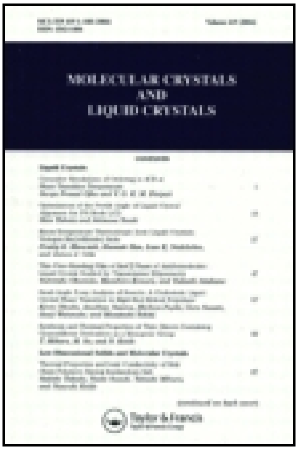

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Proton Spin Relaxation Study of the Dipolar Spin System in Nematic Liquid Crystals

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Proton Spin Relaxation Study of the Dipolar Spin System in Nematic Liquid Crystals

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The proton spin dipolar relaxation time was measured in the mesophases of p-azoxyanisole, p-n-hexyloxyazoxybenzene, p-n-heptyloxyazoxybenzene and p-methoxybenzylidene-p-n-butylaniline as a function of temperature and frequency. It was found that the dipolar spin systems in the nematic crystalline phase are predominantly relaxed by the orientational order fluctuations. This is manifested by the magnetic field effects on the order fluctuation modes.

INTRODUCTION

Recently, some attempts[1,2] have been made to study the molecular dynamics in liquid crystals[3] by means of the proton dipolar spin relaxation time T_{1D} as a function of temperature and frequency. In the liquid crystal p-n-heptyloxyazoxybenzene (HOAB), T_{1D} was measured both in the nematic and smectic-C phases at 37 MHz. It was found that T_{1D} increases with increasing temperature in the smectic-C phase but is constant in the nematic mesophase. The temperature dependence of T_{1D} in the nematic phase differs from that of T_1 measurements.[1,4] This investigation, however, fails to decide whether the proton dipolar spin system in the nematic phase of HOAB is relaxed by the long range order fluctuations[3] or by the usual diffusion mechanisms. The other liquid crystal studied[2] is p-azoxyanisole (PAA). In its nematic phase, T_{1D} was also found to be insensitive to temperature and frequency independent within a narrow frequency range (i.e. 24-32 MHz). It was concluded[2] that the dipolar spin system is relaxed not only by mechanisms which are effective in the laboratory frame (viz. T_1 measurements) but also by an additional relaxation mechanism. The present work was undertaken to study proton dipolar spin systems in several liquid crystals, including HOAB and PAA, as a function of temperature and frequency. It is believed that this may help to elucidate the nature of relaxation mechanisms in the dipolar spin system. In particular, since the spin-lattice relaxation measurements of the dipolar system are performed at an effective field of zero strength, the magnetic field effects on the collective order fluctuations[5] will be observed in T_{1D} measurements at various magnetic field strengths if the order fluctuations are a dominant relaxation mechanism.

EXPERIMENTAL

The nematic liquid crystals used in the present investigation were obtained commercially. All samples were sealed in a vacuum without further purification by the freeze-melt method. HOAB and p-n-hexyloxyazoxybenzene (HAB) were obtained from Eastman Kodak, the zone-refined PAA from Princeton Organics and p-methoxybenzylidene-p-n-butylaniline (MBBA) from Vari-light Corporation, Cincinnati.

The measurements of T_{1D} were made with a Bruker B-KR 322S pulsed spectrometer using the three pulse Jeener-Broekaert sequence.[6] The temperatures of the sample were maintained by nitrogen gas flow with a gradient across the sample of the order of 0.5°C. Measurements in the smectic-C phase of HOAB were always made after the sample was heated to about 20°C above the smectic-C-to-nematic phase transition ($T_{S\text{-}N}$). The accuracy in T_{1D} measurements is about ±5%.

REVIEW OF THE THEORY

The theory of nuclear spin-lattice relaxation in nematic liquid crystals based on a simplified model of magnetic dipolar interaction between a pair of ortho proton spins on a benzene ring has been discussed by many authors.[7,8,9] The dipolar interaction is modulated both by the short range molecular reorientations and by the collective order fluctuations. The effects of a magnetic field (H) on the order fluctuations have been discussed by deGennes and the Orsay Liquid Cristal Group.[5] Their results were used to derive[8,10] the following expression for spectral density,

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

Where S is the order parameter, K the Frank elastic deformation constant, η the viscosity, ω the Larmor frequency and R is defined as $\Delta\chi H^2/\eta$ where $\Delta\chi$ is the anisotropic part of the diamagnetic susceptibility. Two limiting cases are of interest. When $R \ll \omega$, viz. no magnetic field effects, $J_1(\omega) \propto \omega^{-1/2}$. This has been well verified in T_1 measurements of PAA.[11] In the other extreme $R \gg \omega$, the magnetic field effects on the spin-lattice relaxation can be observed. In this case,

$$J_1(\omega \rightarrow 0) \propto H^{-1} \tag{2}$$

This limiting case may be observed[10] by measuring $T_{1\rho}$, the spin-lattice relaxation time in the rotating frame, at a small rotating magnetic field $H_1(\gamma H_1 \ll R)$

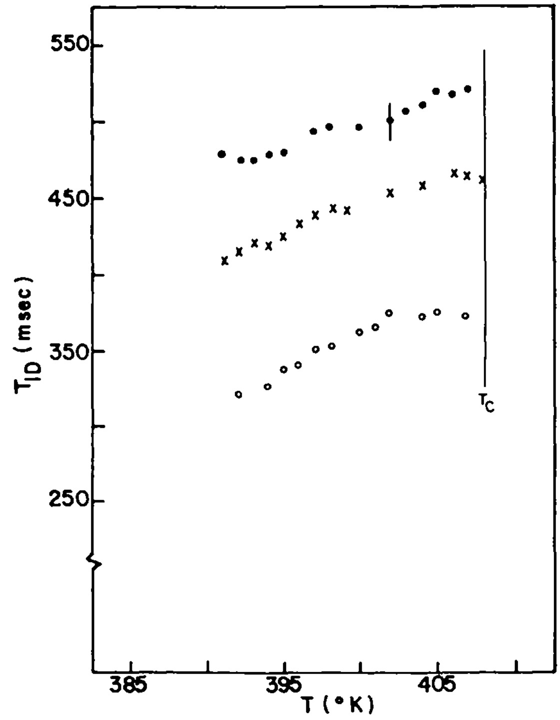

FIGURE 1: The proton dipolar spin relaxation time versus temperature in the nematic phase of PAA. ●, X and ○ denote measurements at 60, 46 and 14 MHz respectively.

while varying the external magnetic field. Since the simple relation $T_{1D}^{-1} \alpha J_1(O)$ is approximately valid, measurements of T_{1D} at various external fields are ideal for detecting any magnetic field effect on the collective order fluctuation modes provided that these modes are the dominant relaxation mechanisms for the dipolar spin system.

RESULT AND DISCUSSION

The measurements of T_{1D} at various Larmor frequencies in the liquid crystals PAA, HAB and HOAB are presented as a function of temperature in figures 1-3 respectively. The above compounds are in a homologous series. T_{1D} was also measured in HAB and HOAB as 211 and 184 msec respectively, at 30 MHz and at a temperature of 390°K.

The clear points (T_C) for PAA, HAB and HOAB are respectively 408, 400 and 397°K. No smectic phase was observed in HAB, while HOAB has a $T_{S\text{-}N}$ at

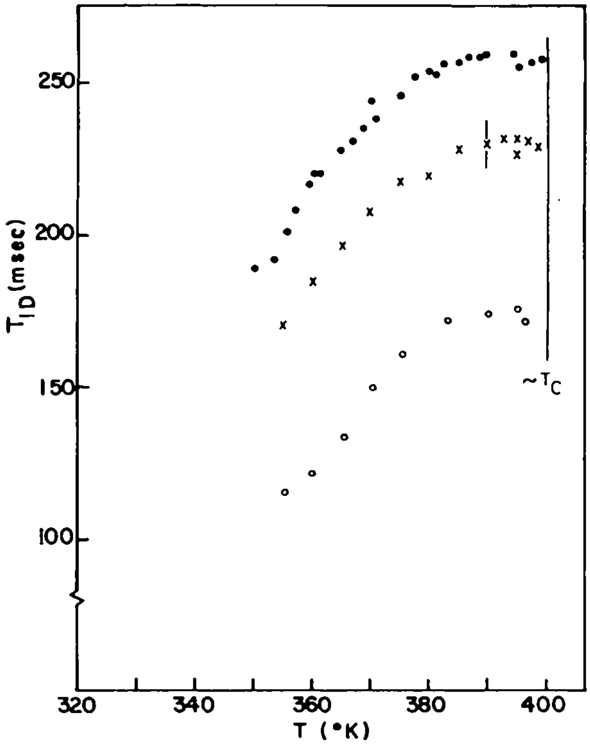

FIGURE 2: The proton dipolar spin relaxation time versus temperature in the nematic phase of HAB. ●, X and O denote measurements at 60, 46 and 14 MHz respectively.

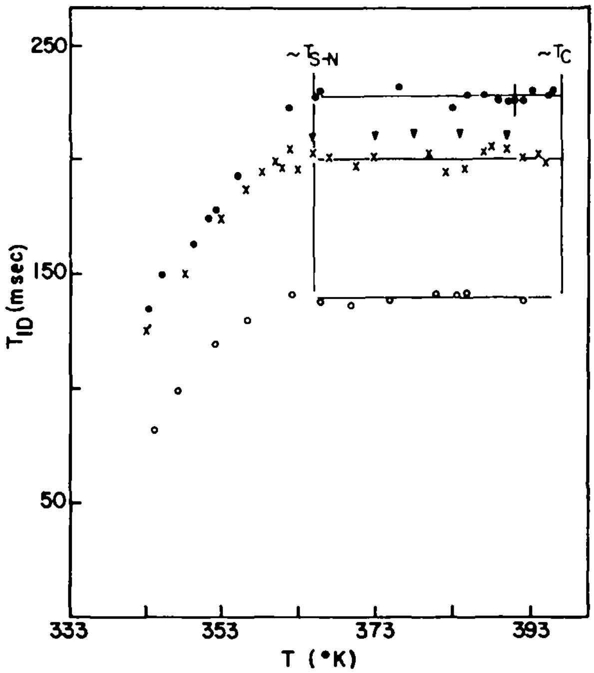

FIGURE 3: The proton dipolar spin relaxation time versus temperature in HOAB. ●, ▼, X and ○ denote measurements at 60, 53, 46 and 14 MHz respectively.

about 365°K. The data for MBBA are shown in figure 4. T_{1D} was also measured at room temperature (298°K) at a few additional Larmor frequencies. Their values are 42, 50 and 56.5 msec at 8, 22 and 30 MHz respectively. At 302°K, T_{1D} is equal to 59 and 64 msec at 23 and 30 MHz respectively. The clear point in our MBBA samples is ~316.5°K.

Temperature dependence

In the nematic phase of the liquid crystals investigated in the present work, T_{1D} was found to be temperature dependent except in HOAB where T_{1D} was constant in agreement with the earlier data.[1] In PAA, T_{1D} depends on temperature weakly (fig. 1) but is not a constant as suggested by sharp et al.[2], while in MBBA the temperature dependence of T_{1D} is rather strong (fig. 4). In HAB (fig. 2), T_{1D} remains constant to about 20° below T_C and then decreases as the solid phase is approached. In all these compounds, T_{1D} values were found to be about four times smaller than their corresponding T_1 values.[1,4,12,13] Except in HOAB, the T_{1D} temperature dependence is similar to T_1. T_{1D} was found to be temperature dependent in the smectic-C phase of HOAB (fig. 3). It may by governed by a thermally activated process, such as "diffusion". In this phase, T_{1D} was also found to be independent of sample rotation in the magnetic field.

Frequency dependence

The frequency dependence of proton T_1 measurements in liquid crystals has been used to infer the dominant mechanism for spin relaxation. Recently, Vilfan et al.[11] have shown by means of a frequency study that the proton T_1 in PAA and in MBBA are respectively controlled by long range order fluctuations and translational diffusion. The diffusion constant deduced by them in the nematic phase of MBBA is, however, an order of magnitude smaller than the value obtained by a direct diffusion measurement.[14] The magnetic field effects on the order fluctuations were studied[10] in MBBA by means $T_{1\rho}$ measurements at a field strength of two to ten kilogauss. The result shows no field effects although there is a definite trend for a higher $T_{1\rho}$ value with higher magnetic field. The above experiments suggest that in MBBA, the orientational order fluctuations

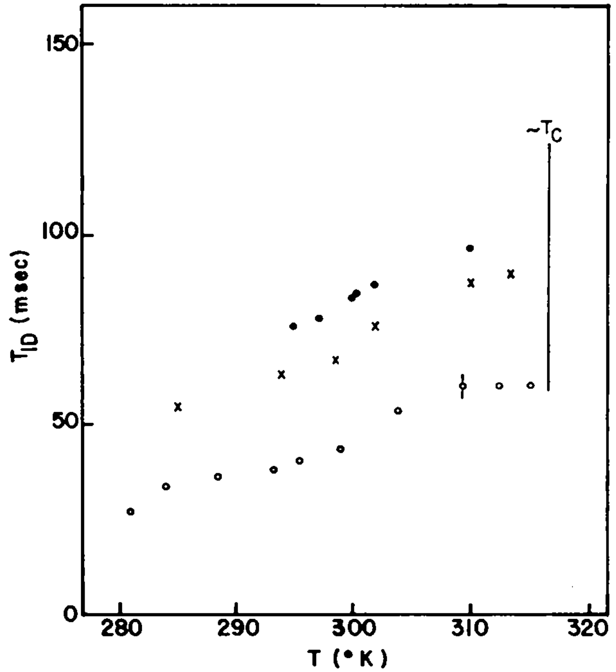

FIGURE 4: The proton dipolar spin relaxation time versus temperature in the nematic phase of MBBA. ●, X and o denote measurements at 60, 46, and 14 MHz respectively.

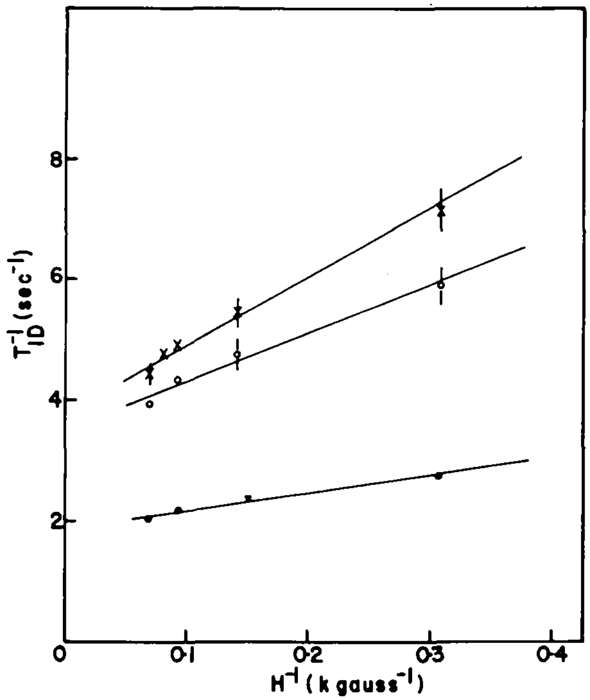

FIGURE 5: The reciprocal of proton dipolar spin relaxation time versus the reciprocal of magnetic field strenght in PAA, HAB and HOAB. ● and ▾ denote respectively our measurements and that of Sharp et al. in PAA at 400°K. ○ denotes measurements in HAB at 390°K and X in the nematic phase of HOAB.

may be more effective in relaxing the proton dipolar spin reservoir than the Zeeman reservoir. In figure 5, a plot of the reciprocal of T_{1D} versus $1/H$ is presented for PAA, HAB and HOAB.[15] It is seen that $1/T_{1D}$ follows the linear relationship of equation (2) in a magnetic field strength between 3 and 14 k gauss. It is interesting to note that for this homologous series, the condition for equation (2) to be valid (i.e. $R \gg \omega$) is satisfied at least down to 3 k gauss. Figure 5 therefore shows that the magnetic field does influence the order fluctuations when relaxing the proton dipolar spin system. It is noted also that the earlier T_{1D} measurements[1] in HOAB are slightly shorter. In the nematic phase of MBBA, the reciprocal of T_{1D} is plotted against $1/H$ at 298 and 302°K as shown in figure 6. The linear dependence between $1/T_{1D}$ and $1/H$ only holds down to a field of 5 k gauss. The deviation below this field strength can be understood by the fact that η in MBBA is about a factor of 15 larger than that of PAA.[16] Hence the condition $(\frac{\Delta\chi H^2}{\eta} \gg \omega)$ is not satisfied at low field. Since $\Delta\chi$ is similar

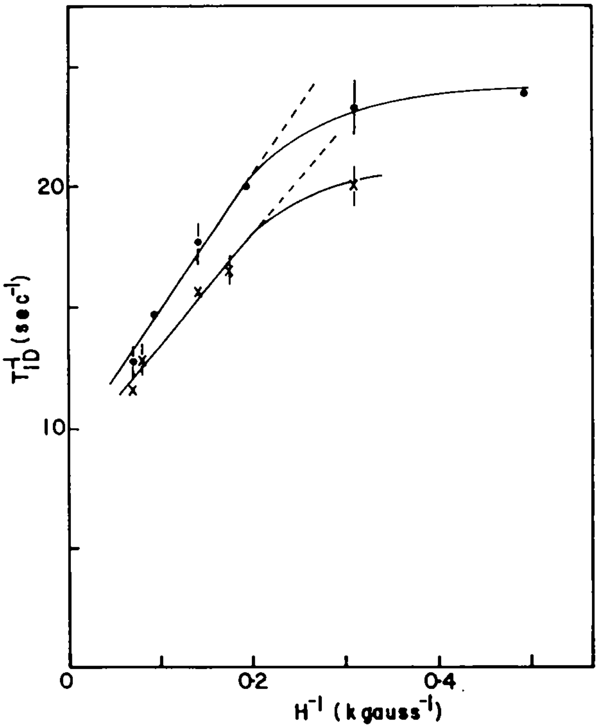

FIGURE 6: The reciprocal of proton dipolar spin relaxation time versus the reciprocal of magnetic field strength in MBBA. X and ● denote measurements at 302°K and 298°K.

for both PAA and MBBA, one would not expect to see any similar devation in PAA until H is below 1.5 k gauss.

The present work indicates that the proton dipolar spin systems in the nematic liquid crystals studied are predominantly relaxed by the orientational order fluctuations. This is identified through the characteristic field dependence of T_{1D}. However, other mechanisms such as the wagging of the end chains or spin diffusion may be needed to account for the magnitude of the dipolar spin relaxation rate. In particular, these are responsible for the intercepts at infinite magnetic field in figure 5 and 6. The fact that T_{1D} does not have an angular dependence in the smectic-C phase of HOAB implies that the relaxation mechanisms are possibly intermolecular processes. It may also be that the molecules in the smectic-C phase have a limited ability to follow the magnetic field.[17] At present, the relaxation mechanisms in the smectic phase of liquid crystals are not as well understood as in the nematic phase.

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