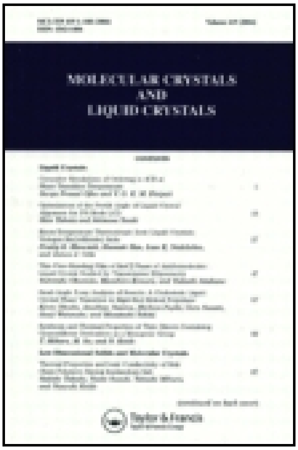

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Molecular Dynamics of p-Brome-p-n-Hexyloxybenzylidene Aniline in the Smectic B Phase by Proton NMR Relaxation

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Molecular Dynamics of p-Brome-p-n-Hexyloxybenzylidene Aniline in the Smectic B Phase by Proton NMR Relaxation

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The dynamics of a smectic B phase is studied for the p-brome-p-n-hexyloxybenzylidene aniline (6Br) by the proton NMR technique. The proton spin lattice relaxation time has been measured as a function of frequency and as a function of temperature over the whole mesomorphic phases and in the isotropic phase up to 14 C above the clearing point. The relaxation measurements for the smectic B phase are discussed in terms of potential contributions of various molecular motions, but translational self-diffusion and rotations/reorientions explain well the relaxation. In the high frequency limit the relaxation is dominated by rotations/reorientations while the translational self diffusion is dominant in the low frequency region. The results reflect the particular distribution of asymmetric molecules in the smectic layers.

Keywords: molecular dynamics, smectic B, NMR relaxation

I. INTRODUCTION

In the smectic B phases of liquid crystals only a restricted number of papers reporting studies of molecular dynamics by Nuclear Magnetic Resonance have been published so far.[7,12]

Here we give new results obtained with a liquid crystal of asymmetric molecules. Systematic measurements of the proton spin lattice relaxation time T_1 were performed as a function of temperature and Larmor frequency in the smectic B, smectic A and isotropic phases of p-brome-p-n-hexyloxybenzylidene aniline (6Br), but the discussion is concentrated on the data relative to the smectic B phase. In section

2 we mention the techniques used in this work and we present the experimental data. In section 3 we analyse the experimental data, relative to the S_B phase, in terms of different mechanisms which are expected to contribute to the relaxation namely translational self-diffusion, rotations/reorientations and order director fluctuations, and we contrast the experimental data to those theoretical models proposed for the nuclear spin lattice relaxation. The results so obtained are discussed in section 4.

II. EXPERIMENTAL TECHNIQUES AND EXPERIMENTAL DATA

The synthesis of p-brome-p-n-hexyloxybenzylidene aniline (6Br) was described in Reference 1. Its molecular structure is given in Figure 1.

After purification, the sample (0.5 cm^3) used in our NMR experiment was degassed and sealed in an evacuated glass tube (Ø = 10 mm). The degassing pressure was less than 10^{-4} mbar. This compound shows enantiotropic smectic A and smectic B phases with transition temperatures given by:

$$K \xrightarrow{74\ \mathrm{C}} S_B \xleftrightarrow{102\ \mathrm{C}} S_A \xleftrightarrow{105.5\ \mathrm{C}} I$$

Measurements of the spin lattice relaxation time were performed at seven different frequencies between 8.2 and 84 MHz. For each frequency the temperature was varied over the whole mesomorphic phase and at least up to 10 C above the clearing point. T_1 was measured by the $\pi - \tau - \pi/2$ pulse sequence with a Bruker SXP/4-100 MHz spectrometer. The temperature of the sample was controlled to within ± 0.3 C and the estimated error in the value of T was less than 1 C.

Figure 2 displays the experimental results of T_1 as a function of the temperature for two frequencies of work. The results obtained at five other frequencies are omitted in Figure 2 for the sake of clarity, but they partially reappear in Figures 3 and 4 where we show the

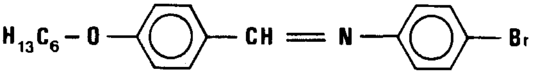

FIGURE 1 Molecular structure of 6Br.

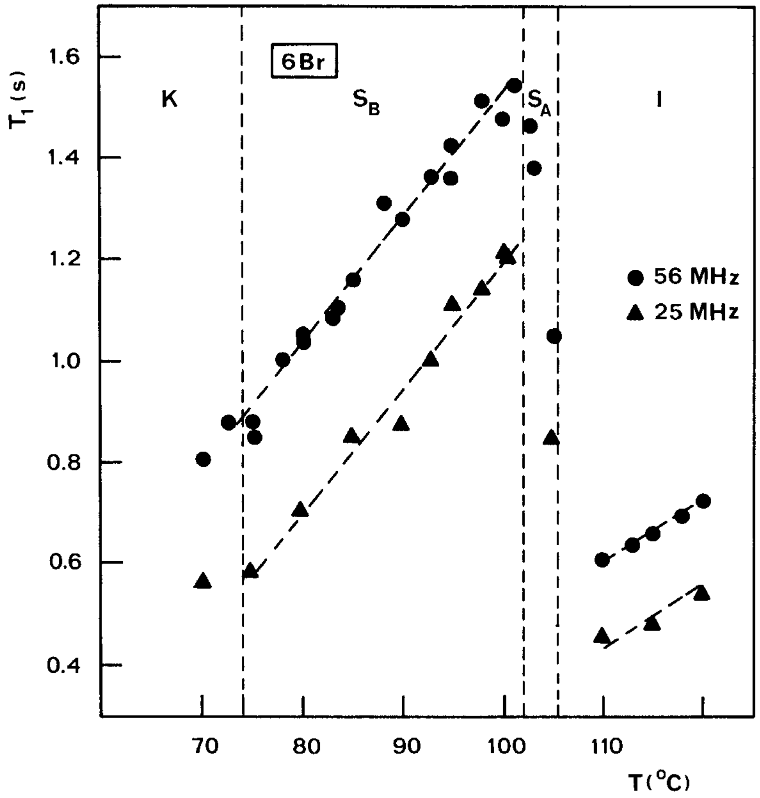

FIGURE 2 Temperature dependence of the proton T_1 in 6Br from 120 to 70 C at 25 and 56 MHz.

frequency dependence of $1/T_1$ at two given temperatures in the S_B phase. These figures also show the contributions of different mechanisms to the overall relaxation which were found as explained in section 3 of this paper.

III. ANALYSIS OF THE DATA RELATIVE TO THE SMECTIC B PHASE

In the smectic B phase the data were analysed in terms of three mechanisms of relaxation, namely translational self diffusion, rotations/reorientations and order director fluctuations.

To describe self diffusion we use the Zumer and Vilfan theory[12] for S_B phases:

$$\left(\frac{1}{T_1}\right)_{S_D} = \alpha_{ef}\, P_1\, (\omega\tau_\perp,\ D_\perp/D_\parallel,\ \ell/d,\ a/d,\ \Delta) \qquad (1)$$

where

$$\alpha_{ef} = \frac{9}{8}\gamma^4\hbar^2\, n/d^3{}_{ef}$$

In expression (1) $\tau_\perp$ is the mean time between jumps within layers, ω is the Larmor frequency, $D_\perp$ and $D_\parallel$ are the diffusion coefficients, ℓ the molecular length, d the fundamental distance in the hexagonal lattice, a the distance of closest approach of nuclei belonging to molecules of adjacent layers, Δ the angle between the static magnetic field and the normal to the smectic layers, P_1 is a complex function of the described terms, γ is the proton giromagnetic ratio, h is the Planck's constant, n is the density of spins and d_{ef} is the effective distance between molecules within the smectic layers taking in account fast local positional fluctuations[12,15] and also in our case the particular distribution of asymmetric molecules in the smectic layers.[2] In the P_1 function we impose values with physical meaning to the described quotients ($D_\perp/D_\parallel = 2$,[14] $\ell/d = 5$, $a/d = 0{,}5$ with $d = 5$ Å) [2] and we admit the polycrystalinity of the sample due to the detected low orientation in the magnetic field.

The rotations of molecules around his long molecular axes, nearly isotropic motions of aliphatic chains and also orientational fluctuations of the long molecular axis, are described by super-position of Lorentzians but in our region of frequencies these contributions are reduced to constant terms only dependent on temperature:[6,7,13]

$$\left(\frac{1}{T_1}\right)_R = A \qquad (2)$$

The possibility of order director fluctuations could play an important role in the relaxation in ordered smectic phases is contradicted by our results. In fact if we fit the experimental data with the superposition of expressions (1), (2) and with the classical contribution B $\omega^{-1/2}$ due to order director fluctuation for different temperatures with α_{ef}, A and B as free parameters and varying $\tau_\perp$ between possible

TABLE I

Parameters associated to the fits represented in Figures 3 and 4

T(C)	n(spins/cm^3)	$\tau_\perp(s)$	$D_\perp$(cm^2 s^{-1})	$A(s^{-1})$	$\alpha_{ef}(s^{-2})$
95	4.49×10^{22}	7.0×10^{-9}	8.9×10^{-8}	0.55	3.95×10^7
85	4.47×10^{22}	1.5×10^{-8}	4.2×10^{-8}	0.77	4.00×10^7

values for a S_B phase[14] we find that only a restricted number of fits has coherence and physical meaning and for those fits the contribution B $\omega^{-1/2}$ is negligible in our domain of frequencies.

In those circumstances we fit the data only with the two first described contributions:

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{S_D} + A \tag{3}$$

As an example in table I the parameters associated with two of the best and coherent fits obtained at T = 95 C and T = 85 C are described. These fits are represented in Figures 3 and 4.

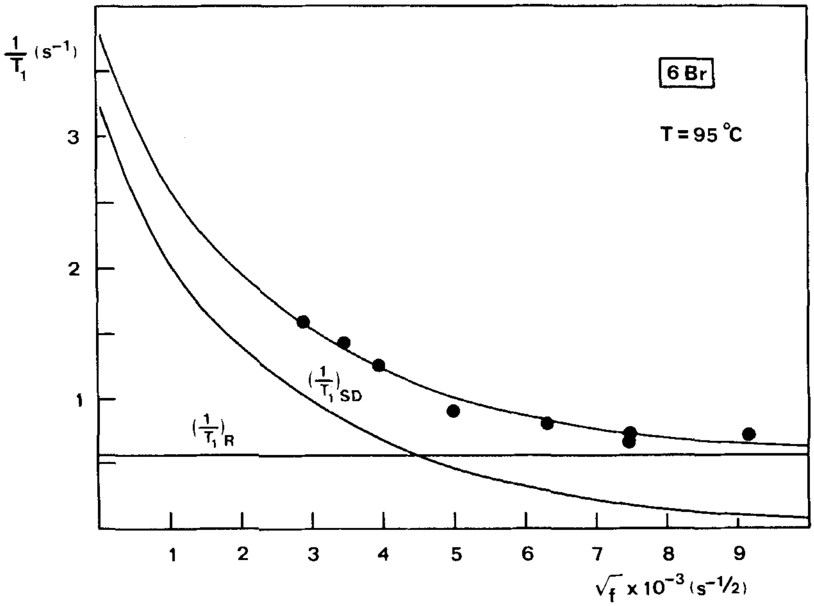

FIGURE 3 Frequency dependence of T_1^{-1} in the smectic B phase of 6Br at T = 95 C.

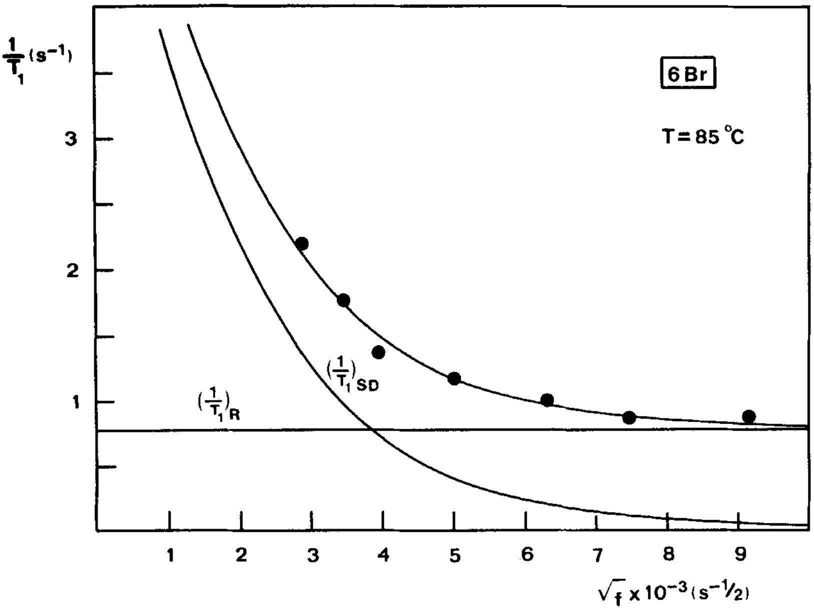

FIGURE 4 Frequency dependence of T_1^{-1} in the smectic B phase of 6Br at T = 85 C.

IV. DISCUSSION OF THE RESULTS AND CONCLUSION

We do not know results of direct measurements of the diffusion coefficients in the smectic B phase of 6Br, however the values of $D_\perp$ obtained from the fits represented in Figures 3 and 4 are reasonable for a smectic B phase.[14] The values of α_{ef} obtained in the best fits, for different temperatures, are similar but they are low ($d_{ef} \simeq$ 8,9 Å). These values must reflect the particular distribution of asymmetric molecules in the smectic layers,[2] only with the aromatic cores arranged in a monomolecular layer and with the aliphatic chains melted on each side of the aromatic cores. This particular distribution must also reduce the importance of translational self diffusion. Similar results of α_{ef} were obtained[16] with other similar compounds (6Cl, 6I, 6F) that exhibits the same molecular disposition in the smectic layers; however α_{ef} is strongly increased[17] for other compounds[3] that exhibit a different molecular disposition in the smectic layers.

The obtained values of $(1/T_1)_R$ are in agreement with other published results for ordered smectic phases.[6,7,8,13] This contribution is thermally activated with an activation energy of 5.6 kcal/mol. Clearly this contribution is associated to rotations around the long molecular axes, nearly isotropic motions of chains due to his disposition with a great number of possible conformations,[2] and also orientational fluctuations of the long molecular axes[15] in spite of the small amplitude of these motions. Our estimation gives for the correlation time of these motions values with physical meaning of the order 10^{-11}s.

In conclusion our results confirm that in the ordered smectic phases order director fluctuations are not an important mechanism of relaxation. In the smectic B phase of 6Br the relaxation is very well explained in terms of translational self diffusion and rotations/reorientations. In the high frequency limit the relaxation is dominated by rotations/reorientations while the self diffusion is dominant in the low frequency region.

Acknowledgments

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