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Isomers and Isomerizations of $C_2B_9H_{11}$ and a Comparison of Relative Isomer Stabilities

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Abstract: The *closo*-borane $B_{11}H_{11}^{2-}$ is fluxional in solution. To account for this behavior, Lipscomb and co-workers proposed a mechanism for the reorganization of the deltahedral structure and showed that the process has a low activation barrier. For the corresponding carborane $C_2B_9H_{11}$ only a single isomer has been reported from among 20 possible positional isomers or 30 isomers if optical isomers are included. Presumably, $C_2B_9H_{11}$ rearranges by the same mechanism as $B_{11}H_{11}^{2-}$ and with a low activation energy. The proposed rearrangement can be used to construct a reaction graph that relates the various positional isomers of $C_2B_9H_{11}$. The reaction graph serves as a road map across what would otherwise be a bewildering potential energy surface. Geometry-optimized SCF-MO calculations at the STO-3G level provide energies of individual isomers as specific points on the energy surface. Isomers, rearrangement mechanisms, reaction graphs, and calculated isomer energies allow us to predict that two as yet unreported isomers of $C_2B_9H_{11}$ might be stabilized behind the barriers presented by even higher energy isomers that should block their conversion to the known isomer of lowest energy. We discuss the relationship of the calculated energies with relative isomer stabilities as estimated by empirical valence rules and the rule of topological charge stabilization, and we find that the three models qualitatively reinforce each other and our predictions of isomer stabilities. We note an interesting correlation of the symmetry of a structure with the degree of its corresponding vertex in the reaction graph. We report geometry-optimized ab initio SCF-MO calculated total energies for the remaining 17 isomers of $C_2B_9H_{11}$, completing the series of 52 isomers in 8 polyhedral classes for the *closo*-carboranes $C_2B_{n-2}H_n$ at the same level of approximation.

The *closo*-carboranes $C_2B_{n-2}H_n$, $n = 5-12$, are known for a profusion of isomers and isomerizations.[1,2] In our earlier work on these molecules we used reaction graphs based on isomerization mechanisms and relative energies from ab initio SCF-MO calculations to rationalize the existence or absence of isomers and to predict the stability of addition isomers that have not yet been reported.[3-8] In this paper we consider the isomers of $C_2B_9H_{11}$, including optical as well as positional isomers. Only one isomer is known experimentally. We conclude that the isolation of the new isomers of $C_2B_9H_{11}$ should be possible.

$C_2B_9H_{11}$. The *closo*-borane $B_{11}H_{11}^{2-}$ is fluxional in solution on the ^{11}B NMR time scale.[9,10] To account for the observed framework reorganization, Lipscomb and co-workers[11,12] proposed a mechanism, eq 1, in which a bond shared by two adjacent triangular faces in **1** opens to give a square face in **2**, followed by the closing of the square with a new bond perpendicular to the one lost in **1** to give a new deltahedral structure **3** that is identical with the starting structure except for its orientation in space. Thus, the reorganization is a degenerate rearrangement or a pseudorotation. King has described the topological requirements for degenerate rearrangements.[13,14] The activation barrier for rearrangement of $B_{11}H_{11}^{2-}$ is very low.[10,15] No experimental value for the barrier has been reported, but Kleier, Dixon, and Lipscomb have estimated it to be less than 3 kcal/mol on the basis of PRDDO calculations.[12] A similar "diamond–square–diamond" (DSD) mechanism can explain the observed fluxional behavior of $B_8H_8^{2-}$.[11,16,17] Multiple DSD processes have been proposed to rationalize the observed isomerizations of the *closo*-carboranes $C_2B_4H_6$, $C_2B_5H_7$, $C_2B_8H_{10}$, and $C_2B_{10}H_{12}$.[11,18-24] The principle of conservation of orbital symmetry blocks single DSD rearrangements that have been proposed for $C_2B_3H_5$ and $C_2B_7H_9$, and

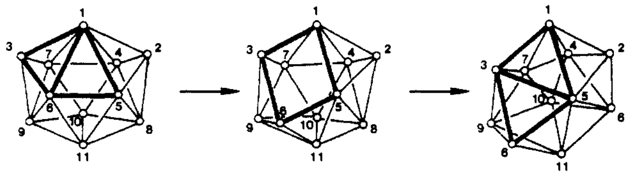

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Table I. Point Groups and Positional Isomers of $C_2B_9H_{11}$

point group	no. of isomers	isomer indices
C_{2v}	3	2,3; 8,9; 10,11
C_s	7	1,2; 1,8; 1,10; 2,8; 2,9; 4,5; 4,7
C_2	1	4,6
C_1	9	1,4; 2,4; 2,6; 2,10; 4,8; 4,9; 4,10; 4,11; 8,10

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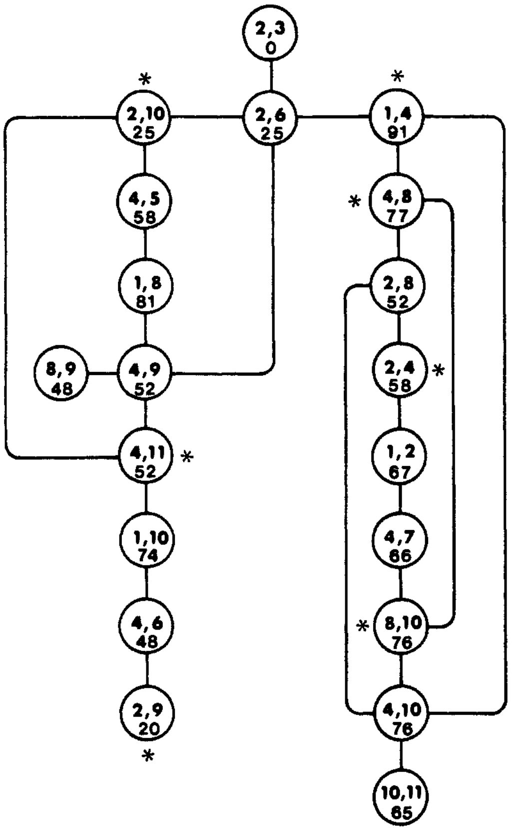

Figure 1. Reaction graph relating the 20 positional isomers of $C_2B_9H_{11}$ by the rearrangement mechanism of eq 1. The pairs of numbers separated by commas are the isomer indices. Beneath each pair of indices is the calculated energy (kcal/mol) of the isomer relative to the most stable 2,3-isomer, which appears at the top of the graph. Isomers 2,9 and 2,8 appear to be in energy wells and should be prevented from rearranging to the lowest energy isomer by barriers at least as high as the energies of the 1,10- and 1,4-isomers.

indeed no rearrangements have been reported for these systems.[3,4,25,26] Lipscomb has suggested that polyhedral rearrangements occurring at high temperatures might involve symmetry crossings of molecular orbitals.[27]

The *closo*-carborane $C_2B_9H_{11}$ is isoelectronic and isostructural with $B_{11}H_{11}^{2-}$. The two-carbon heteroatoms could give rise to a total of 20 positional isomers, but only the 2,3-isomer (**4**) is known.[9,10,28] Table I lists the indices specifying the locations of the carbon atoms for the 20 representative positional isomers. The conventional explanation for the existence of a single isomer is that higher energy isomers, if formed, can easily rearrange to the lowest energy 2,3-isomer through the same mechanism that accounts for the framework reorganization of $B_{11}H_{11}^{2-}$, passing over comparably low activation barriers. In our recent studies of carborane rearrangements we presented a reaction graph in which graph vertices represent each of the 20 possible positional isomers of $C_2B_9H_{11}$ and edges correspond to processes, following eq 1, for the interconversion of isomers. Figure 1 displays a reaction graph for $C_2B_9H_{11}$ that is isomorphic with those graphs we presented previously.[5,8] In Figure 1 and later illustrations the graph vertices are circles containing pairs of indices that specify the positions of the carbons in the polyhedral framework according to the numbering scheme given in **4**. To establish the linkages between isomers or edges joining the vertices of the reaction graph, start with carbons at all possible pairs of position of **1** in eq 1 and determine the isomer corresponding to the new relative positions of the carbons in **3** and identify initial and final structures from among the list of 20 representative isomers. Asterisks next to seven vertices in Figure 1 denote graph loops, edges that begin and end on the same vertex. These represent degenerate rearrangements or pseudorotations, processes in which a bond is broken, a new bond forms, but the resulting structure is identical with the starting structure except for orientation in space and the permutation of otherwise identical atoms.

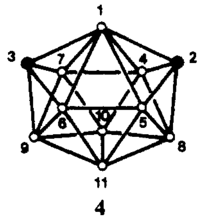

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Table II. Total Energies and Relative Energies of the 20 Positional Isomers of $C_2B_9H_{11}$

isomer	point group	total energy (au)	relative energy (kcal/mol)
1,4	C_1	-300.5190	+91.0
1,8	C_s	-300.5349	+81.0
4,8	C_1	-300.5408	+77.3
8,10	C_1	-300.5423	+76.3
4,10	C_1	-300.5437	+75.5
1,10	C_s	-300.5454	+74.4
1,2	C_s	-300.5566	+67.4
4,7	C_s	-300.5593	+65.7
10,11	C_{2v}	-300.5606	+64.8
2,4	C_1	-300.5707	+58.5
4,5	C_s	-300.5713	+58.1
4,9	C_1	-300.5812	+51.9
2,8	C_s	-300.5816	+51.6
4,11	C_1	-300.5817	+51.6
8,9	C_{2v}	-300.5878	+47.8
4,6	C_2	-300.5879	+47.7
2,6	C_1	-300.6246	+24.6
2,10	C_1	-300.6249	+24.5[a]
2,9	C_s	-300.6324	+19.8[b]
2,3	C_{2v}	-300.6639	0.0[a]

[a] Reference 25. [b] Reference 5.

The reaction graph serves as a road map across what would otherwise be a bewilderingly complicated energy surface. On this surface some high-energy isomers might act as barriers that stabilize other isomers, preventing their rearrangement to the most stable isomer. In previous papers we have used reaction graphs and calculated isomer energies to predict the possible stability of unknown or unreported carborane isomers that might be metastable because of their relative positions on the energy surface. In Figure 1 the known carborane 2,3-$C_2B_9H_{11}$ appears at the top of the graph.

In our previous reports of geometry-optimized ab initio SCF-MO calculations of the *closo*-carboranes[5,29,30] we were able to obtain results for only 3 of the 20 positional isomers of $C_2B_9H_{11}$. In this paper we report the total energies of the remaining 17 and make predictions concerning the yet unreported isomers that might be stabilized behind barriers presented by higher energy isomers. Table II lists total energies (in atomic units) and relative energies (in kilocalories per mole compared to the 2,3-isomer) for the 20 positional isomers of $C_2B_9H_{11}$. These are the results of geometry-optimized ab initio SCF-MO calculations at the STO-3G level.[31] The calculations were executed with the GAUSSIAN 82

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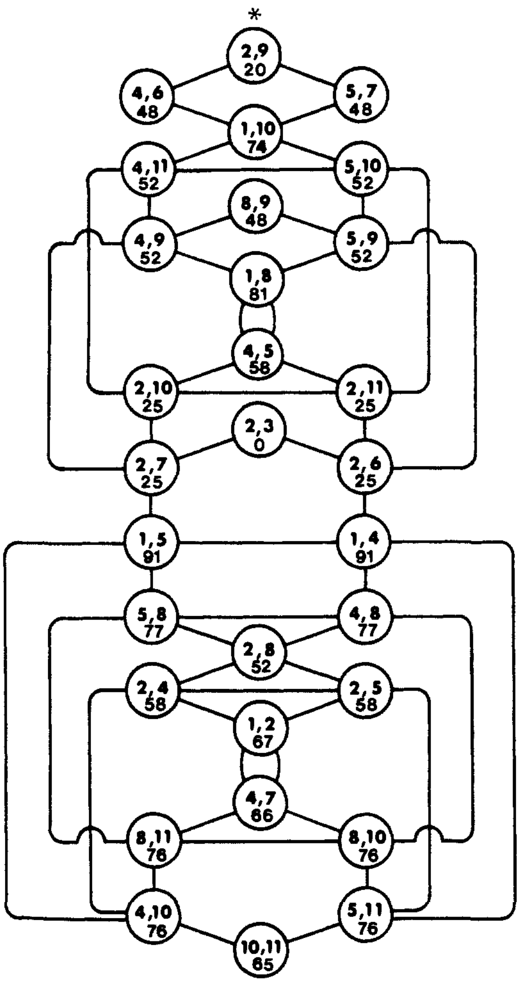

Figure 2. Reaction graph relating the 30 positional and optical isomers of $C_2B_9H_{11}$ by the rearrangement mechanism of eq 1. Enantiomers are paired on either side of the central axis of this figure. Unique positional isomers lie on the axis. Optical isomers should have low barriers to racemization or to rearrangement to lower energy isomers. We do not expect optical isomers to be stable. Isomer stability predictions are the same as those based on Figure 1.

program on the IBM 3081 computer of the Computer Services Division and the GAUSSIAN 86 program on the VAX 11/780 computer in the College of Science and Mathematics at the University of South Carolina. Because we were interested in polyhedral structures similar to **1**, geometry optimizations were carried out under the restriction of the symmetry point group assumed for each isomer. Within this constraint all parameters were optimized. Eigenvalues of the Hessian matrix were not examined. Of course, 9 of the 20 structures have C_1 symmetry or no symmetry constraint at all. In Table II the least stable isomer appears at the top of the list and the most stable or lowest energy isomer is at the bottom. Our choice of the minimal Gaussian basis set was made mainly on the basis of practicality; the calculations for $C_2B_9H_{11}$, even at the STO-3G level, were very slowly convergent and required large amounts of computer time. The use of a limited basis set also has a theoretical justification. We are interested in comparing energies of isomers that share the same polyhedral form but with positions of carbons and borons interchanged. Carbon and boron atoms are similar, and the structures are at least qualitatively the same so one can reasonably hope that electron correlation and basis set errors will largely cancel. McKee reports calculations of other carboranes at various levels of theory that give support to this assumption.[32,33]

As we prepared structural diagrams of the positional isomers for which we planned to do calculations, we realized that pairs of optical isomers or enantiomers are possible for the structures of symmetry point groups C_1 and C_2. Thus, the 10 C_1 and C_2 structures give 10 pairs of optical isomers or a total of 30 optical and positional isomers. Of course, both members of an enantiomeric pair have the same total energy and bond distances so only 20 calculations are necessary to specify energies and structures. But we should have considered optical isomers when we constructed Figure 1. We correct that oversight in Figure 2, where enantiomers are paired on either side of the central axis and unique positional isomers are located on the central stem. When the vertices of each pair of enantiomers are merged, the reaction graph in Figure 2 reduces to that in Figure 1. Vertex 2,9 is the only vertex in Figure 2 with a loop. Relative isomer energies (kcal/mol) appear beneath the corresponding isomer indices inside the circles in Figures 1 and 2.

Table III. Relative Energies of Known Isomers of $C_2B_8H_{10}$ and Predicted Isomers of $C_2B_9H_{11}$ (Energies Relative to the Lowest Energy Isomer and Calculated at the Same Level of Approximation)

carborane	isomer (relative energy, kcal/mol)		
$C_2B_8H_{10}$[a]	1,10 (0)	1,6 (28)	1,2 (54)
$C_2B_9H_{11}$[b]	2,3 (0)	2,9 (20)	2,8 (52)

[a] Reference 5. [b] This work.

From Figure 1 we conclude that it should be possible to prepare 2,9-$C_2B_9H_{11}$. This isomer has a relatively low energy (20 kcal/mol above the observed 2,3-isomer), and it should be stabilized behind a barrier of about 56 kcal/mol presented by the 1,10-isomer along the path 2,9 → 4,6 → 1,10 → 4,11 → 2,10 → 2,6 → 2,3. The 2,9-isomer has a degenerate rearrangement available to it (denoted by an asterisk in Figure 1), and the activation barrier for this rearrangement is likely to be low, comparable to that in $B_{11}H_{11}^{2-}$. Therefore, the 2,9-isomer might be fluxional. This could be detected by ^{11}B or ^{13}C NMR.

Another possible metastable isomer is 2,8-$C_2B_9H_{11}$. This isomer has a higher energy (52 kcal/mol relative to the 2,3-isomer), but it might be stabilized by the highest energy 1,4-isomer or a barrier of about 40 kcal/mol. Immediately adjacent to 2,8 and only 6 kcal/mol above it is the 2,4-isomer. With the addition of another 5–10 kcal/mol as an estimate of the barrier separating 2,4 from 2,8 the 2,4-structure should be thermally accessible to the 2,8-isomer of modest temperatures, and it might be possible to see this rearrangement by NMR.

It is useful to compare relative energies calculated for the $C_2B_9H_{11}$ isomers that we expect to be stable with energies calculated at the same level of approximation for the known isomers of $C_2B_8H_{10}$.[5] The 1,6- and 1,2-isomers of $C_2B_8H_{10}$ have been prepared and can be converted to the most stable 1,10-isomer by pyrolysis.[34-37] For $C_2B_9H_{11}$ only the 2,3-isomer is known, but we predict 2,9- and 2,8-isomers should be stable. The isomers 1,10-$C_2B_8H_{10}$ and 2,3-$C_2B_9H_{11}$ have the lowest calculated energies among the several isomers of the 10- and 11-atom classes of carboranes. Table III shows that 2,9-$C_2B_9H_{11}$ and 1,6-$C_2B_8H_{10}$ both lie 20–30 kcal/mol above the most stable isomer in each class while 2,8-$C_2B_9H_{11}$ and 1,2-$C_2B_8H_{10}$ are 50–55 kcal/mol above the lowest energy isomers. In the 10-atom carboranes the two stable isomers of higher energy are stabilized by even higher energy isomers that intervene along the reaction path. Similarly, in the 11-atom carboranes the barriers approximated by the limiting isomers are at least as high as the corresponding barriers in the 10-atom class. Thus, predictions based on imperfect calculations for $C_2B_9H_{11}$ are comparable to those conclusions for $C_2B_8H_{10}$ based on calculations at the same level of theory but where more experimental information is available.

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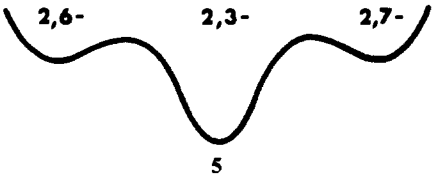
Table IV. Relative Stabilities of Isomers of $C_2B_9H_{11}$

model	most stable, low energy I	II	III	IV	V	least stable, high energy VI
ab initio[a]	2,3 (0)	2,9; 2,6; 2,10 (20–25)	4,6; 8,9; 4,11; 2,8; 4,9 (48–58)	4,5; 2,4; 10,11; 4,7; 1,2 (65)	1,10; 4,10; 8,10; 4,8; 1,8 (75–80)	1,4 (90)
topological charge stabilization[b]	2,3 (−0.180)	2,10; 2,6; 2,4 (−0.145 to 0.140)	2,8; 2,9 (−0.124)	10,11; 4,10; 4,11; 4,5; 4,6; 4,7 (−0.10 to −0.100)	8,10; 4,8; 4,9; 1,2; 8.9 (−0.089 to −0.068)	1,10; 1,4; 1,8 (−0.041 to −0.020)
empirical valence rules	2,3	2,9; 2,6; 2,10	2,8; 2,4	4,6; 4,11; 4,9; 4,5; 8,9	4,7; 4,10; 4,8; 8,10; 10,11	1,2; 1,10; 1,8; 1,4

[a] Relative energies (kcal/mol) in parentheses. [b] Relative energies expressed as charge sums.

The known isomer 2,3-$C_2B_9H_{11}$ has been prepared by degradation of both 1,2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$ (ortho- and meta-isomers, respectively, of the icosahedral carborane).[38] In the 12-atom cage of the ortho-icosahedral carborane, the two carbons are in adjacent positions, and on degradation they move apart to be separated by a boron in the product 2,3-$C_2B_9H_{11}$. These facts suggest that 2,8-$C_2B_9H_{11}$, in which the two carbons are directly attached to each other, is not likely to be prepared by degradation of $C_2B_{10}H_{12}$ isomers. The outlook for 2,9-$C_2B_9H_{11}$ is more promising. To reach 2,9-$C_2B_9H_{11}$ perhaps one could perform the degradation process with the most stable icosahedral borane isomer, 1,12- or *p*-$C_2B_{10}H_{12}$, in which the two carbons are separated by two borons as they would be in the proposed 2,9-$C_2B_9H_{11}$. This process has not been reported.

Figure 2 offers insight into the optical isomer question. Of the 10 enantiomer pairs, 6 are directly linked by a single edge in Figure 2; a single rearrangement through eq 1 is sufficient to interconvert enantiomers. As an example consider the 4,11:5,10 pair. Their energies must be equal, and the activation barrier separating them must be comparable to that for the rearrangement of $B_{11}H_{11}^{2-}$. Therefore, if these enantiomers were at all stable as a positional isomer, they would rapidly interconvert or racemize. Since these optical isomers could not be resolved, it would be a good approximation to merge the pair as a single vertex on the central axis of Figure 2. The remaining four enantiomer pairs are not directly linked, but in each case the members of the pair are connected by a path length of two edges, or they are bridged by one of the unique positional isomers. In each case the bridge has no connections other than those that link it to the enantiomer pair. Two of the pairs also have an additional bridging vertex. Consider the 2,6:2,7 pair bridged by the known 2,3-isomer. The energy profile along the path 2,6–2,3–2,7 must be something like that shown schematically in **5**. The heights of the shoulders separating 2,6 and 2,7 from the central well of 2,3 must be small. Therefore, this pair of enantiomers should quickly rearrange to the unique 2,3-isomer. In each of the other three cases of enantiomers separated by a unique bridging vertex, the bridging isomer has lower energy than the enantiomer pair, also giving an energy profile like **5**. One of the bridging vertices is the 2,8-isomer, which we suspect might be metastable. As previously noted, its central well must be 10–15 kcal/mol below the tops of the barriers to the 2,4:2,5 pair. Thus, we do not expect it to be possible to resolve any optical isomers among the 10 pairs for $C_2B_9H_{11}$.



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Some additional features of Figure 2 are worth noting. Vertices 2,3, 8,9, and 10,11 are of degree 2; i.e., only two edges emanate from each of these vertices. They correspond to the isomers of C_{2v} symmetry, the highest symmetry of this class. The C_2 isomer pair 4,6:5,7 is also of degree 2. Isomers of C_s and C_1 symmetry correspond to vertices of degree 4. The relationship of isomer symmetry to degree of the corresponding vertex in the reaction graph will be the subject of another paper.

Relative Isomer Energies. The relative energies of carborane isomers in Table II can be arranged into six groups on the basis of energy ranges (kcal/mol) with sizable gaps between them: 0, 20–25, 48–58, 65, 75–80, 90. The isomers falling within these groups are identified in the top course of Table IV. The isomers within a group may be very close in energy; some differ by only 0.1 kcal/mol. Despite our expected cancellation of basis set and correlation errors, the energy order within a group must not be well determined. One might reasonably expect improvements in the basis set to rearrange the order of energies of isomers within a group, but the shuffling of isomers from one group to another is much less likely.

Two other models have been used to assess relative energies or stabilities of the isomers of the *closo*-carboranes: empirical valence rules[1,2] and the rule of topological charge stabilization.[39–41] The empirical valence rules were developed to account for observed isomers as the carboranes were first being prepared in the 1960s. The rules are as follows: (i) Carbons prefer to occupy sites of lowest coordination in the polyhedral structure, and (ii) carbons prefer to be as far apart as possible. Conventional valence ideas can rationalize both rules. Carbon is more electronegative than boron. Therefore, a carbon prefers to do less sharing of electrons with less electronegative atoms or to form fewer bonds. The second rule is a result of electrostatic repulsions. The two electronegative carbons in an otherwise boron framework should have negative charges. Separation of the carbons, therefore, reduces repulsions between like charges. Rule i takes precedence over rule ii. In $C_2B_9H_{11}$ positions 2 and 3 are four-coordinate; other positions are five- or six-coordinate. Therefore, carbons should go to positions 2 and 3, satisfying rule i. Since these positions are nonadjacent, rule ii is satisfied as well, although other pairs of sites are more remote from each other. Thus, the empirical valence rules immediately and correctly identify the known 2,3-isomer as being the most stable. In a review of carborane chemistry, Williams used the empirical valence rules to order the stabilities of all 20 $C_2B_9H_{11}$ isomers.[1] In several instances the two rules cannot make distinctions among the stabilities of two or more isomers. Interestingly enough, Williams' table shows the isomers arranged in six groups, and these are shown along the bottom course of Table IV.

The rule of topological charge stabilization is based on the fact that electron count and molecular topology determine electron distribution in a molecule. In the C_{2v} form of $B_{11}H_{11}^{2-}$ 11 boron atoms show 5 different charges (**6**). These charges (Mulliken net atomic populations) for the borons in $B_{11}H_{11}^{2-}$ are from geometry-optimized ab initio SCF-MO calculations at the STO-3G level reported elsewhere.[29] Most of the negative charge in $B_{11}H_{11}^{2-}$ resides on the hydrogens (not shown in **6**). The charges in **6** provide a somewhat better correlation in what follows here than do the extended Hückel charges for $C_{11}^{2-}(C_{2v})$ that we used in an earlier discussion of positional isomers of $C_2B_9H_{11}$.[39] The rule of topological charge stabilization says that more electronegative

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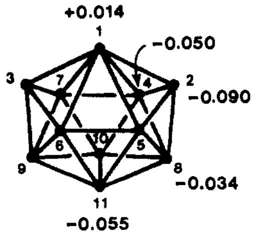

6

heteroatoms are stabilized in those positions where topology produces an accumulation of negative charge in the homoatomic system. Since positions 2 and 3 are the most negative in **6**, they would be preferred locations for the pair of carbon atoms for the most stable isomer of $C_2B_9H_{11}$. For other isomers, consider the charges Q_m and Q_n on sites *m* and *n* in **6**. Assume that the sum $Q_m + Q_n$ is a measure of the energy of the isomer *m,n*-$C_2B_9H_{11}$. For example, the energy of the 2,3-isomer must be related to $Q_2 + Q_3 = 2 \times (-0.090) = -0.180$. Higher in energy would be the 2,10-isomer with $Q_2 + Q_{10} = -0.090 - 0.055 = -0.145$ and so on for the 20 positional isomers of $C_2B_9H_{11}$. In several cases two or more isomers turn out to have the same energy. These charge sums or energies can be divided into six groups, and this has been done in the middle course of Table IV. The rule of topological charge stabilization has been quite successful in correctly ordering the isomer energies of other series of *closo*-carboranes.[29,30,40] We have used similar estimates of relative isomer energies in conjunction with reaction graphs to study the stabilities of heteroatomic and substituted species related to the fluxional ion P_7^{3-}.[41] With so many isomers, $C_2B_9H_{11}$ offers the most challenging test.

The three models agree that the most stable isomer is the 2,3. The empirical valence rules and ab initio calculations both distribute the same three isomers to group II. Beyond these there is little detailed similarity among the compositions of the six groups for the three models. In general one can say that isomers with a carbon at position 2 (four-coordinate; most negative in **6**) are among those at the high-stability, low-energy end of the sequence, and those with a carbon at position 1 (six-coordinate; most positive in **6**) are at the high-energy, low-stability range. But as we can see from reaction graphs, the relationship between energy and stability is not direct. Only the qualitative aspects of energy ordering are useful in predicting stability, and for these the three models agree. In our earlier discussion of the reaction graph we predicted the stability of the unknown isomers 2,8 and 2,9. These fall in groups II or III by the three models. Acting as barriers to the rearrangement of these isomers to the most stable 2,3-isomer are 1,4 and 1,10, which are classified by the three models as members of groups V and VI. Because qualitative, semiquantitative, and quantitative models lead to similar qualitative predictions, we have more confidence in these results.

For this paper we obtained geometry-optimized total energies and bond distances from ab inito SCF-MO (STO-3G) calculations for 17 positional isomers of $C_2B_9H_{11}$. These results, along with those for the other three $C_2B_9H_{11}$ isomers plus structures and energies of the carborane isomers of other classes previously published elsewhere,[5,29,30] constitute a complete set of geometry-optimized calculations at the same level of approximation for $C_2B_{n-2}H_n$, $n = 5$–12, or a total of 52 isomers in 8 polyhedral classes. We plan to submit these data to the Quantum Chemistry Archive of Carnegie-Mellon University.

Conclusions

From reaction graphs based on a proposed rearrangement mechanism and relative energies from ab initio SCF-MO calculations, we predict that 2,9- and 2,8-$C_2B_9H_{11}$ positional isomers should be metastable, blocked from rearranging to more stable structures by higher energy isomers that intervene along the reaction path. So far, only the 2,3-isomer has been prepared. We note that the degree of the vertex in the reaction graph is related to the symmetry of the corresponding isomer: the greater the symmetry, the lower the degree of the vertex. We report geometry-optimized total energies for 17 positional isomers of $C_2B_9H_{11}$, completing a set of calculations at the same level of approximation for a total of 52 polyhedral structures for the $C_2B_{n-2}H_n$.

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Ab Initio Study of the Interaction of Fe, Fe^+, and HFe with H, CH, CH_2, CH_3, and C_5H_5

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Abstract: Ab initio calculations using a single configuration and employing an effective core potential on iron have been used to study the interaction of Fe, Fe^+, and HFe with H, CH, CH_2, CH_3, and C_5H_5. By comparing bond dissociation energies calculated with large basis sets and experiment it was found that trends are well reproduced. For example, the Fe–CH_3 bond is weaker than the Fe–H bond in the neutral complex but stronger in the ionized complex. Also, the Fe—C, Fe═C, and Fe≡C bond dissociation energies are predicted to increase in reasonable agreement with experiment. All H–Fe–X complexes (X = H, CH_3, C_5H_5) are predicted to have quintet ground states with a H–Fe–ligand bond angle of 180°.

In recent years, the unqualified success of theoretical calculations in the area of organic chemistry has been taken largely for granted. In contrast, calculations on unsaturated transition-metal complexes, which are just recently becoming commonplace,[1]

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