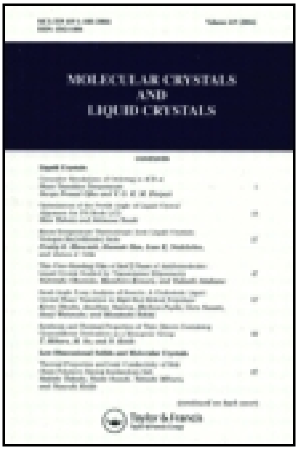

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DMR Study of Molecular Order In A Reentrant Nematic Liquid Crystal

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DMR Study of Molecular Order In A Reentrant Nematic Liquid Crystal

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We report on the measurement of molecular orientational order parameter Q of a perdeuterated 6OCB molecule in a binary mixture of 6OCB/8OCB by means of deuterium quadrupolar splittings. The temperature variation of Q, both of the aromatic and the alkyl deuterons, behaves smoothly through the nematic, smectic A and reentrant nematic phases. These data are in contrast with the prediction of the molecular theory of McMillan-type and the phenomenological theory of Landau-type.

INTRODUCTION

Since the discovery of reentrant phenomenon in liquid crystals in 1975,[1] numerous experiments[2–9] have been carried out to elucidate both the structural and dynamical properties of reentrant mesophases. Molecular orientational order parameter $Q(\equiv S_{ZZ})$, measurable by several experimental techniques, can be valuable in testing the validity of molecular theory of McMillan-type[10] and/or phenomenological theory of Landau-type[2,7,11] for the reentrant polymorphism. Thus far there are contrasting results of Q in binary mixtures that exhibit reentrant mesophases, mainly due to the experimental technique one used. Luckhurst et al.[8] report on the mixture of HBAB/CBOOA that ESR of a steroidal spin-probe gave a smooth temperature dependence of Q through the nematic (N), smectic A(S_A) and reentrant nematic (RN) phases, while ESR of an alkyl spin-probe revealed a steep increase in Q in the RN phase. The behavior of the alkyl spin-probe is also observed in a DMR study[7] of a deuterated solute (*p*-xylene) in a mixture of 4-cyano-4′-hexyloxybiphenyl (60CB) and 4-cyano-4′-octyloxybiphenyl (80CB). However, measurements[3] of the anisotropy of the index of refraction in several 60CB/80CB mixtures show that there was an enhancement in Q in the S_A phase when it is followed by a stable RN phase. The result seems to substantiate the prediction of molecular theory of McMillan-type. The essential difference between the birefringence study[3] and the above ESR and NMR measurements is that the former uses the liquid crystalline molecules while the latter employs impurity probe dissolved in liquid crystals, whose solvation site may depend on the nature of mesophases (in particular at phase transition) and the molecular structure of the probe. To avoid the ambiquity of using probe molecule, Miyajima et al.[6] recently report on a proton NMR lineshape study of a pure compound OBBC which has a RN phase with a wide temperature range. From the dipolar splitting of the phenylene protons, the derived Q was reported to vary smoothly through the N, S_A and RN phases. They conclude that the orientational order of the aromatic core of the molecule is hardly influenced by the presence of a RN phase below the S_A phase. This is of course in contrast with the birefringence study. Furthermore they indicate that the anomalous increase of Q in the RN phase observed by impurity probe may reflect some subtle change in the orientational order of the chain part. Here we report on a DMR study of a mixture of 80CB and perdeuterated 60CB whose quadrupolar splitting of the aromatic and alkyl parts can be followed as a function of temperature in the N, S_A and RN phases.

EXPERIMENTAL

The perdeuterated liquid crystal 60CB-d_{21} (T_c = 75°C) was purchased from Merck Sharp and Dohme Canada Ltd. and the 80CB from BDH Chemicals, Ltd. Both were used without further purification. An unsealed sample of 26 wt.% of 60CB-d_{21} in 80CB was prepared in a 7.5 mm o.d. NMR tube. The transition temperatures of the sample as determined by NMR were about 78, 46 and 28°C for I→N, N→S_A and S_A→RN transitions, respectively. To achieve better temperature homogeneity, the sample was placed in a (10 mm o.d.) water bath whose temperature was monitored by a copper-constantan thermocouple. The temperatures at the water bath were maintained by a nitrogen gas flow with a temperature gradient of better than 0.5°C.

The deuterium NMR spectra were made at 13.81 MHz with a Bruker SXP 4-100 MHz spectrometer equipped with a Nicolet 1180 FFT accessory. The external magnetic field was "locked" at 21.14 kG and its field homogeneity was maximized by proper trimming with

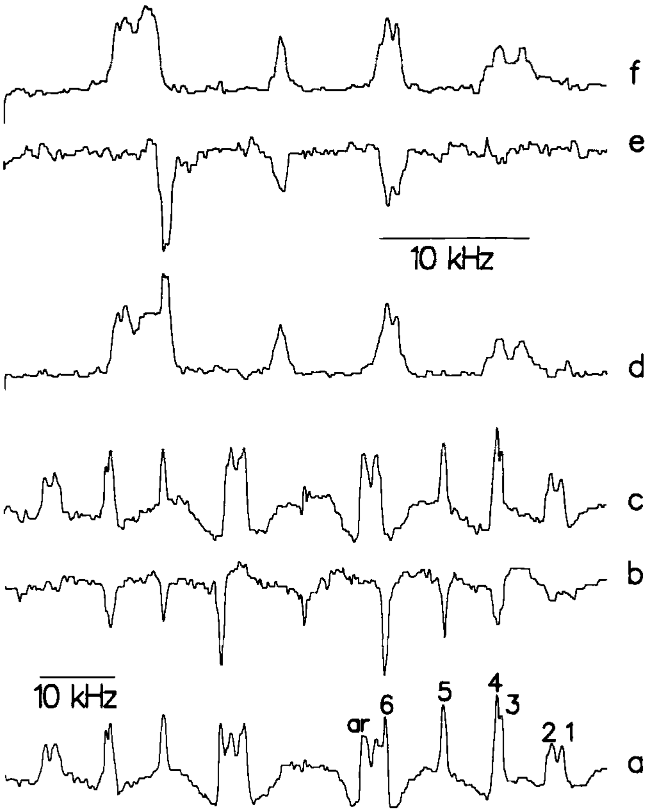

FIGURE 1 Typical DMR spectra of 26 wt.% 6OCB-d_{21} in 8OCB mixture at 30.3°C. While (a)–(c) were obtained by using the FID signal after a $\pi/2$ pulse, (d)–(f) were obtained by quadrupolar echo technique (τ = 150 μs) showing only the right half of the quadrupolar doublets. Number of sweep was 500. (b), (c), (e) and (f) are partially spin-lattice relaxed spectra using the inversion-recovery sequence. (c) and (f) have a recovery time T = 75 ms, while (b) and (e) have T = 1.5 ms.

shim coils. Six DMR spectra were taken at each temperature. Three were taken using quadrature detection from averaging 500 FID signals and three others using $(\pi/2)_x - \tau - (\pi/2)_y$ quadrupolar echo technique with non-quadrature detection and 500 sweeps. Since the aromatic and methyl deuterons produced partially overlapped lines, partially spin-lattice relaxed spectra were taken to null the signal from either the aromatic or the methyl deuterons by taking advantage of their different T_1's. Figure 1 shows a typical set of six spectra in which the partially spin-lattice relaxed spectra allowed us to better determine the quadrupolar splittings of the methyl and aromatic deuterons. The peak assignment gives the numbering of the methylene along the chain starting from the α-methylene which corresponds to no. 1. We assumed that the splittings decrease monotonically along the chain. There are pairing among the splittings of no. 1 and 2 deuterons and of no. 3 and 4 deuterons, thus producing severe overlap in the spectrum.

RESULTS AND DISCUSSION

The quadrupolar splittings of 6OCB-d_{21} molecule in a 26 wt.% 6OCB/8OCB binary mixture are plotted versus temperature in Figure 2. Despite some overlap problems in the DMR spectrum, it can be seen from the figure that both the aromatic and alkyl data show a smooth temperature behavior through the N, S_A and RN phases. These results are surprising in view of the prediction of Q based on either the molecular theory of McMillan-type or the phenomenological theory of Landau-type. For uniaxial phase and idealized cylindrical mesogenic molecule, the quadrupolar splitting at site i, $\Delta\nu_i$, in the fast motion limit can be written as

$$\Delta\nu_i = \frac{3}{2}\left(\frac{e^2qQ}{h}\right)_i < P_2(\cos\theta)P_2(\cos\alpha_i) > P_2(\cos\theta_0) \qquad (1)$$

where θ_0 is the angle between the nematic director $\hat{n}$ and the external magnetic field (here $\theta_0 = 0$ for $\Delta\chi > 0$), θ is the angle between the mesogen symmetry axis (taken usually the long molecular axis) and $\hat{n}$, and α_i is the angle that the ith C-D bond vector makes with the mesogen symmetry axis. In Eq. (1), $\langle \cdots \rangle$ indicates a time average and in the idealized limit wherein extramolecular and intramolecular motion is decoupled, this can be expressed as

$$\langle P_2(\cos\theta)\rangle\langle P_2(\cos\alpha_i)\rangle = \langle P_2(\cos\alpha_i)\rangle Q \qquad (2)$$

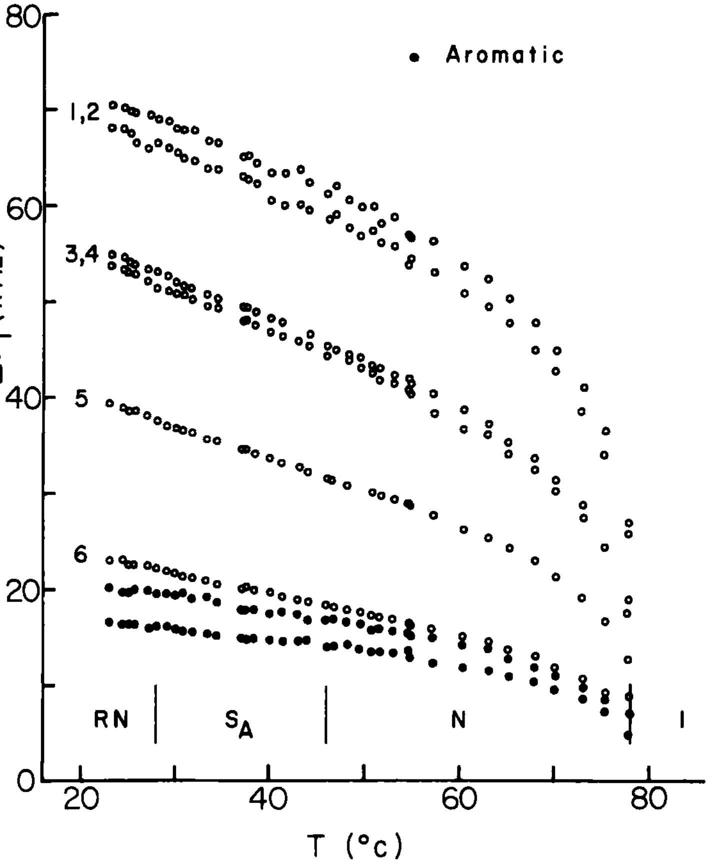

FIGURE 2 Plot of quadrupolar splittings versus the temperature in 26 wt.% 6OCB-d_{21} in 8OCB mixture. The numbering i corresponds to the peak assignment in the DMR spectrum (see text).

With the above approximations, the quadrupolar splitting is directly related to Q of the mesogen and any difference in the temperature behavior of $\Delta\nu_i$ (especially at phase transition) for the aromatic and alkyl sites can only be accounted by their specific internal conformational motions. Thus our data suggest that the temperature dependence of Q derived from both the aromatic and alkyl sites using Eqs. 1 − 2 is in contradiction with the above mentioned theories, i.e. no enhancement in the S_A phase[10,11] and no noticeable increase in the RN phase.[7]

The present study supports the proton NMR lineshape data of Miyajima et al. However it has been suggested[2] that coupling between the nematic and smectic order parameters is important in describing the reentrant phase diagram. Why the Q measurements on the mesogenic molecule, apart from the birefringence study, fail to support the theories is not clear. It is noted, however, that the enhancement of Q in the S_A phase observed by the birefringence study is relatively small (i.e. about 7% at the S_A-RN phase transition and 15% at the S_A-N phase transition). Recent detailed calculations[12] based on the Landau-type theory confirm the enhancement of Q in the S_A phase of reentrant liquid crystals, but the magnitude of δQ could be rather small and is not symmetric as observed in the birefringence study. This may explain why the coupling between the nematic and smectic order parameters does not manifest itself in our Q measurements of the 6OCB molecule.

Acknowledgement

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