Study of the Molecular Dynamics from Deuterium Zeeman and Quadrupolar NMR Relaxation of 4,4′-di-n-Heptylazoxybenzene in the Nematic and Smectic A Phases *

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Z. Naturforsch. **49a,** 311–319 (1994); received August 16, 1993

The deuterium spin-lattice (T_{1Z}) and quadrupolar (T_{1Q}) relaxation times of the liquid crystal 4,4′-Heptyl-azoxybenzene (HAB), deuterated on the aromatic rings and the first methylene group of the chains, have been measured by means of the Jeener-Broekaert pulse sequence at two different frequencies (10 and 46.04 MHz) and throughout the nematic and the smectic A phase. By applying suitable models, we have determined rotational and reorientational diffusion coefficients and evaluated the contribution of the different motions (internal, molecular and collective) to the relaxation. In particular we have found a non negligible contribution from order director fluctuations.

A comparison between the T_{1Z} and T_{1Q} measurements performed by means of Jeener-Broekaert and Wimperis pulse sequences is also shown.

Key words: Liquid crystal, Deuterium NMR, Molecular dynamics, Deuterium relaxation, Director fluctuation.

Introduction

Properties of liquid crystals have often been related to the nature of the aromatic core or to the length and flexibility of the aliphatic chain. Only recently it has been shown that the structure and conformation of the link joining the mesogenic core to the flexible chain could play an important role in the determination of liquid crystal transitional behaviour [1].

In order to investigate the influence of the chains on the orientational order, we have determined, by means of ^{2}H-NMR, the order parameters in the nematic and smectic phases of three closely related mesogens (4,4′-n-heptylazobenzene and 4,4′-n-heptyl- and octyl-azoxybenzene) deuterated in the aromatic core and in the first methylenic group [2]. A different order for the various molecular fragments of the mesogenic molecules has been observed. However, while the quadrupolar splittings of the two aromatic rings, given the low biaxiality of the mesogenic core, showed a constant ratio throughout the temperature range examined, the ratios of the quadrupolar splittings of the methylene deuterons and those of the aromatic deuterons were strongly temperature dependent for all three liquid crystals investigated. This behaviour is indicative of non negligible molecular biaxiality and can be explained by excluding the presence of a single conformation for the CD$_2$-phenyl bond. In order to clarify further the conformational equilibrium of the methylene link, we have undertaken a study of the dynamics of the same series of mesogenic molecules. In [3] the preliminary results obtained by measuring the deuterium spin-lattice relaxation time have been presented.

However the dynamics in liquid crystals is quite complicated and the sole measurements of the longitudinal relaxation time, even if at different frequencies, cannot give detailed information on molecular motions. The molecules, in fact, undergo different types of motion: besides internal dynamics, such as rotations, the molecules are subject to reorientational motion in the anistotropic medium which involves the individual molecules and also the collective excitations due to elastic deformations in the liquid crystalline sample, known as director fluctuations.

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* Presented at the XIIth International Symposium on Nuclear Quadrupole Resonance, Zürich, July 19–23, 1993.

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There have been two main approaches to the study of liquid crystal dynamics: in a first one use has been made of field cycling NMR procedures, which allow to measure relaxation dispersion from few kHz to the MHz regime. These methods, being able to measure the dependence of longitudinal relaxation time (T_1) as a function of the nuclear spin Larmor frequency, are the best for evidencing collective motions. The contribution of director fluctuations to the spectral density $J_1(\omega)$, according to the predictions of Pincus [4] and Blinc [5], have a characteristic $\omega^{-1/2}$ frequency dependence for nematics and possibly a more complicated frequency dependence for smectics and other liquid crystals [6]. Field cycling methods have been extended to liquid crystals with deuterated sites [7], but the attention is still concentrated on collective motions, although assessment of anisotropic reorientational motions is achieved. On the other hand, it is usually possible to separate the contribution of these director fluctuations by measuring individual spectral densities $J_1(\omega)$ and $J_2(2\omega)$ as a function of frequency [8]. Whenever this is performed, by use of suitable pulse sequences which allow the simultaneous measurement of Zeeman and Quadrupolar relaxation times, the spectral densities of the different deuterated sites in the molecule can be used for testing theories of rotational diffusion and internal motions. This, however, is not an easy task and several assumptions have to be made; given the complexity of the motions, a superimposed rotation model has usually been assumed.

Furthermore, the chain dynamics is very complicated. In fact, even if the presence of deuterated chains in the molecule can give additional information on the dynamics, the number of parameters used in the fitting of the various spectral densities can be very high [9], and at the moment only simplified models can be tested.

In this paper attention will be focused on 4,4'-heptylazoxybenzene (HAB) since this mesogen has two reasonably wide nematic and smectic A mesomorphic ranges. An attempt will also be made to evaluate the changes in rotational diffusion at the nematic-smectic A transition.

Experimental

HAB-d$_{12}$ had been synthesised for previous studies according to the procedure described by Van der Veen et al. [10]. This compound shows a smectic A phase from 33.8 to 53.8 °C and a nematic phase from 53.8 to 70.7 °C. A schematic representation of the molecule and the labelling used throughout this paper is shown in Figure 1.

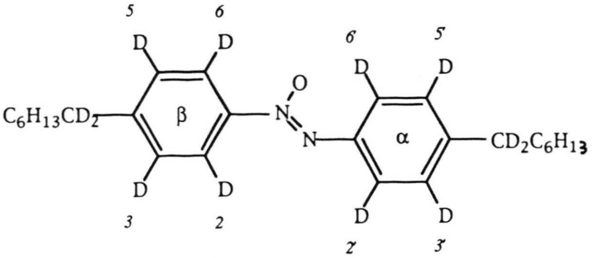

Fig. 1. 4,4'-Heptyl-azoxybenzene-d$_{12}$ (HAB-d$_{12}$).

^{2}H-NMR spectra had been recorded previously [2]: they showed that all deuterons of ring α have the same quadrupolar splitting, while deuterons 2 and 6 of ring β have a quadrupolar splitting slightly different from that of deuterons 3 and 5; the two pairs of aliphatic deuterons show similar quadrupolar splittings giving rise to a single doublet with broad peaks. We were able to distinguish the relaxation times of three types of deuterons: the four deuterons of ring α, a mean value for the four deuterons of ring β and one for the four methylenic deuterons.

The spin-lattice (T_{1Z}) and quadrupolar (T_{1Q}) relaxation times have been determined by means of the Jeener-Broekaert pulse sequence (90_0-D_1-45_{90}-D_2-α) with suitable phase cycling for the suppression of double quantum coherence [11].

The application of the Jeener-Broekaert pulse sequence to the doublet relative to one type of deuterium nuclei changes the intensity of the two peaks in such a way that the sum and the difference of the intensities are respectively related to the relaxation times by the equation

$$M_+(D_2) = 2K \sin\alpha(1 - e^{-D_2/T_{1Z}}), \quad (1\text{a})$$

$$M_-(D_2) = 3K \sin\alpha \cos\alpha \, e^{-D_2/T_{1Q}}), \quad (1\text{b})$$

where α is the flip angle of the monitoring pulse, which is usually chosen around 45° in order to have a large dynamic range, thus being able to measure relaxation of both the sum and difference magnetizations from a single set of recovery curves.

The use of this technique therefore allows the simultaneous determination of the spin-lattice (T_{1Z}) and the quadrupolar (T_{1Q}) relaxation times for one type of deuterium nuclei.

Recently a broadband technique [12], called Wimperis sequence ($90_0-2\tau-67.5_{270}-2\tau-45_{90}-\tau-45_{90}-D_2-\alpha$) has been proposed. Such a sequence eliminates the quadrupolar splitting dependence of the experimental parameters, thus allowing simultaneous measurement of the relaxation times for all different types of deuterons present in the molecule, even if the best value of the parameter τ must be determined experimentally. Some of the measurements, made at 46.04 MHz by means of the Jeener-Broekaert sequence, have been repeated using this technique.

The relaxation times T_{1Z} and T_{1Q} were obtained by means of a three parameter non-linear least squares fit routine run on a PC. The values obtained were used to determine the spectral densities, being

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

$$T_{1Q}^{-1} = 3J_1(\omega) \tag{2b}$$

with $\omega/2\pi$ the Larmor frequency.

The relaxation time measurements were made at two different frequencies (10 and 46.04 MHz) using a Varian XL100 interfaced with a STELAR DS-NMR-386 NMR data acquisition system working at 10 MHz and a Varian VXR-300 working at 46.04 MHz.

The measurements with the Wimperis pulse sequence were made on a Bruker AMX-300 working at 46.04 MHz.

Well resolved spectra were obtained after 800 acquisitions at 10 MHz and after 200 acquisitions at 46.04 MHz. A technique of peak deconvolution was used for the aromatic deuterium signals in the spectra recorded at 10 MHz.

The whole temperature range covering the nematic and smectic A phase was examined. Temperature control was good to 0.1 °C for all instruments.

Theory

In order to treat the complex dynamics in ordered phases, superimposed models have been used to take into account the different types of motion present in the phase. We will briefly consider the models recently used to study the various motions present in uniaxial mesophases and outlined in the introduction.

Molecular Reorientational Motion

Strong collision theories have been used ever since 1967 [13] to model the reorientational motion in ordered media in order to account for the ESR hyperfine linewidths in various systems [14]. They have been used more recently to interpret ^{2}H-NMR relaxation data [15]. Nordio and coworkers [16] have proposed a treatment based on small step rotational diffusion in an anisotropic medium using a restoring potential such as the Maier-Saupe potential. In this model, the rotational diffusion tensor is defined in a molecule fixed frame and is therefore time-independent; the time dependence arises from the transformation to a laboratory fixed frame. The motion is described by the two principal components of an axially symmetric diffusion tensor, $D_\parallel$ and $D_\perp$, which are the rotational diffusion constants of the molecule about the long molecular axis (Z_M) and of the Z_M axis, respectively.

Another model, known as the "third rate anisotropic viscosity model", has been proposed by Vold and Vold [17] which, taking into account the viscosity anisotropy of the mesophase, assumes the rotational diffusion tensor diagonal in the laboratory frame with the z axis along the director and time independent. Thus the reorientational motion is described by the motion of the long molecular axis about the director (α motion) and towards the director (β motion). A third rate constants relative to rotation about the long molecular axis (γ motion), and assumed independent from the overall reorientational motion, is introduced in this model.

For a deuterium which is fixed with respect to the molecular frame, such as a methine deuteron in a linkage group of a mesogenic molecule, the spectral densities in the single exponential approximation are related to the molecular rotational diffusion coefficients by

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

where e^2qQ/h is the quadrupolar coupling constant, the $c_{m_L m_M}$ are the mean squares of the Wigner rotation matrices, β_{M,Q_0} is the angle between the molecular z axis and the C−D bond of interest, and the correlation times $\tau^{(2)}_{m_L m_M}$ are defined as

$$(\tau^{(2)}_{m_L m_M})^{-1} = \frac{D_\perp}{\lambda^{(2)}_{m_L m_M}} + m_M^2(D_\parallel - D_\perp) \tag{4a}$$

in the Nordio model, and

$$(\tau^{(2)}_{m_L m_M})^{-1} = k_{m_M} + \frac{D_\beta}{\lambda^{(2)}_{m_L m_M}} + m_L^2(D_\alpha - D_\beta) \tag{4b}$$

in the "third rate anisotropic viscosity model". The D_i's are the rotational diffusion coefficients mentioned above, the $\lambda^{(2)}_{m_\mathrm{L} m_\mathrm{M}}$ terms depend on the orientational order parameter $\bar{P}_2$, and their values are reported by Agostini et al. [16]. The terms k_{m_M} in the Vold model are given by

$$k_0 = 0\,, \tag{5a}$$

$$k_2 = (3p+1)\,k_1 \tag{5b}$$

and therefore depend on the γ motion. The parameter p can assume values between 0 and 1: one has in the strong collision assumption $p = 0$, while in the small step rotational diffusion model $p = 1$. In the former case results

$$k_{m_\mathrm{M}} = (1 - \delta_{m_\mathrm{M} 0})\, D_\gamma\,. \tag{6}$$

Internal Motions

The internal motions of interest in the type of molecules here considered are rotations of the rigid fragments, such as methylene groups or aromatic rings. This type of motion is usually treated as a free rotation around a C–C bond [18] or as jumps between energetically favourable positions [19], but in all cases it is assumed independent from other motions. Thus, for example, for a ring deuteron or for the methylene group attached directly on the aromatic ring, (3) is modified to include an additional rate constant D_i which describes the free rotation of the ring about the para axis or the free rotation of the C_1–D bond about the ϕ–C_1 bond, respectively:

$$J^{(i)}_{m_\mathrm{L}}(m_\mathrm{L}\,\omega) = \frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2 \cdot \sum_{m_\mathrm{M}=-2}^{2}\ \sum_{m_i=-2}^{2} c_{m_\mathrm{L} m_\mathrm{M}}\,[d^2_{m_i 0}(\beta_{i,\mathrm{Q}_i})]^2\,[d^2_{m_\mathrm{M} m_i}(\beta_{\mathrm{M},i})]^2 \cdot \frac{1}{[(\tau^{(2)}_{m_\mathrm{L} m_\mathrm{M}})^{-1} + (1-\delta_{m_i 0})\,D_i]}\,, \tag{7}$$

where β_{i,Q_i} is the angle between the C–D_i bond and the rotation axis of the i-th fragment, while $\beta_{\mathrm{M},i}$ is the angle between the molecular axis and the rotation axis of the i-th segment.

Collective Motions

The order director fluctuation is a collective motion which comprehends oscillations of several neighbouring molecules about the director of the phase. This type of motion is usually considered negligible above 1 MHz. A simplified theory, which assumes that these order director fluctuations are small and not coupled to reorientational motions, predicts [4, 5] that the contribution to J_1 in the nematic phase is

$$J_1^{(i)\,DF}(\omega) = \frac{e^2qQ}{h}\, A_\mathrm{DF}\,[P_2(\cos\beta_{i,\mathrm{Q}_i})]^2\,\omega^{-1/2}\,, \tag{8}$$

where

$$A_\mathrm{DF} = \left(\frac{3\pi^2}{2}\right)\frac{3kT\,(\bar{P}_2)^2}{4\pi\sqrt{2}\,K\,(D + K/\eta)^{1/2}} \tag{9}$$

with K the average Frank elastic constant, D the average autodiffusion translational constant, η the average viscosity coefficient of the liquid crystal phase, β_{i,Q_i} the angle formed by the C–D bond and the long axis of the rigid fragment under examination, and $\bar{P}_2$ the molecular order parameter.

Order director fluctuations are not predicted to influence J_2. Thus on the basis of this simple theory the inverse square root dependence of J_1 on frequency and the lack of frequency dependence in J_2 should be interpreted as revealing the presence of non negligible order director fluctuations. Moreover, from (8) the spectral density J_1 of the aromatic core deuterons is expected to be insensible to frequency variations since the angle of the corresponding C–D bond with respect to the molecular principal axis is around 60°, a value close to the magic angle where P_2 is 0.

As far as the smectic A phase is concerned, both theoretical [6] and experimental [7] studies indicate a different frequency dependence of the relaxation times with respect to the nematic phase. A similar behaviour in the two phases is however predicted for Larmor frequencies above 1 MHz [6].

Results and Discussion

A series of spectra of HAB-d_{12} obtained with the Jeener-Broekaert pulse sequence at $T = 313$ K with different delays is shown in Figure 2. The comparison of the relaxation times obtained by using the inversion recovery technique, which yields only $T_{1\mathrm{Z}}$, the Jeener-Broekaert and the Wimperis pulse sequences, which yield both $T_{1\mathrm{Z}}$ and $T_{1\mathrm{Q}}$, reveals good agreement especially for the aromatic deuterons which have the smaller quadrupolar splitting. As an example, the data obtained with the three different techniques at $T = 331$ K are shown in Figure 3. In all three types of

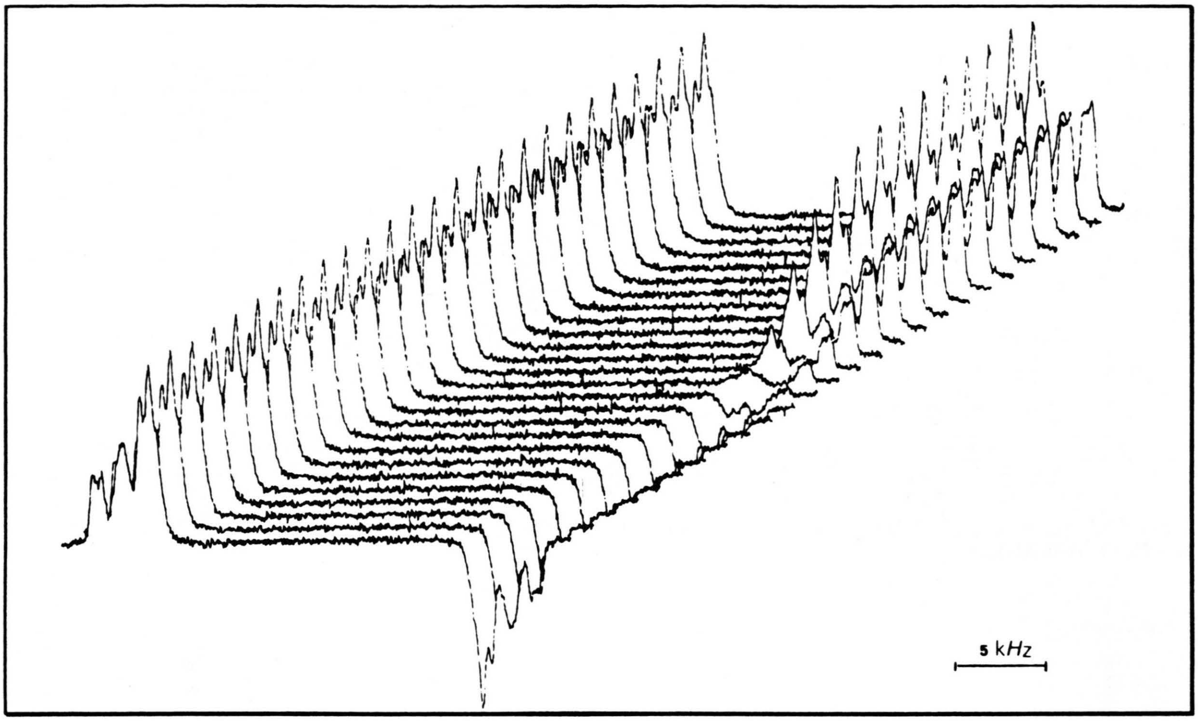

Fig. 2. Series of spectra of the aromatic core of HAB-d_{12} obtained using the Jeener-Broekaert pulse sequence with D_2 varying from 0 to 0.2 s, at $T = 313$ K.

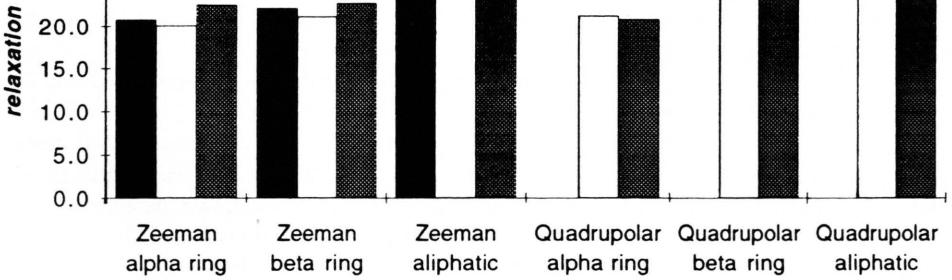

Fig. 3. Relaxation times T_{1Z} and T_{1Q} (msec) of the three types of deuterium nuclei determined at 331 K by means of Inversion-Recovery, Jeener-Broekaert and Wimperis techniques.

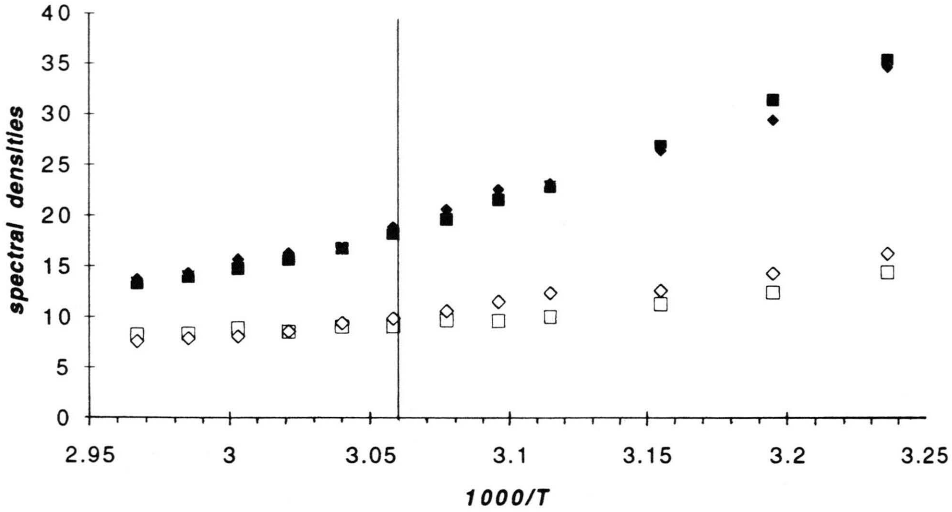

Fig. 4. Spectral densities ($\sec^{-1}$) of deuterium nuclei of ring α vs. $1000/T$ (K^{-1}). The symbols refer to J_1 (◆, ■) and J_2 (◇, □) at 10 and 46.04 MHz, respectively.

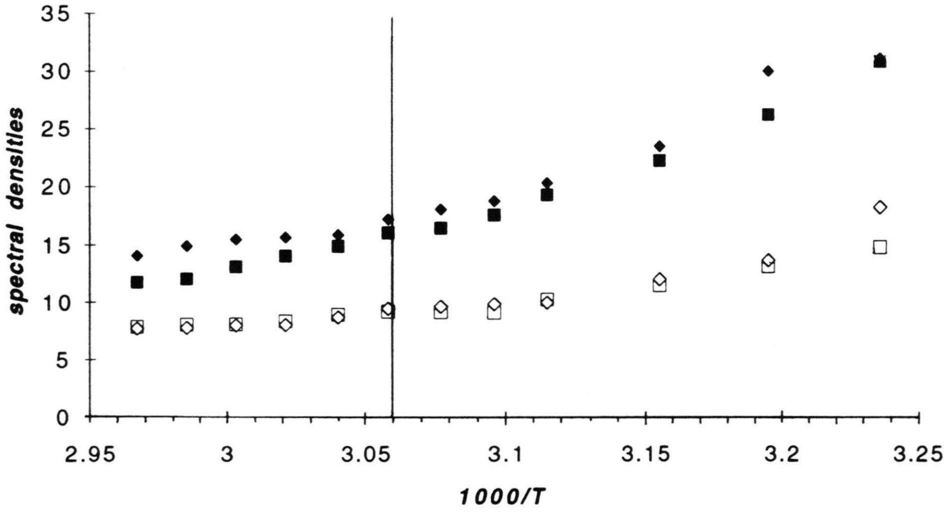

Fig. 5. Spectral densities ($\sec^{-1}$) of deuterium nuclei of ring β vs. $1000/T$ (K^{-1}). The symbols refer to J_1 (◆, ■) and J_2 (◇, □) at 10 and 46.04 MHz, respectively.

experiments the relaxation times are obtained with a maximum error of 5% for the aromatic deuterons and 10% for the aliphatic ones.

In Fig. 4 the temperature dependence of the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ for the aromatic ring α is plotted, while in Fig. 5 the values of $J_1(\omega_0)$ and $J_2(2\omega_0)$ for ring β are shown. As expected, the spectral densities of the aromatic deuterons do not show any frequency dependence. The values of J_2 for the two aromatic rings are practically coincident, while for J_1 the α ring deuterons show slightly bigger values with respect to the β ring deuterons. The ratios J_1/J_2 for the aromatic deuterons assume values between 1.5 and 2.5, in agreement with the values commonly found for thermotropic liquid crystals [17].

The temperature dependence of the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ for the CD_2 deuterons at the two frequencies examined is shown in Figure 6. In this case the frequency dependence is evident and we can therefore infer a contribution to relaxation from director fluctuations. For these deuterons a different trend with respect to temperature is also apparent:

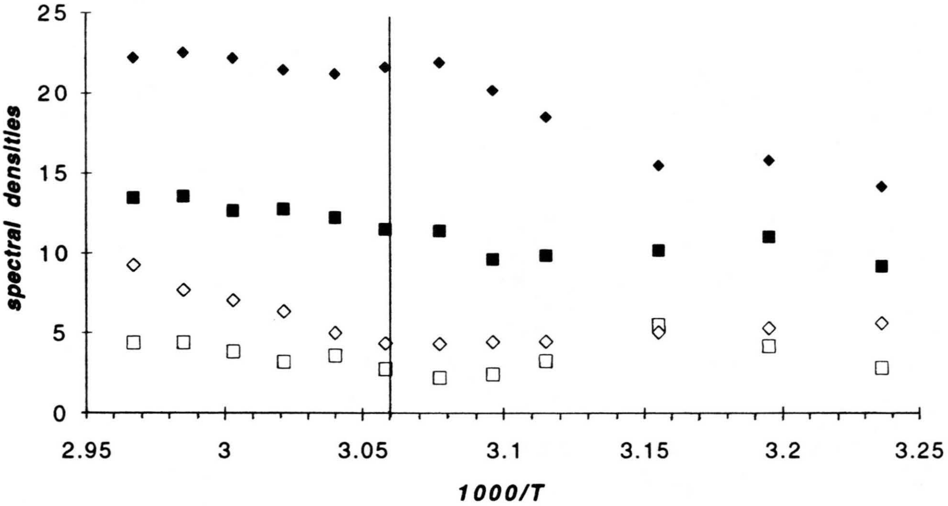

Fig. 6. Spectral densities (sec^{-1}) of deuterium nuclei of the first methylene group of the chains vs. $1000/T$ (K^{-1}). The symbols refer to J_1 (◆, ■) and J_2 (◇, □) at 10 and 46.04 MHz, respectively.

while $J_1(\omega_0)$ and $J_2(2\omega_0)$ of the aromatic deuterons increase monotonically with decreasing temperature, the spectral densities of the aliphatic deuterons decrease in the nematic phase and show a non regular behaviour in the smectic phase. The ratio J_1/J_2 for the aliphatic CD_2 deuterons is nearly double with respect to the same ratio for the aromatic deuterons.

The spectral densities have been interpreted within the small step rotational diffusion model of Nordio with superimposed free rotation for the internal motions ((7) and (4 a)), taking also into account the contribution to $J_1(\omega)$ of the order director fluctuations according to (8). The 12 values of $J_1(\omega)$ and $J_2(2\omega)$ for the different deuterons at the two different frequencies have therefore been used within a non-linear least squares fitting procedure to determine 6 unknowns, i.e. the rotational diffusion constants $D_{\parallel}$ for the spinning motion of the molecule along the main molecular axis, $D_{\perp}$ for the tumbling motion, $D_{R\alpha}$, $D_{R\beta}$ for the rotation of the benzene rings about their para axes, and D_1 for the rotation of the CD_2 group along the C-phenyl bond, in addition to the coefficient A_{DF} which appears in (8).

In the computations, the values of the quadrupolar coupling constants have been assumed to be 185 and 165 kHz for the aromatic and the aliphatic deuterium nuclei, respectively, while the asymmetry parameter η has been neglected. The principal molecular axis has been assumed to lie along the para axis of ring β, which is the most oriented one. The para axis of ring α has been taken at 17° with respect to the long axis according to the findings of [2]. The same should have been done for the two CD_2. In this case, however, since we were not able to distinguish the two different CD_2 groups, which also lie at a different angle with respect to the principal molecular axis, two series of calculations were performed assuming for $\beta_{M,1}$ a value of 0° and 17°, respectively, and taking the average value for the resulting diffusion constant.

In Fig. 7 the diffusion coefficients obtained at the different temperatures examined are reported. The maximum standard deviations are 20% for $D_{\parallel}$, 25% for $D_{R\alpha}$, $D_{R\beta}$, and D_1, 30% for $D_{\perp}$. It can be observed that the values of $D_{\parallel}$, $D_{R\alpha}$, and $D_{R\beta}$ are nearly the same and increase slowly with increasing temperature in both the nematic and smectic phase. $D_{R\beta}$ is always slightly higher than $D_{R\alpha}$ while $D_{\perp}$ is the slowest one and only slightly temperature dependent. In contrast with the other diffusion coefficients, D_1 increases with decreasing the temperature in the nematic phase, while it shows a more complex trend in the smectic A phase; this could be a consequence of pre-transitional phenomena.

An attempt to fit our data with the "third rate anisotropic viscosity model" was also made but did not yield satisfactory results. In fact, the additional diffusion constant introduced in this model was strongly correlated to the diffusion coefficients relative to the ring rotations and therefore no additional information could be obtained.

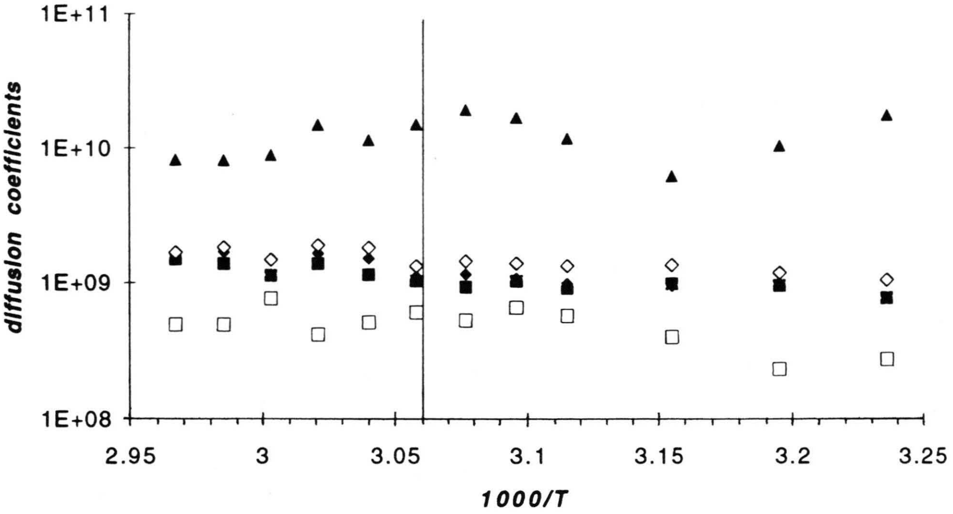

Fig. 7. Diffusion coefficients (sec^{-1}) vs. 1000/T (K^{-1}). The symbols refer to D_1 (▲), $D_{R\beta}$ (◇), $D_{R\alpha}$ (◆), $D_{\parallel}$ (■) and $D_{\perp}$ (□).

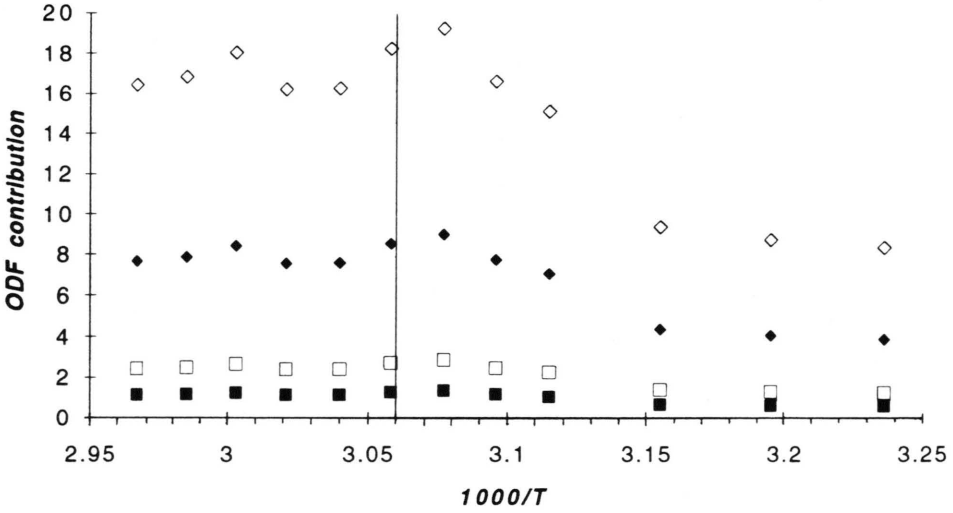

Fig. 8. Contribution of order director fluctuations (ODF) to the spectral density J_1 (sec^{-1}) vs. 1000/T (K^{-1}). The symbols refer to aliphatic deuteria (◇, ◆) and to aromatic deuteria (□, ■) at 10 and 46.04 MHz, respectively.

In Fig. 8 the director fluctuation contributions J_{DF} are shown. The maximum standard deviation for J_{DF} is 10%.

In agreement with the theory, J_{DF} is very low for the aromatic deuterons. For the methylene deuterons, this contribution is poor in the smectic phase at lower temperatures and increases with the temperature, remaining nearly constant in the nematic phase. As expected from theory, J_{DF} is much bigger at the lower frequency.

The experimental values of J_{DF} at some of the temperatures examined have been compared with the values calculated on the basis of (8) by using the known values for the elastic constant and the viscosity coefficient [20, 21], and a value relative to a similar mesogen [22] for the translational autodiffusion coefficient. The order of magnitude of the values thus determined and of those obtained from the fitting procedure is the same.

In most dynamical studies of liquid crystals performed in the MHz region, the order director fluctuation contribution has been assumed negligible. In some cases, however, it has been found to be relevant [23]. Recently, the frequency dependence of the spectral densities has been ascribed to correlated rotations of the different chain segments [9]. If these correlations are taken into account in the theory, however, a dependence of J_2 on frequency is also to be expected. This is not the case of our data, where no such dependence was found.

Conclusions

In agreement with a previous comparison [24], we have found in the present work that the broadband excitation Jeener-Broekaert sequence gives results in agreement with the selective excitation one and is therefore preferable, being less time-consuming.

Notwithstanding the complexity of the problem and the high number of parameters involved, the experiments in this work allow to study in some detail both molecular reorientational and internal motions. The influence of director fluctuations is not negligible, even though it is more relevant at lower frequencies and better investigated by dispersion methods. The combined use of both types of experiments would be very fruitful in the study of the dynamics of liquid crystalline systems.

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