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Proton Spin-Lattice Relaxation in the Nematic Liquid Crystal MBBA†

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Abstract—In the nematic phase of *p*-methoxy benzylidene *p-n*-butylaniline, an increase in the proton spin-lattice relaxation time was observed over a small temperature range above 21 °C. It is proposed that this indicates that additional anisotropic fluctuations, associated with the onset of a biaxial phase, contribute to the proton spin-lattice relaxation in the region of 21 °C. A low frequency collective mode, $\omega_S \sim 50\ \mathrm{sec}^{-1}$, relaxes the dipolar reservoir in the nematic phase. In the isotropic phase at $\omega_L/2\pi = 15$ MHz translation diffusion is the dominant relaxation mechanism.

1. Introduction

An NMR transient study of the liquid crystal *p*-methoxy benzylidene *p-n*-butylaniline,$^{(1)}$ MBBA, which is nematic at room temperature, is reported. In nematic liquid crystals, the relaxation of nuclear spins has been attributed mainly to thermal fluctuations in the orientational order$^{(2-8)}$ and to translational diffusion.$^{(6,9)}$ In a typical liquid crystal, the translational diffusion is fast ($\tau_d \omega_L \ll 1$; τ_d = translational diffusion jump time; ω_L = nuclear Larmor frequency) in both the isotropic and nematic phases. On the other hand, there are several modes of molecular reorientation in the nematic phase. The noncooperative rotational diffusion of individual molecule is certainly slow ($\tau_{\text{tumbling}} > T_2$). However, the short range collective reorientation is fast since it causes some line narrowing.$^{(3)}$ In addition, the long-range collective orientational order fluctuations have a wide frequency spectrum including 'slow' motions. On going to the isotropic phase, there is some persistence

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of the collective modes but the noncooperative rotational diffusion of the molecule becomes fast (i.e., $\tau_{\text{tumbling}} < T_2$).

In several thermotropic materials, short range orientational order effects(6,8,9) influence the spin relaxation above the nematic–isotropic transition temperature; e.g., in the liquid crystal *p*-azoxyanisole (PAA) the proton spins were found(6,9) to relax to some extent by this mechanism even at 15° above T_c. In MBBA, because of a relatively large diffusive relaxation rate, the orientational order fluctuations contribute insignificantly to the nuclear spin relaxation rate in the isotropic phase. An interesting anomaly of the spin relaxation in the laboratory frame was observed in the nematic phase. It is proposed that this anomaly may reflect the development of the biaxial order.

2. Experimental

The liquid crystal MBBA sample of commercial origin (Vari-Light Corporation, Cincinnati) was degassed in a vacuum by the freeze-melt method. Recent measurements(10) of proton T_1 at 33 °C gave lower values than the ones reported in this paper. This difference may be due to a small amount of water in sample.

Proton T_1 measurements (accuracy is ± 5% or better) were performed with a 15 MHz coherent spectrometer while proton $T_{1\rho}$ measurements were carried out with a 30 MHz coherent spectrometer. The temperature was kept within ± 0.1 °C and the temperature gradient across the sample was about 0.2 °C/cm.

3. Results and Discussion

The nematic–isotropic transition is first order, but weak. Short range orientational order effects above T_c were observed in PAA(6,8,9) and MBBA.(11) Nuclear spin relaxation by short range order fluctuations in the isotropic phase of liquid crystals has been expressed in terms of the fluctuations in the local anisotropy.(8) The free energy(11,12,13) in the isotropic phase has a form corresponding to a second-order transition at T^*, plus terms which impose a first order phase transition at slightly higher temperature, T_c. Landau's mean field theory(14) of second order phase transition was, therefore, used in a temperature range not too close to T_c, to give the temperature dependence of the coherence length ξ which is a measure of local order in the isotropic phase. At T_c, ξ is roughly ten times the length of the molecule,(15) i.e., ~200 Å. The spectral density in the short correlation time limit is given by

$$J(\omega) \propto \xi \propto (T - T^*)^{-1/2}.$$

Thus, in the isotropic phase T_1 and T_2 should be proportional to $(T - T^*)^{1/2}$ in the region where ξ is non-zero, if the resonance frequency ω_L is small compared to the frequency of the fluctuations in the local anisotropy.(8)

The proton T_1 data were taken in MBBA at $\omega_L/2\pi = 15$ MHz as a function of temperature (Fig. 1). The nematic-isotropic transition temperature, T_c, of our sample was ~46.5 °C and no discontinuity in the value of T_1 at T_c was observed. In the isotropic phase, the experimental T_1 values below $T \sim 70$ °C show the temperature dependence $(T - T^*)^{1/2}$ with $T^* = T_c - 1$ °C except in the region below $T = T_c + 10$ °C. This plot is obviously fortuitous, as the frequency of fluctuations $(1/\tau)$ in the local anisotropy in MBBA near the T_c is only about 1 MHz.(11) This is much smaller than the frequency of observation ω_L. In the present case $\omega_L \gg 1/\tau$, the orientational modes have the spectral density similar to that in the nematic phase. Hence T_1 has a frequency dependence but does not depend critically on temperature. However, because of the low T_c value in MBBA, even near the clear point the translational diffusion is a very effective relaxation mechanism in the isotropic phase: T_1 values within the entire studied isotropic liquid phase indicate a thermally activated relaxation process with an apparent activation energy of 4.6 Kcal/mole (Fig. 2). Although the value is low compared to 8 Kcal/mole in PAA, it suggests that nuclear spins are relaxed predominantly by translational diffusion. To validate this assertion, measurements of self-diffusion constants in this phase should be made and the activation energy of diffusion compared with the above value.

The T_1 of the benzene-ring protons in nematic liquid crystals (e.g., PAA) is caused largely by the modulation of the dipolar interaction by orientational order fluctuations. The expression for T_1 is given by(3,4)

$$\frac{1}{T_1} = \omega_D{}^2 \frac{S^2}{K} \frac{kT}{(K/\eta + D)^{1/2}} \omega_L^{-1/2} + B(T)$$

where ω_D is a measure for the strength of the dipolar interaction. The

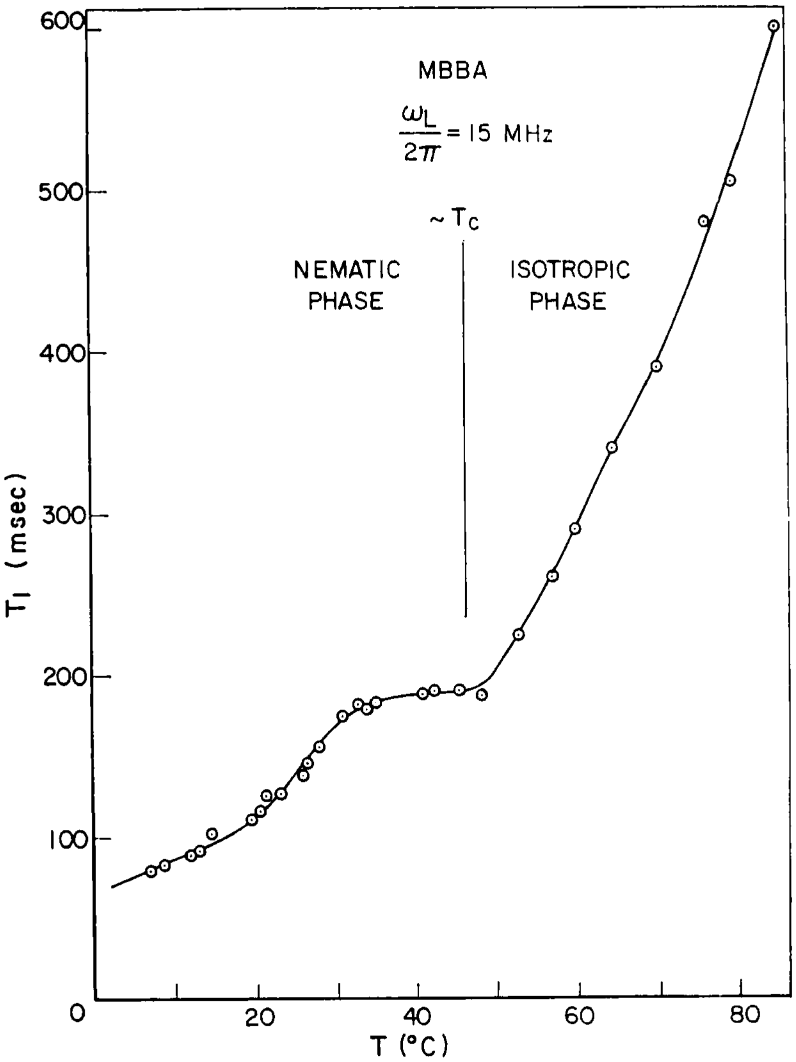

Figure 1. MBBA proton spin-lattice relaxation time T_1 vs. temperature at $\omega_L/2\pi = 15$ MHz.

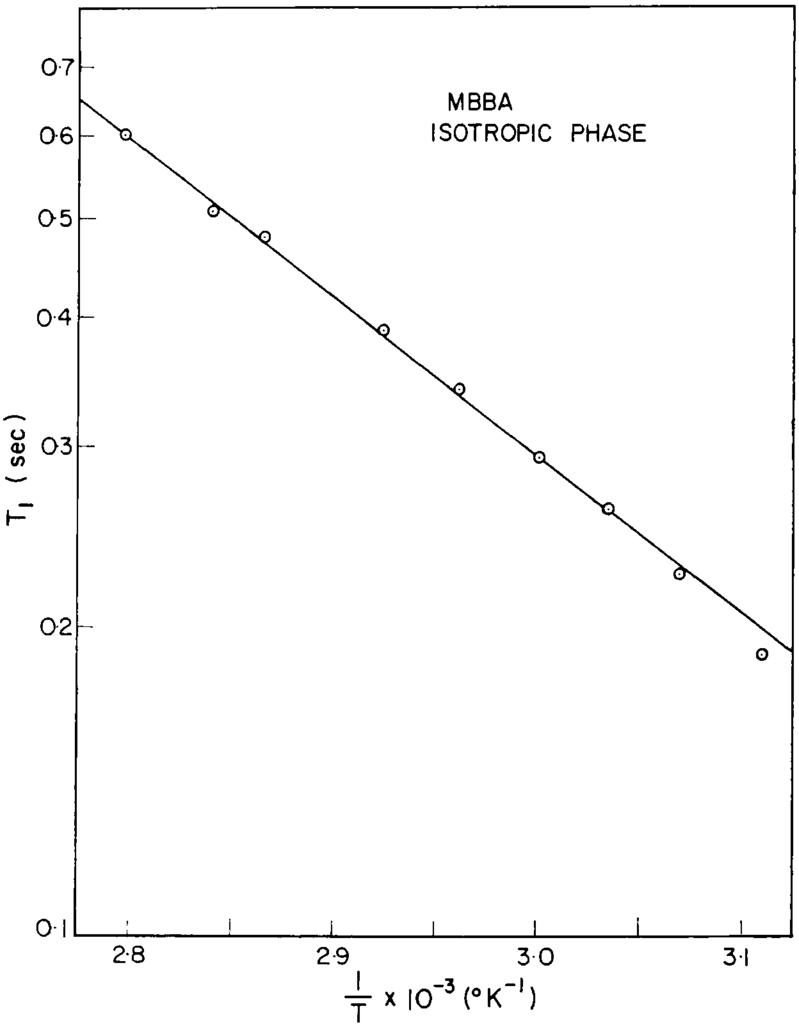

Figure 2. Semilogarithmic plot of proton T_1 vs. inverse temperature in the isotropic phase of MBBA at $\omega_L/2\pi = 15$ MHz.

order parameter is $S = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle$; θ is the angle between the molecular axis and the optical axis. The brackets indicate the time average, T is the absolute temperature, k the Boltzmann constant, ω_L the Larmor frequency, D the diffusion constant, K the Frank elastic deformation constant, and η the viscosity. $B(T)$ is the frequency independent contribution.(4)

The orientational order fluctuation could be identified by its characteristic frequency dependence $\omega_L^{-1/2}$. This relaxation rate, R (ordered), is estimated in MBBA from the order fluctuation rate in PAA using the above $(T_1)^{-1}$ expression and the fact that η for MBBA is about 15 times that of PAA.(16) The magnitude is found to be only about 12% of the observed total relaxation rate just above T_c in MBBA. This makes the analysis in MBBA difficult in the isotropic phase. Even below T_c, this rate is estimated to contribute only some 40% of the observed rate.

In the nematic phase, T_1 increases with temperature. The temperature dependence of T_1 is weak except near 21 °C, where T_1 increases considerably. The weak temperature dependence of T_1 is as expected.(3,4,7) However, the increase in T_1 at ~21 °C, indicates that a change in the dominant spin relaxation mechanism has occurred. In addition, the EPR experiments(17) in MBBA show that there is a definite discontinuity in the effective order parameter at ~22 °C, as the molecular rotation passes from weakly to strongly hindered motion. This change may be explained by Freiser's proposal(18) of a uniaxial–biaxial phase transition. In addition to the long range orientational order fluctuations, one should observe the onset of short range local fluctuations near 21 °C. Such short range order fluctuations are expected to arise from the fluctuation of the second order parameter, describing the biaxial phase at lower temperature. This suggestion is based on the recent demonstration by Haas(19) that MBBA is a biaxial liquid crystal. The analysis of T_1 data is, however, prevented by the lack of knowledge of the translational diffusion in MBBA.

The reciprocal of $T_{1\rho}$ is plotted vs. H_1 at $T = 40$ °C and 22.5 °C, as shown in Fig. 3. For $H_{1\rho} > 9$G, the rate $T_{1\rho}^{-1}$ becomes H_1 independent. Thus $T_{1\rho}^{-1} = R_1 + R_2$, where R_1 and R_2 are the field independent and field dependent components respectively. The rate R_1 represents the contributions from orientational order fluctuations and translational diffusion in their white spectral region. This rate is in the weak collision limit; i.e., $\tau_c \ll T_2$. A slow collective mode,(20) which relaxes the dipolar reservoir, generates the rate R_2. This relaxation is almost in the strong collision limits; i.e., $\tau_c > T_2$ when $H_1 \sim H_L$. The inverse of R_2 is $T'_{1\rho}$, which is equal to the dipolar relaxation time at $H_1 = H_L$.

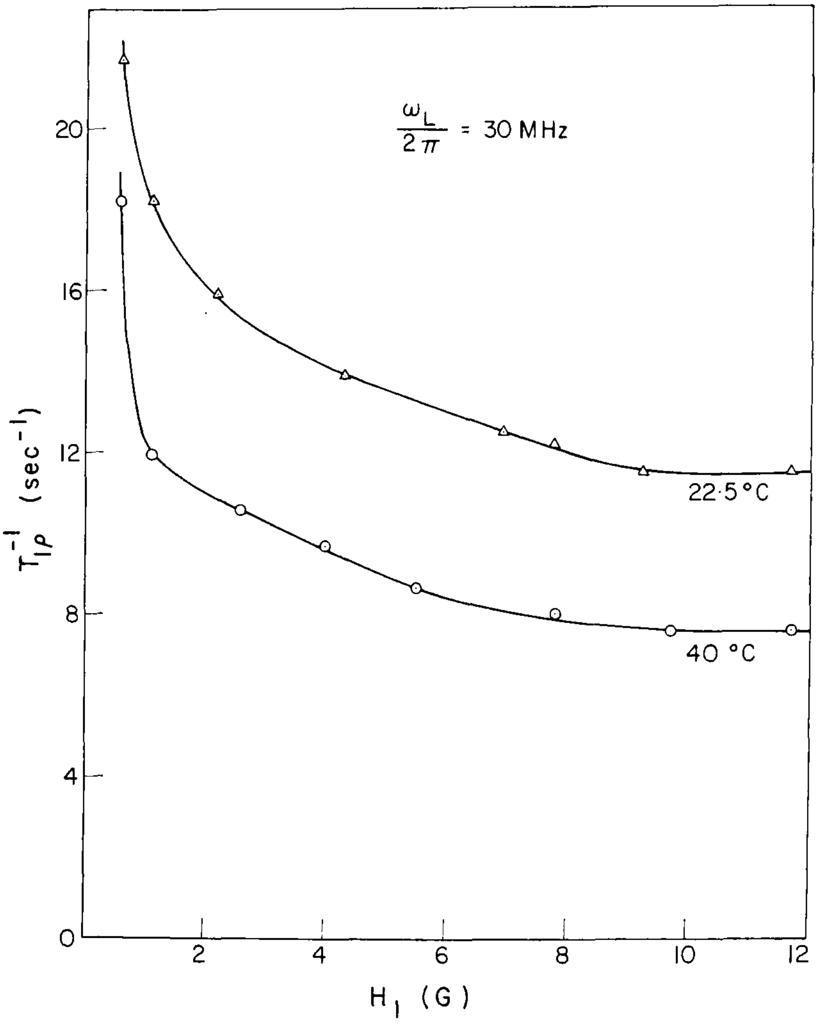

Figure 3. The reciprocal of proton $T_{1\rho}$ vs. the spin-locking field H_1 at $\omega_L/2\pi = 30$ MHz.

In Fig. 4, $T'_{1\rho}$ is plotted against $H_1{}^2$ for both temperatures.(21) At 40 °C, $H_L \sim 1.7$ G, while at 22.5 °C, $H_L \sim 2.3$ G. Considering that only a very small fraction of the local field is changed,(21) the correlation time for the slow collective mode is estimated from Fig. 4, at $H_1 \sim H_L$, to be 20 msec.

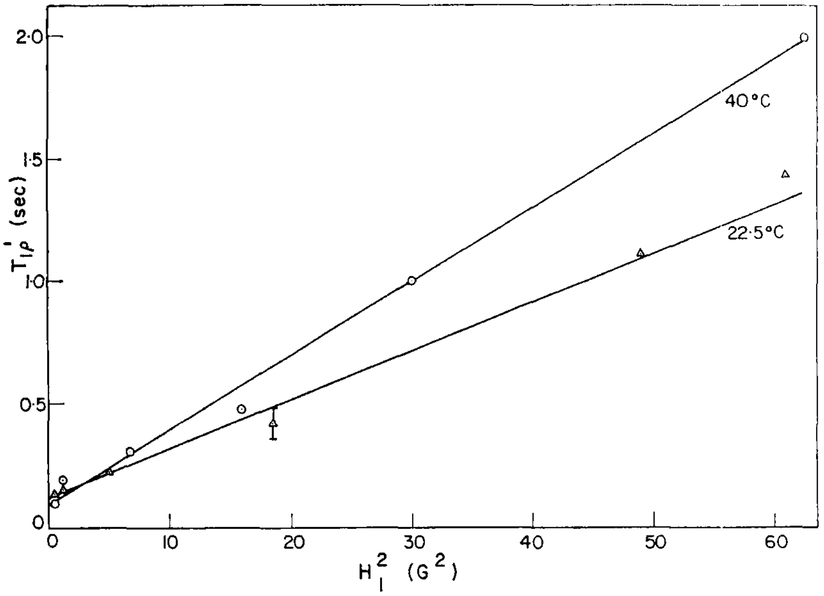

Figure 4. Proton $T'_{1\rho}$ vs. $H_1{}^2$, the square of the spin-locking field (see text).

4. Conclusions

It is proposed that the increase in proton T'_1 values near 21 °C, perceived in the nematic phase of MBBA, indicates that additional anisotropic fluctuations, associated with the onset of a biaxial phase, are contributing to the proton spin relaxation in the region of 21 °C. As noted in the liquid crystal PAA, a low frequency mode, with $\omega_S \sim 50\,\text{sec}^{-1}$, relaxes the dipolar reservoir in the nematic phase of MBBA. At 15 MHz in the isotropic phase the translational diffusion is the predominant relaxation mechanism. Since in the structurally similar liquid crystal PAA just above T_c the hydrodynamic term $A\omega_L^{1/2}$ is(9) about $0.1\,\text{sec}^{-1}$, in MBBA the diffusion relaxation rate would have to be 0.4 sec^{-1} or less near T_c for any study of the orientational order fluctuations in the isotropic phase.

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