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REVIEW

CHIRALITY POLYNOMIALS

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Abstract

Chirality algebra uses ideas from permutation group theory and group representation theory to derive chirality polynomials having appropriate transformation properties for estimation of the magnitude and sign of a given pseudoscalar property (e.g. optical rotation, circular dichroism) for a given skeleton using parameters which depend only upon the ligands located at the specific sites of the skeleton, the particular skeleton, and the particular pseudoscalar property. For all but the simplest skeletons, a qualitatively complete chirality polynomial describing all chirality phenomena associated with the skeleton contains more than one component and thus requires more than one set of ligand parameters. Qualitatively complete chirality polynomials are reviewed for the most important transitive skeletons (i.e. skeletons in which all sites are equivalent), including the polarized triangle, tetrahedron, disphenoid (allene), polarized square, polarized rectangle, polarized pentagon, octahedron, trigonal prism (cyclopropane), and polarized heptagon skeletons.

1. Introduction

Chirality algebra provides a semiempirical approach for understanding molecular pseudoscalar phenomena such as optical rotation, circular dichroism, and optical yields in asymmetric syntheses. Measurements of such pseudoscalar phenomena give real numbers having the following properties:

(1) They depend upon the molecule but not upon its spatial orientation;
(2) They have opposite signs for mirror images, i.e. the two enantiomers of a chiral molecule.

A requirement for chirality algebra is the dissection of a molecule into a collection of ligands attached to an underlying skeleton. Molecules of the greatest interest in the context of this theory have the following features:

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(1) The underlying skeleton is achiral, i.e. contains one or more improper rotation symmetry elements;

(2) The individual ligands are also all achiral;

(3) A sufficiently asymmetrical pattern of ligand substitution (ligand partition) onto the underlying skeleton can destroy all of the improper rotation symmetry elements, thereby leading to a chiral molecule.

Within this context, chirality algebra has the following objectives:

(1) Determination of the ligand partitions for a given molecular skeleton which lead to chiral molecules, namely, how asymmetrical must a ligand partition be to destroy all improper rotation elements (including reflection planes and inversion centers) of an achiral skeleton. Such ligand partitions are called *chiral ligand partitions.*

(2) Determination of mathematical functions (chirality functions) which have appropriate transformation properties under symmetry operations of the skeletal point group for estimation of the magnitude and sign of a given pseudoscalar property (the dependent variable) for a given skeleton using parameters which depend only upon the ligands located at specific sites of the skeleton (the independent variables), the particular skeleton, and the particular pseudoscalar property.

If these chirality functions are polynomials, they can be called more descriptively *chirality polynomials.* Such chirality polynomials may be regarded as initial terms in a Taylor series estimating the magnitudes of pseudoscalar properties.

The fundamental ideas of chirality algebra and the resulting chirality polynomials were first presented by Ruch and Schönhofer [1,2], and are reviewed by Ruch [3] and, in more detail, by Mead [4]. The concepts of qualitative completeness [2–4], qualitative supercompleteness [5], and hyperchirality [6] have arisen from this theory and some of these concepts have led to much controversy and confusion in the literature [7–12]. Meinköhn [13,14] has related chirality polynomials to algebraic invariant theory [15]. The present author [16] has related chirality algebra to the framework groups of Pople [17] and has discussed the systematics of chiral ligand partitions and chirality polynomials for transitive skeletons [18] and for regular polyhedra [19]. Chirality polynomials have been tested experimentally for a number of important transitive skeletons, including the polarized triangle [20] (e.g. phosphines and phosphine oxides), methane [21,22], disphenoid (e.g. allenes [23] and 2,2′-spirobiindanes [24,25]), polarized rectangle (e.g. [2,2]-metacyclophanes [26–28]), polarized pentagon (e.g. cyclopentadienylmanganese tricarbonyl derivatives [29]), cyclopentane [30], and ferrocene [31] skeletons, generally with decreasing degrees of success for skeletons of increasing complexity.

This paper reviews the group-theoretical procedures for obtaining chiral ligand partitions and the corresponding chirality polynomials. These procedures are illustrated for the simplest transitive groups displaying features of interest, including those illustrative of various types of qualitatively complete chirality polynomials. The numbers of sets of separate ligand parameters for qualitatively complete chirality polynomials are noted carefully, and are shown to be responsible for the physical irrelevance of hyperchirality [6] as well as for difficulties in the experimental tests of chirality algebra in all but the simplest skeletons.

2. Skeletons, symmetries, and partitions

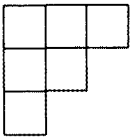
A skeleton having all sites equivalent is called a *transitive* skeleton; otherwise the skeleton is called *intransitive.* A set of equivalent sites in a skeleton is called an *orbit*; the number of sites in an orbit is called the *length* of the orbit. A transitive skeleton thus has only one orbit consisting of all of its sites. A skeleton may be characterized by its *site partition,* which may be represented by a symbol of the type $(a^{b_a}[a-1]^{b_{a-1}}[a-2]^{b_{a-2}} \ldots 1^{b_1})$, where b_k refers to the number of orbits of length k and all non-existent orbit lengths are omitted from this symbol. A transitive skeleton with n sites will have a site partition (n^1) (or (n) suppressing the exponent "1"). Thus, the regular octahedron (O_h point group), a transitive skeleton, has a site partition (6), whereas the trigonal bipyramid (D_{3h} point group), an intransitive skeleton, has a site partition (32), corresponding to the three equivalent equatorial and two equivalent axial sites. Transitive skeletons play a fundamental role in chirality algebra.

Of fundamental importance in chirality algebra is the point group G of the skeleton of interest. The action of any operation of G on the skeleton leads to a characteristic cycle structure, which may be represented as a cycle index term [32–34] or more simply as a *cycle partition,* which is a symbol of the type $(k^{c_k}[k-1]^{c_{k-1}}[k-2]^{c_{k-2}} \ldots 1^{c_1})$, where c_m refers to the number of cycles of length m and all non-existent cycle lengths are omitted from the symbol. For example, the symmetry operations E, C_4, C_3, and i of the O_h point group lead to the cycle partitions (1^6), (41^2), (3^2), and (2^3) on the regular octahedron. All operations in the same conjugacy class of the skeleton point group G lead to the same cycle partition.

The distribution of the ligands on the skeleton is also important in chirality algebra. The *ligand partition* can be depicted by a symbol of the type $(a^{b_a}[a-1]^{b_{a-1}}[a-2]^{b_{a-2}} \ldots 1^{b_1})$, where b_k refers to the number of sets of k identical ligands. In addition, the ligand partition can be equivalently depicted by a collection of boxes called *Young diagrams,* which have the following features:

(1) The rows of boxes represent identical ligands.
(2) The top row is always the longest row and the lengths of the rows decrease monotonically from top to bottom.
(3) The left column is always the longest column and the lengths of the columns decrease monotonically from left to right.

Thus, the ligand partition of the octahedral metal carbonyl complex $(C_6H_5)_3PFe(CO)_3I_2$ is (321) and is represented by the Young diagram



where the "3" and the first row of three boxes represent the three identical CO ligands, the "2" and the middle row of two boxes represent the two identical *I* ligands, and the "1" and the bottom row of a single box represent the single $(C_6H_5)_3P$ ligand.

Young diagrams can be characterized by the following three parameters:

(1) Order (o): This represents the maximum number of identical ligands in the ligand partition and is simply the length of the top row. The order also corresponds to the number of columns in the Young diagram.

(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 and represents the minimum degree of the chirality polynomial for the corresponding ligand partition. The degree of a Young diagram can be calculated by the following equation, where c_k represents the length of column k:

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

For Young diagrams having six or more boxes, there are cases where two or more different Young diagrams with the same number of boxes have the same degree as determined by eq. (1). For example, in the case of Young diagrams having six boxes, both the (41^2) and (3^2) Young diagrams have degree 3 and both the (2^3) and (31^3) Young diagrams have degree 6. In general, Young diagrams having high degrees depict relatively asymmetrical ligand partitions, and Young diagrams having relatively low degrees depict relatively symmetrical ligand partitions. Thus, the degree of a Young diagram may be viewed as a measure of the "asymmetry" of the corresponding ligand partition.

There are four permutation groups which characterize the symmetry of a ligand partition on an underlying skeleton. For a skeleton having n sites, these groups may be summarized as follows:

(1) The symmetric group P_n, consisting of all n! permutations of the n sites.

(2) The skeletal point group G. For an *achiral* skeleton, G can be partitioned

into equal numbers of positive elements (proper rotations including the identity) and negative elements (improper rotations including reflection planes and an inversion center, if present) [4,6]. For a *chiral* skeleton, G contains only positive elements (i.e. only proper rotations including, of course, the identity). Negative elements (improper rotations) are thus absent from chiral skeletons.

(3) The vertical permutation group V of the Young diagram, depicting the ligand partition of interest [4]. This group consists of the direct product [35] of symmetric groups representing all permutations *within* each *column* of the Young diagram. For a Young diagram of order o, this direct product is

$$V = P(c_1) \times P(c_2) \times \ldots \times P(c_o), \tag{2}$$

where c_k is the length of column k (see eq. (1)) and $P(c_k)$ is the symmetric group consisting of all $c_k!$ permutations within column k. Positive elements of V consist of even numbers of two-element transpositions and negative elements of V consist of odd numbers of two-element transpositions, in accord with the standard criterion for the parity of permutation group elements [36].

(4) The horizontal permutation group H of the Young diagram, depicting the ligand partition of interest [4]. This group consists of the direct product [35] of symmetric groups representing all permutations *within* each *row* of the Young diagram. For a Young diagram of index i, this direct product is

$$H = P(r_1) \times P(r_2) \times \ldots \times P(r_i), \tag{3}$$

where r_m is the length of row m and $P(r_m)$ is the symmetric group consisting of all $r_m!$ permutations within row m.

The properties of the groups P_n and G are used to determine chiral ligand partitions for a given skeleton having n sites and skeletal point group G. In general, a skeleton is found to have several chiral ligand partitions of different degrees, as determined by eq. (1). Determination of the chirality polynomials corresponding only to the *lowest* degree chiral ligand partitions requires the use of only the skeletal point group G among the permutation groups listed above. This procedure is used in previous papers by the present author [16,18,19], as well as in the paper on hyperchirality by Dugundji et al. [6]. However, a more general procedure for the determination of chirality polynomials corresponding to *all* chiral ligand partitions (as is required for the study of qualitatively complete chirality polynomials) requires the use of not only the skeletal point group G, but also the groups H and V derived from the Young diagram depicting the chiral ligand partition of interest. This more general procedure was first presented by Ruch and Schönhofer [2] and is described more clearly in Mead's review [4].

A specific feature of the symmetry of achiral skeletons of importance in determining chirality phenomena is the relationship of the reflection planes of the skeleton to its sites. Such reflection planes can be classified into two types: separating planes and non-separating planes [16]. A *separating plane* in a skeleton having n sites contains exactly $n - 2$ of these sites. Conversely, a reflection plane containing less than $n - 2$ sites in a skeleton having n sites is a non-separating plane. Achiral skeletons in which *all* reflection planes are separating planes have been called "category a" or *shoe-like* by Ruch [3], since left-handed and right-handed enantiomers constructed from such skeletons can readily be distinguished like left and right shoes. Skeletons which are not shoe-like have been called "category b" or *potato-like* by Ruch [3], since even though chiral, which member of such an enantiomeric pair is "left-handed" and which is "right-handed" cannot be distinguished by means of an algorithm of a general type described by Ruch.

3. Group representations

Consider a symmetric group P_n. This group contains exactly one conjugacy class [36] for each possible set of positive integers $m_1, m_2, \ldots, m_k$ whose sum $\Sigma_{i=1}^{i=k} m_i = n$ [37]. Such a set of integers is called a *partition* of n and can be depicted by a Young diagram as summarized above. Furthermore, in any finite group there is a one-to-one correspondence between conjugacy classes and irreducible representations [37], as is readily evident by inspection of group character tables. Therefore, the Young diagrams containing n boxes correspond not only to conjugacy classes of the symmetric group P_n, but also to the irreducible representations of P_n. The partitions of n thus relating to the conjugacy classes and irreducible representations of P_n also correspond to partitions of ligands on a skeleton having n sites, as discussed in the previous section.

A chirality function has the so-called pseudoscalar property, which means that it is unaffected by ligand permutations corresponding to proper rotations, but undergoes a change in sign with no change in absolute value under ligand permutations corresponding to improper rotations. As a consequence of this, the representation of the chirality function (i.e. the chiral representation) must contain the *antisymmetric representation* A^-, which is the one-dimensional irreducible representation of all *achiral* point groups having $+1$ characters for all proper rotations and -1 characters for all improper rotations. Thus, the chiral representations of P_n which correspond to chiral ligand partitions are those irreducible representations of P_n which occur in the representation $A^{-\star}$ of P_n *induced* [38,39] by the irreducible representation A^- of the skeletal point group G. The chiral dimensionality X_d corresponds to the number of enantiomer pairs when all sites of the skeleton have different ligands and is equal to the dimensionality of the induced representation, dim $A^{-\star}$, i.e.

$$\dim A^{-\star} = X_d = n!/|G| = I/2, \tag{4}$$

where $|G|$ is the number of elements in G and I is the isomer count as defined by Muetterties [40] and Klemperer [41,42]. The induced representation A^{-*} of P_n is therefore reduced to a sum of irreducible representations of P_n of total dimensionality X_d. Each irreducible representation in this sum corresponds to a chiral ligand partition, which leads to a chirality polynomial using a *different* set of ligand parameters. A sum of the chirality polynomials for each of these individual chiral ligand partitions is needed to describe fully all chirality phenomena for the skeleton in question. Such a sum of chirality polynomials is called a *qualitatively complete* chirality polynomial [2,4], and the individual chirality polynomials making up the sum may be regarded as components of the qualitatively complete chirality polynomial. The chiral ligand partitions of the lowest degree (as defined in eq. (1)) are of particular significance in representing the most "symmetrical" ligand partitions capable of destroying all improper rotations and thereby leading to the lowest degree chirality polynomials or the lowest degree polynomial components for a qualitatively complete chirality polynomial. In the cases of certain regular polyhedral skeletons, there are two or more different ligand partitions of the same degree, which are the lowest degree chiral ligand partitions. Examples are the degree 6 (31^3) and (2^3) chiral ligand partitions for the regular octahedron, the degree 4 (4^2) and (521) chiral ligand partitions for the cube, and the degree 4 (84) and (921) chiral ligand partitions for the regular icosahedron [19]. Such skeletons may be called *chirally degenerate.* The polarized pentagon skeleton as found in cyclopentadienylmanganese tricarbonyl derivatives [29] may also be regarded as chirally degenerate, since the lowest degree and only chiral ligand partition (31^2) corresponds to an irreducible representation of P_5, which occurs *twice* in the representation A^{-*} of P_5 induced by the irreducible representation A^- of the C_{5v} skeletal point group.

The actual process of determining the chiral representations of P_n which correspond to the chiral ligand partitions for a skeleton with n sites and point group G is facilitated greatly if the group induction problem indicated above is converted to a group subduction problem using the Frobenius reciprocity theorem [2,4,18,38,39]. The chiral representations of P_n thus become the representations of P_n *subduced* by G, which contain the antisymmetric representation A^- of G. This leads to the following algorithm for determining the chiral ligand partitions for a skeleton having point group G:

(1) The characters for representations of G subduced by each irreducible representation of P_n are determined from character tables of P_n by copying down the characters of each irreducible representation of P_n for the operations of P_n which are also in G. The required character tables for P_n with $n \leqslant 13$ can be obtained from several sources [43–45]. In order to recognize which operation of P_n corresponds to a given operation of G, the cycle partition of the operation in G is determined and the characters of the operations in the unique conjugacy class of P_n with that particular cycle partition are used.

(2) The characters for the antisymmetric (chiral) representation A^- 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 based on orthogonality relations [37,38] are used to determine which irreducible representations of P_n when restricted only to operations in G contain the representation A^- of G. These irreducible representations of P_n correspond to the chiral ligand partitions for a skeleton with point group G. Note that representations which are irreducible in systems having full P_n symmetry are no longer necessarily irreducible when the symmetry is reduced to G.

4. Algebraic form of the chirality polynomial

The general procedure for determining a chirality polynomial for a given chiral ligand partition of an achiral skeleton consists of the successive application of two projection operators to a monomial derived from the Young diagram corresponding to the chiral ligand partition of interest [4]. The first of these projection operators is the Young operator Y, which is derived from the permutation groups H and V of the Young diagram (eqs. (2) and (3)) with equal numbers of positive and negative terms corresponding to elements of V, the *vertical* permutation group, containing even and odd numbers, respectively, of two-element transpositions. The second projection operator is derived from the skeletal point group G, with equal numbers of positive and negative terms corresponding to the proper and improper rotations, respectively, of G. Application of the Young operator Y can be omitted if chirality polynomials only corresponding to the lowest degree chiral ligand partitions are sought, since the projection operator derived from G then has sufficient terms to generate the full chirality polynomial. This level of simplification was used in some of the previous papers [6,16]. Even more drastically simplified procedures can be used to determine the lowest degree chirality polynomials of shoe-like skeletons or intransitive skeletons [6,16]. On the other hand, qualitatively complete chirality polynomials for a given skeleton consist of sums of chirality polynomial components corresponding to *each* chiral ligand partition, using different sets of ligand parameters for each polynomial in the sum. Determination of qualitatively complete chirality polynomials in general thus requires determination of chirality polynomials corresponding to chiral ligand partitions which are *not* those of lowest degree for the skeleton of interest. In such cases, the full procedure with both projection operators must be used.

The full group-theoretical algorithm for determination of a chirality polynomial in ligand-specific parameters s_k corresponding to a given skeleton, ligand partition, and pseudoscalar measurement can be outlined as follows:

(1) Label the boxes in the Young diagram for the ligand partition of interest with the indices of the skeletal sites corresponding to the particular chiral species

of interest with that ligand partition. These labels correspond to the indices k of the ligand-specific parameters s_k.

(2) Determine from the columns of the labelled Young diagram the monomial arising from the following double product:

$$\prod_{e=1}^{e=\text{order}} \prod_{f=0}^{f=i-1} s_{k_{ef}}^{f} = M(s_1, s_2, \ldots, s_n). \tag{5}$$

In eq. (5), the following should be noted:

(a) The product over e contains one factor for each column of the Young diagram. The index e corresponds to the position of the column relative to the left column, where $e = 1$.

(b) The product over f contains one factor for each box in the Young diagram in column e except for the bottom box, where $f = 0$ and hence $s_{k_{ef}}^{f} = 1$. Thus, if column e has only one box in it, then the factor from column e is unity. Therefore, columns of the Young diagram with only one box in them do not contribute to the monomial in eq. (5). The variable f corresponds to the position of the box relative to the *bottom* box of the column e. In the bottom box, $f = 0$.

(c) The subscript k_{ef} refers to the index entered in the Young diagram box corresponding to column e and row f.

(3) Determine from the Young diagram the corresponding horizontal (H) and vertical (V) permutation groups by eqs. (2) and (3).

(4) Apply the corresponding Young operator Y to the monomial M from eq. (5) to give

$$Y[M(s_1, s_2, \ldots, s_n)] = \sum_{v \in V} \sum_{h \in H} e_v \, hv \star M(s_1, s_2, \ldots, s_n), \tag{6}$$

where h and v represent elements in H and V, respectively; $e_v = +1$ or -1 if the vertical permutation element v consists of an even or odd number, respectively, of two-element transpositions; the summations are taken over all elements v of V and all elements h of H; and the star $\star$ means that the indices $1, 2, \ldots, n$ of the variables s_k in $M(s_1, s_2, \ldots, s_n)$ are permuted by the permutation hv arising from applying first the permutation v and then the permutation h. If the group H has $|H|$ elements and the group V has $|V|$ elements, then the Young operator Y expands the monomial $M(s_1, s_2, \ldots, s_n)$ into a polynomial with $|H|\,|V|$ terms.

(5) Apply permutations corresponding to each of the elements g of the skeletal point group G to the indices of the variables s_k in the polynomial

$Y[M(s_1, s_2, \ldots, s_n)]$ to give the chirality polynomial $X(s_1, s_2, \ldots, s_n)$ defined by

$$X(s_1, s_2, \ldots, s_n) = \sum_{g \in G} e_g g \star Y[M(s_1, s_2, \ldots, s_n)]$$
$$= \sum_{g \in G} e_g g \star \left[\sum_{v \in V} \sum_{h \in H} e_v hv \star M(s_1, s_2, \ldots, s_n) \right], \quad (7)$$

where $e_g = +1$ if g is a proper rotation and $e_g = -1$ if g is an improper rotation. Equation (7) thus represents application of a projection operator corresponding to G.

The polynomial obtained from eq. (7) is usually reduced to a product and/or sum of differences between pairs of ligand parameters $s_k^a - s_i^a$ by standard algebraic methods, which can sometimes involve adding zero in the form

$$0 = K \sum_{k=1}^{k=n} s_k^a - s_k^a, \quad (8)$$

followed by factoring into powers of the type $(s_k - s_m)^a$, where a is a small integer. If the skeleton of interest is shoe-like, having n sites and p planes of symmetry, all of which necessarily are separating planes containing exactly $n - 2$ sites, then the chirality polynomial for its lowest degree chiral ligand partition is the product of differences between pairs of ligand parameters, i.e.

$$X(s_1, s_2, \ldots, s_n) = \prod_{k=1}^{k=p} (s_{a_k} - s_{b_k}), \quad (9)$$

where a_k and b_k are the only two sites outside the separating plane k. Thus, the degree of the chirality polynomial for the lowest degree chiral ligand partition of a shoe-like skeleton is equal to the number of symmetry planes. The introduction of non-separating planes to give a potato-like skeleton leads to sums of differences between pairs of ligand parameters as factors of the chirality polynomials for the lowest degree chiral ligand partitions. The degree of such a chirality polynomial is less than the total number of reflection planes.

Steps (3) and (4) of the above algorithm using the Young operator Y can be omitted for determining chirality polynomials for the *lowest* degree chiral ligand partitions for a given skeleton. In these cases, the group-theoretical algorithm is simplified considerably, as presented in an earlier paper by the author [16]. However, for the determination of chirality polynomials for non-lowest degree chiral ligand partitions of a given skeleton, steps (3) and (4) may be required. The net effect of these additional steps may be regarded as the replacement of the projection operator derived from the skeletal point group G with that derived from a larger group containing G as a subgroup.

Meinköhn [13,14] has used algebraic invariant theory [15] to show that only the chirality polynomials for the lowest degree ligand partitions are required to have the desirable property of depending only upon differences between the ligand parameters. The chirality polynomials for non-lowest degree chiral ligand partitions may also depend only upon differences between the ligand parameters if the ligand partition in question is the lowest degree chiral ligand partition for a larger permutation group L, using the idea of signed permutation groups [18] to extend the concept of chirality to permutation groups L which are not realizable as symmetry groups in three-dimensional space. Consideration of these points leads naturally to the following questions:

(1) Are there ligand partitions which are not the lowest degree chiral ligand partitions for any permutation group? This is certainly the case if only *transitive* permutation groups are considered. The simplest non-trivial cases are the (21^3) and $(2^2 1)$ ligand partitions for five sites, which are not the lowest degree chiral ligand partitions for any of the transitive permutation groups of five objects [18].

(2) Are there ligand partitions corresponding to chirality polynomials which do not depend solely on the differences between the ligand parameters? The simplest example appears to be the (321) chiral ligand partition of the D_{3h} trigonal prism (cyclopropane) skeleton, discussed in greater detail later in this paper. In this case, a larger permutation group L cannot be generated from the D_{3h} skeletal point group through an appropriate Young operation for which (321) is the lowest degree chiral ligand partition.

The determination of chirality polynomials for intransitive skeletons can be simplified by considering each orbit individually and then multiplying together the chirality polynomials for each orbit to give the chirality polynomial for the entire skeleton. Thus, the chirality polynomial for an intransitive skeleton having n sites and q orbits can be determined from the relationship

$$X(s_1, s_2, \ldots, s_n) = \prod_{k=0}^{k=q} X_k , \tag{10}$$

where X_k is the chirality polynomial for orbit k. Different sets of ligand parameters must be used for the chirality polynomials for each orbit. Failure to recognize this point was responsible for the extensive confusion on hyperchirality [6–12] which involves mostly intransitive skeletons, as discussed later. Also note that orbits of length 1 in intransitive skeletons (i.e. isolated sites invariant under all symmetry operations) can be completely ignored in the calculation of all of their chirality polynomials.

This algorithm can be illustrated for the polarized rectangle skeleton, the simplest non-trivial case of a potato-like skeleton. This skeleton has two chiral ligand partitions, namely

(31) (21^2) (11)

corresponding to the Young diagrams

(31) (21^2) (12)

In polarized polygonal skeletons, the top and bottom of the plane of the polygon are differentiated [16] (i.e. "polarized") so that the point group G of the polarized rectangle skeleton is C_{2v}, leading to the following permutation group:

$$G = 1 + (13)(24) - (12)(34) - (14)(23). \tag{13}$$

The signs in front of the permutations in eq. (13) indicate whether they correspond to proper (+) or improper (−) rotations, thereby leading to e_g values of +1 and −1, respectively, in the corresponding projection operator (eq. (7)). The degree of the (31) chiral ligand partition is *one*, leading to the monomial

$$M(31) = s_4. \tag{14}$$

The Young operator is determined as follows:

$$H = P_3(A) \times P_1(B) = 1 + (123) + (132) - (12) - (13) - (23) \tag{15a}$$

$$V = P_2 \times P_1 \times P_1 = 1 - (14) \tag{15b}$$

$$Y[M(31)] = Y(s_4) = 6s_4 - s_1 - s_2 - s_3 - s_2 - s_3 - s_4. \tag{16}$$

Application of the projection operator from the C_{2v} skeletal point group (eq. (13)) to eq. (16) gives the chirality polynomial

$$X(31)(C_{2v}) = (s_4 - s_3) + (s_2 - s_1) \tag{17}$$

after dividing by 6. The degree of the (21^2) chiral ligand partition for the polarized rectangle skeleton is three, leading to the monomial

$$M(21^2) = t_3 t_4^2 \,. \tag{18}$$

The Young operator is determined as follows:

$$H = P_2(A) \times P_1(B) \times P_1(C) = 1 + (12) \tag{19a}$$

$$V = P_3 \times P_1 = 1 + (134) + (143) - (13) - (14) - (34) \tag{19b}$$

$$\begin{aligned} Y[M(21^2)] &= Y(t_3 t_4^2) \\ &= t_3 t_4^2 + t_4 t_1^2 + t_1 t_3^2 - t_1 t_4^2 - t_3 t_1^2 - t_4 t_3^2 \\ &\quad + t_3 t_4^2 + t_4 t_2^2 + t_2 t_3^2 - t_2 t_4^2 - t_3 t_2^2 - t_4 t_3^2 \,. \end{aligned} \tag{20}$$

Application of the projection operator from the C_{2v} skeletal point group (eq. (13)) to eq. (20) gives ultimately the chirality polynomial

$$X(21^2)(C_{2v}) = (t_4 - t_2)(t_3 - t_1)\,[(t_4 - t_3) + (t_2 - t_4)] \tag{21}$$

after dividing by 8. The qualitatively complete chirality polynomial for the polarized rectangle skeleton is the sum of the "s_n-polynomial" in eq. (17) and the "t_n-polynomial" in eq. (21), where the set of "s_n" ligand parameters is different from the set of "t_n" ligand parameters. This chirality polynomial for the polarized rectangle has been used for a study of the molar rotations and circular dichroism in [2,2]-metacyclophanes [26–28], whose C_{2h} transitive skeleton has the same permutations as the C_{2v} polarized rectangle. In these systems, the qualitatively complete chirality polynomial proved to be adequate for predicting experimental pseudoscalar data obtained from electronic transitions in long wave length regions, but not for higher energetic transitions. This offers the possibility to correlate the discrepancies between calculated and observed rotation angles to distinct electronic transitions.

The following features of the above determination of the chirality polynomials for the polarized rectangle skeleton are of interest:

(1) The chirality polynomial for the (21^2) chiral ligand partition of the C_{2v} polarized rectangle is the same as that for the C_{4v} polarized square, for which (21^2) is the lowest degree (and only) chiral ligand partition. The combined effect of the Young operator (eq. (20)) and the C_{2v} projection operator (eq. (13)) is thus equivalent to a C_{4v} projection operator for the (21^2) chiral ligand partition. The C_{4v} permutation group is thus the larger group L for the (21^2) chiral ligand partition of the C_{2v} polarized rectangle skeleton in the sense discussed above.

(2) *Direct* application of the projection operator from the C_{2v} skeletal point group of the polarized rectangle (eq. (13)) to the monomial $t_3 t_4^2$ from eq. (18) without first using the Young operator to give eq. (20) gives

$$C_{2v} \star (t_3 t_4^2) = t_3 t_4^2 + t_1 t_2^2 - t_4 t_3^2 - t_2 t_1^2 , \tag{22}$$

which is *not* identical to the chirality polynomial in eq. (21). This shows how the Young operator derived from the horizontal and vertical permutation groups H and V, respectively, is needed to obtain a chirality polynomial corresponding to a chiral ligand partition which is not that of the lowest degree.

5. Examples of chirality polynomials of transitive skeletons

Table 1 summarizes all of the transitive skeletons having seven or fewer sites and a few having more than seven sites; these skeletons are depicted in fig. 1. Table 2 summarizes the chirality polynomials for all of the transitive skeletons having five or fewer sites. Special features of the transitive skeletons listed in table 1 are noted below:

(1) POLARIZED TRIANGLE AND TETRAHEDRON

These shoe-like skeletons, of considerable chemical significance, are the only possible transitive skeletons containing a single chiral ligand partition of the type (1^n) ($n = 3$ or 4) since they are the only three-dimensional skeletons having symmetries of the corresponding symmetric groups P_n ($n = 3$ and 4). A qualitatively complete chirality polynomial consists of a single component which is a product of all possible differences between ligand parameters and thus has degree $n(n-1)/2$ (table 2). Application of chirality algebra to these skeletons is relatively easy, since only one set of ligand parameters is necessary to give qualitatively complete chirality polynomials. The chirality polynomial for the polarized triangle has been applied to the optical rotations of chiral phosphines and phosphine oxides with reasonable agreement in most cases [20]. The chirality polynomial for the tetrahedron has been applied to methane derivatives [22] with reasonable agreement except for cases where interactions between ligands, such as by hydrogen bonding, tend to favor specific conformations.

(2) DISPHENOID

The shoe-like disphenoid skeleton is found in allene [23] and 2,2′-spirobiindane [24,25] derivatives. This skeleton is derived from the tetrahedron skeleton by distortion to eliminate all C_3 axes. This is the simplest and only shoe-like skeleton having two chiral ligand partitions, namely (1^4) and (2^2). Qualitatively complete

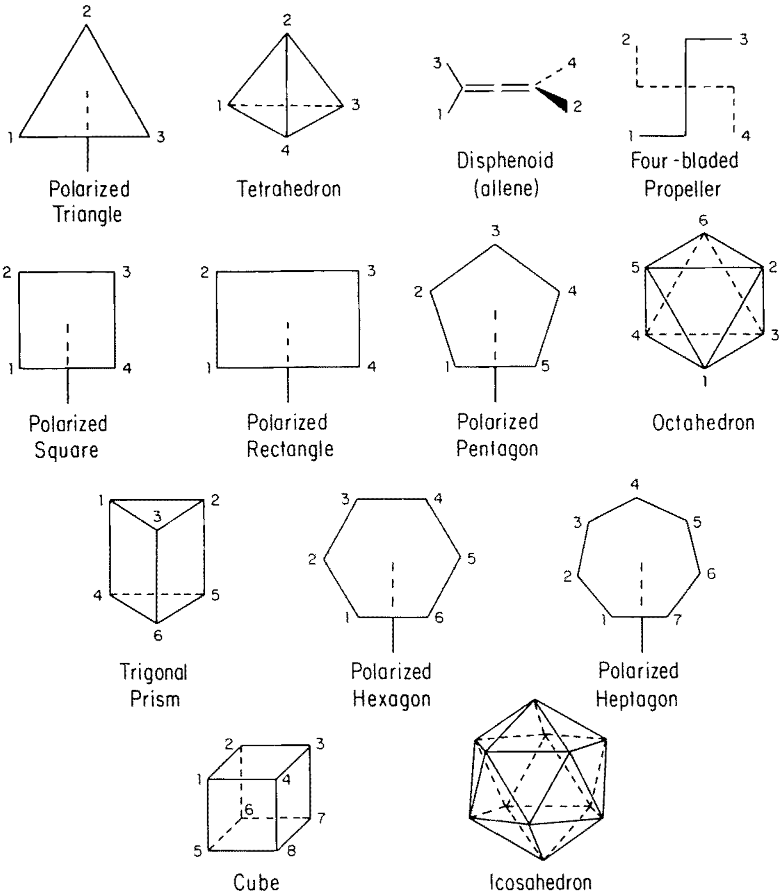
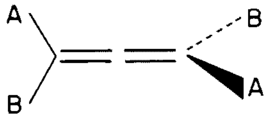


Fig. 1. The transitive skeletons listed in table 1. Numbering schemes are presented for the skeletons whose chirality polynomials are listed in the text or in table 2.

chirality polynomials thus require two sets of ligand parameters, designated in table 2 as s_n and s'_n. Pseudoscalar measurements on chiral allenes having a (2^2) ligand partition, i.e.



can be used to evaluate the s_n parameters since the (1^4) component of the qualitatively complete chirality polynomial then vanishes. Using these s_n parameters, the s'_n parameters can then be evaluated using pseudoscalar measurements on allenes in which all four substituents (ligands) are different. Comparisons of experimental data on the optical rotations of chiral allenes [23] and chiral 2,2′-spirobiindanes [24,25] indicate that the simplest degree 2 polynomial for the (2^2) chiral ligand partition provides a

Table 1

Transitive skeletons discussed in this paper

Skeleton	Chemical examples	Sites	Skeletal point group	Symmetry planes		Sets of ligand parameters[a]	Chiral ligand partitions[b]
				Total	Non-separating		
Polarized triangle	amines, phosphines phosphine oxides	3	C_{3v}	3	0	1	(1^3)
Tetrahedron	CH_4 derivatives	4	T_d	6	0	1	(1^4)
Disphenoid	allenes 2, 2′-spirobiindanes	4	D_{2d}	2	0	2	$(2^2) + (1^4)$
Four-bladed propeller		4	S_4	0	0	3	$(31) + (2^2) + (1^4)$
Polarized square	$C_4H_4Fe(CO)_3$ derivatives	4	C_{4v}	4	2	1	(21^2)
Polarized rectangle	[2, 2] -metacyclophanes[c]	4	C_{2v}	2	2	2	$(31) + (21^2)$
Polarized pentagon	$C_5H_5Mn(CO)_3$ derivatives	5	C_{5v}	5	5	2	$2\,(31^2)$
Octahedron	most ML_6 metal complexes	6	O_h	9	6	2	$(2^3) + (31^3)$
Trigonal prism	cyclopropanes[d]	6	D_{3h}	4	4	6	$(42) + (41^2) + (321) + 2\,(31^3) + (2^3)$
Polarized hexagon	$C_6H_6Cr(CO)_3$ derivatives	6	C_{6v}	6	6	6	$2\,(41^2) + (3^2) + (321) + (31^3) + (2^2 1^2)$
Polarized heptagon	$C_7H_7V(CO)_3$ derivatives	7	C_{7v}	7	7	17	$3\,(51^2) + (43) + 2\,(421) + 3\,(3^2 1)$ $+ (41^3) + 3\,(321^2) + (2^3 1) + 2\,(2^2 1^3)$ $+ (1^7)$
Cube	cubanes	8	O_h	9	9	16	$(521) + (4^2) + (431) + 2\,(51^3)$ $+ 2\,(42^2) + 2\,(421^2) + 2\,(3^2 1^2)$ $+ 2\,(41^4) + (32^2 1) + (2^4) + (321^3)$
Icosahedron	$B_{12}H_{12}^{2-}$ derivatives	12	I_h	15	15	1 176	$2\,(84) + 2\,(921)$ + many higher degree chiral ligand partitions[e]

[a] This column gives the number of sets of different ligand parameters required for a qualitatively complete chirality polynomial.

[b] The chiral ligand partitions are listed in order of ascending degree.

[c] [2, 2] -metacyclophanes actually have the C_{2h} point group, but this is permutationally equivalent to the C_{2v} polarized rectangle.

[d] The trigonal antiprism skeleton with a D_{3d} skeletal point group is permutationally equivalent to the D_{3h} trigonal prism.

[e] For a complete list of the 65 chiral ligand partitions of varying multiplicities for the regular icosahedron, see R.B. King, J. Math. Chem. 1 (1987)45.

Table 2

Some simple chirality polynomials

Skeleton	Chiral ligand partition	Degree	Chirality polynomial
Polarized triangle	(1^3)	3	$(s_3 - s_2)(s_3 - s_1)(s_2 - s_1)$
Tetrahedron	(1^4)	6	$(s_4 - s_3)(s_4 - s_2)(s_4 - s_1)(s_3 - s_2)(s_3 - s_1)(s_2 - s_1)$
Disphenoid (allene)	(2^2)	2	$(s_4 - s_2)(s_3 - s_1)$
Disphenoid (allene)	(1^4)	6	$(s'_4 - s'_3)(s'_4 - s'_2)(s'_4 - s'_1)(s'_3 - s'_2)(s'_3 - s'_1)(s'_2 - s'_1)$
Polarized square	(21^2)	3	$(s_4 - s_3)(s_3 - s_1)[(s_4 - s_3) + (s_2 - s_1)]$
Polarized rectangle	(31)	1	$(s_4 - s_3) + (s_2 - s_1)$
Polarized rectangle	(21^2)	3	$(s'_4 - s'_2)(s'_3 - s'_1)[(s'_4 - s'_3) + (s'_2 - s'_1)]$
Polarized pentagon	(31^2)	3	$(s_5 - s_1)^3 + (s_1 - s_2)^3 + (s_2 - s_3)^3 + (s_3 - s_4)^3 + (s_4 - s_5)^3$
Polarized pentagon	(31^2)	3	$(s'_5 - s'_2)^3 + (s'_1 - s'_3)^3 + (s'_2 - s'_4)^3 + (s'_3 - s'_5)^3 + (s'_4 - s'_1)^3$

good approximation of the experimental data. Experimental data [23] also suggest that the (1^4) "tetrahedral" component of the qualitatively complete $(1^4) + (2^2)$ allene chirality function makes a negligible contribution to the pseudoscalar properties of allene derivatives having four different substituents.

(3) FOUR-BLADED PROPELLER

Further reduction of the symmetry of the disphenoid (allene) skeleton leads to the four-bladed propeller having S_4 symmetry. This skeleton is unusual, since even though it has no reflection planes, it is achiral because of the S_4 and S_4^3 improper rotations in its symmetry point group. The reduction of the symmetry of the disphenoid skeleton to the four-bladed propeller adds the (31) chiral ligand partition of degree 1 so that the four-bladed propeller has a total of three chiral ligand partitions, namely the (1^4) and (2^2) chiral ligands of the disphenoid skeleton and the new (31) chiral ligand partition. This skeleton does not appear to be of particular chemical significance.

(4) POLARIZED SQUARE

The polarized square is the simplest potato-like skeleton. It has a single degree 3 chiral ligand partition, namely (21^2). The $s_4 - s_2$ and $s_3 - s_1$ factors in its chirality polynomial (table 2) correspond to the two σ_d separating planes and the $s_4 - s_3 + s_2 - s_1$ factor corresponds to the two σ_v non-separating planes. In principle, this chirality polynomial can be applied to chiral derivatives of the $C_4H_4Fe(CO)_3$ and $C_5H_5ML_4$

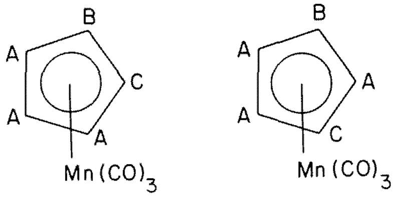
skeletons, but appropriate experimental pseudoscalar measurements are not available on a sufficient variety of such systems to obtain sets of ligand parameters.

(5) POLARIZED RECTANGLE

The polarized rectangle arises from the polarized square by distortion to eliminate the C_4 axis but not the C_2 axis, thereby reducing the symmetry from C_{4v} to C_{2v}. This skeleton has two chiral ligand partitions, namely the (21^2) chiral ligand partition of the polarized square and the new (31) degree 1 chiral ligand partition. The chirality function from the latter chiral ligand partition (table 2) corresponds to the "quadrant rule" [46,47]. The polarized rectangle is discussed in detail in the previous section as an example of the procedure for determining qualitatively complete chirality polynomials.

(6) POLARIZED PENTAGON

The polarized pentagon is the simplest example of a chirally degenerate skeleton since the only chiral ligand partition, namely (31^2), appears twice, corresponding to 1,2 (adjacent) and 1,3 (non-adjacent) positions of the unique substituents (ligands), as illustrated by the cyclopentadienylmanganese tricarbonyl isomers



(23)

The degree 3 chirality polynomials for both (31^2) chiral ligand partitions (table 2) have the same general form, but use different sets of ligand parameters designated as s_n and s_n' $(1 \leqslant n \leqslant 5)$ in table 2. A qualitatively complete chirality polynomial for the polarized pentagon is a sum of four polynomials, namely each of the (31^2) chirality polynomials in table 2 using each of the sets of ligand parameters s_n and s_n' $(1 \leqslant n \leqslant 5)$.

(7) TRIGONAL PRISM

The trigonal prism skeleton found in cyclopropanes is the simplest transitive skeleton which has more than three chiral ligand partitions. The origin of these chiral ligand partitions relates to the alternative origins of the trigonal prism having a D_{3h} skeletal point group of order 12 by reduction of symmetry either from the octahedral skeleton having an O_h skeletal point group of order 48, or from a non-rigid skeleton having a "$T9$" twist skeletal point group [48] of order 36 [18]. The six chiral ligand

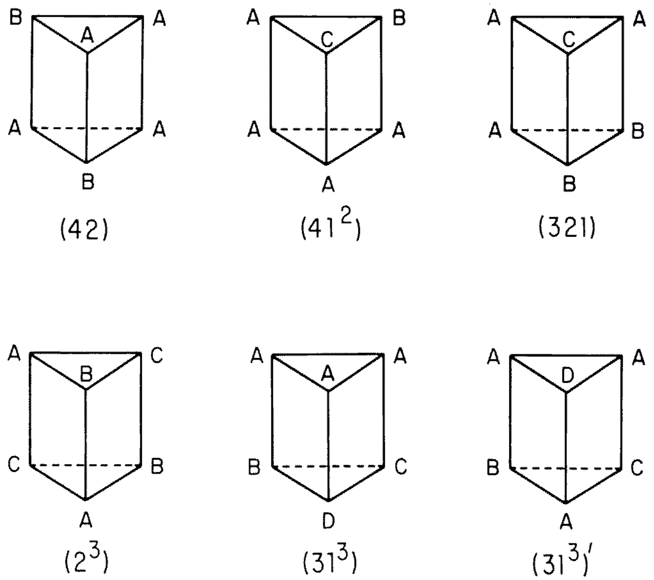


Fig. 2. The six chiral ligand partitions of the trigonal prism (cyclopropane) skeleton.

partitions of the trigonal prism skeleton are illustrated in fig. 2. The corresponding chirality polynomials are the following:

$$X(42)(D_{3h}) = (s_1 - s_2)(s_4 - s_6) - (s_1 - s_3)(s_4 - s_5)$$

(lowest degree chirality polynomial) (24a)

$$X(41^2)(D_{3h}) = (s_1' - s_2')(s_1' - s_3')(s_2' - s_3') - (s_4' - s_5')(s_4' - s_6')(s_5' - s_6')$$

(from the $T9$ twist group [18]) (24b)

$$X(2^3)(D_{3h}) = f(t_n)[g(t_n) + h(t_n)] \tag{24c}$$

$$X(31^3)(D_{3h}) = f(t_n')[g(t_n') - h(t_n')] \tag{24d}$$

from the octahedron, where

$$f(x_n) = (x_1 - x_6)(x_2 - x_4)(x_3 - x_5) \tag{25a}$$

$$\begin{aligned} g(x_n) = {} & (x_1 - x_2)(x_2 - x_3)(x_3 - x_1) + (x_3 - x_6)(x_6 - x_4)(x_4 - x_3) \\ & + (x_1 - x_4)(x_4 - x_5)(x_5 - x_1) + (x_2 - x_5)(x_5 - x_6)(x_6 - x_2) \end{aligned} \tag{25b}$$

$$h(x_n) = (x_1 - x_2 + x_6 - x_4)(x_1 - x_5 + x_6 - x_3)(x_2 - x_5 + x_4 - x_3) \quad (25c)$$

$$\begin{aligned} X(321)(D_{3h}) = {} & (u_1 u_6 - u_3 u_4)(u_4 - u_3)(u_1 - u_6) \\ & + (u_1 u_5 - u_2 u_4)(u_2 - u_4)(u_1 - u_5) \\ & + (u_2 u_6 - u_3 u_5)(u_3 - u_5)(u_2 - u_6) \end{aligned} \quad (24e)$$

$$X(31^3)'(D_{3h}) = f(s''_m)\,[g(s''_m) - h(s''_m)] \quad (24f)$$

from the $T9$ twist group, where the indices m are obtained from the indices n by interchanging the indices 3 and 6.

Thus, six sets of ligand parameters designated above as s_n, s'_n, s''_m, t_n, t'_n, and u_n are needed for a qualitatively complete chirality polynomial for the trigonal prism. The single set of ligand parameters s_n for the trigonal prism skeleton of cyclopropane derivatives can in principle be evaluated from pseudoscalar measurements on chiral cyclopropane derivatives having a (42) ligand partition (e.g. trans-disubstituted cyclopropanes of the type $C_3H_4X_2$), for which all of the above chirality polynomials *except* for the degree 2 $X(42)(D_{3h})$ in eq. (24a) vanish identically. Similarly, the parameters s'_n can be evaluated from the same pseudoscalar measurements on chiral cyclopropane derivatives having a (41^2) ligand partition which is *not* derived from a chiral (42) ligand partition by making the two equivalent ligands different (e.g. cis-disubstituted cyclopropane derivatives of the type C_3H_4XY); in such systems, all chirality polynomials *except* the degree 3 $X(41^2)(D_{3h})$ in eq. (24b) vanish identically. Note also that the degree 4 chirality polynomial $X(321)(D_{3h})$ in eq. (24e) is *not* a function only of the differences between ligand parameters of the type u_n, indicating by Meinköhn's theory [13,14] that there is no transitive signed permutation group [18] on six objects for which (321) is the lowest degree chiral ligand representation.

(8) POLARIZED HEPTAGON

The C_{7v} polarized heptagon (e.g. the $C_7H_7V(CO)_3$ or $C_7H_7Cr(CO)_3^+$ skeletons) has 17 chiral ligand partitions and is chirally degenerate with four degree 3 chiral ligand partitions, namely three (51^2) and one (43) ligand partitions, as the lowest degree chiral ligand partitions. These are illustrated in fig. 3. The corresponding chirality polynomials are the following:

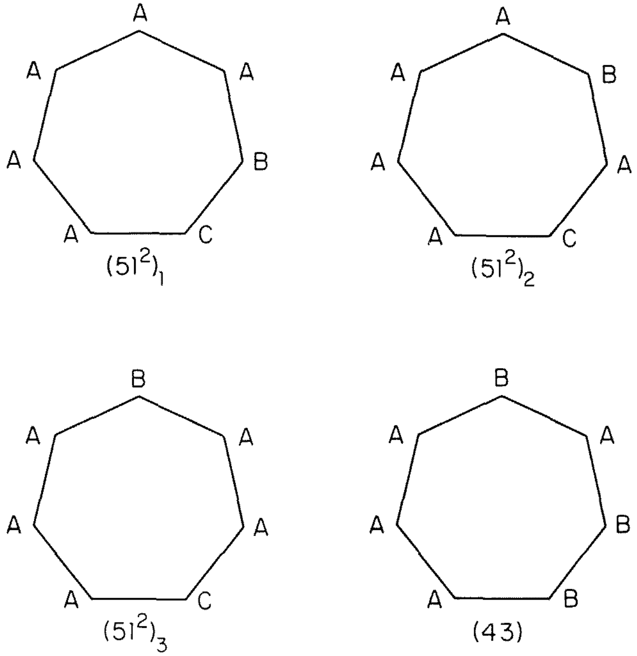


Fig. 3. Schematic representation of the four chiral ligand partitions of the polarized heptagon skeleton.

$$
\begin{aligned}
X(51^2)_k(C_{7v}) = {} & (s_1 - s_{1+k})^3 + (s_2 - s_{2+k})^3 + (s_3 - s_{3+k})^3 + (s_4 - s_{4+k})^3 \\
& + (s_5 - s_{5+k})^3 + (s_6 - s_{6+k})^3 + (s_7 - s_{7+k})^3 \qquad (26)
\end{aligned}
$$

(where $k = 1, 2, 3$ and addition of indices is done modulo 7; different sets of ligand parameters s_n are required for each of the chirality polynomials)

$$
\begin{aligned}
X(43)(C_{7v}) = {} & (t_2 - t_7)(t_3 - t_6)(t_4 - t_5) + (t_3 - t_1)(t_4 - t_7)(t_5 - t_6) \\
& + (t_4 - t_2)(t_5 - t_1)(t_6 - t_7) + (t_5 - t_3)(t_6 - t_2)(t_7 - t_1) \\
& + (t_6 - t_4)(t_7 - t_3)(t_2 - t_1) + (t_7 - t_5)(t_1 - t_4)(t_2 - t_3) \\
& + (t_1 - t_6)(t_2 - t_5)(t_3 - t_4) \qquad (27)
\end{aligned}
$$

For the ligand partitions of the polarized heptagon illustrated in fig. 3, only the corresponding chirality polynomial (eq. (26) or (27)) does not vanish identically, making it possible, in principle, to determine the corresponding ligand parameters from pseudoscalar measurements on sets of the same type of polarized heptagon molecule having the specific degree 3 chiral ligand partition of interest.

(9) CHIRALLY DEGENERATE REGULAR POLYHEDRA

The octahedron, cube, and icosahedron are all examples of chirally degenerate skeletons, namely skeletons having two or more lowest degree chiral ligand partitions. The only chiral ligand partitions for the regular octahedron (table 1) are the degree 6 (2^3) and (31^3) chiral ligand partitions. The corresponding degree 6 chirality polynomials for the octahedron are the same as the chirality polynomials given above in eqs. (24c) and (24d) for the same ligand partitions of the trigonal prism in terms of the degree 3 generating polynomials $f(x_n)$, $g(x_n)$, and $h(x_n)$ (eqs. (25a), (25b), and (25c), respectively) measuring the effects of the three σ_h separating reflection planes, the four C_3 axes, and the three C_4 axes, respectively. Two sets of ligand parameters are thus sufficient for a qualitatively complete chirality polynomial for the octahedron. The set of chiral ligand partitions for the cube is much more complicated, so that 16 different sets of ligand parameters are necessary for a full qualitatively complete chirality polynomial, thereby making such a polynomial intractable. However, many of these components of such a qualitatively complete chirality polynomial vanish identically when the ligand partition of the cube has some symmetry analogous to what is noted above for the trigonal prism skeleton. The chirality polynomials for the lowest degree chiral ligand partitions (4^2) and (521) of the cube can be expressed as

$$X(4^2)(O_h) = -2g(s_n) \tag{28a}$$

$$X(521)(O_h) = f(s'_n) - 2g(s'_n), \tag{28b}$$

where $f(x_n)$ and $g(x_n)$ are the degree 4 generating polynomials

$$\begin{aligned} f(x_n) = {} & (x_1 - x_7)^2 [(x_2 - x_5)(x_3 - x_6) - (x_4 - x_5)(x_3 - x_8)] \\ & - (x_2 - x_8)^2 [(x_1 - x_3)(x_4 - x_5) - (x_3 - x_6)(x_5 - x_7)] \\ & - (x_3 - x_5)^2 [(x_1 - x_6)(x_2 - x_4) - (x_6 - x_8)(x_4 - x_7)] \\ & + (x_4 - x_6)^2 [(x_1 - x_8)(x_2 - x_5) - (x_3 - x_8)(x_2 - x_7)] \end{aligned} \tag{29a}$$

$$\begin{aligned} g(x_n) = {} & (x_1 - x_3)(x_2 - x_7)(x_6 - x_8)(x_5 - x_4) \\ & - (x_1 - x_8)(x_2 - x_4)(x_6 - x_3)(x_5 - x_7) \end{aligned} \tag{29b}$$

measuring the effects of the four S_6 and the C_4 axes, respectively, of the cube. The qualitatively complete chirality polynomial for the regular icosahedron is so complicated that 1176 sets of ligand parameters are theoretically necessary for the full polynomial (table 1). The icosahedron is fourfold chirally degenerate, with the degree 4 (84) and (921) chiral ligand partitions each appearing twice as the lowest degree chiral ligand partitions. A degree 4 chirality polynomial corresponding to all four of these lowest degree chiral ligand partitions of the icosahedron can be expressed as a sum of 120 products of two squared differences between ligand parameters, of which 60 such products have the form p^2m^2 and the other 60 products have the form p^2o^2, where p, m and o represent differences between parameters for pairs of ligands in antipodal (para), nonadjacent nonantipodal (meta), and adjacent (ortho) positions, respectively, of the icosahedron [19]. The validity of this chirality polynomial, however, assumed that the same set of ligand parameters can be used for all four lowest degree chiral ligand partitions contributing to this polynomial, in contradiction to the general ideas outlined in this paper and in more detail in the original Ruch/Schönhofer paper [2]. However, if this simplifying assumption is not made, the chirality polynomial for the icosahedron is clearly intractable, even for the most symmetrically substituted chiral icosahedra.

6. Hyperchirality

in 1976, Dugundji, Marquarding and Ugi (DMU) introduced the idea of hyperchirality in a very detailed paper [6]. They defined a hyperchiral family as a set of all distinct permutation isomers which have in common the same group of ligand permutations representing the rotations, and also have in common that coset of ligand permutations which represent the conversion of each isomer into its respective enantiomer. They suggest the existence of pseudoracemic pairs of non-enantioneric hyperchiral permutation isomers whose chirality observations have the same absolute value but opposite algebraic signs. These ideas of hyperchirality provoked considerable controversy in the literature [7–11] shortly after their publication. The present author has reexamined this controversy and arrived at the following conclusions:

(1) There appears to be nothing significantly incorrect with the rather elegant ideas of permutation group theory presented in the original DMU hyperchirality paper [6].

(2) There is, however, a major flaw in the application of chirality algebra to the hyperchiral systems in the DMU paper [6]. The authors incorrectly assume that isomers having the same group of ligand permutations must necessarily give the same chirality functions, thereby predicting the same absolute value for a given pseudoscalar measurement. In making this incorrect assumption, DMU ignore the need for different sets of ligand parameters for each orbit of an intransitive skeleton and for each component of a qualitatively complete chirality polynomial corresponding to different chiral ligand partitions, such as the two or more lowest degree chiral ligand partitions of a chirally degenerate skeleton. Examination of the hyperchiral skeletons discussed by DMU (table 3 and fig. 4) reveals that most of them, including those of greatest chemical significance, are either intransitive (e.g. sulfurane, puckered cyclobutane,

Table 3

Skeletons having hyperchiral families, discussed by Dugundji, Marquarding and Ugi (DMU)[a, b]

Skeleton	Number in DMU paper[a]	Point group symmetry	Number of sites	Number of orbits	Site partition	Chemical examples
Sulfurane	23	C_{2v}	4	2	(2^2)	SF_4 derivatives (sulfuranes)
4-bladed propeller	26	S_4	4	1	(4)	Spiroalkanes in DMU paper, but see text
Polarized pentagon	30	C_{5v}	5	1	(5)	$C_5H_5Mn(CO)_3$ derivatives
Polarized heptagon	31	C_{7v}	7	1	(7)	$C_7H_7V(CO)_3$ derivatives
Planar cyclobutane	27	D_{4h}	8	1	(8)	Planar cyclobutane derivatives
Puckered cyclobutane	32	D_{2d}	8	2	(4^2)	Actual cyclobutane derivatives
Rigid propane	29	C_{2v}	8	4	(2^4)	Propane derivatives
Norbornanone	43	C_{2v}	8	2	(4^2)	Norbornanone derivatives
Staggered metallocene	33	D_{5d}	10	1	(10)	Rigid ferrocene derivatives

[a] See J. Dugundji, D. Marquarding and I. Ugi, Chem. Scripta 9(1976)74, for a more detailed description of these skeletons.
[b] These skeletons are depicted in fig. 4.

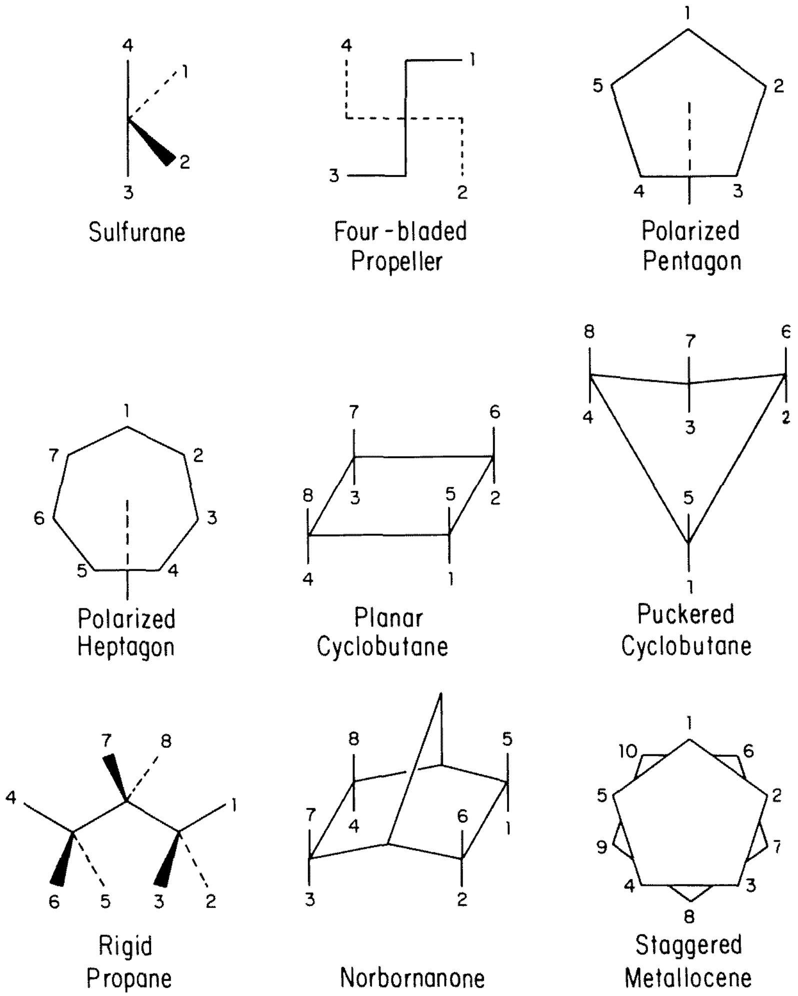


Fig. 4. The nine skeletons having non-trivial hyperchiral families listed in table 3 and discussed by Dugundji, Marquarding and Ugi (DMU) [6].

rigid propane, norbornanone) or chirally degenerate (e.g. polarized pentagon, polarized heptagon, staggered metallocene) and thus require more than one set of ligand parameters, even for the lowest degree chirality polynomials. In general, this required use of different sets of ligand parameters leads to different chirality polynomials for pseudoracemic pairs of non-enantiomeric hyperchiral permutation isomers. This leaves only the S_4 four-bladed propeller and the D_{4h} planar cyclobutane as transitive chirally non-degenerate skeletons having non-trivial hyperchirality families. Neither of these two skeletons is chemically relevant, since the four-bladed propeller does not fully represent the symmetry of spiroalkanes and cyclobutanes are not planar. Thus, this simple analysis of the hyperchiral skeletons discussed by DMU (table 3 and fig. 4) indicates that hyperchirality is not likely to have any experimentally observable consequences, and therefore is physically irrelevant.

7. Summary and outlook

Chirality algebra uses ideas from permutation group theory and group representation theory to derive chirality polynomials having appropriate transformation properties for estimation of the magnitude and sign of a given pseudoscalar property for a given skeleton, using parameters which depend only upon the ligands located at the specific sites of the skeleton, the particular skeleton, and the particular pseudoscalar property. For all but the simplest skeletons, a qualitatively complete chirality polynomial, describing all chirality phenomena associated with the skeleton, contains more than one component and thus requires more than one set of ligand parameters. Chirality polynomials can provide useful semi-empirical estimates of experimental optical rotation and circular dichroism data for molecules based on certain simple skeletons, particularly skeletons having only three or four sites and each reflection plane passing through all but two sites (i.e. "shoe-like" skeletons) such as the methane, allene, 2,2′-spirobiindane, phosphine, and phosphine oxide skeletons. However, for more complicated skeletons, the number of required independent sets of ligand parameters for a qualitatively complete chirality polynomial can present a major obstacle to their application for the estimation of experimental chirality measurements. In addition, attempts to apply even a qualitatively complete chirality polynomial to the estimation of experimental optical rotation and circular dichroism data for [2,2]-metacyclophanes [26–28], based permutationally on the relatively simple polarized rectangle skeleton, reveal aspects of chirality phenomena in these systems which are not adequately approximated by chirality polynomials derived using only group-theoretical ideas such as those outlined in this paper.

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