The $1,2$-isomer complies in only one of the two positions, while in the $2,3$-isomer neither carbon occupies a site of greater electron density. The predicted order of relative stabilities agrees with what is known experimentally about $C_2B_3H_5$ isomers. The $1,5$-isomer is the only known unsubstituted isomer.[19] The $1,2$-isomer exists only as the methyl-substituted form,[20] and the $2,3$-isomer has not been reported in any form.

The empirical valence rules of Williams predict the same order of stabilities. Apical positions 1 and 5 are three-coordinate, while the equatorial sites 2, 3, and 4 are four-coordinate. Cabon atoms occupying positions 1 and 5 would have lower coordination number and be as far apart as possible. The $1,2$-isomer would have adjacent carbons one of which would be in the prefered three-coordinate position. The $2,3$-isomer would have two adjacent, four-coordinate carbons, offending both rules that govern preferred stability.

$B_6H_6^{2-}$ **and** $C_2B_4H_6$. $B_6H_6^{2-}$ has octahedral geometry. The six vertices of an octahedron are equivalent so the charges on the atoms of the C_6^{2-} reference frame must be identical. Topological charge stabilization suggests that the introduction of electronegative heteroatoms will destabilize such a system. Nevertheless, both of the two possible carborane isomers, $1,6$-$C_2B_4H_6$ and $1,2$-$C_2B_4H_6$, are known.[21-23] Consider the atomic charges that

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result when a single nitrogen heteroatom is introduced into one of the equivalent positions of the C_6^{2-} octahedral reference frame to make C_5N^-. In this perturbed system (10) charges are no longer uniform and topological charge stabilization ideas can be used to predict the preferred locations for the second heteroatom. The perturbing heteroatom at position 1 (indicated by • in 10) produces another large negative charge at position 6. Therefore, 1,6-$C_2B_4H_6$

10   **11**   **12**
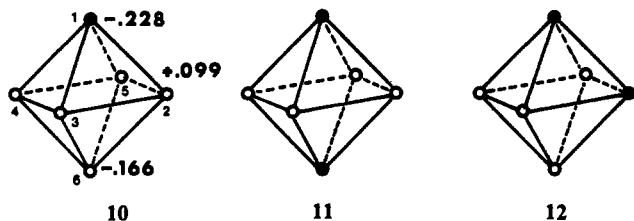
(11) should be more stable than the 1,2-isomer (12). This prediction agrees with the experimental report that the 1,2-isomer quantitatively rearranges to the 1,6-isomer on heating at 250 °C.[24] Other thermal stability observations also suggest that the 1,6-isomer is the more stable.[21]

$B_7H_7^{2-}$ **and** $C_2B_5H_7$. The structures of $B_7H_7^{2-}$ and its heteroatomic analogue, $C_2B_5H_7$, are pentagonal bipyramids.[25] The charge distribution for the uniform reference frame (13) shows the equatorial positions to be favored for replacement by more electronegative heteroatoms. For the pentagonal bipyramid there are four possible isomers of $C_2B_5H_7$: 1,2-, 1,7-. 2,3-. and 2,4-. On the basis of the charge distribution of the uniform reference frame (13), the 2,3- and 2,4-isomers should be the most stable

13   **14**
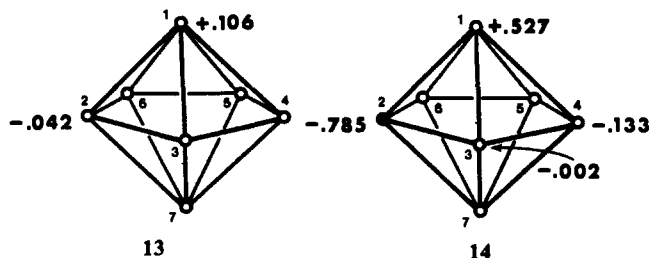
but otherwise of comparable stability. Since the equatorial sites of the uniform reference frame are already negative, we chose to introduce a perturbing electronegative heteroatom at one of them, position 2. This produced a redistribution of charge (14), from which it can be seen that equatorial positions nonadjacent to the perturbing heteroatom are more negatively charged than the adjacent positions. giving the following order of stabilities: 2,4- > 2,3- > 1,2- > 1,7-. Only the 2,4-isomer has been prepared.[26]

$B_8H_8^{2-}$ **and** $C_2B_6H_8$. The shape of $B_8H_8^{2-}$ in the solid state is that of a bisdisphenoid or a slightly distorted dodecahedron having D_{2d} symmetry.[27] Other structures are suspected in solution.[28] In the uniform reference frame (15) the four-coordinate positions 1, 2, 7, and 8 are all equivalent as are the five-coordinate sites 3, 4, 5, and 6. The four-coordinate sites are negative with respect to the five-coordinate sites, making the 1,2- and 1,7-carborane isomers preferred but indistinguishable. The introduction of a perturbing electronegative heteroatom at position 1 redistributes charge (16). Now positions 1 and 7 are the most negative. making 1,7-$C_2B_6H_8$ the most stable of all possible isomers. Indeed, of the six possible isomers only 1,7-$C_2B_6H_8$ is known.[29]

$B_9H_9^{2-}$ **and** $C_2B_7H_9$. $B_9H_9^{2-}$ and $C_2B_7H_9$ have structures of a tricapped trigonal prism (17).[17,30] Six carborane isomers are

15   **16**

17   **18**   **19**
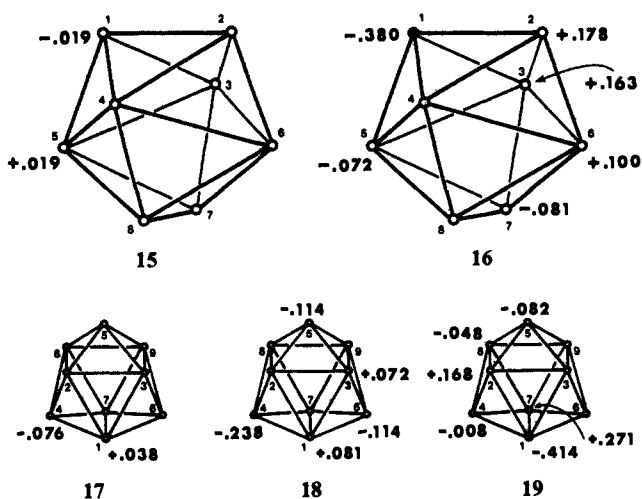
possible. The six vertices of the prism are equivalent and five-coordinate. The three verticies (4, 5. and 6) that cap the rectangular faces of the prism are equivalent and four-coordinate. and they carry negative charge with respect to the five-coordinate sites. Therefore, the 4,5-$C_2B_7H_9$ isomer should be the most stable and in fact it is the only isomer known experimentally. In other work it became important to try to order the stabilities of all six $C_2B_7H_9$ isomers, so we repeated charge density calculations with a single perturbing, more electronegative heteroatom first at a cap, position 4 (18). and then at a prism vertex, position 1 (19). The resulting stability orders are as follows:

unperturbed: 4,5- > 3,4- ∼ 1,4- > 1,8- ∼ 1,2- ∼ 1,7-

perturbed at 4: 4,5- > 3,4- > 1,4-

perturbed at 1: 1,5- (=3,4-) > 1,8- > 1,4- > 1,2- > 1,7-

For the cap (4) perturbed results we can order only three isomers because one heteoatom must always be at a cap. There are five isomers for which at least one atom is at a prism vertex. Since the unperturbed results indicate that a single heteroatom perfers to be at a cap rather than at a prism vertex, in the combined results below we give precedence to the cap perturbed order over the prism vertex perturbed order.

combined: 4,5- > 3,4- > 1,4- > 1,8- > 1,2- > 1,7-

$B_{10}H_{10}^{2-}$ **and** $C_2B_8H_{10}$. The atoms of $B_{10}H_{10}^{2-}$ are arranged in a bicapped square antiprism (20).[31,32] This symmetrical structure has only two different kinds of atoms. Square face capping positions 1 and 10 are negative with respect to the other eight mutually equivalent sites that define the antiprism. Of the seven positional isomers that are possible for the carborane $C_2B_8H_{10}$. three isomers or their derivatives are known: 1,10-, 1,2-. and 1,6-. From the distribution of charges in 20 the rule of topological

20   **21**   **22**
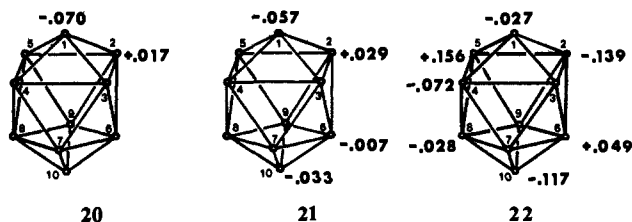
charge stabilization predicts the 1,10-isomer to be the most stable followed by the 1,2- and 1,6-isomers which would have comparable stabilities. In order to distinguish between the 1,2- and 1,6-isomers we introduced a perturbing electronegative heteroatom at position

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Table I. Structures and Relative Stabilities of Carboranes, $C_2B_{n-2}H_n$

related boron hydride	geometry	known carboranes in order of decreasing stabilities	predicted order of isomeric stabilities
$B_5H_5^{2-}$ (6)	trigonal bipyramid	$1,5\text{-}C_2B_3H_5 > 1,2\text{-}C_2B_3H_5{}^a$	1,5- > 1,2- > 2,3-
$B_6H_6^{2-}$ (10)	octahedron	$1,6\text{-}C_2B_4H_6 > 1,2\text{-}C_2B_3H_5{}^a$	1,6- > 1,2-
$B_7H_7^{2-}$ (13, 14)	pentagonal bipyramid	$2,4\text{-}C_2B_5H_7 > 2,3\text{-}C_2B_5H_7$	2,4- > 2,3- > 1,2- > 1,7-
$B_8H_8^{2-}$ (15, 16)	dodecahedron	$1,7\text{-}C_2B_6H_8$	1,7- > 1,5- > 1,6-
$B_9H_9^{2-}$ (17, 18, 19)	tricapped trigonal prism	$4,5\text{-}C_2B_7H_9$	4,5- > 3,4- > 1,4- > 1,8- > 1,2- > 1,7-
$B_{10}H_{10}^{2-}$ (20, 21, 22)	bicapped square antiprism	$1,10\text{-}C_2B_8H_{10} > 1,6\text{-}C_2B_8H_{10} > 1,2\text{-}C_2B_8H_{10}{}^a$	1,10- > 1,6- > 1,2- > 2,4- > 2,7- > 2,6- > 2,3-
$B_{11}H_{11}^{2-}$ (23)	octadecahedron	$2,3\text{-}C_2B_9H_{11}$	2,3- > 2,10- > 2,4-
$B_{12}H_{12}^{2-}$ (24)	icosahedron	$1,12\text{-}C_2B_{10}H_{12} > 1,7\text{-}C_2B_{10}H_{12} > 1,2\text{-}C_2B_{10}H_{12}$	1,12- > 1,7- > 1,2-

^{a} Known only as methyl-substituted derivative.

1 of the uniform reference frame. The resulting modified charge distribution (21) shows positions 6, 7, 8, and 9 to be negative with respect to 2, 3, 4, and 5. Therefore, the relative stabilities of the $C_2B_8H_{10}$ isomers should be as follows: 1,10- > 1,6- > 1,2-. These conclusions are in accord with experimental results. Two indicators of this stability order are the ease of degradation by basic reagents and the quantitative rearrangement of different isomers when heated. The 1,6-$C_2B_8H_{10}$ isomer is easily degraded by ethanolic KOH or piperidine while the 1,10-isomer is highly resistant to such reagents.[33] Furthermore, pyrolysis of the 1,2-isomer leads to the 1,6-isomer[34] which upon further pyrolysis leads quantitatively to the 1,10-isomer.[35] In order to rank the stabilities of the other four carborane isomers, 2,3-, 2,4-, 2,6-, and 2,7-, yet another perturbation calculation of charge densities is needed, this one (22) with the heteroatom located at position 2. These suggest the order 2,4- > 2,7- > 2,6- > 2,3-. Giving precedence to conclusions based on the unperturbed calculations and those with the perturbing heteroatom at position 1 leads to the final combined ordering of isomer stabilities: 1,10- > 1,6- > 1,2- > 2,4- > 2,7- > 2,6- > 2,3-.

$B_{11}H_{11}^{2-}$ **and** $C_2B_9H_{11}$. The structure of $B_{11}H_{11}^{2-}$ is octadecahedral, related to a bicapped pentagonal antiprism with one of the antiprism vertices removed (23). In this structure of rather

23
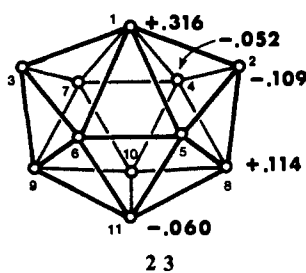
low C_{2v} symmetry, position 1 is unique, positions 2 and 3, 8 and 9, and 10 and 11 constitute pairs of equivalent atoms, while positions 4, 5, 6, and 7 are equivalent. There are 20 different positional isomers possible for $C_2B_9H_{11}$. From the charge distribution in the uniform reference frame (23), one can see that the most stable isomer should be 2,3-$C_2B_9H_{11}$. Indeed, only the 2,3-isomer is known in this class.[16,36]

$B_{12}H_{12}^{2-}$ **and** $C_2B_{10}H_{12}$. $B_{12}H_{12}^{2-}$ has icosahedral geometry and its charge distribution is uniform. Topological charge stabilization predicts that the introduction of a heteroatom into the uniform reference frame is destabilizing. Still, all three of the possible isomers of $C_2B_{10}H_{12}$ exist: 1,2-, 1,7- and 1,12-$C_2B_{10}H_{12}$.[37-39]

Introduction of a perturbing heteroatom in position 1 produces the charge arrangement shown in **24**, with four different kinds of sites. Locating carbons at the most negative sites produces

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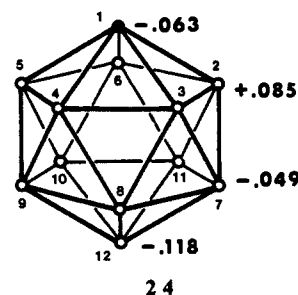
the following order of stability for the $C_2B_{10}H_{12}$ isomers: 1,12- > 1,7- > 1,2-. This is in agreement with thermal data which show that 1,2-$C_2B_{10}H_{12}$ rearranges upon heating to 1,7-$C_2B_{10}H_{12}$ which upon further heating rearranges to the 1,12-isomer.[40]

Comparisons with Other Work

The relative stabilities among carborane positional isomers predicted by using the rule of topological charge stabilization are summarized in Table I. Experimental heats of formation of these isomers are not available for direct verification of the predictions. However, experimental evidence concerning relative stabilities can be deduced from observed thermal rearrangements and the assumption that for cases in which only a single structure is known it is probably the form of lowest energy. This data has been mentioned in the previous section, and conclusions based on this empirical information are also summarized in Table I. The topological charge stabilization predictions agree perfectly with assessments based on available experimental evidence.

The empirical valence rule predictions of relative stabilities of carborane positional isomers have also been collected.[41] They also agree with experimental results, on which the rules were based. Topological charge stabilization and the empirical valence rules

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Table II. Relative Electron Densities at Individual Atoms in $B_nH_n^{2-}$ as Calculated by Different Methods

$B_nH_n^{2-}$	rel atomic charges	method (ref)
$B_5H_5^{2-}$ (6)	1 > 2	this work: EHMO (42): PRDDO (43)
$B_7H_7^{2-}$ (13)	2 > 1	this work: EHMO (42): PRDDO (43): MNDO (44)
$B_8H_8^{2-}$ (15)	1 > 3	this work: MNDO (44)
	3 > 1	PRDDO (43)
$B_9H_9^{2-}$ (17)	4 > 1	this work: PRDDO (43): MNDO (44)
$B_{10}H_{10}^{2-}$ (18)	1 > 2	this work: PRDDO (43): MNDO (44): NEMO (45)
$B_{11}H_{11}^{2-}$ (20)	2 > 10 > 4 > 8 > 1	this work
	2 = 4 > 10 = 8 > 1	MNDO (44)
	2 > 8 > 10 = 4 > 1	PRDDO (43)

Table III. Relative Stabilities of Carborane Isomers Based on Calculated Total Energies

carborane	rel stabilities	method ref
$C_2B_3H_5$	1.5- > 1,2- > 2.3-	EHMO (42): CNDO/2 (46): MNDO (47): PRDDO (43): STO-3G (49, 52): 4-31G (49)
$C_2B_4H_6$	1.6 > 1,2-	EHMO (42); PRDDO (43): INDO (50): STO-3G (48): extended Gaussian (50): minimal basis set STO (53)
	1.2- > 1.6-	CNDO/2 (46): NEMO (51)
$C_2B_5H_7$	2.4- > 2,3- > 1.2- > 1.7-	EHMO (42)
	2.4- > 2.3- > 1.7-	MNDO (47)
	2.3- > 2,4- > 1.2- > 1.7-	CNDO/2 (46)
$C_2B_7H_9$	no isomers compared	
$C_2B_7H_9$	no isomers compared	
$C_2H_8H_{10}$	1.10- > 1.6-	MNDO (47)
$C_2B_9H_{11}$	no isomers compared	
$C_2B_{10}H_{12}$	1,12- > 1.7- > 1.2-	PRDDO (43): CNDO/2 (46): INDO (50); MNDO (47)
	1,7- > 1,12- > 1.2-	EHMO (42)
	1.7- > 1,2- > 1,12	NEMO (51)

can make many predictions concerning the unknown higher energy isomers. It is not surprising that the two methods project a few differences in the order of stabilities among some of these higher energy isomers. For $C_2B_6H_8$, topological charge stabilization predicts the 1,5-isomer to be less stable than 1,7- but more stable than 1,6-. The empirical valence rules put the 1,2-isomer in this intermediate position. A few small differences in detail also exist between the two sets of predictions of relative stabilities among the possible but unknown higher energy isomers of the 9-, 10-, and 11-atom cages.

The empirical valence rules and the rule of topological charge stabilization are related but not equivalent. The traditional valence rules constitute an example of empirically based statements of topological rules. These rules are incomplete in that they depend on an unstated number of valence electrons that occupy the system of molecular orbitals and which therefore determine the distribution of electron density. There are many examples of pairs of systems with the same molecular structure but different numbers of valence electrons. Three such pairs are the following: pentalene and pentalene dianion,[1] porphine and B_8S_{16},[54] and normal adamantane-like molecules such as $(HC)_4S_6$ and those with fewer valence electrons such as $(HC)_4(BR)_6$.[2] For each of these pairs, differences in numbers of valence electrons produce differences in electron distributions calculated for an appropriate reference frame. These isostructural but non-isoelectronic systems do not necessarily share the same set of counting rules for preferred valency. Therefore rules derived empirically for one system may not be transferrable to others. In the carboranes, for example, carbon atoms prefer lower coordination sites than do borons, but in the cage-type molecule $(HC)_4(BR)_6$ the reverse is true. However, charge distributions for these systems can be easily calculated and used as a basis for locating atoms of different kinds within a given structure.

Topological charge stabilization and the empirical valence rules start from different points of view. Following the empirical valence rules one attempts to locate a pair of electronegative heteroatoms in a framework that presumably is homogeneous. Using the rule of topological charge stabilization one starts with a homoatomic framework that already has non-uniform charges as a result of topology. The fact that these systems already have sites of enhanced and diminished electron charge is not part of empirical valence theory, and yet it appears to be a principle of wide generality that directs the realization of particular arrangements of atoms within a given molecular structure.

Many molecular orbital calculations have been reported for the $B_nH_n^{2-}$ series and $C_2B_{n-2}H_n$ isomers. Their results generally lend support to the conclusions of the rule of topological charge stabilization. Let us begin by comparing charge densities. Ours were

calculated from wave functions obtained by the simplest of three-dimensional semiempirical molecular orbital methods carried out for a homoatomic model system without hydrogen substituents but having the same number of valence electrons and the same three-dimensional form as the carboranes under consideration. Such naiveté must surely be suspect. Yet our charge distributions are qualitatively the same as those for the $B_nH_n^{2-}$ series as obtained by EHMO,[42] PRDDO,[43] MNDO,[44] and NEMO[45] calculations. Table II compares the ordering of atomic charges for those $B_nH_n^{2-}$ species in which symmetry allows two or more atoms to have different charges. For the most part the agreement is remarkable. The reversal of charge order for $B_8H_8^{2-}$ by the PRDDO method might be a misprint. If so, disagreements would occur for only $B_{11}H_{11}^{2-}$, the least symmetric member of the series and with five different kinds of sites, but disagreement is not so serious as to lead to different predictions for the lowest energy isomer, based on charge density patterns. Thus, the charge densities we calculated for the simplest possible reference frame appear to be adequate for the job of predicting relative stabilities of isomers using the rule of topological charge stabilization. Although charge density patterns in $B_nH_n^{2-}$ have been reported previously, none of those authors has mentioned using those patterns to account for the relative stabilities of the isoelectronic carborane isomers $C_2B_{n-2}H_n$.

Various molecular orbital methods have been used to calculate total molecular energies of carborane isomers in order to establish their relative stabilities.[42,43,46-53] Table III summarizes the relative stabilities of carborane isomers based on calculated total energies. Comparing these orders with those in Table I, one sees that the rule of topological charge stabilization yields qualitative results as good as or better than the most rigorously calculated total energies. It is interesting to note that interpretations based on charges calculated from extended Hückel wave functions give better agreement with experiment on isomer stabilities than do total energies calculated from the same wave functions. An analysis of the successes and failures of these methods is beyond the scope of this paper, but we do note that applications of more rigorous theoretical methods to the problem of relative stabilities of positional isomers do not necessarily lead to better agreement with experiment.

Summary

We have used the extended Hückel method to generate a pattern of charge densities for a homoatomic reference frame that is isoelectronic and isostructural with a group of heteroatomic positional isomers. Why those charge distributions turn out as

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they do is in itself an interesting question that can be addressed by qualitative molecular orbital theory[6] and will be the subject of another study. The pattern of topologically determined charge densities in the homoatomic frame allowed us to order the relative stabilities of the heteroatomic isomers. For structures of particularly high symmetry, the charge densities in the homoatomic system were everywhere the same. In these cases we introduced a single heteroatom that sufficiently perturbed the system to allow accurate prediction of the location of the second heteroatom. The results summarized in Table I are in excellent agreement with experiment and with more detailed calculations. We have been able to make more predictions of relative stabilities of carborane positional isomers than can be confirmed with available experimental evidence or with total energies calculated by advanced molecular orbital methods. A remarkable feature of Table III is the lack of any calculations for two or more isomers for $C_2B_6H_8$, $C_2B_7H_9$, or $C_2B_9H_{11}$. We are now completing a series of ab initio SCF-MO calculations at the same level of basis set for the complete series $C_2B_{n-2}H_n$ and including several isomers in each

case. The results will be published elsewhere.

The rule of topological charge stabilization is easy to apply. Even such a crude method as the extended Hückel method is apparently adequate to produce the pattern of charge densities from which reliable predictions of structures and relative stabilities can be made. The predictions could be useful as a guide to future synthetic efforts. Topological charge stabilization can serve as a unifying principle for the organization or systemization of chemical information.

Angular Preferences of Intermolecular Forces around Halogen Centers: Preferred Directions of Approach of Electrophiles and Nucleophiles around the Carbon-Halogen Bond[1a]

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Abstract: During our studies of Se⋯Se interactions in selenides, it was observed that halogen atoms X of C-X bonds were engaged in both a "head-on" and a "side-on" fashion to Se atoms. To understand such interactions, we have analyzed the crystallographic environment around halogen centers and find that, in general, "electrophiles" tend to approach halogens of C-X (X = Cl, Br, I) at an angle of $\sim 100°$ and nucleophiles at $\sim 165°$ and that C—X⋯X—C type interactions fall into two groups, one forming an "electrophile–nucleophile pairing" interaction and the other forming no such pairing. These interactions are interpreted in terms of HOMO and LUMO frontier orbitals centered on the halogens and the approaching atoms. Such "electrophile–nucleophile pairing" interactions are quite general for several systems like sulfides and selenides and no doubt are important in the interaction of small molecules containing halogens since halogen atoms often are in a situation to make short contact with a variety of other atoms, owing to their exposed positions in many molecules.

Although the potential energy between two atoms that are parts of a molecule must have a complicated and specific dependence on their relative orientations, in most calculations, this orientational dependence of energy contribution is either lost or modified due to the use of spherically symmetric atom-atom potentials. Introduction of an anisotropic potential introduces complexities in modelling atom-atom interactions. Besides, such anisotropic potential parameters are not known and are not readily calculable. Consequently, even at the cost of accuracy, only spherically symmetric potential functions are usually used in calculating potential energy values.[2] To regard the attractive and repulsive terms of the potential function as spherically symmetric ignores the nonsphericity of the electron distribution[3a] and density[3b] and the anisotropic shapes of atoms.[4,5] Earlier studies from our

laboratories and elsewhere have shown (from an examination of nonbonded interatomic distances in crystals) that when two chemical groups come within the sum of the van der Waals radii of contacting atoms, certain directional preferences exist depending on the chemical nature and stereochemistry of the contacting atoms and groups.[5-10] Such intermolecular associations have been

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