JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office.

VOLUME 97, NUMBER 7 APRIL 2, 1975

Permutational Isomerism

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Abstract: The various rearrangements of the ligands of a generalized polyhedron are classified into modes and labeled group theoretically in terms of double cosets. A physical definition of a mode is given and shown to lead to a mathematical description which differs from previous ones. An *ansatz* is proposed such that the unimolecular rate constants for the various rearrangements depend in a simple manner on the mode to which they belong. The equations governing nmr line shapes are also considered and the various modes have been classified in terms of their distinguishability in nmr experiments. Comparisons are made with other approaches to a mathematical description of permutational isomerism.

1. Introduction

There has long been interest[1] in rearrangements of the ligands on a molecular skeleton during a unimolecular isomerization process. In cases where there are a large number of ligands which may undergo rearrangement these considerations become somewhat complex and approaches based on formal group theoretical labeling of isomers[2] and "modes" of rearrangement[3-8] have been discussed.

In the present paper the various rearrangements of the ligands of a generalized polyhedron are classified into modes and labeled group theoretically in terms of double cosets. Section 2 of the manuscript reviews briefly the formulation which Ruch and coworkers have employed for the labeling of permutational isomers. This formulation is then developed by appending some simple equilibrium applications.

In section 3 the various rearrangements of the ligands are classified in terms of modes and the mathematical manner in which the modes are labeled by double cosets is described. The formal definition of a mode of rearrangement which is presented differs from previous formal definitions;[5-7] however, it does agree with the examples given in most cases and in particular with those of Gielen and Vanlautem[3] and Musher.[4] It is argued on physical grounds that the different modes should involve the various "symmetrically similar" rearrangements as well as any additional rearrangements which are obtained by a rotation of the molecule as a whole. It is also considered important to emphasize the distinction between a rearrangement mode and a rearrangement mechanism or reaction pathway.

In section 4 the physical argument in favor of the mode concept is completed by proposing an *ansatz* such that the rate constants for the various rearrangements depend in a simple way on the mode to which they belong. The kinetic equations governing the unimolecular isomerization processes are developed both in terms of this *ansatz* and also in terms of the labeling system which is presented in sections 2 and 3. The development of these kinetic equations is similar to that discussed by Brocas and Willem;[8] however, it is much more general since it is not restricted to either the trigonal bipyramidal or to equally energetic isomers.

The equations governing nmr line shapes are considered in section 5 and the various modes are classified in terms of their distinguishability in nmr experiments. Some details of the theory of double cosets are presented in appendix A. Additional details regarding the kinetic equations of section 4 are set forth in appendix B; a particularly simple form for these equations emerges in the "high-temperature limit." Finally, the application of the present formalism to the trigonal bipyramidal and octahedral skeletal geometries is exemplified in Appendices C and D, respectively.

2. Permutational Isomers

Permutational isomers[1] are compounds which have in common the same molecular skeleton and set of ligands but differing in the relative distribution of ligands on the skeletal positions. The n skeletal positions are labeled by the indices $s_1, s_2, \ldots, s_n$ and the n ligands by the indices $l_1, l_2, \ldots l_n$. A particular *permutamer* in which ligand l_i occupies skeletal position s_i is denoted by

$$\begin{pmatrix} l \\ s \end{pmatrix} = \begin{pmatrix} l_1\, l_2 \ldots l_n \\ s_1\, s_2 \ldots s_n \end{pmatrix} \tag{1}$$

Different permutamers may be generated by permuting the ligand and/or skeletal indices. However, some permutations may yield experimentally indistinguishable structures. We let $\underset{\sim}{R}_s$ denote the group of permutations on s indices which, independently of the ligand distribution, yields indistinguishable structures. The group $\underset{\sim}{R}_s$ usually involves all proper rotations of the point group of the skeleton; any improper rotations would also be included if the experiments considered do not distinguish chirality. If the experiments considered have a characteristic time of measurement less than that corresponding to an internal motion (*e.g.*, rotation, inversion, or puckering), then the permutations representing such motions may also be included in $\underline{R}_s$. In the present discussion it will be assumed that $\underline{R}_s$ consists solely of the permutations corresponding to the proper rotations of the point group corresponding to the skeletal geometry. The symbol $\underline{R}^l$ denotes the group of permutations on l-indices which, independently of the skeleton, gives indistinguishable substances. For instance, in the complex ion $[Co(NH_3)_4Cl_2]^+$ $\underline{R}_s = \underline{O}_h$ and $\underline{R}^l = \underline{S}_4 \times \underline{S}_2$ where $\underline{S}_4$ permutes the four NH_3 ligands and $\underline{S}_2$ permutes the two Cl^- ligands. One usually says that $\underline{R}^l$ permutes among identical ligands; however, the question of which is identical depends on the particular experiment; for instance, isotopes of the same element might be experimentally indistinguishable by, *e.g.*, electronic spectroscopy, although distinguishable by nmr.

It is obvious that the use of permutations on both ligand and skeletal indices is redundant. Thus we let $\underline{R}_l$ be the group of permutations on s indices which is isomorphic[9] to $\underline{R}^l$. The rationale for this definition is seen on noting that

$$P^l\binom{l}{s} = \binom{P^l l}{s} = \binom{l}{P_l^{-1}s} = P_l^{-1}\binom{l}{s} \tag{2}$$

where P^l is a permutation acting on the l-indices and P_l the isomorphic permutation acting on the s indices. $\underline{S}_n$ denotes the symmetric group of all permutations acting on s indices. It is apparent that the permutamer $R^lQ_sP\binom{l}{s}$ is indistinguishable from $P\binom{l}{s}$ for all $R^l \in \underline{R}^l$, $Q_s \in \underline{R}_s$ and $P \in \underline{S}_n$. However,

$$R^lQ_sP\binom{l}{s} = Q_sPR^l\binom{l}{s} = Q_sP(R_1)^{-1}\binom{l}{s} \tag{3}$$

Thus formally a single permutational isomer is defined[2] to be a collection of all permutamers $Q_sPR_l\binom{l}{s}$ with R_l and Q_s ranging over all the elements of $\underline{R}_l$ and $\underline{R}_s$. These sets, which label the permutational isomers

$$\underline{R}_sP_i\underline{R}_l = \{R_sP_iQ_l; R_s \in \underline{R}_s, Q_l \in \underline{R}_l\} \tag{4}$$

are termed $(\underline{R}_s,\underline{R}_l)$ "double cosets." A selection of group theoretical properties of these double cosets is presented in appendix A. Thus, the symmetric group is a disjoint sum of double cosets

$$\underline{S}_n = \sum_i \underline{R}_sP_i\underline{R}_l \tag{5}$$

where P_i is a generator or representative of the ith double coset. The number of permutational isomers is the same as the number of $(\underline{R}_s,\underline{R}_l)$ double cosets, and methods for calculating this number are available.[2,10]

Next the double coset labeling system is developed by considering the equilibrium concentrations of the various permutational isomers. Thus, let $[P]$ denote the concentration of the permutamer $P\binom{l}{s}$ where $\binom{l}{s}$ is a standard permutamer. At equilibrium there exists a Boltzmann distribution

$$[P]/[Q] = e^{-E_P/kT}/e^{-E_Q/kT} \tag{6}$$

where E_P and E_Q are the internal energies[11] of the permutamers, k is Boltzmann's constant, and T is the absolute temperature. Then, letting $[i]$ denote the concentration of the permutational isomer associated with the ith double coset, $\underline{R}_sP_i\underline{R}_l$, we have

$$\frac{[i]}{[i']} = \frac{\sum_{P \in \underline{R}_sP_i\underline{R}_l}[P]}{\sum_{P' \in \underline{R}_lP_{i'}\underline{R}_l}[P']} = \frac{l_i[P_i]}{l_{i'}[P_{i'}]} \tag{7}$$

where l_i is the number of isoenergetic permutamers in the ith double coset. The energy difference

$$E_i - E_{i'} = kT\ln\frac{l_{i'}[i']}{l_i[i]} \tag{8}$$

involves not only the equilibrium concentrations but also the ratios $l_i/l_{i'}$ of the number of permutamers in each double coset. Actually these ratios are well known although usually identified in a different manner. From appendix A it is seen that l_i is the order of $\underline{R}_l$ times the order of $\underline{R}_s$ divided by the order of $\underline{R}_s \cap P_i\underline{R}_lP_i^{-1}$. Thus

$$l_i/l_{i'} = d_{i'}/d_i \tag{9}$$

It should be noted that $\underline{R}_s \cap P_i\underline{R}_lP_i^{-1}$ is the point group of the permutamer $P_i\binom{l}{s}$, as contrasted to $\underline{R}^s$, the point group of the skeleton. Thus seeing that d_i is the order of the point group of the ith isomer, d_i is identified as the so-called *symmetry number*[11] for that isomer. If eq 9 is substituted into eq 8 with the above interpretation of d_i the resulting formula corresponds to the one given by Mayer and Mayer.[12]

3. Permutational Isomerization

It has been demonstrated that on applying a permutation $P \in \underline{S}_n$ to one permutamer $\binom{l}{s}$ a new permutamer, of possibly a different isomer, is obtained. Thus these permutations might also be associated with permutational isomerization processes. Indeed, if $P \in \underline{S}_n$ permutes skeletal index s_i to s_j, then the corresponding *rearrangement* moves the ligand l_j initially on s_j to position s_i, which was originally occupied by ligand l_i. Each rearrangement has one or more reaction pathways associated with it; for instance, for $P = (ij)$, a transposition between nearest neighbor ligands, one pathway might involve a simultaneous clockwise rotation by π about an axis midway between the two equilibrium skeletal positions, while a second pathway might involve a similar counterclockwise rotation (Figure 1). In general the number and accessibility of the various pathways depends upon the fine details of the potential hypersurface. Furthermore, upon application of $P \in \underline{S}_n$ to the various permutamers in a given single isomer double coset it is seen that a number of permutamers belonging to several new isomers may result. That is, a single rearrangement $P \in \underline{S}_n$ can give rise to several products even if there is only one reactant isomer. Thus in order to specify an explicit reaction *mechanism* one needs to know the reactant, the product, the type (or mode) of rearrangement, and the pathway which is consistent with that rearrangement. The utility of the concept of rearrangement will depend ultimately on its physical separability from these closely associated items which together constitute a reaction or reaction mechanism.

Next a particular isomer, I_0, is formally considered in which all positions have chemically identical ligands. (In the following paragraph it might be advantageous to imagine the ligands on different sets of sites being physically, but not chemically, distinguishable, as perhaps with different isotopes.) Now two rearrangements are defined to be *mode* (or *rate*) *equivalent* if they have the same rate constant when applied to I_0. A maximal set of mode-equivalent rearrangements is called a *mode.* Thus a maximal classification is achieved such that if two rearrangements of a general isomer with the same skeleton as I_0 could possibly have the same rates, consistent with the skeletal symmetry, then they will occur in the same mode.

In group-theoretically identifying the modes the skeletal point group is denoted by $\underline{G}$. If $\underline{G}$ contains no improper rotations, then $\underline{G} = \underline{R}_s$; while if $\underline{G}$ contains an improper rotation σ, then $\underline{G} = \underline{R}_s + \sigma\underline{R}_s$. Since the rearrangement $G^{-1}PG$, with $G \in \underline{G}$, $P \in \underline{S}_n$, is obtained by first rotating the ligands by G, second applying P, and third back rotating the ligands, it is seen that $G^{-1}PG$ and P are rate equiv-

Table I. Different Nomenclatures for Analogous Concepts

Present nomenclature	Gielen and Vanlautem[3]	Musher[4]	Hasselbarth and Ruch[7]	Jesson, Meakin, Muetterties *et al.*[5]	Klemperer[6]
(Rearrangement) mode with hindered rotation			Symmetry equivalent rearrangements	Basic permutational set	Indistinguishable permutational isomerization reactions
(Rearrangement) mode with free rotation	Undistinguishable permutations or chemical processes	Mode or rearrangement	Mode equivalent rearrangements	Collection of basic permutational sets	Nondifferentiable permutational isomerization reactions
Nmr-equivalent modes		Observable process		Indistinguishable basic permutational sets	

alent. That is if we trace out the direct pathways for P and $G^{-1}PG$ on two models of the skeleton, then the two tracings would look identical upon either an improper or a proper rotation. Furthermore, rotational motion of the molecule as a whole is often considered to have little effect on the chemical properties. Here it is considered that the rotational motion of a molecule does not influence the rate constants for the rearrangements of a given mode, hence P and PR_s with $R_s \in \underline{R}_s$ are rate equivalent. If some rotational motion of the molecule were hindered, *e.g.*, in a crystalline matrix, then different PR_s could be associated with different rate constants, and only the subgroup of $\underline{R}_s$ corresponding to unhindered rotation would be used to relate mode-equivalent rearrangements. Here it is considered that all rotations are unhindered. Finally, rearrangements related by time reversal symmetry will also be mode equivalent. Thus, P and P^{-1} are mode equivalent. In general it is seen that P, $G^{-1}PGR_s$, and $G^{-1}P^{-1}GR_s$ are contained in the same mode for all $R_s \in \underline{R}_s$ and $G \in \underline{G}$. Now noting that

$$QPQ^{-1}R = QPS \qquad (10)$$

is an expression in which Q and S range over $\underline{R}_s$ as Q and R do, it is apparent that each mode is a union of sets such as $\underline{R}_sP\underline{R}_s$. These sets are $(\underline{R}_s, \underline{R}_s)$ double cosets. Explicitly then the formal specification of a mode is

$$\text{mode } m = \underline{R}_sP_m\underline{R}_s + \underline{R}_s\sigma P_m\sigma^{-1}\underline{R}_s + \underline{R}_sP_m^{-1}\underline{R}_s + \underline{R}_sP_m^{-1}\sigma^{-1}\underline{R}_s \qquad (11)$$

where $\sigma = 0$ if the point group $\underline{G}$ contains no improper rotations. If these double cosets are abbreviated to $\underline{D}_m$, $\underline{D}_{\sigma m}$, $\underline{D}_{\bar{m}}$, and $\underline{D}_{\sigma\bar{m}}$, respectively, then

$$\text{mode } m = \underline{D}_m + \underline{D}_{\sigma m} + \underline{D}_{\overline{m}} + \underline{D}_{\sigma\overline{m}} \qquad (12)$$

It is seen that each rearrangement mode may consist of several $(\underline{R}_s,\underline{R}_s)$ double cosets. In general a mode will consist of 1, 2, or 4 double cosets. This last statement can be proved if it is noted that $\underline{R}_s$ is a normal subgroup of $\underline{G}$. Then

$$\sigma\underline{R}_s = \underline{R}_s\sigma = \sigma^{-1}\underline{R}_s = \underline{R}_s\sigma^{-1} \qquad (13)$$

and

$$\begin{aligned} \underline{D}_m = \underline{D}_{\overline{m}} &\Leftrightarrow \underline{D}_{\sigma m} = \sigma\underline{D}_m\sigma^{-1} = \underline{D}_{\sigma\overline{m}}, \ \sigma \neq 0 \\ \underline{D}_m = \underline{D}_{\sigma m} &\Leftrightarrow \underline{D}_{\overline{m}} = \underline{D}_{\sigma\overline{m}} \qquad (14) \\ \underline{D}_m = \underline{D}_{\sigma\overline{m}} &\Leftrightarrow \underline{D}_{\overline{m}} = \underline{D}_{\sigma m} \end{aligned}$$

In addition it is seen that whenever there is equality among any of the double cosets in eq 12 that it must appear in pairs with never a lone triple. Of course, one takes $\underline{D}_{\sigma m} = \underline{D}_{\sigma\bar{m}} = 0$, if $\underline{G}$ contains no improper rotations, but the inequality $\underline{D}_m \neq \underline{D}_{\bar{m}}$ is still possible.

The formal definition of a rearrangement mode which has been presented above is not exactly the same as previous analogous formal definitions.[5-7] The nomenclature is in general different with different authors[3-7] and is reviewed and summarized in Table I. The present nomenclature is the most similar to that of Musher[4] and Hasselbarth and Ruch.[7]

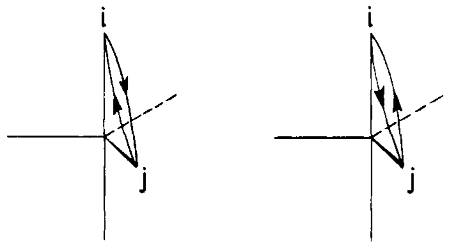


Figure 1. Two possible pathways for the same rearrangement $P = (ij)$.

The reference isomer I_0 was introduced only in order to define a mode. The rearrangements of a particular mode may also be applied to other isomers with different numbers of different ligands, and in such cases the various rearrangements within the same mode may be associated with distinct rate constants. Nevertheless, it is still possible that only rearrangements from one mode are of importance and/or that the rate constants for rearrangements within a single mode are simply related. The usefulness of the concept of a mode depends on the reflection in the experimental data of mode properties in a manner decoupled from the other concepts which constitute a theory of a reaction mechanism.

4. Kinetic Equations

The rate constant which carries one permutamer $P\binom{l}{s}$ to another permutamer $Q\binom{l}{s}$ *via* the rearrangement QP^{-1} is denoted $k(P \rightarrow Q)$. Now the rate constants $k(P \rightarrow Q)$ depend in general not only on the rearrangement mode but also on the reactant and product. In order to delineate the potential utility of the concept of a mode it is proposed that the rate constant be factored into three portions

$$k(P \rightarrow Q) = k_{P^{-1}Q}\, e^{aE_P/kT} e^{-bE_Q/kT} \qquad (15)$$

where the first factor $k_{P^{-1}Q}$ depends only on the mode to which $P^{-1}Q$ belongs, the second factor is a Boltzmann-like term for the reactant, and the third factor is a Boltzmann-like term for the product. Although this proposal is an assumption it does have some reasonable characteristics which are now described.

At equilibrium the ratio of the forward and reverse rate constants is given by

$$\frac{k(P \rightarrow Q)}{k(Q \rightarrow P)} = \frac{[Q]}{[P]} = e^{(E_P-E_Q)/kT} \qquad (16)$$

and substitution of eq 15 into eq 16 gives

$$a + b = 1 \qquad (17)$$

The most reasonable choice for a and b is the symmetric one $a = b = \frac{1}{2}$. It should be noted that this *ansatz* for the rate constants now satisfies the detailed balance conditions of eq 16; this is of interest because this condition has not been a characteristic of previous (usually implied rather than explicit) *ansätze*. In fact, previous considerations seem to have been based upon the implicit assumption that the rate constants are dependent only on the mode.

The $a = b = \frac{1}{2}$ choice can be suggested by a plausibility argument based on absolute rate theory.[13] In this theory the primary temperature dependence of $k(P \rightarrow Q)$ results from the Boltzmann equilibration between the reactant and an activated transition state with energy $E_{P\leftrightarrow Q\ddagger}$. If it is assumed that the transition state energy is a mode-dependent distance, $E_{QP\ddagger^{-1}}$, above the average of the reactant and product energies

$$E^{\ddagger}{}_{P\leftrightarrow Q} = E^{\ddagger}{}_{QP^{-1}} + \tfrac{1}{2}(E_P + E_Q) \tag{18}$$

then according to absolute rate theory the rate constants are given by

$$k(P \rightarrow Q) = Ae^{-(E^{\ddagger}{}_{P\leftrightarrow Q} - E_P)/kT} = \{Ae^{-E_{QP^{-1}}/kT}\}e^{E_P/2kT}e^{-E_Q/2kT} \tag{19}$$

In this manner one obtains the $a = b = \frac{1}{2}$ *ansatz*, and the term in brackets in eq 19 is identified as the mode-dependent factor $k_{QP^{-1}}$. This hypothesis does not seem unreasonable to chemical intuition. Indeed, other hypotheses, such as the assumption that the transition state is a constant (mode-dependent only) energy above the reactant state, are seen to be internally inconsistent since this could not be true for both the forward and reverse reactions (unless the reactant and product fortuitously possess equal energies).

Assuming only unimolecular isomerizations the kinetic equations are now

$$\frac{\mathrm{d}[P]}{\mathrm{d}t} = -\sum_{Q\in \underline{S}_n} (k_{QP^{-1}})e^{(E_P - E_Q)/2kT}[P] + \sum_{Q\in \underline{S}_n} (k_{PQ^{-1}})e^{(E_Q - E_P)/kT}[Q] = \sum_{Q\in \underline{S}_n} k_Q\{-e^{(E_P - E_{QP})/2kT}[P] + e^{(E_{Q^{-1}P} - E_P)/2kT}[Q^{-1}P]\} \tag{20}$$

Recalling that the k_Q are the same for all Q in the same $(\underline{R}_s,\underline{R}_s)$ double coset, one obtains

$$\frac{\mathrm{d}[P]}{\mathrm{d}t} = \sum_m^{\mathrm{DC}} \frac{k_m}{d_m} \sum_{R,\, S\in \underline{R}^s} \{-e^{(E_P - E_{RP_mSP})/2kT}[P] + e^{(E_{RP_m^{-1}SP})/2kT}[RP_m^{-1}SP]\} \tag{21}$$

Next if it is assumed that P is in the ith $(\underline{R}_s,\underline{R}_l)$ double coset (which labels the isomers) summation over the elements of this double coset yields

$$\frac{\mathrm{d}[i]}{\mathrm{d}t} = \sum_m^{\mathrm{DC}} \frac{k_m}{d_m} \sum_{R,\, S,\, T\in \underline{R}_s} \sum_{U\in \underline{R}_l} \times \frac{1}{d_i}\{-e^{(E_i - E_{RP_mSTPU})/2kT}[TPU] + e^{(E_{RP_m^{-1}STPU} - E_i)/2kT}[RP_m^{-1}STPU]\} \tag{22}$$

If the symbols $\underline{D}_m$ and $\underline{D}_i$ denote the sums over the elements in their respective $(\underline{R}_s,\underline{R}_s)$ and $(\underline{R}_s,\underline{R}_l)$ double cosets, it follows that

$$\underline{D}_m\underline{D}_i = \sum_{i'} (i'|mi)\underline{D}_{i'} \tag{23}$$

where the $(i'|mi)$ are scalars determined from the theory of double cosets. Then

$$\frac{\mathrm{d}[i]}{\mathrm{d}t} = \sum_{i'}^{\mathrm{DC}} \sum_m^{\mathrm{DC}} k_m\{-(i'|mi)e^{(E_i - E_{i'})/2kT}[i] + (i'|mi)e^{(E_{i'} - E_i)/2kT}[i']\} \tag{24}$$

it is noted that all $[Q]$ in the same $(\underline{R}_s,\underline{R}_l)$ double cosets are equal, since they simply represent the concentrations of different permutamers of the same isomer.

The set of eq 24 represents the final form for describing the general case. The number of variable concentrations $[i]$ appearing in eq 24 is in fact the number of isomers. General methods are available[14] for solving such coupled kinetic equations, and this is discussed further in appendix B; also a high-temperature solution (*i.e.*, when the differences of energies of the various isomers are essentially small compared to kT) is obtained. It should be noted that the solutions for different numbers of identical ligands can[8] be related to one another. In particular cases the rate constants, k_m, for only one particular mode may be sufficiently large to warrant attention so that the m summation in eq 24 could be truncated. Finally, it is apparent that each mode consists of 1, 2, or 4 $(\underline{R}_s,\underline{R}_l)$ double cosets so that the k_m's for different double cosets could be identical, within our *ansatz*.

5. Nmr-Equivalent Modes

Frequently one finds ligands which are single atoms or ions which also have a nonzero nuclear spin. In such cases nmr spectra may be observed; however, the nmr lines may be broadened or coalesced if there is a sufficiently fast exchange among the like nuclei. Here like nuclei do not necessarily have identical environments. Rather it is just the nmr-equivalent nuclei interrelated by elements of the full point group $\underline{R}_l \cap \underline{R}_s$ which would have identical nmr spectra. Only rearrangements permuting like nuclei among themselves are to be considered, since only these may take place sufficiently rapidly ($\simeq 10^{-6}$ sec) with any likelihood of influencing the nmr line shapes. Thus it is seen that the rearrangements in the mth mode which should be considered are those in the set

$$\{\text{mode } m\} \cap \underline{R}_l \tag{25}$$

Now the nmr line intensity at frequency ν is given by[15]

$$I(\nu) \sim I_m(\mathbf{P}\cdot\mathbf{A}^{-1}\cdot\mathbf{1}) \tag{26}$$

where **P** and **1** are vectors and **A** is the Kubo-Sack matrix with the (a,b)th matrix element given by

$$A_{ab} = -\alpha_a\delta_{ab} + \sum_m [p_{ab}{}^{(m)} - (1 - p_{ab}{}^{(m)})\delta_{ab}](1/\tau_m) \tag{27}$$

The only dependence of $I(\nu)$ on the rearrangement (or exchange) of like nuclei arises in the lifetimes, τ_m, for a given mode m and in the $p_{ab}{}^{(m)}$, which is the average fraction of sites with environment b changed into sites with environment a by rearrangements in the set in eq 25. Often it is anticipated that only one mode is of importance so that the sum in eq 27 is restricted to that mode with the corresponding τ_m treated as a parameter.

The $p_{ab}{}^{(m)}$ may be computed from a consideration of the appropriate double cosets. If $\underline{R}_{\mathrm{eq}}$ denotes the group of permutations among nmr-equivalent nuclei then double coset decomposition yields

$$\underline{R}_l = \sum_n \underline{R}_{\mathrm{eq}}G_n\underline{R}_{\mathrm{eq}} \tag{28}$$

where the $\underline{G}_n$ are double coset multipliers for the $(\underline{R}_{\mathrm{eq}},\underline{R}_{\mathrm{eq}})$ double coset decomposition of $\underline{R}_l$. Since $\underline{R}_l$ and $\underline{R}_{\mathrm{eq}}$ are both products of symmetric groups, each double coset $\underline{R}_{\mathrm{eq}}G_n\underline{R}_{\mathrm{eq}}$ is uniquely labeled by a double coset symbol D^n, with the (a,b)th element $(D_{ab}{}^n)$ being the number of b sites changed to a sites by the elements of that double coset. (See appendix A.) It is then obvious that the rearrangements of the set

$$\{\text{mode } m\} \cap \underline{R}_{\mathrm{eq}}G_n\underline{R}_{\mathrm{eq}} \tag{29}$$

are those rearrangements of mode m which interchange equivalent sites in accordance with the double coset symbol

$\underline{D}^n$. Furthermore, if l_{mn} and l_m represent the orders of eq 29 and 25, respectively, and N_a denotes the number of a sites, then the fraction of spins on b sites which are changed to a sites by the rearrangements in eq 29 is $D_{ab}{}^n/N_b$, and the fraction of allowed rearrangements in mode m which have the double coset symbol $\underline{D}^n$ is l_{mn}/l_m. Thus, the average fraction of b sites changed to a sites by the rearrangements of eq 25 is

$$\mathrm{p}_{ab}{}^{(m)} = \sum_n \frac{l_{mn}}{l_m} \frac{D_{ab}{}^n}{N_b} \tag{30}$$

If two different modes give rise to the same $\mathbf{p}^{(m)}$ matrix of eq 30, then an nmr experiment would not distinguish between these two modes of rearrangement. Such modes may be termed nmr equivalent and they are determined only by computing and comparing the $\mathbf{p}^{(m)}$ matrices of eq 30.

A different but related approach has been employed by Jesson, Meakin, Muetterties, et al.,[5] and by Klemperer.[6] In these other works the full molecular point group $\underline{R}_l \cap \underline{R}_s$ of proper rotations is used to carry out double coset decompositions of $\underline{R}_l$; these $(\underline{R}_l \cap \underline{R}_s, \underline{R}_l \cap \underline{R}_s)$ double cosets are termed "collections of basic permutational sets" [5] or "nondifferentiable permutational isomerization reactions" [6] and they play a role analogous to the mode concept which is discussed here. For example, the actual molecular point group for $(CH_3)_2NPF_4$ would be $\underline{C}_{2v}$, whereas the idealized skeletal point group used in the mode concept here would be $\underline{D}_{3h}$. Thus in these other works the elements of one of these collections of basic permutational sets all possess identical rate constants, whereas the elements of a mode do not necessarily do so. If the definition of a collection of basic permutational sets were extended to include the possibility of inverse and inverted double cosets (similar to those in the mode description of eq 11) and if $\underline{R}_{\mathrm{eq}}$ is equal to $\underline{R}_l \cap \underline{R}_s$, then this extended collection of basic permutational sets would be given by eq 29. In general, however, $\underline{R}_{\mathrm{eq}} \supseteq \underline{R}_l \cap \underline{R}_s$, so that the set of eq 29 will be at least as large as a collection of basic permutational sets.

6. Conclusion

The concept of a permutational isomerization process has been discussed with emphasis on the mode concept of Musher.[4] Its potential utility especially with regard to rate constant *ansätze*, as in section 4, has been argued to be an integral part of the mode concept. Indeed these *ansätze* are here viewed to be necessary for a complete and useful mode concept. The labeling of both isomers and modes in a group theoretical manner has been indicated and used. Finally an attempt has been made to indicate the nature of the assumptions which are introduced and the reasons for making them.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant GP 38027X) and the Robert A. Welch Foundation for generous financial support. The authors also appreciate helpful discussion with Dr. James G. Nourse of Princeton University.

Appendices

A. Theory of Double Cosets. Consider a group $\underline{G}$ with two subgroups $\underline{H}$ and $\underline{K}$. Then the $(\underline{H},\underline{K})$ *double cosets* of $\underline{G}$ are

$$\underline{H}G\underline{K} \equiv \{HGK; H \in \underline{H}, K \in \underline{K}\} \tag{A.1}$$

It is shown in standard group theory texts that these double cosets (DC's) are disjoint and that $\underline{G}$ is uniquely decomposed into

$$\underline{G} = \sum_q \underline{H}G_q\underline{K} \tag{A.2}$$

where q labels the distinct DC's and G_q is an arbitrary element from the qth double coset. Furthermore, if h, k, and d_q are the orders of the sets $\underline{H}$, $\underline{K}$, and $\underline{H} \cap G_q\underline{K}G_q{}^{-1}$, then the order of the DC $\underline{H}G_q\underline{K}$ is

$$l_q = hk/d_q \tag{A.3}$$

If D_r, D_q, and $D_{q'}$ represent the group algebraic sums over the (l_r, l_q, and $l_{q'}$) elements in the DC's $\underline{H}G_r\underline{H}$, $\underline{H}G_q\underline{K}$, and $\underline{H}G_{q'}\underline{K}$, then

$$D_rD_q = \sum_{q'} (q' \,|\, rq) D_{q'} \tag{A.4}$$

where the scalar coefficients $(r'|rq)$ are given by[15]

$$(q' \,|\, rq) = hd_{q'}/d_rd_q = |G_r\underline{H}G_q \cap \underline{H}G_{q'}\underline{K}| \tag{A.5}$$

These coefficients also appear in using *dc matrices* $\mathbf{D}^q$ with matrix elements

$$D_{ij}{}^q \equiv \sum_{G \in \underline{H}G_q\underline{K}} (1/h) |C_i\underline{H} \cap GC_j\underline{K}| \tag{A.6}$$

where C_i and C_j are left coset multipliers of $\underline{H}$ and $\underline{K}$ in $\underline{G}$. These linearly independent DC matrices multiply thus[16]

$$\mathbf{D}^r\mathbf{D}^q = \sum_{q'} (q' \,|\, rq) \mathbf{D}^{q'} \tag{A.7}$$

in close analogy to (A.4). Each DC matrix $\mathbf{D}^r$ for $(\underline{H},\underline{H})$ DC's may be interpreted as an incidence matrix for a directed *DC graph*, which also is in unique correspondence with the DC's. (These graphs may be used to yield topological representations[17] of the rearrangement mode associated with $(\underline{R}_s,\underline{R}_s)$ DC's of section 3.)

Next $\underline{G}$ is considered to be a permutation group on a set Ω of indices. A subset Δ of Ω is called a *fixed block* if

$$\underline{G}\Delta \equiv \{Gx; G \in \underline{G},\ x \in \Delta\} \subseteq \Delta \tag{A.8}$$

A minimal fixed block Δ is called an *orbit*. If $\{\Delta_a; a$ ranging$\}$ and $\{\Gamma_b; b$ ranging$\}$ represent the orbits of $\underline{H} \subseteq \underline{G}$ and $\underline{K} \subseteq \underline{G}$, then a *DC symbol* D^q is defined by

$$D_{ab}{}^q \equiv |\Delta_a \cap G_q\Gamma_b| \tag{A.9}$$

Different DC symbols must arise from different DC's. In addition[18] if $\underline{H}$ and $\underline{K}$ are simple products of disjoint symmetric groups then each DC yields a unique DC symbol. More generally if $\underline{H}$ and $\underline{K}$ have normal subgroups $\underline{H}'$ and $\underline{K}'$ which are simple products of symmetric groups, then the $(\underline{H}',\underline{K}')$ DC symbols correspond to unique disjoint collections of $(\underline{H},\underline{K})$ DC symbols, such that all the DC symbols in one such collection differ only in the permutation of rows and columns. Again if $\underline{H}$ and $\underline{K}$ are the first of these special cases then

$$d_q = \prod_a \prod_b (D_{ab}{}^q!) \tag{A.10}$$

More generally in the second of these special cases if n_q represents the number of $(\underline{H}',\underline{K}')$ DC symbols in the collection for the qth $(\underline{H},\underline{K})$ DC, then

$$d_q = \frac{1}{n_q} \frac{h}{h'} \frac{k}{k'} \prod_{ab} (D_{ab}{}^q!) \tag{A.11}$$

where h, h', k, and k' are the orders of $\underline{H}$, $\underline{H}'$, $\underline{K}$, and $\underline{K}'$ and any DC symbol in the collection is used in the product over a and b. Further $(\underline{H},\underline{H})$ DC symbols may be interpreted as incidence matrices for a corresponding DC diagram. (These DC diagrams often are in close correspondence with the usual diagrammatic representations[3-6] of the manner in which the related mode moves the ligands about in a complex.) Such DC symbols may also be employed to carry out the multiplications of (A.5) or (A.7).

B. Solving the Kinetic Equations. Consider first a general set of coupled first-order rate equations

$$\frac{\mathrm{d}}{\mathrm{d}t} C_i = \sum_j K_{ij} C_j \tag{B.1}$$

where

$$K_{ij} \equiv k(j \rightarrow i), \quad i \neq j$$
$$K_{ii} \equiv -\sum_{j \neq i} k(i \rightarrow j) \tag{B.2}$$

This may be rewritten in matrix form

$$\frac{d}{\mathrm{d}t}\mathbf{C} = \mathbf{KC} \tag{B.3}$$

Then[14] this system of equations may be decoupled if **K** can be brought to diagonal form. However, since **K** is neither Hermitian nor normal, it is necessary to demonstrate that it can be diagonalized. To see this the following detailed balance conditions should be noted

$$\frac{K_{ij}}{K_{ji}} = \frac{k(j \rightarrow i)}{k(i \rightarrow j)} = \frac{e^{-E_i/kT}}{e^{-E_j/kT}} \tag{B.4}$$
$$i \neq j$$

where in general the E_i are free energies. Then defining matrices

$$\Lambda_{ij} \equiv \delta_{ij} e^{E_i/2kT}$$
$$\mathbf{K}^{\Lambda} \equiv \Lambda \mathbf{K} \Lambda^{-1} \tag{B.5}$$

it is apparent that

$$\frac{K_{ij}^{\Lambda}}{K_{ji}^{\Lambda}} = \frac{\Lambda_{ii}K_{ij}\Lambda_{jj}^{-1}}{\Lambda_{jj}K_{ji}\Lambda_{ii}^{-1}} = \frac{K_{ij}\Lambda_{ii}^{2}}{K_{ji}\Lambda_{jj}^{2}} = 1_j, \tag{B.6}$$
$$i \neq j$$

hence, since **K** is real, it is seen $\mathbf{K}^{\Lambda}$ is real symmetric. Then

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{C}^{\Lambda} = \frac{\mathrm{d}}{\mathrm{d}t}\Lambda\mathbf{C} = \Lambda\mathbf{K}\Lambda^{-1}\Lambda\mathbf{C} = \mathbf{K}^{\Lambda}\mathbf{C}^{\Lambda} \tag{B.7}$$

where $\mathbf{C}^{\Lambda} \equiv \Lambda\mathbf{C}$ is simply a rescaled concentration vector. Since $\mathbf{K}^{\Lambda}$ is real symmetric, it has real eigenvalues and can be diagonalized by a unitary transformation, whereupon (B.7) can be decoupled and easily solved.

Now for the present case of interest, *i.e.*, for $a = b = \frac{1}{2}$ (as discussed in section 4)

$$K_{P,Q}^{\Lambda} = k_{PQ^{-1}} \quad P \neq Q$$
$$K_{P,P}^{\Lambda} = K_{P,P} = -\sum_{Q \neq P} k_{QP^{-1}} e^{(E_P - E_Q)/2kT} \tag{B.8}$$

and the rescaled concentrations are

$$\{P\} = e^{E_P/2kT}[P] \tag{B.9}$$

Then eq 20 takes the simple form

$$\frac{\mathrm{d}}{\mathrm{d}t}\{P\} = -\sum_{Q \in \underline{S}_n} k_{QP^{-1}} e^{(E_P - E_Q)/2kT}\{P\} + \sum_{Q \in \underline{S}_n} k_{PQ^{-1}}\{Q\} \tag{B.10}$$

Equation 24 could similarly be simplified. In general the matrix $\mathbf{K}^{\Lambda}$ is best diagonalized on a computer.

In the high-temperature limit, however, $\mathbf{K}^{\Lambda}$ may be factorized extensively using group theory, and indeed in many cases the factorization may be complete. Noting the expansions

$$\begin{aligned} e_{rs}^{\alpha} &= \frac{f^{\alpha}}{n!}\sum_{P \in \underline{S}_n} [P^{-1}]_{sr}^{\alpha} P \\ P &= \sum_{\alpha rs} [P]_{rs}^{\alpha} e_{rs}^{\alpha} \end{aligned} \tag{B.11}$$

where $n!$ is the order of the group $\underline{S}_n$ and $[P]_{rs}^{\alpha}$ is the (*r,s*)th matrix element of the αth irreducible representation (of dimension f^{α}) for the permutation *P*. Then substitution in (B.10) gives (B.12).

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\{e_{rs}^{\alpha}\} &= \frac{f^{\alpha}}{n!}\sum_{P \in \underline{S}_n} \frac{\mathrm{d}}{\mathrm{d}t}[P^{-1}]_{sr}^{\alpha}\{P\} = \\ &\frac{f^{\alpha}}{n!}\sum_{P \in \underline{S}_n}\sum_{Q} [P^{-1}]_{sr}^{\alpha} K_{P,Q}^{\Lambda}\{Q\} = \\ &\sum_{\beta tu}\left(\frac{f^{\alpha}}{n!}\sum_{P,Q} [P^{-1}]_{sr}^{\alpha} K_{P,Q}[Q]_{tu}^{\beta}\right)\{e_{tu}^{\beta}\} \end{aligned} \tag{B.12}$$

It is now obvious that

$$K_{P,Q}^{\Lambda} = K_{PQ^{-1},1}^{\Lambda} \tag{B.13}$$

at least for all $P \neq Q$. For $P = Q$ it is noted that in the high-temperature limit

$$K_{P,P}^{\Lambda} \longrightarrow -\sum_{Q \neq P} k_{QP^{-1}} = -\sum_{R \in \underline{S}_n} k_R \tag{B.14}$$

so that (B.13) is correct for $P = Q$ in this limit. An approximation for $K_{P,P}^{\Lambda}$ which satisfies (B.13) and which is valid at slightly lower temperatures is

$$K_{P,P}^{\Lambda} \simeq -\frac{1}{n!}\sum_{Q,R \in \underline{S}_n} k_{QR^{-1}} e^{(E_R - E_Q)/2kT} \tag{B.15}$$

Hence assuming that (B.13) is valid for all *P* and *Q*. the coefficient of $\{e_{tu}^{\beta}\}$ in (B.12) became

$$\begin{aligned} &\frac{f^{\alpha}}{n!}\sum_{P,R} [P^{-1}]_{sr}^{\alpha} K_{P,R^{-1}P}^{\Lambda}[R^{-1}P]_{tu}^{\beta} \simeq \\ &\frac{f^{\alpha}}{n!}\sum_{w}\sum_{R} K_{R,1}^{\Lambda}[R^{-1}]_{tw}^{\beta}\sum_{P}[P^{-1}]_{sr}^{\alpha}[P]_{wu}^{\beta} = \\ &\delta_{\alpha\beta}\delta_{su}\sum_{R} K_{R,1}^{\Lambda}[R^{-1}]_{tr}^{\alpha} \end{aligned} \tag{B.16}$$

utilizing the orthogonality theorem for irreducible representations. The kinetic equations are, therefore

$$\frac{\mathrm{d}}{\mathrm{d}t}\{e_{rs}^{\alpha}\} = \sum_{t}\left(\sum_{R \in \underline{S}_n} K_{R,1}^{\Lambda}[R^{-1}]_{tr}^{\alpha}\right)\{e_{ts}^{\alpha}\} \tag{B.17}$$

It should be noted that the equations with different values of αs are decoupled; thus there is only a maximum of f^{α} coupled equations. In general further decoupling may be achieved. To see this note that $K_{R,1}^{\Lambda} = K_{Q,1}^{\Lambda}$ if *R* and *Q* are contained in the same $(\underline{R}_s,\underline{R}_s)$ double coset. Then the coefficient of $\{e_{ts}^{\alpha}\}$ in (B.17) is seen to be

$$\begin{aligned} &\sum_{Q \in \underline{S}_n} K_{Q,1}^{\Lambda}[Q^{-1}]_{tr}^{\alpha} = \\ &\sum_{m}\frac{1}{d_m}\sum_{R,S \in \underline{R}_s} K_{RP_mS,1}^{\Lambda}[(RP_mS)^{-1}]_{ts}^{\alpha} = \\ &\sum_{m}\frac{K_{P_m,1}^{\Lambda}}{d_m}\sum_{uv}\sum_{S \in \underline{R}_s}[S]_{tu}^{\alpha}[P_m^{-1}]_{uv}^{\alpha}\sum_{R \in \underline{R}_s}[R]_{vr}^{\alpha} \end{aligned} \tag{B.18}$$

Now if the irreducible representations of $\underline{S}_n$ are chosen to be symmetry adapted to $\underline{R}_s$, then the matrix elements $[R]_{tu}^{\alpha}$ are either 0 or a matrix element of an irreducible representation for $\underline{R}_s$. Furthermore, the rows and columns of irreducible representations of $\underline{S}_n$ are labeled by the irreducible representations of $\underline{R}_s$. Also using the orthogonality theorem for irreducible representations of $\underline{R}_s$, it is apparent that $\Sigma_{R \in \underline{R}_s} [R]_{tu}^{\alpha}$ is zero unless both *t* and *u* are associated with the identity irreducible representations of $\underline{R}_s$ Consequently, letting ρ label the different rows of α of $\underline{S}_n$ labeled by the identity representation of $\underline{R}_s$ results in

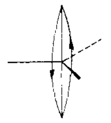
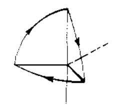
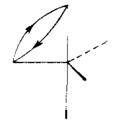
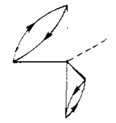
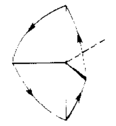
$$\frac{\mathrm{d}}{\mathrm{d}t}\{e_{\rho\sigma}^{\alpha}\} = \sum_{\tau}\left(\sum_{m} K_{P_m,1}^{\Lambda}\frac{|\underline{R}_s|^2}{d_m}\right)\{e_{\tau\sigma}^{\alpha}\} \tag{B.19}$$

C. The Trigonal Bipyramid. The vertices of the trigonal bipyramidal skeleton are labeled in the manner indicated in Figure 2. The skeletal point group for proper rotation is

$$\begin{aligned} \underline{R}^s &= \underline{D}_3 \\ &= \{1, (345), (354), (12)(34), (12)(45), (12)(35)\} \end{aligned} \tag{C.1}$$

The axial (A) and equatorial (E) ligands are identified as forming the two orbits (appendix A) of $\underline{D}_3$. Thus the $(\underline{D}_3,\underline{D}_3)$ double cosets in $\underline{S}_5$ will have DC symbols of the form

Table II. Trigonal Bipyramid Modes with Double Coset Symbol and Double Coset Representative

m				d_m
0+	$\begin{Bmatrix}2 & 0\\0 & 3\end{Bmatrix}_+$	$G_{0+} = 1$ identity		6
0− = (*aa*)	$\begin{Bmatrix}2 & 0\\0 & 3\end{Bmatrix}_-$	$G_{0-} = (12)$		6
1+ = (*aee*)	$\begin{Bmatrix}1 & 1\\1 & 2\end{Bmatrix}_+$	$G_{1+} = (134)$		1
1− = (*ae*)	$\begin{Bmatrix}1 & 1\\1 & 2\end{Bmatrix}_-$	$G_{1-} = (13)$		1
2+ = (*ae*)(*ae*)	$\begin{Bmatrix}0 & 2\\2 & 1\end{Bmatrix}_+$	$G_{2+} = (13)(24)$		2
2− = (*aeae*)	$\begin{Bmatrix}0 & 2\\2 & 1\end{Bmatrix}_-$	$G_{2-} = (1324)$		2

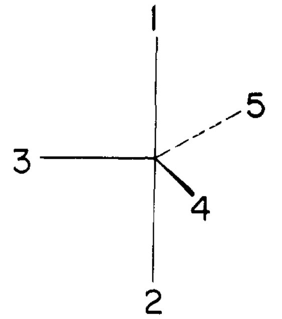


Figure 2. Numbering convention for the trigonal bipyramid.

$$\begin{Bmatrix}D_{AA}{}^q & D_{AE}{}^q\\ D_{EA}{}^q & D_{EE}{}^q\end{Bmatrix} \tag{C.2}$$

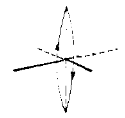
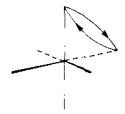
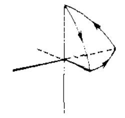
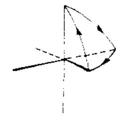
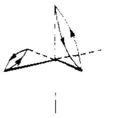
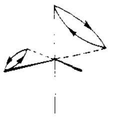
with the sum of row A or column A being 2 (the number of axial ligands) and the sum of row B or column B being 3 (the number of equatorial ligands). In the trigonal bipyramid case point group parity determined by the correspondence to proper or improper rotations, and permutation parity, determined by the evenness or oddness of a permutation, are the same. In addition since

$$\underline{D}_{3h} = \underline{S}_2 \times \underline{S}_3 = \underline{D}_3 + \sigma\underline{D}_3 \tag{C.3}$$

is a direct product of axial and equatorial symmetric groups $\underline{S}_2$ and $\underline{S}_3$, these DC symbols are in unique correspondence with the $(\underline{D}_{3h},\underline{D}_{3h})$ DC's, each of which decomposes into two $(\underline{D}_3,\underline{D}_3)$ DC's of different parities. Thus the additional specification to be appended to the DC symbols to obtain unique correspondence with the $(\underline{D}_3,\underline{D}_3)$ DC's is then simply the parity label, + or −. The completed DC symbols are given in Table II where also a DC representative and a diagram of a representative rearrangement is shown. In this case each $(\underline{R}_l,\underline{R}_l)$ double coset forms an individual mode.

D. The Octahedron. The vertices of the octahedral skeleton are labeled in the manner indicated in Figure 3. Then

Table III. Octahedral Modes and Double Coset Symbols and Double Coset Representatives

	m			
	0+	$\begin{Bmatrix}2 & 0 & 0\\0 & 2 & 0\\0 & 0 & 2\end{Bmatrix}_+$	$G_{0+} = 1$	
	0− = (*tt*)	$\begin{Bmatrix}2 & 0 & 0\\0 & 2 & 0\\0 & 0 & 2\end{Bmatrix}_-$	$G_{0-} = (12)$	
	1 = (*cc*)	$\begin{Bmatrix}2 & 0 & 0\\0 & 1 & 1\\0 & 1 & 1\end{Bmatrix}$	$G_1 = (13)$	
2+	2++ = (*ccc*)	$\begin{Bmatrix}1 & 1 & 0\\0 & 1 & 1\\1 & 0 & 1\end{Bmatrix}_{++}$	$G_{2++} = (135)$	
	2−− = (*ccc*)	$\begin{Bmatrix}1 & 1 & 0\\0 & 1 & 1\\1 & 0 & 1\end{Bmatrix}_{--}$	$G_{2--} = (153)$	
2−	2+− = (*cc*)(*cc*)	$\begin{Bmatrix}1 & 1 & 0\\0 & 1 & 1\\1 & 0 & 1\end{Bmatrix}_{+-}$	$G_{2+-} = (13)(46)$	
	2−+ = (*cc*)(*cc*)	$\begin{Bmatrix}1 & 1 & 0\\0 & 1 & 1\\1 & 0 & 1\end{Bmatrix}_{-+}$	$G_{2-+} = (15)(46)$	

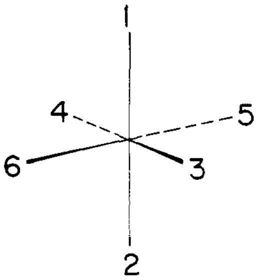


Figure 3. Numbering convention for the octahedron.

the skeletal point group for proper rotations is

$$\begin{aligned}\underline{R}^s &= \underline{O}\\ &= \{1, (3645), (34)(56), (3546),\\ &\quad (1324), (12)(34), (1423),\\ &\quad (1526), (12)(56), (1625),\\ &\quad (136)(245), (163)(254),\\ &\quad (135)(246), (153)(264),\\ &\quad (146)(235), (164)(253),\\ &\quad (145)(236), (154), (263),\\ &\quad (12)(36)(45), (12)(35)(46), (13)(24)(56),\\ &\quad (16)(25)(34), (14)(23)(56), (15)(26)(34)\}\end{aligned} \tag{D.1}$$

In this case the entire set of sites forms an orbit, so it is necessary to consider blocks which are not fixed. The pairs of opposite skeletal sites

$$\{1, 2\}, \{3, 4\}, \text{ and } \{5, 6\} \tag{D.2}$$

form mutually conjugate blocks and may be used to construct DC symbols for the $(\underline{O},\underline{O})$ DC's in $\underline{S}_6$. Again an extra specifying label is required in order to label uniquely each $(\underline{O},\underline{O})$ DC. In the octahedral case permutation and point group parity are not in correspondence. However,

$$\underline{O}_h = (\underline{S}_2 \times \underline{S}_2 \times \underline{S}_2)\underline{S}_3{}^* = \underline{O} + \sigma\underline{O} \qquad (\mathrm{D}.3)$$

where the $\underline{S}_2$ symmetric groups permute indices within the blocks of (D.2) and the $\underline{S}_3{}^*$ symmetric group permutes the blocks among themselves. Then the $(\underline{O}_h,\underline{O}_h)$ DC's which are uniquely labeled by DC symbols each decompose into 1, 2, or 4 $(\underline{O},\underline{O})$ DC's; for a particular DC, say $\underline{O}_h G_q \underline{O}_h$. this decomposition would depend on which, if any, of the sets

$$\underline{O}G_q\underline{O},\ \underline{O}G_q\sigma\underline{O},\ \underline{O}\sigma G_q\underline{O},\ \text{and}\ \underline{O}\sigma G_q\sigma\underline{O} \qquad (\mathrm{D}.4)$$

are distinct. Thus if all these four sets were equal, no extra specifying label would be appended; if all of these sets were distinct, the labels ++, +−, −+, and −− would be appended; and, if there were just two distinct sets

$$\underline{O}G_q\underline{O} = \underline{O}\sigma G_q\sigma\underline{O}\ \text{and}\ \underline{O}G_q\sigma\underline{O} = \underline{O}\sigma G_q\underline{O} \qquad (\mathrm{D}.5)$$

then the labels + and − would be appended. The various DC symbols and DC representatives are indicated in Table III.

It is to be noted that the DC's $m = 2{+}{+}$ and $m = 2{-}{-}$ are reflections, and inverses too, of one another; they thus form a single mode, denoted $m = 2+$. Also the DC's $m = 2{+}{-}$ and $m = 2{-}{+}$ are reflections of one another, so that they too form a single mode, denoted $m = 2-$. Thus although there are seven $(\underline{O},\underline{O})$ DC's there are only five modes.

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The NH_2 Substituent Effect on the Properties of Ionic Compounds

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Received March 23, 1974

Abstract: Electronic structure calculations on NH_2 carbonium ions, their neutral precursors, and related amines have been carried out in order to analyze more closely the unusual stabilizing property of NH_2 groups on the electronic structure of ions. The rotational barriers in guanidinium, amidinium, and immonium are predicted as well as proton affinities of the imines from which these carbonium ions are formed by protonation. The substituent stabilizing effects for carbonium ions are compared with those expected for carbanions and it is found that the BH_2 group is the most effective at stabilizing a neighboring carbanion center, with an NH_2 group relatively ineffective.

The electronic structure of single substituted carbonium ions CH_2R^+ has been previously studied by one of us[1] and it has been determined that the NH_2 group is unusually effective at stabilizing the carbonium ion center. In this work, we extend our studies to examine multiply substituted carbonium ions, amidinium and guanidinium, in order to compare their electronic structure stability and properties with immonium $CH_2NH_2^+$.

This large stabilizing effect of an NH_2 group on carbonium ions has important conformational consequences and so the rotational barriers in immonium, amidinium, and guanidinium are of interest.