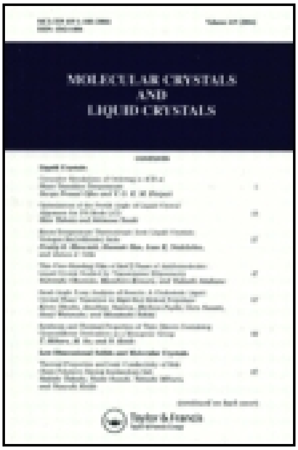

Molecular Crystals and Liquid Crystals

Electron Paramagnetic Resonance Studies of Heisenberg Spin Exchange in a Nematic Liquid Crystal

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Electron Paramagnetic Resonance Studies of Heisenberg Spin Exchange in a Nematic Liquid Crystal

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The effects of Heisenberg spin exchange on the linewidths of the nitroxide free radical di-*tert*-butyl nitroxide (DTBN) in the nematic liquid crystal N-(*p*-Methoxybenzylidene)-*p*-butylaniline (MBBA) have been measured as a function of the temperature and concentration of the free radical. At higher temperatures (>20°C) the spectra are analyzed in terms of spin exchange interactions using Freed's formalism, modified to take into account the anisotropic nature of the viscosity of the liquid crystal. At lower temperatures (<20°C) it is observed that magnetic dipole-dipole interactions between partially oriented DTBN molecules becomes important.

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INTRODUCTION

The translational and rotational diffusion coefficients for a molecule in an isotropic liquid may be approximated, respectively, by[1]

$$D_{tr} = \frac{kT}{6\pi\alpha\eta}$$
$$D_{rot} = \frac{kT}{8\pi\alpha^3\eta} \tag{1}$$

where T is the temperature, η the liquid viscosity, and α the hydrodynamic radius of the molecule. The linear dependence upon T/η of these coefficients has been verified in a large number of experiments.[2]

Electron paramagnetic resonance (EPR) of stable nitroxide radicals is uniquely suited to study both translational[3,4,5,6] and rotational[7] diffusion in liquids because, in one experimental arrangement, one may measure both of these quantities separately, whereas other methods do not have this capability. For example, the direct determination of translational diffusion may be obtained by means of mass diffusion experiments[8] and nuclear magnetic resonance (NMR) pulsed field gradient spin-echo experiments.[9] Information on rotational diffusion is possible through dielectric relaxation experiments,[10] analysis of the infrared and Raman band shapes,[11] and NMR spectroscopy.[9] EPR studies of stable nitroxides in a variety of liquids have been carried out[12,13] and have shown that the ratio of D_{tr} to D_{rot} does not depend on solvent type in isotropic liquids.[13]

It would be very interesting to study rotational and translational diffusion in liquid crystals using the EPR of stable nitroxide radicals. Certainly, anisotropic rotation has been observed in many liquid crystals by magnetic resonance spectroscopy.[14] In addition, translational diffusion, also anisotropic,[15] has recently been studied using NMR[16] and radioactive carbon-14 tagging techniques.[17]

In a liquid crystal, the viscosity as measured by several classical techniques shows an abrupt change upon passing through the mesophase-isotropic transition temperature, T_c.[18,19] Intuitively, one would not expect the translational diffusion to be *discontinuous* at the clearing point, thus modification of D_{tr} in Eq. (1) is necessary. The present work is addressed to this modification which involves introducing into Eq. (1) an effective viscosity, η_{eff}.

The physical technique used to investigate translational motion is the Heisenberg Spin Exchange (HSE) of the nitroxide free radical di-*tert*-butyl nitroxide (DTBN) in the nematogen, N-(*p*-Methoxybenzylidine)-*p*-butylaniline (MBBA). We show that the use of an effective viscosity, η_{eff}, derived from viscosity coefficients measured by Martinoty and Candau,[18] who employed a shear waves reflectance technique, leads to Heisenberg spin exchange frequency that varies linearly with T/η_{eff} and is continuous through the nematic-isotropic transition temperature.

The main effort of the present work is to characterize the HSE properties in a liquid crystal. This is the first step in a program of research in these laboratories in which we seek an understanding of the relationship between rotational and translational diffusion in liquid crystals. In addition, we present some experimental results for which we have no complete analysis yet. We speculate that these results may be due to magnetic dipole-dipole interactions between the electron spins of the nitroxide radicals in the ordered phase.[20]

EXPERIMENTAL

EPR spectra at X-band were recorded with a Varian reflection-type spectrometer using 100 kHz magnetic field modulation and dual cavity techniques. DTBN in water was used as a standard and an isotropic nitrogen hyperfine coupling constant, $a_N = 17.1$ G and a g-value, $g = 2.0053$ were assumed. Temperature control was achieved with a Varian 4557 variable temperature accessory. The sample temperature was measured to ±0.5°C with a copper/constantan thermocouple placed in the nitrogen stream slightly above the microwave cavity.

The nematogen, MBBA, was obtained commercially from Eastman Organic Chemicals and used without further purification. The DTBN was prepared according to the method described by Hoffmann *et al.*[21] DTBN was introduced into the liquid crystal, the concentration being determined volumetrically. Non-degassed samples were sealed in capillary tubes. Several samples were prepared in 4 mm I.D. quartz tubes to check for sample size effects on the results and there proved to be none.

THEORY

The theory of spin exchange between free radicals in solution has been discussed by several authors.[3, 4, 5, 6] Our discussion draws heavily on the work of Freed and coworkers[3,4] and we adopt their notation. It has been shown that the exchange frequency, ω_{HE}, is given by

$$\omega_{HE} = \tau_2^{-1} [1 + J^{-2} \tau_1^{-2}]^{-1} , \tag{2}$$

where J is minus two times the exchange integral for the unpaired electrons on neighboring radicals, τ_2 is the mean time between successive new bimolecular collisions of radicals and τ_1 is the mean lifetime of an interacting radical pair. For simple Brownian diffusion of neutral radicals in an isotropic liquid

$$\tau_2^{-1} = 4\pi d \, D_{tr} \, N \tag{3}$$

$$\tau_1^{-1} = (6D_{tr}/d^2)\exp[U(d)/kT] \qquad (4)$$

where N is the number density of radicals, d is the interaction distance for exchange, D_{tr} is the translational diffusion coefficient given in Eq. (1), and U(d) is the intermolecular potential energy of interaction between the uncharged radical pairs.

Strong exchange is characterized by $(J\tau_1)^2 >> 1$ and for this case, $\omega_{HE} = \tau_2^{-1}$, thus, according to Eqs. (1) and (3), ω_{HE} is a linear function of T/η. Intermediate exchange is characterized by $(J\tau_1)^2 \approx 1$ and the full expression for ω_{HE} given in Eq. (2) must be retained.

Using Freed's formalism, it follows that in the limit of slow-exchange, ω_{HE} is related to the Lorentzian first derivative line-width of the $M_I = 0$ hyperfine line by

$$\omega_{HE} = 2.28 \times 10^7\,[\delta - \delta(0)]\ \text{sec}^{-1}\ , \qquad (5)$$

where δ and $\delta(0)$ are the linewidths in Gauss, in the presence and absence of spin exchange, respectively.

The quantity of interest in this work is τ_2^{-1}, the frequency of bimolecular collisions between radicals. In the case of strong spin exchange, $\omega_{HE} = \tau_2^{-1}$, is a linear function of T/η having a slope g which extrapolates to zero at $T/\eta = 0$, therefore

$$\tau_2^{-1} = g\,(T/\eta)\ . \qquad (6)$$

For the case of intermediate exchange the full expression given by Eq. (2) must be used. Therefore, the frequency of bimolecular collisions will be given by

$$\tau_2^{-1} = \omega_{HE}/p\ , \qquad (6a)$$

where

$$p = [1 + J^{-2}\tau_1^{-2}]^{-1}\ . \qquad (7)$$

We note that Eq. (2) implies that a plot of ω_{HE} *versus* T/η will exhibit curvature and in addition, assuming the validity of Eqs. (1), (3) and (4), that Limit $T/\eta \to 0$ $\omega_{HE} = 0$.

In a nematic liquid crystal, Eqs. (3) and (4) require modification. Recently, Yun and Fredrickson[17] have shown that in the presence of an external magnetic field, mass diffusion in the nematogen, *p*-azoxyanisole, is transversely isotropic about the direction of the applied field. These authors define an axially symmetric diffusion coefficient tensor with principal components $D^{\parallel}$ and $D^{\perp}$ representing the diffusivity when the magnetic field is parallel and perpendicular to the mass flux, respectively. Their experiments[17] indicate that self-diffusion changes continuously (also indicative that the viscosity changes continuously) across the nematic-isotropic transition temperature and that the diffusion coefficient in the disoriented phase, D_0, is given by

$$D_0 = 1/3\,(D^{\parallel} + 2D^{\perp})\ . \qquad (8)$$

We make the plausible assumption that MBBA may be so characterized and replace D_{tr} in Eqs. (3) and (4) by

$$D_{tr} = 1/3\,(D^{\parallel} + 2D^{\perp}) = \frac{kT}{6\pi a \eta_{eff}}\ , \tag{9}$$

where we have defined an "effective" viscosity for the purpose of bimolecular collision rates as

$$\eta_{eff}^{-1} = 1/3\,[(\eta^{\parallel})^{-1} + 2(\eta^{\perp})^{-1}]\ . \tag{10}$$

To compute η_{eff} one needs to measure $\eta^{\parallel}$ and $\eta^{\perp}$ and we have chosen to use the values of these quantities in MBBA as measured by a shear waves reflectance technique.[18]

RESULTS

The nematic-isotropic transition temperature was lowered by the addition of DTBN as expected. Most of the results discussed here were obtained from samples containing 6.0×10^{-2} M DTBN, and for these samples the transition temperature was approximately 37°C.

The EPR spectra of DTBN in MBBA are typical nitroxide spectra showing three sharp hyperfine lines separated by the isotropic hyperfine coupling constant, a_N.[22] It was observed that a_N varies with temperature and this behavior is shown in Figure 1 which is a plot of a_N as a function of the temperature. The nematic-isotropic phase transition temperature is indicated by the arrow in Figure 1. From the value of the measured magnetic field difference between the $M_I = -1$ and $M_I = +1$ lines, we may compute the order parameter. Following Shutt *et al.*,[23] the expression for the order parameter is

$$\sigma_z = \frac{3}{2b}\,(\langle a\rangle - a)\ , \tag{11}$$

where a is the nitrogen hyperfine splitting between the $M_I = -1$ and $M_I = +1$ lines, $\langle a\rangle$ is the average experimental nitrogen hyperfine splitting in the nematic phase between the $M_I = \pm 1$ components, and b is the difference between the parallel and perpendicular components of the (assumed axial) hyperfine coupling tensor. We take $a = 31.0 \pm 0.1$ G, the value measured in isotropic MBBA, and $b = 25.0 \pm 0.1$ G as taken from measurements on dilute DTBN oriented in a host crystal.[24] The maximum value of $\sigma_z = -0.042$ at $T = 10°C$.

The linewidths, as measured between points of maximum slope (δ), of the $M_I = 0$ EPR line of DTBN as a function of radical concentration is shown in Figure 2 for three temperatures: two corresponding to the isotropic phase and one corresponding to the nematic phase of MBBA.

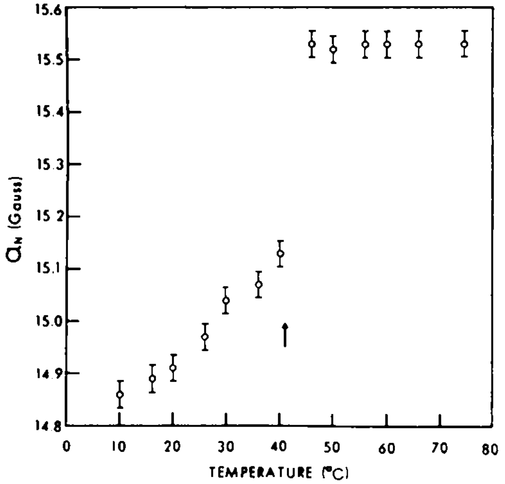

FIGURE 1 The nitrogen hyperfine coupling constant as a function of temperature for 3×10^{-4} M DTBN in MBBA. The nematic-isotropic transition temperature of the solution was 41°C.

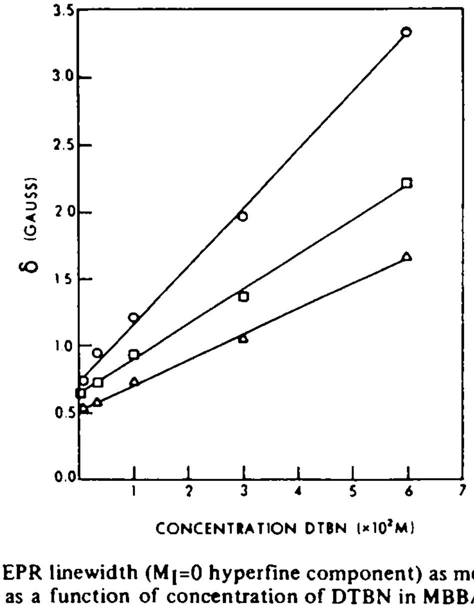

FIGURE 2 The EPR linewidth ($M_I=0$ hyperfine component) as measured between points of maximum slope as a function of concentration of DTBN in MBBA at 72.5°C, ○; 47.5°C, □; and 25°C, △. The solid lines are linear least squares fit to the data.

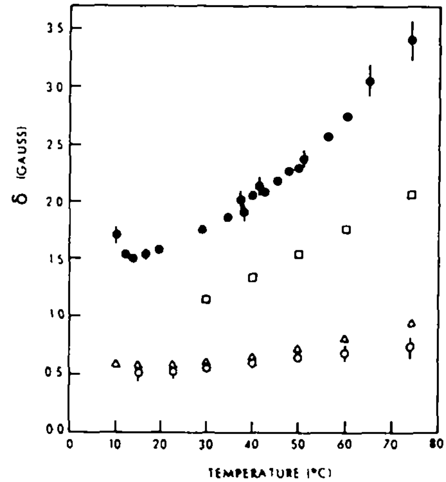

FIGURE 3 The EPR linewidth (M_I=0 hyperfine component) of DTBN in MBBA as a function of temperature for DTBN concentrations of 6 x 10^{-2} M, •; 3 x 10^{-2} M, □; 3.3 x 10^{-3} M, △; and 5.5 x 10^{-4} M, ○. Note that at temperatures below ~15°C the linewidth increase upon decreasing temperature for the 6 x 10^{-2} M solution.

The linewidth variations as a function of the temperature of the $M_I = 0$ hyperfine line of DTBN at various radical concentrations are shown in Fig. 3. The curves in Figure 3 show the same qualitative behaviour for the linewidths of DTBN *versus* temperature and radical concentration in MBBA above 15°C as they do in isotropic liquids, that is, the linewidth increases with increasing temperature, probably due to spin-rotational interactions[25] and in addition, increases with increasing radical concentration due to Heisenberg spin exchange.[3, 4, 5, 6] Furthermore, unlike ordinary liquids, it is noted that at temperatures below 15°C the linewidth of DTBN in MBBA *increases* with decreasing temperature and that this increase is concentration dependent. This behavior has recently been observed by Devaux *et al.*[20] for spin-labeled phospholipids incorporated into membranes and is attributed to the magnetic dipole-dipole interactions between the electron spins of the nitroxide groups. For DTBN in MBBA this interaction is large and one of obvious interest, but for the present, we avoid this temperature region in order to evaluate the spin exchange frequency, ω_{HE}, using Freed's formalism.

Thus, we compute ω_{HE} for the 6.0 x 10^{-2} M solution of DTBN in MBBA using Eq. (5), regarding the linewidth of the 5.5 x 10^{-4} M concentration as δ(0). We restrict the linewidth range such that $\omega_{HE}/2\pi < 0.3\ a_N$ so that overlapping of the lines is not a problem.[6] We plot in Figure 4, ω_{HE} *versus* T/η and in Figure 5, ω_{HE} *versus* T/η_{eff}. The viscosities involved are tabulated in Table I and are

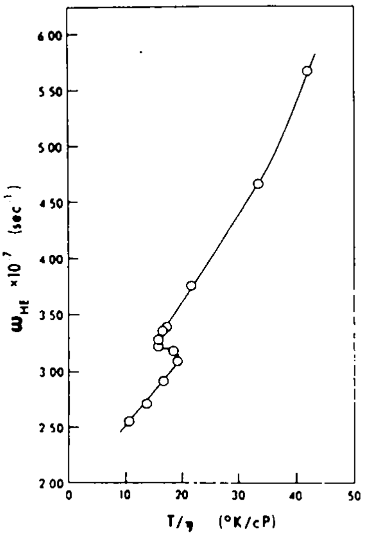

FIGURE 4 The Heisenberg spin exchange frequency *versus* T/η for 6 x 10^{-2} M DTBN in MBBA where η is the viscosity as measured by a capillary method.

taken from the results of Martinoty and Candau[18] assuming $\eta = \eta_0$, $\eta^{\parallel} = \eta_a$, and $\eta^{\perp} = \eta_c$, using those author's notation. In the isotropic range, we take $\eta_{eff} = \eta_0$, where η_0 was measured by the shear waves reflectance technique. Figure 4 shows a curious behavior of ω_{HE}, arising from the fact that η_0, measured by a capillary method, is the viscosity coefficient appropriate for molecules aligned with the flow and ignores the transverse coefficient. Figure 5 shows a smooth variation of ω_{HE} through the nematic-isotropic phase transition in agreement with our intuitive expectations. In addition, the variation of ω_{HE} as a function of T/η_{eff} is

TABLE I

Temperature (°C)	η_a(cP)[a]	η_c(cP)[a]	η_0(cP)[a]	η_{eff}(cP)[b]
20	33.9	56.2	43.1	46.1
25	26.9	41.4	34.5	35.1
30	21.5	30.9	27.8	27.0
35	17.4	23.2	22.6	20.9
40	14.1	17.6	18.5	16.3

[a] Viscosities measured by shear waves reflectance technique (ref. 18).
[b] Computered from Eq. (10).

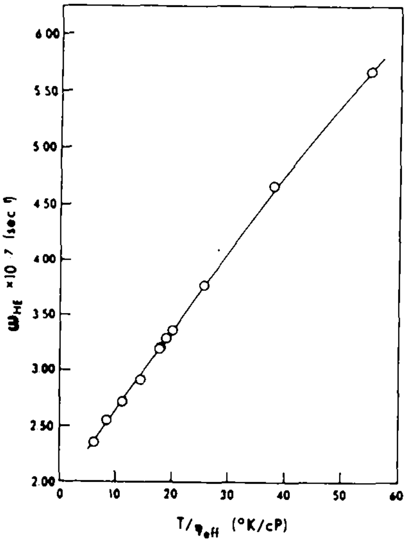

FIGURE 5 The Heisenberg spin exchange frequency *versus* T/η_{eff} for 6×10^{-2} M DTBN in MBBA where η_{eff} is given in Eq. (10). The nematic-isotropic phase transition is at T/η_{eff} ~17°K/cP. Note the smooth transition of the spin exchange frequency through the phase transition.

nearly linear, showing a slight concave downward curvature. This linear behavior, as we have noted above, is consistent with strong exchange [i.e. $(J\tau_1)^2 >> 1$], however, we note that ω_{HE} extrapolates to a non-zero value at $T/\eta_{eff} = 0$. This kind of behavior has been noted for peroxylamine disulfonate (PADS) in water[4] and was interpreted as being due to *intermediate* exchange.

Following Eastman *et al.*,[4] we define

$$\bar{\omega}_{HE} \equiv (T/\eta_{eff}) \frac{d\,\omega_{HE}}{d\,(T/\eta_{eff})} \tag{12}$$

TABLE II

Values of $(J\tau_1)$ and K for 6×10^{-2} M DTBN in MBBA.

Temperature (°C)	$(J\tau_1)$	p^a	$K(M^{-1}sec^{-1})^b$	$K(M^{-1}sec^{-1})^c$
25	1.29	0.623	0.70×10^9	0.68×10^9
47.5	1.63	0.724	0.81	0.81
72.5	2.00	0.799	1.15	1.16

[a] Computed from Eq. (7).
[b] Computed from Eqs. (6a) and (15) using linewidth –vs– T/η_{eff} data.
[c] Computed from Eq. (16) using linewidth –vs– radical concentration data.

from which

$$(J\tau_1)^{-2} = \frac{\omega_{HE} - \bar{\omega}_{HE}}{\omega_{HE} + \bar{\omega}_{HE}} . \tag{13}$$

Values of ω_{HE} are taken from Figure 5 and $\bar{\omega}_{HE}$ from the slope of the curve in Figure 5. Table II lists the value of $(J\tau_1)$ at the three temperatures corresponding to the curves in Figure 2. Also given in Table II are values of p computed from Eq. (7) and values of the bimolecular rate constant

$$K = (\tau_2 C)^{-1} , \tag{15}$$

where C is the molar concentration of DTBN, and τ_2^{-1} is given in Eq. (6a).

An alternative method of obtaining the bimolecular rate constant involves the study of the linewidth as a function of C at a given temperature, as in Figure 2. Denote the slope of the linear curve of δ *versus* C, by h, then[4]

$$K = 2.28 \times 10^7 \ h/p. \tag{16}$$

One must make measurements of δ as a function of T/η in order to compute p and thus K using this method. For comparison, the values of K as deduced from Figure 2 are included in Table II. There is complete agreement of the bimolecular rate constant as computed from the concentration dependence of δ and the bimolecular rate constant as computed from the T/η_{eff} dependence of δ.

DISCUSSION

Heisenberg spin exchange interactions yield information about the diffusion controlled bimolecular collision rate between radicals in liquids and thus, supplies information about the translational diffusion coefficient, D_{tr}. We have shown that the collision rate K is a smooth fuction of T/η_{eff}, where η_{eff} is given by Eq. (10), even through the nematic-isotropic transition temperature. This behavior lends credence to the Stokes-Einstein model adopted here to the nematic mesophase. The values of the bimolecular rate constant are somewhat smaller here than in more conventional solvents.[3, 4, 6]

Additionally, in the case of intermediate exchange, information on the interacting pair may be obtained. Thus, the fact that intermediate exchange is observed opens the possibility that details of the exchange interaction between partially oriented radicals of varying structures may be studied. Further work with larger radicals and radicals with different geometries is now being carried out.

We do not observe an extrapolation of $[\delta - \delta(0)]$ to zero as $T/\eta_{eff} \to 0$, as is expected. Indeed we measure an increase in linewidth upon lowering the temperature at low values of T/η_{eff} which we attribute to magnetic dipole-dipole coupling. We have avoided the region of low T/η_{eff} in the present work, but clearly magnetic dipolar coupling between partially oriented radicals would be an interesting area of experimental and theoretical research.

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