TOPOLOGICAL ASPECTS OF CHEMICALLY SIGNIFICANT POLYHEDRA

R.B. KING

Department of Chemistry, University of Georgia, Athens, GA 30602, USA

Abstract

This paper considers both static and dynamic properties of chemically significant polyhedra. Static properties of polyhedra consider relationships between the numbers and degrees/sizes of polyhedral vertices, edges, and faces; polyhedral symmetries; and numbers of topologically distinct polyhedra of various types. Dynamic properties of polyhedra involve studies of polyhedral isomerizations from both macroscopic and microscopic points of view. Macroscopic aspects of polyhedral isomerization can be described by graphs called topological representations in which the vertices correspond to different permutational isomers and the edges to single degenerate polyhedral isomerization steps. Such topological representations are presented for isomerizations of polyhedra having five, six, and eight vertices. Microscopic aspects of polyhedral isomerizations arise from consideration of the details of polyhedral topology, such as the topological aspects of diamond–square–diamond processes. In this connection, Gale diagrams are useful for describing isomerizations of five- and six-vertex polyhedra, including the Berry pseudorotation of a trigonal bipyramid through a square pyramid intermediate and the Bailar or Ray and Dutt twists of an octahedron through a trigonal prism intermediate.

1. Introduction

An important concept for the description of molecular structures is that of a polyhedron. In this connection, a polyhedron may be regarded as a set in three-dimensional space consisting of (zero-dimensional) points, namely the vertices; (one-dimensional) lines connecting some pairs of the vertices, namely the edges; and (two-dimensional) surfaces formed by the edges, namely the faces. Polyhedra may appear in molecular structures either as coordination polyhedra in which the vertices represent ligands surrounding a central atom, or as cluster polyhedra in which the vertices represent multivalent atoms and the edges represent bonding distances. Deltahedra, which are polyhedra in which all faces are triangles, often play special roles in molcular structures such as those of the cage boranes and carboranes.

This paper focuses on topological aspects of chemically significant polyhedra. Topology is the area of mathematics which in the abstract sense involves the study of neighborhood relationships in sets. This leads to the concept of a topological space, which has a precise mathematical definition [1]. However, here it suffices to regard polyhedra as a special type of topological space in which the vertices are members of the set and the edges describe neighborhood relationships.

Both static and dynamic properties of polyhedra are of chemical interest. Static properties of polyhedra include relationships between the numbers and degrees/sizes of polyhedral vertices, edges, and faces; polyhedral symmetries; and numbers of topologically distinct polyhedra of various types. Dynamic properties of polyhedra include considerations of polyhedral isomerizations from both macroscopic and microscopic points of view. In this context, a polyhedral isomerization step involving conversion of one permutational isomer to another may be defined as a deformation of a specific polyhedron P_1 until the vertices describe a new polyhedron P_2. Of particular interest are sequences of two polyhedral isomerization steps $P_1 \rightarrow P_2 \rightarrow P_3$, leading to a so-called degenerate polyhedral isomerization in which P_3 is topologically equivalent to P_1, although with some permutation of vertices not necessarily the identity permutation. Polyhedral isomerizations may be treated from either the macroscopic or microscopic points of view. The macroscopic view of polyhedral isomerizations describes relationships between permutational isomers using graphs called topological representations [2], in which the vertices correspond to different permutational isomers and the edges to single degenerate polyhedral isomerization steps. The microscopic view of polyhedral isomerizations elucidates possible single polyhedral isomerization steps by considering details of polyhedral topology, including possible diamond−square−diamond processes and more general methods for five- and six-vertex polyhedra based on Gale transformations [3].

This paper summarizes highlights of the static topology of polyhedra, as well as both the macroscopic and microscopic aspects of polyhedral isomerizations. Further details of many of these points are presented in a recent review [4].

2.   Static polyhedron topology

Of basic importance are the following relationships between possible numbers and types of vertices (v), edges (e), and faces (f) of polyhedra:

(1) Euler's relationship [5]:

$$v - e + f = 2. \tag{1}$$

(2) Relationship between the edges and faces:

$$\sum_{i=3}^{v-1} if_i = 2e. \tag{2}$$

In eq. (2), f_i is the number of faces with i edges. This relationship arises from the fact that each polyhedral edge is shared by exactly two faces. Since no face can have fewer edges than the three of a triangle, the following inequality must hold in all cases:

$$3f \le 2e. \tag{3}$$

(3) Relationship between the edges and vertices:

$$\sum_{i=3}^{v-1} i v_i = 2e. \tag{4}$$

In eq. (4), v_i is the number of vertices where i edges meet (i.e. a number of vertices of degree i). This relationship arises from the fact that each polyhedral edge joins exactly two vertices. Since no polyhedral vertex can have a degree less than three, the following inequality must hold in all cases:

$$3v \le 2e. \tag{5}$$

Note the similar forms of eqs. (2) and (4) and of eqs. (3) and (5).

(4) Totality of faces:

$$\sum_{i=3}^{v-1} f_i = f. \tag{6}$$

(5) Totality of vertices:

$$\sum_{i=3}^{v-1} v_i = v. \tag{7}$$

Equation (6) relates the f_i's to f and eq. (7) relates the v_i's to v.

In generating actual polyhedra, the operations of capping and dualization are often important. Capping a polyhedron P consists of adding a new vertex above the center of one of its faces F, followed by adding sufficient edges to connect the new vertex with each vertex of F. Such capping gives a new polyhedron P' having one more vertex than P. Capping a triangular face leads to the relationships $v' = v + 1$, $e' = e + 3$, $f' = f + 2$. In general, capping a face with f_k edges leads to the relationships $v' = v + 1$, $e' = e + f_k$, $f' = f + f_k - 1$. A given polyhedron P can be converted into its dual $P*$ by locating the centers of the faces of $P*$ at the vertices of P and the vertices of $P*$ above the centers of the faces of P. Two vertices in the dual $P*$ are connected by an edge when the corresponding faces in P share an edge. A pair of dual polyhedra P and $P*$ has the following properties:

(1) The numbers of vertices, edges, and faces in such a pair of dual polyhedra satisfy the relationships $v* = f$, $e* = e$, $f* = v$.

(2) Dual polyhedra have the same symmetry elements and thus belong to the same symmetry point group.

(3) Dualization of the dual of a polyhedron leads to the original polyhedron.

(4) The degrees of the vertices of a polyhedon P correspond to the number of edges in the corresponding face of its dual $P*$ and vice versa.

The duals of the cube, regular (I_h) dodecahedron, and n-fold (D_{nh}) prisms are the regular (O_h) octahedron, the regular (I_h) icosahedron, and the n-fold (D_{nh}) bipyramids, respectively. The regular (T_d) tetrahedron and n-fold (C_{nv}) pyramids are self-dual, i.e. their dualization leads to a polyhedron topologically equivalent to the original polyhedron.

The problem of the classification and enumeration of polyhedra is complicated. Thus, there appear to be no formulas, direct or recursive, from which the number of topologically distinct polyhedra having a given number of vertices, edges, faces, or any combination of these elements can be calculated. Furthermore, existence of a set of v, v_i, e, f, and f_i values satisfying simultaneously eqs. (1), (2), (4), (6), and (7) does not guarantee the existence of a polyhedron having these values. For example, Duijvestijn [6] has demonstrated the non-existence of an 11-vertex deltahedron having 10 vertices of degree 5 and 1 vertex of degree 4, even though the corresponding values of $v = 11$, $e = 27$, $f = 18$, $v_4 = 1$, $v_5 = 10$, $v_i = 0$ ($i \neq 4, 5$), $f_3 = 18$, $f_i = 0$ ($i \neq 3$) satisfy the required eqs. (1), (2), (4), (6), and (7). Duijvestijn and Federico [7] have enumerated by computer the polyhedra having up to 22 edges according to their numbers of vertices, edges, and faces, as well as their symmetry groups. Their work shows that there are 1, 2, 7, 34, 257, 2606, and 32,300 topologically distinct polyhedra with 4, 5, 6, 7, 8, 9, and 10 vertices or faces, respectively. Britton and Dunitz [8] have tabulated the properties of all 301 topologically distinct polyhedra having eight or fewer vertices. The duals of these 301 polyhedra (i.e. all polyhedra having eight or fewer faces) are described by Federico [9].

3. Macroscopic aspects of polyhedral isomerizations

The macroscopic description of polyhedral isomerizations uses topological representations [2], which are graphs representing the relationship between different polyhedra with v vertices as well as the different permutational isomers of a given polyhedron. Such graphs correspond to special cases of rearrangement graphs, which can be applied to a number of chemical problems. In such a graph, the vertices correspond to isomers and the edges correspond to isomerization steps. The number of vertices corresponds to the isomer count

$$I = v!/|R|, \tag{8}$$

where $|R|$ is the number of proper rotations in the symmetry point group. The degree d of a vertex corresponds to the number of new permutational isomers generated in a single step from the isomer represented by the vertex in question; this is called the connectivity of the isomer. In the cases of topological representations containing vertices corresponding to topologically distinct polyhedra P, P', P'', etc., the following condition must apply:

$$Id = I'd' = I''d'', \text{ etc.} \tag{9}$$

This condition is called the closure condition.

A simple example of a topological representation is provided in the four-vertex system by the degenerate planar isomerization of a tetrahedron into its enantiomer through a square planar intermediate [2]. The isomer count for the tetrahedron I_{tet} is $4!/|T| = 24/12 = 2$ and the isomer count for the square I_{sq} is $4!/|D_4| = 24/8 = 3$. A topological representation of this process is a $K_{2,3}$ bipartite graph, which is derived from the trigonal bipyramid by deletion of the three equatorial–equatorial edges (fig. 1). The two axial vertices correspond to the two tetrahedral
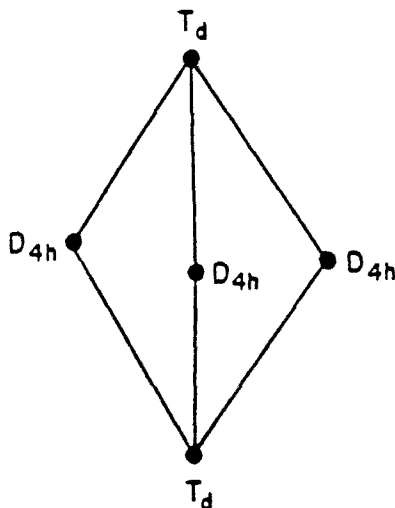

Fig. 1. The $K_{2,3}$ bipartite graph as a topological representation of the degenerate planar isomerization of a tetrahedron (T_d) into its enantiomer through a square planar intermediate (D_{4h}).

isomers and the three equatorial vertices correspond to the three square planar isomers. The connectivities of the tetrahedral (d_{tet}) and square planar (d_{sq}) isomers are 3 and 2, respectively, in accord with the degrees of the corresponding vertices of the $K_{2,3}$ graph (fig. 1). This topological representation satisfies the closure conditon (eq. (9)), since $(2)(3) = I_{tet}d_{tet} = (3)(2) = I_{sq}d_{sq} = 6$.

Some interesting graphs are found in the topological representations of the five-vertex trigonal bipyramid. The trigonal bipyramid has an isomer count $I = 5!/|D_3| = 120/6 = 20$, corresponding to 10 enantiomer pairs. A given trigonal bipyramid isomer can be described by the labels of its two axial positions. A topological representation of the degenerate isomerizations of the 20 trigonal bipyramid isomers through square pyramid intermediates (Berry pseudorotation process [10,11]) is the Desargues–Levy graph (fig. 2). The 20 vertices of degree 3 depict the 20 trigonal bipyramid isomers (i.e. $I_{tbp} = 20$ and $d_{tbp} = 3$), whereas the midpoints of the 30 edges depict the 30 square pyramid isomers (i.e. $I_{sp} = 30$ and $d_{sp} = 2$) so that
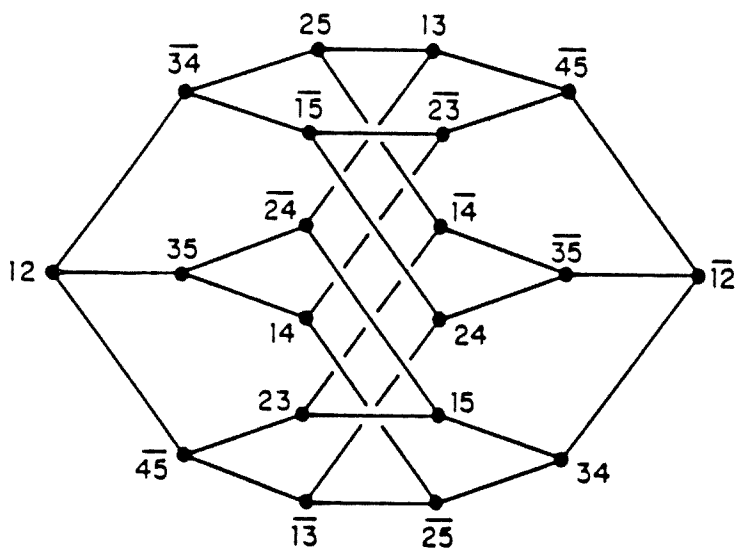
Fig. 2. The Desargues–Levy graph as a topological representation of the dsd isomerizations of the 20 trigonal bipyramid isomers through square pyramid intermediates.

the closure condition (eq. (9)) is satisfied [12]. A topological representation of the degenerate isomerizations of the 10 trigonal bipyramid enantiomeric pairs through similar Berry pseudorotation processes [10, 11] leads to the ten-vertex Petersen's graph (fig. 3), which also satisfies the closure condition.
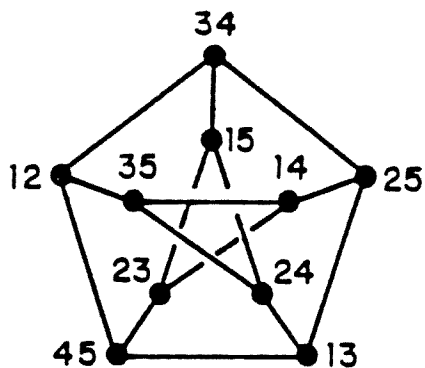

Fig. 3. The Petersen's graph as a topological representation of the dsd isomerizations of the 10 enantiomer pairs of the trigonal bipyramid isomers.

Useful topological representations can also be obtained for six-vertex systems [13]. Here, the process of interest is the isomerization of the octahedron through a trigonal prismatic intermediate, which is the underlying topology of both the Bailar [14] and Ray and Dutt [15] twists for octahedral M(bidentate)$_3$ chelates. The isomer counts are $I_{\text{oct}} = 6! / |O| = 720/24 = 30$ for the octahedron and $I_{\text{tp}} = 6! / |D_3| = 720/6 = 120$ for the trigonal prism. A regular (I_h) dodecahedron in double group form can serve as the topological representation of this process [13]. The midpoints of the 30 edges are the 30 octahedron isomers. Line segments across a pentagonal face connecting these edge midpoints correspond to degenerate isomerizations of these 30 octahedron isomers through trigonal prism intermediates located at the edge midpoints. Thus, each of the 12 (pentagonal) faces of the regular dodecahedron contains 10 trigonal prism isomers. Figure 4 depicts
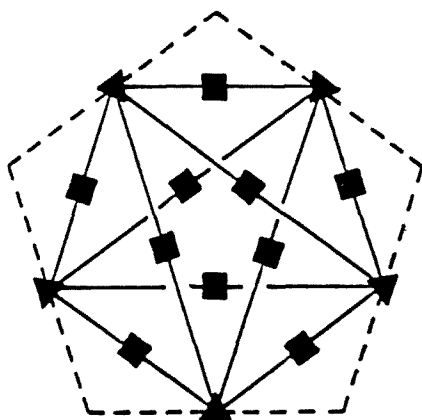

Fig. 4. One of the twelve pentagonal faces of the I_h double group (pentagonal) dodecahedron used as a topological representation for the triple dsd isomerization of the octahedron (O_h) through a trigonal prismatic intermediate (D_{3h}).

one of the 12 pentagonal faces of this double group regular dodecahedron topological representation; the 10 lines on this face representing isomerization processes form a K_5 complete graph [16]. Since the connectivities of the octahedron (d_{oct}) and trigonal prism (d_{tp}) are 8 and 2, respectively, $I_{\text{oct}} d_{\text{oct}} = I_{\text{tp}} d_{\text{tp}} = 240$, so that the closure condition (eq. (9)) is satisfied.

Development of topological representations for systems having more than six vertices is complicated by intractably large isomer counts. However, this difficulty can be alleviated if subgroups of the symmetric groups P_n ($n = 7$, 8, etc.) can be found which contain all of the symmetries of all of the polyhedra of interest. This is not possible for the seven-vertex system since there is no subgroup of the symmetric group P_7 which contains both the fivefold symmetry of the pentagonal bipyramid

and the three-fold symmetry of the capped octahedron. However, the eight-vertex system is more favorable in this connection since the wreath product group $P_4[P_2]$ of order 384 [17–19] contains all of the symmetries of the cube, hexagonal bipyramid, square antiprism, and bisdisphenoid ("D_{2d} dodecahedron"), which are all of the eight-vertex polyhedra of actual or potential chemical interest [20,21]. The major effect of reducing the symmetry by a factor of 105 ($= 3 \times 5 \times 7$) in going from P_8 to $P_4[P_2]$ is the deletion of fivefold and sevenfold symmetry elements, which are not found in actual eight-vertex polyhedra other than the chemically uninteresting heptagonal pyramid. Restricted isomer counts $I^* = 384/|R|$ based on subgroups of the wreath product group $P_4[P_2]$ rather than the symmetric group P_8 are the manageable numbers 16, 32, 48, and 96 for the cube, hexagonal bipyramid, square antiprism, and bisdisphenoid, respectively. Topological representations based on the wreath product group $P_4[P_2]$ rather than the symmetric group P_8 are called hyperoctahedrally restricted since $P_4[P_2]$ is the four-dimensional symmetry group of the four-dimensional analogue of the octahedron as well as that of its dual, namely the tesseract or four-dimensional cube.
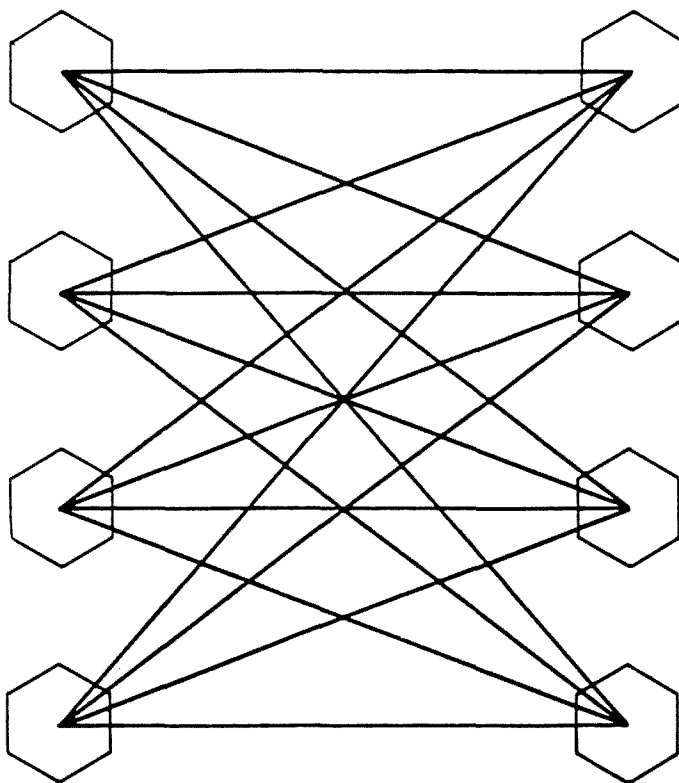

Fig. 5. The $K_{4,4}$ bipartite graph topological representation of the hyperoctahedrally restricted permutational isomerizations involving the cube (hexagon centers) and hexagonal bipyramid (edge midpoints). The processes depicted here require the accessibility of f orbitals and thus are mainly restricted to actinide chemistry.
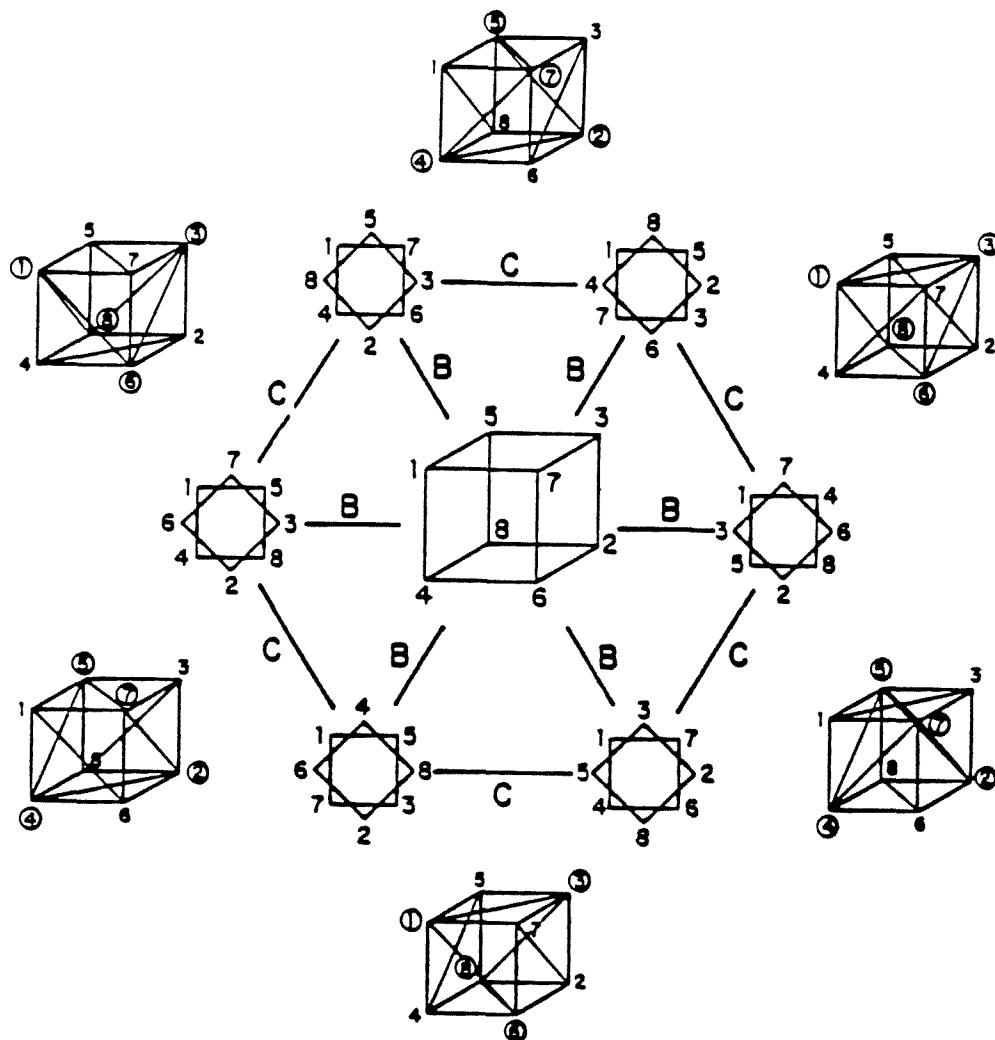
Fig. 6. Details of the hexagon in the topological representation in fig. 5. The vertices represent square antiprism isomers and the edge midpoints represent bisdisphenoid ("D_{2d} dodecahedron") isomers. The processes depicted here do not require the availability of f orbitals and thus can occur with central metal atoms having only s, p, and d orbitals energetically available.

Using these ideas, hyperoctahedrally restricted topological representations for isomerizations of four types of eight-vertex polyhedra are depicted in figs. 5 and 6 [22]. Figure 5 is a $K_{4,4}$ bipartite graph in which 8 cube enantiomer pairs are located at the centers of the hexagons and 16 hexagonal bipyramid enantiomer pairs are located at the edge midpoints. Since neither the cube nor the hexagonal bipyramid can be formed using only s, p, and d orbitals [23], this portion of the topological representation is not accessible if only s, p, and d orbitals are available for chemical bonding.

The detailed structure of a hexagon corresponding to a given pair of cube enantiomers is depicted in fig. 6. The vertices of the hexagon correspond to the square antiprisms that can be generated from the cube in the center by twisting opposite pairs of faces. The midpoints of the hexagon edges correspond to bisdisphenoid enantiomer pairs. Traversing the circumference of a given hexagon corresponds to a sequence of degenerate polyhedral rearrangements interconverting the bisdisphenoids located at the midpoints of two joined hexagonal edges through the square antiprism intermediate represented by the vertex joining the edges through what is called below a double diamond–square–diamond process. Since both the bisdisphenoid and square antiprism can be formed using only s, p, and d orbitals, the circumference of the hexagon (fig. 6) is accessible in ML_8 complexes, where M has the usual sp^3d^5 valence orbital manifold. However, interconversions between hexagons as depicted in fig. 5 require f orbitals and are thus restricted to actinide chemistry, where the valence shell includes f orbitals [24].

4. Microscopic aspects of polyhedral isomerizations

Now let us examine some microscopic aspects of polyhedral isomerizations. As early as 1966, Lipscomb [25] described framework rearrangements (isomerizations) in boranes and carboranes in terms of diamond–square–diamond (dsd) processes. Such a dsd process in a polyhedron occurs at two triangular faces sharing an edge and can be depicted as follows:

$$(10)$$

10a   10b   10c
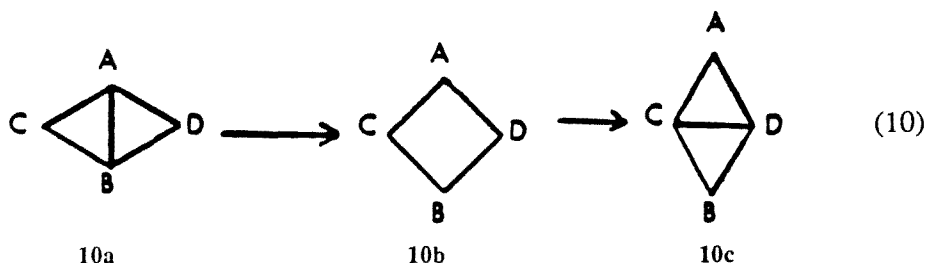
In such a process, a configuration such as **10a** can be called a dsd situation and the edge AB can be called a switching edge. If a, b, c, and d are taken to represent the degrees of the vertices A, B, C, and D, respectively, then the dsd type of the switching edge AB can be represented as $ab(cd)$. The quadrilateral face formed in structure **10b** can be called a pivot face.

Consider a deltahedron having e edges. Such a deltahedron has e distinct dsd situations, one corresponding to each of the e edges acting as a switching edge. Applications of the dsd process at each of the switching edges in a deltahedron leads to a new deltahedron. In cases where the new deltahedron is topologically identical to the original deltahedron, the switching edge can be said to be degenerate. The dsd type of a degenerate switching edge $ab(cd)$ can be seen by application of the process **10a** → **10b** → **10c** to satisfy the conditions:

$$c = a - 1 \quad \text{and} \quad d = b - 1 \quad \text{or} \quad c = b - 1 \quad \text{and} \quad d = a - 1. \tag{11}$$

A deltahedron having one or more degenerate edges is inherently fluxional, whereas a deltahedron without degenerate edges is inherently rigid.

The conditions in eq. (11) can be used to check chemically significant four- to twelve-vertex deltahedra for inherent rigidity or fluxionality with the following results:

(1) *Tetrahedron*: No dsd process of any kind is possible since the tetrahedron is the K_4 complete graph [16]. A tetrahedron is therefore inherently rigid.

(2) *Trigonal bipyramid*: The three edges connecting pairs of equatorial vertices are degenerate switching edges of the type 44(33). A dsd process using one of these edges as the switching edge, thereby involving a square pyramid intermediate, corresponds to the Berry pseudorotation [10, 11], which is believed to be the mechanism responsible for the stereochemical non-rigidity of trigonal bipyramid molecules and which is depicted in the topological representations in figs. 2 and 3.

(3) *Octahedron*: The highly symmetrical octahedron has no degenerate edges and is therefore inherently rigid.

(4) *Pentagonal bipyramid*: The seven-vertex pentagonal bipyramid has no degenerate edges and thus by definition is inherently rigid. However, a dsd process using a 45(44) edge of the pentagonal bipyramid (namely the edge connecting an equatorial vertex with an axial vertex) gives a capped octahedron. The capped octahedron is a low-energy polyhedron for ML_7 coordination complexes [26] but a forbidden polyhedron for boranes and carboranes because of its degree 3 vertex (tetrahedral chamber) [27]. This suggests fluxionality for ML_7 complexes, but not for pentagonal bipyramid boranes and carboranes.

(5) *Bisdisphenoids* ("D_{2d} *dodecahedron*"): The eight-vertex bisdisphenoid has 4 pairwise degenerate edges, which are those of the type 55(44) located in the subtetrahedron consisting of the degree 5 vertices of the bisdisphenoid. Thus, two successive, or more likely concerted, (parallel) dsd processes involving opposite 55(44) edges will convert one bisdisphenoid into another bisdisphenoid through a square antiprism intermediate, as depicted in the circumference of the hexagon in fig. 6. Thus, a bisdisphenoid is inherently fluxional.

(6) *4,4,4-Tricapped trigonal prism*: The 4,4,4-tricapped trigonal prism has 3 degenerate edges, which are those of the type 55(44) corresponding to the "vertical" edges of the trigonal prism. This suggests inherent fluxionality for this nine-vertex polyhedron. A dsd process using one of these degenerate edges as the switching edge involves a C_{4v} 4-capped square antiprism intermediate [28].

(7) *4,4-Bicapped square antiprism*: This ten-vertex deltahedron has no degenerate edges and is inherently rigid.

(8) *Edge-coalesced icosahedron*: This eleven-vertex deltahedron, which is the polyhedron found in $B_{11}H_{11}^{2-}$ and $C_2B_9H_{11}$ [29], has 4 degenerate edges, all of the type 56(45), indicating inherent fluxionality.

(9) *Icosahedron*: This highly symmetrical twelve-vertex deltahedron has no degenerate edges and is therefore inherently rigid.

This simple analysis indicates that in deltahedron molecules the 4-, 6-, 10-, and 12-vertex systems are inherently rigid; the 5-, 8-, 9-, and 11-vertex systems are inherently fluxional; and the rigidity of the 7-vertex system depends upon the energy difference between the two most symmetrical seven-vertex deltahedra, namely the pentagonal bipyramid and the capped octahedron. However, inherent fluxionality is not sufficient for actual fluxionality. Thus, orbital symmetry analyses by Gimarc and Ott on dsd processes in the five-vertex trigonal pyramid carboranes [30] and the nine-vertex tricapped trigonal prism boranes and carboranes [31] indicate that single dsd processes in these cases are blocked by crossings of filled and vacant molecular orbitals. A subsequent, more general study by Mingos and Johnston [32] indicates that single dsd processes in boranes and carboranes, which occur through an intermediate of C_{4v} symmetry, are orbitally forbidden (e.g. those in $B_5H_5^{2-}$ and $B_9H_9^{2-}$), but those which occur through an intermediate of C_{2v} or C_s symmetry are orbitally allowed (e.g. those in $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$). These orbital symmetry analyses apply to polyhedra consisting of light atoms using only s and p valence orbitals such as boron or carbon, and cannot be extended directly to transition metal clusters using d orbitals of the vertex atoms. In addition, such orbital symmetry analyses are not applicable to coordination polyhedra rather than cluster polyhedra.

The above microscopic approach for studying polyhedral isomerizations assumes dsd processes to be the fundamental building blocks. This is supported by a more general method [3] for examining all possible isomerizations involving non-planar intermediates of polyhedra having "few" (i.e. ≤ 6) vertices using a method developed by Gale [33] in 1956 for studying d-dimensional polytopes having only a few more than the minimum $d + 1$ vertices. Thus, if P is a d-dimensional polytope having v vertices, a Gale transformation leads to a Gale diagram of P consisting of v points in $(v - d - 1)$-dimensional space in one-to-one correspondence with the vertices of P [34]. The procedures for obtaining Gale transforms and Gale diagrams of polyhedra and polytopes are described in detail elsewhere [3,4,33–36], and they will not be repeated here since the equations are rather lengthy.

The Gale diagram of a polytope P is significant in that it provides a method for determining the topological properties of P such as the subsets of the vertices that define faces of P, the combinatorial types of these faces, etc. Of particular significance in the present context is the fact that the topological properties of a polytope P which can be determined by the Gale diagram include all possible isomerizations of P to other polytopes having the same number of vertices and embedded in the same number of dimensions as P. Also of particular importance

is the fact that if v is not much larger than d (i.e. if $v \le 2d$), then the dimension of the Gale diagram is less than that of the original polytope P.

Now consider polyhedra in the ordinary three-dimensional space of interest in chemical structures. Gale diagrams of five- and six-vertex polyhedra can be embedded into one- and two-dimensional space, respectively, thereby simplifying the analysis of possible vertex motions leading to isomerizations of these polyhedra of possible chemical interest. Thus, the (one-dimensional) Gale diagrams of five-vertex polyhedra can only contain the points 0, 1, and -1 of the straight line of varying multiplicities m_0, m_1, and m_{-1}, respectively, where $m_0 \ge 0$, $m_1 \ge 2$, and $m_{-1} \ge 2$. The (two-dimensional) Gale diagrams of six-vertex polyhedra can only contain the center and circumference of the unit circle. Figure 7 depicts the Gale diagrams for the two topologically distinct five-vertex polyhedra (trigonal bipyramid and square pyramid) and the seven topologically distinct six-vertex polyhedra. The Gale diagrams of the six-vertex polyhedra are drawn to maximize the symmetry and the number of balanced diameters, i.e. diameters having points at each end. Each such balanced diameter corresponds to a quadrilateral face in the corresponding six-vertex polyhedron.

The following properties of Gale diagrams of dimension 2 or lower impose important restrictions on configurations of points which can be Gale diagrams:

(1)   A line passing through the central point of a Gale diagram bisects the space of the Gale diagram into two halfspaces. Each such halfspace must contain at least 2 vertices (or 1 vertex of multiplicity 2) in the Gale diagram, not including any vertices actually on the bisecting line. Such a halfspace is called an open halfspace. Violation of this condition corresponds to a polyhedron with the impossible property of at least one vertex pair not connected by an edge which is closer in three-dimensional space than another vertex pair connected by an edge.

(2)   A coface of a polyhedron is the set of vertices remaining after forming a face of the polyhedron. The regular octahedron is unusual among polyhedra in that all of its faces are also cofaces. The interior of the figure formed by connecting the vertices of a Gale diagram corresponding to a coface must contain the central point. Furthermore, the central point is a vertex of a Gale diagram if and only if the corresponding polyhedron is a pyramid. In this case, the central vertex corresponds to the apex of the pyramid, which is the coface corresponding to the base of the pyramid.

Non-planar isomerizations of five- and six-vertex polyhedra correspond to allowed vertex motions in the corresponding Gale diagrams in fig. 7. In this context, an allowed vertex motion is the motion of one or more vertices which converts the Gale diagram of a polyhedron into that of another polyhedron with the same number of vertices without ever passing through an impossible Gale diagram, such as one with an open halfspace containing only one vertex of unit multiplicity. Since two
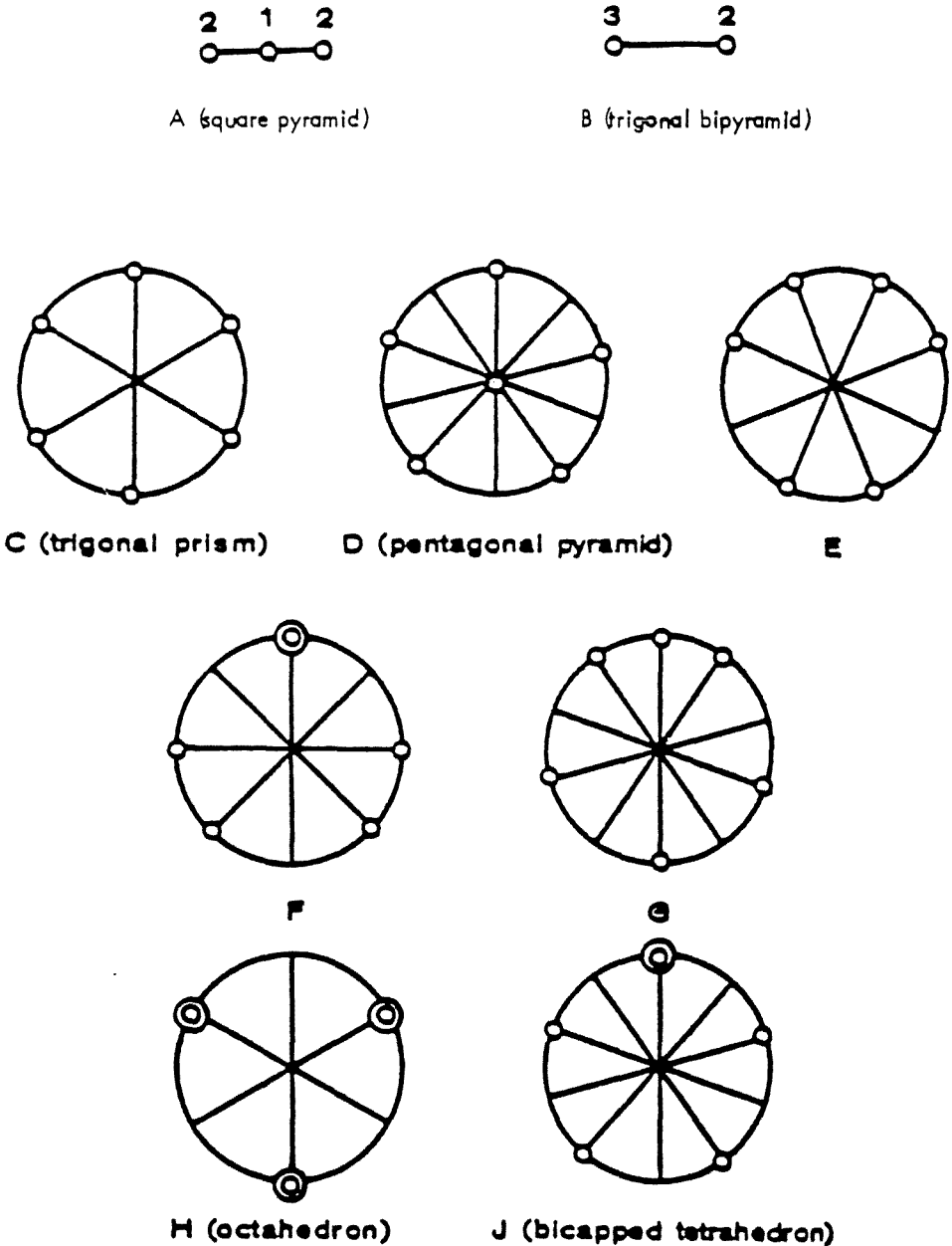
Fig. 7. Gale diagrams for the two topologically distinct five-vertex polyhedra and the seven topologically distinct six-vertex polyhedra.

polyhedra are topologically equivalent if and only if their Gale diagrams are isomorphic [34], such allowed vertex motions are faithful descriptions of all possible polyhedral isomerizations not involving planar isomerizations.
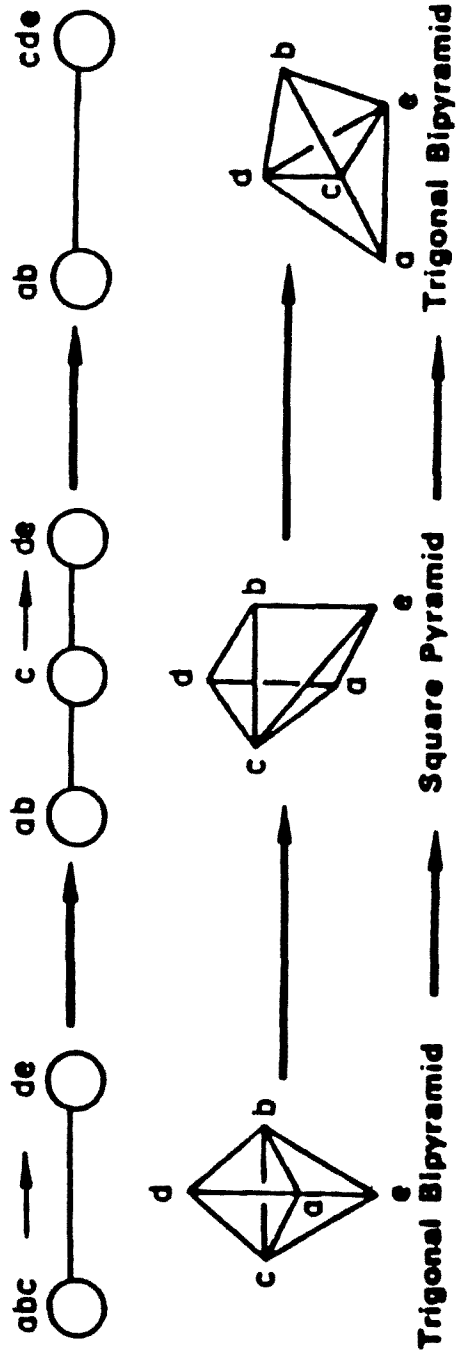
Fig. 8. Gale diagrams for a single dsd degenerate isomerization of a trigonal bipyramid through a square pyramid intermediate (Berry pseudorotation).
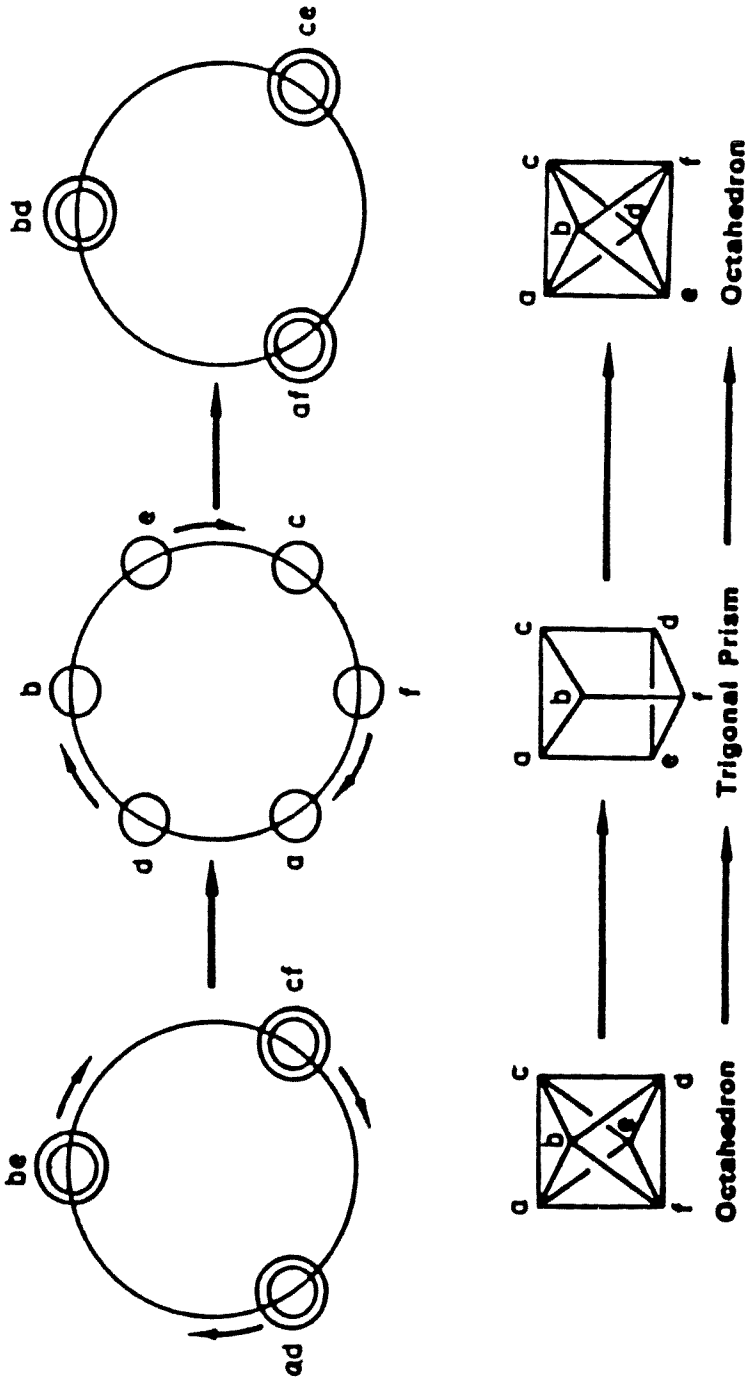
Fig. 9. Gale diagrams for a triple dsd degenerate isomerization of an octahedron through a trigonal prism intermediate (Bailar twist, and Ray and Dutt twist).

The application of Gale diagrams to the study of isomerizations of five-vertex polyhedra is nearly trivial but provides a useful illustration of this method. The only allowed vertex motion in a Gale diagram of a trigonal bipyramid is the motion of 1 point from the vertex of multiplicity 3 through the center point to the vertex originally of multiplicity 2 (fig. 8). This interchanges the vertices of multiplicities 2 and 3 and leads to an equivalent Gale diagram corresponding to an isomeric trigonal bipyramid. The motion through the center point of the Gale diagram corresponds to the generation of a square pyramid intermediate in the dsd process corresponding to the Berry pseudorotation [10,11]. This analysis of the Gale diagrams of the two possible five-vertex polyhedra shows clearly that the only geometrically possible isomerizations of five-vertex polyhedra not involving planar pentagon intermediates can be described as successive dsd processes corresponding to successive Berry pseudorotations.

Gale diagrams are also useful for the study of isomerizations of six-vertex polyhedra [3,35,36]. Such isomerizations are described by allowed motions of the vertices of the Gale diagrams along the circumference of the unit circle, or through the center in the case of polyhedral isomerizations involving a pentagonal pyramid intermediate. In this way, all degenerate isomerizations of six-vertex polyhedra not involving planar hexagon intermediates can be decomposed into a sequence of eight fundamental processes [3]. Two of these fundamental processes involve a pentagonal pyramid intermediate, whereas the remaining six processes are variations of single or multiple dsd processes. Of particular chemical interest is the triple dsd degenerate isomerization of an octahedron through a trigonal prism intermediate, as described by the Gale diagrams in fig. 9. The Bailar twist [14] and the Ray and Dutt twist [15] of six-coordinate $M(bidentate)_3$ chelates are examples of this type of isomerization.

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