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# Classification of Rearrangement Mechanisms and Dynamic Stereochemistry

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We review some aspects of dynamic stereochemistry related to the classification theory of rearrangement mechanisms. This classification is based on the symmetry of the molecular skeleton and has been widely used in connection with nuclear magnetic resonance line shape analysis. It is also related to the Longuet-Higgins approach to nonrigidity and may be used to predict the consequences of various tunneling mechanisms in rotation or vibration spectroscopy.

**KEY WORDS:** Modes of rearrangements; Longuet-Higgins groups; nonrigid molecules; dynamic stereochemistry.

One hundred years ago, van't Hoff postulated a tetrahedral structure for the carbon atom, a discovery that originated the development of stereochemistry. At the present time, our knowledge of molecular structure has reached an impressive degree of sophistication.

Every molecule is characterized by a set of parameters, such as bond lengths, bond angles, and dihedral angles defining the three-dimensional structure of its equilibrium configuration. The molecules may also be classified according to their symmetry, which is expressed by a symmetry point group containing proper and eventually improper symmetry operations.

Molecular movements either conserve the interatomic distances of the molecular framework or they do not. Translation and rotation belong to the first type. Clearly vibration belongs to the second type. During a vibrational movement, the nuclear displacements remain small compared to the

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molecular dimensions. The bond lengths and angles take on values which are close to the equilibrium ones. The point representing the $3N$-6 internal coordinates remains in the neighborhood of a minimum of the potential hypersurface. The $3N$-6 internal coordinates may also undergo modifications of larger amplitude and the point representing them may even jump from one minimum of the potential hypersurface to another. If this occurs with a period comparable to the observational time scale, the molecule is said to be nonrigid.

The aim of dynamic stereochemistry is to study molecular nonrigidity. Of particular importance is the knowledge of the pathways leading from one potential minimum to another. These pathways are usually characterized by the barrier height and the coordinates of the saddle points.

From the point of view of molecular nonrigidity, ammonia is an interesting molecule. Fifty years ago, Barker(1) observed the splitting of the vibration transitions and attributed this fact to the tunneling of the nitrogen atom through the plane of the three hydrogens. This type of tunneling is known as molecular inversion and may be described by an operator $\mathscr{I}$ which inverts the positions of the nuclei about the center of mass. It transforms a configuration $A$ into its mirror image $B$. When labels are attributed to the hydrogen atoms, $A$ and $B$ are not superposable by a rotation of the molecule (see Fig. 1). As a result of the tunneling connecting $A$ and $B$ the vibration energy levels occur in pairs. The distance between two pairs is equal to $h\nu_0$, where $\nu_0$ is the vibration frequency. The splitting between the two levels of a pair depends upon the barrier and the mass of the particle undergoing tunneling. By using the WKB method, and starting from the experimental value of this splitting, Dennison and Uhlenbeck(2)

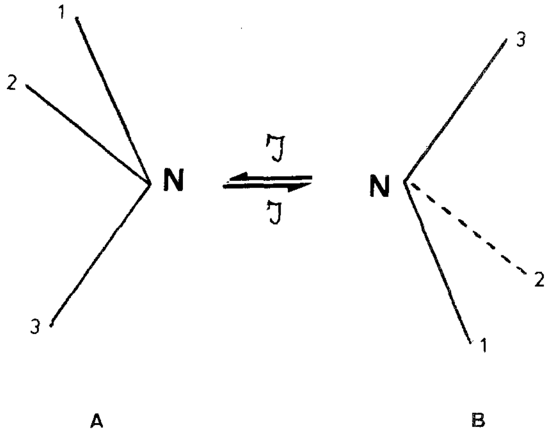

Fig. 1. Inversion represented by the operator $\mathscr{I}$.

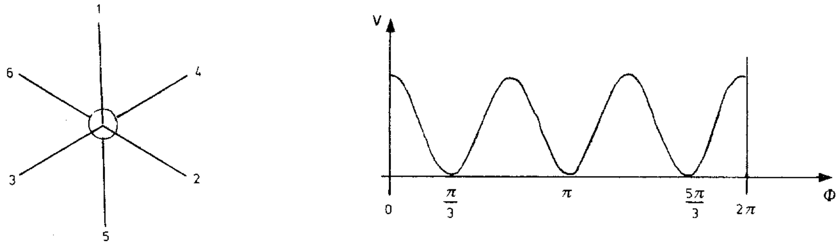

Fig. 2. Hindered internal rotation in ethane.

have computed the distance between the potential minima corresponding to each configuration. Hence, ammonia is not only the simplest nonrigid molecule, but also the first to have been studied from both experimental and theoretical points of view. Detailed reviews concerning the inversion problem may be found in the literature,(3,4) but let us mention that the inversion barrier for $NH_3$ is about 6 kcal/mole.(5,6)

Formally, the operator $\mathcal{I}$ may also be applied to a configuration $A$ of any nonplanar molecule and yield a mirror image $B$ which is nonsuperposable to $A$. However, for many molecules, such as $CH_4$ or $CH_3Cl$, tunneling between the two configurations occurs with a negligible rate, once each $10^9$ years.(7) This figure should be compared to the tunneling frequency of $NH_3$: $2 \times 10^{10}$ cycles per second in the fundamental vibrational state.

Ethane displays another type of nonrigidity, consisting of hindered internal rotation about the carbon–carbon bond. The staggered equilibrium configuration is shown in Fig. 2. The potential energy versus the angle $\phi$ (i.e., the dihedral angle $H_1$–C–C–$H_4$) is also shown in Fig. 2. The internal rotation interconverts three equilibrium configurations corresponding to potential minima instead of two as in the case of inversion. The barrier height is about 3 kcal/mole. This result was first obtained from heat capacity and entropy measurements.(8,9)

Group theory has been widely used to understand the spectroscopic properties of rigid as well as of nonrigid molecules. The determination of the eigenvalues of the molecular Hamiltonian, which is of major importance for the spectroscopist, is indeed considerably simplified when the symmetry of this operator is exploited. In 1924, the vibrations of polyatomic molecules were first studied in connection with symmetry properties.(10) The electronic structure and states of such molecules have been discussed in terms of group theory by Mulliken.(11)

Since these early times, the use of group theory in molecular spectroscopy of rigid molecules has become very popular and classical textbooks deal with these problems (see, for instance, Refs. 12–16). More recently, group theory has been applied to the discussion of spectroscopic properties of nonrigid molecules. In his famous paper of 1963, Longuet-Higgins refers to "the pioneer work of Wilson and his colleagues" in the domain of symmetry properties of nonrigid molecules. The normal vibrations of ethane were investigated by Howard,(17) assuming an internal rotation about the carbon–carbon bond. In its staggered (rigid) equilibrium configuration, the point group of ethane may be written (see Fig. 2):

$$G = A \cup A\sigma \tag{1}$$

where

$$\begin{aligned} A = \{&I, (123)(456), (132)(465), (15)(36)(24),\\ &(14)(26)(35), (16)(25)(34)\} \end{aligned} \tag{2}$$

and

$$\begin{aligned} A\sigma = \{&(15)(26)(34), (142536), (163524), (23)(46),\\ &(12)(56), (13)(45)\} \end{aligned} \tag{3}$$

The group $A$ represents the proper symmetry operations and is isomorphic to $D_3$.(15,16) The permutational symbols[2] appearing in its expression refer respectively to the identity operation ($I$), to the two operations corresponding to the threefold axis ($2C_3$), and to the three twofold axes ($3C_2'$). The set $A\sigma$ is the product of $A$ by any improper symmetry operation $\sigma$. It contains permutational symbols referring respectively to the inversion ($i$), which is a symmetry operation of the centrosymmetric molecule (not to be confused with $\mathscr{I}$, an operator describing the inversion of a centrosymmetric or noncentrosymmetric, nonrigid molecule), to two operations corresponding to the sixfold rotation–reflection axis ($2S_6$), and to the three symmetry planes intersecting along the carbon–carbon bond ($3\sigma_d$). The group $G$ is isomorphic to $D_{3d}$. Taking into account the fact that the total energy of ethane is invariant under a reflection about a plane perpendicular to the molecule axis, Howard(17) used a group isomorphic to $D_{3h}$ (of order 12) instead of $D_3$ in order to derive the spectroscopic properties of ethane. Wilson(18) showed that "the permutations of the hydrogen atoms in ethane which are equivalent to rotations of the molecule (including internal rotation) form a group of 18 operations." Wilson also studied the torsional–rotational levels of $CH_3BF_2$.(19) As may be seen in Fig. 3, this molecule possesses no more than one symmetry plane (when $\varphi = 0$ or $\varphi = \pi/2$) in its

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[2] It is convenient to label independently skeleton sites and ligands. An ordered molecule (OM) is any distribution of the $n$ ligands on the $n$ skeleton sites. A permutational symbol moves the ligands on the fixed skeleton sites: for instance, (123) means that ligand on site 1 replaces ligand on site 2, that ligand on site 2 replaces ligand on site 3, and that ligand on site 3 replaces ligand on site 1. In Figs. 1 and 2 we show reference ordered molecules (ROM), where ligand and site labels coincide.

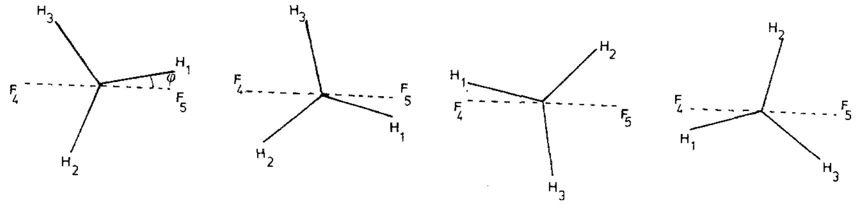

Fig. 3. Four configurations of $CH_3$–$BF_2$.

equilibrium configuration. A given hydrogen atom, say 1, has four quasi-eclipsed positions, when $\varphi \neq 0$ and $\varphi \neq \pi/2$. Hence a group of order 12 (isomorphic to $C_{6v}$) may be used to classify the states of this nonrigid molecule.

These few examples show that some remarkable and intuitive attempts to describe the symmetry properties of nonrigid molecules were elaborated very early. However, the decisive result in this domain is due to Longuet-Higgins, who extended the concept of molecular symmetry group to nonrigid molecules(20): "the symmetry group of such a molecule is the set of (i) all feasible permutations of positions and spins of identical nuclei and (ii) all feasible permutation-inversions, which simultaneously invert the coordinates of all particles in the center of mass."

Longuet-Higgins' paper was the starting point of many very fruitful discussions about the structure of molecular symmetry groups.(21–23) These different approaches have been discussed, compared, and reviewed in more recent publications.(24–26) A new approach was developed by Günthard and coworkers,(27) who introduced the concept of isometric groups and applied it to various situations of physical interest. The reader interested in recent progress in the study of spectroscopic properties of nonrigid molecules may consult the textbook of Bunker.(28)

Until now we have discussed only one of the possible experimental consequences of molecular nonrigidity, namely the spectroscopic modifications in the rotation and vibration domains. However, since the beginning of the 1950's, due to the development of nuclear magnetic resonance, another way of investigating the properties of nonrigid molecules has become available through the observation of the chemical exchange. In 1953, Gutowsky and Saika(29) predicted the possibility to observe chemical exchange and proposed the appropriate modification of the Bloch equations.(30) Three years later, Gutowski and Holm(31) observed a doublet due to a chemical shift between the *cis* and *trans* methyl groups in *N*,*N*-dimethylformamide (see Fig. 4). Due to the internal rotation about the carbon–nitrogen bond, the two components of the doublet coalesce into a single one at higher temperature. This early observation of the chemical

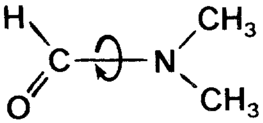

Fig. 4. Hindered rotation in N, N-dimethylformamide.

exchange was the starting point of many very important NMR investigations of nonrigid molecules. The most significant contributions to the experimental and theoretical knowledge in this domain have been reviewed recently.(32) For the present purpose we want to focus on some particular aspects which are closely related to the development of the so-called permutational approach to stereochemistry,(33) i.e., the use of permutation groups in classifying intra- or intermolecular reaction mechanisms. Penta-(34) and hexacoordinate molecules have been widely discussed in this context.

The equilibrium configuration of phosphorus pentafluoride, $PF_5$, has been obtained by electron diffraction.(35) This molecule is of trigonal bipyramidal form with two axial fluorines (on the threefold axis) and three equatorial fluorines (in the plane perpendicular to this axis). The $^{19}F$ NMR spectrum of $PF_5$ showed two components of apparently different intensity. This was attributed to a chemical shift difference between the axial and equatorial fluorines, the intensity ratio being due to the population ratio (2/3) of the axial and equatorial sites.(36) However, improved observations revealed that the two components were in fact of equal intensity and that their splitting was field independent. This is incompatible with a splitting arising from a chemical shift difference, but suggests "that the electron distribution must be very nearly the same about the structurally distinguishable apex (axial) and meridian (equatorial) fluorines in $PF_5$, at least when averaged over the lifetime of NMR states" and that the splitting of the components is due to phosphorus–fluorine coupling.(37)

The first proposal of a mechanism leading to an average between axial and equatorial fluorines was due to Berry.(38) It consists of a simultaneous deformation of the $F_aPF_a$ bond angle from $\pi$ to $2\pi/3$ and of one of the $F_ePF_e$ bond angles from $2\pi/3$ to $\pi$. One of the equatorial fluorines remains unaffected during this movement and is called the pivot (see Fig. 5). For a given configuration, any equatorial fluorine can play the role of the pivot; hence the two axial fluorines can be averaged with any pair of equatorial fluorines and therefore the Berry mechanism is a possible explanation of the observations of Gutowsky *et al.*(37) It explains equally well a similar observation for $Fe(CO)_5$ by $^{13}C$ NMR spectroscopy.(39) It is, however, not the only candidate to achieve complete ligand exchange in trigonal bipyramidal pentacoordinate molecules. Other possibilities have been suggested: exchange between one axial and one equatorial ligand [(*ae*) ex-

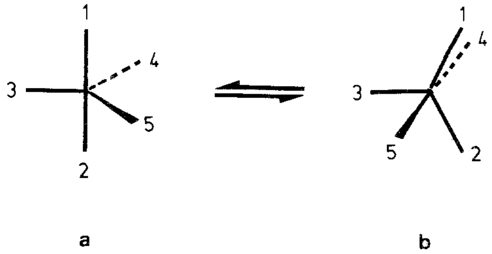

Fig. 5. Berry mechanism ($F_3$ is the pivot).

change],(40) cyclic exchange between one axial and two equatorial ligands [(*aee*) exchange],(40) and also double axial equatorial exchange [(*ae*)(*ae*) exchange].(41,42)

Exchange between two equatorial ligands [(*ee*) exchange](40) has also been proposed, but it does not lead to the observed average between NMR signals of axial and equatorial ligands. Finally, we recall the Turnstile mechanism,(43) which may be described as an (*ae*) exchange and a cyclic (*aee*) exchange occurring simultaneously. It is important to note that this mechanism, although apparently different from the Berry one, generates after one step the same three configurations as the Berry pseudorotation. This illustrates the fact that the number of imaginable mechanisms giving rise to ligand exchange in trigonal bipyramids is practically unlimited, at least if one does not worry about chemical likelihood. However, the total number of configurations $z$ is limited:

$$z = |S_n|/|A| \tag{4}$$

where $S_n$ is the symmetric group of the permutations of $n$ objects of order $|S_n|$. Here $z = 5!/6 = 20$. Hence, by applying once a given mechanism to a starting configuration, one generates one or more of these 20 configurations (including mechanisms that do not interconvert configurations). Therefore, the number of independent mechanisms (i.e., giving rise to different configurations) must be limited: for pentacoordinate complexes of trigonal bipyramidal form and for hexacoordinate octahedra, the permutations of $S_5$ and $S_6$, respectively, have been classified according to their cyclic structure and according to the configuration to which they give rise, starting from an arbitrary given one.(44)

The above considerations should convince the reader that the need for a precise, mathematically founded classification of exchange mechanisms had become apparent by the end of the 1960s. In 1970, Ruch *et al.*,(45) using the well-known group-theoretical concept of double cosets,(46) derived a formula giving the number of isomers for a molecular skeleton of given symmetry with $n$ sites bearing $n_A$ ligands of type $A$, $n_B$ of type $B$, with

$n_A + n_B + \cdots = n$. This formula generalizes Eq. (4) and is equivalent to Polyà's counting formula.(47) The classification theory of intramolecular rearrangements or exchange phenomena can also be expressed in terms of double cosets. It is based on the definition of a mode of rearrangements (see, for instance, Refs. 33, 34, 41, 48). A mode of rearrangements is a set of rearrangement pathways or exchange mechanisms which are indistinguishable because: (a) they are characterized by the same initial and final configurations; (b) they must occur with the same rate constant; (c) they are related by a combination of the two preceding equivalence relations.

The mathematical expressions corresponding to this definition have been worked out by Hässelbarth and Ruch(48) and by Klemperer.(49–54) For instance, it may be shown that the set of permutations

$$M(x) = (AxA) \cup (A\sigma x\sigma^{-1}A) \tag{5}$$

represents(48) a mode of rearrangements, whereas the set

$$F(x) = AxA \tag{6}$$

corresponds to the set of nondifferentiable permutational isomerization reactions(49) in chiral environment. In these expressions, $\cup$ means union and $x$ represents a permutation of the group of allowed permutations (here $S_n$). The sets $AxA$ and $A\sigma x\sigma^{-1}A$ are double cosets whose generators are the permutations $x$ and $\sigma x\sigma^{-1}$, respectively. In the case of pentacoordinate trigonal bipyramids, the group $S_5$ is partitioned into six modes of rearrangements $M(x_i)$. They are listed in Table I, where we also give the generators $x_i$ (see the site labels in Fig. 5a) as well as typical mechanisms for each mode. The connectivity(40) $\delta_i$ is the number of configurations reached in one step of mode $M(x_i)$. For instance, $\delta_1 = 3$ for the mode $M(x_1)$ containing the Berry mechanism, since this mechanism can arise about three pivots. Note also that $\sum_i \delta_i = z$. Indeed, starting from a given configuration, the configurations reached in one step of modes $M(x_i)$ and $M(x_k)$ are different. Finally, any mechanism not listed in Table I will belong to one and only one mode and will be indistinguishable from other

**Table I. Modes of Rearrangement for Trigonal Bipyramids**

| $M(x_i)$ | $x_i$ | Mechanism | $\delta_i$ |
|---|---|---|---|
| $M(x_0)$ | $I$ | Overall rotation | 1 |
| $M(x_1)$ | (1425) | (*aeae*), Berry, Turnstile | 3 |
| $M(x_2)$ | (145) | (*aee*) | 6 |
| $M(x_3)$ | (14) | (*ae*) | 6 |
| $M(x_4)$ | (14)(25) | (*ae*)(*ae*) | 3 |
| $M(x_5)$ | (45) | (*ee*) | 1 |

mechanisms of this mode. For instance, Berry and Turnstile are indistinguishable, at least insofar as we are only concerned with the configurations they generate.

Formulas (5) and (6) are valid when $M(x)$ and $F(x)$ contain the permutation $x^{-1}$. If this is not the case, $M(x)$ and $M(x^{-1})$ [or $F(x)$ and $F(x^{-1})$] are distinct sets and the sets $M(x) \cup M(x^{-1})$ or $F(x) \cup F(x^{-1})$ must be used instead of $M(x)$ and $F(x)$, respectively.(51, 55, 56) Indeed, as a consequence of the principle of detailed balance,(57) the permutations $x$ and $x^{-1}$ represent equiprobable interconversions.

It is now time to discuss some applications of the above classification principles to NMR line shape analysis. We first notice that the group $H$ leaving the effective NMR Hamiltonian invariant is in general different from the point group $G$.(58) The group $G$ is a subgroup of $H$ or is $H$ itself. Hence, the number $z_{\mathrm{NMR}}$ of NMR configurations,(59)

$$z_{\mathrm{NMR}} = |S_n|/|H| \tag{7}$$

is smaller than (or equal to) $z$. There is a one-to-one correspondence between NMR configurations and effective NMR Hamiltonians. Starting from the fact that a reaction detectable by dynamic NMR implies a switch from one effective NMR Hamiltonian to another, Klemperer has defined(60) the set of NMR nondifferentiable reactions:

$$N(x) = HxH$$

It has been shown that each permutation of $N(x)$ gives rise to the same NMR line shape, as calculated from the evolution of the density matrix.(61)

The use of the principle of detailed balance(57) leads to the definition of the so-called NMR mode,

$$M_{\mathrm{NMR}}(x) = (HxH) \cup (Hx^{-1}H) \tag{8}$$

This operator should be used instead of $M(x) \cup M(x^{-1})$ to discuss NMR line shape.(59, 62) Due to the relation between $H$ and $G$, the NMR mode $M_{\mathrm{NMR}}(x)$ contains in general more than one set $M(x_i) \cup M(x_i^{-1})$. For instance, in the case of trigonal bipyramids [where each $M(x_i)$ contains $x_i^{-1}$]

$$\begin{aligned} M_{\mathrm{NMR}}(x_0) &= M(x_0) \cup M(x_5) \\ M_{\mathrm{NMR}}(x_1) &= M(x_1) \cup M(x_4) \\ M_{\mathrm{NMR}}(x_2) &= M(x_2) \cup M(x_3) \end{aligned} \tag{9}$$

so that each NMR mode contains two rearrangement modes. These considerations may be applied to $(CH_3)_2NPF_4$ (see Fig. 6). The dimethylamino group of this molecule remain in equatorial position.(63) Hence, there is a one-to-one correspondence between the isomerization modes of this mole-

Fig. 6. Structure of a substituted fluorophosphorane.

cule and those of $PF_5$ given in Table I (the only difference is that the connectivities are 1, 1, 4, 4, 1, 1 in the present case). In particular, Eqs. (9) remain applicable for a molecule of the structure given in Fig. 6. The $^{31}P$ NMR line shape analysis of $(CH_3)_2NPF_4$ has been performed by Whitesides and Mitchell.$^{(64)}$ Such an analysis consists of a comparison between a set of experimental spectra (observed at different temperatures) and a set of computer-simulated spectra (computed for different values of the exchange rate constant). Each NMR mode gives rise to a set of simulated spectra. The NMR mode leading to the best fit between the experimental set and the simulated set of spectra contains the mechanism responsible for the observed exchange phenomenon. In the case of $(CH_3)_2NPF_4$ the best fit was obtained with $M_{\mathrm{NMR}}(x_1)$,$^{(64)}$ and hence the Berry mechanism is a candidate to explain the observed coalescence, whereas (*ae*) and (*aee*) are not.

It is worthwhile to notice that in the present example computer simulation is not really necessary to discriminate between $M_{\mathrm{NMR}}(x_1)$ and $M_{\mathrm{NMR}}(x_2)$. Indeed, the central line of the slow exchange first-order spectrum of $(CH_3)_2NPF_4$, drawn schematically in Fig. 7, must remain sharp when $M_{\mathrm{NMR}}(x_1)$ is operative, whereas a broadening of this line must occur when $M_{\mathrm{NMR}}(x_2)$ represents the permutational character of the exchange.$^{(65)}$

This example shows the interest of first-order spectra: in such cases, simple examination of the coalescence pattern may lead to the suitable discrimination. Such a simplification has often been exploited in the study of nonrigidity (see, for instance, Refs. 66, 67). The possibility of other applications of this type have been discussed in detail elsewhere.$^{(33,68)}$

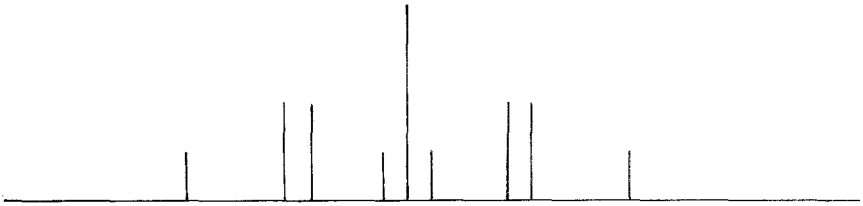

Fig. 7. Slow exchange spectrum of $(CH_3)_2NPF_4$ (schematic).

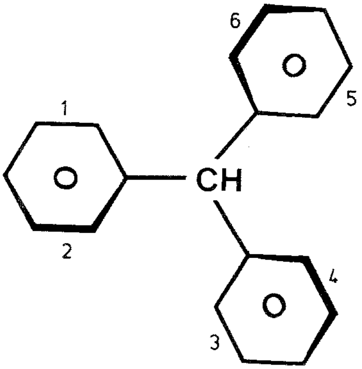

Fig. 8. Propeller conformation of triphenylmethane.

Dynamic nuclear magnetic resonance line shape analysis has also been used in the domain of organic stereochemistry: Mislow and coworkers have published an extremely significant series of papers concerning organic propellers and their stereochemistry. Triarylmethanes, triarylboranes, and tetraarylethanes are examples of such molecules. Their properties have been reviewed in various publications.(69–72) For instance, we discuss triphenylmethane, whose propeller conformation is drawn in Fig. 8.

This molecule possesses a threefold axis along the bond between hydrogen and the central carbon. This carbon lies above the reference plane, i.e., the plane of the three carbon atoms bound to the central one. The three aryl rings are twisted in such a way that the edges 2, 4, 6 lie outside the cone generated by the three carbon–carbon bonds starting from the central carbon atom. The edges 1, 3, 5 lie inside this cone. The helicity of the propeller is due to the fact that the three rings are twisted in the same sense. Change of helicity may occur with passage of the rings through a situation where they are either tangent or normal to the cone. The last case is referred to as the ring flip. For triarylmethanes the observed threshold rearrangement is of the two-ring flip type, i.e., two of the three rings undergo a torsional movement of the flip type. This property has been established by Mislow by using dynamic NMR line shape analysis. The concepts of residual stereoisomerism and stereotopism,(73) introduced by Mislow and coworkers, are useful tools to understand these phenomena. Permutation groups and classification theory have been used extensively by Mislow and coworkers, who have really introduced such descriptions in organic dynamic stereochemistry. They have also studied the so-called stereochemical correspondence defined as "an intrinsic stereochemical similarity between molecular systems which is independent of widely different structural properties."(69,74) For instance, triarylboranes and hexacoordinate trischelates are stereochemically correspondent.(74) The same rela-

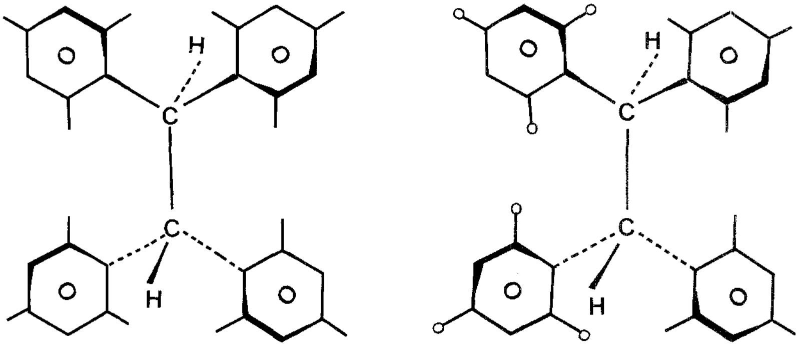

Fig. 9. 1, 1, 2, 2-Tetramesitylethane (left) and 1, 2-dimesityl-1, 2-bis(2, 4, 6-trimethoxyphenyl) ethane (right). Bars on the phenyl rings denote methyl substituents, bars with dots designate methoxy substituents.

tion exists(74) between interconversion of trigonal bipyramidal isomers via the Berry mechanism and 1, 2 shifts of ethyl cations.(75)

One of the most striking features of the work of Mislow is the large amount of information that has been obtained about propellers by combining experimental observations on a given unsubstituted skeleton and on various species differing among each other by their substitution pattern. For instance, the modes of rearrangement of 1, 1, 2, 2-tetramesityl ethane and of 1, 2-dimesityl-1, 2-bis(2, 4, 6-trimethoxyphenyl)ethane have been discussed(71,72) (see Fig. 9) under the assumption that the distortions introduced by the various substitution patterns are small and that there is no interdigitation of the energy levels of pathways belonging to several modes.(72) Such an assumption also underlies the theoretical description of the relation between rearrangement modes of idealized (unsubstituted) and distorted (substituted) skeletons(56,76) and the theoretical description of generalized stereoisomerization modes.(77)

We now come back to the discussion of the influence of nonrigidity on the rotation and/or vibration spectra of polyatomic molecules, since it appears to be related to the classification theory of intramolecular rearrangements. In 1966, Dalton(78) established the relation between the group defined by Longuet-Higgins(20) and the explicit expressions for the approximate energy eigenvectors of a nonrigid molecule. These are formed from linear combination of rigid molecule states based on different configurations. Dalton also established the explicit relation between the configurations reached in one step by a feasible tunneling and the Longuet-Higgins group $Q$: let

$$Rx_1, Rx_2, \ldots, Rx_d \tag{10}$$

represent the $d$ cosets associated to these configurations, where $R$ is the Hougen(79) group, isomorphic to the point group $G$ defined above. Then $Q$ is defined as the set of all distinct products of permutations of the form

$$r_\alpha x_i r_\beta x_k \cdots r_\gamma x_l \tag{11}$$

where $r_\alpha$, $r_\beta$, and $r_\gamma$ represent any element of $R$ and where $x_i$, $x_k$, and $x_l$ are any of the generators $x_1, x_2, \ldots, x_d$. This group allows one to establish the splitting scheme of any rigid molecule symmetry species into the species of the nonrigid molecule. Dalton was also able to obtain formulas giving the statistical weights of the nonrigid molecule levels as well as selection rules between such levels.

These considerations were applied to $SF_4$(78) and $PF_5$(80) under the assumption that both molecules undergo Berry pseudorotation. In the case of $PF_5$, the energies of the nonrigid molecule levels were parametrized, i.e., the energy shifts between a rigid molecule level and the nonrigid levels of the multiplet into which it splits were expressed as multiples of a unique but unknown parameter.

As pointed out by Dalton,(78) the spectroscopic consequences of other mechanisms could also be worked out. The classification theory of rearrangement mechanisms played an important role in this respect. Indeed, the mode of rearrangement given in Eq. (5) defines unambiguously the set of configurations to be used in Dalton's procedure [Eqs. (10) and (11)]. It has been possible to derive in a systematic way(81) the Longuet-Higgins groups from the modes of rearrangement defined in Eq. (5). The argument uses the multiplication table of the modes. This multiplication table(82–84) in the case of $PF_5$ was obtained in 1971 and is probably the first stereochemical application of double coset algebra. It has been used to associate a Longuet-Higgins group to each mode of $PF_5$.(81)

The knowledge of these groups has led to the determination of the splitting schemes, statistical weights, and selection rules for nonrigid molecule levels. It has been shown that, on the basis of these results, the experiment proposed by Dalton would not lead to any discrimination among the modes $M(x_1)$, $M(x_2)$, $M(x_3)$, or $M(x_4)$.(85) However, when the nonrigid molecule energy levels are parametrized, it appears that the theoretical spectra (splitting scheme, statistical weights, selection rules, *and* parametrized levels) are distinguishable.(86) More precisely, $M(x_1)$ and $M(x_4)$ generate theoretical spectra which are different from those obtained from $M(x_2)$ and $M(x_3)$, and the spectra for $M(x_1)$ and $M(x_4)$ are also distinct from each other. It has been suggested that microwave spectroscopy(80) or Doppler-free, high-resolution infrared spectroscopy could be used to detect the predicted effects and to distinguish $M(x_2)$ plus $M(x_3)$ from $M(x_1)$ and $M(x_4)$.(86) To appreciate the interest of such a possibility, we should compare it to the results of NMR line shape analysis. We have already pointed out that $PF_5$ is too fast to allow a detailed line shape analysis, at least at the present time.(37,87) The same is true for $Fe(CO)_5$.(39,88,89) For many slower molecules, NMR line shape analysis leads to the conclusion that $M(x_1)$ *or* $M(x_4)$ is responsible for their nonrigidity,(88,90) but distinction between $M(x_1)$ and $M(x_4)$ is impossible because of the relation between the symmetry group $G$ and the group $H$ leaving the effective spin Hamiltonian invariant.

To conclude, we may say that dynamic stereochemistry appears to be a domain where the use of groups and in particular of permutation groups is especially useful. There exists a strong interaction between the theoretical approach developed by Ruch and Klemperer and experimental investigation in the domain of NMR line shape analysis. An important amount of mechanistic information concerning hypervalent molecules (for instance, penta- and hexacoordinate complexes) has been obtained by combining experimental NMR results and permutational analysis.(32,33)

We think that permutational analysis is also a method which is able to predict the consequences of nonrigidity in rotation and vibration spectroscopy. Unfortunately, at the present time very few experimental results are available concerning discrimination between modes by this type of spectroscopy. Some effort has been made in order to interpret spectroscopic results for $XeF_6$ in terms of tunneling via some rearrangement modes.(91) but for $PF_5$ and related molecules(92) the predicted features have not yet been observed. We hope that the theoretical results will stimulate experimental investigation in this domain.

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