where $C = Ng^2\beta^2S(S + 1)/3k$, using ten terms in the series, results in $J/k = 18.5\ (\pm 0.7)$°K and $g = 2.11$. This fit is within the estimated error and is a considerable improvement over the Curie–Weiss fit, although deviations do occur at temperatures below 35°K. The satisfactory fit to a Heisenberg two-dimensional model for this compound along with the large values for the susceptibility close to the transition at low fields, as well as the field dependence of the susceptibility (decreasing the field increases the susceptibility above the transition), strongly suggests that spins are aligned ferromagnetically within the two-dimensional network of square-planar chlorocuprate(II) ions and at about 11.8°K order antiferromagnetically in three dimensions with these ferromagnetic planes aligned antiparallel to one another. As observed in $(C_2H_5NH_3)_2CuCl_4$ the ferromagnetic exchange is apparently significantly larger than the antiferromagnetic coupling between planes, for the susceptibility is dominated above the transition by this ferromagnetic coupling.

Preliminary single-crystal susceptibility and magnetization measurements confirm this general picture with the easy axis of magnetization (the *c* crystallographic axis) showing a possible spin flop or metamagnetic transition. Further investigation of these field induced transitions in this interesting, highly two-dimensional compound are in progress with an aim toward mapping out the various phase boundaries and comparing the anisotropy field to $[C_2H_5NH_3]_2CuCl_4$.

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Observation of *z*-Axis Anisotropic Motion of a Nitroxide Spin Label

Sir:

Lipid spin labels are providing useful information on the fluidity in the lipid phases of membrane model systems and biological membranes.[1,2] The long axis of the lipid usually corresponds to the nitroxide *x*, *y*, or *z* axis (see Figure 1), and studying anisotropic motion about these principal axes is an important step in understanding membrane spin labeling experiments. We recently obtained well-defined examples of *x*- and *y*-axis anisotropic motion by trapping spin labels in the tubular cavities of thiourea and *β*-cyclodextrin inclusion crystals.[3] We now report the first observation of *z*-axis anisotropic motion. This study relies on 35 GHz electron spin resonance measurements, where differences in *g* values produce a much larger effect than in the conventional 9.5 GHz esr spectra.

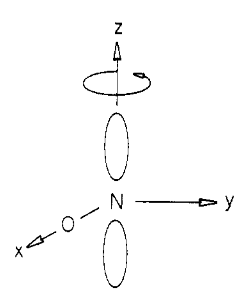


Figure 1. The nitroxide coordinate system.

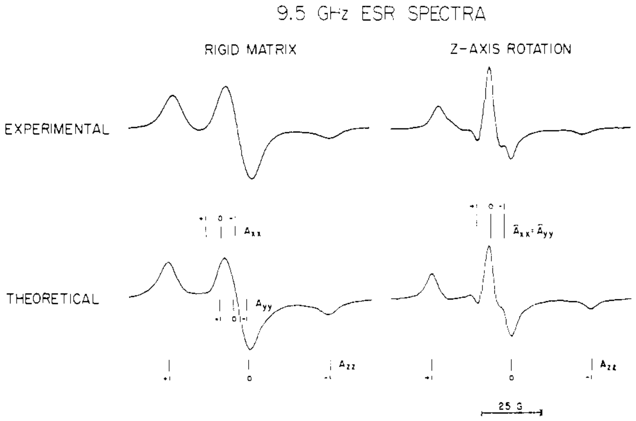
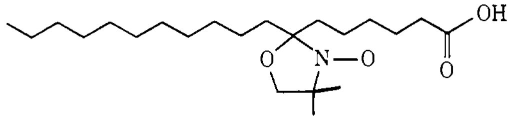


Figure 2. Experimental 9.5-GHz esr spectra of 7-doxylstearic acid trapped in *γ*-cyclodextrin at −196° (left spectrum), 24° (right spectrum), and the theoretical spectra for the rigid matrix and *z*-axis rotation. The principal values of the *A* and *g*-value matrix used in the simulations were those measured for 2-doxylpropane: $A_{xx} = 5.9$ G, $A_{yy} = 5.4$ G, $A_{zz} = 32.9$ G, $g_{xx} = 2.0088$, $g_{yy} = 2.0058$, and $g_{zz} = 2.0022$ (P. Jost, L. J. Libertini, V. C. Hebert, and O. H. Griffith, *J. Mol. Biol.*, **59**, 77 (1971)). To simulate *z*-axis rotation A_{xx}, A_{yy}, g_{xx}, and g_{yy} were replaced by $\overline{A_{xx}} = \overline{A_{yy}} = \frac{1}{2}(5.9 + 5.4) = 5.6$ G, and $\overline{g_{xx}} = \overline{g_{yy}} = \frac{1}{2}(2.0088 + 2.0058) = 2.0073$. The peak to peak widths of the Lorentzian lines were 3.8 and 6.0 G for the calculated *z*-axis motion and rigid matrix spectra, respectively. The indices +1, 0, and −1 refer to the *z* components of the nuclear spin angular momentum.



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The lipid spin label 7-doxylstearic acid (**1**) (the 4′,4′-dimethyloxazoladine-*N*-oxyl derivative of ketostearic acid) was obtained from Syva Associates and *γ*-cyclodextrin (**2**) (*γ*-Schardinger dextrin) was prepared as described previously.[4,5] The lipid spin label **1** was trapped in the host **2** by shaking together a solution of 0.5 mg of **1** in 0.8 ml of cyclohexane with a second solution of 40 mg of **2** in 0.8 ml of water. The resulting precipitate was washed with cyclohexane and then dried. It is well known that the nitroxide *z* axis of **1** is essentially parallel to the long axis of the extended stearic acid chain,[1,6] so that this molecule is a good candidate for the study of *z*-axis anisotropic motion. The 9.5- and 35-GHz esr spectra were recorded on

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(1) P. Jost, A. S. Waggoner, and O. H. Griffith, "Structure and Function of Biological Membranes," L. Rothfield, Ed., Academic Press, New York, N. Y., 1971, Chapter 3.

(2) H. M. McConnell and B. G. McFarland, *Quart. Rev. Biophys.*, **3**, 91 (1970).

(3) G. B. Birrell, S. P. Van, and O. H. Griffith, *J. Amer. Chem. Soc.*, **95**, 2451 (1973).

(4) D. French, M. L. Levine, J. H. Pazur, and E. Norberg, *J. Amer. Chem. Soc.*, **71**, 353 (1949).

(5) D. French, *Advan. Carbohyd. Chem.*, **12**, 189 (1957).

(6) A. S. Waggoner, T. J. Kingzett, S. Rottschaefer, O. H. Griffith, and A. D. Keith, *Chem. Phys. Lipids*, **3**, 245 (1969).

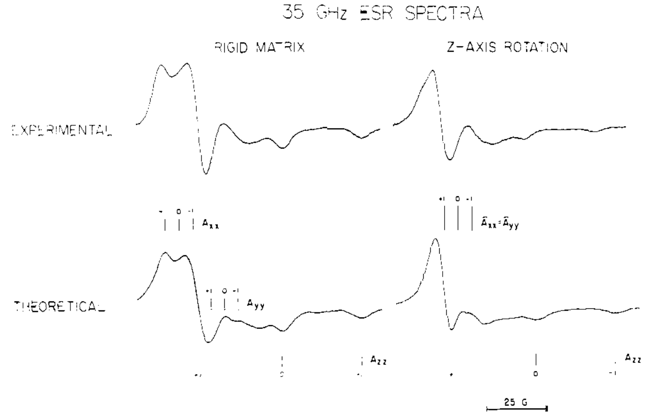

Figure 3. The 35-GHz experimental and calculated esr spectra for the sample of Figure 2. The coupling constants and *g* values used to obtain the theoretical spectra are the same as in Figure 2. The peak to peak Lorentzian line widths were 6.0 G for both simulations.

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 $\bar{A}_{xx} = \bar{A}_{yy} = {}^1/_2(A_{xx} + A_{yy})$ and $\bar{g}_{xx} = \bar{g}_{yy} = {}^1/_2(g_{xx} + g_{yy})$ (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 $2A_{zz}$ (∼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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[7] L. J. Libertini and O. H. Griffith, *J. Chem. Phys.*, **53**, 1359 (1970).

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 noninterconvertible 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 ^{1}H 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-

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[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).