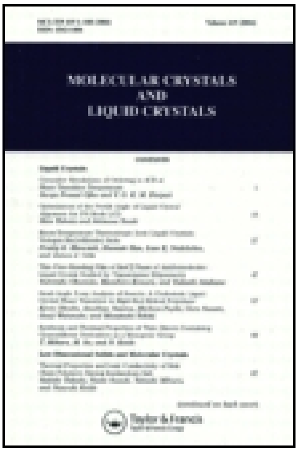

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Deuterium Spin-Lattice Relaxation in Thermotropic Liquid Crystals. Study of 4,4′-di-n-heptylazobenzene, 4,4′-di-n-heptylazoxybenzene and 4,4′-di-n-octylazoxybenzene

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Deuterium Spin-Lattice Relaxation in Thermotropic Liquid Crystals. Study of 4,4′-di-n-heptylazobenzene, 4,4′-di-n-heptylazoxybenzene and 4,4′-di-n-octylazoxybenzene

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The deuterium Zeeman spin-lattice relaxation times T_{1Z} in 4,4′-di-n-heptylazobenzene (HB), 4,4′-di-n-heptylazoxybenzene (HAB), and 4,4′-di n-octylazoxybenzene (OAB) deuterated on the aromatic rings and on the first methylene group of the chains were measured at 10 and 46.04 MHz by means of the inversion-recovery technique. Measurements were made throughout the mesomorphic range and also in the isotropic phase. The relaxation rates show a discontinuity at the isotropic-nematic transition for all deuterons not ascribable to the onset of orientational order. The trends of lnR are linear within the different phases except near phase transitions, and allow to obtain apparent activation energies for the overall motions of the different C—D bonds.

INTRODUCTION

The orientational ordering of three liquid crystal molecules (4,4′-di-n-heptylazobenzene (HB), 4,4′-di-n-heptylazoxybenzene (HAB), and 4,4′-di n-octylazoxybenzene (OAB)), and of a series of solutes dissolved in them, in the full range of the mesomorphic phases, has been examined previously by means of ^{2}H-NMR.[1,2] This study, in addition to reveal a different order for the various molecular fragments of the mesogenic molecules, has shown that the aromatic core of the liquid crystal molecules has a very low biaxiality. A quite different behaviour was shown by solutes having the same aromatic core as the solvent, like azoxybenzene, for which an appreciable biaxiality was found. In order to better understand the different orientational behaviour of these compounds, especially near phase transitions, it is important to obtain information on the dynamics of the aromatic core and that of the chains.

Measurement of relaxation rates provides a powerful method of studying the dynamics in condensed phases. Deuterium nuclear magnetic resonance spectroscopy in particular has revealed a powerful technique in studying liquid crystal molecules[3-14] in that it provides well resolved spectra in both the isotropic and in the liquid crystalline phases, therefore giving information on specific deuterated sites. Determination of relaxation rates of individual nuclei is therefore possible throughout the mesomorphic and isotropic range. The spectral resolution arises from the large differences in the partially averaged quadrupolar interactions in the liquid crystal phases, while in the isotropic phase it is determined by small differences in chemical shifts. Deuterium spin-lattice relaxation, moreover, arises essentially from intramolecular interactions; their treatment is therefore simpler than that of proton. These features of ^{2}H-NMR allow to investigate relaxation behaviour close to the phase transition and to reveal interesting pre-transitional effects as well as discontinuities in the relaxation rate at the transition.

Using suitable NMR pulsed techniques[15] it is possible to determine different spectral densities of motion the temperature and frequency dependence of which give information on different types of molecular motions.

We report here on a preliminary study on T_{1Z} relaxation of the three liquid crystalline compounds HB, HAB, and OAB, for the moment directing our attention essentially to the aromatic core. The measurements have been made at two frequencies throughout the mesomorphic range and extended to the isotropic phase.

EXPERIMENTAL

The liquid crystal molecules studied are schematically shown in Figure 1. The samples of the partially deuterated liquid crystals were available from the previous study[1]. HAB and OAB give a nematic and smectic A phase while HB gives only a nematic phase. Transition temperatures are given in Table I. The nematic range of OAB is very small and the smectic phase coexists with the nematic phase. Spin-lattice relaxation rates at different temperatures were determined for the different deuterons at two different frequencies using the inversion recovery pulse sequence with composite pulse technique $90°_x$-τ-$180°_y$-τ-$90°_x$-τ_1-$90°_x$ with phase cycling using values of τ of the order of 10 μsec. A Varian XL100 interfaced with a STELAR DS-NMR-386 NMR data acquisition system working at 10MHz and a Varian VXR-300 working at 46.04 MHz were used. The spectra were obtained after 16 acquisitions in the isotropic phase and 400 in the ordered phases at 10 MHz and 8 and 100 respectively at 46.04 MHz. Temperature control was good to 0.1° for both instruments.

The relaxation time T_1 was obtained by means of a three parameter non-linear least squares fit routine run on a PC. The resulting relaxation rates $R = (T_1)^{-1}$ are presented in logarithmic plots against the inverse of temperature in Figures 2–4 (errors are within 8%).

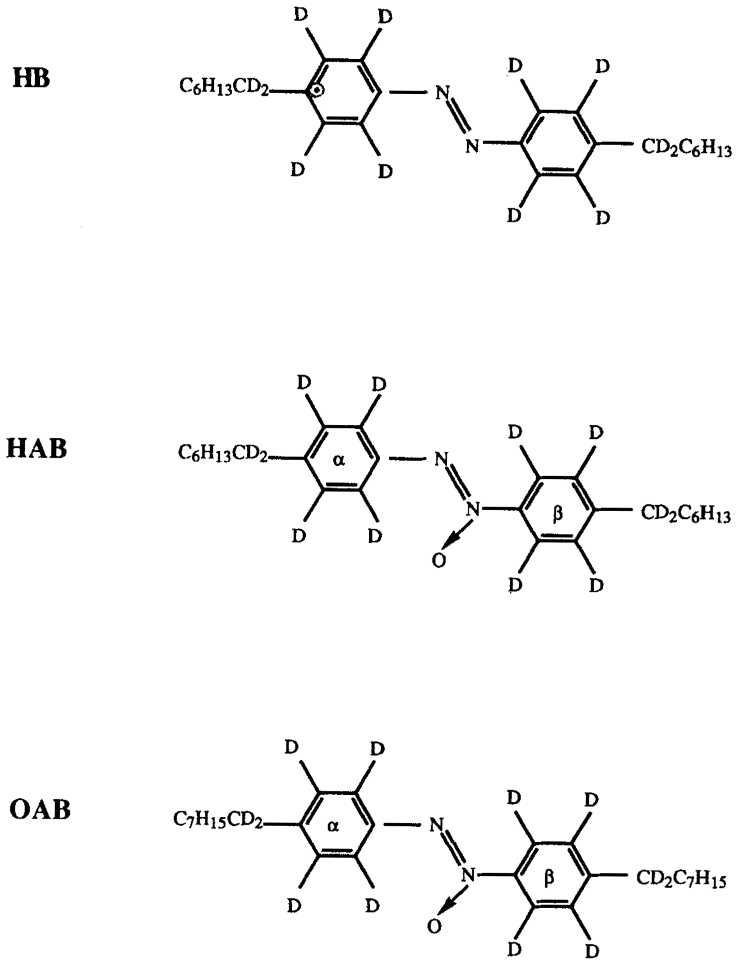

FIGURE 1 Schematic representation of the three molecules examined with the labelling used.

RESULTS AND DISCUSSION

Deuteron relaxation is essentially due to the modulation of the intramolecular interaction between its nuclear quadrupole moment and the electric field gradient acting on the nucleus. The molecular motions which modulate these interactions are therefore molecular reorientations, internal rotations and order director fluctuations. The total relaxation rate can thus be approximated to the sum of four contributions:

$$T_1^{-1} = T_{1I}^{-1} + T_{1R}^{-1} + T_{1\mathrm{ODF}}^{-1} + T_{1\mathrm{cross}}^{-1} \qquad (1)$$

The cross term arises from coupling between reorientational motion and collective

TABLE I

Temperature range for the different phases of the pure compounds

	Range (°C)	
	smectic	nematic
di-n-heptylazobenzene		33 - 48
di-n-heptylazoxybenzene	33.8 - 53.8	53.8 - 70.7
di-n-octylazoxybenzene	38.8 - 64.4	64.4 - 66.6

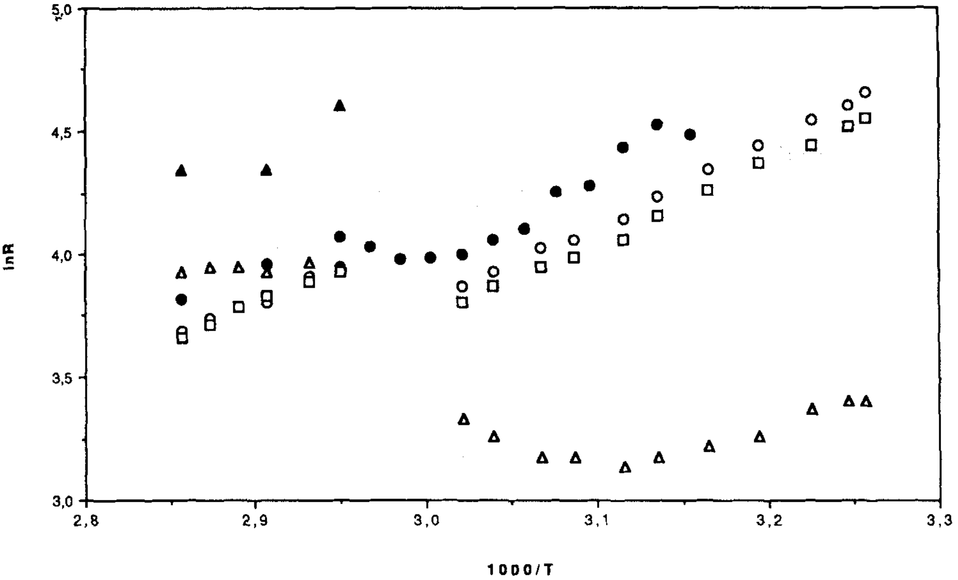

FIGURE 2 The natural logarithm of the relaxation rates for the deuterons in HAB: (▲ and △) methylenic deuterons at 10 and 46 MHz respectively; (●) aromatic deuterons at 10 MHz; (○) ring α deuterons at 46 MHz; (□) ring β deuterons at 46 MHz.

order fluctuations.[16,17] This term however is predicted to be negligible.[17] The order director fluctuation term, if relevant, should give a square root dependence on frequency, while, on the basis of the existing theories,[17] the remaining terms are predicted to be frequency dependent only for liquid crystals with high viscosity. The relaxation times measured for the aromatic deuterons of OAB and HAB are practically independent of frequency in the range 10–46 MHz. In fact director fluctuations are not expected to contribute considering the orientation of the aromatic C—D bonds near the magic angle. In the single elastic constant approximation, this term can be simply evaluated, being[18]:

$$\left(\frac{1}{T_1}\right)_{\mathrm{ODF}} = \frac{9}{32}\left(\frac{e^2qQ}{\hbar}\right)^2 \frac{kT}{\sqrt{2}\pi} \frac{1}{K\sqrt{D+\dfrac{K}{\eta}}} \frac{1}{4\sqrt{\omega_L}} S^2 \,(1\text{-}3\cos^2\beta)^2 \tag{2}$$

with (e^2qQ/h) the quadrupolar coupling constant, K the mean elastic constant, D

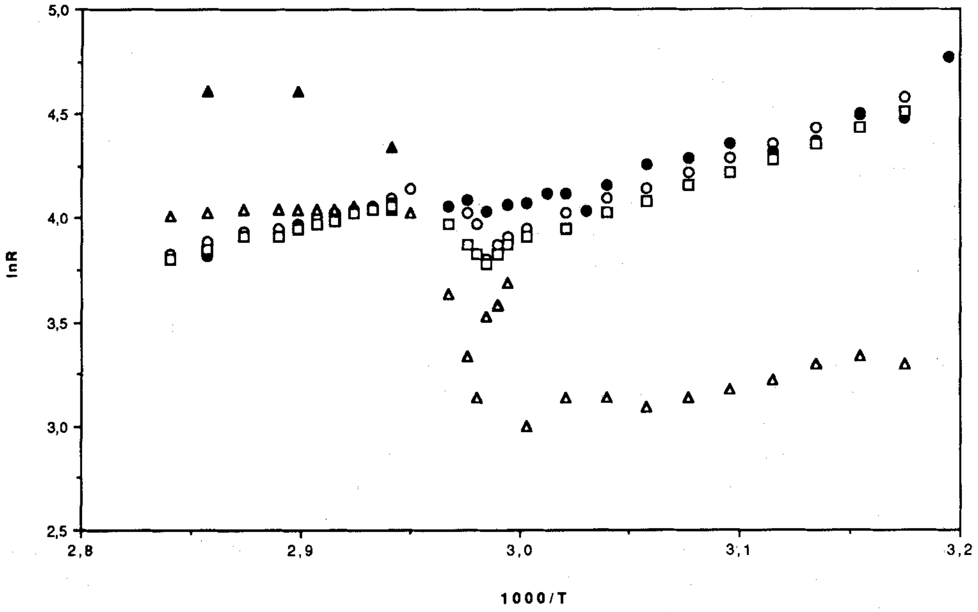

FIGURE 3 The natural logarithm of the relaxation rates for the deuterons in OAB: (▲ and △) methylenic deuterons at 10 and 46 MHz respectively; (●) aromatic deuterons at 10 MHz; (○) ring α deuterons at 46 MHz; (□) ring β deuterons at 46 MHz.

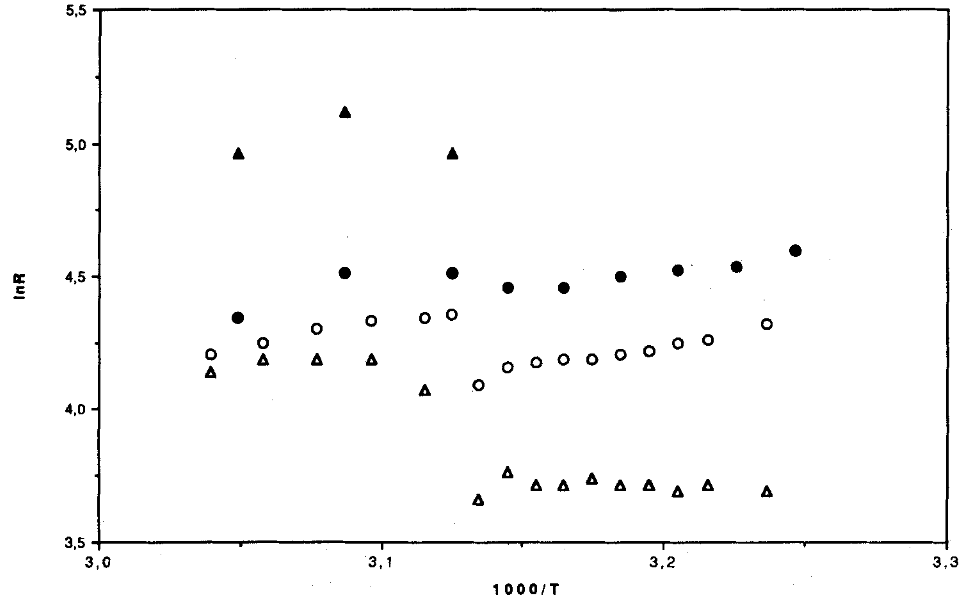

FIGURE 4 The natural logarithm of the relaxation rates for the deuterons in HB: (▲ and △) methylenic deuterons at 10 and 46 MHz respectively; (● and ○) aromatic deuterons at 10 and 46 MHz respectively.

the diffusion constant, η the viscosity, ω_L the Larmor frequency, S the molecular order parameter and β the angle between the C—D bond under examination and the molecular axis. Within this approximation the contribution of this term to the total relaxation rate for the three compounds under examination is of the order of 0.1%. The frequency dependence observed for HB and also for the chains of OAB and HAB could arise from other motions. Frequency dependence has been observed in other liquid crystal compounds of low viscosity[4,6] in disagreement with existing models. In particular in a preliminary study of 4-n-pentyl-d_{11}-4′-cyanobiphenyl-d_4[4] the frequency dependence of relaxation rates has been found to be site dependent with the strongest effect on the first methylene group. According to Dong[14] the frequency dependence of relaxation rates for chain deuterons can be qualitatively predicted if all possible configurations are considered when modeling internal rotations. In order to treat the contributions of internal and reorientational motions to the total relaxation rate however, measurements of the different spectral densities of motion at least at three frequency values are necessary. However, even if our data are relative only to two frequencies, some observations can be made by analysing the trend of the data in the different phases and for the different deuterons. The spin-lattice relaxation rate of a given deuteron depends upon the motions of the C—D bond of interest in the laboratory frame but also on the local order parameter P_2^{CD} along the C—D bond, since the orientation of the principal axis of the quadrupolar interaction tensor, usually assumed along the C—D bond, determines the degree of contribution of the different motions to relaxation. It has been shown by Beckmann *et al.*[10] that a simple expression can be obtained for the spin-lattice relaxation rate in terms of the local order parameter by making a few assumptions. The authors express the spectral density functions as:

$$J_{m_L}(m_L\omega_0) = (F^{(2,0)})^2 \int_0^\infty \overline{D^2_{0m_L}\{\Omega_{LM}(0)\}D^{2*}_{0m_L}\{\Omega_{LM}(t)\}}\cos(m_L\omega_0 t)dt \qquad (3)$$

where the molecular frame chosen is the principal frame for the quadrupolar interaction tensor, usually assumed of cylindrical symmetry about the C—D bond direction of the deuterium site under examination; $F^{(2,0)}$ is the 0th component of the irreducible spherical tensor representing the quadrupolar interaction in the laboratory frame; $D^2(\Omega_{LM})$ are Wigner rotation matrices[19] with Ω_{LM} indicating the set of Euler angles which define the orientation of the molecule in the laboratory frame.

The first simplifying assumption made[10] is that the correlation function can be written as a product of a time independent term and a time dependent one:

$$\overline{D^2_{0m_L}\{\Omega_{\mathrm{LM}}(0)\}D^{2*}_{0m_L}\{\Omega_{\mathrm{LM}}(t)\}} = \overline{|D^2_{0m_L}|^2}g_0(t) \qquad (4)$$

A further assumption made, which is consistent with the strong collision model for the reorientational motion,[20] is that the reduced correlation function $g_0(t)$ is independent of m_L. With this simplification, Equation (3) becomes[10]:

$$J_{m_L}(m_L\omega_0) = (F^{(2,0)})^2\, \overline{|D^2_{0m_L}|^2}\tau^0_{CD} \qquad (5)$$

with:

$$\tau_{CD}^{0} = \int_{0}^{\infty} g_0(t)dt$$

an apparent correlation time resulting from different motions.

The spin-lattice relaxation rate is related to the spectral density functions $J_1(\omega)$ and $J_2(\omega)$:

$$R = J_1(\omega) + 4J_2(2\omega) \tag{6}$$

Substituting the corresponding expression for the spectral density functions according to Equation 5, and expressing the product of the Wigner rotation matrices in terms of the Legendre polynomials $P_L(\cos\beta)$ by means of the Clebsch-Gordan series,[19] the relaxation rate can be rewritten as:

$$R^{i} = (F_{i}^{(2,0)})^{2}(1 - \overline{P_{2}^{i}})\tau_{i}^{0} \tag{7}$$

where P_2^i is the order parameter along the C—D bond under examination.

The relation expressed in Equation (7) between the relaxation rate of the ith deuteron and P_2^i is quite useful since the orientational order parameters are easily determined from quadrupolar splittings, as widely illustrated in a previous work,[1] and the relaxation data can be discussed in terms of such parameters.

The data recorded at 46.04 MHz and reported in Figures 2, 3 and 4 relative to the three liquid crystal molecules respectively, show that in the ordered phases the α methylenic deuterons have a lower relaxation rate with respect to the aromatic ones and, for OAB and HAB, where two types of aromatic rings are present, ring α has a higher rate with respect to ring β (see Figure 1 for the labelling of the molecules), even if the difference is sensibly lower. In the ordered phases at 10 MHz, instrumental limits prevented a significant determination of T_1 for the methylenic deuterons and the discrimination between T_1 of the α and β ring deuterons. In the isotropic phase, the methylenic deuterons have a higher relaxation rate than the aromatic ones in the cases of HB at 10 MHz and HAB and OAB at both 10 and 46.04 MHz.

We will specifically consider the data relative to HAB in the nematic and smectic regions, the orientational order of which has been studied in greater detail. Here the orientational parameters reveal that ring β is more oriented with respect to ring α; this indicates that the principal axis of the molecule is closer to the C_2 axis of the β phenyl ring. The molecular axis has been therefore assumed coincident with the ring β axis and the order parameters have been related to such axis. The order parameters along the two C—D bonds under examination result to be both negative with $|P_2|$ of the C—D_β bond larger than that of the corresponding bond in ring α. If the two deuterons had the same quadrupolar interaction tensor and same apparent correlation time, on the basis of Equation (7), we would expect the deuteron of ring β to have a larger value of R at all temperatures. Actually the deuteron of ring α has a value of relaxation rate 5 to 10% larger than that of ring β at all temperatures. This difference could be justified by a difference of 10 kHz in the quadrupolar coupling constant, a difference which has been observed in some aromatic compounds,[21] or by assuming a greater value of τ_i^0 for ring α with respect to ring β.

As far as the methylene deuterons are concerned, the data clearly reveal a smaller value of τ_i^0 with respect to the aromatic ones.

If we consider the logarithm of the relaxation rates of one type of deuteron throughout the temperature range studied we observe that, within the different phases, the trend with the inverse of temperature is linear. Exceptions are in the regions close to nematic-isotropic phase transitions and for the nematic phase of OAB. This phase however has a very small range of existence for the pure compound (only 2°); in presence of impurities, as in our case, this nematic phase practically represents a transition from smectic to isotropic phase. Moreover, there is discontinuity in the relaxation rate at the isotropic-nematic transition. This discontinuity could be due to discontinuity in P_2 which goes from 0 to a finite value. If the linear trends in the nematic phase of HAB and HB are extrapolated into the isotropic phase, assuming a continuous change in τ_i^0 at the isotropic-nematic transition and exploiting our detailed knowledge of P_2 near the transition temperature, the trends for the isotropic phase predicted on the basis of Equation (7) lie in general below the experimental data. The predicted values of R_I/R_N for HAB at the isotropic-nematic transition are compared with the values obtained extrapolating the experimental trends within the different phases to transition in Table II. The discrepancy is particularly evident in the case of the methylenic deuterons. All this reflects changes in motion expected on entering the nematic phase due to changes in anisotropy of molecular rotation as well as changes in internal motions. If a non-negligible contribution of order director fluctuations to the total relaxation rate were present, it would cause an increase of R on going from the isotropic to the nematic phase, being $R_{1_{\mathrm{ODF}}} = 0$ in the isotropic phase and positive in the nematic phase. The trend of the data at the transition can be justified only assuming that the contribution to the relaxation rate of internal rotations and molecular reorientations, which we will indicate as R_{mol}, has a different temperature dependence in the two phases and a discontinuous change in R_{mol} at the transition is expected. The results relative to the chain deuterons, together with the strong frequency dependence observed, possibly ascribable to internal rotations, seem to indicate that the change at the transition is probably due mainly to a change in internal motions.

The small variation in the linear trend of $\ln R$ with $1/T$ on going through the smectic-nematic phase transition of HAB can be explained just with a change in P_2 only for the methylenic deuterons (see Table II) while the aromatic deuterons show a stronger decrease in R on going from smectic to nematic with respect to the one predicted assuming a variation of orientational order only. This seems to indicate that also for this phase transition there is a variation in R_{mol}, and in particular in internal rotations for the aromatic rings, while molecular rotations and internal motions of the chain do not change.

The experimental relaxation times are strongly temperature dependent; this indicates that the deuteron spin relaxation is thermally activated. In particular $\ln R$ varies linearly with the inverse of temperature over a wide temperature range of

TABLE II

Predicted theoretical and experimental values of the ratios of relaxation rates in the nematic and isotropic phase at the NI transition and in the smectic and nematic phase at the SN transition for HAB

	R_N/R_I		R_N/R_{Sm}	
	theor.	exp.	theor.	exp.
D_α	0.969	0.923	0.995	0.921
D_β	0.962	0.882	0.995	0.931
D_1	0.844	0.538	0.985	0.985

TABLE III

Experimental apparent activation energies E_i^{CD} in kJ mol^{-1}

	smectic phase	nematic phase	isotropic phase
HAB			
ring α	28.9 ± 1.0	24.7 ± 1.0	23.7 ± 1.0
ring β	26.4 ± 1.0	22.1 ± 1.0	24.1 ± 1.0
CD_2	16.3 ± 1.0		1.8 ± 1.0
OAB			
ring α	30.6 ± 1.0		21.7 ± 1.0
ring β	29.4 ± 1.0		20.8 ± 1.0
CD_2	14.0 ± 1.0		4.1 ± 1.0
HB			
ring		13.6 ± 1.0	14.6 ± 1.0
CD_2		1.3 ± 1.0	5.8 ± 1.0

the different phases for all deuterons. In the isotropic phase, where the order parameters P_2 are 0, such linear dependence indicates that spin relaxation is dominated by motions with $\omega_0\tau_i^0 << 1$ and τ_i^0 obeys an Arrhenius type relationship:

$$\tau_i^0 = \tau_{i\infty}^0 \exp(E_i^{CD}/RT) \tag{8}$$

The values of the activation energy E_i for the different deuterons in the isotropic phase can therefore be obtained from the slopes of the trends of $\ln R_i$ with $1/T$. The values thus obtained, and reported in Table III, are apparent activation energies arising from the combination of all motions. If the slopes of the trends relative to the ordered phases, corrected for the effect of the temperature dependent factor $(1\text{-}P_2)$, are interpreted in an analogous way, a general reduction of the apparent activation energy on going from the smectic phase to the nematic and then to the isotropic phase is found. The deuterons of the first CD_2 group of the chain have in all cases smaller activation energy with respect to the aromatic deuterons. This could be associated with the higher order parameters observed for the methylene deuterons, which increase the contribution to the relaxation rate from molecular libration about the short molecular axis, a process expected to have lower activation energy, or with the internal rotation around the phenyl-C_1 bond as we shall see later.

Strongly activated relaxation rates were observed previously for aromatic deuterons in MBBA[22] and 4O.8[23] and were interpreted as suggesting that these deuterons relax predominantly by fast rotation of the whole molecule about the long molecular axis or by internal rotation of the aromatic ring. As already mentioned, our data do not allow us to evaluate the different contributions to the total relaxation rate. However we can try to roughly estimate the relative importance of the two types of motion mentioned above by making some assumptions. Using the superimposed free rotations model in the fast motion limit, assuming that internal and external motions are decoupled, the relaxation rate for the first CD_2 deuterons and for the aromatic deuterons can be expressed in terms of the reduced Wigner functions as[10]:

$$R_i = (F_i^{(2,0)})^2[2(1 + \overline{P_2})(d^2_{02}(\beta_i))^2\{(\tau_M^{(2)})^{-1} + \tau_i^{-1}\}^{-1} + (2 - \overline{P_2})(d^2_{01}(\beta_i))^2\{(\tau_M^{(1)})^{-1} + \tau_i^{-1}\}^{-1} + (d^2_{00}(\beta_i))^2\tau_M^{(0)}] \quad (9)$$

with the index *i* either equal to 1 for the methylene group or to *R* for the aromatic ring and τ_M the molecular rotational correlation time. For simplicity we will assume here that $\tau_M^{(2)}$, $\tau_M^{(1)}$, and $\tau_M^{(0)}$ are of the same order of magnitude. Moreover, due to the relative magnitudes of the reduced Wigner matrix elements, the last term in Equation (9) is small in comparison with the other two. Therefore we can write:

$$R_i = (F_i^{(2,0)})^2[2(1 + \overline{P_2})(d^2_{02}(\beta_i))^2 + (2 - \overline{P_2})(d^2_{01}(\beta_i))^2]\tau_i' \quad (10)$$

where:

$$\tau_i'^{-1} = \tau_M^{-1} + \tau_i^{-1}$$

The composite correlation time τ' should have a biexponential temperature dependence. As already observed, ln$R$, and therefore τ', has a linear trend with $1/T$ and therefore does not allow to determine E_i and E_M separately but furnishes a combined value E_{iM}. The values obtained by means of a fitting procedure for E_{RM} and E_{1M} for HAB in the different phases are given in Table IV. The fact that the data can be fitted with a single exponential seems to indicate that either $\tau_M >> \tau_R,\tau_1$ or $\tau_M << \tau_R,\tau_1$. If the latter case were true we would obtain similar values

TABLE IV

Combined reorientational and internal motion activation energy for the aromatic (E_{RM}) and the aliphatic (E_{1M}) deuterons of HAB

	smectic phase	nematic phase	isotropic phase
E_{RM}	27.0 ± 1.0	21.0 ± 1.0	23.8 ± 1.0
E_{1M}	15.2 ± 1.0		1.8 ± 1.0

of R for all deuterons, aromatic and methylenic, in a molecule. As evident from the data this is not the case. Therefore the data seem to indicate that the relevant motion is the internal rotation.

CONCLUSIONS

Deuterium relaxation times furnish much information on the molecular dynamics in liquid crystals. Certainly more insight into the problem can be obtained by measurements of the different spectral densities of motion at different frequencies but even in that case the dynamical results are not easily obtained and some motional model has to be used.

The determination of the spectral densities $J_1(\omega)$ and $J_2(\omega)$ for the same compounds studied in this work by means of the Jeener-Broekaert pulse sequence is in progress.

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