tering factors in the analytical form and anomalous dispersion factors were taken from ref 13. Final atomic coordinates are given in Table I, and selected bond lengths and angles in Table II.

Acknowledgment. We thank NATO for the provision of a travel grant, the British Council (Rome) for support, and Johnson-Matthey plc for a generous loan of platinum salts.

Supplementary Material Available: Tables of full bond lengths and angles, anisotropic thermal parameters, and H atom coordinates (4 pages); a listing of structure factors (21 pages). Ordering information is given on any current masthead page.

---

(13) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

Contribution from the Departments of Chemistry, University of South Carolina,
Columbia, South Carolina 29208, and Furman University, Greenville, South Carolina 29613

Calculations for Various Structural Forms of $B_{12}H_{12}^{2-}$ as Clues to the Possible Mechanisms for the Isomerizations of $C_2B_{10}H_{12}$

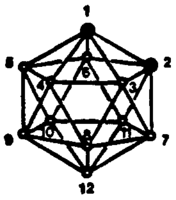
Benjamin M. Gimarc,[*,†] D. Scott Warren,[†] Jane J. Ott,[‡] and Carl Brown[‡]

Received August 10, 1989

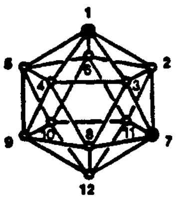
We report the results of geometry-optimized AM1 and ab initio SCF-MO calculations at the STO-3G level for $B_{12}H_{12}^{2-}$ in several structural forms that represent intermediates in various mechanisms proposed for the isomerization of the carboranes *o*-, *m*-, and *p*-$C_2B_{10}H_{12}$. We assume that the energies of the $B_{12}H_{12}^{2-}$ structures, relative to that of the regular icosahedron, represent estimates of activation barriers that the corresponding carboranes might meet along the proposed mechanisms. Structures studied were the regular icosahedron (I_h), an icosahedron of D_{3h} symmetry, the cuboctahedron (O_h), the bicapped pentagonal prism (D_{5h}), the anticuboctahedron (D_{3h}), the tetracapped cube (D_{4h}), the truncated tetrahedron (T_d), and a hexagonal antiprism (D_{6d}). Structural parameters and total energies of these structures are tabulated. Each mechanism can be represented by a reaction graph, the connectivity of which describes the pattern of isomeric conversions for $C_2B_{10}H_{12}$. An acceptable mechanism must have a low activation barrier and require minimal atomic motions, and its reaction graph must account for the experimental observations of isomerizations. The lowest energy pathway seems to be one involving triangular-face rotation. Next higher in energy is the mechanism that passes through the cuboctahedral structure. Carborane isomerization reactions pass through specific transition-state isomers. Lacking calculated energies for these isomers, one can estimate their relative stabilities qualitatively by empirical valence rules and the rule of topological charge stabilization. These considerations give insight into the details of individual processes and, together with the calculated energy results for $B_{12}H_{12}^{2-}$, provide new support for triangular-face rotation as the mechanism that can best account for the observed isomerizations of *o*-, *m*-, and *p*-$C_2B_{10}H_{12}$.

Introduction

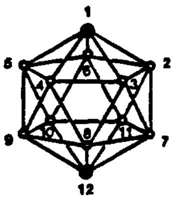
The polyhedral carboranes, $C_2B_{n-2}H_n$, are related to the *closo*-boranes, $B_nH_n^{2-}$ ($5 \leq n \leq 12$). The boron or carbon atoms are linked together to form polyhedral structures with triangular faces. A hydrogen substituent is attached in the position exo to each boron or carbon. The carboranes share the structures of corresponding borane dianions; in each case, two carbon atoms replace a pair of B^- entities. The location of the carbon heteroatoms in the polyhedral cage creates the possibility of positional isomers, and indeed two or more isomers are known for the carboranes where n = 5, 6, 7, 10, and 12. For icosahedral $C_2B_{10}H_{12}$, three isomers are possible (**1**–**3**) and all three have been prepared and characterized.[1-3] The two carbons can be separated by paths of a single-bond distance (1,2, **1**), two bond lengths (1,7, **2**), or three bond lengths (1,12, **3**). Occasionally, the three isomers are referred to as ortho, meta, or para, respectively. Relative stabilities of the three isomers have been rationalized by empirical valence rules[4,5] and the rule of topological charge stabilization,[6] substantiated by the results of ab initio SCF-MO calculations,[7] and confirmed by experimental observations of thermally induced interconversions among the isomers. These methods all agree that the para isomer (1,12) is more stable than the meta (1,7), which in turn is more stable than the ortho isomer (1,2). Heating at 500 °C converts 1,2 into 1,7. At higher temperatures (615 °C), only small amounts of the 1,12-isomer are formed as 1,7-$C_2B_{10}H_{12}$ decomposes.[3] Experiments with substituted 12-atom *closo*-carboranes and -boranes tend to confirm the conclusion that 1,2- and 1,7-isomers interconvert but do not easily rearrange to the 1,12-isomer and that isomerizations occur intramolecularly.[8] The activation barrier to rearrangement of 1,2-$C_2B_{10}H_{12}$ is 62 kcal/mol.[9] The barrier to $B_{12}H_{12}^{2-}$ rearrangement has been estimated to exceed 80 kcal/mol.[10]



1



2



3

Intramolecular thermal isomerizations have been observed to occur in other carboranes as well. In these framework reorganizations, bonds break and are replaced by new bonds and carbon heteroatoms are shifted to new positions, but the process occurs in such a way that the original structural form of the polyhedron is restored. Twenty-five years ago, Lipscomb proposed a general mechanism for the isomerization of the *closo*-boranes and -carboranes. In a classic review,[11] Lipscomb suggested that the re-

---

[†] University of South Carolina.

[‡] Furman University.

(1) Potenza, J. A.; Lipscomb, W. N. *Inorg. Chem.* **1966**, *5*, 1471–1477, 1478–1482, 1483–1488.

(2) Potenza, J. A.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1966**, *56*, 1917–1919. Beall, H.; Lipscomb, W. N. *Inorg. Chem.* **1967**, *6*, 874–879.

(3) Papetti, S.; Heyling, T. L. *J. Am. Chem. Soc.* **1964**, *86*, 2295.

(4) Williams, R. E.; Gerhart, F. J. *J. Am. Chem. Soc.* **1965**, *87*, 3513–3515.

(5) Williams, R. E. In *Progress in Boron Chemistry*; Brotherton, R. J., Steinberg, H., Eds. Pergamon: Oxford, England, 1970; Vol. 2, p 37.

(6) Ott, J. J.; Gimarc, B. M. *J. Am. Chem. Soc.* **1986**, *108*, 4303–4308.

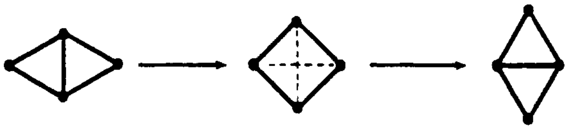
(7) Ott, J. J.; Gimarc, B. M. *J. Comput. Chem.* **1986**, *7*, 673–692.

(8) Hertler, W. R.; Knoth, W. H.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 5434–5439.

(9) Salinger, R. M.; Frye, C. L. *Inorg. Chem.* **1965**, *4*, 1815–1816.

(10) Muetterties, E. L.; Knoth, W. H. *Polyhedral Boranes*; Marcel Dekker: New York, 1968; p 69.

arrangements take place through a process in which a bond forming the edge between two adjacent triangular faces of the polyhedron breaks and is replaced by a new bond that is perpendicular to the lost bond. Initial and final structures contain pairs of edge-fused triangles or diamonds, while the intermediate structure contains a square face. Lipscomb called this process a diamond–square–diamond (DSD) rearrangement:



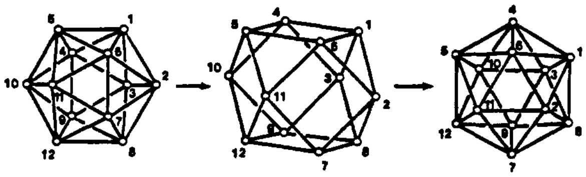
His proposal grew out of earlier studies of particular systems.[12-14] Muetterties and co-workers contributed considerable insight, based on both experimental and theoretical studies, to specific borane and carborane rearrangement processes.[8,15-24] In our previous theoretical studies of the *closo*-boranes and -carboranes, we found support for DSD rearrangements in the 7-, 8-, 10-, 11-, and, possibly, 9-atom cages but not for the 5-atom carborane.[25-27] In this paper, we consider rearrangements of the 12-atom cage.

Calculated Structures for $B_{12}H_{12}^{2-}$

We report the results of Gaussian 82 ab initio SCF–MO calculations at the STO-3G level for $B_{12}H_{12}^{2-}$ in various structural forms proposed as transition states or intermediates in intramolecular rearrangements.[28] One of our reviewers suggested that we carry out calculations of vibrational frequencies for each proposed structure to determine whether that structure represents a true minimum on the energy surface. For a true minimum, all calculated frequencies must be real; if one or more of these frequencies is imaginary, then the corresponding structure is not a minimum on the energy surface. When we attempted to implement this suggestion for our STO-3G structures, we found that it would require more computer resources than we were willing to devote to this problem. Therefore, we executed a series of geometry-optimized semiempirical AM1 calculations, including calculations of vibrational frequencies.[29] The AM1 calculations are quite economical, they provide an additional set of relative energy comparisons among the various structures, and they also give us some information about the positions of the structures on the energy surface. We combine these calculated results with mechanistic proposals and their corresponding reaction graphs and compare conclusions with the reported experimental observations to evaluate the mechanisms.

Our use of the STO-3G basis set for this work deserves some criticism. Previously, and with apparent success, we compared carborane isomer energies calculated at this level.[7] Because we were comparing positional isomers of the same polyhedral form, we were reasonably confident that correlation and basis set errors might largely cancel. In the present work, we compare energies of different polyhedra. In this situation, cancellation of errors is more problematic. These and other difficulties apply to the AM1 calculations. We used the AM1 routines included in the Gaussian 88 package.[30] Unfortunately, AM1 has not been parametrized for boron, for which the program takes MNDO/3 parameters by default. Finally, we can only hope that there is some parallel between energy surfaces from AM1 and STO-3G calculations. Despite these limitations, the AM1 and ab initio STO-3G methods allow us to survey a larger number of different proposed intermediate structures, and at a higher level of theory than has yet been reported. In several instances, the calculated energy differences are large enough to allow confident conclusions.

The Cuboctahedral Intermediate. Equation 1 is the mechanism that Lipscomb and Britton[12] proposed for the isomerization of $C_2B_{10}H_{12}$. This mechanism involves six simultaneous DSD processes to reach the cuboctahedral intermediate **4**. Starting with carbon atoms in all possible pairs of positions in the icosahedron on the left, noting their relative positions in the rearranged icosahedron on the right, and expressing each isomer involved as one of the three representative isomers 1,2, 1,7, or 1,12 lead to the reaction graph **5** corresponding to eq 1. Asterisks above the isomer indices in **5** indicate that rearrangements of the starred isomers are possible that carry that isomer into itself. For example, starting with carbons in positions 1 and 12 on the left leads to an isomer on the right in which the two carbons are still three bond distances apart. The most significant feature of **5** is that it is a disconnected graph. Although a number of processes interconvert isomers 1,2 and 1,7, none converts either of these isomers to 1,12 or the reverse. The experimental observations of thermal isomerization seem to support the disconnected graph **5** and therefore eq 1 as adequately describing the framework reorganization. The conversion of 1,7 to 1,12 is more difficult than the interconversion of 1,2 and 1,7. Therefore, the 1,2 → 1,7 isomerization might follow eq 1 and its corresponding disconnected graph **5**. The small amount of 1,12 formed as 1,7 decomposes has suggested that this rearrangement might follow a different mechanism that allows connection between 1,7 and 1,12 and has a higher activation energy.



4

(1)

$$\overset{*}{1,2} \rightleftarrows \overset{*}{1,7} \qquad\qquad \overset{*}{1,12}$$

5

Our ab initio calculations for $B_{12}H_{12}^{2-}$ reveal that the cuboctahedral structure **4** is 210 kcal/mol higher in energy than the regular icosahedral form. Total energies and structural parameters for both ab initio STO-3G and AM1 results are given in Table I. The energy difference between cuboctahedral and icosahedral $B_{12}H_{12}^{2-}$ is an estimate of the activation barrier for the carborane isomerizations through a cuboctahedral intermediate. This remarkably large value for an activation barrier would seem to be too large to account for observed isomerizations of $C_2B_{10}H_{12}$. What alternative isomerization mechanisms and intermediate structures might be involved?

---

(11) Lipscomb, W. N. *Science* **1966**, *153*, 373–378.

(12) Lipscomb, W. N.; Britton, D. *J. Chem. Phys.* **1960**, *33*, 275–280.

(13) Kaczmarczyk, A.; Dobrott, R. D.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1962**, *48*, 729–733.

(14) Hoffmann, R.; Lipscomb, W. N. *Inorg. Chem.* **1963**, *2*, 231–232.

(15) Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1966**, *5*, 1955–1960.

(16) Muetterties, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5097–5102.

(17) Muetterties, E. L.; Storr, A. T. *J. Am. Chem. Soc.* **1969**, *91*, 3098–3099.

(18) Muetterties, E. L.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 7520–7522.

(19) Muetterties, E. L. *Tetrahedron* **1974**, *30*, 1595–1604.

(20) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748–1756.

(21) Muetterties, E. L.; Hoel, E. L.; Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1975**, *14*, 950–951.

(22) Guggenberger, L. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 7221–7225.

(23) Muetterties, E. L.; Beier, B. F. *Bull. Soc. Chem. Belg.* **1975**, *84*, 397–406.

(24) Muetterties, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 1636–1643; *Rec. Chem. Prog.* **1970**, *31*, 51–88.

(25) Gimarc, B. M.; Ott, J. J. *Inorg. Chem.* **1986**, *25*, 83–85.

(26) Gimarc, B. M.; Ott, J. J. *Inorg. Chem.* **1986**, *25*, 2708–2711.

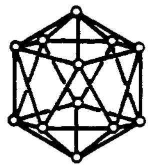
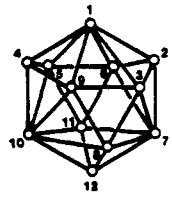
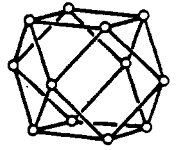
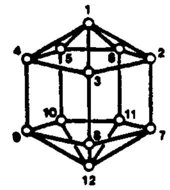
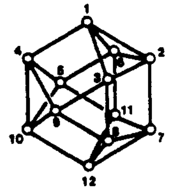
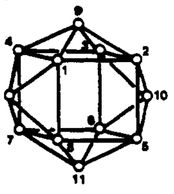
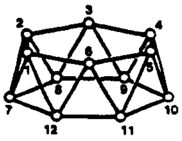
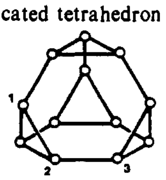
(27) Gimarc, B. M.; Ott, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 1388–1392.

(28) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. *Gaussian 82 Revision H Version*; Carnegie-Mellon University: Pittsburgh, PA, 1984.

(29) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

(30) Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. *Gaussian 88*; Gaussian, Inc.: Pittsburgh, PA, 1988.

Table I. Optimized Structures and Energies of Various Forms of $B_{12}H_{12}^{2-}$: Bond Distances in Å, Heats of Formation (HF) and Total Energies (ET) in hartrees, Relative Energies (EREL) in kcal/mol

structure	AM1	ab Initio
regular icosahedron (I_h) 	B–B = 1.811 B–H = 1.160 HF = −0.231 313 4 EREL = 0.0	B–B = 1.771 B–H = 1.153 ET = −299.506 EREL = 0.0
icosahedron (D_{3h}) 	B_1–B_2 = 1.772 B_1–B_3 = 2.002 B_2–B_3 = 1.646 B_3–B_8 = 1.785 B_1–H = 1.165 B_2–H = 1.159 B_3–H = 1.166 HF = −0.072 367 6 EREL = +99.7	B_1–B_2 = 1.782 B_1–B_3 = 1.933 B_2–B_3 = 1.608 B_3–B_8 = 1.769 B_1–H = 1.157 B_2–H = 1.151 B_3–H = 1.154 ET = −299.2751 EREL = +144.9
cuboctahedron (O_h) 	B–B = 1.757 B–H = 1.164 HF = −0.026 539 6 EREL = +128.5	B–B = 1.735 B–H = 1.155 ET = −299.1699 EREL = +211.0
bicapped pentagonal prism (D_{5h}) 	B_1–B_2 = 1.761 B_2–B_3 = 1.754 B_2–B_7 = 1.838 B_1–H = 1.161 B_2–H = 1.166 HF = +0.066 839 2 EREL = +187.1	B_1–B_2 = 1.717 B_2–B_3 = 1.701 B_2–B_7 = 1.966 B_1–H = 1.152 B_2–H = 1.154 ET = −299.1495 EREL = +223.8
anticuboctahedron (D_{3h}) 	B_1–B_2 = 1.758 B_1–B_4 = 1.740 B_3–B_8 = 1.785 B_1–B_3 = 1.758 B_1–H = 1.166 B_3–H = 1.168 HF = −0.009 211 6 EREL = +139.4	B_1–B_2 = 1.687 B_1–B_4 = 1.791 B_3–B_8 = 1.766 B_1–B_3 = 1.733 B_1–H = 1.156 B_3–H = 1.158 ET = −299.1311 EREL = +235.3
tetracapped cube (D_{4h}) 	B_1–B_2 = 2.038 B_1–B_9 = 1.693 B_1–B_4 = 1.981 B_1–H = 1.169 B_9–H = 1.160 HF = +0.069 683 1 EREL = +188.9	B_1–B_2 = 2.076 B_1–B_9 = 1.669 B_1–B_4 = 1.840 B_1–H = 1.151 B_9–H = 1.159 ET = −299.1275 EREL = +237.6
hexagonal antiprism (D_{6d}) 	B_1–B_2 = 1.719 B_1–B_7 = 1.849 B–H = 1.177 HF = +0.085 515 6 EREL = +198.8	B_1–B_2 = 1.741 B_1–B_7 = 1.811 B–H = 1.165 ET = −299.005 EREL = +314.3
truncated tetrahedron (T_d) 	B_1–B_2 = 1.562 B_2–B_3 = 1.757 B–H = 1.180 HF +0.225 478 3 EREL = +286.6	B_1–B_2 = 1.821 B_2–B_3 = 1.579 B–H = 1.167 ET = −298.7513 EREL = +473.7

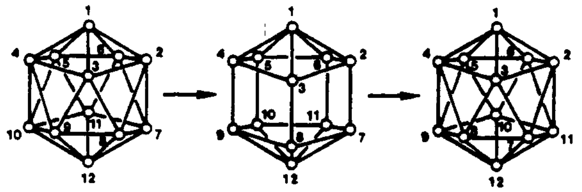
Muetterties and co-workers have proposed different mechanisms for icosahedral isomerizations.[24] Some of these do not involve DSD processes. Fuller and Kepert have used an empirical potential model to estimate relative energies for various $B_nH_n^{2-}$ polyhedra.[31] For $B_{12}H_{12}^{2-}$ alone, they evaluated 17 possible structures, at least some of which are reasonable structures for carborane rearrangement intermediates. Fuller and Kepert calculated a total bond energy function

$$U = \sum_{i<j} (1/r_{ij}^2 - 1/r_{ij})$$

where r_{ij} are distances between atoms i and j. Results of their calculations show that the regular icosahedron is the most stable of the various structures they studied for $B_{12}H_{12}^{2-}$. Higher in energy were the C_{3h} icosahedron and the bicapped pentagonal prism (D_{5h}). Higher still was the cuboctahedron. Dewar and McKee have reported geometry-optimized MNDO calculations on regular icosahedral $B_{12}H_{12}^{2-}$ as well as the D_{3h} icosahedron, the bicapped pentagonal prism, the cuboctahedron, and the anticuboctahedron.[32] Wales and Stone have carried out optimized ab initio SCF-MO calculations with the 4-31G basis set for $B_{12}H_{12}^{2-}$ in regular icosahedral, cuboctahedral, and bicapped-pentagonal-prismatic geometries.[33] These studies suggest isomerization pathways that might have lower energy barriers than those encountered in eq 1.

One of the obvious limitations of eq 1 is the energy required to break six bonds to form the cuboctahedron **4**. Wales and Stone have noted that mechanisms involving fewer DSD processes are favored.[33] For example, $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ can rearrange with only a single DSD process and these ions are known to be fluxional on the NMR time scale. Rearrangements of the $C_2B_5H_7$ and $C_2B_8H_{10}$ cages involve two DSD processes, and these require thermal activation. The still higher temperatures needed for the interconversion of $C_2B_{10}H_{12}$ isomers indicate that two or more DSD processes must be involved. These ideas lead us to expect that low-energy reaction paths are those that involve intermediate or transition-state structures that can be reached by breaking few bonds.

The Bicapped Pentagonal Prism. Equation 2 shows the bottom pentagonal pyramid of an icosahedron rotating with respect to a fixed top pyramid.[34] The intermediate structure is a bicapped pentagonal prism (D_{5h}). This rearrangement requires five simultaneous DSD processes. The reaction graph for eq 2 is **6**.



(2)

$$\overset{*}{1,2} \underset{5}{\overset{5}{\rightleftarrows}} \overset{*}{1,7} \underset{5}{\overset{5}{\rightleftarrows}} 1,12$$

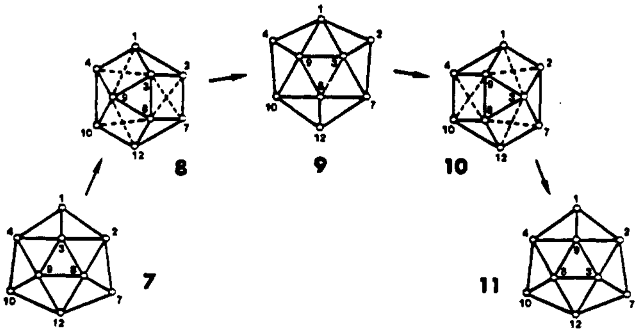
6

Our ab initio calculations put the energy difference between $B_{12}H_{12}^{2-}$ in bicapped-pentagonal-prismatic and regular octahedral forms at 224 kcal/mol. If this is an estimate of the activation barriers for the carborane rearrangement, then the bicapped pentagonal prism is only 10 kcal/mol above or comparable to the cuboctahedron as an intermediate in carborane rearrangements.

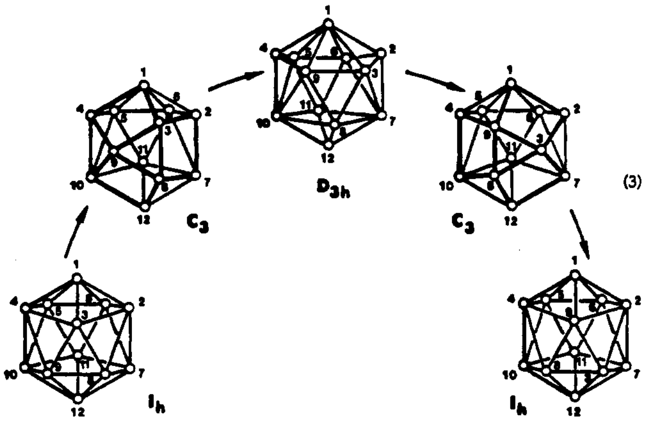
Triangular Face Rotation. Muetterties proposed a triangular-face rotation (TFR) as a possible framework reorganization mechanism for the icosahedron.[24] Other authors have recently shown interest in this process.[33,35] The following scheme is a modification of Muetterties' proposal. Diagrams **7–11** show only

---

(31) Fuller, D. J.; Kepert, D. L. *Inorg. Chem.* **1982**, *21*, 163–167; *Polyhedron* **1983**, *2*, 749–759.
(32) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1978**, *17*, 1569–1581.
(33) Wales, D. J.; Stone, A. J. *Inorg. Chem.* **1987**, *26*, 3845–3850.
(34) Grafstein, D.; Dvorak, J. *Inorg. Chem.* **1963**, *2*, 1128–1133.
(35) Wales, D. J.; Mingos, D. M. P.; Zhenyang, L. *Inorg. Chem.* **1989**, *28*, 2754–2764.



a portion of the icosahedral structure, and that portion is depicted as though it were flat. The triangular face (3, 8, 9) rotates clockwise by 120° from **7** to **11**. As drawn here, this mechanism consists of two consecutive steps, with each step involving three simultaneous DSD processes at **8** and **10**. Equation 3 attempts to show what the overall process looks like for the full 12-atom cage. The reaction graph corresponding to the TFR mechanism, eq 3, is **12**. The numbers above and below the arrows count the number of individual processes relating connected pairs of isomers. Although the 1,7- and 1,12-isomers are connected in **12**, this result might still be consistent with the experimental observations of $C_2B_{10}H_{12}$ isomerizations because there are twice as many routes between 1,2 and 1,7 as between 1,7 and 1,12, suggesting that the 1,2 to 1,7 isomerization is more probable, but this feature alone is probably not sufficient to account for the extreme difficulty in the conversion of the 1,7-isomer into the 1,12-isomer. The energy of the D_{3h} icosahedron is 144.9 kcal/mol above that of the regular icosahedron. The total energy and bond distances for the D_{3h} icosahedron calculated at the STO-3G level appear in Table I.

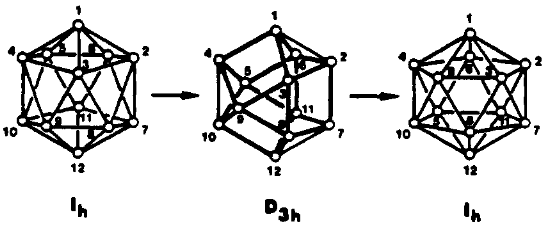


(3)

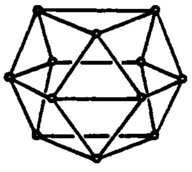
$$\overset{*}{1{,}2} \underset{6}{\overset{6}{\rightleftarrows}} \overset{*}{1{,}7} \underset{3}{\overset{3}{\rightleftarrows}} 1{,}12$$

12

Equation 4 describes a double-TFR mechanism in which opposing triangular faces rotate in opposite directions by 60°. In these pictures, the front triangle (3, 8, 9) rotates clockwise, while the rear triangle (5, 6, 11) rotates counterclockwise. This mechanism involves six simultaneous DSD processes in the intermediate D_{3h} structure. The contrarotation of opposing triangular faces requires shorter movement of each atom through space than is necessary in equation 3. The reaction graph for the double-TFR mechanism is identical with the one for the single-TFR rearrangement (**12**). The intermediate structure of D_{3h} symmetry in eq 4 is the anticuboctahedron (**13**) proposed by Fuller and Kepert.[31] Their empirical potential model gave this structure a fairly high energy.



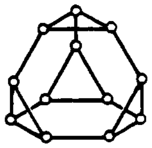
(4)



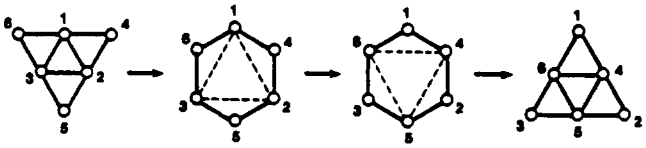
13

Our ab initio SCF–MO results (Table I) show that the anticuboctahedron (**13**) is 235 kcal/mol above that of the regular icosahedron and 24 kcal/mol above that of the cuboctahedron (**4**).

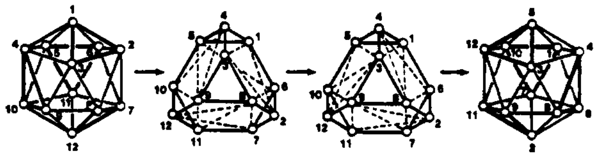
The Truncated Tetrahedron. Muetterties proposed a truncated tetrahedral structure **14** as a possible intermediate for isomerization of icosahedral $C_2B_{10}H_{12}$.[24] The surface of this structure has four hexagonal faces, each of which shares three edges with the other hexagons. Four triangles join the hexagons. The triangles are formed by slicing off the four corners of a tetrahedron. A hexagonal face might be formed in an icosahedral surface by the following triangle–hexagon–triangle process.



14



The atoms that comprise the central triangular unit (1, 2, 3) of the larger triangle on the left become the outside vertices in the triangle on the right. Each hexagonal face in **14** results from breaking three bonds among four unit triangles, or a total of twelve broken bonds in the icosahedron produce the truncated tetrahedron **14**. The energy required for all this bond breaking is likely to be too large to allow the truncated tetrahedron to be a realistic intermediate. Equation 5 shows what the process must be like.



(5)

Heavy lines in the icosahedron on the left denote those triangles that disappear to make the hexagons. Heavy lines in the icosahedron on the right emphasize new triangles that formed within the hexagons to regenerate the icosahedron. Relative to the foreground triangle (3, 8, 9), which for the illustration is fixed throughout the process, other atoms must move through considerable distances during the rearrangement. Equation 5 is unlikely on the grounds of both energetics and dynamics suggested by Muetterties.[21] The many bonds to be broken to reach the intermediate structure require too much energy, and too much motion is required for atoms to reach their final positions. The reaction graph **15** relates isomers through the mechanism of equation 5.

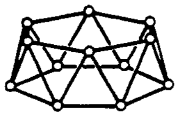
The ab initio calculated energy of the truncated tetrahedral (**14**) form of $B_{12}H_{12}^{2-}$ is 474 kcal/mol above that of the icosahedron, eliminating eq 5 as a realistic isomerization pathway and

$$\overset{*}{1,2} \underset{12}{\overset{12}{\rightleftarrows}} \overset{*}{1,7} \underset{6}{\overset{6}{\rightleftarrows}} 1,12$$

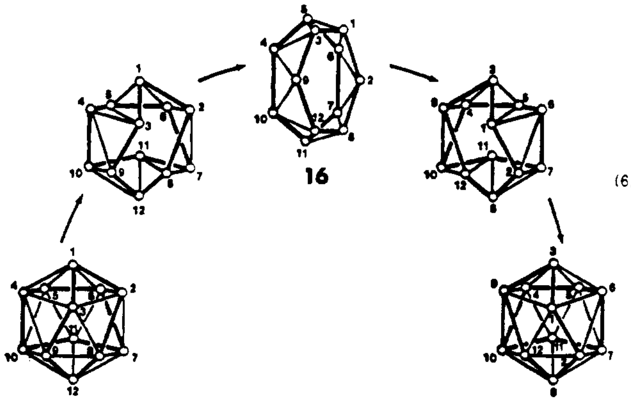
15

the truncated tetrahedron as a possible intermediate. Total energy and structural parameters for **14** are contained in Table I.

The Hexagonal Antiprism. Fuller and Kepert suggested a hexagonal antiprism **16** as a possible structure for the 12-atom cage.[31] This particular structure was among the highest in energy of the 17 structures they evaluated with their empirical potential model. Equation 6 shows how the hexagonal antiprism could serve as a transition state in the isomerization of icosahedral carboranes. To form the hexagonal antiprism (**16**) from the regular icosahedron in equation 6 requires the excising of eight bonds in the icosahedron and the formation of two new bonds (3–5 and 8–11). Bold lines in structures in equation 6 outline the perimeters of the hexagons of **16** that are maintained throughout the reaction. These diagrams reveal two severe limitations of the mechanism. First, the process involves the breaking of a large number of bonds, suggesting a high activation energy. Second, unfolding the icosahedral arrangement of atoms to give the hexagonal antiprism **16** and subsequent recoiling to produce a rearranged regular icosahedron involve extensive motion of atoms through space, violating the dynamical or least motion principle mentioned by Muetterties.[21] Indeed, the calculated energy of the hexagonal antiprism (D_{6d}) is high, 317 kcal/mol above that of the regular icosahedron. Total energy and optimized bond distances appear in Table I. The reaction graph for eq 6 is **17**. By linking all three isomers, the reaction graph **17** provides an avenue for direct conversion of 1,2 to 1,12, which appears to be inconsistent with experimental observations. Thus, several features serve to eliminate eq 6 from serious consideration as a reaction mechanism for carborane isomerizations.



16

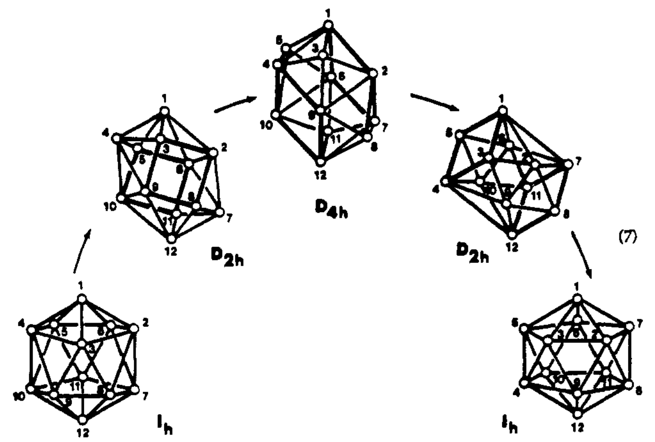


(6)

$$\begin{tikzcd} & 1,12 \arrow[dl, shift left] \arrow[dr, shift left] & \\ 1,2 \arrow[ur, shift left] \arrow[rr, shift left] & & 1,7 \arrow[ul, shift left] \arrow[ll, shift left] \end{tikzcd}$$

17

Consecutive DSD Processes. For the isomerization to pass through the cuboctahedral intermediate (**4**) would require the opening of six bonds before new bonds are formed. The high calculated energy of the cuboctahedral intermediate apparently reflects the large energy required to break these bonds. A mechanism with fewer simultaneous DSD processes might have a lower activation barrier. Equation 7 displays a mechanism involving three sequential or consecutive double-DSD processes.



(7)

Because the same bonds are broken and formed as in the cuboctahedral mechanism, eq 7 has the same disconnected reaction graph as eq 1. In these diagrams bonds 3–8 and 5–11 break in the initial icosahedron to open squares in the first D_{2h} structure. New 2–9 and 6–10 bonds then close the squares to give diamonds, and 2–6 and 9–10 bonds open to give another pair of opposed squares in the tetracapped cube (D_{4h}) structure. These squares are closed with the formation of 1–7 and 4–12 bonds and a third pair of square faces open in the second D_{2h} structure with the breaking of 1–4 and 7–12. Finally, 1–5 and 8–11 bonds close to regenerate a regular icosahedron. The ab initio calculated energy of the tetracapped cube (D_{4h}) form of $B_{12}H_{12}^{2-}$ is 237.5 kcal/mol above that of the regular icosahedral structure. Table I contains the structure and total energy. This result is slightly higher than but comparable to that of the cuboctahedron itself. Attempts to optimize a structure with D_{2h} symmetry led to the tetracapped cube (D_{4h}).

Kharas and Dahl[36] have proposed a variation of eq 7 in which the icosahedron undergoes a single-DSD process (3⋯8, 2–9), producing a tetracapped cuneane structure, followed by the opening of three bonds (5⋯11, 2⋯6, 9⋯10) and the formation of one bond (6–10) to give a tetracapped cube identical with the central D_{4h} structure of eq 7. The tetracapped cube collapses to another tetracapped cuneane, which then rearranges to an icosahedron. Although they occur in a different sequence, the same bonds are broken and formed as in eqs 1 and 7. Therefore, the Kharas–Dahl mechanism has the same reaction graph as eq 1 and the activation energy can be no lower than that of the tetracapped cube of eq 7. Therefore, this process does not require a separate analysis.

Summary of Computational Results

Table II compares relative energies of various structures for $B_{12}H_{12}^{2-}$ as calculated at different levels of theory by Dewar and McKee,[32] Fuller and Kepert,[31] and Wales and Stone[33] and in our ab initio STO-3G and AM1 work described here. The empirical potential model of Fuller and Kepert yields energy values in arbitrary units. For these comparisons, we have multiplied their energies by 1500, which makes the energy they obtained for the D_{3h} icosahedron approximate that reported for this structure by Dewar and McKee. Thus calibrated, the remaining empirical potential energies fall remarkably close to those of the MNDO calculations. The AM1 results are also fairly close to the MNDO energies of Dewar and McKee, with the exception of the bicapped pentagonal prism, for which the MNDO energy appears to be low. Our ab initio STO-3G relative energies are uniformly high compared with our AM1 results and the MNDO results of Dewar and McKee. The ab initio energies of Wales and Stone, who used a superior (4-31G) basis set, are comparable to ours for the bicapped pentagonal prism but fall midway between ours and the MNDO and AM1 results in the case of the cuboctahedron. Both sets of ab initio calculations place the bicapped pentagonal prism at an energy higher than that of the cuboctahedron. The MNDO

---

(36) Kharas, K. C. C.; Dahl, L. F. *Adv. Chem. Phys.* **1988**, *70*, Part II, 1–43.

Table II. Relative Energies (kcal/mol) Determined by Different Theoretical Methods for $B_{12}H_{12}^{2-}$ in Various Structural Forms

structure	empirical potential[a,b]	MNDO[c]	AM1[d]	ab Initio STO-3G[d]	ab Initio 4-31G[e]
regular icosahedron, I_h	0	0	0	0	0
icosahedron, D_{3h}	88	89.9	99.7	144.9	
cuboctahedron, O_h	129	126.6	128.5	211.0	163
bicapped pentagonal prism, D_{5h}	96	109.3	187.1	223.8	225
anticuboctahedron, D_{3h}	116	130.0	139.4	235.3	
tetracapped cube, D_{4h}	120[f]		188.9	237.6	
hexagonal antiprism, D_{6h}	511		198.8	314.3	
truncated tetrahedron, T_d	884		286.6	473.7	

[a] Fuller and Kepert.[31] [b] Fuller and Kepert's unitless energies have been multiplied by 1500 to give the D_{3h} icosahedron a relative energy close to that for the MNDO calculation. [c] Dewar and McKee.[32] [d] This work. [e] Wales and Stone.[33] [f] Value reported for the elongated cuboctahedron, probably closest to the tetracapped cube.

Table III. Numbers of Imaginary Vibrational Frequencies, Obtained at the AM1 Level, for Each of the Structures Considered

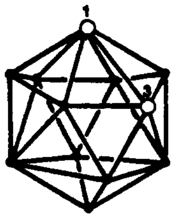
structure	no. of imaginary frequencies
regular icosahedron, I_h	0
icosahedron, D_{3h}	3
cuboctahedron, O_h	4
bicapped pentagonal prism, D_{5h}	4
anticuboctahedron, D_{3h}	6
tetracapped cube, D_{4h}	7
hexagonal antiprism, D_{6d}	9
truncated tetrahedron, T_d	9

and empirical potential results reverse the relative stabilities of cuboctahedron and bicapped pentagonal prism compared to the ab initio results. Table III shows the number of imaginary vibrational frequencies as obtained by AM1 calculations for each of the eight structures considered here. Only the lowest energy structure, the regular icosahedron, corresponds to a minimum on the energy surface. Wales and Stone have also analyzed calculated force constants for the cuboctahedron and bicapped pentagonal prism and found that neither structure corresponds to a true transition state at the 4-31G level of approximation. Of the various proposed intermediate or transition-state structures, the D_{3h} icosahedron has the lowest energy as obtained by empirical potential, MNDO, AM1, and ab initio STO-3G calculations, suggesting eq 3 as the most likely carborane rearrangement pathway. But a transition-state structure is characterized by having a single imaginary vibrational frequency as well as low energy. The three imaginary frequencies (Table III) obtained by AM1 calculations for the D_{3h} icosahedron prove that this structure is not the transition state we are looking for. We chose the D_{3h} icosahedron because it is the structure of highest symmetry that could be encountered along the TFR pathway. But rearrangement by TFR could be achieved through a structure of lower symmetry. An appealing structure is the C_{3v} icosahedron that can be formed from the D_{3h} (eq 3) by allowing the rotating triangular face to be different in size from the fixed triangle behind and by distorting the planar hexagon of the D_{3h} structure by alternately raising and lowing vertices to give a chair form. Our attempts to optimize the geometry of such a structure under C_{3v} symmetry constraints led back to the higher symmetry D_{3h} icosahedron. This result proves nothing about the C_{3v} icosahedron as a possible transition state, but it does suggest that, along the TFR pathway, a transition state of less than maximum symmetry will not likely be trapped in optimum form by the techniques we have relied on in this work. We can still argue, however, that if it is not the transition state for the TFR process, the D_{3h} structure might lie somewhere near a less symmetric transition state, perhaps higher in energy or perhaps lower, and therefore the D_{3h} icosahedron could serve as an idealized form of the TFR transition state. This is what we have assumed for the discussion in the following section.

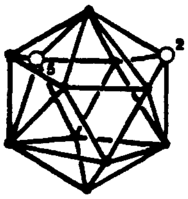
Finally, none of the ab initio results, ours or those of Wales and Stone, are anywhere close to 80 kcal/mol, the estimated lower limit for the activation barrier to rearrangement of $B_{12}H_{12}^{2-}$. These differences raise apprehensions about basis set and electron correlation errors implicit in such calculations. Despite the limitations of the various calculations, ab initio, semiempirical, and empirical potential, and the apparent unsuitability of all the structures evaluated here as possible transition states, eq 3 or a related TFR process remains the most likely explanation of the rearrangement of $C_2B_{10}H_2$ isomers.

Application to $C_2B_{10}H_{12}$

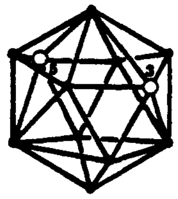
Now let us look in detail at the individual isomers of intermediate or transition-state carborane structures that would be encountered along the reaction pathways of the various proposed mechanisms. Consider the triangular-face rotation, eq 3, that passes through the idealized D_{3h} icosahedral intermediate and is associated with reaction graph **12**. The 1,2 to 1,7 rearrangement passes either of the two isomers of idealized D_{3h} icosahedral geometry: 1,3 (**18**) or 2,5 (**19**). Of the six processes indicated in **12** linking 1,2 and 1,7 by eq 3, three pass through the 1,3-intermediate and the other three go through 2,5. For the conversion of 1,7 to 1,12 only the 3,5-isomer (**20**) of the intermediate icosahedron is involved.



18

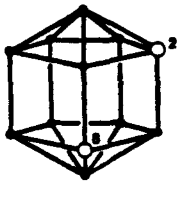


19

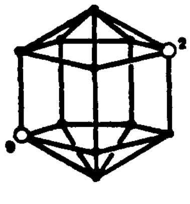


20

For the rearrangement by way of the bicapped pentagonal prism (BPP) as shown in eq 2 and associated reaction graph **6**, the conversion of 1,2 to 1,7 encounters the BPP isomer 2,8 (**21**) while the isomerization of 1,7 to 1,12 goes through the BPP isomer 2,9 (**22**).



21



22

From previously reported ab initio SCF-MO calculations at the STO-3G level, we know the relative energies of the three carborane isomers.[7] They are as follows (in kcal/mol relative to the lowest energy isomer, 1,12): 1,12-isomer, 0; 1,7-isomer, 4.6; 1,2-isomer, 26.8. It would be desirable to have ab initio estimates of the relative energies of carborane isomers in those transition-state or intermediate structures involved in the proposed rearrangement schemes, and indeed we are actively engaged in such calculations. But in the meantime, it is possible for us to predict the relative stabilities of intermediates or transition states using the same two sets of qualitative rules that have been successfully engaged to order the energies or stabilities of the isomers of the deltahedral carboranes, $C_2B_{n-2}H_n$ (n = 5–12): empirical valence rules[4,5] and the rule of topological charge stabilization.[37–41] Both sets of rules correctly predict the order of stabilities among known isomers in each polyhedral class, and they agree reasonably well with each other and with ab initio SCF results for the much larger number of possible carborane isomers that have never been prepared.[4,5,6,41]

The empirical valence rules are (i) carbons prefer to occupy sites of lowest coordination in the polyhedral structure and (ii) carbons prefer to be as far apart as possible. Rule i takes precedence over rule ii. Since carbon is more electronegative and contributes more electrons than boron, carbon prefers to do less electron sharing or to form fewer bonds. The more electronegative carbons should carry negative charges and electrostatic repulsions would therefore keep carbons as far apart as possible and surrounded by the more positive borons. In applying the empirical valence rules to the isomers of the D_{3h} icosahedron, notice that atoms 1, 7, and 10 are 6-coordinate, positions 2, 4, and 12 are 4-coordinate, and the other six locations are 5-coordinate. For the three isomers involved in eq 3 the relative stabilities are ordered by rule i:

2,5 (4-coord, 5-coord) > 3,5 (5-coord, 5-coord) >
1,3 (6-coord, 5-coord)

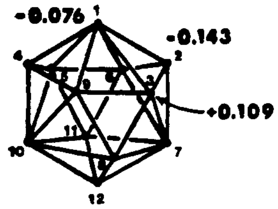
The instability of high energy of 1,3 is emphasized by rule ii: this isomer has adjacent carbons, an unlikely arrangement.

For the BPP structure, each of the isomers 2,8 and 2,9 has both carbons at 5-coordinate sites, so rule i does not apply and rule ii determines the stability order

2,9 (three bonds) > 2,8 (two bonds)

because the two carbons in 2,9 are separated by a path of three bonds compared to two bonds in 2,8. As an estimate of the energy effect such a difference might produce, refer to the structures of *m*- and *p*-$C_2B_{10}H_{12}$, **2** and **3**, which differ structurally by the separation of the pair of carbons by two and three bonds, respectively, and differ in energy by about 5 kcal/mol.

The rule of topological charge stabilization is based on the fact that electron count and molecular topology determine the distribution of electrons in a molecule. The normalized charges[39] (Mulliken net atom populations modified by an additive constant to sum to zero) for a homoatomic reference structure that is isostructural and isoelectronic with the D_{3h} icosahedron of $B_{12}H_{12}^{2-}$ appear in **23**. There are three sets of equivalent sites, each with a different charge determined by the connectivity of the structure. The rule of topological charge stabilization says that more electronegative heteroatoms (in this case, the carbons) are stabilized in those positions where topology produces an accumulation of electron density in the homoatomic reference system. Suppose we take as a measure of the energy of the carborane isomer m,n the sum of the charges $Q_m + Q_n$ at the corresponding locations in the reference frame **23**, with the most negative sum indicating the most stable isomer. The rule of topological charge stabilization then gives the following order of stabilities to the D_{3h} icosahedral carborane isomers involved in eq 3



23

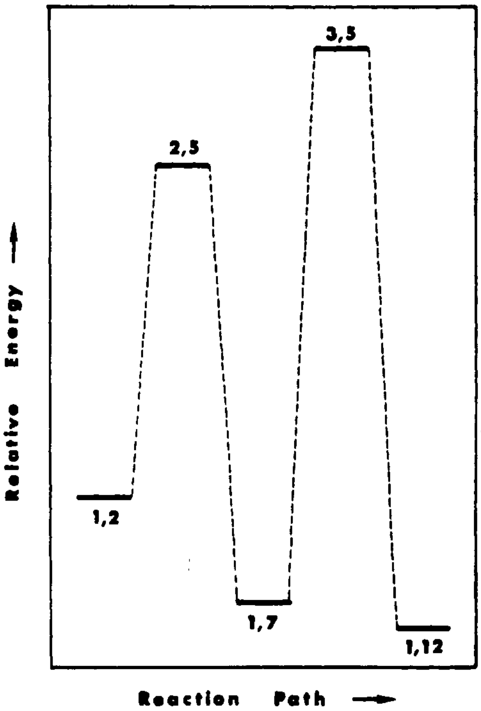
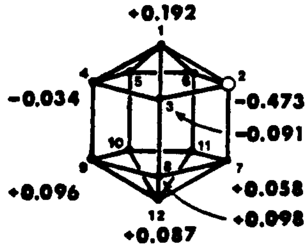


Figure 1. Schematic energy profile along reaction graph **12** corresponding to eq 3 and passing through the D_{3h} icosahedral transition state or intermediate.

2,5 (−0.143 + 0.109 = −0.034) > 1,3 (+0.03) > 3,5 (+0.218)

For the BPP structure the two isomers **21** and **22** have carbons located at the vertices of the pentagonal prism, positions that by symmetry must have equal charges in the homoatomic reference structure. At this level, the rule of topological charge stabilization cannot distinguish between BPP 2,8 and 2,9. But we can use the following perturbation approach. Suppose we put an electronegative heteroatom at one of the 10 equivalent positions and recalculate the normalized charges, as in **24**. In this case, the relative energies of the isomers are determined by the charges of the location of the second carbon, 8 or 9. Since these two charges are virtually identical, the two isomers must have comparable stability, perhaps with 2,9 slightly more stable because atom 9 is slightly less positive than atom 8:



24

2,9 (+0.96) > 2,8 (+0.98)

Now let us use these relative stabilities to draw conclusions about the relative merits of different pathways proposed for icosahedral rearrangements. For eq 3 and reaction graph **12**, the competing processes relating 1,2 and 1,7 involving D_{3h} isomers 2,5 and 1,3. Both the empirical valence rules and the rule of topological charge stabilization predict that 2,5 offers a lower energy pathway than does 1,3. Therefore, the 1,2 → 1,7 isomerization should prefer the 2,5-isomer. Although there are six processes relating 1,2 and 1,7 in **12**, the three processes involving the 1,3 crossing are probably not available because of the high energy. For the 1,7 → 1,12 isomerization only the 3,5-isomer is

---

(37) Gimarc, B. M. *J. Am. Chem. Soc.* **1983**, *105*, 1979–1984.
(38) Gimarc, B. M.; Joseph, P. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 506–507.
(39) Gimarc, B. M.; Ott, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 4298–4303.
(40) Gimarc, B. M.; Ott, J. J. *Inorg. Chem.* **1989**, *28*, 2560–2564.
(41) Gimarc, B. M.; Dai, B.; Warren, D. J.; Ott, J. J. *J. Am. Chem. Soc.* **1990**, *112*, 2597–2601.

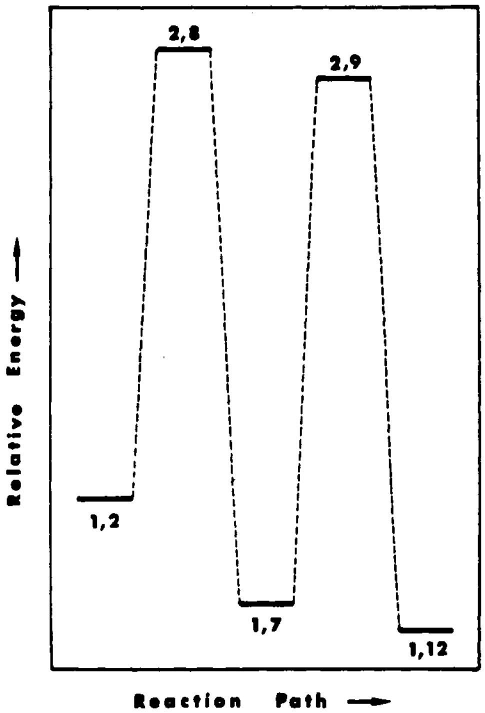


Figure 2. Schematic energy profile along reaction graph 6 corresponding to eq 2 and involving the bicapped-pentagonal-prismatic (BPP) structure.

involved. Both the empirical valence rules and the rule of topological charge stabilization predict that 3,5 on the 1,7 → 1,12 transit is higher than 2,5 on the 1,2 → 1,7 crossing. The relative energies of carborane isomers and intermediate structures are summarized schematically in Figure 1. The barrier facing the 1,7 → 1,12 conversion is high. Not only is the 3,5-intermediate higher absolutely than 2,5, but the 1,7-isomer starts its rearrangement more than 20 kcal/mol lower in energy than does the 1,2-isomer for its isomerization. This difference in activation energies might be enough to account for the experimentally observed differences in isomerization of 1,2 to 1,7 to 1,12.

Now apply the same reasoning to the isomerization according to eq 2 through the BPP intermediate and reaction graph 6. Both qualitative rules say 2,9 has lower energy than 2,8, but probably not by much. Figure 2 represents the potential surface along reaction graph 6. The activation barrier facing 1,7 may still be larger than that in front of 1,2, but surely the relative sizes of the two barriers are closer than those for eq 3, which involve the D_{3h} icosahedron. The relative heights of activation barriers in Figure 1 are more likely to account for the experimental observations of carborane rearrangements than those in Figure 2. These arguments, coupled with the results that, for $B_{12}H_{12}^{2-}$, the D_{3h} icosahedron has a lower energy than does the D_{5h} bicapped pentagonal prism, give new support to the triangular-face rotation as the mechanism most likely to account for the isomerization of $C_2B_{10}H_{12}$.

Wu and Jones have recently reported the results of a fascinating series of experiments on the rearrangements of substituted isomers of $C_2B_{10}H_{12}$.[42] In their experiments the carboranes are substituted with a group that bridges one of the carbons to an immediately adjacent boron. The span of the bridge is too short to allow the substituted carbon and attached boron to move apart from each other. Rearrangement experiments with substituted carboranes have been done previously, but the large numbers of isomers that formed greatly complicated the interpretation of results. The bridging substituent, however, limits the number of possible isomers to a manageable few. Wu and Jones have interpreted their observations according to several rearrangement mechanisms involving transition-state structures of the cuboctahedron, the bicapped pentagonal prism, and the D_{3h} icosahedron. They conclude that only the triangular-face rotation process, eq 3, can account for all the isomers produced and their individual rates of appearance. Although their work would seem to decide the argument over the mechanism of rearrangement of $C_2B_{10}H_{12}$ isomers in favor of triangular-face rotation, Wu and Jones note that substituted carboranes rearrange more easily than do unsubstituted carboranes, an observation that to some might suggest different rearrangement processes followed by substituted and unsubstituted $C_2B_{10}H_{12}$.

Acknowledgment. This research was sponsored in part by the National Science Foundation through Grant Nos. CHE-8703461 to the University of South Carolina and CHE-8712230 to Furman University. J.J.O. and C.B. thank the Duke Endowment and the Dreyfus Foundation for project support.

---

(42) Wu, S.-h.; Jones, M., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 5373–5384.