This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 23 February 2013, At: 08:11
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Quadrupole and Proton Spin-Lattice Relaxation in the Nematic Liquid Crystalline Phase

J. J. Visintainer [a], J. W. Doane [a] & D. L. Fishel [a]
[a] Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio, 44240
Version of record first published: 28 Mar 2007.

To cite this article: J. J. Visintainer , J. W. Doane & D. L. Fishel (1971): Quadrupole and Proton Spin-Lattice Relaxation in the Nematic Liquid Crystalline Phase, Molecular Crystals and Liquid Crystals, 13:1, 69-84

To link to this article: http://dx.doi.org/10.1080/15421407108083538

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable

for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

Molecular Crystals and Liquid Crystals. 1971. Vol. 13, pp. 69–84
Copyright © 1971 Gordon and Breach Science Publishers
Printed in Great Britain

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

Quadrupole and Proton Spin-Lattice Relaxation in the Nematic Liquid Crystalline Phase†‡

J. J. VISINTAINER, J. W. DOANE

Department of Physics and Liquid Crystal Institute
Kent State University
Kent, Ohio 44240

and

D. L. FISHEL

Department of Chemistry and Liquid Crystal Institute
Kent State University
Kent, Ohio 44240

Received October 19, 1970; *in revised form December* 14, 1970

Abstract—Measurements of the quadrupole and proton spin-lattice relaxation times, T_1, in selectively deuterated terephthalbis-(4-amino-fluorobenzene) as well as proton relaxation in other compounds are compared with a calculation for T_1 which recognizes molecular reorientations in addition to the collective order fluctuations. Further, spin-lattice relaxation times in the rotating frame have been measured in *p*-methoxybenyzlidene-*p'*-butylaniline to determine the effect of an applied magnetic field on spin-lattice relaxation. These measurements, made at a constant spin-locking field strength, are found to be independent of the strength of the applied magnetic field up to 10 kG.

Introduction

The existence of long range order fluctuations[1,2] in liquid crystals is clearly established by the light scattering properties of these systems.[3,4] Nuclear spin-lattice relaxation is also sensitive to these collective modes,[5] but they are affected by a different regime of the fluctuation spectrum. That is, measurements of the spin-lattice relaxation time T_1, at normal NMR frequencies correspond to wave-

† This research was sponsored in part by the Air Force Office of Scientific Research, Office of Aerospace Research, U.S. Air Force, under Contract No. F44620-69-C-0021.

‡ Presented at the Third International Liquid Crystal Conference, Berlin, August 24–28, 1970.

lengths of these modes which are more than an order of magnitude shorter than the wavelength of light.

Nearly all of the T_1 measurements in liquid crystals to date have been on the proton spins.[6-9] While theory can, within reason, account for these measurements, the agreement between theory and experiment has not been as good as one would like. For example, the frequency dependence of T_1 for protons in *p*-azoxyanisole follows the expression $T_1 = A + B\omega^{1/2}$. A theory[10,5] of T_1 for protons based on order fluctuations gives the $\omega^{1/2}$ dependence but fails to account for the intercept A. The temperature dependence, however, appears to be in good agreement with the theory[5] if one recognizes the presence of molecular reorientations in addition to the long range order fluctuations.

There are two possible causes for the discrepancy in the frequency dependence. First, T_1 measurements for protons are sensitive to those fluctuation modes near their short wavelength limit. The quadratic dispersion relation which describes these collective modes would not be expected to hold in this short wavelength regime and would therefore affect the frequency dependence of T_1. A second and perhaps more realistic reason for the discrepancy is that the mechanism which has been used in calculating T_1 for protons has been too simple. In these calculations it has been assumed that the nuclear dipole–dipole interaction has been modulated by fluctuations in the orientation of the molecule. One might also expect the translational motion of neighboring molecules to modulate the interaction and also relax the spins.

In this paper we describe $T_{1\rho}$ measurements[11] in a nematic liquid crystal. These measurements are sensitive to those fluctuations where the quadratic dispersion relation is thought to be valid. Since magnetic field effects on the collective modes[2] are thought to be significant in this range we also present $T_{1\rho}$ measurements at different magnetic field strengths. To check the spin-lattice relaxation mechanism we have made measurements of the quadrupole spin-lattice relaxation times for a selectively deuterated liquid crystalline molecule. The proton spin-lattice relaxation in this system was measured as well. The spin-lattice relaxation measurements for deuterons should give better agreement with theory, as one would not expect the quadrupole interaction in these systems to be as

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

strongly perturbed by the motion of neighboring molecules. To compare the dipole with the quadrupole relaxation we have generalized the theory[5] for T_1.

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

Theory

A theory for the temperature dependence as well as the frequency dependence of T_1 in nematic liquid crystals has been described in an earlier paper.[5] In that paper it was shown that a calculation of T_1 should be based not only for the collective order fluctuations but also the molecular reorientations which are characteristic of liquid crystals. An expression for T_1 was calculated for the specific case where the internuclear vector responsible for spin-lattice relaxation was parallel to the molecular axis. For the data presented in this paper it will be necessary to generalize that expression for T_1 to account for the case where the internuclear vector of the dominant dipole–dipole interaction is at some arbitrary angle with respect to the molecular axis.

The nuclear spin-lattice relaxation time for two like nuclei of spin $\frac{1}{2}$ having a constant separation distance may be expressed as[11]

$$T_1^{-1} = \tfrac{9}{8}\gamma^4\hbar^2 r^{-6}[J_1(\omega) + J_2(2\omega)] \tag{1}$$

where γ is the nuclear gyromagnetic ratio and r is the internuclear separation distance. The $J_h(\omega)$ are the Fourier intensities at the frequency ω of the correlation functions given by the expression

$$J_h(h\omega) = \int_{-\infty}^{\infty} \langle F_h(0)\, F_h^*(t)\rangle\, e^{ih\omega t}\, dt \tag{2}$$

for $h = 1, 2$ and where

$$\begin{aligned} F_0(t) &= 1 - 3n^2 \\ F_1(t) &= (l + im)n \\ F_2(t) &= (l + im)^2 \end{aligned} \tag{3}$$

The direction cosines l, m and n describe the internuclear vector **r** in the laboratory coordinate system (x, y, z) with the z-axis in the direction of the magnetic field **H**. It is the time dependence of l, m and n which must be described in order to determine T_1.

We visualize the molecules in nematic liquid crystals as reorienting about a nematic director **N** which is itself executing small fluctuations

about the preferred direction of orientation which is the direction of the magnetic field **H**. In order to describe the instantaneous orientation of **N** in **H** we follow the same prescription as used in an earlier paper[5] by making a transformation of the direction cosines to a frame (primed frame in Fig. 1) where the Z'-axis is parallel to $\mathbf{N}(\mathbf{r}, t)$. In order to account for the fact that the internuclear vector may not lie along the molecular axis we make a second transformation to a frame which is fixed to the molecule with the Z_0-axis parallel to the long axis of the molecule. The transformed direction cosines become

$$\begin{bmatrix} (l+im)/\sqrt{2} \\ (l-im)/\sqrt{2} \\ n \end{bmatrix} = M^{-1}(\phi, \delta\theta, \Psi)M^{-1}(\alpha, \beta, \gamma) \begin{bmatrix} (l_0+im_0)/\sqrt{2} \\ (l_0-im_0)/\sqrt{2} \\ n_0 \end{bmatrix} \quad (4)$$

where ϕ, $\delta\theta$, Ψ and α, β, γ are the appropriate Euler angles[12] for each successive transformation and the matrices M^{-1} are

$$\begin{bmatrix} e^{i(\phi+\psi)} & 0 & \frac{-i}{\sqrt{2}} e^{i\phi}\,\delta\theta \\ 0 & e^{-(\phi+\psi)} & \frac{i}{\sqrt{2}} e^{-i\phi}\,\delta\theta \\ \frac{-i}{\sqrt{2}} e^{i\psi}\,\delta\theta & \frac{i}{\sqrt{2}} e^{-i\psi}\,\delta\theta & 1 \end{bmatrix}$$

and

$$\begin{bmatrix} e^{i(\alpha+\gamma)}\frac{(1+\cos\beta)}{2} & e^{i(\alpha-\gamma)}\frac{(1-\cos\beta)}{2} & \frac{-i}{\sqrt{2}} e^{i\alpha}\sin\beta \\ e^{i(-\alpha+\gamma)}\frac{(1-\cos\beta)}{2} & e^{-i(\alpha+\gamma)}\frac{(1+\cos\beta)}{2} & \frac{i}{\sqrt{2}} e^{-i\alpha}\sin\beta \\ \frac{-i}{\sqrt{2}} e^{i\gamma}\sin\beta & \frac{i}{\sqrt{2}} e^{-i\gamma}\sin\beta & \cos\beta \end{bmatrix}$$

It is the time dependence contained in the first transformation matrix which is governed by the order fluctuations, that is, fluctuations in $\mathbf{N}(\mathbf{r}, t)$. As deviations in the orientation of **N** are small, only the terms to the first order in $\delta\theta$ are retained. The second transformation matrix describes the reorientation of the molecule. If we take the

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

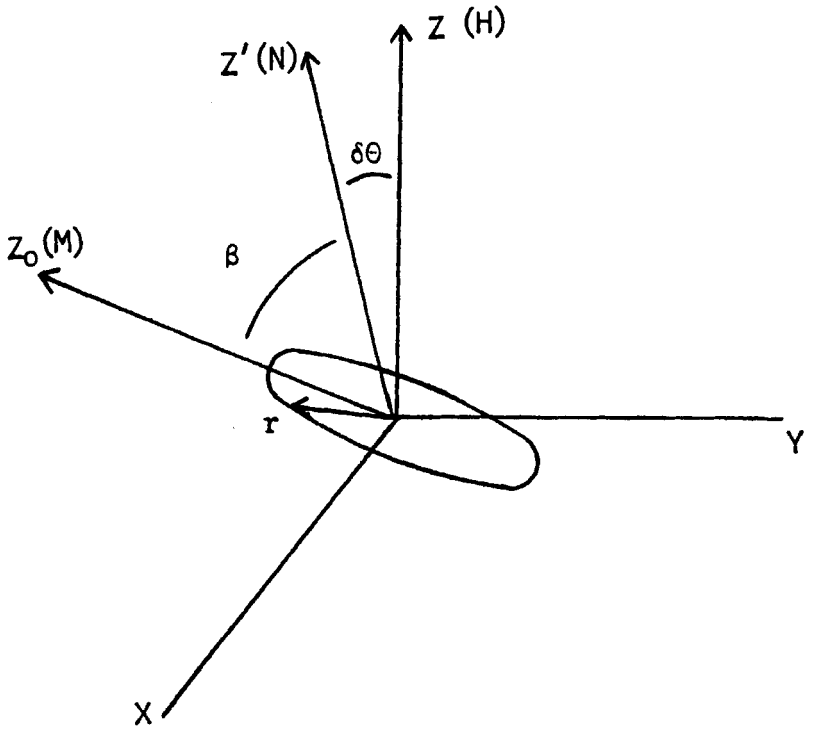

Figure 1. The internuclear vector **r** and the various coordinate systems: the laboratory frame with the z-axis in the direction of the applied magnetic field, **H**; the primed frame with the z'-axis in the direction of the instantaneous nematic director, **N**; and molecular frame with the z_0-axis parallel to the long axis of the molecule.

molecule to be cylindrically symmetric or rod shaped it is free to rotate about its long axis while its long axis is partially ordered about **N**. The direction cosines l_0, m_0 and n_0 describe **r** in the molecular frame and are taken to be fixed as a rigid molecule is assumed.

Using Eq. (4) the correlation functions in Eq. (2) take on the form

$$\langle F_1(0)F_1^*(t)\rangle = \tfrac{1}{16}\langle (e^{i\phi(0)}\,\delta\theta(0)\,e^{-i\phi(t)}\,\delta\theta(t)) \cdot \times (1-3\cos^2\beta(0))\,(1-3\cos^2\beta(t))\rangle F_0^2 \qquad (5)$$

$$+\text{SIMILAR TERMS}$$

The terms not shown in Eq. (5) all contain terms periodic in γ and α. By assuming the fluctuations of the director to be uncoupled from

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

the molecular reorientations and by noting the large disparity in time scales between the two motions Eq. (5) becomes[5]

$$\langle F_1(0)\, F_1^*(t)\rangle = \tfrac{1}{16}\langle e^{i\phi(0)}\,\delta\theta(0)\, e^{-i\phi(t)}\,\delta\theta(t)\rangle \cdot \times \langle 1 - 3\cos^2\beta(0)\rangle^2 F_0^2 \qquad (6)$$

where $F_0 = 1 - 3n_0^2$.

The terms periodic in γ and α which were not written down in Eq. (5) all average to zero. Since all of the terms in $\langle F_2(0)\, F_2^*(t)\rangle$ are periodic in γ and α this correlation function does not contribute. The terms $\delta\theta\, e^{i\phi}$ are the fluctuations $\delta\mathbf{N}$ studied by the Orsay Liquid Crystal Group. The second term on the right in Eq. (6) is the square of the degree of order, S, and Eq. (6) can thus be written

$$\langle F_1(0)\, F_1^*(t)\rangle = \tfrac{1}{4}\langle \delta N(0)\,\delta N(t)\rangle\, S^2(1 - 3\cos^2\theta_0)^2 \qquad (7)$$

where θ_0 is the fixed angle between the internuclear vector and the long axis of the molecule. From Eq. (2) it follows that

$$J_1(\omega) = \tfrac{1}{4}S^2(1 - 3\cos^2\theta_0)^2 \int_{-\infty}^{\infty} \langle \delta N(0)\,\delta N(t)\rangle\, e^{i\omega t}\, dt \qquad (8)$$

The long range order fluctuations involve modes in which the frequency[1] associated with a wave vector q is $\omega(q) = i(Kq^2 + \Delta\chi H^2)/\eta$ where K is the deformation constant of the nematic liquid crystal; η, an average of the Leslie coefficients; $\Delta\chi$, the anisotropic part of the diamagnetic susceptibility and H the strength of the external magnetic field in which the liquid crystal sample resides. The thermal amplitude[1] of the modes is $kT/(Kq^2 + \Delta\chi H^2)V$ where V is the volume and $Kq^2 + \Delta\chi H^2$ is the energy density of mode q.

The correlation function $\langle \delta N(0)\,\delta N(t)\rangle$ based on these modes was first worked out by Pincus[10] then by Blinc[7] who included the magnetic field terms. The effect of the magnetic field on T_1 is discussed in the next section.

Magnetic Field Effects on Spin-Lattice Relaxation

The effects of an external magnetic field on order fluctuations have been discussed by deGennes and the Orsay Liquid Crystal Group.[1] The results of their theory have been applied by Blinc *et al.*[7] to calculate the correlation function $\langle \delta N(0)\,\delta N(t)\rangle$ in Eq. (8). Using their results Eq. (8) becomes

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

$$J_1(\omega) = \frac{1}{8\pi}(1 - 3\cos^2\theta_0)^2 \frac{S^2}{K^{3/2}} \frac{kT\eta^{1/2}}{[1 + (R/\omega)^2]^{1/4}} \frac{\sin[\frac{1}{2}\tan^{-1}(\omega/R)]}{\sin[\tan^{-1}(\omega/R)]} \frac{1}{\omega^{1/2}} \tag{9}$$

where $R = \Delta\chi H^2/\eta$.

If we take $\Delta\chi \approx 10^{-5}$, $\eta \sim 10^{-2}$ poise and $H \sim 10^4\,G$ as typical values for these parameters then we obtain $R \sim 10^5\,\mathrm{sec}^{-1}$. It is seen from Eq. (9) that for values of $\omega \approx R = 10^5\,\mathrm{sec}^{-1}$, one would expect to observe magnetic field effects. Experimentally, this can be accomplished in two ways: by use of $T_{1\rho}$ measurements[11] or by making T_1 measurements on nuclear spins which have low values of γ. The use of $T_{1\rho}$ measurements have the advantage that one can hold ω in Eq. (9) constant by making all of the measurements at the same magnitude of the rotating magnetic field H_1 while the external magnetic field H is varied.

We have made $T_{1\rho}$ measurements on protons in *p*-methoxybenzylidene-*p'*-*n*-butylanaline (MBBA) over a variety of magnetic field strengths for constant values of $H_1 = 13 \pm 2G$. It is seen from Eq. (9) that if ω or γH_1 is sufficiently small one might expect the condition $R \gg \omega$ to be met. In this case it follows from Eq. (9) that for constant ω

$$J_1(\omega)^{-1} \propto H. \tag{10}$$

If on the other hand $R \ll \omega$, that is no external field effects, $J(\omega)$ is of course independent of H.

The results of $T_{1\rho}$ measurements are shown in Fig. 2. The measurements were made on a Brüker B-KR-332s pulsed system with the sample maintained at the temperature $T_{\mathrm{red}} = 96$. The result shows no field effects within the error of the experiment although there is a trend in the direction predicted by Eq. (9) if these effects were becoming significant at the values of H_1 used. It would therefore seem appropriate to neglect the effect of the applied magnetic field on spin-lattice relaxation measurements.

Temperature and Frequency Dependence of T_1

Using Eqs. (1) and (8) we write T_1 for protons as

$$T_1^{-1} = \tfrac{9}{32}\gamma^4\hbar^2 r^{-6}(1 - 3\cos^2\theta_0)^2 S^2 \int_{-\infty}^{\infty} \langle \delta N(0)\, \delta N(t)\rangle\, e^{i\omega t}\, dt \tag{11}$$

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

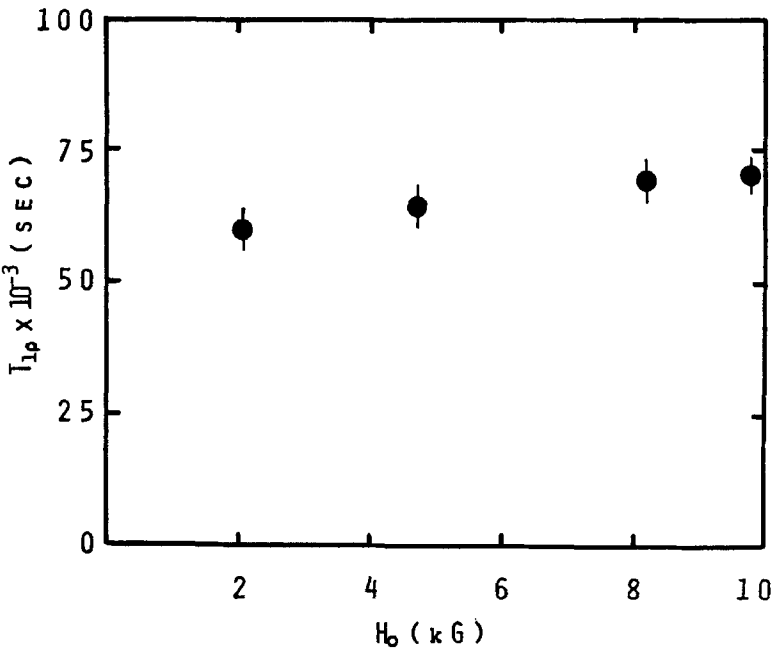

Figure 2. Spin-lattice relaxation in the rotating frame for proton spins in MBBA at $T_{red} = 96$ where the spin-locking field strength H_1 was kept at a constant value of 13 G while the applied magnetic field H was varied.

Since magnetic field effects can be neglected we follow Pincus[10] in calculating $\langle \delta N(0)\, \delta N(t) \rangle$. Including the diffusion constant, D, the expression for T_1^{-1} now becomes

$$T_1^{-1} = \frac{9}{16\sqrt{2}\pi} \frac{\gamma^4 \hbar^2}{r^6} (1 - 3\cos^2\theta_0)^2 \frac{S^2}{K} \frac{kT}{(K/\eta + D)^{1/2}} \frac{1}{\omega^{1/2}} \qquad (12)$$

Equation (12) can be easily adapted to spin 1 nuclei which relax via the quadrupole interaction. The quadrupole Hamiltonian for a spin of 1 is formally equivalent to the dipole–dipole interaction Hamiltonian for two interacting nuclei of spin $\frac{1}{2}$ provided $(\gamma\hbar)^2/r^3$ is replaced by $e^2qQ/2$ where q is the electric field gradient, Q the quadrupole moment of the nucleus and e the electronic charge. If θ' is now taken to be the angle between the direction of the principal axis of the field gradient and the molecular axis, T_1^{-1} becomes

$$T_1^{-1} = \frac{9}{64\sqrt{2}\pi} \frac{e^4 q^2 Q^2}{\hbar^2} (1 - 3\cos^2\theta')^2 \frac{S^2}{K} \frac{kT}{(K/\eta + D)^{1/2}} \frac{1}{\omega^{1/2}} \qquad (13)$$

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

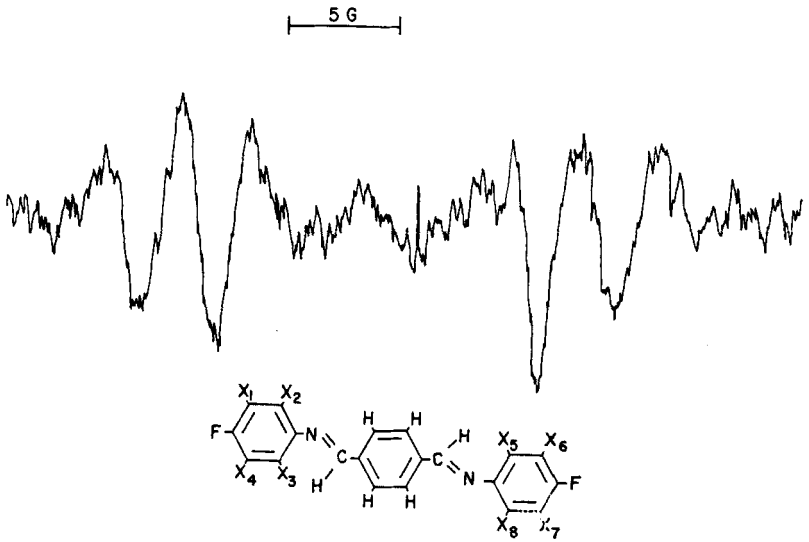

Figure 3. The molecule and deuteron spectra for terephthalbis-(4-animo-fluorobenzene), TAFB, in the nematic liquid crystalline phase at $T = 163\,^{\circ}\mathrm{C}$. The deuterated positions are the x positions in the diagram.

We compare these relationships with measured values of T_1 for protons in terephthalbis-(4-amino-fluorobenzene), TAFB and deuterons in TAFB-d_8. The molecular structure of TAFB-d_8 is shown in Fig. 3 along with its corresponding quadrupole spectra. Figure 4 shows T_1 for protons in TAFB at temperatures extending through the nematic range and into the isotropic liquid at frequencies 8 MHz, 20 MHz and 50 MHz. The values of T_1 for the deuterons in TAFB-d_8 are shown in Fig. 5. These plots are made versus $T_{\mathrm{red}} = 100\,T/T_k$ where T is the absolute temperature and T_k the absolute temperature of the clearing point.

With exception of special cases[13] the temperature dependence for the protons in TAFB is typical of that seen in compounds such as p-azoxyanisole. That is, the variation throughout the nematic range is not large; less than a factor of two. The same appears to be true for deuterons. In order to make a fit of Eqs. (12) and (13) to the data it would be necessary to know the details of the temperature dependence of the Leslie coefficients as well as the diffusion constant. Unfortunately, such information is not available although a rough approximation can be made. Since $K \propto S^2$, Eqs. (12) and

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

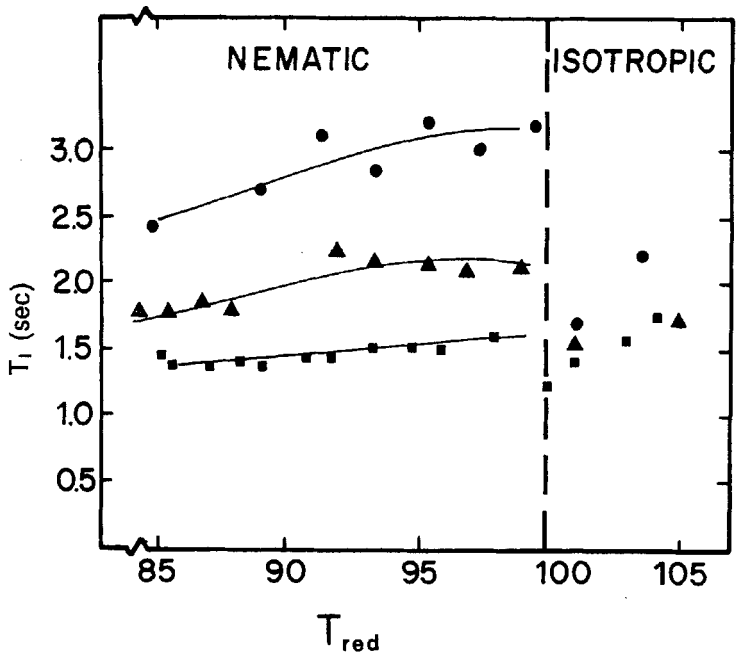

Figure 4. Proton spin-lattice relaxation times versus reduced temperature in TAFB at 8 MHz (squares), 20 MHz (triangles) and 50 MHz (circles).

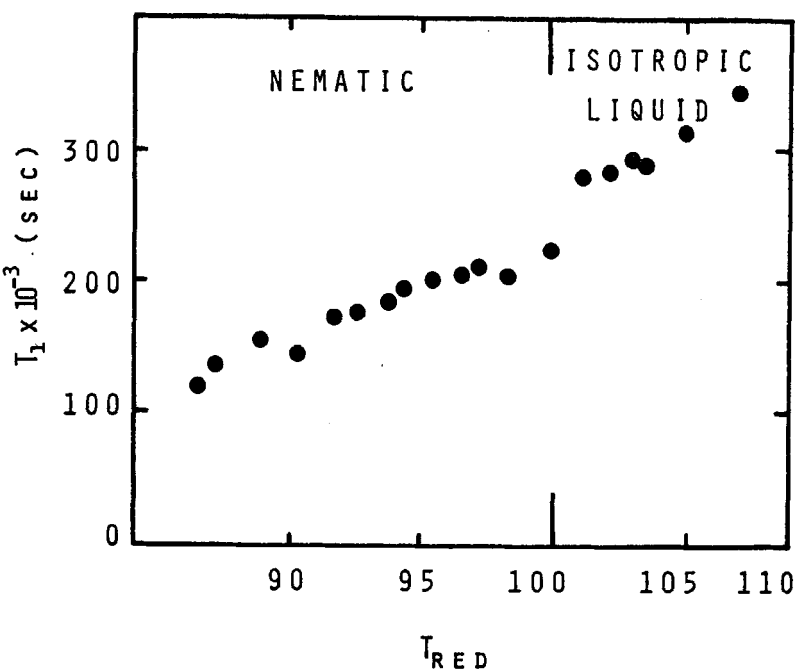

Figure 5. Quadrupole spin-lattice relaxation times for deuterons in TAFB-d_8 taken at a frequency of 8 MHz.

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

(13) predict $T_1 \propto D^{1/2}/T$ for modes whose lifetimes are diffusion limited and $T_1 \propto S/\eta T$ for those which are not. Since neither of the last two expressions are expected to be strongly temperature dependent the data would not appear to contradict the theory.

The measured frequency dependence of T_1 for three different compounds is shown in Fig. 6. Within experimental error the data appear to follow the relation $T_1 = A + B\omega^{1/2}$. On the basis of Fig. 6 one would not expect a large variation of $T_{1\rho}$ for varying values of H_1 where H_1 is kept greater than the dipolar line width. This is in fact what is seen in Fig. 7 for MBBA. The implications of this measurement are discussed in a latter section. Similar data have been observed for PAA.[14] The finite value of the intercept A

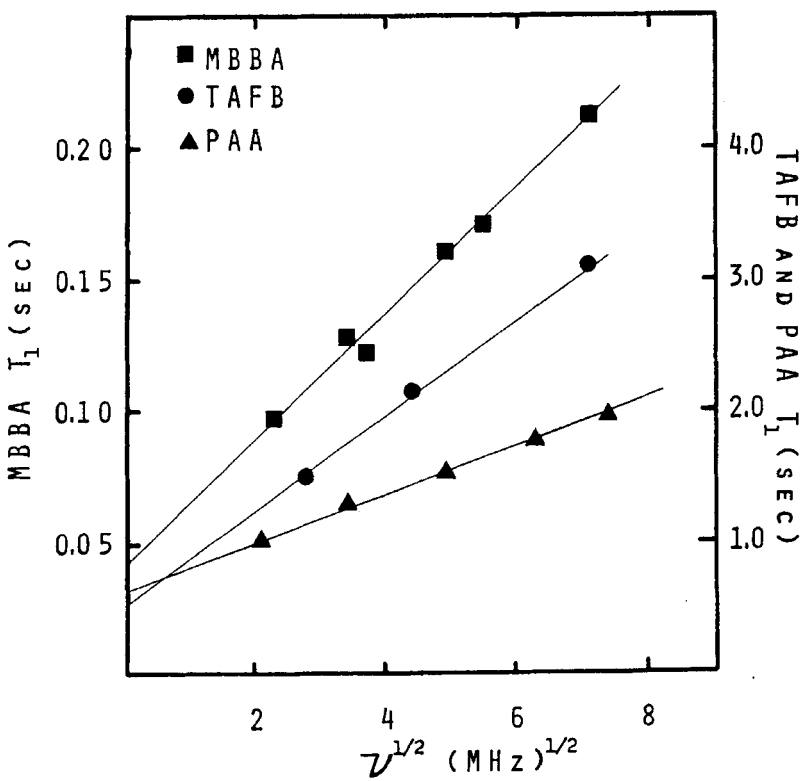

Figure 6. Frequency dependence of the proton spin-lattice relaxation times for: *p*-methoxybenzylidene-*p'*-butylaniline, MBBA, at $T_{red} = 96$; terephthalbis-(4-animo-fluobenzene), TAFB, at $T_{red} = 96$; and *p*-azoxyanisole, PAA at $T_{red} = 99$.

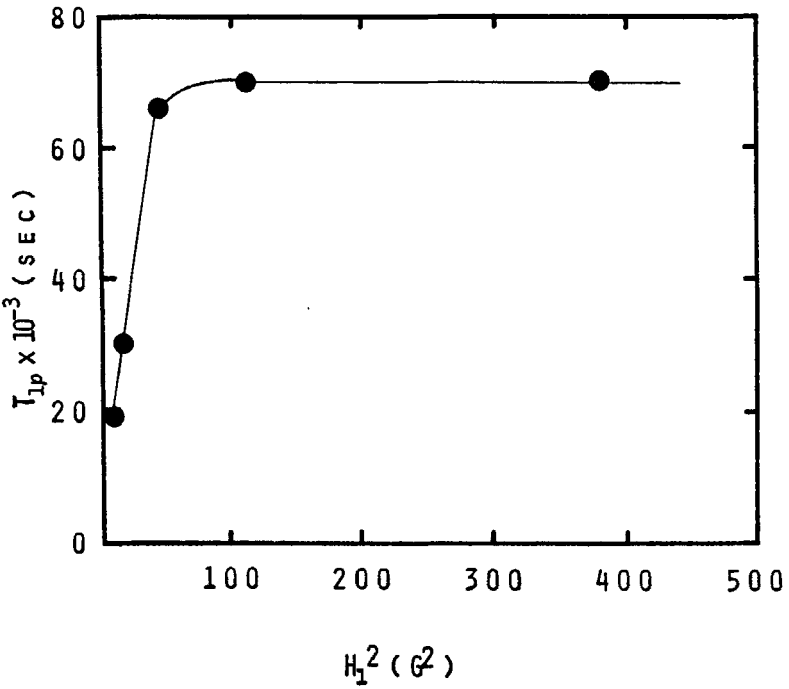

Figure 7. Spin-lattice relaxation in the rotating frame for M protons in MBBA at $T_{red} = 96$ in which the spin-locked field strength, H_1, was varied.

is disturbing since it is not predicted by the theory described in this paper. There is a tendency at first to attribute the intercept to other additive frequency independent relaxation mechanisms; however, this would give $T_1^{-1} = A + B\omega^{-1/2}$ which is not what is observed.

As a check on the mechanism used in arriving at Eqs. (11) and (12) we have calculated and measured the ratio of $(T_1)_{\text{Proton}}/(T_1)_{\text{Quad}}$ in TAFB-d_8. Reasoning that the quadrupole relaxation would be less likely to be affected by neighboring molecules it would stand a greater chance of agreeing with theory. Using Eqs. (12) and (13) we get

$$\frac{(T_1)_{\text{dipole}}}{(T_1)_{\text{quad}}} = \frac{(e^2qQ/2\hbar)^2(1-3\cos^2\theta')^2}{(\gamma^2\hbar/r^3)^2(1-3\cos^2\theta_0)^2} = \frac{(\Delta H)_Q^2}{(\Delta H)_D^2} \tag{14}$$

Using 19 G for quadrupole splitting from Fig. 3 and 3.6 G for the dipole splitting[15] at the same $T_{red} = 87$, we obtain a ratio of

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

$[(T_1)_P/(T_1)_Q]_{calc} = 30$. This is to be compared with the measured value of 10 taken from Figs. 4 and 5 at $T_{red} = 87$. This would tend to indicate that the protons are being relaxed at least in part by intermolecular interactions. It should be mentioned here that the value of T_1 for protons in TAFB and in TAFB-d_8 at 8 MHz was the same within experimental error.

Another test of the mechanism was to dissolve into MBBA a solute which had a considerably smaller degree of order than the liquid crystal solvent. Since $T_1 \propto S^{-2}$ one would expect a larger value for T_1 for the solute. It is possible to measure T_1 for the protons of the solute apart from the liquid crystal protons provided the disparity in their respective values of T_2 is large enough. Such is the case for tetramethylsilane (TMS) dissolved in MBBA. The value of T_2 for TMS in MBBA is 0.3 sec while it is $\sim 10^{-4}$ sec for the protons in MBBA. One can then observe a spin-echo from the TMS alone from which T_1 can be measured. The measured values of T_1 are

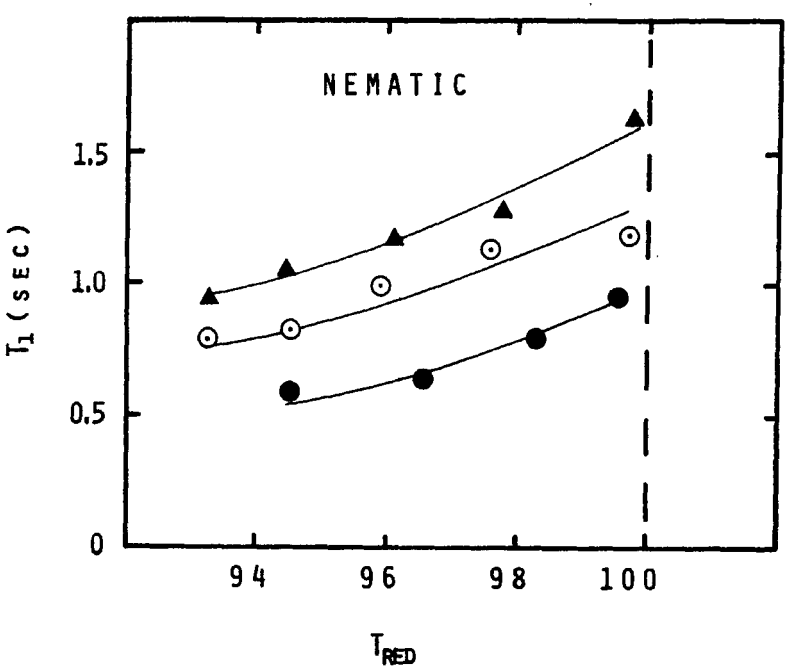

Figure 8. Temperature and frequency dependency of T_1 for protons in TMS dissolved in MBBA. 50.2 MHz (triangles), 24.2 MHz (open circles), and 12.0 MHz (Closed Circles).

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

shown on Fig. 8. Although they are larger than that of MBBA (Fig. 6) at the same frequency, nothing quantitative can be derived since one is not sure of the magnitude of cross-relaxation processes. It is interesting that frequency dependence is still observed. Since the degree of order of TMS[16] is so small one would not expect to see a frequency dependence at all although as mentioned earlier the TMS spins might be cross-relaxing with the MBBA spins and thereby displaying their T_1 character.

The diffusion rate of the TMS molecules in the liquid crystalline matrix has been measured. These measurements are described in an adjoining article.

Preparation of Deuterated TAFB

Terephthal-*bis*(4-fluoroaniline)-2, 3, 5, 6, 2′, 3′, 5′, 6′-d_8 was synthesized from terephthalaldehyde and 4-fluoroaniline-2, 3, 5, 6-d_4 by refluxing an ethanol solution. Recrystallization from ethanol (3*X*) gave the pure anil (67%) mp, 151–151.5° (crystal-nematic), clearing temperature, 235–236° (nematic-isotropic). Mass analysis (with an AEI MS-12 mass spectrometer operated at 70 eV, 100 μA ionizing current, 8 kV accelerating potential, 1500 resolving power) gave the parent ion (m/e 328) as the most intense peak in the spectrum with the M-1 (m/e 327) ion at 66.4% relative intensity. Non-deuterated terephthal-*bis*(4-fluoroaniline) has an M-1 (m/e 319) ion at 83.5% relative intensity. Low voltage (nominal instrument reading: 8 eV, 20 μA ionizing current) spectra of either deuterated or non-deuterated anil show only the parent ion and no M-1 ion. These results indicate there was no significant contamination with anil only partly deuterated on the terminal aromatic rings.

The 4-fluoroaniline-2, 3, 5, 6-d_4 used for synthesis† of the anil was itself prepared (overall yield: 14.9%) from benzene-d_6 (99.5% minimum isotopic purity) by the sequence: mononitration, reduction to aniline-d_5, conversion to fluorobenzene-d_5 (Schiemann reaction), nitration and reduction. The 4-nitrofluorobenzene-2, 3, 5, 6-d_4 was separated from isomers by vacuum fractional distillation. The two reduction steps were accomplished by treatment of a refluxing

† Details for preparation of deuterated TAFB may be obtained by corresponding to one of the authors D.L.F.

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

alcoholic solution with hydrazine and palladium. Mass analysis of the aniline derivatives showed ratios of the parent and M-1 ions comparable to those for non-deuterated derivatives confirming that no hydrogen exchange occurred during reduction.

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013

Discussion

As described earlier, one would expect the theoretical frequency dependence to be more in accord with $T_{1\rho}$ than T_1 measurements particularly in the case of proton spins. This follows from the argument that T_1 measurements may be sensitive to those fluctuation modes near their cut-off wavelength whereas $T_{1\rho}$ measurements are not. From Eq. (12) one would expect an $H_1^{1/2}$ dependence for $T_{1\rho}$. On the contrary, we find from Fig. 7 that there is little variation of $T_{1\rho}$ with H_1 for values of H_1 greater than the line width. This seems to be consistent with the T_1 measurements as there is also seen to be little variation of T_1 in the region near the intercept in Fig. 6 from 0.1 to 0.5 MHz which is the region of $T_{1\rho}$ measurements. No short wavelength limiting effects therefore appear to be present. These results in addition to the results of the $(T_1)_D/(T_1)_Q$ ratio indicate that intermolecular dipole–dipole interactions are important in proton spin-lattice relaxation. Further, quadrupole spin-lattice relaxation on deuterons, N^{14}, etc. would appear to be a better process for studies of fluctuation phenomena in liquid crystals. Some of these studies have already been made.[17]

Acknowledgements

We are indebted to Mr. Ying Yen Hsu for a significant portion of the synthetic work and to Mr. Howard J. Eyman for the mass analyses. One of us J.W.D. would like to acknowledge Dr. D. S. Moroi for his helpful remarks on the T_1 calculation. For mass spectra determination we are indebted to the National Science Foundation for the AEI MS 12 mass spectrometer purchased in part with funds provided by NSF Departmental Instrument Grant GP–8539.

REFERENCES

1. The Orsay Liquid Crystal Group, *J. Chem. Phys.* **51**, 816 (1969).
2. Brown, G. H., Doane, J. W. and Neff, V. D., *Critical Reviews in Solid State Sciences*, Vol. 1 (The Chemical Rubber Co., Cleveland, Ohio).
3. deGennes, P. G., *Mol. Cryst. and Liq. Cryst.* **7**, 325 (1969).
4. deGennes, P. G., *Compt. Rend.* **266**, 15 (1968).
5. Doane, J. W. and Johnson, D. L., *Chem. Phys. Letters* **6**, 291 (1970).
6. Doane, J. W. and Visintainer, J. J., *Phys. Rev. Letters* **23**, 1421 (1969).
7. Blinc, R., Hogenboom, D. L., O'Reilly, D. E. and Peterson, E. M., *Phys. Rev. Letters* **23**, 969 (1969).
8. Weger, M. and Cabane, P., *J. Phys. (Paris) Colloq.* **7100**, 72 (1969).
9. Dong, Ronald Y. and Schwerdtfeger, C. F., *Solid State Commun.* **8**, 707 (1970).
10. Pincus, P., *Solid State Commun.* **7**, 415 (1969).
11. Abragam, A., *The Principles of Nuclear Magnetism* (Oxford Univ. Press, London, 1961), pp. 291 and 560.
12. The Euler angles used here follow the convention of H. Goldstein, *Classical Mechanics* (Addison-Wesley Publishing Company, Inc. Cambridge, Mass., 1950), pp. 107–109.
13. Dong, Ronald Y., Marusic, M. and Schwerdtfeger, C. F., *Solid State Commun.* **8**, 1577 (1970).
14. Dong, Ronald Y., Forbes, W. F. and Pintar, M. M. (to appear in *Solid State Commun.*).
15. Bravo, N., Doane, J. W., Arora, S. L. and Fergason, J. L., *J. Chem. Phys.* **50**, 1398 (1969).
16. Snyder, L. C. and Meiboom, S., *J. Chem. Phys.* **44**, 4057 (1966).
17. Cabane, B. and Clark, W. G., *Phys. Rev. Letters* **25**, 91 (1970).

Downloaded by [Tomsk State University of Control Systems and Radio] at 08:11 23 February 2013