filter until the CT absorptions of the EDA complex were bleached (2-15 min). Crystals of the photoproduct 1 sometimes formed spontaneously upon irradiation. Concentration of the reaction mixture in vacuo allowed the collection of the major products by filtration. Recrystallization from a mixture of either methylene chloride–carbon tetrachloride or methylene chloride–hexane below room temperature afforded the pure products for characterization. Additional material was obtained by rapid removal of the solvent from the original filtrate and fractional crystallization of the residue. Typically, a solution of 128 mg (0.50 mmol) of 9-bromoanthracene and 100 mg of TNM (0.51 mmol of TNM) dissolved in 5 mL of CH_2Cl_2 was irradiated for ~10 min. The solvent was evaporated and the yellow residue was taken up in ~3 mL of CH_2Cl_2 and ~1 mL of CCl_4 was added. Over a period of several hours, colorless crystals formed which were collected by filtration, washed thrice with small portions of cold CCl_4, and air dried to afford 136 mg (60%) of I (R = Br) as colorless plates. The molecular structures of the photoadducts I with R = Br and Ph were determined by X-ray crystallography at the Molecular Structure Center of Indiana University by Dr. J. C. Huffman. The crystallographic and structural details are contained in the Center reports No. 83066 and No. 83077.

The absorption spectra of the transient arene cation radicals and the trinitromethide anion radical were obtained by the spectroelectrochemical technique with use of the gold minigrid electrode described previously.[18]

Acknowledgment. J. M. Masnovi and J. K. Kochi thank the National Science Foundation and the Robert A. Welch Foundation for financial support. We thank J. C. Huffman for the X-ray crystallographic determination of the photoadducts I shown in Figure 2.

Double Cosets and Enumeration of Permutational Isomers of Fixed Symmetry

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Abstract: When a molecular skeleton with n sites and symmetry group G carries n_x ligands of type X, n_y of type Y, etc., the resulting isomers are distributed among several symmetries. We show that the numbers v_γ^{GB} of isomers of symmetry γ obey a system of linear and inhomogeneous equations, as shown by eq 12. The linear coefficients $p_{\beta\gamma}^G$ and the independent terms $p_{\beta B}^{S_n}$ appearing in this system are related to the double-coset structure of G and S_n, respectively, and are easy to calculate by standard group theoretical methods. Unfortunately, the rank of $p_{\beta\gamma}^G$ is smaller than the number of v_γ^{GB} unknowns. Hence, the system can only be solved if some of the unknowns are calculated independently. However, in practice, some of the v_γ^{GB} numbers are easy to obtain either because they are vanishing for any ligand partition (phantom subgroups of G) or because they are readily found by inspection, as it is the case when isomers of high symmetry γ have to be enumerated. Therefore, the relations established in this paper do yield an efficient method to enumerate permutational isomers of fixed symmetry. It is remarkable that the calculations required only involve enumeration of double cosets. The present method is applied to the dodecahedrane skeleton. The number of isomers of fixed symmetry and corresponding to the formula $C_{20}H_{20-n}X_n$ have been obtained (n = 0, 1, 2, ..., 10).

I. Introduction

For 15 years, double-coset algebra has been used to enumerate permutational isomers, rearrangements, and reactions. In *static* stereochemistry, the pioneer work is due to Ruch et al.[1] who showed that a permutational isomer (in fact an achiral isomer or a pair of enantiomers) is in one-to-one correspondance with a double-coset Gx_iB in S_n. Here G, B, and S_n are sets of permutations representing, respectively, the group of symmetry operations of the molecular skeleton, the group of permutations of identical ligands, and the symmetric group of degree n (n is the number of sites of the skeleton). The permutation x_i is the representative of Gx_iB and belongs to S_n. In the above paper, the equivalence between the double-coset formalism and Polya's enumeration procedure[2] was also established. For details, notations, and further references, see for instance ref 3.

Group theoretical methods have also been developed to solve the problem of the enumeration of all the distinct stereoisomers of defined constitution. This has been possible by the use of the so-called *configuration* symmetry group.[4]

The importance of double cosets in *dynamic* stereochemistry has been stressed by Hässelbarth and Ruch[5] and by Klemperer.[6-12] These authors showed that the enumeration of permutational and polytopal rearrangements or reactions is again related to double-coset counting. The concept of generalized modes of rearrangements introduced by Nourse[13] is also based on double-coset algebra. This very compact and elegant formalism gives the *total* number (i.e., from every isomer to every isomer) of polytopal rearrangements for a given molecular skeleton and a given ligand partition (for details see for instance ref 3).

The relevance of these mathematical developments to concrete physical and chemical situations has been widely exemplified in the recent literature. In particular, there has been a very strong interaction between the dynamic nuclear magnetic resonance (line-shape analysis) and the permutation description of magnetic site exchange.[3,12,14] The concepts of residual stereoisomerism and stereotopism[15-17] are also related to these algebraic methods. In

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the domain of rotation–vibration spectroscopy, nonrigid molecular level splittings have been predicted on the basis of modes of rearrangements and double-coset structure.[18-22] This structure is moreover of importance to describe the path of steepest descent and transition states[23,24] of self-inverse or non-self-inverse rearrangements.[25] The chirality or achirality of such path and transition states has been discussed on the same basis.[26]

We now come back to static stereochemistry. As we have recalled it above, the number of double cosets Gx_iB gives the *total* number of permutational isomers arising when a molecular skeleton of symmetry group G bears a ligand partition (n_x ligands of type X, n_y of type Y, etc.) described by the group B. However, one could moreover ask how much isomers have a *fixed* symmetry. For instance, in the case of a trigonal-bipyramidal skeleton such as PF_5 ($G = D_{3h}$) and considering a ligand partition PX_3YZ ($n_x = 3$, $n_y = 1$, $n_z = 1$, i.e., $B = S_3S_1S_1$), there are four permutational isomers corresponding to the four double cosets GxB in S_n. Among these four, one is of C_{3v} and three of C_s symmetry.

Hence, the question to be answered is the following: when n_x ligands of type X, n_y of type Y, etc. are distributed on a molecular skeleton of symmetry G, how many isomers are there for each possible symmetry?

This chemical problem has been studied independently by W. Hässelbarth.[27] According to this author, the number of isomers of fixed symmetry constitute the solution of a system of linear inhomogeneous equations which differs from ours. In this approach, the matrix of linear coefficients, known in the mathematical literature as the Burnside table of marks of the group G, has a nonvanishing determinant. The independent terms are the number of H-invariant elements of the G-set M, for any subgroup H from the conjugacy class **H**. These results are based on previous mathematical work.[28-30] This very compact and elegant result has the advantage to involve a nonsingular matrix, but it requires the manipulation of mathematical objects which are not very familiar to the chemical community. In contrast, the method proposed here makes only use of double cosets which have been widely used beforehand in stereochemistry.[1,3-13,17,19-22,25,26]

In section II we show that the number of isomers of *fixed* symmetry characterizing such a distribution satisfy a system of *linear and nonhomogeneous equations*. The linear coefficients and the independent terms entering this system are only related to the double-coset structure of the groups S_n and G and are easy to calculate. We also discuss the properties of the linear coefficients: they form a square matrix whose rank is smaller than its dimension. Hence, the system may only be solved if some of the unknowns, i.e., some of the numbers of isomers of fixed symmetry, have been determined a priori. These considerations are illustrated in the concrete and well-known case of all the ligands partitions of the trigonal-bipyramidal skeleton such as PF_5.

In section III, we apply the above theoretical results to the enumeration of the isomers of fixed symmetry of the dodecahedrane $C_{20}H_{20}$ skeleton. We limit ourselves to the ligand partition $C_{20}H_{20-n}X_n$ ($n = 0, 1, ..., 10$) but any ligand partition could be treated similarly. We show that, in practice, the isomers of *high* symmetry are easy to enumerate by inspection. Once this result is obtained, it is an easy task to derive the numbers of isomers of *lower* symmetry from the system of equations they have to satisfy.

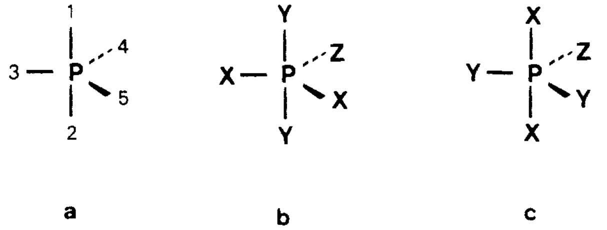

Figure 1. Two isomers b and c with the same G_i.

II. Theory

In the following paragraphs, we will frequently refer to the partition of a group S into double cosets relative to two of its subgroups K and L

$$S = \bigcup_i Ks_iL \qquad (1)$$

where $\bigcup$ means union and where $s_i \in S$. The number of Ks_iL double cosets in S will be denoted by p^S_{KL}. It has been shown that[1,3]

$$p^S_{KL} = \frac{|S|}{|K||L|} \sum_y \frac{|K\cap C(y)||L\cap C(y)|}{|C(y)|} \qquad (2)$$

Here C(y) is the conjugation class of the element y in S, $|C(y)|$ is the number of elements in C(y), i.e., its order, and $\cap$ means intersection. This equation shows that p^S_{KL} is easy to calculate if one knows the number of elements of K and L belonging to a given class C(y) of S. Practical examples are worked out elsewhere (see for instance ref 3).

The number v^{GB} of permutational isomers corresponding to a given ligand partition B and a molecular skeleton of symmetry G has been related to double cosets.[3] Indeed,

$$v^{GB} = p^S_{GB} \qquad (3)$$

when a pair of enantiomers is considered as a *single* isomer and where the groups S_n, G, and B have been defined in the preceding section. A similar formula yields the number w^{AB} of permutational isomers when enantiomers are considered as *distinct* isomers

$$w^{AB} = p^S_{AB} \qquad (4)$$

where A is the group of proper operations of the molecular skeleton. In this paper, we will only discuss properties related to v^{GB}, but similar results can be obtained for w^{AB} when A is used instead of G.

Since we need the permutational expression of G and B, we first label the n sites of the molecular skeleton.[1,3,6-12] A permutation such as (123) will mean the ligand on site 1 replaces the ligand on site 2 which replaces that on site 3 which replaces that on site 1. Once the skeleton sites are labeled, the permutational expression of G is fixed. On the contrary, the permutational expression of B will also depend on the ligand partition and on the distribution of the ligands on the sites. For instance, for the above PX_3YZ case, $B = S_3(123)S_1(4)S_1(5)$ when Y and Z are on sites 4 and 5 but $B = S_3(245)S_1(1)S_1(3)$ when they are on 1 and 3. Here $S_3(245)$ means that S_3 involves the sites 2, 4, and 5. Hence, if we start with a fixed distribution of the ligands on the skeleton, B is also fixed.

The isomer represented by the double coset Gx_iB has a symmetry group whose permutational expression is given by[31]

$$G_i = G\cap x_iBx_i^{-1} \qquad (5)$$

where $x_i \in S_n$. Of course, any $x_i' \in Gx_iB$ may be used as representative of Gx_iB. When x_i' is used in eq 5 instead of x_i, the resulting symmetry is either G_i or the conjugate gG_ig^{-1} ($g\in G$) of G_i. We do not need to distinguish between G_i and one of its conjugates gG_ig^{-1} since they represent the symmetry groups of two identical ligand distributions, up to proper or improper rotation g of the molecular skeleton. Hence, each double coset or isomer

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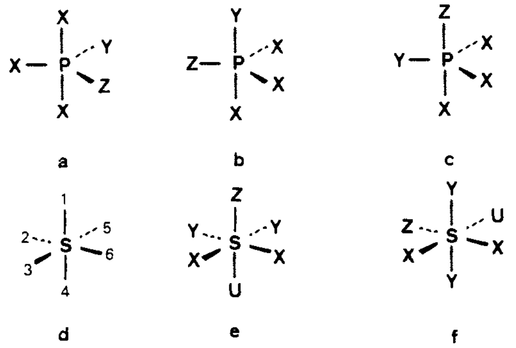

Figure 2. Schönflies symbols and G_i groups.

gives rise to a well-defined symmetry group G_i.

The reverse is not true because two different isomers could well possess the same G_i. This is illustrated in Figure 1, where a shows the skeleton labeling and where b and c show two different isomers of the trigonal bipyramid in the ligand partition PX_2Y_2Z and having the same G_i, i.e.,

$$G_i = \{I, (12)(35), (12), (35)\}$$

The aim of this paper is to answer the following question:[27] for a fixed skeleton symmetry G and a fixed ligand partition, how are the υ^{GB} isomers (see eq 3) distributed according to the isomer symmetries G_i? Of course, the G_i are one of the subgroups of G. It is easy to eastablish the complete list of point groups which are subgroups of the point group of the molecular skeleton. This yields a set of Schönflies symbols.[33] For instance, when $G = D_{3h}$, this set is $\{C_1, C_s, C_2, C_3, D_3, C_{2v}, C_{3v}, C_{3h}, D_{3h}\}$. But this set is not sufficient for the present purpose. Indeed, it could happen that the same Schönflies symbol refers to G_i groups which are not conjugated to each other by some g. Two examples of this situation are given in Figure 2. First, the isomers a, b, and c of the partition PX_3YZ are all of C_s symmetry. However, one should distinguish a from b and c: in a, the ligand distribution preserves the horizontal plane σ_h of D_{3h}, whereas in b and c the vertical plane σ_v is preserved. We propose to call these symmetries C_{sh} and C_{sv}, respectively. Using the labeling of Figure 1, one notes that

$$G_i = \{I, (12)\} \qquad \text{for a}$$
$$G_i = \{I, (45)\} \qquad \text{for b and c} \qquad (6)$$

Clearly, these two G_i groups are *not* conjugated to each other by any g since σ_h and σ_v belong to different classes of $G = D_{3h}$. We want therefore to count separately isomers of symmetry C_{sh} (here a) and those of symmetry C_{sv} (here b and c). Hence, the complete set $\{\gamma\}_{D_{3h}}$ relative to the subgroups of $G = D_{3h}$ will include the modified Schönflies symbols C_{sv} and C_{sh}:

$$\{\gamma\}_{D_{3h}} = \{C_1, C_{sh}, C_{sv}, C_2, C_3, D_3, C_{2v}, C_{3v}, C_{3h}, D_{3h}\} \qquad (7)$$

The second example of Figure 2 refers to $G = O_h$ (as for a SF_6 molecule) and to the ligand partition SX_2Y_2ZU. The labeling of the skeleton is shown in d. Two isomers of C_s symmetry are shown in e and f where σ_d and σ_h are, respectively, preserved by the ligand distribution

$$G_i = \{I, (25)(36)\} \qquad \text{for e}$$
$$G_i = \{I, (14)\} \qquad \text{for f} \qquad (8)$$

These two situations could be distinguished by the use of C_{sd} and C_{sh} instead of the current Schönflies symbol C_s. Note again that these two G_i are not conjugated by any g.

The above modification of Schönflies symbols has some relation with the framework groups introduced by Pople:[34] both originate from the need for more precise information than the usual point group notation. Moreover, in the case of isomers e and f in Figure 2, C_{sd} and C_{sh} correspond to different framework groups, i.e., $C_s[\sigma(SZU)X(X_2Y_2)]$ and $C_s[\sigma(SX_2ZU)X(Y_2)]$, respectively. On the contrary, isomers a $[C_{sh}]$ and b and c $[C_{sv}]$ have the same framework group, namely, $C_s[\sigma(PXYZ)X(X_2)]$. Hence, in this last example, the modified Schönflies symbols lead to a sharper distinction than the framework groups. Is this really necessary or, in other words, to which extent are a, b, and c different? If we forget that they all look like a trigonal bipyramid, we may image that in the plane σ, the bond angle $X\hat{P}Y$ is the same in a, b, and c and that the same is true for the bond angles $X\hat{P}Z$ and $Y\hat{P}Z$. Similarly, we may imagine that the two X ligands out of the plane are disposed in the same way in a, b, and c. Hence a, b, and c could be identical, at least if we only use the information contained in the framework group concept. However, if we assume that the ligands X, Y, and Z are isotopes, then the angles in a, b, and c will be approximately the same as in the original trigonal bipyramid. Then, a, b, and c will be different and the distinction C_{sh} vs. C_{sv} will be meaningful. Isotopic substitution is clearly a situation where the different ligand induces a so-called slight distortion[3,35,36] of the molecular skeleton. But the assumption of slight distortion is certainly valid for a much larger category of substitutions. For instance, the stereochemistry of $Fe(CO)_{5-x}(PF_3)_x$ ($x = 0$–4) is compatible with the assumption that (CO) and (PF_3) ligands induce slight distortions of the molecular skeleton.[37] Another example is provided by a molecule such as $CH_2[(C_6H_5)Sn(SCH_2CH_2)_2NCH_3]_2$, where two tin atoms are connected to a bridging CH_2 and are each surrounded by a tridentate ligand and by a phenyl group.[38] A severe distortion from ideal trigonal-bipyramidal geometry for the tin atoms could have been expected. Surprisingly enough, the solid-state structure reveals that almost all bond angles around the tin atoms differ from their ideal value by less than 10%.

Hence, in the forthcoming discussion, we will assume that the molecular skeleton is only slightly distorted by the presence of different ligands. This assumption has been widely used in the study of propeller molecules (see e.g., ref 17) and is the basis of the isomer enumeration[1] given by eq 3. In this context, the introduction of modified Schönflies symbols is of importance.

Let υ_γ^{GB} be the number of isomers having the same point group γ, for given ligand partition B (henceforth, by γ, we mean one of the subgroups of G, i.e., a Schönflies or a modified Schönflies symbol). Clearly, the υ_γ^{GB} must obey

$$\sum_\gamma \upsilon_\gamma^{GB} = \upsilon^{GB} \qquad (9)$$

For the PX_3YZ case, $G = D_{3h}$, $\upsilon^{GB} = 4$, all the υ_γ^{GB} are zero except $\upsilon_{C_{3v}}^{GB} = 1$, $\upsilon_{C_{sh}}^{GB} = 1$, and $\upsilon_{C_{sv}}^{GB} = 2$.

The integers υ_γ^{GB} must satisfy another relation which is easily deduced from eq 1. One starts from the standard relation[39]

$$|Gx_iB| = \frac{|G||B|}{|G \cap x_iBx_i^{-1}|} = \frac{|G||B|}{|G_i|} \qquad (10)$$

where eq 5 has been used. When this is compared with eq 1, one obtains,

$$\frac{|S_n|}{|G||B|} = \sum_{i=1}^{\upsilon^{GB}} |G_i|^{-1}$$

In the above sum, the terms corresponding to the same point group γ may be put together. Hence,

$$\frac{|S_n|}{|G||B|} = \sum_\gamma \frac{\upsilon_\gamma^{GB}}{|\gamma|} \qquad (11)$$

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Table I. Values of $|\beta \cap C(\mathrm{y})|$ according to the Subgroups and Classes of D_{3h}

	$C(\mathrm{y})$					
β	I	σ_h	$3\sigma_v$	$2C_3$	$3C_2$	$2S_3$
C_1	1					
C_{sh}	1	1				
C_{sv}	1		1			
C_2	1				1	
C_3	1			2		
D_3	1			2	3	
C_{2v}	1	1	1		1	
C_{3v}	1		3	2		
C_{3h}	1	1		2		2
D_{3h}	1	1	3	2	3	2

This relation is readily verified on the above example [$|S_n| = 120$, $|G| = 12$, $|B| = 6$, $v^{GB}_{C_{3v}} = 1$, $v^{GB}_{C_{sh}} = 1$, $v^{GB}_{C_{sv}} = 2$, $|C_{3v}| = 6$, $|C_{sv}| = |C_{sh}| = 2$].

In simple cases, eq 9 and 11 may be used to test the number v^{GB}_{γ} when these have been found by inspection. For more complicated situations, these relations are still useful but they are not sufficient to determine the v^{GB}_{γ}.

In fact, it is possible to show (see Appendix A) that these coefficients obey the following set of relations (see also ref 27–30):

$$p^{S_n}_{\beta B} = \sum_{\gamma} p^{G}_{\beta\gamma} v^{GB}_{\gamma} \tag{12}$$

where $p^{S_n}_{\beta B}$ and $p^{G}_{\beta\gamma}$ are defined by relations similar to eq 1 and 2 and may be easily calculated by using eq 2. In practice, the group G of proper symmetry operations and the group S_n are fixed by the choice of the molecular skeleton.

Hence, for each ligand partition B, eq 12 represents a set of r linear equations in the r unknowns v^{GB}_{γ} (r is the number of subgroups of G, i.e., $r = 10$ for $G = D_{3h}$ as shown by eq 7).

It is interesting to examine eq 12 in two limiting situations: (a) $\beta = C_1$. In this case $p^{S_n}_{\beta B} = |S_n|/|B|$ and $p^{G}_{\beta\gamma} = |G|/|\gamma|$, and therefore eq 12 reduces to eq 11.

(b) $\beta = G$. Then, eq 3 is used, $p^{S_n}_{\beta B} = v^{GB}$ and $p^{G}_{\beta\gamma} = 1$ and therefore eq 12 reduces to eq 9. Hence eq 9 and 11 are merely particular cases of the general relation shown in eq 12. It should also be pointed out that eq 12 has a very simple structure since it is only related to double-coset structure of the groups S_n and G.

In order to get some insight into eq 12, we illustrate it on a well-known example, the trigonal-bipyramidal skeleton, where $G = D_{3h}$ and $S_n = S_5$.

We first calculate the $p^{G}_{\beta\gamma}$ by using standard group theoretical techniques (see, e.g., ref 3). As shown by eq 2, we need to know the classes $C(\mathrm{y})$ of G and the number of elements of β or γ ($|\beta \cap C(\mathrm{y})|$ or $|\gamma \cap C(\mathrm{y})|$) belonging to each of them. This is shown in Table I for each of the six classes of D_{3h} and for the ten subgroups of D_{3h} listed in eq 7. Combining eq 2 and the information contained in Table I, it is an easy matter to obtain the $p^{G}_{\beta\gamma}$. The result is displayed in matrix form in Table II. Note that $p^{G}_{\beta\gamma} = p^{G}_{\gamma\beta}$ and that $p^{G}_{\beta\gamma} = 1$ when $\beta = G$ and that $p^{G}_{\beta\gamma} = |G|/|\gamma|$ when $\beta = C_1$.

The values of $p^{S_n}_{\beta B}$ are obtained in a similar way[3] for each of the subgroups β of G listed in eq 7 and for each of the seven partitions of the five ligands. The result is shown in Table III where $p^{S_n}_{\beta B}$ appears as a matrix with ten lines (β) and seven columns (B). Using eq 2, 3, and 4, it appears that

$$p^{S_n}_{\beta B} = 1 \qquad \text{when all the ligands are identical}$$

$$p^{S_n}_{\beta B} = \frac{|S_n|}{|\beta|} \qquad \text{when they are all different}$$

$$p^{S_n}_{\beta B} = \frac{|S_n|}{|B|} \qquad \text{when } \beta = C_1$$

$$p^{S_n}_{\beta B} = v^{GB} \qquad \text{when } \beta = G = D_{3h}$$

$$p^{S_n}_{\beta B} = w^{\mathrm{AB}} \qquad \text{when } \beta = A = D_3$$

and these properties are easy to verify on Table III.

It can also be seen on Table III that the $p^{S_n}_{\beta B}$ are the same for C_{sh} and C_{sv}. This suggests that Schönflies symbols are sufficient to determine $p^{S_n}_{\beta B}$. This, is however, not true: the above equality results from the fact that in the present case, application of eq 2 requires knowing the number of elements of β belonging to a given class of S_n, i.e., having a given cyclic structure.[3] Accidentally, the G_i groups associated to C_{sh} and C_{sv} have the same number of permutations of a given cyclic structure (see eq 6). On the contrary, the G_i groups associated to C_{sd} and C_{sh} (see Figure 2 (e and f) do not have the same number of permutations of given cyclic structure (see eq 8). Hence, the corresponding $p^{S_n}_{\beta B}$ would be different.

In the present case, the number of isomers v^{GB} for any ligand partition are well-known.[1,3,40,41] It is moreover easy to obtain the point group for each of them. The numbers of isomers v^{GB}_{γ} for each ligand partition and point group are listed in Table IV. It should be noted that some subgroups ($\gamma = C_2$, C_3, D_3, C_{3h}) of $G = D_{3h}$ do never appear. This can be understood on the basis of Pople's[34] classification in terms of framework groups (see Appendix B).

It is now an easy task to *verify* the validity of eq 12. One has merely to perform matrix multiplication of $p^{G}_{\beta\gamma}$ (Table II) by each column of v^{GB}_{γ} (Table IV) and to verify that this yields the corresponding column of $p^{S_n}_{\beta B}$ (Table III). This is indeed true and this means that eq 12 is verified for any of the seven ligand partitions.

It is of course more satisfactory to *solve* eq 12 and to obtain the value of the unknowns v^{GB}_{γ} for each ligand partition. Unfortunately, the determinant of $p^{G}_{\beta\gamma}$ is vanishing. The rank of this matrix is discussed in Appendix C. It is found that it is at most equal to 6 since 4 relations of the type

$$\sum_{\beta} a_{\beta} p^{G}_{\beta\gamma} = 0 \tag{13}$$

can be easily found between the 10-line vectors of $p^{G}_{\beta\gamma}$. The values of the a_{β} coefficients are given in Appendix C (Table XII). Hence, redundant equations have to be suppressed in eq 12 and six unknowns can be expressed as linear functions of four other unknowns considered as independent variables. This is possible provided the determinant obtained by suppressing the four redundant lines and the four columns corresponding to the independent variables does no longer vanish. There are many possible choices of the suppressed lines and columns. In the present case, it is convenient to suppress the lines and columns corresponding to the "phantom" subgroups, i.e., those for which v^{GB}_{γ} is zero for all ligand partitions. The remaining $p^{G}_{\beta\gamma}$ determinant is equal to 1. Hence, $p^{G}_{\beta\gamma}$ is of rank 6, and the corresponding system has a unique solution yielding the value of the 6 remaining v^{GB}_{γ} unknowns, as listed in Table IV.

III. Application to Dodecahedrane

The unsubstituted $C_{20}H_{20}$ dodecahedrane was first synthetized 4 years ago.[42] This molecule possesses the highest conceivable symmetry. Its point group is I_h of order 120. Substituted mono-[43] and dimethyl[44] derivatives have also been obtained. The *total* number of isomers for mono-, di-, tri-, and tetrasubstituted dodecahedranes has been obtained[43] by using Polya's counting theorem.[2,45] The number of isomers of fixed symmetry for substituted dodecahedrane will soon be of interest to organic chemists. Therefore, the theoretical considerations of the preceding section will be applied to this enumeration problem. We limit ourselves to the $C_{20}H_{20-n}X_n$ ligand partitions ($n = 0, 1...,$

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(44) See, for instance: Paquette, L. A.; Balogh, D. W.; Usha, R.; Kountz, D.; Christoph, G. G. *Science (Washington, D.C.)* **1981**, *211*, 575.

(45) See also: Harary, F.; Palmer, E. M.; Robinson, R. W.; Read, R. C. in "Chemical Applications of Graph Theory"; Balaban, A. T., Ed.; Academic Press: New York, 1976.

Table II. $p^G_{\beta\gamma}$ Matrix for the Trigonal-Bipyramidal Skeleton ($G = D_{3h}$)

	γ									
β	C_1	C_{sh}	C_{sv}	C_2	C_3	D_3	C_{2v}	C_{3v}	C_{3h}	D_{3h}
C_1	12	6	6	6	4	2	3	2	2	1
C_{sh}	6	6	3	3	2	1	3	1	2	1
C_{sv}	6	3	4	3	2	1	2	2	1	1
C_2	6	3	3	4	2	2	2	1	1	1
C_3	4	2	2	2	4	2	1	2	2	1
D_3	2	1	1	2	2	2	1	1	1	1
C_{2v}	3	3	2	2	1	1	2	1	1	1
C_{3v}	2	1	2	1	2	1	1	2	1	1
C_{3h}	2	2	1	1	2	1	1	1	2	1
D_{3h}	1	1	1	1	1	1	1	1	1	1

Table III. $p^{S_n}_{\beta B}$ Vectors for All the Ligand Partitions of the Trigonal-Bipyramidal PF_5 Molecule ($G = D_{3h}$)

	ligand partition						
β	PX_5	PX_4Y	PX_3Y_2	PX_3YZ	PX_2Y_2Z	PX_2YZU	PXYZUV
C_1	1	5	10	20	30	60	120
C_{sh}	1	4	7	13	18	33	60
C_{sv}	1	4	7	13	18	33	60
C_2	1	3	6	10	16	30	60
C_3	1	3	4	8	10	20	40
D_3	1	2	3	4	6	10	20
C_{2v}	1	3	5	8	11	18	30
C_{3v}	1	3	4	7	8	13	20
C_{3h}	1	2	3	5	6	11	20
D_{3h}	1	2	3	4	5	7	10

Table IV. Number of Isomers v^{GB}_γ for Each Ligand Partition B of the Trigonal Bipyramid ($G = D_{3h}$) according to Their Point Group γ

	ligand partition						
γ	PX_5	PX_4Y	PX_3Y_2	PX_3YZ	PX_2Y_2Z	PX_2YZU	PXYZUV
C_1					1	3	10
C_{sh}				1		1	
C_{sv}			1	2	2	3	
C_2							
C_3							
D_3							
C_{2v}		1	1		2		
C_{3v}		1		1			
C_{3h}							
D_{3h}	1		1				

10), but there is no difficulty to obtain the same enumeration for any ligand partition.

We apply eq 12 in which the $p^G_{\beta\gamma}$ matrix and the $p^{S_n}_{\beta B}$ vectors have to be calculated first. The set $\{\gamma\}_{I_h}$ of Schönflies symbols relative to the subgroups of I_h is readily established. Note that in this case, nonconjugated G_i groups have different Schönflies symbols, in contradistinction to the D_{3h} and O_h cases discussed before (see Figure 2). This originates from the fact that in I_h, all the symmetry operations of the same kind (reflexions, 2-, 3-, or 5-fold rotations, improper 6- or 10-fold rotations) belong to the same class. Since there are 22 subgroups of I_h, the $p^G_{\beta\gamma}$ matrix is of dimension 22. Despite this, the calculation of its matrix elements is not a formidable task. By using eq 2, it is seen that one needs the classes $C(y)$ of I_h and the number of elements $|\beta \cap C(y)|$ which are common to a given subgroup of I_h and to $C(y)$. The list of $|\beta \cap C(y)|$ is given in Table V. The $p^G_{\beta\gamma}$ are readily obtained by standard techniques. For details see, for instance, ref 3. The result is shown in Table VI. Clearly $p^G_{\beta\gamma}$ is a symmetrical matrix. Moreover, when $\beta = G$, $p^G_{\beta\gamma} = 1$, and when $\beta = C_1$, $p^G_{\beta\gamma} = |G|/|\gamma|$.

The $p^{S_n}_{\beta B}$ are column vectors of dimension 22. There are 11 such vectors since we consider 11 ligand partitions. There is no difficulty in obtaining them by using eq 2. The result is shown in Table VII. When all the ligands are identical, $p^{S_n}_{\beta B} = 1$, whereas $p^{S_n}_{\beta B} = |S_n|/|\beta|$ when they are all different. When $\beta = C_1$, $p^{S_n}_{\beta B} = |S_n|/|B|$, and when $\beta = G$ or A, $p^{S_n}_{\beta B} = v^{GB}$ or w^{AB}, respectively (see eq 3 and 4). Hence, the lines I and I_h of Table VII contain some of the v^{GB} and w^{AB} calculated recently[43] and denoted, respectively, N_s and N_p in this paper. From the values of v^{GB} and w^{AB}, it is easy to obtain the total number of achiral isomers a and the total number of pairs of enantiomers e[1,3]

$$a = 2v^{GB} - w^{AB}$$

$$e = w^{AB} - v^{GB}$$

The remaining task is now to *solve* eq 12, i.e., to calculate v^{GB}_γ for each of the ligand partitions considered here: to each of the 11 column vectors $p^{S_n}_{\beta B}$ of Table VII will correspond a v^{GB}_γ column

Table V. Values of $|\beta \cap C(y)|$ according to the Subgroups and Classes of I_h

	$C(y)$									
β	I	$12C_5$	$12{C_5}^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12{S_{10}}^3$	$20S_6$	15σ
C_1	1									
C_s	1									1
C_i	1					1				
C_2	1				1					
C_3	1			2						
C_5	1	2	2							
D_2	1				3					
D_3	1			2	3					
D_5	1	2	2		5					
C_{2v}	1				1					2
C_{3v}	1			2						3
C_{5v}	1	2	2							5
C_{2h}	1				1	1				1
D_{2h}	1				3	1				3
D_{3d}	1			2	3	1			2	3
D_{5d}	1	2	2		5	1	2	2		5
S_6	1			2		1			2	
S_{10}	1	2	2			1	2	2		
T	1			8	3					
T_h	1			8	3	1			8	3
I	1	12	12	20	15					
I_h	1	12	12	20	15	1	12	12	20	15

Table VI. $p^G_{\beta\gamma}$ Matrix for the Dodecahedral Skeleton ($G = I_h$)

	γ																					
β	C_1	C_s	C_i	C_2	C_3	C_5	D_2	D_3	D_5	C_{2v}	C_{3v}	C_{5v}	C_{2h}	D_{2h}	D_{3d}	D_{5d}	S_6	S_{10}	T	T_h	I	I_h
C_1	120	60	60	60	40	24	30	20	12	30	20	12	30	15	10	6	20	12	10	5	2	1
C_s	60	32	30	30	20	12	15	10	6	17	12	8	16	9	6	4	10	6	5	3	1	1
C_i	60	30	60	30	20	12	15	10	6	15	10	6	30	15	10	6	20	12	5	5	1	1
C_2	60	30	30	32	20	12	18	12	8	16	10	6	16	9	6	4	10	6	6	3	2	1
C_3	40	20	20	20	16	8	10	8	4	10	8	4	10	5	4	2	8	4	6	3	2	1
C_5	24	12	12	12	8	8	6	4	4	6	4	4	6	3	2	2	4	4	2	1	2	1
D_2	30	15	15	18	10	6	12	8	6	9	5	3	9	6	4	3	5	3	4	2	2	1
D_3	20	10	10	12	8	4	8	6	4	6	4	2	6	4	3	2	4	2	4	2	2	1
D_5	12	6	6	8	4	4	6	4	4	4	2	2	4	3	2	2	2	2	2	1	2	1
C_{2v}	30	17	15	16	10	6	9	6	4	10	7	5	9	6	4	3	5	3	3	2	1	1
C_{3v}	20	12	10	10	8	4	5	4	2	7	6	4	6	4	3	2	4	2	3	2	1	1
C_{5v}	12	8	6	6	4	4	3	2	2	5	4	4	4	3	2	2	2	2	1	1	1	1
C_{2h}	30	16	30	16	10	6	9	6	4	9	6	4	16	9	6	4	10	6	3	3	1	1
D_{2h}	15	9	15	9	5	3	6	4	3	6	4	3	9	6	4	3	5	3	2	2	1	1
D_{3d}	10	6	10	6	4	2	4	3	2	4	3	2	6	4	3	2	4	2	2	2	1	1
D_{5d}	6	4	6	4	2	2	3	2	2	3	2	2	4	3	2	2	2	2	1	1	1	1
S_6	20	10	20	10	8	4	5	4	2	5	4	2	10	5	4	2	8	4	3	3	1	1
S_{10}	12	6	12	6	4	4	3	2	2	3	2	2	6	3	2	2	4	4	1	1	1	1
T	10	5	5	6	6	2	4	4	2	3	3	1	3	2	2	1	3	1	4	2	2	1
T_h	5	3	5	3	3	1	2	2	1	2	2	1	3	2	2	1	3	1	2	2	1	1
I	2	1	1	2	2	2	2	2	2	1	1	1	1	1	1	1	1	1	2	1	2	1
I_h	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Table VII. $p^S_{\beta B}$ Vectors for the Ligand Partitions $C_{20}H_{20-n}X_n$ ($n = 0,1,...,10$) of the Dodecahedral Skeleton ($G = I_h$)

	n										
β	0	1	2	3	4	5	6	7	8	9	10
C_1	1	20	190	1140	4845	15 504	38 760	77 520	125 970	167 960	184 756
C_s	1	12	102	588	2461	7 824	19 496	38 928	63 202	84 232	92 644
C_i	1	10	100	570	2445	7 752	19 440	38 760	63 090	83 980	92 504
C_2	1	10	100	570	2445	7 752	19 440	38 760	63 090	83 980	92 504
C_3	1	8	64	384	1623	5 172	12 930	25 860	42 000	56 000	61 612
C_5	1	4	38	228	969	3 104	7 752	15 504	25 194	33 592	36 956
D_2	1	5	55	285	1245	3 876	9 780	19 380	31 650	41 990	46 378
D_3	1	4	37	192	834	2 586	6 525	12 930	21 105	28 000	30 932
D_5	1	2	24	114	507	1 552	3 936	7 752	12 702	16 796	18 604
C_{2v}	1	7	57	303	1261	3 948	9 836	19 548	31 762	42 242	46 518
C_{3v}	1	6	39	210	850	2 658	6 581	13 098	21 217	28 252	31 072
C_{5v}	1	4	26	132	523	1 624	3 992	7 920	12 814	17 048	18 744
C_{2h}	1	6	56	294	1253	3 912	9 808	19 464	31 706	42 116	46 448
D_{2h}	1	4	34	156	657	1 992	4 992	9 816	16 014	21 184	23 420
D_{3d}	1	3	23	105	440	1 329	3 331	6 549	10 679	14 126	15 620
D_{5d}	1	2	16	66	275	812	2 032	3 960	6 470	8 524	9 448
S_6	1	4	34	192	819	2 586	6 486	12 930	21 036	28 000	30 848
S_{10}	1	2	20	114	489	1 552	3 888	7 752	12 618	16 796	18 504
T	1	3	19	99	423	1 296	3 270	6 480	10 560	14 010	15 486
T_h	1	2	12	54	223	666	1 670	3 282	5 344	7 068	7 820
I	1	1	6	21	96	262	681	1 302	2 157	2 806	3 158
I_h	1	1	5	15	58	149	371	693	1 135	1 466	1 648

vector whose elements are the number of isomers of the substituted dodecahedrane for the considered ligand partition.

The same pitfall occurs as for the trigonal-bipyramidal case: the $p^G_{\beta\gamma}$ matrix has a vanishing determinant and the system of eq 12 may not be solved immediately. In Appendix C, we show that 14 relations of the type of eq 13 may be found. Hence, the rank of $p^G_{\beta\gamma}$ is at most equal to 8, and in the system of eq 12, at least 14 equations are redundant and have to be suppressed. For each ligand partition, it will be possible to express 8 v^{GB}_γ in terms of the remaining 14 ones considered as independent variables. This is true provided one obtains a nonvanishing determinant by suppressing 14 redundant lines and the 14 columns corresponding to the independent variables in $p^G_{\beta\gamma}$. When the 14 suppressed lines and columns are C_5, D_2, D_3, D_5, C_{2v}, C_{3v}, C_{2h}, D_{2h}, D_{3d}, S_{10}, T, T_h, I, I_h, the value of the remaining determinant is 4096. The values of the 8 remaining v^{GB}_γ may be found only if the values of these 14 v^{GB}_γ are calculated independently for each ligand partition. This will be done in the next paragraphs.

First, the values of v^{GB}_γ when $\gamma = C_5$, D_5, S_{10}, and I are zero for each ligand partition (phantom subgroups, see Appendix B). Hence, we have still to calculate v^{GB}_γ for $\gamma = D_2$, D_3, C_{2v}, C_{3v}, C_{2h}, D_{2h}, D_{3d}, T, T_h, and I_h and for any ligand partition.

Table VIII. Subspaces and k Values for Some Subgroups of $G = I_h$

γ	subspaces	k values	total no. atoms
D_2	O,C_2,C_2',C_2'',X	1,2,2,2,4	0,0,0,0,20
D_3	$O,C_3,3C_2,X$	1,2,3,6	0,2,0,18
C_{2v}	C_2,σ_v,σ_v',X	1,2,2,4	0,4,4,12
C_{3v}	$C_3,3\sigma_v,X$	1,3,6	2,6,12
C_{2h}	O,C_2,σ_h,X	1,2,2,4	0,0,4,16
D_{2h}	$O,C_2,C_2',C_2'',\sigma,\sigma',\sigma'',X$	1,2,2,2,4,4,4,8	0,0,0,0,4,4,4,8
D_{3d}	$O,C_3,3C_2,3\sigma_d,X$	1,2,6,6,12	0,2,0,6,12
T	$O,4C_3,3C_2,X$	1,4,6,12	0,8,0,12
T_h	$O,4C_3,3C_2,3\sigma_h,X$	1,8,6,12,24	0,8,0,12,0
I_h	$O,6C_5,10C_3,15C_2,15\sigma,X$	1,12,20,30,60,120	0,0,20,0,0,0

The subspaces relative to each of these subgroups and the k values for each subspace are listed in Table VIII. We now apply Pople's method[34] for each ligand partition $C_{20}H_{20-n}X_n$. Hence, we have to find the sets $(i_1,i_2,...)$ $(j_1,j_2,...)$ such that

$$i_1k_1 + i_2k_2 + ... = n$$
$$j_1k_1 + j_2k_2 + ... = 20 - n \qquad (14)$$

by trying successively each of the subgroups of Table VIII. This

Table IX. Number of Isomers v_γ^{GB} for the Ligand Partitions $C_{20}H_{20-n}X_n$ (n = 0,1,...,10) of the Dodecahedral Skeleton ($G = I_h$)

	n										
γ	0	1	2	3	4	5	6	7	8	9	10
C_1				5	28	112	284	603	975	1336	1448
C_s			1	8	13	33	47	81	96	124	112
C_i									2		2
C_2			1		8		23		43		54
C_3				1	1	1	2	6	2	4	8
C_5†											
D_2*									1		
D_3*							1		1		
D_5†											
C_{2v}*			2		3		8		9		12
C_{3v}*		1		1	2	1	1	3	1	2	4
C_{5v}						2					2
C_{2h}*					1		3		2		4
D_{2h}*					1				1		
D_{3d}*			1				1		1		
D_{5d}											2
S_6							1				
S_{10}†											
T*					1						
T_h*									1		
I†											
I_h*	1										

Table X. Phantom Subgroups of $G = D_{3h}$ (Trigonal Bipyramid)

γ	subspaces	k values
C_{3h}	O, C_3, σ_h, X	1,2,3,6
D_3	$O, C_3, 3C_2$, X	1,2,3,6
C_3	C_3, X	1,3
C_2	C_2, X	1,2

Table XI. Phanton Subgroups of $G = I_h$ (Dodecahedron)

γ	subspaces	k values
C_5	C_5, X	1,5
D_5	$O, C_5, 5C_2$, X	1,2,5,10
S_{10}	O, C_5, X	1,2,10
I	$O, 6C_5, 10C_3, 15C_2$, X	1,12,20,30,60

is facilitated by noting that the total number of atoms in each subspace is fixed by the geometry of the dodecahedron. These numbers are also listed in Table VIII. The sets found in this way may, as pointed out previously,[34] correspond to higher symmetry than the starting one. Such solutions are eliminated. The remaining ones are listed in Figure 3 for each value of n and each of the symmetries listed in Table VIII. There are two views of the dodecahedron, one along the C_3 axis ($\gamma = D_3$, C_{3v}, and D_{3d}, and one along (one of) the C_2 axis for the other subgroups. Some of the symmetry elements have been represented on the drawings. The X ligands have been represented by dots, open circles, or squares, (above, under, or on the plane of the drawing, respectively). The (i_1,i_2,...) (j_1,j_2,...), symbols obtained by solving eq 14 are also shown. The values of v_γ^{GB} are easily found by this procedure. They are listed in Table IX where the symmetries for which this enumeration technique has been used are indicated by an asterisk. Note that for $\gamma = I_h$, the only nonvanishing v_γ^{GB} is for $n = 0$.

Using these figures and the fact that there are four phantom subgroups (indicated by a dagger in Table IX), we may now come back to eq 12 and obtain the v_γ^{GB} values for $\gamma = C_1$, C_s, C_i, C_2, C_3, C_{5v}, D_{5d}, and S_6. The results are also shown in Table IX. Hence, the v_γ^{GB} values for each of the considered ligand partitions and each symmetry have been obtained.

IV. Conclusion

Establishing the list of all the permutational isomers for a given ligand partition and a given skeletal symmetry is a rather difficult task when the total number of ligands increases and when the skeleton becomes more symmetric: omission and/or repetition of isomers of low symmetry is almost unavoidable. It is of course

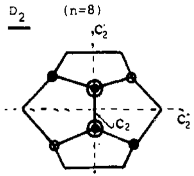
Table XII. Coefficients $a_\beta/|\beta|$ in Equation 22 ($G = D_{3h}$)

β	C_1	C_{sh}	C_{sv}	C_2	C_3	D_3	C_{2v}	C_{3v}	C_{3h}	D_{3h}
	3			-3	-1	1				
	3		-3		-1			1		
	2	-1	-1	-1			1			
					2	-1		-1	-1	1

Table XIII. Coefficients $a_\beta/|\beta|$ in Equation 22 ($G = I_h$)

β	C_1	C_s	C_i	C_2	C_3	C_5	D_2	D_3	D_5	C_{2v}	C_{3v}	C_{5v}	C_{2h}	D_{2h}	D_{3d}	D_{5d}	S_6	S_{10}	T	T_h	I	I_h
	2	-2		-1						1												
	3	-3			-1						1											
	5	-5				-1						1										
	2			-3			1															
	3			-3	-1			1														
	5			-5		-1			1													
	6	-3	-1	-3										1								
	6	-3		-3											1		-1					
	10	-5		-5												1		-1				
	2	-1	-1	-1									1									
	4				-4		-1												1			
			4											-1			-4			1		
	30			-15	-10	-6															1	
			30										-15				-10	-6				1

D_2 (n=8)



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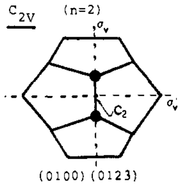
C_{2V} (n=2)



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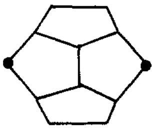

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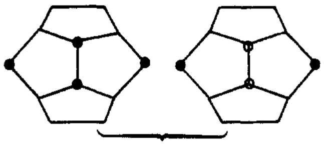
(n=4)



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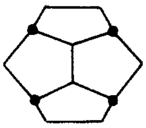

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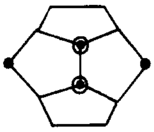
(n=6)



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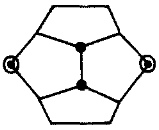

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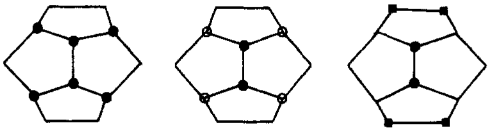

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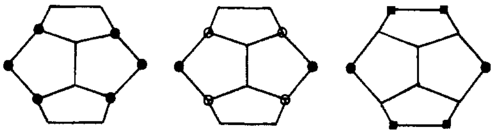

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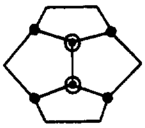
(n=8)



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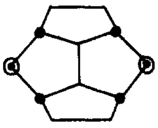

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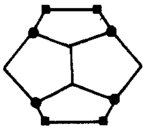

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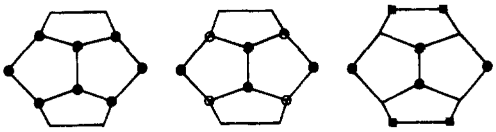

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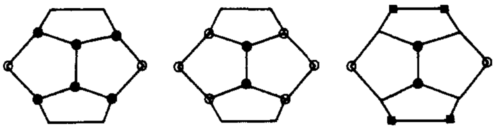

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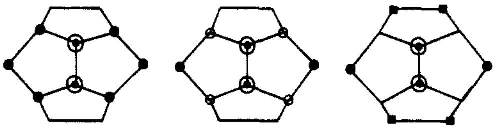
(n=10)



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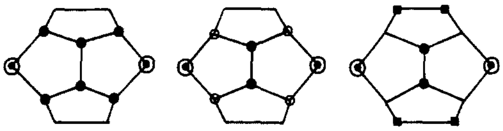

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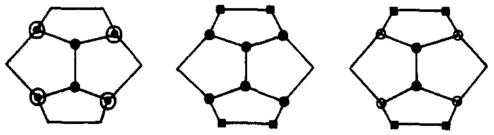

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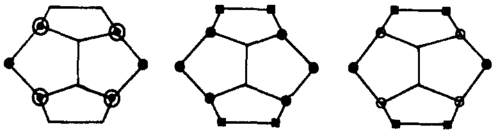
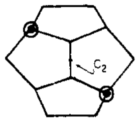


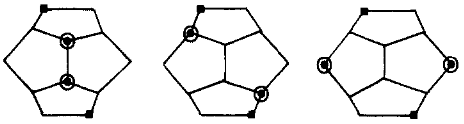
(0012) (0211)

C_{2h} (n=4)



(0001) (0023)

(n=6)



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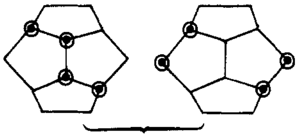
(n=8)



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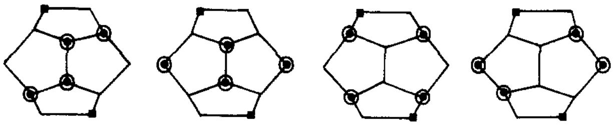
(n=10)



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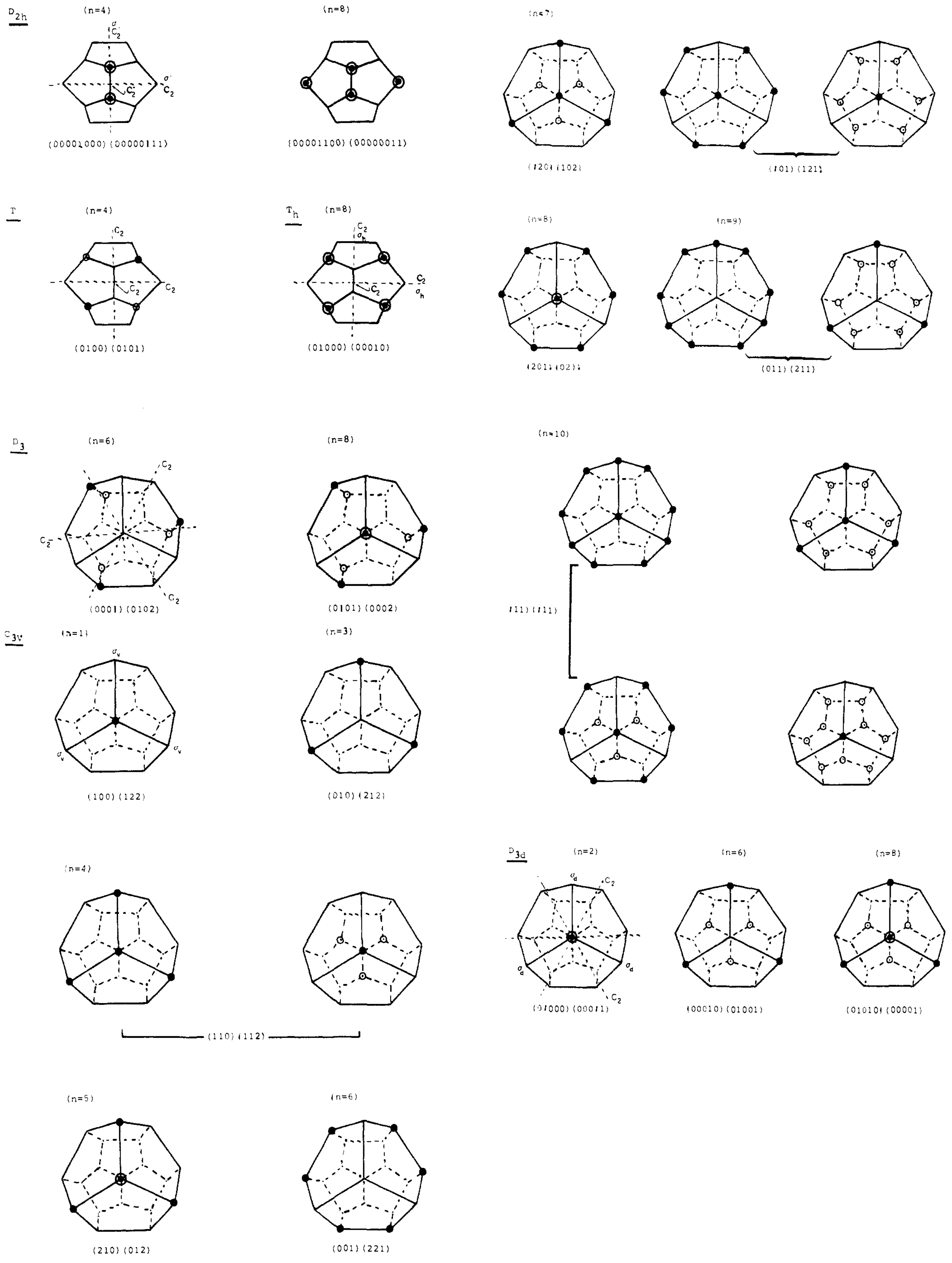

Figure 3. Isomers of $C_{20}H_{20-n}X_n$ of particular symmetries (see text).

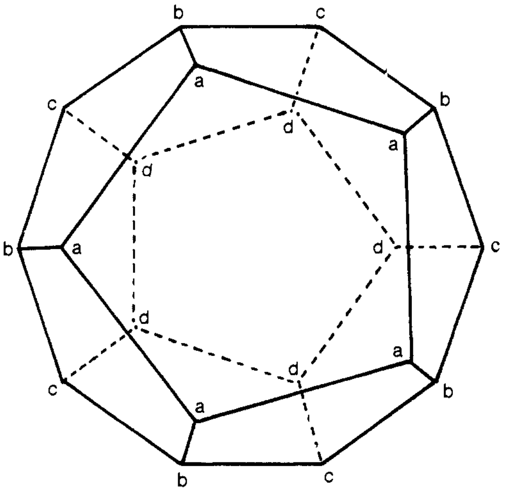

Figure 4. Dodecahedron viewed along C_5 axis.

possible to check such a list of verifying whether the *total* number of isomers found by inspection was equal to the number v^{GB} calculated by group theoretical methods.[1]

The present paper allows to calculate *separately* the number v_γ^{GB} of isomers of symmetry γ. Hence, the above verification can now be made for each possible symmetry. This will seriously reduce the risk of omitting isomers.

As we have shown, the v_γ^{GB} obey a system of equations which can only be solved if some v_γ^{GB} are calculated independently. In fact, this is not a very serious limitation since, in practice, some of the v_γ^{GB}'s are easy to obtain either because they are vanishing for any ligand partition (phantom subgroups of G) or because they are readily found by inspection, as it is the case when isomers of high symmetry have to be enumerated. One should note that for these symmetrical isomers, Pople's method[34] is a very efficient tool which facilitates the enumeration.

The system of equations for v_γ^{GB} is a linear and inhomogeneous one. The linear coefficients $p_{\beta\gamma}^G$ and the inhomogeneous terms $p_{\beta B}^{S_n}$ are related to the double-coset structure of G and S_n, respectively. They are easy to calculate by standard group theoretical techniques.[3] For a given molecular skeleton, $p_{\beta\gamma}^G$ has to be calculated only once, whereas $p_{\beta B}^{S_n}$ depends also on the ligand partition.

Using previous mathematical work,[28,30] W. Hässelbarth[27] has shown independently that the v_γ^{GB} are the solution of a system of linear inhomogeneous equations whose coefficients form the Burnside table of marks. The determinant arising from this table is nonvanishing—in contradistinction to what occurs in our method—hence, this approach does not require the calculation of some v_γ^{GB} independently.

However, since double cosets are rather familiar to theoretical stereochemists (see ref 3 and references cited there), one might expect that the present method, which only involves double-coset enumeration, will provide a convenient tool to calculate the number of isomers of fixed symmetry.

Acknowledgment. We want to acknowledge pertinent comments of Dr. R. Willem during this work and the help of Dr. D. Berckmans in computational problems. We also like to thank Dr. W. Hässelbarth for communication of his manuscript prior to publication. His remarks and criticism have inspired modifications of the original text, in particular the present shortened version of Appendix A.

Appendix

A: **Proof of Equation 12.** We start from the partition of G into double cosets relative to β and G_j:

$$G = \bigcup_k \beta g_k G_j \tag{15}$$

Since β is a subgroup of G, it is possible to decompose the double coset Gx_jB into double cosets relative to β and B

$$Gx_jB = \bigcup_l \beta g_l' x_j B \tag{16}$$

where g_k and g_l' belong to G. When eq 5 is used, it is possible to show that the number p_{β,G_j}^G of (β,G_j) double cosets in G is equal to the number q_j of (β,B) double cosets in Gx_jB. Since

$$S_n = \bigcup_j Gx_jB$$

one obtains

$$p_{GB}^{S_n} = \sum_j q_j = \sum_j p_{\beta B_j}^G$$

In the sum over j, the terms corresponding to the same point group γ may be grouped together. This gives eq 12

$$p_{GB}^{S_n} = \sum_\gamma p_{\beta\gamma}^G v_\gamma^{GB}$$

B: **Phantom Subgroups.** For the case $G = D_{3h}$ (trigonal bipyramid), we have noticed that there are no isomers of point group C_2, C_3, D_3, and C_{3h} in spite of the fact that these are subgroups of G. This may be explained in terms of the framework groups introduced by Pople.[34] We will also show that for $G = I_h$, there are no isomers of C_5, D_5, S_{10}, and I point groups. These will be called "phantom subgroups".

We first list "phantom subgroups" for $G = D_{3h}$, their subspaces, and the corresponding k values (in the same order as the subspaces). This is done in Table X (for details and notation, see ref 34).

We consider a ligand partition $PX_aY_bZ_cU_dV_e$, where the integers a–e ... range from 0 to 5 inclusively and where $a + b + ... = 5$. Following the method of Pople, we have to find the sets $(i_1,i_2,...)$ for each ligand species and such that

$$i_1k_1 + i_2k_2 + ... = 1 \quad \text{(for P)} \tag{17}$$

$$j_1k_1 + j_2k_2 + ... = a \quad \text{(for X)} \tag{18}$$

and so on.

When the subgroup is C_{3h}, we may exclude any ligand partition where one of the integers a,b is equal to one. Indeed, if $a = 1$, for instance, then the set $(i_1,i_2,...)$ is (1000) for the ligand X. (See eq 18.) But this is also the case for the ligand P. Hence, two ligands X and P are located in the center, O, which is excluded. The only remaining ligand partitions are PX_5 and PX_3Y_2. As shown by Pople,[34] there is no C_{3h} framework group for PX_5 molecules. For PX_3Y_2, the only possible $(i_1,i_2,...)$ $(j_1,j_2,...)$ $(l_1,l_2,...)$ sets are (1000)(0010)(0100). This corresponds to D_{3h} symmetry instead of C_{3h} [P in the center, two equivalent Y on C_3, three equivalent X on σ_h]. Hence, C_{3h} is excluded.

The arguments excluding D_3 are similar to those used for C_{3h}.

When the subgroup is C_3, we first suppose that none of the integers a, b, etc., are bigger than 2. Then the use of eq 17 and 18 imposes that all the ligands are on the C_3 axis; hence, the molecular is linear. Such a solution is excluded since the resulting symmetry is not a subgroup of D_{3h}, a fact which contradicts eq 5. If, on the contrary, one integer, say a, is at least 3, then the use of eq 17 and 18 leads to other solutions than the linear molecules, namely

PX_5: (10)(21)

PX_4Y: (10)(11)(10)

PX_3Y_2: (10)(01)(20)

PX_3YZ: (10)(01)(10)(10)

They all correspond to a situation where there are three equivalent X ligands in the subspace X and the remaining ligands on the C_3 axis. This corresponds to C_{3v} symmetry instead of C_3. Hence, C_3 is excluded. Note that C_3 frameworks for PX_5 molecules were already excluded.[34]

Finally, when the subgroup is C_2, it is easy to verify that there are three types of solutions of eq 17 and 18: (a) those where all the ligands are on the C_2 axis (linear), (b) those where two ligands of the same species are in the X subspace (planar), and (c) those where four ligands are in the X subspace. The solutions leading to linear molecules are excluded for the same reason as before. Solutions of type b exist for all ligand partitions except PXYZUV. For instance, for PX_3Y_2, one obtains (10)(30)(01) which means P and 3X ligands on the C_2 axis and 2Y ligands in the X subspace, i.e., C_{2v} symmetry.[46] For the other ligand partitions, a similar conclusion can be reached. Hence, C_2 solutions of type b are also excluded. Type c solutions exist for several ligand partitions

PX_5 (10)(12)

PX_4Y: (10)(02)(10)

PX_3Y_2: (10)(11)(01)

PX_2Y_2Z: (10)(01)(01)(10)

They are all characterized by the fact that two planes interesecting along the C_2 axis each contain two of the four ligands of the X subspace. These two planes are *not perpendicular* to each other (otherwise one should have C_{2v} symmetry instead of C_2). In the original $D_{3h}[O(P),C_3(X_2),3\sigma_v(X)]$ framework, the four ligands which are not on a given C_2 axis lie pairwise in two *perpendicular* planes. Therefore, the type c solutions of C_2 framework symmetry are not compatible with eq 5. They differ from it through an additional distortion, namely the fact that the two above planes are no longer perpendicular.[31] If we limit ourselves to subgroups described by eq 5, we may conclude that C_2 is also excluded.

We now establish that for dodecahedrane ($G = I_h$) C_5, D_5, S_{10}, and I are also phantom subgroups. In Table XI, the subspaces and k values of these subgroups are recalled.[34] In the discussion, we omit the carbon skeleton and only consider the ligands. A ligand partition will be symbolized by $X_aY_bZ_c$... where the 20 integers a,b,c range from 0 to 20 inclusively and where $a + b + c + ... = 20$. We note that in $C_{20}H_{20}$, the center O and the C_2 and C_5 axis contain no atoms. We admit that this will still be the case for any ligand partition. Hence, in the sets $(i_1,i_2,...)(j_1,j_2,...)$, the i and j values corresponding to these subspaces will be vanishing. This restriction can only be fulfilled for a small number of ligand partitions, once the subgroup is specified. These ligands partitions and the resulting $(i_1,i_2,...)(j_1,j_2,...)$ etc. sets are given below

C_5: X_{20}: (04)
$X_{15}Y_5$: (03)(01)
$X_{10}Y_{10}$: (02)(02)
$X_{10}Y_5Z_5$: (02)(01)(01)
$X_5Y_5Z_5U_5$: (01)(01)(01)(01)
D_5: X_{20}: (0002)
$X_{10}Y_{10}$: (0001)(0001)
S_{10}: X_{20}: (002)
$X_{10}Y_{10}$: (001)(001)
I: X_{20}: (00100)

We now apply eq 5 with $G = I_h$ for each of these ligand partitions. The discussion is facilitated by using Figure 4. Clearly, X_{20} leads to $G_i = I_h$. For $X_{15}Y_5$, there are two possibilities (two choices of x_i). The Y ligands may occupy the vertices a of one pentagonal face of the dodecahedron (see Figure 4). Then $G_i = C_{5v}$. Otherwise the Y ligands are on the first neighbors b of the vertices of such a face and again $G_i = C_{5v}$. For $X_{10}Y_{10}$, there are four possibilities for the X or Y ligands: (ab), (ac), (ad), and (bc). The resulting G_i are C_{5v}, C_{5v}, D_{5d}, and D_{5d}, respectively. When the partition is $X_{10}Y_5Z_5$, the X ligands are on (ab), (ac), (ad), or (bc) and G_i is C_{5v} in any case. For the ligand partition $X_5Y_5Z_5U_5$, G_i is also C_{5v}. Hence, the subgroups C_5, D_5, S_{10}, and I are excluded. Of course, we have again limited our discussion to subgroups compatible with eq 5. Additional distortions[31] have been excluded (see the discussion of the trigonal bipyramid).

C. Rank of $p^G_{\beta\gamma}$. According to eq 2, $p^G_{\beta\gamma}$ may be written

$$p^G_{\beta\gamma} = \frac{|G|}{|\beta||\gamma|} \sum_{y} \frac{|\beta \cap C(y)||\gamma \cap C(y)|}{|C(y)|} \tag{19}$$

where $C(y)$ denotes the classes of G.

We want to examine the possibility that the lines (or columns) of this matrix are linearly dependent vectors, i.e., that

$$\sum_{\beta} a_\beta p^G_{\beta\gamma} = 0 \tag{20}$$

Indeed, if at least one relation of this type exists (with the a_β not all vanishing), then the determinant of $p^G_{\beta\gamma}$ will vanish.

If eq 20 is verified, then, using eq 19 yields

$$\sum_{y} \frac{|\gamma \cap C(y)|}{|C(y)|} \sum_{\beta} a_\beta \frac{|\beta \cap C(y)|}{|\beta|} = 0 \tag{21}$$

Hence,

$$\sum_{\beta} a_\beta \frac{|\beta \cap C(y)|}{|\beta|} = 0 \tag{22}$$

is a sufficient condition for the determinant of $p^G_{\beta\gamma}$ to be vanishing. This last relation means that the $r|\beta \cap C(y)|$ vectors of dimension C are linearly dependent (C is the number of classes of G and r the number of its subgroups).

We first examine the case of the trigonal bipyramid. Here $C = 6$ and $r = 10$ as shown on Table I where the 10 $|\beta \cap C(y)|$ vectors are represented. Since the number linearly independent vectors cannot exceed the dimension of the space (here $C = 6$), these vectors must satisfy at least four linear relations of the type eq 22. These four relations are easy to find on Table I. For instance, it is clear that when one substracts the line C_3 from the line D_3, one obtains, up to a factor of 3, the same vector as if one substracts the line C_1 from the line C_2. The coefficients $a_\beta/|\beta|$ to be put in eq 22 and corresponding to this relation appear in the first line of Table XII. The other lines of this table can be found similarly. Hence, there are at least four relations of the type of eq. 20, and the rank of $p^G_{\beta\gamma}$ is at most six. It is found that it is exactly six since the determinant obtained by suppressing the lines and columns C_2, C_3, D_3, and C_{3h} in $p^G_{\beta\gamma}$ is equal to one.

Similar considerations are valid for the dodecahedral skeleton ($G = I_h$). Here, $r = 22$ and $C = 10$ as shown on Table V. The 22 $|\beta \cap C(y)|$ vectors of this table cannot be linearly independent since the space is 10 dimensional. It is also seen on this table that the 22 vectors do not have 10 independent components but at most 8. Indeed, for all vectors, the components corresponding to the classes $12C_5$ and $12C_5^2$ of I_h are equal. The same is true for the classes $12S_{10}$ and $12S_{10}^3$. Hence, there are at least 14 relations of the type of eq 22 to be found, and the rank of $p^G_{\beta\gamma}$ cannot exceed 8. In Table XIII, the coefficients appearing in eq 22 for each of the above 14 relations are shown. The matrix $p^G_{\beta\gamma}$ is exactly of rank 8 since the determinant obtained by suppressing the lines and columns C_5, D_2, D_3, D_5, C_{2v}, C_{3v}, C_{2h}, D_{2h}, D_{3d}, S_{10}, T, T_h, I, and I_h in $p^G_{\beta\gamma}$ is equal to 4096.

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[46] In terms of framework group, this leads to $C_{2v}[C_2(PX_3),\sigma_v(Y_2)]$. It should be noted that when eq 5 is applied with $G = D_{3h}$ (more precisely $D_{3h}[O(P),C_3(X_2),3\sigma_v(X)]$, in the ligand partition PX_3Y_2 and when two of the three X of the $3\sigma_v$ space are replaced by Y ligands, then the resulting framework group is $C_{2v}[C_2(PX),\sigma_v(X_2),\sigma_v(Y_2)]$ and not $C_{2v}[C_2(PX_3),\sigma_v(Y_2)]$. In this sence, the former C_{2v} framework is a subgroup of the D_{3h} one, whereas the latter C_{2v} framework is not.