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Substitution symmetry

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Pólya's enumeration theory and its generalizations are refined to count derivatives of symmetrical parent compounds with any specified subsymmetry. Equivalently, enumeration of orbits of mappings, upon which a group acts by acting on their domain and their range, is refined to count orbits with stabilizers in any specified conjugacy class of subgroups.

Key words: Enumeration under group action—symmetry of derivatives—automorphism group of patterns—table of marks

1. Introduction: The problem of substitution symmetry

Suppose that the corners of a cube are to be colored, four of them black, the other four ones white. By inspection one finds seven distinct figures:

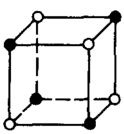

Fig. 1

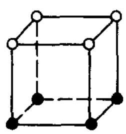

Fig. 2

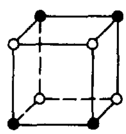

Fig. 3

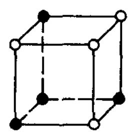

Fig. 4

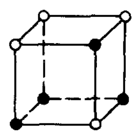

Fig. 5

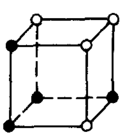

Fig. 6

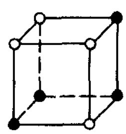

Fig. 7

There are further colorations, of course, but any of these can be transformed into one of the Figs. 1-7 by a suitable proper rotation from the point symmetry group of the cube.

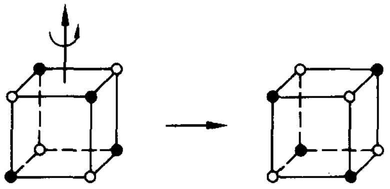

Fig. 8

Hence the Figs. 1–7 exhaust all possible colorations – up to spatial orientation. If we agree upon non differentiating between mirror image colorations as well, Figs. 1–5 remain distinct while one of the Figs. 6 and 7 becomes superfluous. Thus, according as the proper rotational or the full rotation/reflection symmetry of the cube is taken into account, we are left with 7 or 6 symmetry types of colorations, respectively. Suitable translations of the terms "corners of a cube", "colors" and "symmetry group of the cube" yield numerous variations on this theme, like e.g.

i) Permutational isomers

corners of a cube → sites of a molecular skeleton
colours → types of (unidentate, structureless) ligands
symmetry group of the cube → symmetry group of the skeleton.

The symmetry types of colorations correspond to permutational isomers, or to enantiomeric pairs of permutational isomers and achiral ones, respectively.

ii) Graphs

corners of a cube → edges of a regular n-simplex
colors → black, white
symmetry group of the cube → symmetry group of the regular n-simplex
(proper and improper operations).

The symmetry types of colorations with m edges coloured black, the rest of them white, may be interpreted as unlabeled graphs with n vertices and m edges.

Besides the gross enumeration of symmetry types, which is largely covered by the well-known Pólya method [1], there is a variety of more intricate enumeration problems which might be termed "enumeration of symmetry types with prescribed structural properties". Referring to permutational isomers, the most immediate and important structural property is their point symmetry (its counterpart for graphs being their automorphism group). It is evident, that the point symmetry of permutational isomers depends on the composition of the ligand assortment. While "homosubstituted" derivatives (ligands of the same type exclusively) have the symmetry of the skeleton, "heterosubstitution" (ligands of different types) will generally destroy some of the symmetry elements, thus leading to a subsymmetry of the skeleton symmetry. In the limiting case of exclusively different ligands there is no symmetry left at all – apart from symmetry operations fixing all the sites, as occur with planar or linear skeletons.

This paper investigates problems in "substitution symmetry", a typical question being: given a molecular skeleton with n sites and an assortment of $n_1+n_2+\cdots+n_\lambda=n$ ligands of types $1,2,\ldots,\lambda$, how are the symmetries of the permutational isomers distributed among the various subsymmetries of the skeleton symmetry?

For the introductory example, inspection provides the following result, where proper rotational and rotation/reflection symmetries have been listed separately.

Table 1.

	1	2	3	4	5	6	7
Proper rotational symmetry	T	C_4	D_2	C_3	E	C_2	C_2
Rotation/reflection symmetry	T_d	C_{4v}	D_{2h}	C_{3v}	C_s	C_2	C_2

To be more specific, this article provides solutions to the following questions: given a symmetric molecular skeleton,

i) which subsymmetries can be reached at all by substitution?
ii) which is the number of derivatives, with ligands of λ given types, and with some specified subsymmetry?
iii) how many permutational isomers are there, for a given gross formula $n_1, n_2, \ldots, n_\lambda$, and with some specified subsymmetry?

We do not restrict ourselves to the case of structureless ligands, i.e. where symmetry operations of the skeleton merely permute the positions of ligands, but we also admit some ligand structure, to the effect that symmetry operations act on the ligand types as well, as e.g. occurs with reflections in the presence of chiral ligands.

Of course, our results are not restricted to discussing the symmetries of derivatives of symmetrical parent compounds (though this is the typical application that we have in mind). It refers to orbits of mappings between finite sets, upon which a group acts by either acting on the domain, exclusively, or by acting both on domain and range, simultaneously. These are the settings considered in Pólya's enumeration theory [1] and its generalizations by de Bruijn [2], Harary [3, 4], and many others. Our presentation follows that of a recent paper [5], where the present author proposes a natural generalization of de Bruijn's and Harary's power group approach. The results of this note apply to whatever discrete structures, that are parametrized by orbits of mappings between finite sets.

The general problem behind that of substitution symmetry may be stated as follows: Given a set on which a group acts, which is the number of orbits with stabilizers in a given conjugacy class of subgroups? It turns out that this is the permutation representation analogue of the well-known problem to determine the multiplicity of an irreducible linear representation in a reducible one. The notions as well as the basic results of this theory are quite old; they already go back to Burnside [6], with modern presentations given by Dress [7] and by

Knutson [8]. The related question of how to resolve a compound permutation character into a sum of simple ones was treated by Foulkes [9, 10]. But it remained for Stockmeyer [11] and White [12] to provide explicit answers. Later, Plesken [13] covered these results by a general theory of groups acting on lattices, and Kerber and Thürlings [14, 15] derived generating functions for the numbers of symmetry types of mappings with specified stabilizer class and content, while simultaneously and independently the present author was active in this field as well [16]. This treatment aims at implementing these results into chemical combinatorics, some part of which program is covered by a short account of Davidson [17], and to extend them to simultaneous action of a group on the domain and the range of mappings. Last but not least, to our feeling, the present paper provides the by far most simple access to the results in the mathematical literature.

2. General theory: Orbits and their symmetries

A finite group G is said to *act* on a finite set M if the elements of G act as permutations on M, more explicitly, if to each $g \in G$ a permutation $\sigma_g \in \mathrm{Sym}(M)$ is associated such that the mapping $\sigma\colon g \mapsto \sigma_g$ is a homomorphism from G to $\mathrm{Sym}(M)$, the symmetric group of M. That is

$$\sigma_g \sigma_{g'} = \sigma_{gg'} \quad \text{for any } g, g' \in G. \tag{1}$$

Synonymously, M affords a *permutation representation* of G, or M is a *G-set.* The action of the group G induces an equivalence relation on the set M,

$$m' \sim m \Leftrightarrow \exists g \in G\colon m' = \sigma_g(m), \tag{2}$$

due to which this set decomposes into equivalence classes, its *orbits* with respect to the group action. For $m \in M$, the symbol $O_G(m)$ will denote the orbit that contains m, so

$$O_G(m) := \{m' = \sigma_g(m) | g \in G\}. \tag{3}$$

The action of G associates to each $m \in M$ a subgroup of G, its *stabilizer*

$$G_m := \{g \in G | \sigma_g(m) = m\}, \tag{4}$$

which is related to the orbit $O_G(m)$ by the fact that the orbit length $|O_G(m)|$, i.e. the number of elements in the orbit, is given by the stabilizer index.

$$|O_G(m)| = \frac{|G|}{|G_m|}. \tag{5}$$

By the dual construction, a subset of M is assigned to each group element $g \in G$: the set M_g of its *fixed points,*

$$M_g := \{m \in M | \sigma_g(m) = m\}. \tag{6}$$

The numbers of fixed points,

$$f(g) := |M_g|, \tag{7}$$

provide the key to the enumeration of orbits through the

Cauchy–Frobenius Lemma[1]. *The number of orbits of a G-set equals the average number of fixed points of the group elements.*

$$\text{no. of orbits} = \langle f(g)\rangle_{g\in G} := \frac{1}{|G|}\sum_{g\in G} f(g). \tag{8}$$

Example 1. Symmetric polyhedra provide immediate illustrations of the notions mentioned above. Any covering operation of a polyhedron induces a permutation of its corners as well as of its edges, its faces and so on, and the effect of two consecutive covering operations is the same as that of their product (by the very definition of composition for covering operations). So, e.g., let M denote the set of corners of a symmetric polyhedron and let G be its point-symmetry group. Any covering operation $g \in G$ results in a permutation $\sigma_g \in \mathrm{Sym}(M)$ of the polyhedron's corners, such that $\sigma_g\sigma_{g'} = \sigma_{gg'}$ holds[2] for any two elements $g, g' \in G$. So G properly acts on M. The orbits of this action are the subsets of symmetry equivalent corners, the stabilizer of a corner accounts for its site symmetry, and fixed points are points on the rotation axis for proper rotations, and points in the mirror plane for reflections.

Symmetry-equivalent corners have the same site-symmetry. This observation is covered by the general fact, that elements in the same orbit have conjugate stabilizers. In fact,

$$G_{gm} = gG_m g^{-1} \tag{9}$$

holds, where we have abbreviated $\sigma_g(m)$ to gm. Moreover, as $m' \in O_G(m)$ runs through an orbit, the stabilizers $G_{m'}$ run through a complete conjugacy class of subgroups of G (possibly several times), say

$$\mathbb{H} := \{H' = gHg^{-1} | g \in G\}, \tag{10}$$

for $G_m = H$. Hence any orbit is associated with a conjugacy class of subgroups, which we are going to refer to as to the *symmetry of that orbit*, since conjugate subgroups of a point-symmetry group constitute symmetry-equivalent realizations of the same subsymmetry.

The natural question then is: given a G-set M and a conjugacy class $\mathbb{H}$ of subgroups of G, how many orbits with symmetry $\mathbb{H}$ are there? Let us denote this number by $o_{\mathbb{H}}$, so

$$o_{\mathbb{H}} := \text{no. of orbits, consisting of elements with stabilizers in } \mathbb{H}. \tag{11}$$

[1] Which is usually, but erroneously, attributed to Burnside, cf. [18]

[2] Depending on whether symmetry operations are defined with respect to spatially-fixed or to body-fixed symmetry elements, and whether permutations are interpreted in the passive or in the active way, $\sigma: g \mapsto \sigma_g$ is either a proper homomorphism ($\sigma_g\sigma_{g'} = \sigma_{gg'}$) or an antihomomorphism ($\sigma_g\sigma_{g'} = \sigma_{g'g}$). Since the notion of group action could as well be defined in the latter fashion, with all results remaining to be the same, this makes no essential difference. Moreover, if so desired, such 'flaw of beauty' can be easily eliminated by taking inverses

If $G_m = H$, then among the $G_{m'}$ with $n' \in O_G(m)$ the conjugates gH_g^{-1} all occur equally often. Hence $o_{\mathbb{H}}$ is proportional to the number

$$s_H = \text{no. of elements of } M \text{ with } H \text{ as their stabilizer.} \tag{12}$$

The precise relation between $o_{\mathbb{H}}$ and s_H, with $H \in \mathbb{H}$ being of course arbitrary, reads

$$s_H = o_{\mathbb{H}} \cdot \frac{|G|/|H|}{[\mathbb{H}]}, \tag{13}$$

where the enumerator, $|G|/|H|$, is the common length of all the orbits with symmetry $\mathbb{H}$, and where $[\mathbb{H}]$ denotes the number of subgroups in the conjugacy class $\mathbb{H}$.

As a rule, these numbers are much harder to calculate than a related third number, namely the number i_H of H-invariant elements of M, i.e. the number of $m \in M$ which are common fixed points to all the $h \in H$ in a given subgroup H of G.

$$i_H := \text{no. of elements } m \in M \text{ with } hm = m \text{ for all } h \in H. \tag{14}$$

As we shall see, given all the i_H, we can (at least in principle) calculate the s_H, and from them our final objects, the numbers $o_{\mathbb{H}}$, are obtained by multiplication with a simple factor. Let us start from an equivalent expression for the numbers

$$i_H = \text{no. of } m \in M \text{ with } G_m \geqslant H, \tag{15}$$

where we use the signs $\geqslant$ and $\leqslant$, respectively, to denote the subgroup relation, i.e. $H \leqslant G$ as well as $G \geqslant H$ means that H is a subgroup of G. From the expression above, the following equation is obvious

$$i_H = \sum_{H \leqslant K \leqslant G} s_K. \tag{16}$$

We rewrite it in the form

$$i_H = \sum_{K \leqslant G} \zeta(H, K) s_K, \tag{17}$$

where

$$\zeta(H, K) = \begin{cases} 1 & \text{if } H \leqslant K \\ 0 & \text{otherwise} \end{cases}.$$

With a suitable numbering of the subgroups of G, e.g. according to their cardinalities, the matrix of the coefficients $\zeta(H, K)$ is triangular, with diagonal elements all ones. These matrices are invertible; so there are coefficients $\mu(H, K)$ by means of which the system (17) of linear equations is solved, i.e. such that

$$s_H = \sum_{K \leqslant G} \mu(H, K) i_K. \tag{18}$$

In more advanced terms, ζ is the Zeta-function of the subgroup lattice of G, μ is its Möbius-function, and the numbers s_H are obtained from the i_H by Möbius inversion, cf. [19] for an introduction to these notions.

The size of the system (17) of linear equations can be reduced from the number of subgroups of G to the number of conjugacy classes of such subgroups by using the fact that both the s_H and i_H are constant on classes of conjugate subgroups. The matrix associated with the Zeta-function, reduced to conjugacy classes of subgroups by partial summation, then yields the so-called *table of marks* of G, a notion which is due to Burnside [6].

Let us now proceed along these lines. So, for this purpose, let $\mathcal{T}$ be a transversal from the conjugacy classes of subgroups of G, i.e. a collection of subgroups, one from each conjugacy class. Then the reduced form of (17) reads

$$i_H = \sum_{K \in \mathcal{T}} [H \leqslant \mathbb{K}] s_K, \tag{19}$$

where, of course, H also runs through $\mathcal{T}$, and where the coefficient $[H \leqslant \mathbb{K}]$ denotes the number of conjugates of K that contain H as a subgroup. Since it is the orbit numbers $o_{\mathbb{K}}$ that we are looking for, we include the proportionality (13), yielding

$$i_H = \sum_{K \in \mathcal{T}} \frac{|G|[H \leqslant \mathbb{K}]}{|K|[\mathbb{K}]} o_{\mathbb{K}}. \tag{20}$$

The matrix of the coefficients

$$M_{\mathbb{H}\mathbb{K}} := \frac{|G|[H \leqslant \mathbb{K}]}{|K|[\mathbb{K}]} \tag{21}$$

is called the table of marks of the group G. Let us now write $i_{\mathbb{H}}$ for the constant number i_H, $H \in \mathbb{H}$. Then we may summarize our result as follows.

Theorem. *Let M be a G-set. Then the numbers $o_{\mathbb{K}}$ of orbits with symmetry $\mathbb{K}$, $\mathbb{K}$ being a conjugacy class of subgroups of G, constitute the solution of the system of linear equations*

$$i_{\mathbb{H}} = \sum_{\mathbb{K}} M_{\mathbb{H}\mathbb{K}} o_{\mathbb{K}},$$

where the coefficients are the entries of the table of marks of G, and where $i_{\mathbb{H}}$ is the number of H-invariant elements of M, for any subgroup H from the conjugacy class $\mathbb{H}$.

It is important to note that the table of marks does not depend on the particular G-set but only on the structure of the subgroup lattice. So it is the same in any problem, and it is a reasonable task to tabulate these objects, which will be done for the point-groups in collaboration with A. Kerber/Bayreuth [20]. The second ingredient that is needed in order to calculate numbers of orbits with specified symmetry, are the fixed point numbers $i_{\mathbb{H}}$, and that is where the particular permutation representation enters. Let us close this paragraph with a very simple

Example 2. A trigonal bipyramid,

$$G = D_3 = \{e,\ c_3,\ c_3^2,\ c_2,\ c_2',\ c_2''\}$$

$$M = \{1, 2, 3, 4, 5, 6\}$$

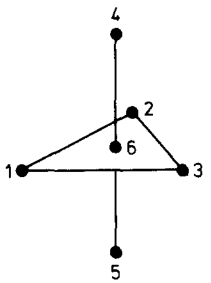

Fig. 9

subgroup lattice

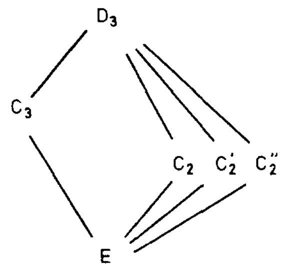

Fig. 10

fixed point numbers

$i_{D_3} = 1$

$i_{C_3} = 3$

$i_{C_2} = i_{C_2'} = i_{C_2''} = 2$

$i_E = 6$

$$\begin{bmatrix} i_{\mathbb{D}_3} \\ i_{\mathbb{C}_3} \\ i_{\mathbb{C}_2} \\ i_{\mathbb{E}} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 1 & 2 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 1 & 2 & 3 & 6 \end{bmatrix} \begin{bmatrix} o_{\mathbb{D}_3} \\ o_{\mathbb{C}_3} \\ o_{\mathbb{C}_2} \\ o_{\mathbb{E}} \end{bmatrix}$$

$$o_{\mathbb{D}_3} = 1, \quad o_{\mathbb{C}_3} = 1, \quad o_{\mathbb{C}_2} = 1, \quad o_{\mathbb{E}} = 0,$$

in agreement with the subsequent sketch of these orbits.

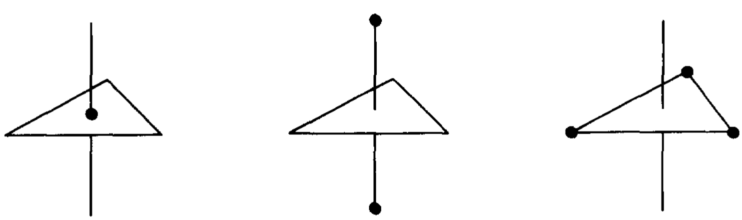

Fig. 11

3. Orbits of mappings and their symmetries

We are now going to apply the general results of the preceding paragraph to G-sets of a particular type: to sets of mappings between two finite sets, on which a group acts by acting on the domain, and, possibly, on the range as well. The first one is the typical scenario of Pólya's theory [1]. It starts from a G-set P, and from another finite set L (without any group action on it), and next considers the set L^P of all mappings from P to L

$$L^P := \{\varphi | \varphi : P \to L\}. \tag{22}$$

Let $\pi_g \in \mathrm{Sym}(P)$ denote the permutation by which $g \in G$ acts on P. Then

$$g : \varphi \mapsto \varphi \circ \pi_g^{-1} \tag{I}$$

defines an action of G on L^P. Here the symbol $\circ$ is used for the composition of mappings, that is, for a mapping φ and a permutation π, $\varphi \circ \pi$ denotes the mapping that takes $i \in P$ into $\varphi(\pi(i))$. The other case of interest is that where G acts on L as well. So let both, P and L, be G-sets on which $g \in G$ acts as $\pi_g \in \mathrm{Sym}(P)$ and $\lambda_g \in \mathrm{Sym}(L)$, respectively. Then G acts on L^P by simultaneously acting on P and on L according to

$$g : \varphi \mapsto \lambda_g \circ \varphi \circ \pi_g^{-1}. \tag{II}$$

This type of action was recently discussed [5] as a generalization of the de Bruijn type [2], which arises naturally in "chemical combinatorics" on the next level beyond Pólya's pure domain action.

Since the theory presented here most immediately applies to derivatives of symmetrical parent compounds, which we also had in mind when choosing the letters P and L for domain and range of mappings instead of D and R, we shall use this picture in order to explain why we consider L^P with the actions of type I and II of a group on it. For this purpose, let $P = \{1, 2, 3, \ldots\}$ denumerate the *positions* (sites), where substitution may take place in a given parent compound, and let $L = \{A, B, C, \ldots\}$ be a collection of *ligand types* (types of substituents). Mappings from P to L obviously represent distributions of ligands of types in L over the sites of the molecular skeleton in question, if $\varphi(i) = X$ is taken to say that there is a ligand of type X at site i. Let the skeleton have a non-trivial symmetry, and denote by G the corresponding point-symmetry group, by R its subgroup of proper rotations, and by S the coset of improper rotations and reflections. Of course, S need not exist, namely if the skeleton is chiral. In this setting, one readily identifies symmetry equivalent distributions, that are mutually transformed by proper rotations $r \in R$, to represent the same derivative. If, moreover, enantiomers need not be distinguished, mutual transforms by improper rotations $s \in S$ are identified as well. Evidently, covering operations of the (spatially fixed) skeleton permute the distributions. Moreover, on any distribution, the effect of two consecutive covering operations is the same as that of their product (by the very definition of composition for point-symmetry operations). So the group acts on the set L^P of distributions, and derivatives are orbits with respect to its subgroup R, while a G-orbit represents either a mirror image pair of chiral derivatives or an achiral compound.

There are now several possibilities, of increasing complexity, of how this action looks like in detail. First and foremost, a covering operation acts on distributions by removing the ligands from their original positions to other sites, i.e. by permuting the positions of the ligands. Note that this site permutation is the same for all distributions, irrespectively of the kind of ligands that are moved. If the ligand symmetry is sufficiently high, this rearrangement will be the only effect. Otherwise it may happen that a covering operation, besides moving the ligands, also changes their types. For instance, improper rotations and reflections take any chiral ligand into its mirror image - wherever it is situated. Finally, and most awkwardly to deal with, the fate of a ligand may depend on its initial and final position, as will be the case if a ligand type has to be considered a chiral one at some sites and an achiral one at others. Let us now translate these descriptions of covering operations acting on distributions into definitions of how a group G acts on a set L^P of mappings. This is conveniently done by describing the image φ' of a general mapping $\varphi \in L^P$ under a general group element $g \in G$.

First, G acts through site permutations exclusively. So there is a permutation representation of G on P, $g \mapsto \pi_g$, and $g \in G$ acts on $\varphi \in L^P$ through taking to site $\pi_g(i)$ whatever ligand type $X \in L$ is assigned to $i \in P$ by the mapping φ. The image φ' is therefore given by $\varphi'(\pi_g(i)) = X$ if $\varphi(i) = X$, equivalently

$$\varphi'(i) = \varphi(\pi_g^{-1}(i)),$$

or (23)

$$\varphi' = \varphi \circ \pi_g^{-1} \text{ as a shorthand notation.}$$

Second, G acts on the ligands as well, irrespectively of their position. So a permutation representation of G on L, $g \mapsto \lambda_g$, is operative in addition, and $g \in G$ acts on $\varphi \in L^P$ by taking to $\pi_g(i)$ the image $X = \varphi(i)$ of i under φ, while transforming it into $\lambda_g(X)$. This amounts to $\varphi'(\pi_g(i)) = \lambda_g(X)$ if $\varphi(i) = X$, equivalently,

$$\varphi'(i) = \lambda_g(\varphi(\pi_g^{-1}(i))),$$

or (24)

$$\varphi' = \lambda_g \circ \varphi \circ \pi_g^{-1}.$$

Third, and last, there is an individual[3] permutation representation of G on L, $g \mapsto \lambda_g^{(i)}$, for any site $i \in P$, and $g \in G$ takes $X = \varphi(i)$ into $\lambda_g^{(i)}(X) = \varphi'(\pi_g(i))$, i.e.

$$\varphi'(i) = \lambda_g^{(i)}(\varphi(\pi_g^{-1}(i))). \tag{25}$$

The most simple action next to that by pure site permutation occurs in the case of derivatives of an achiral parent compound, where the ligands are allowed to be chiral (but sufficiently symmetric with respect to proper rotations). The proper rotations $r \in R$ exclusively permute the positions, while improper rotations and reflections $s \in S$ moreover take any chiral ligand into its mirror image. That is, the point-symmetry group G acts as follows

$$g : \varphi \mapsto \lambda_g \circ \varphi \circ \pi_g^{-1}, \tag{26}$$

[3] The same for all sites in an orbit of P

where the π_g are the usual site permutations, and where $\lambda_r = \varepsilon$, the identity permutation, for all $r \in R$, and $\lambda_s = \tau$, the product of transpositions (XX^*) of mirror image ligand types X and X^*, for all $s \in S$. Of course we assume that X^* is in L if X is.

Our final objects are the numbers of orbits with specified symmetry. For their calculation we need, apart from the table of marks of the group in question, the fixed point numbers i_H for a transversal of the conjugacy classes of subgroups of G.

So, first, let a group G act on L^P by site permutations exclusively, i.e. according to

$$g: \varphi \mapsto \varphi \circ \pi_g^{-1}. \tag{27}$$

A mapping φ is a fixed point to all the elements h in a given subgroup $H \leqslant G$ if and only if

$$\varphi(\pi_h(i)) = \varphi(i) \text{ for any } i \in P,\ h \in H. \tag{28}$$

In other words: φ has to be constant on the H-orbits of P. Let P/H denote the collection of these orbits and $|P/H|$ their number. Then $H \leqslant G$ has

$$|L|^{|P/H|} \tag{29}$$

fixed points in L^P. Making use of the general result of Theorem 1 we end up with

Corollary 1. *Let a group G act on L^P by acting on P exclusively. Then the numbers $o_{\mathbb{K}}$ of orbits with symmetry $\mathbb{K}$ constitute the solution of the system of linear equations*

$$|L|^{|P/H|} = \sum_{\mathbb{K}} M_{\mathbb{HK}} o_{\mathbb{K}}.$$

In case that G acts on L^P by simultaneously permuting sites and ligand types, i.e. according to

$$g: \varphi \mapsto \lambda_g \circ \varphi \circ \pi_g^{-1}, \tag{30}$$

the fixed point numbers i_H are obtained in a similar manner. A mapping φ is H-invariant if and only if, for any $h \in H$, $\lambda_h \circ \varphi = \varphi \circ \pi_h$. That is: the images under φ of the sites in an H-orbit of P have to match each other in the sense that

$$\varphi(i) = X \Rightarrow \varphi(\pi_h(i)) = \lambda_h(X). \tag{31}$$

Moreover, the image of any site $i \in P$ has to be invariant under the H-stabilizer of i,

$$\varphi(i) = X \text{ and } \pi_h(i) = i \Rightarrow \lambda_h(X) = X. \tag{32}$$

So let $T_H \subset P$ be a transversal (i.e. a system of representatives) from the H-orbits of P. For $t \in T_H$, let H_t denote its stabilizer. Finally, let $f(H_t)$ denote the number of H_t-invariant elements of L. Then, from the previous necessary and sufficient condition, the number of fixed points in L^P, common to all elements of a subgroup

$H \leqslant G$ follows to be

$$\prod_{t \in T_H} f(H_t), \tag{33}$$

since, for any H-orbit of P, the image of one site t determines those of all the other sites, and this single image moreover has to H_t-invariant. Evidently, this expression reduces to the previous one, (29), in case that H acts trivially on L. Summarizing, we have

Corollary 2. *Let a group G act on L^P by acting on P and on L simultaneously. Then the numbers $o_{\mathbb{K}}$ of orbits with symmetry $\mathbb{K}$ constitute the solution of the linear system*

$$\prod_{t \in T_H} f(H_t) = \sum_{\mathbb{K}} M_{\mathbb{H}\mathbb{K}} o_{\mathbb{K}}.$$

Let us apply this result to the case of chiral ligands, i.e. $G = R \dot{\cup} S$ acts according to

$$g: \varphi \mapsto \lambda_g \circ \varphi \circ \pi_g^{-1}, \tag{34}$$

$$\text{where} \begin{cases} \lambda_r = \varepsilon & \text{for any } r \in R \\ \lambda_s = \tau & \text{for any } s \in S\text{'} \end{cases}$$

ε being the identity permutation, while τ replaces each chiral ligand type by its mirror image.

If $H \leqslant R$ is a subgroup of proper rotations, the expression (33) for its fixed point number reduces to

$$|L|^{|T_H|} = |L|^{|P/H|}, \tag{35}$$

where the exponent is the number of H-orbits of P. Now let H contain improper rotations and reflections as well, $H \cap S \neq \varnothing$. Then the crucial point is whether the H-stabilizer $H_t = H \cap G_t$ of some site t consists of proper rotations exclusively ($H_t \leqslant R$), or whether it includes improper ones as well ($H_t \cap S \neq \varnothing$). For rationalizing the final result, let us call a site $i \in P$ to be H-chiral, if $H_i \cap S = \varnothing$, and H-achiral, if $H_i \cap S \neq \varnothing$, of course. Denoting by C_H and A_H the subsets of P of H-chiral and H-achiral sites, respectively, and, finally, by L_α the subset of L of achiral ligand types, we end up with the expression

$$|L|^{|C_H/H|} \cdot |L_\alpha|^{|A_H/H|} \tag{36}$$

for the fixed point number of a subgroup H. As before $|P/H|$, the exponents are the numbers of H-orbits of the sets in question. The fact that, in any invariant distribution, exclusively achiral ligands are at achiral sites, properly matches intuition. As an example, only such distributions can be invariant under a reflection that have exclusively achiral ligands in the mirror plane.

Example 3. A trigonal pyramid

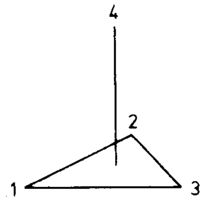

Fig. 12

$G = C_{3v} = \{e, c_3, c_3^2, \sigma, \sigma', \sigma''\}$

$P = \{1, 2, 3, 4\}$

$L = \{A, C, C^*\}$, an achiral ligand type and a mirror image pair of chiral ones

subgroups

C_{3v}

$C_3 = \{e, c_3, c_3^2\}$

$\boldsymbol{\sigma} = \{e, \sigma\}$, and conjugates

$E = \{e\}$

table of marks

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 1 & 2 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 1 & 2 & 3 & 6 \end{bmatrix}$$

C_{3v}: orbits of achiral sites $\{1, 2, 3\}, \{4\}$

C_3: orbits of sites $\{1, 2, 3\}, \{4\}$

$\boldsymbol{\sigma}$: $\begin{cases} \text{orbits of achiral sites } \{1\}, \{4\} \\ \text{orbits of chiral sites } \{2, 3\} \end{cases}$

E: orbits of sites $\{1\}, \{2\}, \{3\}, \{4\}$

where we have chosen σ to be the reflection at the plane through 1 and 4. The fixed point numbers then are

$$C_{3v}\colon 1^2, \quad C_3\colon 3^2, \quad \boldsymbol{\sigma}\colon 1^2 3^1, \quad E\colon 3^4.$$

The numbers of C_{3v}-orbits with the corresponding symmetries are given in the next line

$$\mathbb{C}_{3v}\colon 1, \quad \mathbb{C}_3\colon 4, \quad \mathbb{\sigma}\colon 2, \quad \mathbb{E}\colon 11.$$

Let us check these numbers by drawing some figures, where we have to note that a C_{3v}-orbit either corresponds to a single chiral compound or a mirror image pair of chiral ones. So orbits with symmetry $\mathbb{C}_{3v}$, $\mathbb{\sigma}$ belong to the first category,

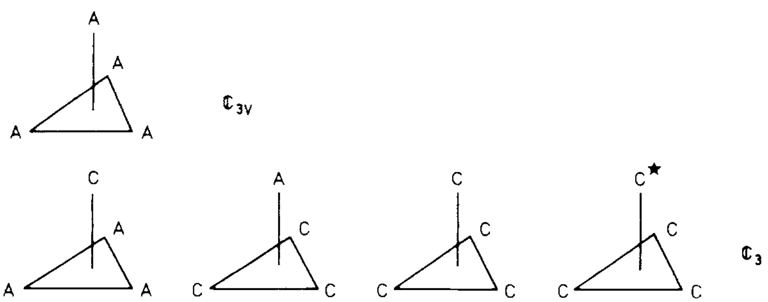

Fig. 13

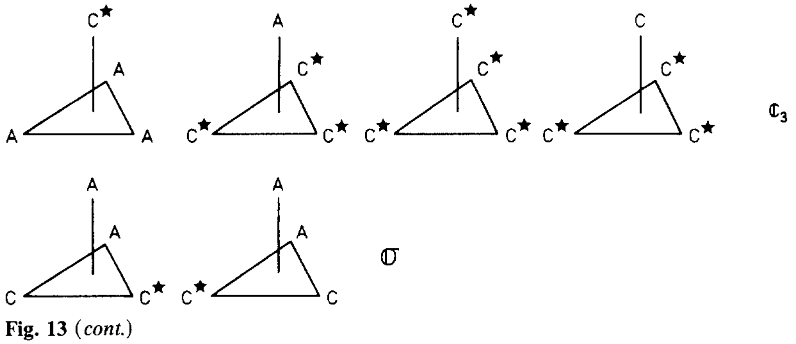

Fig. 13 (*cont.*)

while those of symmetry $\mathbb{C}_3$, $\mathbb{E}$ make up the second one, and there are 11 more mirror image pairs of derivatives without any symmetry. In comparison, with three achiral ligand types, $L=\{A_1, A_2, A_3\}$, the fixed point numbers and the numbers of orbits for the subsymmetries of $\mathbb{C}_{3v}$ turn out as follows

$$C_{3v}\colon 3^2,\quad C_3\colon 3^2,\quad \sigma\colon 3^3,\quad E\colon 3^4$$

$$\mathbb{C}_{3v}\colon 9,\quad \mathbb{C}_3\colon 0,\quad \boldsymbol{\sigma}\colon 18,\quad \mathbb{E}\colon 3.$$

Finally, for two achiral types, $L=\{A, B\}$, the corresponding result is

$$C_{3v}\colon 2^2,\quad C_3\colon 2^2,\quad \sigma\colon 2^3,\quad E\colon 2^4$$

$$\mathbb{C}_{3v}\colon 4,\quad \mathbb{C}_3\colon 0,\quad \boldsymbol{\sigma}\colon 4,\quad \mathbb{E}\colon 0.$$

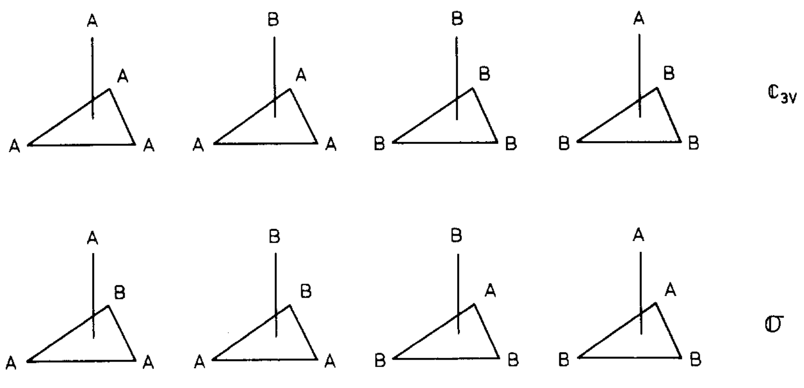

Fig. 14

As a general rule, replacing pairs of achiral ligand types by mirror image pairs of chiral ones does not change the number of derivatives. However, it increases the number of chiral ones at the expense of achiral compounds.

Explicitly, among the compounds deriving from an achiral parent with point-symmetry group $G=R\,\dot\cup\,S$ and from $l=l_\alpha+l_\chi$ ligand types, l_α achiral ones and $\frac{1}{2}l_\chi$ enantiomeric pairs, there are

$$z_\alpha=\langle l^{c_{\text{even}}(\pi_s)}\, l_\alpha^{c_{\text{odd}}(\pi_s)}\rangle_{s\in S}$$

achiral ones, while their total number is

$$z = z_\alpha + z_\chi = \langle l^{c(\pi_r)} \rangle_{r \in R}.$$

In these expressions, the brackets denote averages over the improper rotations and reflections, and over the proper rotations, respectively, in the point-symmetry group. The c's stand for the numbers of cycles, with even lengths, with odd lengths, or in total, in the disjoint cycle decomposition of the site permutations in question. Clearly, then, if the number l_α of achiral ligand types is reduced at the expense of the number l_χ of chiral ones (i.e. while keeping their sum $l = l_\alpha + l_\chi$ constant), the number z_α of achiral derivates likewise decreases at the expense of the number z_χ of chiral ones. More precisely, z_α never increases. It is at most constant, and this happens if (and only if) there are no improper symmetry operations $s \in S$ that mutually permute an odd number of sites. The most simple such case is that of a parent compound with a mirror plane as its only symmetry element, and with two symmetry equivalent sites outside that plane.

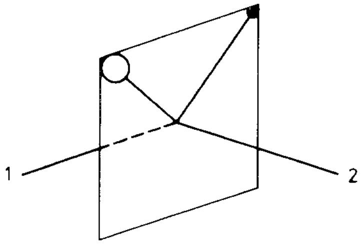

Fig. 15

With two achiral ligand types A and B there are four compounds AA, AB, BA, BB, among which AA and BB are achiral while AB, BA are enantiomers. With two mirror image chiral types C and C^*, however, it is just the other way around: the two meso isomers CC^* and C^*C are achiral, while CC and C^*C^* constitute a mirror image pair.

Ascent in symmetry from C_s to C_{2v}, like in the figure below, reduces the number of derivatives from four to three. At the same time, it turns the previous "exceptional" case into a "normal" one, i.e. now passing from $\{A, B\}$ to $\{C, C^*\}$ reduces the number of achiral compounds at the expense of the number of chiral ones.

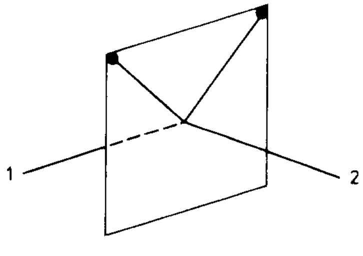

Fig. 16

AA and BB remain to be achiral, of course, while the former mirror image pair AB, BA collapses into a single achiral compound $AB = BA$. On the other hand, CC and C^*C^* remain to be chiral, while the former two achiral meso forms CC^* and C^*C coincide.

4. Substitution symmetry and gross formula

In the manner of writing H^2O instead of H_2O, the *gross formula* attributes to any mapping $\varphi: P \to L$ a monomial

$$GF(\varphi) := \prod_{X \in L} X^{J_\varphi(X)}, \tag{37}$$

where $J_\varphi(X)$ is the number of times that $X \in L$ appears as the image of a site $i \in P$, i.e. $J_\varphi(X) =$ no. of $i \in P$ such that $\varphi(i) = X$. The function J_φ is called the *content* of the mapping φ, and this is the customary object in the mathematical literature, while we keep closer to chemistry by using the gross formula monomial instead.

Evidently, the gross formula of mappings from P to L is invariant under site permutations $\pi \in \mathrm{Sym}\,(P)$. Hence it is, of course, invariant under the action of any group G via site permutations π_g,

$$g: \varphi \mapsto \varphi \circ \pi_g^{-1}. \tag{38}$$

Therefore, all the subsets of L^P for the various possible gross formulas are *G-subsets*, i.e. they are closed with respect to the action of G, which makes them G-sets by themselves. We may therefore ask the same questions as before with reference to these G-subsets of L^P, i.e. ask for the number of derivatives with specified symmetry *and* gross formula. So we need to know the corresponding fixed-point numbers. In the present case of type I actions, a mapping $\varphi \in L^P$ is H-invariant, i.e. a common fixed-point to all the elements $h \in H$ of a subgroup $H \leqslant G$, precisely if it is constant on the H-orbits of P. So we may sum up the gross formula monomials of the H-invariant mappings as follows

$$\begin{aligned}\sum_{\varphi \in L^P}^{(H\text{-inv.})} GF(\varphi) &= \sum_{\varphi \in L^P}^{(H\text{-inv.})} \prod_{i \in P} \varphi(i) \\ &= \sum_{\psi \in L^{P/H}} \prod_{Q \in P/H} \psi(Q)^{|Q|} \\ &= \prod_{Q \in P/H} \left(\sum_{X \in L} X^{|Q|} \right) \\ &= \prod_{k \geq 1} \left(\sum_{X \in L} X^k \right)^{p_k(H)} .\end{aligned} \tag{39}$$

Here P/H denotes the collection of H-orbits of P, with Q varying through this set, and $|Q|$ being the length of the orbit Q. Finally, $p_k(H)$ is used to denote the number of H-orbits of P with length k. The essential step in performing this summation is the interchange of sum and product, a well-known trick in Pólya enumeration theory. From the previous expression we can obtain the numbers of H-invariant mappings, for any gross-formula, by expanding the polynomials

$$\prod_{k\geq 1}\left(\sum_{X\in L} X^k\right)^{p_k(H)} \tag{40}$$

into sums of monomials. Evidently,

$$\prod_{k\geq 1}\left(\sum_{X\in L} X^k\right)^{p_k(H)} = \sum_J i(H,J) \prod_{X\in L} X^{J(X)}, \tag{41}$$

where the right hand sum is over all possible contents of mappings from P to L, i.e. the right hand expression is the sum of all possible gross formula monomials, with the corresponding numbers $i(H, J)$ of H-invariant mappings as their coefficients. So we have found

Lemma 1. *If G acts by site permutations exclusively, the generating function for the numbers $i(H, J)$ of H-invariant mappings with content J is given by the polynomial*

$$\prod_{k\geq 1}\left(\sum_{X\in L} X^k\right)^{p_k(H)}.$$

That is: the numbers $i(H, J)$ are the coefficients of the monomials

$$\prod_{X\in L} X^{J(X)}$$

in the expression above, where $p_k(H)$ denotes the number of H-orbits of P of length k.

If G acts on L as well, the gross formula of mappings is no longer invariant under G, i.e. the gross formula is not a common property to all the mappings within an orbit any more. For example, if G is the point-symmetry group of an achiral skeleton, and if chiral ligands are admitted, mirror image chiral compounds have mirror image gross formulas, unless the gross formula is racemic. But the way out is pretty obvious [5]. Let G act on L^P according to

$$g: \varphi \mapsto \lambda_g \circ \varphi \circ \pi_g^{-1}. \tag{42}$$

Then G acts on the set of gross-formula monomials in a natural fashion

$$g: \prod_{X\in L} X^{J(X)} \mapsto \prod_{X\in L} \lambda_g(X)^{J(X)}. \tag{43}$$

Let us now define a *generalized gross formula* to be an orbit of monomials over L. These orbits are the natural substitutes of gross formulas, when the group in question acts on the ligands as well, since the gross formula of mappings within an orbit ranges precisely over an orbit of gross formulas. So the subsets of mappings with GF in a given GGF constitute G-subsets of L^P again, and we may ask for the distribution of their orbits over the various subsymmetries of G. We will again need the corresponding fixed-point numbers, and we will proceed in the very same manner as before, by summing up the GF of the H-invariant mappings, resulting in a generating function for the numbers $i(H, J)$ of H-invariant mappings with content J. Summing these, in turn, over the GF within a GGF, provides us with the fixed-point numbers we need. Let us skip the computation and only state the result.

Lemma 2. *If G acts through permutations of sites and of ligands, simultaneously, the generating function for the numbers $i(H, J)$ of H-invariant mappings with content J is given by*

$$\prod_{t \in T_H} \left(\sum_{X \in \mathrm{Fix}(H_t)} \prod_{Y \in O_H(X)} Y^{|O_H(t)|/|O_H(X)|} \right).$$

Here T_H is again a transversal from the H-orbits of P, $\mathrm{Fix}(H_t)$ denotes the set of H_t-invariants in L, and $O_H(\cdot)$ is an H-orbit of sites or of ligand types, respectively.

We will apply these results to example 3, thus refining the previous calculation.

Example 3′:

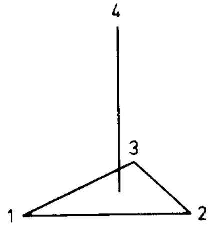

Fig. 17

A trigonal pyramid, $G = C_{3v}$

$L = \{A_1, A_2, A_3\}$, three achiral types

generating function of the $i(H, J)$:

$$\prod_{k \geq 1} \left(\sum_{X \in L} X^k \right)^{p_k(H)}$$

subgroup	orbit lengths	generating function
C_{3v}	3, 1	$(A_1^3 + A_2^3 + A_3^3)(A_1 + A_2 + A_3)$
C_3	3, 1	$(A_1^3 + A_2^3 + A_3^3)(A_1 + A_2 + A_3)$
σ	2, 1, 1	$(A_1^2 + A_2^2 + A_3^2)(A_1 + A_2 + A_3)^2$
E	1, 1, 1, 1	$(A_1 + A_2 + A_3)^4$.

The next two tables display the fixed-point numbers $i(H, J)$ and the inverse of the matrix of marks, while the final one gives the numbers of orbits, $o(\mathbb{H}, J)$, with specified symmetry and gross formula. Of course we need not consider all the possible monomials $A_1^{n_1} A_2^{n_2} A_3^{n_3}$, but only one of each type, i.e. for each partition of the number 4 into at most three parts, $4 = n_1 + n_2 + n_3$. So we take $n_1 \geq n_2 \geq n_3$. There are, evidently, $3GF$ of type A_1^4, $6GF$ of type $A_1^3 A_2$, $3GF$ of type $A_1^2 A_2^2$, and again $3GF$ of type $A_1^2 A_2 A_3$.

Table 2.

$i(H, L)$	A_1^4	$A_1^3 A_2$	$A_1^2 A_2^2$	$A_1^2 A_2 A_3$
C_{3v}	1	1	0	0
C_3	1	1	0	0
σ	1	2	2	2
E	1	4	6	12

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 & 0 \\ -1 & 0 & 1 & 0 \\ \frac{1}{2} & -\frac{1}{6} & -\frac{1}{2} & \frac{1}{6} \end{bmatrix}$$

Table 3.

$o(\mathbb{H}, J)$	A_1^4	$A_1^3A_2$	$A_1^2A_2^2$	$A_1^2A_2A_3$
$\mathbb{C}_{3v}$	1	1	0	0
$\mathbb{C}_3$	0	0	0	0
$\mathbb{C}_s$	0	1	2	2
$\mathbb{E}$	0	0	0	1

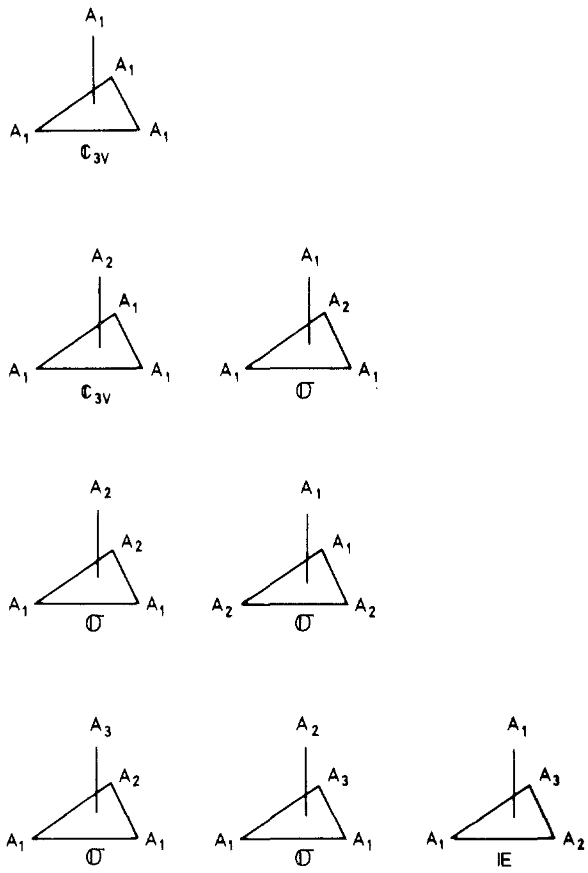

Fig. 18

The second part of this example refers to $L = \{A, C, C^*\}$, one achiral type and a mirror image pair of chiral ones. The generating function to be used is

$$\prod_{t \in T_H} \left(\sum_{X \in \mathrm{Fix}(H_t)} \prod_{Y \in O_H(X)} Y^{|O_H(t)|/|O_H(X)|} \right).$$

Table 4.

subgroup H	T_H	the H_t	the Fix(H_t)
C_{3v}	1, 4	σ, C_{3v}	$\{A\}, \{A\}$
C_3	1, 4	E, C_3	L, L
σ	1, 2, 4	σ, E, σ	$\{A\}, L, \{A\}$
E	1, 2, 3, 4	E, E, E, E	L, L, L, L

Table 5.

subgroup H	generating function
C_{3v}	A^4
C_3	$(A^3+C^3+C^{*3})(A+C+C^*)$
σ	$(A^2+2CC^*)A^2$
E	$(A+C+C^*)^4$

The next table again displays the fixed-point numbers $i(H, J)$, for any racemic gross formula and one from each mirror image pair of chiral gross formulas. In the last table, the orbit numbers are given, specified by symmetry and generalized gross formula.

Table 6.

fixed point numbers	A^4	C^4	A^3C	C^3A	C^3C^*	A^2C^2	C^2C^{*2}	A^2CC^*	C^2C^*A
C_{3v}	1	0	0	0	0	0	0	0	0
C_3	1	1	1	1	1	0	0	0	0
σ	1	0	0	0	0	0	0	2	0
E	1	1	4	4	4	6	6	12	12

Table 7.

orbit numbers	A^4	C^4 C^{*4}	A^3C A^3C^*	C^3A $C^{*3}A$	C^3C^* $C^{*3}C$	A^2C^2 A^2C^{*2}	C^2C^{*2}	A^2CC^*	C^2C^*A $C^{*2}CA$
$\mathbb{C}_{3v}$	1	0	0	0	0	0	0	0	0
$\mathbb{C}_3$	0	1	1	1	1	0	0	0	0
$\mathbb{\sigma}$	0	0	0	0	0	0	0	2	0
$\mathbb{E}$	0	0	1	1	1	2	1	1	4

We have already shown the figures with symmetries $\mathbb{C}_{3v}$, $\mathbb{C}_3$, and $\mathbb{\sigma}$. So it remains to display the 11 mirror image pairs with no symmetry at all. We give only one from each pair.

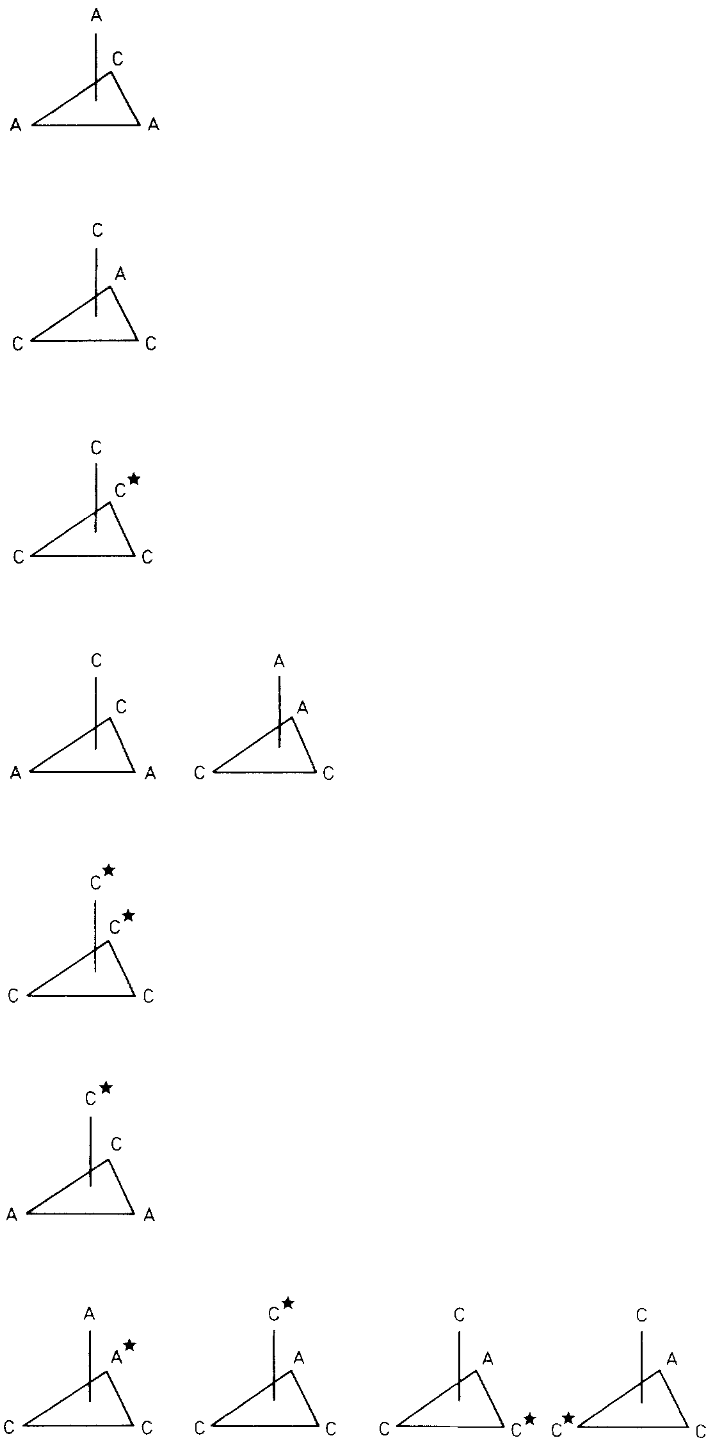

Fig. 19

Choosing our examples among the derivatives of achiral parent compounds, admitting chiral (but otherwise sufficiently symmetric) ligands, amounts to the most simple case of non-trivial action of G on L besides that on P. Somewhat more vivid action takes place in distributions of arrows over the corners of a regular polygon, where the arrows may point upward, downward, clockwise, counterclockwise, or to the center. An example of this type was employed in a preceding paper [5] in another context, namely for a square. We do not use this example here, because its symmetry group D_{4h} already has more than ten conjugacy classes of subgroups. The subgroup D_4 of proper rotations is better manageable, with eight being the number of classes, but then the action is equivalent to that in the chiral ligand cases.

If G acts by site permutations exclusively, the use of generating functions can be avoided, since there is a simple closed form expression available [16] for the fixed-point numbers $i(K, J)$. This is, of course, much more satisfactory from the theoretical point of view, but it also has practical implications in case that one is not interested in the complete set of data for the various gross formulas but rather for some single such contents.

So we let again G act on L^P by acting on P,

$$g\colon \varphi \mapsto \varphi \circ \pi_g^{-1}, \tag{44}$$

and we ask for the number of K-invariant mappings of content J, with K a subgroup of G. The key to these numbers is provided by the observation, that the subsets of mappings with some fixed content are just the orbits of the symmetric group S_P[4] which acts on L^P according to

$$\pi\colon \varphi \mapsto \varphi \circ \pi^{-1}. \tag{45}$$

Evidently, site permutations do not change the content of mappings, and, in reverse, any two mappings with the same content can be mutually transformed by some site permutation. The stabilizer of a mapping φ is a direct product of symmetric groups, each of them referring to one of the "homogeneously substituted" subsets of sites,

$$\varphi^{-1}(X) := \{i \in P \mid \varphi(i) = X\}, \tag{46}$$

i.e. to the sets of preimages of the ligand types in L. Permutation groups of this type are often [21] called Young-subgroups (of the symmetric group in question), and therefore we denote this stabilizer by Y_φ. Explicitly, we then have

$$\{\pi \in S_P \mid \varphi \circ \pi^{-1} = \varphi\} = Y_\varphi = \mathop{\times}_{X \in L} S_{\varphi^{-1}(X)}. \tag{47}$$

Now let K be a subgroup of G, and denote by $K^{(P)}$ its image as a group of site permutations

$$K^{(P)} := \{\pi_k \in S_P \mid k \in K\}. \tag{48}$$

[4] Now we write S_P as a short form of Sym (P).

It immediately follows, that a mapping φ is K-invariant if and only if $K^{(P)} \leqslant Y_\varphi$. This is the starting point for calculating the number $i(K, J)$ of K-invariant mappings with content J as follows. Let φ be a mapping with this content. Then we already know from the previous observations, that any other mapping of the same content can be written as $\varphi \circ \pi^{-1}$ with $\pi \in S_P$. Moreover, two permutations $\pi, \sigma \in S_P$ generate the same mapping, $\varphi \circ \pi^{-1} = \varphi \circ \sigma^{-1}$, if they are in the same left coset of Y_φ, different mappings otherwise. Noting that the stabilizer of a mapping $\varphi \circ \pi^{-1}$ is the conjugate Young-subgroup $\pi Y_\varphi \pi^{-1}$, as the final ingredient, we arrive at

$$i(K, J) = \frac{1}{|Y_\varphi|} \cdot \text{no. of } \pi \in S_P \text{ such that } K^{(P)} \leqslant \pi Y_\varphi \pi^{-1}. \tag{49}$$

Up to now this is merely a reformulation in terms of permutations taking the part of mappings. We may now, however, substitute a single permutation $\kappa \in S_P$ for the subgroups K or $K^{(P)}$, respectively, as follows. Let $\kappa \in S_P$ be such that the sets of sites in its cycles (in other words: the orbits of the cyclic group $\langle \kappa \rangle$ generated by κ) coincide with the K-orbits of P. Then, for any Young-subgroup $Y \leqslant S_P$,

$$K^{(P)} \leqslant Y \Leftrightarrow \kappa \in Y. \tag{50}$$

So we may replace $K^{(P)}$ by κ as follows

$$\begin{aligned} i(K, J) &= \frac{1}{|Y_\varphi|} \cdot \text{no. of } \pi \in S_P \text{ such that } \kappa \in \pi Y_\varphi \pi^{-1} \\ &= \frac{1}{|Y_\varphi|} \cdot \text{no. of } \pi \in S_P \text{ such that } \pi^{-1} \kappa \pi \in Y_\varphi. \end{aligned} \tag{51}$$

With π running through S_P, the conjugates of κ, $\pi^{-1}\kappa\pi$ run through the conjugacy class C_κ of κ,

$$C_\kappa = \{\pi^{-1}\kappa\pi \mid \pi \in S_P\}, \tag{52}$$

and they do it with constant frequency, which then is $|S_P|/|C_\kappa|$. So we arrive at

$$i(K, J) = \frac{|S_P|}{|Y_\varphi|} \frac{|C_\kappa \cap Y_\varphi|}{|C_\kappa|}. \tag{53}$$

These numbers are easily accessible if the cyclic notation of permutations is employed. Explicitly, C_κ is the class of permutations, which have the K-orbit lengths of P as their cycle lengths. Let us collect these results in terms of

Lemma 3. *Let G act by site permutations exclusively, and let J be a content. Then, for any subgroup $K \leqslant G$, the number of K-invariant mappings of content J is given by*

$$i(K, J) = \frac{p!}{|Y|} \frac{|C_\kappa \cap Y|}{|C_\kappa|},$$

where C_κ is the conjugacy class associated with the partition of $p = |P|$ into K-orbit *lengths. Y is any Young-subgroup of those associated with another partition of p: the one made up by the frequencies $J(X)$ of the ligand types, i.e. the type of gross formula.*

Let us illustrate this result by means of the colorations of the cube from the introduction.

Example 4. A cube, the corners of which are colored black or white, its pure rotational symmetry being considered. So we have $P=\{1,\ldots,8\}$, $L=\{B, W\}$, $G=O$, the octahedral group. Finally, we specify the gross formula to be B^4W^4.

The octahedral group has five conjugacy classes of elements:

i) the identity e,
ii) six 180°-rotations c_2 about axes passing through the midpoints of opposite edges of the square,
iii) three 180°-rotations c_2' about axes passing through the midpoints of opposite faces,
iv) eight 120°-rotations c_3 about axes passing through opposite corners,
v) six 90°-rotations c_4 about the c_2'-axes again.

Correspondingly, the list of conjugacy classes of subgroups of O starts as follows

$\mathbb{E}$:	the class of the identity subgroup	E,
$\mathbb{C}_2$:	six cyclic subgroups of the type	$C_2=\langle c_2\rangle$,
$\mathbb{C}_2'$:	three cyclic subgroups of the type	$C_2'=\langle c_2'\rangle$,
$\mathbb{C}_3$:	four cyclic subgroups of the type	$C_3=\langle c_3\rangle$,
$\mathbb{C}_4$:	three cyclic subgroups of the type	$C_4=\langle c_4\rangle$.

Any cyclic subgroup C_n can be extended to a dihedral group D_n; however, the D_2 partly coincide. So the list continues as follows

$\mathbb{D}_2$:	three dihedral groups of the type	D_2,
$\mathbb{D}_2'$:	one dihedral group of the type	D_2',
$\mathbb{D}_3$:	four dihedral groups of the type	D_3,
$\mathbb{D}_4$:	three dihedral groups of the type	D_4.

With $\mathbb{T}$ and $\mathbb{O}$, the classes of the tetrahedral group and of the octahedral group itself the list comes to an end.

The scheme below shows a condensed version of the subgroup lattice of O: the collection of conjugacy classes, ordered according to $\mathbb{H} \leqslant \mathbb{K}$ if and only if there are $H \in \mathbb{H}$ and $K \in \mathbb{K}$ such that $H \leqslant K$.

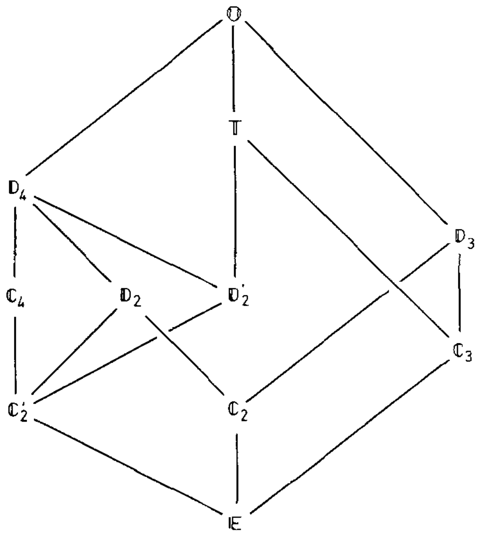

Fig. 20

The next table is that of the marks. The zero entries above the diagonal have been omitted.

Table 8.

	$\mathbb{O}$	$\mathbb{T}$	$\mathbb{D}_4$	$\mathbb{D}_3$	$\mathbb{C}_4$	$\mathbb{D}_2$	$\mathbb{D}_2'$	$\mathbb{C}_3$	$\mathbb{C}_2$	$\mathbb{C}_2'$	$\mathbb{E}$
$\mathbb{O}$	1										
$\mathbb{T}$	1	2									
$\mathbb{D}_4$	1	0	1								
$\mathbb{D}_3$	1	0	0	1							
$\mathbb{C}_4$	1	0	1	0	2						
$\mathbb{D}_2$	1	0	1	0	0	2					
$\mathbb{D}_2'$	1	2	3	0	0	0	6				
$\mathbb{C}_3$	1	2	0	1	0	0	0	2			
$\mathbb{C}_2$	1	0	1	2	0	2	0	0	2		
$\mathbb{C}_2'$	1	2	1	0	2	2	6	0	0	4	
$\mathbb{E}$	1	2	3	4	6	6	6	8	12	12	24

Table 9 displays, for any class $\mathbb{K}$ of subgroups $K \leq O$, the partition of $p=8$ into K-orbit lengths, the size of the conjugacy class C_κ, the cardinality of the intersection $C_\kappa \cap Y$ with a Young-subgroup of type $S_4 \times S_4$, and, finally, the number of K-invariant mappings with gross formula B^4W^4. We employ the notation $[1^{\alpha_1}2^{\alpha_2}\dots n^{\alpha_n}]$ for the partition of n with α_i summands i.

Table 9.

	C_κ	$\lvert C_\kappa\rvert$	$\lvert C_\kappa \cap S_4 \times S_4\rvert$	$i(K, B^4 W^4)$
$\mathbb{O}$	[8]	5040	0	0
$\mathbb{T}$	$[4^2]$	1260	36	2
$\mathbb{D}_4$	[8]	5040	0	0
$\mathbb{D}_3$	[62]	3360	0	0
$\mathbb{C}_4$	$[4^2]$	1260	36	2
$\mathbb{D}_2$	$[4^2]$	1260	36	2
$\mathbb{D}_2'$	$[4^2]$	1260	36	2
$\mathbb{C}_3$	$[31^2]$	1120	64	4
$\mathbb{C}_2$	$[2^4]$	105	9	6
$\mathbb{C}_2'$	$[2^4]$	105	9	6
$\mathbb{E}$	$[1^8]$	1	1	70

The corresponding system of linear equations is readily solved, resulting in the spectrum of orbit symmetries as follows.

$\mathbb{O}$	$\mathbb{T}$	$\mathbb{D}_4$	$\mathbb{D}_3$	$\mathbb{C}_4$	$\mathbb{D}_2$	$\mathbb{D}_2'$	$\mathbb{C}_3$	$\mathbb{C}_2$	$\mathbb{C}_2'$	$\mathbb{E}$
0	1	0	0	1	1	0	1	2	0	1

As a final remark, based upon a one-to-one correspondence between K-invariant mappings of type II and certain K-invariant mappings of type I, a direct approach to the fixed-point numbers $i(K, J)$ for type II actions (i.e. where G acts on P and on L, simultaneously) has been outlined in [16]. The resulting closed form expression is, however, a rather complicated one, and so we will not discuss it here.

5. Qualitative discussion: Which subsymmetries are realized?

In the preceding paragraphs we have provided the tools for enumerating substitution patterns (i.e. orbits of mappings) by substitution symmetry. For this purpose, the table of marks of the group in question is needed as well as the list of fixed-point numbers of its various subgroups. Now we are interested in learning which subsymmetries occur at all among the symmetries of substitution patterns. Of course we can answer that question by calculating, for any subsymmetry, the corresponding number of patterns and see whether it turns out to be zero or not, but we should like to know whether there is a direct and more simple approach. We restrict ourselves to type I actions, i.e. a group G acts on L^P by acting on P exclusively,

$$g : \varphi \mapsto \varphi \circ \pi_g^{-1}. \tag{54}$$

Our question now is: given a conjugacy class $\mathbb{H}$ of subgroups of G, is there an orbit of mappings with symmetry $\mathbb{H}$? Equivalently, we may ask: given a subgroup H of G, does there exist a mapping $\varphi \in L^P$ with stabilizer $G_\varphi = H$? For answering these questions, the notion of a partition of a set – to be distinguished from that of a partition of a number – turns out to be useful.

Let a set P be subdivided into mutually disjoint non-empty subsets A_i,

$$P = \bigcup_i A_i, \quad A_i \cap A_j = \varnothing. \tag{55}$$

The collection $\mathscr{A} = \{A_1, A_2, \ldots\}$ of the subsets A_i is called a partition of P. Often, the subsets A_i are called the blocks of the partition $\mathscr{A}$. Another partition $\mathscr{B}$ of P is called finer than $\mathscr{A}$ (synonymously, $\mathscr{B}$ is a sub-partition of $\mathscr{A}$), if $\mathscr{B}$ is obtained from $\mathscr{A}$ by partitioning its blocks A_i, in other words, if any block B_j is contained in one of the blocks A_i. We write $\mathscr{B} \leqslant \mathscr{A}$ to denote this event. Of course, any partition $\mathscr{A}$ of P is associated with a partition α of $p = |P|$, which is made up by the block lengths $a_i = |A_i|$,

$$p = \sum_i a_i. \tag{56}$$

There are now partitions of the set of sites, P, associated with any subgroup $H \leqslant G$ and with any mapping $\varphi \in L^P$ as follows.

i) the orbit-partition $\mathscr{B}_H$ of a subgroup $H \leqslant G$ is the partition of P into H-orbits.
ii) the fibre-partition $\mathscr{A}_\varphi$ of a mapping $\varphi \in L^P$ is the partition of P into the subsets of preimages of the elements in L, $\mathscr{A}_\varphi = \{A_X \neq \phi\}$, where $A_X = \{i \in P \mid \varphi(i) = X\}$.

Again we denote by G_φ the stabilizer of φ,

$$G_\varphi = \{g \in G \mid \varphi \circ \pi_g^{-1} = \varphi\}. \tag{57}$$

We know already, that a mapping φ is H-invariant if and only if φ is constant on the H-orbits of P. In other words

$$H \leqslant G_\varphi \Leftrightarrow \mathscr{B}_H \leqslant \mathscr{A}_\varphi. \tag{58}$$

Now let H and K be subgroups of G with the same orbit-partition, and let H be a subgroup of K. Then H cannot be the stabilizer of some mapping φ, since any H-invariant map is automatically K-invariant as well. So the conjugacy class $\mathbb{H}$ is not among the candidates for symmetries of substitution patterns. And we can go on: if H and K have a common orbit partition, the same applies to the subgroup $\langle H, K\rangle$ generated by H and K, and from that we conclude that among all the subgroups with the same orbit partition there is a maximal one, and this is the only candidate for being the stabilizer of some mapping. And these maximal subgroups *are* indeed stabilizers of mappings. Namely, let $H \leqslant G$ be maximal in the previous sense, and let $\varphi \in L^P$ be such that $\mathscr{A}_\varphi = \mathscr{B}_H$. Then $G_\varphi = H$. As a final remark, the lattice of these maximal subgroups is isomorphic to the refinement lattice of their orbit partitions in the sense that

$$H \leqslant K \Leftrightarrow \mathscr{B}_H \leqslant \mathscr{B}_K. \tag{59}$$

The implication $H \leqslant K \Rightarrow \mathscr{B}_H \leqslant \mathscr{B}_K$ is evident. In reverse, let H not be a subgroup of K. Then H and K generate a group $\langle H, K\rangle$, that is a genuine supergroup of K and has the same orbit partition as K. But then K was not maximal, in contradiction to our starting assumptions.

Example 5

Let $P=\{1,2,3,4\}$ be the corners of a square, and choose G to be C_{4v}, i.e. the symmetry of the square as an object in the plane. The figure below shows its lattice of subgroups, together with their orbit partitions. The encircled subgroups are the maximal ones, for their respective partitions, while the other ones fail to meet this condition. The figures at the end demonstrate that it is exactly the conjugacy classes of these maximal subgroups that occur among the symmetries of substitution patterns. The subgroups of C_{4v} are identified as the symmetries of distortions of the square, where this appears to be necessary.

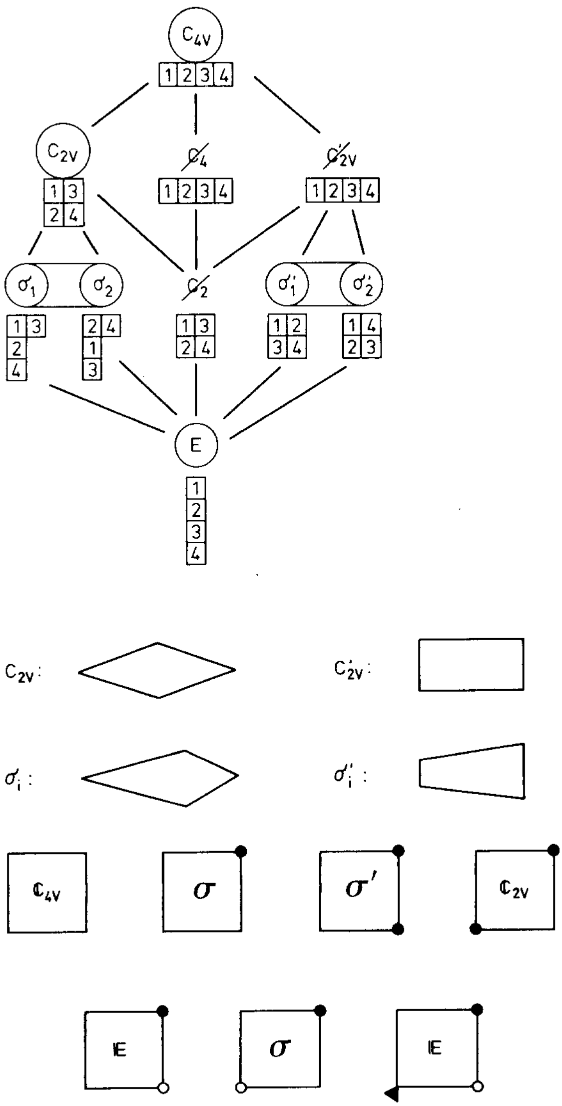

Fig. 21

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