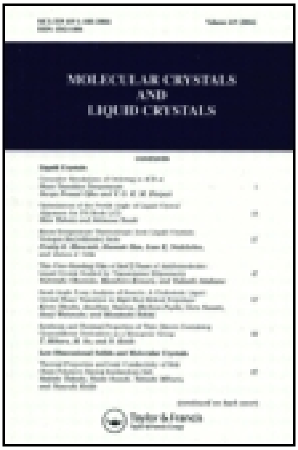

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Proton Spin Relaxation in a Reentrant Nematic Liquid Crystal Mixture

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PROTON SPIN RELAXATION IN A REENTRANT NEMATIC LIQUID CRYSTAL MIXTURE

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ABSTRACT

Proton spin-lattice relaxation time was measured at the nematic-smectic A and smectic A-reentrant nematic transitions in four different binary mixtures of 8OCB and 6OCB. An asymmetric behavior of T_1 in the nematic phase above and below the smectic A phase was found.

I. INTRODUCTION

Cladis[1,2] was first to observe the nematic (N)-smectic A(S_A)-reentrant nematic (RN) phase sequence in binary mixtures of certain bilayer smectics at atmospheric pressure and in pure smectic liquid crystals at high pressure. The low temperature RN is called "reentrant" to distinguish it from the high temperature nematic phase, though they appear to be optically identical.[2] More recently the reentrant phenomenon is observed in pure compounds at atmospheric pressure.[3,4]

A phenomenological Landau theory has been proposed[5] to describe the reentrant behavior in liquid crystals. This involves an additional free energy term which couples density and composition of a binary mixture to the smectic order parameter ψ. According to the above Landau theory, there is no essential difference between the high and low temperature nematic phases. However there remains some uncertainty in the nature of RN phase, in particular its dynamic properties. Also little is known about the S_A-RN transition.

Nuclear spin relaxation is useful to study dynamic properties of liquid crystals.[6] The relaxation mechanisms in nematic liquid crystals are now well understood. Generally speaking proton T_1 in low viscosity nematics (e.g. p-azoxyanisole) is relatively insensitive to temperature, while in high viscosity nematics (e.g. p-methoxybenzylidene-p-n-butylaniline) it increases with increasing temperature. In the former nematics, the dominant relaxation mechanism is orientational order director fluctuations (ODF) which are characteristic to liquid crystals, whereas in the latter molecular self diffusion appears to be a dominant feature giving the observed temperature dependence. Here we present the results of a proton spin-lattice relaxation study of the N-S_A and S_A-RN transitions in binary mixtures of octyloxycyanobiphenyl (8OCB) and hexyloxycyanobiphenyl (6OCB). 6OCB has a nematic phase but no stable S_A phase. Because of the very large dipole associated with the nitrile bond, the alkyloxycyanobiphenyl compounds form antiparallel associated pairs[2] in mesophases. According to Cladis[2,7], mixtures with more than 22 wt. % but less than 29 wt. % 6OCB show the following transitions with decreasing temperature: isotropic (I), N, S_A, RN, solid. We have studied four different mixtures in this concentration range.

II. EXPERIMENTAL

Proton spin-lattice relaxation time (T_1) was measured as a function of temperature at ω_L = 30 MHz in four different 8OCB-6OCB mixtures, three of which exhibit reentrant nematic phase. All T_1 measurements were made by cooling sample from the isotropic phase. The pure liquid crystals were obtained from BDH Chemicals, Ltd. and used without further purification. The compositions of the mixtures were determined to better than ± 0.5 wt. %. As shown in figure 1, the transition temperatures of our mixtures determined by NMR agree well with the values reported by Cladis et al. The proton FID signal was used to distinguish between S_A and N (or RN) phases since signal in S_A phase narrowed as sample was rotated by the magic angle of 54.7°. All samples were degassed by the freeze-pump-thaw method and sealed in 7.5 mm o.d. NMR tube under vacuum.

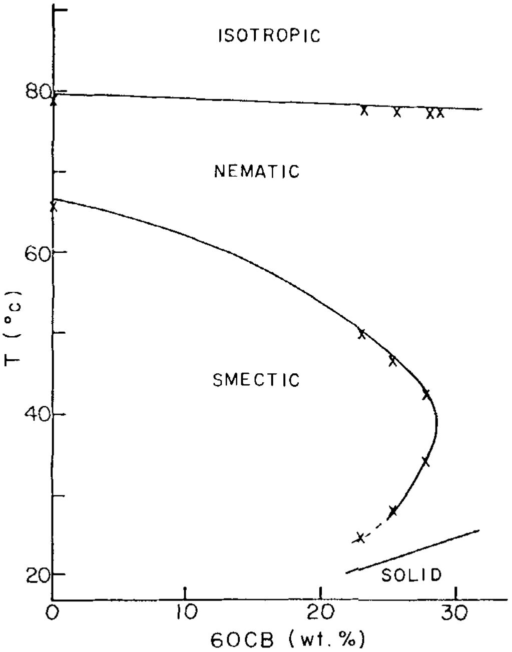

FIGURE 1 Phase diagram of binary mixture of 6OCB in 8OCB. Solid phase lines are from reference 7.

T_1 was measured using 180°-τ-90° sequence with a home-built variable frequency coherent pulsed NMR spectrometer equipped with a BNC-12 (Nicolet) FFT accessories. The main components are a Rockland Model 5600 synthesizer, an Amplifier Research Model 200L power amplifier and an Arenberg Model WA-600-E-DC amplifier and preamp. The NMR probe is placed in an oven constructed by using a copper cylinder wrapped with heating coil. The temperature of the oven is controlled with a Thermal Electric Model 32422 temperature controller. The sample temperature was monitored with a copper-constantan thermocouple and the temperature gradient across the sample was better than 0.5°C.

III. RESULTS AND DISCUSSION

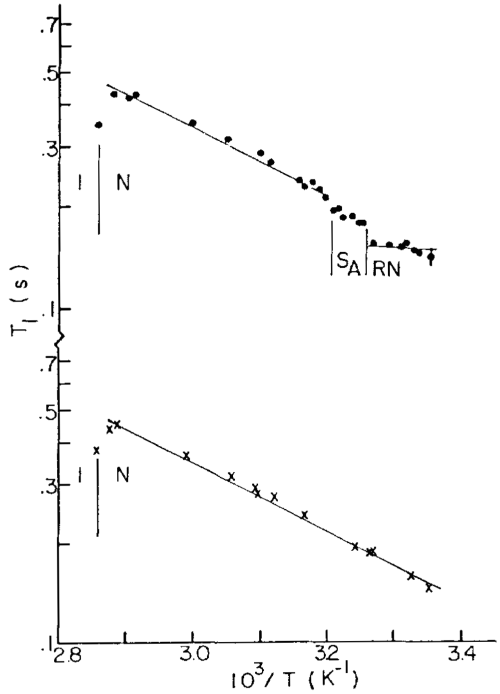

FIGURE 2 Plot of proton T_1 versus the reciprocal temperature. X and ● denote data for ~28.4 wt. % and for 27.7 wt. % respectively.

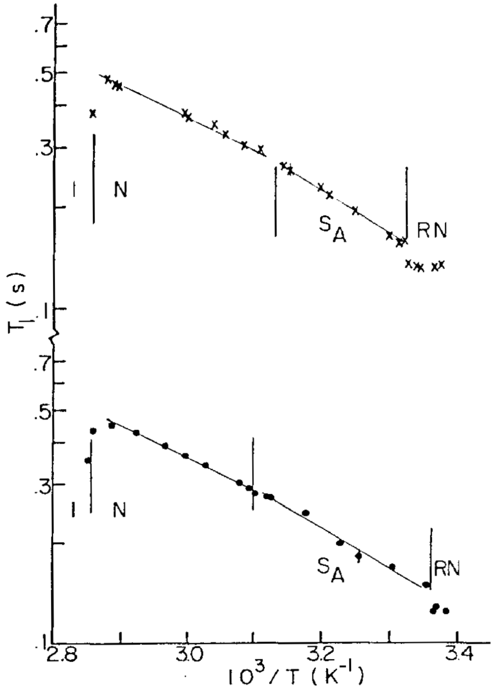

FIGURE 3 Plot of proton T_1 versus the reciprocal temperature. X and ● denote data for 25.2 wt. % and for 22.9 wt. % respectively.

Plot of proton T_1 versus the reciprocal of temperature is shown for ~28.4 and 27.7 wt. % of 6OCB mixtures in figure 2 and for 25.2 and 22.9 wt. % of 6OCB mixtures in figure 3. The value of T_1 and its temperature dependence in the nematic phase of our mixtures appear to be indifferent to the relative concentration of 6OCB and 8OCB, though the temperature range of the high temperature nematic increases with increasing 6OCB concentration. For the ~28.4 wt. % mixture, no S_A phase is detected and proton T_1 is thermally activated (see figure 2) over the nematic range of ~23° to 77°C with an activation energy $E_a = 4.7 \pm 0.2$ k cal/mole. The corresponding E_a for the 27.7 wt. %, 25.2 wt. % and 22.9 wt. % of 6OCB mixtures are equal to 4.7 ± 0.2, 4.5 ± 0.2 and 4.6 ± 0.2 k cal/mole, respectively. We think that the thermal activation process is molecular self diffusion which modulates the intermolecular dipolar interactions among protons. This relaxation mechanism is expected to be effective even in the S_A phase. Thus it is not surprising that no observable discontinuity in T_1 is seen at the N-S_A transition in three of our mixtures. However, the activation energy E_a in the S_A phase is slightly higher than that of nematic phase, i.e. $E_a \approx 5.6 \pm 0.4$ k cal/mole. There is a small but discontinuous jump in T_1 at the S_A-RN transition and in the limited range of RN phase, T_1 is independent of temperature within experiment error in our three mixtures. It is noted that the value of T_1 in the RN phase decreases with decreasing concentration of 6OCB. This concentration dependence of T_1 value is probably due to the decrease in the S_A-RN transition temperature. The fact that the temperature dependence of proton T_1 differs in the nematic phase above and below the S_A phase seems to indicate the dynamics of the high temperature nematic and reentrant nematic phases are different. Further experiments such as T_1 frequency dependence study may shed light on the dynamical properties of reentrant nematic phase. It would seem that the molecular self diffusion, an effective relaxation mechanism in the high temperature nematic and smectic A phases of the binary mixtures of 8OCB/6OCB, becomes too slow to be effective in the reentrant nematic phase. Thus other relaxation mechanisms such as ODF may account for the observed temperature independent T_1 in this phase.

To conclude, we report here difference in proton T_1 at the N-S_A and the S_A-RN transitions. The observed asymmetric behavior of T_1 about the S_A phase may be due to quantitative difference in the short range order in the two nematic phases.

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REFERENCES

1. P.E. Cladis, Phys. Rev. Lett., 35, 48 (1975); P.E. Cladis, R.K. Bogardus, W.D. Daniels and G.N. Taylor, Phys. Rev. Lett., 39, 720 (1977)
2. D. Guillon, P.E. Cladis and J. Stamatoff, Phys. Rev. Lett., 41, 1598 (1978)
3. F. Hardouin, G. Sigaud, M.F. Archard and H. Gasparoux, Solid State Commun., 30, 265 (1979); N.H. Tinh and H. Gasparoux, Mol. Cryst. Liq. Cryst. Lett., 49, 287 (1979)
4. D. Demus, G. Pelzl, A. Wiegeleben and W. Weissflog, Mol. Cryst. Liq. Cryst. Lett., 56, 289 (1980); 295 (1980)
5. P.S. Pershan and J. Prost, J. Phys. (Paris), 40, L-27 (1979)
6. C.G. Wade, Annu. Rev. Phys. Chem., 28, 47 (1977); V. Graf, F. Noack and M. Stohrer, Z. Naturforsch Teil, A 32, 61 (1977)
7. F.R. Bouchet and P.E. Cladis, Mol. Cryst. Liq. Cryst. Lett., (in press)