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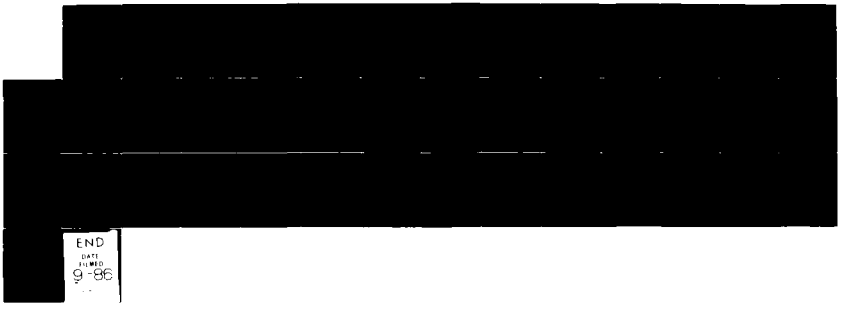

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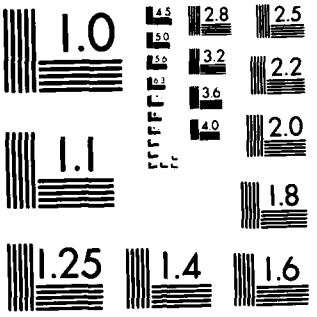

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ABSTRACT. Some topological properties of polyhedra are summarized with particular reference to properties relevant to polyhedral isomerizations such as inherent rigidity or fluxionality. Among the chemically significant deltahedra, the tetrahedron, octahedron, 4,4bicapped square antiprism, and icosahedron are inherently rigid whereas the normally encountered 5, 8, 9, and 11 vertex deltahedra are inherently fluxional. Topological representations are graphs in which the vertices correspond to different polyhedral isomers and the edges

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represent single polyhedral isomerization steps. The Petersen's and Desargues-Levy graphs are topological representations of 5 vertex systems and the double group pentagonal dodecahedron with K_5 complete graphs on each of the 12 faces is a topological representation of a 6 vertex system. Additional ideas including hyperoctahedral restriction are necessary for tractable topological representations of systems having more than 6 vertices. Thus a hyperoctahedrally restricted topological representation of an 8 vertex system is a $K_{4,4}$ bipartite graph of hexagons with cubes at the vertices of the $K_{4,4}$ graph, hexagonal bipyramids at the edge midpoints of the $K_{4,4}$ graph, square antiprisms at the vertices of the 8 hexagons, and bisdisphenoids at the midpoints of the edges of the 8 hexagons. In the study of 5 and 6 vertex polyhedra, Gale transformations can be used to reduce their effective dimensionalities to 1 and 2, respectively, so that all possible types of their non-planar isomerizations can be found in these spaces of lower dimensionality. The observations arising from this application of Gale transformations provides useful insights relating to isomerizations of 7 and 8. vertex polyhedra although an exhaustive treatment of the latter is clearly intractable.

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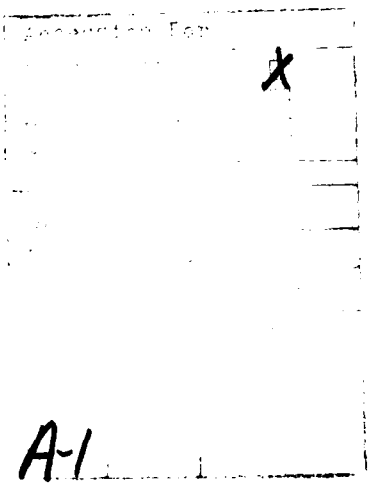
Topological Aspects of Polyhedral Isomerizations

by

R.B. King



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TOPOLOGICAL ASPECTS OF POLYHEDRAL ISOMERIZATIONS

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ABSTRACT. Some topological properties of polyhedra are summarized with particular reference to properties relevant to polyhedral isomerizations such as inherent rigidity or fluxionality. Among the chemically significant deltahedra, the tetrahedron, octahedron, 4,4-bicapped square antiprism, and icosahedron are inherently rigid whereas the normally encountered 5, 8, 9, and 11 vertex deltahedra are inherently fluxional. Topological representations are graphs in which the vertices correspond to different polyhedral isomers and the edges represent single polyhedral isomerization steps. The Petersen's and Desargues-Levy graphs are topological representations of 5 vertex systems and the double group pentagonal dodecahedron with K_5 complete graphs on each of the 12 faces is a topological representation of a 6 vertex system. Additional ideas including hyperoctahedral restriction are necessary for tractable topological representations of systems having more than 6 vertices. Thus a hyperoctahedrally restricted topological representation of an 8 vertex system is a $K_{4,4}$ bipartite graph of hexagons with cubes at the vertices of the $K_{4,4}$ graph, hexagonal bipyramids at the edge midpoints of the $K_{4,4}$ graph, square antiprisms at the vertices of the 8 hexagons, and bisdisphenoids at the midpoints of the edges of the 8 hexagons. In the study of 5 and 6 vertex polyhedra, Gale transformations can be used to reduce their effective dimensionalities to 1 and 2, respectively, so that all possible types of their non-planar isomerizations can be found in these spaces of lower dimensionality. The observations arising from this application of Gale transformations provides useful insights relating to isomerizations of 7 and 8 vertex polyhedra although an exhaustive treatment of the latter is clearly intractable.

1. INTRODUCTION

A key concept for the description of chemical structures is that of a polyhedron. In three-dimensional space a polyhedron may be regarded as a set consisting of (zero-dimensional) points, namely the vertices; (one-dimensional) lines connecting some of the vertices, namely the edges; and (two-dimensional) surfaces formed by the edges, namely the faces. Polyhedra appear in chemical structures in two principal ways: coordination polyhedra in which the vertices represent ligands surrounding a central atom which is often, but not always, a metal, and cluster polyhedra in which the vertices represent multivalent atoms and the edges represent bonding distances. In chemical contexts deltahedra, in which all faces are triangles, often play a special role.

The role of polyhedra in the static description of chemical structures makes the dynamic properties of polyhedra also of considerable interest. This chapter summarizes some mathematical approaches for the study of the dynamic properties of polyhedra. Such methods use extensively the ideas taken from the area of mathematics known as topology, which, in the abstract sense, may be regarded as the study of neighborhood relationships in sets. This leads to the concept of a topological space, which has a precise mathematical definition [1]. However, it is sufficient here to regard polyhedra as a special type of topological space in which the vertices are the members of the set and the edges are used to determine neighborhood relationships.

The central concept in the study of the dynamic properties of polyedra is that of a polyhedral isomerization. In this context a polyhedral isomerization may be defined as a deformation of a specific polyhedron P_1 until the vertices define a new polyhedron P_2. Of particular interest are sequences of two polyhedral isomerization steps $P_1 \rightarrow P_2 \rightarrow P_3$ in which the polyhedron P_3 is combinatorially equivalent to the polyhedron P_1 (i.e., the "same" polyhedron) although with some permutation of the vertices not generally the identity permutation. Such a polyhedral isomerization sequence of the type $P_1 \rightarrow P_2 \rightarrow P_3$ in which P_1 and P_3 are combinatorially equivalent may be called a degenerate polyhedral isomerization with a P_2 as the intermediate polyhedron. A degenerate polyhedral isomerization with a planar intermediate "polyhedron" (actually a polygon) may be called a planar polyhedral isomerization. The simplest example of a planar polyhedral isomerization is the interconversion of two tetrahedra (P_1 and P_3) through a square planar intermediate P_2. Except for this simplest example, planar polyhedral isomerizations are unfavorable owing to excessive intervertex repulsion and, in the case of ML_n coordination complexes, unfavorable or impossible hybridizations of the available M valence orbitals.

Polyhedral isomerizations may be treated from either the macroscopic or microscopic points of view. Initial work in this area, pioneered by Muetterties [2-5], Gielen [6-13], Klemperer [14-16], and Brocas [17], focussed on the macroscopic picture, namely relationships between different permutational isomers. Such relationships

may be represented by graphs called topological representations in which the vertices correspond to different permutational isomers and the edges to single degenerate polyhedral isomerization steps. My much more recent work treats the microscopic picture in which the details of polyhedral topology are used to elucidate possible single polyhedral isomerization steps, namely which types of isomerization processes are possible. This chapter presents a general view of both approaches and presents key literature references for the reader wishing further details.

2. POLYHEDRON TOPOLOGY

Before considering the dynamics of polyhedra it is first necessary to consider the static topology of polyhedra. Of basic importance are relationships between possible numbers and types of vertices (v), edges (e), and faces (f) of polyhedra. In this connection the following elementary relationships are particularly significant [18]:

(1) Euler's relationship:

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

This arises from the properties of ordinary three-dimensional space [19].

(2) Relationship between the edges and faces:

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

In equation 2 f_i is the number of faces with i edges (i.e., f_3 is the number of triangular faces, f_4 is the number of quadrilateral faces, etc.). This relationship arises from the fact that each 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:

$$3f \leq 2e \tag{3}$$

(3) Relationship between the edges and vertices:

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

In equation 4 v_i is the number of vertices of degree i (i.e., having i edges meeting at the vertex). This relationship arises from the fact that each edge joins exactly two vertices. Since no vertex

of a three-dimensional polyhedron can have a degree less than three, the following inequality must hold in all cases:

$$3v \leq 2e \tag{5}$$

Note the similar forms of equations 2 and 4 and of equations 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 equation 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_1 consists of adding a new vertex above the center of one of its faces F_1 followed by adding edges to connect the new vertex with each vertex of F_1. This capping process gives a new polyhedron P_2 having one more vertex than P_1. If a triangular face is capped, the following relationships will be satisfied where the subscripts 1 and 2 refer to P_1 and P_2, respectively: $v_2 = v_1 + 1$; $e_2 = e_1 + 3$; $f_2 = f_1 + 2$. In general if a face with f_k edges is capped, the following relationships will be satisfied: $v_2 = v_1 + 1$; $e_2 = e_1 + f_k$; $f_2 = f_1 + f_k - 1$. 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. The process of dualization has the following properties:
(1) The numbers of vertices and edges in a pair of dual polyhedra P and P* 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 polyhedron correspond to the number of edges in the corresponding face polygons of its dual.

The problem of classification and enumeration of polyhedra is a complicated one. Thus there appear to be no formulas, direct or recursive, for which the number of combinatorially distinct polyhedra having a given number of vertices, edges, faces, or any given combin-

ation of these elements can be calculated [20,21]. Duijvestijn and Federico have enumerated by computer the polyhedra having up to 22 edges according to their numbers of vertices, edges, and faces and their symmetry groups and present a summary of their methods, results, and literature references to previous work [22]. Their work shows that there are 1, 2, 7, 34, 257, 2606, and 32300 combinatorially distinct polyhedra with 4, 5, 6, 7, 8, 9, and 10 faces or vertices, respectively. Federico [23] has tabulated the detailed properties of all 301 combinatorially distinct polyhedra having eight or fewer faces. By dualization (see above) the information in this list can be converted to information for all combinatorically distinct polyhedra having eight or fewer vertices. This information from Federico's work [23] has played a key role in my recent work on polyhedral dynamics. Even more recently I became aware of a similar listing of all polyhedra having eight or fewer vertices [24] in a journal more familiar to chemists and not requiring dualization before use.

Some of the properties of polyhedra having relatively few vertices are listed in Tables 1-3. This includes almost all of the polyhedra of chemical significance. Table 1 lists all 10 polyhedra having 6 or fewer vertices, Table 2 lists all 34 polyhedra having 7 vertices, and Table 3 lists the important polyhedra having 8 vertices as well as a few polyhedra having 9 to 12 vertices.

Polyhedra of greatest significance in coordination chemistry are those that can be formed by the nine s, p, and d orbitals in the sp^3d^5 valence orbital manifold accessible to transition metals. There are, however, some polyhedra having fewer than nine vertices which cannot be formed by these orbitals; such polyhedra are called forbidden polyhedra [25]. Group theoretical arguments show that polyhedra of the following types are always forbidden polyhedra:
(1) Polyhedra having eight vertices, a direct product symmetry group $R \times C_s$ or $R \times C_i$ (R contains only proper rotations), and the plane C_s fixing either 0 or 6 vertices.
(2) Polyhedra having a six-fold or higher C_n rotation axis.
However, these conditions are not necessary for a polyhedron to be forbidden since in addition to one forbidden 7-vertex polyhedron (the hexagonal pyramid) and ten forbidden 8-vertex polyhedra (including the cube, the D_{3d} bicapped octahedron, the D_{3h} 3,3-bicapped trigonal prism, and the hexagonal bipyramid) satisfying one or both of the above conditions, there are two forbidden C_{3v} 8-vertex polyhedra which satisfy neither of the above conditions.

Within the context of the polyhedra tabulations in Tables 1-3 and the concept of forbidden polyhedra, the polyhedra appearing as coordination polyhedra can be examined. The most prevalent coordination polyhedra for coordination numbers 4 to 8 are depicted in Figure 1. For coordination numbers 4 and 6 the tetrahedron and octahedron, respectively, dominate except in special cases [26,27]. For coordination number 5 the trigonal bipyramid and square pyramid are of similar energies [26] and the prototypical polyhedral isomerization involves their interconversion [28,29]. These two polyhedra, like the tetrahedron for coordination number 4, are the only possible

TABLE 1

PROPERTIES OF ALL POSSIBLE FOUR-, FIVE-, AND SIX-VERTEX POLYHEDRA

Polyhedron name (if any)	Vertices	Edges	Faces	Symmetry	v_3	v_4	v_5	f_3	f_4	f_5	Gale Diagram[c]	Federico Number of Dual[d]
Tetrahedron	4	6	4	T_d	4	0	0	4	0	0		1
Trigonal bipyramid	5	9	6	D_{3h}	2	3	0	6	0	0	B	2
Square pyramid	5	8	5	C_{4v}	4	1	0	4	1	0	A	3
Octahedron	6	12	8	O_h	0	6	0	8	0	0	H	7
Bicapped tetrahedron	6	12	8	C_{2v}	2	2	2	8	0	0	J	4
Diagonally deficient cube	6	11	7	C_{2v}	2	4	0	6	1	0	F	8
	6	11	7	C_s	3	2	1	6	1	0	G	5
"Irregular hexahedron"	6	10	6	C_2	4	2	0	4	2	0	E	9
Pentagonal pyramid	6	10	6	C_{5v}	5	0	1	5	0	1	D	6
Trigonal prism	6	9	5	D_{3h}	6	0	0	2	3	0	C	10

(a) The designations v_n refer to the numbers of vertices of degree n.
(b) The designations f_3, f_4 and f_5 refer to the numbers of faces which are triangles, quadrilaterals, and pentagons, respectively.
(c) The letters refer to the Gale diagrams depicted in Figure 7.
(d) The numbers refer to the number of the dual polyhedron in Table 1 of P.J. Federico, Geometriae Dedicata 3, 469 (1981).

TABLE 2

PROPERTIES OF THE 34 SEVEN-VERTEX POLYHEDRA

Edges	Faces	Symmetry	Vertex Types[a] v_3	v_4	v_5	v_6	Face Types[b] f_3	f_4	f_5	f_6	dsd rigidity index[c]	distinctive features[d]	Listing Numbers[e] F	BD
A) Deltahedra														
15	10	C_{2v}	2	3	0	2	10	0	0	0	2	$2v_6$	11	2
15	10	C_{3v}	3	0	3	1	10	0	0	0	2	$1v_6$ + C_3 axis	12	1
15	10	C_2	2	2	2	1	10	0	0	0	1	$1v_6$ + C_2 axis	13	3
15	10	C_{3v}	1	3	3	0	10	0	0	0	2	capped octahedron	20	4
15	10	D_{5h}	0	5	2	0	10	0	0	0	2	pentagonal bipyramid	23	5
B) Polyhedra having One Quadrilateral Face														
14	9	C_s	3	2	1	1	8	1	0	0	2	$0e_{33}$	14	6
14	9	C_1	3	2	1	1	8	1	0	0	1	$1e_{33}$	15	7
14	9	C_{2v}	2	4	0	1	8	1	0	0	2		16	10
14	9	C_s	3	1	3	0	8	1	0	0	2	$3e_{45}$	21	8
14	9	C_s	3	1	3	0	8	1	0	0	1	$2e_{45}$	22	9
14	9	C_s	2	3	2	0	8	1	0	0	2	$0e_{55}$	24	11
14	9	C_1	2	3	2	0	8	1	0	0	1	$1e_{55}$	25	12
14	9	C_s	1	5	1	0	8	1	0	0	1		28	13

TABLE 2 (Continued)

Edges	Faces	Symmetry	Vertex Types[a]				Face Types[b]				dsd rigidity index[c]	distinctive features[d]	Listing Numbers[e]	
			v_3	v_4	v_5	v_6	f_3	f_4	f_5	f_6			F	BD
C) Polyhedra having Two Quadrilateral Faces														
13	8	C_{2v}	4	2	0	1	6	2	0	0	2		18	16
13	8	C_1	4	1	2	0	6	2	0	0	2	2connected e_{33}	26	17
13	8	C_2	4	1	2	0	6	2	0	0	0	2 disconnected e_{33}	27	18
13	8	C_2	3	3	1	0	6	2	0	0	1	$1e_{44}$	30	21
13	8	C_s	3	3	1	0	6	2	0	0	2	$2e_{44}$	31	22
13	8	C_1	3	3	1	0	6	2	0	0	1	$2e_{44}$	32	20
13	8	C_1	3	3	1	0	6	2	0	0	1	$3e_{44}$	33	19
13	8	C_{2v}	2	5	0	0	6	2	0	0	1	4-capped trigonal prism ($1e_{33}$)	36	23
13	8	C_2	2	5	0	0	6	2	0	0	2	$0e_{33}$	37	24
D) Polyhedra having Three or Four Quadrilateral Faces														
12	7	C_s	5	1	1	0	4	3	0	0	1		35	28
12	7	C_{3v}	4	3	0	0	4	3	0	0	0	3-capped trigonal prism, SD	39	32
12	7	C_{3v}	4	3	0	0	4	3	0	0	1	SD	40	29
12	7	C_2	4	3	0	0	4	3	0	0	0	SD	41	31

TABLE 2 (Continued)

Edges	Faces	Symmetry	Vertex Types[a] v_3	v_4	v_5	v_6	Face Types[b] f_3	f_4	f_5	f_6	dsd rigidity index[c]	distinctive features[d]	Listing Numbers[e] F	BD
12	7	C_1	4	3	0	0	4	3	0	0	1	$1v_3$ surrounded by $3v_4$, SD	42	30
11	6	C_{2v}	6	1	0	0	2	4	0	0	0	4 quadrilateral faces	44	34
E) Polyhedra having Pentagonal or Hexagonal Faces														
13	8	C_s	4	2	0	1	7	0	1	0	1	3-capped pentagonal pyramid	17	14
13	8	C_s	3	3	1	0	7	0	1	0	1		29	15
12	7	C_1	5	1	1	0	5	1	1	0	1	SD	34	26
12	7	C_s	4	3	0	0	5	1	1	0	1		38	27
11	6	C_s	6	1	0	0	3	2	1	0			43	33
12	7	C_{6v}	6	0	0	1	6	0	0	1		hexagonal pyramid	19	25

(a) The designations v_n refer to the numbers of vertices of degree n.
(b) The designations f_3, f_4, f_5, and f_6 refer to the numbers of faces which are triangles, quadrilaterals, pentagons, and hexagons, respectively.
(c) The dsd rigidity index is defined in the text.
(d) Distinctive features include special names for the polyhedra, the presence or absence of vertices (v_n) or edges ($e_m e_n$) of distinctive types, and/or self-duality (SD). The edge designation $e_m e_n$ refers to an edge connecting a vertex of degree m with one of degree n.
(e) F: number of the dual polyhedron in Table 1 of P.J. Federico, Geometriae Dedicata, 3, 469 (1981); BD: number of polyhedron in Figure 4 of D. Britton and J.D. Dunitz, Acta Cryst. A29, 362 (1973).

TABLE 3

PROPERTIES OF SELECTED POLYHEDRA HAVING FROM EIGHT TO TWELVE VERTICES

Polyhedron Name	Vertices	Edges	Faces	Symmetry	Vertex types				Face types			
					v_3	v_4	v_5	v_6	f_3	f_4	f_5	f_6
A) Selected Polyhedra with Eight Vertices												
Bisdisphenoid (D_{2d}-Dodecahedron)	8	18	12	D_{2d}	0	4	4	0	12	0	0	0
Hexagonal bipyramid	8	18	12	D_{6h}	0	6	0	2	12	0	0	0
sym-Tetracapped tetrahedron	8	18	12	T_d	4	0	0	4	12	0	0	0
4,4-Bicapped trigonal prism	8	17	12	C_{2v}	0	6	2	0	10	1	0	0
Square antiprism	8	16	10	D_{4d}	0	8	0	0	8	2	0	0
Cube	8	12	6	O_h	8	0	0	0	0	6	0	0
B) A Few Polyhedra having from Nine to Twelve Vertices												
4,4,4-Tricapped trigonal prism	9	21	14	D_{3h}	0	3	6	0	14	0	0	0
4-Capped square antiprism	9	20	13	C_{4v}	0	5	4	0	12	1	0	0
4,4-Bicapped square antiprism	10	24	16	D_{4d}	0	2	8	0	16	0	0	0
3,4,4,4-Tetracapped trigonal prism	10	24	16	C_{3v}	1	3	3	3	16	0	0	0
sym-Tetracapped octahedron	10	24	16	T_d	4	0	0	6	16	0	0	0

TABLE 3 (Continued)

Polyhedron Name	Vertices	Edges	Faces	Symmetry	Vertex types				Face types			
					v_3	v_4	v_5	v_6	f_3	f_4	f_5	f_6
Dual of square antiprism	10	16	8	D_{4d}	8	2	0	0	0	8	0	0
$B_{11}H_{11}^{2-}$ polyhedron[c]	11	27	18	D_{2v}	0	2	8	1	18	0	0	0
Pentacapped trigonal prism	11	27	18	D_{3h}	2	3	0	6	18	0	0	0
Icosahedron	12	30	20	I_h	0	0	5	0	20	0	0	0
Cuboctahedron	12	24	14	O_h	0	12	0	0	8	6	0	0

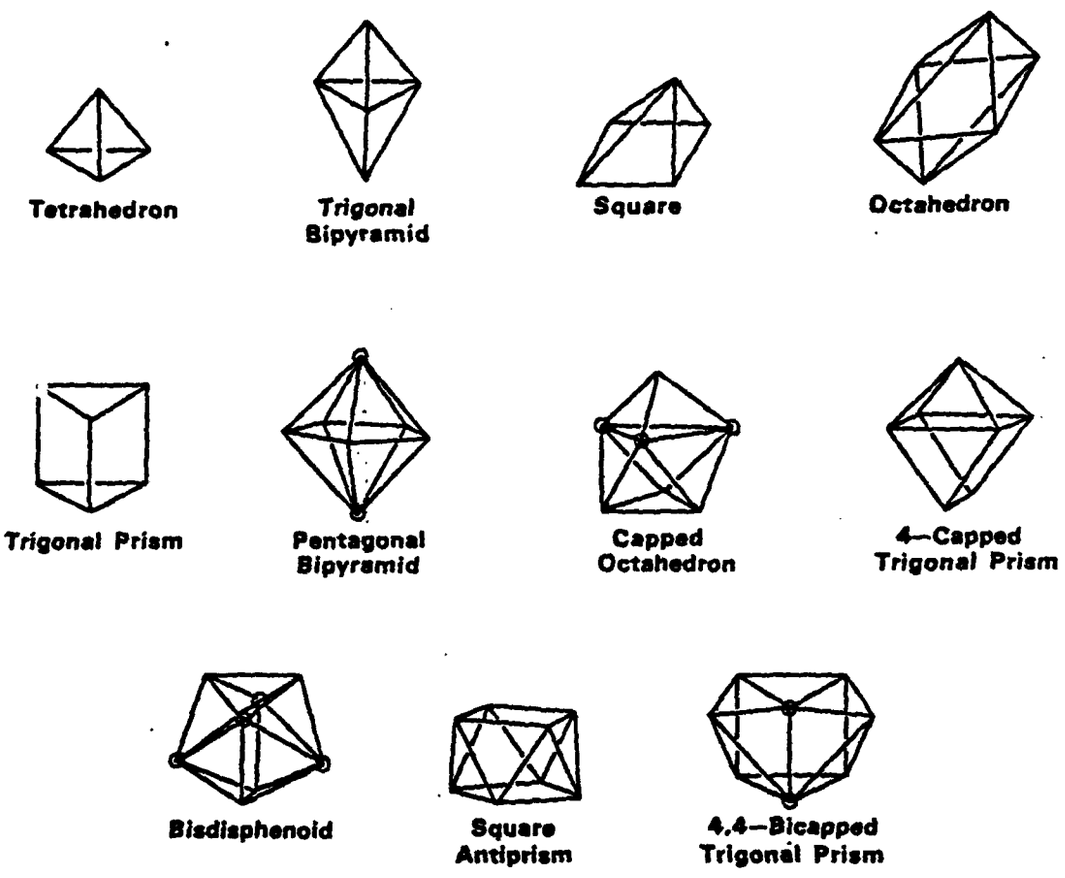


Figure 1: Some chemically significant polyhedra having from four to eight vertices. Degree five vertices are circled for clarity.

polyhedra for their coordination numbers. Interpretation of coordination number 7 can be based on three prototypical polyhedra, namely the pentagonal bipyramid, the capped octahedron, and the 4-capped trigonal prism. However, some of the lower symmetry polyhedra in Table 2 are also found [30]. The prevalent polyhedra for all of these coordination numbers are <u>deltahedra</u>, namely the tetrahedron, trigonal bipyramid, octahedron, pentagonal bipyramid, and capped octahedron for coordination numbers 4, 5, 6, 7, and 7, respectively. In most cases maximizing the number of polyhedral edges by having only triangular faces (i.e., the equality in equation 3), minimizes the Coulombic repulsion energies between ligands located at the vertices [26, 27, 30, 31].

In consideration of possible polyhedra for coordination number 8, many of the polyhedra of obviously high symmetry, notably the cube, are forbidden polyhedra (see above) and thus cannot be formed by sp^3d^4 hybrids. However, the two most prevalent polyhedra for coordination number 8, namely the square antiprism and the bisdisphenoid (<u>much</u> more often called the (D_{2d}) dodecahedron but this is very confusing because of the existence of the very different (I_h) regular (pentagonal) dodecahedron) can be derived from the cube from distortions which place the eight ligands at the vertices in positions accessible through sp^3d^4 hybrids but retaining the maximum symmetry consistent with this requirement. Distortion of a cube to a square antiprism simply involves a 45° twist of one face relative to the opposite face. Distortion of a cube to a bisdisphenoid involves squeezing along the six diagonals depicted in Figure 1. This method of depicting the topology of the bisdisphenoid, although not metrically accurate, often facilitates viewing important topological relationships in this chemically important polyhedron. In Figure 1 the four degree 5 vertices of the bisdisphenoid are circled in order to distinguish them clearly from the four degree 4 vertices.

3. POLYHEDRAL ISOMERIZATIONS

Consider an ML_n coordination compound having n ligands or a cluster compound having n vertices. There are a total of n! permutations of the sites occupied by these ligands or vertices. These permutations form a group of order n! called the <u>symmetric group</u> [32,33] and conventionally designated by S_n (although I have used P_n for the symmetric group in some of my papers in order to avoid confusion with improper rotations [34], also designated by S_n). The symmetric group S_n is the automorphism (symmetry) group of the <u>complete graph</u> K_n, which consists of n vertices with an edge between every pair of vertices for a total of n(n-1)/2 edges.

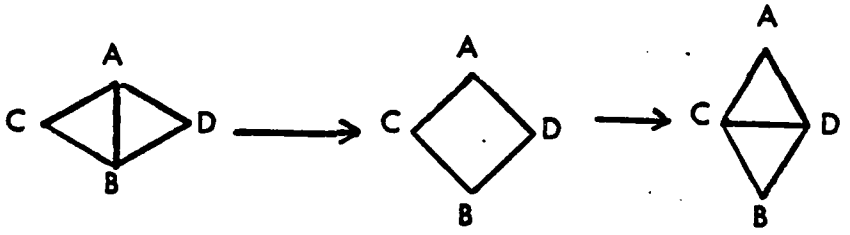
Now consider the symmetry point group G (or, more precisely, the framework group [35]) of the above ML_n coordination compound or n-vertex cluster compound. This group has $|G|$ operations of which $|R|$ are proper rotations [34]: $|G|/|R| = 2$ if the compound is achiral and $|G|/|R| = 1$ if the compound is chiral (i.e., has no improper rotations). The n! distinct permutations of the n sites

in the coordination compound or cluster are divided into n!/|R| right cosets [15] which represent the permutational isomers since the permutations corresponding to the |R| proper rotations of a given isomer do not change the isomer but merely rotate it in space. This leads naturally to the concept of isomer count, I, namely

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

Similarly the quotient $E = n!/|G| = 2I$ for a given chiral polyhedron corresponds to the number of enantiomeric pairs. The isomer count, I, indicates the complexity of macroscopic models for polyhedral isomerizations, such as topological representations discussed below.

Now let us consider some microscopic aspects of polyhedral isomerizations. As early as 1966 Lipscomb [36] 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:



(9)

9a **9b** **9c**

In this process a configuration such as **9a** 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, in structure **9a**, then the dsd type of the switching edge AB can be represented as ab(cd). In this designation the first two digits refer to the degrees of the vertices joined by AB and the two digits in parentheses refer to the degrees of the two vertices not joined by AB but contained in the faces (triangles) having AB as the common edge (i.e., C and D in structure **9a**). The quadrilateral face formed in structure **9b** can be called a pivot face.

In his pioneering paper Lipscomb [36] described some possible framework rearrangements of the polyhedra found in cage boranes and carboranes having from 5 to 12 vertex atoms. Fifteen years later [37] I reexamined this question in light of advances in known experimental information on polyhedral chemical systems as well as improved understanding in polyhedral topology. Subsequently [38] I developed a mathematical approach for examining all possible non-planar rearrangements of polyhedra having few (i.e., ≤ 6) vertices using a method developed by Gale [39] in 1956 for studying d-dimensional polytopes having only a few more than the minimum d+1 vertices. This work [38] confirmed the crucial role of dsd-processes conjectured so success-

fully by Lipscomb [36] and also provided insight for more detailed study of isomerizations of polyhedra having seven [40] and eight [41] vertices.

Consider a deltahedron with e edges. Such a deltahedron has e distinct dsd situations, one corresponding to each of the e edges acting as the switching edge. Applications of the dsd process at each of the dsd situations in a given deltahedron leads in each case to a new deltahedron. In most cases the new deltahedron is relatively unsymmetrical and also may have vertices of degree 3 leading to tetrahedral chambers which are unfavorable in polyhedral boranes [42]. However, in some cases the new deltahedron is identical to the original deltahedron. In these cases the switching edge can be said to be degenerate. A dsd process involving a degenerate switching edge represents a pathway for a degenerate polyhedral isomerization of the deltahedron. A deltahedron having one or more degenerate edges is inherently fluxional whereas a deltahedron without degenerate edges is inherently rigid.

The dsd type of a degenerate edge ab(cd) can be seen by application of the process 9a → 9b → 9c to satisfy the following conditions:

$$c = a-1 \text{ and } d = b-1 \text{ or } c = b-1 \text{ and } d = a-1 \qquad (10)$$

Using these conditions chemically significant deltahedra can be very easily checked for the presence of one or more degenerate edges with the following results:

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

(2) Trigonal Bipyramid: The three edges connecting pairs of equatorial vertices are degenerate edges of the type 44(33). A dsd process using one of these degenerate edges as the switching edge and involving a square pyramid intermediate corresponds to the Berry pseudorotation [28,29] which is believed to be the mechanism responsible for the stereochemical non-rigidity of trigonal bipyramidal complexes, even at relatively low temperatures [29,43].

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

(4) Pentagonal Bipyramid: The 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) will give a capped octahedron. The capped octahedron is a low energy polyhedron for ML_7 coordination complexes [30] but a forbidden polyhedron for boranes and carboranes because of its tetrahedral chamber [42]. This suggests that ML_7 complexes will be fluxional but that pentagonal bipyramidal boranes and carboranes will not be fluxional.

(5) Bisdisphenoid (Figure 1): The bisdisphenoid has four pairwise degenerate edges, which are those of the type 55(44) located in the subtetrahedron consisting of the degree 5 vertices of the bisdisphenoid (those circled in Figure 1). Thus two successive or more likely

concerted (parallel) dsd processes involving opposite 55(44) edges (i.e., a pair related by a C_2 symmetry operation) will convert one bisdisphenoid into another bisdisphenoid through a square antiprismatic intermediate. Thus a bisdisphenoid, like the trigonal bipyramid discussed above, is inherently fluxional.

(6) 4,4,4-Tricapped Trigonal Prism: The three edges of the type 55(44) corresponding to the "vertical" edges of the trigonal prism are degenerate. A dsd process using one of these degenerate edges as the switching edge involves a C_{4v} 4-capped square antiprism intermediate. Nine-vertex systems are therefore inherently fluxional.

(7) 4,4-Bicapped Square Antiprism: This polyhedron has no degenerate edges and is inherently rigid.

(8) The C_{2v}-$B_{11}H_{11}^{2-}$ Polyhedron: The four edges of the type 56(45) are degenerate. This eleven-vertex deltahedron is therefore inherently fluxional.

(9) Icosahedron: This highly symmetrical polyhedron, like the octahedron, has no degenerate edges and is therefore inherently rigid.

This simple analysis indicates that in deltahedral species 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 7-vertex deltahedra, namely the pentagonal bipyramid and the capped octahedron. This can be compared with experimental fluxionality observations by boron-11 NMR on the deltahedral borane anions $B_nH_n^{2-}$ ($6 \leq n \leq 12$) [37] where the 6, 7, 9, 10, and 12 vertex systems are found to be rigid and the 8 and 11 vertex systems are found to be fluxional. The only discrepancy between experiment and this very simple theory is the 9 vertex system.

Gimarc and Ott have done orbital symmetry analyses on dsd processes in the five-vertex trigonal bipyramidal carboranes [44] and the nine-vertex tricapped trigonal prismatic boranes and carboranes [45]. They find that the single dsd processes in both cases are blocked by crossings of filled and vacant molecular orbitals but that a double dsd process in the tricapped trigonal prism is orbital symmetry allowed. Their analysis applies to polyhedra of light atoms using only s and p valence orbitals such as boron or carbon. The symmetry forbidden nature of the single dsd process in the tricapped trigonal prism suggests an explanation for the experimentally observed rigidity of tricapped trigonal prismatic $B_9H_9^{2-}$ in contrast to the inherent fluxionality of this polyhedron (see above). The Gimarc-Ott analysis [44,45] cannot be extended directly to transition metal clusters involving d orbitals of the vertex atoms and is not applicable to coordination rather than cluster polyhedra.

4. TOPOLOGICAL REPRESENTATIONS OF POLYHEDRAL ISOMERIZATIONS

Topological representations are graphs representing the relationship between the different permutational isomers of a given polyhedron. 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 $I = n!/|R|$ (equation 8) [2]. The degree of a vertex corresponds to the number of new permutational isomers generated from the isomer represented by the vertex in a single step; this is called the connectivity.

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 (Figure 2). The two axial vertices correspond to the two tetrahedral isomers and the three equatorial vertices correspond to the three square planar isomers. The connectivities of the tetrahedral (δ_{tet}) and square planar (δ_{sq}) isomers are 3 and 2, respectively, in accord with the degrees of the corresponding vertices of the $K_{2,3}$ graph (Figure 2). Thus $I_{tet}\,\delta_{tet} = I_{sp}\,\delta_{sp} = 6$; this is an example of the closure condition $I_a\,\delta_a = I_b\,\delta_b$ required for a topological representation with vertices representing more than one type of polyhedron.

Some interesting graphs are found in the topological representations of the five-vertex trigonal bipyramidal systems. The trigonal bipyramid has an isomer count $I = 5!/|D_3| = 120/6 = 20$ corresponding to 10 enantiomeric pairs. A given trigonal bipyramidal isomer can be described by the labels of its two axial positions (i.e., the single pair of vertices not connected by an edge) with a bar used to distinguish enantiomers. In a single degenerate dsd isomerization of a trigonal bipyramid through a square pyramid intermediate, both axial vertices in the original trigonal bipyramid become equatorial vertices in the new trigonal bipyramid leading to a connectivity of three for dsd isomerizations of trigonal bipyramids. The corresponding topological representation thus is a 20 vertex graph in which each vertex has degree 3. However, additional properties of dsd isomerizations of trigonal bipyramids exclude the (pentagonal) I_h dodecahedron as a topological representation unless double group form is used to produce pseudohexagonal faces [2]. A graph suitable for the topological representation of dsd isomerizations of trigonal bipyramids is the Desargues-Levy graph, depicted in Figure 3 (top).

Less complicated but still useful topological representations can be obtained by using each vertex of the graph to represent a set of isomers provided that each vertex represents sets of the same size and interrelationship and each isomer is included in exactly one set. A simple example is the use of the Petersen's graph (Figure 3: bottom) as a topological representation of isomerizations of the 10 trigonal bipyramid enantiomer pairs ($E = 5!/|D_{3h}| = 120/12 = 10$) by dsd processes. The use of Petersen's graph for this purpose relates to its being the odd graph O_3 where an odd graph O_k is defined as follows [46]: its vertices correspond to subsets of cardinality k-1 of a set S of cardinality 2k-1 and two vertices are adjacent if and only if the corresponding subsets are disjoint.

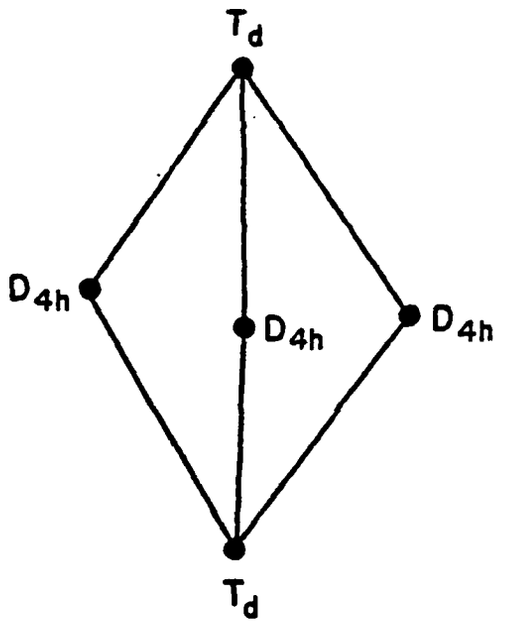


Figure 2: The $K_{2,3}$ bipartite graph as a topological representation of the degenerate planar isomerization of a tetrahedron (T_d) into its enantiomer through a square planar intermediate (D_{4h}).

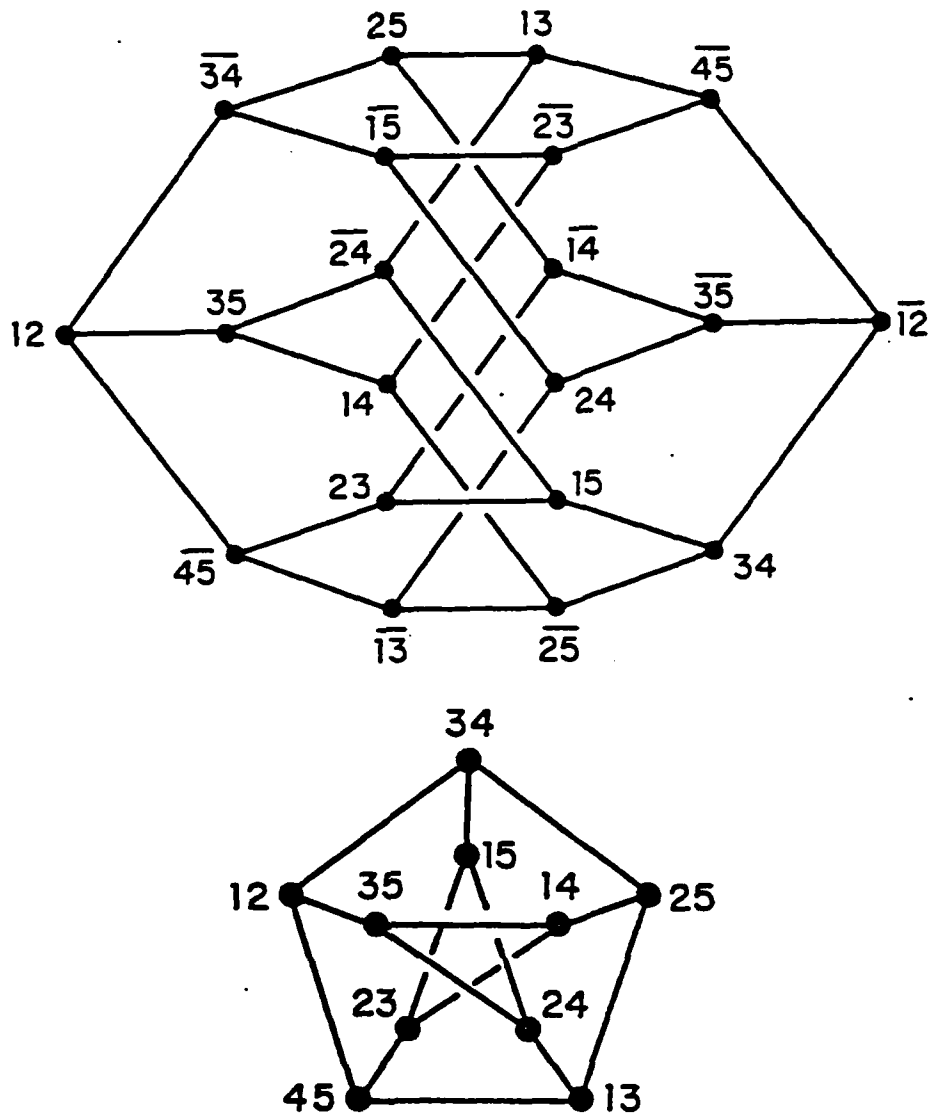


Figure 3: Topological representation of the isomerizations of trigonal pyramids through dsd processes (Berry pseudorotations). The two digits represent labels for the axial positions with a bar used to indicate an enantiomer. Top: Desargues-Levy graph as a topological representation for dsd isomerizations of the 20 trigonal bipyramid isomers. Bottom: The Petersen's graph as a topological representation for dsd isomerizations of the 10 enantiomer pairs of the trigonal bipyramid isomers.

Useful topological representations can also be obtained for six-vertex systems [4]. Here the process of interest is the degenerate triple dsd isomerization of the octahedron through a trigonal prismatic intermediate, which is the underlying topology of both Bailar [47] and Ray and Dutt [48] twists for octahedral M(bidentate)$_3$ chelates. The isomer counts are $I_{oct} = 6!/|O| = 720/24 = 30$ for the octahedron and $I_{tp} = 6!/|D_3| = 720/6 = 120$ for the trigonal prism. A pentagonal (I_h) dodecahedron in double group form can serve for the topological representation for this process [4]. The midpoints of the 30 edges are the 30 octahedron isomers. Line segments across a pentagonal face connecting these edge midpoints correspond to triple dsd isomerization processes; the midpoints of these lines correspond to the 120 trigonal prismatic isomers with 10 such isomers being located in each of the 12 faces of the pentagonal dodecahedron. Figure 4 depicts one of the 12 pentagonal faces of this double group pentagonal dodecahedral representation; the ten lines on this face representing isomerization processes form a K_5 graph. This system is closed since the connectivities of the octahedron (δ_{oct}) and trigonal prism (δ_{tp}) are 8 and 2, respectively, leading to the closure relationship $I_{oct}\ \delta_{oct} = I_{tp}\ \delta_{tp} = 240$.

Development of topological representations for systems having more than 6 vertices is complicated by intractably large isomer counts. Thus the isomer count of the seven-vertex polyhedron with the largest number of symmetry elements, namely the pentagonal bipyramid, is $7!/|D_5| = 5040/10 = 504$. Similarly the isomer counts of the cube, hexagonal bipyramid, square antiprism, and bisdisphenoid are 40320/24 = 1680, 40320/12 = 3360, 40320/8 = 5040, and 40320/4 = 10080, respectively. Graphs corresponding to topological representations of permutational isomerizations involving such large numbers of polyhedral isomers are clearly unwieldy and unmanageable.

The problem of representing permutational isomerizations in seven- and eight-vertex polyhedra can be simplified if subgroups of the symmetric groups S_n (n = 7, 8) can be found which contain all of the symmetries of all of the polyhedra of interest. However, this is <u>not</u> possible for the seven-vertex system since there is no subgroup of S_7 that contains both the five-fold symmetry of the pentagonal bipyramid and the three-fold symmetry of the capped octahedron. However, the situation with the eight-vertex system is more favorable since the wreath product group [49,50,51] $S_4[S_2]$ of order 384 contains all of the symmetries of the cube, hexagonal bipyramid, square antiprism, and bisdisphenoid [52], which are all of the eight-vertex polyhedra of actual or potential chemical interest. The major effect of reducing the symmetry by a factor of 105 (= 3 x 5 x 7) in going from S_8 to $S_4[S_2]$ is the deletion of five-fold and seven-fold symmetry elements. Such symmetry elements are not of interest in this context since none of the 257 eight-vertex polyhedra have five-fold symmetry elements [23,24] and the only eight-vertex polyhedron having a seven-fold symmetry element is the heptagonal pyramid, which is not of interest in this particular chemical context. Restricted isomer counts $I^* = 384/|R|$ based on subgroups of the wreath product group

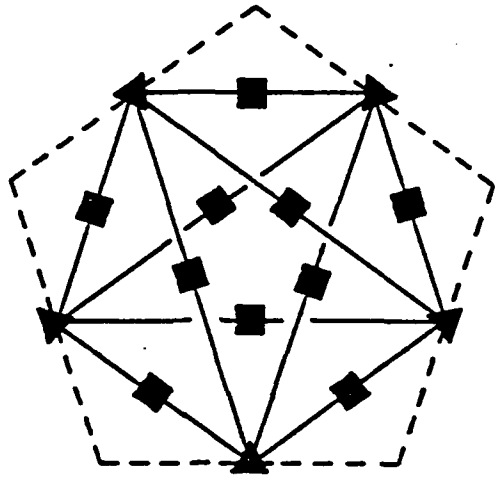


Figure 4: One of the twelve pentagonal faces of the I_h double group (pentagonal) dodecahedron used as a topological representation for the degenerate triple dsd isomerization of the octahedron (O_h) through a trigonal prismatic intermediate (D_{3h}). The five triangles at the midpoints of the sides of the face represent five of the 30 octahedron permutational isomers whereas the ten squares at the midpoints of the edges of the K_5 graph drawn on the face represent 10 of the 120 trigonal prism permutational isomers.

$S_4[S_2]$ rather than the symmetric group S_8 are the more manageable numbers 16, 32, 48, and 96 for the cube, hexagonal bipyramid, square antiprism, and bisdisphenoid, respectively.

The concept of restricting vertex permutations in eight-vertex systems to the wreath product group $S_4[S_2]$ rather than the fully symmetric S_8 group can be restated in graph-theoretical terms using the hyperoctahedral graph H_4 [46]. Therefore such a restriction of permutations from S_8 to $S_4[S_2]$ can be called a hyperoctahedral restriction. The hyperoctahedral graphs underlying this restriction are designated as H_n and have 2n vertices and 2n(n-1) edges with every vertex connected to all except one of the remaining vertices so that each vertex of H_n has degree 2(n-1). The name "hyperoctahedral" comes from the fact that an H_n graph is the 1-skeleton of the analogue of the octahedron (the "cross-polytope") in n-dimensional space [19]. The hyperoctahedral graphs H_2 and H_3 thus correspond to the square and octahedron, respectively. The $S_4[S_2]$ wreath product group is the automorphism (symmetry) group of the hyperoctahedral graph H_4 just as the S_8 symmetric group is the automorphism group of the complete graph K_8. Note that the hyperoctahedral graph H_4 is the 1-skeleton of the four-dimensional cross polytope, which is the dual of the tesseract, the four-dimensional analogue of the cube.

Using these ideas topological representations for isomerizations of eight-vertex polyhedra are depicted in Figures 5 and 6 [53]. Vertices and edge midpoints in these representations correspond to the $E^* = 384/|G|$ hyperoctahedrally restricted enantiomer pairs (E^* = 8, 16, 24, and 48 for the cube, hexagonal bipyramid, square antiprism, and bisdisphenoid, respectively) except because of the hyperoctahedral reduction in symmetry, the number of points for the square antiprism must be doubled [53]. Figure 5 is a $K_{4,4}$ bipartite graph in which the 8 cube enantiomer pairs are located at the centers of the hexagons and the 16 hexagonal bipyramid enantiomer pairs are located at the edge midpoints. Since both the cube and hexagonal bipyramid are forbidden polyhedra (i.e., cannot be formed using only s, p, and d orbitals [25]), this portion of the topological representation for hyperoctahedrally restricted eight-vertex systems 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 Figure 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 double dsd processes interconverting the bisdisphenoids located at the midpoints of two joined hexagonal edges meeting at a vertex through the square antiprism intermediate represented by the vertex joining the edges. Since both the bisdisphenoid and square antiprism can be formed using only s, p, and d orbitals, the circumference of the hexagon is accessible in ML_8 systems where M has the usual sp^3d^5 orbital manifold. Thus in the usual situation

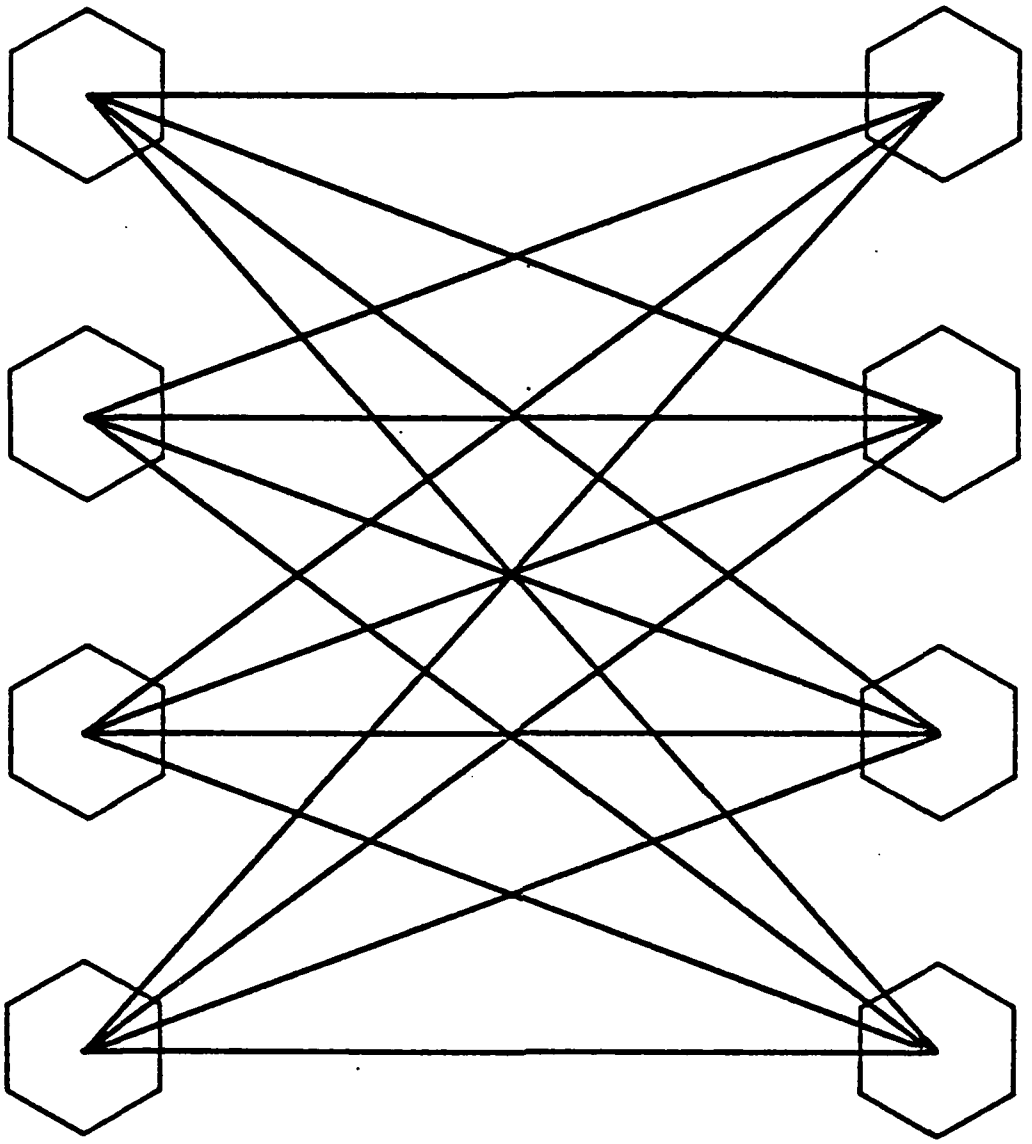


Figure 5: The $K_{4,4}$ bipartite graph topological representation of the hyperoctahedrally restricted permutational isomerizations involving the cube, hexagonal bipyramid, square antiprism, and bisdisphenoid. The hexagons represent the eight cube hyperoctahedrally restricted enantiomeric pairs; the 16 edges connecting the hexagons (i.e., the midpoints of the edges of the $K_{4,4}$ bipartite graph) represent the 16 hexagonal bipyramid hyperoctahedrally restricted enantiomeric pairs; the 48 vertices of the eight hexagons represent 48 isomeric square antiprisms, and the midpoints of the 48 edges of the eight hexagons represent the 48 bisdisphenoid hyperoctahedrally restricted enantiomeric pairs.

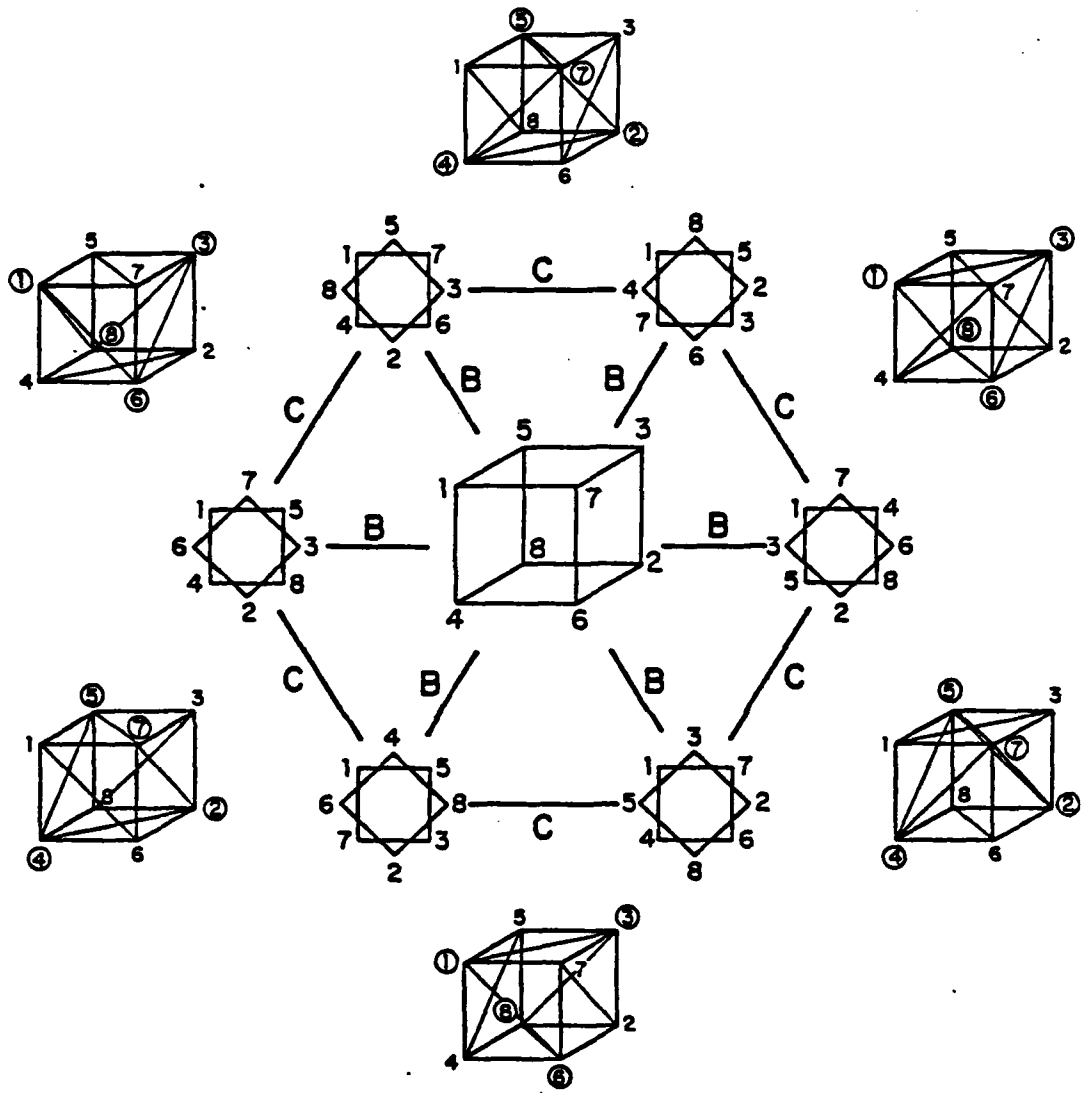


Figure 6: Details of the hexagon in the topological representation in Figure 5. The spokes B represent quadruple dsd square antiprism-cube-square antiprism isomerizations and the edges C represent double dsd bisdisphenoid-square antiprism-bisdisphenoid with a cube in the center of the hexagon, six isomeric square antiprisms at the vertices of the hexagon, and six isomeric bisdisphenoids at the midpoints of the edges of the hexagon.

not involving f orbitals, isomerizations are restricted to the circumference of a given hexagon in Figure 5 and cannot occur from one hexagon to another.

5. GALE TRANSFORMATIONS AND GALE DIAGRAMS

Consider a polytope P in d-dimensional space R^d. The minimum number of vertices of such a polyhedron is d + 1 and there is only one such polyhedron, namely the d-simplex [19]. The combinatorially distinct possibilities for polytopes having only d + 2 and d + 3 vertices (polyhedra with "few" vertices) are also rather limited and through a Gale transformation [54] can be represented faithfully in a space of less than d dimensions. More specifically, if P is a d-dimensional polytope with v vertices, a Gale transformation leads to a Gale diagram of P consisting of v points in v-d-1 dimensional space R^{v-d-1} in one-to-one correspondence with the vertices of P [54]. From the Gale diagram it is possible to determine all of the combinatorial properties of P such as the subsets of the vertices of P that define faces of P, the combinatorial types of these faces, etc. Of particular significance in the present context is the fact that the combinatorial properties of a polytope P which can be determined by the Gale diagram include all possible isomerizations (rearrangements) of P to other polytopes having the same number of vertices and imbedded 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 $v \leq 2d$), then the dimension of the Gale diagram is smaller than that of the original polytope P.

Now consider polyhedra in the ordinary three-dimensional space of interest in chemical structures (i.e., d = 3). Gale diagrams of five- and six-vertex polyhedra can be imbedded into one- and two-dimensional space, respectively, thereby simplifying analysis of their possible vertex motions leading to non-planar polyhedral isomerizations of these polyhedra of possible interest in a chemical context.

In order to obtain a Gale diagram for a given polyhedron, the polyhedron is first subjected to a Gale transformation. Consider a polyhedron with v vertices as a set of v points $X_1, \ldots, X_v$ in three-dimensional space R^3. These points may be regarded as three-dimensional vectors $X_n = (x_{n,1}, x_{n,2}, x_{n,3})$, $1 \leq n \leq v$, from the origin to the vertices of the polyhedron. In addition consider a set of points D(A) in v-dimensional space R^v, $A = (a_1, \ldots, a_v)$ such that the following sums vanish:

$$\sum_{i=1}^{v} a_i x_{i,k} = 0 \text{ for } 1 \leq k \leq 3 \tag{11a}$$

$$\sum_{i=1}^{v} a_i = 0 \tag{11b}$$

Equation 11a may also be viewed as three orthogonality relationships

between the v-dimensional vector $A = (a_1, \ldots, a_v)$ and the three v-dimensional vectors $(x_{1,k}, x_{2,k}, \ldots, x_{v,k})$, $1 \leq k \leq 3$. Now consider the locations of the vertices of the polyhedron as the following v x 4 matrix:

$$D_0 = \begin{pmatrix} x_{1,1} & x_{1,2} & x_{1,3} & 1 \\ x_{2,1} & x_{2,2} & x_{2,3} & 1 \\ \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \\ x_{v,1} & x_{v,2} & x_{v,3} & 1 \end{pmatrix} \tag{12}$$

Consider the columns of D_0 as vectors in R^v. Since D_0 has rank 4 the 4 columns of D_0 are linearly independent. Hence the subspace $M(X)$ of R^v represented by these four linearly independent columns has dimension 4. Its orthogonal complement $M(A)^{\perp} = \{A \in R^v \mid A \cdot X = 0 \text{ for all } X \in M(X)\}$ coincides with $D(A)$ defined above by equations 11a and 11b. Therefore:

$$\dim D(A) = \dim M(A)^{\perp} = v - \dim M(X) = v-4 \tag{13}$$

Now define the following v x (v-4) matrix:

$$D_1 = \begin{pmatrix} a_{1,1} & a_{1,2} \cdots a_{1,v-4} \\ a_{2,1} & a_{2,2} \cdots a_{2,v-4} \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ a_{v,1} & a_{v,2} & a_{v,v-4} \end{pmatrix} \tag{14}$$

The v rows of D_1 may be considered as vectors in v-4 dimensional space; conventionally the jth row is denoted by $\bar{x}_j = (a_{i,1}, a_{j,2}, \ldots, a_{j,v-4})$ for $j = 1, \ldots, v$.

The final result of this construction is the assignment of a point $\bar{x}_j$ in v-4 dimensional space (R^{v-4}) to each vertex x_j of the polyhedron. The collection of v points $\bar{x}_1, \ldots, \bar{x}_v$ in R^{v-4} is called a Gale transform of the set of vertices $x_1, \ldots, x_v$ of the polyhedron in question. The following features of a Gale transform of a polyhedron should be noted:

(1) Gale transforms $\bar{x}_j$ and $\bar{x}_k$ of two or more vertices of a polyhedron may lead to the same point (i.e., the same v-4 coordinates) in v-4 dimensional space (R^{v-4}). In other words some points of a Gale transform may have a multiplicity greater than one so that the Gale transform of a polyhedron in such cases contains fewer distinct points than the polyhedron has vertices.

(2) The Gale transform depends upon the location of the origin in

the coordinate system. Therefore, infinitely many Gale transforms are possible for a given polyhedron. Geometrically a Gale transform of a polyhedron corresponds to a projection of the v vertices of a v-1 dimensional simplex into a v-4 dimensional hyperplane [54,55]. Since infinitely many such projections are possible, the Gale transform for a given polyhedron is not unique.

In practice, it is easier to work with Gale diagrams corresponding to Gale transforms of interest. Consider a Gale transform of a polyhedron having v vertices $\bar{x}_1, \ldots, \bar{x}_v$ as defined above. The corresponding Gale diagram $\hat{x}_1, \ldots, \hat{x}_v$ is defined by the following relationships

$$\hat{x}_i = 0 \text{ if } \bar{x}_i = 0 \tag{15a}$$

$$\hat{x}_i = \bar{x}_i / \| \bar{x}_i \| \quad \text{if } \bar{x}_i \neq 0 \tag{15b}$$

In equation 15b $\| \bar{x}_i \|$ is the length of the vector $\bar{x}_i$ (i.e., $\sqrt{a_{i,1}^2 + a_{i,2}^2 + \ldots + a_{i,v-4}^2}$). If v-4 = 1 (i.e., v = 5), Gale diagrams can only contain the points of the straight line 0,1, and -1 of varying multiplicities m_0, m_1, and m_{-1}, respectively, where $m_0 \geq 0$, $m_1 \geq 2$, and $m_{-1} \geq 2$. If v-4 = 2 (i.e., v = 6) Gale diagrams can only contain the center and circumference of the unit circle. These two types of Gale diagrams (Figure 7) are of interest for the study of polyhedral isomerizations since they represent significant structural simplifications of the corresponding polyhedra.

The following properties of Gale diagrams are of interest since they impose important restrictions on configurations of points which can be Gale diagrams:

(1) A v-5 dimensional plane or hyperplane passing through the central point of the Gale diagram bisects the space of the Gale diagram into two halfspaces. Each such halfspace must contain at least two vertices (or one vertex of multiplicity 2) of the Gale diagram not including any vertices actually in the bisecting plane or hyperplane. Such a halfspace is called an open halfspace. Violation of this condition corresponds to a polyhedron with the impossible property of at least one pair of vertices not connected by an edge which is closer in three-dimensional space than another pair of vertices which is connected by an edge.

(2) The set of vertices of a polyhedron not forming a given face or edge of the polyhedron is called a coface of the polyhedron. The regular octahedron is unusual since all of its faces are also cofaces corresponding to other faces. The interior of the figure formed by connecting the vertices of a Gale diagram corresponding to a coface must contain the central point.

(3) The central point is a vertex of a Gale diagram if and only if the corresponding polyhedron is a pyramid. The central vertex of such a Gale diagram corresponds to the apex of a 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 Figure 7. In this context an allowed vertex motion of a Gale

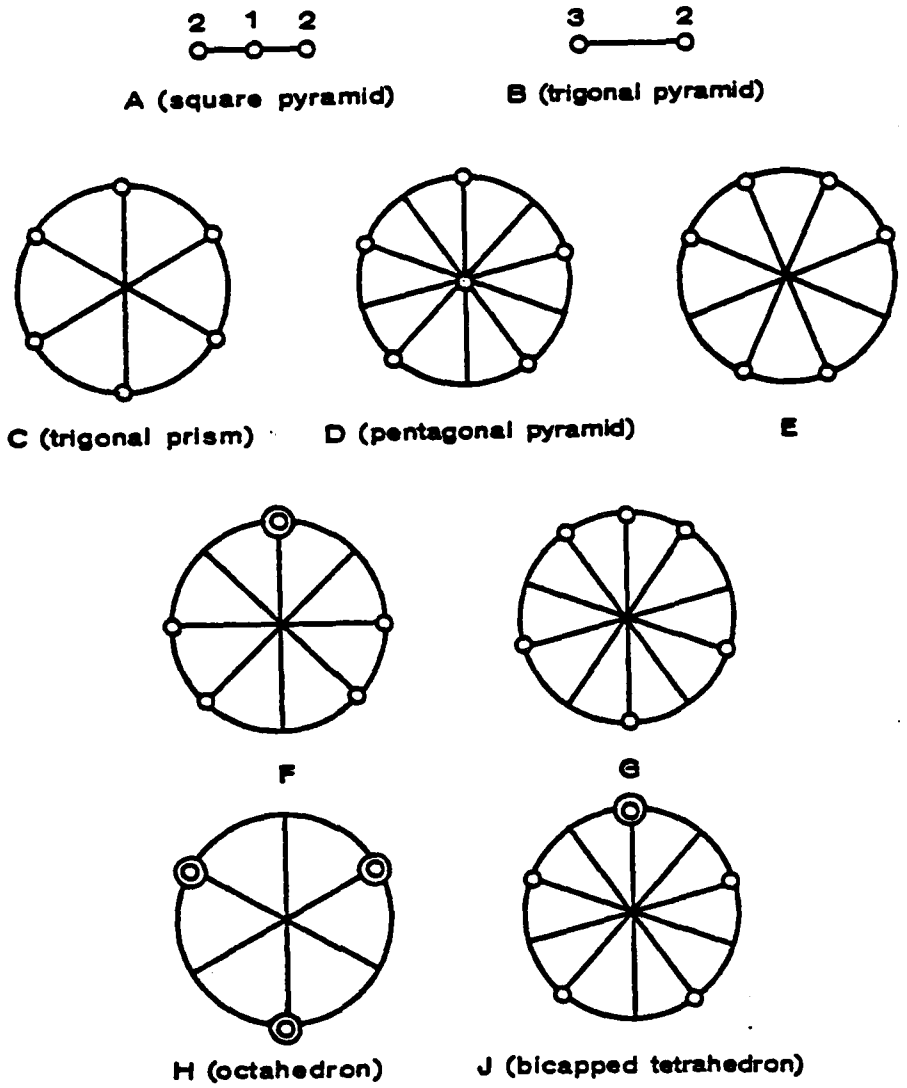


Figure 7: Gale diagrams for the two combinatorially distinct five-vertex polyhedra and the seven combinatorially distinct six-vertex polyhedra. The properties of these polyhedra are listed in Table 1. In the six-vertex Gale diagrams vertices of multiplicity 1 are represented by a single circle and vertices of multiplicity 2 are represented by a double circle.

diagram 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 polyhedra are combinatorially equivalent if and only if their Gale diagrams are isomorphic [54], such allowed vertex motions of Gale diagrams are faithful representations of all possible non-planar polyhedral isomerizations.

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 possible five-vertex polyhedra are the square pyramid and trigonal bipyramid. Their Gale diagrams (A and B, respectively, in Figure 7) are the only two possible one-dimensional five-vertex Gale diagrams which have the required two vertices in each open halfspace (i.e., $m_1 \geq 2$ and $m_{-1} \geq 2$). The only allowed vertex motion in a Gale diagram of a trigonal bipyramid involves motion of one point from the vertex of multiplicity 3 through the center point to the vertex originally of multiplicity 2 (Figure 8, top). 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 non-planar degenerate isomerization of a trigonal bipyramid. This, of course, is the Berry pseudorotation process which is the prototypical dsd process as discussed above. The choice of three points to move away from the vertex of multiplicity 3 in the Gale diagram of a trigonal bipyramid corresponds to the presence of three degenerate edges in a trigonal bipyramid (see above). This analysis of the Gale diagrams of the two possible five-vertex polyhedra shows clearly that the only possible non-planar isomerizations of five-vertex polyhedra can be represented as successive dsd processes corresponding to successive Berry pseudorotations.

Gale diagrams are also useful for the study of isomerizations of six-vertex polyhedra [38]. In this case there are seven combinatorially distinct six-vertex polyhedra (Table 1). The corresponding Gale diagrams are derived from two-dimensional ($v-4 = 6-4 = 2$) Gale transforms and thus have vertices on the circumference of the unit circle. In addition, the center of the circle is a vertex of the Gale diagram for the pentagonal pyramid. The maximum multiplicity of a vertex in the Gale diagram of a six-vertex polyhedron is 2 since otherwise there would be open halfspaces containing only one point (i.e., one of the open semicircles obtained by bisecting the unit circle using the diameter containing the vertex of multiplicity $\geq$ 3).

The Gale diagrams of six-vertex polyhedra can be visualized most clearly if all of the diameters containing vertices are drawn as in Figure 7. Such Gale diagrams are called standard Gale diagrams [54]. Some standard Gale diagrams have diameters with vertices of unit multiplicity at <u>each</u> end. The two vertices of such a <u>balanced</u> diameter [38] form an edge which is a coface corresponding to a quadri-

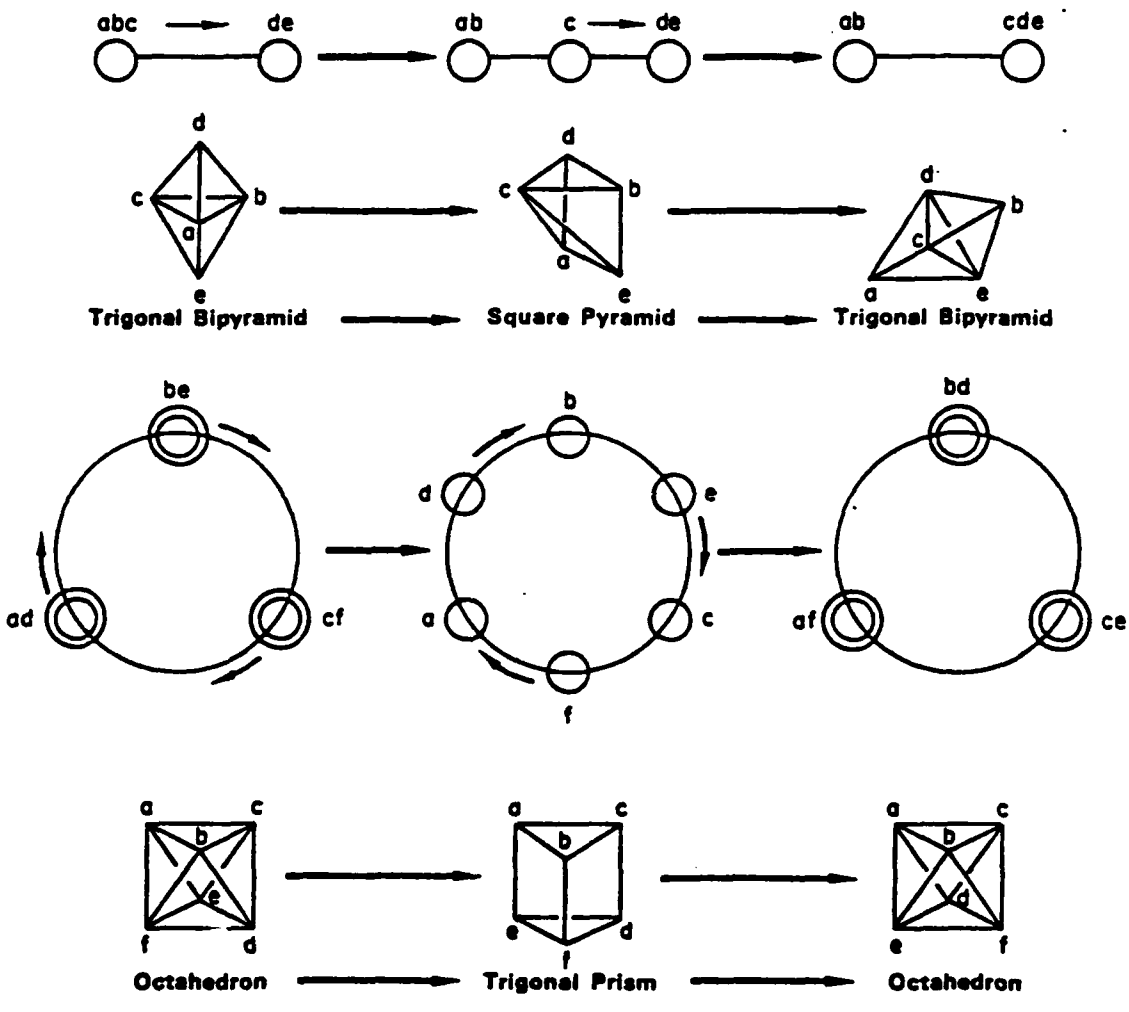


Figure 8: Examples of the use of Gale diagrams to depict polyhedral isomerizations. Top: the single dsd degenerate isomerization of a trigonal bipyramid through a square pyramid intermediate (Berry pseudorotation); bottom: the triple dsd degenerate isomerization of an octahedron through a trigonal prism intermediate (Bailar twist). Vertices are labeled with lower case letters and the motions in the Gale diagrams are indicated by arrows.

lateral face of the polyhedron. Therefore, the number of balanced diameters in a Gale diagram of a six vertex polyhedron is equal to the number of quadrilateral faces of the polyhedron.

Polyhedral isomerizations in six-vertex polyhedra may be represented by allowed motions of the vertices of their Gale diagrams along the circumference of the unit circle or through the center in the case of polyhedral isomerizations involving a pentagonal pyramid intermediate (not pentagonal bipyramid as erroneously stated in my earlier paper [38]). However, vertex motions are not allowed if at any time they generate one or more forbidden diameters containing three (or more) vertices.

Using these techniques all non-planar degenerate isomerizations involving six-vertex polyhedra can be decomposed into sequences of the eight fundamental processes listed in Table 4. The following aspects of these processes are of particular interest:

(1) The triple dsd process interconverting octahedra through a trigonal prismatic intermediate (H → C → H) and represented by the sequence of Gale diagrams in Figure 8 in which the vertices of the polyhedra are labeled for clarity appears in a chemical context as the Bailar twist [47] and the Ray and Dutt twist [48] for six-coordinate chelates of the type M(bidentate)$_3$. Both of these processes involve the same type of rearrangement of the polyhedral vertices but have different types of edges in the trigonal prismatic intermediate bridged by the bidentate ligand.

(2) The only possible single true dsd degenerate isomerization in six vertex deltahedra (J → G → J) involves the bicapped tetrahedron (J) such as is found in $Os_6(CO)_{18}$ [56].

(3) Two of the eight fundamental six-vertex degenerate isomerization processes (J → D → J and G → D → G) involve a pentagonal pyramidal intermediate (D). Processes involving an f_n face ($n \geq 4$) as a pivot face in the intermediate polyhedron (i.e., the face across which edges are broken and made) may be called an n-pyramidal process since the simplest examples involve an n-gonal pyramid intermediate. Using this terminology the dsd process can be called a 4-pyramidal process since its simplest example involves the degenerate isomerization of a trigonal bipyramid through a square pyramid intermediate. Thus in theory each new number of vertices v can introduce a new (v-1)-pyramidal process. However, these processes rapidly become increasingly unfavorable in ML_n complexes as the number of vertices in the pivot face increases owing to the general unfavorability of large numbers of coplanar ligands L. The resulting assumption that 4-pyramidal processes (i.e., dsd processes) are more favorable than any higher n-pyramidal process ($n \geq 5$) can be used to reduce the numbers of possible isomerization processes in seven-vertex and certain subsets of eight-vertex polyhedra to more manageable amounts (see the next section).

TABLE 4

THE EIGHT FUNDAMENTAL DEGENERATE NONPLANAR ISOMERIZATION PROCESSES OF SIX-VERTEX POLYHEDRA

Process[a]	Process Type[b]
H→C→H	3 dsd (Bailar and Ray and Dutt twists)
J→G→J	dsd'
J→D→J	5-pyramidal
G→E→G	dsd'
G→D→G	5-pyramidal
F→H→F	sds
F→E→F	dsd'
E→C→E	dsd or dsd'

(a) The polyhedra are designated by letters used in Figure 7.

(b) The dsd' and sds processes are minor variations on the dsd process discussed in the text. For a more detailed discussion of these rather subtle points see R.B. King, Theor. Chim. Acta, 64, 439 (1984).

6. SEVEN- AND EIGHT-VERTEX POLYHEDRA

In the study of isomerizations in seven-vertex polyhedra Gale transformations offer no advantage since they no longer provide dimensionality reduction. Thus for $v = 7$, the dimensionality of the Gale transform is $v-4 = 7-4 = 3$. Instead, an effective approach has been to consider first the intermediate polyhedra P_2 in isomerizations of the types $P_1 \rightarrow P_2 \rightarrow P_3$ in which P_1 and P_3 have the same number of edges and P_2 has one less edge than P_1 and P_3 [40]. Such P_2 polyhedra must necessarily have at least one non-triangular face and can conveniently be called non-deltahedra. The five seven-vertex deltahedra (Table 2) thus cannot be intermediate polyhedra P_2 in such polyhedral isomerizations. This reduces the number of possible sevenvertex intermediate polyhedra to 29 seven-vertex non-deltahedra. Furthermore, one of these non-deltahedra, namely the hexagonal pyramid, can be the intermediate polyhedron only in energetically unfavorable 6-pyramidal processes. For the remaining 28 seven-vertex non-deltahedra, it is feasible to draw diagonals across the non-triangular faces in all possible ways, thereby generating all possible transformations $P_1 \rightarrow P_2$ and $P_2 \rightarrow P_3$ involving the non-deltahedron in question as P_2; drawing diagonals in this manner can be called <u>diagonalization</u>. Using this approach a non-deltahedron P_2 can be the intermediate polyhedron in a degenerate polyhedral isomerization $P_1 \rightarrow P_2 \rightarrow P_3$ if and only if two or more different ways of diagonalizing a non-triangular face of P_2 lead to the same polyhedron corresponding to P_1 in one case and P_3 in the other case. If the non-triangular face of P_2 being diagonalized is quadrilateral, such an isomerization is a single dsd process. Such <u>degenerate</u> isomerization processes are not particularly common especially for intermediate polyhedra P_2 having only one quadrilateral face. Thus only one of the five seven-vertex deltahedra, namely the one of lowest symmetry (C_2), can undergo degenerate isomerization through a single dsd process. The other seven-vertex deltahedra require multiple dsd processes or energetically relatively unfavorable 5-pyramidal or 6-pyramidal processes for their degenerate polyhedral isomerizations.

These considerations allow the definition of a <u>dsd rigidity index</u> of a polyhedron P_1 as the number of edges that must be removed from P_1 in a dsd manner (i.e., converting two triangular faces sharing an edge into a single quadrilateral face) in order to give an intermediate polyhedron P_2, which upon adding back the same number of edges in a different way gives a polyhedron P_3 combinatorially equivalent to P_1, namely $P_1 \rightarrow P_2 \rightarrow P_3$ is a degenerate isomerization involving only dsd processes. Table 2 listing the 34 seven-vertex polyhedra included their dsd rigidity indices. Four of the five seven-vertex deltahedra have a dsd rigidity index of 2 which means that a degenerate isomerization must involve loss of two edges to give an intermediate polyhedron having two quadrilateral faces. The most chemically interesting such processes are the degenerate double dsd isomerizations of the pentagonal bipyramid and the capped octahedron through 4-capped trigonal prismatic intermediates since all three of these polyhedra

(Figure 1) are of chemical significance [30]. Four of the 28 seven-vertex polyhedra having only triangular and quadrilateral faces cannot undergo degenerate isomerizations involving only dsd (4-pyramidal) processes and therefore have a dsd rigidity index of zero. The degenerate isomerizations of such polyhedra must involve less energetically favorable n-pyramidal ($n \geq 5$) processes. None of the seven-vertex polyhedra having a dsd rigidity index of zero has been found to be chemically significant.

Some additional considerations become necessary for the study of isomerizations in eight-vertex polyhedra because of the large number of possible polyhedra. Thus there are 257 combinatorically distinct eight-vertex polyhedra [23,24] of which 14 are deltahedra. However, of these deltahedra only the bisdisphenoid and hexagonal bipyramid lack tetrahedral chambers and the hexagonal bipyramid is one of the forbidden polyhedra discussed above which cannot be formed using only s, p, and d orbitals. Thus the special role of the bisdisphenoid among eight-vertex polyhedra is readily apparent.

In order to make tractable the study of isomerizations of the large numbers of eight-vertex polyhedra the following assumptions were introduced [41]:

(1) Only dsd processes (i.e., 4-pyramidal rather than n-pyramidal, $n \geq 5$, processes) were considered for energetic reasons discussed above.

(2) Only symmetrical parallel multiple dsd processes were considered. In a symmetrical multiple dsd process, the quadrilateral pivot faces are equivalent because of the symmetry of the intermediate polyhedron.

(3) Only such dsd processes in the 14 combinatorially distinct deltahedra were considered since minimum energy coordination polyhedra are expected to be deltahedra or polyhedra such as the square antiprism which are derived from deltahedra through low energy processes.

This study revealed the unusual property of the bisdisphenoid in undergoing degenerate single, double, and quadruple dsd processes as depicted in Figure 9. Note also in Figure 9 the two distinct ways of depicting a bisdisphenoid topologically as a cube plus six diagonals which may be called the tetrahedral and rectangular presentations according to the orientation of the four degree 5 vertices (circled in Figure 9) on the underlying cube. In Figure 9 presentations are selected for the bisdisphenoid so that the pivot face(s) for the isomerizations are faces of the underlying cube. The tetrahedral presentation of the bisdisphenoid involves less distortion than the rectangular presentation. Therefore isomerizations in which the bisdisphenoid can be depicted in the tetrahedral presentation on an underlying cube having one or more of its faces as pivot faces are probably more favorable than those requiring rectangular presentations. This suggests that the double dsd isomerizations of the cube involving a square antiprism intermediate (Figure 9 middle) should be the most favorable of the three processes in Figure 9. This is consistent with the observation that next to the bisdisphenoid the square antiprism is the most prevalent eight-vertex coordination polyhedron [57].

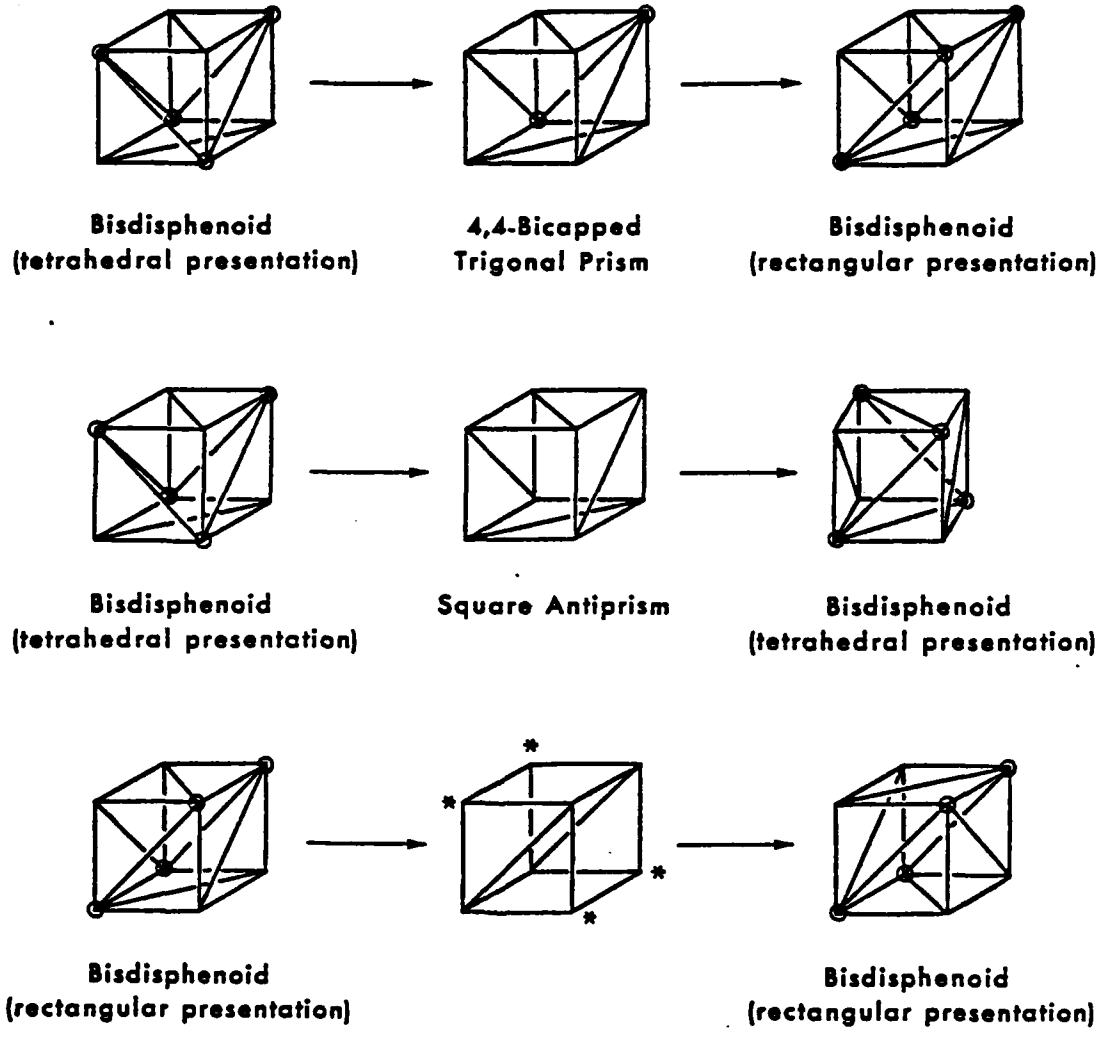


Figure 9: Degenerate dsd isomerizations of the bisdisphenoid. Top: a single dsd isomerization involving a 4,4-bicapped trigonal prism intermediate; middle: a double dsd isomerization involving a square antiprism intermediate; bottom: a quadruple dsd isomerization involving an intermediate polyhedron with four triangular and four rectangular faces. For clarity degree 5 vertices are circled and degree 3 vertices are starred.

7. ACKNOWLEDGMENT

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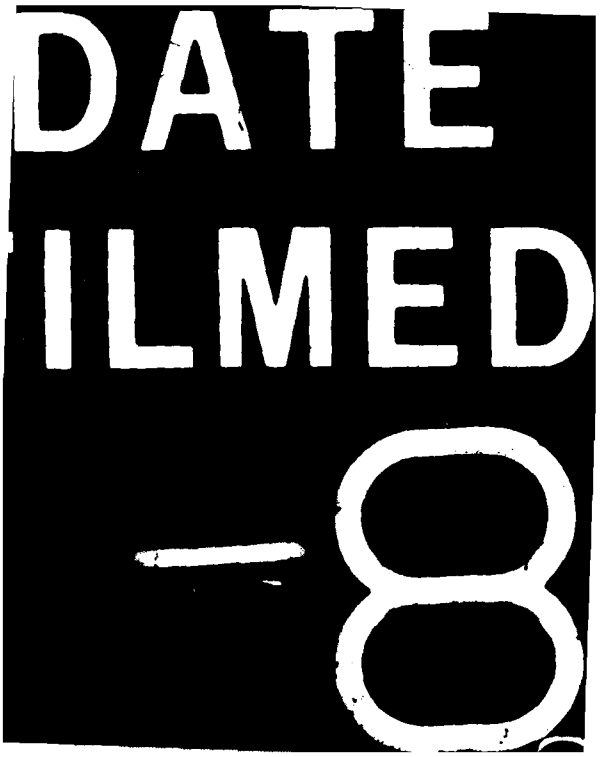
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