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ORIGINAL PAPER

Permutational isomers on a molecular skeleton with neighbor-excluding ligands

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Abstract Permutational isomers of ligands substituted on a molecular skeleton are studied under a condition on the ligand placement which excludes a second ligand of the same type at a neighboring skeletal site. General theory to treat such a circumstance is developed to identify a correspondence between isomers and suitable double cosets of groups involving permutations of ligands amongst skeletal sites. Then this theory is illustratively applied for a selection of skeletons, including an experimentally realized hexamalono-buckminsterfullerene skeleton, with 12 ligation locations.

Keywords Symmetry · Isomers · Enumeration · Permutations · Double cosets · Exclusionary ligation · Hexamalono-buckminsterfullerene

1 Introduction

The characterization of arrangements of substituents on a fixed skeleton is a long-studied isomer problem in chemistry. In particular Polya gave [1–3] a seminal formulation and constructive enumeration, the ideas being of a general sort to enumerate symmetry mediated equivalence classes of mappings, often now described in many mathematics combinatorics texts, typically with little or no reference to chemistry. There are a couple collections [4,5] of chemical applications. Read [6] reviews Polya's work, its chemical aspects, and subsequent work including that in the chemical literature up through ∼1985. There are more recent chemical reviews [7–10], while Fujita's [11] and El-Basil's [12] books describe substitutional-isomer enumeration for isomers of particular subsymmetries of the overall symmetry of the parent skeleton. Kerber [13] gives a comprehensive description of the different mathematical

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developments concerning this general subject describable as "enumeration under group action". Notably Kerber's book includes Ruch et al. [14] elegant recasting of the theory in terms of double cosets, such as typically is not presented in combinatorics texts. This approach makes little use of auxiliary nomenclature and concepts not already present in group theory—while at the same time Ruch et al. approach uses more group-theoretic ideas than explicitly identified in Polya's approach. Ultimately it is not so clear whether the two approaches are fully equivalent, in that Polya's original approach entailed a special choice of one of the subgroups (the "ligand subgroup") appearing more generally in the double cosets of the theory of Ruch et al. And though deBruijn [15] has extended the Polya enumeration theory to allow a more general such subgroup, there is a yet further generalization [16] of the categories of equivalence classes possible within the framework of Ruch et al.—to so-called "double classes".

Throughout all this work the qualitative symmetry-mediated behavior of the ligands being substituted on the skeleton is centrally relevant. Different qualitative presumptions concerning these ligands have been made at different times:

- Polya's work [1,2] assumed geometrically structureless ligands attached "independently" at skeletal sites. That is, the ligands are presumed to be placeable one to a site, with the ligands only distinguished by labels (or "colors" in Polya's language) independent of the group action and position.
- Hasselbarth and Ruch extended [17] applications to ligands which have an internal chirality, so that improper rotations on the system as a whole (including both skeleton and ligands) change the ligands' chiralities. See also Fujita's later work [11].
- The possibility of bidentate (or more generally polydentate) ligands were treated [18], though the "solution" is not what is frequently desired as it allows all possible bindings between the skeletal sites and the chelate ligation sites (so that different ends of a bidentate ligand may be inordinately far apart).
- Special chemical "ligational" substructures were considered [19] which only in a loose sense could be termed ligands, changing under certain (even "proper-rotational") symmetry transformations on the system (the ligational substructures in effect being part of the skeleton).
- Balasubramanian [7] generalized the idea of independent ligands to allow them to transform like selected non-totally symmetric irreducible representations, so that, the ligand designation might incorporate their internal states (say of spin).

The bulk of the chemical work [4,5] follows Polya with independent structureless ligands, as also does the work of Fujita [11] and El-Basil [12] on subsymmetry isomer enumeration, and finally the great bulk of Kerber's book [13]. Especially in one commentary [18] it was noted that there are very many chemical isomer-enumeration problems not readily treatable by Polya's classical theory, or even by various extensions [20–24] of it—one such problem being that where the presence of a ligand of one type at a site selects for another at a neighboring site.

Here one special sort of problem where a ligand at one site precludes like ligands at neighboring sites is addressed—and "solved". This special "ligand exclusionary" problem occurs when the various sites fall into pairs such that ligation at one site of a pair solely excludes ligation at the other site of the pair. A particular case of this

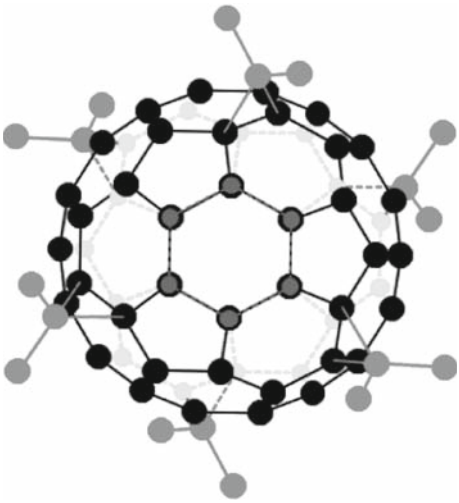

Fig. 1 The hexamalonic-buckminsterfullerene species of $\mathfrak{T}_h$ symmetry. The malonic acid moieties are appear around the periphery, with the O & H atoms suppressed. The C_{60} atoms on the "back-side" of the C_{60}-skeleton are with 6 of them hidden behind the central 6 carbons of the "front-side"

circumstance occurs with the decarboxylation of a highly symmetric hexa-malonic acid derivative of buckminsterfullerene, $C_{60}[:C(CO_2H)_2]_6$, such as experimentally obtained and investigated by Cerar et al. [25]. This novel C_{60}-derivative is of $\mathfrak{T}_h$ symmetry and is depicted in Fig. 1. There each degree-1 site is the C atom of a carboxylate group which is reactive to decarboxylation if the nearby carboxylate position is not already decarboxylated. That is, the ligand substitution here is of an H atom in place of a carboxylic-acid group, but such that no more than one carboxylate group of any one of the malonic acid moieties may be so substituted (i.e., with elimination of CO_2). The general theory for such *exclusionary substitution* then is here developed within the framework of double cosets. This hexa-malonic-C_{60} example, as well as a few related examples, are illustratively treated by this theory.

1.1 General formulation

A set S of *skeletal sites* is presumed, each site to be occupied by a ligand from a *ligand* set L. In the formulation of Ruch et al. [14] the situation bears a close similarity to real-space model building (and to molecular reality) where the number N of ligands to be attached to the skeleton exactly matches the number of skeletal sites to which they are to be attached. That is, the sets S and L have the same number N of members, and one may assume a special one-to-one correspondence φ from L to S specifying a *reference* assignment of ligands to skeletal sites. Different *arrangements* (or "configurations" of ligands on sites) may be associated with permutations of the sites relative to the ligands (after making the correspondence φ) or with permutations of the ligands relative to the sites (before making the correspondence φ). Thus there are two different sets of permutations, $\mathfrak{S}_S$ *and* $\mathfrak{S}_L$ acting either on S or L, and one might be tempted to take two notations for the two types of permutations. But we use just a single notation for the members of this single overall abstract group $\mathfrak{S}_{[N]}$ of permutations on the set $[N] \equiv \{1, 2, 3, \ldots, N\}$ of position labels, and we use the position of $P \in \mathfrak{S}_{[N]}$

relative to φ to indicate whether P acts on S or on L. That is, in $P\varphi$, the permutation $P \in \mathfrak{S}_{[N]}$ acts on site labels, whereas in φP , now P acts on ligand labels. Of course there is redundance in permuting ligands relative to sites and in permuting sites relative to ligands—this fact being manifested by the relation $P\varphi = \varphi P^{-1}$. Moreover, there are fundamental symmetries involving both the sites and the ligands, such that these symmetries dictate the "isomeric" equivalence of different arrangements. The sites are considered to have a *skeletal symmetry group* $\mathfrak{G}_S$ consisting of (certain) permutations of the skeletal-site labels. Also the ligands are considered to have a *ligand symmetry group* $\mathfrak{G}_L$ consisting of permutations of the ligand labels. Arrangements resulting from the permutation of sites by elements of $\mathfrak{G}_S$ or of the ligands by elements of $\mathfrak{G}_L$ are considered *equivalent*—that is, these arrangements identify the same *isomer*. Thence for $P_S \in \mathfrak{G}_S$, $P_L \in \mathfrak{G}_L$, and $Q \in \mathfrak{S}_{[N]}$, the arrangements $P_S\varphi Q P_L$ and φQ are equivalent. But also this means that $\varphi P_S^{-1} Q P_L$ and φQ are equivalent, and indeed we might say that $P_S^{-1} Q P_L$ and Q are *equivalent*, and denote this by $P_S^{-1} Q P_L \sim Q$. As a consequence

$$P \sim Q \Leftrightarrow \quad P \in \mathfrak{G}_S Q \mathfrak{G}_L \equiv \{A Q B \,|A \in \mathfrak{G}_S, B \in \mathfrak{G}_L\} \tag{1}$$

this set being termed a *double coset*—or more precisely a $(\mathfrak{G}_S, \mathfrak{G}_L)$-double coset, in $\mathfrak{S}_{[N]}$. That is, the isomers are in one-to-one correspondence with these double cosets. See also some reviews [10,13].

This formalism is somewhat different than that of Polya, and actually applies to circumstances beyond those originally identified by Polya, including our considered circumstance, with exclusionary locationing of ligands. As noted by Ruch et al. [14] the enumeration of $(\mathfrak{A}, \mathfrak{B})$-double cosets in a group $\mathfrak{G}$ is given by a convenient formula of Frobenius [26]

$$z = \frac{|\mathfrak{G}|}{|\mathfrak{A}|\,|\mathfrak{B}|} \sum_{\rho}^{\mathfrak{G}} \frac{\left|\mathfrak{A} \cap C_\rho\right| \left|\mathfrak{B} \cap C_\rho\right|}{\left|C_\rho\right|} \tag{2}$$

where $|T|$ denotes the order of a set T, and the sum is over *conjugacy classes* C_ρ of the parent group $\mathfrak{G}$. Since via (1) double cosets correspond to isomers, the enumeration of isomers is then accomplished by (2).

Though not needed to make the new development of the following section, it is informative to recall the traditional case of independent ligands without exclusionary locationing, for which $\mathfrak{G} = \mathfrak{S}_{[N]}$. Then the conjugacy classes (of $\mathfrak{S}_{[N]}$) have an especially simple and well-known characterization, as all those permutations with a given (disjoint) *cycle structure*, whence the class label ρ is identified to a partition of N, and conveniently represented as

$$\rho = (1^{\rho_1} 2^{\rho_2} 3^{\rho_3} \ldots N^{\rho_N}) \tag{3}$$

where ρ_m is the number of disjoint m-cycles occurring in a permutation of this class (Thence $\sum_i i\rho_i = N$). Moreover, the number of elements of C_ρ is given by a simple (and well known) formula

$$\left|C_\rho\right| = N! \prod_i i^{\rho_i} \cdot \rho_i! \tag{4}$$

For a particular skeletal group, it often occurs that the group $\mathfrak{A} = \mathfrak{G}_S$ has elements in relatively few classes of $\mathfrak{S}_{[N]}$, so that only a few $\left|\mathfrak{A} \cap C_\rho\right| = \left|\mathfrak{G}_S \cap C_\rho\right|$ appearing in (2) are $\neq 0$. The traditional Polya problem is solved taking $\mathfrak{B}$ to be a product of disjoint symmetric groups for separate sets of distinguishable ligands—that is, if $L = \bigcup_\beta B_\beta$ with B_β the set of (identical) ligands of type β, then $\mathfrak{B} = \mathfrak{G}_L = \prod_\beta^\times \mathfrak{S}_{B_\beta}$, and the intersections $\left|\mathfrak{B} \cap C_\rho\right|$ (for ρ for which $\left|\mathfrak{G}_S \cap C_\rho\right| \neq 0$) are relatively easy to determine, and some of these may turn out to be 0. This then provides a means for enumerating isomers [via (2)], such as is much more efficient than hand generation if the circumstance is at all complicated. Indeed it often is quite efficient even when the number of isomers precludes their individual computer generation.

2 The case with exclusionary ligands

The implementation of our condition of a ligand of a given type excluding another of the same type at a neighbor site is straight-forward so long as each site has just one such neighbor site, as we now assume. A site and its unique neighbor subject to exclusion are termed a *near-pair*. Then the set of N sites is partitioned into $n \equiv N/2$ near-pairs. The ligand set L is presumed to include no more of the exclusionary ligands than may be accommodated, and the reference assignment φ is imagined to satisfy this exclusionary condition. Then not all the arrangements (of ligands on sites) are to be allowed—more particularly only those which do not permute two of the exclusionary ligands to a near-pair of sites of S. That is, not all $P \in \mathfrak{S}_{[N]}$ are to be allowed for arrangements φP—indeed we may constrain them to be a member of a subgroup of $\mathfrak{S}_{[N]}$ which permutes near-pairs as a whole amongst themselves, while also possibly interchanging the two sites within a near-pair. Then let $\mathfrak{S}^*_{[n]}$ denote the group which permutes whole near-pairs around amongst themselves, and let $\mathfrak{E}_i \equiv \{I, \varepsilon_i\}$ denote the two-element *exchange* group with ε_i the permutation exchanging the two members of the ith near-pair, and also let $\mathfrak{E}_{[n]} \equiv \prod_i^{\in[n]} \mathfrak{E}_i$. Then the full group of allowed permutations to be considered is

$$\mathfrak{G} = \mathfrak{S}^*_{[n]} \mathfrak{E}_{[n]} \tag{5}$$

If the two sites of the ith near-pair are denoted i_a and i_b, then ε_i is just the transposition $(i_a i_b)$. Much as in the standard treatment at the end of the last section, the allowed isomers correspond to $(\mathfrak{G}_S, \mathfrak{G}_L)$-double cosets now in $\mathfrak{G}$. But care needs to be exercised with the ligand group $\mathfrak{B} = \mathfrak{G}_L$, as the traditional-case for m non-exclusionary ligands generally gives elements not in the overall group $\mathfrak{G}$ of now allowed permutations. But this is fairly easily resolved, on restriction to the part of this conventional group shared with the now allowed overall group $\mathfrak{G}$.

As a first circumstance consider the case of exactly m ligands of a single type to be substituted, while all the $N - m$ others are the single "unsubstituted" (perhaps undecarboxylated) type. Then for the ordinary non-exclusionary case the ligand group is $\mathfrak{B} = \mathfrak{G}_L = \mathfrak{S}_{[m]} \times \mathfrak{S}_{[m+1,N]}$, where $[l, m]$ denotes the set of integers i which are

$\geq l$ and $\leq n$, for instance, with $[m+1, N] \equiv \{m+1, m+2, \ldots, N\}$. But if these m substituent ligands (or decarboxylations) are exclusionary, then

$$\mathfrak{B} = \mathfrak{G}_L = (\mathfrak{S}_{[m]_a} \times \mathfrak{S}_{[n-m,n]_a \cup [n]_b}) \cap \mathfrak{G} = (\mathfrak{S}^*_{[m]} \times \mathfrak{S}^*_{[m+1,n]})\mathfrak{E}_{[m+1,n]} \tag{6}$$

where $[n]_a \equiv \{1_a, 2_a, \ldots, n_a\}$ and $[n]_b \equiv \{1_b, 2_b, \ldots, n_b\}$. The generation of isomers is equivalent to the generation of the consequent $(\mathfrak{G}_S, \mathfrak{G}_L)$-double cosets in $\mathfrak{G}$.

Enumeration is done by the same general double-coset formula (2) as before, with ρ now identifying conjugacy classes for the group $\mathfrak{G}$ of (5) rather than the group $\mathfrak{S}_{[N]}$. As shown in the appendix, the conjugacy classes of this group of (5) are not so very much different in nature than those for $\mathfrak{S}_{[n]}$—the classes of $\mathfrak{G}$ involve partitions of n much as the classes of $\mathfrak{S}_{[N]}$ involve partitions of N. The elements of $\mathfrak{G}$ of (5) turn out to be of the form $P^*\varepsilon_T$ for $P^* \in \mathfrak{S}^*_{[n]}$ and for $\varepsilon_T \equiv \prod_i^{\in T} \varepsilon_i$ with $T \subseteq [n]$ corresponding to some subset of near-pairs. Moreover the conjugacy classes of $\mathfrak{G}$ are specified: first by the disjoint cycle structure of $P^* \in \mathfrak{S}^*_{[n]}$ (viewed as a permutation of near-pairs), and second by a sequence of "parities" $s = \pm$ associated with each cycle appearing in P^*. For a given cycle C in P^* there may be different ε_j comprising ε_T with j also a member of the cycle C, and the parity of the number of such ε_j is the *parity* s associated to the cycle C. As a consequence, it is convenient to label the conjugacy classes of $\mathfrak{G}$ as

$$\rho \equiv (1_+^{\rho_{1+}} 1_-^{\rho_{1-}} 2_+^{\rho_{2+}} 2_-^{\rho_{2-}} 3_+^{\rho_{3+}} \ldots n_-^{\rho_{n-}}) \tag{7}$$

where ρ_{is} is the number of length-i cycles with a parity of s $(= \pm)$ for the number of ε_k associated to a cycle. Moreover there is a simple formula for the order of a class of $\mathfrak{G} = \mathfrak{S}^*_{[n]}\mathfrak{E}_{[n]}$, namely as

$$\left|C_\rho\right| = n! \prod_i \{2^{(i-1)(\rho_{i+}+\rho_{i-})}/(i^{\rho_{i+}+\rho_{i-}} \cdot \rho_{i+}!\rho_{i-}!)\} \tag{8}$$

also as shown in the appendix. Thus the isomer count, for m exclusionary ligands, is

$$z_m = \frac{|\mathfrak{G}|}{|\mathfrak{G}_S| \left|\mathfrak{S}^*_{[m]} \times \mathfrak{S}^*_{[m+1,n]}\mathfrak{E}_{[m+1,n]}\right|} \times \sum_\rho^{\mathfrak{G}} \frac{\left|\mathfrak{G}_S \cap C_\rho\right| \left|(\mathfrak{S}^*_{[m]} \times \mathfrak{S}^*_{[m+1,n]}\mathfrak{E}_{[m+1,n]}) \cap C_\rho\right|}{\left|C_\rho\right|} \tag{9}$$

Noting that $|\mathfrak{G}| = n!2^n$ and $\left|\mathfrak{S}^*_{[m]} \times \mathfrak{S}^*_{[m+1,n]}\mathfrak{E}_{[m+1,n]}\right| = m!(n-m)!2^{n-m}$, the pre-factor before the summation in (9) becomes

$$\text{pre-fac} = \frac{2^m}{|\mathfrak{G}_S|} \binom{n}{m} \tag{10}$$

The $\left|(\mathfrak{S}^*_{[m]} \times \mathfrak{S}^*_{[m+1,n]}\mathfrak{E}_{[m+1,n]}) \cap C_\rho\right|$ are obtained by factoring ρ in all possible ways consonant with the group factors $\mathfrak{S}^*_{[m]}$ and $\mathfrak{S}^*_{[m+1,n]}\mathfrak{E}_{[m+1,n]}$—that is, the $\rho_{i\pm}$ parts $i_\pm$ for each i are put together to form two new class labels $\rho[m]$ and $\rho[m+1,n]$ for the first m and last $n-m$ permutation indices, with the condition that only i_+ parts go into $\rho[m]$. Then

$$\left|(\mathfrak{S}^*_{[m]} \times \mathfrak{S}^*_{[m+1,n]}\mathfrak{E}_{[m+1,n]}) \cap C_\rho\right| = \sum_{\rho[m],\rho[m+1,n]}^{\text{factors}} \left|\mathfrak{S}^*_{[m]} \cap C_{\rho[m]}\right| \cdot \left|\mathfrak{S}^*_{[m+1,n]}\mathfrak{E}_{[m+1,n]} \cap C_{\rho[m+1,n]}\right| \tag{11}$$

where the terms in this last summation are given as in (4) and (8). This is not really so different from the computation of $\left|\mathfrak{G}_L \cap C_\rho\right|$ as appears in the traditional non-exclusionary circumstance.

But there might be more than one type of exclusionary ligand, or there may be several types of non-exclusionary ligands. What is relevant here is the pairs of ligands allowed to share a near-pair of sites—each possible pair of ligands allowed at a near-pair behaves like a single *pair-ligand* substitutable at a near-pair (of sites) as a whole. With the presumption that they are otherwise independent, $\mathfrak{G}_S$ becomes a (disjoint) product of groups $\mathfrak{S}^*_{B_\beta}$ (for ordinary non-exclusionary pair-ligands) and $\mathfrak{S}^*_{B_\beta}\mathfrak{E}_{B_\beta}$ (for our current exclusionary ligands). The conjugacy classes of these are characterized (in accordance with the preceding discussion), along with the order $\left|\mathfrak{G}_S \cap C_\rho\right|$ which involves products of what might be denoted $\left|\mathfrak{S}^*_{B_\beta} \cap C_\rho\right|$ and $\left|\mathfrak{S}^*_{B_\beta}\mathfrak{E}_{B_\beta} \cap C_\rho\right|$. This then completes our general method for the enumeration of such ligand-exclusionary isomers.

3 Applications to skeletons of different malonate moieties

First, a preliminary example much simpler than that indicated in our target case of Fig. 1 might be considered. That is, a preliminary very simple skeleton is considered, involving just 3 malonate moieties, as in Fig. 2. Here the 3-fold dihedral symmetry group is $\mathfrak{D}_{3h}$, or in consonance with Fig. 2,

$$\begin{aligned}\mathfrak{D}_{3h} &= \{I, \sigma_h\}\mathfrak{C}_{3v}\\ \mathfrak{C}_{3v} &= \{I, \sigma_v\}\mathfrak{C}_3\\ \mathfrak{C}_3 &= \{I, C_3, C_3^2\}\end{aligned}$$

And the different group elements if considered as permutations can be represented as

$$\begin{aligned}\sigma_h &= (1_a1_b)(2_a2_b)(3_a3_b)\\ \sigma_v &= (1_a)(1_b)(2_a3_a)(2_b3_b)\\ C_3 &= (1_a2_a3_a)(1_b2_b3_b)\end{aligned}$$

where we use a notation with $(i_1, i_2, \ldots, i_m)$ denoting the cyclic permutation which takes $i_1 \mapsto i_2$, $i_2 \mapsto i_3$, …, and $i_m \mapsto i_1$. The overall group $\mathfrak{G} = \mathfrak{S}^*_{[3]}\mathfrak{E}_{[3]}$for

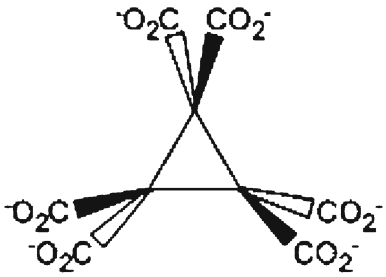

Fig. 2 A trimalonic-cyclopropane structure, with the central atoms of each malanoic acid being a member of the cyclopropane ring

exclusionary substitution has

$$\begin{aligned}\mathfrak{S}^*_{[3]} &= \{I, (123)^*, (132)^*, (12)^*, (23)^*, (31)^*\} = \mathfrak{C}_{3v}\\ \mathfrak{E}_{[3]} &= \mathfrak{E}_1\mathfrak{E}_2\mathfrak{E}_3\\ \mathfrak{E}_i &= \{I, (i_a i_b)\}\end{aligned}$$

where we have used the notation from the appendix with $P^* \equiv P_a P_b$ for which P_c denotes just a permutation of the indices $[n]_c \equiv \{1_c, 2_c, \ldots, n_c\}$ for $c \in \{a, b\}$. E.g., $(123)^* = (1_a 2_a 3_a)(1_b 2_b 3_b)$ and $(12)^* = (1_a 2_a)(1_b 2_b)$. Thence it may be seen that the elements of $\mathfrak{D}_{3h}$ fall into 6 conjugacy classes

$$\{I\}, \{C_{2a}, C_{2b}, C_{2c}\}, \{C_3, C_3^{-1}\}, \{\sigma_h\}, \{\sigma_{bc}, \sigma_{ca}, \sigma_{ab}\}, \{S_6, S_6^{-1}\}$$

which also fall in different $\mathfrak{G}$-conjugacy classes, respectively with

$$\rho = (1^3_+),\ (1_+2_+), (3_+), (1^3_-), (1_-2_+), (3_-)$$

in the notation of (7). The relevant data for these classes, along with the numbers of their elements in $\mathfrak{D}_{3h}$ and $\mathfrak{G}_L = (\mathfrak{S}^*_{[m]} \times \mathfrak{S}^*_{[m+1,n]})\mathfrak{E}_{[m+1,n]}$ is summarized in Table 1. The central area of this table gives the different values of $\left|\mathfrak{G}_L \cap C_\rho\right|$ with the different rows identified by different substituent numbers m (and associated $\mathfrak{G}_L$) appearing in the left-hand central area of the table, while the columns of this central area are identified by different classes C_ρ with the ρ-labels appearing in the top central portion of the table. The center part of the bottom row of the table gives the different values of $\left|\mathfrak{G}_S \cap C_\rho\right|$, again with the different ρ indicated in the top central portion of the table. Then for a given number m of substituents, one combines triples of elements $(\left|\mathfrak{D}_{3h} \cap C_\rho\right|, \left|\mathfrak{G}_L \cap C_\rho\right|$, and $\left|C_\rho\right|)$ together as $\left|\mathfrak{D}_{3h} \cap C_\rho\right| \cdot \left|\mathfrak{G}_L \cap C_\rho\right| / \left|C_\rho\right|$ and sums on ρ to obtain the sum-part Σ_m of (9). Multiplication by the pre-factor of (10), then gives the isomer counts z_m, all as summarized in the right-hand central portion of the table. Of course, the isomers for the simple skeleton of Fig. 2 may be easily worked out by hand, without any of this general group-theoretic machinery. But the pattern of calculation is the same in the following less trivial examples.

For the hexamalonate-C_{60} species of Fig. 1, the skeletal symmetry group is of a tetrahedral symmetry. If improper rotations are precluded, then the group is just the proper-rotational order-12 tetrahedral group $\mathfrak{T}$, and with its use, one identifies *stereo-isomers* (for which chiral structures are distinguished). If the improper rotations

Table 1 Enumeration of exclusionary isomers for the $n = 3$ $\mathfrak{D}_{3h}$-skeleton

m	$\lvert\mathfrak{G}_L \cap C_\rho\rvert$	ρ						Pre-fac	Σ_m	z_m
		(1_+^3)	(1_+2_+)	(3_+)	(1_-^3)	(1_-2_+)	(3_-)			
0	$\lvert C_\rho\rvert$	1	6	8	1	6	8	1/12	12	1
1	$\lvert\{I, \sigma_v\}\mathfrak{E}_{\{2,3\}} \cap C_\rho\rvert$	1	2	0	0	0	0	1/2	2	1
2	$\lvert\{I, \sigma_v'\}\mathfrak{E}_3 \cap C_\rho\rvert$	1	1	0	0	1	0	1	2	2
3	$\lvert\mathfrak{C}_{3v} \cap C_\rho\rvert$	1	3	2	0	0	0	3/2	3	2
	$\lvert\mathfrak{G}_L \cap C_\rho\rvert = \lvert\mathfrak{D}_{3h} \cap C_\rho\rvert$	1	3	2	1	3	2	Total = 6		

are included, then the group $\mathfrak{T}_h = \mathfrak{T} \cdot \{I, \hat{i}\}$ includes the inversion $\hat{i}$, and with its use, one identifies *structural* (or constitutional) *isomers* (where enantiomers are not distinguished). The elements of $\mathfrak{T}_h$ fall into 6 conjugacy classes

$$\{I\}, \{C_{2x}, C_{2y}, C_{2z}\}, \{C_{3a}, C_{3a}^{-1}, C_{3b}, C_{3b}^{-1}, C_{3c}, C_{3c}^{-1}, C_{3d}, C_{3d}^{-1}\},$$

$$\{\hat{i}\}, \{\sigma_{yz}, \sigma_{zx}, \sigma_{xy}\}, \{S_{3a}, S_{3a}^{-1}, S_{3b}, S_{3b}^{-1}, S_{3c}, S_{3c}^{-1}, S_{3d}, S_{3d}^{-1}\}$$

To treat the traditional case where the ligands are non-exclusionary, say as concerns the formation of methyl esters, these elements then are identified to different conjugacy classes of $\mathfrak{S}_{[N]}$. Indeed, they occur in just 5 $\mathfrak{S}_{[N]}$-conjugacy classes, as

$$\rho = (1^{12})\ ,\ (2^6), (3^4), (2^6), (1^4 2^4), (6^2)$$

If there are m methylations (say for the first m ligands), then the ligand group is $\mathfrak{G}_L = \mathfrak{S}_{[m]} \times \mathfrak{S}_{[m+1,N]}$. The resultant (nonexclusionary) computations paralleling those of the preceding (exclusionary) case then appear as in Table 2, which however does not show rows for more than n $(= N/2 = 6)$ substituents, since we know (because of the symmetry between interchange of substituted and unsubstituted sites) that the later isomer counts are trivially given via $z_m = z_{N-m}$. Here even for $m \leq 6$ certainly many of these have a pair of methyl groups in the same malonic acid moiety. The parallel to the computation of Table 1 is seen to be quite close, and the summary in this Table 2 may be observed to closely parallel the usual Polya-theoretic approach (by way of cycle indices).

Next consider the exclusionary case, as with decarboxylation where removal of CO_2 from any of the carboxylic acid group inhibits decarboxylation at the second carboxylic acid group of that malonic-acid moiety. Again Cerrar et al. [25] have prepared the water-soluble hexamalonate-C_{60} species, which further they have found under mildly basic conditions releases CO_2 molecules up to the point of 6 of them, but no more, and each CO_2 from different malonate groups. Thence our modification of the Polya enumeration applies. The overall group is $\mathfrak{G} = \mathfrak{S}_{[6]}^* \mathfrak{E}_{[6]}$, and the elements of $\mathfrak{T}_h$ as already identified may be verified to fall into six different $\mathfrak{G}$-conjugacy classes, as

Table 2 For non-exclusionary isomers of the $N = 12$ $\mathfrak{T}_h$-C_{60}skeleton

m	$\lvert\mathfrak{G}_L \cap C_\rho\rvert$	ρ					Pre-fac	Σ_m	z_m
		(1_+^6)	(2^6)	(3^4)	$(1^4 2^4)$	(6^2)			
0	$\lvert C_\rho\rvert$	1	10395	246400	51975	6652800	1/24	24	1
1	$\lvert(\mathfrak{S}_{\{1\}} \times \mathfrak{S}_{[2,12]}) \cap C_\rho\rvert$	1	0	0	17325	0	1/2	2	1
2	$\lvert(\mathfrak{S}_{\{1,2\}} \times \mathfrak{S}_{[3,12]}) \cap C_\rho\rvert$	1	945	0	7875	0	11/4	20/11	5
3	$\lvert(\mathfrak{S}_{[1,3]} \times \mathfrak{S}_{[4,12]}) \cap C_\rho\rvert$	1	0	4480	4725	0	55/6	78/55	13
4	$\lvert(\mathfrak{S}_{[1,4]} \times \mathfrak{S}_{[5,12]}) \cap C_\rho\rvert$	1	315	0	3255	0	165/8	72/55	27
5	$\lvert(\mathfrak{S}_{[1,5]} \times \mathfrak{S}_{[6,12]}) \cap C_\rho\rvert$	1	0	0	2625	0	33	38/33	38
6	$\lvert(\mathfrak{S}_{[1,6]} \times \mathfrak{S}_{[7,12]}) \cap C_\rho\rvert$	1	225	1600	2475	14400	77/2	100/77	50
	$\lvert\mathfrak{G}_L \cap C_\rho\rvert = \lvert\mathfrak{T}_h \cap C_\rho\rvert$	1	4	8	3	8	Total = 220		

Table 3 For exclusionary isomers of the $N = 12$ $\mathfrak{T}_h$ -C_{60} skeleton

m	$\lvert\mathfrak{G}_L \cap C_\rho\rvert$	ρ						Pre-fac	Σ_m	z_m
		(1_+^6)	$(1_-^2 2_+^2)$	(3_+^2)	(2_+^3)	$(1_+^2 1_-^2 2_+)$	(6_+)			
0	$\lvert C_\rho\rvert$	1	180	640	120	180	3840	1/24	24	1
1	$\lvert(\mathfrak{S}_{\{1\}} \times \mathfrak{S}_{[2,6]}\mathfrak{E}_{[2,6]}) \cap C_\rho\rvert$	1	0	0	0	60	0	1/2	2	1
2	$\lvert(\mathfrak{S}_{[2]} \times \mathfrak{S}_{[3,6]}\mathfrak{E}_{[3,6]}) \cap C_\rho\rvert$	1	12	0	12	18	0	5/2	8/5	4
3	$\lvert(\mathfrak{S}_{[3]} \times \mathfrak{S}_{[4,6]}\mathfrak{E}_{[4,6]}) \cap C_\rho\rvert$	1	0	16	0	9	0	20/3	27/20	9
4	$\lvert(\mathfrak{S}_{[4]} \times \mathfrak{S}_{\{5,6\}}\mathfrak{E}_{\{5,6\}}) \cap C_\rho\rvert$	1	3	0	6	6	0	10	6/5	12
5	$\lvert(\mathfrak{S}_{[5]} \times \mathfrak{S}_{\{6\}}\mathfrak{E}_{\{6\}}) \cap C_\rho\rvert$	1	0	0	0	0	0	8	1	8
6	$\lvert\mathfrak{S}_{[6]} \cap C_\rho\rvert$	1	0	40	15	0	120	8/3	7/4	5
	$\lvert\mathfrak{G}_L \cap C_\rho\rvert = \lvert\mathfrak{T}_h \cap C_\rho\rvert$	1	3	8	1	3	8	Total = 40		

$$\rho = (1_+^6),\ (1_-^2 2_+^2),\ (3_+^2),\ (2_+^3),\ (1_+^2 1_-^2 2_+),\ (6_+)$$

Following the discussion at the end of the preceding section, and taking the decarboxylated malonic acid moieties to be the first m (e.g., in the reference structure), it is seen that these exclusionary "ligands" manifest a symmetry $\mathfrak{S}^*_{[m]}$, while the remaining $n - m$ pair-ligands consist of fully undecarboxylated malonic acid moieties and manifest a symmetry $\mathfrak{S}^*_{[m+1,n]}\mathfrak{E}_{[m+1,n]}$. Thus the ligand symmetry group is $\mathfrak{G}_L = \mathfrak{S}^*_{[m]} \times \mathfrak{S}^*_{[m+1,n]}\mathfrak{E}_{[m+1,n]}$. The resultant enumeration is reported in Table 3. One can see the parallel to the calculation for the earlier simpler $\mathfrak{D}_{3h}$ skeleton (summarized in Table 1), as well as the parallel to the calculation for the "standard" Polya enumeration (as in Table 2) for the present $\mathfrak{T}_h$-symmetry buckminsterfullerene derivative.

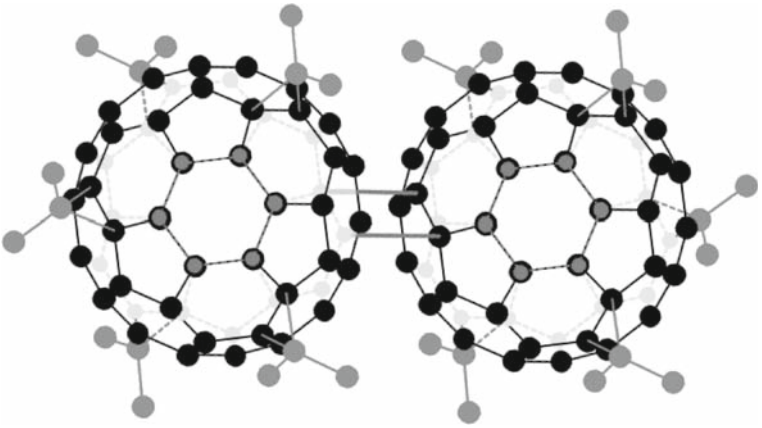

Fig. 3 A dimer of pentamalonic-C_{60} units, having an overall $\mathfrak{D}_{2h}$ symmetry. The central bonds indicate the two single bonds interconnecting the two C_{60} moieties. Again the O and H atoms on the peripheral malonic acid moieties are suppressed

But these ideas can be extended to yet further cases with exclusionary locationing of ligands. A slightly larger case is found in the deca-malonic acid derivative of two Buckminsterfullerenes joined to one another by a pair of single bonds to adjacent sites where previously we placed a 6th malonate, as in Fig. 3. The consequent skeletal symmetry group is just the dihedral group $\mathfrak{D}_{2h} = \mathfrak{D}_2 \cdot \{I, \hat{i}\}$, or if chiral structures are to be distinguished, it is just $\mathfrak{D}_2$. The overall group is $\mathfrak{G} = \mathfrak{S}^*_{[10]}\mathfrak{E}_{[10]}$, and the eight elements of $\mathfrak{D}_{2h}$ may be seen to fall into five different $\mathfrak{G}$-conjugacy classes, as

$$\rho = (1_+^{10}),\ (1_+^4 1_-^2 2_+^2),\ (1_+^2 1_-^4 2_+^2),\ (1_-^2 2_+^4) \quad \text{for} \quad I, \sigma_x, \sigma_y, C_{2z}$$
$$\& \quad \rho = (2_+^5) \quad \text{for} \quad C_{2x}, C_{2y}, \sigma_z, \hat{i}$$

Since $\mathfrak{D}_{2h}$ is smaller than the hexamalanato-C_{60} $\mathfrak{T}_h$ group, the application is simpler in some ways, though the number of skeletal positions is nearly twice as great, and the consequent isomer counts are somewhat larger, as seen in Table 4, which again parallels the earlier tables. Though with care and effort one might attempt the counts of Table 3 by hand, the results of Table 4 surely are beyond such traditional hand manipulation and generation of structures.

Further, though our Tables 1–4 have been illustrated for structural isomers, using a symmetry group including all improper rotations, the data of these tables readily allow the construction of corresponding tables for stereoisomers, using the symmetry group exclusively corresponding to proper rotations. The group of proper rotations is a subgroup, of half the size, so that all that changes are the intersection numbers in the bottom row of the tables, as well as the prefactors, which are all just twice as large.

It may be noted that there are other more brute-force conceptually simple means by which to generate the isomer counts. So long as the number of substitution sites is not overly great, one may constructively generate isomers. And this has been done [27], to check the above enumerations, and to deal further with individual properties and the underlying reaction network, at least for the hexamalono-C_{60} case.

Table 4 For exclusionary isomers of the $N = 20$ $\mathfrak{D}_{2h}$-$(C_{60})_2$ skeleton

m	$\lvert\mathfrak{G}_L \cap C_\rho\rvert$	ρ					Pre-fac	Σ_m	z_m
		(1_+^{10})	$(1_+^4 1_-^2 2_+^2)$	$(1_+^2 1_-^4 2_+^2)$	$(1_-^2 2_+^4)$	(2_+^5)			
0	$\lvert C_\rho\rvert$	1	37800	37800	75600	30240	1/8	8	1
1	$\lvert(\mathfrak{S}_{\{1\}} \times \mathfrak{S}_{[2,10]}\mathfrak{E}_{[2,10]}) \cap C_\rho\rvert$	1	15120	7560	0	0	5/2	8/5	4
2	$\lvert(\mathfrak{S}_{[2]} \times \mathfrak{S}_{[3,10]}\mathfrak{E}_{[3,10]}) \cap C_\rho\rvert$	1	5880	1680	3360	1680	45/2	22/15	33
3	$\lvert(\mathfrak{S}_{[3]} \times \mathfrak{S}_{[4,10]}\mathfrak{E}_{[4,10]}) \cap C_\rho\rvert$	1	2520	630	0	0	120	13/12	130
4	$\lvert(\mathfrak{S}_{[4]} \times \mathfrak{S}_{[5,10]}\mathfrak{E}_{[5,10]}) \cap C_\rho\rvert$	1	1305	225	540	360	420	23/21	460
5	$\lvert(\mathfrak{S}_{[5]} \times \mathfrak{S}_{[6,10]}\mathfrak{E}_{[6,10]}) \cap C_\rho\rvert$	1	750	75	0	0	1008	515/504	1030
6	$\lvert(\mathfrak{S}_{[6]} \times \mathfrak{S}_{[7,10]}\mathfrak{E}_{[7,10]}) \cap C_\rho\rvert$	1	450	45	180	180	1680	291/280	1746
7	$\lvert(\mathfrak{S}_{[7]} \times \mathfrak{S}_{[8,10]}\mathfrak{E}_{[8,10]}) \cap C_\rho\rvert$	1	315	0	0	0	1920	121/120	1936
8	$\lvert(\mathfrak{S}_{[8]} \times \mathfrak{S}_{\{9,10\}}\mathfrak{E}_{\{9,10\}}) \cap C_\rho\rvert$	1	210	0	105	210	1440	149/144	1490
9	$\lvert(\mathfrak{S}_{[9]} \times \mathfrak{E}_{\{10\}}) \cap C_\rho\rvert$	1	0	0	0	0	640	1	640
10	$\lvert\mathfrak{S}_{[10]} \cap C_\rho\rvert$	1	0	0	0	945	128	9/8	144
	$\lvert\mathfrak{G}_L \cap C_\rho\rvert = \lvert\mathfrak{T}_h \cap C_\rho\rvert$	1	1	1	1	4	Total = 7614		

4 Conclusion

The classical Polya-theory has been nicely extended within an alternative [14] double-coset framework to encompass a special circumstance of exclusionary locationing of ligands when there is but a single neighbor skeletal site from which like ligands are to be excluded. An illustration has been made for the case of malonic acid residues arranged on different skeletons, including the $\mathfrak{T}_h$-buckminsterfullerene arrangement, experimentally realized in the work of Cerar et al. [25]. But we have applied it to several other species, including those of Figs. 2–5, though computational tabulations were not explicitly displayed for the species of Figs. 4–5. The various overall isomer counts for both exclusionary and non-exclusionary cases are summarized in Table 5 for all the different skeletons entertained in the preceding section. In this table the counts of structural (or constitutional) isomers are given as a sum of two numbers a and c, with a the number of isomers which are achiral and c the number which are chiral (enantiomeric) pairs. That is, the computations of the earlier section were also repeated using the more discerning achiral skeletal groups $\mathfrak{G}_S$ comprised solely from proper rotations. The resultant stereoisomer counts are $a + 2c$, while the structural isomer counts are $a + c$, whence one sees that the differences between these two corresponding isomer counts give c. From Table 5, ones sees that when for our two C_{60}-based skeletons, the number of ligands is one less than the maximum, every isomer is chiral.

It may be mentioned that Polya's "cycle-index" approach might also be extended to deal with the present case of exclusionary ligands. With the special type of exclusion

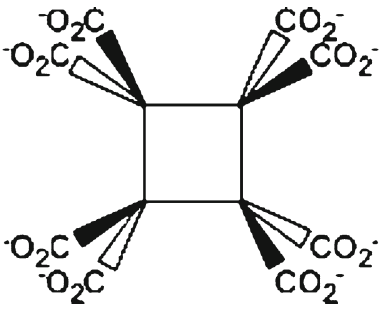

Fig. 4 A tetramalonic-cyclobutane structure, with the central atoms of each malanoic acid being a member of the cyclobutane ring

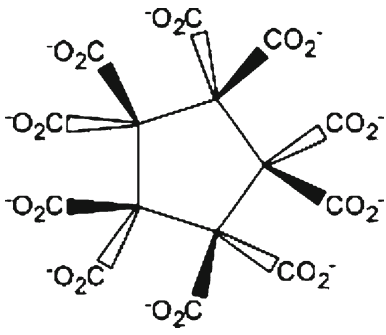

Fig. 5 A pentamalonic-cyclopentane structure, paralleling those of Figs. 2 and 4

Table 5 Summary counts for the various structures

m	$\mathfrak{D}_{3h}$		$\mathfrak{D}_{4h}$		$\mathfrak{D}_{5h}$		$\mathfrak{T}_h$		$\mathfrak{D}_{2h}$	
	Ex	Nonex	Ex	Nonex	Ex	Nonex	Ex	Nonex	Ex	Nonex
0	1+0	1+0	1+0	1+0	1+0	1+0	1+0	1+0	1+0	1+0
1	1+0	1+0	1+0	1+0	1+0	1+0	1+0	1+0	3+1	3+1
2	1+1	2+1	3+1	4+1	2+2	3+2	2+2	3+2	14+19	17+19
3	2+0	2+1	2+1	3+2	4+1	4+3	2+7	5+8	20+110	35+125
4		2+1	4+0	7+3	3+3	7+7	3+9	9+18	54+406	105+570
5		1+0		3+2	4+0	6+10	0+8	10+28	44+986	164+1856
6		1+0		4+1		7+7	2+3	14+36	84+1662	340+4720
7				1+0		4+3		10+28	32+1904	420+9480
8				1+0		3+2		9+18	56+1434	662+15494
9						1+0		5+8	0+640	658+20666
10						1+0		3+2	16+128	822+22778
11								1+0		658+20666
12								1+0		662+15494
13										420+9480
14										340+4720
15										164+1856
16										105+570
17										35+125
18										17+19
19										3+1
20										1+0

applying only to disjoint pairs, one may imagine a line drawn between the two sites of each such near-pair, and inquire about the symmetry classes of ways to orient different numbers of these lines—an orientation being a direction for the line segment, indicated by an arrow placed on the line segment. One may imagine that unoriented line segments in which neither site is occupied by a ligand, while for an oriented line segment the arrow points from the site occupied by an exclusionary ligand, to the other unoccupied member of the pair. In any event some elaboration has been made [28] of classical Polya theory to deal with oriented line-segment problems not unlike this.

Also the method as outlined here applies with greater numbers of types of ligands, just entailing further choices for the ligand group $\mathfrak{G}_L$. But it might also be mentioned that much the same idea applies with a greater number of exclusions manifested by an exclusionary ligand, so long as the sets of sites which are judged as neighbors fall into disjoint sets of otherwise mutual neighbors. That is, one deals with near-triples, or near-quadruples, etc. in place of the present consideration of near-pairs. A nice example of exclusionary substitution occurs at each C-atom of a hydrocarbon when the substituting ligand is OH.

At the same time there remain many unresolved problems of isomerism characterization. A first problem is the development of a general systematic scheme to treat isomerism when the exclusionary ligands at a skeletal site have several neighbor skeletal sites from which like ligands are excluded but without the subsets of mutually neighboring exclusionary sites falling into disjoint subsets. Also there is a question of the problem [18] for bidentate ligands in requiring the 2 ligation sites of such a biden-

tate species to be located at neighboring sites—again for the general case when there is more than one neighbor site of the skeleton. Indeed these two problems are complementary, with both viewable as generally demanding attention to "connectivity" (of skeletal and ligand sites). That is, both problems demand incorporation of information beyond the (ordinary) symmetry of the skeleton and ligands—it here being understood that "symmetry" refers both to geometric symmetry and to symmetry of ligand identity.

Finally beyond isomer enumeration, the use of the double-coset correspondents could be individually generated, such as done by Brown et al. [29,30]. Indeed elsewhere we deal [27] with individual generation to address further questions for the $\mathfrak{T}_h$-hexamalanato-C_{60} case. One such further (fundamental combinatorial) question concerns which m-ligand isomers give rise to each given $m+1$-ligand isomer. Thus both as regards extensions of enumerative procedures, and as regards further characterization, much remains to be done with (isomer) combinatorial theoretics.

Acknowledgement Acknowledgement is made (through Grant BD-0894) to the Welch Foundation of Houston, Texas.

Appendix—$\mathfrak{G} = \mathfrak{S}^*_{[n]}\mathfrak{E}_{[n]}$ and its conjugacy classes

First, a more explicitly detailed designation of the various groups may be made, for the case when there are N sites partitionable into $n = N/2$ near-pairs. If the near-pairs are designated by the integers $[n] \equiv \{1, 2, \ldots, n\}$, the two sites of the ith near-pair might be distinguished as i_a and i_b, $i \in [n]$. Then in correspondence to each permutation P in $\mathfrak{S}_{[n]}$, there are corresponding permutations $P_a \in \mathfrak{S}_{[n]_a}$ and $P_b \in \mathfrak{S}_{[n]_b}$ (with $[n]_c \equiv \{1_c, 2_c, \ldots, n_c\}$, $c \in \{a, b\}$) such that

$$P_a j_c = \begin{cases} (Pj)_a, & c = a \\ j_b, c = b(\neq a) \end{cases} \quad \& \quad P_b j_c = \begin{cases} j_a, c = a(\neq b) \\ (Pj)_b, c = b \end{cases}$$

Then $\mathfrak{S}^*_{[n]} = \{P_a \cdot P_b \,\big|\, P \in \mathfrak{S}_{[n]}\}$. Also $\mathfrak{E}_i = \{1, \varepsilon_i\}$ with ε_i the permutation $(i_a i_b)$ that exchanges i_a & i_b.

It is clear that the two component groups $\mathfrak{S}^*_{[n]}$ and $\mathfrak{E}_{[n]}$ have only one element in common, the identity I. If P is a simple permutation of the indices $[n]$, and P^* is the corresponding permutation of near-pairs, then one sees that

$$P^*\varepsilon_U = (P^*\varepsilon_U P^{*-1})P^* = \varepsilon_{PU} P^*$$

where $\varepsilon_U \equiv \prod_i^{\in U} \varepsilon_i$, $U \in [n]$, and where $PU \equiv \{Pi \,|\, i \in U\}$. Thus the set of $P^*\varepsilon_U$ are closed under multiplication and so form a group. Thus we have:

Proposition 1 *The elements of $\mathfrak{S}^*_{[n]}\mathfrak{E}_{[n]}$ form a group and are uniquely specified in the form $P^*\varepsilon_U$, for $P^* \in \mathfrak{S}^*_n$ and $\varepsilon_U \in \mathfrak{E}_{[n]}$ for $U \subseteq [n]$.*

Clearly now $P \in \mathfrak{S}_{[n]}$ has a disjoint cycle decomposition into a set D_P of disjoint cycles, and one has $P^* = \prod_C^{\in D_P} C^*$. Moreover, such a cycle involves a subset of

elements of $[n]$, and we identify this subset by $[C]$, whence a corresponding factorization of an arbitrary element of $\mathfrak{E}_{[n]}$ is possible as $\varepsilon_U = \prod_C^{\in D_P} \varepsilon_{U\cap[C]}$, with it being understood that if $U \cap [C]$ is the empty set $\emptyset$, then $\varepsilon_\emptyset = I$. Thus we have a general factorization:

Proposition 2 *Each element $P^*\varepsilon_U$ of $\mathfrak{S}^*_{[n]}\mathfrak{E}_{[n]}$ with $P = \prod_C^{\in D_P} C$ is a unique product of factors $C^*\varepsilon_{U\cap\{C\}}$ each acting on disjoint near-site sets [C] for $C \in D_P$.*

To understand the conjugacy class structure of $\mathfrak{G}$, one then considers conjugation of these different factors. For a general $Q \in \mathfrak{S}_{[n]}$ and a general cyclic permutation $C = (i_1 i_2 \dots i_k)$, $k \geq 1$, it is known that $Q(i_1 \dots i_k)Q^{-1} = (Qi_1 \dots Qi_k)$, which we denote as C_Q. Then the result of conjugation by $Q^* \in \mathfrak{S}^*_{[n]}$ is

$$Q^* \cdot C^*\varepsilon_{U\cap[C]} \cdot Q^{*-1} = C^*_Q \varepsilon_{QU\cap Q[C]}$$

Moreover, for a general $\varepsilon_T \in \mathfrak{E}_{[n]}$, one has

$$\varepsilon_T \cdot C^*\varepsilon_{U\cap[C]} \cdot \varepsilon_T^{-1} = C^* \cdot C^{*-1}\varepsilon_T C^* \cdot \varepsilon_{U\cap[C]}\varepsilon_T = C^* \cdot \varepsilon_{C^{-1}T}\varepsilon_{U\cap[C]}\varepsilon_T$$

But the ε_i all commute with one another and are involutary ($\varepsilon_i^2 = I$), so that the resulting product of the various ε_R is relatively simple. First, the ε_i factors in ε_T with $i \notin [C]$ are not moved by C, so that these factors cancel between $\varepsilon_{C^{-1}T}$ and ε_T, and we may assume without loss of generality that $T \subseteq [C]$, and in fact because of the "independence" of the different single near-pair factors ε_i, we can consider them one at a time. First in the trivial case that $|[C]| = 1$, one has $\varepsilon_i C \varepsilon_i^{-1} = \varepsilon_i C \varepsilon_i = \varepsilon_i^2 = I$ and $\varepsilon_i \cdot C\varepsilon_i \cdot \varepsilon_i^{-1} = \varepsilon_i$, so that this conjugation does not change parity. Then in the non-trivial case when $|[C]| \neq 1$, it is seen that $C^{-1}i$ and i must be distinct for $i \in [C]$, whence for $\varepsilon_i \cdot C^*\varepsilon_U \cdot \varepsilon_i^{-1} = C^* \cdot \varepsilon_{C^{-1}i}\varepsilon_U\varepsilon_i$, just 4 different things can happen:

- first, both $i \in U$ and $C^{-1}i \in U$, whence $\varepsilon_{C^{-1}i}\varepsilon_U\varepsilon_i = \varepsilon_{U\setminus\{i,C^{-1}i\}}$ (where $U\setminus V$ denotes the subset of U with any elements of V removed); or
- second, $i \in U$ and $C^{-1}i \notin U$, whence $\varepsilon_{C^{-1}i}\varepsilon_U\varepsilon_i = \varepsilon_{\{C^{-1}i\}\cup U\setminus\{i\}}$; or
- third, $i \notin U$ and $C^{-1}i \in U$, whence $\varepsilon_{C^{-1}i}\varepsilon_U\varepsilon_i = \varepsilon_{\{i\}\cup U\setminus\{C^{-1}i\}}$; or
- fourth, $i \notin U$ and $C^{-1}i \notin U$, whence $\varepsilon_{C^{-1}i}\varepsilon_U\varepsilon_i = \varepsilon_{\{i,C^{-1}i\}\cup U}$.

That is, the number of ε_j which survive in $\varepsilon_{C^{-1}i}\varepsilon_U\varepsilon_i$ is changed by -2, 0, or +2 from the number in ε_U, so that the parity s of this number is unchanged. Also if one chooses $i \in U$, it is seen that the result for $\varepsilon_{C^{-1}i}\varepsilon_U\varepsilon_i$ either has 2 fewer such ε_j or else moves one of the original ε_j in $\varepsilon_{C^{-1}i}\varepsilon_U\varepsilon_i$ one position around the cycle C—and such a conjugacy transformation may be repeated to move the moved index around further till it impinges next to another remaining ε_k, whereafter an application of another conjugacy transformation could be applied to eliminate ε_k and $\varepsilon_{k\pm1}$, and thereby diminish their number by 2 again. Thus given any number m of ε_j in ε_U their number can be reduced to either 0 or 1 as m is of even or odd parity, using a sequence of conjugacy transformations by suitable ε_i. But also such conjugacy transformations are seen to be able to increase the number of ε_j up to a maximal set of the same parity. Thus it is seen that conjugacy transformations conserve the disjoint cycle structure and that they conserve the parity of the number of ε_j associated to each such cycle.

Theorem 3 *The classes of* $\mathfrak{S}^*_{[n]}\mathfrak{E}_{[n]}$ *are identified uniquely to two things:*

- *first, the disjoint cycle structure of the earlier propositions; and*
- *second, the parity of the number of* ε_j *associated to each such disjoint cycle.*

Thus the conjugacy classes are neatly identified as in Eq. (7).

Now we address the order of these conjugacy classes. First note that the number of ways to partition the digits of $[n]$ into $\sum_i (\rho_{i+} + \rho_{i-})$ distinguished sets such that there are $\rho_{i+} + \rho_{i-}$sets of size i, is given by the multinomial coefficient $n! \big/ \prod_i (i!)^{(\rho_{i+}+\rho_{i-})}$. But if the ρ_{is} sets, for particular $i \in [n]$ and $s \in \{+,-\}$, are not to be distinguished, then this reduces this count by division by a factor $\prod_i \rho_{i+}!\rho_{i-}!$. That is, we have $n! \big/ \{\prod_i (i!)^{(\rho_{i+}+\rho_{i-})}\rho_{i+}!\rho_{i-}!\}$ ways to partition $[n]$ into $\rho_{i+} + \rho_{i-}$sets of size-i sets with those associated to the same parity s not distinguished, while those associated to different parities are. From any one of these size-$i$sets $[C]$ associated to a parity s , there are $(i-1)!$ possible i-cycles and $\frac{1}{2}\cdot 2^i$ possible members of $\mathfrak{E}_{[C]}$ consisting of a parity-s number of factors ε_i, $i \in [C]$. That is, for a given partitioning of $[n]$ involving ρ_{is} size-i sets associated to parity s, there are $(i-1)!^{\rho_{is}}2^{(i-1)\rho_{is}}$ possible group elements for each i and s. Putting the partition count $n! \big/ \{\prod_i (i!)^{(\rho_{i+}+\rho_{i-})}\rho_{i+}!\rho_{i-}!\}$ together with the associated overall group-element count of $\prod_i \{(i-1)!2^{(i-1)}\}^{(\rho_{i+}+\rho_{i-})}$, we obtain:

Theorem 4 *The order of the conjugacy class* $\rho \equiv (1_+^{\rho_{1+}}1_-^{\rho_{1-}}2_+^{\rho_{2+}}2_-^{\rho_{2-}}3_+^{\rho_{3+}}\ldots n_-^{\rho_{n-}})$ *of* $\mathfrak{S}^*_{[n]}\mathfrak{E}_{[n]}$ *is given by* $\left|C_\rho\right| = n!\prod_i \{2^{(i-1)(\rho_{i+}+\rho_{i-})}/(i^{\rho_{i+}+\rho_{i-}}\cdot\rho_{i+}!\rho_{i-}!)\}$.

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