CHEMICAL APPLICATIONS OF TOPOLOGY AND GROUP THEORY. XXI: CHIRALITY IN TRANSITIVE SKELETONS AND QUALITATIVE COMPLETENESS [1]

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Abstract

This paper unifies the following ideas for the study of chirality polynomials in transitive skeletons: (1) Generalization of chirality to permutation groups not corresponding to three-dimensional symmetry point groups leading to the concepts of signed permutation groups and their signed subgroups; (2) Determination of the total dimension of the chiral ligand partitions through the Frobenius reciprocity theorem; (3) Determination of signed permutation groups, not necessarily corresponding to three-dimensional point groups, of which a given ligand partition is a maximum symmetry chiral ligand partition by the Ruch−Schönhofer partial ordering, thereby allowing the determination of corresponding chirality polynomials depending only upon differences between ligand parameters; such permutation groups having the point group as a signed subgroup relate to qualitative completeness. In the case of transitive permutation groups on four sites, the tetrahedron and polarized square each have only one chiral ligand partition, but the allene and polarized rectangle skeletons each have two chiral ligand partitions related to their being signed subgroups of the tetrahedron and polarized square, respectively. The single transitive permutation group on five sites, the polarized pentagon, has a degenerate chiral ligand partition related to its being a signed subgroup of a meta-cyclic group with 20 elements. The octahedron has two chiral ligand partitions, both of degree six; a qualitatively complete chirality polynomial is therefore homogeneous of degree six. The cyclopropane (or trigonal prism or trigonal anti-prism) skeleton is a signed subgroup of both the octahedron and a twist group of order 36; two of its six chiral ligand partitions come from the octahedron and two more from the twist group. The polarized hexagon is a signed subgroup of the same twist group but not of the octahedron and thus has a different set of six chiral ligand partitions than the cyclopropane skeleton. Two of its six chiral ligand partitions come from the above twist group of order 36 and two more from a signed permutation group of order 48 derived from the $P_3[P_2]$ wreath product group with a different assignment of positive and negative operations than the octahedron.

1.   Introduction

A number of chemically significant phenomena such as optical rotation and circular dichroism relate to *pseudoscalar measurements*, which give real numbers having the following two properties:

(1) They depend upon the measured object but not its spatial orientation;
(2) They have opposite signs for mirror images such as the two enantiomers of a chiral molecule.

This interest in pseudoscalar measurements has led to the geometrical and algebraic study of chirality [2−8]. Such studies have the following objectives:

(1) Determination of the ligand partitions for a given molecular skeleton which lead to chiral systems, namely how asymmetrical must a ligand partition be before all improper rotation symmetry elements S_n (including reflection planes $S_1 \equiv \sigma$ and inversion centers $S_2 \equiv i$) of an achiral skeleton are destroyed.
(2) Determination of mathematical functions (chirality functions) by which the magnitude and sign of a given pseudoscalar property (the dependent variable) can be calculated for a given skeleton using parameters which depend only upon the ligands located at specific sites on the skeleton (the independent variables).

Chirality algebra dissects a molecule into a collection of ligands and an underlying skeleton. A molecule with a monocentric skeleton may be represented as ML_n, in which M is a metal or other central atom and the n ligands L may or may not be equivalent. Polycentric skeletons such as allene and cyclopropane are also of interest and can be analogously represented. In this paper, as well as in a previous paper by King [8], the ligands L are assumed to be *achiral*.

The previous paper by King [8] on chirality relates chirality functions to framework groups [9], a method for describing the symmetry of skeletons having a finite number of sites. In this connection, the sites in a given skeleton may be divided into orbits, where sites in a given orbit are symmetry equivalent, namely interchangeable by a symmetry operation of the skeleton. A skeleton in which all sites are symmetry equivalent thus has only one orbit and is called a *transitive* skeleton. The chirality functions for transitive skeletons are the basic building blocks for chirality functions of all skeletons, since the chirality function of a given intransitive skeleton is the product of a chirality function of its individual orbits which correspond to transitive subskeletons having a smaller number of sites [8].

This paper presents a number of details which are important in understanding various aspects of chirality algebra in the limited number of transitive skeletons having six or less sites. These include the most important skeletons for building chiral molecules such as methane, allene, and cyclopropane derivatives; cyclobutadiene, cyclopentadienyl, and benzene metal complexes; and octahedral metal complexes. In addition, signed permutation groups and their signed subgroups are defined which relate to qualitatively complete chirality polynomials.

2.   Groups and generators

Certain elements of a given discrete group G form a set of its *generators* if every element of G is expressible as a finite product of their (positive or negative) powers [10]. A set of relations satisfied by the generators of G is called a *presentation* of G if *every* relation satisfied by the generators is an algebraic consequence of the particular relations of the presentation. The presentations of the permutation groups of the transitive skeletons of interest are given in table 1. More extensive listings of the presentations of all possible distinct permutation groups of up to seven objects are given by Miller [11]; a similar listing of presentations of all possible distinct permutation groups on eight objects is given by Burns [12]. A much more recent listing of all *transitive* groups on up to eleven objects and their generators is given by Butler and McKay [13].

In order to extend the concept of chirality to the presentations of permutation groups, a sign (positive or negative) must be assigned to each group element so that the identity operation is positive and the following symbolic relationships are satisfied:

$$(+)(+) = (+) \tag{1a}$$

$$(+)(-) = (-) \tag{1b}$$

$$(-)(-) = (+). \tag{1c}$$

The process of assigning signs to group elements satisfying (1a)–(1c) describes a homomorphism from G to the cyclic multiplicative group on the two elements $(1, -1)$, namely the Z_2 group. A permutation group having such sign assignments for each element is a *signed permutation group*. In signed permutation groups corresponding to three-dimensional point groups, the positive group elements are the proper rotations including the identity and the negative group elements are the improper rotations including an inversion center and reflection planes. In general, a given presentation of a permutation group may admit more than one self-consistent sign assignment satisfying eqs. (1a)–(1c). Thus, the permutation groups of the polarized square and allene skeletons in table 1 have the same presentation but different sign assignments relating to the fact that the operation of period four (ab in table 1) is a proper rotation (C_4) in the polarized square, but an improper rotation (S_4) in the allene skeleton. Also, alternative sign assignments are possible for the presentation of the octahedron (e.g. a negative and b positive in table 1), but these do not correspond to actual point groups.

The signed permutation group of an *achiral* skeleton contains equal numbers of positive and negative elements. The positive elements form a *chiral* subgroup of index two. Introduction of nonequivalent ligands at the sites of the achiral skeleton in

Table 1

Transitive permutation groups having three to six sites corresponding to three-dimensional point and framework groups

Skeleton	Sites	Symmetry operations	Point group	Framework group	Presentation
Polarized triangle	3	6	C_{3v}	$C_{3v}[3\sigma_v(L)]$	$a^2 = b^2 = (ab)^3 = 1$; a, b neg
Tetrahedron	4	24	T_d	$T_d[4C_3(L)]$	$a^2 = b^3 = (ab)^4 = 1$; a neg; b pos
Polarized square	4	8	C_{4v}	$C_{4v}[2\sigma_v(L_2)]$	$a^2 = b^2 = (ab)^4 = 1$; a, b neg
Allene	4	8	D_{2d}	$D_{2d}[2\sigma_d(L_2)]$	$a^2 = b^2 = (ab)^4 = 1$; a neg; b pos
Polarized rectangle	4	4	C_{2v}	$C_{2v}[X(L_4)]$	$a^2 = b^2 = (ab)^2 = 1$; a, b neg
Polarized pentagon	5	10	C_{5v}	$C_{5v}[5\sigma_v(L)]$	$a^2 = b^2 = (ab)^5 = 1$; a, b neg
Octahedron	6	48	O_h	$O_h[3C_4(L_2)]$	$a^2 = b^6 = (ab^2)^4 = (ab^3)^2 = 1$; a pos; b neg
Polarized hexagon	6	12	C_{6v}	$C_{6v}[3\sigma_v(L_2)]$	$a^2 = b^2 = (ab)^6 = 1$; a, b neg
Cyclopropane	6	12	D_{3h}	$D_{3h}[3C_2(L_2)]$	$a^2 = b^2 = (ab)^6 = 1$; a neg; b pos

general reduces the symmetry of the system by destroying some of the symmetry elements of the unlabeled skeleton. The resulting smaller signed permutation group can still contain equal quantities of positive and negative elements (an achiral group) or only positive elements (a chiral group). In this abstract manner, chirality can be studied without using the concepts of proper and improper rotations. This allows the extension of the concept of chirality to permutation groups not isomorphic to three-dimensional point groups. An example of such a permutation group is the order 72 $P_2[P_3]$ wreath product auromorphism group of the non-planar $K_{3,3}$ bipartite graph.

Permutation groups may also be characterized by their cycle indices [14] $Z(G)$, which are polynomials of the form

$$Z(G) = \frac{1}{|G|} \sum_{i=1}^{i=c} a_i x_1^{c_{i2}} x_2^{c_{i2}} \dots x_n^{c_{in}} . \tag{2}$$

In eq. (2) the terms and indices have the following significance:

$|G| =$ number of elements in the permutation group,

$n =$ number of sites in the permutation group,

$c =$ number of terms in the cycle index,

$a_i =$ number of elements in the permutation group having the indicated cycle structure,

$x_k =$ dummy variable referring to cycles of length k,

$c_{ik} =$ exponent indicating the number of cycles of length k in term i.

Signed permutation groups may be characterized analogously by their *signed cycle indices*, in which each term is preceded by a plus or minus sign depending upon whether the term corresponds to a positive or negative element of the corresponding permutation group. The signed cycle index $Z^{\pm}(G)$ thus may be expressed as follows:

$$Z^{\pm}(G) = \frac{1}{|G|} \sum_{i=1}^{i=c} (\text{sgn}) a_i x_1^{c_{i1}} x_2^{c_{i2}} \dots x_n^{c_{in}} , \tag{3}$$

where

$(\text{sgn}) = +$ if the group element is positive

$(\text{sgn}) = -$ if the group element is negative.

By way of illustration, the signed cycle indices for the polarized square and allene permutation groups are listed below:

(A) *Polarized squares*

$$Z^{\pm}(G) = \frac{1}{8}(x_1^4 + 2x_4 + x_2^2 - 2x_1^2 x_2 - 2x_2^2) \tag{4}$$

(B) *Allene skeleton*

$$Z^{\pm}(G) = \frac{1}{8}(x_1^4 - 2x_4 + x_2^2 - 2x_1^2 x_2 + 2x_2^2). \tag{5}$$

Note that the signed cycle indices $(Z^{\pm}(G)$ from eq. (3)) for these two distinct skeletons are different, whereas the regular cycle indices $(Z(G)$ from eq. (2)) are identical. Thus, signed cycle indices $Z^{\pm}(G)$ provide more information than ordinary cycle indices $Z(G)$ and this additional information is essential for the study of chirality. Furthermore, in the case of achiral point groups the signed cycle index as defined by eq. (3) corresponds to the generalized character cycle index [15−17] for the antisymmetric irreducible representation A^- having $+1$ characters for all proper rotations and -1 characters for all improper rotations. For brevity, the factor $1/|G|$ will be omitted from cycle indices and signed cycle indices in this paper.

An element of a permutation group *may* be assigned a sign (positive or negative) as outlined above but *must* have a *parity* (even or odd). Thus, the parity of a permutation is odd or even depending upon whether the *total* number of cycles of *even* length in the permutation is odd or even, respectively. Equivalently, the parity of a permutation is odd or even depending upon whether the number of two-site transpositions in the permutation is odd or even, respectively [18]. Such an assignment of odd and even parities to elements of a permutation group G describes another homomorphism from G to Z_2.

A permutation group must contain either only even permutations or equal numbers of even and odd permutations. In an ordinary signed permutation group, all positive elements (namely, proper rotations in three-dimensional point groups) are even permutations and all negative elements (namely, improper rotations in three-dimensional point groups) are odd permutations; if this is not the case, the signed permutation group is *extraordinary*. (In a previous paper [8], ordinary groups were called normal, but this terminology can be confusing since a normal subgroup, discussed below, refers to a totally different concept.) The signed permutation groups of the tetrahedron and allene skeletons are ordinary and those of the polarized square, polarized rectangle, polarized pentagon, and octahedron skeletons are extraordinary. Extraordinary signed permutation groups may be characterized by the *anomalous* terms in their signed cycle indices, where an anomalous term is a positive term corresponding to an odd permutation or a negative term corresponding to an even permutation.

The assignment of signs to each element of a permutation group to give a signed permutation group provides a method for defining a new type of subgroup relationship. Thus, a signed permutation group H is a *signed subgroup* of a signed permutation group G if all of the operations of H are contained in G *with the same signs*. In order for a group H to be a signed subgroup of group G, the signed cycle index of G, $Z^{\pm}(G)$, must contain *with the proper sign* (but not necessarily the same numerical coefficient) each term in the signed cycle index of H, $Z^{\pm}(H)$. Thus, any anomalous terms in the signed cycle index of H must be found in the signed cycle index of any group G of which H is a signed subgroup. For this reason, the anomalous terms of the signed cycle indices of signed permutation groups are convenient indi- ators of possible signed subgroup relationships important for the study of qualitative mpleteness in chirality functions.

It is instructive to compare the properties os signed subgroups with those of ormal subgroups. A signed permutation group K is a *normal* subgroup of a signed permutation group G if K consists only of *complete* conjugacy classes of G [19]. In order for a group K to be a normal subgroup of group G, the signed cycle index of G, $Z^{\pm}(G)$, must contain each term in the signed cycle index of K, $Z^{\pm}(K)$, with the proper sign and generally the same numerical coefficient. An exception to the latter condition can occur when a single signed cycle index term of G corresponds to two or more classes of elements having the same cycle structure. Note that all normal subgroups of G are signed subgroups. However, not all subgroups of G are signed subgroups and not all signed subgroups of G are normal subgroups.

The following groups are significant in the study of the chirality algebra of an *achiral* skeleton having n sites:

P_n : the symmetric group on n sites having $n!$ elements.

G : the three-dimensional symmetry point group of the skeleton.

R : the subgroup of index 2 in the achiral G consisting of only its proper rotations (positive elements).

N : the normalizer of G in P_n, namely the largest subgroup of P_n containing G as a *normal* subgroup. This defines the total permutations of a set of isomers whose symmetry point groups contain exactly the same set of ligand permutations and has led to the mathematically interesting [6,20] but physically dubious [21–23] concept of "hyperchirality".

M : a *maximum* symmetry signed permutation group on n objects which has the *least* symmetrical chiral ligand partition of G as its *most* symmetrical chiral ligand partition using the Ruch–Schönhofer partial ordering relating to the degree of the corresponding chirality polynomial. This relates to the concept of qualitative completeness [4,5] and a similar group can be defined for the concept of qualitative supercompleteness [7].

Since G is a normal subgroup of N, N can be expressed as the semidirect product [24,25]

$$N = G \wedge N/G = G \wedge H. \tag{6}$$

In a few but not all cases, the signed subgroup G is also a normal subgroup of M so that M can also be expressed as a semidirect product

$$M = G \wedge M/G = G \wedge C. \tag{7}$$

The group H contains one element corresponding to each diastereomer ("member of a hyperchiral family" [6]) having the same set of ligand permutations in its symmetry point group and therefore the same chirality polynomial. The group C, when it exists, contains one element corresponding to each diastereomer which, when present in equal quantities in the set of diastereomers represented by C, leads to a mixture for which the lowest degree of chirality polynomial vanishes identically [4,5]. A major portion of the confusion in the literature arises from the fact that N and M and thus H and C are defined very differently, and thus are not necessarily the same. Thus, G must be a normal subgroup of N but may be only a signed subgroup of M.

The relationship between the groups P_n, G, R, N, M, H, and C for an achiral skeleton can be summarized by the following scheme:
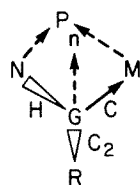

Fig. 1.

In this scheme, a dotted arrow represents a subgroup relationship which *cannot* be normal for $n \geqslant 5$, a solid arrow represents a signed subgroup relationship which can or cannot be normal, a wedge represents a subgroup relationship which *must* be normal, and the groups indicated next to the wedges and the solid arrow are the corresponding quotient groups [see eqs. (6) and (7)].

3.   Isomer count and group representation theory

Consider a skeleton having n sites. The number of permutations of these n sites is $n!$ These permutations may be partitioned into $n!/|R|$ sets of $|R|$ permutations each, where $|R|$ is the order of the proper rotation subgroup of the skeleton. The number $n!/|R|$ is, of course, the *isomer count* I of the skeleton [26–28]. This section uses group representation theory [25,29] to relate the isomer count to the sum of the dimensions of the chiral representations which, in turn, are closely connected with chiral ligand partitions and chirality functions. Some related ideas are presented rather differently elsewhere [5,25]. In this section, subgroup relationships are *not* signed.

A chirality function has the property that it is unaffected by ligand permutations corresponding to proper rotations (i.e. positive permutation group elements) but undergoes a change in sign with no change in absolute value with ligand permutations corresponding to improper rotations (i.e. negative permutation group elements). 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, namely $X(G, A^-, C_n) = +1$, and -1 characters for all improper rotations, namely $X(G, A^-, S_n) = -1$.

Consider the point group G of a skeleton having n sites as a subgroup of the corresponding symmetric group P_n. In order to determine which of the irreducible representations Γ_r of P_n correspond to chiral ligand partitions, the standard procedure [5] involves subduction [25,29] of these representations of P_n by its subgroup G. The characters of the subduced representation Γ_r, namely $X(P_n, \Gamma_k, g)|_G$ for the operations g in G contained in P_n, are equal to the characters of the corresponding representation and operation in P_n using the cycle partitions of the symmetry operations in G and permutations in P_n as a basis for comparison. In general, irreducible representations of P_n may lead to *reducible* representations when subduced by G. Such subduced representations may contain the antisymmetric representation A^- which indicates the chirality of the ligand partition corresponding to the irreducible representation of P_n in question.

In order to determine whether the subduced representation contains the antisymmetric representation A^-, standard orthogonality methods [25,29,30] are applied using the following scalar product of two character vectors:

$$\#(A^-)_r = \frac{1}{|G|} [X(G, A^-)] \cdot [X(P_n, \Gamma_r)_G] . \tag{8}$$

In eq. (8), the symbols have the following significance:

$\#(A^-)_r$ = the number of times that the antisymmetric representation A^- appears in the representation of G subduced by the rth irreducible representation Γ_r of P_n.

$|G|$ = the number of operations in G.

$X(G, A^-)$ = a $|G|$-dimensional vector having $+1$ for the coordinates corresponding to proper rotations of G and -1 for the coordinates corresponding to the improper rotations of G corresponding to the definition of the antisymmetric representation A^-.

$X(P_n, \Gamma_k)|_G$ = another $|G|$-dimensional vector having the coordinates $[X(P_n, \Gamma_r, e)|_G, X(P_n, \Gamma_r, g_2)|_G, \ldots, X(P_n, \Gamma_r, g_{|G|})|_G]$, where e is the identity operation of G and $g_2, g_3, \ldots, g_{|G|}$ are the remaining (non-identity) operations of G listed in the same order as in $X(G, A^-)$.

In order to obtain all of the chiral ligand partitions of the skeleton in question, eq. (8) must be applied successively to all irreducible representations of P_n as indexed by r. This separately tests all possible ligand partitions for chirality

This method is actually the most convenient method if specific information on chiral ligand partitions is sought, such as might be required for construction of specific chirality functions. However, if the objective is only to obtain some insight regarding the variety of chiral representations (chiral ligand partitions) through a parameter that might be called the chiral dimensionality X_d, then a further mathematical analysis of the problem suggests a more direct approach.

The characters $X(P_n, \Gamma_r, g)|_G$ appearing as components in the character vector $X(P_n, \Gamma_r)|_G$ used in eq. (8) arise from subduction of an irreducible representation Γ_r of the symmetric group P_n by its subgroup G. The opposite process is possible, namely *induction* of a representation Λ of G into the larger group P_n of which G is a subgroup. Gorenstein [29] provides a useful summary of this induction process. Let a_i, $1 \leqslant i \leqslant |G|$, be a complete set of coset representatives of G in P_n. Let Λ be a representation of G and let its dimension be d. The definition of Λ can be extended to all of P_n by setting p equal to the $d \times d$ zero matrix for all permutations p found in P_n but not in G. The following equation is then used to define a map Λ^*:

$$p\Lambda^* = ((a_i \, pa_j^{-1})\Lambda) \quad p \in P_n. \tag{9}$$

Thus, $p\Lambda^*$ is a $|G| \times |G|$ matrix of blocks whose (i, j)th entry is the $d \times d$ matrix $(a_i \, pa_j^{-1})\Lambda$. In general, we call Λ^* the representation of P_n *induced* by the representation Λ of G. The characters of the induced representation can be found using the following formula [25,29] after setting $X(G, \Lambda, p) = 0$ for permutations of p of P_n *not* found in G:

$$X(P_n, \Lambda^\star, p) = \frac{1}{|G|} \sum_{u \in P_n} X(G, \Lambda, upu^{-1}) \text{ for all } p \text{ in } P_n. \tag{10}$$

Furthermore, the dimension of a representation $\Lambda^\star$ of P_n induced by a representation Λ of G can be found using the following equation, since $|P_n| = n!$:

$$\dim \Lambda^\star = \frac{n!}{|G|} \dim \Lambda. \tag{11}$$

Scalar products of character vectors are useful for determining the irreducible representations contained in a reducible representation according to the orthogonality relationships as exemplified by eq. (8). The Frobenius reciprocity theorem [25,29] relates such character vector products involving subduced and induced characters, as represented by the following equation using the notation introduced above and referring to the case of interest in this work in which symmetry point group G is a subgroup of the symmetric group P_n:

$$\left\{ [X(G, \Lambda)] \cdot [X(P_n, \Gamma_r)|_G] \right\}_G = \left\{ [X(P_n, \Lambda^\star)] \cdot [X(P_n, \Gamma_r)] \right\} P_n. \tag{12}$$

Now let Λ be the antisymmetric representation A^-. Then combining eqs. (8) and (12) shows the equivalence of the following procedures:

(1) Subduction: Determination of the number of times that the antisymmetric irreducible representation A^- of the point group G appears in the representation Γ_r of P_n subduced by G as represented in eq. (8). Note that in general the irreducible representation Γ_r of P_n becomes reducible after subduction by G.

(2) Induction: Determination of the irreducible representations Γ_r of P_n which occur in the representation $A^{-\star}$ of P_n induced by the irreducible representation A^- of the point group G.

Now consider the dimensionality of the induced representation $A^{-\star}$. Since the antisymmetric representation A^- is always one-dimensional, eq. (11) indicates that the dimensionality of $A^{-\star}$ is $n!/|G|$. This means that the sum of the dimensions of the irreducible representations Γ_r of P_n contained in $A^{-\star}$ (i.e. the representations Γ_a corresponding to chiral ligand partitions) must also be $n!/|G|$. Note the close relationship of this quantity to the isomer count $I = n!/|R|$ discussed above. For an achiral framework group, $n!/|G| = I/2 = n!/|R|$ since $|G| = 2|R|$. The quantity $n!/|G|$ thus corresponds to the number of enantiomer pairs when all n sites of the skeleton have different ligands and may be called the *chiral dimensionality* X_d. The

chiral dimensionality rapidly increases as the number of sites n increases, indicating that the set of chiral ligand partitions also rapidly becomes large and therefore complicated. For example, in the cube, which has eight sites and the O_h point group of order 48, the chiral dimensionality is $8!/48 = 840$, indicating a complicated set of chiral ligand partitions even for this very symmetrical polyhedron. This complicated set of chiral ligand partitions for the cube is listed in one of Ruch and Schönhöfer's papers [4]. For this reason, the detailed discussion of the chiral ligand partitions and chirality polynomials in this paper will be limited to transitive skeletons having no more than six sites.

4.   Chirality polynomials

The subduction procedure outlined above and described in detail elsewhere [5,8] can be used to determine the irreducible representations of the symmetric group corresponding to the chiral ligand partitions for a given skeleton. The sum of the dimensions of these chiral representations must equal the chiral dimensionality $X_d = n!/|G|$; this relationship can be used to check the subduction calculations. Furthermore, a partial ordering of the chiral ligand partitions is possible based on the corresponding Young diagrams [4,5]. This partial ordering corresponds to the degrees of the corresponding chirality polynomials as calculated by a group-theoretical algorithm [6,8] and is used to define the relative symmetries of different ligand partitions throughout this paper. In its most convenient forms [6,8], the group-theoretical algorithm uses the permutations of all operations of the symmetry point group on the skeletal sites, i.e. the permutations of the corresponding framework group [8,9].

Chirality polynomials are most useful is they can express the magnitudes and signs of pseudoscalar properties as functions which depend only upon the *differences* between the parameters assigned to ligands at the various sites of the skeleton in question. By using algebraic invariant theory, Meinköhn [31,32] has shown that only the lowest degree of chirality polynomials for a given skeleton (framework group) are required to have this desirable property of depending only upon the differences between the ligand parameters.

Previous studies of chirality algebra [4,5,8] have focused on identifying the Ruch—Schönhofer maximum symmetry ligand partition making chiral a given achiral skeleton by destroying all of the improper rotation symmetry elements. This relates to calculating the lowest degree chirality polynomial, namely a chirality polynomial which must depend only upon the differences between the ligand parameters [31,32]. This problem can be "inverted" to give the following problem: Find the permutation group on n objects for which a given partition of n ligands is a maximum symmetry chiral ligand partition by the Ruch—Schönhofer partial ordering [4,5], thereby allowing the determination of a chirality polynomial for the ligand partition in question which is required to depend only upon the differences between ligand parameters. This problem has the following aspects of particular interest:

Table 2

Ligand partitions for five sites

Ligand partition	Chirality polynomial degree	Irreducible representation dimension	Signed transitive permutation groups having the ligand partition as a max symmetry chiral ligand partition[a]
(1^5)	10	1	P_5
(21^3)	6	4	(tetrahedron + center)
(2^21)	4	5	(trigonal bipyramid)
(31^2)	3	6	$M_{5''}, D_5$
(32)	2	5	M_5
(41)	1	4	
(5)	0	1	

[a]There is no transitive signed permutation group for which the (21^3) or (2^21) ligand partition is the maximum symmetry chiral ligand partition corresponding to a minimum degree chirality polynomial. In both of these cases, an *intransitive* permutation group is indicated in parentheses having these ligand partitions as the maximum symmetry chiral ligand partition.

Table 3

Transitive signed permutation groups on five and six sites[a]

Butler/McKay label[b]	Other designation[c]	Order	Number of classes	Signed cycle index	Chiral ligand partitions
(A) Five sites					
T5	P_5	120	7	$x_1^5 + 15x_1^3x_2^2 + 20x_1^2x_3 + 24x_5$ $- 10x_1^3x_2 - 20x_2x_3 - 30x_1x_4$	(1^5)
T3	M_5	20	5	$x_1^5 + 5x_1^2x_2^2 + 4x_5 - 10x_1x_4$	$(1^5)+(32)$
T3'	$M_5{}'$	20	5	$x_1^5 + 4x_5 + 5x_1x_4 - 5x_1x_2^2 - 5x_1x_4$	(31^2)
T2	D_5	10	4	$x_1^5 + 4x_5 - 5x_1x_2^2$	$2(31^2)$
(B) Six sites					
T16	P_6	720	11	$x_1^6 + 45x_1^2x_2^2 + 40x_1^3x_3 + 40x_3^2 + 90x_2x_4 + 144x_1x_5$ $- 15x_1^4x_2 - 15x_2^3 - 120x_1x_2x_3 - 90x_1^2x_4 - 120x_6$	(1^6)
T14	$PGL(2,5)$	120	7	$x_1^6 + 15x_1^2x_2^2 + 20x_1^3x_3 + 24x_1x_5$ $- 10x_2^3 - 30x_1^2x_4 - 20x_6$	$(1^6)+(3^2)$
T13	$P_2[P_3]$	72	9	$x_1^6 + 4x_1^3x_3 + 4x_3^2 + 9x_1^2x_2^2 + 18x_2x_4$ $- 6x_1^4x_2 - 12x_1x_2x_3 - 6x_2^3 - 12x_6$	$(1^6)+(2^21^2)$
T13'	$P_2[P_3]'$	72	9	$x_1^6 + 4x_1^3x_3 + 4x_3^2 + 9x_1^2x_2^2 + 6x_2^3 + 12x_6$ $- 6x_1^4x_2 - 12x_1x_2x_3 - 18x_2x_4$	$(21^4)+(2^3)$

Table 3 continued

Butler/McKay label[b]	Other designation[c]	Order	Number of classes	Signed cycle index	Chiral ligand partitions
$T13''$	$P_2[P_3]''$	72	9	$x_1^6 + 4x_1^3x_3 + 4x_3^2 + 9x_1^2x_2^2 + 6x_1^4x_2 + 12x_1x_2x_3 - 6x_2^3 - 12x_6 - 18x_2x_4$	$(3^2) + (51)$
$T11$	$P_3[P_2]$	48	10	$x_1^6 + 9x_1^2x_2^2 + 8x_3^2 + 6x_2x_4 - 3x_1^4x_2 - 7x_2^3 - 6x_1^2x_4 - 8x_6$	$(1^6) + (2^21^2) + (3^2)$
$T11'$	O_h	48	10	$x_1^6 + 8x_3^2 + 3x_1^2x_2^2 + 6x_1^2x_4 + 6x_2^3 - x_2^3 - 8x_6 - 3x_1^4x_2 - 6x_2x_4 - 6x_1^2x_2^2$	$(31^3) + (2^3)$
$T11''$	$P_3[P_2]''$	48	10	$x_1^6 + 3x_1^4x_2 + 3x_1^2x_2^2 + 8x_6 + 8x_3^2 + x_2^3 - 6x_2^3 - 6x_1^2x_2^2 - 6x_1^2x_4 - 6x_2x_4$	$(41^2) + (3^2)$
$T10'$	$P_2[P_3]'/C_2$	36	9	$x_1^6 + 9x_1^2x_2^2 + 4x_1^3x_3 + 4x_3^2 - 18x_2x_4$	$(21^4) + (2^3) + (3^2) + (51)$
$T9$	$P_2[P_3]/C_2$	36	9	$x_1^6 + 9x_1^2x_2^2 + 4x_1^3x_3 + 4x_3^2 - 6x_2^3 - 12x_6$	$(1^6) + (2^21^2) + (3^2) + (51)$
$T9'$	$D_{3h} \times C_3$	36	9	$x_1^6 + 4x_1x_3 + 4x_3^2 + 3x_2^3 + 6x_6 - 9x_1^2x_2^2 - 3x_2^3 - 6x_6$	$(31^3) + (41^2)$
$T8$	$P_3[P_2]/C_2$	24	5	$x_1^6 + 3x_1^2x_2^2 + 8x_3^2 - 6x_2^3 - 6x_1^2x_4$	$(1^6) + (2^21^2) + (41^2) + 2(3^2)$
$T7'$	O_h/C_2	24	5	$x_1^6 + 3x_1^2x_2^2 + 8x_3^2 - 6x_1^2x_2^2 - 6x_2x_4$	$(31^3) + (2^3) + (41^2) + (3^2)$
$T6$		24	8	$x_1^6 + 3x_1^2x_2^2 + 8x_3^2 - x_2^3 - 3x_1^4x_2 - 8x_6$	$(1^6) + (2^21^2) + (31^3) + (2^3) + (3^2)$

Table 3 continued

Butler/McKay label[b]	Other designation[c]	Order	Number of classes	Signed cycle index	Chiral ligand partitions
T5		18	9	$x_1^6 + 4x_1^3 x_3 + 4x_3^2 - 3x_2^3 - 6x_6$	$(1^6) + (2^2 1^2) + (31^3) + (41^2) + (3^2) + (51)$
T3		12	6	$x_1^6 + 3x_1^2 x_2^2 + 2x_3^2 - 4x_2^3 - 2x_6$	$(1^6) + 2(2^2 1^2) + (321) + 2(3^2) + (41^2) + (51)$
T3'	D_{3h} or D_{3d}	12	6	$x_1^6 + 2x_3^3 + 3x_2^3 - x_2^3 - 3x_1^2 x_2^2 - 2x_6$	$(2^3) + 2(31^3) + (321) + (41^2) + (42)$
T3"	C_{6v}	12	6	$x_1^6 + 2x_3^2 + x_2^3 + 2x_6 - 3x_1^2 x_2^2 - 3x_2^3$	$(2^2 1^2) + (31^3) + (321) + (3^2) + 2(41^2)$

[a] This includes groups *not* corresponding to three-dimensional point or framework groups.
[b] See ref. [13].
[c] P_n = symmetric group, M_n = metacyclic group, $P_n[P_m]$ = wreath product group; different extraordinary signed permutation groups with the same unsigned cycle index are differentiated by primes.

(1)   Solution of this problem provides a group theoretical approach to the search for qualitatively complete chirality polynomials [4,5]. In this context, a chirality polynomial is said to be *qualitatively complete* if there is no nonracemic isomer mixture for which it vanishes identically [5]. The permutation groups M for the *least* symmetrical chiral ligand partitions may define quotient groups [e.g. C of eq. (7)], which in turn define permutations leading to nonracemic isomer mixtures for which lower degree chirality polynomials derived from *more* symmetrical chiral ligand partitions vanish. In these cases, a chirality polynomial derived from a less symmetrical chiral ligand partition must be added to the lowest degree chirality polynomial in order to obtain a qualitatively complete chirality polynomial.

(2)   The permutation group M may *not* always correspond to an actual three-dimensional point group, i.e. a framework group [9] having n sites. Therefore, *all* transitive permutation groups of degree n (i.e. those permuting n objects) [11−13] are potentially important to the study of qualitatively complete chirality functions, not just those realizable as three-dimensional point or framework groups.

(3)   Since the treatment of qualitatively complete chirality functions may require consideration of permutation groups which are not realizable as three-dimensional point or framework groups, the generalization of chirality to signed permutation groups having characteristic signed cycle indices [eq. (3)] is required.

(4)   Signed permutation groups on n objects of which the framework group G is a signed subgroup are important to this treatment, as exemplified by the group M defined above. In order for G to be a signed subgroup of M, the same anomalous terms in the signed cycle index of G must be present in the signed cycle index of M. This facilitates greatly the search for signed permutation groups M that can correspond to ligand permutations leading to nonracemic isomer mixtures for which some chirality polynomials corresponding to G may vanish.

(5)   There are ligand partitions for which there is no possible *transitive* signed permutation group having as its lowest degree chirality polynomial a polynomial corresponding to the ligand partition in question. The simplest such cases are the (21^3) and $(2^2 1)$ ligand partitions on five sites (table 2), which lead to the lowest degree chirality polynomials for the *intransitive* framework groups [9] $T_d[O(L), 4C_3(L)]$ (tetrahedron + center) and $D_{3h}[C_3(L_2), 3C_2(L)]$ (trigonal bipyramid), respectively, but not for any *transitive* signed permutation groups of degree five (table 3).

The general ideas outlined in this section are illustrated in the relatively simple cases of the transitive skeletons with four sites, and are then extended to the more interesting transitive skeletons with five and six sites.

5.   Transitive skeletons having four sites

The four transitive signed permutation groups on four objects have the four non-trivial possible partitions of four ligands as their highest symmetry chiral ligand

partitions by the Ruch–Schönhofer partial ordering [4,5]. Thus, the ligand partitions (1^4), (21^2), (2^2), and (31) corresponding to irreducible representations of the symmetric group P_4 ($\approx T_d$) of dimensions 1, 3, 2, and 3, respectively, are the highest symmetry chiral ligand partitions for the T_d tetrahedron, C_{4v} polarized square, D_{2d} allene, and C_{2v} polarized rectangle, respectively. The ligand partitions (1^4) and (21^2) are the only chiral ligand partitions for the tetrahedron and polarized square in accord with their chiral dimensionalities $X_d = n!/|G|$ of 24/24 = 1 and 24/8 = 3, respectively. However, both the allene and polarized rectangle skeletons have two chiral representations namely (1^4) + (2^2) of total dimension 3 for the allene skeleton $(24/|D_{2d}| = 3)$ and (21^2) + (31) of total dimension 6 for the polarized rectangle skeleton $(24/|C_{2v}| = 6)$. Thus, a single chirality polynomial is qualitatively complete for the tetrahedron or polarized square, whereas two-component chirality polynomials are required in the cases of allene and the polarized rectangle for qualitative completeness. This fundamental point is already recognized in the original papers by Ruch and Schönhofer [4] and Mead [5] on chirality functions. However, the full permutation group theoretical significance of this situation has not been clearly stated.

Consider first the following three permutation isomers having the allene skeleton with the framework group $D_{2d}[2\sigma_d(L_2)]$:
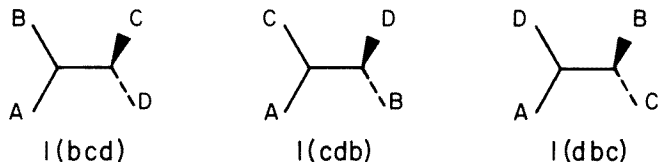

I(bcd)   I(cdb)   I(dbc)

Fig. 2.

These isomers are related by keeping ligand *A* fixed and permuting ligands *B*, *C*, and *D* in a threefold "symmetry" operation. The set of three isomers I(*bcd*), I(*cdb*), I(*dbc*) thus forms a group isomorphic to the cyclic group C_3 based on the ligand permutations required to form a given number of the set from a reference isomer, say I(*bcd*), taken as the identity element of the group.

The lowest degree chirality polynomial corresponding to the (2^2) ligand partition for one of the above isomers, say I(*bcd*), is the following polynomial of degree 2:

$$(2^2)[I(bcd)] = (B - A)(D - C). \tag{13}$$

In eq. (13) and in the following similar equations, the letters representing the ligands are also taken to mean the corresponding chirality polynomial parameters, for brevity and to avoid too many confusing indices.

The chirality polynomial in eq. (13) has a major flaw, namely it vanishes identically for a nonracemic mixture of equal quantities of the three isomers $I(bcd)$, $I(cdb)$, and $I(dbc)$, i.e.

$$X(2^2)[I(bcd) + I(cdb) + I(dbc)] \equiv 0. \tag{14}$$

In order to obtain a chirality polynomial without this flaw, it is necessary to use a polynomial of degree 6 derived from the other chiral ligand partition of the allene skeleton, namely (1^4). However, a chirality polynomial obtained from this chiral ligand partition and the permutations of the D_{2d} symmetry point group of the allene skeleton using the standard group-theoretical algorithm [6,8] will *not* be a function only of the differences between the ligand parameters. In order to obtain a chirality polynomial from the chiral ligand partition (1^4), which must be a function only of the differences between ligand parameters, it is necessary to use the permutations from a group of degree 4 for which the ligand partition (1^4) is the lowest degree chiral ligand partition. This permutation group [M in eq. (7)] is, of course, that of the tetrahedron $T_d \approx P_4$ (table 1). From the ligand partition (1^4) and the permutation group T_d (*not* D_{2d}), the following chirality polynomial of degree 6 is obtained using the standard group-theoretical procedure [6,8]:
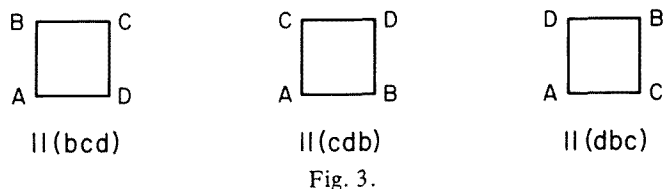
$$X(1^4)[I(bcd)] = (s_2 - s_1)(s_3 - s_1)(s_4 - s_1)(s_3 - s_2)(s_4 - s_2)(s_4 - s_3). \tag{15}$$

In eq. (15) and in similar following equations, a variable s_k represents the parameter of the ligand located at site k of the skeleton.

The chirality polynomial of eq. (15) is familiar as the lowest degree chirality polynomial for a tetrahedral skeleton such as methane. Furthermore, this chirality polynomial does *not* vanish for a nonracemic mixture of equal quantities of the three isomers $I(bcd)$, $I(cdb)$, and $I(dbc)$.

The observations outlined above suggest that T_d plays the role of M and C_3 plays the role of C [see eq. (7)]. The group D_{2d} is a signed subgroup of T_d and represents the symmetry of the allene skeleton. The group C_3 represents the permutations forming the isomers of the nonracemic mixture (i.e. $I(bcd) + I(cdb) + I(dbc)$) for which the lowest degree chirality polynomial of the allene skeleton vanishes. The nonracemic mixture of equal quantities of $I(bcd)$, $I(cdb)$, and $I(dbc)$ has the higher effective permutational symmetry T_d relative to the D_{2d} permutational symmetry of a single isomer, and this higher symmetry is reflected in the form of the chirality polynomial required in order to avoid its vanishing for a nonracemic mixture. In other words, the vanishing of the degree 2 polynomial of eq. (13) for the nonracemic mixture of equal quantities of $I(bcd)$, $I(cdb)$, and $I(dbc)$ is diagnostic of a higher effective symmetry for this system.

It is instructive to compare this property of the allene skeleton with that of the polarized square skeleton, which has (21^2) as its only chiral ligand partition. A set of polarized square isomers analogous to I(bcd), I(cdb), and I(dbc) is the following:

$$\text{II}(bcd) \qquad \text{II}(cdb) \qquad \text{II}(dbc)$$

Fig. 3.

The chirality polynomial corresponding to the (21^2) ligand partition has degree 3 and can be represented as follows:

$$X(21^2)[\text{I}(bcd)] = (s_2 - s_1)(s_4 - s_3)[(s_1 - s_3) + (s_2 - s_4)]. \qquad (16)$$

For a nonracemic mixture of equal quantities of the three isomers II(bcd), II(cdb), and II(dbc), this polynomial has the following value:

$$X(21^2)[\text{II}(bcd) + \text{II}(cdb) + \text{II}(dbc)]$$

$$= 2[(AC + DB)(B - D) + (AD + BC)(C - B) + (AB + CD)(D - C)] \neq 0. \qquad (17)$$

The added $[(s_1 - s_3) + (s_2 - s_4)]$ factor of the degree 3 polynomial (16) prevents eq. (17) from vanishing for the nonracemic mixture of equal quantities of II(bcd), II(cdb), and II(dbc). The single chirality polynomial of eq. (16) is thus qualitatively complete. Note also that the C_{4v} point group of the polarized square is *not* a signed subgroup of the tetrahedron (T_d), since the cycle index term x_4 corresponds to a positive operation (C_4) in C_{4v} but a negative operation (S_4) in T_d.

The remaining transitive skeleton with four sites is the polarized rectangle which has two chiral ligand partitions, namely the degree 1 (31) partition and the degree 3 (21^2) partition. The lowest degree chirality polynomial is therefore the following degree 1 (linear) polynomial:

$$X(31) = (s_1 - s_3) + (s_2 - s_4). \qquad (18)$$

This polynomial, however, vanishes for the nonracemic mixture of equal quantities of the following two isomers:

B ☐ A   C ☐ B
A ☐ C   A ☐ A

III (bac)   III (cba)

Fig. 4.

However, the following degree 3 polynomial from the (21^2) chiral ligand partition [compare eq. (16)] does not vanish for this isomer mixture:

$$X(21^2) \, [\text{III}(bac) + \text{III}(bca)]$$

$$= (B-A)(C-A)[A-A+B-C] + (C-A)(A-B)[A-B+C-A]$$

$$= 2(B-A)(C-A)(B-C). \tag{19}$$

In this connection, note the following:

(1) The ligand partition in the nonracemic isomer pair $\text{III}(bac) + \text{III}(cba)$ is (21^2), in accord with the ligand partition leading to the polynomial in eq. (19).
(2) C_{2v} is a normal subgroup of C_{4v}.
(3) C_{4v} can be represented by the following semidirect product [24,25]:

$$C_{4v} = C_{2v} \wedge C_2. \tag{20}$$

Thus, the groups C_{4v}, C_{2v}, and C_2 correspond to the groups M, G, and C, respectively, in eq. (7).

6.   Transitive skeletons having five sites

There are only four transitive signed permutation groups on five sites (table 2). Furthermore, three of these signed permutation groups do not correspond to framework groups [9] having five sites; these are the following:

(1) The symmetric group P_5 having 120 operations.
(2) The ordinary metacyclic group M_5 having 20 operations and the following signed cycle index:

$$x_1^5 + 5x_1 x_2^2 + 4x_5 - 10x_1 x_4. \tag{21}$$

(3) The extraordinary metacyclic group M_5, having 20 operations and the following signed cycle index:

$$x_1^5 + 4x_5 + 5x_1 x_4 - 5x_1 x_2^2 - 5x_1 x_4. \tag{22}$$

Signed permutation groups on five sites thus represent the simplest examples of the extension of the concept of chirality to permutation groups not corresponding to three-dimensional point groups or framework groups. The two signed metacyclic groups M_5 and M_5, are derived from the same underlying unsigned group but with different assignments of positive and negative operations. They thus have the same cycle index [eq. (2)] but different *signed* cycle indices [eq. (3)]. One of these meta-cyclic groups, M_5, is ordinary and its chiral ligand partitions are the one-dimensional (1^5) partition of the symmetric group P_5 and the five-dimensional (32) ligand parti-tion. The other metacyclic group, M_5, is extraordinary, with the anomalous signed cycle index terms $+5x_1 x_4$ and $-5x_1 x_2^2$ and has a single chiral ligand partition, namely the six-dimensional (31^2). This latter metacyclic group is important in under-standing the chirality polynomials of the single type of *transitive* skeleton having five sites, namely the polarized pentagon. In general, extraordinary signed permutation groups appear to arise more frequently in chirality algebra than related ordinary signed permutation groups.

The only *transitive* signed permutation group on five sites which corresponds to a three-dimensional point group is the polarized pentagon, framework group $C_{5v}[5\sigma_v(L)]$, isomorphic to the D_5 dihedral group and corresponding to, for example, the cyclopentadienyl-manganese tricarbonyl (cymantrene) skeleton. This skeleton has been treated in some detail both in a previous paper [8] and in an earlier paper by Dugundji et al. [6], but also exhibits some other interesting features in the context of the present paper. The polarized pentagon has only one chiral ligand partition, namely the six-dimensional (31^2) partition also found in the extraordinary metacyclic group M_5,. However, the (31^2) chiral ligand partition appears twice in the polarized pentagon. This degeneracy is in accord with its chiral dimensionality of $5!/|C_{5v}| = 12$ and corresponds to two distinctive chiral isomers having the (31^2) ligand partition and depicted as follows:
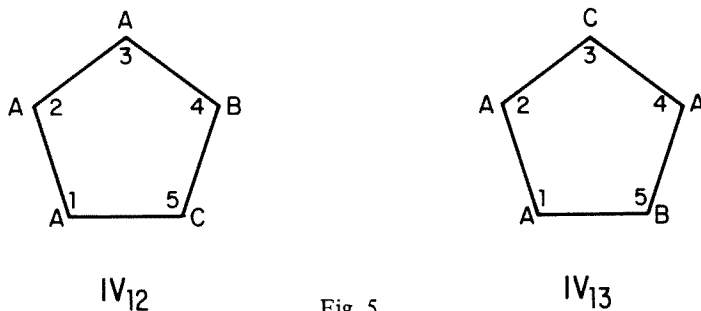

IV$_{12}$ Fig. 5.   IV$_{13}$

Using the standard group-theoretical algorithm [6,8], the following chirality polynomials of degree 3 can be obtained from isomers IV_{12} and IV_{13}, respectively:

$$X(31^2)_{12}(C_{5v})$$

$$= (s_5 - s_1)^3 + (s_1 - s_2)^3 + (s_2 - s_3)^3 + (s_3 - s_4)^3 + (s_4 - s_5)^3 \qquad (23a)$$

$$X(31^2)_{13}(C_{5v})$$

$$= (s_5 - s_2)^3 + (s_1 - s_3)^3 + (s_2 - s_4)^3 + (s_3 - s_5)^3 + (s_4 - s_1)^3. \qquad (23b)$$

However, the polynomial $X(31^2)_{12}(C_{5v})$ [eq. (23a)] vanishes for the chiral isomer IV_{13} and the polynomial $X(31^2)_{13}(C_{5v})$ [eq. (23b)] vanishes for the chiral isomer IV_{12}. Therefore, neither of these chirality polynomials is qualitatively complete. Their sum is qualitatively complete and is equal to the degree 3 polynomial obtained by applying the standard group-theoretical algorithm to either IV_{12} and IV_{13} using the extraordinary metacyclic group $M_{5'}$, which is the signed permutation group generated by the ten symmetry permutations of one C_{5v} isomer and the $x_1 x_4$ cycle index permutation necessary to convert one isomer into the other. The chirality polynomial of the extraordinary metacyclic group $M_{5'}$ can be represented as the following sum:

$$X(31^2)(M_{5'}) = (31^2)(C_{5v})_{12} + (31^2)(C_{5v})_{13}. \qquad (24)$$

Some of these observations on transitive signed permutation groups on five sites are summarized in table 3, particularly the transitive signed permutation groups (table 2) having a given chiral ligand partition as a maximum symmetry chiral ligand partition by the Ruch−Schönhofer partial ordering [4,5].

7. Transitive skeletons having six sites

There are three transitive skeletons having six sites, the octahedron $O_h [3 C_4(L_2)]$ having 48 symmetry operations and a chiral dimensionality of $6!/|O_h| = 720/48 = 15$, and the polarized hexagon $C_{6v}[3\sigma_v(L_2)]$ and cyclopropane skeleton $D_{3h}[3C_2(L_2)]$ (trigonal prism) having 12 symmetry operations and chiral dimensionalities of $720/12 = 60$. The permutation groups of the polarized hexagon and cyclopropane skeletons have the same cycle indices [eq. (2)], but differ in the assignments of positive and negative operations (table 1) and therefore have different signed cycle indices (eq. (3) and table 2). All three of these skeletons are extraordinary and there-

fore cannot contain the fully asymmetric (1^6) chiral ligand partition. Other transitive permutation groups on six sites (table 3) do not correspond to actual point or framework groups.

The octahedron, like the polarized pentagon discussed above, has two chiral ligand partitions of the same degree, namely the degree 6 ligand partitions (31^3) and (2^3) of dimensions 10 and 5, respectively, leading to the required chiral dimensionality of 15, and corresponding to the following two ligand distributions:
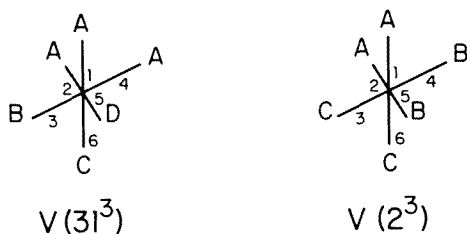
Fig. 6

The degree 6 chirality polynomials for both of the chiral ligand partitions of the octahedron can be expressed in terms of the same three degree 3 polynomials $f(s_n)$, $g(s_n)$, and $h(s_n)$ as follows $(1 \leqslant n \leqslant 6)$:

$$X(2^3) = f(s_n) [g(s_n) + h(s_n)] \tag{25a}$$

$$X(31^3) = f(s_n) [g(s_n) - h(s_n)] , \tag{25b}$$

where

$$f(s_n) = (s_1 - s_6)(s_2 - s_5)(s_3 - s_4) \tag{26a}$$

$$g(s_n) = (s_1 - s_2)(s_2 - s_3)(s_3 - s_1) + (s_3 - s_6)(s_6 - s_5)(s_5 - s_3)$$

$$+ (s_1 - s_5)(s_5 - s_4)(s_4 - s_1) + (s_2 - s_4)(s_4 - s_6)(s_6 - s_2) \tag{26b}$$

$$h(s_n) = (s_1 - s_2 + s_6 - s_5)(s_1 - s_4 + s_6 - s_3)(s_2 - s_4 + s_5 - s_3). \tag{26c}$$

The degree 3 polynomials $f(s_n)$, $g(s_n)$, and $h(s_n)$ measure the effects of the separating [8] reflection planes (σ_h), the threefold rotation axes (C_3), and the fourfold rotation axes (C_4), respectively, of the octahedron on the pseudoscalar properties evaluated by

the chirality polynomial. Because of the same degrees of both chiral ligand partitions of the octahedron, a *homogeneous* qualitatively complete chirality polynomial $X_{QC}[O_h]$ can be expressed as follows:

$$X_{QC}[O_h] = f(s_n)[w_1 g(s_n) + w_2 h(s_n)]. \tag{27}$$

In eq. (27), the coefficients w_1 and w_2 are *weighting* coefficients that control the proportions of $X(31^3)$ and $X(2^3)$ in the homogeneous $X_{QC}[O_h]$. Also the following relationships are found involving $f(s_n)$, $g(s_n)$, and $h(s_n)$, where $O_h \star (a^m b^n c^p \dots)$ schematically indicates the permutations of a monomial of the form $a^m b^n c^p \dots$ under the 48 operations of the octahedral group as when applying the group-theoretical algorithm [6,8]:

$$f(s_n)h(s_n) = -f(s_n)g(s_n) + f(s_n)p(s_n) \tag{28}$$

$$f(s_n)g(s_n) = O_h \star (a^3 b^2 c) + O_h \star (a^2 b^2 cd) \tag{29}$$

$$f(s_n)h(s_n) = -O_h \star (a^3 b^2 c) + O_h \star (a^2 b^2 cd) \tag{30}$$

$$f(s_n)p(s_n) = (2)O_h \star (a^2 b^2 cd) \tag{31}$$

This leads to the following results in accord with the full group-theoretical algorithm for the calculation of the chirality polynomials for the (2^3) and (31^3) chiral ligand partitions of the octahedron:

$$X(2^3) = f(s_n)g(s_n) + f(s_n)h(s_n) = (2)O_h \star (a^2 b^2 cd) \tag{32}$$

$$X(31^3) = f(s_n)g(s_n) - f(s_n)h(s_n) = (2)O_h \star (a^3 b^2 c). \tag{33}$$

The remaining two transitive skeletons having six sites have only 12 symmetry operations and therefore have chiral dimensionalities of 60. Because of these large chiral dimensionalities, the sets of chiral ligand partitions for these skeletons are larger and more complicated than the examples discussed above. Understanding these systems is therefore facilitated by searching for larger signed permutation groups of degree 6 for which the signed permutation groups of these transitive skeletons are signed subgroups. The anomalous terms of the signed permutation groups can serve as a guide for this purpose.

Consider first the skeleton represented by the framework group $D_{3h}[3C_2(\mathbb{L}_2)]$ or the permutationally equivalent $D_{3d}[3\sigma_d(L_2)]$ corresponding to, for example, the cyclopropane skeleton as well as the trigonal prism or antiprism [8]. The anomalous terms in the signed cycle index of the corresponding signed permutation group are $+x_2^3$ and $-x_1^2 x_2^2$ (table 3). The largest signed permutation groups having both of these anomalous terms in their signed cycle indices are the octahedron O_h of order 48, chiral dimensionality $720/48 = 15$, and the chiral ligand partitions (31^3) and (2^3) (see above) and a group designated in table 3 as $T9'$ of order 36, chiral dimensionality $720/36 = 20$, and the ten-dimensional chiral ligand partitions (31^3) and (41^2). The trigonal antiprism or the permutationally equivalent trigonal prism arises by removal of the C_4 axis from the octahedron and is a signed subgroup of the octahedron. The $T9'$ signed permutation group of order 36 is a "twist group" derived from a trigonal prism by adding a threefold twist operation $T3$ of cycle structure $x_1^3 x_3$ in which one of the parallel triangular faces of the trigonal prism is twisted by $120°$ while leaving the other triangular face fixed.

The trigonal prism signed permutation group $D_{3h}[3C_2(L_2)]$ contains no less than the six chiral ligand partitions $(2^3) + 2(31^3) + (321) + (41^2) + (42)$, in accord with its chiral dimensionality of 60. The chiral ligand partitions $(2^3) + (31^3)$ of degree 6 relate to the generation of this signed permutation group by removal of the C_4 axis from the octahedron, whereas the chiral ligand partitions (31^3) and (41^2) of degrees 6 and 3, respectively, relate to the generation of the $D_{3h}[3C_2(L_2)]$ signed permutation group from the twist group $T9'$ by removal of the T_3 twist operation defined above. Thus, reduction of the symmetry to $D_{3h}[3C_2(L_2)]$ adds only two new chiral ligand partitions, namely (321) and (42); the latter leads to the following lowest degree chirality polynomial of degree 2:

$$X(42)\,(D_{3h}) = (s_1 - s_2)\,(s_4 - s_6) - (s_1 - s_3)\,(s_4 - s_5). \tag{34}$$

This chirality polynomial vanishes for the following chiral isomer (VI) having a (31^3) ligand partition, indicating that it is not qualitatively complete:
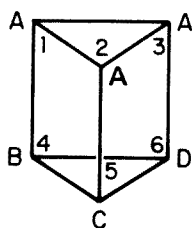

VI

Fig. 7.

This chiral isomer effectively has the twist operation T_3 discussed above as a "symmetry operation", since leaving the bottom BCD face fixed and rotating the top AAA face by $120°$ around the C_3 axis leads to a configuration indistinguishable from the original configuration. This indicates that a chirality polynomial derived from the twist group $T9'$ must be added to the polynomial 34 in order to obtain a qualitatively complete chirality function for the trigonal prism (cyclopropane) skeleton.

Now consider the polarized hexagon skeleton $C_{6v}[3\sigma_v(L_2)]$ which also has chiral dimensionality 60 and six chiral ligand partitions, namely $(2^2 1^2) + (31^3) + (321) + (3^2) + 2(41^2)$. In this case, the anomalous signed cycle index terms are $+x_2^3$, $+x_6$, and $-x_1^2 x_2^2$. The anomalous signed cycle index term $+x_6$ found in $C_{6v}[3\sigma_v(L_2)]$ prevents it from being a signed subgroup of the octahedron for which the x_6 signed cycle index term is not anomalous. However, all three of the anomalous signed cycle index terms in C_{6v} are also present in the twist group $T9'$ (table 3), and indeed the chiral ligand partitions of $T9'$, namely (31^3) and (41^2), are among those found in $C_{6v}[3\sigma_v(L_2)]$. In addition, the polarized hexagon is a signed subgroup of the extraordinary signed wreath product group $T11''$ or $P_3[P_2]''$ (table 3) which has the chiral ligand partitions (41^2) and (3^2). The group $T11''$ is derived from the same unsigned wreath product group $P_3[P_2]$ as the octahedron, but has a different assignment of positive and negative operations (table 3). The reduction of the symmetry to $C_{6v}[3\sigma_v(L_2)]$ adds only two new chiral ligand partitions, namely (321) and $(2^2 1^2)$. The action of the T_3 twist operation of the twist group $T9'$ on a polarized hexagon can be visualized as leaving three alternate vertices (e.g. 1, 3, and 5 in VII below), fixed while rotating the other three vertices through a C_3 operation, thereby leading
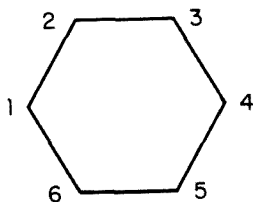
VII

Fig. 8.

to the required $x_1^3 x_3$ cycle index term for the twist operation. The polarized hexagon may also be obtained from the extraordinary wreath product group $P_3[P_2]''$ ($T11''$) by removal of the period four operation $x_2^2 x_4$ (now a negative operation rather than a positive operation in the octahedon O_h or $T11'$) and the $x_1^4 x_2$, $x_1^2 x_2^2$, and $x_2 x_4$ operations generated from it. Thus, the generation of the polarized hexagon from the large groups $T9'$ and $P_3[P_2]''$ is completely analogous to the generation of the trigonal prism $D_{3h}[3C_2(L_2)]$ from the larger groups $T9'$ and O_h ($T11'$).

Table 4

Ligand partitions for six sites

Ligand partition	Chirality polynomial degree	Irreducible representation dimension	Transitive signed permutation groups having the ligand partition as a max symmetry chiral ligand partition
(1^6)	15	1	P_6
(21^4)	10	5	
$(2^2 1^2)$	7	9	$P_2[P_3]$
(31^3)	6	10	O_h
(2^3)	6	5	O_h, $P_2[P_3]'$
(321)	4	16	
(41^2)	3	10	$P_3[P_2]''$, $D_{3h} \times C_3$, O_h/C_2, C_{6v}
(3^2)	3	5	$P_3[P_2]''$, O_h/C_2, C_{6v}
(42)	2	9	D_{3h}, D_{3d}
(51)	1	5	
(6)	0	1	

Some of these observations on transitive signed permutation groups on six sites are summarized in table 4, particularly the transitive signed permutation groups (table 3) having a given chiral ligand partition as a maximum symmetry chiral ligand partition.

8.   Summary

This paper unifies the following ideas from diverse sources for the study of chirality polynomials in transitive skeletons:

(1) The concept of chirality is generalized to permutation groups not corresponding to three-dimensional symmetry point groups by introducing the ideas of signed permutation groups, signed cycle indices, and signed subgroups (sect. 2).

(2) The Frobenius reciprocity theorem [29] provides a basis for determining the total dimension of the set of chiral ligand partitions (chiral dimensionality), thereby indicating the complexity of a qualitatively complete chirality polynomial (sect. 3).

(3) Signed permutation groups of which a given ligand partition is the maximum symmetry chiral ligand partition by the Ruch–Schönhofer partial ordering

[4,5] allow the determination of corresponding chirality polynomials which are required to depend only upon differences between ligand parameters by Meinköhn's algebraic invariant theory [31,32] (sect. 4). Such signed permutation groups need not correspond to actual three-dimensional point groups, thereby making necessary the generalization of chirality noted above. These signed permutation groups relate to the permutations within nonracemic isomer mixtures for which qualitatively *in*complete chirality of insufficient degree can vanish, thereby indicating a higher effective symmetry of such systems. In all cases, the actual symmetry point group of the skeleton must be a signed subgroup of any larger permutation group indicating such higher effective symmetries.

These ideas are illustrated for the limited number of possible transitive skeletons having four (tetrahedron, polarized square, allene, polarized rectangle), five (polarized pentagon), and six (octahedron, cyclopropane, polarized hexagon) sites. All skeletons having seven or more sites have such high chiral dimensionalities that study of their chiral ligand partitions by these methods appears intractably complicated.

Acknowledgements

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