Molecular Dynamics in the Columnar and Lamellar Mesophases of a Liquid Crystal of Biforked Molecules

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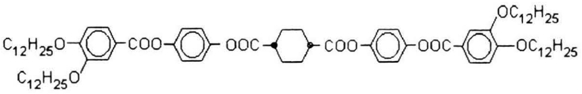
In this work we present the first study of molecular dynamics in the S_C and ϕ_h mesophases of a liquid crystal of biforked molecules. This study was performed by means of proton NMR relaxation measurements obtained at different temperatures in the studied phases, combining standard and fast field-cycling techniques in order to cover a large domain of Larmor frequencies (100 Hz–300 MHz). The experimental results were analysed considering the potential contributions of different relaxation mechanisms, namely local molecular rotational reorientations, self-diffusion and collective movements. The description of the contributions of the rotational reorientations and self-diffusion mechanisms are not quite different in the two studied phases. The main distinction in the molecular dynamics is found in the low Larmor frequency range dominated by the collective movements. While in the S_C phase this contribution can be described by the law characteristic of smectic layer undulations, the contribution of the collective movements in the ϕ_h phase can be assigned to elastic deformation of the columns.

Key words: NMR, Proton Relaxation, Molecular Dynamics, Biforked Molecules, ϕ_h Mesophase.

Introduction

In recent years it was noticed that molecules differing in shape from the usual rod-like or disc-like one give rise to new kinds of liquid crystals [1–3]. The recently discovered biforked mesogens [2, 4–5] belong to this category, the same compound exhibiting both columnar and lamellar mesophases. The compound **1** studied in this work,

(1)



with the phase transitions

$$K \xrightarrow[113\,^{\circ}\mathrm{C}]{} S_C \xleftrightarrow[149\,^{\circ}\mathrm{C}]{} \phi_h \xleftrightarrow[156\,^{\circ}\mathrm{C}]{} I,$$

is an example of such behaviour [5]. The ϕ_h phase, originally discovered in the phasmidic mesogens, is a special hexagonal columnar mesophase where the columnar cross-section is composed of clusters of molecules (3 in the case of phasmidic mesogens or ≈4.5 in the case of biforked mesogens [1]). In [6] a description of the molecular packing in the ϕ_h phase of **1** is given, based on a model previously proposed for a hexacatenar compound [3]: n elongated molecular hard moieties compose the core of a columnar plate, which is surrounded by an aliphatic crown, n being calculated from the ratio of the columnar plate's volume, obtained by X-ray scattering, and of the molecular volume, determined by dilatometry. According to this model, the low enthalpy- and molecular volume-changes in the transition between the smectic C (S_C) and the ϕ_h phases indicate that the structure of the ϕ_h phase at local level is not very different from the one of the S_C phase.

This similarity is favoured by the high tilt angles (≈60° for the molecular hard core) observed in the S_C phase of this kind of compounds: the hexagonal columnar structure of the ϕ_h phase results from the segregation of the smectic layers into columns as a consequence of the increasing disorganisation of the aliphatic chains caused by the increase of the temperature. In this process, the relative position of the molecular cores inside each column remains similar to the one initially existing in the S_C phase [6].

In order to better understand the relationship between the molecular structure of such systems and the

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corresponding molecular dynamics we present in this paper a comparative NMR study of the S_C and ϕ_h phases exhibited by the compound **1**. This study was carried out by means of proton spin-lattice relaxation (T_1) measurements in a very broad domain of Larmor frequencies (100 Hz–300 MHz), combining standard and fast field-cycling NMR techniques. Angular dependent proton NMR spectra at the Larmor frequency of 60 MHz were also obtained, as well as angular dependent T_1 data. The T_1 relaxation dispersion results, obtained for several temperatures covering the isotropic, ϕ_h and S_C phases, were then interpreted considering the potential contributions of the different types of molecular motions expected in the referred mesophases – namely local molecular rotational reorientations, self-diffusion and collective movements.

This system allows for the comparison between the dynamic behaviour of quite different liquid crystalline arrangements – lamellar and columnar – of the same molecules. The most direct evidence of our study is the clear distinction between the T_1 dispersion in the low frequency range, which is explained by the type of collective motions arising from the different global nature of the two mesophases – lamellar (S_C) and columnar (ϕ_h). The particular molecular structure of this kind of compounds – a rod-like body with two flexible molecular chains in each extremity – required the introduction of a new relaxation model for the rotational reorientations, which takes into account the relative reorientations of the chains with respect to the molecular core.

1. Experimental Techniques and Results

The T_1 data for Larmor frequencies ($\omega/2\pi$) between 100 Hz and 1 MHz were obtained using a fast field-cycling spectrometer [7] with a polarisation and detection field of 0.215 T and a switching time of 2–3 ms. The high frequency T_1 data (above 4 MHz) were obtained in two conventional pulsed NMR spectrometers (BRUKER SXP 4–100 and BRUKER MSL 300) using the inversion recovery sequence with phase cycling ($(\pi)_x-(\pi/2)_{x,-x}$) for suppression of the DC bias.

The samples consisted of a few hundred milligrams of liquid crystalline material sealed under moderate vacuum ($<10^{-4}$ Torr) in NMR glass tubes. The data were recorded after the sample had been heated to the isotropic phase and then slowly cooled (<1 °C/min) in the presence of the magnetic field. The temperature was controlled within ± 0.5 °C.

The T_1 dispersion curves in the isotropic, ϕ_h and S_C phases are presented in Figures 1 and 2. No angular variation was found in the T_1 measurements or in the proton spectra obtained at the Larmor frequency of 60 MHz for the two mesophases. This fact, together with the symmetry properties of the ϕ_h phase, allows us to conclude that the sample was not oriented by the magnetic field, which means that it has the characteristics of a crystalline powder. The simple qualitative comparison between the T_1 data in the three phases leads to the following conclusions:

a) The T_1 dispersion behaviour in the high frequency range ($\nu > 10-20$ MHz) is similar in the isotropic, S_C and ϕ_h phases.
b) At low frequencies ($\nu < 10-20$ kHz) the T_1 dispersion depends strongly on the phase. The most obvious feature is the absence of T_1 dispersion in this frequency range for the isotropic phase. Therefore, the T_1 dispersion in this frequency region for the ϕ_h and S_C phases must be attributed to a mechanism which is not expected to exist in the isotropic phase, which is the case for the collective movements. Most likely the difference between the T_1 dispersion behaviour in the ϕ_h and S_C phases for this frequency range indicates a distinction between the collective movements in these two phases. Actually, this is expected since the liquid crystalline arrangements (columnar and lamellar) are considerably different in the two mesophases.
c) At intermediate frequencies (20 kHz $< \nu <$ 10 MHz) the T_1 dispersion in the S_C phase is different from the one observed in the isotropic and ϕ_h phases but this difference is not so remarkable as at low frequencies.

In order to compare theory and experiment, we fitted the T_1^{-1} dispersion data, for different temperatures, with the theoretical expressions which represent the sum of the contributions of the different movements to the relaxation rate, according to equation (1) and the special models given in Section 2.2.

Consistency of the fits for different temperatures in the same phase was obtained using Arrhenius type dependencies for the involved correlation times. The respective activation energies were determined by the fitting process.

2. Theory

2.1. Potential Contributions to the Relaxation Rate

Three relaxation mechanisms were considered as potential contributions to the relaxation rate in the

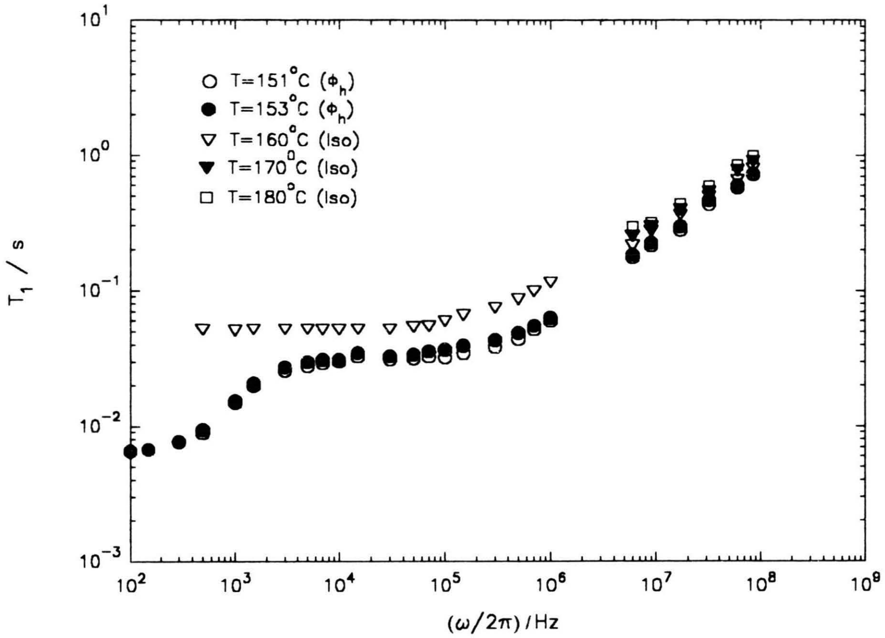


Fig. 1. T_1 versus proton Larmor frequency ($\omega/2\pi$) in the isotropic and ϕ_h phases.

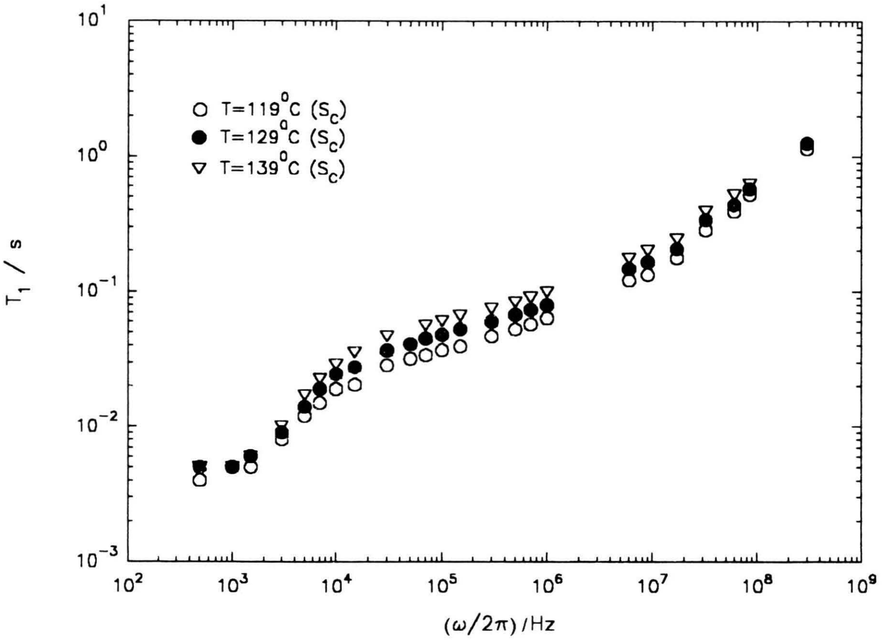


Fig. 2. T_1 versus proton Larmor frequency ($\omega/2\pi$) in the S_C phase.

analysed mesophases, namely collective movements (CM), self-diffusion (SD) and local molecular rotational reorientations (ROT). The overall relaxation rate is given by

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

neglecting cross terms between the different mechanisms as usually assumed in liquid crystalline phases [8].

Each contribution to the overall relaxation rate is given in terms of the spectral densities, $J^{(k)}(\omega)$, for relaxation by dipolar coupling, by [9]

$$T_1^{-1}=\frac{9}{8}\left(\frac{\mu_0}{4\pi}\right)^2\gamma^4\hbar^2\left[J^{(1)}(\omega)+J^{(2)}(2\omega)\right], \qquad (2)$$

where γ is the gyromagnetic ratio of the proton.

When the sample is not aligned, the spectral densities for the powder sample can be obtained from those for the aligned monodomain using

$$[J^{(k)}(\omega)]_{\text{polycrystal}}=\sum_{n=0}^{2}\left(\frac{1}{2}\int_0^{\pi} f_{kn}(\Delta)\sin(\Delta)\,\mathrm{d}\Delta\right)\cdot J^{(n)}(\omega,\Delta=0) \qquad (3)$$

with [10]

$$f_{kn}=\frac{1}{8}\begin{bmatrix} 8-24\cdot\sin^2\Delta+18\cdot\sin^4\Delta & 144(\sin^2\Delta-\sin^4\Delta & 9\cdot\sin^4\Delta \\ 2\cdot(\sin^2\Delta-\sin^4\Delta) & 8-20\cdot\sin^2\Delta+16\cdot\sin^4\Delta & 2\cdot\sin^2\Delta-\sin^4\Delta \\ 2\cdot\sin^4\Delta & 16(2\cdot\sin^2\Delta-\sin^4\Delta & 8-8\cdot\sin^2\Delta+\sin^4\Delta \end{bmatrix}, \qquad (4)$$

where Δ is the angle between the director of a local domain and the external Zeeman field. Substituting the results of the integrals (3) in (2) we get for the relaxation rate

$$[T_1^{-1}]_{\text{polycrystal}}=\frac{9}{8}\left(\frac{\mu_0}{4\pi}\right)^2\gamma^4\hbar^2\sum_{k=0}^{2}p_k\cdot\left[J^{(k)}(\omega)+J^{(k)}(2\omega)\right] \qquad (5)$$

with

$$p_0=\frac{1}{30},\quad p_1=\frac{2}{5},\quad p_2=\frac{1}{10}\quad\text{and}$$

$$J^{(k)}(\omega)\equiv J^{(k)}(\omega,\Delta=0).$$

2.2. Models Proposed to Describe the Relaxation Mechanisms

2.2.1. Smectic C Phase

In the S_C phase three mechanisms were proposed as effective contributions to the relaxation rate, namely a) collective movements, b) self-diffusion and c) local molecular rotational reorientations:

a) Layer undulations were considered as the contribution of collective motions to the relaxation rate in the S_C phase. This type of mechanism predicts a law for the relaxation rate proportional to ω^{-1} [11] with low (ω_{LC}) and high (ω_{HC}) cut-off frequencies which express respectively the existence of a maximum and a minimum wavelength for the collective fluctuation modes. The respective spectral densities can be written as

$$[J^{(k)}(\omega)]_{\text{CM}}=\frac{A}{\omega}\delta_{k1}\cdot\left[\frac{2}{\pi}\arctan\left(\frac{\omega_{HC}}{\omega}\right)-\frac{2}{\pi}\arctan\left(\frac{\omega_{LC}}{\omega}\right)\right], \qquad (6)$$

where A is a constant related to the viscoelastic properties of the material [11] and δ_{k1} is the Kronecker symbol.

b) To describe the self-diffusion's contribution we used the theory of Vilfan and Žumer for anisotropic diffusion in the smectic A phase, adapted to the smectic C phase, which gives the following expression for the spectral densities [12],

$$[J^{(k)}(\omega)]_{\text{SD}}=\frac{n\,\tau_\perp}{d^3}R^{(k)}\left(\omega\,\tau_\perp,\frac{\langle r_\perp^2\rangle}{d^2},\frac{D_\parallel}{D_\perp},\frac{\ell}{d},\varphi\right), \qquad (7)$$

where n is the spin density, $\tau_\perp$ the mean time between two successive intra-layer jumps, $\langle r_\perp^2\rangle$ the mean square width of intra-layer jumps, ℓ and d are the length and the diameter of the molecules, respectively, $D_\parallel$ and $D_\perp$ are the inter and intra-layer diffusion coefficients, respectively, and φ is the tilt angle of the smectic C phase. The Eq. (7) is approximately obtained when rotating the spectral densities presented in [12] by the tilt angle φ [10, 13].

c) The contribution of the molecular rotational reorientations to the relaxation rate was described by a generalisation of the Woessner model [14, 15], where the reorientation of the aliphatic chains relative to the molecular core is taken into account together with the global rotational reorientations of the whole molecule.

Two reasons initiated the introduction of a new model in order to explain the contribution of rotations to the spin-lattice relaxation rate:

a) The fact that the molecule of the compound studied in this work has four chains and not 1 or 2 as in calamitic liquid crystals.

b) The total number of protons in the chains is approximately 4 times greater (100:26) than the number of protons in the molecular core, which means that the specific contribution of the chain's protons to the relaxation may considerably contribute to the overall relaxation rate.

Assuming that the chains may rotate or reorientate relative to the core, a description of the rotational reorientations based on models [16, 17], which consider molecules as ellipsoid-like objects, would be a too drastic approximation in this case.

Neglecting the contribution to the relaxation from proton pairs with elements belonging to different parts of the molecule (core-chain or different chains), we obtain

$$[J^{(k)}(\omega)]_{\mathrm{ROT}} = \frac{N_{\mathrm{core}}}{N_0}\,[J^{(k)}_{\mathrm{core}}(\omega)]_{\mathrm{ROT}} + \sum_{\mathrm{chains}} \frac{N_{\mathrm{chain}}}{N_0}\,[J^{(k)}_{\mathrm{chain}}(\omega)]_{\mathrm{ROT}}\,, \tag{8}$$

where $[J^{(k)}_{\mathrm{core}}(\omega)]_{\mathrm{ROT}}$ and $[J^{(k)}_{\mathrm{chain}}(\omega)]_{\mathrm{ROT}}$ are the rotational reorientations spectral densities for the core and for the chains, N_{core} is the number of protons of the core and N_{chain} is the number of protons in one chain.

For the contribution of the core we follow the procedure of Woessner [14, 15] and [17, 18] which gives

$$[J^{(k)}_{\mathrm{core}}(\omega)]_{\mathrm{ROT}} = \frac{4}{3}\,C_k \sum_{\ell=-2}^{2} A_\ell \langle [d^{(2)}_{\ell k}(\beta)]^2\rangle \frac{\tau_\ell}{1+\omega^2\tau_\ell^2}\,, \tag{9}$$

where $C_0=6$, $C_{\pm 1}=1$, $C_{\pm 2}=4$, $d^{(2)}_{\ell k}(\beta)$ is the second rank reduced Wigner rotation matrix, and the τ_ℓ's are

$$\tau_0=\tau_{\mathrm{S}}\,, \quad \frac{1}{\tau_{\pm 1}} = \frac{5}{6\,\tau_{\mathrm{S}}} + \frac{1}{6\,\tau_{\mathrm{L}}}\,, \quad \frac{1}{\tau_{\pm 2}} = \frac{1}{3\,\tau_{\mathrm{S}}} + \frac{2}{3\,\tau_{\mathrm{L}}}\,. \tag{10}$$

τ_{S} and τ_{L} are the correlation times for rotations around the short and long molecular core axis, respectively. The factors A_ℓ are given by

$$A_\ell = \frac{1}{N_0}\sum_{j>i}^{N_0} \frac{1}{8\,r_{ij}^6} \begin{bmatrix} 2(3\cos^2\alpha_{ij}-1)^2; & \ell=0 \\ 3\sin^2(2\,\alpha_{ij}); & \ell=\pm 1 \\ 3\sin^4\alpha_{ij}; & \ell=\pm 2 \end{bmatrix}, \tag{11}$$

where N_0 is the number of protons in one molecule, r_{ij} is the proton-proton distance and α_{ij} is the angle between the proton-proton axis and the long molecular axis. For the evaluation of the A_ℓ factors we took the summation only over the protons of the core, considering the molecule in the all-trans configuration. According to [19], $\langle [d^{(2)}_{\ell k}(\beta)]^2\rangle$ may be written in terms of ensemble avarages of the second and fourth rank Legendre polynomials S and $\langle \mathrm{P4}\rangle$ of the angle β between the director and the long molecular axis, namely

$$S = \tfrac{1}{2}\langle 3\cos^2\beta - 1\rangle\,,$$

$$\langle P_4\rangle = \tfrac{1}{8}\langle 35\cos^2\beta - 30\cos^2\beta + 3\rangle\,, \tag{12}$$

as

$$\langle [d^{(2)}_{\ell k}(\beta)]^2\rangle = \frac{1}{35}\begin{bmatrix} 7+10\,S+18\langle P_4\rangle & 7+5\,S-12\langle P_4\rangle & 7-10\,S+3\langle P_4\rangle \\ 7+5\,S-12\langle P_4\rangle & \tfrac{1}{2}(14+5\,S+16\langle P_4\rangle) & 7-5S-2\langle P_4\rangle \\ 7-10\,S+3\langle P_4\rangle & 7-5\,S+2\langle P_4\rangle & \tfrac{1}{2}(14+20\,S+\langle P_4\rangle) \end{bmatrix}, \tag{13}$$

To calculate the relaxation due to the rotations of the chains we generalised this model in order to describe the global movement of the chains as a combination of the rotation of the chain in a frame attached to the core of the molecule and the rotation of the molecule in the director's frame as shown in Figure 3. The spectral density for the rotation of the chains can thus be written as

$$[J^{(k)}_{\mathrm{chain}}(\omega)]_{\mathrm{ROT}} = \frac{1}{N_{\mathrm{chain}}} \sum_{i<j}^{N_{\mathrm{chain}}} \int_{-\infty}^{+\infty} \cdot \langle [F^{(k)*}_{ij}(0)\cdot F^{(k)}_{ij}(t)]_{\mathrm{LAB}}\rangle \cdot e^{i\omega t}\,\mathrm{d}t \tag{14}$$

with

$$[F^{(k)}_{ij}(t)]_{\mathrm{LAB}} = \sum_{\ell=-2}^{2}\sum_{m=-2}^{2} D^*_{k\ell}(\alpha_{\mathrm{M}}, \beta_{\mathrm{M}}, \gamma_{\mathrm{M}}) \cdot D^*_{\ell m}(\alpha_{\mathrm{C}}, \beta_{\mathrm{C}}, \gamma_{\mathrm{C}})\,[F^{(m)}_{ij}(t)]_{\mathrm{CHAIN}}\,, \tag{15}$$

where $D_{k\ell}$ are the second rank Wigner rotation matrices, α_{M}, β_{M}, γ_{M} and α_{C}, β_{C}, γ_{C} are the Euler angles which define the position of the molecular axis in the director's frame and the position of the chain axis in the molecular frame (see Fig. 3), respectively, and $F^{(k)}_{ij}$ are the spherical harmonics of the dipolar hamiltonian. The generalisation of the procedure used to obtain (9) gives

$$[J^{(k)}_{\mathrm{chain}}(\omega)]_{\mathrm{ROT}} = \frac{4}{3}\,C_k \sum_{\ell,m=-2}^{2} A_m \cdot \langle [d^{(2)}_{\ell k}(\beta_m)]^2\rangle \langle [d^{(2)}_{\ell m}(\beta_{\mathrm{C}})]^2\rangle \frac{\tau_{\ell m}}{1+\omega^2\tau_{\ell m}^2} \tag{16}$$

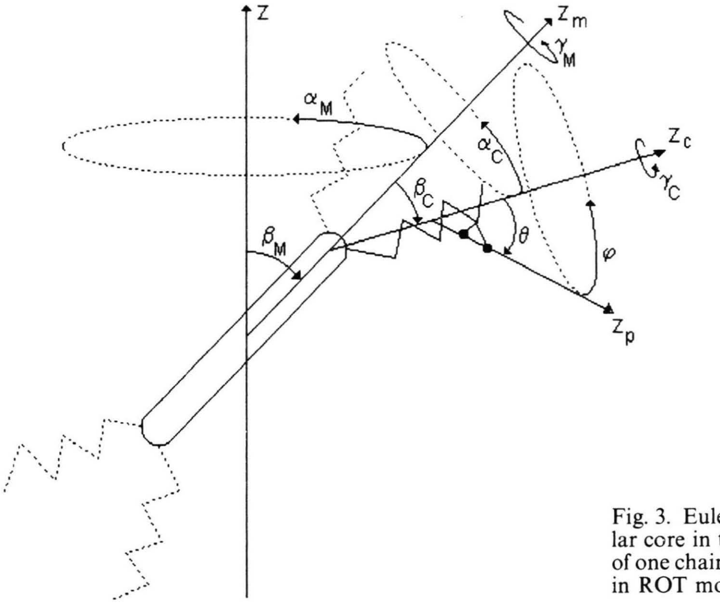


Fig. 3. Euler angles which define the position of the molecular core in the director's frame ($\alpha_M, \beta_M, \gamma_M$) and the position of one chain in the molecular frame ($\alpha_C, \beta_C, \gamma_C$) as considered in ROT model for rotational reorientations.

with

$$\frac{1}{\tau_{\ell m}} = \frac{1}{\tau_\ell^M} + \frac{1}{\tau_m^C}. \tag{16a}$$

τ_ℓ^M may be expressed by (10) in terms of the correlation times τ_S and τ_L for the rotations of the molecular core. τ_m^C will be defined by extension of (10) in terms of the transversal (τ_S^C) and longitudinal (τ_L^C) correlation times for the rotation of the chains in the frame attached to the molecular core as

$$\tau_0 = \tau_S^C, \quad \frac{1}{\tau_{\pm 1}^C} = \frac{5}{6\tau_S^C} + \frac{1}{6\tau_L^C}, \quad \frac{1}{\tau_{\pm 2}^C} = \frac{1}{3\tau_S^C} + \frac{2}{3\tau_L^C}. \tag{17}$$

The factors A_m are calculated as in (11) but considering only the protons of the *chain*. Equation (13), which is valid for $\langle [d_{k\ell}^{(2)}(\beta_M)]^2 \rangle$, also applies to $\langle [d_{\ell m}^{(2)}(\beta_C)]^2 \rangle$ substituting S and $\langle P_4 \rangle$ by the ensemble averages of the second and fourth rank Legendre polynomials of the angle β_C between the molecular long axis and the long axis of the chain, namely

$$S_C = \tfrac{1}{2}\langle 3\cos^2\beta_C - 1\rangle,$$
$$\langle P_4 \rangle_C = \tfrac{1}{8}\langle 35\cos^4\beta_C - 30\cos^2\beta_C + 3\rangle. \tag{18}$$

2.2.2. ϕ_h Phase

As we will see later, the peculiar structural characteristics of the ϕ_h phase put some problems concerning the interpretation of the relaxation results related with this phase. In general terms we verify, as in the S_C phase, that the overall frequency dependence of the relaxation rate in this phase indicates the presence of three main relaxation mechanisms.

In the low frequency range, below 3 kHz, where the contribution of collective modes to the relaxation rate is dominant, the relaxation rate is substantially different from the one observed in the S_C phase. This fact is not unexpected since the structural characteristics of the ϕ_h phase (columnar) – and thus also the expression of the respective collective movements – are different from those of the S_C phase (lamellar). Therefore dominant collective movements in this phase were considered to be elastic deformations of the columns. The contribution of this mechanism to the relaxation rate is described by a model introduced by Žumer and Vilfan for columnar phases of discotic liquid crystals [20].

In this model, bending and compression of the columns are taken into account. Following the procedure described in [20] and [21], the spectral density for collective movements may be written as

$$[J^{(k)}(\omega)]_{CM} = \delta_{k1}\frac{C}{\omega}\int_{u_0}^{1}\sqrt{u} \cdot \left[\arctan\left(\frac{R}{u}\frac{\omega_{HC}}{\omega} + u\frac{\omega_{HC}}{\omega}\right) - \arctan \cdot \left(\frac{R_1}{u}\frac{\omega_{HC}}{\omega} + u\frac{\omega_{HC}}{\omega}\right)\right] du \tag{19}$$

with

$$R = \frac{B q^2_{\perp \mathrm{HC}}}{K_3 q^4_{\parallel \mathrm{HC}}}, \quad R_1 = \frac{B q^2_{\perp \mathrm{LC}}}{K_3 q^4_{\parallel \mathrm{HC}}},$$

$$u_0 = \left(\frac{q^2_{\parallel \mathrm{LC}}}{q^2_{\parallel \mathrm{HC}}}\right), \quad \omega_{\mathrm{HC}} = \frac{K_3 q^2_{\parallel \mathrm{HC}}}{\eta},$$

where C is a constant related to the viscoelastic parameters of the material, K_3 and B are elastic constants, respectively, for bending and compression of the columns and η is the corresponding effective viscosity $q_{\parallel \mathrm{HC}}$ and $q_{\perp \mathrm{HC}}$ are the components of the largest wave-vector of the deformations, respectively parallel and perpendicular to the columns $q_{\parallel \mathrm{LC}}$ and $q_{\perp \mathrm{LC}}$ are the corresponding values for the smallest wave-vector of the columns' deformations. We verified numerically that the existence of a minimum value for the components of the wave-vector associated with the columns' elastic fluctuations is negligible for any physically acceptable values of the involved parameters. Under this condition, also assumed in [20] and [21], Eq. (19) simplifies to

$$[J^{(k)}(\omega)]_{\mathrm{CM}} = \delta_{k1} \frac{C}{\omega} \int_0^1 \sqrt{u} \tag{20}$$

$$\cdot \left[\arctan\left(\frac{R}{u}\frac{\omega_{\mathrm{HC}}}{\omega} + u\frac{\omega_{\mathrm{HC}}}{\omega}\right) - \arctan\left(u\frac{\omega_{\mathrm{HC}}}{\omega}\right)\right] \mathrm{d}u\,.$$

The asymptotic limit of this function is independent of the frequency for low frequencies and is proportional to $1/\omega^2$ for high frequencies.

In the high frequency region, above 10 MHz, where local molecular rotational reorientations are the dominant mechanism, the frequency dependence of the relaxation rate is quite similar to the one observed in the S_C phase, indicating that the model used to describe this mechanism in the S_C phase is also appropriate for the ϕ_h phase.

Due to the peculiar liquid crystalline arrangement of the ϕ_h phase, none of the available models in the literature is strictly applicable to the description of the relaxation produced by self-diffusion in this phase. Although the ϕ_h phase exhibits a columnar structure, the model of Žumer and Vilfan for diffusion in discotic columnar mesophases [20] is actually not adequate because the cross-section of the columns in the ϕ_h phases is composed of several molecules which may diffuse individually. There is no physical reason for these molecules to diffuse together as groups equivalent to the discs present in the discotic columnar phases. Moreover it does not seem very realistic to consider for the biforked molecules the azimuthal symmetry that is assumed for the discotic molecules in the Žumer and Vilfan model for discotic columnar phases. Therefore, based on the similarity between the S_C and ϕ_h phases at the local level, which is compatible with the structure described in [6], we considered the Vilfan and Žumer theory for the diffusion [12] used for the S_C phase as a possible approximation for the relaxation produced by self-diffusion in this phase.

3. Analysis of the Experimental Results

The relaxation models described in Sect. 2 were used to fit the experimental results by a computer assisted non-linear least-squares method.

3.1. S_C *Phase*

The best fit obtained for the S_C phase at $T = 129\,°\mathrm{C}$ is presented in Figure 4. The values of the parameters for the different models appear in Table 1.

The rotational reorientations process was verified to be the dominant mechanism at high frequencies in the S_C phase. We used (8)–(18) in order to account for the contribution of these movements. For the order parameters S, S^C, P_4 and P_4^C we assumed approximate values based on the characteristics of the phase and of the mesogens. For the nematic order parameter we considered a typical average value for smectic phases with liquid-like layers $S \approx 0.7$ [22, 23]. For the order parameter S^C associated with the order of the chains we assumed an approximate value $S^C \approx 0.3$ based on molecular order studies for discotic liquid crystals [24]. The approximate values of $\langle P_4 \rangle$ and $\langle P_4^C \rangle$ were

Table 1. Model parameters obtained from the fits in the S_C phase.

$T/°\mathrm{C}$		119	129	139
CM Model	$A/10^{53}\ \mathrm{m}^{-6}$	3.8	3.4	3.2
	$(\omega_{\mathrm{LC}}/2\pi)/10^3\ \mathrm{Hz}$	1.2	1.2	1.2
	$(\omega_{\mathrm{HC}}/2\pi)/10^6\ \mathrm{Hz}$	380	380	380
SD Model	$d/10^{-10}\ \mathrm{m}$	5.0	5.0	5.0
	$\tau_{\perp}/10^{-9}\ \mathrm{s}$	6.9	5.0	3.7
$E = 42\ \mathrm{kJ \cdot mol^{-1}}$	$D_{\perp}/10^{-12}\ \mathrm{m^2\,s^{-1}}$	9.1	12.5	17.1
ROT Model	$\tau_S/10^{-9}\ \mathrm{s}$	2.8	2.4	2.1
(8)–(18)	τ_S/τ_L	6	6	6
	$\tau_S^C/10^{-11}\ \mathrm{s}$	6.0	5.0	4.3
$E = 16\ \mathrm{kJ \cdot mol^{-1}}$	τ_S^C/τ_L^C	6	6	6

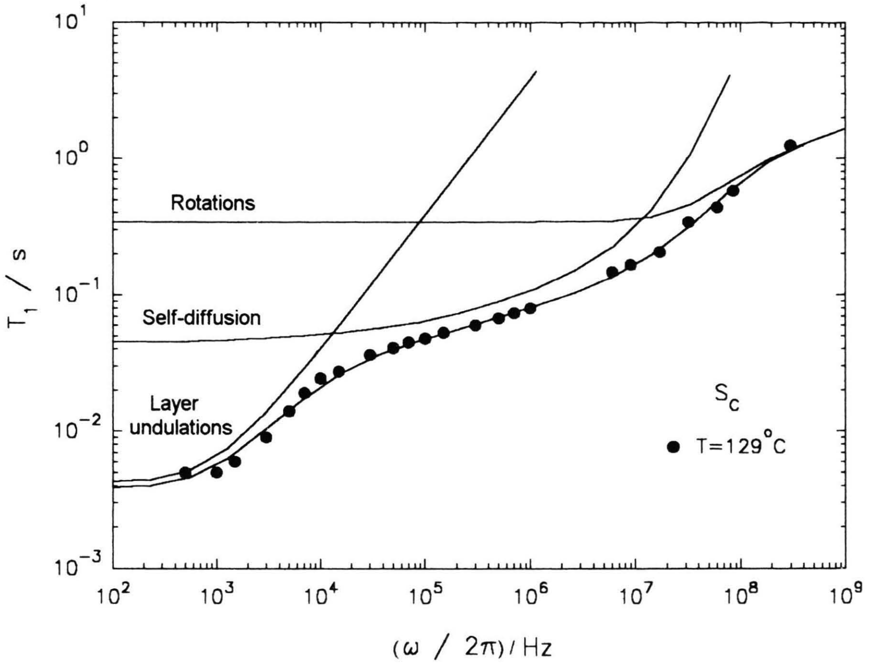


Fig. 4. Best fit of T_1 data as a function of proton Larmor frequency $(\omega/2\pi)$ at 129 °C (S_C phase) using (6) for the contribution of collective movements, (7) for the contribution of self-diffusion and the ROT contribution according to (8)–(18) with the optimized model parameters given in Table 1 and assumptions given by (21).

obtained from S and S^C using the expression $\langle P_4 \rangle \approx 5 \cdot S^2/7$ [25]. Nevertheless it was subsequently verified that the fits are not very sensitive to these order parameters.

The correlation times τ_S^C and τ_L^C obtained by (16) and (17) for the reorientations of chains are compatible to others reported in the literature for chain movements [26, 27].

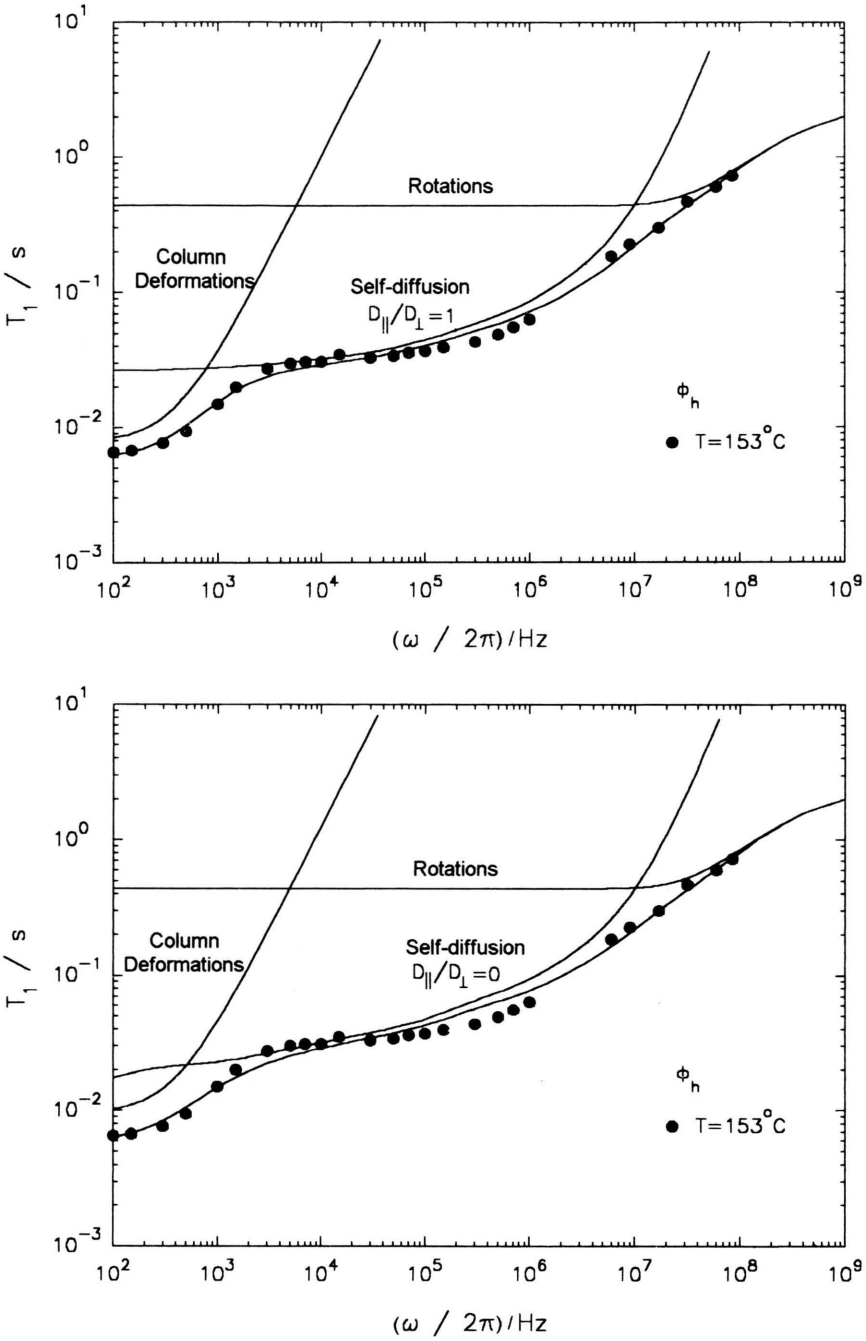
The values of τ_S/τ_L and τ_S^C/τ_L^C obtained with this model are in good agreement with those expected considering the anisotropy of the molecular core and of the chains in the all-trans configuration [28]. The obtained temperature dependence of the correlation times is compatible with the assumption that this is a thermally activated process with an activation energy $E = 16$ kJ mol^{-1}.

Self-diffusion was verified to be the dominant relaxation mechanism at intermediate frequencies (0.1 MHz $< \nu < 10$ MHz) in the S_C phase. The value considered for the spin density was $n = 5.7 \times 10^{28}$ spins m^{-3}. In (7) we used the following fixed parameters [6, 12, 29]:

$$\frac{\langle r_\perp^2 \rangle}{d^2} = 1, \quad \frac{D_\parallel}{D_\perp} = 1, \quad \frac{\ell}{d} = 11. \tag{21}$$

Our calculations are independent of the tilt angle of the phase, φ, because this parameter is averaged out in the case of a powder sample as we can easily verify applying (3), (4) and (7) with $\Delta = \varphi$. The values of $\tau_\perp$ obtained from the fits for the three measured temperatures in the S_C phase are of the order of 10^{-9} s and are compatible with a thermally activated process with an activation energy of 42 kJ mol^{-1}. The values of $\tau_\perp$ and $D_\perp$ obtained for the S_C phase and the respective activation energy, presented in Table 1, are similar to values for the same phase reported in [29–30]. The value of d (that may be assigned to the spacing corresponding to the lateral intermolecular interaction between the molecular hard cores) is in good agreement with the structural results presented in [6]. In fact, the d value obtained from the fits to the relaxation results (5 Å) is only slightly higher than the values obtained by X-ray diffraction. This small difference may be explained by the fact that X-ray studies, as pointed out in [6], underestimate the molecular diameter because of the neglected contribution of the alkyl chains.

The fits confirmed that collective fluctuation modes are the dominant relaxation mechanism at low frequencies ($\nu < 10$ kHz) in the S_C phase. The ω^{-1} dependence resulting from the layer undulation mechanism is in good agreement with our data in this phase. Similar values for the observed low and high cut-off frequencies can be found in the literature for disordered layer smectic phases in other liquid crystalline materials [30].



Figs. 5A and 5B. Best fits of T_1 data as a function of proton Larmor frequency ($\omega/2\pi$) at 153 °C (ϕ_h phase) using (20) for the contribution of collective movements in columnar phases, (7) for the contribution of self-diffusion (respectively with $D_\parallel/D_\perp=1$ and $D_\parallel/D_\perp=0$) and ROT contribution according to (8)–(18) with the optimized model parameters given in Table 2.

3.2. ϕ_h Phase

The best fits obtained for the ϕ_h phase, for $T=153\,^\circ$C, are presented in Figs. 5A and 5B. The values of the parameters for the different models appear in Table 2.

As in the S_C phase, the rotational reorientations process was verified to be the dominant mechanism at high frequencies in the ϕ_h phase. Equations (8)–(18), considered for the description of this process in the S_C phase, lead to the same conclusions for both the S_C and ϕ_h phases. Considering again the similarity at

Table 2. Model parameters obtained from the fits in the ϕ_h phase.

$T/°\mathrm{C}$		153	
CM Model (19)–(20)	$C/10^{51}\,\mathrm{m}^{-6}$	2.7	2.7
	$R/10^{-7}$	1.0	1.0
	$\omega_{HC}/2\pi)/10^6$ Hz	2.0	2.0
SD Model	$d/10^{-10}$	5.7	5.7
	$\tau_\perp/10^{-9}$ s	12.4	10.9
	$D_\parallel/D_\perp$	1	0
	$D_\perp/10^{-12}\,\mathrm{m}^2\,\mathrm{s}^{-1}$	6.6	7.5
ROT Model (8)–(18)	$\tau_S/10^{-9}$ s	1.8	1.8
	τ_S/τ_L	6	6
	$\tau_S^C/10^{-11}$ s	4.4	4.4
	τ_S^C/τ_L^C	6	6

local level between the S_C and ϕ_h phase we assumed for (9) and (16) the same order parameters (S, S^C, $\langle P_4\rangle$ and $\langle P_4^C\rangle$) as for the S_C phase. As in the S_C phase we verified that the assumption of these values was not critical for the results obtained from the fits.

In the ϕ_h phase, as in the S_C phase, self-diffusion was verified to be the dominant relaxation mechanism at intermediate frequencies (0.1 MHz $< \nu <$ 10 MHz). We used, as an approximation to account for the contribution of the self-diffusion process, the Vilfan and Žumer model for relaxation due to self-diffusion in smectic phases with liquid-like layers [12]. Due to the structural differences between the S_C and ϕ_h phases we considered for the parameter $D_\parallel/D_\perp$ (ratio between the diffusion coefficients for inter- and intra-layer movements) the limiting values of 1 (as assumed in the S_C phase) and zero. The latter is associated with the possibility of strong constraints in "inter-layer" movements due to the limitations of diffusion between columns in comparison with: i) diffusion along the columns; ii) diffusion inside the clusters which constitute the cross-section of the columns.

The values considered in this phase for the spin density and for the parameter $\langle r_\perp^2\rangle/d^2$ (see (21)) were the same as used for the S_C phase. For the parameter ℓ/d we used alternatively the values 11 (as in the S_C phase) and 13. This variation of ℓ/d could be due to the possible greater closeness (and consequent elongation) of the molecules inside the clusters compared to the situation verified in the S_C phase. Nevertheless we verified that the changing of this parameter from 11 to 13 does not affect considerably the values of the diffusion constants obtained from the fits.

The best fits using the Vilfan and Žumer model of self-diffusion [12] are obtained for values of the mean time between intra-layer jumps, $\tau_\perp$, of the order of 10^{-8} s and diffusion coefficients of the order of $10^{-12}\,\mathrm{m}^2\,\mathrm{s}^{-1}$. As we can see in Figs. 5A and 5B, the fit with $D_\parallel/D_\perp = 1$ is better than the one obtained for $D_\parallel/D_\perp = 0$. As in the S_C phase, the value of d obtained from the fits (that we assign to the mean transverse distance between the hard cores) is in good agreement with the value calculated from the X-ray diffraction data (5.4 Å as determined in [6]). Once again, the value obtained by the relaxation results (5.7 Å) is only slightly higher than the one determined from the X-ray scattering measurements.

The achievement of good fits to the experimental relaxation results, in the ϕ_h phase, with the same diffusion model used for the lamellar phase (with similar values of the diffusion coefficients and geometric parameters compatible with the X-ray diffraction results – see Tables 1 and 2) is an indication of the structural similarity of both phases at local level, as proposed by the packing model detailed in [6].

The fits confirmed, as in the S_C phase, that collective fluctuation modes are the dominant relaxation mechanism at low frequencies ($\nu <$ 10 kHz) in the ϕ_h phase. The assumption that collective modes in this phase are essentially different from those observed in the S_C phase is supported by the fact that the model of Žumer and Vilfan for collective movements in columnar phases [20] fits very well our data for the ϕ_h phase. Nevertheless, as much as it is known by the authors, there are no results available in the literature for similar phases in order to allow a comparative conclusion regarding the model parameters obtained from the fit.

The difference between the relaxation results in this phase relative to those of the S_C phase was confirmed by a test fit of the $1/\omega$ law, (6), associated with possible "layer" undulations which had a very conclusive result. From that fit we obtain physically unacceptable results, in particular to the maximum and minimum cut-off frequencies. The values obtained for these parameters have the same order of magnitude ($\approx$1 kHz). This would mean that the maximum and minimum wavelength associated with the collective modes would be practically identical, which is not physically reasonable. This conclusion allows us to exclude the "layer" undulation mechanism in the description of the relaxation in the ϕ_h phase.

4. Conclusions

In the analysis of the relaxation measurements we considered molecular rotational reorientations, self-diffusion and collective movements as potential contributions to the overall relaxation rate in the S_C and ϕ_h mesophases.

The contribution from local molecular rotational reorientations dominates the relaxation rate at high frequencies for the S_C and ϕ_h mesophases. A similar description of this mechanism in these two phases is compatible with our data. The fits with the rotational model described by (9) and (16), which takes into account the rotation of the chains relative to the molecular core, give correlation times of the order of 10^{-9} s (τ_S) and 10^{-10} s (τ_L) for the global rotation, and of 10^{-11} s (τ_S^C) and 10^{-12} s (τ_L^C) for the rotation of the chains. The values of the τ's for the rotation of the chains relative to the core are similar to values of correlation times for chains' movements presented in [26, 27].

Self-diffusion is the dominant mechanism of relaxation at intermediate frequencies in the two studied mesophases. The relaxation due to self-diffusion in the S_C phase is well described using the curves obtained from Vilfan and Žumer model (7) for values of $\tau_\perp$ of the order of 10^{-9} s. From these values we obtain diffusion coefficients, $D_\perp$, of the order of 10^{-11} m^2 s^{-1}. The values of $\tau_\perp$ obtained in the S_C phase show an Arrhenius type dependence on the temperature with an activation energy of 42 kJ mol^{-1}. The best fit obtained for the ϕ_h phase, using as an approximation the same diffusion model as for the S_C phase, gives times between intra-layer jumps, $\tau_\perp$, of the order of 10^{-8} s and diffusion coefficients of the order of 10^{-12} m^2 s^{-1}. The values of the parameter d obtained from the fits to our relaxation results are in good agreement with the size of the mean intermolecular lateral interaction distance between the molecular hard-cores as determined by the X-ray diffraction study presented in [6].

The compatibility of the relaxation results with a similar description of the molecular rotational reorientations and self-diffusion mechanisms in the S_C and ϕ_h phases (leading, in both phases, to consistent values of correlation times for rotational reorientations and diffusion coefficients), together with the structural analysis given in [6], may be considered as an indirect indication of the similarity at local level between the structure of these two mesophases.

A clear distinction between the collective fluctuation modes is the most evident difference found in the molecular dynamic behaviour of the ϕ_h phase when compared with the S_C phase of the biforked liquid crystal considered in this work. The contribution of these movements dominates the overall relaxation rate at low frequencies in both the S_C and ϕ_h phases. Nevertheless, while in the S_C phase the T_1 dispersion at low frequencies is well described by a ω^{-1} law characteristic of layer undulations, the T_1 data for the ϕ_h phase in the same frequency range are better described by a different law which can be ascribed to elastic deformations of the columns.

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