

Enumeration of polycarborane isomers: especially dicarboranes

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Abstract Various sorts of isomer enumeration problems are addressed in the context of polycarboranes, with special illustrative focus on the case of dicarboranes, for which then various numerical results are given. A systematic and general Pólya-theoretic methodology is used to make the computations, including some new techniques being applicable to a wide range of nano-structures built from a framework of like local subunits.

Keywords Isomer enumerations · Structural isomers · Stereoisomers · Dicarborane isomers · Polycarboranes

1 Prelude

Carboranes and more general polycarboranes are of interest [1–4] as fundamental nano-structures for use in the construction of various nano-devices. The carborane unit is especially attractive as a fairly well understood building block such that each icosahedral carborane unit offers a multiplicity of bonding directrices for potential neighboring carborane units—so that thereby a wide variety of nano-structures are possible. But also given a nano-structure one might be interested in the variety of

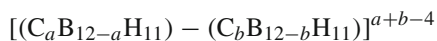
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possible patterns of substitution on it, say so as to “tune” the properties of the underlying structures. Enumerations and further global characterizations of such different patterns of substitution then form the general problems here addressed.

For a concrete illustration consider two carboranes $[C_cB_{12-c}H_{12}]^{c-2}$ in the shape of icosahedra where there are $c = 1$ or 2 carbon atoms. Then one H atom bonded to a C atom may be deleted from each of these two icosahedra, whereafter the two radicals are joined together to obtain a bridged dicarborane species



when a or $b = 2$, then the second carbon atom in the carborane can be connected *ortho*, *meta*, or *para* to the bridge connection. Figure 1 shows a borane dimer, with $a = b = 1$; there positions 2, 11, and 12 are *ortho*, *meta*, and *para* to position 1 (in either of the borane units). One can now seek isomer counts for substitution of H atoms by X, where X might for instance represent F or CH_3 . We presume that rotation about the central bridge bond is allowed. This does not necessarily assume that internal rotation is free, but rather that it takes place on a sufficiently short time scale. But still there are different possible types of isomers to consider: structomers, diastereomers, and stereomers. Each type of isomer is distinguished by suitable features. The *structomers* entail just the characterization of the isomers in terms of the parent skeletal graph—here involving bonds between the neighbor vertices in each of the molecular icosahedra, as well as the bridge bond (or edge), and perhaps the bonds from each X to the corresponding B or C atom of the icosahedra—these structomers are more often called “structural isomers” or “constitutional isomers”.

Here just such isomer counts of a few types are made, by way of Pólya’s theory [5–8] of enumeration under group action, using the so-called “cycle index”. This is used to enumerate different types of isomers (structural isomers, diastereomers, and stereoisomers). And as is prototypical here, when the symmetry group of the underlying skeleton (on which substitutions are made) is comprised from a local part leaving units fixed (here carborane units) times a global part interchanging different units, a general theory is here formulated to facilitate the requisite constructions. This then

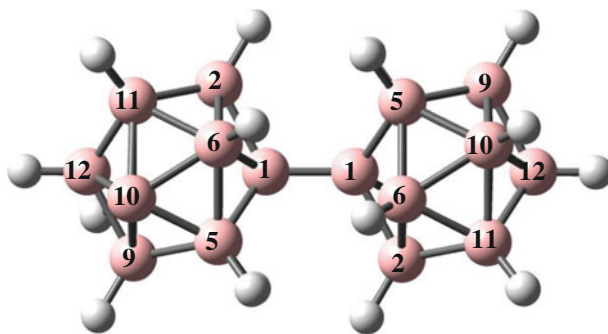


Fig. 1 Borane dimer, showing just the half of the dimer closer to the viewer. Carbon atoms sit preferentially at the bridge positions 1

extends some earlier¹ [9, 10] similar theory for the special subcase when this symmetry group turns out to be a “wreath product”. This yields what might be termed different types of isomer “sub-counts”.

2 Isomer characterization

For the $a = b = 1$ case, the permutation symmetry groups associated with each of these types of isomers (structomer, diastereomer, or stereomer) may be explicitly identified. We label the two different component icosahedra $[\text{CB}_{11}\text{H}_{12}]^-$ of the dicarborane by a and b , and also identify separate permutation groups associated to corresponding icosahedra by these subscripts a and b . Thus we have fivefold rotation groups for each icosahedron C_{5a} and C_{5b} . But also (for $a = b$) there are local reflection groups $\text{C}_{va} \equiv \{I, \sigma_a\}$ and $\text{C}_{vb} \equiv \{I, \sigma_b\}$ involving a reflections σ_a and σ_b , reflecting in a plane through a bridge atom and the atom opposite (*i.e.*, *para* to it) in the single icosahedron a or b . In addition, there is twofold rotation group C'_2 interchanging polyhedra, and there is $\text{C}_{vab} \equiv \{I, \sigma_a\sigma_b\}$ which involves the simultaneous reflection of both polyhedra (but does not include the reflection of one without the reflection of the other). Then the groups associated to each type of isomer count are:

- stereomer: $(\text{C}_{5a}\text{C}_{5b})\text{C}'_2$
- diastereomer: $(\text{C}_{5a}\text{C}_{5b})\text{C}_{vab}\text{C}'_2$
- structomer: $(\text{C}_{5va}\text{C}_{5vb})\text{C}'_2$ (where $\text{C}_{5v} = \text{C}_5\text{C}_v$)

That is, two conformations are to be counted as equivalent under the group corresponding to the given type of isomer—and the enumerations for a given number n of substituents X are just for the number of equivalence classes for all the $\binom{22}{n}$ different possible conformations. With these various groups represented in terms of permutations on the possible substitution sites, the isomer enumeration is conveniently carried out via Pólya’s theory [5–8]—using so called “cycle indices”.

For the case of $a = b = 2$ where the second C in each icosahedron is placed *para* to the bridge C atom, the groups are designated in the same manner. The isomer counts then are the same as those resulting for the $a = b = 1$ case.

For the case $a = 1$ and $b = 2$ with the second C in the second icosahedron in the *para* position, the groups are only slightly modified, just with the C'_2 factor missing from each of these groups.

The remaining cases involve at least one icosahedron with a C atom off of what otherwise would be a fivefold axis. That is, for these cases there is an icosahedron cage with a C-atom either *ortho* or *meta* to a bridge C atom. If there is just one such off-center C atom, say the b icosahedron, then the groups are:

- stereomer: C_{5a}
- diastereomer: $(\text{C}_{5a})\text{C}_{vab}$
- structomer: $\text{C}_{5va}\text{C}_{vb}$

¹ See Part 25 of Pólya in ref. 5, or pages 99, 119–121, 136 of Pólya & Read in ref. 6, or page 98ff of Harary & Palmer in ref. 8.

If $a = b = 2$ and both icosahedra have both icosahedra with off-axis C atoms, there is a possibility that both are the same type (both o , or both m), in which case the relevant groups are:

- stereomer: C'_2
- diastereomer: C'_2C_{vab}
- structomer: $C_{va}C_{vb}C'_2$

But (still with $m = n = 2$) if they are different types (*ortho* and *meta*), then

- stereomer: $\{I\}$
- diastereomer: C_{vab}
- structomer: $C_{va}C_{vb}$

Again in all these cases the Pólya theory is applicable.

3 Methodology for counting isomers

To solve any one of these isomer counting problems one needs the so-called “cycle index” for the relevant group G of permutations. In general a permutation P on a set of N labels (here identifying the substitution sites) is a product of a number $|P|_l$ of disjoint cycles of different lengths $l = 1$ up to N . Evidently then $\sum_{c=1}^N |P|_c = N$, and for each $P \in G$ we further introduce products $\prod_{l=1}^N s_l^{|P|_l}$ with the s_l being variables, and we might even further let χ^λ denote some character of G . Then the χ^λ -cycle index for a subset $S \subseteq G$ is

$$Z_\lambda(S) \equiv \frac{1}{|S|} \sum_{P \in S} \chi^\lambda(P) \cdot \prod_{l=1}^N s_l^{|P|_l} \quad (1)$$

when $S = G$ (and perhaps χ^λ is irreducible), this reduces to Balasubramanian's χ^λ -cycle index [11], and if further χ^λ is taken to be the identity irreducible representation, then this further specializes to Pólya's [5, 6] standard cycle index, which then is simply denoted $Z(G)$. Pólya's theorem then says that if one takes $s_l \equiv 1 + x^l$, $Z(G)$ becomes a polynomial (in x) for which the coefficient of x^n is the number of n -fold substituted isomers (for our single substituent X beyond H) as mediated by the group G .

In the case of polycarboranes the whole group G can be built up from pieces associated with the compound icosahedral units, just a and b for dicarboranes. In particular we utilize

$$\begin{aligned} Z(C_5) &= \frac{1}{5} \{s_1^{11} + 4s_1s_5^2\} \\ Z(C_5\sigma) &= \frac{1}{5} \{5s_1^3s_2^4\} = s_1^3s_2^4 \\ Z(\sigma) &= s_1^3s_2^4 \end{aligned} \quad (2)$$

The utilization of these simple single-unit cycle indices to determine the desired cycle indices for various multi-unit species is described in a later section.

Numerical results for the $[\text{CB}_{11}\text{H}_{11}]_2^{2-}$ dicarborane case are given in Table 1 showing the results for each of the 3 types of isomers contemplated, as well as the counts of diastereomers which correspond either to enantiomeric pairs or individual achiral structures. In Table 2 just the structomer counts for the remaining types of dicarboranes are given, with *o*, *m*, *p* labelling *ortho*, *meta*, and *para* units (with *c* = 2 carbons), while \emptyset labels units with just a single C atom (at the bridgehead). These tables report results just for $n = 0 \rightarrow 11$ substituents (all of the same kind X), as it is understood that the isomer counts at n and $22 - n$ are the same (as is evident upon interchange of H and X).

4 Further enumerative characterization

In addition one may consider the respective numbers α and χ of achiral and chiral diastereomers. Given the numbers $\#_{\text{ster}}$ and $\#_{\text{diast}}$ of stereomer and diastereomer counts (at a given n), we have

Table 1 Isomer counts for $(\text{C}_{5va}\text{C}_{5vb})\text{C}_2'$ -symmetric skeletons $\emptyset - \emptyset$ or $p - p$

| n | $\emptyset - \emptyset$ and $p - p$ | $\emptyset - p$ | $\emptyset - o$ and $\emptyset - m$ | $m - m$ and $o - o$ | $o - m$ |
|-----|-------------------------------------|-----------------|-------------------------------------|---------------------|-----------|
| 0 | 1 | 1 | 1 | 1 | 1 |
| 1 | 3 | 6 | 10 | 7 | 14 |
| 2 | 15 | 27 | 61 | 59 | 111 |
| 3 | 50 | 100 | 268 | 306 | 612 |
| 4 | 156 | 303 | 923 | 1,293 | 2,555 |
| 5 | 391 | 782 | 2,630 | 4,219 | 8,438 |
| 6 | 886 | 1,749 | 6,347 | 11,335 | 22,581 |
| 7 | 1,704 | 3,408 | 13,064 | 24,856 | 49,712 |
| 8 | 2,908 | 5,774 | 22,940 | 45,572 | 90,970 |
| 9 | 4,226 | 8,452 | 34,320 | 69,694 | 139,388 |
| 10 | 5,350 | 10,642 | 47,312 | 89,980 | 179,718 |
| 11 | 5,748 | 11,496 | 47,384 | 97,772 | 195,544 |
| 12 | 5,350 | 10,642 | 43,712 | 89,980 | 179,718 |
| 13 | 4,226 | 8,452 | 34,320 | 69,694 | 139,388 |
| 14 | 2,908 | 5,774 | 22,940 | 45,572 | 90,970 |
| 15 | 1,704 | 3,408 | 13,064 | 24,856 | 49,712 |
| 16 | 886 | 1,749 | 6,347 | 11,335 | 22,581 |
| 17 | 391 | 782 | 2,630 | 4,219 | 8,438 |
| 18 | 156 | 303 | 923 | 1,293 | 2,555 |
| 19 | 50 | 100 | 268 | 306 | 612 |
| 20 | 15 | 27 | 61 | 59 | 111 |
| 21 | 3 | 6 | 10 | 7 | 14 |
| 22 | 1 | 1 | 1 | 1 | 1 |
| Sum | 37,128 | 73,984 | 295,936 | 592,416 | 1,183,744 |

Table 2 Structomer counts for various types of dicarbonanes

| n | # _{ster} | # _{diast} | # _{struc} | χ | α | χ' | α' |
|-----|-------------------|--------------------|--------------------|--------|----------|---------|-----------|
| 0 | 1 | 1 | 1 | 0 | 1 | 0 | 1 |
| 1 | 3 | 3 | 3 | 0 | 3 | 0 | 3 |
| 2 | 17 | 15 | 15 | 2 | 13 | 0 | 15 |
| 3 | 66 | 50 | 50 | 16 | 34 | 0 | 50 |
| 4 | 231 | 158 | 156 | 73 | 85 | 2 | 154 |
| 5 | 655 | 411 | 391 | 244 | 167 | 20 | 371 |
| 6 | 1,663 | 984 | 886 | 679 | 305 | 98 | 788 |
| 7 | 3,560 | 2,016 | 1,704 | 1,544 | 472 | 312 | 1,392 |
| 8 | 6,578 | 3,628 | 2,908 | 2,950 | 678 | 720 | 2,188 |
| 9 | 10,142 | 5,498 | 4,226 | 4,644 | 854 | 1,272 | 2,954 |
| 10 | 13,246 | 7,122 | 5,350 | 6,124 | 998 | 1,772 | 3,578 |
| 11 | 14,412 | 7,724 | 5,748 | 6,688 | 1,036 | 1,976 | 3,772 |
| 12 | 13,246 | 7,122 | 5,350 | 6,124 | 998 | 1,772 | 3,578 |
| 13 | 10,142 | 5,498 | 4,226 | 4,644 | 854 | 1,272 | 2,954 |
| 14 | 6,578 | 3,628 | 2,908 | 2,950 | 678 | 720 | 2,188 |
| 15 | 3,560 | 2,016 | 1,704 | 1,544 | 472 | 312 | 1,392 |
| 16 | 1,663 | 984 | 886 | 679 | 305 | 98 | 788 |
| 17 | 655 | 411 | 391 | 244 | 167 | 20 | 371 |
| 18 | 231 | 158 | 156 | 73 | 85 | 2 | 154 |
| 19 | 66 | 50 | 50 | 16 | 34 | 0 | 50 |
| 20 | 17 | 15 | 15 | 2 | 13 | 0 | 15 |
| 21 | 3 | 3 | 3 | 0 | 3 | 0 | 3 |
| 22 | 1 | 1 | 1 | 0 | 1 | 0 | 1 |
| Sum | 86,736 | 47,496 | 37,128 | 39,240 | 8,256 | 10,368 | 26,760 |

$$\#_{\text{ster}} = \alpha + 2\chi \quad \text{and} \quad \#_{\text{diast}} = \alpha + \chi \quad (3)$$

(as each member of an enantiomeric pair is counted but once for a diastereomer). Thus

$$\alpha = 2\#_{\text{diast}} - \#_{\text{ster}} \quad \text{and} \quad \chi = \#_{\text{ster}} - \#_{\text{diast}} \quad (4)$$

We recall that *scalar* properties (boiling and melting points, heats of formation and vaporization, densities, specific heats, magnetic susceptibilities, polarizabilities, solubilities in achiral solvents, etc) are the same for the two members of an enantiomeric pair of stereomers, so that $\#_{\text{diast}}$ counts the number of different sets of scalar properties achievable either for different pure stereomers or for the different racemates (as so often arise with asymmetric syntheses)—though the racemates have many scalar properties different than the corresponding pure stereomers.

It is readily seen that these results may be re-expressed in terms of our generalized cycle indexes. We denote the stereomer group by $\mathbf{G}_{\text{stereo}}$ and the diastereomer group by $\mathbf{G}_{\text{diast}} = \mathbf{G}_{\text{stereo}} \oplus \sigma_{ab}\mathbf{G}_{\text{stereo}}$, where σ_{ab} is our overall reflection. Also we let

$\lambda = \text{anti}$ denote the antisymmetric irreducible representation which has character $= +1$ on $\mathbf{G}_{\text{stereo}}$ and $= -1$ on the coset $\sigma_{ab}\mathbf{G}_{\text{stereo}}$. Then $Z_{\text{anti}}(\mathbf{G}_{\text{diast}})$ is the counting polynomial for enantiomeric pairs, and $Z(\sigma_{ab}\mathbf{G}_{\text{stereo}})$ is the counting polynomial for achiral species.

A similar consideration may be made for the relation between structomers and diastereomers. That is, if we imagine that a scalar property depends purely on the graphical structure of a molecule, then (for our dicarboranes) there will be pairs of diastereomers having the same values for such scalar properties—and each such pair will be grouped together in a single structomer. Various gas phase scalar properties might reasonably be imagined to closely manifest such a diastereomeric independence, but in condensed phases the scalar properties should depend some on the geometric characteristics so as to distinguish diastereomers corresponding to the same structomer. We might denote the number of such pairs as χ' and the number of structomers corresponding to a single diastereomer by α' . Then (for our dicarboranes)

$$\#_{\text{diast}} = \alpha' + 2\chi' \quad \text{and} \quad \#_{\text{struc}} = \alpha' + \chi' \quad (5)$$

and

$$\alpha' = 2\#_{\text{diast}} - \#_{\text{ster}} \quad \text{and} \quad \chi' = \#_{\text{ster}} - \#_{\text{diast}} \quad (6)$$

which in close correspondence with the relations between stereomers and diastereomers. It may be noted that with polycarboranes with ≥ 3 carborane units, one structomer may correspond to a greater number of diastereomers. Again generating polynomials $Z_{\text{anti}}(\mathbf{G}_{\text{struct}})$ and $Z(\sigma_a\mathbf{G}_{\text{diast}})$ apply for χ' - and α' -counting.

Results for the $a = b = 1$ dicarborane (and also the $a = b = 2$ *para-para* carborane) are given in Table 1. Similar results are readily obtainable for all the other cases of Table 2.

Another type of isomer sub-count entails the enumeration of the numbers of isomers which have particular numbers of substituents X in each of the different carborane units. For the illustrative dicarborane case we thus seek isomer counts $\#_{m,n}$ with m and n substituents in each carborane unit. There of course is a problem as to whether the two units are of the same type (o , m , p , or \emptyset). But again all this is treatable via a modest extension of the standard Pólya theory, as explained in the next section. Example numerical results are given in Table 3 for the $a = b = 1$ (or $\emptyset - \emptyset$ case).

Finally the Pólya theory (and associated cycle indices) apply even if there are more than one substituent to replace H. One merely introduces a variable t_X for each type of substituent X , and takes $s_m = 1 + \sum_X t_X^m$, whence the overall coefficient of $\prod_X t_X^{m_X}$ in Z gives the number of isomers with m_X substituents of type X . That is, this just entails further manipulation of a now more elaborate multi-variable polynomial. A super-count $\#_{\text{total}}(m_{\text{sub}})$ of all these isomers with any number of substitutions with m_{sub} possible types of substituents taking place is readily obtainable on taking all these $t_X = 1$. For instance, for the diastereomeric case, these net numbers of isomers are:

$$\#_{\text{total}}(m_{\text{sub}}) \approx 3.7 \times 10^4, 1.77 \times 10^8, 9.1 \times 10^{10}, 1.21 \times 10^{13} \quad (7)$$

Table 3 Structomer unit subcounts for dicarborane skeletons $\emptyset - \emptyset$ or $p - p$

| m \ n | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|-------|-----|-------|-------|--------|--------|--------|--------|-------|-------|-----|----|----|
| 0 | 1 | | | | | | | | | | | |
| 1 | 3 | 6 | | | | | | | | | | |
| 2 | 11 | 33 | 66 | | | | | | | | | |
| 3 | 33 | 99 | 363 | 561 | | | | | | | | |
| 4 | 66 | 198 | 726 | 2,178 | 2,211 | | | | | | | |
| 5 | 94 | 282 | 1,034 | 3,102 | 6,204 | 4,465 | | | | | | |
| 6 | 94 | 282 | 1,034 | 3,102 | 6,204 | 8,836 | 4,465 | | | | | |
| 7 | 66 | 198 | 726 | 2,178 | 4,356 | 6,204 | 6,204 | 2,211 | | | | |
| 8 | 33 | 99 | 363 | 1,089 | 2,178 | 3,102 | 3,102 | 2,178 | 561 | | | |
| 9 | 11 | 33 | 121 | 363 | 726 | 1,034 | 1,034 | 726 | 363 | 66 | | |
| 10 | 3 | 9 | 33 | 99 | 198 | 282 | 282 | 198 | 99 | 33 | 6 | |
| 11 | 1 | 3 | 11 | 33 | 66 | 94 | 94 | 66 | 33 | 11 | 3 | 1 |
| Sum | 416 | 1,242 | 4,477 | 12,705 | 22,143 | 24,017 | 15,181 | 5,379 | 1,056 | 110 | 9 | 1 |

for $\#_{\text{total}}(m_{\text{sub}}) = 2, 3, 4, 5$. With many different types of substituents, one naturally anticipates that the remnant symmetry of the substituted species more typically is naught but the identity group. Were this to be the case then $\#_{\text{total}}(m_{\text{sub}})$ should approach $(m_{\text{sub}} + 1)^{22} / |\mathbf{G}|$, again as we expect for larger values of m_{subs} . Indeed for the present diastereomer case (with $\mathbf{G} = \mathbf{G}_{\text{diast}}$ of order 200), we have

$$(m_{\text{sub}} + 1)^{22} / |\mathbf{G}_{\text{diast}}| \approx 2.1 \times 10^4, 1.57 \times 10^8, 8.0 \times 10^{10}, 1.19 \times 10^{13} \quad (8)$$

Evidently one need not go to overly large m_{subs} to obtain a couple digits of accuracy. The analogous expression $\binom{22}{n} \cdot m_{\text{subs}}^n$ which one might imagine when the total number of substituents beyond H is just n cannot of course be expected to work well when n is small.

5 Methodology for general polycarboranes

Much as the counts for our dicarboranes could be built up in terms of each component icosahedral group, there are rather similar ideas applicable to the polycarborane case. That is, it might be imagined that we have a whole sequence of carborane units, which fall into classes γ which have the bonds to other carborane groups in similar positions. That is, if a carborane unit is removed from the whole nano-structure while marking the atoms where the bridge bonds to other units occur, then the members of this class are to be isomorphic. Evidently whatever molecular permutation group we have to designate our isomers can only interchange site labels between carborane units belonging to the same class, allowing that there can be component permutations which permute the labels around within individual units. Then one can generally present our isomer group in the form

$$\mathbf{G} = \left(\bigcup_x \mathbf{G}_0 P_x \right) \cdot \mathbf{T} \quad (9)$$

where: \mathbf{G}_0 is a product over groups each of which permutes labels within an individual unit; the union is disjoint; the P_x permute the labels within units but generally in a correlated way; the parenthetical part forms a group (leaving indices within carborane units); and \mathbf{T} is a group based on the interchanges of the different units. When the set of P_x form a group \mathbf{P} (as often occurs here), \mathbf{G} is [7] the “semi-direct product” of $\mathbf{G}_0\mathbf{P}$ and \mathbf{T} , or of \mathbf{G}_0 and \mathbf{PT} —and yet further $\mathbf{G}_0\mathbf{P}$ is the semi-direct product of \mathbf{G}_0 and \mathbf{P} . But for our purposes it is of value to keep separate account of \mathbf{G}_0 and \mathbf{P} (and \mathbf{T}) as they each manifest different sorts of actions on our set of substitution sites. As an example for the $a = b = 1$ dicarborane case of diastereomers: $\mathbf{G} = (\mathbf{C}_{5a}\mathbf{C}_{5b})\mathbf{C}_{\text{vab}}\mathbf{C}'_2$, $\mathbf{G}_0 = (\mathbf{C}_{5a}\mathbf{C}_{5b})$, $\mathbf{T} = \mathbf{C}'_2$, and the set \mathbf{P} of P_x is $\mathbf{C}_{\text{vab}} = \{I, \sigma_a\sigma_b\}$. The existence of this general decomposition follows in that there is a subgroup \mathbf{G}_{fix} of \mathbf{G} which moves no labels between units, and this group \mathbf{G}_{fix} itself has a maximal subgroup $\mathbf{G}_0 = \prod_{\text{C}}^{\text{units}} \mathbf{G}_{\text{C}}$ which is expressible as a simple product of groups \mathbf{G}_{C} acting on each unit C independently. Indeed this subgroup \mathbf{G}_{fix} must be normal, and there is a set $\{P_x\}$ of coset multipliers for \mathbf{G}_0 in \mathbf{G}_{fix} . Then evidently \mathbf{T}

is the factor group of G_{fix} in G . A special case of all this occurs when P is just the identity, and the result is what is called a “wreath” product, such as have been dealt with before (see footnote 1) [9] in the context of Pólya enumeration theory.

The point of this decomposition (of the symmetry group) is that it provides a neat means by which to treat the cycle index of G , as

$$Z(G) = \sum_T \sum_x \prod_{\gamma}^{T\text{-cycles}} Z(G_{C(\gamma)} P_{xC(\gamma)} \cdot T_{\gamma}) \quad (10)$$

where the product is over the different disjoint cycles (of unit labels) occurring in T with $C(\gamma)$ a representative unit in the cycle. Notably

$$Z(G_{C(\gamma)} P_{xC(\gamma)}) = \frac{1}{|G_{C(\gamma)}|} \sum_P^{\in G_{C(\gamma)}} \prod_{l=1}^N s_l^{|P|_l} \quad (11)$$

which clearly is something which depends on just a single unit. And rather similarly, if such a disjoint cycle γ of T is of length m (involving m units), then very similarly we have

$$Z(G_{C(\gamma)} P_{xC(\gamma)} \cdot T_{C(\gamma)}) = \frac{1}{|G_{C(\gamma)}|} \sum_P^{\in G_{C(\gamma)}} \prod_{l=1}^N s_{lm}^{|P|_l} \quad (12)$$

where the dependence on $T_{C(\gamma)}$ comes in very simply. In fact, every such possible component single-unit Z is rather much like what we already have encountered in our exemplar dicarborane case. Every case with a unit attached to another is exactly as given in eqn (2), while for a degree-2 unit (attached to 2 other units) the possible forms are similar to those in eqn. (2) except with one factor of s_1 is missing (as these units have just 10 possible substitutional positions), and for a degree-3 unit, another factor of s_1 is missing.

Thence rather general polycarborane substitutional isomers can be handled, in a relatively nice manner. Yet also these constructions lend themselves to the construction of a polynomial to enumerate “unit-subcounts” of isomers, having different numbers of substituents in different units—basically one just needs to introduce a counting variable t_C for each carborane unit c .

6 Conclusion

It is seen that Pólya counting theory is readily applicable to deal with the enumeration of different sorts of isomers (stereomers, diastereomers, and structomers). Modest elaborations of this theory facilitate the readiness of computations on such multiunit structures—when the overall symmetry is viewed as a product of the local symmetry of the individual sub-units (here carboranes) and the global symmetry involving the interchange of the different subunits. Yet further modest extensions enable different

sorts of sub-counts of isomers. This then adds to the list of further properties which can be obtained via Pólya-theoretic generating functions—there having been a fair number of interesting graphical properties [12, 13] dealt with previously via Pólya-theoretic methods for the case of different sorts of acyclic hydrocarbons—indeed with sufficient graphical properties to represent different chemico-physical properties in a standard (group-function-theoretic [14, 15]) fashion. Some graph-theoretic quantities (such as various combinatorially defined “twists”, “curvatures”, or “torsions”) may even relate to geometric structure, so that information on such might also be gained by way of graphical combinatorics. It might also be mentioned that substitutional isomers can further be fit into a substitution-reaction poset [16] which then may be utilized [17] in organizing or fitting properties of the species within the poset. Evidently there is an increasing degree of promise of further insight from such combinatorial mathematical approaches.

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