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Proton NMR study of CBOOA, NBOOA, and their chain-deuteriated homologues in smectic A_d and nematic mesophases†

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The nature of the smectic A_d to nematic phase transition and the modes of molecular motion were investigated for the homologous mesogens, CBOOA, NBOOA, and their chain-deuteriated compounds. In NBOOA, the S_{A_d}–N phase transition was found to be first order with a pronounced pretransitional decrease of the orientational order parameter, $\langle P_2 \rangle$, both above and below the transition point, while in CBOOA the anomaly in $\langle P_2 \rangle$ was very small. Despite the different behaviours in terms of the orientational order, the dynamical aspects of molecular motion, probed by the NMR relaxation, are quite similar. The motional mode characteristic of the N phase is order director fluctuation, but translational self-diffusion becomes the dominant relaxation mechanism in the S_{A_d} phase. It is also recognized that the relative importance of these mechanisms changes in a continuous manner as a function of temperature.

1. Introduction

4-Octyloxy-*N*-(4-cyanobenzylidene)aniline (CBOOA) is a well known mesogen which exhibits a smectic A_d (S_{A_d}) to nematic (N) phase transition. McMillan's early study [1] that pointed out a possible second order nature of this phase transition has since stimulated a good number of experimental studies [2–7]. Some of the experiments suggested the existence of a first order component, but in neither adiabatic [8] nor recent AC [9] calorimetric studies, was observed the associated latent heat. In addition, Cladis and her co-workers have found a further unusual phase sequence for CBOOA, i.e. isotropic (I)–N–S_{A_d}–reentrant nematic (RN), on lowering the temperature under high pressures [10, 11]. On the other hand, the physical properties of NBOOA [4-octyloxy-*N*-(4-nitrobenzylidene)aniline, the nitro counterpart of CBOOA] have been revealed only recently [12–15]. Prasad *et al.* [14] found that the S_{A_d}–N phase boundary was nearly a straight line on the p–T phase diagram, and the RN phase did not appear up to 2 kilobars. Recently this S_{A_d}–N transition was shown by us to be of first order [9]. It is therefore interesting to investigate the difference in the nature of the S_{A_d}–N phase transitions of these two homologues. In order to obtain information on the temperature dependence of the orientational order parameter and the modes of molecular motion, proton and deuterium NMR studies were carried out. The chain-deuteriated compounds, CBOOA-d_{17} and NBOOA-d_{17}, were used to resolve the information from the core and chain moieties.

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2. Experimental

The syntheses of NBOOA and CBOOA have been described in our previous paper [15]. NBOOA-d_{17} and CBOOA-d_{17} were prepared by the same procedure using 1-bromooctane-d_{17} (MSD Isotopes, Merck Frosst Canada Inc.) as an alkylating reagent. The transition temperatures were S_{A_d}–355·9 K–N–378·7 K–I for CBOOA-d_{17} and S_{A_d}–349·9 K–N–357·5 K–I for NBOOA-d_{17}, and were not seriously affected by the chain-deuteriation. Proton NMR experiments were performed with a home-made Fourier transform NMR spectrometer. Spin–lattice relaxation rates were measured in the laboratory frame (T_1^{-1}) and the dipolar frame (T_{1D}^{-1}). The latter was measured with a technique of adiabatic demagnetization in the rotating frame (ADRF) [16, 17] at 30 MHz. The recovery of magnetization was found to be of exponential form throughout the experiments.

3. Results and discussion

3.1. *Orientational order parameter for the molecular core*

Figure 1 shows examples of the proton NMR spectra of NBOOA and NBOOA-d_{17} in the S_{A_d} phase. It is clear from the comparison of these spectra that the central component and the outer doublet are due to chain and core moieties, respectively. The second rank orientational order parameter for the molecular core, $\langle P_2 \rangle$, was obtained from the splitting, $\Delta\nu$, of the dipolar doublet via the equation [18]

$$\Delta\nu = (3/2\pi)\gamma_p^2 \hbar r^{-3} P_2(\cos\Phi)\langle P_2 \rangle, \qquad (1)$$

where γ_p is the gyromagnetic ratio of a proton, r is the nearest interproton distance within a phenylene ring, Φ is the angle between the interproton vector and the molecular long axis, and $P_2(x)$ is the second Legendre polynomial. Figure 2 shows the temperature dependence of $\langle P_2 \rangle$ for CBOOA-d_{17}, and figure 3 shows the results for NBOOA and NBOOA-d_{17}. In estimating $\langle P_2 \rangle$, the values of r and Φ were taken to be 0·245 nm and 10° respectively from the molecular structures. The $\langle P_2 \rangle$ value for CBOOA-d_{17} exhibits a monotonic temperature dependence throughout the S_{A_d} and N phases with little anomaly at the S_{A_d}–N transition point, $T_{S_{A_d}N}$. The results for CBOOA were almost the same as those for CBOOA-d_{17}, which is consistent with the previous

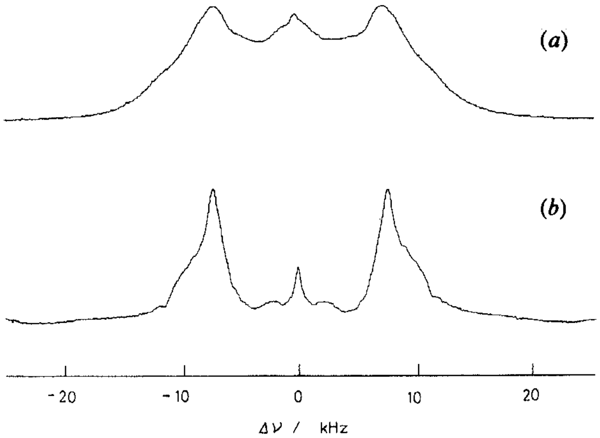


Figure 1. Proton NMR spectra, measured at 30 MHz, of (*a*) NBOOA and (*b*) NBOOA-d_{17} in the S_{A_d} mesophase.

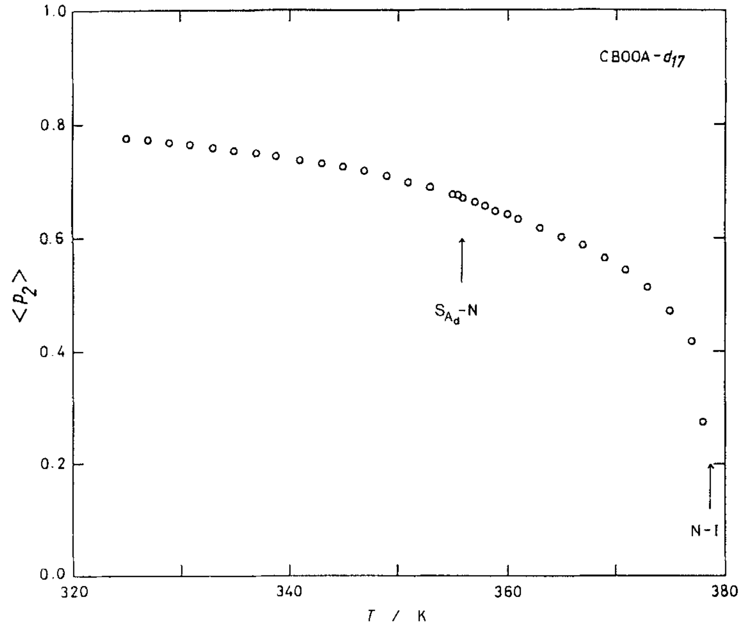
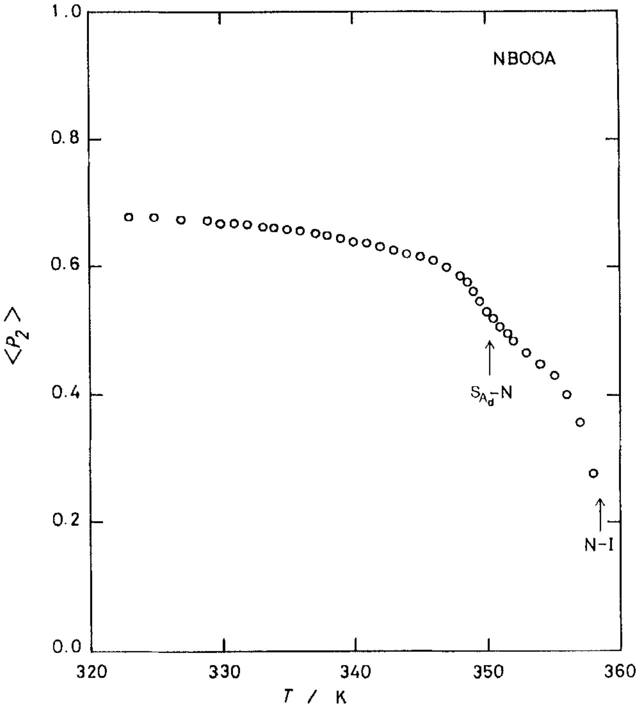


Figure 2. Temperature dependence of the second rank orientational order parameter $\langle P_2 \rangle$ for the molecular core in CBOOA-d_{17}.

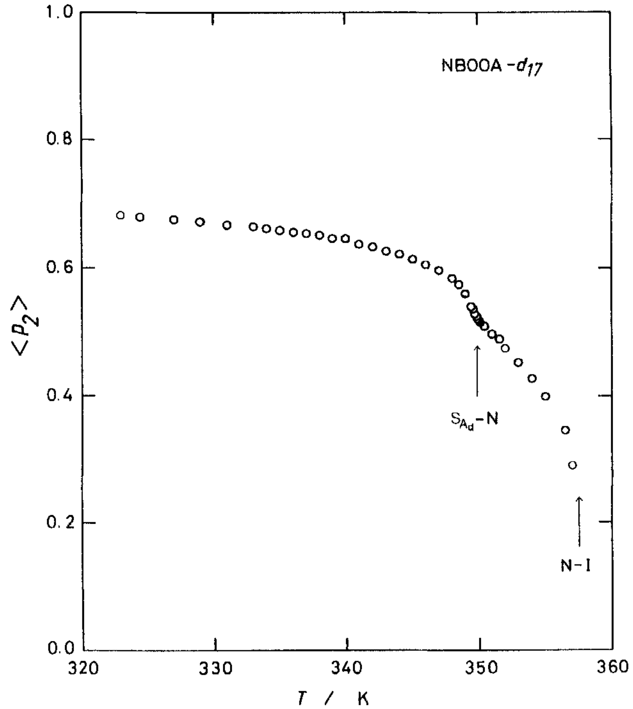
magnetic anisotropy experiments with CBOOA [6]. Similar NMR results have been obtained for OBBC, another reentrant mesogen [19, 20]. For both NBOOA and NBOOA-d_{17}, however, $\langle P_2 \rangle$ shows a significant anomaly at $T_{S_{A_d}N}$. It is clear from figures 3 (a) and (b) that the temperature derivative, $\partial\langle P_2 \rangle/\partial T$ is discontinuous at $T_{S_{A_d}N}$. Since the accuracy of the measurements are higher for the chain deuteriated compound, detailed measurements were conducted for NBOOA-d_{17}; an expanded view of $\langle P_2 \rangle$ versus T in the vicinity of $T_{S_{A_d}N}$ is given in figure 3 (c). One can see here a discontinuous change in $\langle P_2 \rangle$ of around 0·001 at the transition point. In spite of this first order nature, a pronounced pretransitional decrease in $\langle P_2 \rangle$ was found on both sides of $T_{S_{A_d}N}$ for NBOOA and NBOOA-d_{17}, unlike for the known S_{A_d}–N phase transitions, showing a strong coupling between orientational and translational orders.

3.2. *Spin–lattice relaxation in CBOOA and CBOOA-d_{17}*

Figure 4 represents the temperature dependence of the spin–lattice relaxation rates, T_1^{-1} (measured at 7·5 and 30 MHz) and T_{1D}^{-1} for CBOOA and CBOOA-d_{17}. One of the significant features on the observed relaxation rates of the Zeeman order is that T_1^{-1} decreases with temperature in the S_{A_d} phase, but increases with temperature in the N phase. It has been well conceived that the decreasing profile of T_1^{-1} versus temperature comes mainly from the translational self-diffusion of the molecules (TSD) in liquid crystals as well as in conventional liquids [20, 21]. The observed Arrhenius-type relaxation behaviour in the S_{A_d} mesophase is explained by this mechanism. However, the T_1^{-1} in the N phase shows an inverse dependence on temperature. The TSD mode cannot explain this behaviour because the correlation time for the diffusion is faster in the N phase, and so this mode becomes less effective to T_1^{-1} at higher temperatures.


NBOOA
$\langle P_2 \rangle$
1.0
0.8
0.6
0.4
0.2
0.0
320
330
340
350
360
T / K
S_{A_d}-N
N-I

(a)


NBOOA-d_{17}
$\langle P_2 \rangle$
1.0
0.8
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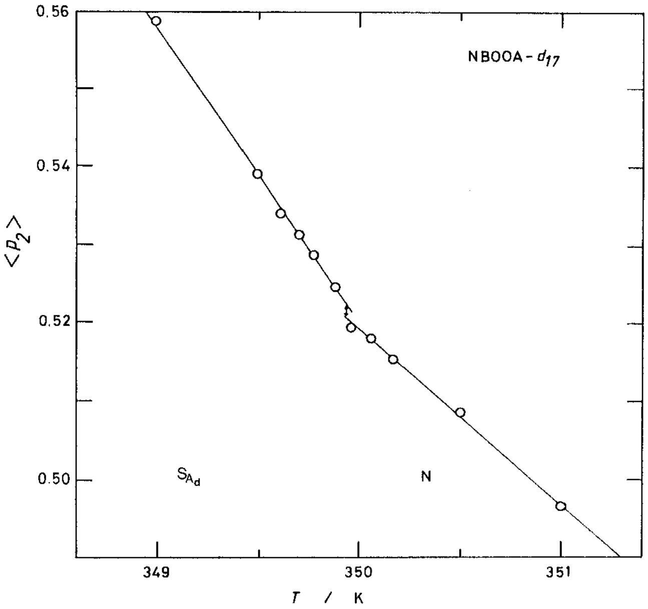
S_{A_d}-N
N-I

(b)



(c)

Figure 3. Temperature dependence of the second rank orientational order parameter $\langle P_2 \rangle$ for the molecular core in NBOOA and NBOOA-d_{17}. (a) NBOOA; (b) NBOOA-d_{17}; and (c) an expanded view near the phase transition point $T_{S_{A_d}N}$ of NBOOA-d_{17}.

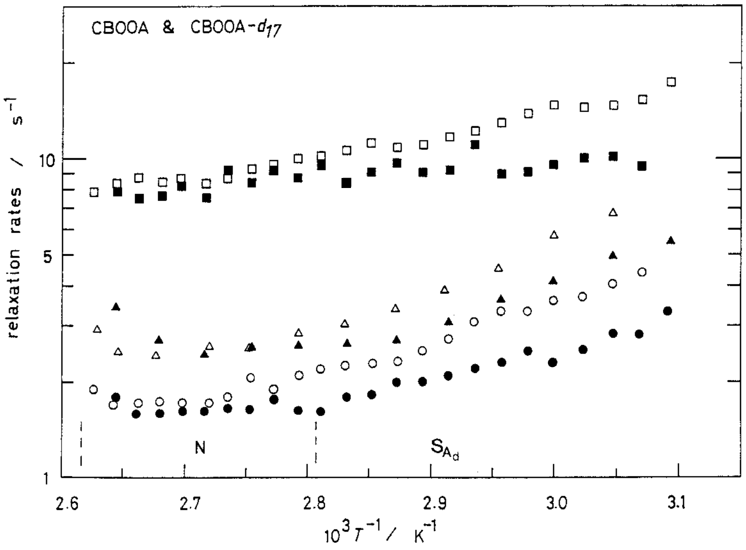


Figure 4. Temperature dependence of the proton spin–lattice relaxation rates in CBOOA and CBOOA-d_{17}. The symbols, ○ (T_1^{-1} at 30 MHz), △ (T_1^{-1} at 7·5 MHz), and □ (T_{1D}^{-1}) stand for the relaxation rates for CBOOA, and ● (T_1^{-1} at 30 MHz), ▲ (T_1^{-1} at 7·5 MHz), and ■ (T_{1D}^{-1}) stand for those in CBOOA-d_{17}.

Therefore, as an additional contribution, the order director fluctuation (ODF), a collective mode characteristic of liquid crystals, is considered. We now briefly sketch the treatment of spin–lattice relaxation due to ODF in the context of elastic continuum theory. The spin–lattice relaxation of aromatic protons caused by ODF is calculated by the formula [22],

$$T_{1\,\mathrm{ODF}}^{-1} = Cr^{-6}P_2^2(\cos\Phi)\langle P_2\rangle^2(k_\mathrm{B}T/\sqrt{2}\pi)(\eta/K^3)^{1/2} \times \omega_0^{-1/2}[1-(2\sqrt{2}/\pi)(\omega_0/\omega_\mathrm{c})^{1/2}+\ldots], \tag{2}$$

$$C=(3/2)I(I+1)\gamma_\mathrm{p}^4\hbar^2, \tag{3}$$

for a pair of nuclear spins distance r apart. Here η is the effective viscosity coefficient for director fluctuation, K is the Frank's elastic constant under the one-elastic constant approximation ($K=K_1=K_2=K_3$), and ω_c is the cut-off frequency defined by

$$\omega_\mathrm{c}=Kq_\mathrm{c}^2/\eta=(K/\eta)(2\pi/a)^2, \tag{4}$$

where q_c is the higher cut-off wavenumber, and a is a quantity related to a molecular length. If $\omega_\mathrm{c} \gg \omega_0$ due to low viscosity in the N phase, $T_{1\,\mathrm{ODF}}^{-1}$ will be large enough to overcome the decrease in T_1^{-1} caused by TSD. Taking an approximation from the elastic theory, $K \propto \langle P_2\rangle^2$, the temperature dependence of T_1^{-1} is determined by

$$T_{1\,\mathrm{ODF}}^{-1} \propto (\sqrt{\eta}/\langle P_2\rangle)k_\mathrm{B}T, \tag{5}$$

which can lead to a weakly increasing T_1^{-1} with temperature. It may be seen from figure 4 that the enhancement of T_1^{-1} is not large at 30 MHz as compared with T_1^{-1} at 7·5 MHz, suggesting that the cut-off effect is not negligible at 30 MHz (ω_c is not far larger than this NMR frequency). The cut-off effect should be significant at lower temperatures due to high viscosity, and the $T_{1\,\mathrm{ODF}}^{-1}$ may be depressed since the second term in equation (2) does not vanish. This leads to a change in the dominant relaxation mechanism from ODF to TSD, and then reversal of the temperature dependence of T_1^{-1} is expected.

The present experimental results show that the director fluctuation is the predominant contribution to T_1^{-1} in the N phase, but the translational diffusion to T_1^{-1} in the $\mathrm{S_{A_d}}$ mesophase. It is noteworthy at this stage that the contribution from nematic-like director fluctuation remains in the $\mathrm{S_{A_d}}$ mesophase, as signified by the fact that no discontinuous change in T_1^{-1} was observed at $T_{\mathrm{S_{A_d}N}}$, and that the temperature dependence of T_1^{-1} is very small in the $\mathrm{S_{A_d}}$ mesophase. Evidence for the existence of this kind of fluctuation is available for other $\mathrm{S_{A_d}}$ liquid crystals [20, 23, 24].

Let us now examine the difference in relaxation rates between CBOOA and CBOOA-d_{17}. It is interesting to compare the differences in the $\mathrm{S_{A_d}}$ and N phases; the relaxation of CBOOA is generally faster than that of CBOOA-d_{17} in the $\mathrm{S_{A_d}}$ mesophase, while in the N phase, the difference is small at 30 MHz, and is reversed at 7·5 MHz. The enhancement of relaxation rate by chain-deuteriation can be expected only when the relaxation is governed mainly by ODF. The ODF-assisted relaxation is caused mainly by the modulation of intramolecular dipole–dipole interaction among ring protons while the contribution from the chain protons is small. Since the observed relaxation rate is an average of the core and chain contributions, the relaxation rate in the fully protonated compound is reduced by the slowly-relaxing chain protons. In the chain-deuteriated compound, the ODF-induced relaxation is observed in a more straightforward way. If, on the other hand, the relaxation is governed by TSD, the process involves mainly the intermolecular dipole–dipole interactions. Intramolecular spin relaxation is not induced by translational diffusion of an elongated molecule in the ordered fluid as long as the angle between the external magnetic field and the molecular long axis is conserved during diffusion. Then the chain-deuteriation will make the relaxation rates to about $9/26 \fallingdotseq 0{\cdot}35$ because of a reduced number of intermolecular pairwise interactions. Our experimental finding is consistent with the above model and indicates again that the director fluctuation dominates T_1^{-1} and T_{1D}^{-1} in the N phase, but the contribution from self-diffusion becomes significant in the S_{A_d} phase of CBOOA. It is also recognized from figure 4 that the reduction of the relaxation rate by chain-deuteriation is not large. The values of T_1^{-1} for CBOOA-d_{17} amount to 70 per cent of those in CBOOA even at the lowest temperature. This fact shows that the intramolecular mechanism still operates in the S_{A_d} mesophase. It is most likely to be either the nematic-like director fluctuation or the self-diffusion coupled with the director fluctuation where the molecular long axis rotates during the process of diffusion.

In order to further confirm our assessment of the relaxation mechanisms, the Larmor-frequency dependence of T_1^{-1} was analysed. Figure 5 represents the temperature dependence of the ratio of the relaxation rates, $\alpha \equiv T_1^{-1}$ (7·5 MHz)/T_1^{-1} (30 MHz). Equation (2) predicts a characteristic frequency dependence, $T_1^{-1} \propto \omega_0^{-1/2}$ ($\alpha = 2{\cdot}0$ in this case) in the ODF-assisted relaxation in low viscosity nematics. However, the observed values are less than 2·0 over the whole temperature range studied, and show that the ODF mode does not solely account for the values of T_1^{-1} even in the N phase. Figure 5 also shows that α is comparatively large in the high and low temperature limits, but small near the S_{A_d}–N phase transition region. It is reasonably understood that the growth of α at high and low temperature regions is due to excitation of the ODF mode and to the increase of the low frequency components of molecular self-diffusion, respectively.

In the case of relaxation of the dipolar order (T_{1D}^{-1}), the temperature dependence is generally smaller than that of T_1^{-1}, and an especially notable fact is that T_{1D}^{-1} is almost independent of temperature for CBOOA-d_{17}. For both samples T_{1D}^{-1} (measured at 30 MHz) is about five times larger than T_1^{-1} (30 MHz) in the N phase, showing the presence of a very slow motional mode. Note that the dipolar energy ($H_D/h < 20$ kHz) is by more than three orders of magnitude smaller than the Zeeman energy. However, the

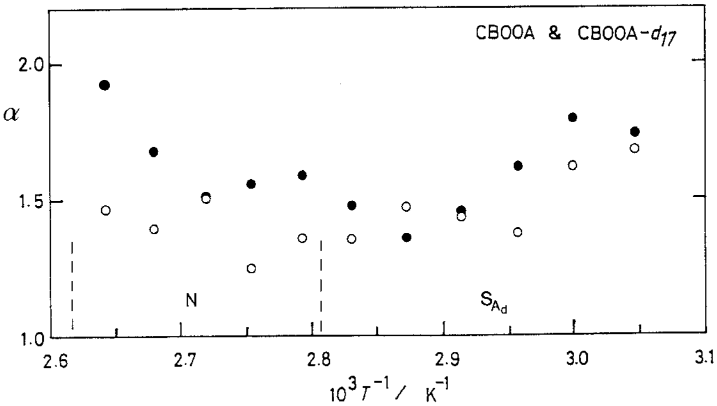


Figure 5. The ratio of Zeeman relaxation rates measured at different Larmor frequencies, $\alpha \equiv T_1^{-1}$ (7·5 MHz)/T_1^{-1} (30 MHz), as a function of temperature in CBOOA (○) and CBOOA-d_{17} (●).

positive gradient of $\log(T_1^{-1})$ against T^{-1} in the S_{A_d} phase, as shown in figure 4, proves that the diffusion-induced T_1^{-1} is in the higher temperature branch of its Zeeman relaxation maximum, and so the diffusion mechanism cannot explain the large difference between T_{1D}^{-1} and T_1^{-1} in the N phase. Director fluctuation is, on the other hand, a long wavelength mode, and has a larger spectral density at lower frequencies. The very small temperature dependence of T_{1D}^{-1}, and a large difference between T_{1D}^{-1} and T_1^{-1} in the N phase are attributable to this mechanism. Figure 4 also shows that the difference between T_{1D}^{-1} and T_1^{-1} becomes smaller as the temperature is lowered in the S_{A_d} phases of either of the samples. An interpretation is as follows. If the cut-off effect on the nematic-like director fluctuation becomes serious in the lowest temperature region of the S_{A_d} phase, the predominant mechanism will switch over to the self-diffusion. Because the diffusion-induced T_1^{-1} is in the higher temperature branch of its Zeeman relaxation maximum, the correlation time for diffusion almost satisfies the extreme-narrowing condition, and so the difference in relaxation rates comes close to the limiting case for uncorrelated fast motion, $T_{1D}^{-1} = 2T_1^{-1}$ [25].

All the above analyses show that the characteristic molecular motional modes for the spin–lattice relaxation in the cyano compounds are the nematic order director fluctuation in the N phase, and translational self-diffusion in the S_{A_d} phase. It is clear, however, that the two modes do not solely account for the process in either phase. It should be stressed that nematic-like order director fluctuation persists in the S_{A_d} mesophase.

3.3. *Spin–lattice relaxation in NBOOA and NBOOA-d_{17}*

The experimental results of T_1^{-1} and T_{1D}^{-1} for NBOOA and NBOOA-d_{17} are shown in figure 6, and the frequency dependence of T_1^{-1} is depicted in figure 7. The results are generally similar to those for the cyano compounds: (1) as the temperature increases,

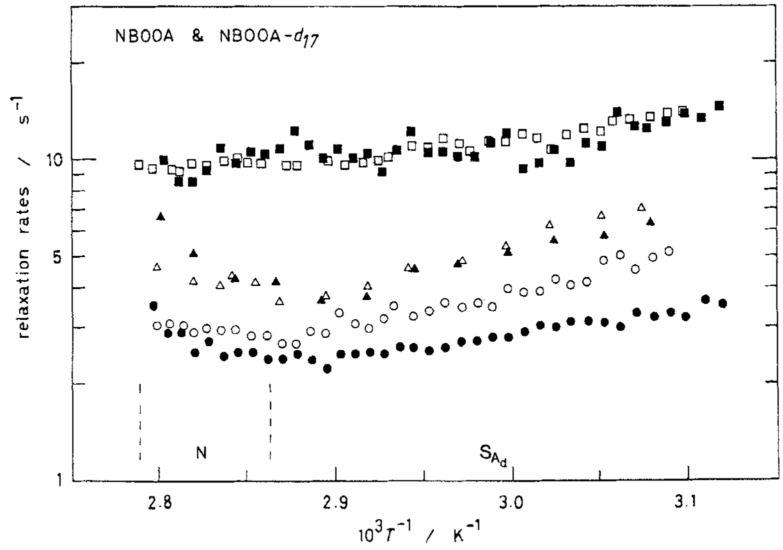


Figure 6. Temperature dependence of the proton spin–lattice relaxation rates in NBOOA and NBOOA-d_{17}. The symbols, ○ (T_1^{-1} at 30 MHz), △ (T_1^{-1} at 7·5 MHz), and □ (T_{1D}^{-1}) stand for the relaxation rates for NBOOA, and ● (T_1^{-1} at 30 MHz), ▲ (T_1^{-1} at 7·5 MHz), and ■ (T_{1D}^{-1}) stand for those in NBOOA-d_{17}.

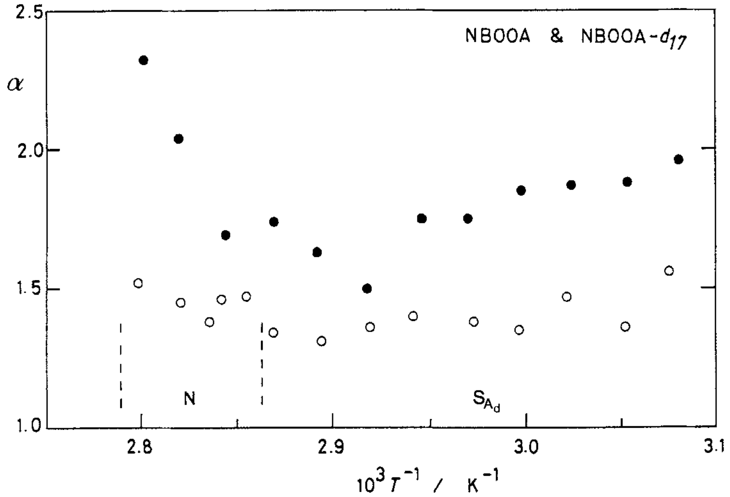


Figure 7. The ratio of Zeeman relaxation rates measured at different Larmor frequencies, $\alpha \equiv T_1^{-1}$ (7·5 MHz)/T_1^{-1} (30 MHz), as a function of temperature in NBOOA (○) and NBOOA-d_{17} (●).

T_1^{-1} decreases in the S_{A_d} phase, while it increases in the N phase, (2) the relative magnitudes of T_1^{-1} (7·5 MHz) for chain-protonated and chain-deuteriated compounds are reversed as the phase changes from N to S_{A_d}, (3) T_1^{-1} is strongly dependent on frequency in the high temperature limit of the N phase and the low temperature limit of S_{A_d} phase, but not in the S_{A_d}–N phase transition region, (4) T_{1D}^{-1} is almost independent of temperature. Thus the general features of the molecular motion are similar for CBOOA and NBOOA as probed by the NMR relaxation, in spite of the difference in the nature of the S_{A_d}–N phase transition.

4. Conclusion

In NBOOA, the nitro counterpart of CBOOA. The S_{A_d}–N phase transition was found to be of first order with pronounced pretransitional decrease of the orientational order parameter, $\langle P_2 \rangle$, both above and below the transition point, while in CBOOA the anomaly in $\langle P_2 \rangle$ was very small. In spite of the different behaviour of the orientational order parameter, the dynamical aspects of molecular motion are similar as shown by the NMR relaxation measurements. In either of the mesogens, the motional mode characteristic of the liquid-crystalline phases are order director fluctuation in the N phase and translational self-diffusion in the S_{A_d} phase. It was also recognized, however, that both of these modes contribute in each of the mesophases to varied degrees. The transition from S_{A_d} to N phases seems to be almost continuous from a viewpoint of NMR relaxation.

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