

in the presence of substantial barriers to internal rotation the group relaxation would not be expected to be independent of the over-all relaxation process. From the plot of a' vs. $a''\omega$ approximate limiting relaxation times may be estimated. It is found that the longest relaxation time at 20° cannot be shorter than 26×10^{-18} sec. and the shortest relaxation time cannot be longer than 12×10^{-12} sec. Due to the long extrapolation, the arc intercept at infinite frequency, a_∞ , of phenylacetonitrile at 60° should be regarded as approximate. Still, $a_\infty - a_D$ is considerably larger than the corresponding difference for anisole and indicates a substantial amount of torsional vibration.

The dielectric constant and loss data for 1-naphthaleneacetonitrile and 1-(chloromethyl)naphthalene fit well on Cole-Cole arcs showing only one relaxation time for the former and a slight distribution of relaxation times for the latter. The relaxation times of the rigid α -chloronaphthalene,¹⁸ α -bromonaphthalene,¹⁹ α -nitronaphthalene,²⁰ and α -naphthyl isocyanate²¹ molecules in benzene solution at 20° are, respectively, 15.8×10^{-12} , 18×10^{-12} , 22.8×10^{-12} , and 31.5×10^{-12} sec. The relaxation times found for 1-(chloromethyl)naphthalene and 1-naphthaleneacetonitrile fit in well

(18) H. Kramer, *Z. Naturforsch.*, **15a**, 66 (1960).

(19) F. Hufnagel, *ibid.*, **15a**, 723 (1960).

(20) R. W. Rampolla and C. P. Smyth, *J. Am. Chem. Soc.*, **80**, 1057 (1958).

(21) B. R. Jolliffe and C. P. Smyth, *ibid.*, **80**, 1064 (1958).

with the series given above and should, therefore, be interpreted as arising from over-all relaxation. The effect of the steric repulsion of the 8-hydrogen has been observed¹⁴ previously in the considerably longer relaxation times of the methoxy- and ethoxynaphthalenes with the substituent group in the 1-position as compared to those with the group in the 2-position.

The Stuart-Briegleb molecular models indicate strong steric repulsion between the 8-hydrogen and the methoxy or ethoxy group in the 1-position, but somewhat less hindrance to group rotation than in the cases of the CH_2Cl and CH_2CN groups, the complete rotation of which appears to be impossible without great distortion of the bond angles. The absence of any detectable contribution from group relaxation confirms the existence of the steric blocking indicated by the molecular models for the 1-naphthaleneacetonitrile and 1-(chloromethyl)naphthalene molecules, but the contributions from hindered group rotation found for 1-methoxy- and 1-ethoxynaphthalene show a degree of molecular flexibility not inherent in the models. The short and practically identical relaxation times found^{22,23} for the hydroxyl group in the 1- and 2-positions are consistent with the smallness of steric hindrance to rotation shown by the models for the 1-position and its absence for the 2-position.

(22) F. K. Fong and C. P. Smyth, *J. Phys. Chem.*, **67**, 226 (1963).

(23) F. K. Fong and C. P. Smyth, *J. Am. Chem. Soc.*, **85**, 548 (1963).

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Theory of Line Widths in Electron Spin Resonance Spectra: Motion of Methyl Groups¹

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RECEIVED APRIL 18, 1964

The relaxation-matrix theory of line widths in electron spin resonance spectra has been employed to analyze the line-width effects arising from the motions of methyl groups in π -electron free radicals. Broadening of the lines can result because the methyl-proton hyperfine splittings are a function of the angle of orientation of the methyl group, and thus the splittings fluctuate as this angle varies. The motion of the methyl groups is treated by a Brownian motion model assuming a free rotatory diffusion about the C-C bond between the methyl group and the aromatic system to which it is bonded, and also by a jump model in which the group can undergo transitions from one to another of three different equilibrium orientations. Radicals with several methyl groups are analyzed as having either completely correlated or completely uncorrelated motions. The correlated motions are approximated by assuming a gear-like interleaving without slip of the hydrogen atoms on methyl groups substituted at adjacent positions on an aromatic ring. When the motions of the methyl group cause large contributions to the line width, the central pair of lines from the splittings by one methyl group are predicted to be broad and the end lines narrow. When there are two or four methyl groups in the radical, large line-width contributions lead to a spectrum in which every third line is narrow while the remaining lines are broad, an effect which is analogous to the alternating line-width phenomenon. For very rapid rotations, nonsecular as well as secular line-width contributions are important, and consequently the nondiagonal relaxation matrix for the case of one methyl group has been analyzed in detail. None of these effects of methyl-group rotations has been observed in the e.s.r. spectra of aromatic radicals, and from the negative results it is possible to estimate that the relaxation time τ_c for the rotation of the methyl groups is less than 10^{-8} sec. The predicted effects are most likely to be found by low-temperature studies on radicals which have large methyl-proton hyperfine splittings and highly hindered methyl groups.

I. Introduction

In a number of recent studies³⁻¹¹ on the electron spin resonance spectra of aromatic free radicals in solution, anomalous line-width variations have been found

(1) This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. AF-AFOSR-285-63, and by the National Science Foundation through Grant No. NSF-GP-1370.

(2) National Science Foundation Predoctoral Fellow, 1959-1962.

(3) J. R. Bolton and A. Carrington, *Mol. Phys.*, **5**, 161 (1962).

(4) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 1156 (1962).

(5) J. H. Freed, P. H. Rieger, and G. K. Fraenkel, *ibid.*, **37**, 1881 (1962).

that are attributable to modulations of the isotropic hyperfine interactions. Some of the effects observed

(6) J. R. Bolton, A. Carrington, and P. F. Todd, *Mol. Phys.*, **6**, 169 (1963).

(7) E. de Boer and E. L. Mackor, *Proc. Chem. Soc.*, 23 (1963).

(8) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, in press. It has come to our attention that A. Horsfield, J. R. Morton, and D. H. Whiffen [*Mol. Phys.*, **5**, 115 (1962)] have observed line-width effects from methyl-group motions in the solid state. Their observations come within the scope of the theory presented here. See also I. Miyagawa and K. Itoh, *J. Chem. Phys.*, **36**, 2157 (1962).

(9) A. Carrington, *Mol. Phys.*, **5**, 425 (1962).

(10) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

References to this work will be designated by I.

(11) J. H. Freed and G. K. Fraenkel, to be published.

have arisen from the motion of hydroxyl-group protons^{3,6,9}; others from perturbations of the spin-density distribution in nitro groups (either because of rotational motions or because of fluctuating interactions with the solvent)^{4,5,8,10,11}; and in one case⁷ the jumping of an alkali metal cation between two different positions in an anion radical was detected. The most striking width variation discovered is a line-width alternation in which every other line in the spectrum is anomalously broadened. Some of the radicals investigated, such as the dihydroxydurene (1,4-dihydroxy-2,3,5,6-tetramethylbenzene) cation,³ the dinitrodurene (1,4-dinitro-2,3,5,6-tetramethylbenzene) anion,^{4,8} and the 2,6-dinitrotoluene anion,⁸ have hindered methyl groups, but no line-width effects due specifically to the methyl-group motions have been observed.⁸ In the present investigation, we examine the implications of these negative results and inquire into the nature of the line-width variations that might be expected from the motions of methyl groups in aromatic free radicals.

The hyperfine splitting from the protons of a methyl group that is substituted in an aromatic free radical is expected to be a function of the orientation of the group with respect to the π -electron framework¹²⁻¹⁶; minimum splitting is predicted for a proton which lies in the plane of the π -electron system, and maximum splitting for a proton rotated by 90° out of the plane. The fluctuations in the splittings from a rapidly rotating methyl group cannot be detected by measuring the positions of the hyperfine lines in the spectrum, however, because the positions are determined by the time-average value of the splittings. But the fluctuations do alter the spectrum since, through a second-order perturbation, they contribute to the line widths. We shall examine the effects of the methyl-group motions by means of the recently developed theory of e.s.r. line widths.¹⁰ This theory is formulated in terms of a relaxation matrix which determines the time dependence of the density matrix of the spin system.

For free radicals in solution, two types of motion have to be specified in order to determine the relaxation matrix: the over-all tumbling of the radical as a whole and the rotation of the methyl groups relative to the rest of the molecule. Molecular tumbling motions were first treated as a Brownian motion rotatory diffusion by Debye in his classic work on dielectric absorption and relaxation in polar liquids. These developments were reviewed and summarized in his book "Polar Molecules,"¹⁷ first published in 1929. The Debye theory was carried over by Bloembergen, Purcell, and Pound¹⁸ in formulating a theory of relaxation in the n.m.r. spectra of liquids, and his ideas have been used since with little change.¹⁹⁻²² The motions

of methyl groups have been examined in a number of studies, and in particular there is an extensive series of investigations on solids using n.m.r. methods by Gutowsky and co-workers.²³ Both classical reorientations of the methyl group and quantum-mechanical tunneling were considered by these authors. A quantum-mechanical treatment is required for analyzing internal rotations in gaseous molecules and is probably also satisfactory for the motions of methyl groups in solids,²³ but a classical stochastic diffusion model is likely to be reasonably suitable for liquids because of the strong influence of the solvent interactions and the low potential barriers for methyl-group rotations.²³ We therefore treat both the over-all tumbling motion of the radical and the methyl-group rotations as a Brownian motion rotatory diffusion. The quantitative details of such a model are not expected to be correct, but the form of the results should be indicative of the main factors of importance. We also use a jump model in which the orientation of the methyl group is limited to three conformations in dynamic equilibrium with each other. This model has the virtue of being quite simple and in a sense it possesses some of the features of a quantum-mechanical tunneling process. A number of the radicals of interest contain several methyl groups, and we treat these on the assumption that the motions of the different groups are either uncorrelated or locked together in a completely correlated manner.

II. Calculation of the Spectral Densities

The spin Hamiltonian of a free radical with fluctuating isotropic hyperfine interactions contains the term¹⁰

$$\hbar|\gamma_e| \sum_i a_i(t) \mathbf{I}_i \cdot \mathbf{S} \quad (2.1)$$

where $a_i(t)$ is the instantaneous value of the isotropic hyperfine splitting (in gauss) and \mathbf{I}_i is the nuclear spin angular momentum operator for the i th nucleus. The spin-angular momentum operator for the electron is \mathbf{S} , and its magnetogyric ratio is γ_e . The splittings of the lines in the e.s.r. spectrum (for molecules tumbling rapidly in solution) are determined by the time-average values of the hyperfine interactions, $\bar{a}_i = \langle a_i(t) \rangle$, while line broadening comes about because of the time dependence of the $a_i(t)$. The contribution to the line broadening and relaxation which arises from modulation of the isotropic hyperfine interaction is quantitatively determined by the second-order effects of the perturbing Hamiltonian¹⁰

$$\hbar\delta\mathcal{C}^{(1)}(t) = \hbar|\gamma_e| \sum_i [a_i(t) - \bar{a}_i] \mathbf{I}_i \cdot \mathbf{S} \quad (2.2)$$

and the time-dependent quantities needed to calculate the line widths are the correlation functions $g_{ij}^{(1)}(\tau)$ for two nuclei i and j ,

$$g_{ij}^{(1)}(\tau) = \gamma_e^2 \langle [a_i(t) - \bar{a}_i][a_j(t + \tau) - \bar{a}_j] \rangle \quad (2.3)$$

The line widths are related to the eigenvalues of the relaxation matrix,¹⁰ and the elements of this matrix are linear combinations of the spectral densities $j_{ij}^{(1)}(\omega)$. These spectral densities are the Fourier transforms of the correlation functions

$$j_{ij}^{(1)}(\omega) = \langle^{1/2} \int_{-\infty}^{\infty} g_{ij}^{(1)}(t) \exp(-i\omega t) dt \quad (2.4)$$

(23) See E. O. Stejskal, D. E. Woessner, T. C. Farrar, and H. S. Gutowsky, *ibid.*, **31**, 55 (1959), and references cited therein.

(12) R. Bersohn, *J. Chem. Phys.*, **24**, 1066 (1956).

(13) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

(14) D. B. Chesnut, *J. Chem. Phys.*, **29**, 43 (1958).

(15) C. Heller and H. M. McConnell, *ibid.*, **32**, 1535 (1960).

(16) A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.*, **4**, 425 (1961).

(17) P. Debye. "Polar Molecules," Dover Publications, Inc., New York, N. Y., 1954.

(18) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

(19) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961.

(20) D. E. Woessner, *J. Chem. Phys.*, **37**, 647 (1962).

(21) H. Shimizu, *ibid.*, **37**, 765 (1962).

(22) See, however, W. B. Moniz, W. A. Steele, and J. A. Dixon, *ibid.*, **38**, 2418 (1963).

where $\omega/2\pi$ is the frequency of the transition induced by the perturbation. In the high-field approximation which is applicable to most experiments on free radicals, it is permissible to approximate¹⁰ the frequencies ω by either $\omega = 0$ or $\omega = \omega_0$, where $\omega_0/2\pi$ is the Larmor frequency of the e.s.r. experiment. Since the other interactions which can cause line broadening are neglected in the present calculations, we will normally suppress the superscript (I) referring to modulation of the "isotropic" interaction in equations for the correlation functions and spectral densities.

Both the time dependence of the angle of orientation of the methyl groups and the relation between the methyl-proton hyperfine splitting and this angle affect the values of the correlation functions. We next turn to a consideration of the dependence of the hyperfine splittings on the angle of orientation and then proceed to a detailed specification of the motion using the models described in the Introduction. It will be assumed that the motions of the methyl groups are independent of the over-all tumbling of the molecule.

A. Angular Dependence of the Hyperfine Splittings.—The instantaneous isotropic hyperfine splitting from the i th proton in a rotating methyl group that is bonded to a planar π -electron system can be represented by a Fourier series in the angle of orientation θ_i . We define θ_i as the dihedral angle between the plane of the aromatic system and the plane determined by the i th proton, the methyl carbon atom, and the contiguous carbon atom of the aromatic system (the C-C-H_{*i*} plane). If, except for the methyl group, the molecule is planar, the splitting $a_i(\theta_i)$ is an even function of θ_i ; and if the threefold symmetry axis of the methyl group is also a twofold axis of the rest of the molecule, there can only be even harmonics in the Fourier series. The splitting can then be written as a Fourier cosine series in $2n\theta_i$

$$a_i(\theta_i) = A_i + \sum_{n=1}^{\infty} B_{i,n} \cos 2n\theta_i \quad (2.5)$$

Even if the aromatic system is not strictly planar, or if the methyl-group C₃ axis is not a C₂ axis for the rest of the molecule, the methyl-proton splitting is still probably determined to a good first approximation by the π -electron spin density on the contiguous atom of the aromatic system; and thus, departures from eq. 2.5 are likely to be small. Valence-bond calculations²⁴ indicate that the variation of the hyperfine splitting with angle is rather well represented by a $\cos 2\theta_i$ dependence, and for this reason, and also to keep the ensuing formulas as simple as possible, terms with $n > 1$ will be omitted. The orientations of the three protons in a single methyl group are necessarily interrelated if bending motions are excluded, and therefore we can write

$$\theta_i = \theta + \alpha_i \quad (2.6a)$$

with

$$\alpha_1 = 0, \alpha_2 = 2\pi/3, \alpha_3 = -2\pi/3 \quad (2.6b)$$

for the orientation of the individual protons. If the motion is one in which the average of $\cos 2\theta$ is zero, $\langle a_i(\theta_i) \rangle = A_i$; and since the A_i and $B_{i,1}$ are inde-

pendent of i , the expression for the splitting becomes (approximately)

$$a_i(\theta_i) = \bar{a} - b \cos 2\theta_i \quad (2.7)$$

where \bar{a} is the (average) methyl-group proton hyperfine splitting. Since the minimum splitting, corresponding to the planar conformation, is undoubtedly quite small, the magnitude of b is probably close to that of \bar{a} , $b \cong \bar{a}$.

When two methyl groups are substituted at adjacent positions on an aromatic ring, there is crowding and partial interleaving of the hydrogen atoms. Thus, studies of hexamethylbenzene²⁵ are consistent with the picture that at low temperatures (*ca.* 110°K.) the methyl-group carbon atoms lie in the plane of the benzene ring and the hydrogen atoms are interleaved with each other in a gear-like manner. As the temperature is increased, the methyl groups tend to rotate without any slipping of gears, but at higher temperatures slipping takes place.²⁶ We first consider the limit of completely interlocked methyl groups.

When there is no slipping, the turning of one methyl group in a clockwise direction causes the adjacent group to turn in a counterclockwise direction. Let the protons of the first methyl group be numbered 1, 2, and 3 in the clockwise direction, and those in the second group 4, 5, and 6 in the counterclockwise direction. Then if the two methyl groups are rigidly locked together, the orientations of the protons are interrelated by $\theta_{i+3} = -\theta_i$, and since, by eq. 2.7 $a_i(\theta_i)$ is an even function of θ_i , $a_{i+3}(\theta) = a_i(\theta)$, where $\theta = \theta_i$. The perturbing Hamiltonian, eq. 2.2, is therefore invariant to an interchange of protons ($i+3$) and i , so that protons ($i+3$) and i are completely equivalent (see section III below and I,¹⁰ section IV.B.1). It follows¹⁰ that for $i, j = 1, 2, \text{ or } 3$

$$j_{ij}(\omega) = j_{i+3,j}(\omega) = j_{i+3,j+3}(\omega) \quad (2.8)$$

The six protons may conveniently be collected into three completely equivalent subgroups: protons 1 and 4 are placed in subgroup 1, protons 2 and 5 in subgroup 2, and protons 3 and 6 in subgroup 3. Then if u, v ($= 1, 2, 3$) refer to the subgroups and i, j ($= 1, 2, 3$) to the protons in a single methyl group, the spectral densities for the subgroups (j_{uv}) are equal to the corresponding spectral densities for the protons of a single methyl group (j_{ij}), *i.e.*, $j_{uv} = j_{ij}$. The spectral densities j_{uv} based on completely equivalent subgroups are useful in setting up the relaxation matrix in terms of the coupled representation (see below, section III, and I, section IV.B.2). Correlated motions may also take place in a radical like the dinitrodurene anion because the nitro groups can cause the methyl groups on one side of the ring to rotate in synchronism with those on the other side. If all the methyl groups are rigidly locked together, there are again three sets of completely equivalent subgroups; but now each subgroup contains four completely equivalent protons instead of two.

In a radical containing two sterically independent methyl groups as, for example, in the *p*-xylene or 3,5-dimethylnitrobenzene anions, the motions of the two groups are probably completely uncorrelated. The

(25) O. Schnepf, *J. Chem. Phys.*, **29**, 56 (1958).

(26) C. A. Coulson and D. Stocker, *Mol. Phys.*, **2**, 397 (1959).

(24) M. Karplus, private communication.

spectral densities $j_{ij}(\omega)$ referring to nuclei i and j in different methyl groups are then zero.

These two models for radicals with more than one methyl group represent the extreme possibilities of completely coupled and uncoupled motions. Our calculation for the rigidly locked-together motions is inadequate to the extent that quantum-mechanical tunneling acts as a decoupling mechanism even when there is no slipping of gears. Ordinarily, however, the uncorrelated-motion model is probably more suitable because slipping seems to occur, as indicated by hexamethylbenzene,^{25,26} except at very low temperatures.

B. Brownian Motion Model.—The Brownian motion for free rotational diffusion is described by the Langevin equation

$$\frac{d^2\theta}{dt^2} + \beta\theta = A(t) \quad (2.9)$$

where $A(t)$ is a random acceleration, and βI is the rotational friction constant, with I being the moment of inertia of the rotor. Debye¹⁷ suggested that often rotating solute molecules could be approximated as spheres and that Stoke's relation $\beta I = 8\pi\eta a^3$ could be used as an estimate of the friction constant. Here a is the radius of the sphere and η the (effective) viscosity of the fluid. The probability of finding the rotor at any orientation θ_0 ($0 \leq \theta_0 \leq 2\pi$) is independent of θ_0 and is just

$$W(\theta_0)d\theta_0 = (1/2\pi)d\theta_0 \quad (2.10)$$

while the conditional probability that the orientation is θ at the time τ if it was θ_0 at the time $\tau = 0$ is²⁷

$$P(\theta_0|\theta, \tau)d\theta = (4\pi D\tau)^{-1/2} \exp[-(\theta - \theta_0)^2/4D\tau]d\theta \quad (2.11)$$

Here D is the rotatory diffusion constant and is given in terms of the friction constant by the Einstein relation

$$D = kT/(\beta I) \quad (2.12)$$

where k is the Boltzmann constant and T the absolute temperature. Equation 2.11 only holds for long times, *i.e.*, $\tau \gg \beta^{-1}$. Since the rotating group can make many complete revolutions during the time τ , the angle θ in eq. 2.11 can be anywhere in the range $-\infty \leq (\theta - \theta_0) \leq \infty$.

The applicability of these Brownian motion equations to the rotation of a methyl group is of course open to question. Certainly the formulation of the friction constant in terms of the radius, moment of inertia, and viscosity is not quantitatively correct, and the Langevin equation itself may be invalid for this problem. Nevertheless, eq. 2.11 is a reasonable and simple type of distribution function to represent the motion, and in effect we are assuming that the classical motion of macroscopic bodies is an adequate first approximation to the motion of the methyl group. As indicated in the Introduction, quantum mechanical models which neglect intermolecular interactions are not good descriptions of the methyl group motion in liquids. A free rotatory diffusion has been used rather than one

corresponding to a hindered internal rotation because to our knowledge the difficult detailed solutions of the appropriate Brownian motion equations for this problem have not been carried out.²⁸ Since the barrier to internal rotation of methyl groups is small, however, the free rotatory diffusion should represent a reasonable first approximation except at very low temperatures.

The correlation functions (eq. 2.3) for a single methyl group undergoing free rotational diffusion are readily computed from eq. 2.10 and 2.11 for the distribution functions. If the hyperfine splittings vary with angle according to eq. 2.7, we have

$$\begin{aligned} g_{ij}(\tau) &= \gamma_e^2 b^2 (\cos 2\theta_i(t) \cos 2\theta_j(t + \tau)) \\ &= \gamma_e^2 b^2 \int_0^{2\pi} d\theta_{i0} W(\theta_{i0}) \cos 2\theta_{i0} \times \\ &\quad \int_{-\infty}^{\infty} d\theta_j P(\theta_{i0}|\theta_j, \tau) \cos 2\theta_j \\ &= (\gamma_e^2 b^2 / 2\pi) \int_0^{2\pi} d\theta_0 \cos [2(\theta_0 + \alpha_i)] \times \\ &\quad \cos [2(\theta_0 + \alpha_j)] \int_{-\infty}^{\infty} d\theta P(\theta_0|\theta, \tau) \cos [2(\theta - \theta_0)] \\ &= (1/2) \gamma_e^2 b^2 \cos [2(\alpha_i - \alpha_j)] \exp(-4D\tau) \end{aligned} \quad (2.13)$$

where the α_i are defined by eq. 2.6b. The spectral densities, eq. 2.4, are therefore

$$j_{11}(\omega) = j_{ii}(\omega) = (1/2) \gamma_e^2 b^2 \tau_0 (1 + \omega^2 \tau_0^2)^{-1} \quad (2.14a)$$

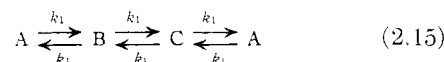
$$j_{12}(\omega) = j_{ij}(\omega) = -(1/2) j_{11}(\omega), \quad i \neq j \quad (2.14b)$$

where

$$\tau_0^{-1} = 4D \quad (2.14c)$$

Here D is the rotatory "diffusion constant" of the methyl group.

C. Three-jump Model.—We assume the methyl group can have only three orientations (A, B, C) which differ from each other by rotations through 120°. These three orientations are in dynamic equilibrium according to the equations



where k_i is a "rate constant," and we assume that the time between jumps from one orientation to another is long compared to the duration of a jump. This is perhaps a more reasonable picture than Brownian motion diffusion in case there is an appreciable energy barrier to reorientation. The "rate constant" k_1 can include the effects of quantum-mechanical tunneling as well as passage over a classical activation barrier.

By setting up the rate equations for the populations in the three states, it is readily shown that the conditional probabilities are

$$P(A|A\tau) = (1/3)[1 + 2 \exp(-3k_1\tau)] \quad (2.16a)$$

$$P(A|B\tau) = P(A|C\tau) = (1/3)[1 - \exp(-3k_1\tau)] \quad (2.16b)$$

with similar relations if the rotor is in orientation B or C at $\tau = 0$ instead of state A. The *a priori* probabilities are, of course, $W(A) = W(B) = W(C) = (1/3)$. Gutowsky, *et al.*,²³ have obtained similar equations. Computation of the correlation functions and spectral

(27) S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943); G. E. Uhlenbeck and L. S. Ornstein, *Phys. Rev.*, **36**, 823 (1930); M. C. Wang and G. E. Uhlenbeck, *Rev. Mod. Phys.*, **17**, 323 (1945).

(28) But see M. Goldstein, *J. Chem. Phys.*, **39**, 243 (1963), where some preliminary results are discussed.

densities gives results identical with eq. 2.14 when eq. 2.7 is assumed except that now

$$\tau_0^{-1} = 3k_1 \quad (2.17)$$

More generally, if eq. 2.7 is not used, $^{1/2}b^2$ in eq. 2.14 is replaced by

$$[(^{1/3})(a_1^2 + a_2^2 + a_3^2) - \bar{a}^2] \quad (2.18)$$

where a_1 , a_2 , and a_3 are the hyperfine splittings from the different protons in one of the three allowed orientations and \bar{a} is the average of these splittings.

III. Secular Contributions to the Line Widths

In this section we shall determine the line widths when the only spectral densities of importance are those for which $\omega = 0$. These are called the secular contributions and correspond to terms which do not result from energy interchange between the spin system and its surroundings. The modulation of the isotropic interaction gives a secular part which arises from the $I_{iz}S_z$ term and a nonsecular part from the $I_i^+S^-$ terms. For a Debye-type dispersion as in eq. 2.14, the nonsecular terms can be neglected when the correlation time τ_0 is long enough so that $(\omega_0\tau_0)^2 \gg 1$ ($\omega_0/2\pi$ is the Larmor frequency of the e.s.r. experiment). Secular terms contribute only diagonal elements to the relaxation matrix, and therefore the determination of the line widths is particularly simple if they are the only terms which make a major contribution to the line broadening. It is important to note, however, that other significant interactions (particularly the anisotropic intramolecular dipolar interaction between the unpaired electron and the nuclear magnetic moments) may cause appreciable line-broadening effects that are not entirely secular,^{10,29} and in such circumstances the results of the present section may require generalization.^{10,30} Nonsecular isotropic contributions will be discussed in section IV.

The transverse relaxation time $T_{2,\mu}$ and the width (in gauss) $[|\gamma_e|T_{2,\mu}]^{-1}$ of the μ th transition in the e.s.r. spectrum are determined from the eigenvalues λ_μ of the relaxation matrix by¹⁰ $[-\lambda_\mu]^{-1} = T_{2,\mu}$. Each transition is of Lorentzian shape, but since the different transitions in a degenerate line may have different widths, the over-all shape of such a line may not be Lorentzian.^{10,31} The secular (sec.) contribution of modulations of the isotropic hyperfine splittings to the width of the μ th component of the k th line in the spectrum is given by eq. 4.46 of I

$$[T_{2,\mu}^{(k)}(\text{I}; \text{sec.})]^{-1} = \sum_{i,j} j_{ij}^{(I)}(0)m_i m_j \quad (3.1)$$

where m_i is the z component of the spin angular momentum of the i th nucleus. For a single methyl group with spectral densities given by eq. 2.14

$$[T_2^{(M)}(\text{I}; \text{sec.})]^{-1} = (^{1/8})j_{11}(0)[9 - 4M^2] \quad (3.2)$$

where M is the sum of the z components of the proton nuclear spin angular momenta [$M = \pm(^{3/2}), \pm(^{1/2})$].

(29) D. Kivelson, *J. Chem. Phys.*, **27**, 1087 (1957); **33**, 1094 (1960).

(30) The pseudo-secular part of the anisotropic intramolecular dipolar interaction is comparable in magnitude to the secular part and gives rise to off-diagonal elements in the relaxation matrix. When these contributions are sufficiently large, the entire relaxation matrix must be considered independent of whether or not the nonsecular parts from modulation of the isotropic splittings are important.

(31) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, in press

The width contributions from eq. 3.2 are listed in Table I.

TABLE I
SECULAR LINE WIDTH CONTRIBUTIONS, CORRELATED METHYL GROUPS

No. of methyl groups	M^a	$\{M_1, M_2, M_3\}^{a,b}$	Degeneracy, D_μ	$[T_{2,\mu}^{(M)}(\text{I}; \text{sec.})]^{-1}/j_{11}^{(I)}(0)$
1	$^{3/2}$	$^{1/2}, ^{1/2}, ^{1/2}$	1	0
	$^{1/2}$	$[^{1/2}, ^{1/2}, -^{1/2}]$	3	1
2	3	1, 1, 1	1	0
	2	[1, 1, 0]	6	1
	1	[1, 0, 0]	12	1
		[1, 1, -1]	3	4
	0	0, 0, 0	8	0
		1, 0, -1	12	3
4	6	2, 2, 2	1	0
	5	[2, 2, 1]	12	1
	4	[2, 1, 1]	48	1
		[2, 2, 0]	18	4
	3	1, 1, 1	64	0
		[2, 1, 0]	144	3
		[2, 2, -1]	12	9
	2	[1, 1, 0]	288	1
		[2, 0, 0]	108	4
		[2, 1, -1]	96	7
	[2, 2, -2]	3	16	
1		[1, 0, 0]	432	1
		[1, 1, -1]	192	4
		[2, 0, -1]	144	7
		[2, -2, 1]	24	13
	0	0, 0, 0	216	0
		[1, -1, 0]	576	3
		$[\pm 2, \mp 1, \mp 1]$	96	9
	[2, -2, 0]	36	12	

^a M_i is the sum of the z components of the nuclear spin angular momenta of the i th completely equivalent subgroup, and $M = \sum M_i$. The widths for positive and negative M are the same.
^b Brackets indicate that permutations of $\{M_1, M_2, M_3\}$ are included as well as the particular order of values listed.

When the radical contains several methyl groups all with the same average proton hyperfine splitting, and thus forming a set of equivalent protons,¹⁰ it is convenient to collect the protons into *completely* equivalent subgroups. Two equivalent protons are *completely* equivalent if the perturbing Hamiltonian, eq. 2.2, is invariant to an interchange of their positions. If protons i and j are in the same completely equivalent subgroup u , the spectral densities satisfy the relations (see I, section IV.B.1) $j_{11} = j_{jj} = j_{ij} = j_{uu}$, and for nuclei within the same equivalent group but different completely equivalent subgroups, $j_{uu} = j_{vv}$. If u and v are different completely equivalent subgroups, $j_{uv} \neq j_{vu}$. We write

$$M_u = \sum_{i \text{ in } u} m_i \quad (3.3)$$

for the sum of the z components of the nuclear spin angular momenta m_i in the u th completely equivalent subgroup, with a similar expression for M_v , the nuclei in the v th completely equivalent subgroup. Equation 3.1 can then be rewritten as

$$[T_{2,\mu}^{(M)}(\text{I}; \text{sec.})]^{-1} = j_{11}^{(I)}(0)M^2 + \sum_{u \neq v} [j_{uv}^{(I)}(0) - j_{11}^{(I)}(0)]M_u M_v \quad (3.4)$$

where

$$M = \sum_u M_u = \sum_i m_i$$

is the sum of the z components of the nuclear spin angular momenta of all the methyl-group protons. For interleaved, correlated, rotating methyl groups there are three different completely equivalent subgroups ($u = 1, 2, 3$), $j_{11}(0)$ is given by eq. 2.14a, and $j_{uv}(0) = -(1/2)j_{11}(0)$ for $u \neq v$, as in eq. 2.14b. If the radical contains two interleaved correlated methyl groups, there are two protons in each completely equivalent subgroup, and if it contains four, there are four protons in each subgroup, so that the possible values of M_u are $M_u = \pm 1, 0$ and $M_u = \pm 2, \pm 1, 0$, respectively, and the statistical weights are 1:2:1 and 1:4:6:4:1. The line widths of the components are given in Table I for these two cases.

If there are several methyl groups undergoing uncorrelated motions, eq. 3.1 reduces to

$$[T_{2,\mu}^{(M)}(\mathbf{I}; \text{sec.})]^{-1} = (1/8)j_{11}(0)\sum_i (9 - 4M_i^2) \quad (3.5)$$

where $j_{11}(0)$ is given by eq. 2.14a and M_i is the sum of the z components of the angular momenta of the protons in the i th methyl group ($M_i = \pm(3/2), \pm(1/2)$) with statistical weights 1:3:3:1). The widths from this equation are given in Table II for two and four uncorrelated methyl groups.

TABLE II
SECULAR LINE WIDTH CONTRIBUTIONS, UNCORRELATED
METHYL GROUPS

No. of methyl groups	M^a	$[M_1, M_2, M_3, M_4]^{a,b}$	Degen-eracy, D_μ	$[T_{2,\mu}^{(M)}(\mathbf{I}; \text{sec.})]^{-1/2} j_{11}^{(1)}(0)$
2	3	$3/2, 3/2$	1	0
	2	$[3/2, 1/2]$	6	1
	1	$[3/2, -1/2]$	6	1
		$1/2, 1/2$	9	2
	0	$[3/2, -3/2]$	2	0
		$[1/2, -1/2]$	18	2
4	6	$3/2, 3/2, 3/2, 3/2$	1	0
	5	$[3/2, 3/2, 3/2, 1/2]$	12	1
	4	$[3/2, 3/2, 3/2, -1/2]$	12	1
		$[3/2, 3/2, 1/2, 1/2]$	54	2
	3	$[3/2, 3/2, 3/2, -3/2]$	4	0
		$[3/2, 3/2, 1/2, -1/2]$	108	2
		$[3/2, 1/2, 1/2, 1/2]$	108	3
	2	$[3/2, 3/2, 1/2, -3/2]$	36	1
		$[3/2, 3/2, -1/2, -1/2]$	54	2
		$[3/2, 1/2, 1/2, -1/2]$	324	3
		$[1/2, 1/2, 1/2, 1/2]$	81	4
	1	$[3/2, 3/2, -3/2, -1/2]$	36	1
		$[3/2, -3/2, 1/2, 1/2]$	108	2
		$[3/2, 1/2, -1/2, -1/2]$	324	3
		$[1/2, 1/2, 1/2, -1/2]$	324	4
	0	$[3/2, 3/2, -3/2, -3/2]$	6	0
		$[3/2, -3/2, 1/2, -1/2]$	216	2
		$[\pm 3/2, \mp 1/2, \mp 1/2, \mp 1/2]$	216	3
$[1/2, 1/2, -1/2, -1/2]$		486	4	

^a M_i is the sum of the z components of the nuclear spin angular momenta of the i th methyl group, and $M = \sum M_i$. The widths for positive and negative M are the same. ^b Brackets indicate permutations of $[M_1, M_2]$ or $[M_1, M_2, M_3, M_4]$ are included as well as the particular order of values listed.

The results in Table I show that for a single methyl group the motional modulation of the isotropic splitting makes no contribution to the secular part of the line

width for the $M = \pm(3/2)$ lines, and adds $j_{11}(0)$ to the width of the $M = \pm(1/2)$ lines. If this modulation contributes significantly to the total line width, the central pair of lines will thus be broader than the outer pair.

When there are either two or four methyl groups, either with correlated or uncorrelated motions, the line-width pattern is rather complex, but in the limit of very large $j_{11}(0)$ every third line is narrow and all other lines broad. For the correlated motions of two methyl groups, the narrow lines correspond to $M = 3, 0, -3$ with statistical weights 1:8:1, while for the uncorrelated motion the statistical weights are 1:2:1. For four methyl groups, the narrow lines have quantum numbers $M = 6, 3, 0, -3, -6$ with statistical weights 1:64:216:64:1 or 1:4:6:4:1, respectively, for correlated or uncorrelated motions. When $j_{11}(0)$ is not very large compared to the other line-broadening mechanisms, numerical calculations of the over-all absorption curve resulting from the superposition of individual Lorentzian-shaped components of different widths are required to obtain the predicted widths. One example of such a calculation is given in Table III for

TABLE III
LINE WIDTHS AND SHAPES, FOUR CORRELATED METHYL
GROUPS^a

M^b	Degen-eracy, D_M	Width, ^c δ_M	Amplitude, ^d A_M	Reduced amplitude, A_M/D_M	Shape factor, S_M
6	1	1.15	0.413	0.413	0.743
5	12	2.31	1.24	.103	.743
4	66	2.36	5.16	.078	.660
3	220	1.20	28.1	.128	.429
2	495	2.37	31.2	.063	.595
1	792	2.38	47.2	.060	.581
0	924	1.21	96.1	.104	.390

^a Calculated for four equivalent correlated methyl groups from results in Table I taking $|\gamma_e|^{-1}j_{11}^{(1)}(0) = |\gamma_e|^{-1}X = 1.0$ gauss. Here X is the contribution to $[T_{2,\mu}^{(M)}]^{-1}$ from line-broadening mechanisms other than modulations of the isotropic hyperfine splitting, and is taken to be a constant for all component transitions. ^b M is the sum of the z components of the nuclear spin angular momenta of all 12 protons. ^c Width between extrema of the first derivative of the spectrum. ^d Peak-to-peak amplitude of the first derivative of the spectrum. The area of the absorption for unit statistical weight and half half-width of 1.0 gauss is normalized to unity.

the case of four equivalent correlated methyl groups. The numerical values used are $|\gamma_e|^{-1}j_{11}^{(1)} = |\gamma_e|^{-1}X = 1.0$ gauss where X is the contribution to $[T_{2,\mu}^{(M)}]^{-1}$ from other line-broadening effects and is assumed to be a constant for all components. The computation was performed on an IBM 7090 computer using a program developed by Dr. S. Goodman. Each component was taken to be of Lorentzian shape and with the line width given by the values in Table I (e.g., for $M = 4$, two lines were superimposed with widths of 2.0 and 5.0 gauss and with statistical weights of 48 and 18, respectively). The amplitudes and widths were obtained by interpolation from the computed numerical tabulations of the first derivative of the over-all superimposed spectrum as a function of magnetic field. The results show the characteristic narrowness of every third line, and the last column indicates the departures from Lorentzian shape. The shape factor

$$S_M = (A_M/D_M)^{1/2}\delta_M \quad (3.6)$$

tabulated in this column is a constant for lines of the same shape and has the value 0.743 for an appropriately normalized Lorentzian.²¹

The narrowness of every third line predicted for the spectra from two and four methyl groups, as well as the broadening of the two central lines for a single methyl group, is analogous to the alternating line-width phenomena.³⁻⁹ The line-width variations predicted here for methyl groups, however, have not been observed.³ The experimental situations most likely to show these effects are discussed briefly in section V, but their absence implies that the nonsecular contributions may also be important. These are considered in the next section.

IV. Nonsecular Contributions to the Line Width

The importance of the nonsecular contributions

	1	2	3	4	5	6	7	8	9
	<i>aa'</i>	<i>bb'</i>	<i>cc'</i>	<i>ab'</i>	<i>ac'</i>	<i>ba'</i>	<i>bc'</i>	<i>ca'</i>	<i>cb'</i>
<i>aa'</i>	$A + B$	0	0	C	C	C	0	C	0
<i>bb'</i>	0	$A + B$	0	C	0	C	C	0	C
<i>cc'</i>	0	0	$A + B$	0	C	0	C	C	C
<i>ab'</i>	C	C	0	B	C	0	0	0	C
<i>ac'</i>	C	0	C	C	B	0	C	0	0
<i>ba'</i>	C	C	0	0	0	B	C	C	0
<i>bc'</i>	0	C	C	0	C	C	B	0	0
<i>ca'</i>	C	0	C	0	0	C	0	B	C
<i>cb'</i>	0	C	C	C	0	0	0	C	B

arising from modulations of the methyl-proton splittings by rotational motions depends on the correlation time τ_0 for the motion. We can use the fact that no effects attributable to methyl-group rotations have been observed⁸ in order to set an upper limit for τ_0 employing, for comparison, the magnitude of the secular contributions alone. Assuming $b \cong \bar{a}$ in eq. 2.7, and using eq. 2.14 and 3.1, we find

$$[|\gamma_e|T_{2,\mu}^{(M)}(I; \text{sec.})]^{-1} = (1/2)|\gamma_e|b^2\tau_0 \cong 8.8 \times 10^6 \bar{a}^2 \tau_0 \text{ gauss} \quad (4.1)$$

where \bar{a} is in gauss and τ_0 in seconds. The experimental data, although fragmentary,⁸ indicate that the contributions from eq. 4.1 are probably less than 0.1 gauss, and since typical splittings are a few gauss in magnitude, τ_0 is probably of the order of 10^{-8} or less. Thus, $\omega_0\tau_0$ might be comparable to or less than unity, and the nonsecular contributions are not necessarily negligible. In this section we therefore examine the nonsecular line-width effects for a single methyl group.

Straightforward calculation shows that the motional modulation of the isotropic splitting contributes

$$[T_2^{(\pm 3/2)}(I; \text{nonsec.})]^{-1} = (3/4)j_{11}^{(1)}(\omega_0) \quad (4.2)$$

to the nonsecular (nonsec.) part of the width of the $M = \pm(3/2)$ lines. The relaxation matrix for the $M = \pm(1/2)$ lines is not diagonal, however, and requires detailed investigation. Let us designate the wave functions for the spin states of the $M = 1/2$ line by

$$\begin{aligned} |a\rangle &= |1/2; 1/2, 1/2, -1/2\rangle \\ |b\rangle &= |1/2; 1/2, -1/2, 1/2\rangle \\ |c\rangle &= |1/2; -1/2, 1/2, 1/2\rangle \end{aligned} \quad (4.3)$$

$$\begin{aligned} |a'\rangle &= |-1/2; 1/2, 1/2, -1/2\rangle \\ |b'\rangle &= |-1/2; 1/2, -1/2, 1/2\rangle \\ |c'\rangle &= |-1/2; -1/2, 1/2, 1/2\rangle \end{aligned}$$

in the notation $|\gamma\rangle = |m_s; m_1, m_2, m_3\rangle$ where m_s is the z component of the electron spin angular momentum and m_i is the z component of spin angular momentum of the i th proton. A complete treatment would include the anisotropic intramolecular dipolar and g -tensor interactions, but for simplicity we shall only calculate the matrix for the isotropic hyperfine interaction. These other terms are readily included. From eq. 4.46, 4.48, and 4.53 of I, the appropriate part of the relaxation matrix is found to be that shown in eq. 4.4

where, for the special case of isotropic splitting only using eq. 2.14

$$A = -(3/4)j_{11}^{(1)}(0) \quad (4.5a)$$

$$B = -(1/4)[j_{11}^{(1)}(0) + 3j_{11}^{(1)}(\omega_0)] \quad (4.5b)$$

$$C = (1/8)j_{11}^{(1)}(\omega_0) = (1/18)(A - 3B) \quad (4.5c)$$

The relaxation matrix relates the matrix elements of the x component of the electron spin angular momentum in the interaction representation, $\langle\beta|S_x^\dagger(t)|\beta'\rangle$, to the time derivatives, $(d/dt)\langle\alpha|S_x^\dagger(t)|\alpha'\rangle$ [eq. 2.15 of I]

$$\frac{d}{dt} \langle\alpha|S_x^\dagger(t)|\alpha'\rangle = \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'} \langle\beta|S_x^\dagger(t)|\beta'\rangle \quad (4.6)$$

Denoting the $\langle a|S_x^\dagger(t)|a'\rangle$ matrix element by $S_1(t)$, the $\langle b|S_x^\dagger(t)|b'\rangle$ element by $S_2(t)$, etc., according to the numbering of the columns in eq. 4.4, and using the rules obtained in I, section VII, it is readily shown that $S_1(t) = S_2(t) = S_3(t)$ and that $S_4(t) = S_5(t) = S_6(t) = S_7(t) = S_8(t) = S_9(t)$. Using the procedures in I, section VII, the 9×9 matrix in eq. 4.4 can thus be reduced to a 2×2 matrix, and the two related differential equations are

$$\begin{aligned} \frac{dS_1(t)}{dt} &= (A + B)S_1(t) + 4CS_4(t) \\ \frac{dS_4(t)}{dt} &= 2CS_1(t) + (B + 2C)S_4(t) \end{aligned} \quad (4.7)$$

The solution for $S_1(t)$, the only matrix element which determines the spectrum, is

$$S_1(t) = S_1(0)(1/2D)[(D + A - 2C)\exp(\lambda_+t) + (D - A + 2C)\exp(\lambda_-t)] \quad (4.8)$$

where

$$D = [(A - 2C)^2 + 32C^2]^{1/2} \quad (4.9)$$

$$\lambda_{\pm} = (1/2)(A + 2B + 2C \pm D) = -[T_{2,\pm}^{(1/2)}]^{-1} \quad (4.10)$$

The spectrum, eq. 2.13 and 3.5 of I, is thus

$$I(\omega) = (3/2\pi D) \left[(D + A - 2C) \frac{T_{2,+}^{(1/2)}}{1 + [T_{2,+}^{(1/2)}]^2(\omega - \omega_{1/2})^2} + (D - A + 2C) \frac{T_{2,-}^{(1/2)}}{1 + [T_{2,-}^{(1/2)}]^2(\omega - \omega_{1/2})^2} \right] \quad (4.11)$$

and consists of two superimposed Lorentzian-shaped lines with transverse relaxation times $T_{2,\pm}^{(1/2)}$ and statistical weights $3(D \pm A \mp 2C)/2D$. The line for $M = -(1/2)$ has the same shape function and width as the line for $M = (1/2)$, but its center is of course at a different frequency, and if interactions other than modulation of the isotropic interaction were included this symmetry would not necessarily hold. In the limit that the nonsecular contributions can be neglected, $C = 0$, $B = (1/3)A$, and a single Lorentzian-shaped line is obtained of width $j_{11}^{(1)}(0)$, as in Table I. In the extreme narrowing limit, $\omega_0\tau_0 \ll 1$, we have $j_{11}^{(1)}(\omega_0) = j_{11}^{(1)}(0)$, the widths become $[T_{2,\pm}^{(1/2)}]^{-1} = (5/4)[1 \pm (1/5)\sqrt{6}]j_{11}^{(1)}(0)$, and the statistical weights are $(3/2)[1 \pm (2/3)^{1/2}]$.

In general, numerical calculations of the spectrum (eq. 4.11) as a superposition of Lorentzian-shaped lines must be performed as in section III in order to obtain the widths and amplitudes. Under conditions that the modulation of the isotropic interaction for a single methyl group would be large enough to be detectable, and in the absence of complications from other line-broadening mechanisms, the non-Lorentzian shape resulting from the nonsecular contributions could be distinguished from the Lorentzian shape predicted

for the secular contribution by studies of the line-shape factor S_M , eq. 3.6.³¹

V. Conclusions

Our calculations show that modulation of the methyl-proton hyperfine splittings by rotational motion of the methyl groups can cause several interesting line-width effects. For a single methyl group, the central pair of lines is predicted to be broader than the outer pair, and if the rotational motion is fast ($\omega_0\tau_0 \gtrsim 1$), so that nonsecular contributions are important, the central lines are non-Lorentzian in shape. The presence of large secular line-width effects of this type causes every third line in the spectra from radicals with either two or four equivalent methyl groups to be sharp compared to the other lines, and thus an effect analogous to the alternating line-width phenomenon is predicted. The variation of the widths from line to line if the motions of the several methyl groups are uncorrelated with each other is different in detail from that found if they are interlocked so as to move in a completely correlated manner.

None of the predicted effects has yet been observed, and although good quantitative experimental estimates of the upper limits of the line-width variations are not available, eq. 4.1 and the experimental data⁸ indicate that in the compounds studied the correlation times τ_0 for the rotation of methyl groups are no larger than about 10^{-8} sec. Since the line-width effects vary approximately as the square of the hyperfine splitting (\bar{a}) and linearly with the correlation time (τ_0), radicals with methyl groups that have large methyl-proton splittings and are highly hindered should be studied at low temperatures if the predicted line-width anomalies are to be observed.

Throughout the calculations, the line-broadening effects of such important mechanisms as the anisotropic intramolecular dipolar and g -tensor interactions have been neglected. Their inclusion would not be expected to alter the qualitative nature of the predictions, but if relevant experimental data become available, it would probably become necessary to include these effects in the calculations. The present discussion has also neglected the contributions from spin-density modulations¹¹ such as those that can arise from the motions of other substituents in the radical or from solvent perturbations. Effects of this type are important in radicals like the dihydroxydurene cation.³