Isomerization of Carboranes $C_2B_6H_8$, $C_2B_8H_{10}$, and $C_2B_9H_{11}$ by the Diamond-Square-Diamond Rearrangement

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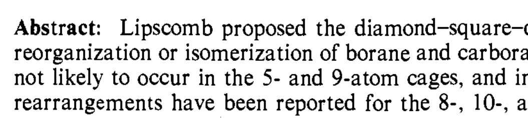
Abstract: Lipscomb proposed the diamond-square-diamond (DSD) mechanism as a general scheme for the framework reorganization or isomerization of borane and carborane deltahedra. In previous papers we have argued that this process is not likely to occur in the 5- and 9-atom cages, and indeed, rearrangements of these systems have not been observed. But rearrangements have been reported for the 8-, 10-, and 11-atom cages. In this paper we consider several proposed DSD rearrangements using the reaction graphs or pathways that correspond to these mechanisms and relative isomer energies obtained from ab initio SCF MO calculations. We report optimized geometries and energies for the 2,7- and 2,4-isomers of $C_2B_8H_{10}$ and for 2,9-$C_2B_9H_{11}$. If isomerizations follow DSD pathways, we predict the unknown isomer 1,2-$C_2B_6H_8$ to be metastable relative to the 1,7-isomer that is known experimentally. We found that the ab initio total energy of 2,7-$C_2B_8H_{10}$, an unknown isomer, is slightly lower than that of the 1,2-isomer which has been prepared. The reaction pathway linking the isomers of $C_2B_8H_{10}$ shows that the 2,7-isomer is an intermediate between two known isomers of lower energy while the 1,2-isomer is stabilized behind a barrier presented by a higher energy isomer. Ab initio energies and reaction graphs combine with experimental information on the existence and reactivities of isomers to provide further support for DSD mechanisms.

The *closo*-boranes and carboranes, $B_nH_n^{2-}$ and $C_2B_{n-2}H_n$, have polyhedral structures with triangular faces.[1,2] They are sometimes called deltahedra. A single hydrogen substituent is attached by a normal electron-pair bond in the exo position to each boron and carbon atom of the structural cage. In a now classic review, Lipscomb proposed a general mechanism for the framework reorganization or isomerization of deltahedral structures.[3] He proposed that rearrangements take place by a diamond-square-diamond (DSD) process in which a bond shared by two adjacent triangular faces breaks and a new bond, perpendicular to the lost bond, forms to join the pair of atoms in the two-triangle diamond:



Such a rearrangement will be significant only if it regenerates the structure of the starting deltahedron. In the boranes this produces a degenerate rearrangement or pseudorotation. In the carboranes the process can move the pair of carbon heteroatoms to different sites within the framework of the cage to produce positional isomers. Lipscomb's proposal developed as a generalization of mechanistic considerations for specific molecules.[4-6] As a special case, these rearrangements include the Berry pseudorotation that has been proposed to explain the fluxional behavior of PCl_5 and related molecules.[7] The DSD mechanism has been used to account for observed rearrangements in the polyhedral cages of metal clusters. Even after 20 years the DSD mechanism still serves as a stimulus for experimental and theoretical research.[8-10]

We have recently used simple molecular orbital calculations and orbital symmetry arguments to conclude that single DSD processes must face high activation energy barriers for framework reorganizations for $C_2B_3H_5$, $C_2B_7H_9$, and their related *closo*-boranes, $B_5H_5^{2-}$ and $B_9H_9^{2-}$.[11,12] Indeed, these systems are not known to isomerize or rearrange. But experimental and theoretical evidence support DSD rearrangements in other systems. The $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ anions are known to be fluxional in solution on the NMR time scale.[13-16] Although many isomers are possible for $C_2B_6H_8$ and $C_2B_9H_{11}$, only a single isomer is known for each of these carboranes. Williams[1] proposed that those carboranes for which only one structure is known form a class in which isomerization reactions are particularly facile, with presumably low activation barriers allowing higher energy isomers to rearrange to the most stable structure in each case. Using PRDDO MO calculations, Lipscomb and co-workers have shown that DSD rearrangements of $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ are allowed and have low activation energies.[17,18] Three isomers of $C_2B_8H_{10}$ are known, and these can be interconverted by pyrolysis. A DSD mechanism has been proposed for the isomeriaztion.

We became interested in DSD rearrangements as a result of ab initio calculations we performed to obtain total energies of carborane isomers for comparison with orders of relative stabilities predicted by empirical valence rules and the rule of topological charge stabilization.[19,20] In several instances, during ab initio calculations for higher energy isomers of $C_2B_6H_8$ and $C_2B_9H_{11}$, we found that starting geometries chosen to approximate those of higher energy carborane isomers rearranged to the structures of lower energy isomers in the course of geometry optimization.

$C_2B_6H_8$. Both $B_8H_8^{2-}$ and $C_2B_6H_8$ have dodecahedral or bisdisphenoid (idealized D_{2d}) structures in the solid state.[21-23] The situation for $B_8H_8^{2-}$ is more complicated in solution where NMR spectra have been interpreted as resulting from square antiprism (D_{4d}) or bicapped (rectangular face) triangular prism (C_{2v}) structures.[13] The solution structures are highly dependent on the polarity of the solvent. $B_8H_8^{2-}$ is fluxional in solution, with all boron atoms equivalent, indicating low activation barriers for rearrangements. King has recently studied $B_8H_8^{2-}$ polyhedra and

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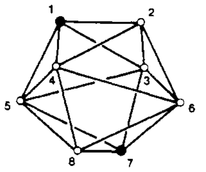
rearrangements using group theory and topology.[24]

Although seven isomers are possible for $C_2B_6H_8$, only the 1,7-isomer (**1**, where the two carbon heteroatoms are represented by ●) has been prepared and characterized.[22,23] We attempted



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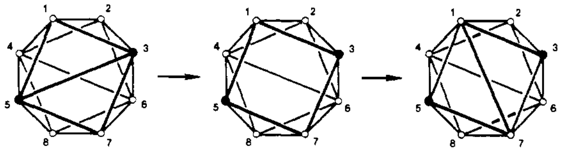
to obtain structures and total energies from ab initio SCF MO calculations at the STO-3G level for seven isomers, but we were successful in locating minima for only six of them.[19] The order of stabilities established by calculated total energies agrees with our predictions of relative stabilities based on the rule of topological charge stabilization.[20]

$$\underset{0}{1,7} > \underset{27.6}{1,6} > \underset{29.5}{1,2} > \underset{37.1}{1,3} > \underset{53.8}{1,5} > \underset{63.3}{3,4} > 3,5$$

The numbers appearing below the positions of the carbon heteroatoms in the sequence of isomers are energies (in kcal/mol) relative to the energy of the most stable isomer, 1,7-$C_2B_6H_8$. Repeated attempts to optimize structures that we felt approximated that of 3,5-$C_2B_6H_8$ led to the structure for the 1,7-isomer. Examination of calculated structures generated during the optimization procedure indicated that the computational rearrangement followed the DSD pathway proposed by Lipscomb,[3] elaborated by Muetterties,[16] and shown in eq 1. Equation 1

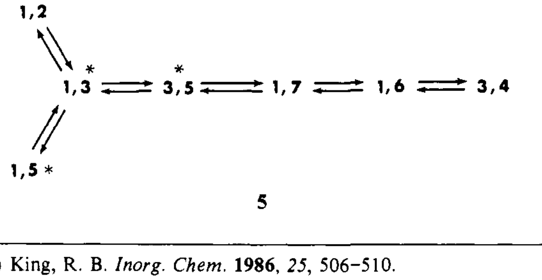


2 **3** **4** (1)

regenerates in **4** the same polyhedral structure of **2**. The two carbons, located at adjacent, 5-coordinate positions in **2**, move to nonadjacent, 4-coordinate positions in **4**, an arrangement equivalent to the 1,7-isomer (**1**) except for labeling and the orientation of the figure in space. The intermediate structure **3** is related to the bicapped trigonal prism. The 3-fold axis of the prism passes through triangles 1,4,5 and 3,6,7 with capping atoms at 2 and 8. If all eight atoms were borons, **3** would have C_{2v} symmetry. Throughout eq 1 the structures maintain a C_2 axis (perpendicular to the plane of the page and passing through the centers of **2**, **3**, and **4**).

Other isomerizations are possible. For example, if the two carbons are located at positions 5 and 7 in **2** (an arrangement equivalent to the 1,3-isomer), eq 1 produces a framework reorganization but leaves the carbons in positions equivalent to the 1,3-isomer. (The carbons are at adjacent 4- and 5-coordinate positions; eq 1 reverses the coordination numbers of those positions.) Such a process is said to be degenerate or a pseudorotation. We observed this degenerate rearrangement in our geometry optimization calculations.

Following the isomerizations that result from starting with carbon atoms at all possible pairs of positions in **2** and proceeding through eq 1 to the rearranged product **4** reveals a branched-chain relationship or reaction graph (**5**) for the isomers of $C_2B_6H_8$:



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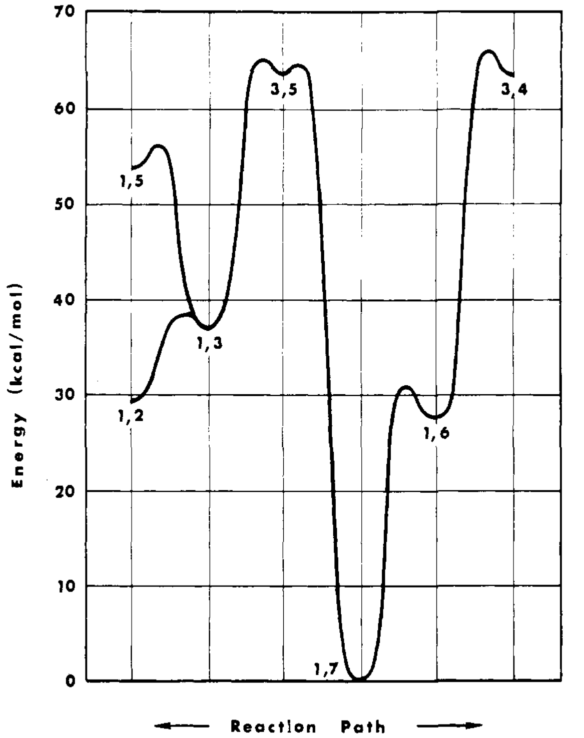

Figure 1. Schematic potential energy surface along the reaction pathway **5**, obtained from eq 1, relating the seven isomers of $C_2B_6H_8$. The energy of the 3,5-isomer is unknown but assumed to be at least as high as that of the 3,4-isomer. Energies of the other isomers were obtained by STO-3G calculations. Activation barriers are unknown but assumed small.

Asterisks in **5** designate those isomers which are capable of undergoing degenerate rearrangements.

Using PRDDO MO calculations, Kleier and Lipscomb have studied the rearrangement of $B_8H_8^{2-}$ through eq 1.[17] They find that the barrier to rearrangement through the C_{2v} intermediate (**3**) is quite low, less than 4 kcal/mol, in qualitative agreement with the observed fluxional behavior of $B_8H_8^{2-}$. Although the energy surface for rearrangement of the corresponding carborane $C_2B_6H_8$ is more complicated than that of $B_8H_8^{2-}$, activation barriers separating individual carborane isomers should be low.

Figure 1 displays the energies of the various carborane isomers along the reaction pathway (**5**) available by eq 1. We prepared Figure 1 assuming that the energy of the 3,5–isomer is at least as high as that of the 3,4-isomer and that the energy barriers between adjacent isomers are small. We have a result based on an assumed, nonoptimal geometry showing that the energy of the 3,5-isomer is no more than 106 kcal/mol above that of 1,7-$C_2B_6H_8$. (It is possible, of course, that the 3,5-structure may not correspond to a relative minimum on the energy surface.) If isomers interconvert by eq 1, then they do so along the energy surface presented in Figure 1, and therefore one would not expect to be able to isolate the 1,6- and 3,4-isomers because these are separated from the most stable 1,7-isomer by very low activation barriers, much as Williams imagined.[1] But 1,5- and 1,3-$C_2B_6H_8$ might rearrange to the 1,2-isomer, which should be metastable, being separated from the 1,7-isomer by an activation barrier of more than 30 kcal/mol. Therefore, if isomerization occurs by eq 1, we predict that preparation and isolation of 1,2-$C_2B_6H_8$ should be feasible. So far, only the 1,7-isomer has been reported.

Equation 2 is a double DSD rearrangement of the eight-atom polyhedron, connecting disbisphenoids **6** and **8** through a square antiprism intermediate **7** with idealized D_{4d} symmetry. This process was first proposed by Muetterties and co-workers.[16,25,26]

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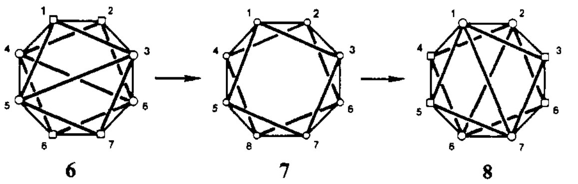
Notice that diagonals 4–6 and 3–5 disappear in **6** to reappear at 1–7 and 2–8 in **8**.



6 **7** **8** (2)

Starting with carbons at all possible pairs of positions in **6** and carrying through to **8**, eq 2 shows that carborane isomers are related through the three-component, disconnected reaction graph **9**. Since the reaction graph is disconnected, the double DSD mechanism of eq 2 does not allow the interconversion of all shown isomers of $C_2B_6H_8$. The disbisphenoids **6** and **8** contain two sets of equivalent sites: the four 4-coordinate sites (designated by □ in **6** and **8**) and the four 5-coordinate positions (○). Equation 2 converts 4-coordinate sites in **6** into 5-coordinate sites in **8**. Therefore, this process could account for the observed equivalence of boron atoms in the ^{11}B NMR studies of $B_8H_8^{2-}$.

$$1,2 \rightleftarrows 3,5 \rightleftarrows 1,7 \rightleftarrows 3,4$$

$$\overset{*}{1,3} \rightleftarrows 1,5$$

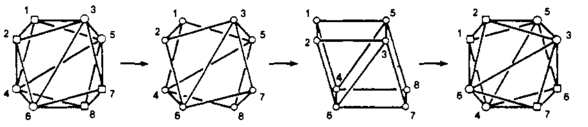
$$\overset{*}{1,6}$$

9

Even if interconversions within a particular component of **9** occur with low activation energies, conversions between isomers in different components (by way of some unknown process, not eq 2) are likely to have higher activation barriers; otherwise, we would be studying that unknown, lower energy process. Consider the four-vertex component of **9**. Isomers 1,2 and 1,7 are separated by the high-energy 3,5-isomer just as they are in the reaction graph **5** for eq 1. Therefore, if the rearrangement proceeds by eq 2, it should be possible to isolate 1,2-$C_2B_6H_8$ and probably the 1,3- and 1,6-isomers as well.

MO correlation diagrams by Kleier and Lipscomb suggest that eq 1 and 2 are allowed by the principle of conservation of orbital symmetry.[17] Furthermore, their results for $B_8H_8^{2-}$ show that the D_{4d} intermediate **7** has an energy that is an order of magnitude higher than that of the C_{2v} intermediate **3** relative to the disbisphenoid D_{2d} (**2** or **6**). Thus, barriers in eq 2 may be 10 times higher than those in eq 1.

Equation 3 is a quadruple DSD rearrangement proposed by King.[24] Equation 3 leads to the five-component disconnected reaction graph **10**. Equation 3 and reaction graph **10** are not able to exchange atoms between the sets of 4- and 5-coordinate sites. Furthermore, it does not suggest an easy pathway from 3,5- to 1,7-isomers or a degenerate rearrangement for 1,3 that we observed during computer optimizations of isomer geometries.



(3)

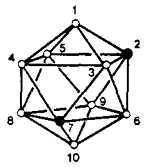
$$1,6 \rightleftarrows 1,3 \rightleftarrows 1,5$$

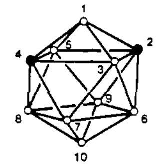
$$\overset{*}{1,2} \quad \overset{*}{1,7} \quad \overset{*}{3,4} \quad \overset{*}{3,5}$$

10

$C_2B_8H_{10}$. $B_{10}H_{10}^{2-}$ and $C_2B_8H_{10}$ have bicapped square antiprism structures.[27,28] Seven isomers are possible for $C_2B_8H_{10}$, but only three are known experimentally: 1,10-**11**, 1,6-**12**, and 1,2-**13**. Pyrolysis of the 1,2-isomer produces the 1,6-isomer, which on further pyrolysis gives the 1,10-isomer.[28-31]

Table I. Bond Distances and Total Energies of 2,7-$C_2B_8H_{10}$ and 2,4-$C_2B_8H_{10}$ from Geometry-Optimized ab Initio SCF MO Calculations at the STO-3G Level[a]





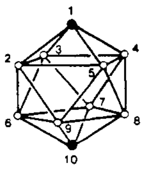
2,7-$C_2B_8H_{10}$[b] point group C_2		2,4-$C_2B_8H_{10}$[c] point group C_{2v}	
C_2B_1	1.626	C_2B_1	1.601
C_2B_3	1.769	C_2B_3	1.750
C_2B_5	1.774	C_2B_6	1.751
C_2B_6	1.694	B_1B_3	1.694
C_2B_9	1.738	B_3B_6	1.774
B_1B_3	1.671	B_6B_7	1.826
B_1B_4	1.675	B_6B_{10}	1.681
B_1B_5	1.690	B_6B_9	1.854
B_3B_4	1.827	C_2H	1.081
B_3B_6	1.826	B_1H	1.146
B_4B_5	1.814	B_3H	1.148
B_4B_8	1.822	B_6H	1.148
B_5B_8	1.759	$B_{10}H$	1.144
C_2H	1.080		
B_1H	1.145		
B_3H	1.148		
B_4H	1.147		
B_5H	1.148		

[a] All bond distances are in Å. [b] Total energy is −275.6553 au. [c] Total energy is −275.6430 au.

Table II. Relative Stabilities of $C_2B_8H_{10}$ Isomers as Predicted by Qualitative and Quantitative Methods

empirical valence rules[a]	1,10 > 1,6 > 1,2 > 2.7 > 2,4 > 2,6 ~ 2,3
topological charge stabilization[b]	1,10 > 1,6 > 1,2 > 2,4 > 2,7 > 2,6 > 2,3
ab initio, STO-3G[c]	1,10 > 1,6 > 2,7 > 1,2 > 2,4 > 2,6 > 2,3
	0 28.1 53.2 54.0 61.0 73.7 74.0

[a] Reference 1. [b] Reference 20. [c] Reference 19; decimal sequence contains relative energies in kcal/mol.



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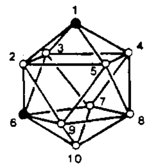

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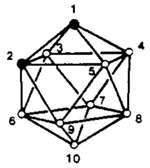

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In our earlier ab initio study of carborane isomer energies, we obtained energies of five of the seven isomers of $C_2B_8H_{10}$.[19] For this report we have calculated total energies and optimized structures for the two remaining isomers. Table I contains the total energies and optimized bond distances of 2,7- and 2,4-$C_2B_8H_{10}$ as calculated at the STO-3G level,[32] comparable with the values we reported previously for the other isomers. Our original motivation for the ab initio calcuation of total energies

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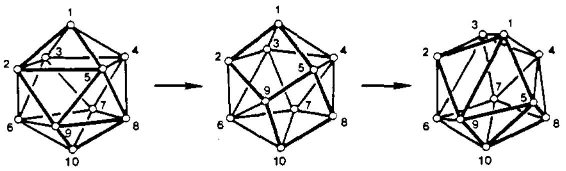
of carborane isomers was to determine the order of stabilities for comparison with qualitative orderings of stabilities based on empirical valence rules[1,2] and the rule of topological charge stabilization.[20] Table II displays these comparisons. Except for an interchange of order of stabilities for the 2,7- and 2,4-isomers, the two qualitative schemes are in substantial agreement. Both rules predict the isomers 1,10, 1,6, and 1,2 to be the most stable, which seems to be consistent with the fact that these three are the experimentally known isomers. Therefore, we were quite surprised when we found that the ab initio total energy of 2,7-$C_2B_8H_{10}$ falls slightly below that of the 1,2-isomer, one of the experimentally known isomers. Indeed, the energies of the 2,7-, 1,2-, and 2,4-isomer are relatively close. We did our calculations using the minimal basis set. Improvements in basis set quality or the inclusion of correlation corrections might alter the ordering of these three isomers. But, as we will show, the order predicted by ab initio calculations at the STO-3G level is not inconsistent with the fact that 2,7-$C_2B_8H_{10}$ has never been isolated although 1,10-, 1,6-, and 1,2-isomers have all been prepared.

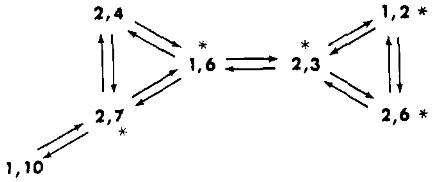
Kaczmarczyk, Dobrott, and Lipscomb[5,6] proposed a DSD process to account for the isomerization of disubstituted $B_{10}H_{10}^{2-}$, and this process was clearly elaborated as a double DSD process, eq 4, by Hertler, Knoth, and Muetterties in their studies of the equilibrium among isomers of $B_{10}H_8R_2$.[33,34] Lipscomb pointed out that this process would also explain the isomerization of $C_2B_8H_{10}$.[3]

Notice that the 4-fold axis of the antiprism, passing through vertices 1 and 10 in **14**, reappears through 2 and 8 in **16**. As related by eq 4, the seven isomers of $C_2B_8H_{10}$ can isomerize through the reaction graph **17**. Asterisks in **17** denote isomers that can undergo degenerate rearrangements. Although Hertler and co-workers[33] did not construct the reaction graph **17**, they included in their paper the pair-wise connections from which **17** can be constructed. In **17** the two low-energy isomers 1,10 and 1,6 are separated by the 2,7-isomer. Therefore, the barrier preventing the conversion of 1,6 to 1,10 is around 25 kcal/mol, the energy difference between 2,7- and 1,6-isomers, plus the activation barrier between 2,7- and 1,10-isomers, which is assumed to be small. The 1,2-isomer must be separated from the lower energy 1,6-isomer by a barrier of at least 20 kcal/mol, the energy difference between 2,3- and 1,2-isomers, plus a small barrier separating 2,3 and 1,6. Thus, the known isomers 1,10, 1,6, and 1,2 are in energy pockets separated from each other by thermally accessible energy barriers that can be approximated by the energies of higher energy isomers along the reaction pathway. Even if the unknown 2,7-isomer has a lower energy than the known 1,2-isomer, we do not anticipate the future isolation of the 2,7-isomer because it is on an energy crest between the two lowest energy isomers 1,10 and 1,6. The relative calculated total energies, the known isomers, and the reaction pathway based on eq 4 combine to present a consistent story.



(4)

14 **15** **16**



17

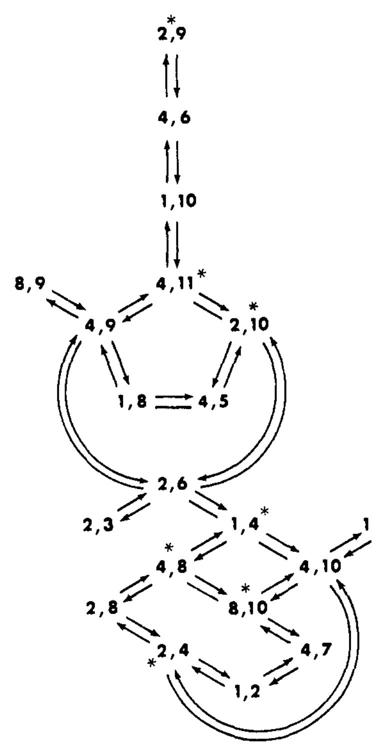
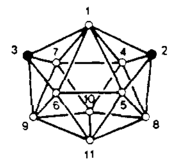
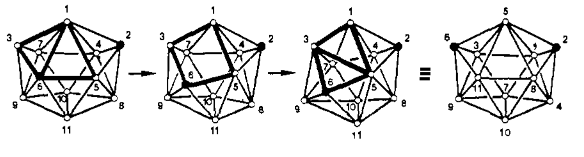


Figure 2. Reaction pathway or reaction graph relating the 20 isomers of $C_2B_9H_{11}$ by degenerate rearrangements. The 2,3-isomer is known experimentally and predicted to have the lowest energy.

$C_2B_9H_{11}$. $B_{11}H_{11}^{2-}$ and $C_2B_9H_{11}$ have octadecahedral structures that have been described as related to a bicapped pentagonal antiprism with one of the antiprism vertices removed.[14,15,35] There are 20 possible isomers of $C_2B_9H_{11}$, but only 2,3-$C_2B_9H_{11}$ (**18**) has been isolated and characterized. $B_{11}H_{11}^{2-}$ in solution is fluxional on the NMR time scale.[35] Equation 5 shows a DSD process, proposed by Lipscomb.[3] This particular illustration shows the 2,6-isomer rearranging into a structure (**21**, **21'**) identical with the 2,3-isomer (**18**) except for labeling and orientation in space. When we attempted to obtain an optimized structure from ab initio SCF MO calculations for 2,6-$C_2B_9H_{11}$ this framework reorganization resulted.[19] We also obtain rearrangements of 4,11 into 2,10 and of 4,6 into 2,9. The reaction graph corresponding to eq 5 is shown in Figure 2. This connected graph demonstrates that all isomers can interconvert through one or a sequence of single DSD processes of the type given by eq 5. Kleier, Dixon, and Lipscomb[18] have studied this process using PRDDO MO calculations for $B_{11}H_{11}^{2-}$. They found that the intermediate **20**, of C_s symmetry, was less than 1 kcal/mol higher in energy than



18



(5)

19 **20** **21** **21'**

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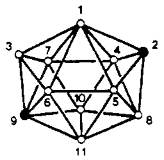
Table III. Bond Distances and Total Energy of 2,9-$C_2B_9H_{11}$ from Geometry-Optimized ab Initio SCF MO Calculations at the STO-3G Level[a]



2,9-$C_2B_9H_{11}$[b]
point group C_s

C_2B_1	1.639	B_1B_6	2.010	C_2H	1.077
C_2B_4	1.568	B_3B_6	1.646	C_9H	1.080
C_2B_8	1.694	B_4B_7	1.836	B_1H	1.154
C_9B_3	1.687	B_4B_8	1.807	B_3H	1.146
C_9B_6	1.723	B_4B_{10}	1.764	B_4H	1.150
C_9B_{10}	1.692	B_6B_{11}	1.788	B_6H	1.149
B_1B_3	1.706	B_8B_{10}	1.754	B_8H	1.147
B_1B_4	2.065	$B_{10}B_{11}$	1.857	$B_{10}H$	1.148

[a] All bond distances are in Å. [b] Total energy is −300.6324 au.

initial and final C_{2v} structures **19** and **21**.

The rule of topological charge stabilization[20] predicts the following order for the four most stable isomers of $C_2B_9H_{11}$:

$$\begin{array}{ccccccc} 2,3 & > & 2,10 & > & 2,6 & > & 2,9 \\ 0 & & 25.4 & & 20.4 & & \end{array}$$

Again, numbers appearing below the isomer designations in the sequence are energies (in kcal/mol) relative to the lowest energy 2,3-isomer. The energies were obtained from ab initio SCF MO calculations with the STO-3G basis set. We reported total energies and optimized structures of the 2,3- and 2,10-isomers in our earlier study. Table III contains the corresponding information for the 2,9-isomer. The qualitative ordering sequence is not completely consistent with calculated energies. The isomers 2,3, 2,6, and 2,10 are linked together near the center of Figure 2. The relatively low-energy 2,9-isomer appears at a terminal position at the top of the diagram. Calculation of geometry-optimized energies of many or all of the remaining 17 isomers of $C_2B_9H_{11}$ might reveal metastable isomers protected from rearrangement by higher energy isomers as we predict for $C_2B_6H_8$ and $C_2B_7H_9$. Such a project, even at the STO-3G level, would require more computer time than we expect to have available to us in the near future.

Conclusions

We have used reaction pathways connecting carborane isomers through DSD framework reorganizations and estimates of relative stabilities of isomers based on minimal basis set but geometry-optimized ab initio SCF MO calculations to rationalize the existence of particular isomers and experimental observations of the rearrangements of $C_2B_6H_8$, $C_2B_8H_{10}$, and $C_2B_9H_{11}$ and to predict the metastability of an isomer that has not yet been reported. It should be possible to isolate 1,2-$C_2B_6H_8$ because it is separated from the minimum energy 1,7-isomer by energy barriers that result from the interposition of higher energy isomers along the reaction pathway. We report total energies and geometry-optimized structures at the STO-3G level for 2,7-$C_2B_8H_{10}$, 2,4-$C_2B_8H_{10}$, and 2,9-$C_2B_9H_{11}$. These results supplement our earlier set of molecular structure calculations at the same level of theory for *closo*-carboranes and boranes. We found the energy of unknown 2,7-$C_2B_8H_{10}$ to be slightly lower than that of one of the known isomers of this carborane. However, we do not expect 2,7-$C_2B_8H_{10}$ to be isolated because it is an intermediate on the reaction pathway between two lower energy isomers.

The results of our calculations and our examination of reaction graphs based on DSD framework reorganizations combine with the experimental work of others to support the proposal of DSD rearrangements for the 8-, 10-, and 11-atom boranes and carboranes. But the proof of any mechanistic proposal must be infinitely difficult. Indeed, other mechanisms have been suggested for these rearrangements. Johnson[37] has proposed a single-edge cleavage process as a general mechanism for polyhedral rearrangements, and this mechanism merits serious study, particularly for the five- and six-atom cages. Finally, the framework reorganizations of the *closo*-boranes and carboranes are examples of degenerate cage rearrangements or pseudorotations, processes known to occur in other species such as the bullvalenes[38,39] and the P_7^{3-} ion.[40] Although the mechanisms of the various rearrangements differ in detail, they constitute a larger class of processes of importance to both organic and inorganic chemistry.

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Characterizing the 2-Norbornyl Cation in the Gas Phase

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Contribution from the Chemistry Department, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4. *Received August 4, 1986*

Abstract: The gas-phase heat of formation, $\Delta H_f°$, of the 2-norbornyl cation has been reassessed as 767 ± 5 kJ mol^{-1} by considering all available experimental data. This ion can be distinguished in the gas phase from isomeric $[C_7H_{11}]^+$ species by its collisional activation mass spectrum which, unlike all other $[C_7H_{11}]^+$ ions studied, contained a significant peak at m/z 66, $[C_5H_6]^{\bullet+}$. Its charge stripping mass spectrum was similarly structure-diagnostic in that it alone lacked peaks corresponding to $[C_7H_{10}]^{2+}$ and $[C_7H_{11}]^{2+}$.

The solution chemistry of the 2-norbornyl cation has been a topic of interest and controversy since 1949 when Winstein and Trifan[1] first proposed that the ion has a nonclassical bridged structure. Indeed, a recent issue of *Accounts of Chemical Research*[2] contained a series of articles about the structure and chemistry of this celebrated species.

Although a number of mass spectral investigations of $[C_7H_{11}]^+$ ions derived from 2-norbornyl compounds have been reported,[3]

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