were obtained for d^8 and solved. Determinants for the quartet d^7 states are obtained by reversing the signs of all diagonal elements in the triplet determinants. Energy-level diagrams for d^7 and d^8 with different Δ_1/Δ_2 values have been constructed using Δ_2/B as a variable and $C = 4B$. Diagrams of this type are shown in Figure 10. Calculations were also performed for the d^8 case with $0° \leqslant \theta \leqslant 60°$ using a constant α value of 77° inasmuch as the available structural data (Table I) do not indicate a large variation of this angle with ϕ. A procedure similar to that for the $\phi = 0°$ case was used with appropriate values of angular coordinates in eq 12–14. Calculations were carried out with $e_\sigma = 3B$–$6B$, $e_{\pi^s} = e_{\pi^c} = 0$, and with $e_\sigma = 4B$, $e_{\pi^s} = 0.2e_\sigma$, $e_{\pi^c} = 0$; in all cases $C = 4B$. One such energy-level diagram is given in Figure 11 and illustrates the usual order of triplet states for a given ϕ over the range of parameterization.

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Enumeration of Permutational Isomerization Reactions. II[1]

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Received April 13, 1972

In a previous paper, classes of symmetry equivalent permutational isomerization reactions were defined and exhaustively enumerated for symmetric molecules with identical substituents.[1] In the present paper this treatment is extended to molecules whose substituents are not necessarily identical. The generalized treatment is used to enumerate all distinct permutational isomerization reactions of molecules MH_nP_4, $n = 1, 2, 3$, or 4, where M is a transition metal, H is a hydride ligand, and P is a trisubstituted phosphorus ligand. The importance of these results for the interpretation of temperature-dependent nmr line-shape behavior is stressed.

I. Introduction

It will be assumed throughout this paper that the reader is familiar with the author's paper, "Enumeration of Permutational Isomerization Reactions"[1] (EPIR-I). In EPIR-I, classes of symmetry equivalent permutational isomerization reactions are defined, assuming that all ligands which are permuted are identical. All permutational isomers of a given molecule must have in common the same molecular skeleton. If all the ligands are not identical, then the permutation of two nonidentical ligands may lead to a change in molecular geometry and therefore a change in the molecular skeleton. Such a permutation would not define a permutational isomerization reaction. In the case of molecules of the type MH_nP_4 (see Figure 1), the P ligands and H ligands are clearly not identical and the methods of EPIR-I become chemically meaningless.

In the following section, the concepts defined in EPIR-I will be generalized to allow enumeration of the permutational isomerization reactions of molecules with sets of nonidentical ligands. These concepts will then be used to treat molecules of the type MH_nP_4.

II. Generalized Definitions

A. The Group of Allowed Permutations.—As in EPIR-I, permutational isomers[3] are defined as "chemical compounds which have in common the same molecular skeleton and set of ligands, differing only by the distribution of ligands on the skeletal positions." The set of indexed unidentate ligand labels $\mathbf{L}_l = \{l_1, l_2, \ldots, l_n\}$ and the set of indexed skeletal position labels $\chi_s = \{s_1, s_2, \ldots, s_n\}$ are combined to form a $2 \times n$ matrix $\binom{l}{s}$. Thus

$$\begin{pmatrix} l \\ s \end{pmatrix} = \begin{pmatrix} 12\ldots n \\ ij\ldots k \end{pmatrix}$$

lists the ligand indices in the top row and below each ligand index is placed the index of the skeletal position which that ligand occupies. A permutational isomerization reaction is described by a permutation p_i which acts on the indices of the skeletal positions. The set of all permutations which describe permutational isomerization reactions and/or point group operations forms a group called the *group of allowed permutations*.

In EPIR-I it is assumed that all n ligands are identical and therefore any one of the $n!$ permutations in the symmetric group S_n is an allowed permutation. If all n ligands are not identical, then some elements in S_n do not represent permutational isomerization reactions and the group of allowed permutations must be a subgroup of S_n. Consider, for example, the isomers shown in Figure 2. The permutation $p_i = (1)(2)(3)(4)(56)$ will convert isomer a into isomer b if skeletal positions are indexed as in Figure 1. Since a and b are permutational isomers, p_i represents a permutational isomerization reaction; *i.e.*, p_i is an allowed permutation. The permutation $q_i = (1)(25)(3)(4)(6)$ converts isomer a into isomer c. Since a and c are polytopal isomers[4] but not permutational isomers, q_i does not represent a permutational isomerization reaction; *i.e.*, q_i is not an allowed permutation. As defined above, permutational isomers must have in common the same molecular skeleton. Isomers a and c clearly do not: a has a C_{2v} molecular skeleton, while c has a D_{4h} molecular skeleton.

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(3) I. Ugi, D. Marquarding, H. Klusacek, G. Gokel, and P. Gillespie, *Angew. Chem.*, **82**, 741 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 703 (1970).

(4) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969).

These considerations show that the group of allowed permutations consists of those permutations which permute skeletal positions that are occupied by identical ligands. This subgroup of S_n may be defined precisely. If the molecule in question has m different types of ligands, χ_s is partitioned into m subsets such that the skeletal positions in each subset are occupied by identical ligands. For a molecule of type MH_2P_4 (see Figure 1) $m = 2$ and $\chi_s = \{s_1, s_2, s_3, s_4, s_5, s_6\}$. χ_s is partitioned into two subsets $\chi_s^P = \{s_1, s_2, s_3, s_4\}$ and $\chi_s^H = \{s_5, s_6\}$. Since an allowed permutation may permute any elements within χ_s^P and/or any elements within χ_s^H, there exist $4!\cdot 2!$ allowed permutations. This group of permutations is defined as $S_4 + S_2$, the direct sum[5] of the symmetric groups S_4 and S_2. In general, if a molecule has m different types of ligands and n_i ligands of type i, then the group of allowed permutations is $\Sigma_{i=1}^{m} S_{n_i}$, where the summation implies direct sums.

Distinguishable and differentiable permutational isomerization reactions are defined as in EPIR-I, keeping in mind that the group of allowed permutations is in general $\Sigma_{i=1}^{m} S_{n_i}$, not S_n. In the remainder of this section, formulas for counting these reactions will be provided. Lest he become suspicious of the purely mathematical nature of these definitions, the reader should keep in mind the usefulness of the definitions in solving chemical problems. As will be demonstrated in the following section, knowledge of the number of reactions differentiable in a totally symmetric environment is essential for the interpretation of temperature-dependent nmr spectra. Reactions which are formally nondifferentiable in a chiral environment must generate identical topological representations, as demonstrated elsewhere.[6] Sets of reactions distinguishable in a chiral or totally symmetric environment are physically meaningful only when a molecule is fixed in a symmetric environment, but these sets are in addition of help in generating sets of differentiable reactions. They are also helpful in relating isomerization mechanisms to isomerization reactions.

B. Enumeration Procedures.—Formulas for enumerating reactions may not be taken directly from EPIR-I because the problem of counting conjugacy classes or double cosets is more involved in $\Sigma_{i=1}^{m} S_{n_i}$ than in S_n. Before addressing this problem, the concept of cyclic index used in EPIR-I must be generalized. In order to minimize notational complexities, only the case of $m = 2$ is discussed here. Extension of all definitions and theorems to the case of an arbitrary m is evident and will be omitted.

If a permutation group H acts on the union of two disjoint sets χ_s^1 and χ_s^2 such that every $h_i \epsilon \mathrm{H}$ permutes only elements of χ_s^1 among themselves and elements of χ_s^2 among themselves, then the *generalized cyclic type* of $h_q \epsilon \mathrm{H}$ is defined by the array $(j_1, j_2, \ldots, j_{n_1};\ k_1, k_2, \ldots, k_{n_2})$, where the permutation h_q contains j_i cycles of length i which permute elements in χ_s^1 and k_l cycles of length l which permute elements in χ_s^2. For example, if S_3 acts on $\{1, 2, 3\}$, S_4 acts on $\{4, 5, 6, 7\}$ and $\mathrm{H} = S_3 + S_4$, then the generalized cyclic type of $h_q = (12)(3)(4)(567)$ is $(1, 1, 0;\ 1, 0, 1, 0)$.

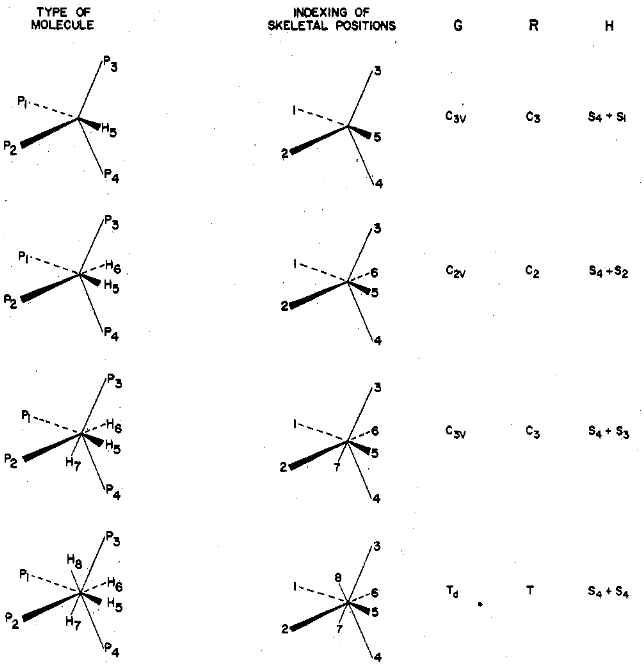

Figure 1.—Molecules of the type MH_nP_4, $n = 1, 2, 3$, and 4, where H is a hydride ligand, M is a transition metal, and P is a trisubstituted unidentate phosphorus ligand. G is the molecular point group, R is the group of proper rotation operations in G, and H is the group of allowed permutations.

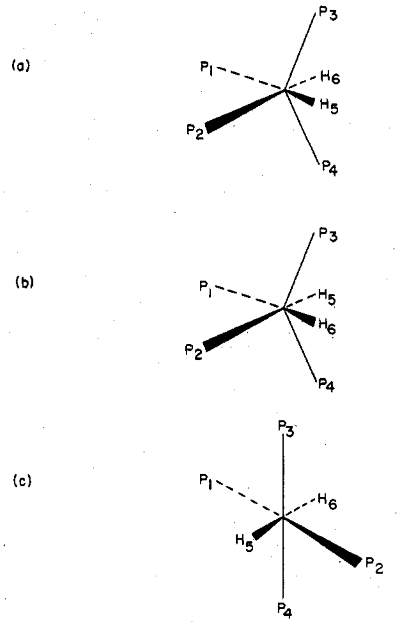

Figure 2.—Three isomers of the type MH_2P_4.

If two permutational isomerization reactions are formally indistinguishable in a chiral or totally symmetric environment, then they must be of identical generalized cyclic type. Accordingly, eq 1 defines the isomerization counting polynomial F_I which counts, with respect to generalized cyclic type, the number of distinguishable permutational isomerization reactions in a totally symmetric environment.

$$F_I(\mathrm{G};\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) \equiv \sum_{j_1, j_2, \ldots, j_{n_1};\ k_1, k_2, \ldots, k_{n_2}} A'_{j_1 j_2 \cdots j_{n_1}, k_1 k_2 \cdots k_{n_2}} \times a_1^{j_1} a_2^{j_2} \ldots a_{n_1}^{j_{n_1}} b_1^{k_1} b_2^{k_2} \ldots b_{n_2}^{k_{n_2}} \quad (1)$$

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[5] For a rigorous definition of this operation, see ref 1.

[6] W. G. Klemperer, *J. Amer. Chem. Soc.*, **94**, 6940 (1972).

Here, G is the permutation group generated by the molecular point group acting on the indices of the skeletal positions, n_1 and n_2 are the number of skeletal positions occupied by ligands of type 1 and type 2, respectively, and the summation extends over all generalized cyclic types found in $S_{n_1} + S_{n_2}$. Each coefficient $A'_{j_1j_2\cdots j_{n_1},k_1k_2\cdots k_{n_2}}$ is the number of distinguishable permutational isomerization reactions in a totally symmetric environment of generalized type $(j_1, j_2, \ldots, j_{n_1};\ k_1, k_2, \ldots, k_{n_2})$. The a_i's and b_i's are variables which allow identification of the coefficients. Note that if $n_1 = n$ and $n_2 = 0$, then eq 1 reduces to eq 3 in EPIR-I.

The isomerization counting polynomial F_I may be derived from a polynomial F which counts the number of conjugacy classes in the group of allowed permutations with respect to G. This polynomial, defined in eq 2, has the same general form as F_I. $A_{j_1j_2\cdots j_{n_1},k_1k_2\cdots k_{n_2}}$

$$F(\mathrm{G};\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) \equiv \sum_{j_1,j_2,\ldots,j_{n_1};\ k_1,k_2,\ldots,k_{n_2}} A_{j_1j_2\cdots j_{n_1},k_1k_2\cdots k_{n_2}} \times a_1^{j_1}a_2^{j_2}\cdots a_{n_1}^{j_{n_1}}b_1^{k_1}b_2^{k_2}\cdots b_{n_2}^{k_{n_2}} \qquad (2)$$

is the number of conjugacy classes of generalized cyclic type $(j_1, j_2, \ldots, j_{n_1};\ k_1, k_2, \ldots, k_{n_2})$ in $S_{n_1} + S_{n_2}$ with respect to G.

The polynomial Y, defined in eq 3, is needed to relate F_I and F. The general form of this polynomial

$$Y(\mathrm{G};\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) \equiv \sum_{j_1,j_2,\ldots,j_{n_1};\ k_1,k_2,\ldots,k_{n_2}} C_{j_1j_2\cdots j_{n_1},\ k_1k_2\cdots k_{n_2}} \times a_1^{j_1}a_2^{j_2}\cdots a_{n_1}^{j_{n_1}}b_1^{k_1}b_2^{k_2}\cdots b_{n_2}^{k_{n_2}} \qquad (3)$$

is similar to that of F and F_I. Here $C_{j_1j_2\cdots j_{n_1},k_1k_2\cdots k_{n_2}}$, however, is the number of conjugacy classes of generalized cyclic type $(j_1, j_2, \ldots, j_{n_1}; k_1, k_2, \ldots, k_{n_2})$ in G containing permutations generated by proper rotations.

The relationship among the polynomials F_I, F, and Y is given in eq 4. Equation A3, given in the Appendix,

$$F_I(\mathrm{G};\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) = F(\mathrm{G};\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) - Y(\mathrm{G};\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) \qquad (4)$$

is used to calculate $F(\mathrm{G};\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2})$. $Y(\mathrm{G};\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2})$ may be calculated using information found in standard group character tables.

If instead of a totally symmetric environment we consider permutational isomerization reactions distinguishable in a chiral environment, eq 4 changes only insofar as G is replaced by R, where R is the permutation group consisting of all operations in G which are generated by proper rotations. Equation 5 allows calculation of the appropriate counting polynomial for reactions distinguishable in a chiral environment.

$$F_I(\mathrm{R};\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) = F(\mathrm{R};\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) - Y(\mathrm{R};\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) \qquad (5)$$

We now turn our attention from permutational isomerization reactions that are distinguishable to those that are formally differentiable. As in EPIR-I the number of permutational isomerization reactions differentiable in a chiral environment is designated D'_R. If D_R is the number of double cosets generated by R in $S_{n_1} + S_{n_2}$, then $D'_\mathrm{R} = D_\mathrm{R} - 1$. Equation A8 is used to calculate D_R. In a totally symmetric environment, D'_G is the number of formally differentiable reactions. D_G is the number of double cosets generated by G in $S_{n_1} + S_{n_2}$. If G contains improper rotations, then $D'_\mathrm{G} = D_\mathrm{G}$. If G contains no improper rotations, then $D'_\mathrm{G} = D_\mathrm{G} - 1$. D_G may be calculated using eq A8.

III. Examples

The definitions given above and the theorems given in the Appendix will now be used to treat nonrigid molecules of the type MH_nP_4 shown in Figure 1. Certain molecules of this type may undergo permutational isomerization *via* intermediate polytopal configurations having connectivities[4] greater than two. In this case a "linear combination"[7] of certain formally differentiable permutational isomerization reactions may be needed to characterize the rearrangement. In this section, only those mechanisms will be considered which involve intermediate configurations having connectivities equal to two. Thus only one permutational isomerization reaction will be needed to characterize the rearrangement.

Of particular interest here is the number of differentiable permutational isomerization reactions in a totally symmetric environment. For molecules of the type MH_2P_4, Meakin, *et al.*,[7] have defined "equivalent basic sets" of permutations which consist of permutations that are indistinguishable by temperature-dependent nmr line-shape analysis. Generalizing their arguments, permutational isomerization reactions nondifferentiable in a totally symmetric environment will yield identical temperature-dependent line shapes. By "identical" we mean of course identical to the order of approximation implied by the "jump model" used to simulate nmr spectra of nonrigid systems. Therefore the number of permutational isomerization reactions differentiable in a totally symmetric environment is the maximum number of permutational isomerization reactions which will lead to different temperature-dependent nmr line shapes.

As was stressed in EPIR-I, assignment of a rearrangement reaction to a system of isomers does not specify a rearrangement mechanism, although it does exclude certain mechanisms. However, if specific assumptions are made concerning the possible rearrangement mechanisms, it may be possible to place the postulated mechanisms in a one-to-one correspondence with permutational isomerization reactions differentiable in a totally symmetric environment. The experimental temperature-dependent nmr line-shape behavior can then be compared to the simulated nmr spectra generated by the various differentiable reactions, and a mechanism may be assigned to the rearrangement. The validity of such an assignment depends on the validity of the preliminary assumptions concerning the mechanism, while the feasibility of such an assignment of course depends on the complete resolution of experimental spectra and the correct

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(7) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971).

assignment of chemical shifts and coupling constants to the pertinent nuclei.

In the examples given below, results will be interpreted assuming a mechanism where the approximately tetrahedral framework formed by the phosphorus ligands may be distorted (or rotated) but not inverted during the course of the rearrangement reaction, while the hydride ligands may move from one face of the distorted tetrahedron to another. Such a mechanism, first proposed by Meakin, *et al.*,[7] is called a "tetrahedral tunneling" mechanism. It may be expected to occur for molecules MH_nP_4 when M is small and P ligands are bulky. In these cases the four P ligands should closely approximate a tetrahedron.

All of the results given below could presumably be obtained by computer analysis,[7] but the present treatment provides a more inexpensive and convenient alternative.

A. MHP_4 Molecules.—$MH(PF_3)_4$, M = Co, Rh, Ir, are molecules of this type[8] (see Figure 1). Their structure can be described either as a distorted trigonal bipyramid with the H ligand occupying an axial position or a distorted tetrahedron formed by the P ligands with an H ligand occupying a tetrahedral face.[10] In either case, the point group of the skeletal framework is C_{3v}. The group of allowed permutations is $S_4 + S_1$. The order of this group is only $4! \cdot 1! = 24$ and the distinguishable and differentiable permutational isomerization reactions may be obtained by inspection. The combinatorial formulas given in the Appendix will be employed, however, to illustrate the meaning and use of these formulas.

First, the distinguishable permutational isomerization reactions in a chiral environment are enumerated using eq 6, which is obtained by letting $R = C_3$ in eq 5.

$$F_I(C_3;\ a_1, a_2, a_3, a_4;\ b_1) = F(C_3;\ a_1, a_2, a_3, a_4;\ b_1) - Y(C_3;\ a_1, a_2, a_3, a_4;\ b_1) \quad (6)$$

$F(C_3;\ a_1, a_2, a_3, a_4;\ b_1)$ is calculated using eq A3, letting $W = C_3$, $n_1 = 4$ and $n_2 = 1$. Consulting Table I, $|C_3| = 3$. The first summation, $\Sigma_{r_i \epsilon C_3}$, extends over the three operations (1)(2)(3)(4)(5), (1)(234)(5), and (1)(243)(5). Each term in the summation is dependent only on the generalized cyclic type of r_i. Thus the terms corresponding to the last two operations will be identical.

For the first term the generalized cyclic type $(d_1, d_2, d_3, d_4;\ e_1)$ of r_i = (1)(2)(3)(4)(5) is (4, 0, 0, 0; 1). This term is the product of two quantities: the first is determined by d_1, d_2, d_3, d_4; the second is determined by e_1. The calculation of each quantity follows the procedure used in EPIR-I. The first quantity is

$$4!1^4\left\{\sum_{(p)} \prod_{m=1}^{4} \left[(m^{p_m} \cdot p_m!)^{-1} \cdot \left(1^{-1}\sum_{q|1}\phi(q) a_{mq}{}^{1/q}\right)^{p_m}\right]\right\} = 4!1^4\{[(1^4 \cdot 4!)^{-1}(a_1{}^1)^4] + [(1^2 \cdot 2!)^{-1}(a_1{}^1)^2] \times [(2^1 \cdot 1!)^{-1}(a_2{}^1)^1] + [(1^1 \cdot 1!)^{-1}(a_1{}^1)^1][(3^1 \cdot 1)^{-1}(a_3{}^1)^1] + [(2^2 \cdot 2!)^{-1}(a_2{}^1)^2] + [(4^1 \cdot 1!)^{-1}(a_4{}^1)^1]\} = a_1{}^4 + 6a_1{}^2a_2{}^1 + 8a_1{}^1a_3{}^1 + 3a_2{}^2 + 6a_4{}^1 \quad (7)$$

Here, the sum over the partitions (p_1, p_2, p_3, p_4) of $d_l = 4$ is taken in the order (4, 0, 0, 0), (2, 1, 0, 0), (1, 0, 1, 0), (0, 2, 0, 0), (0, 0, 0, 1). The second quantity is given by eq 8.

$$1!1^1\left\{\sum_{(t)} \prod_{m=1}^{1} [(m^{t_m} \cdot t_m!)^{-1} \cdot \left(1^{-1}\sum_{r|1}\phi(r) b_{mr}{}^{1/r}\right)^{t_m} = b_1{}^1 \right. \quad (8)$$

For the second term, the generalized cyclic type $(d_1, d_2, d_3, d_4;\ e_1)$ of r_i = (1)(234)(5) is (1, 0, 1, 0; 1). As above, this term is the product of two quantities: the first is determined by d_1, d_2, d_3, d_4; the second is determined by e_1. Since $e_1 = 1$ as before, the second quantity is given by eq 8. The first quantity is given by eq 9.

$$\prod_{l=1}^{4} d_l!l^{d_l} \sum_{(p)} \prod_{m=1}^{d_l} [m^{p_m} \cdot p_m!]^{-1} \cdot \left[l^{-1}\sum_{q|l}\phi(q) a_{mq}{}^{l/q}\right]^{p_m} = \{a_1{}^1\}\left\{1!3^1\left[(1^1 \cdot 1!)^{-1}\left(3^{-1}\sum_{q|3}\phi(q) a_q{}^{3/q}\right)^1\right]\right\} = \{a_1{}^1\}\{[a_1{}^3 + 2a_3{}^1]\} = a_1{}^4 + 2a_1{}^1a_3{}^1 \quad (9)$$

All of this information is combined in eq 10. The

$$F(C_3;\ a_1, a_2, a_3, a_4;\ b_1) = {}^1/_3\{[a_1{}^4 + 6a_1{}^2a_2{}^1 + 8a_1{}^1a_3{}^1 + 3a_2{}^2 + 6a_4{}^1][b_1{}^1] + 2[a_1{}^4 + 2a_1{}^1a_3{}^1][b_1{}^1]\} = a_1{}^4b_1{}^1 + 2a_1{}^2a_2{}^1b_1{}^1 + 4a_1{}^1a_3{}^1b_1{}^1 + a_2{}^2b_1{}^1 + 2a_4{}^1b_1{}^1 \quad (10)$$

result may be checked by calculating $F(C_3;\ 1, 1, 1, 1;\ 1)$ using eq A7 and comparing this number with the sum (here, 10) of the coefficients in eq 10.

Next, we calculate the second term on the right side of eq 6 using information given in Table I.

TABLE I

CONJUGACY CLASSES OF THE PERMUTATION GROUP GENERATED WHEN THE POINT GROUP C_3 OPERATES ON THE SKELETAL POSITIONS OF A MOLECULE MHP_4[a]

Point group operation	Induced permutation	Generalized cyclic type
E	(1)(2)(3)(4)(5)	(4, 0, 0, 0; 1)
C_3	(1)(234)(5)	(1, 0, 1, 0; 1)
C_3^{-1}	(1)(243)(5)	(1, 0, 1, 0; 1)

[a] Skeletal positions are indexed as in Figure 1.

$$Y(C_3;\ a_1, a_2, a_3, a_4;\ b_1) = a_1{}^4b_1{}^1 + 2a_1{}^1a_3{}^1b_1{}^1 \quad (11)$$

Substituting eq 10 and 11 into eq 6, we obtain the isomerization counting polynomial for permutational isomerization reactions distinguishable in a chiral environment.

$$F_I(C_3;\ a_1, a_2, a_3, a_4;\ b_1) = 2a_1{}^2a_2{}^1b_1{}^1 + 2a_1{}^1a_3{}^1b_1{}^1 + a_2{}^2b_1{}^1 + 2a_4{}^1b_1{}^1 \quad (12)$$

The corresponding polynomial for reactions distinguishable in a totally symmetric environment, given in eq 13, may be generated in a similar fashion.

$$F_I(C_{3v};\ a_1, a_2, a_3, a_4;\ b_1) = 2a_1{}^2a_2{}^1b_1{}^1 + a_1{}^1a_3{}^1b_1{}^1 + a_2{}^2b_1{}^1 + a_4{}^1b_1{}^1 \quad (13)$$

With eq 12 and 13 in hand, complete sets of permutational isomerization reactions distinguishable in a chiral and in a totally symmetric environment are easily generated. These sets are given in the first two columns of Table II.

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(8) P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 1797 (1971). For studies on other molecules of this type, see ref 9.

(9) J. P. Jesson in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, pp 173–178, and references therein.

(10) B. A Frenz and J. A. Ibers, *Inorg. Chem.*, **9**, 2403 (1970). For the structure of $RhH[P(C_6H_5)_3]_4$ see R. W. Baker and P. Pauling, *Chem. Commun.*, 1495 (1969).

TABLE II
DISTINGUISHABLE AND DIFFERENTIAL PERMUTATIONAL ISOMERIZATION REACTIONS OF MOLECULES MHP_4[a]

Distinguishable in a chiral environment	Distinguishable in a totally symmetric environment	Differentiable in a chiral environment	Differentiable in a totally symmetric environment
(1)(23)(4)(5)	(1)(23)(4)(5)	(1)(23)(4)(5)	(1)(23)(4)(5)
(123)(4)(5) (132)(4)(5) (13)(24)(5)	(123)(4)(5) (13)(24)(5)	(123)(4)(5)	(123)(4)(5)
(13)(2)(4)(5) (1243)(5) (1342)(5)	(13)(2)(4)(5) (1243)(5)	(13)(2)(4)(5)	

[a] Skeletal positions are indexed as in Figure 1. In each column, a double line separates sets of reactions nondifferentiable in a totally symmetric environment. A single line then divides one of these sets into subsets of reactions nondifferentiable in a chiral environment.

Using eq A8, the numbers of differentiable permutational isomerization reactions in a chiral environment and in a totally symmetric environment are calculated as $D'_{C_3} = 3$ and $D'_{C_{3v}} = 2$, respectively. In a totally symmetric or in a chiral environment, if two reactions are indistinguishable, then they are also nondifferentiable. By partitioning a complete set of distinguishable reactions into subsets of nondifferentiable reactions, a complete set of differentiable reactions can be obtained (see Table II). In a totally symmetric environment, the distinguishable reactions p_i and p_j are nondifferentiable if p_i and $g_k \cdot p_j$, $g_k \epsilon G$, are indistinguishable. In a chiral environment, the distinguishable reactions p_i and p_j are nondifferentiable if p_i and $r_k \cdot p_j$, $r_k \epsilon R$, are indistinguishable.

A set of two reactions differentiable in a totally symmetric environment is shown in Figure 3. Since (1)(23)(4)(5) is generated by a point group operation in C_{3v}, this reaction cannot be detected by the nmr technique. Because $D'_{C_{3v}} = 2$, all permutational isomerization reactions not generated by point group operations will lead to identical temperature-dependent nmr line-shape simulations using the "jump model." Thus virtually no mechanistic information may be inferred from temperature-dependent nmr line-shape analysis.

The permutational isomerization reaction (123)(4)(5) drawn in Figure 3 is implied by the "tetrahedral tunneling" mechanism: in the reactant isomer, the hydride ligand occupies the $P_3P_2P_4$ face (trans to P_1) and in the product the hydride ligand occupies the $P_1P_2P_4$ face (trans to P_3). Thus the "tetrahedral tunneling" mechanism will lead to temperature-dependent nmr line-shape behavior.

Following the procedure used in this example, additional formulas and tables may be derived for the remaining examples B through D.

B. MH_2P_4 Molecules.—$FeH_2[P(OC_2H_5)_3]_4$[7,11] is one of many known molecules of this type having the cis configuration shown in Figure 1. This geometrical configuration can be described as either a distorted octahedron with cis H ligands or a distorted tetrahedron formed by P ligands with both H ligands occupying tetrahedral faces.[12] In either case, the point group symmetry of the skeletal framework is C_{2v}.

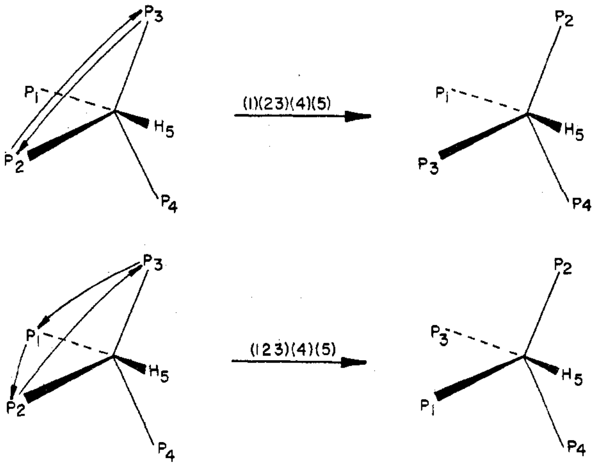

Figure 3.—Two permutational isomerization reactions of molecules MH_2P_4 differentiable in a totally symmetric environment. Skeletal positions are indexed as in Figure 1.

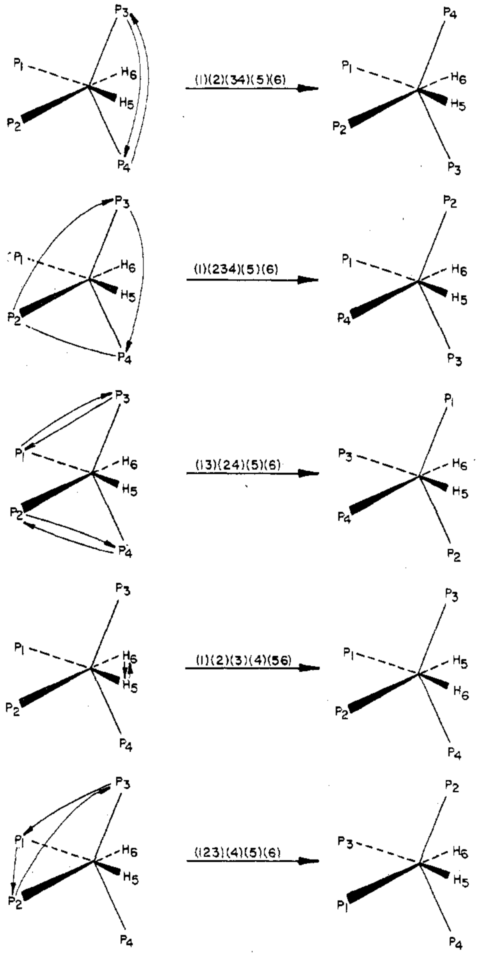

Figure 4.—Five permutational isomerization reactions of molecules MH_2P_4 differentiable in a totally symmetric environment. Skeletal positions are indexed as in Figure 1.

Isomerization counting polynomials are given in eq 14 and 15. Also, $D'_{C_2} = 15$ and $D'_{C_{2v}} = 5$. Sets

$$F_I(C_2;\ a_1, a_2, a_3, a_4;\ b_1, b_2) = 4a_1{}^2a_2{}^1b_1{}^2 + 4a_1{}^1a_3{}^1b_1{}^2 + 3a_2{}^2b_1{}^2 + 4a_4{}^1b_1{}^2 + a_1{}^4b_2{}^1 + 4a_1{}^2a_2{}^1b_2{}^1 + 4a_1{}^1a_3{}^1b_2{}^1 + 2a_2{}^2b_2{}^1 + 4a_4{}^1b_2{}^1 \quad (14)$$

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[11] For related molecules, see ref 9, pp 118–119, 180–189, and references therein.

[12] L. J. Guggenberger, D. D. Titus, M. T. Flood, R. E. Marsh, A. A. Orio, and H. B. Gray, *J. Amer. Chem. Soc.*, **94**, 1135 (1972).

TABLE III

DISTINGUISHABLE AND DIFFERENTIABLE PERMUTATIONAL ISOMERIZATION REACTIONS OF MOLECULES MH_2P_4[a]

Distinguishable in a chiral environment	Distinguishable in a totally symmetric environment	Differentiable in a chiral environment	Differentiable in a totally symmetric environment
(1)(2)(34)(5)(6) (12)(3)(4)(56)	(1)(2)(34)(5)(6) (12)(3)(4)(56)	(1)(2)(34)(5)(6)	(1)(2)(34)(5)(6)
(1)(234)(5)(6) (132)(4)(56)	(1)(234)(5)(6) (132)(4)(56)	(1)(234)(5)(6)	(1)(234)(5)(6)
(1)(243)(5)(6) (123)(4)(56)		(1)(243)(5)(6)	
(13)(2)(4)(5)(6) (1234)(56)	(13)(2)(4)(5)(6) (1234)(56)	(13)(2)(4)(5)(6)	
(1)(23)(4)(5)(6) (1342)(56)		(1)(23)(4)(5)(6)	
(13)(24)(5)(6) (14)(23)(56)	(13)(24)(5)(6) (14)(23)(56)	(13)(24)(5)(6)	(13)(24)(5)(6)
(14)(23)(5)(6) (13)(24)(56)		(14)(23)(5)(6)	
(1423)(5)(6) (1324)(56)	(1423)(5)(6) (1324)(56)	(1423)(5)(6)	
(1324)(5)(6) (1423)(56)		(1324)(5)(6)	
(1)(2)(3)(4)(56) (12)(34)(5)(6)	(1)(2)(3)(4)(56) (12)(34)(5)(6)	(1)(2)(3)(4)(56)	(1)(2)(3)(4)(56)
(12)(3)(4)(5)(6) (1)(2)(34)(56)	(12)(3)(4)(5)(6) (1)(2)(34)(56)	(12)(3)(4)(5)(6)	
(123)(4)(5)(6) (1)(243)(56)	(123)(4)(5)(6) (1)(243)(56)	(123)(4)(5)(6)	(123)(4)(5)(6)
(132)(4)(5)(6) (1)(234)(56)		(132)(4)(5)(6)	
(1342)(5)(6) (1)(23)(4)(56)	(1342)(5)(6) (1)(23)(4)(56)	(1342)(5)(6)	
(1234)(5)(6) (13)(2)(4)(56)		(1234)(5)(6)	

[a] Skeletal positions are indexed as in Figure 1. In each column, double lines separate sets of reactions nondifferentiable in a totally symmetric environment. Single lines then divide these sets into subsets of reactions nondifferentiable in a chiral environment.

$$F_I(C_{2v};\ a_1, a_2, a_3, a_4;\ b_1, b_2) = 3a_1{}^2a_2{}^1b_1{}^2 + 2a_1{}^1a_3{}^1b_1{}^2 + 2a_2{}^2b_1{}^2 + 2a_4{}^1b_1{}^2 + a_1{}^4b_2{}^1 + 3a_1{}^2a_2{}^1b_2{}^1 + 2a_1{}^1a_3{}^1b_2{}^1 + a_2{}^2b_2{}^1 + 2a_4{}^1b_2{}^1 \quad (15)$$

of distinguishable and differentiable reactions are given in Table III. Figure 4 shows five permutational isomerization reactions differentiable in a totally symmetric environment.

Assuming "tetrahedral tunneling," there exist four possible mechanistic types: (a) one hydride ligand moves to an unoccupied face and the other hydride ligand remains fixed, (b) both hydride ligands move to unoccupied faces, (c) the two hydride ligands are exchanged, and (d) one hydride ligand moves to an unoccupied face while the other hydride ligand moves to the face previously occupied by the first hydride ligand. Consulting Figure 4, we see that mechanism a implies reaction (1)(234)(5)(6), b implies (13)(24)(5)(6), c implies (1)(2)(3)(4)(56), and d implies (123)(4)(5)(6). Therefore, these four mechanisms will in theory be detectable and differentiable by temperature-dependent nmr studies.

C. MH_3P_4 Molecules.—As shown in Figure 1, the geometric configuration of these molecules may be described as a distorted tetrahedron of P ligands with H ligands occupying three faces. The compound $ReH_3[P(C_6H_5)_3]_4$ has been characterized,[13] but detailed structural work has not been reported. Since the rhenium atom is quite large, one would not necessarily expect the structure to conform to the idealized structure just mentioned. An analogous molecule with a first-row central metal atom would probably be amenable to the present treatment.

Isomerization counting polynomials are given in eq 16 and 17. Also, $D'_{C_3} = 19$ and $D'_{C_{3v}} = 7$. Sets

$$F_I(C_3;\ a_1, a_2, a_3, a_4;\ b_1, b_2, b_3) = 2a_1{}^2a_2{}^1b_1{}^3 + a_2{}^2b_1{}^3 + 4a_1{}^1a_3{}^1b_1{}^3 + 2a_4{}^1b_1{}^3 + a_1{}^4b_1{}^1b_2{}^1 + 6a_1{}^2a_2{}^1b_1{}^1b_2{}^1 + 3a_2{}^2b_1{}^1b_2{}^1 + 8a_1{}^1a_3{}^1b_1{}^1b_2{}^1 + 6a_4{}^1b_1{}^1b_2{}^1 + 2a_1{}^4b_3{}^1 + 4a_1{}^2a_2{}^1b_3{}^1 + 2a_2{}^2b_3{}^1 + 6a_1{}^1a_3{}^1b_3{}^1 + 4a_4{}^1b_3{}^1 \quad (16)$$

$$F_I(C_{3v};\ a_1, a_2, a_3, a_4;\ b_1, b_2, b_3) = 2a_1{}^2a_2{}^1b_1{}^3 + a_2{}^2b_1{}^3 + 2a_1{}^1a_3{}^1b_1{}^3 + a_4{}^1b_1{}^3 + a_1{}^4b_1{}^1b_2{}^1 + 4a_1{}^2a_2{}^1b_1{}^1b_2{}^1 + 2a_2{}^2b_1{}^1b_2{}^1 + 4a_1{}^1a_3{}^1b_1{}^1b_2{}^1 + 3a_4{}^1b_1{}^1b_2{}^1 + a_1{}^4b_3{}^1 + 2a_1{}^2a_2{}^1b_3{}^1 + a_2{}^2b_3{}^1 + 3a_1{}^1a_3{}^1b_3{}^1 + 2a_4{}^1b_3{}^1 \quad (17)$$

of distinguishable and differentiable reactions are given in Table IV. Figure 5 shows seven permutational isomerization reactions differentiable in a totally symmetric environment.

"Tetrahedral tunneling" of hydride ligands leads to six different mechanistic types: (a) one hydride ligand moves to the unoccupied face, the other two remaining fixed, (b) one hydride ligand moves to the unoccupied face, a second hydride ligand moves to the previously occupied face, and the third hydride ligand remains

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[13] L. Malatesta, M. Freni, and V. Valenti, *Angew. Chem.*, **73**, 273 (1961).

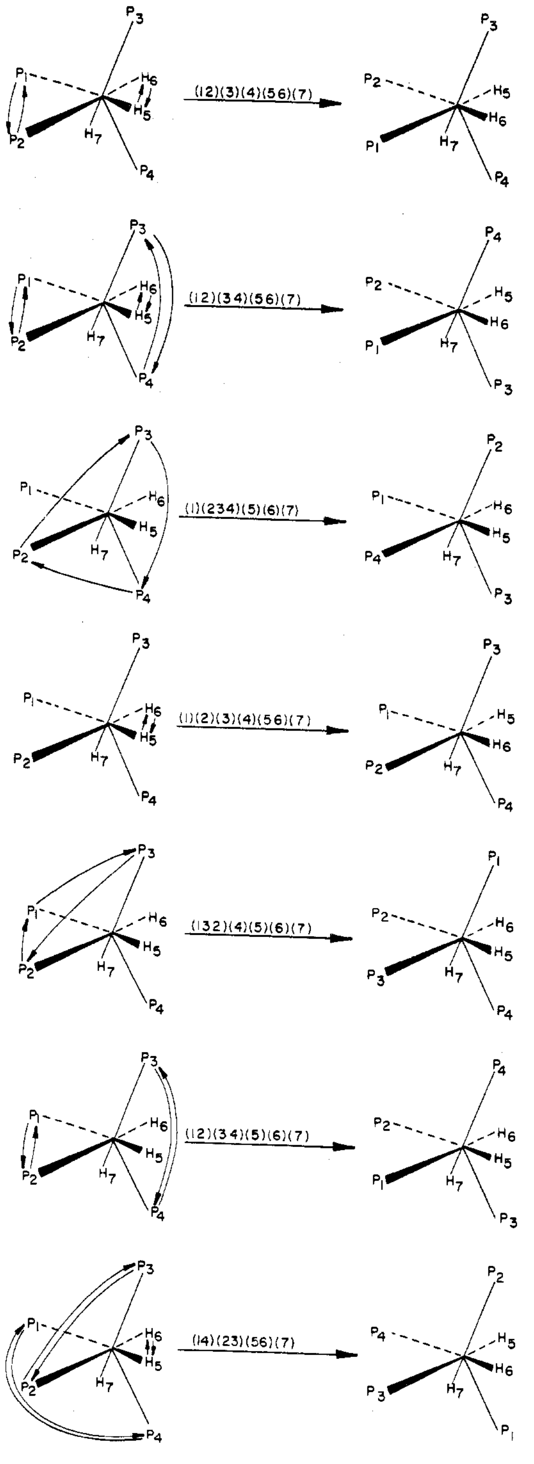

Figure 5.—Seven permutational isomerization reactions of molecules MH_3P_4 differentiable in a totally symmetric environment. Skeletal positions are indexed as in Figure 1.

fixed, (c) one hydride ligand remains fixed and the other two are permuted, (d) all three hydride ligands are cyclically permuted, (e) one hydride ligand moves to the unoccupied face and the other two hydride ligands are permuted, and (f) one hydride ligand moves to the unoccupied face, a second hydride ligand moves to the face previously occupied by the first hydride ligand, and the third hydride ligand moves to the face previously occupied by the second hydride ligand. These mechanisms are easily related to permutational isomerization reactions by identifying each "tetrahedral" face with the phosphorus ligand trans to that face. For example, see (12)(34)(56)(7) shown in Figure 5. In the reactant isomer, H_5 is on the face trans to P_1, H_6 is trans to P_2, and H_7 is trans to P_3; in the product isomer, H_5 is trans to P_1, H_6 is trans to P_2 and H_7 is trans to P_4. Therefore, H_5 and H_6 remain fixed while H_7 has moved to the previously unoccupied face. Of course the tetrahedron of phosphorus atoms has not been inverted. Inspecting the remaining reactions in Figure 5, we see that mechanism a implies reaction (12)(34)(56)(7), b implies (1)(234)(5)(6)(7), c implies (1)(2)(3)(4)(56)(7), d implies (132)(4)(5)(6)(7), e implies (12)(34)(5)(6)(7), and f implies (14)(23)(56)(7). Therefore all six mechanisms imply reactions which are theoretically detectable and differentiable by temperature-dependent nmr studies.

D. MH_4P_4.—Molecules of this type which have been studied using the variable-temperature nmr technique include $MoH_4[P(C_6H_5)_2CH_3]_4$,[14,15] $WH_4[P(C_6H_5)_2CH_3]_4$,[15] and $WH_4[P(C_6H_5)(CH_3)_2]_4$.[15] Available experimental data are consistent with the T_d symmetry of the idealized structure given in Figure 1, where hydride ligands occupy the faces of a tetrahedron formed by phosphorus ligands. We shall assume this symmetry to be appropriate for some molecules of this type, in particular those with bulky phosphorus ligands and a small central metal atom.[14]

Isomerization counting polynomials are given in eq 18 and 19. Also, $D'_T = 11$ and $D'_{T_d} = 5$. Sets

$$\begin{aligned} F_I(T;\ a_1, a_2, a_3, a_4;\ b_1, b_2, b_3, b_4) ={}& a_1^4b_1^2b_2^1 + \\ & 2a_1^4b_1^1b_3^1 + a_1^4b_2^2 + a_1^4b_4^1 + a_1^2a_2^1b_1^4 + 4a_1^2a_2^1b_1^2b_2^1 + \\ & 4a_1^2a_2^1b_1^1b_3^1 + 3a_1^2a_2^1b_2^2 + 4a_1^2a_2^1b_4^1 + 2a_1^1a_3^1b_1^4 + \\ & 4a_1^1a_3^1b_1^2b_2^1 + 6a_1^1a_3^1b_1^1b_3^1 + 2a_1^1a_3^1b_2^2 + \\ & 4a_1^1a_3^1b_4^1 + a_2^2b_1^4 + 3a_2^2b_1^2b_2^1 + 2a_2^2b_1^1b_3^1 + \\ & 2a_2^2b_2^2 + 3a_2^2b_4^1 + a_4^1b_1^4 + 4a_4^1b_1^2b_2^1 + 4a_4^1b_1^1b_3^1 + \\ & 3a_4^1b_2^2 + 4a_4^1b_4^1 \end{aligned} \tag{18}$$

$$\begin{aligned} F_I(T_d;\ a_1, a_2, a_3, a_4;\ b_1, b_2, b_3, b_4) ={}& a_1^4b_1^2b_2^1 + \\ & a_1^4b_1^1b_3^1 + a_1^4b_2^2 + a_1^4b_4^1 + a_1^2a_2^1b_1^4 + 3a_1^2a_2^1b_1^2b_2^1 + \\ & 2a_1^2a_2^1b_1^1b_3^1 + 2a_1^2a_2^1b_2^2 + 2a_1^2a_2^1b_4^1 + a_1^1a_3^1b_1^4 + \\ & 2a_1^1a_3^1b_1^2b_2^1 + 3a_1^1a_3^1b_1^1b_3^1 + a_1^1a_3^1b_2^2 + 2a_1^1a_3^1b_4^1 + \\ & a_2^2b_1^4 + 2a_2^2b_1^2b_2^1 + a_2^2b_1^1b_3^1 + a_2^2b_2^2 + 2a_2^2b_4^1 + \\ & a_4^1b_1^4 + 2a_4^1b_1^2b_2^1 + 2a_4^1b_1^1b_3^1 + 2a_4^1b_2^2 + \\ & 3a_4^1b_4^1 \end{aligned} \tag{19}$$

of distinguishable and differentiable reactions are given in Table V. Figure 6 shows five permutational isomerization reactions differentiable in a totally symmetric environment.

Inspecting Figure 6, we notice that all the possible "tetrahedral tunneling" mechanisms imply permutational isomerization reactions differentiable in a totally symmetric environment; *i.e.*, all four mechanisms imply reactions which are in theory detectable and differentiable by temperature-dependent nmr studies.

Acknowledgments.—I am indebted to Dr. Bertram Frenz for helpful discussions concerning the structures of molecules treated in this paper.

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[14] J. P. Jesson, E. L. Muetterties, and P. Meakin, *J. Amer. Chem. Soc.* **93**, 5261 (1971).

[15] B. Bell, J. Chatt, G. J. Leigh, and T. Ito, *J. Chem. Soc., Chem. Commun.*, 34 (1972).

TABLE IV

DISTINGUISHABLE AND DIFFERENTIABLE PERMUTATIONAL ISOMERIZATION REACTIONS OF MOLECULES MH_3P_4[a]

Distinguishable in a chiral environment	Distinguishable in a totally symmetric environment	Differentiable in a chiral environment	Differentiable in a totally symmetric environment
(12)(3)(4)(56)(7)	(12)(3)(4)(56)(7)	(12)(3)(4)(56)(7)	(12)(3)(4)(56)(7)
(12)(34)(56)(7) (124)(3)(56)(7) (142)(3)(56)(7)	(12)(34)(56)(7) (124)(3)(56)(7)	(12)(34)(56)(7)	(12)(34)(56)(7)
(1)(2)(34)(5)(6)(7) (1342)(576) (1234)(567)	(1)(2)(34)(5)(6)(7) (1342)(576)	(1)(2)(34)(5)(6)(7)	
(1)(234)(5)(6)(7) (12)(34)(567) (1)(243)(576)	(1)(234)(5)(6)(7) (12)(34)(567) (1)(243)(576)	(1)(234)(5)(6)(7)	(1)(234)(5)(6)(7)
(1)(243)(5)(6)(7) (12)(34)(576) (143)(2)(567)		(1)(243)(5)(6)(7)	
(1)(24)(3)(56)(7) (1432)(56)(7) (1234)(56)(7)	(1)(24)(3)(56)(7) (1432)(56)(7) (1234)(56)(7)	(1)(24)(3)(56)(7)	
(14)(2)(3)(56)(7) (1243)(56)(7) (1342)(56)(7)		(14)(2)(3)(56)(7)	
(1)(2)(3)(4)(56)(7) (123)(4)(56)(7) (132)(4)(56)(7)	(1)(2)(3)(4)(56)(7) (123)(4)(56)(7)	(1)(2)(3)(4)(56)(7)	(1)(2)(3)(4)(56)(7)
(13)(2)(4)(5)(6)(7) (1)(23)(4)(576) (13)(2)(4)(567)	(13)(2)(4)(5)(6)(7) (1)(23)(4)(576)	(13)(2)(4)(5)(6)(7)	
(132)(4)(5)(6)(7) (1)(2)(3)(4)(567) (123)(4)(576)	(132)(4)(5)(6)(7) (1)(2)(3)(4)(567) (123)(4)(576)	(132)(4)(5)(6)(7)	(132)(4)(5)(6)(7)
(123)(4)(5)(6)(7) (1)(2)(3)(4)(576) (132)(4)(567)		(123)(4)(5)(6)(7)	
(13)(2)(4)(56)(7)	(13)(2)(4)(56)(7)	(13)(2)(4)(56)(7)	
(1)(23)(4)(56)(7)		(1)(23)(4)(56)(7)	
(12)(34)(5)(6)(7) (1)(234)(576) (134)(2)(567)	(12)(34)(5)(6)(7) (1)(234)(576)	(12)(34)(5)(6)(7)	(12)(34)(5)(6)(7)
(1)(2)(34)(56)(7) (1423)(56)(7) (1324)(56)(7)	(1)(2)(34)(56)(7) (1423)(56)(7)	(1)(2)(34)(56)(7)	
(14)(23)(56)(7) (1)(234)(56)(7) (1)(243)(56)(7)	(14)(23)(56)(7) (1)(234)(56)(7) (1)(243)(56)(7)	(14)(23)(56)(7)	(14)(23)(56)(7)
(13)(24)(56)(7) (134)(2)(56)(7) (143)(2)(56)(7)		(13)(24)(56)(7)	
(1342)(5)(6)(7) (1)(2)(34)(567) (1243)(576)	(1342)(5)(6)(7) (1)(2)(34)(567) (1243)(576)	(1342)(5)(6)(7)	
(1243)(5)(6)(7) (1)(2)(34)(576) (1432)(567)		(1243)(5)(6)(7)	

[a] Skeletal positions are indexed as in Figure 1. In each column, double lines separate sets of reactions nondifferentiable in a totally symmetric environment. Single lines then divide these sets into subsets of reactions nondifferentiable in a chiral environment.

Appendix

Two theorems are proved here. Theorem I provides a formula for calculating $F(W; a_1, a_2, \ldots, a_{n_1}; b_1, b_2, \ldots, b_{n_2})$ needed above in eq 4 and 5. Theorem II provides a formula for calculating D_W needed for the calculation of D'_R and D'_G. First, however, the definitions of cyclic type and cyclic index are generalized. Definitions of all other terms used below may be found in the Appendix of EPIR-I.

A. Definititions.—Let H be a permutation group degree m acting on the set B, $|B| = m$. Assume that B is the disjoint union of the two sets B_1 and B_2, $|B_1| = n_1$ and $|B_2| = n_2$. Assume further that every permutation $h_q \epsilon$H permutes only elements of B_1 among themselves and elements of B_2 among themsleves. Then the *generalized cyclic type* of $h_q \epsilon$H is defined by $(j_1, j_2, \ldots, j_{n_1}; k_1, k_2, \ldots, k_{n_2})$ where j_i is the number of disjoint cycles in h_q of length i which permute elements in B_1 and k_l is the number of disjoint cycles in h_q of length l which permute elements in B_2. The

TABLE V

DISTINGUISHABLE AND DIFFERENTIABLE PERMUTATIONAL ISOMERIZATION REACTIONS OF MOLECULES MH_4P_4[a]

Distinguishable in a chiral environment	Distinguishable in a totally symmetric environment	Differentiable in a chiral environment	Differentiable in a totally symmetric environment
(12)(3)(4)(56)(7)(8)	(12)(3)(4)(56)(7)(8)	(12)(3)(4)(56)(7)(8)	(12)(3)(4)(56)(7)(8)
(1243)(5687)	(1243)(5687)		
(1)(2)(3)(4)(56)(7)(8)	(1)(2)(3)(4)(56)(7)(8)	(1)(2)(3)(4)(56)(7)(8)	(1)(2)(3)(4)(56)(7)(8)
(12)(34)(5)(6)(78)	(12)(34)(5)(6)(78)		
(132)(4)(56)(7)(8)	(132)(4)(56)(7)(8)		
(123)(4)(56)(7)(8)			
(132)(4)(5768)	(132)(4)(5768)		
(123)(4)(5867)			
(12)(34)(5786)	(12)(34)(5786)		
(12)(34)(5678)			
(12)(3)(4)(5)(6)(7)(8)	(12)(3)(4)(5)(6)(7)(8)	(12)(3)(4)(5)(6)(7)(8)	
(12)(3)(4)(56)(78)	(12)(3)(4)(56)(78)		
(12)(3)(4)(586)(7)	(12)(3)(4)(586)(7)		
(12)(3)(4)(568)(7)			
(1243)(5)(687)	(1243)(5)(687)		
(1342)(576)(8)			
(1243)(57)(68)	(1243)(57)(68)		
(1432)(58)(67)			
(1)(2)(3)(4)(576)(8)	(1)(2)(3)(4)(576)(8)	(1)(2)(3)(4)(576)(8)	(1)(2)(3)(4)(576)(8)
(123)(4)(5)(6)(7)(8)	(123)(4)(5)(6)(7)(8)		
(132)(4)(567)(8)	(132)(4)(567)(8)		
(132)(4)(586)(7)	(132)(4)(586)(7)		
(123)(4)(58)(67)	(123)(4)(58)(67)		
(12)(34)(587)(6)	(12)(34)(587)(6)		
(1)(2)(3)(4)(567)(8)		(1)(2)(3)(4)(567)(8)	
(132)(4)(5)(6)(7)(8)			
(123)(4)(576)(8)			
(123)(4)(568)(7)			
(132)(4)(57)(68)			
(12)(34)(5)(687)			
(12)(3)(4)(5)(68)(7)	(12)(3)(4)(5)(68)(7)	(12)(3)(4)(5)(68)(7)	
(12)(3)(4)(5678)	(12)(3)(4)(5678)		
(1243)(56)(7)(8)	(1243)(56)(7)(8)		
(1432)(5786)	(1432)(5786)		
(12)(3)(4)(58)(6)(7)		(12)(3)(4)(58)(6)(7)	
(12)(3)(4)(5786)			
(1432)(56)(7)(8)			
(1243)(5678)			
(1)(2)(3)(4)(56)(78)	(1)(2)(3)(4)(56)(78)	(1)(2)(3)(4)(56)(78)	(1)(2)(3)(4)(56)(78)
(132)(4)(568)(7)	(132)(4)(568)(7)		
(123)(4)(586)(7)			
(12)(34)(5)(6)(7)(8)	(12)(34)(5)(6)(7)(8)		
(12)(34)(57)(68)	(12)(34)(57)(68)		
(12)(34)(58)(67)			
(12)(3)(4)(5)(6)(78)	(12)(3)(4)(5)(6)(78)	(12)(3)(4)(5)(6)(78)	
(12)(3)(4)(5867)	(12)(3)(4)(5867)		
(12)(3)(4)(5768)			
(1243)(58)(6)(7)	(1243)(58)(6)(7)		
(1342)(58)(6)(7)			
(1243)(5786)	(1243)(5786)		
(1)(2)(3)(4)(5786)	(1)(2)(3)(4)(5786)	(1)(2)(3)(4)(5786)	(1)(2)(3)(4)(5786)
(12)(34)(5768)	(12)(34)(5768)		
(132)(4)(5)(6)(78)	(132)(4)(5)(6)(78)		
(123)(4)(5)(6)(78)			
(132)(4)(5867)	(132)(4)(5867)		
(123)(4)(5768)			
(12)(34)(58)(6)(7)	(12)(34)(58)(6)(7)		
(12)(34)(5)(68)(7)			
(12)(3)(4)(587)(6)	(12)(3)(4)(587)(6)	(12)(3)(4)(587)(6)	
(12)(3)(4)(578)(6)			
(12)(3)(4)(57)(68)	(12)(3)(4)(57)(68)		
(12)(3)(4)(58)(67)			
(1243)(5)(678)	(1243)(5)(678)		
(1342)(567)(8)			
(1243)(5)(6)(7)(8)	(1243)(5)(6)(7)(8)		
(1423)(56)(78)	(1423)(56)(78)		

[a] Skeletal positions are indexed as in Figure 1. In each column, double lines separate sets of reactions nondifferentiable in a totally symmetric environment. Single lines then divide these sets into subsets of reactions nondifferentiable in a chiral environment.

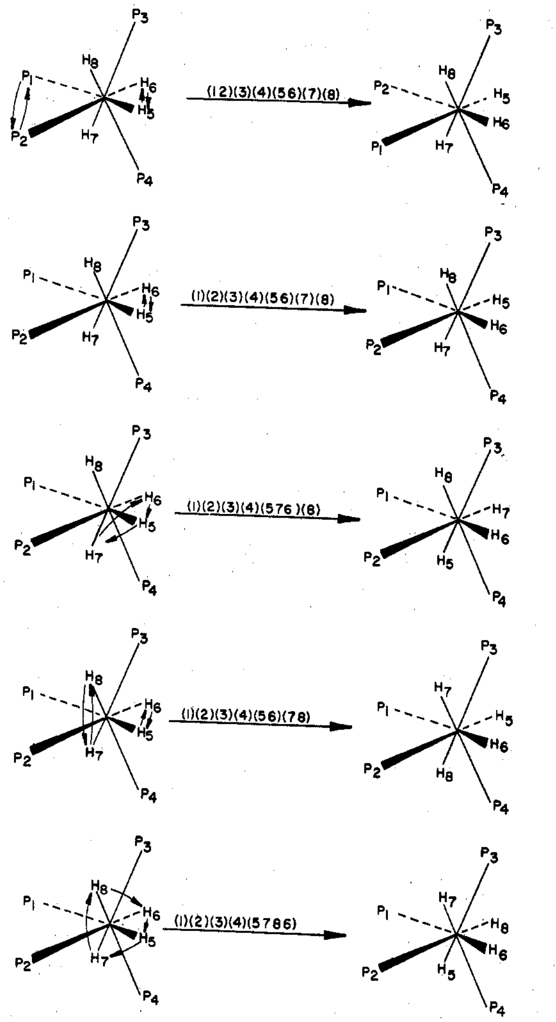

Figure 6.—Five permutational isomerization reactions of molecules MH_3P_4 differentiable in a totally symmetric environment. Skeletal positions are indexed as in Figure 1.

generalized cyclic index of H is defined by

$$Z(\mathrm{H};\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) \equiv \sum_{h_q \in \mathrm{H}} a_1^{j_1} a_2^{j_2} \ldots a_{n_1}^{j_{n_1}} b_1^{k_1} b_2^{k_2} \ldots b_{n_2}^{k_{n_2}} \quad \text{(A1)}$$

In eq A1, the summation extends over all operations h_q in H, the j_i's and k_i's indicate the generalized cyclic type of each h_q as defined above, and the a_i's and b_i's are dummy variables.

The concept of a generalized cyclic index was introduced by Pólya,[16] formalized by Robinson,[17] and extended further by de Bruijn.[18] If H is the direct sum of H_1 and H_2, where H_1 acts on B_1 and H_2 acts on B_2, Pólya's[19] reasoning demonstrates that eq A2 may be used to calculate the generalized cyclic index of H given the cyclic indices of H_1 and H_2.

$$Z(\mathrm{H}_1 + \mathrm{H}_2;\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) = Z(\mathrm{H}_1;\ a_1, a_2, \ldots, a_{n_1}) \cdot Z(\mathrm{H}_2;\ b_1, b_2, \ldots, b_{n_2}) \quad \text{(A2)}$$

B. Theorem I. Theorem.—Let the symmetric permutation groups S_{n_1} and S_{n_2} act on the disjoint sets B_1 and B_2, respectively, $|B_1| = n_1$, $|B_2| = n_2$. The group $\mathrm{H} \equiv S_{n_1} + S_{n_2}$ acts on B, the union of B_1 and B_2. W is an arbitrary subgroup of H.

If $A_{j_1 j_2 \ldots, j_{n_1} k_1 k_2, \ldots, k_{n_2}}$ is the number of conjugacy classes in H with respect to W of cyclic type $(j_1, j_2, \ldots, j_{n_1};\ k_1, k_2, \ldots, k_{n_2})$ and

$$F(W;\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) \equiv \sum_{j_1, j_2, \ldots, j_{n_1};\ k_1, k_2, \ldots, k_{n_2}} A_{j_1 j_2 \ldots j_{n_1}, k_1, k_2, \ldots, k_{n_2}} \times a_1^{j_1} a_2^{j_2} \ldots a_{n_1}^{j_{n_1}} b_1^{k_1} b_2^{k_2} \ldots b_{n_2}^{k_{n_2}}$$

the summation extending over all generalized cyclic types found in H, then

$$F(W;\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) = |W|^{-1} \sum_{w_i \in W} \left\{ \prod_{l=1}^{n_1} d_l! l^{d_l} \sum_{(p)} \prod_{m=1}^{d_l} [m^{p_m} \cdot p_m!]^{-1} \cdot [l^{-1} \sum_{q|l} \phi(q) a_{m_q}{}^{l/q}]^{p_m} \right\} \cdot \left\{ \prod_{u=1}^{n_2} e_u! u^{e_u} \sum_{(t)} \prod_{m=1}^{e_u} [m^{t_m} \cdot t_m!]^{-1} \cdot \left[u^{-1} \sum_{r|u} \phi(r) b_{m_r}{}^{u/r} \right]^{t_m} \right\} \quad \text{(A3)}$$

where $(d_1, d_2, \ldots, d_{n_1};\ e_1, e_2, \ldots, e_{n_2})$ is the generalized cyclic type of $w_i \epsilon W$; $\Pi_{l=1}{}^{n_1}$ is the product over only those l, $1 \leq l \leq n_1$, for which $d_l \neq 0$; $\Pi_{u=1}{}^{n_2}$ is the product over only those u, $1 \leq u \leq n_2$, for which $e_u \neq 0$; $\Sigma_{(p)}$ sums over the partitions $(p_1, p_2, \ldots, p_{d_l})$ of d_l; and $\Sigma_{(t)}$ sums over all the partitions $(t_1, t_2, \ldots, t_{e_u})$ of e_u. All other symbols were defined in EPIR-I.

Proof.—This proof is not presented in detail since its course parallels the proof of theorem I in EPIR-I.

A permutation group $\pi(W)$ acting on H is defined as in EPIR-I. Burnside's Lemma implies eq A4.

$$A_{j_1 j_2 \ldots j_{n_1}, k_1 k_2 \ldots k_{n_2}} = |W|^{-1} \sum_{w_i \in W} \chi_{j_1 j_2 \ldots j_{n_1}, k_1 k_2 \ldots k_{n_2}}[\pi(w_i)] \quad \text{(A4)}$$

$\chi_{j_1 j_2 \ldots j_{n_1} k_1 k_2 \ldots k_{n_2}}[\pi(w_i)]$ is the number of $h_q \epsilon \mathrm{H}$ of generalized cyclic type $(j_1, j_2, \ldots, j_{n_1};\ k_1, k_2, \ldots, k_{n_2})$ which $\pi(w_i)$ leaves fixed. If $(d_1, d_2, \ldots, d_{n_1};\ e_1, e_2, \ldots, e_{n_2})$ is the generalized cyclic type of w_i, then $\chi_{j_1 j_2 \ldots j_{n_1}, k_1 k_2 \ldots k_{n_2}}[\pi(w_i)]$ is the coefficient of $a_1^{j_1} a_2^{j_2} \ldots a_{n_1}^{j_{n_1}} b_1^{k_1} b_2^{k_2} \ldots b_{n_2}^{k_{n_2}}$ in the expression

$$\left| \sum_{l=1}^{n_1} S_{d_l}[C_l] + \sum_{u=1}^{n_2} S_{e_u}[C_u] \right| Z\left(\sum_{l=1}^{n_1} S_{d_l}[C_l] + \sum_{u=1}^{n_2} S_{e_u}[C_u];\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2} \right) \quad \text{(A5)}$$

In eq A5 the summation $\Sigma_{l=1}{}^{n_1}$ extends over only those l, $1 \leq l \leq n_1$, for which $d_l \neq 0$, and the summation $\Sigma_{u=1}{}^{n_2}$ extends over only those u, $1 \leq u \leq n_2$, for which $e_u \neq 0$. Consequently

$$F(W;\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2}) = |W|^{-1} \sum_{w_i \in W} \left| \sum_{l=1}^{n_1} S_{d_l}[C_l] + \sum_{u=1}^{n_2} S_{e_u}[C_u] \right| \cdot Z\left(\sum_{l=1}^{n_1} S_{d_l}[C_l] + \sum_{u=1}^{n_2} S_{e_u}[C_u];\ a_1, a_2, \ldots, a_{n_1};\ b_1, b_2, \ldots, b_{n_2} \right) \quad \text{(A6)}$$

Using eq A2 given above and formulas presented in

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[16] G. Pólya, *Acta Mathematica*, **68**, 145 (1937).

[17] R. W. Robinson, *J. Combinatorial Theory*, **4**, 181 (1968).

[18] N. G. de Bruijn, *Nieuw Archief Wiskunde*, (2) **19**, 89 (1971).

[19] Reference 16, pp 174, 177.

the proof of theorem I in EPIR-I, eq A3 can be derived from eq A6.

As in EPIR-I, eq A7 is of interest.

$$F(W;\ 1, 1, \ldots, 1;\ 1, 1, \ldots, 1) = |W|^{-1} \sum_{w_i \epsilon W} \left(\prod_{l=1}^{n_1} d_l!l^{d_l} \right) \left(\prod_{u=1}^{n_2} e_u!u^{e_u} \right) \quad \text{(A7)}$$

C. Theorem II. Theorem.—B_1, B_2, H, B, and W are defined as in theorem I. If D_W is the number of equivalency classes (double cosets Wh_iW) generated in H when h_i, $h_j \epsilon$H are considered equivalent if $h_i = w_k \cdot h_j \cdot w_h$ for some w_k, $w_h \epsilon W$, then

$$D_W = |W|^{-2} \sum_W{}' (h_{d_1 d_2 \cdots d_{n_1}, e_1 e_2 \cdots e_{n_2}})^2 \times \left(\prod_{l=1}^{n_1} d_l!l^{d_l} \right) \left(\prod_{u=1}^{n_2} e_u!u^{e_u} \right) \quad \text{(A8)}$$

where Σ'_W sums over the generalized cyclic types $(d_1, d_2, \ldots, d_{n_1};\ e_1, e_2, \ldots, e_{n_2})$ of operations in W and $h_{d_1 d_2 \cdots d_{n_1}, e_1 e_2 \cdots e_{n_2}}$ is the number of operations in W of generalized cyclic type $(d_1, d_2, \ldots, d_{n_1};\ e_1, e_2, \ldots, e_{n_2})$.

Proof.—This proof is not presented in detail since its course parallels the proof of theorem II in EPIR-I.

The group W^W acting on elements in H is defined as in EPIR-I. Then Burnside's Lemma implies

$$D_W = |W|^{-2} \sum_{(w_i, w_k) \epsilon W^W} \chi(w_i, w_k) \quad \text{(A9)}$$

where $\chi(w_i, w_k)$ is the number of h_i in H which satisfy eq A10

$$h_i(w_k) = w_i \quad \text{(A10)}$$

Arguments used in EPIR-I show that eq A11 will hold if w_i and w_k are of the same cyclic type $(d_1, d_2, \ldots, d_{n_1};\ e_1, e_2, \ldots, e_{n_2})$. If w_i and w_k are not of the

$$\chi(w_i, w_k) = \left(\prod_{l=1}^{n_1} d_l!l^{d_l} \right) \left(\prod_{u=1}^{n_2} e_u!u^{e_u} \right) \quad \text{(A11)}$$

same cyclic type, $\chi(w_i, w_k) = 0$. Equations A9 and A11 are combined as in EPIR-I to yield eq A8.

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A Restatement of Polya's Theorem

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Received May 2, 1972

Polya's theorem is restated in a manner which may lead to greater ease of isomer enumeration and aid in the formulation of individual isomers. Several examples are treated.

A restatement of Polya's theorem in terms of invariance to covering operations may lead to a greater ease of isomer enumeration and aid in the formulation of the structure of individual isomers. The restatement[1] is as follows: the total number of (theoretically possible) stereoisomers of a molecule will be the number of distinguishable configurations of the molecule in a fixed coordinate system which are invariant under each operation of the rotational group (including the identity operation) divided by the total number of operations of the rotational group of the parent geometry. If the full covering group is used (*i.e.*, improper rotations are included) the result is the number of geometric isomers.

The distinguishable configurations invariant under the identity operation are simply the set of all distinguishable configurations, *i.e.*, the number of permutations of the ligands taken one at a time. The number of these depends only on the number of ligands of each type to be added and may be calculated from

$$P_1{}^n = \frac{n!}{n_a!n_b!n_c!\ldots}$$

where n is the total number of ligands, n_a is the number of A groups, n_b the number of B groups, etc. If only one ligand of each type is present ($n_a = n_b = n_c = \ldots = 1$) then $P_1{}^n = n!$ and the total isomers possible will be $n!/h$ where h is the order of the rotational group. This leads to the well-known (at least for the first few members) results shown in Table I.

TABLE I

MAXIMUM NUMBER OF STEREOISOMERS FOR A GIVEN PARENT GEOMETRY[a]

Coordin no.	Geometry and rotational group	No. of isomers
4	Tetrahedron T	$4!/12 = 2$
	Sq plane D_4	$4!/8 = 3$
	Sq pyr C_4	$4!/4 = 6$
	Boat D_2	$4!/4 = 6$
5	Trigonal bipyr D_3	$5!/6 = 20$
	Sq pyr C_4	$5!/4 = 30$
	Pentagon C_5	$5!/10 = 12$
6	Octahedron O	$6!/24 = 30$
12	Icosahedron I	$12!/60 = 7,983,360$

[a] Maximum achieved only when all ligands are different; planar geometries yield optically inactive isomers, and others give $n/2$ enantiomorphic pairs.

In order for a configuration to be invariant under a C_n operation, any ligands which do not fall on the C_n axis must be in sets of n similar ligands. Groups falling on the C_n axis belong to "sets of one." Each C_n opera-

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(1) Although this restatement is essentially contained in one of Polya's original papers {*Acta Mat.* (*Uppsala*), **68**, 145 (1937)} the implications and simplifications have been overlooked in the recent literature concerned with isomers. A partial summary in English of this paper of Polya appears in a chapter by Uhlenbeck and Ford in "Studies in Statistical Mechanics," Vol. I, J. DeBoer and G. E. Uhlenbeck, Ed., Interscience, New York, N. Y. (North-Holland Publishing Co., Amsterdam), 1962.