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# Diamond–Square–Diamond Isomerization of $C_2B_5H_7$

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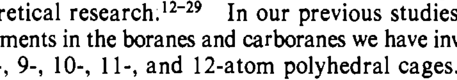
The *closo*-borane $B_7H_7^{2-}$ and the related carborane $C_2B_5H_7$ have pentagonal-bipyramidal shapes. Although four isomers of the carborane are possible, only two have been prepared. Interconversion of these two unsubstituted isomers has never been observed, but the substituted 2,3-isomer has been converted into the 2,4-isomer and the isomerizations of B-monosubstituted and B,B′-disubstituted 2,4-$C_2B_5H_7$ have been extensively studied experimentally by Onak. The rearrangements of substituents have been explained as resulting from diamond–square–diamond (DSD) framework reorganizations that move substituent-bearing boron atoms to new positions while the two carbons remain at nonadjacent equatorial sites in the pentagonal bipyramid. Similar rearrangements might move one or both carbons to interconvert carborane isomers themselves. We have geometry-optimized ab initio SCF MO energies for the four carborane isomers. We have plotted these energies along the reaction coordinate indicated by the proposed DSD mechanism. The plot rationalizes the existence of only two carborane isomers. Further calculations reveal additional details of the DSD process. Relative energies for the monomethyl- and dimethyl-substituted isomers of 2,4-$C_2B_5H_7$ are also included.

## Introduction

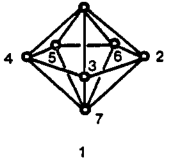
The *closo*-boranes $B_nH_n^{2-}$ and the related carboranes $C_2B_{n-2}H_n$ have polyhedral structures with triangular faces.[1,2] Some of the carboranes are known to isomerize. For example, heating causes the interconversion of positional isomers of $C_2B_4H_6$, $C_2B_8H_{10}$, and $C_2B_{10}H_{12}$.[3-7] The boranes $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ are observed to undergo rapid structural rearrangement in solution.[8-10] In a classic review, Lipscomb proposed a general mechanism for the structural reorganization of the *closo*-boranes and -carboranes.[11] In this process a bond shared by two adjacent polyhedral triangular faces, the switching edge, disappears and is replaced by a new bond perpendicular to the original bond, joining previously nonadjacent atoms. Lipscomb called this process the diamond–square–diamond (DSD) rearrangement:



We are interested in only those rearrangements that restore the original polyhedral shape while allowing atoms to move to new positions within that structural framework, because these are the isomerizations that *closo*-carboranes have been observed to undergo. Lipscomb's suggestion developed from earlier work on specific carboranes. For over 20 years this proposal has been a source of stimulation for a considerable amount of experimental and theoretical research.[12-29] In our previous studies of DSD rearrangements in the boranes and carboranes we have investigated the 5-, 8-, 9-, 10-, 11-, and 12-atom polyhedral cages.[30-34] In this paper we consider DSD rearrangements in $B_7H_7^{2-}$ and $C_2B_5H_7$. We also report results concerning some substituted carboranes. Unless specified otherwise, all results are ab initio SCF MO calculations at the STO-3G level. These were done by using the Gaussian-80 program on a MicroVax II computer.[35]

### $C_2B_5H_7$ and $B_7H_7^{2-}$

$B_7H_7^{2-}$ and $C_2B_5H_7$ have pentagonal-bipyramidal shapes (**1**).



**1**

Of the four possible isomers of $C_2B_5H_7$, only the 2,4- and 2,3-isomers have been prepared.[36-38] Our previously reported geometry-optimized ab initio SCF MO calculations at the STO-3G level indicate the order of isomer stabilities given in **2**. The

| 2,4 | > | 2,3 | > | 1,2 | > | 1,7 |
|---|---|---|---|---|---|---|
| 0 | | 24.2 | | 49.8 | | 79.8 |

**2**

numbers appearing beneath the isomer designations in **2** are energies (in kcal/mol) relative to the most stable 2,4-isomer. This

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‡ University of South Carolina.

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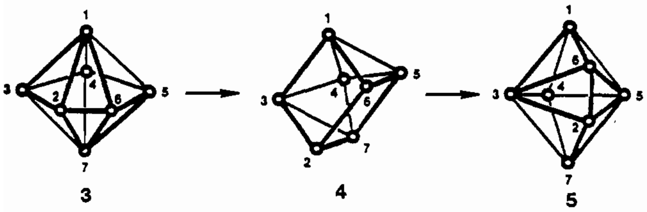
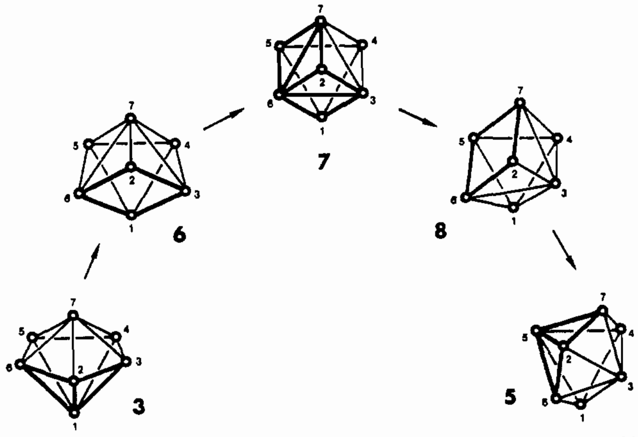
order of stabilities is in agreement with predictions based on the rule of topological charge stabilization and on empirical valence rules developed for the *closo*-carboranes[2,5,39-43] and with recent [MP2/6-31G*] calculations done by McKee.[44] The order also agrees with experimental evidence so far as it goes.[29,38,45] The 2,4-isomer has been produced in quantity as the *C,C'*-dimethyl derivative. Unsubstituted 2,3-$C_2B_5H_7$ has been prepared only in very small amounts. The remaining 1,2- and 1,7-isomers are unknown.

Although the *closo*-boranes $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ are fluxional, $B_7H_7^{2-}$ is not. While there is no evidence for the thermal conversion between the high-energy 2,3-$C_2B_5H_7$ into the more stable 2,4-isomer, the interconversion between the diethyl-substituted isomers has been observed. For *B*-chloro-substituted derivatives of the 2,4-frame, the Onak group finds the activation barrier to isomerization to be around 45 kcal/mol.[46] Beck, Kahn, and Sneddon report that when 2,3-$Et_2$-2,3-$C_2B_5H_5$ is heated to 320 °C 81% is converted to the 2,4-$Et_2$-2,3-$C_2B_5H_5$ isomer.[45] Over a number of years, Onak and co-workers have reported an extensive series of experiments they have carried out on the interconversion of B-monosubstituted and B,B'-disubstituted isomers of 2,4-$C_2B_5H_5XY$.[46-50] The Onak group explains their observations as the results of DSD rearrangements that have substituent-bearing boron atoms to new positions in the pentagonal bipyramid while regenerating the 2,4-carborane isomer cage. Onak and co-workers propose three isomerization processes.[46] In equation 1 two DSD processes occur simultaneously and the reaction passes through a transition-state structure **4** that can be described as a trigonal prism with one capped rectangular face. Imagine breaking bonds 1–2 and 6–7 in **3** to produce the capped trigonal prism **4** with two open squares and then forming new bonds 3–6 and 2–5 to yield the new pentagonal bipyramid **5**. The overall process is a pseudorotation or a degenerate rearrangement. Onak refers to **4** as an unstable arachno structure. An alternative way to view this rearrangement is to imagine twisting the 2–6 equatorial edge by 90°, as demonstrated by McKee.[44]



(1)

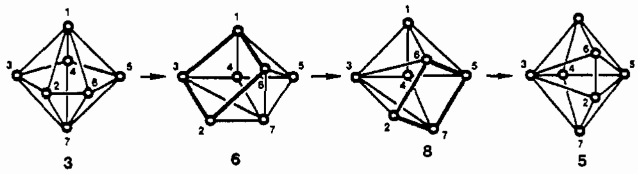
Equation 2 consists of the same two DSD processes as in eq 1, but here they occur consecutively rather than simultaneously.



(2)

The 1–2 bond in **3** opens the square in **6** followed by the closing of the 3–6 bond to form **7**. Then the 6–7 bond opens to give **8** and the 2–5 bond closes to form the pseudorotated pentagonal bipyramid **5**. The intermediate structure **7** is a capped octahedron. The structures in eq 2 are drawn from a perspective from which it is easy to visualize the 3-fold axis of the capped octahedron **7**, which Onak calls a hypercloso structure. He refers to the intervening structures **6** and **8** as unstable nido structures.

Equation 3 involves overlapping consecutive DSD processes.



(3)

First the apex–equatorial bond 1–2 breaks in **3**, leading to the unstable nido structure **6**. The square hole in **6** closes to a diamond with the formation of the 3–6 bond, while the 6–7 bond opens to give the equivalent unstable nido structure **8**. Finally, the 2–5 bond forms to close the square and regenerate the pentagonal bipyramid **5**.

These three paths differ in the details of their transition-state or intermediate structures and the synchronization of bond opening and closing, but they are equivalent in that the same bonds are broken and formed and, more importantly, they start from the same initial structure and lead to an identical terminal structure.

King has applied group theory and topological arguments to the study of a wide range of seven-vertex polyhedra.[51] He classifies the intermediate **4** in eq 1 as having a DSD rigidity index of 2 because two edges of the pentagonal bipyramid **3** must be lost to open two quadrilateral faces to give **4**. He also shows DSD graphs relating the degenerate rearrangement of the pentagonal bipyramid through the unstable nido structure **6**, which has a DSD rigidity index of 1.

Suppose we start in eq 1 with a pair of carbon heteroatoms at positions 2 and 4 in the structure **3**, the cage of which otherwise consists of borons. A structural reorganization occurs through eq 1, but it leads to a tipped pentagonal bipyramid in which the two heteroatoms are once more in nonadjacent equatorial sites. Thus, eq 1 starting with carbons at positions 2 and 4 and utilizing the 1–2 and 6–7 bonds as switching edges represents not an isomerization but a degenerate rearrangement of the 2,4-isomer of $C_2B_5H_7$. If the carbons are located in positions 4 and 6, the same degenerate rearrangement is observed. If we start with the carbons at different positions or use different switching edges, other rearrangements are observed. Imagine the same process starting with the two carbons at positions 1 and 2. One carbon would be at an apical position, the other in an equatorial site. Following atoms 1 and 2 in **3** through eq 1 shows the heteroatoms move to nonadjacent equatorial sites in **5** to produce a structure equivalent

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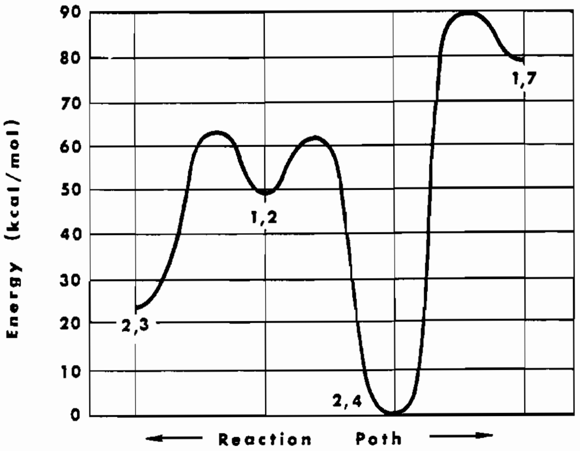


**Figure 1.** Energy (in kcal/mol) along the reaction coordinate for the isomerization of $C_2B_5H_7$. Activation barriers between isomers are unknown but are assumed to be small.

to the 2,4-isomer. Thus, eq **1** can convert 1,2-$C_2B_5H_7$ into the 2,4-isomer. By starting with carbon atoms at all possible pairs of positions in **3**, following through to **5**, and expressing the results as one of the four representative isomers specified in **2**, we can produce the reaction graph **9**, which shows how the four positional

$$2,3^* \rightleftarrows 1,2^* \rightleftarrows 2,4^* \rightleftarrows 1,7$$

**9**

isomers can interconvert through eq 1 and, because of their equivalence, by eq 2 and 3 as well. Asterisks in the reaction graph **9** denote isomers for which the equations permit degenerate rearrangements such as the one we described for the 2,4-isomer. The studies by Onak and associates of the isomerizations of boron-substituted 2,4-$C_2B_5H_7$ make use of the degenerate rearrangement allowed for the 2,4-isomer; the borons can move from one location to another while returning the carbons to nonadjacent equatorial sites. Their observations and kinetic data substantiate an overall double-DSD process common to eq 1, 2, and 3.

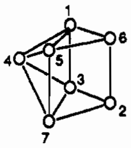
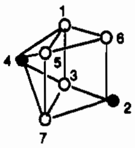
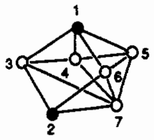
We know geometry-optimized ab initio SCF MO energies for the four isomers shown in **2**, and we have plotted these as the potential energy profile along the reaction graph as shown in Figure 1. This figure has been constructed by using only the relative minima corresponding to the various isomers and the sequence of isomers along the reaction coordinate. The shapes of the curves between these minima and the heights of the maxima depend on the details of the reaction process, eq 1, 2, or 3. Even without knowledge of the details about the actual intermediates that intervene between isomers we can see that the two experimentally observed isomers, the 2,3- and 2,4-species, are separated by an energy barrier at least as high as the energy of the intervening 1,2-isomer. The activation barrier for the conversion of the 2,3- to the 2,4-isomer is at least 25 kcal/mol, high enough to stabilize the 2,3-isomer from converting the 2,4-species at room temperature. If the barriers surrounding the 1,2- and 1,7-isomers are small, then we would not expect to be able to isolate these isomers because they could easily rearrange to the 2,4- or 2,3-species. Thus, the facts that the 2,4- and 2,3-isomers have been prepared but not the 1,2- and 1,7-species are consistent with the calculated isomer energies and the reaction graph sequence based on the processes proposed by Onak and co-workers.

## Determination of the Most Probable Path

**Homoatomic Case.** In order to determine the most probable path followed by the substituted carboranes reported by Onak, we first performed calculations on the different intermediates that would arise for the homoatomic $B_7H_7^{2-}$ ion in each of the different paths.

Consider first eq 1. This process is guaranteed to be symmetry-allowed because no element of symmetry is maintained during the conversion between **3** and **4**. Geometry-optimized ab initio SCF MO calculations show the capped trigonal prism to be 76.6 kcal/mol higher in energy than the pentagonal bipyramid for homoatomic $B_7H_7^{2-}$. In this comparison between two totally different structures, the capped trigonal prism and the pentagonal bipyramid, it is less likely that errors due to basis set and neglect of correlation energy would cancel as they apparently do when the structures of the same polyhedral form such as the positional isomers in $C_2B_5H_7$ are compared. The optimized bond distances for the capped trigonal prism are given in Table I.

**Table I.** Bond Distances and Total Energies for $B_7H_7^{2-}$ and 2,4-$C_2B_5H_7$ as Capped Trigonal Prisms and 1,2-$C_2B_5H_7$ in the Unstable Nido Conformation[a]

| | <br>**4''**<br>$B_7H_7^{2-}$ | <br>**4'**<br>2,4–$C_2B_5H_7$ | <br>**6'**<br>1,2–$C_2B_5H_7$ |
|---|---|---|---|
| point group | $C_{2v}$ | $C_s$ | $C_s$ |
| bond dist | $B_1B_3$, 1.743 | $C_2B_3$, 1.624 | $C_1B_3$, 1.866 |
| | $B_1B_4$, 1.661 | $C_2B_6$, 1.463 | $C_1B_4$, 1.544 |
| | $B_1B_5$, 1.698 | $C_4B_1$, 1.648 | $B_3B_4$, 1.708 |
| | $B_1B_6$, 1.796 | $C_4B_3$, 1.558 | $B_3B_7$, 1.906 |
| | $B_2B_6$, 1.542 | $B_1B_3$, 1.914 | $B_3B_5$, 1.760 |
| | $B_1H$, 1.161 | $B_1B_5$, 1.539 | $B_4B_7$, 1.716 |
| | $B_2H$, 1.172 | $B_1B_6$, 1.904 | $C_1H$, 1.082 |
| | $B_4H$, 1.157 | $C_2H$, 1.850 | $C_2H$, 1.083 |
| | | $C_4H$, 1.078 | $B_3H$, 1.151 |
| | | $B_1H$, 1.146 | $B_4H$, 1.147 |
| | | $B_3H$, 1.151 | $B_7H$, 1.149 |
| | | $B_6H$, 1.555 | |
| total energy | −174.2763 | −200.6769 | −200.6933 |

[a] All geometry-optimized bond distances are in Å and total energies in au. Calculations are at the STO-3G level.

Consider symmetry elements associated with structures in eq 2. A plane of symmetry maintained through the process **3** → **6** → **7**. In the second half of the rearrangement **7** → **8** → **5**, the 6–7 bond in **7** breaks to give the open square in **8** followed by the formation of a 2–5 bond to regenerate the pentagonal bipyramid **5**, now oriented with the 5-fold rotational axis passing through atoms 3 and 5. Throughout the second half of this rearrangement a single plane of symmetry is maintained, this one passing through atoms 2, 3, and 5. Therefore, no symmetry element is carried through the entire process **3** → **5**.

In the process **3** ($D_{5h}$) → **6** ($C_s$) → **7** ($C_{3v}$), orbital degeneracies in **3** are lost in **6** and new (and different) degeneracies appear in **7**. It turns out that the HOMO and LUMO of **7** are degenerate, establishing an open-shell electron configuration. This degeneracy could be predicted from the simple rule developed by Wales and Stone.[52] Using a model derived from tensor spherical harmonics, they have determined that an intermediate having a single atom on a 3-fold or higher major axis of symmetry will contain a degenerate HOMO–LUMO pair. The capped octahedron **7** contains a 3-fold axis. Although the overall rearrangement of eq 2 does not maintain an element of symmetry throughout by which orbitals can be classified, the fact that the HOMO must rise to touch the LUMO in the transitional state **7** suggest that this structure has a high energy and therefore that eq 2 is not a likely mechanism for the rearrangement.

The HOMO–LUMO degeneracy of the capped octahedron holds only for the boron hydride $B_7H_7^{2-}$. For the carborane isomers $C_2B_5H_7$, however, the introduction of the carbon heteroatoms eliminates the 3-fold axis, thus removing the requirement of orbital degeneracies. But presumably the nodal properties of the carborane MOs are similar to those of $B_7H_7^{2-}$. The largest HOMO–LUMO gap obtained from stationary-point calculations (all main-frame bond distances were 1.7 Å and all distances to H were 1.1 Å) for the carboranes in a capped-octahedral configuration is only 7.6 kcal/mol. This suggests a high energy barrier

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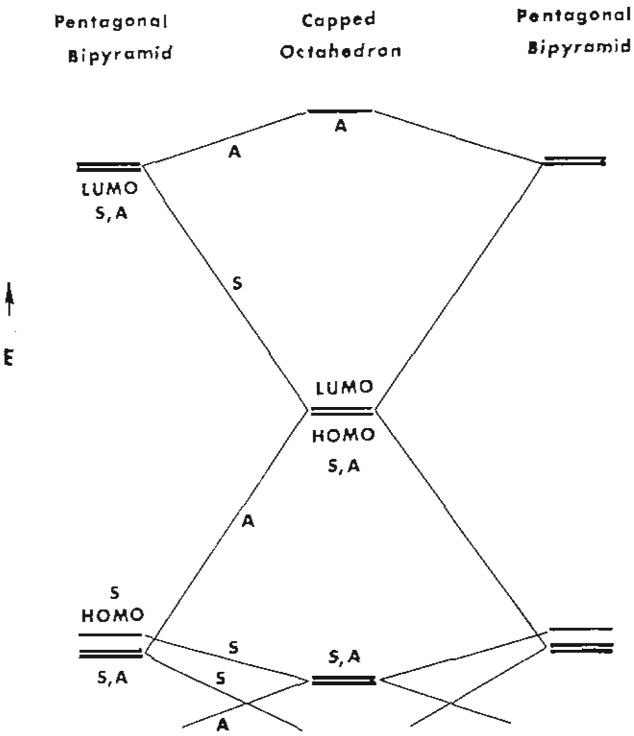


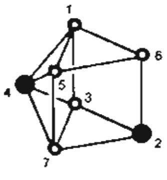
**Figure 2.** Correlation of orbital energy levels between the pentagonal bipyramid and the capped octahedron for $B_7H_7^{2-}$ around the HOMO–LUMO gap.

between the initial and final pentagonal bipyramids via a capped-octahedral intermediate.

The molecular orbitals of the pentagonal bipyramid and the capped octahedron can be classified with respect to the plane of symmetry that is maintained through the process **3** → **6** → **7**. The molecular orbitals are either symmetric (S) or antisymmetric (A) with respect to this plane. The peculiar correlations of MOs around the HOMO–LUMO gap are known in Figures 2 and 3, which include energy levels from extended Hückel calculations. Figure 3 includes AO composition diagrams for the MOs involved. Because of the differences in symmetry and structure between the pentagonal bipyramid and capped octahedron the relations in AO composition between connected MOs are far from obvious.

**Heteroatomic Case.** The replacement of two $B^-$ entities by two carbon atoms allows for more than one possible starting structure and/or intermediate. Inspection of the figures drawn in eq 1, 2, and 3 reveals that a degenerate rearrangement occurs for the equivalent starting 2,4- and 4.6-structures.

First consider the reaction path described by eq 1. Both of the equivalent starting 2,4- and 4.6-structures would pass through a common intermediate, **4′**. This intermediate is found to be 72.4 kcal/mol higher in energy than the 2,4-isomer. McKee calculates the energy to be only 60.6 kcal/mol above that of the 2,4-isomer at the [MP2/6-31G*] level.[44] (This structure is lower in energy than the unknown 1,7-pentagonal-bipyramidal isomer.) The geometry-optimized bond distances obtained for the structure are reported in Table I.



**4′**

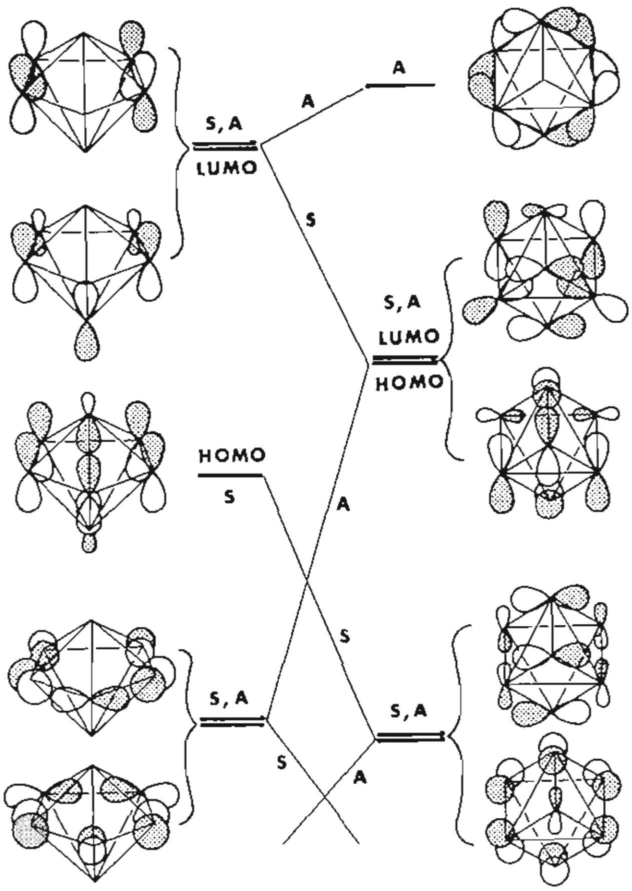
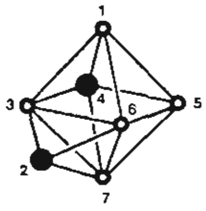
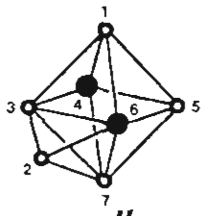


**Figure 3.** MO composition diagram of those orbitals shown in Figure 2.

While the open-shell electron configuration for the capped octahedron for $B_7H_7^{2-}$ indicates that eq 2 is unlikely, it is still interesting to examine the structures that would intervene if this route were accessible. Following eq 2 for the equivalent 2,4- and 4,6-structures leads to two different capped octahedral intermediates:



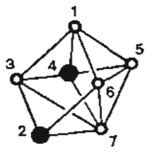
**7′**



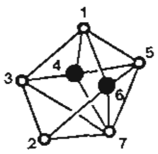
**7″**

Stationary-point calculations with all main-frame bond distances equal to 1.7 Å and all distances to H as 1.1 Å show these two structures to be about 230 kcal/mol higher in energy than the 2,4-pentagonal-bipyramidal structure. Geometry optimizations of the capped octahedron **7′** led to the unstable nido structure **6′**. The structure obtained for **6′** is shown in Table I. This structure is, however, not an intermediate that would be found in the degenerate rearrangement of the 2,4-isomer but it is rather an intermediate that would appear in the nondegenerate rearrangement which converts the 1,2-isomer into the 2,4-isomer via eq 3. McKee also reports the existence of a similar but more open structure.[44] Geometry optimizations for the capped octahedron **7″** led to the capped trigonal prism **4′**. These results do not provide us with a barrier height for eq 2; however, they do indicate that the two strucures **7′** and **7″** are not the relative minima along the reaction path that we would expect them to be if eq 2 were a likely mechanism.

Equation 3 would also lead to two possible intermediates:



**6″**



**6‴**

**Table II.** Relative Energies and Enthalpies (in kcal/mol) for Methyl-Substituted Derivatives of 2,4-$C_2B_5H_7$

| compd | $\Delta H^a$ | $\Delta E^b$ | $\Delta H^c$ |
|---|---|---|---|
| 3-$CH_3$ | 0 | 0 | 0 |
| 1-$CH_3$ | 0.707 | 0.94 | 0.76 |
| 5-$CH_3$ | 0.987 | 1.82 | 1.23 |

[a] Totally optimized MNDO results.[34] [b] Ab initio SCF MO results at the STO-3G level (this work). [c] Experimental results.[32]

We were unsuccessful in locating structures of minimum energy for **6″** and **6‴**. Upon geometry optimization both structures converged to the 2,4-$C_2B_5H_7$ pentagonal bipyramid. The starting structures were 68.8 and 108.8 kcal/mol above the final 2,4-pentagonal-bipyramidal structure.

The inability to locate stationary points for the unstable nido and capped-octahedral structures could indicate poor starting structures. If our starting structure is reasonably close to that of a local minimum (i.e. a reactive intermediate), as is the case for the capped trigonal prism, we find no difficulty in getting an optimized structure. However, if the structure in actuality represents that of a transition state, then the starting geometry must be such that the Hessian matrix initially contains one negative eigenvalue for a successful geometry optimization. Such a starting structure is difficult to generate. We were unable to do so.

### Barrier Heights for Nondegenerate Rearrangements

To obtain approximate barrier heights for the nondegenerate rearrangements that interconvert all of the possible isomers according to the reaction graph **9**, geometry optimizations were attempted for all possible intermediates that would be formed in either eq 1 or eq 3. The structure **6′**, which intermediates between the 1,2- and 2,4-isomers via eq 3, lies 12 kcal/mol above the 1,2-pentagonal-bipyramidal structure. All other intermediates converged on the pentagonal bipyramid.

### Substituted Carboranes

After heating a sample of 5-$(CH_3)$-2,4-$C_2B_5H_6$ to 295 °C, Onak et al. found the sample to contain an equilibrium mixture of all possible B-substituted isomers. Assuming a DSD mechanism, the following equilibria are established:

$$\text{5-(CH}_3\text{)-2,4-C}_2\text{B}_5\text{H}_6 \rightleftarrows \text{1-(CH}_3\text{)-2,4-C}_2\text{B}_5\text{H}_6 \rightleftarrows \text{3-(CH}_3\text{)-2,4-C}_2\text{B}_5\text{H}_6$$

An alternate trigonal face rotation mechanism (TRF), which is cleverly eliminated by Onak, would also provide a mixture of boron-substituted isomers but the reaction path would afford the sequence

$$\text{1-(CH}_3\text{)-2,4-C}_2\text{B}_5\text{H}_6 \rightleftarrows \text{5-(CH}_3\text{)-2,4-C}_2\text{B}_5\text{H}_6 \rightleftarrows \text{3-(CH}_3\text{)-2,4-C}_2\text{B}_5\text{H}_6$$

From percent composition data Onak calculates the equilibrium constants for both mechanisms. Using these rate constants, they predict the percent composition curves (rate profile) for 3-$(CH_3)$-2,4-$C_2B_5H_6$ in each of the mechanisms. Actual measurements taken then on the rearrangment of 3-$(CH_3)$-2,4-$C_2B_5H_6$ show the rate profile to match the predicted DSD curves but not the predicted TRF curves.

**Table III.** Relative Energies and Enthalpies (in kcal/mol) for Dimethyl-Substituted Derivatives of 2,4-$C_2B_5H_7$

| compd | $\Delta H^a$ | $\Delta E^b$ | $\Delta H^c$ |
|---|---|---|---|
| 1,3-$(CH_3)_2$ | 0 | 0 | 0 |
| 1,5-$(CH_3)_2$ | 0.940 | 1.71 | 1.38 |
| 1,7-$(CH_3)_2$ | 0.537 | 1.21 | 1.22 |
| 3,5-$(CH_3)_2$ | 0.093 | 0.53 | 0.53 |
| 5,6-$(CH_3)_2$ | 1.512 | 2.50 | 2.28 |

[a] Totally optimized MNDO results.[34] [b] Ab initio SCF MO results at the STO-3G level (this work). [c] Experimental results.[32]

Onak et al. used their experimental equilibrium data obtained in the observed rearrangements of the monomethyl-substituted carboranes to determine the enthalpy differences between various mono- and polysubstituted carborane derivatives. Tables II and III show the relative energies obtained in our calculations for comparison.

### Conclusion

Justification can be made for the existence of only two out of four possible isomers of $C_2B_5H_7$ by considering their relative energies and position along the reaction coordinate, which interconverts all isomers according to a double diamond–square–diamond rearrangement mechanism. The two known isomers of lower energy are separated by one of the higher energy isomers. This barrier prevents the interconversion between the two known isomers, allowing both species to be isolated. However, it is speculated that barriers between the high- and low-energy isomers are small, allowing the higher energy isomers to rearrange to the more stable structures. Optimum structures and energies for all but one of the possible intermediates were unobtainable, as the geometry optimizations led to the pentagonal bipyramids.

Onak has observed the degenerate rearrangement of boron-substituted $C_2B_5H_7$ in which the borons exchange places but the carbons return to their nonadjacent equatorial positions. To explain his results, he proposes three different possible double diamond–square–diamond sequences. The least likely of the three is the mechanism sequence that contains a capped-octahedral intermediate. Our calculations do not lead us to a definite preference for either of the other two possible mechanism sequences.

Calculations done on monomethyl- and dimethyl-substituted carboranes were in agreement with Onak's experimentally determined relative stabilities.

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**Registry No.** **2** (2,3-isomer), 30347-95-6; **2** (1,2-isomer), 25036-76-4; **2** (1,7-isomer), 25036-79-7; **4′**, 20693-69-0; **4″**, 12430-07-8; 3-$CH_3$-2,4-$C_2B_5H_6$, 23940-13-8; 1-$CH_3$-2,4-$C_2B_5H_6$, 23810-31-3; 5-$CH_3$-2,4-$C_2B_5H_6$, 23810-32-4; 1,3-$(CH_3)_2$-2,4-$C_2B_5H_5$, 68297-89-2; 1,5-$(CH_3)_2$-2,4-$C_2B_5H_5$, 68238-17-5; 1,7-$(CH_3)_2$-2,4-$C_2B_5H_5$, 23753-78-8; 3,5-$(CH_3)_2$-2,4-$C_2B_5H_5$, 68238-16-4; 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$, 58548-76-8.