the density calculated for two dimers per unit cell, 1.55 g cm^{-3}, agrees well with the experimental value, 1.56 g cm^{-3}, obtained by the flotation method in a mixture of *n*-heptane and carbon tetrachloride. Intensity data were collected by the θ–2θ scan technique; a total of 2289 unique reflections were collected and 1272 of those were selected as above background on the basis that $\sigma(I)/I < 0.30$. The reflections were corrected for Lorentz and polarization effects and calculated absorption corrections were applied. The structure was determined by the heavy-atom method and refined, using anisotropic temperature factors for all nonhydrogen atoms (hydrogen atoms have not been included in these calculations), to a conventional R value, $R = (\Sigma|F_o - F_c|)/(\Sigma|F_o|)$, of 0.0796 and a weighted R_w value, $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$, of 0.0657 using a weighting scheme based on counting statistics ($w = 4I/\sigma(I)^2$) and minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. Further refinement is in progress but the main features of the structure are apparent at this stage.

The unit cell contains two discrete centrosymmetric, dimeric units that, although crystallographically independent, are virtually identical. The structure is illustrated in Figure 1 and the values for bond distances and bond angles are the average values for the two units (the greatest difference in corresponding bond distances or bond angles was only four times the estimated standard deviation). Within each unit, the coordination of the copper is essentially planar (the copper is only 0.02 Å out of the least-squares plane of the four donor atoms and none of the donor atoms is more than 0.01 Å out of that plane), and there are only small deviations from planarity for the copper atom and the entire tetradentate ligand associated with it (the greatest deviation from the plane of the donor atoms is 0.46 Å for C9). The square-planar copper(II) complexes are connected into dimers by hydrogen bonding of the alcohol group of one complex and the alkoxide group of the other to form an eight-membered ring. The average oxygen–oxygen distance of 2.29 (1) Å is shorter than any hydrogen bonded oxygen–oxygen distance previously reported and is almost as short as the fluorine–fluorine distance[5] in the HF_2^- ion (2.26 Å); the observation that the compound retains the dimeric units when dissolved in chloroform is a further indication that strong hydrogen bonds exist within these units.

Although the average copper–copper distance for the two units is 4.979 (6) Å, the room temperature magnetic moment of 1.69 BM per gram atom of copper is below the spin-only value for one unpaired electron, 1.73 BM; the moment drops to 1.56 BM at 193°K and to 1.14 BM at 77°K. These values are indicative of antiferromagnetic coupling with a coupling constant, J, of approximately 100 cm^{-1}. Although much larger coupling constants have been observed for binuclear copper(II) complexes, the value is surprisingly large in view of the copper–copper distance and the nature of the bridging; the only coupling mechanism which seems at all reasonable for this compound is indirect coupling *via* a σ pathway. It is not clear, however, which factor—the greater copper–copper distance, the absence of a π pathway, or the different types of bridging—causes the coupling to be less than that observed for many oxygen-bridged copper complexes with a copper–copper distance of approximately 3.0 Å.

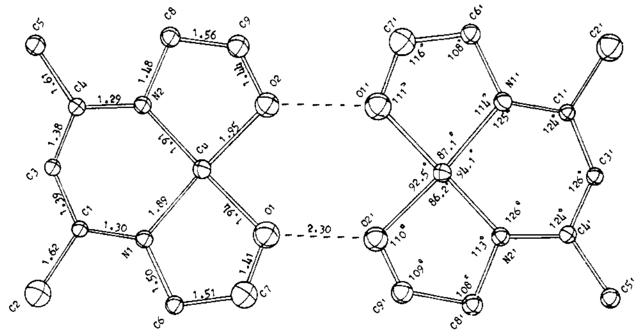

Figure 1. Molecular structure of the dinuclear complex, $[CuC_9H_{16}N_2O_2]_2$, showing all nonhydrogen atoms. Bond distances and bond angles are average values for the two independent molecules in the unit cell; standard deviations of all bond lengths are in the range 0.01–0.03 Å and standard deviations of all bond angles are in the range 0.6–23.°.

We have also prepared and studied the corresponding nickel(II) complex and found it to be isostructural with the copper(II) complex; in fact, the only significant differences in the two structures were the C–CH_3 distances (1.53 Å and 1.52 Å for the nickel compound). The C–CH_3 values for the nickel structure are in good agreement with previous structures; we have no explanation for the longer distances observed for the copper compound at this point in the refinement. The only previous example of cooperative hydrogen bonding in transition metal complexes was a cobalt(III)–nickel(II) complex[6] with 2-aminoethanol ligands which involved hydrogen bonding between octahedral faces of the two complexes. Further work on the synthesis, structure, and magnetic properties of hydrogen bonded polynuclear complexes is in progress.

Acknowledgment. This work was supported by National Science Foundation Grant GP-20885. Funds from the Quality Improvement Program of the State of Georgia for the purchase of X-ray diffraction equipment are gratefully acknowledged; the help of the Rich Electronic Computer Center of Georgia Institute of Technology with computations is appreciated.

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(5) L. Helmholz and M. T. Rogers, *J. Amer. Chem. Soc.*, **61**, 2590 (1939).

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J. A. Bertrand,* F. T. Helm
School of Chemistry, Georgia Institute of Technology
Atlanta, Georgia 30332

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Line-Shape Effects in the Electron Spin Resonance Spectra of Fluoroalkyl Radicals[1]

Sir:

The study of temperature-dependent line shapes in solution esr spectra of acyclic alkyl radicals has yielded valuable information concerning the barriers hindering internal rotations and the equilibrium conformations in

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(1) Presented in part at the First Winter Fluorine Conference, St. Petersburg, Fla., Jan 1972, and at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973.

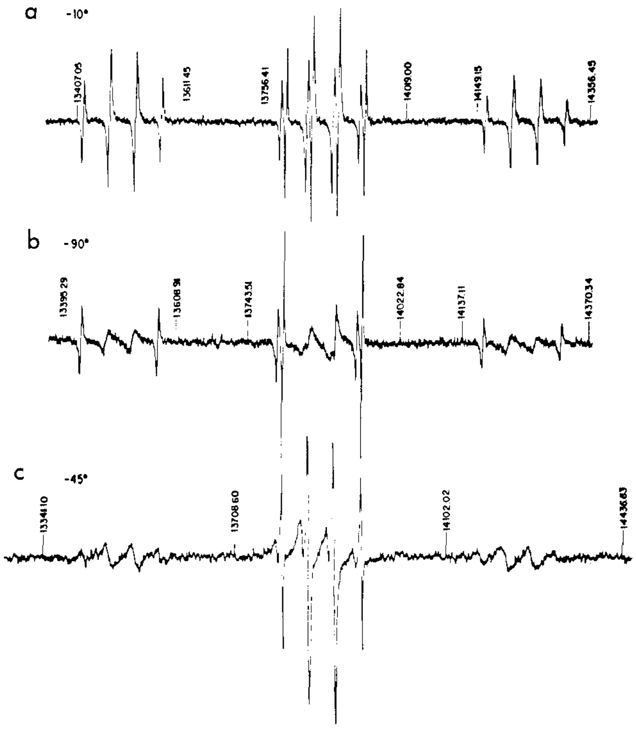

Figure 1. Esr spectra of the perfluoroethyl radical obtained by photolysis of perfluoropropionyl peroxide (a) in dichlorodifluoromethane at −10°, (b) in dichlorodifluoromethane at −90°, and (c) in a completely halogenated fluorocarbon oil of high viscosity (see text) at −45°. In the absence of unusual relaxation processes, the inner two lines of all four quartets in the spectrum should be of equal height.

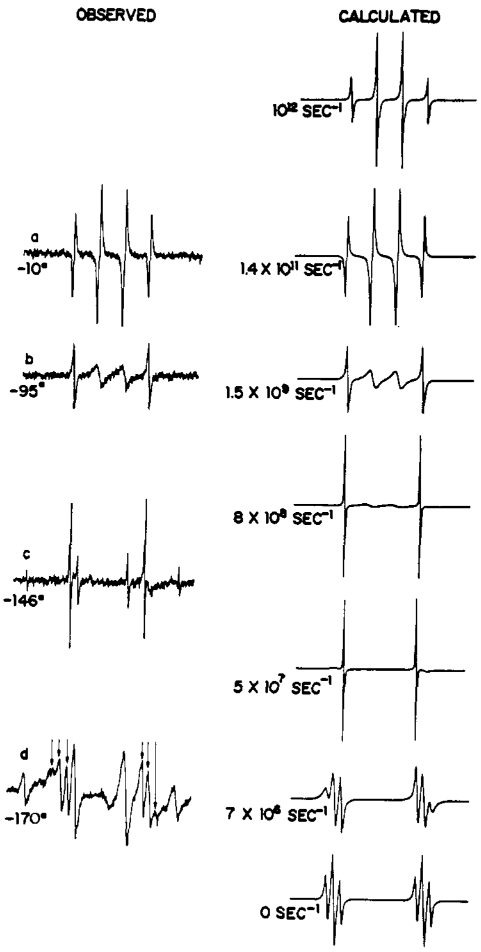

Figure 2. Line-shape changes with temperature in the spectrum of perfluoroethyl radical due to hindered internal rotation of the CF_3 group. Spectra a and b were obtained by photolysis of perfluoropropionyl peroxide in CCl_2F_2 and represent the downfield $M^{\alpha\text{-F}} = 1$ lines. Spectra c and d were obtained by photolysis of *tert*-butyl perfluoropropionyl perester in $CClF_3$ at −146 and −170° and show the central region of the spectrum containing the $M^{\alpha\text{-F}} = 0$ lines. At these temperatures, the wing lines are broadened beyond detection. Spectra c and d are complicated by the presence of a quartet of 22.86 G attributed to the methyl radical of unknown provenance. At −146° the downfield $I^{\alpha\text{-F}} = 1$ lines (second-order components) are obliterated by dipolar line broadening. The calculated spectra were obtained by the density matrix method.

these radicals.[2] Although some esr studies on partially fluorinated alkyl radicals have been reported,[3] little is known about the internal motions and the conformational preferences of their perfluoro analogs for which solution esr spectra have not been available until very recently.[1,4] We report here the esr spectra of a few simple perfluoroalkyl radicals and the dynamic information which can be extracted from the analysis of their temperature-dependent line shapes.

The perfluoroethyl radical was generated over a broad temperature range by photolysis of perfluoropropionyl peroxide or perfluoropropionic acid *tert*-butyl perester[5] in various Freon solvents (*e.g.*, CCl_2F_2, $CClF_3$, $CClF_2$-CCl_2F, and mixtures thereof). At −10° (Figure 1a) the spectrum consists of a large triplet of 87.7 G due to two α-fluorines split into quartets of 11.43 G by three β-fluorines ($g = 2.00386$). The central components of the triplet ($M_I^{\alpha\text{-F}} = 0$ lines) are further split by second-order effects[6] into doublets corresponding to the two possible values of the resultant nuclear angular momentum for the α-fluorines $I^{\alpha\text{-F}} = 1,0$. The relative amplitudes of the spectrum, however, deviate from the expected ratios. Two distinct line-shape effects become important as the temperature is lowered: first, the broadening of the inner two lines of the quartets associated with the β-fluorines and, second, the broadening of the outer lines of the triplet ($M_I^{\alpha\text{-F}} = \pm 1$ lines) and of the downfield second-order components ($M_I^{\alpha\text{-F}} = 0$, $I^{\alpha\text{-F}} = 1$ lines) associated with the two α-fluorines. The latter effect has a strong *viscosity* dependence. Figure 1c shows the spectrum of the C_2F_5 radical at −45° obtained by photolysis of perfluoropropionyl peroxide in a Halocarbon oil (series 25.7/100) in which the wing lines of the triplet and the downfield second-order components are nearly obliterated by line broadening while the central quartet ($I^{\alpha\text{-F}} = 0$ lines) is unaffected by the viscosity of the medium.

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(2) (a) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971); (b) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971); J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, No. 24, 147 (1970).

(3) (a) A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys. Lett.*, **5**, 552 (1970); (b) D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6485 (1972); (c) A. Hudson and K. D. J. Root, *Advan. Magn. Resonance*, **5**, 1 (1971).

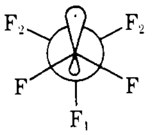
(4) (a) R. V. Lloyd and M. T. Rogers, *J. Amer. Chem. Soc.*, **95**, 1512 (1973); (b) R. W. Fessenden has observed the spectrum of the perfluoroethyl radical by radiolysis of solid C_2F_6 (private communication).

(5) *Cf.* J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969).

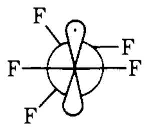
(6) R. W. Fessenden, *J. Chem. Phys.*, **37**, 747 (1962).

The viscosity-independent broadening of the central lines of the quartets ($M_I^{\beta\text{-F}} = \pm 1/2$ lines) is caused by hindered rotation of the trifluoromethyl group about the C–C bond axis and is shown as a function of temperature in Figure 2. The spectrum at −170° shows the incipient formation of two triplets of 3.14 G separated by 40.4 G indicating two equivalent β-fluorines and a unique β-fluorine in the most stable conformation of the radical. *Opposite signs* for these two coupling constants must be taken for their weighted average to be 11.37 G in close agreement with the 11.43 G quartet splitting at higher temperatures. Knowledge of the spectral parameters in the slow-exchange limit allows the spectra to be fitted by the density matrix method[2b,7] (Figure 2). An activation energy of 2.85 kcal/mol is obtained for the rate process which exchanges one of the two equivalent β-fluorines with the unique β-fluorine.

The presence of a substantial barrier to internal rotation in the perfluoroethyl radical should be contrasted with the essentially free rotation in the ethyl[2,8] and the 2,2,2-trifluoroethyl radicals.[3] In these species the radical sites are planar and the molecules possess sixfold axes of internal rotation. Sixfold barriers typically have magnitudes of only a few hundred calories/mole. A barrier of 2.85 kcal mol^{-1} is, therefore, indicative of a threefold axis of internal rotation which obtains in a perfluoroethyl radical with a strongly pyramidal radical center. This conclusion is entirely consistent with the magnitude of the α-fluorine coupling,[9] and is also borne out by INDO calculations[10] as a function of the nonplanarity angle θ (defined as the angle between the C–C axis and the bisector of the $F_\alpha CF_\alpha$ angle) and the angle of rotation about the C–C axis.[11] An energy minimum is obtained for conformation I with $\theta = 30°$.[12] At present we cannot exclude a motion of coupled inversion and rotation with barriers of comparable heights (2.9 kcal/mol) and proceeding through a common transition state II as being responsible for the observed linewidth effect.



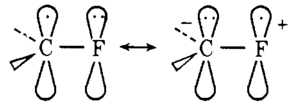
I



II

a_α (calcd), 96.7 G; (exptl) 87.6 G
a_1 (calcd), 184.6 G; (exptl) $\pm$40.4 G
a_2 (calcd), 6.9 G; (exptl) $\mp$3.14 G

The viscosity-dependent selective line broadening (Figure 1) is due to a different relaxation process brought about by the modulation of the anisotropic (dipolar) component of the hyperfine coupling tensor for the α-fluorines by the tumbling motion in solution.[13] This component is very large because of contributions of structures such as III which place unpaired spin density in fluorine 2p orbitals. This line-shape effect is thus ubiquitous for radicals with α-fluorines, and it is also displayed by the trifluoromethyl radical which was chosen for a more quantitative study since its F hyperfine tensor is known from a single-crystal esr study.[14] The CF$_3$ radical (a^F = 144.1 G at −90°) was generated from CF$_3$Br by a novel general technique for the production of fluoroalkyl radicals consisting in the photolysis of mixtures of a fluoroalkyl bromide, a dialkyl phosphite, and di-*tert*-butyl peroxide.[15] At −141° (Figure 3b) the wing lines ($M_I^F = \pm 3/2$) and the downfield second-order components ($M_I^F = \pm 1/2$, $I^F = 3/2$) are severely broadened and appear with reduced amplitudes.[16] The sharper central lines ($M_I^F = \pm 1/2$, $I^F = 1/2$) are also significantly broader at −141° than at −90°.



III

The spin Hamiltonian for a system undergoing dipolar relaxation may be written as

$$H = H_0 + H_d'(t) \qquad (1)$$

where H_0 gives the positions of the lines of the esr spectrum and $H_d'(t)$ represents the randomly fluctuating electron–nuclear dipolar interaction. The equation of motion for the spin density vector $\boldsymbol{\rho}$ in Liouville space for such a system can be written as

$$\frac{d\boldsymbol{\rho}}{dt} = -i\mathbf{L}\boldsymbol{\rho} + \mathbf{R}(\boldsymbol{\rho} - \boldsymbol{\rho}_0) \qquad (2)$$

where **L** is the Liouville operator corresponding to the Hamiltonian H_0, **R** is the relaxation matrix, and $\boldsymbol{\rho}_0$ is the spin density matrix at thermal equilibrium. In the coupled representation $|(I_1,I_2, \ldots)IM_ISM_s\rangle$ **L** is almost diagonal and the transverse relaxation time for the $\alpha \leftrightarrow \beta$ transition is given to first order by

$$[T_{2d}(\alpha{\leftrightarrow}\beta)]^{-1} = -R_{\alpha\beta:\alpha\beta} \qquad (3)$$

Assuming a set of completely equivalent fluorine nuclei with an axially symmetric hyperfine coupling tensor the dipolar contribution to the line width of the (M_I, I) hyperfine component is given by[17]

$$[T_{2d}(M_I,I)]^{-1} = (A_{\parallel}^2/80)\{[3I(I+1) + 5M_I^2]J_0 + [7I(I+1) - M_I^2]J_w\} \qquad (4)$$

where $A_{\parallel}$ is the parallel component of the anisotropic part of the hyperfine tensor in angular frequency units,

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(7) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971).

(8) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); (b) R. W. Fessenden, *J. Chim. Phys. Physicochim. Biol.*, **61**, 1570 (1964).

(9) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965); (b) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *ibid.*, **48**, 4802 (1968).

(10) (a) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968); (b) we obtained a copy of the program CNINDO, written by P. A. Dobosh, from the Quantum Chemical Program Exchange, Indiana University.

(11) The calculations assume tetrahedral angles for the CF$_3$ group, equal C–F bond lengths of 1.33 Å, a C–C bond of 1.50 Å, and an FCαF angle of 115°.

(12) The lack of agreement between calculated and experimental β-fluorine coupling constants is noteworthy. It appears to be an intrinsic feature of the CNINDO program (G. R. Underwood, private communication). Variations of bond length and distortions at the β-carbon did not produce sensibly smaller values for the coupling to the β-fluorine contained in the plane of symmetry of conformation I.

(13) Line-shape effects of this type for several RCF$_2$ radicals have been reported by another group of investigators while this work was near completion (J. Cooper, A. Hudson, R. A. Jackson, and M. Townson, *Mol. Phys.*, **23**, 1155 (1972)).

(14) M. T. Rogers and L. D. Kispert, *J. Chem. Phys.*, **46**, 3193 (1967).

(15) (a) P. J. Krusic, P. Meakin, and B. S. Smart, manuscript in preparation; (b) *cf.* A. G. Davies, D. Griller, and B. P. Roberts, *J. Amer. Chem. Soc.*, **94**, 1782 (1972).

(16) This effect for the CF$_3$ radical was noted by Fessenden and Schuler[9a] but was not interpreted by them.

(17) A. D. McLachlan, *Proc. Roy. Soc. Ser. A.*, **280**, 271 (1964).

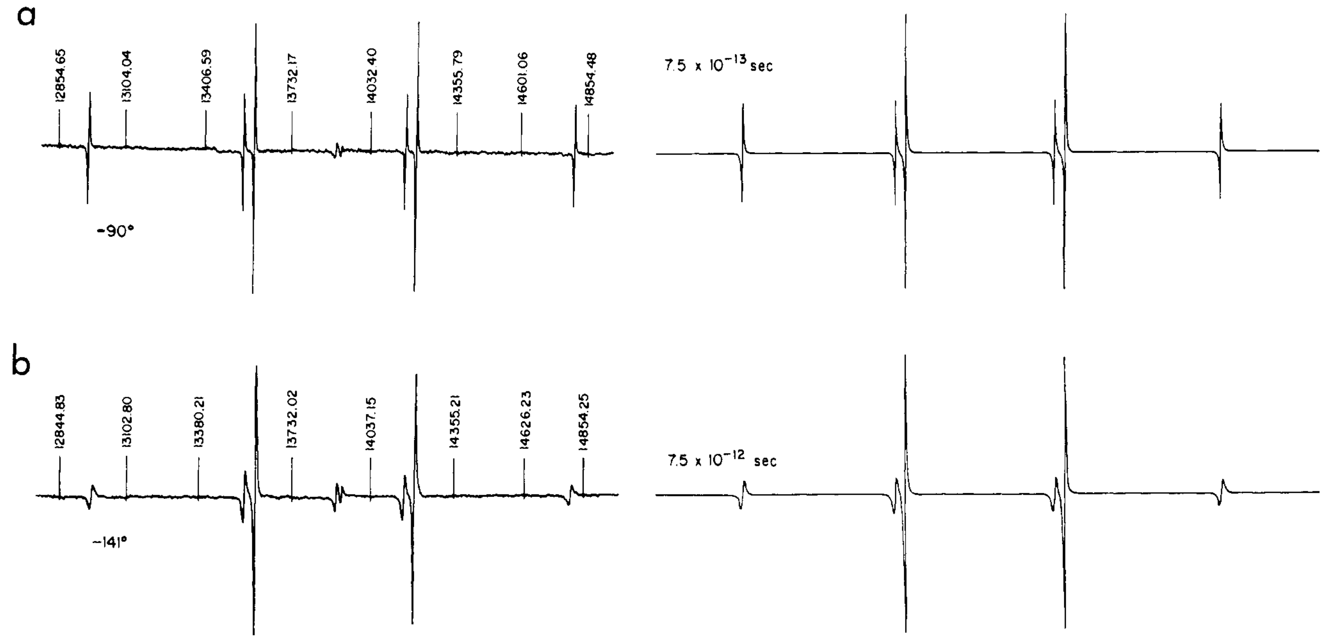


Figure 3. Esr spectra of the trifluoromethyl radical at two temperatures with the calculated spectra (Redfield relaxation matrix theory) for two rotational correlation times. The radical was generated by photolysis of a solution containing di-*tert*-butyl peroxide, dimethyl phosphite, and bromotrifluoromethane (1:1:5, v/v/v).

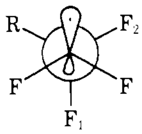
$J_0 = 2\tau_c$, $J_w = 2\tau_c(1 + \omega^2\tau_c^2)^{-1}$, and τ_c is the correlation time for the rotational tumbling. The details of the line-shape calculations will be reported elsewhere.[18]

The experimental spectra for the $\cdot CF_3$ radical were fit by this theory using Lorentzians with line-width parameters $T_2(M_I,I)$ given by

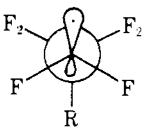
$$[T_2(M_I,I)]^{-1} = [T_{2d}(M_I,I)]^{-1} + T_{2o}^{-1}$$

where T_{2o} accounts for other relaxation processes. In these calculations $A_{\parallel}$ was taken to be 108 G[14] and T_{2o} was chosen to give best agreement with the experimental spectra ($T_{2o} = 75 \times 10^{-9}$ sec). It is seen in Figure 3 that the agreement is quite good. The resulting rotational correlation times (Figure 3) compare well with values for small molecules obtained by other means.[19]

We also examined the spectra of the *n*-perfluoropropyl[1,4] and *n*-perfluoroheptyl radicals from the corresponding bromides. At −60° the spectrum of the former consists of a triplet of triplets caused by the two α-fluorines (86.2 G) and the two β-fluorines (15.1 G) split into quartets by the γ-fluorines (3.61 G). At room temperature the spectrum of the latter is likewise a triplet of triplets (86.0 and 16.4 G) split into an apparent quintet of 1.5 G. The α-fluorine couplings indicate radical sites of comparable geometry to that in perfluoroethyl. In both radicals the magnitudes of the β-fluorine couplings *increase* notably as the temperature is raised. Save for the dipolar broadening of the wing lines, particularly severe for the *larger* heptyl radical, no additional line-shape effect was apparent down to −100°. This behavior is consistent with the presence of a barrier to rotation about the C_α–C_β bonds with minima corresponding to conformations IV and V. Conformation V should lead to the smallest value



IV



V

for the β-fluorine coupling (*cf.* I). The observation of a positive temperature coefficient for $a_{\beta\text{-F}}$ must then mean that this rotamer is the more populated at low temperatures and hence the more stable. A fuller analysis of the internal dynamics in these and other perfluoroalkyl radicals is in progress.

Acknowledgments. We are grateful to Professor J. K. Kochi (Indiana) for a sample of perfluoropropionic acid *tert*-butyl perester, to Dr. D. P. Carlson (Du Pont) for samples of perfluoropropionyl peroxide, and to Mr. B. F. Gordon for technical assistance.

P. Meakin, P. J. Krusic*
Central Research Department[20]
E. I. du Pont de Nemours & Company, Experimental Station
Wilmington, Delaware 19898

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[18] P. Meakin and J. P. Jesson, *J. Magn. Resonance*, **11**, 182 (1973). The line widths were calculated using a modified version of a computer program written for the simulation of multipulse and Fourier transform nmr experiments. This program calculates all of the elements of the relaxation matrix in Liouville space in the basis in which the Liouville operator is diagonal. The spectrum is then calculated by diagonalizing ($R - iL$). In this particular case the computer program gives results in agreement with those from eq 4.

[19] W. G. Rothschild, *J. Chem. Phys.*, **59**, 3265 (1970).

(20) Contribution No. 2051.

A Photochemical Reaction with a Preequilibrium Step. Acid-Catalyzed Photochemical Wallach Rearrangement

Sir:

Under excitation by 320-nm monochromatic light, azoxybenzene undergoes an isomerization to *o*-hydroxyazobenzene, the well-known photo-Wallach rearrangement.[1]

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(1) E. Buncel in "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1968.