CHEMICAL APPLICATIONS OF TOPOLOGY AND GROUP THEORY. XXIV: CHIRALIZATION OF CHEMICALLY SIGNIFICANT POLYHEDRA [1]

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Abstract

Permutation group-theoretical methods are used to study the chiralization of achiral polyhedral skeletons with v vertices by successive ligand replacement. Starting from the fully symmetrical ligand partition (v), such chiralization processes may be characterized either by the minimum number of ligand replacement steps m, or the minimum number of different kinds of ligands i, required to destroy all improper rotations. These parameters are trivially related to the lowest degree chiral ligand partition(s) as determined by the subduction of the skeleton point group G into the corresponding symmetric group S_v by the procedure of Ruch and Schönhofer. Two different chiralization pathways with different values of m and i are found for the octahedron, cube, hexagonal bipyramid, and icosahedron. Many less symmetrical chemically significant polyhedra have the degree 2 ligand partition $(v-2, 2)$ as the lowest degree chiral ligand partition and thus have only one chiralization pathway. Such polyhedra include the bicapped tetrahedron, trigonal prism, capped octahedron, bisdisphenoid, square antiprism, 4,4,4-tricapped trigonal prism, 4-capped square antiprism, 4,4-bicapped square antiprism, and the cuboctahedron.

1. Introduction

Consider an achiral polyhedral skeleton having identical achiral ligands at each of its v vertices. The successive replacement of these ligands L_1 by other achiral ligands $L_2, \ldots, L_{v-1}$ different from L_1 will at some point destroy all improper rotation symmetry elements (including reflection planes and the inversion center, if present), leading to a chiral system. Such a process can be called the *chiralization* of the achiral polyhedral skeleton. Sokolov [2] has shown that the chiralization of polyhedra can be defined in two different ways, namely by the minimum number of ligand replacement steps m, or the minimum number of different kinds of ligands i, required to destroy all improper rotations. The values of m and i as well as v are definite characteristics of the polyhedron in question although, as noted below, some polyhedra may have more than one chiralization pathway.

This paper develops these ideas of Sokolov in terms of the chirality algebra pioneered by Ruch and Schönhofer [3–5], reviewed by Mead [6], and discussed in three previous papers of this series [7–9]. The chiralization parameters m and i are simply related to the Young diagrams corresponding to the most symmetrical chiral ligand partitions by the Ruch–Schönhofer partial ordering [4,6]. In addition, this paper develops the concept of multiple chiralization pathways and extends the concept of chiralization to a wider range of chemically significant polyhedra than those treated by Sokolov [2].

2. Background

Consider the full symmetric group P_n containing $n!$ elements. This group contains exactly one conjugacy class and hence one irreducible representation [10] for each possible set of positive integers $m_1, m_2, \ldots, m_k$ whose sum $\Sigma_{i=1}^{i=k} m_i = n$. Such a set of positive integers is called a partition of n. A given partition of n can be depicted by n boxes arranged so that the successive rows contain $m_1, m_2, \ldots, m_k$ boxes, where $m_i \geqslant m_{i+1}$. Such an arrangement of boxes is called a Young diagram [10]. A Young diagram is drawn so that the top row is the longest row and the left column is the longest column.

Chirality algebra uses Young diagrams to represent ligand partitions where the rows correspond to identical ligands. Ligand partitions can also be represented by symbols of the type $(a_1^{b_1} a_2^{b_2} \ldots a_p^{b_p})$, where a_i and b_i are small integers and $a_m > a_{m+1}$ $(1 \leqslant m \leqslant p)$ [7]. In this symbol for a ligand partition there are b_i sets of a_i identical ligands. In the description of ligand partitions by Young diagrams, the following three parameters can be used to classify the Young diagrams.

(1) Order (o): This represents the maximum number of identical ligands in the ligand partition and is simply the length of the top row.

(2) Index (i): This represents the number of different ligands in the ligand partition and is simply the length of the left column.

(3) Degree (g): This provides a basis for ordering Young diagrams (the Ruch–Schönhofer partial ordering) and represents the minimum degree of the corresponding ligand-specific chirality polynomial [4,6,7]. The degree of a Young diagram can be calculated by the following equation:

$$g = \tfrac{1}{2} \sum_{k=1}^{k=\text{order}} c_k(c_k - 1). \qquad (1)$$

In eq. (1), c_k represents the length of column k.

The Ruch–Schönhofer partial ordering of Young diagrams can also be described in terms of the so-called *transfer condition* [6]. In such terms, a Young diagram $Y^{(p)}$

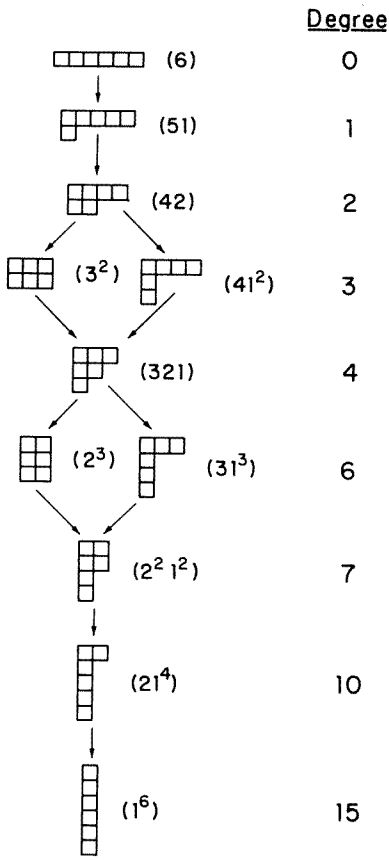

Fig. 1. Lattice of Young diagrams and ligand partitions for six ligand sites.

smaller than a given Young diagram $Y^{(r)}$ (i.e. of lower symmetry by the Ruch–Schönhofer partial ordering) can always be obtained from $Y^{(r)}$ by moving boxes downward without at any time producing an array of boxes which violates the requirement of a Young diagram that the lengths of the rows and columns decrease monotonically from the top row and the left column, respectively. This process can continue until the fully asymmetric Young diagram representing the ligand partition (1^n) is reached. The partial ordering of the Young diagrams can then be depicted by a lattice representing allowed movements of boxes from a given Young diagram to give higher degree Young diagrams representing less symmetrical ligand partitions. Thus, the lattice in fig. 1 depicts the Ruch–Schönhofer partial ordering for all of the Young diagrams having six boxes, corresponding to all possible partitions of six ligands. Note the bifurcations in this lattice moving towards maximum degree (i.e. maximum asymmetry and downwards in fig. 1) at the Young diagrams corresponding to the degree

2 (42) and degree 4 (321) ligand partitions to give the degree 3 (3^2) and (41^2) and degree 6 (2^3) and (31^3) ligand partitions, respectively.

In the study of chirality, the minimum degree (maximum symmetry) ligand partitions leading to chiral systems based on an achiral polyhedral skeleton are particularly significant. For this purpose, the chiral ligand partitions can be found by the following group-theoretical procedure [4,6,7].

(1) The characters for the skeletal point group G subduced [4,6,7,11] by each irreducible representation Γ_r of the symmetric group P_n are determined from the character tables of P_n (refs. [12--14]) by copying down the characters of each irreducible representation Γ_r for the operations of P_n which are also in G. In order to recognize which operation in P_n corresponds to a given operation in G, the cycle partition of the operation in G is determined, and the characters of the unique operation in P_n with that cycle partition are used.

(2) The characters of the chiral representation $\Gamma_\star$ of G are determined simply by using +1 for the proper rotations (E, C_n) and −1 for the improper rotations (σ, i, S_n).

(3) Standard group-theoretical methods [11,15,16] are used to determine which representations Γ_r of P_n, when restricted only to operations in G, contain the chiral representation $\Gamma_\star$ of G. Note that representations which are irreducible in systems with full P_n symmetry are no longer necessarily irreducible when the symmetry is reduced to G.

(4) The Young diagrams corresponding to these irreducible representations of the symmetric group P_n correspond to chiral ligand partitions for a skeleton with point group G.

Among the chiral ligand partitions found in this manner, those of lowest degree are particularly significant since they correspond to the maximum symmetry ligand partition leading to a chiral system from an achiral skeleton. The other chiral ligand partitions found in this manner have a more profound permutation group-theoretical significance [8] relating to qualitative completeness [4,6]; they will not be discussed further in this paper.

The two parameters in the Sokolov paper [2] can readily be related to properties of the Young diagrams of the lowest degree chiral ligand partition determined, as outlined above. Thus, the minimum number of chiralization steps m (μ in Sokolov's paper) is simply the difference between the number of vertices and the order (o) of the lowest degree chiral ligand partition. Similarly, the minimum number of different ligands i required for chiralization (ζ in Sokolov's paper) is simply the index of the lowest degree chiral ligand partition, and therefore is given the same symbol for clarity. These relationships allow the group-theoretical algorithm outlined above (rather than trial and error) to be used to determine the Sokolov chiralization parameters, thereby making feasible the determination of these parameters for a wider range of chemically significant polyhedra. Of particular interest is the discovery of

several polyhedra having multiple chiralization pathways, arising from bifurcations in the corresponding Young diagram lattice.

3. Results

Table 1 summarizes the chiralization parameters for the most chemically significant polyhedra having from four to twelve vertices. The information presented in this table includes the lowest degree chiral ligand partitions and the corresponding degeneracies, degrees g, order o, indices i, and chiralization steps m. In addition, the number of nonidentical vertices N and the number of different binary ratios BR are presented for comparison with those parameters of Sokolov [2].

Of particular interest is the discovery of four polyhedra, namely the octahedron, cube, hexagonal bipyramid, and icosahedron, which have two different chiralization pathways leading to two different lowest degree chiral ligand partitions having the same degrees. Such polyhedra may be called *bifurcately chiralizable*. This possibility was not explicitly recognized in the 1976 paper by Sokolov [2].

The origin of bifurcately chiralizable polyhedra can best be illustrated by the simplest such polyhedron, namely the regular octahedron, using the six-box Young diagram lattice depicted in fig. 1. The bifurcation at the ligand partition (42) in this lattice is responsible for the bifurcate chiralizability of the octahedron. Thus, the three-step ($m = 3$) chiralization of the octahedron to the (31^3) chiral ligand partition proceeds along the sequence (6) → (51) → (41^2) → (31^3) in fig. 1, noting that direct routes from the (51) to the (41^2) and from the (41^2) to the (31^3) ligand partitions can be taken avoiding the (42) and (321) ligand partition intermediates. Similarly, the four-step ($m = 4$) chiralization of the octahedron to the (2^3) chiral ligand partition proceeds along the sequence (6) → (51) → (42) → (321) → (2^3) in fig. 1, noting that a direct route from the (42) to the (321) ligand partition can be taken avoiding the (3^2) or (41^2) ligand partition intermediate. Similar alternative chiralization pathways can be found for the cube, hexagonal bipyramid, and icosahedron using the more complicated Young diagram lattices for 8, 8 and 12 boxes, respectively.

Most chemically significant polyhedra having v vertices, where $v \geqslant 6$, which have only one chiralization pathway (i.e. are not bifurcately chiralizable) have sufficiently low symmetries that the degree 2 ligand partition $(v - 2, 2)$ with $i = m = 2$ is already chiral. This corresponds to a two-step chiralization process $(v) \rightarrow (v - 1, 1) \rightarrow (v - 2, 2)$ which stops before reaching any bifurcations in the Young diagram lattice. Examples of such polyhedra (table 1) include the bicapped tetrahedron, trigonal prism, capped octahedron, bisdisphenoid, square antiprism, 4, 4, 4-tricapped trigonal prism, 4-capped square antiprism, 4, 4-bicapped square antiprism, and the cuboctahedron.

Table 1

Some polyhedra and their chiralization[a]

Polyhedron	v	e	f	Point group	Chiral ligand partitions[b]	Chiralization[c] g	o	i	m	N	BR
Tetrahedron	4	6	4	T_d	(1^4)	6	1	4	3	1	1
Trigonal bipyramid	5	9	6	D_{3h}	$(2^2 1)$	4	2	3	3	2	3
Square pyramid	5	8	5	C_{4v}	(31^2)	3	3	3	2	2	3
Octahedron	6	12	8	O_h	(2^3)	6	2	3	4	1	2
Octahedron	6	12	8	O_h	(31^3)	6	3	4	3	1	2
Bicapped tetrahedron	6	12	8	C_{2v}	2(42)	2	4	2	2	3	7
Trigonal prism	6	9	5	D_{3h}	(42)	2	4	2	2	1	3
Pentagonal bipyramid	7	15	10	D_{5h}	2(421)	4	4	3	3	2	4
Capped octahedron	7	15	10	C_{3v}	(52)	2	5	2	2	3	6
Bisdisphenoid[d]	8	18	12	D_{2d}	3(62)	2	6	2	2	2	7
Hexagonal bypyramid	8	18	12	D_{6h}	(4^2)	4	4	2	4	2	5
Hexagonal bipyramid	8	18	12	D_{6h}	2(521)	4	5	3	3	2	5
Square antiprism	8	16	10	D_{4d}	2(62)	2	6	2	2	1	4
Cube	8	12	6	O_h	(4^2)	4	4	2	4	1	3
Cube	8	12	6	O_h	(521)	4	5	3	3	1	3
4,4,4-tricapped trigonal prism	9	21	14	D_{3h}	2(72)	2	7	2	2	2	6
4-capped square antiprism	9	20	13	C_{4v}	2(72)	2	7	2	2	3	7
4,4-bicapped square antiprism	10	24	16	D_{4d}	2(82)	2	8	2	2	2	7
$B_{11}H_{11}^{2-}$ polyhedron[e]	11	27	18	C_{2v}	(10,1)	1	10	2	1	5	20
Icosahedron	12	30	20	I_h	2(84)	4	8	2	4	1	3
Icosahedron	12	30	20	I_h	2(921)	4	9	3	3	1	3
Cuboctahedron	12	24	14	O_h	(10,2)	2	10	2	2	1	4

[a] v = number of vertices; e = number of edges; f = number of faces.

[b] Only the lowest degree chiral ligand partition is listed. The octahedron, hexagonal bipyramid, cube, and icosahedron are listed twice since there are two different lowest degree chiral ligand partitions for these polyhedra. The numbers in front of the parentheses indicate the degeneracies.

[c] g = degree of the lowest degree chirality polynomial; o = order of the corresponding Young diagram (length of the longest row); i = index of the corresponding Young diagram (length of the longest column); m = number of ligand substitution steps from the ligand partition (v) in which identical ligands are present at all vertices; N = number of non-equivalent vertices; BR = number of non-equivalent binary relations. See Sokolov, Russ. J. Struct. Chem. 17(1976)642 for a more detailed discussion of the last two parameters.

[d] The bisdisphenoid is most frequently called the (D_{2d}) dodecahedron in chemical contexts, although this latter term invites confusion with the (regular, I_h) pentagonal dodecahedron.

[e] For a more detailed description of this 11-vertex C_{2v} polyhedron, see fig. 5 of Klanberg and Muetterties, Inorg. Chem. 5(1966)1855.

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