Figure 3. The 35-GHz experimental and calculated esr spectra for the sample of Figure 2. The coupling constants and g values used to obtain the theoretical spectra are the same as in Figure 2. The peak to peak Lorentzian line widths were 6.0 G for both simulations.

Varian E-3 and V-4502 spectrometers, respectively. The computer simulated spectra were obtained using a program for a randomly oriented sample based on the familiar equations $g = g_{xx} \sin^2 \theta \cos^2 \phi + g_{yy} \sin^2 \theta \sin^2 \phi + g_{zz} \cos^2 \theta$ and $A = (A_{xx}^2 \sin^2 \theta \cos^2 \phi + A_{yy}^2 \sin^2 \theta \sin^2 \phi + A_{zz}^2 \cos^2 \theta)^{1/2}$ where g and A are the g value and splitting constant at a given orientation, g_{xx}, g_{yy}, g_{zz} and A_{xx}, A_{yy}, A_{zz} are the principal values of the ^{14}N hyperfine matrix and the g value matrix, respectively, and θ, ϕ are the usual angles in spherical coordinates.[7]

The 9.5-GHz esr spectra of 1 in 2 at 24 and $-196°$ are shown in the top row of Figure 2. The corresponding theoretical spectra are given in the bottom half of Figure 2. In simulating rapid motion about the z axis of a nitroxide, the principal values A_{zz} and g_{zz} remain unchanged, but A_{xx}, A_{yy}, g_{xx}, and g_{yy} are replaced by the motion averaged values $\overline{A_{xx}} = \overline{A_{yy}} = \frac{1}{2}(A_{xx} + A_{yy})$ and $\overline{g_{xx}} = \overline{g_{yy}} = \frac{1}{2}(g_{xx} + g_{yy})$ (the proof parallels the y axis case given in ref 3). It is clear from the calculated spectra of Figure 2 that there are only minor differences between the line shapes for z-axis rotation and a rigid matrix at the conventional microwave frequency of 9.5 GHz. The reason for this is readily seen from the line positions at the principal orientations, as indicated in Figure 2. The maximum splitting in both spectra is $2A_{zz}$ ($\sim$64 G), and the only differences are relatively small shifts in the x and y principal values. The agreement between calculated and experimental spectra is very good, particularly since the line width was the only parameter varied to achieve a visual fit with the experimental spectra.

The corresponding 35-GHz experimental and theoretical esr spectra are shown in Figure 3. We note that there are now major differences between spectra calculated for z-axis rotation and for the rigid matrix. The hyperfine splitting and g-value parameters are the same, but the relative shifts of each three-line spectrum increase by a factor of 12,500 G/3400 G = 3.7 as, given by the familiar expression $h\nu = g\beta H$ where ν is the microwave frequency and H is the magnetic field. The overall splitting in the powder spectrum at 35 GHz is no longer $2A_{zz}$ (see principal line positions in

Figure 3), and z-axis rotation is readily distinguished from the rigid matrix limit. The agreement between the theoretical and experimental spectra is very good, and once again the only independent parameter was the line width. Based on this good agreement between experimental and theoretical spectra we conclude that the spin label 7-doxylstearic acid is either rotating or undergoing rapid large amplitude oscillations about the nitroxide z axis in the γ-cyclodextrin host at room temperature. In contrast, at $-196°$ the esr spectra approach the rigid glass limit. The prominent changes brought about by z-axis rotation are the decrease in overall splitting and the coalescence of the two low field peaks in the 35-GHz spectrum. We note the sensitivity of 35-GHz spectra to z-axis motion renders this a useful general approach for the investigation of anisotropic motion of lipid spin labels in membrane models and biological membranes.

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Separation of Conformational Diastereomers in a Triarylmethane. A Novel Type of Stereoisomerism[1]

Sir:

In a recent analysis of stereoisomerism and stereoisomerization in compounds displaying restricted rotation of aryl groups,[2] we remarked that a molecule of the type Ar_3ZX containing a chiral center (Z) and three aryl groups (Ar) differing in constitution and lacking a local C_2 axis can exist in 32 stereoisomeric propeller forms, and that for such a compound, "four nonintercovertible isomers exist even when interconversions by the two-ring flip are rapid, consisting of two diastereomeric dl pairs." We now wish to report the experimental verification of this analysis.

Racemic 1-(2-methoxynaphthyl)-1-(2-methylnaphthyl)-1-(3-methyl-2,4,6-trimethoxyphenyl)methane (1) was synthesized by condensation of 1-(2-methoxynaphthyl)-1-(2-methylnaphthyl)methanol and 2,4,6-trimethoxytoluene in nitromethane with H_2SO_4 as a catalyst. Purification of the product mixture afforded a sample of 1, mp 160–195°. The ^1H nmr spectrum (benzene-d_6, hexamethyldisiloxane as internal reference) of this material featured two singlets in the methyl proton region at δ 2.26 and 2.33 ppm, due to the diastereotopic methylnaphthyl groups. The intensity ratio of these two signals revealed that the product consisted of a ca. 60:40 mixture of diastereomers 1a and 1b, respectively. Several recrystallizations of this ma-

(1) This work was supported by the National Science Foundation (GP-30257).
(2) D. Gust and K. Mislow, J. Amer. Chem. Soc., 95, 1535 (1973).

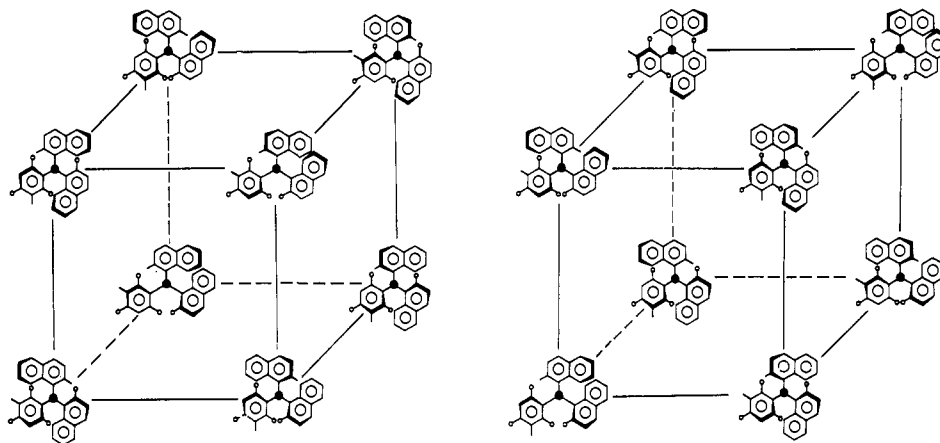(7) L. J. Libertini and O. H. Griffith, J. Chem. Phys., 53, 1359 (1970).

Figure 1. The 16 structures depict one-half of the 32 possible stereoisomers of **1** (the ones having the *R* configuration at the chiral center). The 16 isomers are grouped into two sets of eight each, shown at the corners of the two cubes. The edges connecting the structures represent stereoisomerization pathways by the two-ring flip mechanism. 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.

terial from benzene gave an analytical sample[3] of **1a**, more than 95% diastereomerically enriched, mp 210–213°. From the mother liquors a fraction,[3] mp 158–163°, was obtained, consisting of **1a** and **1b** in a ratio of ca. 30:70. The rate of interconversion of the diastereomers was determined by conventional means and gave $\Delta G^{\neq}_{122}$ = 30.6 kcal/mol for **1a** → **1b** and $\Delta G^{\neq}_{122}$ = 30.4 kcal/mol for the reverse process.[4]

It has been shown[5] that the two-ring flip is the stereoisomerization mechanism of lowest energy (threshold mechanism) in all systems of the type Ar_3Z and Ar_3ZX thus far examined where such isomerization occurs by correlated rotation of the aryl groups. In addition, for systems where two-ring flip pathways for stereoisomerizations requiring higher energies are available, these pathways are evidently followed preferentially.[5] This conclusion applies with equal force to the present case, where all stereoisomerizations by this mechanism occur rapidly on the nmr time scale at ambient temperatures. However, given the substitution pattern of **1**, rapid stereoisomerization by two-ring flips is incapable of interconverting all diastereomeric conformations.[2] Consequently, a novel type of stereoisomerism arises.

The various interconversion pathways by the two-ring flip mechanism are shown in Figure 1. The cube on the left might be taken to represent one of the diastereomers, arbitrarily **1a**, whereas the other represents the second diastereomer, arbitrarily **1b**.

The key features to be noted are the following. First, each of the three aryl rings in **1a** or **1b** may rotate by multiples of π radians in the course of the two-ring flips without achieving interconversion of **1a** and **1b**. Thus, there is no restriction on the torsional angle of any of the individual aryl groups, the only constraint being a mechanistic one. Another way of putting it is that the restriction lies in the relationship of the torsional angles of the three groups, rather than in the absolute value of each. In consequence, conventional definitions of "conformer" which are couched in terms

of torsional angles around a single bond appear to be inadequate to deal with the present case, without modification, since it is difficult to see how any such definition is capable of differentiating **1a** and **1b**, which are, after all, diastereomeric *conformers*. By the same token, any one of the eight rapidly interconverting forms depicted at the vertices of either cube in Figure 1 may be taken as a representative conformation for **1a** or **1b**.

Second, it must be emphasized that the existence of separable diastereomers **1a** and **1b** (*residual stereoisomerism*) depends primarily on the structural and mechanistic constraints described above, and only secondarily on steric congestion about the central atom. A system with bulkier blocking substituents (*e.g.*, methyl in place of some of the methoxy groups) would presumably exhibit a barrier to diastereomerization substantially higher than 31 kcal/mol.

It remains to consider the mechanism for the interconversion of **1a** and **1b**. As previously indicated[2] such interconversion could in principle occur by either a one- or a three-ring flip. On the basis of empirical force field calculations,[5] we conclude that the mechanism in question is the one-ring flip.

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Photoisomerization of β-Diketones and β-Keto Esters

Sir:

While studying the photo-Fries rearrangement[1] of enol esters, we have observed that the β-diketones formed were affected by light, resulting in a shift of their enol–keto equilibrium ratio. Recently a similar change in the enol content of ethyl acetoacetate under the influence of ultraviolet (uv) irradiation was de-

(3) All compounds exhibited analytical and spectral properties consistent with the given structural assignments.

(4) The same value for the equilibrium constant (K = 0.7 for **1a** ⇌ **1b** at 122°) was obtained starting either with **1a** or with material enriched in **1b**.

(5) P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, in press; J. D. Andose and K. Mislow, *ibid.*, in press.

(1) Part of a Ph.D. Thesis to be submitted by D. Veierov to the Feinberg Graduate School of the Weizmann Institute of Science. For previous publications on this subject see: M. Gorodetsky and Y. Mazur, *Tetrahedron*, **22**, 3607 (1966), and references cited therein.