

DETAILS OF THE REACTION GRAPHS FOR INTRAMOLECULAR ISOMERIZATIONS OF THE CARBORANES

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Received 29 December 1989

Abstract

From proposed mechanisms for framework reorganizations of the carboranes $C_2B_{n-2}H_n$, $n = 5-12$, we present reaction graphs in which points or vertices represent individual carborane isomers, while edges or arcs correspond to the various intramolecular rearrangement processes that carry the pair of carbon heteroatoms to different positions within the same polyhedral form. Because they contain both loops and multiple edges, these graphs are actually pseudographs. Loops and multiple edges have chemical significance in several cases. Enantiomeric pairs occur among carborane isomers and among the transition state structures on pathways linking the isomers. For a carborane polyhedral structure with n vertices, each graph has $n(n-1)/2$ graph edges. The degree of each graph vertex and the sum of degrees of all graph vertices are independent of the details of the isomerization mechanism. The degree of each vertex is equal to twice the number of rotationally equivalent forms of the corresponding isomer. The total of all vertex degrees is just twice the number of edges or $n(n-1)$. The degree of each graph vertex is related to the symmetry point group of the structure of the corresponding isomer. Enantiomeric isomer pairs are usually connected in the graph by a single edge and never by more than two edges.

1. Introduction

The *closo*-boranes $B_nH_n^{2-}$ and their isostructural, isoelectronic analogs, the carboranes $C_2B_{n-2}H_n$, $n = 5-12$, have closed polyhedral structures with triangular faces, as shown in fig. 1 [1,2]. The $n = 8$ and $n = 11$ boranes are known to be fluxional and isomerization reactions have been observed in the carboranes of $n = 6, 7, 10$ and 12 . The phenomena of carborane isomers and isomerizations have been a source of fascination to chemists for over twenty-five years. Various mechanisms have been proposed to account for the observed reorganization of these polyhedral structures. Most of the proposed mechanisms have involved the diamond-square-diamond (DSD) process [3]. A bond that serves as a shared edge between a pair of fused triangular

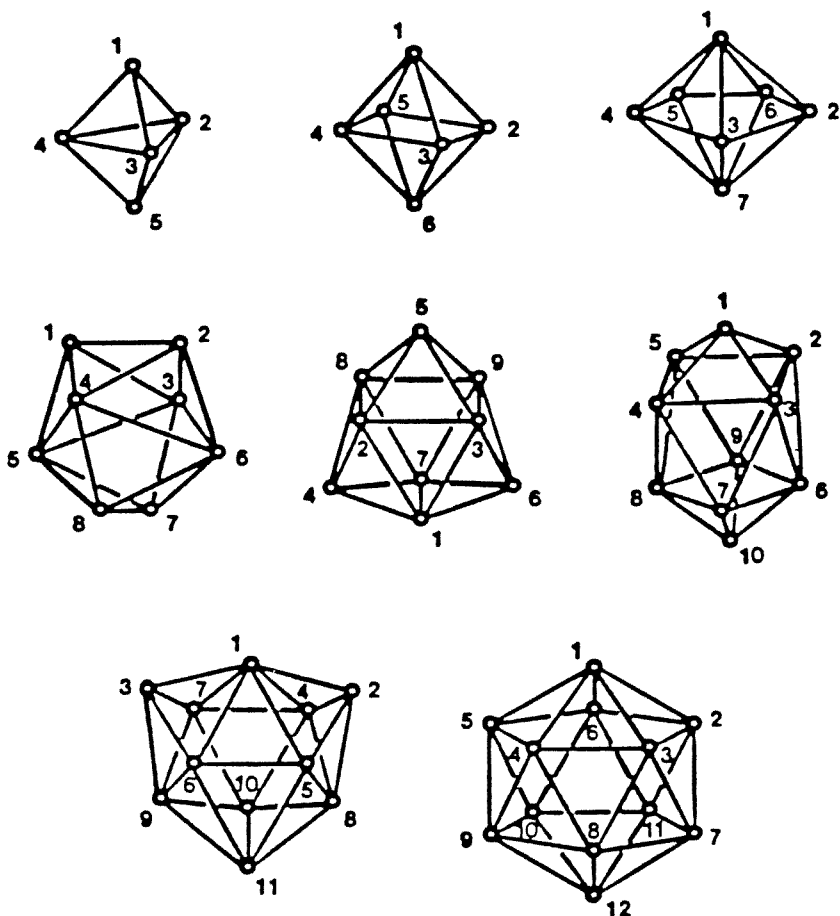
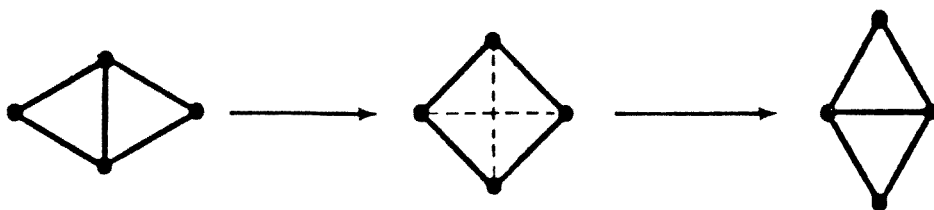


Fig. 1. The polyhedral structures of the *closo*-carboranes $C_2B_{n-2}H_n$, $n = 5-12$.



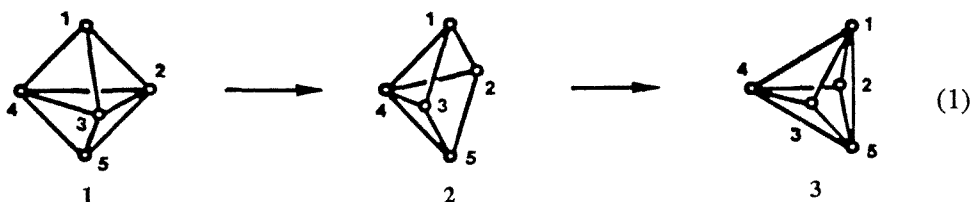
faces breaks, opening a square face which is then closed by a new bond which forms perpendicular to the one broken, regenerating two shared-edge triangles. Such rearrangements are significant if they produce structures that have the same polyhedral form as the starting structure. Thus, the reorganization is a degenerate rearrangement

or a pseudorotation. King has described the topological requirements for degenerate rearrangements [4,5].

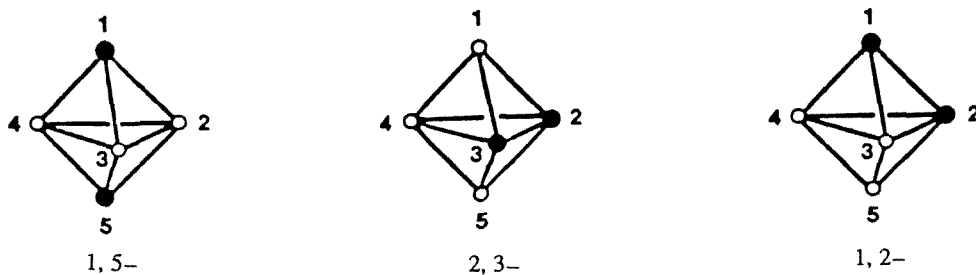
We have represented these rearrangement processes by reaction graphs in which the graph vertices indicate particular carborane isomers and the edges joining the vertices correspond to specific rearrangement processes [6,7]. Such reaction graphs serve as road maps across the energy surface. Total molecular energies from *ab initio* SCF MO calculations for individual carborane isomers locate specific points on the energy surface. Using reaction graphs and calculated energies, we have been able to account for observed isomerization reactions and the existence of known carborane isomers, and in several cases to predict the possible metastability of isomers that have not yet been reported [7–13]. Reaction graphs describing intramolecular isomerizations in other systems have also been investigated [14]. In this paper, we consider the mathematical properties of reaction graphs for the carboranes in greater detail.

2. $C_2B_3H_5$

Equation (1) shows the diamond–square–diamond rearrangement that has been proposed for the isomerization of trigonal bipyramidal $C_2B_3H_5$ through a square pyramidal transition state structure to a regenerated trigonal bipyramid [15]. There

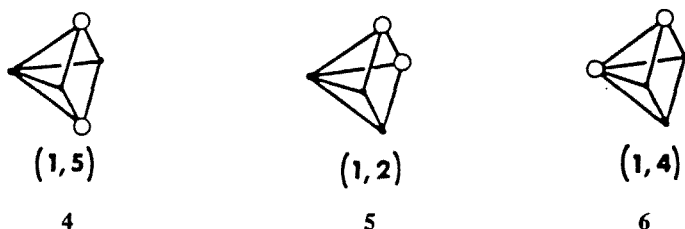


are three possible isomers of $C_2B_3H_5$: both carbons in apical positions, 1, 5–, both in equatorial positions, 2, 3–, and one carbon in an apical site while the other is in an equatorial location, 1, 2–, where the pairs of indices specify the locations of the



carbon heteroatoms in the polyhedral structure according to the numbering scheme of the reactant structure in eq. (1) or fig. 1. Suppose we start with carbons in all

possible pairs of positions in **1** and note where they appear in **3**, referring both initial and final structures to the three representative isomers above. There are five possible choices for the location of the first carbon and four remaining positions for the location of the second carbon or a total of $5 \times 4 = 20$ possible position pairs. However, since interchanges of the locations of the two carbons are indistinguishable for identical carbons, we can reduce the number of starting positions to ten, or in general $n(n-1)/2$, where n is the number of vertices in the carborane polyhedron. Although the ten possible starting positions must correspond to only 3 carborane isomers, they specify ten processes that lead from reactant **1** to product **3**. These processes pass through ten square pyramidal intermediate or transition state structures **2**, but only three nonequivalent structures **4**, **5** and **6** are possible. In particular, there are two equivalent structures with the carbons in diagonal basal positions **4**, four equivalent structures with adjacent basal carbons **5**, and four equivalent structures with both apical and basal carbons **6**. The vertex indices follow the numbering scheme of the



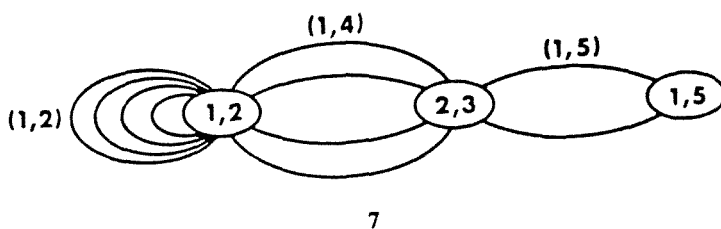
transition state structure **2** in the equation and are enclosed in parentheses to specify them as the representative transition state isomeric structures and to distinguish them from the representative deltahedral carboranes.

As an example, suppose we start with carbons in positions 3 and 4 in **1**. Except for rotation in space, this arrangement is equivalent to starting with the 2, 3- isomer. At the transition state **2**, the carbons are in apical and basal positions corresponding to the transition state isomer (1, 4) or **6**. Finally, in **3**, the carbons are in apical-equatorial locations that specify the 1, 2- carborane isomer. Therefore, isomerization of 2, 3- to 1, 2- passes through the (1, 4) transition structure. Following the processes that result from the other nine starting locations for pairs of carbon atoms, one can obtain the information summarized in table 1. This information can be displayed more vividly in the form of a reaction graph **7**. The vertices, ovals enclosing the carborane isomer indices, are connected by edges that correspond to rearrangement processes that pass through transition state isomeric structures specified in parentheses besides each edge. In particular, two processes involving transition structure (1, 5) or its equivalent by rotation link carborane isomers 2, 3- and 1, 5-, four processes connect isomers 1, 2- and 2, 3- through (1, 4), and four processes denoted by graph loops that begin and end on the vertex 1, 2- indicate pseudorotations that pass through

Table 1

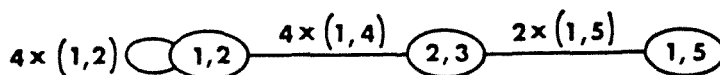
Isomerization processes and transition state structures for $C_2B_3H_5$ following eq. (1)

Isomerization process	Transition state isomer	Number of equivalent transition state structures
1, 5- - 2, 3-	(1, 5)	2
1, 2- - 2, 3-	(1, 4)	4
1, 2- - 1, 2-	(1, 2)	4



transition state structures equivalent to (1, 2). Notice that no edges connect vertices 1, 2- and 1, 5-. The fact that an isomer, such as 2, 3- in this example, has available to it different reaction processes with different numbers of channels may be chemically significant in those cases where activation energies of the processes happen to be equal. Ten edges, or in general $n(n-1)/2$, connect the graph. Since 7 contains both loops and multiple edges, it is more accurately described as a *pseudograph* [16].

The information in 7 is portrayed more economically in 8, where numbers of edges or loops are denoted by numbers multiplying the specified transition state structures. The degree of each vertex is the number of edges that begin or end at the



Degree of vertex	12	6	2
Isomer point group	C_s	C_{2v}	D_{3h}

8

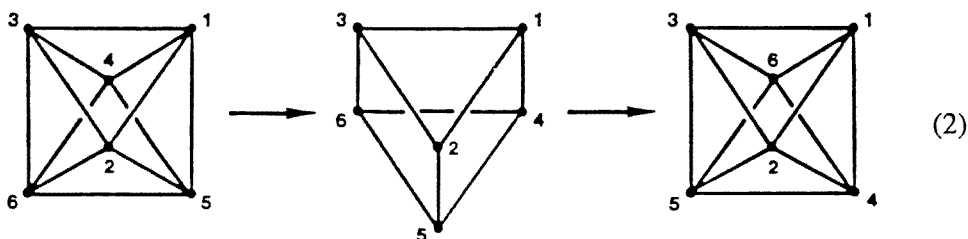
vertex. For example, the 1, 2- vertex has four edges to 2, 3- plus four loops, each beginning and ending on 1, 2-, for a total of $4 \times 2 + 4 = 12$ edges emanating from vertex 1, 2-. The degree of each vertex is just twice the number of rotationally equivalent structures for each isomer. Consider the following accounting. There is

only one way to represent the apical–apical isomer 1, 5– under the numbering scheme of the reactant in eq. (1). There are three rotationally equivalent structures for the equatorial–equatorial isomer: 2, 3–, 2, 4–, and 3, 4–. Six rotationally equivalent structures have carbons at both axial and equatorial sites: 1, 2–, 1, 3–, 1, 4–, 2, 5–, 3, 5–, and 4, 5–. Each of these ten structures represents the end of an edge in the reaction graph under the numbering scheme of the reactant in eq. (1). A duplicate set of edge endings is represented by structures at the product end in eq. (1). Therefore, doubling of the numbers of rotationally equivalent structures gives the degrees of 2, 6, and 12 for the isomers 1, 5–, 2, 3–, and 1, 2–, respectively. The sum of the degrees of all three vertices is 20, or twice the number of edges. The total degree counts the ends of the edges, and since each edge must have two ends, the total degree must be twice the number of edges or $n(n-2)$. First shown by Euler, this is the oldest theorem of graph theory [16]. Notice that higher symmetry isomers correspond to vertices of lower degree.

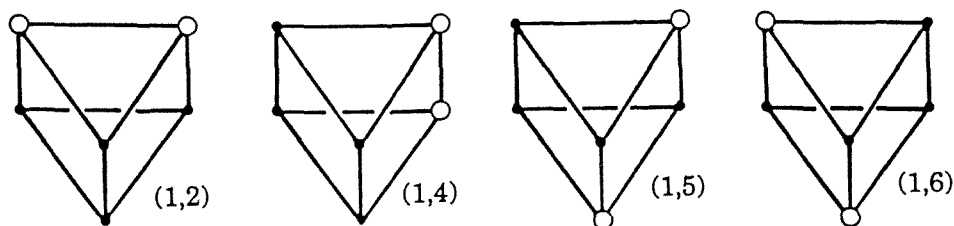
Although eq. (1) would appear to be a textbook example of the DSD mechanism, our previous studies revealed the crossing of HOMO and LUMO in the transition structure **2**, indicating that this process violates the principle of conservation of orbital symmetry and therefore probably has a very high activation energy [17]. This conclusion is consistent with experimental facts; rearrangements of $C_2B_3H_5$ isomers have never been observed.

3. $C_2B_4H_6$

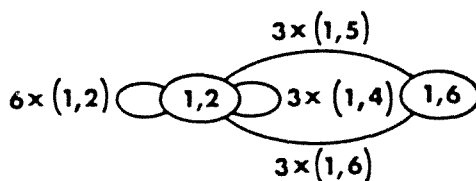
Equation (2) shows a mechanism that has been proposed for the interconversion of the two isomers of $C_2B_4H_6$ [15]. This equation consists of three simultaneous DSD processes. It can also be considered a triangular face rotation (TFR) in which the rear



face (4, 5, 6) rotates by 120° with respect to a fixed front face (1, 2, 3). A total of $6 \times 5/2 = 15$ processes are involved in the framework reorganizations of the two possible isomers of $C_2B_4H_6$: 1, 2– and 1, 6–. These processes pass through four non-equivalent trigonal prism transition structures: (1, 2), (1, 4), (1, 5) and (1, 6). There are six structures rotationally equivalent to (1, 2), corresponding to the six triangular face edges in the trigonal prism. Three structures are equivalent to (1, 4), in which carbons are of the ends of edges that connect the two triangles. The six structures in



which carbons are located at the ends of the diagonals of the three rectangular faces give rise to three pairs of structures, each member represented by (1, 5) and (1, 6), which are nonsuperimposable mirror images of each other or enantiomers. Equation (2) leads to the reaction graph **9**. A total of nine loops, three involving (1, 4)



Degree of vertex	24	6
Isomer point group	C_{2v}	D_{4h}

9

and six passing through (1, 2), permit the pseudorotation or degenerate rearrangement of $1, 2-C_2B_4H_6$. Of fifteen possible processes, only six connect the two isomers, three through each member of the enantiomeric pairs (1, 5) and (1, 6). Since (1, 5) and (1, 6) differ only as mirror images of each other, they have the same energies, so all six processes face the same activation barrier. Enantiomeric (chiral) processes are paired on either side of the main axis in **9**. Processes that are unique (achiral) except for rotation in space lie on the main axis of the graph. The more symmetric isomer has a vertex of lower degree in **9**.

Both isomers 1, 2- and 1, 6- have been prepared. Although thermal isomerization of 1, 2- to 1, 6- has been accomplished, McKee has shown that the rearrangement apparently goes through a mechanism other than that of eq. (2) [18].

4. $C_2B_5H_7$

There are four possible isomers of $C_2B_5H_7$: 1, 2-, 2, 3-, 2, 4-, and 1, 7-. Equation (3), requiring a double DSD process, has been proposed as a mechanism for observed isomerization [19]. There are $7 \times 6/2 = 21$ processes involving an equal

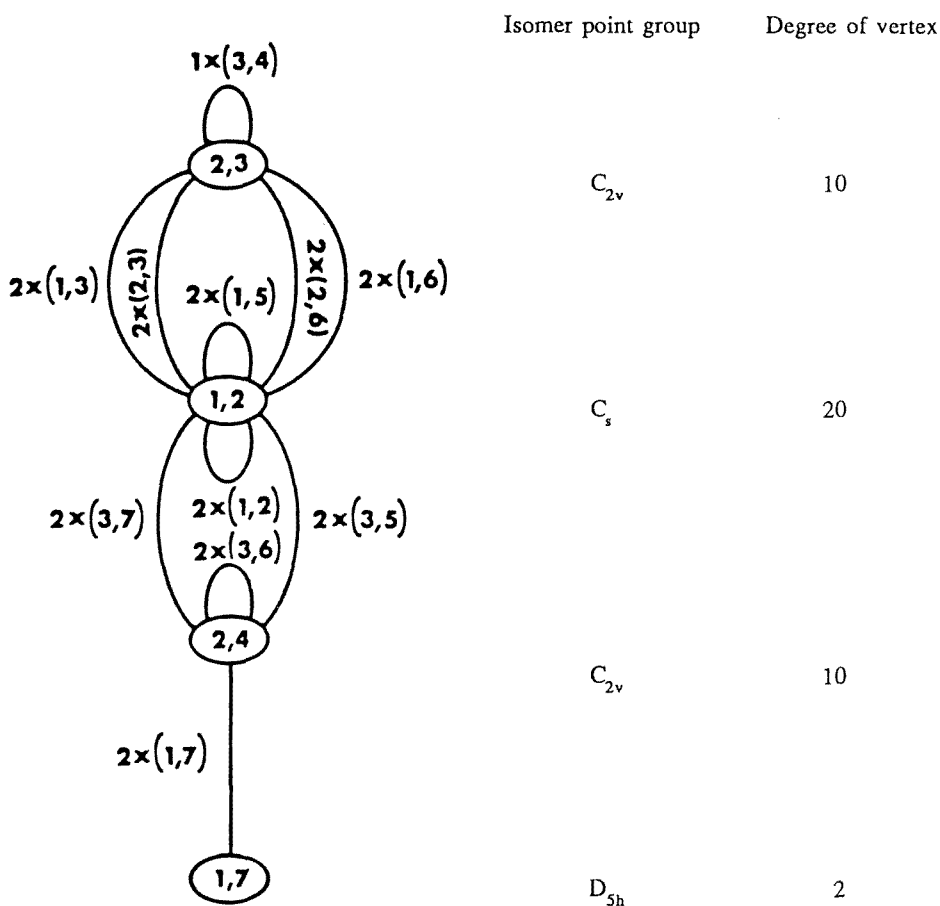
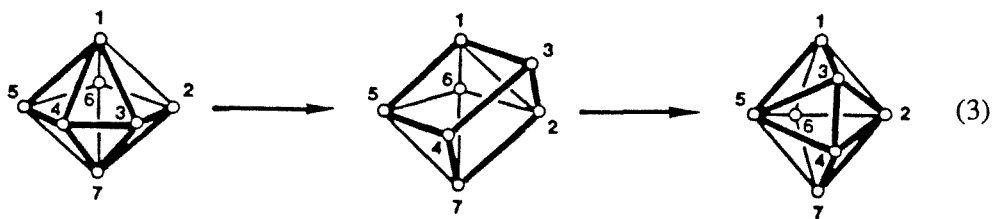
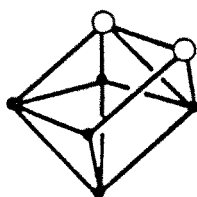


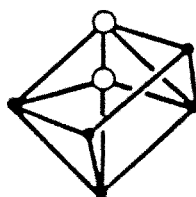
Fig. 2. Reaction graph for the isomerization of $C_2B_3H_7$ by eq. (3). Processes that lie on either side of the central axis involve enantiomeric transition structures, while those on the central axis are unique except for rotation in space.

number of isomeric transition structures which can be divided into eleven nonequivalent isomer classes, including three different sets of enantiomeric pairs. Isomers, processes, and transition structures are summarized in the reaction graph in fig. 2. Edges that

are paired on either side of the central axis of the figure correspond to processes that involve enantiomeric transition structures such as the loops (1, 2) and (1, 5). Edges or loops that lie on the central spine correspond to processes that involve transition structures that are unique except for rotation in space. Two different types of processes connect the isomers 1, 2- and 2, 3-. One type passes through the enantiomeric transition structures (1, 3) and (2, 3), the other goes by way of another set of enantiomers (1, 6) and (2, 6). These two enantiomeric sets



(1, 3); (2, 3)



(1, 6); (2, 6)

should have different energies; hence, one set of pathways will be preferred. The two links between 1, 2- and 2, 4- go by way of opposite members of an enantiomeric pair (3, 5) and (3, 7). The two processes for degenerate rearrangement of 1, 2- $C_2B_5H_7$ are nonequivalent.

Thermal conversion of 2, 3- into 2, 4- $C_2B_5H_7$ has been achieved. The isomerization of substituted derivatives of 2, 4- $C_2B_5H_7$ has been extensively studied by Onak and coworkers [19-23]. Their experimental results support the mechanism represented by eq. (3) and can be accounted for by processes involving the loops on the 2, 4- vertex in fig. 2.

5. $C_2B_6H_8$

There are four possible unique isomers and three possible enantiomeric isomer pairs for $C_2B_6H_8$:

Unique	Enantiomeric pairs
1, 2- (C_{2v})	1, 3-; 1, 4- (C_1)
1, 5- (C_s)	1, 7-; 1, 8- (C_2)
1, 6- (C_s)	3, 5-; 4, 5- (C_2)
3, 4- (C_{2v})	

This makes a total of ten possible isomers and ten vertices in the reaction graph. Only the 1, 7- isomer has been reported. Although $B_8H_8^{2-}$ is fluxional, no evidence of optical activity or fluxional racemization of 1, 7- $C_2B_6H_8$ has been mentioned in the literature.

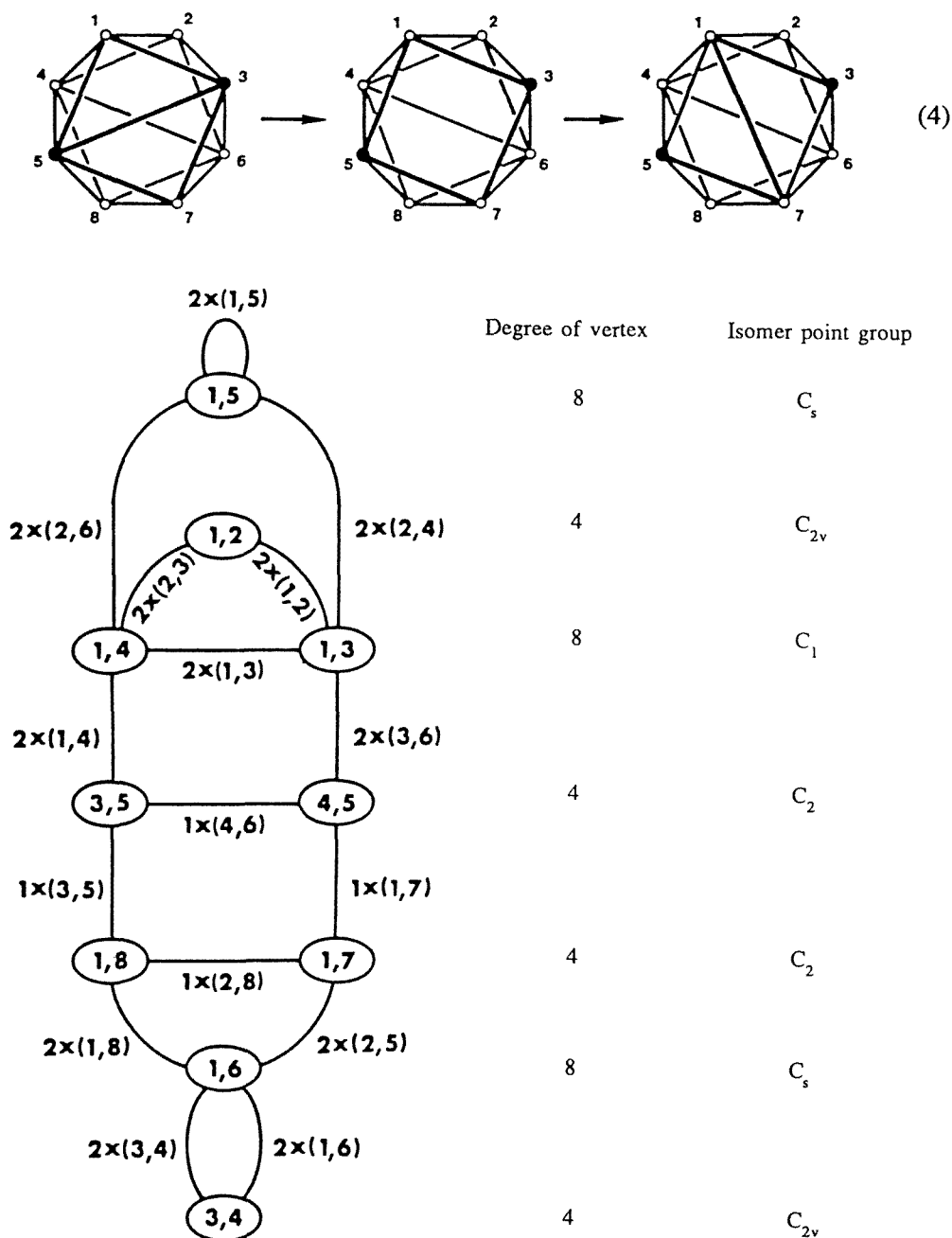


Fig. 3. The reaction graph for isomerization of $C_2B_6H_8$ by eq. (4).

Equation (4) describes a single DSD process that has been proposed to account for the fluxionality of $B_8H_8^{2-}$ [3,24]. The isomerization of the corresponding carborane $C_2B_6H_8$ would presumably follow a similar path. The transition structure in eq. (4)

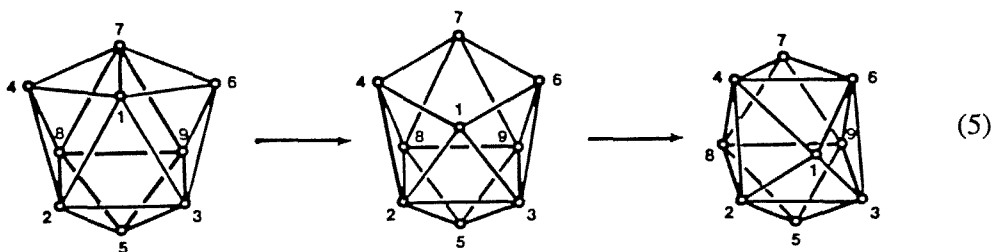
has sixteen different isomers, including two unique isomers, two sets of equivalent pairs, and six sets of enantiomeric pairs. Figure 3 displays the reaction graph for equation (4). Enantiomeric pairs of isomers lie on either side of the central axis of the figure and are directly linked by isomerization processes. These three direct connections plus the loop on vertex 1, 5– involve the four unique isomeric transition structures. The six enantiomeric pairs of transition structures are related to matching pairs of processes on either side of the central axis in fig. 3.

6. $C_2B_7H_9$

For this carborane, there should be four possible unique isomers and two enantiomeric pairs:

Unique	Enantiomeric pairs
1, 2– (C_5)	1, 4–; 1, 6– (C_1)
1, 5– (C_5)	1, 8–; 1, 9– (C_2)
1, 6– (C_{2v})	
4, 5– (C_{2v})	

Equation (5) presents a single DSD process of the isomerization $C_2B_7H_9$ [25].



The thirty-six processes operate through ten transition structures, including two sets of enantiomeric pairs with each member of the pair represented by four rotationally equivalent structures. These isomers, processes and transition structures are summarized in fig. 4. Enantiomeric pairs of isomers and processes involving enantiomeric transition structures are related across the central axis of fig. 4. Vertices on the axis represent unique carborane isomers. Notice that members of the enantiomeric pairs 1, 8– and 1, 9– and 1, 4– and 1, 6– are directly linked in fig. 4.

In an earlier publication, we showed that eq. (5) is not allowed by the principle of conservation of orbital symmetry [8]. Equation (6), which has been proposed as an alternative [25], is allowed although, for structural reasons, the transition structure probably presents a high activation barrier. Equation (6) involves a double DSD process.

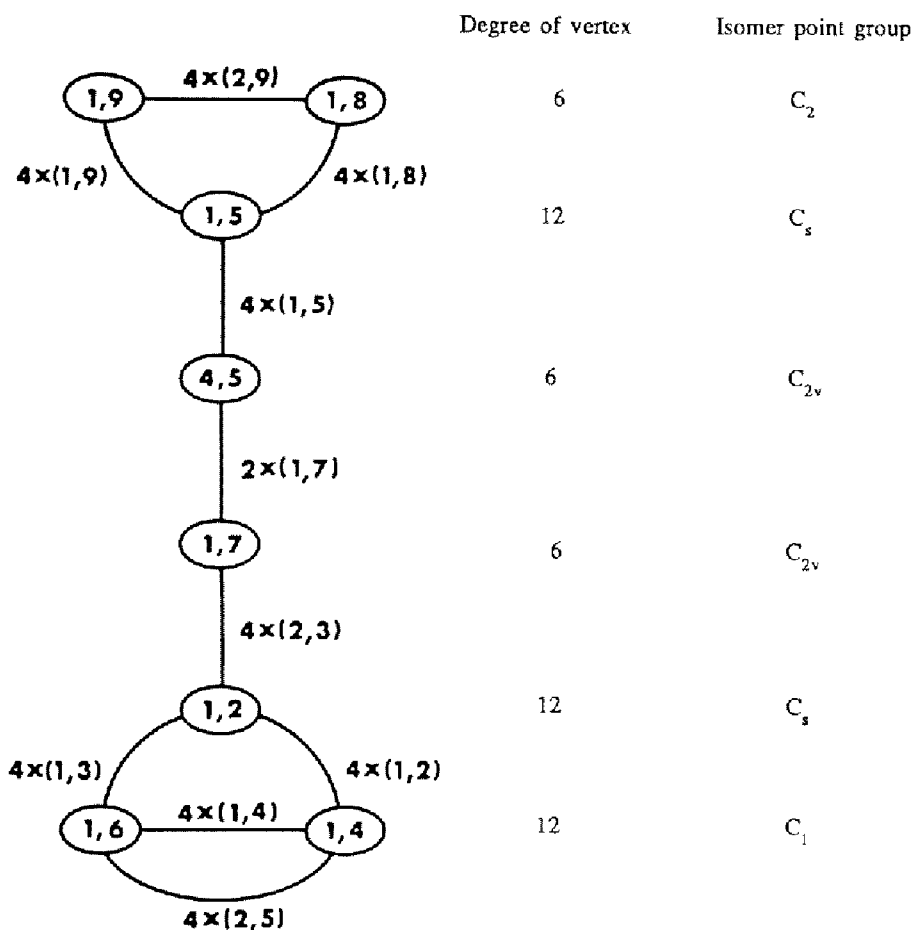


Fig. 4. Reaction graph for the isomerization of $C_2B_7H_9$ by the single DSD process of eq. (5).

The corresponding reaction graph is shown in fig. 5. This has been drawn with unique isomers along the central axis with enantiomeric pairs symmetrically disposed on either side. Similarly, isomerization processes involving enantiomeric transition structures are matched on either side of the central axis. In our previous work, we ignored the differences between enantiomeric pairs 1, 4-; 1, 6- and 1, 8-; 1, 9-. If we fuse these optical isomers into one another and denote graph loops by asterisks, we obtain the hexagonal graph 10 we reported earlier [8].

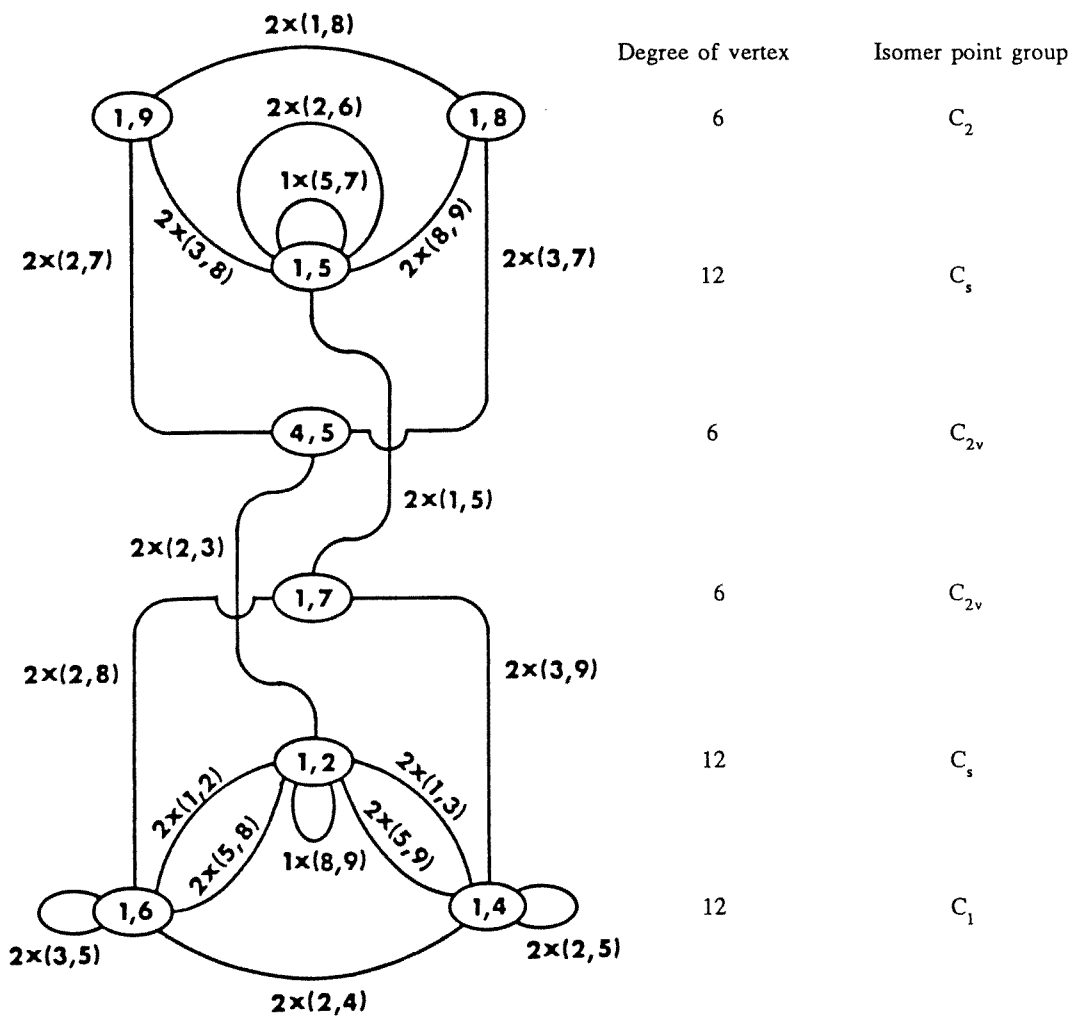
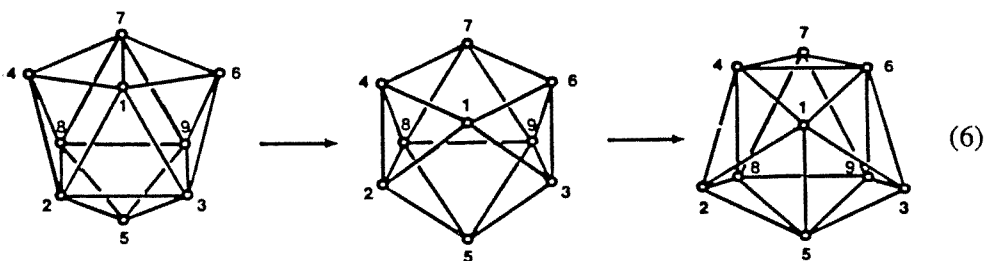
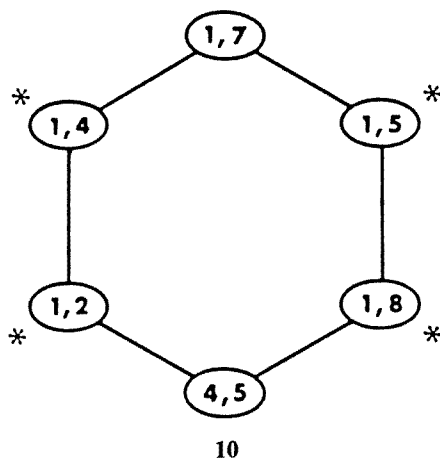


Fig. 5. Reaction graph for the isomerization of $C_2B_7H_9$ by the symmetry allowed double DSD mechanism of eq. (6).



Although the reaction mechanisms of eqs. (5) and (6) lead to quite different reaction graphs, figs. 4 and 5, respectively, the degrees of corresponding vertices are identical because they are determined by the numbers of rotationally equivalent structures, not by the details of the mechanism.

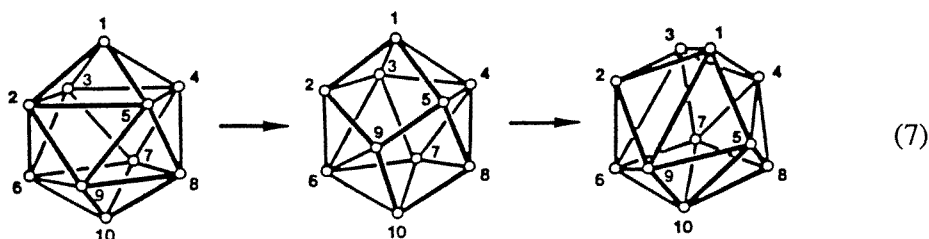
$B_9H_9^{2-}$ is not fluxional. Only one carborane isomer, 4,5- $C_2B_7H_9$, has been reported, but we predict that others should be stable.

7. $C_2B_8H_{10}$

There are nine possible isomers of $C_2B_8H_{10}$, including two pairs of enantiomers:

Unique	Enantiomeric pairs
1, 10- (D_{4d})	2, 6-; 2, 7- (C_1)
1, 2- (C_s)	2, 8-; 2, 9- (C_1)
1, 6- (C_s)	
2, 3- (C_s)	
2, 4- (C_{2v})	

Equation (7) is the double DSD mechanism that has been proposed for the rearrangement [3,15,26-28].



There are twenty-four different transition structures, including three unique isomers, five sets of equivalent pairs, and eight enantiomeric pairs. The reaction graph in fig. 6 summarizes the forty-five possible rearrangement paths.

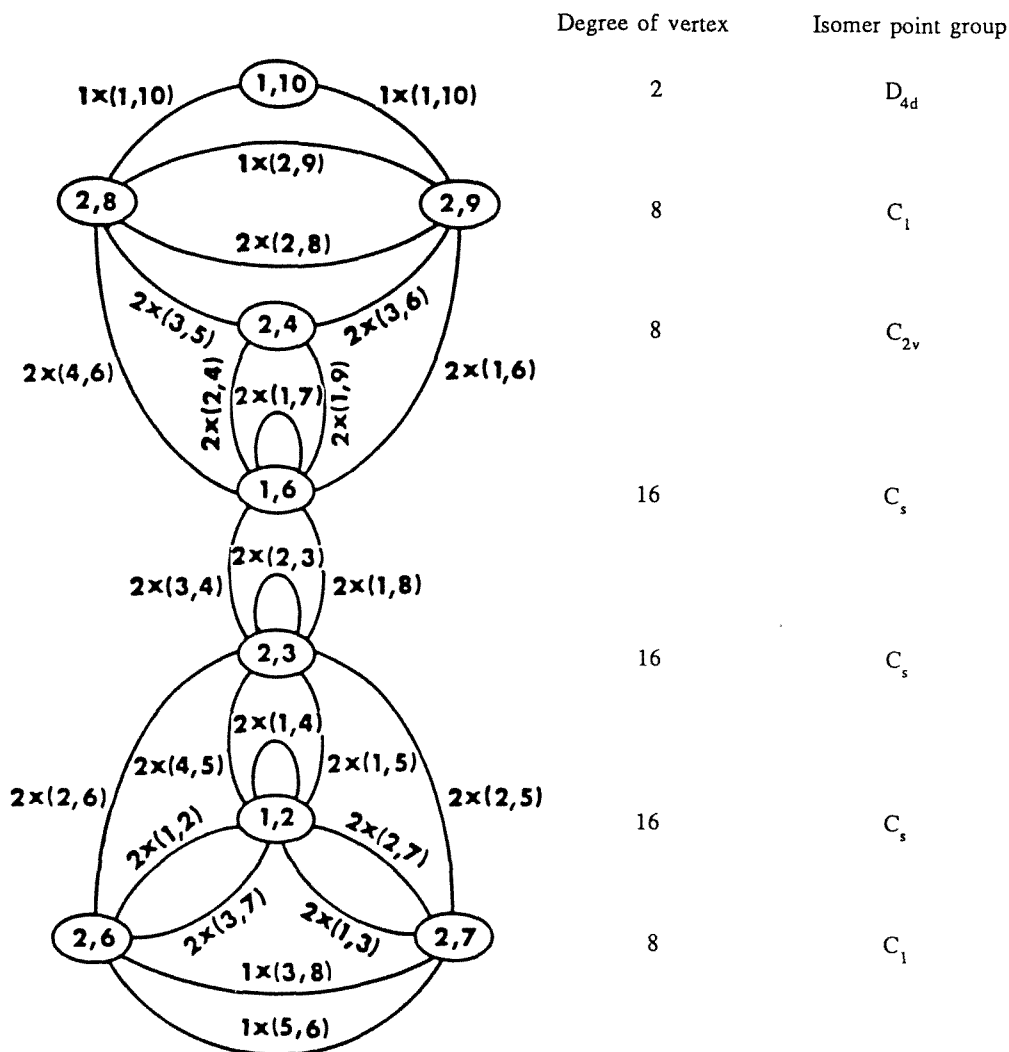


Fig. 6. Reaction graph for the isomerization of $C_2B_8H_{10}$ by eq. (7).

The 1,2-, 1,6-, and 1,10- isomers of $C_2B_8H_{10}$ have been prepared and quantitative isomerizations of 1,2- into 1,6- and of 1,6- into 1,10- have been observed.

8. $C_2B_9H_{11}$

Equation (8) is a mechanism that has been proposed to account for the observed fluxional behavior of $B_{11}H_{11}^{2-}$ in solution [3,29]. Only a single isomer of $C_2B_9H_{11}$ has been prepared although thirty isomers are possible, including ten enantiomeric pairs:

Unique		Enantiomeric pairs	
1, 2- (C_s)	2, 9- (C_s)	1, 4-; 1, 5- (C_1)	4, 8-; 5, 8- (C_1)
1, 8- (C_s)	4, 5- (C_s)	2, 4-; 2, 5- (C_1)	4, 9-; 5, 9- (C_1)
1, 10- (C_s)	4, 7- (C_s)	2, 6-; 2, 7- (C_1)	4, 10-; 5, 11- (C_1)
2, 3- (C_{2v})	8, 9- (C_{2v})	2, 10-; 2, 11- (C_1)	4, 11-; 5, 10- (C_1)
2, 8- (C_s)	10, 11- (C_{2v})	4, 6-; 5, 7- (C_2)	8, 10-; 8, 11- (C_1)

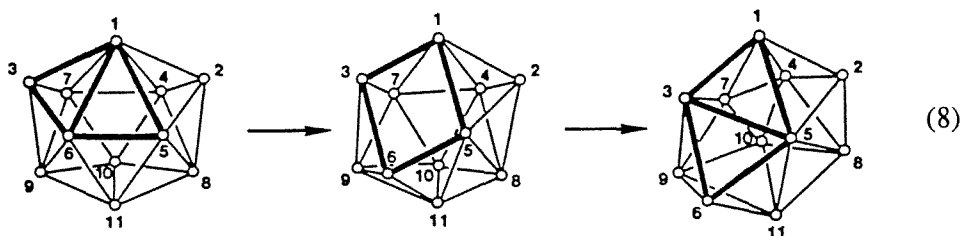


Table 2

Isomer point group and corresponding vertex degree in fig. 7 for the thirty possible isomers of $C_2B_9H_{11}$ as related by eq. (8).

Isomer	Degree of vertex	Isomer point group
2, 3-; 8, 9-; 10, 11-	2	C_{2v}
1, 2-; 1, 8-; 1, 10-; 2, 8-; 2, 9-; 4, 5-; 4, 7-	4	C_s
4, 6-; 5, 7-	2	C_2
1, 4-; 1, 5-; 2, 4-; 2, 5-; 2, 6-; 2, 7-; 2, 10-; 2, 11-; 4, 8-; 5, 8-; 4, 9-; 5, 9-; 4, 10-; 5, 11-; 4, 11-; 5, 10-; 8, 10-; 8, 11-	4	C_1

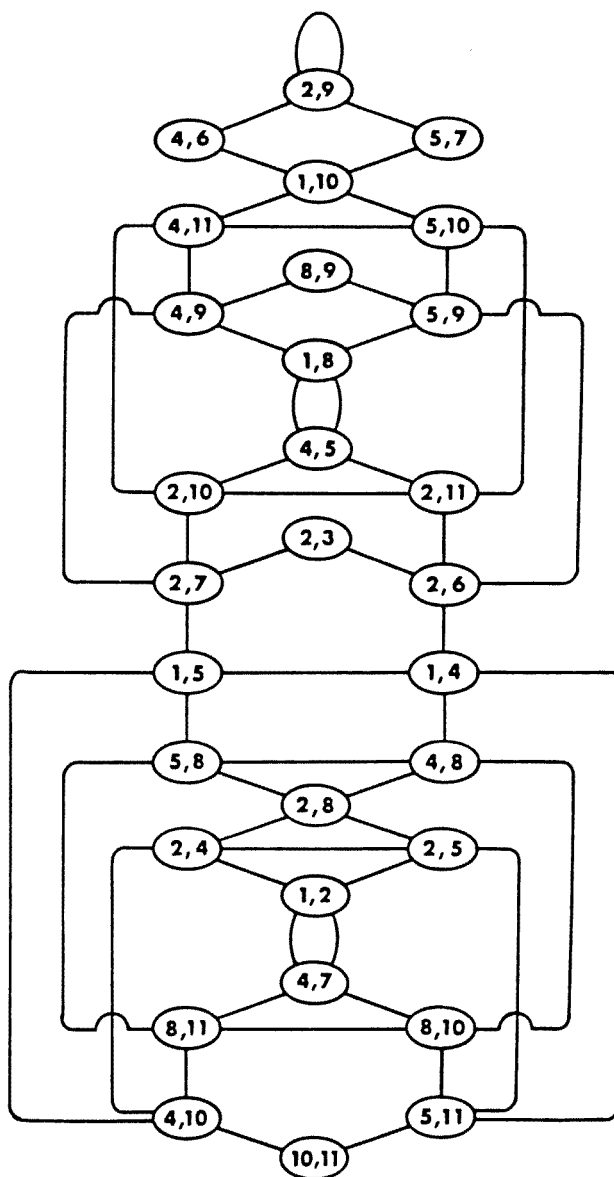


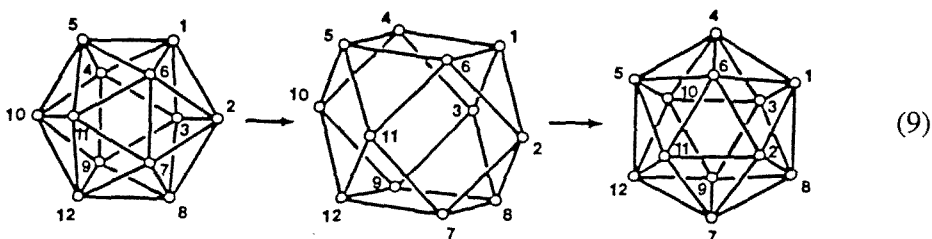
Fig. 7. Reaction graph for the isomerization of $C_2B_9H_{11}$ by eq. (8).

There are fifty-five possible processes, each involving a different transition structure of which there are seven unique isomers and twenty-four enantiomeric pairs. The reaction graph is shown in fig. 7. The seven unique transition structures correspond to the direct interconversion links connecting six of the ten pairs of optical isomers plus the degenerate rearrangement or loop on 2, 9-. The seven unique transition

structure isomers have carbons that lie either on the symmetry plane or on opposite sides of the symmetry plane of the transition structure. Table 2 relates isomer point group and degree of vertex for the thirty possible isomers of $C_2B_9H_{11}$ in fig. 7 as generated from eq. (8).

9. $C_2B_{10}H_{12}$

Three isomers of icosahedral $C_2B_{10}H_{12}$ are possible: 1, 2- (C_{2v}), 1, 7- (C_s), and 1, 12- (D_{5h}). All three have been prepared and characterized [30-32]. On pyrolysis, the 1, 2- isomer can be converted into the 1, 7- isomer. Further pyrolysis of the 1, 7- isomer yields only a small amount of 1, 12-, which is formed as 1, 7- decomposes. $B_{12}H_{12}^{2-}$ is not fluxional. Equation (9) describes one of several proposed isomerization



mechanisms for $C_2B_{10}H_{12}$. This one passes through a cuboctahedral transition structure and requires six simultaneous DSD processes [3,33]. The corresponding reaction graph is **11**. The most interesting feature of **11** is the fact that it is a disconnected

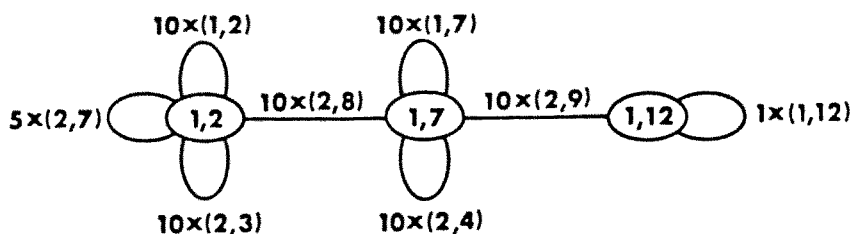
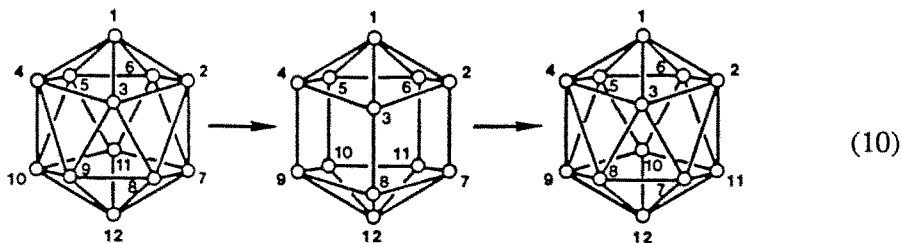


Degree of vertex	60	60	12
Isomer point group	C_{2v}	C_s	D_{5h}

11

graph. No process in eq. (9) connects the 1, 12- isomer with either 1, 2- or 1, 7-. This has long been considered as evidence in support of eq. (9) as the mechanism for isomerization of 1, 2- into 1, 7- because it fits with the experimental observation that conversion of 1, 7- into 1, 12- is much more difficult than the 1, 2- to 1, 7- isomerization. The two rearrangements were assumed to proceed by different mechanisms. Recent calculations at various levels of theory show that other proposed transition state structures probably have lower energies than the cuboctahedron [13,34,35].

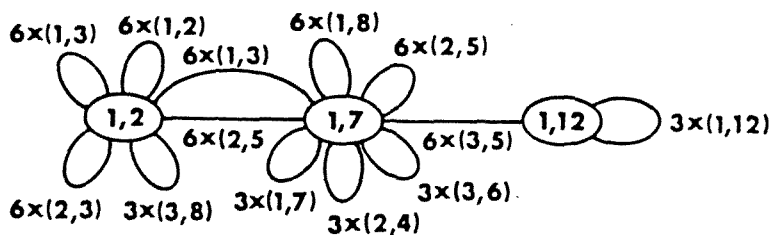
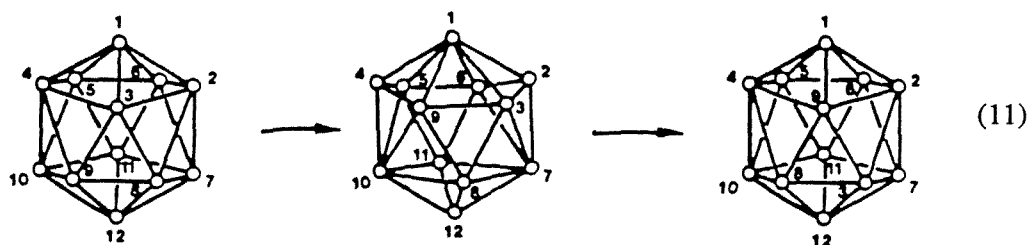
Equation (10) shows an alternative isomerization mechanism that passes through a bicapped pentagonal prism structure and involves five simultaneous DSD processes [36]. The corresponding reaction graph is **12**. The degree of each vertex in connected graph **12** is identical to that of the corresponding vertex in the disconnected graph **11**.



Degree of vertex	60	60	12
Isomer point group	C_{2v}	C_s	D_{5h}

12

Another alternative mechanism is that of eq. (11). This one involves an intermediate structure of D_{3h} icosahedral symmetry [37]. Equation (11) can be described as a triple DSD process or a single TFR mechanism. Imagine the triangle 3, 8, 9 rotating clockwise by 120° from reactant to product. The corresponding reaction graph is **13**. Again, the degree of each vertex in **13** is identical to those of corresponding vertices in **11** and **12** because the degree of a vertex is determined by the number of rotationally equivalent forms of the corresponding isomer. From energies considered elsewhere, we believe that the TFR rotation, eq. (11), is the most likely candidate to explain the observed isomerizations of $C_2B_{10}H_{12}$ [13].



Degree of vertex	60	60	12
Isomer point group	C_{2v}	C_s	D_{5h}

13

10. Topological representations and closure

In the late 1960's, Muetterties used graph theory to describe rearrangements of polyhedral molecular structures. He assigned the term *topological representation* to what we in this paper call a *reaction graph* [38,39]. Muetterties' work was quite general. He considered all possible permutational isomers of n identical but distinguishable polyhedral vertices which might be atoms in a polyhedral structure such as those of the *closo*-boranes or ligands surrounding a central metal atom. For the larger of the polyhedra that we consider here, enormous numbers of permutational isomers are possible and these could be conveniently generated only by computer. The large number of isomers present further problems, including the generation of graphs that are too large to be illustrated and which require higher dimensionality than can be conveniently represented. We tremendously simplify the problem for the carboranes by the restriction of indistinguishability of isomers that differ by permutations only among the carbons or only among the borons. In our most complicated case, the number of isomers is only thirty.

The vertices of Muetterties' topological representations correspond to two sets of polyhedral isomers G_A and G_B . Rearrangement processes would carry polyhedra of set G_A into polyhedra of a different form in G_B . Further rearrangements would return these structures to the polyhedra of set G_A . Applied to our studies, the G_A

polyhedra would be the deltahedral structures of the carborane isomers, represented in the reaction graphs by ovals surrounding carbon indices, while the G_B set would contain the transition structural isomers with one or more square faces and indicated by carbon indices enclosed in parentheses beside the edges linking the deltahedral vertices. If we wished to make our graphs follow the conventions of the topological representations of Muetterties, we could include the transition structure isomers as vertices, perhaps by enclosing the corresponding indices by boxes and inserting these directly into the graph edges.

Muetterties pointed out that the condition of *closure* applies to topological representations of polyhedral rearrangements. If the sum of the degrees of all the vertices in the isomer set G_A equals the sum of degrees of all vertices in G_B , then the topological representation is said to be *closed*. This simply means that the topological representation has no dangling edges that are not connected to vertices. In the same sense, the reaction graphs we show here are closed.

11. Summary

We list the following observations or conclusions concerning reaction graphs of the n -polyhedral boranes:

- (i) The number of possible isomerization processes is $n(n - 1)/2$. This is the total number of edges in the reaction graph.
- (ii) The total degree of a reaction graph is twice the number of edges or $n(n - 1)$.
- (iii) The degree of each vertex is twice the number of rotationally equivalent structures of the corresponding isomer.
- (iv) The degree of each vertex is directly related to the symmetry point group of the corresponding isomer.
- (v) Isomers with structures of higher symmetry have corresponding graph vertices of lower degree.
- (vi) Vertices associated with optical isomers are usually separated in the reaction graph by walks of a single step (i.e. directly connected) and are in no instances further removed than two steps.
- (vii) The graph edge connecting members of an enantiomeric pair passes through a transition structure in which the two carbons are symmetrically disposed with respect to a plane of symmetry, either both carbons on the plane or both on opposite sides of the plane. If the connection is by a single step, the symmetric structure is a transition structure. If the connection is by way of a two-step process, the symmetric structure is one of the unique carborane isomers.
- (viii) Reaction graphs are closed.

Acknowledgements

This research was sponsored in part by the National Science Foundation through Grant No. CHE-8703461 to the University of South Carolina. One of us (B.M.G.) gratefully acknowledges the hospitality of the Department of Chemistry, Harbin Normal University, Harbin, China, where some of the research described here was accomplished.

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