

Correlated Rotation in Complex Triarylmethanes. I. The 32-Isomer System and Residual Diastereoisomerism^{1,2}

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Abstract: A triarylmethane has been prepared with three different aryl groups lacking local C_2 axes. As predicted by an earlier analysis, this compound exists in two diastereomeric forms even when all interconversions by the usual two-ring flip mechanism are rapid (residual diastereoisomerism). The two diastereomers have been separated; the barrier to isomerization is *ca.* 30.5 kcal/mol. The interconversion between the diastereomers is ascribed to the one-ring flip mechanism. A noteworthy feature of this novel type of stereoisomerism, and a consequence of the occurrence of correlated rotation, is that although two separable conformers exist, there are no restrictions upon the torsional angles of the individual aryl rings. Examples of the same phenomenon in molecules of the type Ar_3Z , Ar_2ZX , and Ar_2ZXY are discussed.

In an earlier paper,⁴ we offered an analysis of the conformational statics and dynamics of propeller-like molecules in which two or three aryl groups are bonded to a central atom. More recently, this analysis was applied in the experimental study of some molecules of types Ar_3Z ^{5,6} and Ar_3ZX .⁶⁻⁸ The major conclusion of this body of work was that the two-ring flip is the stereoisomerization mechanism of lowest energy (threshold mechanism) in all systems of this type thus far examined. In addition, for systems where two-ring flip pathways for stereoisomerizations requiring higher energies are available, it was found that these pathways are followed preferentially.

Our original analysis⁴ yielded the conclusion that a more complex molecule of the type Ar_3ZX , containing a chiral center (Z) and three aryl groups (Ar) differing in constitution and lacking local C_2 axes coincident with the bonds to the central atom, exists in 32 stereoisomeric propeller forms. It was then noted that even when interconversions among these forms by the two-ring flip mechanism are rapid, four isomers (two diastereomeric *dl* pairs) still exist, and that interconversion of these four isomers may only be achieved by additional stereoisomerization mechanisms. In the present paper, we report the experimental confirmation of this analysis and discuss some of its implications for stereochemistry. This paper, and the one immediately following⁹ which deals with triarylmethanes of lesser complexity, are both designed to illustrate how the interplay of structure and mechanism in such systems leads to novel stereochemical phenomena.

(1) This work was supported by the National Science Foundation (GP-30257).

(2) A portion of this work has appeared in preliminary form: P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 8172 (1973).

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(4) D. Gust and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 1535 (1973).

(5) J. F. Blount, P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 7019 (1973); J. P. Hummel, D. Gust, and K. Mislow, *ibid.*, in press.

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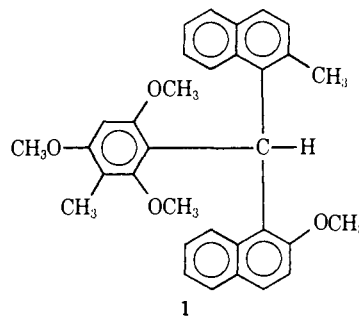
(7) (a) P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, **96**, 2165 (1974); (b) J. D. Andose and K. Mislow, *ibid.*, **96**, 2168 (1974); (c) P. Finocchiaro, D. Gust, and K. Mislow, *ibid.*, **96**, 2176 (1974).

(8) R. J. Boettcher, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 7157 (1973).

(9) P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, **96**, 3205 (1974).

Results

Racemic 1-(2-methoxynaphthyl)-1-(2-methylnaphthyl)-1-(3-methyl-2,4,6-trimethoxyphenyl)methane (**1**) was prepared by condensation of 1-(2-methoxynaphthyl)-1-(2-methylnaphthyl)methanol and 2,4,6-trimethoxytoluene in nitromethane with H_2SO_4 as catalyst (see Experimental Section). The tempera-



ture-dependent 60-MHz 1H nmr spectrum (pyridine, hexamethyldisiloxane as internal reference) of a sample of the purified product (methyl and methoxy region) is shown in Figure 1. At low temperatures (-40°) the spectrum features a plethora of methyl signals, many of which overlap. This result indicates a mixture of numerous stereoisomers on the nmr time scale, as expected in the light of previous results on related but simpler systems.⁷

As the temperature is raised, many of the signals coalesce as a result of rapid stereoisomerizations, and at 87° the spectrum features only nine signals in the methyl and methoxy region. This spectrum is consistent with a mixture of two diastereomers, **1a** and **1b**. The three signals at high field are aromatic methyl resonances. Comparison with similarly substituted compounds⁹ allows us to assign the two lower intensity resonances to the methylnaphthyl methyl groups of diastereomers **1a** (δ 2.24 ppm, solid arrow) and **1b** (δ 2.31 ppm, hollow arrow). The resonances for the *m*-methyl groups of **1a** and **1b** are accidentally isochronous and appear at δ 2.07 ppm. The ratio of the two diastereomers is readily monitored by the measurement of the relative intensities of the two methylnaphthyl methyl resonances. Thus, the ratio of **1a**:**1b** in this sample at 87° was found to be 45:55. We emphasize at this point that this is not an equilibrium mixture of **1a** and **1b** (see below).

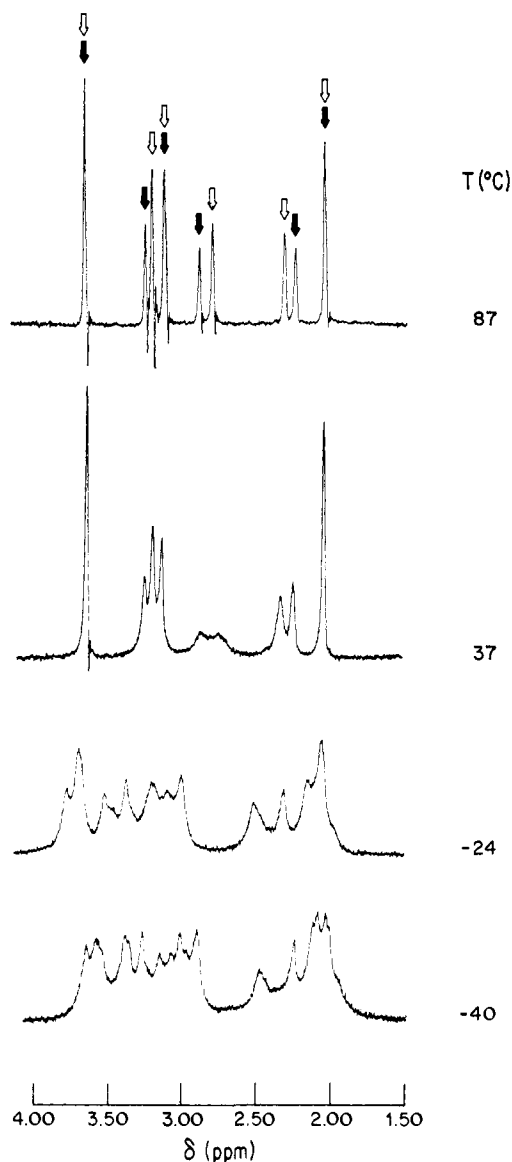


Figure 1. Temperature-dependent 60-MHz ^1H nmr spectrum (methyl and methoxy region) of a 45:55 mixture of **1a** and **1b**, respectively (pyridine, hexamethyldisiloxane as internal reference). The solid arrows indicate resonances due to **1a**; resonances due to **1b** are indicated by hollow arrows.

The methoxy region of the spectrum contains six resonances, whose assignment to individual methoxy groups was not attempted. The resonances of **1a** and **1b** at δ 3.07 and 3.58 ppm are accidentally isochronous, as indicated by the integrated intensities.

Fractional recrystallization of the product mixture yielded a sample of **1a**, mp 210–213°, which was ca. 95% diastereomerically pure (nmr). The 60-MHz ^1H nmr spectrum of this material at 83° in benzene is shown in Figure 2. Comparison of this spectrum with the 87° spectrum in Figure 1 clearly confirms the assignment of resonances for **1a** and **1b** given above, taking into consideration a slight solvent effect on chemical shift. From the mother liquors a fraction, mp 158–163°, was obtained which consisted of a 30:70 mixture of **1a** and **1b**, respectively.

It was found that **1a** and **1b** interconvert upon heating. The rate of isomerization was measured by monitoring the relative intensities of the methylnaphthyl methyl

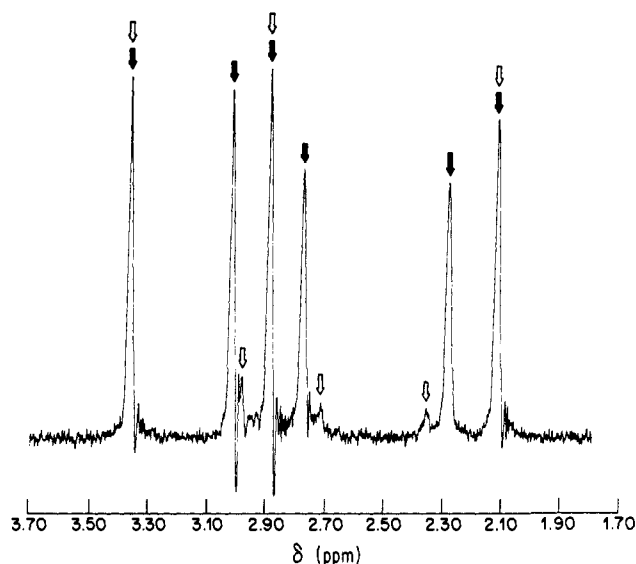


Figure 2. The 60-MHz ^1H nmr spectrum (methyl and methoxy region) of **1a**, ca. 95% diastereomerically enriched (83°, benzene, hexamethyldisiloxane as internal reference). For significance of arrows see Figure 1.

signals as a function of time (Figure 3). The barriers to diastereomerization were found to be $\Delta G^\ddagger_{122} = 30.6$ kcal/mol for **1a** \rightarrow **1b**, and $\Delta G^\ddagger_{122} = 30.4$ kcal/mol for the reverse process, with an equilibrium constant of 0.7 for the reaction **1a** \rightleftharpoons **1b** at 122° (see Experimental Section).

Discussion

Stereochemical Analysis of 1. It was previously shown⁴ that a molecule such as **1** may exist in 32 stereoisomeric propeller forms (16 *dl* pairs), and there are consequently 32 rearrangements¹⁰ which will convert a given isomer of **1** directly into itself or into one of the 31 other isomers. These rearrangements form a mathematical group¹¹ *G* under the operation "fol-

(10) The term "rearrangement" as used here refers only to the net result of the transformation of an initial structure (model of a molecule) to a final structure (model of a molecule). A reaction "mechanism," on the other hand, is a representation of the actual physical changes undergone by a molecule during its transformation from an initial state to a final state. A mechanism has associated with it physical motions, transition states, intermediate structures, and energetics. Thus, a given rearrangement may be realized by a variety of mechanisms, all of which have the net effect of converting a given starting structure to the same final structure.

(11) (a) At several points in this paper we choose to express ourselves in simple set and group theoretical terms, because we feel that such language is capable of providing the clearest, most convenient, and most concise description of the subject. We realize that this approach may in some cases cause a problem in communication, since the use of such terminology is not yet widespread in organic chemistry. For the reader who wishes to learn more about elementary set and group theory, yet who lacks a strong mathematical background, we strongly recommend the highly readable introductory texts by I. Grossman and W. Magnus, "Groups and their Graphs," Random House Inc., New York, N. Y., 1964, and J. A. Green, "Sets and Groups," Routledge and Kegan Paul Ltd., London, 1965. (b) It should be pointed out that this group of order 32 cannot be represented in terms of permutations and inversions on structures such as **1**. For an unsubstituted triphenylmethane the full permutation-inversion group can be expressed as the direct product $S_3[S_2] \times C_1$, where $S_3[S_2]$ is a wreath product of order 48 and can be represented by all permutations of the ortho positions of the three rings which maintain connectivity, and C_1 is a group of order 2 which contains the operation of inversion of all coordinates. The group $S_3[S_2] \times C_1$ can be decomposed into 16 rearrangement modes by forming double cosets of the point group C_2 . Such a result is entirely in agreement with the discussion in this paper using the group $C_2 \times C_2 \times C_2 \times C_2 \times C_2$ and C_2 point-group symmetry. These considerations will be discussed in a future publication. We wish to thank Dr. James G. Nourse for helpful discussions on this subject.

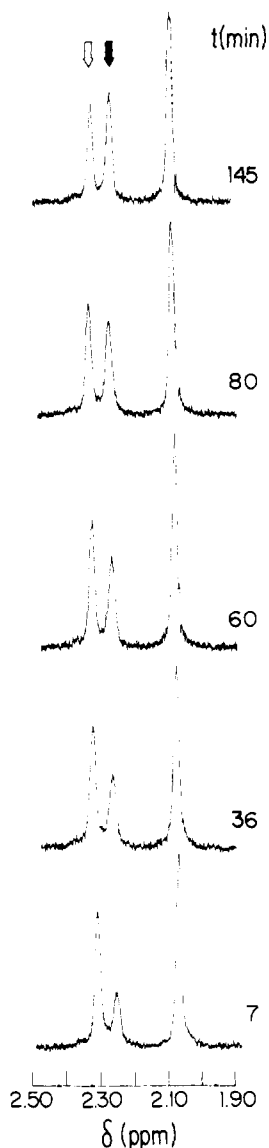


Figure 3. The 60-MHz ^1H nmr spectrum (methyl region) of a 30:70 mixture of **1a** and **1b**, respectively, as a function of time (122° , pyridine, hexamethyldisiloxane as internal reference). The changing ratio of intensities of the two lower field signals reflects diastereomerization. For significance of arrows see Figure 1.

lowed by" which is isomorphic to the abstract group $C_2 \times C_2 \times C_2 \times C_2$. For ease of visualization, these five C_2 subgroups may be associated with five operations of period 2 upon an arbitrary propeller conformation of **1**. These are: rotation of each of the three aryl groups independently by π radians about its bond to the central carbon atom, reversal of the helicity (sense of twist) of the propeller-shaped molecule, and inversion of configuration at the chiral center.

This group of rearrangements **G** may be decomposed into cosets with respect to the subgroup **A** (of index 2 in **G**) of rearrangements which do not involve net inversion at the chiral center, *i.e.*

$$\mathbf{G} = \mathbf{A} \cup i\mathbf{A}$$

where *i* is the rearrangement corresponding to inversion. On the basis of previous work,^{7,12} inversion is not considered to be a feasible rearrangement for **1**

(12) A. Rieker and H. Kessler, *Tetrahedron Lett.*, 1227 (1969).

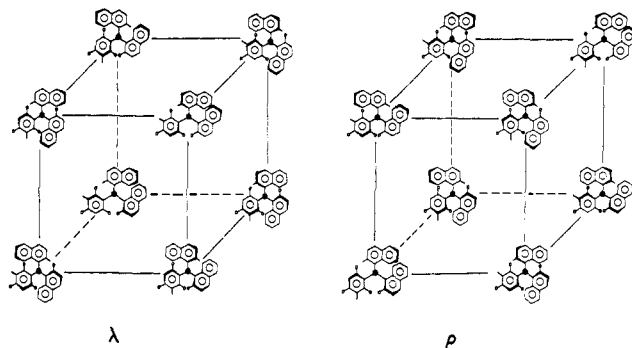


Figure 4. Topological representation of the stereoisomerization pathways for (*R*)-**1** by the two-ring flip mechanism. The enantiomeric set of isomers (having the *S* configuration at the chiral center) and pathways is not shown. The heavy dot in the center of each structure stands for C-H, the small circles denote methoxy groups, and the short lines denote methyl groups. For the meaning of λ and ρ , see text.

under the conditions of the experiment, and therefore we are only concerned with rearrangements belonging to subgroup **A**.

This subgroup may in turn be decomposed into cosets with respect to its subgroup **B** of rearrangements (index 2 in **A**) which do not involve a net reversal of helicity, *i.e.*

$$\mathbf{A} = \mathbf{B} \cup h\mathbf{B}$$

where *h* is the rearrangement corresponding to a net helicity change (net reversal of the sense of twist of the propeller-shaped molecule). Both experimental results^{5,7a,c,13-15} and empirical force field calculations^{7b} indicate that the energetically favored rearrangements of Ar_3Z and Ar_3ZX molecules involve a net reversal of helicity. Thus, we need concern ourselves only with coset $h\mathbf{B}$.

Coset $h\mathbf{B}$ consists of eight rearrangements. These eight rearrangements may be realized mechanistically in terms of the four classes of flip mechanisms (corresponding to four rearrangement modes), *i.e.*, the zero-, one-, two-, and three-ring flips.⁴ As was pointed out above, the two-ring flip is the mechanism of lowest energy for stereoisomerizations of triarylmethanes. The interconversions of the propeller conformations of **1** by this mechanism are presented topologically¹⁶ in Figure 4; only the set of 16 isomers having the *R* configuration at the chiral center is shown. These 16 propeller forms are grouped into two sets of eight each, as depicted in the two cubes. The propeller conformations are shown at the corners of the cubes, and the edges connecting these structures represent stereoisomerization pathways by the two-ring flip mechanisms. Thus, the cube on the left, for example, stands for a set (λ) of eight propeller conformations and the 12 associated interconversion pathways. The second set of eight isomers and 12 interconversion pathways (set ρ) is represented by the cube on the right in Figure 4.

(13) (a) J. S. Hyde, R. Breslow, and C. deBoer, *J. Amer. Chem. Soc.*, **88**, 4763 (1966); (b) L. D. Kispert, J. S. Hyde, C. De Boer, D. LaFollette, and R. Breslow, *J. Phys. Chem.*, **72**, 4276 (1968).

(14) J. W. Rakshys, Jr., S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, **93**, 6522 (1971).

(15) D. Hellwinkel, M. Melan, and C. R. Degel, *Tetrahedron*, **29**, 1895 (1973).

(16) The particular image used here is arbitrary and is chosen only for convenience and clarity. Other representations which maintain the connectivity are equally valid.

Similarly, the 16 isomers of the *S* configuration at the chiral center and their associated rearrangements may be partitioned into two sets, λ and $\bar{\rho}$ (not shown in Figure 4), which are enantiomeric to λ and ρ , respectively.

It was previously reported^{7c} that the flipping of the two mesityl (or 2,6-xylyl) groups in trimesitylmethane and related molecules requires an activation energy of *ca.* 22 kcal/mol, and that replacement of some or all of the *o*-methyl groups by methoxy or benzo groups lowers this barrier. Consequently, since all the aryl groups of **1** are sterically less demanding than mesityl, stereoisomerizations of **1** by the two-ring flip mechanism necessarily occur rapidly at ambient temperatures. This conclusion is borne out by the ¹H nmr spectrum of **1** (Figure 1). At 87°, this spectrum is consistent with rapid stereoisomerizations by the two-ring flip since, as was pointed out above, only two diastereomeric forms of **1** are manifest. If slow stereoisomerization by two-ring flip pathways were to result in the presence of more than two diastereomers, this fact would presumably be indicated by the appearance of other resonance lines; such lines do indeed appear at lower temperatures (Figure 1).

According to our analysis even when stereoisomerizations of **1** by the two-ring flip mechanism are rapid, **1** should still exist as a mixture of two noninterconverting diastereomeric conformers. Stereoisomerization by two-ring flips is indeed rapid at ambient temperatures and it is therefore apparent that **1a** and **1b** are, in fact, these two conformers. Thus, diastereomer **1a** may be associated with one of the sets, λ or ρ , together with its enantiomer ($\bar{\lambda}$ or $\bar{\rho}$). Similarly, **1b** may be associated with the other set, together with its enantiomer. No attempt has been made to identify a given diastereomer with a particular set. In other words, a given racemic diastereomer, **1a** or **1b**, consists of 16 component forms which may be described by two enantiomeric sets (λ and $\bar{\lambda}$, or ρ and $\bar{\rho}$), each of which represents a rapidly interconverting equilibrium mixture of eight propeller structures.

In order to interconvert **1a** and **1b**, a pathway connecting the two cubes λ and ρ must be traversed. Such a pathway cannot, of course, be a two-ring flip. This accounts for the fact that the barrier for interconversion of **1a** and **1b** is as high as 31 kcal/mol, whereas the highest two-ring flip barrier in this system is less than *ca.* 22 kcal/mol, as explained above. In principle, such stereoisomerization could occur by either a one- or three-ring flip mechanism.⁴ Empirical force field calculations for trimesitylmethane^{7b} have yielded rough estimates of energy barriers of *ca.* 80, 47, and 31 kcal/mol for the three-, one-, and two-ring flip mechanisms, respectively. Although we have no experimental basis for distinguishing between the one- and three-ring flip mechanisms for the interconversion of **1a** and **1b**, the trend of these calculations allows us to conclude that the mechanism in question is the one-ring flip.¹⁷

Residual Stereoisomerism. The preceding discus-

(17) The calculated^{7b} barrier (47 kcal/mol) for the one-ring flip of trimesitylmethane is considerably higher than that found experimentally for **1** (31 kcal/mol). This is to be expected, however, since **1** is less sterically congested about the central atom than trimesitylmethane. In addition, refined calculations^{7b} for the two-ring flip of trimesitylmethane have yielded a barrier of *ca.* 20 kcal/mol, compared to the experimentally found^{7a} barrier of 22 kcal/mol. Similar refinements for the one-ring flip might therefore be expected also to yield a lower calculated barrier.

sion quite naturally leads to the question: how is one to describe stereoisomerism of the type encountered in the present work? We propose the following. Let **C** represent the set of stereoisomers which exist for a given molecule when all isomerizations are frozen out. Now, when any given set of stereoisomerizations **M** is allowed to occur, a new set of stereoisomers, **C'**, results. Each element of **C'** consists either of a single stereoisomer from **C** (when it is unaffected by the isomerization in question) or of a rapidly interconverting mixture of two or more stereoisomers from **C**. If **C'** contains more than one element, we will say that the system exhibits *residual stereoisomerism* under the set of isomerizations **M**. For example, since the 16 conformers of (*R*)-**1** which exist in the absence of all isomerizations are reduced to two isomers, (*R*)-**1a** and (*R*)-**1b**, when all two-ring flip interconversions are rapid, (*R*)-**1** is said to exhibit residual stereoisomerism under the two-ring flip mechanism. On the other hand, residual stereoisomerism in this example disappears at elevated temperatures when interconversion between (*R*)-**1a** and (*R*)-**1b** by the one-ring flip is rapid, and only one isomer ((*R*)-**1**) obtains. "Isomerism," in this as in all other cases, is a concept which is tied to the time scale of observation.

The idea of residual stereoisomerism is particularly useful when the set of allowed isomerizations corresponds to a particular rearrangement, rearrangement mode, or set of rearrangement modes, since the occurrence of residual isomerism is then related to the logical partitioning of rearrangements according to skeletal symmetry.¹⁸ In such a case, the set of allowed rearrangements **M** may be used to partition **C** into equivalence classes, each of which corresponds to an element of **C'**.

The use of the term "residual stereoisomerism" leads naturally to similar terms such as "residual diastereoisomerism," "residual enantiomerism," "residual diastereotopicity," etc. The meaning of these designations follows directly from the above discussion. For example, even when interconversion of all conformational diastereomers of **1** by the one- and two-ring flips is rapid, **1** still exhibits residual enantiomerism under the flip mechanisms, since inversion at the chiral center is necessary to interconvert (*R*)-**1** and (*S*)-**1**.

Correlated Rotation and Conformational Isomerism. Conformers are usually defined in terms of the allowed torsional angles about certain bonds. Thus, Klyne and Prelog, for example, state that "The partial conformation of two bonded atoms (X, Y) with all their substituents across the bond (X-Y) may be defined in terms of the *torsion angle between the two most preferred substituents* (one on each atom)."¹⁹ These authors go on to suggest that if this angle is not known exactly, conformers may be described by placing limits upon the allowed torsional angles (syn-periplanar, antiperiplanar, etc.).

The above definition is perfectly adequate for describing the propeller structures at the corners of each cube in Figure 4. However, careful examination of the two diastereomeric sets λ and ρ reveals that when stereoisomerization by the two-ring flip mechanism

(18) (a) E. Ruch, W. Hässelbarth, and B. Richter, *Theor. Chim. Acta*, 19, 288 (1970); (b) E. Ruch and W. Hässelbarth, *ibid.*, 29, 259 (1973).

(19) W. Klyne and V. Prelog, *Experientia*, 16, 521 (1960).

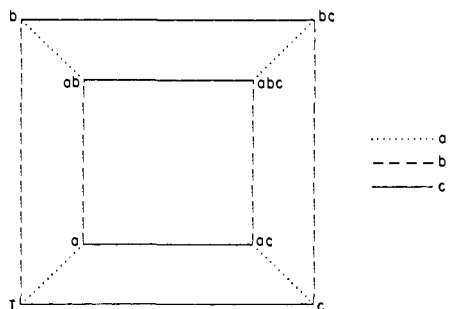


Figure 5. Cayley diagram for the abstract group $C_2 \times C_2 \times C_2$. Vertices represent group elements, and the three types of edges (dotted, dashed, solid) represent the three generators.

is rapid, the two sets cannot be differentiated using this conventional definition, *i.e.*, there are no restrictions upon the individual torsional angles about any of the bonds to the central carbon atom in **1a** and **1b**. Unlike the case of a hindered biaryl, for example, where rotation by 2π radians about the central bond results in interconversion of all stereoisomers, each of the three aryl groups in **1a** and **1b** may rotate by multiples of π radians in the course of the two-ring flips without achieving interconversion of **1a** and **1b**. Instead, the two diastereomers are differentiated by restrictions upon the relationships of the three torsional angles in question, rather than upon their absolute values. In other words, although all three aryl groups in **1a** and **1b** are rapidly spinning (even on the nmr time scale) about their bonds to the central atom during the two-ring flips, the conformations of a given molecule of **1a** and a given molecule of **1b** are never the same. Rapid rotation about the bonds to the central atom is allowed, but the groups are constrained to rotate in a correlated fashion. Thus, the key to the occurrence of this novel type of isomerism is *correlated rotation*.

To our knowledge, the present work provides the first example of the separation of stable stereoisomers in a triaryl system of the type Ar_3ZX . It is important to note that the high barrier to interconversion of **1a** and **1b** depends primarily upon the mechanistic restriction described above, and only secondarily on the degree of steric congestion about the central atom. The interconversion of **1a** and **1b** is due to a one-ring flip, whereas all previously observed diastereomerizations in such systems have occurred by the two-ring flip.

When one considers the propeller conformations in one of the diastereomeric sets, *e.g.*, λ , one may be tempted to look for a *single* unifying structural feature which distinguishes these eight conformations from the eight others in set ρ , *i.e.*, it is tempting to try to discover the singular "difference" between isomers **1a** and **1b**. For example, the methylnaphthyl methyl group of a given propeller structure may be either proximal or distal to the methine hydrogen, and the aryl ring as a whole may be twisted about its bond to the central carbon atom in either a right- or left-handed sense. Similar constraints may be placed upon the other two aryl rings. If one now arbitrarily chooses a conformation from λ , one might see, for example, that the methylnaphthyl methyl group is proximal to the methine hydrogen. However, conformations also exist in ρ which exhibit this feature. In general, one consequence of the fact that there are no restrictions upon the individual

torsional angles of the aryl groups of **1a** and **1b** is that no single structural feature of this type exists which will allow of a differentiation between λ and ρ .

If we seek combinations of two or three such structural features which are unique to one set, our attempts will still be frustrated. Actually, a combination of *four* structural descriptors (proximal *vs.* distal, for each ring, plus sense of twist) is necessary to assign a particular propeller structure to either λ or ρ , given the *R* configuration at the chiral center. However, specification of these four descriptors is tantamount to constructing the structure itself and comparing it with Figure 4. Thus, one is reduced to requiring *all* the information concerning constraints on torsional angles inherent in the eight structures in λ in order to differentiate λ from ρ . This remains true even though alternative descriptions of the relationship of torsional angles in these structures are conceivable (see below).²⁰ The complexity of the isomerism of **1a** and **1b** thus renders it difficult to grasp the essential difference between the two isomers in a straightforward, intuitive way.

Alternative Descriptions of Isomerism in 1. Although isomer **1a** or **1b** may be completely described for our purposes by the appropriate cube diagram, alternative descriptions are conceivable.

One such description hinges upon the concept of a mathematical group of rearrangements. For example, consider any one propeller structure in λ . There exist eight rearrangements¹⁰ which will convert this reference structure directly into itself, and into the seven other isomers within λ . These eight rearrangements form a group under the operation "followed by," and therefore the result (product) of any rearrangement followed by any other rearrangement is itself one of the eight rearrangements. This group of rearrangements is isomorphic to the abstract group $C_2 \times C_2 \times C_2$. There are several ways to define this group. For instance, the group multiplication table could be delineated, the generators and defining relations could be enumerated, or the graph of the group could be constructed. We have found the description of the group by means of its graph (Cayley diagram) to be the most useful representation for our purposes.

A graph of the abstract group $C_2 \times C_2 \times C_2$ is shown in Figure 5. The eight vertices represent the eight group elements, and the edges (dotted, dashed, and solid) represent the three generators of the group (*a*, *b*, and *c*, respectively), *i.e.*, the set of group elements which, in combination, are capable of generating the entire group. Thus, the eight group elements are *I* (identity), *a*, *b*, *c*, *ab*, *ac*, *bc*, and *abc*, as shown in Figure 5.

The graph in Figure 5 is the Cayley diagram of the group of rearrangements discussed above if we identify

(20) It is possible to derive a single rule (*e.g.*, a parity rule which associates a parity change with each element of isomerism, and thus permits assignment of a structure to either λ or ρ on the basis of parity) which will allow one to differentiate λ from ρ . For example, each descriptor might be given the value +1 or -1 for some reference isomer, and the product of the four descriptors of each isomer in λ would then be of the same sign (either +1 or -1), and opposite in sign to the corresponding product in ρ . Alternatively each descriptor might be given the value 0 or 1 for some reference isomer, and the arithmetic sum of the four descriptors of each isomer in λ would then be of the same parity (even or odd), and opposite to that of the corresponding sum in ρ . However, any such rule must still include all the information on the relationships of torsional angles implied by the eight structures in λ (or ρ).

the eight vertices (I, a, b, \dots) with the eight rearrangements, and the three generators with, for example, the three rearrangements which correspond to the three two-ring flips of a propeller structure. The assignment of a particular two-ring flip to a particular generator a, b , or c is completely arbitrary. For example, we might choose to associate rearrangement a with the flipping of the methylnaphthyl and methoxynaphthyl groups, b with the flipping of the methylnaphthyl and methyltrimethoxyphenyl groups, and c with the flipping of the methoxynaphthyl and methyltrimethoxyphenyl groups.

Let us now associate a reference structure (propeller conformation) from λ with the identity rearrangement I . The choice of the reference structure is also entirely arbitrary; any one of the eight structures in λ will do equally well since the Cayley diagram (Figure 5) accommodates any choice. This reference structure together with the Cayley diagram of the group of rearrangements completely and unambiguously describes the isomers and their interconversions represented by cube λ . This is easily understood when we recognize that it is possible to perform a one-to-one mapping of the eight structures in cube λ onto the eight rearrangements (I, a, b, \dots), and of the two-ring flip interconversions (represented by the edges of the cube λ) onto the generators of the group (edges of the Cayley diagram). This accounts for the fact that the Cayley diagram and the cube λ are topologically equivalent (isomorphic).²¹

Alternatively, we may choose a reference structure from ρ and associate it with the identity rearrangement. In this case, the Cayley diagram together with this reference structure completely describes the isomers and interconversions represented by ρ .

Correlated Rotation in Other Systems. One of the key features of isomerism in **1** is that two residual diastereomers exist even when there are no restrictions upon the individual torsional angles of the aryl groups. As was pointed out, correlated rotation is a necessary condition for the observation of this phenomenon. However, it is not a sufficient condition. For example, all of the flip mechanisms involve correlated rotations of the aryl groups, and if only three-ring flip pathways for **1** were being traversed rapidly, eight diastereomeric *dl* pairs would result. However, in contrast to the situation described above for rapid two-ring flips, there would be definite restrictions upon the individual torsional angles of the aryl groups in these diastereomers.

(21) There are numerous other realizations in stereochemistry of the abstract group $C_2 \times C_2 \times C_2$. Three examples are: the group of conformational rearrangements of a molecule of the type Ar_2ZX , such as a diaryl ketone,²² the group of rearrangements of a spirocyclic phosphorane,²² and the group of rearrangements by inversion in a molecule with three chiral centers, such as 2-chloro-3-bromo-5-iodo-*n*-heptane. In this last case, each C_2 subgroup can be thought of as inversion at one of the three chiral centers. The Cayley diagrams for all of these groups of rearrangements are isomorphic to that in Figure 5. However, the first two systems are stereochemically correspondent,^{6,22} *i.e.*, the static as well as dynamic stereochemical features of both systems may be represented by the same abstract model system (an idealized two-bladed propeller). The heptane, on the other hand, is not stereochemically correspondent to the other two systems for, whereas the model^{18b} structures of the rearrangements of Ar_2ZX and the spirocyclic molecule are the same, the mode structure of the rearrangements of the heptane is entirely different. In short, the heptane lacks the symmetry of the two-bladed propeller.⁶ Thus, isomorphic group structure is not a sufficient condition for stereochemical correspondence.

(22) D. Gust, P. Finocchiaro, and K. Mislow, *Proc. Nat. Acad. Sci. U. S.*, **70**, 3445 (1973).

On the other hand, when bis(2,6-xylyl)-1-(2-methylnaphthyl)methane,^{7c} for example, isomerizes rapidly by all possible two-ring flip pathways, although there is no restriction upon the individual torsional angles of the aryl groups, all stereoisomers in this case are interconverted by these flips, and thus there will be no residual stereoisomerism. We conclude that the occurrence of isomerism in the absence of restrictions upon individual torsional angles depends not only upon correlated rotation, but also upon structural factors and substitution patterns. We have already stressed the importance of the substitution pattern with regard to isomerism in **1**. In the following, some other situations will be discussed in which such residual stereoisomerism among conformers may also occur.

If isomerizations of a molecule such as **1** occur rapidly by the one-ring, but not by the two-ring flip mechanism, two diastereomers will still result, and there will also be no restrictions upon torsional angles of individual aryl groups.

Any molecule which is stereochemically correspondent to **1** (*e.g.*, a properly substituted seven-coordinate transition metal tris-chelate complex whose molecular skeleton assumed a C_3 propeller conformation) can in principle exhibit behavior paralleling that described for **1** above.

As was previously shown,^{4,23} a similar situation (*i.e.*, isomerism arising in the absence of restrictions on individual torsional angles) exists in principle in molecules of the type Ar_3Z when all three aryl groups are different, and when these groups lack local C_2 axes coincident with the bonds to the central atom. There are 16 propeller isomers possible for such a molecule, and consequently 16 rearrangements. These rearrangements form a group isomorphic to the abstract group $D_2 \times D_2$ under the operation "followed by." As in the case of molecules of type Ar_2ZX , when stereoisomerization by the two-ring flip mechanism is rapid on the time scale of observation, two residual diastereomers exist, and, granting reversal of helicity in each rearrangement, these isomers can only be interconverted by a one- or three-ring flip. Since the two-ring flip has been found to be the threshold mechanism for triarylcarbenium ions,¹⁴ triarylamines,¹⁵ and triarylboranes,⁵ the detection of such residual diastereomers in these and related Ar_3Z systems should be experimentally realizable.

The stereochemically correspondent (suitably substituted) tris-chelate system^{4,6} is also in principle capable of demonstrating this type of residual stereoisomerism (although, of course, the interconversion mechanisms would not be rotational in nature). However, the actual observation of this phenomenon requires that the isomerization mechanism corresponding to the two-ring flip be of lowest energy. If the threshold mechanism corresponded instead to the one-ring flip, two isomers should also be isolable when interconversions by this mechanism are all rapid. In this event, however, the residual isomers would be enantiomers, rather than diastereomers.⁴ However, in many tris-chelates, the mechanism of lowest energy not involving bond rupture (*i.e.*, the trigonal twist)²⁴ corresponds

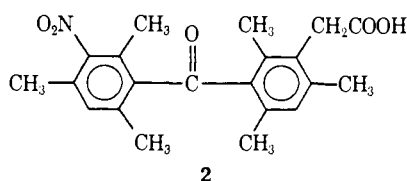
(23) F. Strobusch, *Tetrahedron*, **28**, 1915 (1972).

(24) See, for example, L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, **93**, 360 (1971); S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *ibid.*, **94**, 6411 (1972).

to the three-ring flip. Thus, the possibility of observing isomerization in such systems analogous to that found for **1** appears unlikely, at present.

In diaryl molecules of type Ar_2ZX where the aryl groups differ constitutionally and lack local C_2 axes a related phenomenon is conceivable.⁴ Eight propeller-like stereoisomers (four *dl* pairs) are possible for this system. When interconversion of diastereomers by all eight one-ring flip pathways is rapid on the time scale of observation, there is no restriction upon the individual torsional angles of the aryl groups. However, enantiomerization by the one-ring flip mechanism alone is impossible.²⁵ This is seen to be an example of residual enantiomerism resulting from constraints due to correlated rotation.²⁶

Allen and Moir²⁷ recognized some time ago that enantiomerization in such a system by a "concerted rotation" mechanism corresponding to the one-ring flip is impossible, but the significance of this early observation seems not to have been fully appreciated. For example, Narayanan, *et al.*,²⁸ reported the resolution and optical rotation of ketone **2**. This claim was



disputed by Lauer and Staab,²⁹ who, having found no evidence for restricted rotation in dimesityl ketone and 3,5-dinitro-2,4,6,2',4',6'-hexamethylbenzophenone (**3**) on the nmr time scale, even down to -90° , argued that since **2** is not appreciably more sterically encumbered than these molecules, the barrier to enantiomerization in **2** could not possibly be high enough to permit resolution at ambient temperatures. However, if we examine this problem in the light of the previous analysis,^{4,25} it is apparent that the substitution patterns of dimesityl ketone and **3** are such that in both molecules the aryl groups have local C_2 axes, and thus enantiomerization may occur by the one-ring flip mechanism (which has been calculated to be the threshold mechanism for such ketones).³⁰ In contradistinction, enantiomerization of **2** requires a two- or zero-ring flip in addition to the one-ring flip interconversions. It follows that the claim of Narayanan, *et al.*,²⁸ cannot be refuted solely on the basis of arguments²⁹ derived from studies of dimesityl ketone and **3**.

A final example of conformational isomerism in the absence of restrictions upon individual torsional angles occurs in molecules of type Ar_2ZXY , where the aryl groups differ and lack local C_2 axes. Such molecules

(25) This discussion may be more easily visualized by reference to Figure 10, ref 4.

(26) A similar situation would, in principle, arise in the stereochemically correspondent spirophosphoranes and related systems.^{6,22} However, the threshold mechanisms in the two systems are in general not correspondent (one-ring flip for Ar_2ZX ;²² mode M_1 (e.g., Berry pseudorotation) for the spirophosphoranes).²²

(27) M. Allen and R. Y. Moir, *Can. J. Chem.*, **37**, 1799 (1959).

(28) K. V. Narayanan, R. Selvarajan, and S. Swaminathan, *J. Chem. Soc. C*, 540 (1968).

(29) D. Lauer and H. A. Staab, *Chem. Ber.*, **102**, 1631 (1969).

(30) Crude empirical force field calculations for 2,6,2',6'-tetramethylbenzophenone have yielded energy barriers of ca. 2 and 15 kcal/mol for the idealized one- and two-ring flips, respectively (P. Finocchiaro, unpublished results).

are similar to those of type Ar_2ZX discussed above, except for the additional presence of a chiral center. Thus, when isomerization of such molecules by the one-ring flip pathways is rapid, there are no restrictions upon individual torsional angles, but two residual diastereomers (two *dl* pairs) still result.⁴ When the two aryl groups in an Ar_2ZXY system lack local C_2 axes but do not differ in constitution, the element of central chirality is eliminated, but there still remain eight stereoisomers (four *dl* pairs) which can be partitioned into two enantiomeric sets of four diastereomers each. Although interconversion among isomers within a set may occur by the one-ring flip, interconversion between the sets is possible only by zero- or two-ring flips, and residual enantiomerism thus results. Akkerman, *et al.*,³¹ obtained several such diarylacetic acids in optically active form and measured the barriers to enantiomerization by the two-ring flip. If all one-ring flip pathways in these systems are of lower energy than the two-ring flips, these systems exhibit residual enantiomerism of the type discussed above.

Experimental Section³²

(*dl*)-1-(2-Methoxynaphthyl)-1-(2-methylnaphthyl)methanol. A solution of 1-bromo-2-methylnaphthalene (11.2 g, 50 mmol) in 100 ml of anhydrous ether was treated with *n*-butyllithium (50 mmol, 1.9 *M* in hexane). After 30 min, 2-methoxy-1-naphthaldehyde (9.5 g, 50 mmol), dissolved in 150 ml of benzene, was added dropwise to the solution of the organolithium compound, with stirring at room temperature. After 35 min the mixture was poured onto crushed ice and the organic layer was diluted with chloroform, separated, and dried ($MgSO_4$). The solvent was distilled at reduced pressure, and the crude white solid obtained was recrystallized from a mixture of 60–80° petroleum ether–acetone (80:20) to yield 6.0 g (36%) of white plates; mp 122–123°; 1H nmr $\delta_{CDCl_3}^{TMS}$ 2.25 (2 H, s, CH_3), 3.77 (3 H, s, OCH_3), 4.95 (1 H, d, $^3J_{HH} = 6.6$ Hz, OH), 7.08 to 7.73 (12 H, m, aromatic H plus CH) and 8.46 (1 H, m, aromatic H). Mass spectral analysis was consistent with the assigned structure; exact mass, 328.146143 (calcd, 328.146331).

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.13; H, 6.28.

(*dl*)-1-(2-Methoxynaphthyl)-1-(2-methylnaphthyl)-1-(3-methyl-2,4,6-trimethoxyphenyl)methane (**1**). To a mixture of 1-(2-methoxynaphthyl)-1-(2-methylnaphthyl)methanol (10.0 g, 30 mmol) and 2,4,6-trimethoxytoluene (20 g, 175 mmol) dissolved in 200 ml of nitromethane was added 6 drops of concentrated H_2SO_4 . After 15 min the red solution was poured onto water, the organic layer was extracted with chloroform and dried ($MgSO_4$), and the solvent was distilled at reduced pressure. Addition of a 50:50 mixture of acetone–methanol resulted in the precipitation of a pale yellow solid (4.0 g, 27% yield), mp ca. 160–195°. Tlc analysis of this material, with a 50:50 mixture of $CHCl_3$ and hexane as eluent, showed only a single spot. The 1H nmr spectrum of this material was consistent with the assigned structure and featured absorptions (in benzene- d_6 with hexamethyldisiloxane as internal reference) at δ 2.09 (3 H, s, CH_3), 2.26, 2.33 (3 H, singlets, CH_3), 2.64, 2.81, 2.88 (9 H, br singlets, OCH_3), 3.23 (3 H, s, OCH_3), 5.90, 5.97 (1 H, br singlets, aromatic H), 6.97 (7 H, m, aromatic H plus CH), 7.50 (5 H, m, aromatic H), and 8.15 (1 H, m, aromatic H). This spectrum represents a ca. 60:40 mixture of diastereomers **1a** and **1b**, respectively (see below and text). A direct estimate of the relative proportions of **1a** and **1b** in the crude red oil obtained from the reaction mixture was not possible because this material was contaminated with

(31) O. S. Akkerman and J. Coops, *Recl. Trav. Chim. Pays-Bas*, **86**, 755 (1967); O. S. Akkerman, *ibid.*, **89**, 673 (1970).

(32) Elemental analyses were performed by Schwarzkopf Micro-analytical Laboratories, Woodside, N. Y. Unless specified otherwise, nmr spectra were recorded on a Varian A-60A spectrometer at ambient temperature (ca. 37°) and refer to ca. 20% solutions in $CDCl_3$ containing tetramethylsilane (TMS) as internal reference. Mass spectra were obtained on a AEI MS-9 high-resolution mass spectrometer, with an ionizing voltage of 70 eV. All reactions which involved the use of organometallic compounds as reagents were carried out under a dry high-purity nitrogen atmosphere. Melting points were measured in a Thomas-Hoover apparatus and are corrected.

unreacted starting materials; on the other hand, although addition of acetone-methanol allowed removal of the unreacted materials, a certain amount of fractionation occurred. Attempts to purify this red oil by column chromatography were unsuccessful: both the unreacted materials and the product were eluted at nearly the same rate.

Several recrystallizations of the material with mp 165–190° from benzene gave an analytical sample of **1a** (ca. 95% diastereomerically enriched), mp 210–213° (1.0 g, 25% yield). The ¹H nmr spectrum in benzene-*d*₆ (hexamethyldisiloxane as internal reference) featured resonances at δ 2.08 (3 H, s, CH₃), 2.25 (3 H, br s, CH₃), 2.60 (3 H, br s, OCH₃), 2.78, 2.90 (6 H, br singlets, OCH₃), 3.22 (3 H, s, OCH₃), 5.97 (1 H, s, aromatic H), 6.98 (7 H, m, aromatic H plus CH), 7.50 (5 H, m, aromatic H), and 8.15 (1 H, m, aromatic H). Mass spectral analysis was consistent with the assigned structure; exact mass, 492.230345 (calcd, 492.230045).

Anal. Calcd for C₃₃H₃₂O₄: C, 80.46; H, 6.55. Found: C, 80.50; H, 6.69.

The mother liquors deriving from the recrystallizations of **1a** were combined and recrystallized several times to yield a fraction with mp 199–207°, which showed a ratio **1a**:**1b** of ca. 80:20, by nmr analysis. Exact mass, 492.229881 (calcd, 492.230045). The fragmentation pattern was superimposable with that obtained for **1a**.

Anal. Calcd for C₃₃H₃₂O₄: C, 80.46; H, 6.55. Found: C, 80.23; H, 6.50.

Further recrystallizations of the mother liquors yielded a fraction, mp 158–163°, in which the ratio **1a**:**1b** was ca. 30:70, as determined by nmr analysis. Further enrichment of **1b** in this fraction was not attempted. The ¹H nmr spectrum in benzene-*d*₆ (hexamethyldisiloxane as internal reference) featured resonances at δ 2.08 (3 H, s, CH₃), 2.25, 2.31 (3 H, br singlets, CH₃), 2.63 (3 H, br s, OCH₃), 2.80, 2.82, 2.86 (6 H, br singlets, OCH₃), 3.21 (3 H, s, OCH₃), 5.90, 5.97 (1 H, singlets, aromatic H), 6.98 (7 H, m, aromatic H plus CH), 7.50 (5 H, m, aromatic H), and 8.15 (1 H, m, aromatic H). Mass spectral analysis was consistent with the assigned structure; exact mass, 492.230345 (calcd, 492.230045). The fragmentation pattern was superimposable with that of the other two fractions.

Anal. Calcd for C₃₃H₃₂O₄: C, 80.46; H, 6.55. Found: C, 80.18; H, 6.55.

Equilibration Studies on 1. A pyridine solution of a 70:30 mixture of **1b** and **1a**, respectively, was placed in a thin-walled nmr tube. The probe temperature³³ was set at 122°, and the nmr spectrum in the methyl region was recorded as a function of time (Figure 3). The values of the forward (*k*₁) and reverse (*k*₋₁) rate constants for the equilibration of the diastereomers **1a** ⇌ **1b** at 122° were calculated by use of eq 1, which is an adaptation³⁴ of the usual expression³⁵ for a reversible first-order reaction, where *R* is the ratio of

$$\ln [(R - K)/(1 + R)] = -(k_1 + k_{-1})t \quad (1)$$

diastereomers at time *t* and *K* is the equilibrium constant (i.e., *R* at *t*_∞).

The ratio (*R*) of the two diastereomers was determined from the relative peak areas of the methylnaphthyl methyl proton absorptions as a function of time. In order to determine the equilibrium constant, a pyridine solution of the diastereomers was kept in a constant temperature bath (122°) for ca. 7 hr after which no further change in ratio was observed. The value of *K* was found to be the same, within experimental error, starting from either a 70:30 or a 5:95 ratio of **1b**:**1a**. A value of *K* = 0.7 was found at 122°. A least-squares treatment (correlation coefficient 0.997) of ln [(*R* - *K*)/(1 + *R*)] vs. *t* (eq 1) using 11 data points over a time interval of 145 min and the value of *K*, together with the Eyring equation,³⁶ gave the values of Δ*G*[‡]₁₂₂ for **1** reported in the text.

Nmr Measurements. ¹H nmr spectra were recorded on a Varian A-60A spectrometer equipped with variable-temperature accessories. Temperature measurements were based on the chemical shift separation of the protons of a methanol or an ethylene glycol sample, and utilized the temperature-shift correlation of Van Geet.³³ Temperatures are considered to be accurate to ±2°, although within a given series of measurements smaller differences (ca. ±0.5°) are considered significant. Saturation of the nmr signals was avoided.

(33) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970); **40**, 2227 (1968).

(34) H. S. Gutowsky, J. Jonas, and T. H. Siddall, III, *J. Amer. Chem. Soc.*, **89**, 4300 (1967).

(35) K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill, New York, N. Y., 1965, p 19.

(36) The transmission coefficient was assumed to be unity.

Correlated Rotation in Complex Triarylmethanes. II. The 16- and 8-Isomer Systems and Residual Diastereotopicity¹

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Abstract: The dynamic stereochemistry of two complex triarylmethane systems has been studied. In one of these, the molecule has three different aryl groups, two of which lack local *C*₂ axes coincident with the bonds to the central carbon atom. Although all conformers of this methane are rapidly interconverted at ambient temperatures by two-ring flip pathways, and in spite of the fact that there are no restrictions upon the individual torsional angles of the aryl groups, this compound still exhibits residual diastereotopicity, i.e., the groups in the ortho positions of the ring with a *C*₂ axis still give rise to separate resonances in the ¹H nmr spectrum. Isomerization, presumably by the one-ring flip mechanism, is necessary to cause coalescence of these signals. The barrier for this process is greater than 26 kcal/mol. Residual diastereotopicity is also observed in methanes with three different aryl groups, only one of which lacks a local *C*₂ axis, but in this case all conformers and all diastereomeric environments are averaged by two-ring flips.

In the preceding paper³ we discussed the stereochemistry of a triarylmethane in which the particular substitution pattern (three different rings lacking local

*C*₂ axes) gives rise to 32 propeller forms and in which separation of two stable diastereomers was possible at ambient temperatures. A major conclusion of that work was that for this compound two noninterconvertible diastereomers exist even when interconversion among the propeller forms by the two-ring flip mechanism is rapid (*residual stereoisomerism*), and that there is no restriction upon the torsional angles of the in-

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(3) P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, **96**, 3198 (1974).