

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 <sup>1</sup>H nmr spectrum in benzene-*d*<sub>6</sub> (hexamethyldisiloxane as internal reference) featured resonances at δ 2.08 (3 H, s, CH<sub>3</sub>), 2.25 (3 H, br s, CH<sub>3</sub>), 2.60 (3 H, br s, OCH<sub>3</sub>), 2.78, 2.90 (6 H, br singlets, OCH<sub>3</sub>), 3.22 (3 H, s, OCH<sub>3</sub>), 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 C<sub>33</sub>H<sub>32</sub>O<sub>4</sub>: 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 C<sub>33</sub>H<sub>32</sub>O<sub>4</sub>: 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 <sup>1</sup>H nmr spectrum in benzene-*d*<sub>6</sub> (hexamethyldisiloxane as internal reference) featured resonances at δ 2.08 (3 H, s, CH<sub>3</sub>), 2.25, 2.31 (3 H, br singlets, CH<sub>3</sub>), 2.63 (3 H, br s, OCH<sub>3</sub>), 2.80, 2.82, 2.86 (6 H, br singlets, OCH<sub>3</sub>), 3.21 (3 H, s, OCH<sub>3</sub>), 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 C<sub>33</sub>H<sub>32</sub>O<sub>4</sub>: 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 temperature<sup>33</sup> 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*<sub>1</sub>) and reverse (*k*<sub>-1</sub>) rate constants for the equilibration of the diastereomers **1a** ⇌ **1b** at 122° were calculated by use of eq 1, which is an adaptation<sup>34</sup> of the usual expression<sup>35</sup> 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*<sub>∞</sub>).

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,<sup>36</sup> gave the values of Δ*G*<sup>‡</sup><sub>122</sub> for **1** reported in the text.

**Nmr Measurements.** <sup>1</sup>H 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.<sup>33</sup> 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 Diastereotopicity<sup>1</sup>

Paolo Finocchiaro,<sup>2</sup> Devens Gust, and Kurt Mislow\*

*Contribution from the Department of Chemistry, Princeton University,  
Princeton, New Jersey 08540. Received December 7, 1973*

**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*<sub>2</sub> 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*<sub>2</sub> axis still give rise to separate resonances in the <sup>1</sup>H 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*<sub>2</sub> axis, but in this case all conformers and all diastereomeric environments are averaged by two-ring flips.

In the preceding paper<sup>3</sup> we discussed the stereochemistry of a triarylmethane in which the particular substitution pattern (three different rings lacking local

*C*<sub>2</sub> 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-

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

(2) NATO Fellow, 1972–1973, on leave of absence from the University of Catania, Catania, Italy.

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

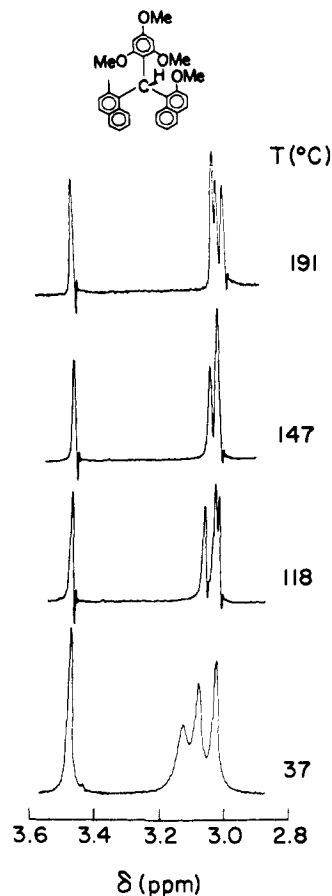
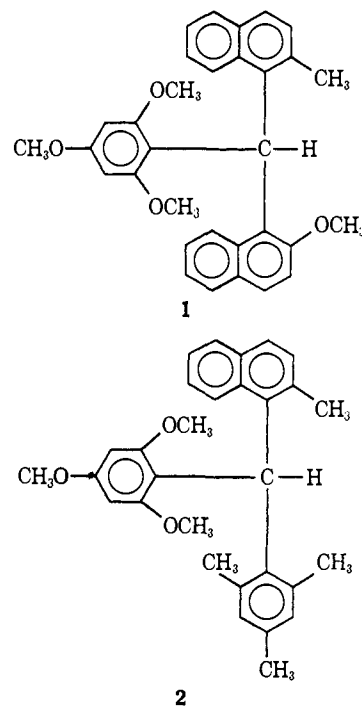


Figure 1. Temperature-dependent 60-MHz  $^1\text{H}$  nmr spectrum (methoxy region) of **1** (1,2,4-trichlorobenzene, hexamethyldisiloxane as internal reference).

dividual aryl groups in the two diastereomers. The key to the phenomenon was shown to be correlated rotation by the two-ring flip mechanism.

The present paper deals with stereoisomerism and stereoisomerization in triarylmethanes of a lower degree of complexity, *i.e.*, triarylmethanes in which all aromatic rings are constitutionally different, but in which only one or two (rather than all three) rings lack local  $C_2$  axes coincident with their bonds to the central carbon atom. Two such compounds are 1-(2-methoxynaphthyl)-1-(2-methylnaphthyl)-1-(2,4,6-trimethoxyphenyl)methane (**1**) (one local  $C_2$  axis) and mesityl-1-(2-methylnaphthyl)-1-(2,4,6-trimethoxyphenyl)methane (**2**) (two local  $C_2$  axes). A variety of stereochemical phenomena are observed for these and related compounds by nmr spectroscopy, and the effects of correlated rotation of the aryl groups are once again in evidence.

**1-(2-Methoxynaphthyl)-1-(2-methylnaphthyl)-1-(2,4,6-trimethoxyphenyl)methane (1).** The temperature-dependent 60-MHz  $^1\text{H}$  nmr spectrum of racemic **1** (methoxy region) is shown in Figure 1. The spectrum at 37° features four methoxy signals in the ratio of intensity of 1:1:1:1. Some of these resonances are broad, but at 118° all have sharpened. By comparison with the spectra of related compounds (**2**, **4**, **5**, and **6**) the signal at  $\delta$  3.48 ppm may be assigned to the *p*-methoxy group, whereas the remaining resonances at higher field correspond to the three *o*-methoxy groups of **1**. One of these resonances arises from the methoxy-



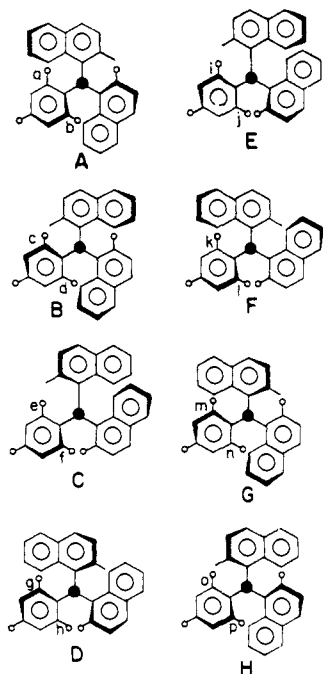
naphthyl group, whereas the other two derive from the trimethoxyphenyl group. We have been unable to assign these resonances further. Since the two *o*-methoxy groups of the trimethoxyphenyl ring give rise to anisochronous signals at ambient temperatures, they are necessarily diastereotopic.

As the temperature is raised above 118°, two of the high-field methoxy signals move together, and at 147° they are isochronous. This behavior, however, does *not* correspond to a coalescence phenomenon resulting from intramolecular motions, since the signals remain sharp and at higher temperatures are seen to separate again. Thus, these two resonances are accidentally isochronous<sup>4</sup> at 147°, the crossover temperature.

(4) A similar situation was recently noted by Schiemenz and Rast,<sup>5</sup> who observed a crossover of resonances due to diastereotopic protons in 1,2,3-triphenyl-2-propanol upon addition of shift reagent. These authors took this occasion to urge that isochrony be operationally defined, the criterion being signal coincidence within the precision of experimental measurement (in the sense of van Gorkom and Hall<sup>6</sup>). While agreeing with this suggestion, we would like to take the present occasion to call attention to the fact that there are *two* kinds of isochrony which are operationally as well as conceptually distinct: *inherent isochrony*, the necessary consequence of nuclear symmetry equivalence, which obtains under all conditions of measurement (noting that symmetry criteria are properly applied only with reference to a given time scale of observation), and *accidental isochrony*, the isochrony of symmetry nonequivalent nuclei, which is observed only under strictly defined conditions of measurement. Under other conditions, such nuclei will be anisochronous. We suggest that this distinction is useful enough to be retained. In the same sense, one might speak of inherent and accidental isogamy (magnetic equivalence in the coupling constant sense).<sup>7</sup> The above dichotomy has its matching counterpart in chirality measurements. *Inherent optical inactivity*, the necessary consequence of molecular achirality (including the "achirality" of *dl* pairs), obtains under all conditions of measurement, whereas *accidental optical inactivity* of chiral compounds (or nonracemic mixtures) is observed only under strictly defined conditions of measurement. Under other conditions, such compounds or mixtures will be optically active. Thus, in complete analogy to the accidental isochrony of two symmetry nonequivalent nuclei at the nul point, where the relative sense of shift (upfield *vs.* downfield) is abruptly reversed by continuously changing conditions (such as a change in temperature, as in the present case, or a change in concentration of shift reagent<sup>8</sup>) the optical rotation of many a chiral compound is exactly *zero* at some nul point, where the relative sign of rotation (plus *vs.* minus) is abruptly reversed by continuously changing conditions (*e.g.*, temperature, solvent, wavelength).

(5) G. P. Schiemenz and H. Rast, *Tetrahedron Lett.*, 1697 (1972).

(6) M. van Gorkom and G. E. Hall, *Quart. Rev., Chem. Soc.*, 22, 14 (1968).



**Figure 2.** The eight stereoisomers of (*R*)-**1** in the propeller conformation. The heavy dot in the center of each structure stands for C-H, the small circles denote methoxy groups, and the short line denotes a methyl group. The diastereomeric environments of the trimethoxyphenyl ring are labeled with lower case letters.

Since the resonances for the diastereotopic *o*-methoxy signals have not coalesced even at 191°, the Gutowsky-Holm approximation<sup>8</sup> and the Eyring equation may be employed to calculate a lower limit for any process which results in the averaging of the diastereotopic methoxy group environments. A value of  $\Delta G^{\ddagger}_{191} > 26$  kcal/mol was thus obtained.

**Analysis of Isomerization in 1.** In order to understand the reason for the diastereotopicity of the two *o*-methoxy groups in **1**, a detailed analysis of isomerism in **1** is required. Compound **1**, as well as the other methanes which will be discussed later, is presumed to adopt a propeller conformation in the ground state, by analogy with all triarylmethanes thus far investigated.<sup>3,9,11</sup> Compound **1** may exist in 16 stereoisomeric propeller forms (eight *dl* pairs). The eight conformers of the *R* configuration at the chiral center are shown in Figure 2.

If all stereoisomerizations of **1** were slow on the nmr time scale, four methoxy proton signals should in principle be observed for each of these diastereomers (in an achiral solvent), resulting in a total of  $4 \times 8 = 32$  methoxy resonances. However, only four such signals are in fact observed at 118°, and at least some of the possible isomerizations of **1** are therefore occurring rapidly on the nmr time scale at this temperature.

Previous work<sup>3</sup> indicates that only eight rearrangements (in the permutational sense) need to be con-

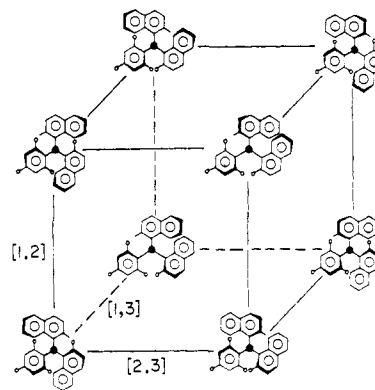
(7) P. Laszlo and P. J. Stang, "Organic Spectroscopy," Harper and Row, New York, N. Y., 1971, pp 103-105.

(8) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(9) See ref 10 and references cited therein.

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

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



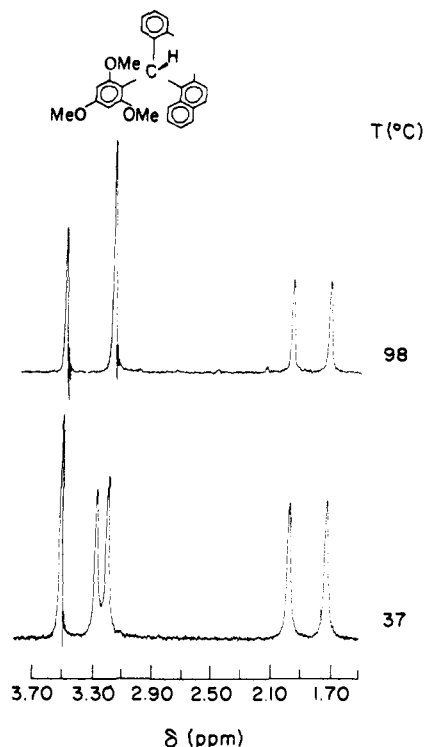
**Figure 3.** Topological representation of the stereoisomerization pathways for (*R*)-**1** by the two-ring flip mechanism. The enantiomeric set of isomers (having the *S* configuration at the chiral center) and pathways is not shown. Numerals in brackets identify the ligands which flip during the conversions: 1 = 2-methyl-1-naphthyl; 2 = trimethoxyphenyl; 3 = 2-methoxy-1-naphthyl.

sidered in molecules of the type  $Ar_3ZX$  such as **1**. These rearrangements may be realized in terms of the four classes of flip mechanisms, *i.e.*, the zero-, one-, two-, and three-ring flips.<sup>10</sup> It was also shown<sup>3</sup> that in 1-(2-methoxynaphthyl)-1-(2-methylnaphthyl)-1-(3-methyl-2,4,6-trimethoxyphenyl)methane (**3**), which has the same ortho substituents as **1**, all stereoisomerizations by the two-ring flip mechanism, which is the mechanism of lowest energy in such systems, require activation energies substantially less than 22 kcal/mol. Consequently, we conclude that all two-ring flip isomerizations of **1** are occurring rapidly on the nmr time scale at ambient temperatures and above.

All isomerizations of (*R*)-**1** by the two-ring flip mechanism are depicted topologically in Figure 3. This figure is arbitrarily drawn in the form of a cube, with the eight isomers of (*R*)-**1** shown at the corners. The 12 edges of the cube represent interconversions of the propeller conformers by the two-ring flips. The numbers in brackets identify the rings which flip during the specified interconversion. Thus, all four vertical edges in Figure 3 represent [1,2]-flips, the edge labeled [2,3] and the three edges parallel to it represent [2,3]-flips, and the remaining four edges denote [1,3]-flips.

It is immediately apparent from Figure 3 that all eight structures are interconverted by the two-ring flip pathways. Thus, at ambient temperatures, (*R*)-**1** consists of only one isomer, which is an equilibrium mixture of eight propeller conformers rapidly interconverting by two-ring flips. (*S*)-**1** consists of a similar set of conformers having the *S* configuration at the chiral center.

However, although all the propeller isomers of (*R*)-**1** are rapidly interconverted by the two-ring flips, the <sup>1</sup>H nmr spectrum still exhibits two resonances for the *o*-methoxy groups of the trimethoxyphenyl ring. The reason for the diastereotopicity of these two groups is not obvious from Figure 3, and we must therefore consider in detail (Table I) the effect of the various two-ring flips upon the environments of these *o*-methoxy groups. The left-hand column of Table I lists the types of two-ring flip pathways, the center column indicates which propeller conformers are interconverted by the pathway in question, and the right-hand column lists the environments of the *o*-methoxy groups of the



**Figure 4.** The 60-MHz  $^1\text{H}$  nmr spectra (methyl and methoxy region) of a 1,2,4-trichlorobenzene solution of **4** (hexamethyldisiloxane as internal reference) at 37 and 98  $^\circ$ .

trimethoxyphenyl ring which are averaged. Table I indicates that although a combination of all [1,2]-, [1,3]-, and [2,3]-flips interconverts all diastereomers, this combination results in two distinct sets of averaged *o*-methoxy environments. Consequently, the two  $^1\text{H}$  nmr signals which are observed for these groups (Figure 1) are accounted for, and the experimentally observed spectra are rationalized in terms of two-ring flips.<sup>12,13</sup>

Since all eight isomers of (*R*)-**1** are interconverted by the two-ring flip pathways, **1** does not exhibit residual diastereoisomerism<sup>3</sup> under this mechanism. This is in contrast to **3** in which all three aryl rings are constitutionally different and lack local  $C_2$  axes. Since one of the aryl rings of **1** possesses such an axis, no residual diastereoisomerism can result. However, note that two diastereotopic *o*-methoxy groups are observed in **1** even when all two-ring flip isomerizations are rapid. This situation is the ghost of the residual isomerism in **3**, and **1** may thus be said to exhibit *residual diastereotopicity* under the two-ring flip mechanism.

Examination of Figure 3 brings to light another feature of **1** which parallels the behavior of **3** discussed in the preceding paper.<sup>3</sup> It will be recalled that **3** exists in two diastereomeric forms although there is no restriction upon the torsional angles of the individual aryl groups. In the case of **1** undergoing rapid two-

(12) A similar analysis for the remaining methoxy and methyl groups of **1** shows that when all two-ring flips are rapid, only one signal is expected for each of these groups. This expectation is borne out by the  $^1\text{H}$  nmr spectra of **1** at ambient temperatures and above (see Experimental Section).

(13) Upon cooling the nmr sample of **1**, below ambient temperatures, a plethora of signals is observed in the methyl and methoxy region of the spectrum. This finding indicates that interconversion of diastereomers is becoming slow on the nmr time scale, as expected in the light of previous results for related systems.<sup>3,11</sup>

**Table I.** Effect of Stereoisomerizations by the Two-Ring Flip Mechanism on the Environments of the *o*-Methoxy Groups of the Trimethoxyphenyl Ring of (*R*)-**1**<sup>a</sup>

Flip pathway	Resulting isomerizations <sup>b</sup>	Resulting exchanges <sup>b</sup>
[1,2]	[A,B] [C,D] [E,F] [G,H]	[a,d][b,c] [e,h][f,g] [i,l][j,k] [m,p][n,o]
[1,3]	[A,E] [B,F] [C,G] [D,H]	[a,i][b,j] [c,k][d,l] [e,m][f,n] [g,o][h,p]
[2,3]	[A,D] [B,C] [E,H] [F,G]	[a,h][b,g] [c,f][d,e] [i,p][j,o] [l,m][k,n]
[1,2] + [1,3] + [2,3]	[A,B,C,D,E,F,G,H]	[a,d,e,h,i,l,m,p] [b,c,f,g,j,k,n,o]

<sup>a</sup> See Figures 2 and 3 for an explanation of numerals and letters.

<sup>b</sup> Capital letters in brackets represent isomers which are interconverted by the pathway in question; lower case letters in brackets designate *o*-methoxy groups whose environments are averaged by the process indicated.

ring flips, there is likewise no restriction upon the torsional angles of the individual aryl groups. Nevertheless, two diastereotopic *o*-methoxy groups are observed. The stereochemical phenomenon which accounts for this behavior is again correlated rotation of the aryl rings. Although there are no restrictions upon the *individual* torsional angles of the rings of **1**, *i.e.*, although the groups are all spinning rapidly about their bonds to the central carbon atom, there still remains a constraint upon the *relationships* of these torsional angles. The angle of a given ring at any time is a function of the angles of the other two. Thus, the same mechanistic feature, correlated rotation, accounts for the behavior of both **1** and **3**. However, since the substitution pattern is different in the two compounds, the effect is manifested in different ways, *i.e.*, residual diastereoisomerism (**3**) *vs.* residual diastereotopicity (**1**).

In order to exchange the diastereotopic *o*-methoxy groups in **1**, a pathway other than the two-ring flip must be traversed; this pathway is presumably<sup>3</sup> the one-ring flip. A lower limit of 26 kcal/mol was obtained for the barrier associated with this process. If we recall that **1** and **3** do not differ appreciably in steric congestion around the central atom (same ortho substituents), a value close to 30 kcal/mol (that found for **3**) may be assigned to the one-ring flip barrier of **1**.

The 60-MHz  $^1\text{H}$  nmr spectrum of racemic 1-(2-methylnaphthyl)-*o*-tolyl-1-(2,4,6-trimethoxyphenyl)methane (**4**) at ambient temperatures also displays two signals of equal intensity for the *o*-methoxy groups at  $\delta$  3.20 and 3.27 ppm (Figure 4). These signals coalesce at 67 $^\circ$ , and the Gutowsky-Holm approximation,<sup>8</sup> together with the Eyring equation, yields  $\Delta G^\ddagger_{67} = 18.5$  kcal/mol. This compound is stereochemically correspondent<sup>14</sup> to **1**, and hence the analysis given above applies with equal force to **4**. Thus, even though all two-ring flip interconversions of **4** are rapid at ambient temperatures, the two *o*-methoxy groups remain diastereotopic. As explained above for **1**, the process of exchanging the environments of these two

(14) K. Mislow, D. Gust, P. Finocchiaro, and R. J. Boettcher, *Fortschr. Chem. Forsch.*, **47**, 1 (1974).

groups ( $\Delta G^\ddagger = 18.5$  kcal/mol) corresponds to the one-ring flip mechanism: substitution of a 2-methoxynaphthyl group by an *o*-tolyl group lowers the barrier considerably (by *ca.* 12 kcal/mol), as expected from the difference in steric bulk of the two groups.

**Mesityl-1-(2-methylnaphthyl)-1-(2,4,6-trimethoxyphenyl)methane (2) and Related Systems.** We shall now discuss isomerism in a group of molecules of type  $\text{Ar}_3\text{ZX}$  in which all three aryl rings are different, but in which only one lacks a local  $C_2$  axis.

For a compound such as **2** eight propeller forms (four *dl* pairs) are possible.<sup>10</sup> The four diastereomeric conformers of (*R*)-**2** are shown in Figure 5. Interconversion among these forms by means of the two-ring flip mechanism is represented topologically in Figure 5, which reveals that the six diastereomeric two-ring flip pathways may be partitioned into three sets, *i.e.*, two [1,2]-flips, two [1,3]-flips, and two [2,3]-flips. The two [2,3]-flips in combination with any one of the other pathways suffice to interconvert all four diastereomers.

Table II lists the environments of the *o*-methyl groups

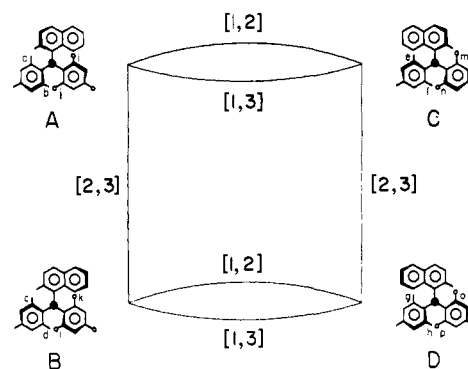
**Table II.** Effect of Stereoisomerizations by the Two-Ring Flip Mechanism on the Environments of the *o*-Methoxy and Mesityl *o*-Methyl Groups of (*R*)-**2**<sup>a</sup>

Flip pathway	Resulting isomerizations <sup>b</sup>	Resulting exchanges <sup>b</sup> <i>o</i> -Me	Resulting exchanges <sup>b</sup> <i>o</i> -OMe
[1,2]	[A,C] [B,D]	[a,f][b,e] [c,h][d,g]	[i,m][j,n] [k,o][l,p]
[1,3]	[A,C] [B,D]	[a,e][b,f] [c,g][d,h]	[i,n][j,m] [k,p][l,o]
[2,3]	[A,B] [C,D]	[a,d][b,c] [e,h][f,g]	[i,j][k,l] [m,p][n,o]
[1,2] + [1,3]	[A,C] [B,D]	[a,b,e,f] [c,d,g,h]	[i,j,m,n] [k,l,o,p]
[1,2] + [2,3]	[A,B,C,D]	[a,d,f,g] [b,c,e,h]	[i,l,m,p] [j,k,n,o]
[1,3] + [2,3]	[A,B,C,D]	[a,d,e,h] [b,c,f,g]	[i,l,n,o] [j,k,m,p]
[1,2] + [1,3] + [2,3]	[A,B,C,D]	[a,b,c,d,e,f,g,h]	[i,j,k,l,m,n,o,p]

<sup>a</sup> See Figure 5 for explanation of numerals and letters. <sup>b</sup> Capital letters in brackets represent isomers which are interconverted by the pathway in question; lower case letters in brackets designate *o*-methoxy or mesityl *o*-methyl groups whose environments are averaged by the process indicated.

of the mesityl ring and of the *o*-methoxy groups of the four isomers of (*R*)-**2** which are exchanged by the various two-ring flip pathways. In the absence of any stereoisomerization, eight signals are expected for each of these two sets of groups, and four signals each are expected for the methylnaphthyl methyl, *p*-methyl, and *p*-methoxy groups. Stereoisomerization by any one of the three sets of two-ring flips will result in pairwise coalescence of all these signals. On the other hand, rapid isomerization by the [2,3]-flips in addition to any *one* of the other two sets (*e.g.*, [2,3] + [1,2] or [2,3] + [1,3]) will cause the coalescence of all diastereotopic methylnaphthyl methyl resonances, as well as all *p*-methyl and *p*-methoxy resonances. However, such a combination will result in *two* *o*-methyl resonances for the mesityl group and *two* *o*-methoxy resonances. Interconversions by all three sets of mechanisms ([2,3] + [1,2] + [1,3]) are necessary for coalescence of these pairs of signals to singlets.

Thus, **2** exhibits residual diastereotopicity under, for example, the combination of [1,3]- and [2,3]-flips. In



**Figure 5.** Topological representation of the stereoisomerization pathways for (*R*)-**2** by the two-ring flip mechanism. The enantiomeric set of isomers (having the *S* configuration at the chiral center) and pathways are not shown. The environments of the *o*-methoxy and mesityl *o*-methyl groups are labeled with lower case letters. Numerals in brackets identify the ligands which flip during the conversions: 1 = 2-methyl-1-naphthyl; 2 = mesityl; 3 = trimethoxyphenyl.

addition, it will be noted that when **2** isomerizes by these two sets of mechanisms there are no restrictions upon the individual torsional angles of the aryl rings. In spite of this fact, two diastereotopic *o*-methyl and *o*-methoxy groups result. This phenomenon is clearly related to similar observations in **1** and **3**, and is another manifestation of correlated rotation of the aryl groups. Since only one of the aryl groups of **2** lacks a local  $C_2$  axis, all diastereomers and all diastereomeric methyl group environments are averaged by the three available sets of two-ring flips, and therefore there is no need to invoke another isomerization mechanism, such as the one-ring flip.

In light of this analysis the experimental <sup>1</sup>H nmr spectrum of **2** as a function of temperature is readily understood. Figure 6 shows the 100-MHz <sup>1</sup>H nmr spectrum of a hexachloro-1,3-butadiene solution of **2** (methyl and methoxy region) in the temperature range 183 to 31°. The spectrum at 183° features five signals at  $\delta$  3.60, 3.13, 2.08, 2.01, and 1.79 ppm, in the ratio of intensities of 1:2:1:1:2, respectively. The signals at  $\delta$  3.13 and 1.79 ppm are assigned to the *o*-methoxy and the mesityl *o*-methyl groups, respectively. The resonances at  $\delta$  2.08 and 2.01 correspond to the other aromatic methyl groups, whereas that at  $\delta$  3.60 ppm derives from the *p*-methoxy group. From the above analysis, it is evident that this spectrum is consistent with rapid isomerization of **2** by all three sets of two-ring flip interconversions.<sup>15</sup>

Upon cooling, the *o*-methoxy signal is seen to split into two signals at  $\delta$  3.48 and 2.89 ppm. Similarly, the signal at  $\delta$  1.79 ppm splits into two resonances (Figure 6). On the basis of the information in Table II, such behavior may be ascribed to the fact that one of the two-ring flips is becoming slow on the nmr time scale at 31°. The barrier for this two-ring flip may be calculated from the coalescence data for either the *o*-methoxy or *o*-methyl resonances, and the Gutowsky-Holm approximation<sup>8</sup> in combination with the Eyring equation may be used to calculate barriers of  $\Delta G^\ddagger_{114} = 19.0$  and  $\Delta G^\ddagger_{86} = 18.6$  kcal/mol from the two coalescences, respectively. These two barriers are the same

(15) Analogy with similar compounds<sup>9,11</sup> allows us to conclude that such interconversions are expected to be rapid at this temperature.

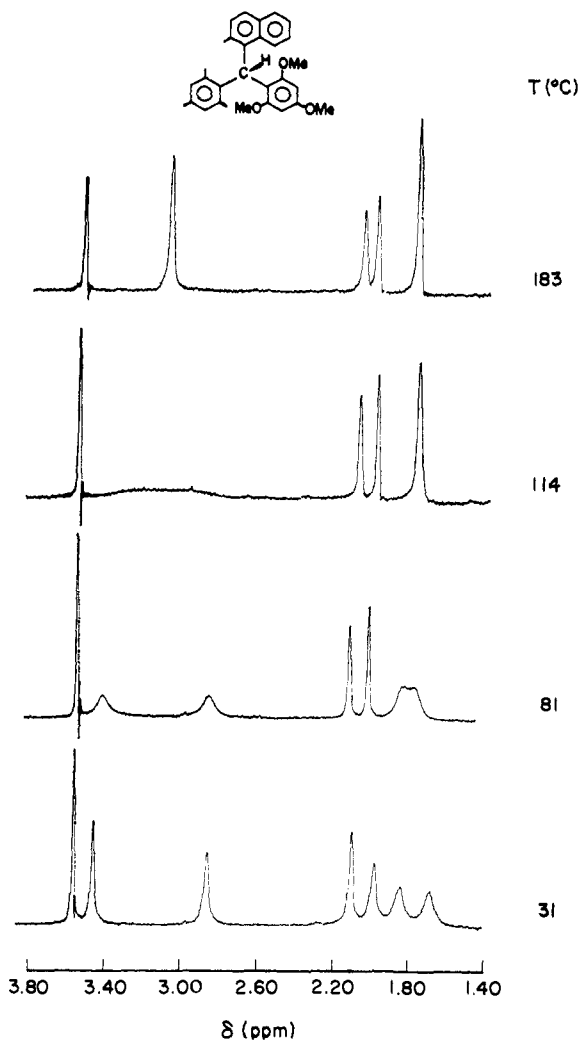


Figure 6. The 100-MHz  $^1\text{H}$  nmr spectra (methyl and methoxy region) of **2** in the range 183 to 31° (hexachloro-1,3-butadiene, hexamethyldisiloxane as internal reference).

within experimental error, as is required by the above analysis.

In Figure 7 is shown the 100-MHz  $^1\text{H}$  nmr spectrum of **2** ( $\text{CDCl}_3\text{-CS}_2$  solution) in the range 31 to  $-68^\circ$ . As the temperature is lowered, each of the two *o*-methoxy and two mesityl *o*-methyl signals is seen to broaden, and at  $-36^\circ$  each of these signals has split into two resonances. This change is accompanied by poorly resolved splitting of the other signals. Such behavior indicates that yet another two-ring flip process has become slow on the nmr time scale (Table II). At *ca.*  $-36^\circ$ , the mixture consists of two diastereomers **2a** (major isomer) and **2b** (minor isomer), each of which has two diastereotopic *o*-methoxy groups and two diastereotopic mesityl *o*-methyl groups. Analysis<sup>16</sup> based on the methoxy resonances yields  $\Delta G^{\ddagger}_{-29} = 13.1$  kcal/mol for the diastereomerization **2a**  $\rightarrow$  **2b** and  $\Delta G^{\ddagger}_{-29} = 12.8$  kcal/mol for the reverse process.

Further cooling results in the appearance of additional resonances (Figure 7). If, at these low temperatures, isomerizations by the lowest energy set of two-ring flips are no longer occurring rapidly on the nmr time scale, other diastereomers (corresponding to A,

(16) H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, **74**, 961 (1970).

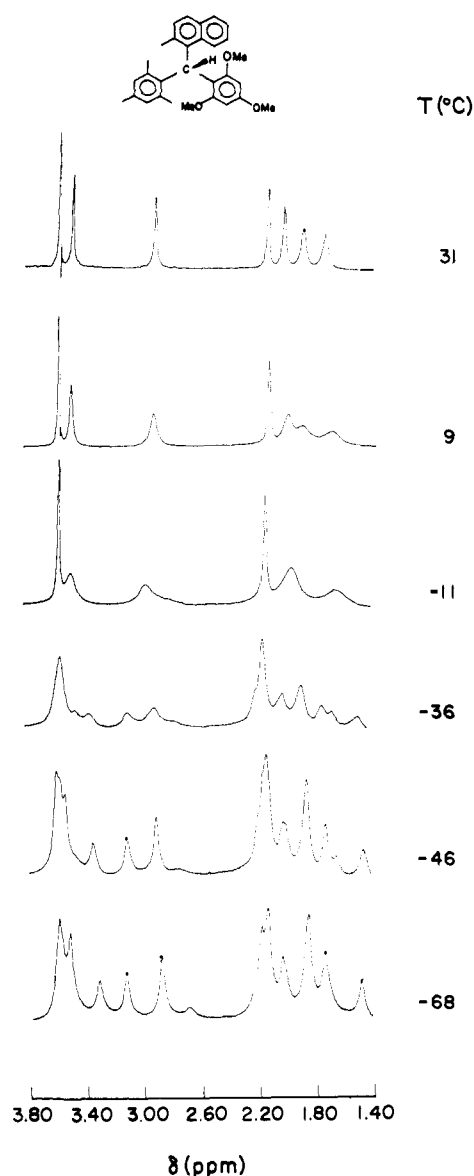


Figure 7. The 100-MHz  $^1\text{H}$  nmr spectra (methyl and methoxy region) of **2** in the range 31 to  $-68^\circ$  ( $\text{CDCl}_3\text{-CS}_2$ , TMS as internal reference).

B, C, D, and their enantiomers) will manifest themselves in the nmr spectrum. The additional resonances observed below  $-36^\circ$  may be ascribed to these isomers. However, because of overlap of resonances and low relative populations of diastereomers, a precise analysis of the low-temperature phenomena was not attempted.

The 60-MHz  $^1\text{H}$  nmr spectrum of racemic mesityl-*o*-tolyl-1-(2,4,6-trimethoxyphenyl)methane (**5**) at  $-51^\circ$  in  $\text{CDCl}_3$  (Figure 8) displays four equal intensity signals in the methyl region at  $\delta$  1.76, 2.03, 2.15, and 2.25 ppm. In the methoxy region, three equal intensity signals are in evidence at  $\delta$  3.42, 3.75, and 3.83 ppm. Coalescence phenomena (discussed below) allow us to assign signals at  $\delta$  1.76 and 2.15 ppm to the mesityl *o*-methyl groups and the resonances at  $\delta$  3.42 and 3.75 ppm to the *o*-methoxy groups. Coalescence of both the *o*-methyl and *o*-methoxy signals occurs at *ca.*  $-10^\circ$  (Figure 8) and analysis<sup>8</sup> yields  $\Delta G^{\ddagger}_{-10} = 13.2$  kcal/mol for both coalescences.

Compound **5** is stereochemically correspondent<sup>14</sup> to **2**, since both are triarylmethanes which have three dif-

ferent aryl rings, one of which lacks a local  $C_2$  axis. Thus, the analysis of **2** is valid for **5**, and shows that the process observed for **5** (coalescence at  $-10^\circ$ ) corresponds to the process observed for **2** (coalescence at  $84$  and  $114^\circ$ ). In both cases, two *o*-methoxy signals coalesce to a singlet, as do two mesityl *o*-methyl signals. Thus, we may ascribe the barrier of  $13.2$  kcal/mol to the highest energy two-ring flip possible for **5**, corresponding to the barrier of  $19$  kcal/mol for **2**.<sup>17</sup>

**Assignment of Isomerization Mechanisms.** Although several isomerization processes have been observed for **2** and related compounds, the nmr evidence by itself does not provide information on the identity of the particular rings which are involved in the flip mechanisms. Is the barrier of *ca.*  $19$  kcal/mol observed for **2**, for instance, associated with the [1,2]-, the [1,3]-, or the [2,3]-flip? Tentative assignments may, however, be made on the basis of analogy with other compounds, as discussed below.

In a previous study of bis(2,6-xylyl)-1-(2-methylnaphthyl)methane,<sup>11b</sup> it was concluded that the barrier for the flipping of a 2,6-xylyl and a 2-methyl-1-naphthyl group in this compound is *ca.*  $19$  kcal/mol. Since **2** possesses essentially the same two groups,<sup>18</sup> it is tempting to conclude that the barrier of *ca.*  $19$  kcal/mol observed for the process of highest energy in **2** corresponds to the flipping of a mesityl and a 2-methyl-1-naphthyl group (*i.e.*, the [1,2]-flip in Figure 5). This conclusion is bolstered by the observation<sup>11b</sup> that the barrier height in the two-ring flip of such compounds appears to depend to a major extent upon the steric parameters of the two flipping groups. The nature of the nonflipping group has relatively little effect upon the barrier, within reasonable limits.

We now turn to the process of lower energy measured for **2** at  $-29^\circ$ , and to the isomerization observed in **5**. The barriers for both of these processes are *ca.*  $13$  kcal/mol. The barrier for enantiomerization of dimesityl-1-(2,4,6-trimethoxyphenyl)methane is also  $\Delta G^\ddagger_{-20} = 13$  kcal/mol.<sup>19</sup> This process has been ascribed to the flipping of a mesityl and a trimethoxyphenyl ring. Reasoning as above, we assign the  $13$ -kcal/mol barriers observed for **2** and **5** to similar two-ring flips, and the  $13$ -kcal/mol barrier of **2** may thus be ascribed to the [2,3]-flip (Figure 5).

Granted the above assignments, the two-ring flips of lowest energy for **2** are by exclusion the [1,3]-flips. These conclusions are consistent with previous estimates in such systems<sup>11b</sup> which suggest that the order of decreasing "steric bulk" is mesityl  $>$  2-methyl-1-naphthyl  $>$  9-anthryl  $>$  2,4,6-trimethoxyphenyl.

**Effect of Correlated Rotation in Other Systems.** Analogs to the stereochemical phenomena observed in the  $Ar_3ZX$  systems discussed above may be found in the related  $Ar_3Z$  systems. For example, in a system such

(17) In the case of 9-anthryl-*o*-tolyl-1-(2,4,6-trimethoxyphenyl)methane (**6**) (stereochemically correspondent<sup>14</sup> to **2** and **5**), the low-temperature  $^1H$  nmr spectrum ( $-65^\circ$ ) features three equal intensity signals for the methoxy groups at  $\delta$  2.96, 3.74, and 3.88 ppm. Coalescence of the signals at  $\delta$  2.96 and 3.88 ppm occurs at  $-37^\circ$ , from which an activation energy of  $\Delta G^\ddagger_{-37} = 11.4$  kcal/mol is calculated.<sup>8</sup> We tentatively ascribe this barrier to the two-ring flip of highest energy in this system.

(18) We make the reasonable assumption that the *p*-methyl group does not contribute significantly to the stereoisomerization barriers of **2**.

(19) Free energy of activation estimated<sup>11b</sup> from published data: M. J. Sabacky, S. M. Johnson, J. C. Martin, and I. C. Paul, *J. Amer. Chem. Soc.*, **91**, 7542 (1969).

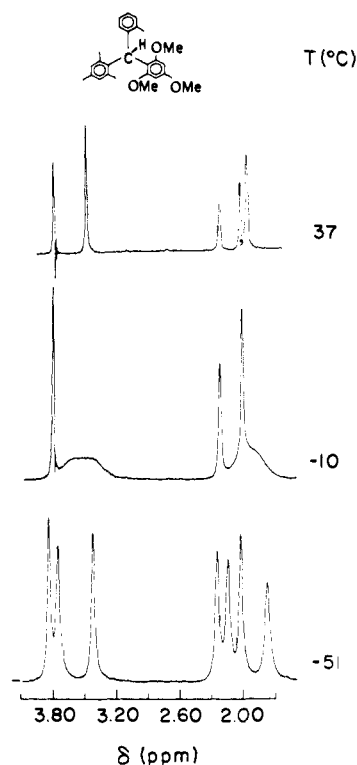


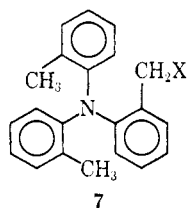
Figure 8. The 60-MHz  $^1H$  nmr spectra (methyl and methoxy region) of a  $CDCl_3$  solution of **5** (TMS as internal reference) in the range  $37$  to  $-51^\circ$ .

as a triarylborane with three different aryl groups, two of which lack local  $C_2$  axes coincident with their bonds to the central atom, isomerizations by the two-ring flip mechanism interconvert all eight stereoisomeric propeller structures (four *dl* pairs).<sup>10</sup> In addition, the diastereomeric environments of the ortho (or meta) positions of the ring with a local  $C_2$  axis are likewise averaged. However, detailed analysis reveals that these ortho (or meta) environments are averaged to two *enantiomeric* sets, rather than to a single set of homotopic positions. Therefore, these two enantiomeric ortho (or meta) environments are in principle distinguishable in a chiral environment. For example, the nmr spectrum of such a compound in a chiral solvent or in the presence of a chiral shift reagent should in principle feature two resonances for the two ortho groups of the ring with a local  $C_2$  axis when interconversions by all two-ring flip pathways are rapid. Such a system may be said to exhibit *residual enantiotopicity* under the two-ring flip mechanism. This residual enantiotopicity will be observed in spite of the fact that there are no restrictions upon the torsional angles of the individual aryl groups when all two-ring flips are rapid, and owes its existence to the occurrence of correlated rotation. Interconversion of the enantiomeric environments discussed above requires isomerizations by a mechanism other than the two-ring flip. Thus, the phenomenon discussed here is seen to be closely related to that found for **1**.

In the case of an  $Ar_3Z$  molecule with three different aryl rings, only one of which lacks a local  $C_2$  axis, similar effects are observed. Four isomers (two *dl* pairs) are possible<sup>10</sup> for such a molecule. Two of the three sets of two-ring flip interconversions are sufficient to interconvert all four isomers. However, the ortho (or meta)

environments of each of the two rings having local  $C_2$  axes are averaged to two enantiomeric environments by these same two-ring flips. Thus, the nmr spectrum of such a compound in a chiral environment would in principle display two resonances for the enantiotopic groups in the ortho (or meta) positions when interconversions of all stereoisomers by only two of the two-ring flips is rapid. Interconversion by the third two-ring flip is necessary to achieve averaging of the enantiomeric environments. Thus, the situation parallels that described above for **2**: in **2**, residual diastereotopicity was observed when isomerizations by two of the three sets of two-ring flips was rapid, whereas in the  $Ar_3Z$  system, residual enantiotopicity would be expected under similar conditions.

Residual diastereotopicity was recently observed by Hellwinkel, *et al.*,<sup>20</sup> in triaryl amines in which all rings lack local  $C_2$  axes, and two of the rings are constitutionally the same. The temperature-dependent  $^1H$  nmr spectra of several amines represented by **7** were



studied,<sup>20</sup> and in each of these compounds, only one isomer was detected at all temperatures investigated. At low temperatures, two resonances were observed for the *o*-methyl groups, and an AB pattern was seen for the methylene protons. Upon warming, the methylene signals were found to coalesce to a singlet with  $\Delta G^\ddagger = ca.$  12–13 kcal/mol, whereas coalescence of the *o*-methyl groups required  $\Delta G^\ddagger = ca.$  18–19 kcal/mol. It was concluded<sup>20</sup> that the lower energy coalescence was the result of the two-ring flip, whereas the coalescence of the methyl groups occurred by the one- or three-ring flip mechanism.

Hellwinkel, *et al.*,<sup>20</sup> analyzed **7** as an  $Ar_3ZX$  system, taking explicit account of the pyramidality at nitrogen. As was previously pointed out,<sup>21</sup> a propeller molecule such as **7** will in fact be pyramidal on the time average, as is required solely on the basis of symmetry arguments. However, since the barrier to inversion at nitrogen in a triarylamine is so low that this process is rapid on the nmr time scale, it makes absolutely no difference whether the nitrogen is pyramidal and is undergoing rapid inversion, or whether it lies motionlessly in the region between the three aryl rings: operationally, these two alternatives are indistinguishable. Consequently, such a system may be much more conventionally and conveniently (yet completely) analyzed as an  $Ar_3Z$  molecule,<sup>10</sup> rather than in terms of the complex network of interconversions among  $Ar_3ZX$  isomers and their intermediate states developed by Hellwinkel, *et al.*<sup>20</sup>

For an  $Ar_3Z$  molecule such as **7**, eight propeller conformations are possible (four *dl* pairs).<sup>22</sup> Intercon-

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

(21) For a complete discussion, see footnote 27, ref 10.

(22) In their topological analysis, Hellwinkel, *et al.*,<sup>20</sup> considered only one of these four possible *dl* pairs (treating the isomers as  $Ar_3ZX$  molecules), ignoring the other propeller forms and postulating instead a multiplicity of hypothetical intermediate structures.

version among all eight isomers may occur by the two-ring flip mechanism. These interconversions, which may be represented topologically by the edges of a cube whose eight vertices correspond to the propeller forms, will result in the coalescence of the methylene protons of **7**, but will not average the environments of the methyl groups, in agreement with experimental findings.<sup>20</sup> Thus, **7** displays residual diastereotopicity under the two-ring flip mechanism.

A related type of residual diastereotopicity may exist in systems of the type  $Ar_2ZXY$ . For example, Akkerman<sup>23</sup> observed resonances for two diastereotopic ortho *tert*-butyl groups in 2,4,2',4'-tetra-*tert*-butyl-6,6'-dimethyldiphenylacetic acid (**8**) by  $^1H$  nmr spectroscopy at ambient temperatures. These resonances coalesced at 140°. Akkerman ascribed the magnetic nonequivalence at ambient temperatures to "slow rotation of the phenyl groups about their bonds to the central atom."<sup>23</sup> However, rapid rotation about these bonds by the one-ring flip mechanism would not result in averaging of all ortho *tert*-butyl signals; such an averaging requires a two- or zero-ring flip in addition to the one-ring flips. Therefore, if isomerization by the one-ring flip is rapid in **8** at ambient temperatures, this compound exhibits residual diastereotopicity, even though there are no restrictions on individual torsional angles.

#### Experimental Section<sup>24</sup>

(*dl*)-Mesityl-1-(2-methylnaphthyl)methanol. Mesityl-1-(2-methylnaphthyl) ketone<sup>25</sup> (3.0 g, 10.4 mmol) was added portionwise, with stirring, to a suspension of  $LiAlH_4$  (0.4 g, 10.4 mmol) in 100 ml of anhydrous ethyl ether, at room temperature. After the addition was completed (15 min), the mixture was carefully hydrolyzed with water and filtered. The solvent was distilled from the resulting filtrate at reduced pressure, and the crude white solid obtained was recrystallized from petroleum ether (60–80°) to yield 2.50 g (83.5%) of white crystals: mp 106–108°;  $^1H$  nmr  $\delta_{CDCl_3}^{TMS}$  2.08 (1 H, s, OH), 2.13 (6 H, s,  $CH_3$ ), 2.23 (3 H, s,  $CH_3$ ), 2.33 (3 H, s,  $CH_3$ ), 6.76 (3 H, s, aromatic H plus CH), and 7.30–8.25 (6 H, m, aromatic H); mass spectral analysis was consistent with the assigned structure; exact mass, 290.167228 (calcd, 290.167056).

*Anal.* Calcd for  $C_{21}H_{22}O$ : C, 86.85; H, 7.64. Found: C, 86.53; H, 7.64.

(*dl*)-Mesityl-1-(2-methylnaphthyl)-1-(2,4,6-trimethoxyphenyl)methane (**2**). Five drops of concentrated  $H_2SO_4$  was added to a mixture of mesityl-1-(2-methylnaphthyl)methanol (1.90 g, 6.55 mmol) and 1,3,5-trimethoxybenzene (4.0 g, 23.8 mmol) dissolved in 100 ml of nitromethane, at room temperature. After 5 min the mixture was poured onto water, and the organic material was extracted with chloroform and dried over  $MgSO_4$ . The solvent was distilled at reduced pressure and the crude white solid obtained was recrystallized from a mixture of ethanol-ethyl acetate (40:60) to yield 2.50 g (87%) of white plates: mp 158–160°;  $^1H$  nmr  $\delta_{CDCl_3}^{TMS}$  1.81 (3 H, s,  $CH_3$ ), 1.96 (3 H, s,  $CH_3$ ), 2.11 (3 H, s,  $CH_3$ ), 2.21 (3 H, s,  $CH_3$ ), 3.01 (3 H, s,  $OCH_3$ ), 3.63 (3 H, s,  $OCH_3$ ), 3.73 (3 H, s,  $OCH_3$ ), 6.00 (1 H, d,  $^4J_{HH} = 2.0$  Hz, aromatic H), 6.15 (1 H, d,  $^4J_{HH} = 2.0$  Hz, aromatic H), 6.63 (1 H, s, aromatic H), 6.70 (2 H, s, CH plus aromatic H), and 7.19–7.62 (6 H, m, aromatic H); mass spectral analysis was consistent with the assigned structure; exact mass, 440.235403 (calcd, 440.235131).

(23) O. S. Akkerman, *Recl. Trav. Chim. Pays-Bas*, **89**, 673 (1970).

(24) 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 an 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.

(25) R. C. Fuson, B. C. McKusick, and F. W. Spangler, *J. Amer. Chem. Soc.*, **67**, 597 (1945).



*Anal.* Calcd for  $C_{30}H_{32}O_3$ : C, 81.78; H, 7.32. Found: C, 81.85; H, 7.40.

(*dl*)-Mesityl-*o*-tolyl-1-(2,4,6-trimethoxyphenyl)methane (5). To a mixture of mesityl-*o*-tolylmethanol<sup>26</sup> (4.0 g, 16.6 mmol) and 1,3,5-trimethoxybenzene (6.5 g, 38.5 mmol) dissolved in 100 ml of nitromethane was added five drops of concentrated  $H_2SO_4$ , at room temperature with stirring. The mixture was worked up as described for 2 and the crude product was recrystallized from ethyl acetate to yield 5.80 g (89%) of white needles: mp 177–179°;  $^1H$  nmr  $\delta_{CDCl_3}^{TMS}$  1.95 (6 H, s,  $CH_3$ ), 2.00 (3 H, s,  $CH_3$ ), 2.21 (3 H, s,  $CH_3$ ), 3.45 (6 H, s,  $OCH_3$ ), 3.80 (3 H, s,  $OCH_3$ ), 6.00 (1 H, s, CH), 6.10 (2 H, s, aromatic H), 6.70 (2 H, s, aromatic H), and 7.00 (4 H, m, aromatic H); mass spectral analysis was consistent with the assigned structure; exact mass, 390.219465 (calcd, 390.219482).

*Anal.* Calcd for  $C_{26}H_{30}O_3$ : C, 79.97; H, 7.74. Found: C, 80.17; H, 7.77.

9-Anthryl *o*-Tolyl ketone. A solution of 9-bromoanthracene (10.0 g, 38.8 mmol) in 200 ml of anhydrous ether was treated with *n*-butyllithium (38.8 mmol, 1.9 M in hexane, Alfa Inorganics). The suspension of the organolithium compound was cooled to ca. –50°, and *o*-methylbenzoyl chloride (6.0 g, 38.8 mmol) dissolved in 30 ml of ether was added with stirring. The mixture was allowed to warm gradually to ca. 20°, and after 30 min it was poured onto crushed ice. The separated organic layer was extracted with ether and dried ( $MgSO_4$ ), and the solvent was removed at reduced pressure. The crude yellow solid obtained was recrystallized from ethanol to yield 11.0 g (96%) of translucent yellow needles: mp 126–127°;  $^1H$  nmr  $\delta_{CDCl_3}^{TMS}$  2.85 (3 H, s,  $CH_3$ ), 7.00, 7.30, 7.80 (12 H, m, aromatic H), and 8.41 (1 H, s, aromatic H); mass spectral analysis was consistent with the assigned structure; exact mass, 296.120401 (calcd, 296.120109).

*Anal.* Calcd for  $C_{22}H_{16}O$ : C, 89.16; H, 5.44. Found: C, 88.97; H, 5.48.

(*dl*)-9-Anthryl-*o*-tolylmethanol, mp 134–136°, was prepared in a manner analogous to that described for mesityl-1-(2-methylnaphthyl)methanol from 9-anthryl-*o*-tolyl ketone and  $LiAlH_4$  (71% yield). The  $^1H$  nmr spectrum featured resonances at  $\delta_{CDCl_3}^{TMS}$  2.21 (3 H, s,  $CH_3$ ), 2.50 (1 H, d,  $^3J_{HH} = ca. 3.8$  Hz, OH), 7.25 (9 H, m, aromatic H plus CH), 7.91 (4 H, m, aromatic H), and 8.38 (1 H, s, aromatic H); mass spectral analysis was consistent with the assigned structure; exact mass, 298.135151 (calcd, 298.135758).

*Anal.* Calcd for  $C_{22}H_{18}O$ : C, 88.56; H, 6.08. Found: C, 88.64; H, 6.01.

(*dl*)-9-Anthryl-*o*-tolyl-1-(2,4,6-trimethoxyphenyl)methane (6). Five drops of concentrated  $H_2SO_4$  was added, with stirring, to a mixture of 9-anthryl-*o*-tolylmethanol (3.4 g, 11.4 mmol) and 1,3,5-trimethoxybenzene (5.0 g, 30 mmol) dissolved in 80 ml of nitromethane, at room temperature. The mixture was worked up as described for 2 and the crude product was recrystallized from acetone–ethanol (80:20) to yield 3.68 g (72%) of pale yellow plates: mp 185–187°;  $^1H$  nmr  $\delta_{CDCl_3}^{TMS}$  1.66 (3 H, s,  $CH_3$ ), 3.30 (6 H, s,  $OCH_3$ ), 3.71 (3 H, s,  $OCH_3$ ), 6.11 (2 H, s, aromatic H), 7.15 (9 H, m, aromatic H plus CH), 8.00 (4 H, m, aromatic H), and 8.32 (1 H, s, aromatic H); mass spectral analysis was consistent with the assigned structure; exact mass, 448.203738 (calcd, 448.203833).

*Anal.* Calcd for  $C_{31}H_{28}O_3$ : C, 83.01; H, 6.29. Found: C, 83.17; H, 6.21.

(*dl*)-1-(2-Methylnaphthyl)-*o*-tolylmethanol, mp 83–85°, was prepared by reduction of the corresponding ketone<sup>27</sup> (prepared from 2-methyl-1-naphthylmagnesium bromide and *o*-methylbenzoyl chloride) with  $LiAlH_4$  as described for mesityl-1-(2-methylnaphthyl)methanol (86.5%). The  $^1H$  nmr spectrum featured resonances at  $\delta_{CDCl_3}^{TMS}$  2.20 (3 H, s,  $CH_3$ ), 2.36 (3 H, s,  $CH_3$ ), 2.68 (1 H, d,  $^3J_{HH} = ca. 3.8$  Hz, OH), 6.60 (1 H, d,  $^3J_{HH} = ca. 3.8$  Hz, CH), and 7.15–8.20 (10 H, m, aromatic H); mass spectral analysis was consistent with the assigned structure; exact mass, 262.135860 (calcd, 262.135758).

*Anal.* Calcd for  $C_{19}H_{18}O$ : C, 86.99; H, 6.92. Found: C, 86.83; H, 8.61.

(*dl*)-1-(2-Methylnaphthyl)-*o*-tolyl-1-(2,4,6-trimethoxyphenyl)methane (4). To a mixture of 1-(2-methylnaphthyl)-*o*-tolylmethanol (2.80 g, 10.7 mmol) and 1,3,5-trimethoxybenzene (5.0 g, 30 mmol) dissolved in 100 ml of nitromethane was added a few drops of concentrated  $H_2SO_4$ , at room temperature, with stirring. The mixture was worked up as described for 2 and the crude material was recrystallized from a mixture of ethanol–acetone (70:30) to yield 3.95 g (90%) of white crystals: mp 158–160°;  $^1H$  nmr  $\delta_{CDCl_3}^{TMS}$  1.92 (3 H, s,  $CH_3$ ), 2.15 (3 H, s,  $CH_3$ ), 3.36 and 3.39 (6 H, singlets,  $OCH_3$ ), 3.73 (3 H, s,  $OCH_3$ ), 6.13 (2 H, s, aromatic H), 6.60 (1 H, s, CH), and 7.05–8.08 (10 H, m, aromatic H); mass spectral analysis was consistent with the assigned structure; exact mass, 412.203432 (calcd, 412.203833).

*Anal.* Calcd for  $C_{28}H_{28}O_3$ : C, 81.52; H, 6.84. Found: C, 81.26; H, 6.98.

(*dl*)-1-(2-Methoxynaphthyl)-1-(2-methylnaphthyl)-1-(2,4,6-trimethoxyphenyl)methane (1). Five drops of concentrated  $H_2SO_4$  was added to a mixture of 1-(2-methoxynaphthyl)-1-(2-methylnaphthyl)methanol<sup>3</sup> (5.0 g, 16.8 mmol) and 1,3,5-trimethoxybenzene (10.0 g, 60 mmol) dissolved in 100 ml of nitromethane, at room temperature, with stirring. The mixture was worked up as described above and the crude product was recrystallized from acetone to yield 5.2 g (65%) of translucent cubes: mp 157–160°;  $^1H$  nmr  $\delta_{CDCl_3}^{TMS}$  2.13 (3 H, s,  $CH_3$ ), 3.13 (3 H, s,  $OCH_3$ ), 3.23 and 3.28 (6 H, br singlets,  $OCH_3$ ), 3.70 (3 H, s,  $OCH_3$ ), 6.10 (2 H, s, aromatic H), 7.20–7.66 (13 H, m, aromatic H plus CH); mass spectral analysis was consistent with the assigned structure; exact mass, 478.214609 (calcd, 478.214396).

*Anal.* Calcd for  $C_{32}H_{30}O_4$ : C, 80.31; H, 6.32. Found: C, 80.09; H, 6.30.

**Dnmr Measurements.** The  $^1H$  nmr spectra were recorded on a Varian A-60A or a Varian HA-100 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.<sup>28</sup> Temperatures are considered to be accurate to  $\pm 2^\circ$ , although within a given series of measurements smaller differences (ca.  $\pm 0.5^\circ$ ) are considered significant. Saturation of the nmr signals was avoided. The HA-100 spectra were calibrated using the difference frequency between the lock signal and pen position (DIFF 1 of the signal monitor) as measured on the V-4315 signal counter. Dnmr samples were ca. 25% v/v solutions with ca. 5% v/v TMS or hexamethyldisiloxane, which were used as the lock signal for the 100-MHz (frequency sweep mode) spectra.

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