Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

A ^{2}H NMR study of orientational order, phase transitions and dynamics in a liquid crystalline compound

D. Catalano[a]; E. Ciampi[a]; K. Fodor-Csorba[b]; C. Forte[c]; M. Geppi[d]; D. Imbardelli[e]
[a] Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa, Pisa, Italy [b] Research Institute for Solid State Physics, Hungarian Academy of Sciences, Budapest, Hungary [c] Istituto di Chimica Quantistica ed Energetica Molecolare, CNR, Pisa, Italy [d] Scuola Normale Superiore, Pisa, Italy [e] Dipartimento di Chimica, Università della Calabria, Rende, Cosenza, Italy

To cite this Article Catalano, D. , Ciampi, E. , Fodor-Csorba, K. , Forte, C. , Geppi, M. and Imbardelli, D.(1996) 'A ^{2}H NMR study of orientational order, phase transitions and dynamics in a liquid crystalline compound', Liquid Crystals, 21: 6, 927 — 932

To link to this Article: DOI: 10.1080/02678299608032912

URL: http://dx.doi.org/10.1080/02678299608032912

LIQUID CRYSTALS, 1996, VOL. 21, NO. 6, 927–932

A ^{2}H NMR study of orientational order, phase transitions and dynamics in a liquid crystalline compound

by D. CATALANO*†, E. CIAMPI†, K. FODOR-CSORBA‡, C. FORTE§,
M. GEPPI¶ and D. IMBARDELLI||
†Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa,
Via Risorgimento 35, 56126 Pisa, Italy
‡Research Institute for Solid State Physics, Hungarian Academy of Sciences,
1525 Budapest, P.O. Box 49, Hungary
§Istituto di Chimica Quantistica ed Energetica Molecolare, CNR,
Via Risorgimento 35, 56126 Pisa, Italy
¶Scuola Normale Superiore, Piazza dei Cavalieri 7, 56127 Pisa, Italy
||Dipartimento di Chimica, Università della Calabria, 87030 Rende (Cosenza), Italy

(*Received 2 January 1996; in final form 13 May 1996; accepted 24 June 1996*)

^{2}H-NMR spectroscopy is employed to investigate the orientational order in the nematic and smectic A, B, and crystal G phases formed by 4-(2-methylbutyl)phenyl 4′*n*-heptylbiphenyl-4-carboxylate-d$_{18}$. Evidence of the lock in the *trans*-conformation of the first two methylene groups of the *n*-heptyl chain is found in the S$_{B}$ and G phases. The dynamics of the aromatic molecular core are studied in a temperature interval including the S$_{A}$–S$_{B}$ transition, by the analysis of the deuterium Zeeman and Quadrupolar relaxation times using the rotational diffusion model. Hence the diffusion constants related to the molecular spinning and tumbling motions are evaluated.

^{2}H NMR spectroscopy, a successful technique in the study of molecular order, phase transitions and dynamics of liquid crystals [1], is here employed to investigate the behaviour of the deuteriated compound **I** of figure 1 (4-(2-methylbutyl)phenyl 4′*n*-heptylbiphenyl-4-carboxylate-d$_{18}$) in its liquid crystalline phases. The synthesis and the sequence of mesophases presented by this compound were reported by Fodor-Csorba *et al.* [2]. The following phase transition sequence was revealed by observation with a polarizing microscope equipped with a hot stage, on cooling:

$$\mathrm{C}+\xleftarrow[40^{\circ}\mathrm{C}]{}\mathrm{G}\xleftarrow[57^{\circ}\mathrm{C}]{}\mathrm{S_B}\xleftarrow[67^{\circ}\mathrm{C}]{}\mathrm{S_A}\xleftarrow[137^{\circ}\mathrm{C}]{}\mathrm{N}\xleftarrow[147{\cdot}2^{\circ}\mathrm{C}]{}\mathrm{I}$$

The layer spacing and molecular dynamics in the liquid crystalline phases have already been studied on the non-deuteriated analogue by dielectric relaxation and neutron scattering [3]. A decrease in layer spacing was found at the S$_{B}$–G transition due to the onset of tilting of the local director inside the smectic planes with respect to the planes. In fact the crystal G phase is characterized by this kind of tilted arrangement, with the molecules hexagonally close packed within the layers.

All the ^{2}H NMR experiments were run at 46·04 MHz. Proton coupled ^{2}H NMR spectra of **I** were recorded in the temperature range between 146°C and 45°C with a Bruker CXP 300 spectrometer and a Varian VXR 300. A selection of the spectra is shown in figure 2. At a high temperature, five quadrupolar doublets, α, β, χ, δ, φ, are evident. Below 71°C the β and χ signals are superimposed. The two doublets δ and φ, with integral ratio 1/5, can be ascribed to the six types of different aromatic deuterons, which, as is usually found [4], show the smallest quadrupolar splitting (except for the methyl deuterons at the end of long alkyl chains). The assignment of the φ signal is not certain and, anyway, it is not essential. By analogy with the spectral analysis of liquid crystals containing the azoxy group [5] (there are no examples of spectra of selectively deuteriated liquid crystals containing the benzoate group), the φ signal could be attributed to the aromatic deuterons nearest to the carbonyl group. The fact that the deuterons on three different aromatic rings exhibit the same quadrupolar splitting over a wide range of temperature most probably indicates that the *para*-axes of the rings are substantially parallel to one another and the C–D directions for these deuterons form the same angle with the *para*-axis. A deviation of 1° from such a regular structure is enough to justify the difference between the δ and φ quadrupolar splittings.

---

*Author for correspondence.

0267–8292/96 $12·00 © 1996 Taylor & Francis Ltd.

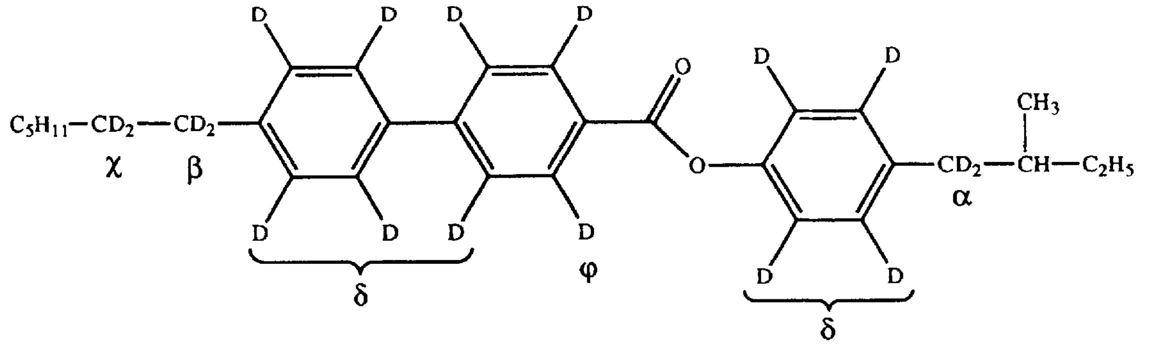

Figure 1. Molecular structure and deuteron labelling.

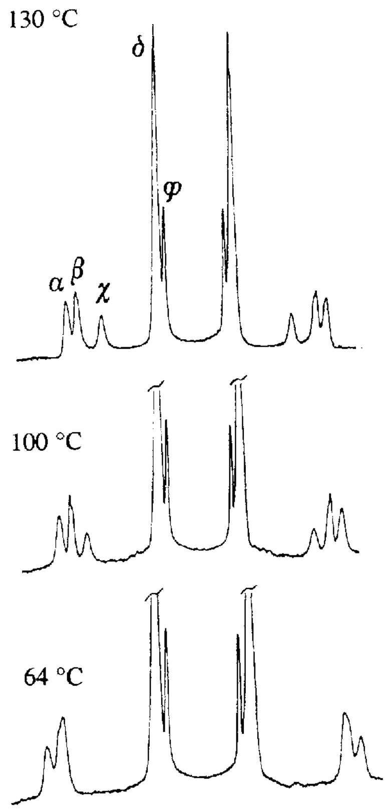

Figure 2. A selection of spectra of compound **I** in its S_A and S_B phases.

A spectrum recorded with proton decoupling at 73°C helps to assign the α, β, χ signals to the relative aliphatic deuterons (see figure 1). In the coupled spectrum, the linewidth of the three signals is about 1800 Hz, 1500 Hz and 1900 Hz, respectively; in the decoupled spectrum, they have the same linewidth of about 1500 Hz. This indicates that the α and χ peaks are due to methylene deuterons close to protonated groups. Consequently, the β signal is assigned to the deuterons of the CD_2 group of the unbranched chain linked to the aromatic core. Moreover, since it has been generally observed that the quadrupolar splittings of methylene deuterons decrease on going along the chain from the aromatic core towards the chain end [4], the largest quadrupolar splitting is assigned to the methylene deuterons on the branched chain. We also notice that both in the coupled and uncoupled spectra, the β peak shows a partially resolved structure due to the geminal D–D coupling, evaluated about 200 Hz, a quite reasonable value for a methylene group linked to a highly oriented aromatic core.

The trends in the quadrupolar splittings with temperature (figure 3), found from the analysis of the ^2H NMR spectra, substantially confirm the series of transition temperatures indicated in the above scheme. Some interesting indications about the molecular organization in the mesophases can be drawn from direct inspection of these trends.

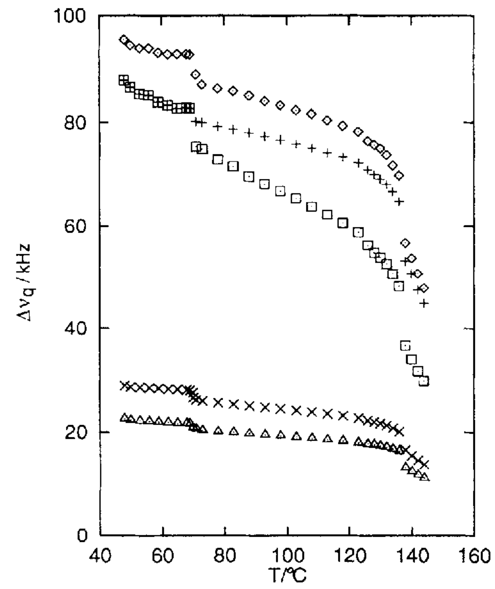

Figure 3. Deuterium quadrupolar splittings vs. temperature. With reference to the nomenclature given to the peaks in figure 2, we have ◇ α, + β, □ χ, × δ and △ φ. The experimental uncertainty on the splittings is about 500 Hz.

As a first point, the increase in all the quadrupolar splittings (absolute values) with decreasing temperature in the tilted G phase indicates that the local phase director inside the smectic layers aligns along the magnetic field in the spectrometer. This alignment confirms the observation that, when a phase sequence includes both G and S_B phases, the smectic planes, rather than the normals to the layers, are tilted relatively to the magnetic field [6].

Looking at the signals due to the three types of alkyl deuterons, we find three very distinct doublets in the nematic and smectic A phases. In general, for methylenic deuterons along a chain, the decrease in the quadrupolar splittings is a consequence of an increase in conformational freedom. In the present case, the difference between the quadrupolar splittings of the β and χ doublets, assigned to the deuterons of the unbranched chain, indicates that rotation around the C–C bond allows a significant percentage of *gauche*-conformation. In fact, contrarily to the *trans*-conformation, in the *gauche*-situation the C–D bonds of the two methylene groups involved have different orientations with respect to the molecular long axis. Below the S_A–S_B transition, the β and χ signals superimpose, suggesting that, in the highly ordered S_B and G phases, the two methylene groups are locked in the most elongated *trans*-conformation. This simple conformational model is also in agreement with the slight increment of layer spacing at the S_A–S_B transition (2·4%) found by neutron scattering [3], and also observed for other liquid crystals [7–9]. Here we have probably met a favourable case in which a phase transition can be associated with a detail of the molecular structure through straightforward measurements of static parameters.

The dynamic behaviour of compound **I** has been investigated around the S_A–S_B transition, by measuring the deuterium Zeeman (T_{1Z}) and Quadrupolar (T_{1Q}) relaxation times in the temperature range between 55°C and 90°C. We used a Bruker AMX 300 spectrometer, having a 90° pulse width of 9 µs, and employed the Wimperis pulse sequence [10] 90_0–$2\tau_1$–$67{\cdot}5_{270}$–$2\tau_1$–45_{90}–τ_1–45_{90}–τ_2–45_0, where τ_1 is a delay of 7·5 µs which is empirically determined. The delay τ_2 was varied between 20 µs and 2 s. Good spectra were obtained after 1000 acquisitions.

The sum (M_+) and the difference (M_-) of the integrals of the two components of a quadrupolar doublet, reported as a function of the variable delay time τ_2, give T_{1Z} and T_{1Q}, respectively, through the two fitting equations:

$$M+(\tau_2)=a\left[1-b\exp\left(-\frac{\tau_2}{T_{1Z}}\right)\right] \qquad (1\,a)$$

$$M-(\tau_2)=c+d\exp\left(-\frac{\tau_2}{T_{1Q}}\right) \qquad (1\,b)$$

The parameters *a*, *b*, *c*, *d* are determined by the fitting procedure together with T_{1Z} and T_{1Q}. These equations differ from those theoretically predicted [11], where $b=1$, $c=0$ and $M-(0)/M_+(\infty)=d/a=1{\cdot}5\sin 45°=1{\cdot}07$. Expression (1 *a*) is analogous to that used to analyse the integral intensity decays from inversion recovery experiments, when the inversion is not complete at vanishing variable delay [12]. For $\tau_2\to\infty$ the integrals of the two peaks of the quadrupolar doublets, which should be equal, show a slight asymmetry due to base line imperfections. This is compensated for by the parameter *c*.

Only an estimate of the order of magnitude has been possible for the relaxation times of the alkyl deuterons, because the combination of large quadrupolar splittings with the relatively long deuterium 90° pulse does not allow the Wimperis pulse sequence to work properly. In the range of temperatures investigated, both T_{1Z} and T_{1Q} have values between 20 and 200 ms and, at each temperature, are greater than the corresponding relaxation times of the aromatic deuterons, as usually found in rod-like mesogens [13, 14]. It must also be pointed out that the complete superposition of the β and χ peaks in the S_B phase would presumably have made impossible a detailed analysis of the dynamic behaviour of the aliphatic methylenes even with more accurate experimental data.

In the following account, we will analyse the results obtained for the aromatic deuterons. By fitting the experimental values of $M_+(\tau_2)$ and $M_-(\tau_2)$ to equation (1 *a*) and (1 *b*), respectively, we find *b* values in the range between 0·94 and 1·0, depending on the temperature. For $\tau_2\to\infty$ the integrals of the two peaks of the quadrupolar doublets differ up to 8% and the parameter *c* is between $-0{\cdot}1$ and 0·1. The parameter *a* is about 2·7 and the ratio $M_-(0)/M_+(\infty)=(d+c)/a$ ranges from 0·9 to 1, probably owing to imperfections in the pulse sequence. The T_{1Z} and T_{1Q} values, determined at different temperatures with experimental errors of about 10%, are reported in figure 4. No difference has been found between the relaxation times of the δ and φ signals.

The spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ are connected to the measured relaxation times by the following equations [11]:

$$\frac{1}{T_{1Z}}=J_1(\omega_0)+4J_2(2\omega_0) \qquad (2\,a)$$

$$\frac{1}{T_{1Q}}=3J_1(\omega_0) \qquad (2\,b)$$

The relaxation times increase with increasing temperature and show a steeper change around the S_A–S_B transition, particularly definite in the case of T_{1Z} (see figure 4). This fact and the consequent trends in spectral densities suggest a different dynamic behaviour in the

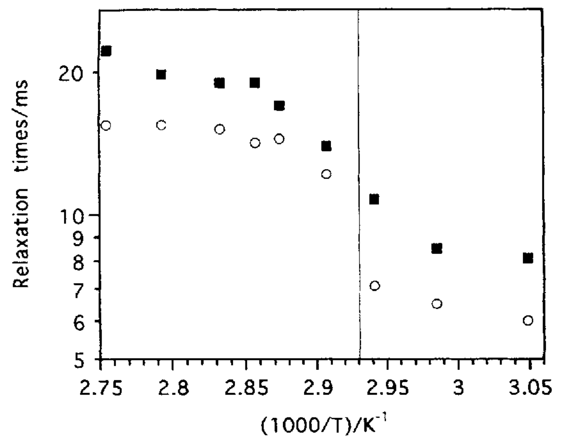

Figure 4. Relaxation times T_{1Z} (○) and T_{1Q} (■) vs. $1000/T$; the uncertainties on T_{1Z} and T_{1Q}, are about 10% of the corresponding values.

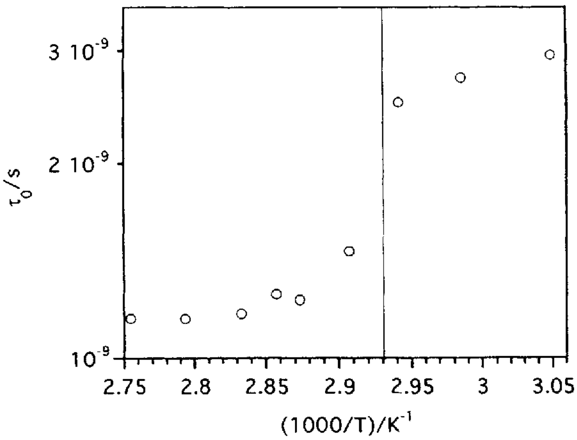

Figure 5. Effective correlation time τ_0 for the global molecular motion according to the Beckmann model as a function of $1000/T$; the uncertainty on τ_0 is about 10% of its value.

two phases. The ratio $J_1(\omega_0)/J_2(2\omega_0)$ for the aromatic deuterons assumes values between 1·2 and 1·7.

As a first approach, we can discuss our experimental data in terms of a simple model, given by Beckmann *et al.* [13], which takes into account only Zeeman relaxation times, T_{1Z}, and uses them to obtain an 'effective' correlation time τ_0 comprising global information about all the motions of the CD bond which contribute to the relaxation. Following this model, in the fast motion regime, the relaxation rate $(R = 1/T_{1Z})$ can be expressed in terms of the local order parameter S_{CD} and of the effective correlation time τ_0:

$$R = (F^{(2,0)})^2 \, (1 - S_{CD})\tau_0 \tag{3}$$

where $F^{(2,0)} = (3/2)^{1/2} q_{CD}$; here q_{CD} is the quadrupolar coupling constant, assumed to be 185 kHz for aromatic deuterons [15]. The local order parameters are easily obtainable from the quadrupolar splittings $\Delta\nu_q$ reported in figure 3, using the following relation:

$$S_{CD} = \frac{2}{3} \frac{\Delta\nu_q}{3q_{CD}} \tag{4}$$

$\Delta\nu_q$ is negative for the deuterons of the aromatic cores of mesogenic molecules highly ordered along the magnetic field and its absolute value increases with decreasing temperature, as does the term $(1 - S_{CD})$ in equation 3. The correlation time τ_0 should also increase when the motions slow down significantly. The values of τ_0 computed for the aromatic deuterons at different temperatures are reported in figure 5. A strong increase of τ_0 at the transition from the smectic A to the smectic B phase is observed, indicating a substantial slowing down of the motions involved in the dynamic behaviour of the aromatic molecular core. In effect, the behaviour of R is dominated by this dynamic effect, rather than by the change of S_{CD}. The slope of the trend of τ_0 within each smectic phase could be connected to the global activation energy of the molecular motions, but could also be physically meaningless as a consequence of the roughness of the model.

In the present case, however, a more detailed analysis is possible exploiting both T_{1Z} and T_{1Q}, on the basis of the model proposed by Nordio and coworkers [16]. These authors describe the molecular reorientation as small step rotational diffusion in the anisotropic environment given by a mean field potential like that of Maier and Saupe. The parameters characterizing the motion are the two principal components, $D_\parallel$ and $D_\perp$, of an axially symmetric diffusion tensor fixed in the molecular frame. $D_\parallel$ and $D_\perp$ represent the rotational diffusion constants of the molecule for its motion about the molecular long axis and for the motion of such an axis, respectively. In applying this model, we have assumed the *para*-axis of the aromatic system to be coincident with the molecular long axis and the molecular ordering and diffusion tensors to be symmetric around such an axis.

The spectral densities are related to the molecular rotational diffusion constants by expression (5), valid in the fast motion limit ($\omega\tau \ll 1$, with ω the Larmor frequency) and when each auto-correlation function is written as a single exponential function [17]:

$$J_{m_L}(m_L\omega) = \frac{3\pi^2}{2} q_{CD}^2 \sum_{m_M=-2}^{2} c_{m_L,m_M}[d^2_{m_M 0}(\beta_{M,Q_0})]^2 \tau^{(2)}_{m_L,m_M} \tag{5}$$

β_{M,Q_0} is the angle between the molecular z axis and the C–D bond of interest, assumed to be 60 degrees in the present case. The c_{m_L,m_M} coefficients are the mean squares of the Wigner rotation matrices and can be expressed in terms of the order parameter of the molecular long axis [18], $\langle P_2 \rangle$, which is simply proportional to S_{CD} for a uniaxial molecule, as we assume for our highly ordered compound, in a uniaxial phase. We evaluate $\langle P_2 \rangle$ as $2S_{CD}/(3\cos^2\beta_{M,Q_0}-1)$ neglecting η, the asymmetry constant of the electric field gradient tensor. The correlation times $\tau^{(2)}_{ML,mM}$ are defined as

$$(\tau^{(2)}_{m_L m_M})^{-1} = \frac{D_\perp}{\lambda^{(2)}_{m_L m_M}} + m_M^2(D_\parallel - D_\perp) \qquad (6)$$

The $\lambda^{(2)}_{m_L m_M}$ terms also depend on the orientational order parameter $<P_2>$ and their values are reported in [17, 18]. Equation (6) is valid for a deuteron which is not subject to internal rotations, as for example the methine deuteron in a substituted benzylidenaniline. For other deuterons, additional diffusion constants should be used to take into account internal motions such as the rotations of the aromatic rings around their *para*-axes or the rotation of methylene fragments around C–C bonds [19, 20], but the determination of these parameters requires the measurement of individual T_{1Z} and T_{1Q} for deuterons on different fragments. As already described, at each temperature, we have just one set of values T_{1Z} and T_{1Q} for all the deuterons of the aromatic core; therefore, we must treat these data as representative of the global motion of the molecular core. The rotation of the various phenyl rings around their *para*-axes or the molecular long axis, will essentially contribute to the value of the $D_\parallel$ diffusion coefficient [21].

The values of $D_\perp$ and $D_\parallel$, determined from the values of the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ according to equations (5) and (6) are reported in figure 6 plotted against $1000/T$. The uncertainty on the plotted coefficients due to the uncertainty on the experimental $\Delta\nu_q$, T_{1Z} and T_{1Q} quantities is contained within 15% of the quoted values. The fast motion limit condition used in equation 5 is satisfied in the present case, $\omega\tau^{(2)}{}_{mL,mM}$ ranging from 5×10^{-4} to 5×10^{-2}. The assumption of a non-zero value for η (namely $\eta = 0{\cdot}04$ [22]) in the evaluation of $\langle P_2 \rangle$ would affect only $D_\perp$, yielding about halved values for this parameter; the following discussion, however, would not change.

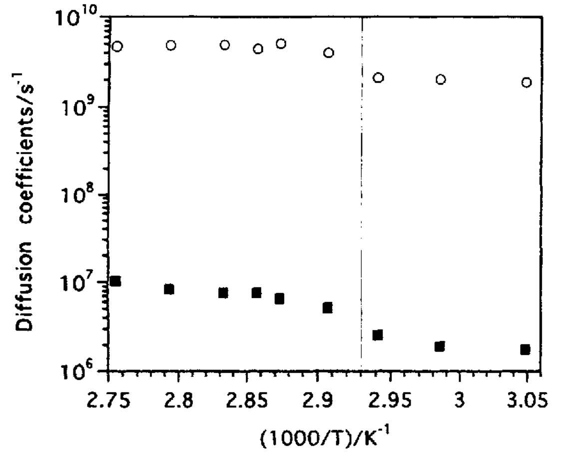

Figure 6. Diffusion coefficients $D_\parallel$ (○) and $D_\perp$ (■) vs. $1000/T$.

It is interesting to point out that, on comparing the espressions of $1/T_{1Z}$ for the two models ([13, 16]), we have found that, in the case under investigation, the relation $\tau_0 \approx 5/D_\parallel$ should roughly hold, as really does happen. In general, it can be verified that for high molecular order, i.e. $P_2 > 0{\cdot}7$, τ_0 is mainly determined by $D_\parallel$, with $\tau_0 \times D_\parallel$ ranging between 4 and 10 if $D_\perp > 5 \times 10^6$. The product rapidly increases above 10 on approaching $D_\perp = 10^6$, particularly for low values of P_2. The values here obtained for $D_\parallel$ are comparable to those reported for various compounds in their nematic, S_A, S_B and S_C phases [19–21, 23–25]. The order of magnitude of $D_\perp$ ($10^6 \div 10^7$) is lower than that reported for the same compounds ($10^7 \div 10^9$).

A change by a factor two in the values of both diffusion coefficients is detected within a range of about 2 K around the transition. $D_\perp$ decreases with decreasing temperature, indicating the existence of an activation energy barrier for the corresponding motion, while $D_\parallel$ is substantially constant within both smectic phases; the ratio $D_\parallel/D_\perp$ is approximately 5×10^2 and 10^3 in the S_A and S_B phases, respectively. These results can be intuitively ascribed to the known differences in the molecular organisation and dynamics in the two kinds of smectic phase. In fact, inside the S_B layers, the molecules assume a local hexagonal packing [26], which does not exist in the S_A layers. A cooperative fluctuation of their long axes, affecting $D_\perp$ occurs, instead of the independent long axial fluctuations characteristic of the S_A phase [27]. All this has been experimentally proved specifically for the non-deuteriated analogue of compound **I** [3]. Moreover, free rotation around the molecular long axis is known to be allowed both in the S_A and S_B phases [26]. However, we must recall that the values of $D_\parallel$ might be mainly determined by the rotation of the phenyl rings around their *para*-axes, rather than by the global molecular rotation. In the analysis here presented, we neglect the possible contribution of the director fluctuations to the relaxation [28]. Measurements at different frequencies are required to check the importance of these fluctuations; anyway, aromatic deuterons are usually rather insensitive to them, owing to the particular orientation of the aromatic CD bonds with respect to the molecular long axis.

In the future, the NMR dynamical study of compound I will be extended to the whole range of temperature over which the compound is liquid crystalline. The new experiments will also embrace the study of the dynamical behaviour of the alkyl chains.

The synthetic work was supported by the research foundation OTKA T020905.

References

[1] J. W. Emsley (editor), 1983, *Nuclear Magnetic Resonance of Liquid Crystals*, NATO ASI Series C, Vol. 141, (Dordrecht: Reidel).

[2] Fodor-Csorba, K., Bata, L., Holly, S., Gács-Baitz, E., and Ujszászy, K., 1993, *Liq. Cryst.*, **14**, 1863.

[3] Bata, L., Pépy, G., and Rosta, L., 1988, *Liq. Cryst.*, **3**, 893.

[4] Beckmann, P. A., Emsley, J. W., Luckhurst, G. R., and Turner, D. L., 1983, *Mol. Phys.*, **50**, 699.

[5] Catalano, D., Forte, C., Veracini, C. A., Emsley, J. W., and Shilstone, G. N., 1987, *Liq. Cryst.*, **2**, 345.

[6] Vaz, M. J., Yaniv, Z., Dong, R. Y., and Doane, J. W., 1985, *J. Magn. Reson.*, **62**, 461.

[7] Seurin, P., Guillon, D., and Skoulios, A., 1981, *Mol. Cryst. liq. Cryst.*, **71**, 51.

[8] Fanelli, E., Melone, S., Torquati, G., Pisipati, V. G. K. M., and Rao, N. V. S., 1987, *Mol. Cryst. liq. Cryst.*, **146**, 235.

[9] Gandolfo, C., Grasso, D., Buemi, G., and Torquati, G., 1988, *Nuovo Cimento*, **10D**, 1363.

[10] Wimperis, S., 1990, *J. Magn. Reson.*, **86**, 46.

[11] Vold, R. L., Dickerson, W. H., and Vold, R. R., 1981, *J. Magn. Reson.*, **43**, 213.

[12] Kowalewski, J., Levy, G. C., Johnson, L. F., and Palmer, L., 1977, *J. Magn. Reson.*, **26**, 533.

[13] Beckmann, P. A., Emsley, J. W., Luckurst, G. R., and Turner, D. L., 1986, *Mol. Phys.*, **59**, 97.

[14] Forte, C., Gandolfo, C., Geppi, M., and Veracini, C. A., 1995, *Mol. Cryst. liq. Cryst.*, **266**, 213.

[15] Emsley, J. W., and Lindon, J. C., 1975, *NMR Spectroscopy Using Liquid Crystal Solvents* (Pergamon Press).

[16] Nordio, P. L., Rigatti, G., and Segre, U., 1972, *J. chem. Phys.*, **56**, 2117.

[17] Agostini, G., Nordio, P. L., Rigatti, G., and Segre, U., 1975, *Atti Accad. Naz. Lincei, Ser. 8*, **13**, 1.

[18] Vold, R. R., and Vold, R. L., 1988, *J. chem. Phys.*, **88**, 1443.

[19] Dong, R. Y., 1988, *J. chem. Phys.*, **88**, 3962.

[20] Dong, R. Y., and Richards, G. M., 1988, *J. Chem. Soc. Faraday Trans.*, **84**, 1053.

[21] Dong, R. Y., 1986, *Mol. Cryst. liq. Cryst.*, **141**, 349.

[22] Ambrosetti, R., Catalano, D., Forte, C., and Veracini, C. A., 1986, *Z. Naturforsch*, **41a**, 431.

[23] Dong, R. Y., and Richards, G. M., 1986, *Mol. Cryst. liq. Cryst.*, **141**, 335.

[24] Dong, R. Y., 1989, *Liq. Cryst.*, **4**, 505.

[25] Forte, C., Geppi, M., and Veracini, C. A., 1994, *Z. Naturforsch*, **49a**, 311.

[26] Petrie, S. E. B., 1979, *Liquid Crystals The Fourth State of Matter*, edited by F. D. Saeva (Marcel Dekker), Chap. 4.

[27] Bata, L., and Buka, A., 1981, *Mol. Cryst. liq. Cryst.*, **63**, 307.

[28] Vold, R. R., and Vold, R. L., 1994, *The Molecular Dynamics of Liquid Crystals*, NATO ASI Series C, Vol. 431, edited by J. W. Emsley and C. A. Veracini (Dordrecht: Reidel), p. 207.