Table of Marks and Double Cosets in Isomer Counting

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Abstract: In recent years, two new formulas have been obtained for the calculation of the number of isomers of each symmetry for a given molecular skeleton and ligand assortment. One, due to Hässelbarth, utilizes the "table of marks" of the skeletal symmetry group; the other, due to Brocas, is based on double coset counting. We present alternate derivations of both from a common starting point, the counting of double cosets, and we show that the Hässelbarth formula also contains terms belonging to the table of marks of the ligand permutation group, so that the formula in reality is entirely in terms of marks, and we exhibit a diagrammatic method for evaluating these marks. We show that the method of Ruch, Hässelbarth, and Richter for calculating the number of optically active and inactive isomers follows from a special case of the Brocas formula, and we indicate how similar special cases can be used to obtain other information about classes of isomers. The Brocas formula contains less information than the Hässelbarth formula, and in general it does not permit a solution of the problem without additional information, which, however, is nearly always available. We show how the Brocas formula can be derived from the Hässelbarth formula, and in the process we obtain a new and practical method for evaluating double coset numbers with the aid of tables of marks. We emphasize the simplicity and utility of the unjustly neglected concept of the table of marks. As examples, all results and techniques are applied to the counting of isomers of the pentaprismane derivatives.

I. Introduction

In recent years, there has been significant progress in the application of group-theoretical methods to the isomer-counting problem. The problem may be stated as follows: Given a molecular skeleton with N sites and with a given point symmetry group, and given an assortment of ligands to be attached to the sites, some of which may be identical, how many chemically different isomers are there? More detailed questions may also be asked, such as the following: How many of the isomers are achiral and how many consist of enantiomeric pairs? How many of the isomers have a given symmetry?

A solution to the problem in terms of a generating polynomial was given in 1937 by Polya.[1] More recent progress began with the pioneering work of Ruch, Hässelbarth, and Richter,[2] who showed how the total number of isomers, and the number of enantiomeric pairs and of achiral isomers, could be calculated by counting double cosets of the skeleton point group and the group of permutations of identical ligands, both regarded as subgroups of the group of permutations of all ligands. The concept of the double coset,[3,4] unfortunately omitted in many familiar treatises on group theory, proves to be very convenient for problems such as isomer counting. The method of ref 2 is exceedingly easy to apply in practice, even when the number of isomers is large, in the hundreds or thousands.

An important further advance was made more recently by Hässelbarth,[5] who developed a most general and elegant method for dealing with counting problems by considering application of symmetry and permutation group elements to general mappings of ligands onto sites. Hässelbarth's method is applicable not only to structureless ligands but also to ones which change under rotations and/or reflections, and it yields solutions to the problem of the number of isomers with each possible symmetry. His solution involves the use of generating polynomials, and of the "table of marks" of a group, a concept going back to Burnside.[6] Even more than double cosets, the concept of the mark is an unjustly neglected one, being omitted even from quite voluminous treatises on the theory of finite groups. As Hässelbarth showed, however, and as we shall also emphasize, the marks are quite easy to understand and obtain, and they are very useful in counting problems.

Another approach to the question of the number of isomers of each symmetry was developed by Brocas,[7] who returned to double coset counting to obtain a formula in terms of double coset numbers involving the number of isomers of each symmetry. His method is less general than Hässelbarth's, being applicable only

to structureless ligands, and it also suffers from the defect that the number of independent equations provided by his formula is in general less than the number of unknowns to be solved for. In practice, however, one nearly always has enough additional information to overcome this difficulty.

In the present article, we attempt to provide more insight into the methods of Hässelbarth and Brocas by discussing their relationship to one another and to the method of ref 2. In the process, we provide alternate derivations of both formulas which may take the results more transparent to some readers. We confine ourselves throughout to structureless ligands.

In section II, we obtain the Hässelbarth mark formula by means of double coset counting. We also show that another quantity used by Hässelbarth, and evaluated by him with the aid of a generating polynomial, is itself a mark, and we provide an alternate diagrammatic method for evaluating it, which in practice proves quite convenient.

Section III discusses the Brocas formula, again starting with double coset counting. Our derivation is somewhat more direct and intuitive than that of Brocas, though closely related to it. We also show that the method of Ruch, Hässelbarth, and Richter for obtaining the number of achiral isomers and enantiomeric pairs is a special case of the Brocas formula. We show how similar special cases can be used to obtain other information.

In section IV, we show how tables of double coset numbers can be obtained from tables of marks, and we use this to show that the Brocas formula is derivable from that of Hässelbarth. In many cases, this method for obtaining double coset counts is more convenient than others customarily used.

Each of sections II–IV is divided into two subsections: subsection A deals with the general theory, while subsection B provides examples by applying the results to the pentaprismane derivatives. The pentaprismane molecule, $C_{10}H_{10}$, with the carbon atoms located at the vertices of a regular pentagonal prism and thus with D_{5h} symmetry, has been synthesized by Eaton, Or, and Branca.[8] It is ideal for providing illustrations of the use of group theoretical

(1) Polya, G. *Acta Math.* **1937**, *68*, 145.
(2) Ruch, E.; Hässelbarth, W.; Richter, B. *Theor. Chim. Acta* **1970**, *19*, 288.
(3) Huppert, B. *Endliche Gruppen I*; Springer-Verlag: Berlin, 1967, pp 94–101.
(4) "Representations of Permutation Groups I"; Kerber, A. *Lecture Notes in Mathematics*; Springer-Verlag: Berlin, 1971; Vol. 240.
(5) Hässelbarth, W. *Theor. Chim. Acta* **1985**, *67*, 339.
(6) Burnside, W. *Theory of Groups of Finite Order*, 2nd ed.; Cambridge University Press: Cambridge, 1911; Reprinted by Dover Publications: New York, 1955; Section 180.
(7) Brocas, J. *J. Am. Chem. Soc.* **1986**, *108*, 1135.
(8) Eaton, P. E.; Or, Y. S.; Branca, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 2134.

methods in isomer counting because it fulfills all three of the most important conditions: namely, (i) the pentaprismane molecule and some of its derivatives actually have been made, so the question is not simply academic; (ii) the group theoretical methods yield results quickly and easily; and (iii) the number of isomers often turns out to be much too large to be obtained by exhaustive counting, illustrating the indispensable nature of the group theoretical methods.

In section V, we use the formula obtained in section IV to obtain an expression for the rank of the double coset matrix, i.e., for the number of independent equations furnished by the Brocas formula. There is some discussion of the results in section VI.

II. Double Cosets and Table of Marks

A. General Theory. Before beginning, we discuss our notation. We use capital Latin letters to denote groups. Usually these will be chosen from the beginning of the alphabet, A–H, but we use S to denote a permutation group. An element of a group will be denoted by a lower case letter, where possible the same letter as that used for the group, perhaps with a subscript. Thus, a or a_j denotes an element of group A. Sometimes we will be forced to use r as well as s for an element of the permutation group.

If F is a subgroup of A, then the script letter $\mathscr{F}^{(A)}$ denotes the set of all subgroups of A which are conjugate to F. If D is another subgroup of A, $\mathscr{F}^{(A)}_{\{D\}}$ denotes the set of subgroups of A which are conjugate to F and which contain D as a subgroup.

We use the standard set-theoretic symbols $\cup$ for union and $\cap$ for intersection. Thus, if A and B are two subgroups of S, A $\cap$ B is the subgroup consisting of all elements contained in both A and B, while A $\cup$ B would denote the set of elements (in general not a subgroup) belonging to A and/or B. The absolute value sign applied to any set denotes the order: $|A|$ is the order of the group A, $|\mathscr{F}^{(A)}|$ is the number of subgroups of A conjugate to F, etc.

We now proceed to a precise formulation of our problem. We are given a skeleton with N sites, to which numbers have been assigned in some convenient way. We are also given N structureless ligands, some of which may be identical with one another. The number of isomers will not depend on the nature of the ligands, but it will depend in general on how many are identical. This is described by the "ligand partition", $P(B)$, which is simply a partition of N into a sum of integers. If for every t, $1 \le t \le N$, there are $u_t(B)$ sets of t identical ligands [of course, some of the $u_t(B)$ can be zero], then we must obviously have

$$\sum_t t u_t(B) = N$$

and the set of the $u_t(B)$ determines $P(B)$ completely. $P(B)$ can also be denoted by a Young diagram $\Delta(B)$ in which the number of rows of length t is $u_t(B)$ for each t. It can also be denoted symbolically in product form:

$$P(B) = \Pi_t t^{u_t(B)}$$

The symmetry group of the skeleton will be denoted by A, and it will have subgroups D, F, G, H, ..., any of which might be the symmetry group of an isomer, or of a distorted version of the skeleton. We will also need the concept of the orbits associated with the group A. An orbit of A is just a set of sites which are equivalent under A, i.e., which are carried into one another by elements of A. The set of orbits of A forms a partition $P(A)$, with all the properties of $P(B)$ just discussed, in which $u_t(A)$ is the number of orbits of length t. For the trigonal bipyramid with D_{3h} symmetry, for example, we have $P(A) = (32)$; for the triangular prism, also with D_{3h} symmetry, $P(A) = (6)$, since all sites are equivalent in this case.

The questions we wish to consider are the following: Given a skeleton and ligand partition, how many isomers are there? Also, how many isomers have some specified property, such as being optically active or inactive? For a given subgroup D of A, how

many isomers have symmetry D?

Let S be the full permutation group of the N ligands among the N sites. Elements of S will be referred to sites, not to ligands; for example, a cyclic permutation (123) would mean that the ligand on site 1 is moved to site 2, that on site 2 to site 3, and that on site 3 to site 1. We denote by L some arbitrarily chosen "standard" isomer, i.e., some assignment of ligands to sites adopted as a starting point. Given the ligand partition $P(B)$, let B denote the group of permutations which, when applied to L, result in permutations of identical ligands, i.e., in no visible change. Evidently, B is just a direct product of permutation groups of t objects for every set of t identical ligands, and its order is

$$|B| = \Pi_t(t!)^{u_t(B)}$$

In order to obtain the Hässelbarth formula, we need to repeat some of the steps in the derivation of ref 2 and diverge from that derivation at an appropriate point. If s is some element of S, we can obtain an isomer L(s) by applying s to L:

$$L(s) = sL \tag{1}$$

The subgroup of permutations which just permute identical ligands when applied to L(s) is evidently

$$B_s = sBs^{-1} \tag{2}$$

Of the $N!$ permutations in S, the ones which leave L(s) unchanged are those that consist of an element b_s from B_s followed by an element a from A, and only those

$$ab_sL(s) = L(s)$$

which, after insertion of (1) and (2), becomes

$$asbs^{-1}L(s) = asbs^{-1}sL = asbL = L(s) \tag{3}$$

The permutations that produce the isomer L(s) are thus all those that can be written in the form asb, which by definition are just the elements of the double coset AsB. The element s is called the generator of the double coset. We will sometimes refer to the double cosets AsB generated by elements of S as S-double cosets of A and B, since there are many groups which contain A and B as subgroups, and double cosets of A and B can be generated within any of them. It is very easy to show[2-4] that any element of the double coset can be considered to be its generator and that the double cosets are disjoint, i.e., that each element of S is a member of one and only one double coset AsB. There is an isomer for each double coset. One also easily shows the following: For fixed s, we allow a and b to run through all the elements of A and B, respectively, and in each case write down the element asb. The number of entries thus produced is $|A||B|$, but the same group element may appear more than once. In fact, all elements belonging to AsB appear the same number of times. The number of times each element appears is thus the number of times s appears. In order to have asb = s, we must have a = $sb^{-1}s^{-1}$, so the number of appearances of each element is $|sBs^{-1} \cap A|$, and the order of the double coset is

$$|AsB| = \frac{|A||B|}{|sBs^{-1} \cap A|} = \frac{|A||B|}{|B_s \cap A|} \tag{4}$$

Obviously, the inverse of (4), summed over all elements of the double coset, each of which can be considered the generator, just gives unity:

$$1 = \frac{1}{|A||B|} \sum_{r \in AsB} |B_r \cap A| \tag{5}$$

Allowing the sum (5) to extend over all r in S gives the total number $Z^{(S)}_{AB}$ of isomers:

$$Z^{(S)}_{AB} = \frac{1}{|A||B|} \sum_{r \in S} |B_r \cap A| \tag{6}$$

Starting with (6), we can generate the elements of B_r for each r, divide them into classes, and note which are also in A. Proceeding in this way, we easily obtain the very useful formula

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(9) The author is indebted to W. Hässelbarth for suggesting the simple method of proof used in this subsection, which replaces a more cumbersome approach used in the original version of this article.

(obtained by a different method in ref 2)

$$Z_{AB}^{(S)} = \frac{|S|}{|A||B|} \sum_C \frac{|C \cap A||C \cap B|}{|C|} \qquad (7)$$

where the sum goes over the classes of S.

As was clearly explained in ref 2, each double coset corresponds to a set of permutations related to one another by combinations of permutations of identical ligands and elements of A. Thus, if A is taken to be the group of proper rotations, permutations related to one another by reflections or inversions are considered to belong to different isomers, and enantiomeric pairs are counted as two isomers. If A is taken to be the full point group including improper operations, an enantiomeric pair counts as one isomer. By combining these two approaches, Ruch, Hässelbarth, and Richter elegantly solve the problem of the number of enantiomeric pairs and achiral isomers.

We now return to (5) and note that, if the sum is extended, not over the entire permutation group, but just over those elements producing isomers possessing some property of interest, one obtains the number of isomers having that property. In particular, we are interested in the number of isomers having a particular symmetry. Evidently, the symmetry group of L(s) is just

$$F_s = B_s \cap A \qquad (8)$$

Also, if $F_r = aF_s a^{-1}$, L(r) and L(s) have the same symmetry, with s and r merely producing different orientations. Thus, the quantity we are looking for is $Z_{AB}^{(S)}(\mathcal{F})$, the number of isomers with symmetry conjugate to F, which is the same as the number of double cosets with this property and is given by

$$Z_{AB}^{(S)}(\mathcal{F}) = \frac{|F|}{|A||B|} Y_{AB}^{(S)}(\mathcal{F}) \qquad (9)$$

where $Y_{AB}^{(S)}(\mathcal{F})$, is the number of elements r of S with the property that $F_r \in \mathcal{F}^{(A)}$. When r runs through all the elements of S, all B_r will be generated equally often, and the same will be true for all conjugate F_r. Hence, (9) can be rewritten in the more directly usable form

$$Z_{AB}^{(S)}(\mathcal{F}) = \frac{|F||\mathcal{F}^{(A)}|}{|A||B|} Y_{AB}^{(S)}(F) \qquad (10)$$

where $Y_{AB}^{(S)}(F)$ is now the number of elements r with the property that $F_r = F$.

Unfortunately, $Y_{AB}^{(S)}(F)$ is hard to calculate directly. Much more easily accessible is $X_{AB}^{(S)}(F)$, the number of r such that $F_r \geq F$ (F_r has F as a subgroup), which is the same as the number of r such that $B_r \geq F$. Dividing through by $|F||\mathcal{F}^{(A)}|$, we transform (10) into

$$\frac{|A|Z_{AB}^{(S)}(\mathcal{F})}{|F||\mathcal{F}^{(A)}|} = \frac{1}{|B|} Y_{AB}^{(S)}(F) \qquad (11)$$

We now sum (11) over all F which contain D as a subgroup (including D and A, of course). The right-hand side obviously just gives $|B|^{-1} X_{AB}^{(S)}$. As for the left-hand side, each term with given $\mathcal{F}$ will be repeated once for each F in $\mathcal{F}^{(A)}$ that has D as a subgroup. We thus find

$$\sum_{\mathcal{F}} \frac{|A||\mathcal{F}_{\{D\}}^{(A)}|}{|F||\mathcal{F}^{(A)}|} Z_{AB}^{(S)}(\mathcal{F}) = \frac{1}{|B|} X_{AB}^{(S)}(D) \qquad (12)$$

The coefficient of $Z_{AB}^{(S)}(\mathcal{F})$ in (12) is clearly a function only of the conjugate sets $\mathcal{D}$ and $\mathcal{F}$, and not of the particular subgroup chosen from each set. It is called the mark of D in F:

$$M_{\mathcal{D}\mathcal{F}}^{(A)} = \frac{|A||\mathcal{F}_{\{D\}}^{(A)}|}{|F||\mathcal{F}^{(A)}|} \qquad (13)$$

As was the case with the double cosets, the value of $M_{\mathcal{D}\mathcal{F}}^{(A)}$ will depend not only on D and F but on the larger group A which has both as subgroups. We will therefore sometimes refer to $M_{\mathcal{D}\mathcal{F}}^{(A)}$ as the A-mark of D in F. If $\mathcal{D}$ and $\mathcal{F}$ are allowed to run over

all the sets of conjugate subgroups of A, the marks can be arranged in a matrix $\mathbf{M}^{(A)}$ which is called the table of marks. Note that the mark (13) is zero unless D is a subgroup of some subgroup belonging to $\mathcal{F}^{(A)}$. Thus, if the subgroup sets are assigned rows and column according to decreasing order, $\mathbf{M}^{(A)}$ has nonzero elements along the main diagonal and zeros to the right and above the main diagonal. $\mathbf{M}^{(A)}$ is evidently invertible, since one sees at a glance that the columns are all linearly independent. Thus, as Hässelbarth[5] has shown, (12) can be solved for the desired quantities $Z_{AB}^{(S)}(\mathcal{D})$.

Burnside's original definition of the mark,[6] translated into more familiar language, states that $M_{\mathcal{D}\mathcal{F}}^{(A)}$ is the number of left (right) cosets of F with respect to A which are left invariant under left (right) multiplication by all elements of D. It is easy to see that this is equivalent to (13): If the coset aF is invariant under D, DaF = aF, it follows that $D \leq aFa^{-1}$. The mark is thus the total number of cosets times the fraction whose generators have this property. But the subgroups aFa^{-1} generated by the coset generators are just all the subgroups belonging to $\mathcal{F}^{(A)}$, each appearing an equal number of times. From this, one immediately obtains (13).

Hässelbarth[5] has obtained a generating polynomial for the evaluation of the right-hand side of (12). We now show that the right-hand side is also a mark. If we generate B_r for each r in S, each group in $\mathcal{B}^{(S)}$ is generated an equal number of times, and this number is just $|S|/|\mathcal{B}^{(S)}|$. $X_{AB}^{(S)}(D)$ is just the number of r such that $B_r \geq D$, so we see that

$$X_{AB}^{(S)}(D) = \frac{|S|}{|\mathcal{B}^{(S)}|} |\mathcal{B}_{\{D\}}^{(S)}| \qquad (14)$$

Combining (12), (13), and (14), we see that

$$\sum_{\mathcal{F}} M_{\mathcal{D}\mathcal{F}}^{(A)} Z_{AB}^{(S)}(\mathcal{F}) = M_{\mathcal{D}\mathcal{B}}^{(S)} \qquad (15)$$

Defining $\bar{\mathbf{M}}^{(A)} = [\mathbf{M}^{(A)}]^{-1}$, we can solve (15) for the desired quantities $Z_{AB}^{(S)}(\mathcal{D})$:

$$Z_{AB}^{(S)}(\mathcal{D}) = \sum_{\mathcal{F}} \bar{M}_{\mathcal{D}\mathcal{F}}^{(A)} M_{\mathcal{F}\mathcal{B}}^{(S)} \qquad (16)$$

The Hässelbarth formula, in the version we will use, is embodied in eq 15 and 16. Our derivation has emphasized its close connection with double coset counting.

As we shall see, the marks are very easy to obtain. Moreover, because of the structure of the table of marks, the inversion is also very easy to carry out, one row at a time. Thus, the number of isomers with given symmetry is *very* easily obtainable with the aid of (15) and (16). That the right-hand side of (15) is also a mark will prove useful in section IV.

We now examine the right-hand side of (15) in more detail, so as to facilitate its evaluation. In our case, B is a direct product of $u_t(B)$ permutation groups of t objects for each t, and S is the full permutation group of N objects, with $|S| = N!$. The number of groups conjugate to B, $|\mathcal{B}^{(S)}|$, is just the number of ways of assigning N objects to the N squares in the Young diagram $\Delta(B)$, without distinguishing between assignments that differ by permutations within rows, and/or by permutations of entire rows of the same length. This combinatorial factor is easily seen to be

$$\frac{N!}{\Pi_t(t!)^{u_t(B)}[u_t(B)]!}$$

We see, therefore, that

$$M_{\mathcal{D}\mathcal{B}}^{(S)} = |\mathcal{B}_{\{D\}}^{(S)}|\Pi_t[u_t(B)]! \qquad (17)$$

A group conjugate to B will contain D as a subgroup if and only if the sites of each orbit of D are occupied by identical ligands, and $|\mathcal{B}_{\{D\}}^{(S)}|$ is the number of ways of achieving this that correspond to distinct groups. This can be evaluated diagrammatically by filling the rows of $\Delta(B)$ with entire rows from $\Delta(D)$. Such a filling is carried out according to the following rules:

(i) Starting with the top row of $\Delta(D)$ and working downward, transfer each entire row of $\Delta(D)$ into a previously empty row of

Table I. Table of Marks of D_{5h}

	D_{5h}	D_5	C_{5v}	C_{5h}	C_5	C_{2v}	C_2	C_{sv}	C_{sh}	C_1
D_{5h}	1	0	0	0	0	0	0	0	0	0
D_5	1	2	0	0	0	0	0	0	0	0
C_{5v}	1	0	2	0	0	0	0	0	0	0
C_{5h}	1	0	0	2	0	0	0	0	0	0
C_5	1	2	2	2	4	0	0	0	0	0
C_{2v}	1	0	0	0	0	1	0	0	0	0
C_2	1	2	0	0	0	1	2	0	0	0
C_{sv}	1	0	2	0	0	1	0	2	0	0
C_{sh}	1	0	0	2	0	5	0	0	10	0
C_1	1	2	2	2	4	5	10	10	10	20

$\Delta(B)$, or into the unfilled portion of a partially filled row.

(ii) Each row transferred must be placed as far to the left as possible in the row in which it is placed (this prevents us from distinguishing between permutations within a row).

(iii) If a row of $\Delta(D)$ is transferred into a previously empty row of $\Delta(B)$, it should go into the highest empty row of given length (this prevents us from distinguishing between permutations of rows of equal length in $\Delta(B)$).

(iv) At the end, all rows of $\Delta(D)$ must be transferred with no overflow.

The number of such fillings is just $|\mathscr{B}_D^{(S)}|$; multiplication by $\Pi_i[u_i(B)]!$ then gives the mark. Alternatively, one could omit rule iii and also omit the multiplicative factor at the end. The procedure is illustrated in Figure 1 for the case in which D has four orbits of length 2, and two of length 1, and in which there are two sets of three identical ligands and two pairs of identical ligands. There are 12 fillings in this case, and we have $u_2(B) = u_3(B) = 2$, with all others zero, so the multiplicative factor is 4, and the mark is 48. Of course, one can often see the result without drawing the diagrams. In the example of Figure 1, one sees that each of the sites E and F must go into rows of length 3, but not both into the same row. Of the four pairs AA, BB, CC, and DD, one must be in the same row with E, one in the same row with F, and the other two in rows by themselves. There are clearly $4 \times 3 = 12$ ways of doing this.

B. Application to Pentaprismane. For pentaprismane, there are 10 sites, and the symmetry of the skeleton, A, is D_{5h}, of order 20. All sites are equivalent under this group, so its orbit structure is just (10). The other sets of conjugate subgroups, with their orders and orbit structures, are as follows:

 Order 10: D_5 (10); C_{5v} (5^2); C_{5h} (10)
 Order 5: C_5 (5^2)
 Order 4: C_{2v} ($4^2 2$)
 Order 2: C_2 (2^5); C_{sv} ($4^2 2$); C_{sh} (2^5)
 Order 1: C_1 (1^{10})

Following Brocas,[7] we denote the subgroup with a single verticle reflection plane by C_{sv}, and that with a horizontal plane by C_{sh}. The subgroups are all invariant except for C_{2v}, C_2, and C_{sh}, for each of which there are five conjugate subgroups.

Counting D_{5h} and C_1, there are thus ten possible symmetries for isomers. As Hässelbarth[5] has pointed out, however, some of these can be eliminated a priori. If H is a subgroup of F, and if the orbits of H are the same as those of F (not just the lengths, but the specific sites involved), then there can be no isomers with symmetry H, since symmetry H would require that the orbits of H be occupied by identical ligands, and any isomer with this property would have the higher symmetry F. Subgroups that can be eliminated in this way are called "phantom subgroups" by Brocas.[7] In our case, the phantom subgroups are D_5, C_{5h}, and C_5. Any isomer invariant under D_5 or C_{5h} would have to have all ligands identical and would have D_{5h} symmetry; an isomer invariant under C_5 must have all sites on each pentagonal face occupied by identical ligands and would have at least C_{5v} symmetry. The number of symmetries that really need to be considered is therefore seven instead of ten; nevertheless, to show the power of the method, we will make no use of this result in the present section.

The D_{5h}-marks for these subgroups have been evaluated with the aid of (13) and are listed in Table I. We indicate with two
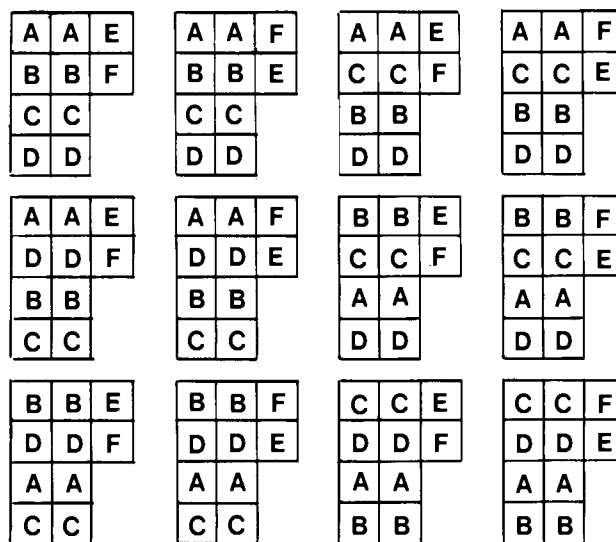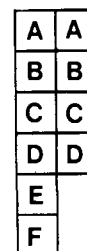
Figure 1. The 12 permissible ways in which the Young diagram representing the ligand partition $(3^2 2^2)$ can be filled with entire rows of the diagram corresponding to orbit lengths $(2^4 1^2)$.

illustrations how the marks are calculated. For all of them, of course, $|A| = 20$. For $D = C_5$, $F = C_{5h}$, we have $|F| = 10$, $|\mathscr{F}^{(A)}| = |\mathscr{F}_{(D)}^{(A)}| = 1$, so (13) yields 2 for the mark. For $D = C_{sv}$, $F = C_{2v}$, we have $|F| = 4$, $|\mathscr{F}^{(A)}| = 5$, but $|\mathscr{F}_{(D)}^{(A)}| = 1$, since only one of the five C_{2v} groups contains a *particular* C_{sv} as subgroup. The value of the mark is therefore unity. The table of marks is thus quickly and easily generated. The matrix inversion is also fast and easy, and the result is given in Table II.

There are 42 possible ligand partitions with ten ligands. To keep the tables to manageable size, we restrict ourselves to the twelve partitions which contain no single ligands. The S-marks of the subgroups of D_{5h} in the twelve selected B groups have been evaluated by the diagrammatic method explained in the last subsection. These too are obtained with ease and are listed in Table III.

From each ligand partition, the number of isomers with each symmetry is obtained with the aid of (16). One simply applies Table II to Table III by matrix multiplication. The resulting isomer numbers are listed in Table IV. Note that the absence of any isomers for the three phantom subgroups falls out automatically. Although the number of isomers, particularly with C_1 symmetry, is often quite large, the generation of Tables I–IV is almost childishly easy. The method of Hässelbarth is therefore practical as well as mathematically appealing.

Table II. Inverse Marks of D_{5h}

	D_{5h}	D_5	C_{5v}	C_{5h}	C_5	C_{2v}	C_2	C_{sv}	C_{sh}	C_1
D_{5h}	1	0	0	0	0	0	0	0	0	0
D_5	-1/2	1/2	0	0	0	0	0	0	0	0
C_{5v}	-1/2	0	1/2	0	0	0	0	0	0	0
C_{5h}	-1/2	0	0	1/2	0	0	0	0	0	0
C_5	1/2	-1/4	-1/4	-1/4	1/4	0	0	0	0	0
C_{2v}	-1	0	0	0	0	1	0	0	0	0
C_2	1/2	-1/2	0	0	0	-1/2	1/2	0	0	0
C_{sv}	1/2	0	-1/2	0	0	-1/2	0	1/2	0	0
C_{sh}	1/2	0	0	-1/10	0	-1/2	0	0	1/10	0
C_1	-1/2	1/4	1/4	1/20	-1/20	1/2	-1/4	-1/4	-1/20	1/20

Table III. S_{10} Marks of D_{5h} and Its Subgroups in Selected B Subgroups

	(10)	(82)	(73)	(64)	(62^2)	(5^2)	(532)	$(4^2 2)$	(43^2)	(42^3)	$(3^2 2^2)$	(2^5)
D_{5h}	1	0	0	0	0	0	0	0	0	0	0	0
D_5	1	0	0	0	0	0	0	0	0	0	0	0
C_{5v}	1	0	0	0	0	2	0	0	0	0	0	0
C_{5h}	1	0	0	0	0	0	0	0	0	0	0	0
C_5	1	0	0	0	0	2	0	0	0	0	0	0
C_{2v}	1	1	0	2	0	0	0	2	0	0	0	0
C_2	1	5	0	10	20	0	0	30	0	60	0	120
C_{sv}	1	5	8	10	20	12	24	30	24	60	48	120
C_{sh}	1	5	0	10	20	0	0	30	0	60	0	120
C_1	1	45	120	210	1260	252	2520	3150	4200	18900	25200	113400

Table IV. Isomer Numbers for Pentaprismane Derivatives of All Symmetries for Selected Ligand Partitions

	(10)	(82)	(73)	(64)	(62^2)	(5^2)	(532)	$(4^2 2)$	(43^2)	(42^3)	$(3^2 2^2)$	(2^5)
D_{5h}	1	0	0	0	0	0	0	0	0	0	0	0
D_5	0	0	0	0	0	0	0	0	0	0	0	0
C_{5v}	0	0	0	0	0	1	0	0	0	0	0	0
C_{5h}	0	0	0	0	0	0	0	0	0	0	0	0
C_5	0	0	0	0	0	0	0	0	0	0	0	0
C_{2v}	0	1	0	2	0	0	0	2	0	0	0	0
C_2	0	2	0	4	10	0	0	14	0	30	0	60
C_{sv}	0	2	4	4	10	5	12	14	12	30	24	60
C_{sh}	0	0	0	0	2	0	0	2	0	6	0	12
C_1	0	0	4	6	52	10	120	142	204	912	1248	5604

III. The Brocas Double Coset Formula

A. General Theory. Consider an isomer L(s), represented by the S-double coset AsB. Each permutation belonging to AsB produces the same isomer, the differences being only in orientation, handedness, and/or permutations of identical ligands. Now suppose that the symmetry of the skeleton is lowered to D, a subgroup of A. A permutation sb applied to the standard molecule L will still produce the same configuration as before, but subsequent application of a permutation a from A may now produce a chemically different species because of the lowered skeletal symmetry. Thus, what was originally one isomer will be "split" into several by the application of elements of A.

An element of A applied to L(s) will produce the same isomer if and only if it is of the form df_s, where d is an element of D, and f_s is an element of the symmetry group F_s, given by (8), of the molecule L(s). If a is an element producing a different isomer, then evidently all members of the A-double coset DaF_s will produce the same isomer. If we denote by $K(D,A,s)$ the number of isomers into which L(s) is split when the symmetry is lowered from A to D, therefore, we have

$$K(D,A,s) = Z_{DF}^{(A)} \tag{18}$$

Note that this is independent of B, and it also depends on s only through the isomer symmetry group F. Because the number of double cosets is the same for conjugate subgroups, the right-hand side of (18) really depends only on the set $\mathcal{F}^{(A)}$ to which F_s belongs. We therefore conclude the following: If the skeletal symmetry is lowered from A to D, an isomer whose symmetry group belongs to the conjugate set $\mathcal{F}$ will be split into a set of isomers whose number is given by

$$K(D,A,\mathcal{F}) = Z_{DF}^{(A)} \tag{19}$$

If we sum (19) over $\mathcal{F}$, the left-hand side sums to the total number

of isomers when the skeletal symmetry is D, while for each $\mathcal{F}^{(A)}$ there is a contribution to the right-hand side for every originally distinct isomer with symmetry in $\mathcal{F}^{(A)}$. We thus obtain the Brocas formula

$$Z_{DB}^{(S)} = \sum_{\mathcal{F}} Z_{DF}^{(A)} Z_{AB}^{(S)}(\mathcal{F}) \tag{20}$$

Our derivation is somewhat more direct and intuitive than that of Brocas,[7] who considers the splitting up of the S-double coset AsB into subdouble cosets $Da_j sB$, and shows (actually only states) that the number of these is the same as the number of A-double cosets of D and F_s. His derivation does not emphasize the interpretation of $K(D,A,\mathcal{F})$ as the number of isomers into which a given one is split by the lowered symmetry.

At first glance, (20) would appear to be an equation similar to (15), which can be solved for the isomer numbers $Z_{AB}^{(S)}(\mathcal{F})$. However, as Brocas[7] has pointed out, it is an immediate consequence of (7) that the number of independent equations produced by (20) cannot be greater than the number of classes of A, and this is often less than the number of possible symmetries, even if the phantom subgroups are eliminated. In practice, for any particular ligand partition, one can always eliminate at leaast one or two nonphantom subgroups by inspection at the start, and in all cases known to the author this additional information is sufficient to solve the problem. On the other hand, the same additional information is available to speed the solution of (15), so its presence is not a persuasive reason for preferring (20). In all cases studied by the author, (15) turns out to be the more convenient method, though both approaches are convenient enough to be useful.

In the author's view, the Brocas formula is less important as a method for solving the full isomer problem than as a convenient way of obtaining information on larger classes of isomers by considering only certain ones of the equations produced by (20).

Table of Marks and Double Cosets in Isomer Counting

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Table V. D_{5h} Double Coset Numbers for D_{5h} and Its Subgroups

	D_{5h}	D_5	C_{5v}	C_{5h}	C_5	C_{2v}	C_2	C_{sv}	C_{sh}	C_1
D_{5h}	1	1	1	1	1	1	1	1	1	1
D_5	1	2	1	1	2	1	2	1	1	2
C_{5v}	1	1	2	1	2	1	1	2	1	2
C_{5h}	1	1	1	2	2	1	1	1	2	2
C_5	1	2	2	2	4	1	2	2	2	4
C_{2v}	1	1	1	1	1	3	3	3	5	5
C_2	1	2	1	1	2	3	6	5	5	10
C_{sv}	1	1	2	1	2	3	5	6	5	10
C_{sh}	1	1	1	2	2	5	5	5	10	10
C_1	1	2	2	2	4	5	10	10	10	20

Table VI. S_{10} Double Coset Numbers of D_{5h} and Its Subgroups with Selected B Subgroups

	(10)	(82)	(73)	(64)	(62²)	(5²)	(532)	(4²2)	(43²)	(42³)	(3²2²)	(2⁵)
D_{5h}	1	5	8	16	74	16	132	174	216	978	1272	5736
D_5	1	7	12	26	136	26	252	330	420	1920	2520	11400
C_{5v}	1	7	16	26	136	32	264	330	432	1920	2544	11400
C_{5h}	1	5	12	22	128	26	252	318	420	1896	2520	11352
C_5	1	9	24	42	252	52	504	630	840	3780	5040	22680
C_{2v}	1	15	32	60	330	66	636	810	1056	4770	6312	28440
C_2	1	25	60	110	640	126	1260	1590	2100	9480	12600	56760
C_{sv}	1	25	64	110	640	132	1272	1590	2112	9480	12624	56760
C_{sh}	1	25	60	110	640	126	1260	1590	2100	9480	12600	56760
C_1	1	45	120	210	1260	252	2520	3150	4200	18900	25200	113400

In particular, consider the case where D is an *invariant* subgroup of A. In that case, it is easy to show from (6) that

$$Z_{DF}^{(A)} = \frac{|A||F \cap D|}{|D||F|} \tag{21}$$

Since $Z_{DF}^{(A)}$ is an integer, it is clear that the index $|F|/|F \cap D|$ must be a divisor of the index $|A|/|D|$. Now consider further the case where $|A|/|D|$ is a prime, q (in practice, nearly always $q = 2$). In that case, $|F|/|F \cap D|$ must be either unity or q, and it will be unity if and only if F is a subgroup of D. For this case, then, (20) becomes

$$Z_{DB}^{(S)} = q\xi(D) + \eta(D) \tag{22}$$

where $\xi(D)$ is the number of isomers whose symmetry group is a subgroup of D, and $\eta(D)$ is the number containing symmetry elements not belonging to D. Equation 22, together with

$$Z_{AB}^{(S)} = \xi(D) + \eta(D) \tag{23}$$

enables one to solve for $\xi(D)$ and $\eta(D)$. In ref 2, D was taken to be the subgroup of pure rotations, so that $\xi(D)$ is the number of enantiomeric pairs and $\eta(D)$ is the number of achiral isomers. This approach is now seen to be a special case of the Brocas formula. This is almost certainly the most important special case, but eq 22 and 23 can equally well be applied to other prime-index invariant subgroups to yield other information on classes of isomers.

B. Application to Pentaprismane. The double coset tables can be worked out straightforwardly with the help of (7) and are listed in Tables V and VI. Since D_{5h} has eight classes, one might hope that (20) would provide as many as eight independent equations, which is larger than the number of nonphantom subgroups. In fact, however, the rank of the matrix obtained from Table V is only six. This does not prevent the solution of the problem, however, as there is enough information available. Of the seven nonphantom subgroups, D_{5h} is a possibility only if all ligands are identical, and in this case it is the only possibility. For any particular ligand partition, therefore, there are really never more than six possibilities (in fact, it is alway easy to eliminate at least one of these), so one can reobtain Table IV from Tables V and VI with the aid of (20) and the additional information. It is also straightforward to check the correctness of Table IV by applying Table V to Table IV by matrix multiplication and verifying that one obtains Table VI. If one is only interested in solving for the isomer numbers, however, eq 15 is much more convenient than (20) for this system. In the first place, Tables I and II are much more easily obtained than Tables V and VI. Moreover, the

working out of Table III by inversion of Table I and subsequent working out of Table IV by matrix multiplication, even without use of additional information, is easier than the solution of (20) with the aid of additional information.

On the other hand, use of eq 22 and 23 yields interesting information in this case. Consider, for example, the ligand partition (532). If we take D to be D_5, we find $\xi = 120$, $\eta = 12$, meaning that there are 120 enantiomeric pairs and 12 achiral isomers. If the carbon atoms on one of the pentagonal faces are replaced by a different isotope, the symmetry is lowered to C_{5v}. Taking D = D_{5v} and using eq 22 and 23, we find that all 132 isomers for this ligand partition would be split into two by this symmetry lowering. Imposition of a preferred sense of rotation around a pentagonal face by means of a magnetic field along the axis of the prism lowers the symmetry to C_{5h}. In this case, we see from eq 22 and 23 that 120 of the isomers would split into pairs, with the remaining 12 remaining invariant. In this way, the Brocas formula proves its usefulness.

IV. Connection between Marks and Double Cosets

A. General Theory. The Hässelbarth formula (15) and the Brocas formula (20) are both equations involving the isomer numbers that one would like to calculate, and straightforwardly calculable properties of the symmetry and permutation groups. Since (15) contains more information than (20), it is clear that (15) is not derivable from (20). In this section, we show that (20) is derivable from (15), and in the process obtain a relation, new as far as we are aware, relating double coset numbers to marks.

We start by noting that the derivation of eq 16 was not in any way dependent on the assumption that the overall group was a permutation group. For any group A with subgroups D, F, H, G, the same derivation used to obtain (16) gives

$$Z_{DF}^{(A)}(\mathcal{G}) = \sum_{\mathcal{H}} M_{\mathcal{GH}}^{(D)} M_{\mathcal{HG}}^{(A)} \tag{24}$$

where $Z_{DF}^{(A)}(\mathcal{G})$ is the number of A-double cosets of D, F whose generators a satisfy $aFa^{-1} \cap D \in \mathcal{G}$.

Summing (24) over $\mathcal{G}$ gives the result

$$Z_{DF}^{(A)} = \sum_{\mathcal{GH}} M_{\mathcal{GH}}^{(D)} M_{\mathcal{HG}}^{(A)} \tag{25}$$

or

$$Z_{DF}^{(A)} = \sum_{\mathcal{H}} Q_{D\mathcal{H}} M_{\mathcal{HG}}^{(A)} \tag{26}$$

with

$$Q_{D\mathcal{H}} = \sum_{\mathcal{G}} M_{\mathcal{GH}}^{(D)} \tag{27}$$

Table VII. Q Matrix for D_{5h} and Subgroups

	D_{5h}	D_5	C_{5v}	C_{5h}	C_5	C_{2v}	C_2	C_{sv}	C_{sh}	C_1
D_{5h}	0	0	0	1/5	1/5	0	1/4	1/4	1/20	1/20
D_5	0	0	0	0	2/5	0	1/2	0	0	1/10
C_{5v}	0	0	0	0	2/5	0	0	1/2	0	1/10
C_{5h}	0	0	0	2/5	2/5	0	0	0	1/10	1/10
C_5	0	0	0	0	4/5	0	0	0	0	1/5
C_{2v}	0	0	0	0	0	0	1/4	1/4	1/4	1/4
C_2	0	0	0	0	0	0	1/2	0	0	1/2
C_{sv}	0	0	0	0	0	0	0	1/2	0	1/2
C_{sh}	0	0	0	0	0	0	0	0	1/2	1/2
C_1	0	0	0	0	0	0	0	0	0	1

Table VIII. Table of Marks for D_5 and C_{5v}

		D_5 C_{5v}	C_5 C_5	C_2 C_{sv}	C_1 C_1
D_5	C_{5v}	1	0	0	0
C_5	C_5	1	2	0	0
C_2	C_{sv}	1	0	1	0
C_1	C_1	1	2	5	10

Table IX. Inverse Marks of D_5 and C_{5v}

		D_5 C_{5v}	C_5 C_5	C_2 C_{sv}	C_1 C_1
D_5	C_{5v}	1	0	0	0
C_5	C_5	-1/2	1/2	0	0
C_2	C_{sv}	-1	0	1	0
C_1	C_1	1/2	-1/10	-1/2	1/10

Table X. Table of Marks of C_{5h}

	C_{5h}	C_5	C_{sh}	C_1
C_{5h}	1	0	0	0
C_5	1	2	0	0
C_{sh}	1	0	5	0
C_1	1	2	5	10

Table XI. Inverse Marks of C_{5h}

	C_{5h}	C_5	C_{sh}	C_1
C_{5h}	1	0	0	0
C_5	-1/2	1/2	0	0
C_{sh}	-1/5	0	1/5	0
C_1	1/10	-1/10	-1/10	1/10

Table XII. Table of Marks of C_5

	C_5	C_1
C_5	1	0
C_1	1	5

Table XIII. Inverse Marks of C_5

	C_5	C_1
C_5	1	0
C_1	-1/5	1/5

Table XIV. Table of Marks of C_{2v}

	C_{2v}	C_2	C_{sv}	C_{sh}	C_1
C_{2v}	1	0	0	0	0
C_2	1	2	0	0	0
C_{sv}	1	0	2	0	0
C_{sh}	1	0	0	2	0
C_1	1	2	2	2	4

Table XV. Inverse Marks of C_{2v}

	C_{2v}	C_2	C_{sv}	C_{sh}	C_1
C_{2v}	1	0	0	0	0
C_2	-1/2	1/2	0	0	0
C_{sv}	-1/2	0	1/2	0	0
C_{sh}	-1/2	0	0	1/2	0
C_1	1/2	-1/4	-1/4	-1/4	1/2

Table XVI. Table of Marks of C_2, C_{sv}, and C_{sh}

			C_2 C_{sv} C_{sh}	C_1 C_1 C_1
C_2	C_{sv}	C_{sh}	1	0
C_1	C_1	C_1	1	2

Table XVII. Inverse Marks of C_2, C_{sv}, and C_{sh}

			C_2 C_{sv} C_{sh}	C_1 C_1 C_1
C_2	C_{sv}	C_{sh}	1	0
C_1	C_1	C_1	-1/2	1/2

It is to be noted that $Q_{\mathcal{DH}} = 0$ unless H is a subgroup of D. More importantly, $Q_{\mathcal{DH}}$ depends only on the groups D and H, and *not* on the larger group A in which they are considered to be contained as subgroups. Thus, with *one* Q matrix, one obtains the number of A-double cosets from the A-marks, and the number of S-double cosets from the S-marks, etc.

If we want to obtain the Q matrix for some group A together with its subgroups, we proceed as follows: For each set of conjugate subgroups $\mathcal{D}^{(A)}$, we select one member D, calculate the table of D-marks, and form the inverse $\bar{M}^{(D)}$. The element $Q_{\mathcal{DH}} = 0$ unless some H in $\mathcal{H}$ is a subgroup of D, in which case $Q_{\mathcal{DH}}$ is just the sum of the elements in the $\mathcal{H}$-column of $\bar{M}^{(D)}$. Then, for *any* group S ≥ A, and *any* subgroup B of S (whether or not it is also a subgroup of A), we obtain the number of S-double cosets of D and B by applying the Q matrix just obtained to the S-marks of H in B arranged in a column, with $\mathcal{H}$ running over the subgroup sets of A (or just those of D if one is interested only in one subgroup of A).

In particular, if we apply the Q matrix of the molecular symmetry group A to both sides of (15), we immediately obtain (20), showing that, as claimed, (20) is a consequence of (15).

B. Application to Pentaprismane. The Q matrix for D_{5h} is easily constructed according to the procedure just described. It is given in Table VII. The first row of the Q matrix consists of the sums of the columns of Table II. For the other rows, we need the marks and inverse marks for the subgroups of D_{5h}, and these are given in Tables VIII–XVII. In the C_{2v} row of Table VII, for example,

the entries in the C_{2v}, C_2, C_{sv}, C_{sh}, and C_1 columns are obtained by summing the columns of Table XV, and the others are zero. One sees at a glance that the rank of Q is 6, since four of the columns are zero and the other six are clearly linearly independent.

It is easy to verify that matrix multiplication of Table I with Table VIII reproduces Table V, and that matrix multiplication of Table III with Table VIII reproduces Table VI. Indeed, this method is just as easy a way of obtaining these tables as direct calculation with eq 7, if not easier. Thus, the results of the previous subsection provide not only a proof that (20) is a consequence of (15) but also a practical alternative method for obtaining tables of double coset numbers.

V. Rank of Q Matrix and Double Coset Matrix

According to Table VII, four of the ten columns of the Q matrix for D_{5h} consist entirely of zeroes, while the others are all linearly

independent. The question naturally arises whether this is a mere artifact or an example of a general result. This question is of interest intrinsically, and also because the rank of the $\mathbf{Q}$ matrix for a group A (the number of its linearly independent columns) is equal to the rank of the double coset matrix, which in turn is equal to the number of independent equations furnished by the Brocas formula. Brocas[7] showed that this cannot be greater than the number of classes of A, but we have seen that it can be smaller. In this section, we obtain an answer to this question by a closer examination of the $\mathbf{Q}$ matrix. In the process, we also obtain an alternate expression for $\mathbf{Q}$-matrix elements.

Given a group D, with $N(D)$ sets of conjugate subgroups (including D itself and the subgroup consisting only of the identity), we have from the definition of the inverse matrix

$$\sum_{\mathcal{H}} \bar{M}^{(D)}_{\mathcal{G}\mathcal{H}} M^{(D)}_{\mathcal{H}\mathcal{J}} = \delta_{\mathcal{G}\mathcal{J}} \tag{28}$$

Summing (28) over $\mathcal{G}$, and remembering the definition (27) of the $\mathbf{Q}$ matrix, we find

$$\sum_{\mathcal{H}} Q_{\mathcal{D}\mathcal{H}} M^{(D)}_{\mathcal{H}\mathcal{J}} = 1 \tag{29}$$

For given D, there are $N(D)$ elements $Q_{\mathcal{D}\mathcal{H}}$ to be determined, and (29) gives exactly $N(D)$ independent equations, since we have already seen that the rank of the table of marks is $N(D)$. The elements of $\mathbf{Q}$ are thus completely determined by (29), and if we can find a solution to (29), that solution will be the unique $\mathbf{Q}$ matrix.

We now assert that

$$Q_{\mathcal{D}\mathcal{H}} = \frac{|\mathcal{H}^{(D)}||H^*|}{|D|} \tag{30}$$

where H* denotes the set of elements belonging to H, but not to any subgroup of H except H itself. To prove the assertion, we evaluate the left-hand side of (29) using (30) for the $\mathbf{Q}$-matrix elements. Denoting the left side of (29) by T, and inserting (30) and the definition of the mark (13), we find

$$T = \frac{1}{|F||\mathcal{F}^{(D)}|}\sum_{\mathcal{H}}|\mathcal{H}^{(D)}||H^*||\mathcal{F}^{(D)}_{(H)}| \tag{31}$$

The sum over $\mathcal{H}$ in (31), we recall, goes only over conjugate sets $\mathcal{H}$ which contain subgroups of F.

We now obtain an expression for $|\mathcal{F}^{(D)}_{(H)}|$ as follows: Let $\mathcal{H}^{(DF)}$ denote the set of members of $\mathcal{H}^{(D)}$ which are subgroups of a given F. (Note that, in general, $\mathcal{H}^{(DF)}$ may contain subgroups not in $\mathcal{H}^{(F)}$.) We now imagine that the conjugate set $\mathcal{F}^{(D)}$ is generated, and a list made of all the members of $\mathcal{H}^{(D)}$ that appear. The number of entries in the list is evidently $|\mathcal{F}^{(D)}||\mathcal{H}^{(DF)}|$. Each group in $\mathcal{H}^{(D)}$ appears the same number of times, and this number is be definition $|\mathcal{F}^{(D)}_{(H)}|$, so we have

$$|\mathcal{F}^{(D)}_{(H)}| = \frac{|\mathcal{F}^{(D)}||\mathcal{H}^{(DF)}|}{|\mathcal{H}^{(D)}|} \tag{32}$$

Inserting (32) into (31), we obtain

$$T = \frac{1}{|F|}\sum_{\mathcal{H}}|H^*||\mathcal{H}^{(DF)}| \tag{33}$$

A little reflection shows, however, that the right-hand side of (33) is just unity. The sum runs over all conjugate sets containing subgroups of F, with the contribution of each multiplied by the number of groups from the set which are subgroups of F. Each subgroup H of F thus contributes H* to the sum. We can imagine going through the subgroups H of F one by one (including C_1 and F itself, of course) and listing the members of H* for each H. Every element of F will eventually be listed, under F* if not elsewhere. But no elements will be listed more than once; for, if d is contained in both H and G, then it is also contained in the smaller subgroup H G, and hence is not a member of H* or G*. The sum in (33) is thus just F, and the right-hand side of (33) is unity, proving that the assertion (30) was correct.

For many groups H, however, H* is an empty set. If h is an element of H, then it is at least a member of one subgroup, namely the cyclic subgroup consisting of the powers of h. If this cyclic subgroup is not equal to H itself, then h is not in H*. Since this argument applies to all elements of H, it follows that H* is empty, and hence all $Q_{\mathcal{D}\mathcal{H}} = 0$, if H is not cyclic. If H is cyclic, however, H* is not empty, and indeed consists of the generators of H. For, if h is a generator of the cyclic group H, then any subgroup containing h must also contain all its powers and must thus be identical with H itself. We conclude, therefore, the following:

(i) The $\mathcal{H}$-column of a $\mathbf{Q}$ matrix will contain nonzero elements if and only if H is a cyclic group.

(ii) The $\mathbf{Q}$ matrix associated with a group D will have just zeroes in the columns corresponding to noncyclic subgroups. The columns corresponding to cyclic subgroups will have nonzero diagonal elements, and zeroes below the main diagonal if the arrangement of rows and columns is in descending order, the convention used in the present article.

(iii) It is an immediate consequence of (ii) that the rank of the $\mathbf{Q}$ matrix, and hence that of the double coset matrix, associated with a group A, is just the number of conjugate sets of *cyclic* subgroups of A. This can never be greater than the number of classes, as noted by Brocas[7], since the cyclic groups generated by elements of the same class are evidently conjugate. It can be smaller, however, since elements from two or more classes can serve as generators for the same cyclic subgroup. This actually happens with D_{5h}. The cyclic subgroup C_5 is generated by elements C_5 and C_5^2, and the cyclic subgroup C_{5h} is generated by S_5 and C_5S_5. The rank of the $\mathbf{Q}$ matrix is therefore just 6, although there are eight classes.

VI. Discussion

We have shown the connection between the various methods used in the isomer-counting problem by deriving both the Hässelbarth and Brocas formulas from a common starting point, the Ruch–Hässelbarth–Richter double coset counting method. By working out the application to pentaprismane, we have also illustrated the practical strengths and weaknesses of each method. For obtaining the complete list of isomer numbers, the Hässelbarth method seems to us clearly superior, from the practical point of view as well as the theoretical one. The table of marks and its inverse are easily obtained, the only disadvantage being perhaps that of unfamiliarity, a difficulty which is easily remedied because of the great simplicity of the concept. We have also shown that the Brocas formula is a consequence of the Hässelbarth formula, and in the process we have developed an alternate method for generating tables of double coset numbers.

Our results are at present still restricted to the case of structureless ligands, so we cannot lay claim to as high a degree of generality and elegance as that possessed by Hässelbarth's treatment.[5] Some of our results can probably be generalized, however, and we plan to investigate this.