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Study of internal ring rotation and molecular reorientation in the liquid crystal 5O.7 by deuterium N.M.R. spectroscopy

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The spectral densities of motion were determined by deuterium N.M.R. relaxation measurements in the nematic, smectic A and smectic C phases of 4-*n*-pentyloxybenzylidene-d_1-4′-heptylaniline and 4-*n*-pentyloxybenzylidene-4′-heptylaniline-2,3,5,6-d_4. By examining two atomic sites on a 5O.7 molecule, we were able to gain information on the reorientation motion and internal rotation of the aniline ring. It was also found that director fluctuations make some contribution to the spectral density $J_1(\omega)$. We use the superimposed rotations model to account for the internal ring motion and the small step rotational diffusion model for the molecular reorientation. The derived rotational diffusion constants for the spinning and tumbling motions appear to give physically plausible activation energies in the mesophases of 5O.7.

1. Introduction

There are various molecular motions in liquid crystals that can be conveniently studied by means of nuclear spin relaxation [1]. For example, deuteron spin ($I = 1$) may be used to probe molecular spinning and tumbling motions, as well as director fluctuations [2] through the modulations of its intramolecular nuclear quadrupole interaction. In the case of a spin being located on a flexible chain of a mesogen, internal segmental motions due to rotation about each C–C bond must also be considered. Motional models are needed to account for the contributions of different types of motion to the deuterium spin relaxation rates. For instance, the small step rotational diffusional model of Nordio *et al.* [3] has been proven by several experimental techniques [4–6] to be useful in describing reorientations of mesogenic molecules in an ordering pseudo-potential. In this model, the molecule is treated as a symmetric-top and its reorientation is characterized by an axially symmetric rotational diffusion tensor whose principal components are $D_\parallel$, the rotational diffusion constant of the molecule about its long molecular axis, and $D_\perp$, the rotational diffusion constant of the long molecular axis. Early attempts [7, 8] to apply this model to the deuterium N.M.R. spectral densities of motion for the aniline ring deuterons in 4-*n*-alkyloxybenzylidene- 4′-alkylaniline-2,3,5,6-d_4 have been met with limited success. The difficulty arises from a lack of sufficient experimental information to properly account for the internal rotation of the aniline ring about its para axis with a rotational diffusion constant D_R. It was therefore assumed that internal ring rotation is too fast to be an effective relaxation mechanism for the phenyl deuterons and that director fluctuations may be ignored based on a geometric argument of the C–D bond in the ring. With these assumptions, the two measured spectral densities, $J_1(\omega_0)$ and $J_2(2\omega_0)$ of the ring deuterons allow a determination of the two model

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parameters $D_\parallel$ and $D_\perp$ in the small step rotational diffusion model. These results indicate that the rotational anisotropy $R(=D_\parallel/D_\perp)$ increases with increasing temperature in the nematic (N) phase in contradiction with an expected value of 1 in the isotropic (I) phase. In addition the temperature dependence of $D_\perp$ in the nematic phase [7, 8] of 4O.8-d_4 and 5O.7-d_4 does not show an Arrhenius-type behaviour. In a more recent study [9], the above difficulty is avoided by looking at the methine deuteron on the linkage group in 1O.4 (MBBA-d_{13}). The $J_1(\omega_0)$ and $J_2(2\omega_0)$ of the methine deuteron are used to determine $D_\parallel$ and $D_\perp$ for the molecular core. Furthermore, the spectral densities from the deuterated butyl chain of 1O.4 enable us to estimate a small contribution from director fluctuations to various deuterons when the segmental motions of the chain are treated using the superimposed free rotations model [10] proposed by Beckmann *et al.* In the liquid crystal 5CB-d_{15} [11], the ring rotation has been explicitly included in the spectral densities of the ring deuterons. This is possible by finding an analytical solution of $D_\parallel$ and $D_\perp$, D_R and D_1 where D_1 is the rotational diffusion constant of the C_α–C_β bond, using the spectral densities of the α deuterons and the ring deuterons. The inclusion of D_R produces a reasonable R value of ~ 14 near the clearing temperature (T_c) in 5CB. In addition the D_R value appears to be intermediate between the $D_\parallel$ and $D_\perp$ values. It would be of interest to see if the inclusion of D_R would resolve some of the difficulties encountered in our earlier studies [7, 8].

In this paper we report our D.M.R. study of the methine deuteron in 5O.7-d_1 (4-*n*-pentyloxybenzylidene-d_1-4′-heptylaniline) and of the ring deuterons in 5O.7-d_4 (especially near T_c). By measuring the spectral densities of motion from two different sites on 5O·7, it is possible to gain information on $D_\parallel$, $D_\perp$ and D_R as well as the contribution from the director fluctuations. In the present study, we report on the data obtained in the nematic, smectic A and C phases of 5O.7-d_1. We have not yet carried out D.M.R. relaxation study in the smectic B and G phases of 5O.7-d_1 owing to inferior signal-to-noise ratio at 15·3 MHz.

2. Experimental

The 5O.7-d_1 sample was purchased from Merck Sharp and Dohme Canada Ltd. and used without further purification. It has a T_c of 348·2 K. The clearing temperature of our 5O.7-d_4 sample (T_c = 350·8 K) was reported [12] about one and a half degrees too low. Sample temperature was controlled by an oven that was connected to an external bath circulator and monitored by a copper-constantan thermocouple. The thermal gradient across the sample (7·5 mm o.d., length $\simeq$ 2 cm) was estimated to be 0·3°C.

The home-built superheterodyne coherent pulsed N.M.R. spectrometer which has been described previously [12], was controlled by a G.E. spectrometer control unit. The deuterium Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin–lattice relaxation times were determined at 15·3 MHz using the Jeener–Broekaert pulse sequence with the appropriate phase-cycling to prevent unwanted coherences and the procedures for data reductions described before [9]. Signal collection was started 30–40 μs after the second monitoring $\pi/4$ pulse and averaged over 1200–3600 scans. Using the above method, T_{1Z} and T_{1Q} of 5O.7-d_4 agree essentially with those reported earlier [7] except perhaps near T_c. Using standard nuclear spin relaxation theory [13] for spin I = 1, the spectral densities of motion $J_1^{(i)}(\omega_0)$ and $J_2^{(i)}(2\omega_0)$ can be obtained for the methine deuteron ($i = 0$) and for the ring deuterons ($i = 1$) by

$$T_{1Z}^{-1} = J_1(\omega_0) + 4J_2(2\omega_0),$$

$$T_{1Q}^{-1} = 3J_1(\omega_0),$$

where $\omega_0/2\pi$ is the Larmor precession frequency.

3. Theory

The nematic order parameter $\bar{P}_2$ was calculated from the quadrupolar splitting of the methine deuteron

$$\Delta\nu_Q^{(0)} = \frac{3}{2}\left(\frac{e^2qQ^{(0)}}{h}\right)\left(\frac{3\cos^2\beta_{M,Q_0} - 1}{2}\right)\bar{P}_2 \tag{1}$$

where the quadrupole coupling constant $e^2qQ^{(0)}/h = 185\,\text{kHz}$ and β_{M,Q_0}, the angle between the methine C–D bond and the long molecular (Z_M) axis, was taken as 68°. $\bar{P}_4$ was calculated from

$$\bar{P}_4 = Z^{-1}\int_0^{\pi} P_4(\cos\beta)\exp(-U(\beta)/kT)\sin\beta\, d\beta \tag{2}$$

using gaussian integration and the Maier–Saupe potential [14], $U(\beta_0)/kT = -\lambda P_2(\cos\beta_0)$ where the partition function Z is

$$Z = \int_0^{\pi} \exp(-U(\beta)/kT)\sin\beta\, d\beta$$

and $\lambda = 4{\cdot}541\bar{P}_2T_c/T$. Both $\bar{P}_2$ and $\bar{P}_4$ are needed [15] to evaluate the mean square of the Wigner rotation matrices, $\langle[D^2_{m_L,m_M}(\Omega_0)]^2\rangle = \kappa(m_L, m_M)$, in the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$, where Ω_0 are the Euler angles describing the instantaneous orientation of the molecule in the liquid-crystalline coordinate system.

In the motional narrowing regime, Redfield's relaxation theory [16] may be used to relate nuclear spin relaxation rates to molecular motions via the spectral densities

$$J_{m_L}(m_L\omega) = \frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2\int_0^{\infty} G_{m_L}(t)\cos(m_L\omega t)dt, \tag{3}$$

where the autocorrelation function $G_{m_L}(t)$ is

$$G_{m_L}(t) = \sum_{m_M}[d^2_{m_M0}(\beta_{M,Q})]^2\langle(D^2_{m_Lm_M}(0) - \overline{D^2_{m_Lm_M}})(D^{2*}_{m_Lm_M}(t) - \overline{D^{2*}_{m_Lm_M}})\rangle, \tag{4}$$

where the subscripts m_L and m_M refer to the projection indices of the corresponding second-rank tensor component of the relaxation hamiltonian in the laboratory and molecular frames, respectively.

We use the superimposed free rotations model in conjunction with the small step rotational diffusion model to account for the molecular reorientation of mesogens in a restoring potential of Maier–Saupe type and the internal ring rotations [7]. The methine proton (or deuteron) at the C=N–C linkage group shows fine dipolar structure due to dipole–dipole interactions with the neighbouring protons in MBBA [17], indicating that it has no internal motion. We therefore assume that reorientation of the methine deuteron reflects that of the 'cylindrical' molecular core. Approximating the autocorrelation functions which consist of multi-exponentials in general, to a single exponential [3] and taking the fast motion limit, $\omega_0\tau^{(2)}_{m_L m_M} \ll 1$, the spectral densities of the methine deuteron in the small step rotational diffusion model are given by

$$J^{(0)R}_{m_L}(m_L\omega_0) = \frac{3\pi^2}{2}\left(\frac{e^2qQ^{(0)}}{h}\right)^2 \sum_{m_M=-2}^{2} \kappa(m_L, m_M)[d^2_{m_M 0}(\beta_{M,Q_0})]^2 \tau^{(2)}_{m_L m_M}, \tag{5}$$

where the superscript R denotes reorientation contribution to the spectral densities. The correlation times $\tau^{(2)}_{m_L m_M}$ are given by

$$(\tau^{(2)}_{m_L m_M})^{-1} = \frac{D_\perp}{\lambda^{(2)}_{m_L m_M}} + m^2_M(D_\parallel - D_\perp), \tag{6}$$

where $\lambda^{(2)}_{m_L m_M}$ depend on the order parameter $\bar{P}_2$ and their values were given by Agostini *et al.* [3]. For the ring deuterons, one obtains from the superimposed rotations model [7]

$$J^{(1)R}_{m_L}(m_L\omega_0) = \frac{3\pi^2}{2}\left(\frac{e^2qQ^{(1)}}{h}\right) \sum_{m_M=-2}^{2} \sum_{m_l=-2}^{2} \{\kappa(m_L, m_M)[d^2_{m_l 0}(\beta_{1,Q_1})]^2$$
$$\times [d^2_{m_M m_l}(\beta_{M,1})]^2 [(\tau^{(2)}_{m_L m_M})^{-1} + (1 - \delta_{0m_l})D_R]^{-1}\}. \tag{7}$$

In writing down the above spectral densities, one has assumed free rotation of the aniline ring about its para (Z_1) axis. β_{1,Q_1} is the angle between the ring C–D bond and the Z_1 axis, while $\beta_{M,1}$ the angle between the Z_1 and Z_M axes. $\beta_{M,1}$ and β_{1,Q_1} assume the values of 8° and 60°, respectively, and $e^2qQ^{(1)}/h$ is taken to be identical to that of the methine deuteron.

Besides the molecular reorientation and internal motions, a collective fluctuation mode known as director fluctuations may also contribute to the spectral densities of motion. If fluctuations in the nematic director have small amplitudes, the only nonzero contribution is $J_1(\omega)$. Since the director fluctuations are slow in comparison with molecular reorientation, the coupling between these two types of motion which gives rise to a small cross term [15, 18], may be neglected. One may write [9] in the one constant approximation,

$$J^{(0)DF}_1(\omega) = A_{DF}[d^2_{00}(\beta_{M,Q_0})]^2\omega^{-1/2} \tag{8}$$

for the methine deuteron, while for the ring deuterons

$$J^{(1)DF}_1(\omega) = A_{DF}[d^2_{00}(\beta_{M,1})]^2[d^2_{00}(\beta_{1,Q_1})]^2\omega^{-1/2}, \tag{9}$$

where

$$A_{DF} = \frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2 \frac{3kT(\bar{P}_2)^2}{4\sqrt{2}\pi K(D + K/\eta)^{1/2}},$$

with K being the average Frank elastic constant, D, the average translational self-diffusion constant and η, the average viscosity coefficient of the sample.

4. Results and discussion

Figure 1 shows the experimental spectral densities of motions $J^{(i)}_1(\omega_0)$ and $J^{(i)}_2(2\omega_0)$ for 5O.7-d_1 and 5O.7-d_4 as a function of reduced temperature T_{red} ($= T/T_c$). The spectral densities of the methine deuteron are larger than the corresponding spectral densities for the ring deuterons and $J^{(i)}_1(\omega_0) > J^{(i)}_2(2\omega_0)$. In general, the spectral

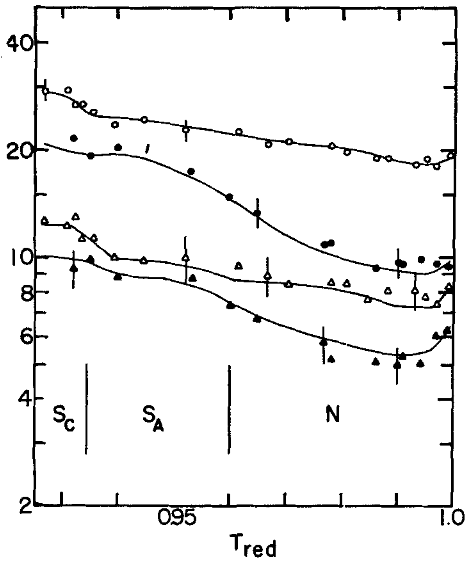

Figure 1. Plots of spectral densities versus the reduced temperature $T_{\rm red}$. Circle and triangle denote experimental $J_1(\omega_0)$ and $J_2(2\omega_0)$, respectively, and the solid curves denote theoretical fits. Open symbols are for 5O.7-d_1, while the close symbols are for 5O.7-d_4.

densities increase with decreasing temperature but show no apparent discontinuity at the phase transitions. Moreover, the spectral densities of the ring deuterons show a stronger temperature dependence. From the quadrupolar splitting of the methine deuteron in 5O.7-d_1, one calculates from equation (1) the order parameter $\bar{P}_2$ which is given as a function of temperature in figure 2. Also shown in the figure are the calculated $\bar{P}_4$ values.

If we assume that director fluctuations play a negligible role in relaxing the methine and ring deuterons, there are three unknowns $D_\parallel$, $D_\perp$ and $D_{\rm R}$ in the superimposed free rotations model. The rotational diffusion constants ($D_\parallel$, $D_\perp$) of the molecular core which appear in the correlation times $\tau^{(2)}_{m_{\rm L}m_{\rm M}}$ may be evaluated from the measured spectral densities of the methine deuteron. The equations for $J_1^{(0){\rm R}}(\omega_0)$ and $J_2^{(0){\rm R}}(2\omega_0)$ from equation (5) were written in terms of R and $D_\perp$ and then combined by eliminating $D_\perp$ to form a quartic in R. The quartic was numerically solved [19] to give R by the method of bisection. The internal ring rotation constant $D_{\rm R}$ was then separately calculated by the method of bisection from $J_1^{(1){\rm R}}(\omega_0)$ and $J_2^{(1){\rm R}}(2\omega_0)$. These $D_{\rm R}$ values were found to be different. In particular, the $D_{\rm R}$ values from $J_1^{(1)}(\omega_0)$ are always smaller than those from $J_2^{(1)}(2\omega_0)$ at the corresponding temperatures, indicating that director fluctuations may make some nonzero contribution to $J_1^{(i)}(\omega_0)$.

We adopt a model in which both the director fluctuations and reorientation/internal motions are effective relaxation mechanisms. The experimental spectral densities can be written as

$$\begin{aligned} J_1^{(i)}(\omega_0) &= J_1^{(i){\rm R}}(\omega_0) + J_1^{(i){\rm DF}}(\omega_0), \\ J_2^{(i)}(2\omega_0) &= J_2^{(i){\rm R}}(2\omega_0). \end{aligned}$$

With the inclusion of director fluctuations, the above $D_\parallel$ and $D_\perp$ values calculated from the methine deuteron would be altered. By varying $A_{\rm DF}$ in equations (8) and (9),

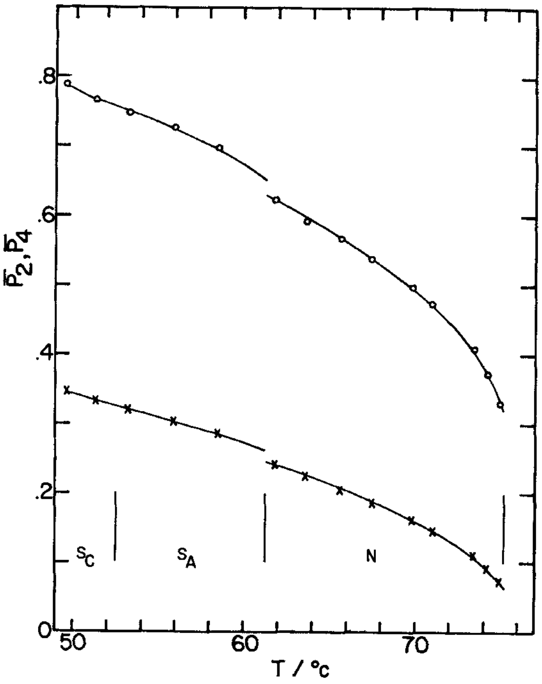

Figure 2. Plots of order parameters $\bar{P}_2$(o) and $\bar{P}_4$(x) versus the temperature for the 5O.7-d_1 sample.

one can obtain the same D_R value from both the $J_1^{(1)}(\omega_0)$ and $J_2^{(2)}(2\omega_0)$. We have chosen to find the rotational diffusion constants to give optimum fit to all four spectral densities by minimizing the sum squared error $\Sigma_i\,(J_i^{\mathrm{expt}} - J_i^{\mathrm{calc}})^2$. The resultant rotational diffusion constants for 5O.7-d_1, are summarized in figure 3 and the fits to the experimental spectral densities appear to be good as indicated by the solid curves in figure 1. In the nematic phase, the contribution of director fluctuations to $J_1(\omega_0)$ amounts to about 13 and 38 per cent of the total for the ring and methine deuterons, respectively. These percent contributions become smaller in the smectic phases as expected. It was found that A_{DF} remains constant at $8{\cdot}8 \times 10^5\,\mathrm{s}^{-3/2}$, indicating that director fluctuations show little temperature dependence with the approximations of the present model. The D_R value is intermediate between the $D_\parallel$ and $D_\perp$ values. A value of about 24 was found for R in the nematic phase, which is not unreasonable for a rodlike molecule like 5O.7. The activation energy E_a for $D_\parallel$ and $D_\perp$ in the nematic phase are roughly the same at a value of 32·7 kJ/mole. While E_a remains the same for $D_\parallel$ as the temperature is lowered into the S_A and S_C phases, higher E_a values are obtained for $D_\perp$ in the S_A (46 kJ/mol) and S_C ($\gtrsim$ 120 kJ/mol) phases. The behavior of $D_\perp$ is not unexpected because the rotation of the long molecular axis should be hindered when molecules form layered structure. However the observed temperature dependence of D_R is unusual. D_R appears to be thermally activated with a rather high E_a value in the S_A phase. It increases upon heating into the nematic phase but shows a maximum in the mid-range and then decreases as T_c is approached. The slowing down of the internal ring rotation near T_c is, however, not expected. Furthermore there is a discontinuous jump at the S_A–S_C phase transition, resulting in a higher D_R value just below the phase transition. This seems to indicate

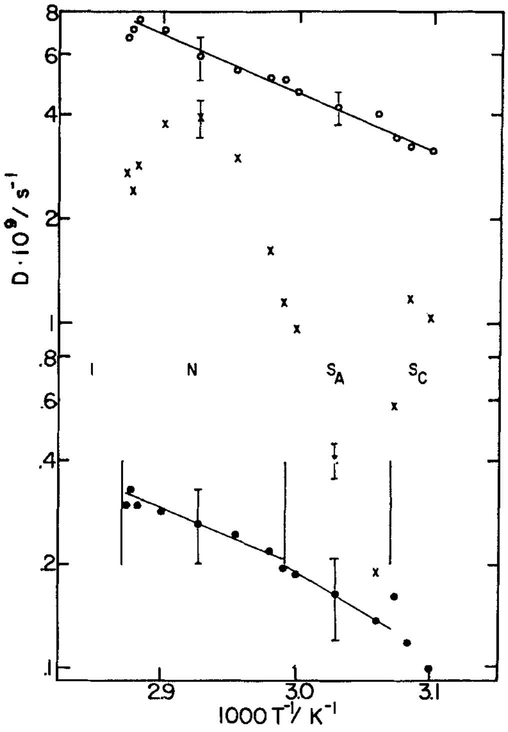

Figure 3. Plots of rotational diffusion constants versus the reciprocal temperature for the 5O.7-d_1 sample. ○, ● and x denote $D_\parallel$, $D_\perp$ and D_R, respectively. The error bars reflect variations of ± 5 per cent in experimental $J_1^{(0)}$ and $J_2^{(0)}$ values keeping A_{DF} constant.

that molecular tilt in the S_C phase has resulted in easier internal ring rotation at the phase transition. Indeed the D_R value just below the S_A–S_C phase transition is similar to that at the S_A–N phase transition in 5O.7. However, one should verify the D_R discontinuity in other liquid crystals. The present analysis fails to predict the slowing down of the spinning motion ($D_\parallel$) which was observed in recent infrared bandshape analyses [20, 21], but seems to force the ring rotation to slow down near T_c. The anomalous behaviour of D_R near T_c may, however, indicate some additional relaxation contributions from, for example, order parameter fluctuations [15]. Further experiments are needed to test this conjecture.

In conclusion, we have shown in the present study that both director fluctuations and internal ring rotations are necessary to account for the observed spectral densities of motion for the ring deuterons of a rodlike liquid crystal. The rotation anisotropy R remains roughly constant in the nematic phase and increases to larger value in the S_C phase of 5O.7. The activation energies for $D_\perp$ in various mesophases of 5O.7 seem to be physically plausible. A recent carbon-13 spin–lattice relaxation study of the protonated aniline carbons [22] in 5O.7 appears to support the above derived rotational diffusion constants. A more critical test of the above results is to compare the experimental ^{13}C spin–lattice relaxation times of the unprotonated aromatic carbons in this molecule with their predicted values. The director fluctuation relaxation factor A_{DF} has been determined by means of proton N.M.R. in many liquid crystals [23]. Unfortunately this value is unavailable for 5O.7. Nevertheless we have compared our A_{DF} value with that of the homologue member MBBA-d_{13} and found that they have the same orders of magnitude after taking into account their different interactions. We conclude by indicating that the superimposed free rotations model in conjunction with the small step rotational diffusion model appears to work satisfactorily for the 5O.7 mesogen.

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