NMR Study of Molecular Dynamics in a D_{ho} Columnar Mesophase

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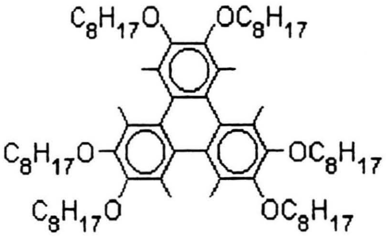
In this paper we report the first molecular dynamics study combining fast field-cycling and conventional NMR techniques in a thermotropic liquid crystal of discotic molecules exhibiting an ordered columnar hexagonal mesophase. Using the association of these techniques we obtained proton T_1 data over a very large domain of Larmor frequencies ($\omega/2\pi$ from 500 Hz to 85 MHz). The proton spin-lattice relaxation results were analysed considering the structure of the mesophase and the types of movements which are expected to influence significantly the relaxation rate, namely local molecular rotational reorientations, inter-columnar self-diffusion and collective movements corresponding to bending and compression of the columns. We verified that these mechanisms dominate the relaxation respectively for high, medium and low Larmor frequencies.

Key words: NMR; Proton Relaxation; Molecular Dynamics; Columnar Hexagonal Mesophases (D_{ho}); Discotic Molecules

Introduction

In this paper we present the first proton NMR molecular dynamics study, using both fast field-cycling [1] and conventional techniques, in an ordered hexagonal columnar phase of discotic molecules.



$$K \xrightarrow{66.8\,°C} D_{ho} \xleftrightarrow{85.6\,°C} I$$

Fig. 1. Molecular structure and phase sequence of the liquid crystal C_8HET.

We obtained T_1 results as a function of temperature and Larmor frequency in the isotropic and columnar hexagonal (D_{ho}) phases of the liquid crystal hexaoctyloxytriphenilene – C_8HET [2] (see in Fig. 1 the molecular structure and phase sequence of this compound). Our results in the D_{ho} phase are interpreted considering the contributions to the relaxation rate, $1/T_1(\nu)$, of the molecular movements which are expected to be observed in this mesophase – namely collective movements (CM), translational self-diffusion (SD) and local molecular rotational reorientations (ROT). The overall relaxation rate is given, in terms of the possible contributions, by

$$T_1^{-1} = (T_1^{-1})_{\mathrm{ROT}} + (T_1^{-1})_{\mathrm{SD}} + (T_1^{-1})_{\mathrm{CM}}. \qquad (1)$$

Crossed terms between different relaxation mechanisms were considered negligible as generally accepted for liquid crystal systems [3].

In the case of a crystalline powder, each of these contributions may be expressed, in terms of the spectral densities for relaxation by dipolar coupling, by [4, 5]

$$[T_1^{-1}]_{\mathrm{polycrystal}} = \frac{9}{8}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4 \hbar^2 \cdot \sum_{k=0}^{2} p_k \left[J^{(k)}(\omega) + 4J^{(k)}(2\omega)\right], \qquad (2)$$

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where γ is the gyromagnetic ratio of the proton, $J^{(k)}(\omega)$ is the spectral density for an aligned sample, and $p_0 = 1/30$, $p_1 = 2/5$, $p_2 = 1/10$.

The global expression of $1/T_1(\omega)$ resulting from these contributions was numerically fitted to our experimental results using the χ^2 minimisation method. These fits allowed us to verify the agreement between the proposed models and our data and to evaluate some physical parameters relevant for the description of the molecular movements in question, namely:

i) Cut-off frequencies resulting from spatial limitations to the collective modes;

ii) Self-diffusion coefficients;

iii) Characteristic time scales for the diffusive and local reorientational movements.

Spectral Densities for the Different Movements in the D_{ho} Mesophase

In order to describe the contribution of the collective movements in the D_{ho} columnar mesophase we used a model of Žumer and Vilfan [6] that takes into account bending and compression of the columns. This model gives the following expression for the spectral densities for an aligned monodomain (director parallel to the magnetic field) [5]:

$$\left[J^{(k)}(\omega)\right]_{\mathrm{CM}} = \delta_{k1}\frac{C}{\omega}\int_0^1 \sqrt{u}\left[\arctan\left(\frac{R}{u}\frac{\omega_{\mathrm{c}}}{\omega}+u\frac{\omega_{\mathrm{c}}}{\omega}\right) - \arctan\left(u\frac{\omega_{\mathrm{c}}}{\omega}\right)\right]\mathrm{d}u \tag{3}$$

with

$$R = \frac{Bq_{\perp\mathrm{c}}^2}{K_3 q_{\|\mathrm{c}}^4}, \quad \omega_{\mathrm{c}} = \frac{K_3 q_{\|\mathrm{c}}^2}{\eta},$$

where C is a constant related to the visco-elastic properties of the liquid crystal in the columnar phase, K_3 and B are elastic constants for bending and compression of the columns, respectively, and η is an effective viscosity. $q_{\perp\mathrm{c}}$ and $q_{\|\mathrm{c}}$ are the maximum components of the wave-vector of collective modes perpendicular and parallel to the director, respectively. This expression is asymptotically independent of ω for low frequencies and proportional to $1/\omega^2$ for high frequencies.

For the description of the contribution of translational self-diffusion we followed a model of Žumer and Vilfan [6], which describes self-diffusion as an inter-columnar jump-process that modulates intermolecular dipolar interactions. The resulting spectral densities for an aligned monodomain are given by

$$\left[J^{(k)}(\omega)\right]_{\mathrm{SD}} = \frac{n\tau}{d^3}R^{(k)}\left(\frac{\ell}{d}, \frac{D_\perp}{D_\|}, \varepsilon, \omega\tau\right), \tag{4}$$

where n is the spin density, τ the mean time between jumps, d the inter-columnar distance (corresponding to the diameter of the disc-like molecule), ℓ the average distance between the centres of two contiguous molecules in a column, $D_\perp$ and $D_\|$ are the diffusion coefficients perpendicular and parallel to the director's direction (along the axis of the columns), respectively, and ε is a parameter dependent on the spins' distribution over the molecular disk. $R^{(k)}$ is an integral function that may be approximated by a Lorentzian type curve [6, 7].

In order to describe the contribution of local molecular rotational reorientation movements we introduced a generalisation of the Woessner model [8] adapted to discotic molecules following the same approach as presented in a recent work on molecular dynamics in a columnar phase of biforked molecules [5]. This model takes into account global reorientations of the molecule and reorientations of the molecular chains relatively to a mean molecular frame. Following the procedure used in [5] we obtain similar expressions for the spectral densities for rotational reorientation-movements. The only difference is that the contribution of the chains is now given by

$$\left[J^{(k)}_{\mathrm{chain}}(\omega)\right]_{\mathrm{ROT}} = \frac{4}{3}C_k \sum_{\ell,m,n=-2}^{2} A_n \left\langle \left[d^{(2)}_{k\ell}(\beta_{\mathrm{M}})\right]^2 \right\rangle \cdot \left[d^{(2)}_{\ell m}(90°)\right]^2 \left\langle \left[d^{(2)}_{mn}(\beta_{\mathrm{C}})\right]^2 \right\rangle \frac{\tau_{\ell n}}{1+\omega^2\tau_{\ell n}^2}, \tag{5}$$

where the reduced Wigner matrix factor $\left[d^{(2)}_{\ell m}(90°)\right]^2$ appears due to the fact that in the case of the D_{ho} phase the chains are in the average perpendicular to the director defined by the direction of the columnar longitudinal axis. All the other factors in (5) are calculated as in [5]. As fitting parameters we considered the correlation times $\tau_\perp$ and $\tau_\|$ for the rotational reorientations of the molecular core and the correlation times $\tau_\perp^{\mathrm{c}}$ and $\tau_\|^{\mathrm{c}}$ for transversal and longitudinal reorientations of the chains in the molecular frame, respectively. These times are used to calculate the parameters $\tau_{\ell n}$ in (5) [5].

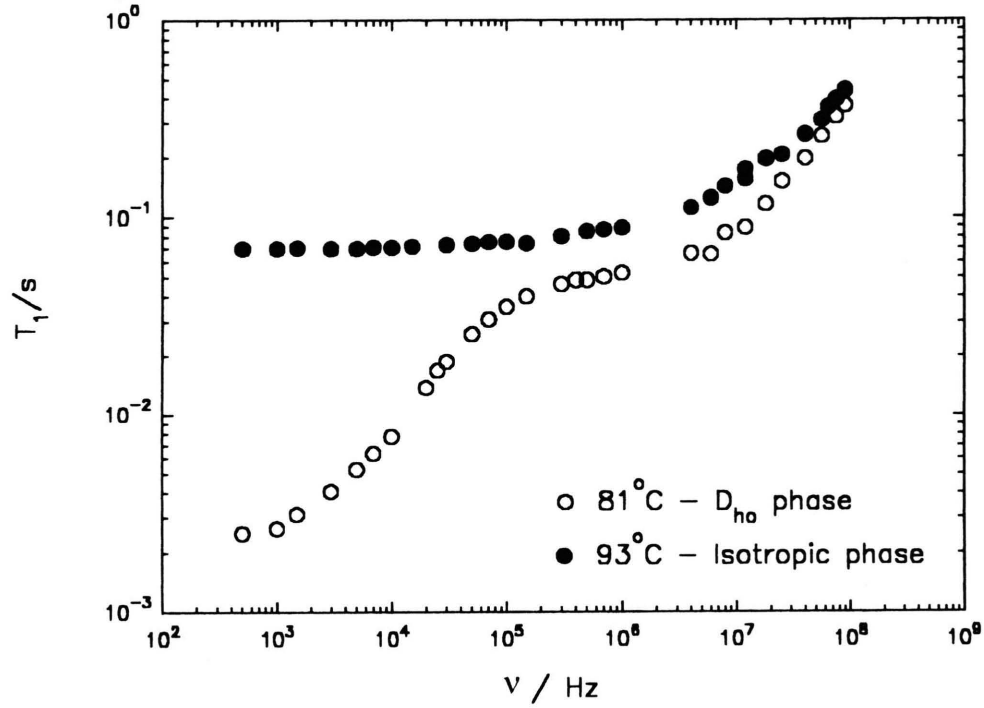

Fig. 2. T_1 versus proton Larmor frequency ($\nu = \omega/2\pi$) in the isotropic and D_{ho} phases.

Results and discussion

In Fig. 2 we present the T_1 values obtained as functions of the frequency in the isotropic and D_{ho} phase of the liquid crystal. The measurements were performed using a field-cycling spectrometer [1] for low Larmor frequencies (500Hz $\leq \omega/2\pi \leq$ 4 MHz) and a variable field BRUKER SXP 4-100 spectrometer for high frequencies (4 MHz $< \nu \leq$ 90 MHz). Additional results for high Larmor frequencies ($\omega/2\pi \geq$ 12 MHz) were also obtained at several different temperatures in the columnar phase. That data allowed us to consider the effect of the temperature on the mechanisms expected to influence the T_1 dispersion in this frequency range.

The most remarkable observation that we can immediately obtain from the data presented in Fig. 2 is the obvious difference between the isotropic and columnar phases with respect to the T_1 dispersion in the low frequency range. This effect is most probably due to some relaxation mechanism that is present in the mesophases and absent in the isotropic phase, as we previously noted [5]. This is precisely the case of the collective movements. Thus, from this qualitative observation, we may conclude that this mechanism is most likely dominant in the frequency region where this difference occurs – the low frequency range.

Table 1. Parameters obtained from the best fit of T_1 data as a function of the Larmor frequency (ω) in the D_{ho} phase using (3) for the contribution of collective movements (CM), (4) for the contribution of self-diffusion (SD) and (5) (and related equations in [5]) for the contribution of local molecular rotational reorientations (ROT).

	Parameter	Temperature T/°C		
		67	73	81
CM Model	$(\omega_c/2\pi)$/MHz	28	28	28
	$R/10^{-7}$	1.0	1.0	1.0
SD Model	$d/10^{-10}$m	23.2	23.2	23.2
	$\ell/10^{-10}$m	3.6	3.6	3.6
	$\tau/10^{-8}$s	1.4	1.2	0.9
	$D_\perp/10^{-10}\text{m}^2\text{s}^{-1}$	1.0	1.2	1.5
E_a = 33 kJ·mol^{-1}	$D_\parallel/10^{-12}\text{m}^2\text{s}^{-1}$	< 6.5	< 5.4	< 4.3
ROT Model	$\tau_\perp/10^{-8}$s	3.0	2.7	2.4
	$\tau_\perp/\tau_\parallel$	13	13	13
	$\tau_\perp^c/10^{-11}$s	2.4	2.2	1.9
E_a = 18 kJ·mol^{-1}	$\tau_\perp^c/\tau_\parallel^c$	12	12	12

The overall relaxation rate in the D_{ho} phase is determined according to (1) and (2) by the summation of the spectral densities given by the models described

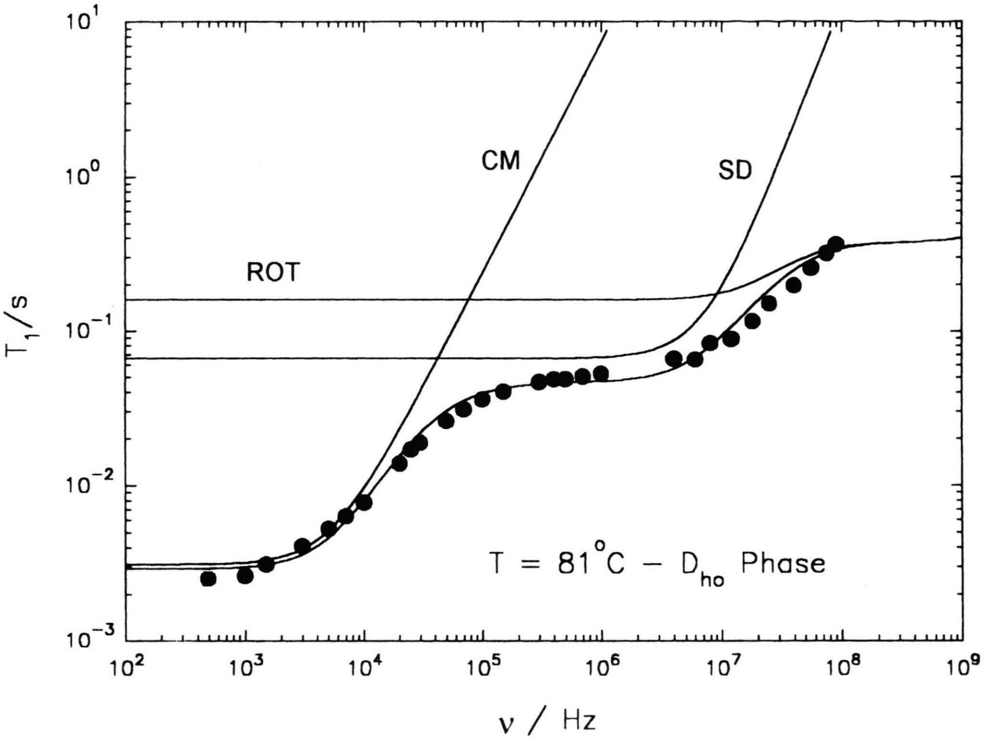

Fig. 3. Best fit of T_1 data as a function of the Larmor frequency in the D_{ho} phase using (3) for the contribution of collective movements (CM), (4) for the contribution of self-diffusion (SD) and (5) (and related equations in [10]) for the contribution of local molecular rotational reorientations (ROT) with the optimised model parameters given in Table 1.

before. Taking into account the characteristics of the studied liquid crystal and the experimental conditions used in the field-cycling and conventional high field NMR measurements, our sample can be considered as a crystalline powder.

The sum resulting from (2) was fitted to the experimental data. In Table 1 we present the set of fitting parameters resulting from the conjoint analysis of our wide frequency range data at 81 °C with high Larmor frequency data for other temperatures in the same mesophase [9]. The data analysis was performed considering the same relaxation models for all the studied temperatures and admitting an Arrhenius type evolution for the characteristic times involved in the thermal activated processes. This applies to the self-diffusion process and also for the correlation times of the local molecular rotational reorientations. The curve corresponding to the best fit at T = 81 °C (D_{ho} phase) is presented in Figure 3.

From the analysis of the experimental results we verify that the three proposed mechanisms – collective motions, self-diffusion and local molecular rotational reorientations – clearly explain the T_1 frequency dispersion in the whole examined frequency range. This result, common to a large number of liquid crystalline systems, was also verified by Vilfan *et al.* in an NMR molecular dynamics study of the homologous compound hexapentoxytriphenylene, C_5HET [7]. Local molecular rotations are dominant at high frequencies ($\omega/2\pi$ > 10MHz) and self-diffusion dominates in the medium frequency range (10 kHz < $\omega/2\pi$ < 10 MHz). From these results it is also possible to confirm the conclusion inferred from the qualitative analysis of the data: that the collective modes dominate the low frequency range ($\omega/2\pi$ < 10 kHz). The theoretical model [6] used to fit the results in this frequency region is in good agreement with the experimental data. The test of the model is even more conclusive as, according to our analysis, the influence of the two remaining mechanisms is very weak in the low frequency region. This means that the relaxation due to collective movements may be explained considering bending and compressing of the columns as the predominant mechanisms in the corresponding frequency range.

In what concerns the self-diffusion mechanism, we obtained for the mean time between inter-columnar jumps, τ, values of the order of 10^{-8} seconds and diffusion coefficients of the order of 10^{-10} m^2s^{-1}. These values are in good agreement with previous studies of molecular dynamics in the D_{ho} phase of the liquid crystal here considered [9]. A similar result is obtained in [7] for the C_5HET ($\tau = 9 \times 10^{-9}$s at 80 °C). The data analysis confirms that self-diffusion may be considered as a thermally activated mechanism with an activation energy, E_a, of 33 kJ·mol^{-1}.

The process of local molecular reorientations is particularly influent in the high frequency range, and the corresponding correlation times are of the order of 10^{-8} seconds and 10^{-11} seconds for the movements of the core and of the chains, respectively. It is worthwhile to notice that, in spite of having a similar characteristic time-scale, in the medium frequency range the rotations of the molecular core are clearly dominated by the self-diffusion mechanism (see Figure 3). This may be explained by the small number of protons of the molecular core. In fact, the much larger number of protons in the chains (17:1) implies that the aliphatic part of the molecule is dominant in the relaxation process. This may probably explain why in [7] the authors could very satisfactorily explain the relaxation in the medium frequency range ruling out the rotational reorientation-mechanism and taking into account only the diffusive movements. As the correlation times for local reorientation movements of the chains are of the order of 10^{-11} seconds, this mechanism, according to (5), becomes dominant at higher frequencies (see Figure 3). It is worthwhile to note the similarity between the correlation times for the rotational reorientations of the chains in our case and that considered in [7] for "the frequency independent contribution explained by the fast local rotation of proton spin pairs". The ratio $\tau_\perp/\tau_\parallel = 13$ of the correlation times for rotations of the molecular core around an axis perpendicular and parallel to the director, respectively, means that the molecules perform much faster reorientation movements around the column axis than perpendicularly to that axis. Actually this is expected considering the structure of the columnar phase. As the columns are separated from each other by the disordered aliphatic medium formed by the *melted* chains, it is reasonable to consider as equivalent any position of the molecule obtained by rotation around the axis of the column, while the closeness of the rigid cores piled up in the central region of the column implies that there must be a well-determined preferable position with respect to rotations around an axis perpendicular to the columnar axis. This means that, most probably the molecules are much freer to rotate around the axis of the column than otherwise. This hypothesis is implicitly assumed in a previous work about molecular dynamics in columnar phases [6] in which only rotations around the columnar axis are considered. The ratio $\tau_\perp^c/\tau_\parallel^c = 12$ between the correlation times for transversal and longitudinal rotational reorientations of the chains is compatible with that expected from the geometric anisotropy of the chains [10].

As a general conclusion, we verified that the large frequency domain attained by means of the conjugation between the fast field-cycling and conventional NMR techniques allowed us to overcome the difficulty stated in [7] of verifying the relative importance of each of the mechanisms contributing to the relaxation rate. This is especially true in the low frequency range where the collective movements, so characteristic of the liquid crystalline state, become most clearly observable.

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