

Electron Spin Resonance Studies of Anisotropic Ordering, Spin Relaxation, and Slow Tumbling in Liquid Crystalline Solvents¹

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A detailed study of anisotropic ordering, line shapes, and relaxation is reported for the perdeuterated 2,2,6,6-tetramethyl-4-piperidone *N*-oxide (PD-Tempone) nitroxide radical in several liquid crystal solvents. The line width results are analyzed in terms of the Polnaszek, Bruno, and Freed (PBF) theory appropriately modified for anisotropic ordering both in the motional narrowing and slow tumbling region. The motional narrowing results are usually consistent with isotropic rotational diffusion, but under a weak (asymmetric) ordering potential, $\langle D_{00}^2 \rangle \approx -0.1$, and activation energies characteristic of the twist viscous properties of the liquid crystal. Anomalous line shape behavior in the incipient slow tumbling region is observed, which is not explained by the extrapolation of the appropriate parameters from the motional narrowing region. This anomaly is discussed in terms of anisotropic viscosity and director fluctuations. The latter is predicted to be of negligible importance for the weakly ordered spin probe, as well as qualitatively of the wrong behavior. Anisotropic viscosity, while apparently able to "explain" the anomaly, leads to physically untenable conclusions. The anomaly is then discussed in terms of slowly fluctuating intermolecular torques, leading to a frequency-dependent diffusion coefficient. While this latter may in part offer an explanation (when one distinguishes between torque components parallel and perpendicular to the director), the implied slowness of the fluctuating torques suggests, from general theory, a new model based upon a local solvent structure around the spin probe which may persist over longer periods than the reorientation time of the spin probe. A simple model calculation of the effects on the ESR relaxation is given. This limiting model is also appropriate for highly structured isotropic liquids. It is shown that such a model could have the same formal spectral effects as anisotropic rotational diffusion, and it would yield non-Debye-like spectral densities of the type that could potentially "explain" the observed incipient slow tumbling anomaly. More general theoretical approaches for the analysis of these effects are briefly discussed.

I. Introduction

In a recent series of papers we have shown the wide range of information that one is able to obtain from ESR relaxation studies about rotational reorientation in liquid and frozen media, when careful studies are made of ESR spectra over the full range from the very fast motional region to the rigid limit.²⁻⁴ These studies, from which estimates could be made of (1) anisotropic rotational diffusion coefficients; (2) frequency dependence of the rotational reorientational correlation functions; (3) the non-Brownian nature of the reorientational process (e.g., large angle jump diffusion); (4) spin-rotational and angular momentum relaxation, were all performed on isotropic liquids containing spin probes. There is currently great interest in the dynamical reorientational properties of liquid crystals which may also be studied by ESR, and this has been reviewed in several places.⁵⁻⁸ There have been several recent studies of the dynamics of nitroxide free radicals in oriented systems such as nematic liquid crystals and lyotropic liquid crystals.⁹⁻¹² However, these studies have been based upon analyses appropriate when the probe motion is rapid, an assumption, we shall see, which is not always justified. Nordio and coworkers have presented a useful analysis of motional narrowing ESR line widths in liquid crystals for Brownian reorientation¹³ which is appropriate for such studies. Polnaszek, Bruno, and Freed (PBF)¹⁴ have generalized this approach to cover the slow tumbling region based on the slow tumbling theory of Freed et al.¹⁵ In that

work PBF also developed improved methods for analyzing the motional narrowing widths; they considered other models for rotational reorientation; and they obtained solutions for rotational diffusion with very strong restoring potentials.

The present work was undertaken to attempt to perform an extensive study of relaxation of nitroxide spin probes in liquid crystal solvents in the spirit of I and II (i.e., to obtain detailed information on rotational anisotropy and the deviations from Brownian motion in ordered fluids) utilizing the PBF theory for the analysis.

It was shown in II that the need for a high degree of spectral resolution for accurate spin relaxation studies could be fulfilled by the use of a perdeuterated spin label 2,2,6,6-tetramethyl-4-piperidone *N*-oxide (PD-Tempone), for which inhomogeneous broadening due to unresolved intramolecular proton or deuteron interactions is minimized. Thus, this probe was used in our most extensive studies, although other nitroxide probes were also used for comparison purposes. Another advantage of using the PD-Tempone probe is the fact that careful and extensive results on isotropic liquids given in II are available for comparison purposes, so that those results in liquid crystals, which are peculiar to these solvents, could be readily distinguished. In fact, as will be seen, such studies proved useful in shedding further light on molecular dynamics in liquids in general, as studied by ESR.

Actually, it was found at an early stage of this work, that

the PBF theory required some generalization before it could be applied to the experiments described here. This is because the ordering of the spin probes is, in general, not axially symmetric. In section II we give the appropriate analysis for rotational diffusion under more general mean field restoring potentials. Also, a more complete discussion of motional narrowing line widths is given, and the importance of frequency-dependent spectral densities, usually ignored by other workers, is stressed. The experimental procedures including analysis of any non-Lorentzian line shapes (in the motional narrowing region) are summarized in section III. The rigid limit spectra and magnetic parameters are discussed in section IV. A detailed discussion of the motional narrowing results including the asymmetric ordering and line width analyses appears in section V. The limitations of the motional narrowing analysis as the motion slows is also discussed there. It was possible, with the small spin probes, to obtain results in the incipient slow tumbling region, and the analysis of these spectra in terms of the PBF theory is discussed in section VI. It is shown there that these spectra have distinctly anomalous behavior.

We have in II and in a recent theoretical study¹⁶ undertaken a detailed statistical mechanical analysis of molecular reorientation to serve as the basis for analyzing unusual relaxation behavior not predicted by simple models of rotational reorientation. This general theory and its applicability to ordered fluids is summarized in section VII. The concept of relatively slowly fluctuating torques is then first discussed from the viewpoint of its effects on a frequency-dependent diffusion coefficient in a manner analogous to that given in II for isotropic liquids. However, because these results imply the existence of torque components fluctuating significantly more slowly than the molecular reorientation, one has, from the general theory,¹⁶ that it is probably more accurate to treat these components as persistent torques (by analogy with the mean field director), against which rotational reorientation takes place, but these torques then relax on a slower time scale. A simple "local structure" model is given in section VII for analyzing such effects, where it is shown that such a mechanism may (1) contribute to "apparent" anisotropic diffusion observations; (2) yield non-Debye-like spectral densities; and (3) possibly explain in part the experimental slow tumbling anomalies. An analysis of ESR effects of hydrodynamic fluctuations in the director based on the approach used in recent discussions of NMR relaxation¹⁷⁻²¹ is given in the Appendix. It is related to, but different from, the nonhydrodynamic "local structure" model of section VII.

Further discussion of the spin relaxation results appears in section VIII and a summary of the conclusions appears in section IX.

II. Rotational Diffusion in Anisotropic Liquids and ESR Line Shapes

The theory for analyzing slow tumbling as well as motional narrowing ESR spectra in liquid crystals has been discussed in detail by PBF. For purposes of the present work, it is necessary to generalize their methods to cases where the ordering of the solute molecule is of lower symmetry than cylindrical, since this was, in general, found to be the case in our current work. Also we give more explicit expressions for line widths in the motional-narrowing region.

Following PBF we may write the perturbing hamiltonian

$$\mathcal{H}_1(\Omega, \Psi) = \sum_{L, K, M} (-1)^K D_{-KM}^L(\Omega) D_{M, M}^L(\Psi) F'_{\mu, i}{}^{(L, K)} A_{\mu, i}{}^{(L, M)} \quad (2.1)$$

where the $F'_{\mu, i}{}^{(L, K)}$ and $A_{\mu, i}{}^{(L, M)}$ are irreducible tensor components of rank L , with F' in molecule-fixed coordinates, while A is a spin operator in the laboratory axes (whose z axis coincides with the applied dc field). Equation 2.1 is based upon two sets of rotations of the coordinate systems: first from the molecular axis system (x', y', z') into the director axis system (x'', y'', z'') with Euler angles $\Omega = (\alpha, \beta, \gamma)$; and then into the laboratory axis system x, y, z with Euler angles Ψ . The orientation of the director relative to the laboratory frame can be specified by the two polar angles θ and φ such that $\Psi = (0, \theta, \varphi)$. More precisely, we mean by the molecular coordinate system (x', y', z') the principal axis system for the orientation of the molecule in the mesophase. It may be necessary to transform from the principal axis system of the magnetic interactions (x''', y''', z''') to the (x', y', z') system with Euler angles Θ , according to

$$F'_{\mu, i}{}^{(L, K)} = \sum_{K'} D_{K, K'}^L(\Theta) F'''_{\mu, i}{}^{(L, K')} \quad (2.2)$$

where $\Theta = (\alpha', \beta', \gamma')$.

A. Rotational Diffusion. The problem of rotational diffusion in nematic solvents has been studied^{13,14} by means of adding the effects of an orienting potential to the rotational diffusion equation for isotropic liquids. The previous authors considered a cylindrically symmetric potential in the diffusion equation, but our results and that of other workers^{22,23} have shown that the ordering tensors for several different free radicals dissolved in various liquid crystals are not axially symmetric. These latter observations imply that the ordering potential is not axially symmetric, and an asymmetric potential should in general be included in the diffusion equation to explain ESR relaxation in the mesophase of liquid crystals. The diffusion equation for a particle undergoing Brownian rotational diffusion in the presence of a potential U is given by^{16,24}

$$\frac{\partial P(\Omega, t)}{\partial t} = -M \cdot \left[R \cdot \frac{MU(\Omega)}{kT} + R \cdot M \right] P(\Omega, t) - \Gamma_{\Omega} P(\Omega, t) \quad (2.3)$$

where $U(\Omega)$ can be taken to be the orienting pseudopotential for a liquid crystal, M is the vector operator which generates an infinitesimal rotation, and is identified with the quantum mechanical angular momentum operator for a rigid rotator, while R is the diffusion tensor of the molecule. Both R and M are defined in the (x', y', z') molecular coordinate system. The angular momentum operator M^{24-26} is defined by

$$M^2 \varphi_{KM}^L(\Omega) = L(L+1) \varphi_{KM}^L(\Omega) \quad (2.4a)$$

$$M_{\pm} \varphi_{KM}^L(\Omega) = [(L \mp K)(L \pm K + 1)]^{1/2} \varphi_{K \pm 1, M}^L(\Omega) \quad (2.4b)$$

$$M_{x'} \varphi_{KM}^L(\Omega) = K \varphi_{KM}^L(\Omega) \quad (2.4c)$$

where $\varphi_{KM}^L(\Omega)$ are the eigenfunctions of M^2 and $M_{z'}$, L is the "angular momentum quantum number", and K is its component along the z' axis and

$$M_{\pm} = M_{x'} \pm iM_{y'} \quad (2.4d)$$

Then $\phi_{KM}^L(\Omega)$ are the normalized generalized spherical harmonics, i.e., eigenfunctions of the rigid rotor:

$$\phi_{KM}^L(\Omega) = \left(\frac{2L+1}{8\pi^2} \right)^{1/2} D_{KM}^L(\Omega) \quad (2.5)$$

When $U = 0$, eq 2.3 is simply the equation for (asymmetric) Brownian rotational diffusion in isotropic liquids. Equation 2.3 is based on the assumption that the external torque \mathbf{T} is derived from the potential $U(\Omega)$:^{16,24,27}

$$\mathbf{T} = iMU(\Omega) \quad (2.6)$$

The equilibrium solution to eq 2.3 is given by

$$P_0(\Omega) = \exp(-U(\Omega)/kT) / \int d\Omega \exp(-U(\Omega)/kT) \quad (2.7)$$

It is convenient to transform the Markov operator Γ_Ω defined in eq 2.3 to a symmetrized form:

$$\tilde{\Gamma}_\Omega = P_0(\Omega)^{-1/2} \Gamma_\Omega P_0(\Omega)^{1/2} \quad (2.8a)$$

and

$$\tilde{P}(\Omega, t) = P_0(\Omega)^{-1/2} P(\Omega, t) \quad (2.8b)$$

Then one obtains the diffusion equation

$$\frac{\partial \tilde{P}(\Omega, t)}{\partial t} = -\tilde{\Gamma}_\Omega \tilde{P}(\Omega, t) \quad (2.9a)$$

where

$$\tilde{\Gamma}_\Omega = \mathbf{M} \cdot \mathbf{R} \cdot \mathbf{M} + \frac{(\mathbf{M} \cdot \mathbf{R} \cdot \mathbf{M} U)}{2kT} + \frac{\mathbf{T} \cdot \mathbf{R} \cdot \mathbf{T}}{(2kT)^2} \quad (2.9b)$$

The restoring potential for liquid crystals can be written in its most general form as

$$U(\Omega) = \sum_{L,K,M} \epsilon_{KM}^L D_{KM}^L(\alpha, \beta, \gamma) \quad (2.10)$$

The assumption of cylindrical symmetry about the director axis, \hat{n} , implies that all averages taken over the angle γ vanish unless $M = 0$.²⁸ The uniaxial property of nematic liquid crystals (i.e., $\hat{n} \equiv -\hat{n}$) implies that L must be even. It is useful to use the linear combinations of the D_{K0}^L which are of definite parity, i.e., the real linear combinations:

$$U(\Omega) = \sum_{\text{even } L} \left(\epsilon_0^L D_{00}^L(\Omega) + \sum_{K > 0} \epsilon_{K\pm}^L [D_{K0}^L(\Omega) \pm D_{-K0}^L(\Omega)] \right) \quad (2.11)$$

These have simpler properties for molecular symmetries less than cylindrical.

Usually one considers only the leading term $\epsilon_0^2 D_{00}^2(\Omega)$, i.e., the Maier-Saupe potential.²⁹ We¹⁴ have already considered the cylindrically symmetric case when $\epsilon_0^4 \neq 0$ as well, but we have shown that typical ESR spectral predictions are not very sensitive to having $\epsilon_0^4 \neq 0$. In general, however, one expects the terms for $L > 2$ to be less important than those for $L = 2$, and we may approximate

$$U(\Omega) \cong \epsilon_0^2 D_{00}^2(\Omega) + \sum_{K > 0} \epsilon_{K\pm}^2 [D_{K0}^2(\Omega) \pm D_{-K0}^2(\Omega)] \quad (2.12)$$

The ϵ_0^2 , $\epsilon_{K\pm}^2 = \epsilon_K^2 \pm \epsilon_{-K}^2$ (with K positive) are themselves second rank irreducible tensor components, so that, in the principal axis of molecular orientation system (x' , y' , z') their cartesian components ϵ_{ij}^2 are diagonalized, with $\text{Tr}_i \epsilon_{ij}^2 = 0$, and complete specification is given by just ϵ_0^2 and $\epsilon_{2\pm}^2$. (Equation 2.12 may be thought of as the scalar product of second rank irreducible tensors.)

TABLE I: Comparison of the Different Schemes of Ordering Parameters^a

Wigner rotation matrices	Saupe's ordering tensor ^b	Snyder's motional constants ^c
$\langle D_{00}^2 \rangle$	O_{zz}	$(5)^{-1/2} C_{3z^2-r^2}$
$\langle D_{20}^2 + D_{-20}^2 \rangle$	$(6)^{1/2} / 2 (O_{yy} - O_{xx})$	$-(2/5)^{1/2} C_{x^2-y^2}$
$\langle D_{10}^2 - D_{-10}^2 \rangle$	$(8/3)^{1/2} O_{xz}$	$(2/5)^{1/2} C_{xz}$
$\langle D_{10}^2 + D_{-10}^2 \rangle$	$i(8/3)^{1/2} O_{yz}$	$i(2/5) C_{yz}$
$\langle D_{20}^2 - D_{-20}^2 \rangle$	$-i(8/3)^{1/2} O_{xy}$	$-i(2/5) C_{xy}$

^a Luz and Meiboom, *J. Chem. Phys.*, 59, 275 (1973), use a set of orientation parameters, C_{qn}^L , which are simply related to our ordering parameter: $\langle D_{kn}^2 \rangle = C_{kn}^2$. ^b Reference 29. ^c Reference 30.

The ordering tensor is defined by

$$\langle D_{KM}^L(\Omega) \rangle = \int d\Omega P_0(\Omega) D_{KM}^L(\Omega) \quad (2.13)$$

where $L = 2$ and $M = 0$. It is also a second rank irreducible tensor whose symmetry properties are related to those of the $\epsilon_{K\pm}^2$. Thus from eq 2.7 and 2.12 and the orthogonality of the $D_{KM}^L(\Omega)$ terms it follows that in the (x' , y' , z') system only $\langle D_{00}^2(\Omega) \rangle$ and $\langle D_{20}^2 + D_{-20}^2 \rangle$ are nonzero, i.e. $\langle D_{KM}^2(\Omega) \rangle$ is also diagonalized. The correspondence between the ordering tensor $\langle D_{KM}^2(\Omega) \rangle$ and those of Saupe²⁹ and Snyder³⁰ is given in Table I. Thus the "diagonalized" potential (retaining only $L = 2$ terms) becomes

$$U(\Omega) = \epsilon_0^2 D_{00}^2(\Omega) + \epsilon_{2+}^2 (D_{20}^2(\Omega) + D_{-20}^2(\Omega)) \quad (2.14)$$

or equivalently

$$U(\alpha, \beta) = \gamma_2 \cos^2 \beta + \epsilon \sin^2 \beta \cos 2\alpha \quad (2.14')$$

where $\epsilon_0^2 = 2\gamma_2/3$ and $\epsilon_{2+}^2 = 2\epsilon(6)^{-1/2}$. For molecules in which the molecular x' and y' axes are aligned to different extents, ϵ is nonzero. If one chooses the orientation coordinate system such that the z' axis tends to align to a greater degree either parallel or perpendicular to the director than both the x' or y' axes, one should have $|\gamma_2| > |\epsilon|$. From Table I it is seen that ϵ is proportional to the difference in the ordering parameters for the y' and x' axes, and the case $\epsilon < 0$ corresponds to the y' axis being ordered preferential to the x' axis along the direction of \hat{n} and/or to the x' axis being ordered to a greater degree perpendicular to the \hat{n} than the y' axis. Note that, if the director is not parallel to the magnetic field, but is rotated by $\Psi = (0, \theta, \varphi)$, the potential parameters for the orientation of the molecule relative to the director are not affected. [Note also that the two-parameter potential enables one to permute the labeling of the principal axes, i.e., if we have $\gamma_{2,z}$, ϵ_z as the potential terms when the magnetic z axis corresponds to the z axis defining the generalized spherical harmonic, then one can write the potential terms with respect to y alignment as $\gamma_{2,y} = -(\gamma_{2,z} - 3\epsilon_z)/2$ and $\epsilon_y = -(\gamma_{2,z} + \epsilon_z)/2$; similarly $\gamma_{2,x} = -(\gamma_{2,z} + 3\epsilon_z)/2$ and $\epsilon_x = (\gamma_{2,z} - \epsilon_z)/2$ (cf. discussion below eq 2.12). It is sometimes true, as will be seen in section V, that such a relabeling of axes can reduce the specification of the potential to just the one parameter γ_2 , or else it may still succeed in keeping ϵ small.]

We may utilize eq 2.6 and 2.4b,c to obtain \mathbf{T} from the potential in eq 2.14²⁶ in terms of its components in the (x' , y' , z') coordinate system

$$\mathbf{T}_\pm = T_{x'} \pm iT_{y'} = \pm i \sin 2\beta [\epsilon e^{i\alpha} - \gamma_2 e^{\pm i\alpha}] \quad (2.15a)$$

$$\mathbf{T}_{z'} = -2\epsilon \sin^2 \beta \sin 2\alpha \quad (2.15b)$$

This permits the determination of the last term on the right-hand side in eq 2.9b once \mathbf{R} is given in the (x', y', z') coordinate system. We shall assume axially symmetric rotation about z' , such that $R_{x'x'} = R_{y'y'} = R_{\perp}$ and $R_{z'z'} = R_{\parallel}$. The second term on the right-hand side of eq 2.9b is found from the well-known form of the operator $\mathbf{M} \cdot \mathbf{R} \cdot \mathbf{M}$.²⁴⁻²⁶ We introduce the definitions

$$\lambda = -\gamma_2/kT \quad (2.16a)$$

and

$$\rho = -\epsilon/kT \quad (2.16b)$$

and obtain for the symmetrized Markov operator defined in eq 2.9

$$\tilde{\Gamma} = \mathbf{M} \cdot \mathbf{R} \cdot \mathbf{M} - f(R_{\perp}, R_{\parallel}, \lambda, \rho, \Omega) \quad (2.17a)$$

where

$$f(R_{\perp}, R_{\parallel}, \lambda, \rho, \Omega) =$$

$$\sum_{L=0,2,4} \left[X_{00}^L D_{00}^L + \sum_{0 < K \leq L} X_{K0}^L (D_{K0}^L + D_{-K0}^L) \right] \quad (2.17b)$$

with

$$X_{00}^0 = -(2/15)[R_{\perp}(\lambda^2 + \rho^2) + 2R_{\parallel}\rho^2] \quad (2.18a)$$

$$X_{00}^2 = 2[R_{\perp}\lambda - [R_{\perp}(\lambda^2 + \rho^2) - 4R_{\parallel}\rho^2]/21] \quad (2.18b)$$

$$X_{00}^4 = 4[2R_{\perp}(\lambda^2 + \rho^2) - R_{\parallel}\rho^2]/35 \quad (2.18c)$$

$$X_{20}^2 = (6)^{1/2}\rho[R_{\perp} + 2R_{\parallel}]/3 + 2R_{\parallel}\lambda/7 \quad (2.18d)$$

$$X_{20}^4 = 4(10)^{1/2}R_{\perp}\rho\lambda/35 \quad (2.18e)$$

$$X_{40}^4 = (8/35)^{1/2}R_{\parallel}\rho^2 \quad (2.18f)$$

One may also write the diffusion equation in terms of the general angular momentum operator \mathbf{N} referred to the director frame.²⁴ This is appropriate when \mathbf{R} is diagonal in this frame, i.e., anisotropic viscosity. One then generates an analogous set of expressions.^{24,31} In particular we assume $R_{xx} = R_{yy} = \hat{R}_{\perp}$, $R_{zz} = \hat{R}_{\parallel}$, and one finds for the components of \mathbf{T} in the (x, y, z) coordinates:

$$\begin{aligned} T_x \pm iT_y &= [2\epsilon \sin \beta \sin 2\alpha \mp \\ &\quad i \sin 2\beta(\gamma_2 - \epsilon \cos 2\alpha)]e^{\pm i\alpha} \quad (2.19a) \\ T_z &= 0 \end{aligned}$$

and

$$\Gamma_{\Omega} = \mathbf{N} \cdot \mathbf{R}_{\Omega} \cdot \mathbf{N} - \hat{R}_{\perp} \hat{f}(\lambda, \rho, \Omega) \quad (2.20a)$$

where

$$\hat{f}(\lambda, \rho, \Omega) = \sum_{L=0,2,4} (\hat{X}_{00}^L D_{00}^L(\Omega) + \sum_{0 < K \leq L} \hat{X}_{K0}^L (D_{K0}^L(\Omega) + D_{-K0}^L(\Omega))) \quad (2.20b)$$

with

$$\hat{X}_{00}^0 = -2(\lambda^2 + 3\rho^2)/15 \quad (2.21a)$$

$$\hat{X}_{00}^2 = 2[\lambda - (\lambda^2 - 3\rho^2)/21] \quad (2.21b)$$

$$\hat{X}_{00}^4 = 4(2\lambda^2 + \rho^2)/35 \quad (2.21c)$$

$$\hat{X}_{20}^2 + 6^{1/2}\rho[1 + 2\lambda/7] \quad (2.21d)$$

$$\hat{X}_{20}^4 = 4(10)^{1/2}\lambda\rho/35 \quad (2.21e)$$

$$\hat{X}_{40}^4 = (8/35)^{1/2}\rho^2 \quad (2.21f)$$

The procedure for solution now follows the general approach of PBF, utilizing the normalized generalized spheri-

cal harmonics of eq 2.5 as an orthonormal basis set. Actually, it is more convenient, as seen from the above discussions, to use the real functions of definite parity:

$$D_{K\pm, M}^L(\Omega) = N_L^{-1/2} \frac{1}{\sqrt{2}} [D_{K, M}^L(\Omega) \pm (-1)^K D_{-K, M}^L(\Omega)] \quad \text{for } K \neq 0 \quad (2.22)$$

Computer programs based on the PBF theory were written for calculating nitroxide line shapes when (1) the asymmetric potential defined by eq 2.14' describes the orientation of a nitroxide radical for which the principal magnetic (x''', y''', z''') and orientation (x', y', z') axes are coincident and (a) eq 2.17 and 2.18 apply or (b) eq 2.20 and 2.21 apply; (2) a Maier-Saupe potential is used, but the z' and z''' axes are tilted by angle β' ; (3) different reorientational models are used for a Maier-Saupe potential with either an axial nitroxide or asymmetric nitroxide. All these programs contain the correction terms for nonsecular contributions to the resonant frequency shifts. Further details, as well as computer-program listings, appear in Polnaszek's thesis.³¹

B. Motional Narrowing Region. Many of the special simplifying features which may be applied to spectra in the motional narrowing region have been discussed by PBF. We extend and apply that discussion to the problems of interest here.

(1) *Effective Spin Hamiltonian and Ordering Parameters.* Here one uses an effective spin hamiltonian

$$\mathcal{H} = \mathcal{H}_0' + \mathcal{H}_1'(\Omega) \quad (2.23a)$$

where

$$\mathcal{H}_0' = \mathcal{H}_0 + \langle \mathcal{H}_1(\Omega) \rangle \quad (2.23b)$$

and

$$\mathcal{H}_1'(\Omega) = \mathcal{H}_1(\Omega) - \langle \mathcal{H}_1(\Omega) \rangle \quad (2.23c)$$

where the averaging implied by the angular brackets is according to the prescription of eq 2.13. When nuclear Zeeman terms are neglected the static spin hamiltonian in the high field approximation is

$$\hbar \mathcal{H}_0 = \langle g \rangle \beta_e B_0 S_z - \hbar \gamma_n \sum_i \langle a_i \rangle S_z I_z \quad (2.24)$$

The apparent g and a values, i.e. $\langle g \rangle$ and $\langle a \rangle$, must be corrected for nonsecular static and dynamic frequency shifts according to the methods discussed by PBF. Thus, for example, for the potential of eq 2.14 and for a molecule in which the (x''', y''', z''') coordinates are the same as the (x', y', z') coordinates, i.e., the magnetic tensor principal axes coincide with the orientational principal axes, one obtains the following equation (for a single nucleus of spin I) for these nonsecular frequency shifts:

$$\begin{aligned} \omega_{\text{corr}} - \omega_{\text{zero order}} &= \Delta\omega(m) = \frac{1}{\omega_0} [I(I+1) - m^2] 2b^2 - \\ &\quad \left\{ \frac{3}{20} (F_0^2 + 2F_2^2) + \frac{3m}{10} (F_0 D_0' + 2F_2 D_2') + \right. \\ &\quad \left. \frac{1}{15} (7I(I+1) - m^2) (D_0^2 + 2D_2^2) + \right. \\ &\quad \left. \left[\frac{3}{28} (F_0^2 - 2F_2^2) + \frac{3m}{14} (F_0 D_0' - 2F_2 D_2') - \right. \right. \\ &\quad \left. \left. \frac{2}{21} (5I(I+1) - 8m^2) (D_0^2 - 2D_2^2) + bD' [I(I+1) - \right. \right. \\ &\quad \left. \left. m^2] \right] \langle D_{00}^2 \rangle + \left(-\frac{3}{14} [F_0 F_2 + m(F_0 D_2' + F_2 D_0')] + \right. \right. \\ &\quad \left. \left. \frac{4}{21} [5I(I+1) - 8m^2] D_0 D_2 \right) \langle D_{20}^2 + D_{-20}^2 \rangle \right\} \frac{\omega_0 \tau_R^2}{1 + \omega_0^2 \tau_R^2} \quad (2.25) \end{aligned}$$

where we are using the notation of I (except that F_2 and D_2 used here have opposite sign than the use in I for the consistent set of conventions needed for anisotropic liquids, cf. Polnaszek's thesis³¹). In principle, terms including $\langle D_{00}^4 \rangle$ and $\langle D_{20}^2 \rangle + \langle D_{-20}^2 \rangle$ can be included but they are negligible (<1% of the sum of the terms retained).

If the magnetic tensors are known, eq 2.13 can then be used to calculate the ordering parameters. For the case in which the asymmetric potential of eq 2.14 is applicable and $\Psi = 0$, the following equations result:

$$\langle D_{00}^2 \rangle = \frac{(\langle a \rangle - a)(g_x - g_y) - (\langle g \rangle - g)(a_x - a_y)}{(a_x - a)(g_x - g_y) - (g_x - g)(a_x - a_y)} \quad (2.26a)$$

$$\langle D_{20}^2 \rangle + D_{-20}^2 = \frac{\sqrt{6}[(\langle a \rangle - a)(g_x - g) - (\langle g \rangle - g)(a_x - a)]}{(g_x - g_y)(a_x - a) - (g_x - g)(a_x - a_y)} \quad (2.26b)$$

[In eq 2.26 and hereafter we shall refer to magnetic tensor components in the x''', y''', z''' axes as the x, y, z components, or else some cyclic permutation of the (x''', y''', z''') axes provided there is no confusion with the laboratory axes.]

With the ordering parameters known, eq 2.13 can be expressed as a system of two integral equations and the potential parameters λ and ρ obtained. Note that, because there are only two experimental observables, viz. $\langle g \rangle$ and $\langle a \rangle$, obtained from a motional-narrowing nematic ESR spectrum of a nitroxide, one can have at most two adjustable parameters, and one must then assume some knowledge of the x', y', z' axis system.³²

For many compounds of appropriate molecular geometry, the one-parameter Maier-Saupe potential may prove sufficient to describe its orientation, and a second parameter, which may then be determined, is the tilt angle of the magnetic z axis with respect to the z' axis. For this case, one obtains the set of equations

$$\cos^2 \beta' = \frac{(a_x - a)(\langle g \rangle - g) - (g_x - g)(\langle a \rangle - a)}{(g_x - g)(\langle a \rangle - a) - (\langle g \rangle - g)(a_x - a_x)} \quad (2.27)$$

$$\langle D_{00}^2(\Omega) \rangle = \frac{\langle a \rangle - a}{(a_x - a_x) \cos^2 \beta' + (a_x - a)} \quad (2.27a)$$

where the magnetic tensor components are in their principal axis system.

Note that the possible solutions of eq 2.27 for β' are $\pm\beta' \pm n\pi$ ($n = 0, 1, 2, \dots$) but, because of the uniaxial property of nematics, they are equivalent.

If there is a static distribution of directors around the laboratory axis, then one would have to use eq 2.1 and average the spectrum over the distribution in Ψ (e.g., a potential such as $V(\Psi) = \mu \cos^2 \theta$).^{3,31}

(2) Relaxation. If we define, as in PBF, the correlation function

$$C(L, L'; m, m', q, q'; \tau) = \langle D_{-m, q}^{(L)}(t) D_{-m', q'}^{(L')*}(t + \tau) \rangle$$

[where the prime on a function is defined by $f'_a(\Omega) = f_a(\Omega) - \langle f_a(\Omega) \rangle$], and its Fourier-Laplace transform (the spectral density function):

$$K(LL', mm', q, q', i\omega) = \int_0^\infty d\tau \exp(-i\omega\tau) C(L, L'; m, m'; q, q'; \tau)$$

then the line widths and other relaxation behavior may be

described in terms of these functions, according to the methods outlined by PBF. In particular one has

$$\text{Re } K(LL', KK', MM'; i\omega) = \sum_n \frac{E_n}{E_n^2 + \omega^2} \times \langle G_0(\Omega) | D_{KM}^L(\Omega) | G_n(\Omega) \rangle \langle G_n(\Omega) | D_{K'M'}^{L'*}(\Omega) | G_0(\Omega) \rangle \quad (2.28)$$

where the $G_n(\Omega)$ are the eigenfunctions of $\tilde{\Gamma}_\Omega$ of eq 2.9b with eigenvalues E_n . Equation 2.28 may be simplified by noting that for general potentials of form eq 2.11 or 2.12, only those K for which $M' = M$ are nonzero, so

$$K(L, L', K, K', M, M', i\omega) = K(L, L', K, K', M, i\omega) \delta_{MM'} \quad (2.29a)$$

We note further that the usual terms of $\mathcal{H}_1(\Omega)$ only require $L = L' = 2$. Also it can be shown for the potential of eq 2.14 that

$$K(2, K, K', M, i\omega) = K(2, -K, -K', M, i\omega) = K(2, K, K', -M, i\omega) = K(2, -K, -K', -M, i\omega) = K(2, K', K, M, i\omega) \quad (2.29b)$$

[For a cylindrically symmetric potential one also has $K = K'$ for nonzero values of K .]¹⁴ Thus, for the asymmetric potential of eq 2.14, the line widths are given

$$T_2^{-1} = \text{Re} \sum_{\substack{K, K', M \\ \alpha, \alpha', \beta, \beta'}} K(2, K, K', M, i\omega) F_{\mu_i}^{(2, K)} F_{\nu_j}^{(2, K')*} \times [A_{\mu_i}^{(2, M)}]_{\alpha\beta} [A_{\nu_j}^{(2, M')}]_{\alpha'\beta'}^* \quad (2.30a)$$

For a single nuclear spin of I , one has the usual dependence of the line width upon the z component of the nuclear spin quantum number, m_I

$$T_2^{-1}(m_I) = A + Bm_I + Cm_I^2 \quad (2.30b)$$

where

$$A - A' = \text{Re} \left\{ \frac{I(I+1)}{3} \gamma_e^2 \sum_{K, K'} D_K D_{-K'} [K(2, K, K', 0, \omega_0) + 3K(2, K, K', 1, \omega_0) + 6K(2, K, K', 2, \omega_0)] + \frac{\hbar^2 \gamma_e^2}{16\beta_e^2} \sum_{K, K'} F_K F_{-K'} [4K(2, K, K', 0, 0) + 3K(2, K, K', 1, \omega_0)] \right\} \quad (2.31a)$$

$$B = -\text{Re} \left\{ \frac{\hbar \gamma_e^2}{\sqrt{6}\beta_e} \sum_{K, K'} D_K F_{-K'} [4K(2, K, K', 0, 0) + 3K(2, K, K', 1, \omega_0)] \right\} \quad (2.31b)$$

$$C = \text{Re} \left\{ \frac{\gamma_e^2}{3} \sum_{K, K'} D_K D_{-K'} [8K(2, K, K', 0, 0) - K(2, K, K', 0, \omega_0) + 6K(2, K, K', 1, \omega_0) - 3K(2, K, K', 1, \omega_0) - 6K(2, K, K', 2, \omega_0)] \right\} \quad (2.31c)$$

where the D_K and F_K are defined as in I; also $\omega_a \approx \omega_\pm = \pm\omega_n + \frac{1}{2}a|\gamma_d|$. Note A' , the residual width, includes all other nuclear-spin independent line-broadening mechanisms. [The units of A , B , and C are sec^{-1} ; for comparison with experimental results, they are multiplied by $2(3)^{-1/2}/|\gamma_d|$ to give values which correspond to peak-to-peak line widths in gauss.] Note that nonsecular terms are readily included in this treatment of ESR line widths in the motional narrowing region of the nematic mesophase. In previous

work nonsecular terms were either neglected or considerably complicated the method.^{9-13,28}

In the isotropic limit, the spectral densities are

$$K(2, K, K', M, \omega) =$$

$$(1/5) \delta_{KK'} \frac{\tau_{LK}^{-1}}{(\tau_{LK}^{-1})^2 + \omega^2} = \frac{1}{5} j_{LK}(\omega) \quad (2.32)$$

and then eq 2.31 corresponds to the equation given for axially symmetric rotational diffusion in I.

For an axially symmetric potential, eq 2.31 can be used to calculate motional narrowing line widths by the substitution of $K_{KM}^{(2)} \delta_{KK'}$ for the $K(2, K, K', M, \omega)$. In this case the $K_{KM}^{(2)}$ for $|\lambda| \leq 1$ may be obtained by a perturbation theory approach and are given by PBF. (Their equations for $K_{KM}^{(2)}$ allow for the K and M to be permuted throughout, to obtain all the needed expressions.)^{33,34}

Programs for the analysis of the motional-narrowing relaxation of a nitroxide with asymmetric magnetic parameters oriented by the asymmetric potential of eq 2.14 are given in Polnaszek's thesis.³¹

III. Experimental Section

A. Sample Preparation. The nitroxide free radical 2,2,6,6-tetramethyl-4-piperidone *N*-oxide (Tempone) and its totally perdeuterated analog (PD-Tempone) were synthesized by Dr. R. P. Mason using the method of Rozantsev.³⁵ The bromoacetamide spin label, 3[[2-[2-(bromoacetamido)ethyl]ethyl]carbamoyl]-5,5-tetramethyl-1-pyrrolidinyloxy (BASL), was purchased from Syva Associates. The α -phenylnitroxyl nitroxide (PNN) was a gift of Dr. G. Rist. The di-*tert*-butyl nitroxide (DTBN) was synthesized by B. Kaplan using the method of Hoffmann et al.³⁶ All free radical nitroxides were used without further purification.

The liquid crystal bis(4'-*n*-octyloxybenzal)-2-chloro-1,4-phenylenediamine (BOCP) was purchased from Aldrich Chemical Corp. and used without further purification. The nematic compounds butyl-*p*-(*p*-ethoxyphenoxy-carbonyl)phenyl carbonate (BEPC), *p*-(*p*-ethoxyphenyl-azo)phenyl hexanoate (PEPH), and *p*-[*N*-(*p*-methoxybenzylideneamino)-*n*-butylbenzene (MBBA) were obtained from Eastman Kodak. BEPC was purified by several recrystallizations from methanol, PEPH was recrystallized from absolute alcohol, and MBBA was purified by vacuum distillation.³⁷ The *p*-ethoxy-*p'*-hexyloxyazobenzene (EHAB) and its nematic precursor *p*-ethoxy-*p*-hexyloxyazobenzene were synthesized as described by Koch³⁸ and recrystallized from ethanol-water mixtures and then from absolute ethanol. The nematic compound *p*-[*N*-(σ -hydroxy-*p*-methoxybenzylidene)amino]-*n*-butylbenzene (OH-MBBA)³⁹ was synthesized by refluxing *p*-*n*-butylaniline (Aldrich) and *p*-methoxy- σ -hydroxybenzaldehyde prepared by the method of Zemplen et al.⁴⁰ in absolute alcohol. Upon recrystallization from methanol, OH-MBBA melted at 42°C. Nematic phase IV, a low melting nematic eutectic, was synthesized by the methods of Steinstrasser and Pohl^{41a} and recrystallized from a methanol-hexane mixture; it was also purchased from EM Laboratories. Nematic phase V,^{41b} a lower melting nematic eutectic composed of 65% phase IV and 35% of another mixture, was obtained from EM Laboratories and used without further purification. The dimethoxyethane (DME) was Eastman White Label and was purified by the methods of Bolton and Fraenkel.⁴² Deoxygenated samples were prepared by

standard methods, and further details may be found in Polnaszek's thesis.³¹

B. ESR Spectrometer. Most of the ESR measurements were performed on a Varian E-12 spectrometer using 10-kHz field modulation, cf. I and II. The temperature in the active region of the cavity was controlled by a Varian E-257 variable temperature control unit and was stable to $\pm 1^\circ\text{C}$. The temperature gradient over the active region of the cavity relative to the center was found to vary with temperature. At room temperature the value was $\pm 0.5^\circ\text{C}$, while at 150°C the gradient increased to $\pm 2^\circ\text{C}$. Other techniques are as described in I and II.

C. Line Width Measurements. All line width measurements were performed with the modulation amplitude set at a value of less than one-tenth of the line width and with the microwave power set well below that required to maximize the signal amplitude. All the spin labels studied had unresolved proton or deuteron hyperfine structure in each of three principal ESR lines. This inhomogeneous broadening causes the line shapes to be non-Lorentzian and to appear to be broader than the true peak-to-peak line width $2|\gamma_d| T_2^{-1}(3)^{-1/2}$. The correct line widths can be obtained as was done in II. One measures the line shape by noting the variation of the derivative half-amplitude as a function of the distance from resonance. This line shape is then compared to a theoretical line shape calculated using a peak-to-peak line width and hyperfine splitting (hfs) constants for the nuclei causing the inhomogeneous broadening. Kreilick using an NMR technique has determined these hyperfine splitting constants in the isotropic phase for Tempone to be $a_{\beta^H} = -0.11$ G and $a_{\gamma^H} = -0.01$ G.⁴³ Because there are 12 β protons and 4 γ protons and a_{γ^H} is so small, the effect of the γ protons was neglected in the line shape simulations.

For Tempone in the isotropic phase of BEPC, a β proton coupling constant of 0.125 ± 0.003 G is needed to fit the observed line shape. In the nematic phase of BEPC the β -proton coupling was found to vary with the temperature as a result of the increase of $\langle D_{K0}^2 \rangle$ with decreasing temperature. If one assumes an axially symmetric potential, the ordering parameter can be determined from the nitrogen hfs using eq 2.27a with $\beta' = 0$. Then one may use this ordering parameter and the isotropic β proton coupling to calculate the z component of the methyl proton hyperfine tensor in the principal axis of the nitrogen magnetic tensors (from eq 2.27a). One obtains $a_z^{H\beta} = -0.739 \pm 0.008$ G and $a_{\perp}^{H\beta} = \frac{1}{2}(a_x + a_y) = 0.182$ G, if one assumes axial symmetry of the methyl proton hyperfine tensor. For PD-Tempone in phase V a similar analysis applied to the β deuteron splittings yields $a_D^{\text{iso}} = -0.0215 \pm 0.0005$ G and $a_z^D = -0.093 \pm 0.007$ G. Since the isotropic splittings, a_N and the a_z^N determined for the rigid limit were nearly identical for PD-Tempone in all the liquid crystal solvents, it was assumed that the a_D and a_z^D were the same for all systems in the liquid and nematic regions. Then, after one has obtained $\langle D_{00}^2 \rangle$ relative to the molecular z axis, this can be used to calculate the $\langle a_D \rangle$ needed for the line shape analysis. The intrinsic peak-to-peak line width for PD-Tempone, or any radical in which the inhomogeneous broadening is due to 12 equivalent deuterons, can be obtained from Figure 1 and knowledge of the deuteron hfs.

In the motional narrowing region, when the variation in the line width among the three nitrogen lines is small compared to the line widths, it is usually more accurate to determine one line width and use the relative amplitude of

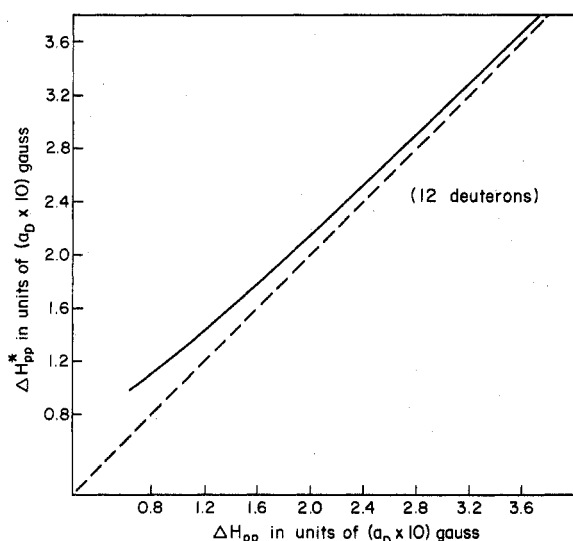


Figure 1. Calibration curve for obtaining the intrinsic derivative line width ΔH_{pp}^* from the observed (inhomogeneous) derivative line width ΔH_{pp} for PD-Tempone involving 12 equivalent deuterons.

the lines to calculate the relative line width of all the lines. This procedure can be readily modified to the case of inhomogeneously broadened lines. After determining $\langle a_D \rangle$ and one line width as described above, one can use that value of $\langle a_D \rangle$ and vary the intrinsic line widths in the line shape program until one obtains the correct intensity ratios. This procedure was applied to all spectra in which the line widths were 1 G or less. For widths >1 G the corrections were less than 1%. [Magnetic field inhomogeneity will not cause serious inhomogeneous broadening of the lines, since it is ~ 5 mG,² whereas the minimum intrinsic line width observed for PD-Tempone in phase V was 134 mG at 67°C.]

Another factor which can affect the observed line shapes in the nematic mesophase is the possibility of the director \hat{n} not being parallel to the dc magnetic field. deGennes has predicted that due to thermal fluctuations the director can have components which are not parallel to the field.⁴⁴ One notes that the resonant positions of the lines will be different for each orientation of the director. If the motion of the director is taken as being slow on the ESR time scale,^{17,44} then each observed line will be a superposition of resonances from different director orientations and any modulation by the motion of the director may be neglected, i.e., one has a static distribution of directors. The total line shape for a distribution of Lorentzians with the director distribution also of a Maier-Saupe form is given by

$$I(B_0) = \int_{-\pi/2}^{\pi/2} \frac{T_2^{-1}(B(\theta) - B_0)}{[(T_2^{-1})^2 + (B(\theta) - B_0)^2]^2} \times \exp(\alpha \sin^2 \theta) \sin \theta d\theta \quad (3.1)$$

where

$$B(\theta) = \{B + m_I[a + D_{00}^2(\theta)\langle D_{00}^2(\Omega) \rangle(a_z - a)] - [I(I+1) - m_I^2][a - \frac{1}{2}D_{00}^2(\theta)\langle D_{00}^2(\Omega) \rangle(a_z - a)]^2/2B_0\} [1 - D_{00}^2(\theta)\langle D_{00}^2(\Omega) \rangle(g_z - g)/g] \quad (3.2)$$

where the $\langle D_{00}^2(\Omega) \rangle$ are the experimentally determined ordering parameters, θ is the angle between \mathbf{B}_0 and \hat{n} , B_0 is the resonant field of the center line in the absence of a potential $= (\omega_0/\gamma_e)$, and $\alpha = -(kT\theta_0^2)^{-1}$ where θ_0 is the root mean square fluctuation in θ^{6a} and we have assumed small

TABLE II: Magnetic Parameters for Nitroxides in Liquid Crystals^a

(A) PD-Tempone in Phase V			
g_x	2.0097 ± 0.0002	A_y, G	5.01 ± 0.2
g_y	2.0062 ± 0.0002	A_z, G	33.7 ± 0.3
g_z	2.00215 ± 0.0001	$\langle A \rangle, G$	14.77 ± 0.3
$\langle g \rangle$	2.0060 ± 0.00017	a_N, G	14.78 ± 0.02
g_s	2.00601 ± 0.00005	A, G	2.2
A_x, G	5.61 ± 0.2	B, G	0.2
(B) Other Systems			
System	A_z	a_N	g

PD-Tempone in Phase IV	33.5	14.75	2.00602
PD-Tempone in BOCP	33.9	14.74	
PD-Tempone in BEPC	33.8	14.79	2.00600
PNN in BEPC	18.1	7.62	
Bromoacetamide spin label in BEPC	33.2	14.62	2.0058

^a Polycrystalline matrices.

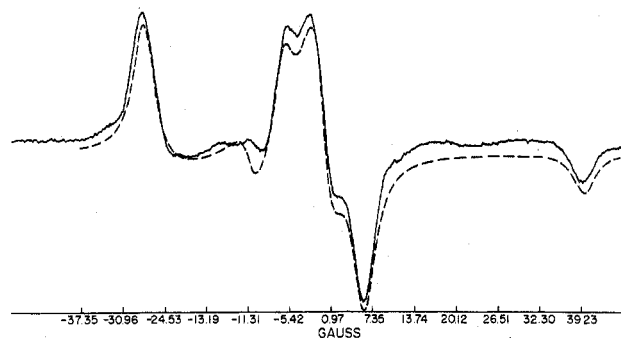


Figure 2. Rigid limit spectrum for PD-Tempone in phase V and simulation based on magnetic parameters given in Table II.

ordering parameters to get a simple result in eq 3.2. [In general, T_2^{-1} will depend on θ , a matter to be discussed in section VII. However for small values of θ_0 expected for this mechanism, it is reasonable to neglect this effect.]

We have observed in our work with PD-Tempone in phases IV and V, marginal asymmetries of the hyperfine lines, which would require values of $\alpha > 100$ (i.e., let R be the ratio of the low-field to high-field extremum intensity of a hyperfine line, then we see $R \sim 0.94$ to 1.0). These values for α are very much larger than those used by Brooks et al.⁴⁵ for VAAC in PAA. Furthermore (1) our observed asymmetries increase with decreasing temperature, or the opposite direction expected for director fluctuations, but in the correct direction if due to slowing of the rate of molecular reorientation; also (2) the high-field line is predicted to have $R > 1$ while we observe $R < 1$, etc. Thus, within experimental error it does not appear that we observe any effects from a static distribution of directors.⁴⁶ Dynamic effects of fluctuations in the director are discussed in section VII and the Appendix.

IV. Determination of Magnetic Tensor Components. Rigid Limit

In order to simulate slow motional spectra and to analyze the data in the motional narrowing region, one must know

the components of the g and A tensors which occur in the spin hamiltonian $\mathcal{H}_1(\Omega)$. We have made our measurements on polycrystalline samples in the manner given in I and II. All of the liquid crystals used froze into amorphous solids when cooled slowly below their nematic range. However, to prevent some residual ordering from being frozen in, the samples were frozen outside the magnet gap or inside the cavity with the magnetic field turned off. MBBA and OH-MBBA, if quick-frozen in liquid nitrogen, formed rigid glasses. However the spectra of PD-Tempone in all the frozen nematics was virtually identical and independent of whether the sample was amorphous or glassy. Also the isotropic a and g values for PD-Tempone in all the liquid crystals studied were nearly equal as shown in Table II. Thus, it was decided to determine accurately the magnetic tensors for PD-Tempone in one system and use these values for all systems and also for Tempone.

The rigid limit spectrum of PD-Tempone in frozen phase V at -190°C is shown in Figure 2. Note the resolution in the central region. For Tempone in the rigid limit, the center region is not resolved because of inhomogeneous broadening due to unresolved proton hyperfine structure. Thus deuteration of the nitroxide spin label is seen to aid in the analysis of the rigid limit spectrum as well as the motional narrowing and slow motional spectra. Further resolution can be obtained by deuteration of the solvent (cf. I and II). The parameters which gave the best fit are given in Table II. A lorentzian line shape gave the best overall fit, although a gaussian shape function appears to fit the extrema better. Note that the theoretical spectrum is slightly lowered from the experimental one, so that the fit in the region -24.53 to -13.19 G is an artifact of the drawing; it is this region for which a gaussian gives a better fit. [We note that rigid limit spectra for PD-Tempone in toluene solvent were more successfully fit with a lorentzian shape, although some features of the spectrum in 85% glycerol were better fit with a gaussian (cf. II).] The form for the orientationally dependent intrinsic line width was assumed to be²

$$T_2^{-1} = A + B \cos^2 \beta \quad (4.1)$$

It was found that the values of A and B of 2.2 ± 0.1 and 0.2 ± 0.1 G, respectively, gave the best fit to the experimental spectrum. It was shown in II that the magnetic parameters and intrinsic line widths for PD-Tempone vary with solvent in nonliquid-crystalline solvents. The near equivalence of these quantities for all the liquid crystals is probably due to chemical similarity of these compounds. Also these results are very similar to the magnetic parameters obtained in II for nonhydrogen-bonding isotropic solvents (e.g., toluene) as one might expect.

There are some differences between the theoretical and experimental spectra. One of the possible causes, which was discussed above, is the residual motion present. It was not experimentally convenient to reduce the temperature further; however the observed spectra changed very little with temperature in this region. The deuterium inhomogeneous broadening is expected to be negligible, since the largest component of the methyl deuterium hyperfine tensor is -0.09 G. Quadrupole terms were neglected in the theoretical hamiltonian used. Dinse et al.³² have measured the quadrupole splitting of a chemically similar nitroxide to be -0.9 G, but the effect of the quadrupole splitting will be to shift the lines corresponding to the x and y orientations by⁴⁷

$$\frac{9}{32} \left(\frac{1}{a_1} \right) \left(\frac{e^2 q Q}{\hbar |\gamma_e|} \right)^2 \approx 0.04 \text{ G} \quad (4.2)$$

which is negligible; also there will be no shift in the lines from the z orientations. Spectra simulated with nuclear Zeeman terms included did not differ from those in which these terms were neglected. It was thought that the small bump appearing near -13 G might be due to the presence of a spectrum arising from ^{15}N ($I = 1/2$). However, simulation performed with parameters appropriate for the ^{15}N species, that was added to the line shape calculated for ^{14}N using the correct isotropic abundances, did not show such a bump nor was the rest of the spectrum affected. Another source of error is the assumption used in the hamiltonian to simulate the spectra that the principal axes of the g and hyperfine tensors coincide. It has been reported that the xy planes differ by 6° for DTBN.⁴⁸ If this were true for PD-Tempone the values for the x and y components may be changed somewhat, but it would be within our error limits. Thus one can be confident that the magnetic parameters given in Table II are fairly accurate.

The spin parameters determined from the rigid limit simulations give the same isotropic values (obtained at temperatures 300° higher) when one averages the values of the principal components. Thus, it is reasonable to believe that the magnetic tensors are temperature independent, so they may be used for all the line shape analyses.

V. Motional Narrowing Results

A. Preliminary Observations. The motional narrowing ESR spectra of all nitroxides consisted of three sharp lines in the isotropic and nematic phases in all liquid crystals studied. If one refers to PBF, one finds that this observation need not in itself be indicative of motional narrowing. The analyses will be given for only the nematic mesophase. [Several of the liquid crystals had underlying smectic mesophases. All the smectic solvents gave spectra which had splitting constants nearly identical with the isotropic splittings and thus were indicative of randomization of the director in the smectic phase. The lines were much broader than the nematic phase and in some cases were asymmetric. This is indicative of the local ordering present in the macroscopically disordered smectic phases.⁸ The nematic compounds which did not have underlying smectic phases all froze to amorphous randomly oriented solid phases. All mesophases could be supercooled considerably below their melting points, and no sudden changes (or discontinuities) were observed in the ESR spectra in this region until the samples froze. Below the freezing point in all systems, the spectra varied continuously with temperature until the rigid limit was reached.]

The nematic-isotropic transition point, T_K , was determined to be the temperature at which the observed splitting constant changed from its isotropic value to a smaller value indicative of the ordering in the nematic phase. Because of the temperature gradient in the cavity as well as impurities in the liquid crystal solvent, it was possible to observe spectra from both phases simultaneously if one was at or near T_K . These transition points and freezing points were dependent upon the concentration of the radical and also upon the specific radical which was dissolved in the nematic solvent. Thus the values of the transition points and freezing points could vary by several degrees from sample to sample.

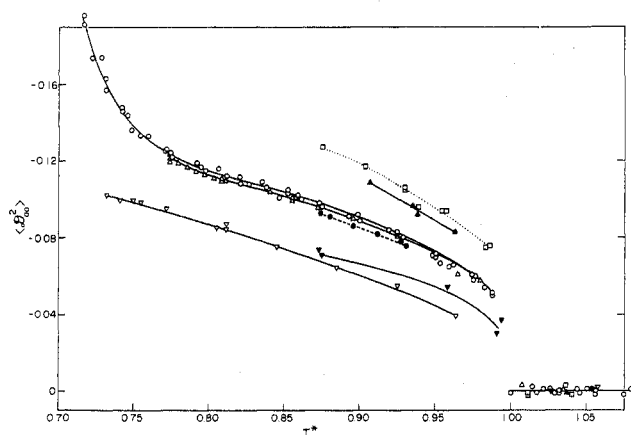


Figure 3. Ordering parameter $\langle D_{00}^2 \rangle_z$ vs. reduced temperature $T^* = T/T_K$ for PD-Tempone in several liquid crystals: (O) phase V; (Δ) phase IV; (\bullet) MBBA; (\blacktriangledown) OHMBBA; (∇) BOCP; (\blacktriangle) BEPC; (\square) Tempone in BEPC.

One finds that phase V and BOCP should be the best liquid crystals in which to do an ESR relaxation study, since they have nematic ranges of over 100° . However phase V freezes at least 80° below BOCP and thus would be a more suitable solvent in which to look for slow-motional effects. When the experimental study was performed, phase V was the lowest melting nematic compound readily available. Radical stability is another factor to be considered in the choice of lower temperature liquid crystals. If the radical is volatile, it may distill out of the liquid crystal when heated in the evacuated sample tubes. Also, as noted previously the temperature gradients in the cavity are much greater at the higher temperatures.

The radical chosen for most of the motional narrowing studies was PD-Tempone. As we have shown, the contribution from inhomogeneous broadening can be completely neglected for spectra having all lines of width 1 G or greater, and the contribution is quite small for narrower lines. The accuracy of the line width measurements is considerably increased compared to proton inhomogeneously broadened lines. The only apparent disadvantage in using PD-Tempone is that, because of its size and geometry, it is not ordered to a large extent in the nematic phase.

B. Order Parameters and Potential Expansion Coefficients. In order to perform relaxation studies, one must know the coefficients in the potential (cf. eq 2.14) which determines the distribution function for the orientation of the radical in the nematic phase. These coefficients can be determined from the ordering parameters calculated in the motional narrowing region.

The ordering parameters $\langle D_{00}^2 \rangle_z$ determined for PD-Tempone in several liquid crystals for the Maier-Saupe potential are plotted vs. T^* in Figure 3 where $T^* = T/T_K$. The magnetic parameters used are those given in Table II for PD-Tempone in phase V. The ordering parameters for a solute molecule in different solvents might be expected to lie on nearly the same line when plotted against T^* . The fact that they do not in all cases shows $\lambda = -\gamma_2/kT$ is a function of the solvent to some extent as well as the radical. In general, it is found that liquid crystals of nearly the same geometry but with different chemical groups in the center orient PD-Tempone to the same amount. For instance, phase V, phase IV, and MBBA have similar alkyl end groups and OH-MBBA and BOCP are laterally substituted liquid crystals with an atom or group on a benzene

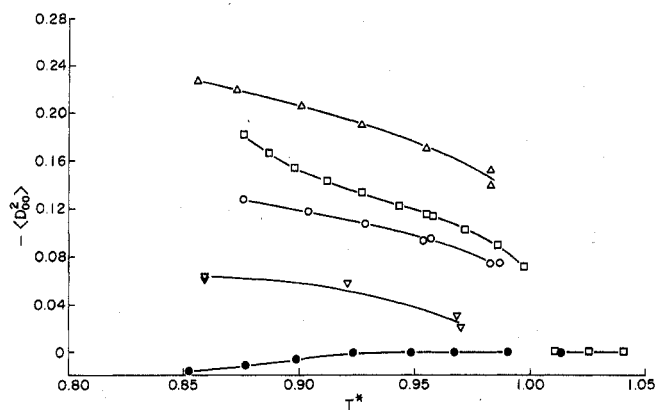


Figure 4. Ordering parameter $\langle D_{00}^2 \rangle_z$ vs. reduced temperature $T^* = T/T_K$ for several nitroxide radicals: (Δ) PNN in BEPC; (\square) BASL in BEPC; (O) Tempone in BEPC; (∇) DTBN in EHAB; (\bullet) MSL in PEPH.

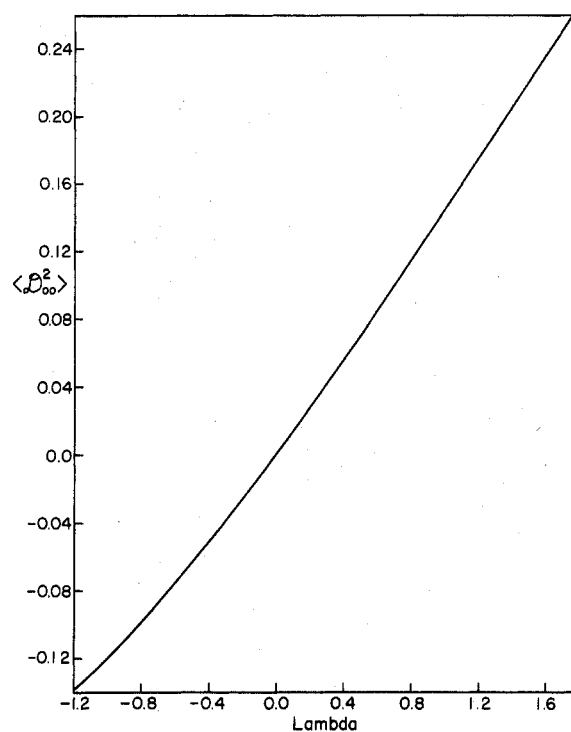


Figure 5. Calibration curve of ordering parameter $\langle D_{00}^2 \rangle_z$ vs. λ for the Maier-Saupe potential.

ring ortho to the center group. The discontinuity in the ordering at the transition point is indicative of a first-order phase transition, whereas the deviation of the observed $\langle D_{00}^2 \rangle_z$ vs. T^* from near linearity for phase V and to a lesser extent phase IV at low T^* is a result of the breakdown of the assumption of motional narrowing upon which eq 2.26 is based.

Further results of $\langle D_{00}^2 \rangle_z$ for different radicals are given in Figure 4. The relationship between λ and $\langle D_{00}^2 \rangle_z$ according to eq 2.13 is given in graphical form in Figure 5 for the range of values of interest. The most ordered system in Figure 3, Tempone in BEPC, is included for comparison. [Also note in Figure 3 that Tempone and PD-Tempone appear to order to a slightly different degree in BEPC. We have not determined whether this is a true effect or whether it reflects differences in sample preparation.⁶⁴ The radical PNN oriented the largest amount, but was found to decom-

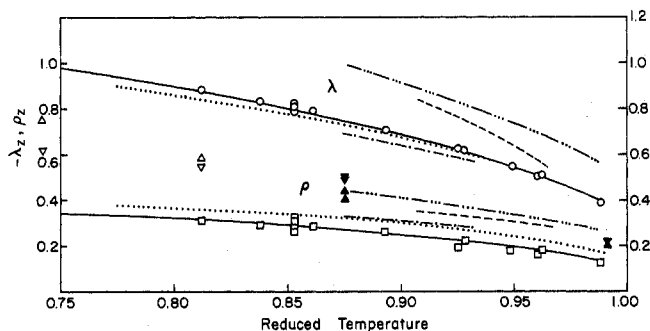


Figure 6. Asymmetric ordering parameters vs. reduced temperature for PD-Tempone in various solvents. The ordering parameters are defined with respect to the z -molecular axis (see text). Solvents are denoted by (—) phase V; (·····) phase IV; (-·-·-) MBBA; (- - - -) BEPC; (-·-·-) Tempone in BEPC; (Δ) for λ_z and (∇) for ρ_z in BOCP; (\blacktriangle) for λ_z and (\blacktriangledown) for ρ_z in OH-MBBA.

pose to another radical after 1 hr or more in the liquid crystals used. The larger bromoacetamide spin label orients to a lesser degree, but it is beginning to show slow motional effects at much more elevated temperatures than PD-Tempone. The curves for DTBN and the maleamide spin label (MSL) are representative of nitroxides which are very weakly ordered and almost not ordered, respectively. However, for MSL this may be due to a tilt of the z axis with respect to the z' axis such that β' is close to the magic angle. [The DTBN reacted to give another spectrum after 1 hr in the isotropic phase of PEPH.]

We now recall that the magnetic tensors of PD-Tempone are not axially symmetric. An examination of a molecular model of PD-Tempone indicates that there is no particular axis in the molecule about which it would prefer to align in a nematic phase. Because of these two reasons, one should be able to determine an ordering tensor for PD-Tempone that need not be axially symmetric. In fact an asymmetric potential (cf. eq 2.12, 2.14) is needed to describe the ordering of PD-Tempone in the mesophase. The second potential parameter is determined utilizing the g values measured for the nematic and isotropic phases. These measured g values were corrected for the static and dynamic nonsecular shifts using eq 2.25. The corrected g and hyperfine values permit the calculation of the two ordering parameters from eq 2.13. It is found that PD-Tempone in phase V orients weakly with the magnetic z axis tending to be perpendicular to the director, the y axis tending to be parallel to the director, and the x axis tending to be oriented nearly at the magic angle. [This implies that if there is a single axis of cylindrical symmetry, it is not one of the magnetic principal axes.]⁴⁹ The values of the two ordering parameters were then used to calculate the potential parameters λ and ρ from eq 2.13. The results are shown in Figure 6 for the z -axis parameters for PD-Tempone and Tempone in several liquid crystals. It can be seen that $|\lambda| > |\rho|$ for all solvents except BOCP and OH-MBBA. However, if one calculates λ and ρ with respect to the y magnetic axis as the primary axis of PD-Tempone from the known values with respect to the z axis, one obtains the result that $\rho_y \approx 0$ for these two solvents. Thus for BOCP and OH-MBBA, the orientation can be described by a Maier-Saupe potential with respect to the y axis. Therefore (by a proper choice of labeling of the magnetic principal axes) it is the first term, i.e., the Maier-Saupe potential, which predominates in the potential expansion for all systems studied. This encourages us in the belief that the two-parameter potential of eq

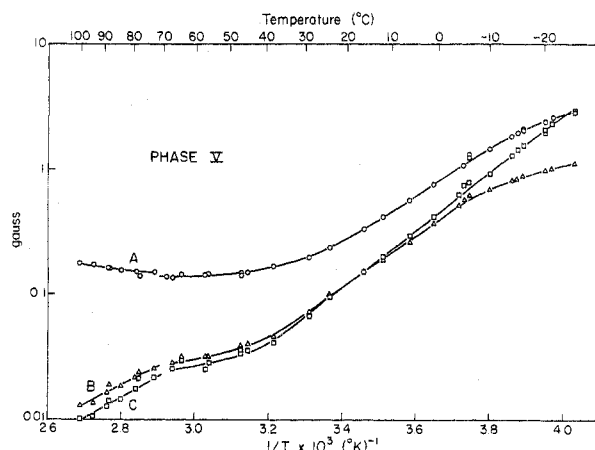


Figure 7. A, B, and C vs. $1/T$ for PD-Tempone in phase V.

2.14 is adequate for dealing with the molecular dynamics. For phase IV and phase V the λ and ρ curves were extrapolated for those values of T^* corresponding to the slow motional region. These values of λ and ρ were used for simulating slow motional spectra.

C. Line Width Analysis. The ESR spectra of PD-Tempone in the nematic phase of a liquid crystal are now analyzed in the motional narrowing region. Because all observed spectra consisted of three lines, one might think that the motional narrowing limit will apply for all temperatures. However, the lines become asymmetric at lower temperatures and the two hyperfine splittings become considerably different. It is in this region that one must use the slow-tumbling theory to simulate the observed spectra. The slow motional spectra of the weakly ordered PD-Tempone are expected to be sensitive to model dependence, anisotropic viscosity, asymmetric molecular reorientation, and the type of liquid crystalline potential used as is readily seen from the examples in PBF. A thorough analysis of the motional narrowing region should help to show which of the above-mentioned processes are important. It is expected that in the absence of any second-order phase transition, the same sort of diffusion process will occur at all temperatures, and one should be able to extrapolate the results of the motional narrowing region into the slow motional region.

The first case to be discussed will be that of PD-Tempone in phase V, a system which exhibits slow motional effects, but, nevertheless, has a long mesomorphic range over which one can observe motional narrowing behavior. The other systems will be analyzed in terms of their similarities or differences to this system. All line widths were measured by the method of relative amplitudes (cf. I and II) and corrected for deuterium inhomogeneous broadening using the ordering parameters given in Figure 3 to calculate the deuterium hfs (cf. section III). All line width data can be expressed as coefficients A, B, and C of eq 2.30b.

(1) **Isotropic Phase.** The line width results for PD-Tempone in the isotropic phase of phase V are shown in Figure 7. Our analysis of the line widths in the isotropic region is identical with that given in I and II. For PD-Tempone in the isotropic phase of phase V, one is in the region $\omega_0^2 \tau_R^2 \sim 1$ where nonsecular terms are expected to be important. If nonsecular terms are included in the calculation of τ_R , one gets the result that τ_R determined from B does not equal τ_R from C for isotropic rotation. In fact τ_R^C / τ_R^B varies from 1.3 near T_K to 1.5 at 99° . If nonsecular terms are neglected,

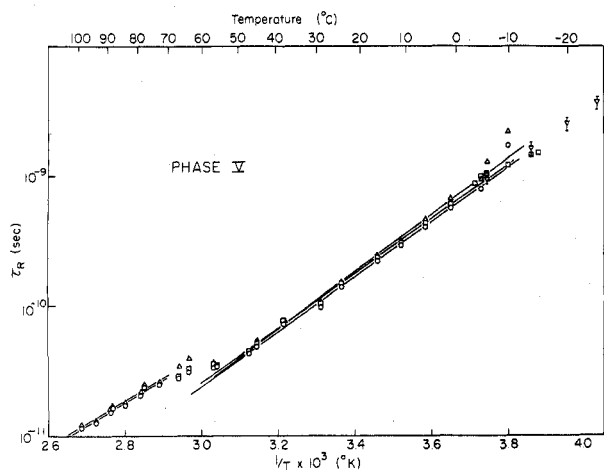


Figure 8. τ_R vs. $1/T$ for PD-Tempone in phase V. The points given by O represent the best fit obtainable for an axial potential allowing for anisotropic viscosity. The results for asymmetric potential with (Δ) anisotropic rotation and with (\square) anisotropic viscosity. For anisotropic viscosity, $\tau_R = \tau_{\hat{A}_{\perp}} = (6\hat{A}_{\perp})^{-1}$, while for anisotropic rotation, $\tau_R = (6\sqrt{R_{\parallel}R_{\perp}})^{-1}$. The best results for an $\epsilon' \neq 1$ are also the same as \square except for the lower temperatures where they are given by ∇ .

the ratio varies from 0.9 to 0.8. The same sort of behavior was found in I and II in the region where $\omega_0^2\tau_R^2 \sim 1$ and was fit in an ad-hoc manner by changing the spectral density function for the nonsecular terms only. That is, the quantity $E_n(E_n^2 + \omega_0^2)^{-1}$ in eq 2.28 is changed to $E_n/(E_n^2 + \epsilon\omega_0^2) = \tau_R/(1 + \epsilon^2\tau_R^2\omega_0^2)$ where ϵ is an adjustable parameter. Calculated rotational correlation times are shown in Figure 8. The standard deviations for the calculated τ_R are $\leq 3\%$ whereas the average value of ϵ is found to be 4.6 ± 1.7 . The parameter ϵ is believed to be indicative of deviations from the assumption of simple Brownian rotational diffusion due to relatively slowly fluctuating torques that induce the reorientation (cf. section VII). This value of ϵ is comparable to the values found in II for the same radical in several isotropic solvents. Another effect which can cause τ_R^B to be unequal to τ_R^C is anisotropic rotational diffusion. In fact, one may analyze for this in the usual way (I, II) to obtain an $N_y = 3.2 \pm 0.5$, which would imply rotation about the y axis (in the magnetic tensor principal axis system). This alternate explanation conflicts with the observations in II that the motion is virtually isotropic in a variety of isotropic solvents. Thus by comparison with the results in I and II, we favor an $\epsilon = 4.6$ and isotropic motion for PD-Tempone in phase V. [One cannot distinguish between the contributions from the two sources from our present data in the isotropic phase, as there are always contributions from nonsecular terms in the range of τ_R 's available. It was possible, however, to make such a distinction in I and II.]

The isotropic-phase results for the other liquid crystals are similar to those for phase V. Results are plotted in Figures 9–12. Again the τ_R 's are all in the range where nonsecular terms will contribute to the line widths. For the case of Tempone in BEPC the data could only be fit by assuming anisotropic rotation about the y axis and one obtains $N_y = 2.3 \pm 0.6$ for $\epsilon = 4.6$. For the other samples N_y is equal to one within the experimental error for $\epsilon = 4.6$. [It is, of course, possible that the magnetic parameters have been sufficiently altered in BEPC to cause an apparent $N_y \neq 1$, cf. II, but it is not likely since a and a_z are essentially the same for BEPC as for the other solutes, cf. Table I.] In the

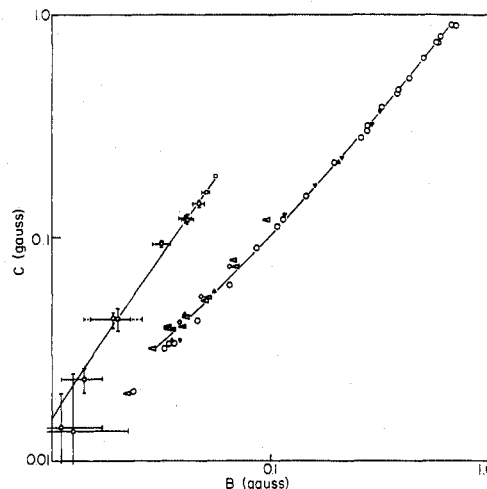


Figure 9. C vs. B for PD-Tempone in several liquid crystals: (O) phase IV; (∇) MBBA; (Δ) OH-MBBA; (\square) BOCB; (\diamond) BEPC; (Δ) Tempone in BEPC.

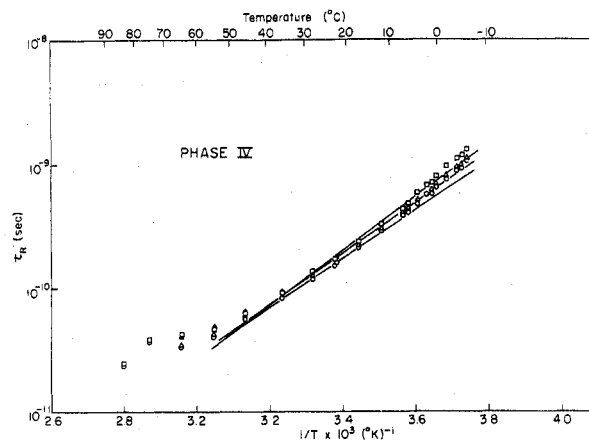


Figure 10. τ_R vs. $1/T$ for PD-Tempone in phase IV. The points given by O, Δ , and \square are as given in Figure 8.

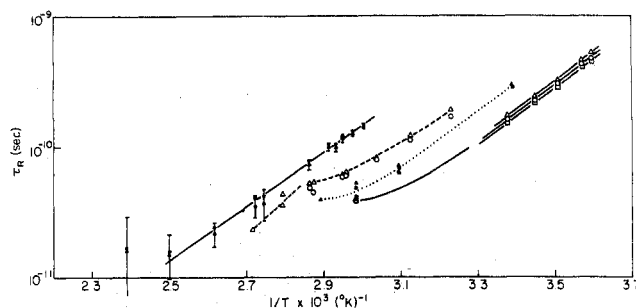


Figure 11. τ_R vs. $1/T$ for PD-Tempone in various nematic solvents. The points O, Δ , and \square are for MBBA solvent, but are otherwise defined as in Figure 8. The points \bullet , \blacktriangle , and \blacksquare are equivalently defined, but for OH-MBBA solvent. The dashed line connects the points for BEPC solvent (Δ for $\epsilon = 1$ and ∇ for $\epsilon = 4.6$).

analysis of motional narrowing spectra in the nematic phase, it will be shown that a smaller value of ϵ approximately equal to 2.2 is needed to satisfactorily explain the line width data in the region where nonsecular terms are expected to contribute to the line widths.

(2) *Nematic Phase.* The line width behavior in the

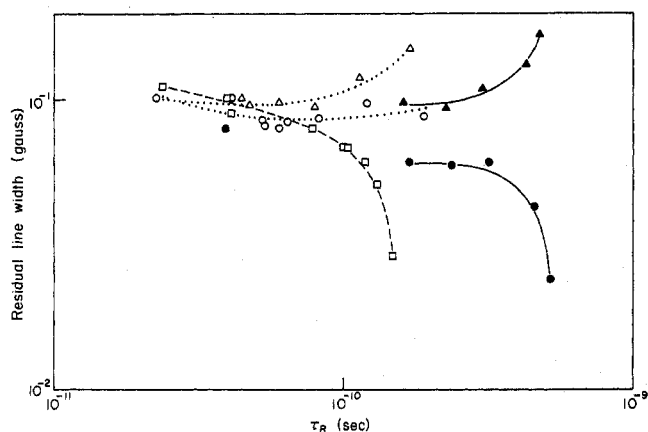


Figure 12. Residual line width A' vs. τ_R for PD-Tempone in a variety of solvents: (—) MBBA, (---) BOCP, and (····) Tempone in BEPC. The ● are MBBA, anisotropic rotation; ▲ are MBBA, anisotropic viscosity; □ are BOCP anisotropic rotation; ○ are BOCP with ϵ' correction; and Δ are Tempone in BEPC.

nematic phase will now be considered. Again we first analyze results for phase V.

The measured A , B , and C for PD-Tempone in the nematic phase of phase V are shown in Figure 8. These results were first analyzed in terms of Brownian rotational diffusion in the presence of an orienting potential. It was first assumed that, except for the orienting potential, the description of the motion should be very similar to that for the isotropic liquid, since the values of τ_R do not change very markedly at the phase transition (cf. Figure 8) nor is the ordering very substantial (cf. Figure 6). Thus we used an $\epsilon \sim 4.6$. When the best single parameter Maier-Saupe potential was used, it was impossible to fit the results, except with a $\tau_R^B \neq \tau_R^C$. However, with the two-parameter potential, one has τ_R^B and τ_R^C more nearly equal. The final adjustment (to the results for $\tau_R \leq 10^{-10}$ sec for $\tau > 23^\circ\text{C}$) was made by fitting ϵ assuming isotropic rotation under the two-term potential. This yielded $\epsilon = 2.9 \pm 2.4$ (or $\epsilon \sim 2.2 \pm 1.4$ neglecting one result). [Alternatively we could have introduced an anisotropic viscosity factor $\tilde{N} = \hat{R}_\parallel/\hat{R}_\perp = 2.8 \pm 1.3$ to "explain" the C/B ratio with $\epsilon \sim 1$, but with \tilde{N} decreasing as the motion slows to $\tau_{R\perp} \sim 10^{-10}$ sec.] Here we let $\tau_R = \tau_{R\perp} = (6\hat{R}_\perp)^{-1}$ and $\tau_{R\parallel} = (6\hat{R}_\parallel)^{-1}$. However, for $T < 20^\circ\text{C}$ (or $\tau_R > 2 \times 10^{-10}$ sec) the C/B ratio is increasing suggesting $\tau_R^C > \tau_R^B$. It is possible to "explain" the increase in C/B as due to anisotropic viscosity (which only affects the C term, since (1) only it has pseudosecular contributions and (2) nonsecular terms are already negligible, cf. eq 5 of I). Such an analysis yields the strange result that for $T < 20^\circ\text{C}$, $\tau_{R\perp}$ continues to increase normally (cf. Figure 8) but $\tau_{R\parallel}$ would have to remain virtually constant (i.e., \tilde{N} would now be increasing rapidly). An alternative explanation, based on the fact that a similar but weaker effect was observed for PD-Tempone in isotropic glycerol- H_2O solvent (II), is that one must modify the pseudosecular spectral densities to

$$j(\omega_a) = \frac{\tau_R}{1 + \epsilon' \omega_a^2 \tau_R^2}$$

by analogy with the nonsecular corrections; but, in general $\epsilon' > \epsilon$. It was found that $\epsilon' \sim 5$ in glycerol. Our results for PD-Tempone in phase V yield $\epsilon' \sim 20$, provided only the pseudosecular spectral densities are corrected in this fashion and this will be discussed in section VII. [Note that this

TABLE III: Activation Energies and Preexponential Factors for Rotational Relaxation of PD-Tempone Dissolved in Several Liquid Crystal Solvents

Solvent	E_a , kcal/mol	A , sec
Phase V	9.6 ± 0.3	$(1.3 \pm 0.6) \times 10^{-17}$
Phase V (solvent) ^a	8.7	
Phase V (isotropic phase)	8.0 ± 0.6	$(2.2 \pm 1.2) \times 10^{-18}$
Phase IV	8.9 ± 0.2	$(4.4 \pm 1.3) \times 10^{-17}$
Phase IV (solvent) ^a	10.1	
BOCP	9.4 ± 0.3	$(1.5 \pm 0.8) \times 10^{-16}$
MBBA	10.2 ± 0.2	$(7.0 \pm 1.6) \times 10^{-18}$
MBBA (solvent) ^a	11.3, 11.9, 10.5	

^a The result for the twist viscosity coefficient from ref 54.

analysis gives values for τ_R that are very nearly the same as the $\tau_{R\perp}$ obtained from an analysis of anisotropic viscosity.] An alternative explanation in terms of the onset of anisotropic molecular reorientation about the molecular y axis, with N_y increasing from 1 to greater than 2, could also "explain" our observation, but, again, we are loathe to accept such a mechanism which "suddenly appears" as a function of τ_R when there are no phase transitions (cf. I and II). Furthermore, such a prediction ultimately leads to a prediction that the residual line widths A' would tend to become negative at the lower temperatures for this mechanism. Our results for isotropic liquids indicate that A' should be increasing linearly with τ_R for $\tau_R > 10^{-10}$ sec (cf. I and II). These matters are further discussed in section VI, since the anomaly becomes more dramatic as the slow tumbling region is reached.

The activation energy and preexponential factor from the best linear fit (i.e., with the ϵ' correction) of $\log \tau_R$ vs. $1/T$ in Figure 8 are given in Table III. The somewhat different results for the isotropic phase are also given in Table III.

The line width results for B and C for Tempone and PD-Tempone in the other liquid crystalline solvents are shown in Figure 9. One can see that the C/B ratio for PD-Tempone in BOCP is quite different than for the other solvents, and it is slightly changed for BEPC. As noted from the results for the isotropic region, PD-Tempone in BEPC appears to rotate 2.3 ± 0.6 times as rapidly about the molecular y axis than the other two axes (provided the correct magnetic parameters are being used) thus one would expect to see differences in the nematic phase. [No line width data were taken for BOCP in the isotropic phase because PD-Tempone either decayed or distilled out of solvent at the high temperatures $> 180^\circ\text{C}$ at which BOCP is isotropic. Note the large errors for B and C in Figure 9 which occur at temperatures $> 100^\circ\text{C}$.]

The results for PD-Tempone in phase IV are very similar to those in phase V, and were analyzed in the same manner. One has in Figure 10 graphs of $\log \tau_R$ vs. $1/T$ for the different assumptions of model. One finds isotropic motion within experimental error and $\epsilon' \approx 20$ –25. The activation energy and preexponential factors are given in Table III. They are close to the results for phase V.

As noted, C/B for PD-Tempone in BOCP differs considerably from C/B in all other nematics (cf. Figure 9). The other line width results for this system are given in Figures 11 and 12. We have already noted that the ordering data for PD-Tempone in BOCP could be fit to a Maier-Saupe

potential with the magnetic tensor y axis as the principal axis for orientation. We have used this potential in the line width analysis. All attempts to calculate correlation times using a modified pseudosecular term or an anisotropic viscosity failed. C/B ratios as large as those observed experimentally could not be predicted.⁵⁰ The magnetic parameters used were those given in Table II for PD-Tempone in phase V, but note that a and a_z are equal to within the experimental error for phase V and BOCP. Thus anisotropic rotation (about the molecular y axis) was introduced to analyze the experimental data. The mean value of N_y was 9.4 ± 1.5 . This result is somewhat surprising considering the molecular structure of PD-Tempone. There can be no hydrogen bonding in this system. Other nonbonded interactions between the oxygens in either the nitroxyl groups or carbonyl group in PD-Tempone and the atoms (even the Cl's) in BOCP seem unlikely. However, BOCP is known to form a smectic C state below the nematic phase. Unfortunately, spectra in this smectic phase were indicative of randomization of the director and could not be used to obtain additional information about this system. The observed anisotropic rotation might possibly be due to pretransitional effects; that is, the layered structure characteristic of the smectic mesophase is beginning to form in the nematic phase. One observes the transition to the smectic phase when this layering phenomenon overwhelms the magnetic free energy, and the layers are oriented randomly with respect to the field. In a very strong magnetic field, one might have an ordered smectic, but that was not achieved in the present case. If one is observing pretransitional effects with the PD-Tempone located in the layers, it should be freer to reorient about the direction in which it aligns, e.g., the y axis, with diffusion about the other axes more strongly hindered. Note that $\tau_{R\perp} \sim 5.0 \times 10^{-10}$ at 58°C , whereas it is $\sim 4 \times 10^{-11}$ for isotropic rotation in phase V and phase IV at that temperature, which is approximately the value of $\tau_{R\parallel} \sim 4.3 \times 10^{-11}$ observed in BOCP.

Another possibility is that the molecule is rotating slowly enough about the y axis that one must simulate the spectra using the slow-tumbling formalism, but this was ruled out by performing the appropriate simulations. They showed that only slight differences $\sim 3\%$ could be caused between the calculated values of B and C and the experimental values. However these differences can be accounted for by the fact that $\tau_{R\parallel}$ is rapid enough to include some nonsecular contributions to the line widths, and our slow motional program neglects these contributions.

The calculated A' , however, was found to decrease with increasing correlation time, which, as already noted, is not the expected behavior. It was believed that a fully sound analysis of the results should involve fitting an $\epsilon' \neq 1$. Rather than add another adjustable parameter to the analysis of the available data, we have set $\epsilon' \approx 15$, essentially the proper value for phases IV and V. The calculated correlation times are changed by no more than 2%, while $N_y = 9.1 \pm 1.0$ or virtually unchanged. The results are given in Figures 11 and 12. The adjusted A' for $\epsilon' \neq 1$ looks somewhat flatter with τ_R than expected. This may be due to (1) our use of an isotropic spin-rotational formula which may well be inadequate for very anisotropic diffusion in an oriented mesophase and/or (2) the anisotropy in the diffusion has been a little overestimated.

The results on Tempone (and some of PD-Tempone) in BEPC show a slightly larger C/B ratio compared to phases IV and V (cf. Figure 9) as was the case in the isotropic

phases. However, the nematic results fit better to an $N_y = 1.6 \pm 0.2$ vs. 2.3 ± 0.6 for the isotropic phase. We cannot, of course, be certain about such small anisotropies without accurate magnetic parameter measurements in the solvent BEPC. Given, in part, the rather short nematic range for this solvent, no further analysis was made, other than that displayed in Figures 11 and 12.

The liquid-crystal MBBA is one of the most commonly used nematic solvents. Line width results for PD-Tempone in this nematic are given in Figure 9, and are found to be very similar to those in phase IV, cf. Figures 11 and 12 and Table III. The last system studied in the motional narrowing region is PD-Tempone in OH-MBBA. The results in Figure 9 and analysis in Figure 11 indicate it too is rotating isotropically. Not enough data were taken to determine an accurate E_a . In fact this was the only system where the freezing point was not reproducible even for the same sample.

Note that the τ_R vs. $1/T$ behavior shown in Figures 8, 10, and 11 for the different systems differs only slightly if one uses an axially symmetric potential rather than the correct asymmetric potential. However, as we have already noted, the different potentials predict quite different results for the detailed dynamics of asymmetric viscosity about the director. Also, if one has anisotropic rotation about a molecular principal axis, but the molecule is aligned asymmetrically, the axial and asymmetric potentials will give quite different results for the correlation times.

VI. Slow Motional Analysis

In this section the theory developed by PBF for simulating slow tumbling ESR line shapes in an anisotropic solvent is applied to the analysis of ESR spectra in the nematic phase.

One must use a slow motional approach, such as that of the stochastic Liouville method, to explain ESR spectra when the motional narrowing theories break down. For isotropic solvents, this occurs when the lines start to become asymmetric and/or the splitting constants begin to deviate from a constant value. In the liquid crystalline phases, however, splitting constant deviations are also due to change of ordering with temperature. Also, one may have asymmetric lines in the motional narrowing region if there is a static distribution of director orientations in liquid crystals. In the previous section the slow motional region was considered to begin when the ordering parameter curve begins to deviate from a smooth curve (nearly linear) when plotted against the reduced temperature T^* as shown in Figures 4 and 6. This begins to occur when the two "observed" splitting constants for the three line nitroxide spectrum became unequal. The two splitting constants should not be exactly equal because of the nonsecular corrections discussed in section II. However the effects observed are much larger than those predicted for nonsecular shifts and also of the wrong sign. In all the nitroxides studied it was noted that a_{01} became less than a_{-10} as the temperature was decreased. This is shown in Table IV for PD-Tempone. [For PD-Tempone, a_{-10} remains nearly constant whereas for the other systems a_{-10} decreases as the temperature decreases. Some g -value measurements performed on PD-Tempone in phase V in this region showed that observed g values began to decrease with decreasing temperature instead of increasing as they had throughout the motional narrowing region.] Thus one should try to fit these effects plus the line width asymmetry (in the absence of di-

TABLE IV: Dynamic Frequency Shifts and Calculated Residual Line Widths for PD-Tempone in Phase V

T, C	τ_R , nsec	Calcd													
		Exptl, G ^{a,b}		A ^c		B ^d		C ^e		D ^f		A', G			
		$\Delta S_{1,0}$	$\Delta S_{0,-1}$	$\Delta S_{1,0}$	$\Delta S_{0,-1}$	$\Delta S_{1,0}$	$\Delta S_{0,-1}$	$\Delta S_{1,0}$	$\Delta S_{0,-1}$	$\Delta S_{1,0}$	$\Delta S_{0,-1}$	A ^c	B ^d	C ^e	D ^f
-6	0.94	-0.03	-0.23	0.00	-0.15	-0.10	-0.33	-0.13	-0.13	-0.03	-0.23	0.60	0.57	0.65	0.5
-14	1.6	+0.07	-0.61	0.09	-0.61	-0.26	-0.66	-0.16	-0.66	-0.16	-0.66	1.0	0.85	-0.15	0.9
-20	2.5	+0.14	-1.35	0.03	-1.27	-0.26	-1.27	-0.07	-1.42	-0.22	-1.47	1.45	1.35	-0.35	1.7
-25	3.6	+0.17	-2.58	-0.21	-2.01	-0.41	-1.51	-0.61	-2.21	-0.51	-2.71	1.75	1.75	-0.4	2.25

^a $\Delta S_{1,0}$ is the difference in shift between the low-field and center lines. $\Delta S_{0,-1}$ is the difference between the center and high-field lines. A positive (negative) ΔS means an apparent increase (decrease) in splitting compared to $\langle a_N \rangle$, which is extrapolated from the higher temperature (a_N), see text. ^b A typical higher temperature result is at +1°C: $\Delta S_{1,0} = -0.01$, $\Delta S_{0,-1} = +0.01$. ^c Calculated with ϵ' (sec) = 1.2, ϵ' (psec) = 19. ^d Calculated with ϵ' (sec) = 4.6, ϵ' (psec) = 15.0. ^e Calculated with ϵ' (sec) = ϵ' (psec) = 1.0. ^f Calculated with anisotropic viscosity model.

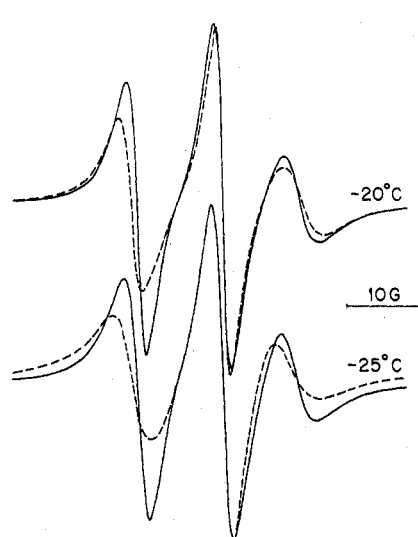


Figure 13. Comparison of experimental and simulated spectra in the incipient slow-tumbling region for PD-Tempone in phase V: (----) experimental result; (—) theoretical result based on isotropic Brownian diffusion with $\tau_R = 2.5 \times 10^{-9}$ sec at -20°C , and $\tau_R = 3.6 \times 10^{-9}$ sec at -25°C ($A' = 0$ G).

rector effects) in the simulation of slow motional spectra in the nematic phase.

The system chosen for a careful slow motional analysis was PD-Tempone in phase V, because it had the largest region of deviation of the splitting constants from near equality, and a thorough study of the motional narrowing region over a long temperature range had been obtained as discussed in the previous section. There, it was shown that PD-Tempone rotates isotropically, but anomalous line width behavior sets in for $\tau_R \geq 2 \times 10^{-10}$ sec. Slow motional type simulations were performed for the spectra taken at 1°C (where $\tau_R = 6 \times 10^{-10}$ sec). The results of this analysis were identical with those from the motional narrowing analysis demonstrating that the anomalous line width behavior is not simply due to the onset of slow tumbling. One finds, from Table IV, that slow-tumbling effects begin to become important for $\tau_R \geq 0.8 \times 10^{-9}$ sec.

We show experimental slow tumbling spectra in Figure 13. The simulated spectra shown in that figure were from the PBF theory using values of λ and ρ extrapolated from Figure 6 to the appropriate temperature with τ_R similarly obtained from Figure 8 for isotropic rotational diffusion. The agreement in Figure 13 is rather poor. This agreement

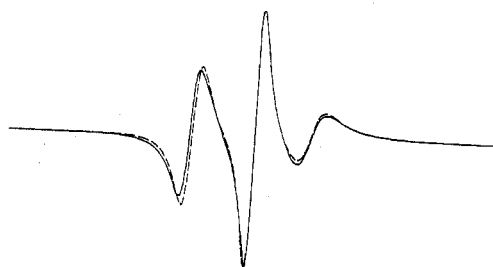


Figure 14. Comparison of experimental (----) and theoretical spectra (—) for PD-Tempone in phase V at -20°C for anisotropic viscosity with $\tau_{R\parallel} = 0.05$ nsec is assumed and $\tau_{R\perp} = 2.5$ nsec ($A' = 1.8$ G).

can be improved by introducing an anisotropic viscosity (cf. section V), but the best fits here suggest that $\tau_{R\parallel}$ must be decreasing with decreasing temperature! (In particular at -20°C one gets $\tau_{R\perp}/\tau_{R\parallel} \approx 50$, cf. Figure 14, while at -25°C one would need a negative $\tau_{R\parallel}$.) Such a result appears to be further demonstration of the invalidity of explaining the anomalies in terms of simple anisotropic viscosity. An anisotropic diffusion mechanism is even less successful in "explaining" the anomaly (it requires negative residual widths, N_y , increasing with decreasing temperature, e.g., $N_y = 3.5$ at -20°C and the agreement is not satisfactory). In both cases, furthermore, one is postulating the sudden onset of anisotropy at a stage when the spectrum is undergoing drastic changes (incipient slow motion) although the liquid crystal exhibits no phase transitions. Again this is taken as clear evidence for the invalidity of such an analysis. In I and II, it was shown that slow-tumbling spectra are particularly sensitive to the reorientational model, i.e., whether the molecule reorients by small (Brownian) or large angle jumps. We show in Figure 15 model-dependent spectra simulated as described by PBF. It is clear that model dependence has only a small effect compared to the anomalous behavior.⁵¹

It was then decided to introduce the fluctuating torque model discussed in II and in the next section, wherein an $\epsilon' > 1$ is introduced to account for moderately slowly fluctuating torques. Various attempts are shown in Figures 16–18. It is clear that the spectra cannot be fit with a single ϵ' , the best fits being obtained for $\epsilon'_{\text{sec}} \sim 1-2$ and $\epsilon'_{\text{psec}} \sim 15-20$ (cf. Figure 18). The main virtue of this analysis is that one is able to use a single set of parameters for all temperatures to achieve reasonable fits. Summaries of the effects of this analysis on the predictions of C vs. B and A vs. τ_R are given in Figures 19 and 20.

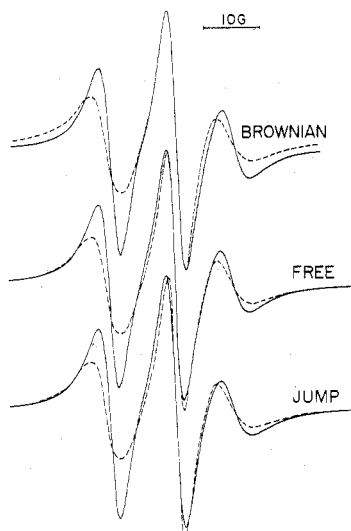


Figure 15. Model dependence and a comparison of experimental (----) and theoretical spectra (—) for PD-Tempone in phase V at -25°C and isotropic rotation with $\tau_R = 3.6 \times 10^{-9}$ sec ($A' = 0$ G). Free diffusion, an approximate inertial model, gives results equivalent to moderate jump diffusion; while the result labeled jump is for strong jump diffusion, cf. ref 2 and 4.

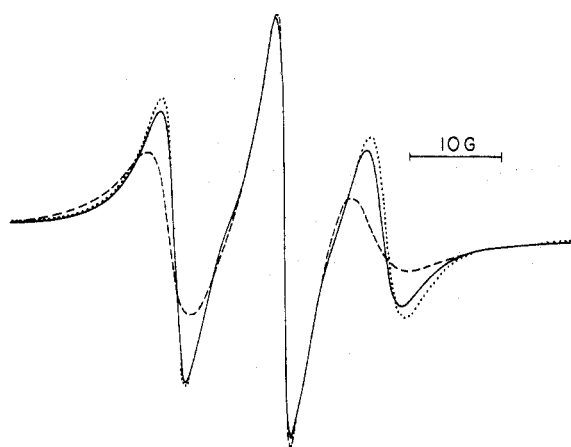


Figure 16. Effects of ϵ' and a comparison of experimental (----) and theoretical spectra (—) for PD-Tempone in phase V at -25°C using a single ϵ' where (—) is for $\epsilon' = 4.6$ ($A' = 1.05$ G) and (· · · ·) is for $\epsilon' = 9.4$ ($A' = 1.6$ G). In both cases $\tau_R = 3.8$ nsec.

The implications of these fits are discussed in the next two sections.

VII. Fluctuating Torque Analysis

In II, a detailed discussion was given of a simple dynamic molecular model involving relatively slowly fluctuating torques, and inertial effects only in very lowest order, which appeared to offer a unified explanation to the relaxation anomalies such as the ϵ , $\epsilon' \neq 1$. The existence of $\epsilon' \sim 15\text{--}20 \gg 1$ in this work again requires that one take cognizance of effects from a careful analysis of molecular dynamics in liquids. In the present case, one has the feature of a highly structured liquid in which the nitroxide probe is dissolved. One may give a general statistical mechanical analysis for the rotational motion of the nitroxide probe (labeled B particle), and obtain a generalized Fokker-Planck equation:¹⁶

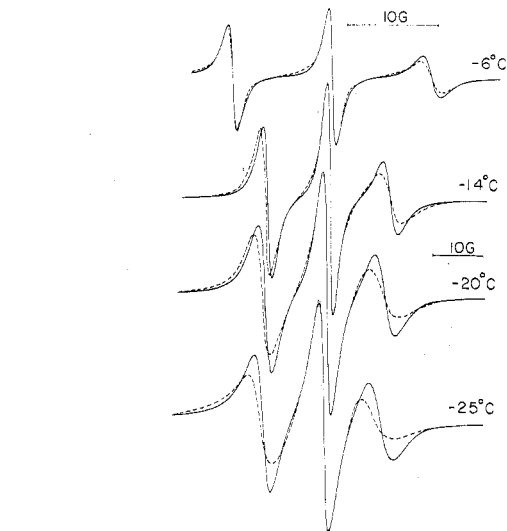


Figure 17. Comparison of experimental (----) and theoretical (—) spectra for PD-Tempone in phase V utilizing $\epsilon'_{\text{sec}} = 4.6$, $\epsilon'_{\text{psec}} = 15$. The values at -6 , -14 , -20 , -25°C are for τ_R 0.9, 1.6, 2.5, 3.6 nsec, respectively, and for A' 0.5, 0.85, 1.25, 1.75 G, respectively.

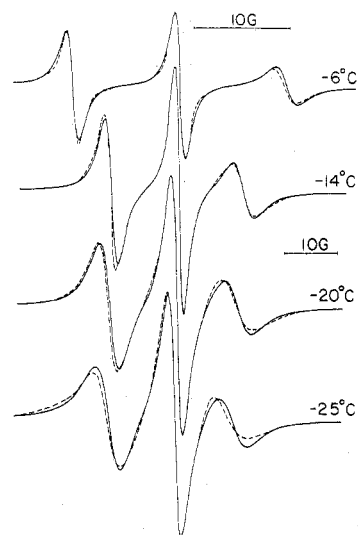


Figure 18. Comparison of experimental (----) and theoretical (—) spectra for PD-Tempone in phase V utilizing $\epsilon'_{\text{sec}} = 1.2$, $\epsilon'_{\text{psec}} = 20$. The values at -6 , -14 , -20 , -25°C are for τ_R 0.9, 1.6, 2.5, 3.6 nsec, respectively, and for A' 0.55, 1.0, 1.45, 1.75 G, respectively.

$$\left[\frac{\partial}{\partial t} + i\omega_B \cdot \mathbf{J}_B + \hat{\mathbf{L}}_B \cdot (\nabla_L)_B + \langle \mathbf{N}_B \rangle \cdot (\nabla_L)_B \right] f_B(t) = (\nabla_L)_B \cdot \int_0^t d\tau \mathbf{G}(t - \tau) \cdot [\omega_B/kT + (\nabla_L)_B] f_B(\tau) \quad (7.1)$$

In eq 7.1, ω_B is the angular velocity of the B particle, \mathbf{L}_B its angular momentum, $\mathbf{J}_B = -i\mathbf{r}_B \times (\nabla_r)_B = -\mathbf{M}$ (cf. eq 2.3–2.4), $\hat{\mathbf{L}}_B \cdot (\nabla_L)_B$ is the precessional term, and $\langle \mathbf{N}_B \rangle$ is the mean-field torque, experienced by the B particle and is equivalent to \mathbf{T} of eq 2.6. The quantity $\mathbf{G}(t)$ is the operator equivalent of the correlation function for the fluctuating or random torques on the B particle. When the assumption is made that angular momentum relaxation occurs very rapidly, then it is possible to introduce a coarse graining in time interval such that the angular momentum is at its

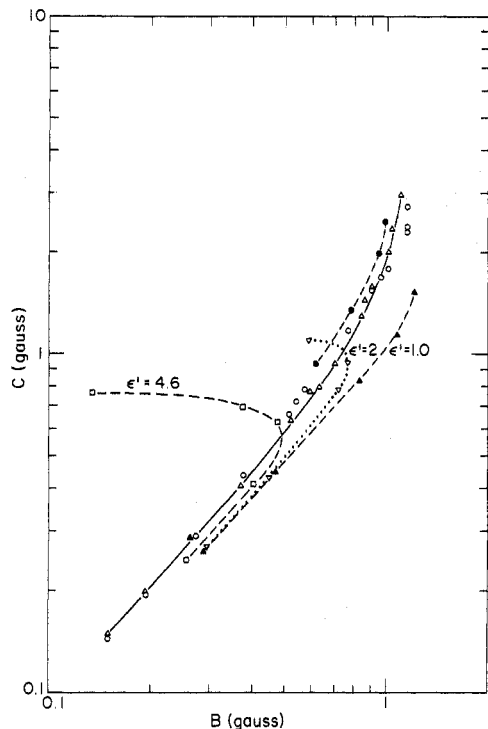


Figure 19. Predictions of C vs. B for PD-Tempone in phase V. The experimental values are given by (O). The predictions for different values of ϵ' are as noted on the figure. The solid curve (and points Δ) correspond to $\epsilon'_{\text{sec}} = 1.2$ and $\epsilon'_{\text{psec}} = 20$.

thermal equilibrium distribution, while the B particle has not appreciably reoriented, nor have the fluctuating components of the torque which are effective in causing the reorientation necessarily relaxed.

In this limit, one may expect to obtain a Smoluchowski-type expression for the reorientational relaxation of the B particle. This limit has been discussed in detail, and one may obtain the result:¹⁶

$$\frac{\partial P(\Omega, t)}{\partial t} = \int_0^t d\tau iJ_B \cdot \mathbf{R}(t - \tau) \cdot \left[iJ_B - \frac{\langle \mathbf{N}_B(t, \Omega) \rangle}{kT} \right] P(\Omega, \tau) \quad (7.2)$$

where the Fourier-Laplace transform of $\mathbf{R}(t)$ is defined by

$$R[s] = (kT)^2 \mathbf{K}^{-1}[s] \quad (7.3)$$

and $\mathbf{K}(t)$ is a simplified, torque correlation function of only Ω_B and t given by the average:

$$\mathbf{K}(t) \equiv \langle R_B(t=0)R_B(t) \rangle \quad \text{where } R_B = \mathbf{N}_B - \langle \mathbf{N}_B \rangle \quad (7.4)$$

over a canonical ensemble of solvent molecules (in the presence of the potential field of the B particle). There is, however, a simplifying assumption in obtaining eq 7.2, viz. that $\mathbf{K}(t)$ should be characterized by a relaxation time τ_M (or spectrum of times) such that $\tau_M \lesssim \tau_R$; i.e., the fluctuating torque components relax in times not long compared to the reorientation time of the B particle. It is then still possible to include any slowly relaxing torques into a redefined time dependent $\langle \mathbf{N}_B(t, \Omega_B) \rangle$ in eq 7.2 such that $\mathbf{R}(t) \rightarrow 0$ in times t over which $\langle \mathbf{N}_B(t, \Omega_B) \rangle$ changes negligibly. [However, $\mathbf{N}_B(t, \Omega_B)$ will then still be a function of those local

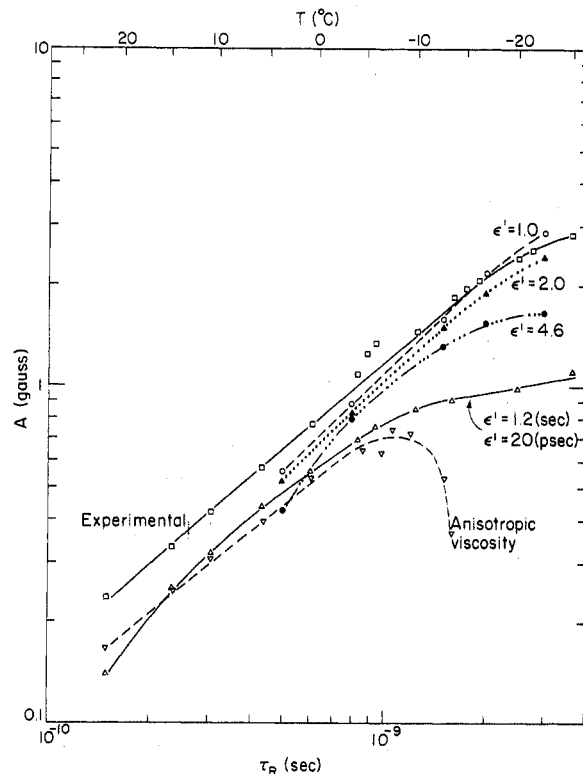


Figure 20. Predictions of A vs. τ_R for PD-Tempone in phase V for different values of ϵ' as noted on the figure. The calculated values are due to \mathbf{g} tensor and dipolar contributions. The experimental values are represented by the points (\square) and the solid line through them.

coordinates and orientations representing the slowly relaxing solvent modes.] Thus the effects of the fluctuating torques are separated into two parts for simplicity: the faster components, which induce the diffusive-type reorientations, and the more persistent components, which represent systematic local torque effects over time scales greater than τ_R , but will average out in times $\tau_X \gg \tau_R, \tau_M$. Fluctuating torque components of order of τ_R will contribute both types of effects, but, because of the greater complexity of their analysis, they are implicitly included in the two limiting types. Our analysis in II for isotropic liquid solvents was based on the model of eq 7.2 where $\langle \mathbf{N}_B(\Omega_B, t) \rangle = 0$. The observation there of $\epsilon, \epsilon' \sim 4$ or 5, corresponds to $\tau_M \sim \tau_R$ and is thus probably at the limit of validity of ascribing the "slowly fluctuating-torques" to $\mathbf{R}_B(t)$. The results in the present work requiring $\epsilon' \sim 15$ –20, as well as the existence of a time-dependent mean-field $\langle \mathbf{N}_B(\Omega_B) \rangle \neq 0$, suggest that this concept of slower fluctuating torque components characterized by a τ_X may well be significant.

Clearly, a complete description of the molecular dynamics is not possible, so we use the above approach to analyze our results. We first discuss the analysis in terms of which the anomalous ϵ' is ascribed to $\mathbf{R}(t)$. Then we discuss a simple limiting model in terms of a τ_X that is suggested by the highly structured properties of liquid crystals. Also, there exists a hydrodynamic model for cooperative fluctuations in the director due to deGennes⁴⁴ and applied to NMR by Pincus.¹⁷ Such long-range hydrodynamic modes are naturally included in an $\langle \mathbf{N}_B(\Omega_B, t) \rangle$ where the time-dependent part of $\langle \mathbf{N}_B \rangle$ is characterized by persistence times $\tau_q \gg \tau_R$. The application of this model to our ESR results is dis-

cussed in the Appendix where it is shown (1) to have negligible predicted effect on our results and (2) to predict spectral anomalies that are qualitatively in the opposite direction to the anomalies observed in the present work.

A. Fluctuating Torques Inducing Reorientation. This is the model used in II, but now applied to a liquid crystalline solvent for which

$$\langle \mathbf{N}_B \rangle \neq 0 \quad (7.5)$$

We assume an exponentially decaying $\mathbf{K}(t) \equiv IkTV^2e^{-t/\tau_M}$ so that the Fourier-Laplace transform of eq 7.2 becomes (for isotropic rotational diffusion):

$$\{s - R(s)[+J_B^2 + iJ_B\langle \mathbf{N}_B \rangle/kT]\}P(\Omega, s) = P(\Omega, t = 0) \quad (7.6)$$

where $s = -i\omega$ and

$$R(\omega) = \frac{kT}{IV^2}(-i\omega + \tau_M^{-1}) \quad (7.7a)$$

so

$$R(0) = kT/IV^2\tau_M \quad (7.7b)$$

One must then diagonalize $\Gamma \equiv J_B^2 - iJ_B\langle \mathbf{N}_B \rangle/kT$ as previously discussed (cf. PBF) in order to obtain the normal modes of relaxation for the particle. It is first advantageous to symmetrize this operator to $\tilde{\Gamma}$ (cf. eq 2.8a). The normal modes for $\tilde{\Gamma}$ will, in general, be linear combinations of the $D_{KM}^L(\Omega) \times [(2L+1)/8\pi^2]^{1/2}$ which we write as $u_{KM}^L(\Omega)$. Since the $u_{KM}^L(\Omega)$ form a complete orthonormal set we may write

$$P(t = 0) = \delta(\Omega - \Omega_0) = \sum_{L', K', M'} u_{K'M'}^{L'}(\Omega_0) u_{K'M'}^{L'}(\Omega) \quad (7.8)$$

with the result for the conditional probability of

$$P(\Omega_0, |\Omega, s) = \sum_{L', K', M'} u_{K'M'}^{L'}(\Omega_0) u_{K'M'}^{L'}(\Omega) [s + E_{K'M'}^{L'} R_1(s)]^{-1} \quad (7.9)$$

where the $E_{K'M'}^{L'}$ are the eigenvalues of $J_B^2 + iJ_B\langle \mathbf{N}_B \rangle/kT$ corresponding to eigenfunctions $u_{K'M'}^L(\Omega)$. These results may be used in the motional narrowing analysis of PBF to give modified spectral density functions, i.e., we now get

$$K_{ab}(s) = \sum_{n \neq 0} \langle u_0(\Omega) | f_a(\Omega) | u_n(\Omega) \rangle \langle u_n(\Omega_0) | f_b(\Omega_0) | u_0(\Omega_0) \rangle / [s + E_{K'M'}^{L'} R_1(s)] \quad (7.10)$$

where $K_{ab}(s)$ is the Fourier Laplace transform of the correlation function of $f_a(t)$ and $f_b(t)$ [cf. section IV of PBF for a more detailed discussion].

One finds that the only change over the motional narrowing theory used in the previous sections is the inclusion of $R(\omega)$ given by eq 7.7. One can also introduce anisotropic diffusion and/or anisotropic viscosity and solve in an analogous manner. In particular, in the latter case, one recovers the old results (cf. eq 2.20) but with

$$\hat{R}_\parallel(\omega) \equiv \hat{R}_\parallel(0)[1 - i\omega\hat{\tau}_{M,\parallel}^{-1}] \quad (7.11a)$$

$$\hat{R}_\perp(\omega) \equiv \hat{R}_\perp(0)[1 - i\omega\hat{\tau}_{M,\perp}^{-1}] \quad (7.11b)$$

i.e., different parallel and perpendicular components of $\hat{R}(0)$ and, in general, different relaxation times for the associated fluctuating torque correlation functions.

The slow tumbling spectra may be analyzed by writing the time-dependent Smoluchowski eq 7.2 in its spin-dependent form,^{4,16} i.e., as a time-dependent SLE. Since this

poses some difficulties in its solution,⁴ we transform to a time-independent augmented SLE in which a specific Markovian model for the fluctuating torques is explicitly included so as to yield results equivalent to the time-dependent SLE, i.e., V and τ_M have the same meaning. The appropriate method is discussed in Appendix D of II, except that here (1) the analysis is based upon the $u_{KM}^L(\Omega)$ rather than the $D_{KM}^L(\Omega)$, (2) $\gamma_L^2 = L(L+1)kT/I$ is then replaced by $E_{KM}^L kT/I$, and (3) $\hat{R}_\parallel(0)\hat{\tau}_{M,\parallel} = kT/IV_\parallel$, $\hat{R}_\perp(0)\hat{\tau}_{M,\perp} = kT/IV_\perp$. This is the approach utilized in analyzing the slow-tumbling (and motional narrowing) spectra in sections VI and V. In particular, for $\hat{R}_\parallel(0) = \hat{R}_\perp(0) = R$ and $V_\parallel = V_\perp = V$ one has $\epsilon'_{L'} = [1 + E_{KM}^L kT/IV^2]^2$ independent of K' and M' . When $V_\parallel \neq V_\perp$ the precise definitions of $\epsilon'_{L'KM'}$ become more complex. However, $\epsilon'_{\text{sec}} \equiv \epsilon'_{2,0,0}$ and $\epsilon'_{\text{psec}} \equiv \epsilon'_{2,0,1}$ are given as the actual corrections needed to adjust the spectral densities: i.e., $j_{L'KM'}(\omega) = \hat{R}_\perp(0)E_{KM}^L / [(\hat{R}_\perp(0)E_{KM}^L)^2 + \epsilon'_{L'KM'}\omega^2]$ (e.g., for zero ordering but still anisotropic viscosity: $\epsilon'_{\text{sec}} = (1 + 6\hat{\tau}_{M,\perp}\hat{R}_\perp(0))^2$ and $\epsilon'_{\text{psec}} = (1 + 5\hat{\tau}_{M,\perp}\hat{R}_\perp(0) + \hat{\tau}_{M,\parallel}\hat{R}_\parallel(0))^2$ and these expressions are useful, though no longer exact, for low ordering).

The values $\epsilon'_{\text{psec}} \sim 15-20$ and $\epsilon'_{\text{sec}} \sim 1-2$ that were found would then have to imply that $V_\parallel^2 < V_\perp^2$ (with $\hat{\tau}_{M,\parallel} > \hat{\tau}_{M,\perp}$ for $\hat{R}_\parallel \sim \hat{R}_\perp$), i.e., the torques inducing reorientation about the axis parallel to the director are rather weak compared to the more normal torques inducing reorientation perpendicular to the director. This would seem to be a reasonable result for a small probe dissolved in a liquid crystal. However, if this were the case, it would be surprising to have $\hat{R}_\parallel(0) \sim \hat{R}_\perp(0)$ as appears to be the case from the experimental analysis. One would require that $V_\parallel^2\tau_{M,\parallel} \sim V_\perp^2\tau_{M,\perp}$. Lastly, we note that $\epsilon'_{\text{psec}} \sim 15-20$ appears to be too large to justify the frequency-dependent diffusion coefficient analysis.

An analogous analysis can, of course, be made in terms of anisotropic diffusion involving $R_\parallel(0)$, $R_\perp(0)$, $\tau_{M,\parallel}$, and $\tau_{M,\perp}$ (cf. ref 16), and this would have the feature of being independent of the macroscopic ordering with respect to the magnetic field, but it would depend on the molecular symmetry.

B. Fluctuations in the Local Structure Parameter. We now consider the case when eq 7.2 may be written as

$$\frac{\partial P(\Omega, t)}{\partial t} = iJ_B \cdot \mathbf{R}(\Omega, t) \cdot [iJ_B - \langle \mathbf{N}_B(t, \Omega) \rangle/kT]P(\Omega, t) \quad (7.12)$$

That is, we neglect any "memory" in \mathbf{R} , and we assume that it is possible to diagonalize \mathbf{R} in either a body-fixed or laboratory-fixed basis such that it is time-independent.^{16,24} However, we let

$$\langle \mathbf{N}_B(t, \Omega) \rangle = \mathbf{T} + \mathbf{T}'(t, \Omega) \quad (7.13)$$

where \mathbf{T} is the true mean field component and \mathbf{T}' is a slowly fluctuating time-dependent component with relaxation time τ_X such that $\tau_X \gg \tau_R$.

This means that $\langle \mathbf{N}_B(t, \Omega) \rangle$ remains essentially constant over time intervals in which the reorientation of the B particle occurs. Thus we may regard \mathbf{T}' as quasistatic, and calculate an ESR line shape due to the combined effects of $\mathbf{T} + \mathbf{T}'$. We shall for the present simple model assume no relation between \mathbf{T} and \mathbf{T}' , so that \mathbf{T}' could also just as well apply to a structured isotropic liquid. Thus $\langle \mathbf{T}' \rangle = 0$ will imply an isotropic distribution of local structure (or order) parameter. This is not an unreasonable model for PD-Tempone which is only weakly ordered in liquid crystals.⁵² [The

other limit, where T' is due to cooperative fluctuations in the static director is discussed in the Appendix as already noted. A related discussion is given for the local director model when T' is a small perturbation on T .]

It is then, in principle, necessary to solve the diffusion equation under the combined torque $T + T'$, but we shall assume both $|T|, |T'| \lesssim kT$ and approximate their effects on the spin relaxation as being additive. Thus, we now consider the case $|T| = 0, |T'| \neq 0$. We may now speak of a "local director" oriented by Euler angles Ψ relative to the laboratory z axis, and a local order or structure parameter

$$S_1 = \langle D_{00}^2(\Omega) \rangle \quad (7.14)$$

for the PD-Tempone relative to this local director (we shall assume axial symmetry of the molecular ordering tensor for simplicity). We first calculate the resonant frequencies and line widths in the motional narrowing region for arbitrary Ψ . Then this result is averaged over an isotropic "reorientation" of Ψ with the rather slow relaxation time τ_X .

The first stage of the calculation is equivalent to that of calculating the resonance frequencies and line widths for a "smectic" liquid crystal in which the director is tilted by Ψ from the laboratory z axis.^{8,9} Therefore we have

$$\overline{\mathcal{H}} = \overline{\mathcal{H}}_0 + \overline{\mathcal{H}}_1(\Psi) \quad (7.15)$$

where $\overline{\mathcal{H}}_1(\Psi)$ is the average over Ω of $\mathcal{H}_1(\Omega, \Psi)$ given by eq 2.1, so

$$\overline{\mathcal{H}}_1(\Psi) = \sum_{\mu, m} S_1 D_{0m}^2(\Psi) F_{\mu, i}^{(2,0)} A_{\mu, i}^{(2, m)} \quad (7.16)$$

Similarly, one may calculate the Ψ -dependent line width $T_2^{-1}(\Psi)$ ^{8,9,12} analogous to eq 2.29–2.31, where, however, the effect of $\Psi \neq 0$ in eq 2.1 is taken into account. In particular, for $\Psi = (0, \theta, \phi)$, and axial symmetry about the director, one obtains the results that eq 2.30–2.31 are again appropriate but with $K = K'$ and the $K(L, K, M, \omega)$ are replaced by $\hat{K}(L, K, M, \omega, \theta)$ given by:

$$\hat{K}(2, K, 0, \omega, \theta) = 1/5 D_k + 2/7 P_2(\cos \theta) E_k + 6/35 P_4(\cos \theta) F_k \quad (7.17a)$$

$$\hat{K}(2, K, 1, \omega, \theta) = 1/5 D_k + 1/7 P_2(\cos \theta) E_k - 4/35 P_4(\cos \theta) F_k \quad (7.17b)$$

$$\hat{K}(2, K, 2, \omega, \theta) = 1/5 D_k - 2/7 P_2(\cos \theta) E_k + 1/35 P_4(\cos \theta) F_k \quad (7.17c)$$

with

$$D_k = K(2, K, 0, \omega) + 2K(2, K, 1, \omega) + 2K(2, K, 2, \omega) \quad (7.18a)$$

$$E_k = K(2, K, 0, \omega) + K(2, K, 1, \omega) - 2K(2, K, 2, \omega) \quad (7.18b)$$

$$F_k = 3K(2, K, 0, \omega) - 4K(2, K, 1, \omega) + K(2, K, 2, \omega) \quad (7.18c)$$

Now these results are averaged over the slower motion that averages out Ψ . Thus $\overline{\mathcal{H}} = \overline{\mathcal{H}}_0$ predicts the isotropic liquid resonance frequencies, while

$$\overline{\hat{K}}(2, K, 0, \omega, \theta) = \overline{\hat{K}}(2, K, 1, \omega, \theta) = \overline{\hat{K}}(2, K, 2, \omega, \theta) = 1/5 D_k \quad (7.19)$$

As long as $S_1 \neq 0$, one finds that $1/5 D_k$ is *unequal* to the isotropic result of eq 2.32. In particular, for $\omega = 0$, one has a simple power series expression for the $K(2, K, M, 0)$ given by

Polnaszek⁸ that is valid for $S_1 < 0.8$. One then finds that

$$D_0(\omega = 0) \simeq [1 + 0.16 S_1 - 2.29 S_1^2 + 0.934 S_1^3] \tau(0)^{-1} \quad (7.20a)$$

and

$$D_2(\omega = 0) [1 + 0.052 S_1 + 0.264 S_1^2 - 0.177 S_1^3] \tau(2)^{-1} \quad (7.20b)$$

Thus the local structure factor $S_1 \neq 0$ tends to lead to differences between the "effective" $\tau(0)^{-1}$ and $\tau(2)^{-1}$. The effect is small for small $S_1 \sim 0.1$ but becomes significant for larger S_1 , where it has the same observable effect as an $R_{\parallel} > R_{\perp}$ for positive S_1 . However, the averaging of the Ψ -dependent parts of $\overline{\mathcal{H}}(\Psi)$ and $T_2^{-1}(\Psi)$ is not very fast. One can then expect residual broadening and frequency shift effects to ensue from this mechanism. In general, this problem can be treated as a slow-tumbling problem by means of the SLE. That is, one may write (cf. eq 2.4 of PBF)

$$\sum_j [\omega \delta_{i,j} + \overline{\mathcal{H}}(\Psi)_{i,j}^x - iT_2^{-1}(\Psi)_{i,j}] Z(\Psi, \omega)_j = (1/2) \omega_1 [S_1^x \rho_0]_i \quad (7.21)$$

where $\text{Im } Z(\Psi, \omega)_j$ refers to the absorption at orientation Ψ for the j th allowed or forbidden transition. Also $\overline{\mathcal{H}}(\Psi)_{i,j}^x$ refers to the matrix element between the i th and j th transitions for the commutator form of $\mathcal{H}(\Psi)$. The diagonal $T_2^{-1}(\Psi)_{i,i}$ correspond to the line widths for the i th transition and are given by eq 2.30–2.31 and 7.17 for the three allowed transitions. The other $T_2^{-1}(\Psi)_{i,i}$ as well as the "off-diagonal" components $T_2^{-1}(\Psi)_{i,j}$ ($i \neq j$) may be obtained by the methods already outlined here, in PBF, and by Freed and Fraenkel.⁵³ One then expands the $Z(\Psi, \omega)_j$ in the complete orthonormal set of spherical harmonics $Y_m^0(\theta, \phi)$ and solves for the coefficient of $Y_0^0(\theta, \phi)$.^{14,15}

We now assume for simplicity that (1) motional narrowing theory applies to averaging Ψ as well as to Ω , (2) the local ordering is small, and (3) the relaxation of $Y_m^2(\theta, \phi)$ is governed by relaxation time τ_X . Then we may obtain an approximate result by retaining only the residual width component from the incomplete averaging of $\overline{\mathcal{H}}_1(\Psi)$ and neglect the higher order width components from Ψ -dependent parts of $T_2(\Psi)_{i,j}^{-1}$ (we are also neglecting for simplicity the mainly dynamic frequency shift terms that arise from cross terms between $\overline{\mathcal{H}}_1(\Psi)$ and $T_2(\Psi)_{i,j}^{-1}$). The final result, which is really for isotropic liquids, but with a dynamical structure, then takes on a simple result. It is, in fact, represented by the basic expression for isotropic liquids given by eq 5 of I except for the simple modifications that

$$j_0(\omega) = \frac{\tau(0)}{1 + \omega^2 \tau(0)^2} \rightarrow \left[D_0(\omega) + \frac{S_1^2 \tau_X}{1 + \omega^2 \tau_X^2} \right] \quad (7.22a)$$

and

$$j_2(\omega) = \frac{\tau(2)}{1 + \omega^2 \tau(2)^2} \rightarrow D_2(\omega) \quad (7.22b)$$

where, when $\omega \tau_R \ll 1$, $D_k(\omega)$ is well represented by $D_k(0)$ given by eq 7.20 (or by eq 4.16 of PBF⁵⁴ and eq 7.18 when the frequency dependence applies). These results are based on a simple exponential relaxation law of the local structure. This is clearly an oversimplification for a liquid crystal where one would expect to have (localized) cooperative modes of rotation yielding more complex frequency dependences (cf. Appendix). The results eq 7.22 still exhibit a more complex ω dependence than the conventional expres-

sions for isotropic liquids. In particular, recognizing that we have $\tau_X \gg \tau_R$, then we may have $\omega^2 \tau_R^2 \ll 1$, while we may have $\omega^2 \tau_X^2 \geq 1$, so that eq 7.22 becomes

$$j_0(\omega) \approx \tau_R(1 + 0.16S_1 - 2.29S_1^2) + S_1^2 \tau_X / [1 + \omega^2 \tau_X^2] \quad (7.23a)$$

and

$$j_2(\omega) \approx \tau_R(1 + 0.052S_1 + 0.264S_1^2) \quad (7.23b)$$

respectively. If we let $S_1 \sim -0.1$ and $\tau_X/\tau_R \sim 10(2)^{1/3}$ then (for $\omega^2 \tau_X^2 \ll 1$) $j_0 \sim 1.12\tau_R$, $j_2 \sim 1.01\tau_R$; however (more generally)

$$j_0(\omega) \approx j_0(0) \left[1 - \frac{S_1^2 \tau_X^3 \omega^2 / \tau_R}{1 + \omega^2 \tau_X^2} \right] \quad (7.24)$$

This may be compared with

$$\frac{\tau_R}{1 + \epsilon' \omega^2 \tau_R^2} \rightarrow \tau_R [1 - \epsilon' \omega^2 \tau_R^2]$$

to yield an

$$\epsilon' \sim \frac{S_1^2 (\tau_X/\tau_R)^3}{1 + \omega^2 \tau_X^2} \sim \frac{20}{1 + \omega^2 \tau_X^2}$$

In the region of $10^{-10} \leq \tau_R \leq 10^{-9}$ when pseudosecular and secular frequencies are important compared to τ_X^{-1} , then eq C2, C3 of II should be used for terms involving $\omega^2 \tau_X^2$. We have performed an analysis analogous to that of Appendix C of II for this local structure mechanism. We have assumed, by analogy to the ordering of the spin probes relative to the main director, that the molecular magnetic z axis orients perpendicular relative to the local ordering. The contributions involving $D_2(\omega)$ of eq 7.22 are then relatively unimportant and we neglect them in the following. One finds that (1) for $\tau_X \lesssim 3 \times 10^{-9}$ sec this mechanism contributes nearly equally to B and C , and the relative contribution to A (i.e., A/B from this mechanism) is comparable to that from the main reorientational process. (2) for $5 \times 10^{-9} \lesssim \tau_X \leq 2.5 \times 10^{-8}$ sec, the contribution to B from this mechanism is decreasing (from $3.2S_1^2$ G to $1.0S_1^2$ G) while that for C first increases before decreasing (i.e., from $4S_1^2$ G to $5S_1^2$ G at 10^{-8} sec to $2.7S_1^2$ G). This has the effect of increasing the overall C/B value in this region. Meanwhile, the contribution to A remains large at $4S_1^2 - 5S_1^2$ G.

These results are clearly in the direction of explaining the observed C/B anomaly as well as the residual A' .

Finally, if we assume that the relaxation of the local structure is somewhat related to the mean field (or director) orientation, we may introduce a $\tau_{X_{\parallel}}$ and a $\tau_{X_{\perp}}$ by analogy to anisotropic viscosity (eq 7.11). One might expect that $\tau_{X_{\perp}}/\tau_{X_{\parallel}} \geq 1$ where $\tau_{X_{\parallel}}$ is the relaxation time of the component parallel to the macroscopic director. One then finds that (3) for $\tau_{X_{\perp}} \lesssim 3 \times 10^{-9}$ sec the effect of $\tau_{X_{\perp}}/\tau_{X_{\parallel}} > 1$ on the contribution to B is negligible, but the contribution to C is enhanced by as much as 50%, while the contribution to A is greatly suppressed; for $5 \times 10^{-9} \lesssim \tau_{X_{\perp}} \leq 2.5 \times 10^{-8}$ sec, the contribution to A increases rapidly, and all other observations for (2) are found except that they are enhanced. (4) Lastly we note that one requires $S_1^2 \sim 0.1$ to get effects of the order observed experimentally (assuming $\tau_{X_{\perp}}/\tau_R \sim 10$). [Note, however that one must introduce a more careful slow tumbling analysis for $|S_1 \mathcal{H}_1|^2 \tau_X^2 \geq 1$, i.e., for $\tau_X \gtrsim 2.5 \times 10^{-9}/S_1$. Note $\tau_R \sim 2.5 \times 10^{-9}$ sec is the related value for slow tumbling in the overall reorientation when the modified analysis of Appendix C of II is used.]

These results are thus quite encouraging in indicating that this dynamic local structure mechanism could explain, at least in part, the observed anomalies. The analysis given here, has, for convenience, been highly approximate, but it should indicate the general spectral features of this mechanism.

VIII. Further Discussion

Here we wish to consider some other aspects of the relaxation studies for comparison with the results in I and II. First we note from Table III that the activation energies for PD-Tempone in the various nematics are all quite similar with preexponential factors of about the same order. For several of our liquid crystals the temperature dependence of the twist viscosity coefficient, γ_1 , which characterizes the viscous torque associated with an angular velocity of the director and has no counterpart in isotropic liquids has been measured.⁵⁴ The activation energies compare favorably to our results (cf. Table III). This appears to demonstrate that the same thermal activation processes are the ones affecting the reorientation of the spin probe. This quantity γ_1 is reasonably associated with \hat{R}_{\perp} . If we make this association, and then employ the Stokes-Einstein relation

$$\tau_R = \frac{4}{3} \frac{\pi r_e^3 \eta}{kT} \quad (8.1)$$

with $\eta \approx \gamma_1$ and r_e the effective rotation radius, then it is possible to obtain r_e from Meiboom and Hewitt's measurements of γ_1 ^{54a} and our experimental τ_R 's for MBBA in the nematic phase. We find $r_e \approx 1.13$ Å (from the range 5–23°C) compared to an estimated hydrodynamic radius r_0 of 3.2 Å (from geometric considerations cf. II), or a value of $\kappa = 0.044$ where $\kappa = (r_e/r_0)^3$. This result for r_e is somewhat smaller than found in isotropic liquids (cf. II), as one would expect for a small solute in a solvent of larger molecules, but it is not very much smaller than the value of 1.46 Å found for glycerol solvent.⁵⁵

One can also estimate the spin-rotational relaxation from the high temperature line width results where $\tau_R \lesssim 10^{-11}$ sec (cf. I and II). Our most useful data for this was from the isotropic phase of phase V. We obtain $(T_2^{\text{SR}})^{-1} = 1.2 \times 10^{-12}/\tau_R$ in gauss (derivative width) compared to the theoretical value of $0.50 \times 10^{-12}/\tau_R$ from simple theoretical considerations (i.e., $\tau_R \tau_J = I/6kT$, cf. II). This experimental result is similar to, but somewhat larger than, the results obtained for isotropic solvents (cf. II where the maximum there was $1 \times 10^{-12}/\tau_R$ in acetone solvent). In terms of a simple jump diffusion model, this result could be interpreted in terms of reorientational jumps of substantial angle (cf. II). However, such information is better obtained from slow tumbling studies as discussed in section VI and in II.

It was shown in II, that a fraction of the low temperature residual width A' is due to intermolecular electron-nuclear spin dipolar interactions, which are modulated by the translational diffusion. There the expression

$$(T_2^{-1})_{\text{dip}} = \gamma_1^2 \gamma_e^2 \hbar I(I+1) \frac{8\pi}{45} \frac{N}{dD} \quad (8.2)$$

was used where N is the density of spins, d is the distance of closest approach of the interacting spins, and $D = \frac{1}{2}(D_0 + D_s)$ the mean diffusion coefficient of the solute (D_0) and solvent (D_s). We estimate $N \approx 4.5 \times 10^{22}$ proton/cm³ using a molecular weight of 274 for phase V and 18.6 protons per molecule (the average of the two compounds) and $\rho = 1.1$ g/cm³ (the value for MBBA at room temperature). Thus

$(T_2^{-1})_{\text{dip}} \approx 3.05 \times 10^{-16}/dD$ in gauss. There are no available data on diffusion coefficients in phase V, and recent results on diffusion coefficients in MBBA show widely divergent results.⁵⁶ If, instead, we use the viscosity $\eta \sim \gamma_1$ for phase V at 23°C^{54b} and then extrapolate this η value using the E_a for rotational diffusion found for PD-Tempone in phase V (cf. Table III), we obtain $\eta \approx 20$ P at -25°C which is the temperature for which a maximum experimental value of $A' = 1.75$ G is achieved. If now, the Stokes-Einstein relation

$$D_i = kT/6\pi\eta r_i \quad (8.3)$$

with r_i the effective translational diffusion radius of the i th molecule is used one gets $(T_2^{-1})_{\text{dip}} \approx 6.8 (r_{\text{red.}}/d)$ G where $r_{\text{red.}} = (r_p r_s)/(r_p + r_s) \approx r_p$ for a small probe molecule. Thus, this very crude analysis could "explain" all of A' with $d \approx 4r_p$. However, one might reasonably expect that the use of $\eta \approx \gamma_1$ overestimates the microviscosity for diffusion of the small solute molecule. (A rough lower limit to η might be $\kappa\gamma_1 \approx 1$ P yielding a much smaller dipolar contribution to A' of ca. 0.34 $(r_{\text{red.}}/d)$ G which is small, but not negligible; this latter value is more consistent with results for toluene solvent cf. II.) The main point really is that the intermolecular dipolar mechanism is expected to make a nontrivial contribution to A' for the lower temperature nematics.⁵⁷

IX. Summary and Conclusions

In this work we have demonstrated how the PBF theory for ESR line shapes in both the slow tumbling and motional narrowing regions may be effectively employed in an analysis of experiments on nitroxides dissolved in liquid crystal solvents. The well-resolved spectra obtained from PD-Tempone were of particular aid for accurate results.

In general, we have found that the ordering of the nitroxide spin probes in the liquid crystal solvents requires a two-term potential function. Appropriate symmetry-dependent potential functions were introduced that very conveniently allow for relabeling of molecular axes. It was then shown how the Brownian diffusion (Smoluchowski) equation may be solved for the more general restoring potentials, and this was incorporated into the PBF theory.

The motional narrowing line width analyses in the isotropic and nematic phases were typically best explained in terms of isotropic rotational diffusion of PD-Tempone for most solvents but under the anisotropic ordering potential. The isotropic diffusion is consistent with recent results for PD-Tempone in normal liquids. The activation energies (E_a) for τ_R in several liquid crystal solvents were quite similar (8.9 to 10.2 kcal/mol) and for the cases it could be compared (MBBA and phase IV), it is rather close to E_a for the measured twist viscosity. This appears to demonstrate a close relation between τ_R and the other viscous processes in the liquid crystals. The isotropic values for E_a appear typically to be a little smaller than the nematic values.

It was also demonstrated in this work that slow-tumbling corrections to the spectra from liquid-crystalline solvents can become important even while they consist of three well-resolved lines. In the present case, these corrections are first manifest in the shifts of the line positions. Failure to include the slow tumbling corrections would then necessarily lead to incorrect results for the ordering parameters, which could incorrectly suggest a "phase transition". It appears to be a general feature of the analysis of ESR spectra involving qualitative spectral changes (such as those which

result from slow tumbling) that inappropriate or inadequate analysis can appear to imply discontinuous behavior characteristic of a "phase transition" even while the actual sample being studied does not have discontinuous behavior over the region studied. In the recent isotropic liquid studies, this principle was invoked to provide information on reorientation by jumps of substantial angle.

The slow motional analysis for PD-Tempone in phase V solvent was based on this principle, i.e., all relevant ordering parameters and τ_R values were extrapolated from the results for the motional narrowing region. However, unlike the studies in isotropic liquids, the predicted spectra in the present case were found to be in poor agreement with experiment. No significant improvement could be achieved by introducing jump diffusion models. Partial success in the slow tumbling fits could be obtained by invoking the rather sudden onset of an anisotropic viscosity mechanism, such that while $\tau_{R\perp}$ is behaving normally, $\tau_{R\parallel}$ even begins to speed up as the temperature is lowered! Furthermore, this violates our principle of invoking a discontinuous change in the absence of phase transitions.

In the recent studies on isotropic solvents it was found necessary to introduce the corrections ϵ and ϵ' for non-Debye-like spectral densities. This was again found to be important for the liquid crystals. Typically $\epsilon \sim 4.6$ (for the nonsecular spectral densities) for the isotropic phases in agreement with the results on isotropic liquids. There appears to be a lowering of this value in the nematic phases, but the analysis is not very certain. It was suggested in previous work that this might be explained in terms of relatively slowly fluctuating torques affecting the rotational diffusion, and a theoretical analysis related this to ϵ and ϵ' in terms of frequency-dependent diffusion coefficients. In this work, we applied this analysis to the ordered solvents in an attempt to explain the slow-tumbling spectral anomaly in terms of $\epsilon' \neq 1$. It was indeed possible to obtain rather good agreement in this way, but only by invoking an anisotropic ϵ' analogous to an anisotropic viscosity such that $\epsilon'_{\text{sec}} \sim 1-2$ and $\epsilon'_{\text{psec}} \sim 15-20$.

This latter large value of ϵ' appears on theoretical grounds to be too large; i.e., if there are important components of the fluctuating torque relaxing considerably slower than τ_R , they should more properly be included into a local structure or ordering term which is relaxing on a longer time scale than τ_R . A simple model for this slowly relaxing local structure was then developed to conveniently predict the effects one might expect on the ESR spectra. The simple model, which neglects any correlated effects between the mean field potential (or director) and the slowly relaxing local structure (and may thus be applied to structured isotropic liquids), is shown first of all to predict, in general, non-Debye-like spectral densities for the rotational reorientation. It is further found that this effect can lead to spectral densities which would appear to imply anisotropic rotational diffusion coefficients, whereas, in effect, the anisotropy is in the local structure. Our analysis of this model shows that it has the potential of explaining, at least in part, the observed slow-tumbling spectral anomalies. The absence of such an anomaly in the higher temperature region where nonsecular terms are important would have to imply important temperature dependence of the local structure, or else a spectral density lacking in high frequency components.

The model of hydrodynamic fluctuations in the director due to deGennes and Pincus is found both qualitatively

and quantitatively to be inconsistent with the observed spectral anomalies. In general, we could find no evidence for this mechanism in our experimental results, but this is consistent with the weak ordering (i.e., $\langle D_{00}^2 \rangle \approx -0.1$) of the PD-Tempone spin probe.

However, our slowly relaxing local structure model would definitely be consistent with (nonhydrodynamic) cooperative reorientational modes of relaxation of the liquid crystal molecules on a time scale faster than director fluctuation, a mechanism which should be associated with a frequency dependence more typical of hydrodynamic modes than with a localized mode.

It is pointed out that a more rigorous (albeit a more complicated) analysis of both the slowly relaxing local structure mechanism and the director fluctuations may be obtained from a solution based upon more general Smoluchowski equations explicitly including the slowly fluctuating torques (as well as the mean-field torques) and introduced into an augmented stochastic Liouville equation, which includes the spin degrees of freedom.

Further experimental and theoretical work on these interesting phenomena is clearly warranted.⁵⁸

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Appendix. Director Relaxation and ESR Line Widths

In this case, the motion which causes modulation of the magnetic tensors can be thought of as arising from two processes: (1) motion of the molecule with respect to the director, and (2) motion of the director axis with respect to the preferred axis of director orientation (fluctuations of the direction of the ordering axis).

The perturbation hamiltonian required to describe the relaxation effects in this case can be written as follows

$$\mathcal{H}_1'(\Omega, \Psi) = \mathcal{H}_1(\Omega, \Psi) - \langle \mathcal{H}_1(\Omega, \Psi) \rangle \quad (\text{A1})$$

with $\mathcal{H}_1(\Omega, \Psi)$ given by eq 2.1.

The orientation-dependent part of the spectral density is required for relaxation and is given by

$$\begin{aligned} \bar{K}_{\text{KMK}'\text{M}'}(\omega) = \sum_{\text{N}, \text{N}'} \int_0^\infty \langle [D_{\text{KN}}^{(2)}(\Omega) D_{\text{NM}}^{(2)}(\Psi) - \\ \langle D_{\text{KN}}^{(2)}(\Omega) D_{\text{NM}}^{(2)}(\Psi) \rangle] [D_{\text{K}'\text{N}'}^{(2)}(\Omega_0) * D_{\text{N}'\text{M}'}^{(2)}(\Psi_0) * - \\ \langle D_{\text{K}'\text{N}'}^{(2)}(\Omega_0) * D_{\text{N}'\text{M}'}^{(2)}(\Psi_0) * \rangle] e^{-i\omega t} dt = \\ \int_0^\infty \bar{C}_{\text{KMK}'\text{M}'}(t) e^{-i\omega t} dt \quad (\text{A2}) \end{aligned}$$

where the $\bar{C}(t)$ is the correlation function. If one assumes that the motion of Ω and of Ψ are independent processes (but see below), then $\bar{C}(t)$ can be written as

$$\begin{aligned} \bar{C}_{\text{KMK}'\text{M}'}(t) = \\ \sum_{\text{N}, \text{N}'} \{ \langle D_{\text{NM}}^{(2)}(\Psi) D_{\text{N}'\text{M}'}^{(2)}(\Psi_0) * \rangle \langle D_{\text{KN}}^{(2)}(\Omega) D_{\text{K}'\text{N}'}^{(2)}(\Omega_0) * \rangle - \\ \langle D_{\text{KN}}^{(2)}(\Omega) \rangle \langle D_{\text{K}'\text{N}'}^{(2)}(\Omega_0) * \rangle \} + \langle D_{\text{KN}}^{(2)}(\Omega) \rangle \langle D_{\text{K}'\text{N}'}^{(2)}(\Omega_0) * \rangle \times \\ [\langle D_{\text{NM}}^{(2)}(\Psi) D_{\text{N}'\text{M}'}^{(2)}(\Psi_0) * \rangle - \langle D_{\text{NM}}^{(2)}(\Psi) \rangle \langle D_{\text{N}'\text{M}'}^{(2)}(\Psi_0) * \rangle] \quad (\text{A3}) \end{aligned}$$

The quantity in square brackets in the first term on the right-hand side of eq A3 is $C_{\text{KNKN}'}(t)$, the correlation function when there is no motion of the director; the evaluation of this quantity is given in section II. The quantity in

brackets in the second term is an analogous expression for the correlation function for motion of the director only. Note that this quantity is multiplied by a product of order parameters for the molecular orientation. In the limit of no director motion $\Psi = \Psi_0 = (0,0,0)$ and $D_{\text{NM}}^{(2)}(\Psi) = \delta_{\text{NM}}$ and the ensemble average over Ψ in the first term becomes $\delta_{\text{NM}} \delta_{\text{N}'\text{M}'}$ and the bracketed quantity in the second term is zero. Thus $\bar{C}_{\text{KMK}'\text{M}'}(t) = C_{\text{KMK}'\text{M}'}(t)$ in this limit. In the limit of $\langle D_{\text{KN}}^{(2)}(\Omega) \rangle = 0$, i.e., no ordering of the molecule by the director, the second term of eq A3 again disappears, but the first term can still be modified by the motion of the director. This latter is a physically unreal result in this limit of no ordering. It arises because the form of eq 2.1 refers the molecular motion relative to a moving (or fluctuating) reference frame, i.e., that of the director. A more rigorous, but more difficult to analyze model, would involve solving for the molecular diffusive motion by means of an equation such as eq 7.2, but with the restoring potential including the director fluctuations.⁶⁵ In such a treatment, the motion of Ω is, in general, dependent upon Ψ . We hereafter neglect any unrealistic effects of director fluctuation on the first term of eq A3 and consider only the effects in the second term of eq A3 which are physically more realistic. This is, in effect, the approach used by several authors,¹⁷⁻²⁰ although they have not discussed these matters.

In order to simplify the evaluation of eq A3, the following assumptions are made. (1) The distribution of director and molecular orientations are axially symmetric with respect to the preferred axis of director orientations. This results in $\text{N} = \text{N}'$, $\text{K} = \text{K}'$, and $\text{M} = \text{M}'$ and the $\langle D_{\text{KN}}^{(2)}(\Omega) \rangle$ are zero unless $\text{K} = \text{N} = 0$.¹⁴ (2) The magnetic tensors have axial symmetry. Thus $\text{K} = 0$ in all terms. (3) The fluctuations in the director are small in amplitude so that the $D_{\text{KN}}^{(2)}(\Psi)$ can be approximated by their forms for small θ given in Appendix B of PBF. Thus the correlation function of eq A3 becomes

$$\begin{aligned} \bar{C}_{0\text{M}}(t) = \sum_{\text{N}} \langle D_{\text{NM}}^{(2)}(\Psi) D_{\text{NM}}^{(2)}(\Psi_0) * \rangle C_{0\text{N}}(t) + \\ \langle D_{00}^{(2)}(\Omega) \rangle^2 [\langle D_{0\text{M}}^{(2)}(\Psi) D_{0\text{M}}^{(2)}(\Psi_0) * \rangle - \langle D_{00}^{(2)}(\Psi) \rangle^2 \delta_{\text{M}0}] \delta_{\text{N}0} \quad (\text{A4}) \end{aligned}$$

Equation A4 will be evaluated by using two different approaches: (1) considering the thermal fluctuations of the director as done by several authors for NMR relaxation,¹⁷⁻²⁰ and (2) considering the motion of the director to be a diffusion process in the presence of a very strong orienting potential. The latter is more appropriate for a localized mode (e.g., the local structure model of section VIIB).

For the thermal fluctuations, one must first expand the $D_{\text{NM}}^{(2)}$ for small θ . Thus eq A4 becomes

$$\begin{aligned} \bar{C}_{0\text{M}}(t) = \sum_{\text{N}} \{ \delta_{\text{NM}} + \frac{\theta \theta_0}{4} (-1)^{\text{N}+\text{M}+1} [\delta_{\text{M}, \text{N}+1} f_+(2, \text{M} - \\ 1) f_-(2, \text{M} - 1) + \delta_{\text{M}, \text{N}-1} f_+(2, \text{M} + 1) f_-(2, \text{M} + \\ 1)] \} e^{i\text{M}(\phi - \phi_0)} C_{0\text{N}}(t) + \langle D_{00}^{(2)}(\Omega) \rangle^2 \langle e^{i\text{M}(\phi - \phi_0)} \theta \theta_0 \rangle^2 \times \\ [\delta_{\text{M}, -1} + \delta_{\text{M}, +1}] \delta_{\text{N}, 0} \quad (\text{A5}) \end{aligned}$$

where the $f_{\pm}(\text{L}, \text{M})$ are defined as in PBF. The quantity

$$\langle \theta \theta_0 e^{i(\phi - \phi_0)} \rangle \approx \langle \delta \hat{n}(\mathbf{r}) \delta \hat{n}(\mathbf{r}_0) * \rangle \quad (\text{A6})$$

where

$$\delta \hat{n}(\mathbf{r}) = \hat{n}(\mathbf{r}) - \hat{n}_0 \quad (\text{A7})$$

is the fluctuating component of the director orientation with the unit vector \hat{n}_0 , the preferred director orienta-

tion.²¹ The quantity $\langle \delta \hat{n}(\mathbf{r}) \delta \hat{n}(\mathbf{r}_0)^* \rangle$ can be evaluated by considering the fluctuation $\delta \hat{n}(\mathbf{r})$ to be a superposition of plane-wave disturbances given by Fourier components:

$$\delta \hat{n}(\mathbf{r}) = V^{-1/2} \delta \hat{n}_q e^{i\mathbf{q} \cdot \mathbf{r}} \quad (\text{A8})$$

where V is the volume. The correlation function for fluctuations of the director becomes²⁰

$$\langle \delta \hat{n}(\mathbf{r}) \delta \hat{n}(\mathbf{r}_0)^* \rangle = \frac{V}{(2\pi)^3} \int_0^{q_c} \frac{kT}{Kq^2 V} \exp\left\{-\frac{Kq^2 t}{\eta}\right\} 4\pi q^2 dq \quad (\text{A9})$$

where $kT/Kq^2 V$ is the thermal amplitude of the modes, Kq^2/η is the damping constant of the slow mode, τ_q^{-1} , and $[V/(2\pi)^3]4\pi q^2$ is the number of states in a volume element $4\pi q^2 dq$, with K the average elastic constant of the liquid crystal. Also, η is the viscosity, and q_c is the wave vector which corresponds to a cutoff in the modes near the molecular length.²⁰ In the true hydrodynamic limit, $q_c \rightarrow \infty$ and the integration in eq A9 is readily performed. For q_c finite, one has

$$\langle \delta \hat{n}(\mathbf{r}) \delta \hat{n}(\mathbf{r}_0)^* \rangle = \frac{kT\eta^{1/2}}{4\pi^{3/2} K^{3/2} t^{1/2}} \Phi[(\omega_c t)^{1/2}] \quad (\text{A10})$$

where $\omega_c = Kq_c^2/\eta$ is the cutoff frequency and $\Phi(\chi)$ is the error or probability function.⁵⁹ Note for $\omega_c \rightarrow \infty$, $\Phi[(\omega_c t)^{1/2}] \rightarrow 1$. Thus the contribution to the correlation function needed for relaxation due to fluctuations of the director is

$$\bar{C}_{01}(t) = \bar{C}_{0-1}(t) = \frac{3kT\eta^{1/2} \langle D_{00}^{(2)}(\Omega) \rangle^2}{8\pi^{3/2} K^{3/2} t^{1/2}} \Phi[(\omega_c t)^{1/2}] \quad (\text{A11})$$

The spectral density then has the form²⁰

$$\bar{K}_{01}(\omega) = \frac{3kT\eta^{1/2} \langle D_{00}^{(2)}(\Omega) \rangle^2}{8\sqrt{2}\pi K^{3/2} \omega^{1/2}} \left\{ 1 - \frac{1}{2\pi} \ln \left| \frac{1 + \sqrt{2\omega/\omega_c} + \omega/\omega_c}{1 - \sqrt{2\omega/\omega_c} + \omega/\omega_c} \right| - \frac{1}{\pi} \arctan(\sqrt{2\omega/\omega_c} + 1) - \frac{1}{\pi} \arctan(\sqrt{2\omega/\omega_c} - 1) \right\} \quad (\text{A12})$$

which is valid for $\omega > 0$. [The discontinuity at $\omega = 0$ would undoubtedly be removed by an analysis recognizing the coupled dependence of Ω upon ψ as discussed above.]

In this case, the ESR line width contribution in gauss due to fluctuations in the director orientation is

$$T_2^{-1} = \frac{|\gamma_e|}{3\sqrt{3}} \left\{ (a_{11} - a_{12})^2 [I(I+1) - m_1^2] \bar{K}_{01}(\omega_{\pm}) + \left[\frac{1}{2}(g_{11} - g_{12})^2 B_0^2 - 2(a_{11} - a_{12})(g_{11} - g_{12}) B_0 m_1 + 2(a_{11} - a_{12})^2 m_1^2 \right] \bar{K}_{01}(\omega_0) \right\} \quad (\text{A13})$$

For typical molecular lengths, i.e., 40 Å for MBBA, one finds $\omega_c \approx 1.9 \times 10^8$. Thus, the nonsecular terms in eq A13 can be neglected as the quantity in brackets $\{ \}$ in eq A12 approaches zero for $\omega_0 \gg \omega_c$. For the pseudosecular terms $\omega_{\pm} \lesssim \omega_c$, and the quantity in brackets is somewhat less than unity (ca. 0.32). Using the values $\eta = \gamma_1$, K_{11} ²¹ and the order parameter for PD-Tempone in MBBA at 23°C, one predicts that the contributions to the A and C line width coefficients to be 0.01 and -0.005 G, respectively, which are too small to be of importance. Also, relaxation due to thermal fluctuations of the director predicts that the C/B ratio should be decreased by this process. Furthermore, these contributions are expected to have little temperature dependence.¹⁸ It is observed in our experiments that the C/B ratio increases substantially with decreasing tempera-

ture. Thus this process cannot account either qualitatively or quantitatively for this behavior.

Note that the average over the director fluctuations in the first term of eq A5 reduces to δ_{NM} as the leading term, and the line width contribution calculated from this term is just that predicted from the rotation of the molecule.

Alternatively one can evaluate the quantity in brackets in the second term of eq A4 by using a formalism which corresponds to the diffusion of a "localized" \hat{n} in the presence of a very strong restoring potential of the form

$$V(\Psi)/kT = \alpha \cos^2 \theta \quad (\text{A14})$$

where the distribution parameter $\alpha \gg 1$. As the potential is a function of θ only, the diffusion equation can be separated into its components by letting¹⁴

$$Y_N^M(\Psi) = y_N^M(\theta) \exp(iM\phi) (2\pi)^{-1/2} \quad (\text{A15})$$

and to lowest order in θ and α^{-1} , one has

$$-D^{-1} \bar{\Gamma}_\theta = \partial^2/\partial \theta^2 + \theta^{-1}(\partial/\partial \theta) - (M/\theta)^2 - \alpha^2 \theta^2 + 2\alpha \quad (\text{A16})$$

where D is the diffusion constant for director motion.¹⁴

The eigenfunctions for this differential equation are given by

$$y_N^{|M|}(\theta) = [2\alpha N!/(N + |M|)!]^{1/2} e^{-\alpha \theta^2/2} (\alpha^{1/2} \theta)^{|M|} L_N^{|M|}(\alpha \theta^2) \quad (\text{A17})$$

where the $L_N^{|M|}(z)$ are the generalized Laguerre polynomials.⁶⁰ The eigenvalues of this equation are

$$W_N^{|M|} = 2\alpha D(2N + |M|) \quad (\text{A18})$$

These eigenfunctions and eigenvalues can be used for the evaluation of the correlation functions for director motion in eq A3 or A4. The quantity in brackets in eq A4 can be rewritten as

$$\hat{C}_{0M}(t) = \langle [D_{0M}^{(2)}(\Psi) - \langle D_{0M}^{(2)}(\Psi) \rangle] [D_{0M}^{(2)}(\Psi_0)^* - \langle D_{0M}^{(2)}(\Psi_0)^* \rangle] \rangle \quad (\text{A19})$$

The evaluation of this integral over all angles Ψ and Ψ_0 requires the conditional probability

$$P(\Psi, \Psi_0, t) = \sum_{N,M} \exp(-W_N^{|M|}(\Psi)t) | Y_N^M(\Psi) \langle Y_N^M(\Psi_0) | \times \left[\frac{P_0(\Psi)}{P_0(\Psi_0)} \right]^{1/2} \quad (\text{A20})$$

Thus we can proceed as in PBF for molecular rotation and finally obtain

$$\hat{C}_{0M}(t) = \sum_{p,q} \langle Y_0^0(\Psi) | D_{0M}^{(2)}(\Psi) | Y_p^q(\Psi) \rangle e^{-W_p^q t} \langle Y_p^q(\Psi_0) | D_{0M}^{(2)}(\Psi_0)^* | Y_0^0(\Psi_0) \rangle \quad (\text{A21})$$

where Σ' means that the term $p = q = 0$ has been omitted. Keeping the leading terms in the $D_{0M}^{(2)}(\Psi)$,¹⁴ one has

$$\hat{C}_{01}(t) = \hat{C}_{0-1}(t) = \sum_{q,p} \langle Y_0^0(\Psi) | e^{i\phi} d_{01}^2(\theta) | Y_p^q(\Psi) \rangle^2 e^{-W_p^q t} \quad (\text{A22})$$

Substituting for the Y_p^q from eq A15 and A17 and for $d_{01}^2(\theta)$ from eq A5, the integral over Ψ in eq A22 becomes

$$\int_0^\infty \theta d\theta \int_0^{2\pi} d\phi (2\alpha)^{1/2} \exp(-\alpha\theta^2) \frac{e^{\pm i\phi}}{\sqrt{2\pi}} \frac{3}{2}\theta \times \left[\frac{2\alpha p!}{(p+|q|)!} \right]^{1/2} \frac{e^{iq\phi}}{\sqrt{2\pi}} (\alpha^{1/2}\theta) L_p^{1/2}(\alpha\theta^2) \quad (\text{A23})$$

The integration over ϕ requires that $q = \mp 1$. Substituting $u = \alpha\theta^2$, the integral over θ now has the form⁵⁹

$$\frac{3}{2} \left[\frac{p!}{\alpha(p+1)!} \right]^{1/2} \int_0^\infty e^{-u} u L_p^{1/2}(u) du = \frac{3}{2} \left[\frac{p!}{\alpha(p+1)!} \right]^{1/2} \frac{\Gamma(p)}{p! \Gamma(0)} = \frac{3}{2\alpha^{1/2}} \delta_{p,0} \quad (\text{A24})$$

The correlation function for localized director motion then is⁶¹

$$\hat{C}_{01}(t) = \left(\frac{9}{4\alpha} \right) e^{-2\alpha D t} \quad (\text{A25})$$

Thus we can define a single correlation time for localized director motion as

$$\tau_D^{-1} = 2\alpha D \quad (\text{A26})$$

and the spectral density for this case is

$$\bar{K}_{01}(\omega_\pm) = \frac{9}{4\alpha} \frac{\tau_D}{1 + (\omega_\pm \tau_D)^2} \langle D_{00}^{(2)}(\Omega) \rangle^2 \quad (\text{A27})$$

and the line width contribution becomes

$$T_2^{-1} = \frac{|\gamma_H|}{3\sqrt{3}} (a_{11} - a_{12})^2 [I(I+1) - m_I^2] \frac{9}{8\alpha^2 D} \langle D_{00}^{(2)}(\Omega) \rangle^2 [1 + (\omega_\pm \tau_D)^2]^{-1} \quad (\text{A28})$$

Again the prediction is that the C line width coefficient resulting from director motion is negative. It has been estimated that $R/D \sim 1000$ ⁶² where R is the rotational rate of the molecule. The values of $\langle D_{00}^{(2)}(\Omega) \rangle^2$ observed experimentally were ~ 0.01 . Thus for $\alpha > 10$ – 100 the line width contribution from this model for director motion is calculated to be negligible compared to that resulting from molecular motion.⁶³

References and Notes

- (1) A preliminary account of this work was given at the Varian Workshop, Vanderbilt University, June 1973. Supported in part by grants from the National Science Foundation, the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Cornell University Materials Science Center.
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- (27) in PBF, $M^2 = -\nabla_\Omega^2$. Note that eq 2.5 of PBF should have been written as $\tilde{Z} \equiv P_0^{-1/2} [Z P_0]$ and eq 2.9 should have $P_0^{1/2}$ instead of $P_0^{-1/2}$.
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- (33) The perturbation eq 4.16 of PBF require some modification. The terms quadratic in λ_2^2 are respectively for eq 4.16a–f: $-(0.0777R_{00} + 0.0434)$; $-(0.1283R_{01} + 0.0262)$; $+(0.0311R_{02} - 0.0149)$; $-(0.2061R_{11} + 0.0481)$; $-(0.0376R_{12} + 0.0066)$; $+(0.0764R_{22} + 0.0062)$. Also the quantity $(\lambda_2^2/48)[s + E_{11}^{(10)}]^{-1}$ must be added to eq 4.16d. Other, more general expansions, based upon the complete computer solutions, may be found in ref 8 and 31.
- (34) If the principal axis of the magnetic tensors and the principal axes of the molecular orientation do not coincide, one must transform between them. It is usually easier to work with the magnetic tensors in the (x' , y' , z') system than the orientation tensor in the (x'' , y'' , z'') system.
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- (49) As noted above, PD-Tempone may not have its principal axes of orientation coincident with the principal axes of the magnetic tensors for several of the nematics studied. If the orienting potential were cylindrically symmetric about a particular molecular axis, then, as shown in section II, it should be possible to relate that axis to one of the principal axes of the magnetic tensor. If this is the case, then the experimentally observed g and A values can be used to determine an ordering parameter and one tilt angle. From eq 2.27 one finds for the tilt angle relative to the z magnetic principal axis, $\beta^* = 33 \pm 1^\circ$, and with the x axis as the principal axis one has $\beta^* = 53 \pm 1^\circ$. However neither of these look reasonable from the point of view of the known structure of Tempone. With the y axis as the principal axis, there is no real solution of eq 2.27 for β^* . Therefore, we shall not consider the effect of the tilt angle any further.
- (50) For anisotropic viscosity in the presence of a weak ordering potential, one can show that this calculated $(C/B)_{\tilde{R}_i \sim 100 \tilde{R}_\perp} = 1.8(C/B)_{\tilde{R}_i = \tilde{R}_\perp}$ for

the λ_y values used for BOCP.

- (51) For ordered liquid solvents it is true that even in the motional narrowing region where the lines are Lorentzian, the widths are somewhat dependent on rotational model. This is because the larger the size of the elementary jump angle, the less the reorientational process is affected by the orienting potential. Our τ_R 's in the motional narrowing region were also estimated by means of a strong jump model (cf. PBF) and this typically yielded values of τ_R that were 5–10% shorter than the analysis based on a Brownian model. This difference was not deemed very significant. All other aspects of the analysis remained essentially unchanged.
- (52) The effect of the weak ordering is to reduce the PD-Tempone line width coefficients by about 30% below what they would be if the ordering potential were zero but τ_R were the same.
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- (55) If we estimate κ from the relation used by J. S. Hwang, D. Kivelson, and W. Z. Plachy [*J. Chem. Phys.*, **58**, 1753 (1973)]

$$\kappa = [6(r_s/r_0) + (1 + r_s/r_0)^{-3}]^{-1}$$

where r_s is the solvent radius ($r_s \approx 14 \text{ \AA}$ for MBBA), then we get $\kappa = 0.038$.

- (56) Thus Zupancic et al. [*Solid State Commun.*, **15**, 227 (1974)] obtained an activation energy E_a for D_{\perp} of 5.4 kcal/mol using an NMR pulse technique, while H. Hakeml and M. M. Labes [*J. Chem. Phys.*, **61**, 4020 (1974)] found $E_a = 17 \pm 2.5$ kcal/mol using an optical method. These results extrapolate to D_{\perp} of 1.4×10^{-7} and $4.4 \times 10^{-10} \text{ cm}^2/\text{sec}$, respectively, at -25°C .
- (57) Hoel and Kivelson [*J. Chem. Phys.*, **62**, 4535 (1975)] have recently suggested that the residual A' in VOAA studies is to be attributed to spin-rotational relaxation in the absence of any other known mechanism. This requires that the spin-rotational relaxation component about the symmetry axis begins to slow down when η/T becomes large enough (instead of typical decrease with η/T). (They do not see the effects of reorientational relaxation about the symmetry axis, because of the symmetry of the magnetic parameters.) We have implicitly argued against such mechanisms in our recent work on nitroxides (ref 3 and II), where R_{\parallel} and R_{\perp} were both observed and varying magnitudes of A' were found. In particular, we summarize for isotropic liquids: (1) $N = R_{\parallel}/R_{\perp}$ was typically found to be constant with temperature, and for PD-Tempone $N \approx 1$, and in all cases $R_{\parallel} \propto R_{\perp} \propto T/\eta$. (2) It is possible for small rotational asymmetry relative to the molecular z axis to significantly affect A' , and there is usually a small contribution from intermolecular electron-nuclear dipolar interactions. (3) The observed A' are typically simply linear in η/T for large enough viscosity. (4) In II they were found to be significantly dependent upon magnetic field, which should not be true for a spin-rotation mechanism, although this observation is dependent upon the rotational model such as implied in (2). Also most important (5) the measurements of W_6 in ref 3 and II from saturation studies show that precisely when A' becomes anomalous (increasing with η/T), the W_6 are decreasing (cf. Figure 12 of II). Since, at the higher temperatures, $W_6 \propto T/\eta$ is found to be virtually equal to $A'/2$ as predicted for a

spin-rotational mechanism [i.e., $T_1(\text{SR}) = T_2(\text{SR})$], then, if A' at the lower temperatures (where $A' \propto \eta/T$) were due to a spin-rotational mechanism, one would still expect $W_6 \approx A'/2$, which it decidedly is not. It appears that A' is due essentially to a purely secular mechanism. Furthermore (6) we have consistently argued against any physical explanations of spectral anomalies which appear to be "turned on", although the sample exhibits no phase transitions. We believe a likely possibility for explaining an anomalous A' could be in terms of modulation of the dipolar and g -tensor terms by rotational reorientation, but where the reorientation is complicated by a slowly relaxing local structure and/or related considerations. (Cf. section VII.) In II it was suggested that (2) above might help to explain the anomalous A' , but more careful considerations show that A/C is not very significantly affected by such small rotational asymmetry, so it would not be a very satisfactory explanation. (We wish to thank Dr. B. Kowert for a helpful discussion on this point.)

- (58) Recent pressure-dependent studies on the PD-Tempone system will be reported on elsewhere: J. S. Hwang, K. V. S. Rao, and J. H. Freed, to be submitted for publication.
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- (61) We can establish a formal equivalence between eq A25 and eq A9 with eq A5 by regarding the result eq A25 as the result for the q th mode and letting $2\alpha D \rightarrow Kq^2/\eta$ while letting $9/4\alpha \rightarrow 3kT/2Kq^2V$ or $D \rightarrow kT/3\eta V$ and $\alpha \rightarrow 3Kq^2V/2kT$.
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- (63) It should be noted that we have avoided the question as to whether a motional-narrowing theory actually applied for the slow director fluctuations. First we should note that the criterion for validity is given by $|\mathcal{J}C_1^2|_{\tau_D^2} \ll 1$ where $|\mathcal{J}C_1^2|^{1/2}$ measures the root mean square value of modulation of $\mathcal{J}C_1(\Psi)$ by the small amplitude director motion. Thus for example, for the diffusion model we require

$$\left[\frac{9}{4\alpha} \langle D_{00}^{(2)}(\Omega) \rangle^2 \frac{\gamma_a^2}{3\sqrt{3}} (a_{\parallel} - a_{\perp})^2 \right] [\tau_D^{-2} + \omega_{\pm}^2]^{-1} \ll 1$$

These conditions should be obeyed in the present case. When they are not obeyed, a slow tumbling theory analogous to PBF for the diffusion model or analogous to that of J. B. Pedersen and J. H. Freed [*J. Chem. Phys.*, **58**, 2746 (1973); **58**, 2869 (1973)], for the hydrodynamic model, should be employed.

- (64) Similar results have been observed in ^2H NMR studies on deuterated stearic acids in the liquid crystalline phase of egg lecithin [G. W. Stockton, C. F. Polnaszek, A. P. Tulloch, F. Hasan, and I. C. P. Smith, *Biochemistry*, submitted for publication]. The ordering parameters for the totally deuterated acids are also reduced compared to those of partially deuterated (at one position) acids.
- (65) NOTE ADDED IN PROOF: Actually by using eq 7.12 and the method outlined in section VIIB, but applied to director fluctuations, it is easy to demonstrate that (1) the analysis involving the second term of eq A3 as given below is indeed appropriate; and (2) the first term of eq A3 is to be replaced by $C_{\text{KMK}'M}(t)$, so the physically unreal feature is indeed removed.