Rotational dynamics of a chiral mesogen by 2H NMR study: can it be anomalous?

Ronald Y. Dong[a]; M. Cheng[a]; K. Fodor-Csorba[b]; C. A. Veracini[c]

[a] University of Manitoba, [b] Research Institute for Solid Physics and Optics, [c] Universita di Pisa,

PLEASE SCROLL DOWN FOR ARTICLE

Rotational dynamics of a chiral mesogen by ^{2}H NMR study: can it be anomalous?

RONALD Y. DONG*, M. CHENG

Department of Physics and Astronomy, University of Manitoba, Winnipeg, MB,
Canada R3T 2N2

K. FODOR-CSORBA

Research Institute for Solid State Physics and Optics,
Hungarian Academy of Sciences, 1525 Budapest, Hungary

and C. A. VERACINI

Dipartimento di Chimica e Chimica Industriàle dell Università di Pisa, 56100 Pisa,
Italy

Deuterium NMR spectroscopy is used to study a ring-deuteriated chiral liquid crystal 4-(2-methylbutyl)oxycarbonylphenyl 4-(10-undecenyloxy)benzoate. The quadrupolar and proton–deuteron dipolar splittings, and deuteron quadrupolar and Zeeman spin-lattice relaxation times were measured as a function of temperature in the smectic A phase at two different Larmor frequencies. The derived spectral densities of motion at different temperatures were analysed simultaneously using a rotational diffusion model which also includes internal ring rotations. Motional parameters ($D_\perp$, $D_\parallel$, D_R) and order parameter tensors (S_{zz}, $S_{xx} - S_{yy}$) were obtained. Although the present data seem insufficient to draw a definitive conclusion, we believe that it is possible for this particular chiral molecule to have $D_\perp > D_\parallel$, which is different from non-chiral rod-like liquid crystals.

1. Introduction

Chiral molecules used to form ferro- and antiferro-electric liquid crystals have recently attracted much attention owing to the observation of a rich variety of chiral subphases [1, 2]. Indeed chirality is now thought of as an important element in creating novel organizations and functions of liquid crystalline materials. Molecular chirality can be created by placing asymmetric carbons in the end chain(s) of a non-chiral liquid crystal molecule. There is now evidence that a chiral chain is motionally hindered in the liquid crystalline phase, as the chain is bent at the chiral centre with respect to the molecular long axis [3–6]. A bent shape increases the molecular biaxiality and moment of inertia. This is consistent with the belief that in order to see macroscopic polarization, rotation around the molecular long axis must be highly restricted. NMR studies of conventional rod-like mesogens have clearly established that the spinning motion

(around the molecular long axis) of the molecule is about two orders of magnitude faster than its tumbling motion (about one of the short axes) [7]. In the present study, the molecule of an optically pure chiral mesogen is found to show rotational behaviours which may be anomalous. Our sample is a partially ring-deuteriated smectogen S-4-(2-methylbutyloxy)carbonylphenyl 4-(10-undecenyloxy)-benzoate (MBPUB-d$_2$) and is studied by means of deuterium NMR spectroscopy. Spectral densities of motion were determined from measurements of the Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times. They are fitted to a small-step rotational diffusion model to obtain motional parameters.

2. Experimental

A home-built superheterodyne coherent pulse NMR spectrometer was operated for deuterons at 15.1 MHz using a Varian 15 in electromagnet and at 46.05 MHz using a 7.1 T Oxford superconducting magnet. The sample was placed in an NMR probe whose temperature was regulated either by an external oil bath circulator or by an air flow with a Bruker BST-1000 temperature

*Author for correspondence; e-mail: dong@brandonu.ca; permanent address: Department of Physics and Astronomy, Brandon University, Brandon, MB, Canada R7A 6A9

controller. The temperature gradient across the sample was estimated to be better than 0.3°C. The $\pi/2$ pulse width of about $4 \mu s$ was produced by an ENI power amplifier. Pulse control and signal collection were performed by a General Electric 1280 computer. Fourier transformation and data processing were done by Spectral Calc and Micro Origin softwares on an IBM-PC computer. A broadband J-B excitation sequence [8] was used to measure simultaneously T_{1Z} and T_{1Q} of the aromatic deuterons. The pulse sequence was modified using an additional monitoring $\pi/4$ pulse to minimize any long term instability of the spectrometer. The data manipulation has been detailed elsewhere [9]. Signal collection was started $10 \mu s$ after each monitoring $\pi/4$ pulse, and averaged for over 1024 scans at 46 MHz and 4096 scans at 15.1 MHz. The experimental uncertainty in these spin-lattice relaxation times was estimated to be $\pm 5\%$. The quadrupolar and dipolar splittings of the aromatic deuterons were determined from an NMR spectrum obtained by Fourier transforming the free induction decay signal after a $\pi/2$ pulse, and had an experimental error of better than $\pm 1\%$.

A typical spectrum of MBPUB-d_2 is shown in figure 1 together with the molecular structure of the mesogen. The permanent dipoles are located mainly on the two carbonyl groups in the molecule and point approximately perpendicularly to the molecular long axis. Although MBPUB has a narrow one degree range of SmC* phase, our sample only shows the SmA phase, with an extended temperature range by supercooling. As seen in the figure, the spectrum consists of a quadrupolar doublet (with a splitting $\Delta \nu_Q$) whose peaks show an additional splitting ($\Delta \nu_d$) due to the dipole–dipole coupling between the deuteron and its nearby proton.
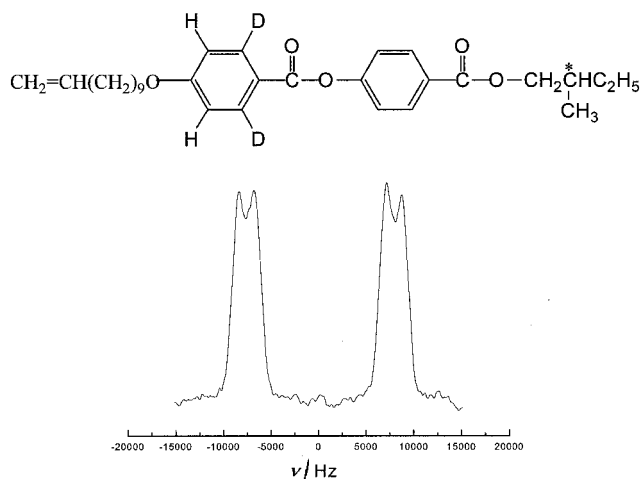

Figure 1.   A typical DMR spectrum of MBPUB-d_2 and its molecular structure.

The observed splittings are a result of the anisotropic motion of molecules within fluid layers in the SmA phase.

3.   Results and discussion

In a previous study [10], the *para*-axes of the phenyl rings were found to make an angle of 12°. We estimate that the molecular z_M axis makes an angle $\theta = 6°$ with the *para*-axis of the deuteriated ring. Using the $\Delta \nu_Q$ and $\Delta \nu_d$, the principal values $P_2 (= S_{zz})$ and $S_{xx} - S_{yy}$ of the order matrix of the molecular core can be determined at each temperature according to:

$$\Delta \nu_Q = -\frac{3}{8} q_{CD} \left[P_2 f(\theta) - \frac{1}{2}(S_{xx} - S_{yy}) g(\theta) \right] \quad (1)$$

$$\Delta \nu_d = -2 K_{DH} \frac{1}{r_{DH}^3} \left[P_2 \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \right.$$
$$\left. - \frac{1}{2}(S_{xx} - S_{yy}) \sin^2 \theta \right] \quad (2)$$

where q_{CD} (185 kHz) is the nuclear quadrupolar coupling constant, K_{DH} (18.434 kHz Å^3) is the D–H dipolar coupling constant, r_{DH} (2.5 Å) is the proton–deuteron distance, and the functions $f(\theta) = 3 \sin^2 \theta + \eta \cos^2 \theta + (\eta - 1)/2$ and $g(\theta) = 1 + 2 \cos^2 \theta + \eta(5 + 2 \sin^2 \theta)/3$ [11]. In equation (1) a nominal value of $\theta_{R,Q} = 60°$ for the angle between the C–D bond and the *para*-axis, and an average of quadrupolar splittings from the two non-equivalent C–D bonds in the (x_M, y_M, z_M) frame have been used. Also, $\eta = 0.04$ is assumed. The derived order parameters are shown in figure 2. These are used to construct the orienting pseudopotential for the spin relaxation study. As seen in the figure, the molecular biaxiality ($S_{xx} - S_{yy}$) is small (*c.* 0.03) and the nematic order parameter P_2 (*c.* 0.7) increases very slightly over the entire SmA phase upon the decreasing temperature.

To study the dynamics of this sample, we have measured the deuteron T_{1Q} and T_{1Z} as a function of temperature at two different Larmor frequencies. From these relaxation times, the spectral densities $J_1(\omega)$ and $J_2(2\omega)$ are obtained as shown in figure 3. We found that both J_1 and J_2 show strong frequency dependences, and increase with decreasing temperature in the SmA phase. The apparently large frequency dependence in J_2 cannot be explained by the well-known relaxation mechanism called order director fluctuations (ODF) [7]. Furthermore, the ring deuteron is known to be insensitive to the ODF because of the orientation of its C–D bond being close to the magic angle. We therefore ignore any contributions from the ODF and choose to explain our spectral density data using the small step rotational diffusion model of Nordio [12], but with a minor modification [13] for a (molecular) biaxial orienting potential.
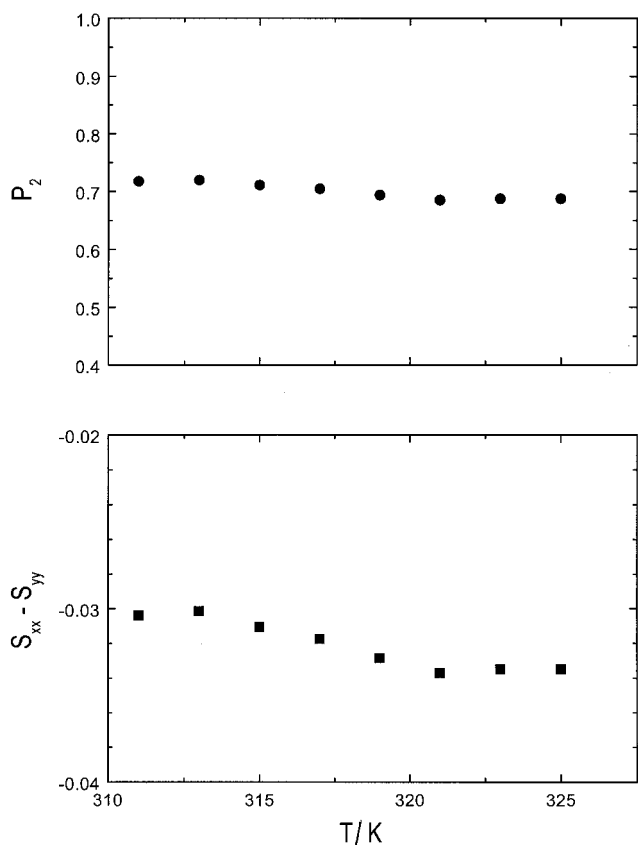
Figure 2.   Plots of order parameters P_2 and $S_{xx} - S_{yy}$ versus temperature.
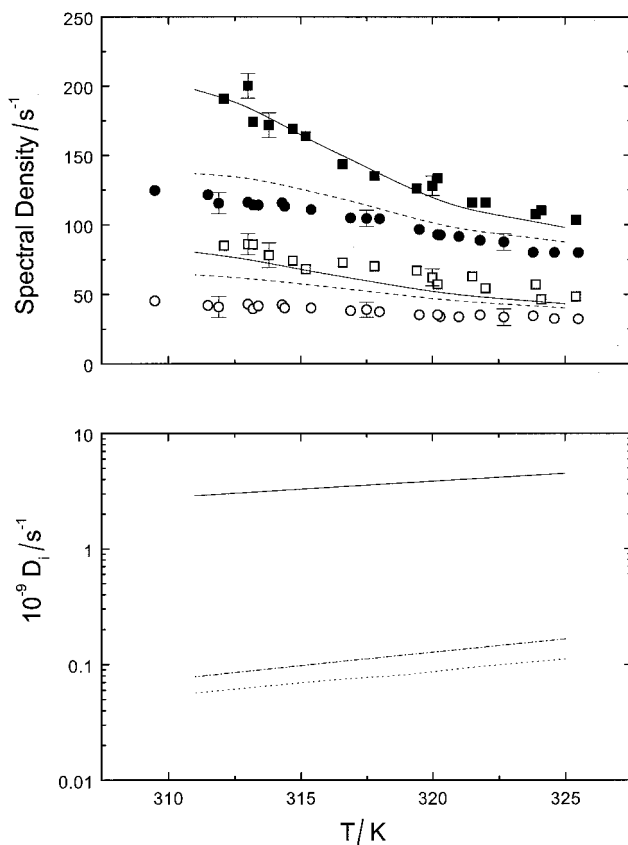

Figure 3.   Upper graph: Plot of spectral densities versus the temperature; closed and open symbols denote $J_1(\omega)$ and $J_2(2\omega)$, respectively; squares and circles denote data collected at 15.1 and 46 MHz, respectively. Solid and dashed lines denote calculated spectral densities at 15.1 and 46 MHz, respectively. Lower graph: Plot of rotational diffusion constants versus the temperature; solid, dash-dotted and dotted lines denote $D_\perp$, D_R and $D_\parallel$, respectively.

We note that the rotational diffusion tensor is diagonal in the (x_M, y_M, z_M) frame with principal values $D_{zz}\ (= D_\parallel)$ and $D_{xx} = D_{yy}\ (= D_\perp)$. Internal ring rotations about its *para*-axis and the overall motion of the molecule are assumed to be uncorrelated so that the superimposed rotations model [14] is used. Furthermore, ring rotations with a rotational diffusion constant D_R may be treated either in the small step diffusive limit [15] or in the strong collision limit [14]. Here the strong collision limit is adopted. Using the notation of Tarroni and Zannoni [13], the ring deuteron spectral density is given by

$$J_m(m\omega) = \frac{3\pi^2}{2}(q_{CD})^2 \sum_n \sum_{n'} \sum_p [d_{po}^2(\theta_{R,Q})]^2 d_{np}^2(\theta) d_{n'p}^2(\theta)$$

$$\times \sum_K \frac{(\beta_{mnn'}^2)_K [(\alpha_{mnn'}^2)_K + (1 - \delta_{po})D_R]}{m^2\omega^2 + [(\alpha_{mnn'}^2)_K + (1 - \delta_{po})D_R]^2} \quad (3)$$

where $(\alpha_{mnn'}^2)_K/D_\perp$, the decay constants, are the eigenvalues and $(\beta_{mnn'}^2)_K$, the relative weights of the exponentials, are the corresponding eigenvectors from diagonalizing the rotational diffusion matrix Γ. The Γ operator contains the orienting potential which is specified by the order parameters of the molecule. Using

an Arrhenius temperature dependence for all three model parameters, i.e.

$$D_\perp = D_\perp^o \exp(- E_a^{D_\perp}/RT) \quad (4)$$

$$D_\parallel = D_\parallel^o \exp(- E_a^{D_\parallel}/RT) \quad (5)$$

$$D_R = D_R^o \exp(- E_a^{D_R}/RT) \quad (6)$$

where $D_\perp^o$, $D_\parallel^o$ and D_R^o are the pre-exponentials, and their corresponding activation energies are $E_a^{D_\perp}$, $E_a^{D_\parallel}$ and $E_a^{D_R}$, respectively, a global analysis of eight different temperatures was carried out to minimize the sum square deviation of experimental and calculated spectral densities with AMOEBA [16]. It is advantageous to rewrite equations (4)–(6) in terms of $D_\perp'$, $D_\parallel'$ and D_R' at $T_{max} = 325$ K, the highest temperature used in the global analysis, since the correlation coefficient between the pre-exponential and its corresponding activation energy is as high as 0.99 [17]. Thus six target parameters $(D_\perp', D_\parallel', D_R'$ and three activation energies) were varied

in the minimization. The quality factor Q is defined by

$$Q = \frac{\sum_k \sum_m \sum_i [J_m^{\text{calc}}(m\omega_i) - J_m^{\text{exp}}(m\omega_i)]_k^2}{\sum_k \sum_m \sum_i [J_m^{\text{exp}}(m\omega_i)]_k^2} \qquad (7)$$

where k is summed over eight temperatures, sum over m is for 1 and 2, and i is for two frequencies.

The calculated spectral densities and the derived model parameters are shown in figure 3, with a $Q = 1.3\%$. Despite the relatively small Q value, there are systematic derivations between the experimental and calculated spectral densities, especially in $J_2(2\omega)$ and at low temperatures. These deviations are largely due to limitations of the adopted motional model. We note that the tumbling motion $(D_\perp)$ is faster than the spinning motion $(D_\parallel)$ which is a surprise. That $D_\parallel$ and D_R values are found to be comparable seems to follow from other non-chiral rod-like mesogens. The slow spinning rate (c. 10^8 s^{-1}) may stem from the bent shape of the molecule and its larger moment of inertia about the long axis. Similar spinning rates have been reported for the SmA phase of other chiral compounds by dielectric spectroscopy [18]. However, the possibility of $D_\perp < D_\parallel$ is addressed below. The activation energies $E_a^{D_\perp}$, $E_a^{D_\parallel}$ and $E_a^{D_R}$ are equal to 26.7, 40.3 and 45.0 kJ mol^{-1}, respectively. The error limit of $E_a^{D_\perp}$ is ± 0.5 kJ mol^{-1}, while that of $E_a^{D_\parallel}$ varies in the range 44.7–38.5 kJ mol^{-1} and that of $E_a^{D_R}$ is 47.9–43.4 kJ mol^{-1}. For a particular target parameter, the error limit was estimated by varying the one under consideration to give an approximate doubling in the Q value while keeping all other target parameters identical to those for the minimum Q. The pre-exponentials $D_\perp^o$, $D_\parallel^o$ and D_R^o are given by 8.74×10^{13}, 3.37×10^{14} and 2.84×10^{15} s^{-1}, respectively. These parameters represent reasonable 'collision' frequencies for the different motional processes. The error limit for $D_\perp^o$ is $(1.08–0.71) \times 10^{14}$ s^{-1}, for $D_\parallel^o$ $(6.8–0.7) \times 10^{14}$ s^{-1}, and for D_R^o $(5.3–0.95) \times 10^{15}$ s^{-1}.

Now the correlation coefficients among various model parameters are discussed. As found before for other liquid crystals, correlation coefficients between the pre-exponentials and their corresponding activation energies in equations (4)–(6) are 0.99 and higher. The correlation coefficients for the remaining pairs of model parameters range between 0.89 and 0.98. For example, values for $(D_\perp^o, D_\parallel^o)$, $(D_\perp^o, D_R^o)$ and $(D_\parallel^o, D_R^o)$ are 0.98, 0.96 and 0.91, respectively. To test for a small $D_\perp$ (c. 10^6 s^{-1}) observed in some ordered smectic phases, we have tried to fit the data by fixing $D_\perp'$ as input, and letting the remaining five target parameters vary in the minimization. We found that the present data set tends to give negative $D_\perp$ values if it is allowed to vary around a value of 5×10^6 s^{-1}. The $D_\perp'$ was then changed to find the best

Q value. We did find another local minimum giving a slightly worse Q value of 1.4% with $D_\parallel > D_\perp$ as in conventional rod-like mesogens. It is noted that the D_R and $D_\perp$ values now become similar. The calculated spectral densities and the derived model parameters are shown in figure 4. The pre-exponentials $D_\perp^o$, $D_\parallel^o$ and D_R^o are given by 1.59×10^{12}, 2.05×10^{16} and 1.43×10^{16} s^{-1}, respectively. The upper error limit of $D_\perp^o$ is 1.6×10^{13} s^{-1}, while its lower limit cannot be determined owing to the fits being insensitive to small $D_\perp$ values. The correlation coefficients between $E_a^{D_\perp}$ and other model parameters in equations (5)–(6) range beween 0.5 and 0.6, while the correlation coefficient between $D_\parallel^o$ and D_R^o is slightly less than 0.99.

As seen from their error limits, the two sets of $D_\perp$ values are distinct from each other. Given that we have only a single deuterated site in MBPUB, the difference in Q values for fitting our relaxation data cannot unambiguously favour one of these two distinct solutions. However, we believe that for chiral mesogens,
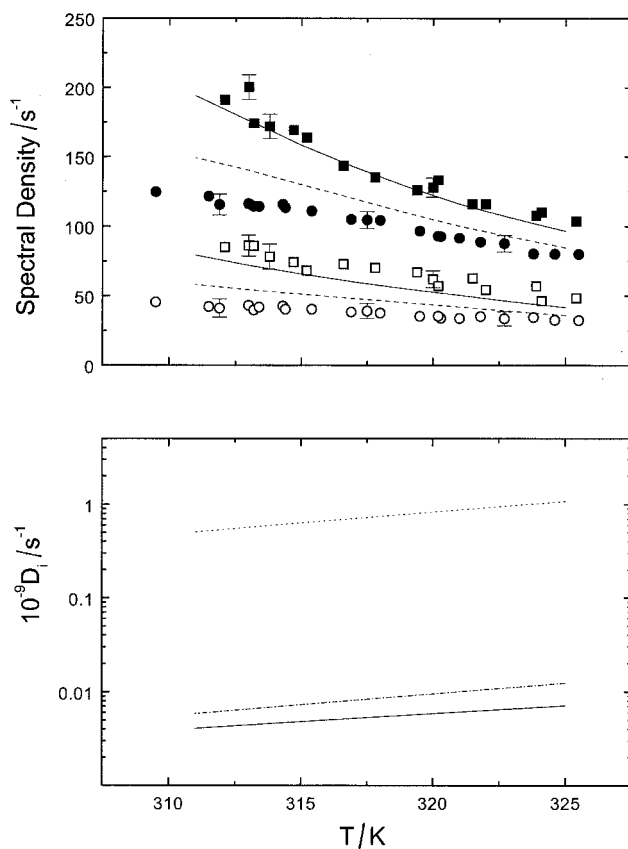

Figure 4. Upper graph: Plot of spectral densities versus the temperature. Closed and open symbols denote $J_1(\omega)$ and $J_2(2\omega)$, respectively; squares and circles denote data collected at 15.1 and 46 MHz, respectively. Lower graph: Plot of rotational diffusion constants versus the temperature; solid, dash-dotted and dotted lines denote $D_\perp$, D_R and $D_\parallel$, respectively.

the possibility of $D_\perp > D_\parallel$ should not be ruled out entirely. In particular, the solution of $D_\perp < D_\parallel$ cannot be achieved in AMOEBA by varying all six target parameters. Moreover, the derived D_R values ($c.\ 10^7\,\mathrm{s}^{-1}$) appear to be too slow for internal ring rotations. Perhaps the fast $D_\perp$ motion is connected to slow motions of the MBPUB molecule about its molecular long axis and the fluid nature within each layer of the SmA phase. Another possibility is the existence of some dipole–dipole correlations across the layers or large undulations of the layers. Further NMR experiments on a chain-deuterated MBPUB and other chiral molecules of similar dimensions should be carried out to see if $D_\perp > D_\parallel$ is indeed valid, at least for some chiral mesogens. When a MBPUB sample with the chiral chain deuteriated is available, the additional relaxation data could be used to test a non-axial rotational diffusion tensor as described in the Tarroni–Zannoni model [13]. Possible anomalous rotational behaviour of such chiral molecules can have significant implications on organizations and packing of tilted molecules in various chiral subphases.

References

[1] GOODBY, J. W., PATEL, J. S., and CHIN, E., 1992, *J. mater. Chem.*, **2,** 197.

[2] ŠKARABOT, M., ČEPIČ, M., ŽEKŠ, B., BLINC, R., HEPPKE, G., KITYK, A. V., and MUŠEVIČ, I., 1998, *Phys. Rev. E*, **58,** 575.

[3] YOSHIDA, S., JIN, B., TAKANISHI, Y., TOKUMARU, K., ISHIKAWA, K., TAKEZOE, H., FUKUDA, A., KUSUMOTO, T., NAKAI, T., and MIYAJIMA, S., 1999, *J. phys. Soc. Jpn.*, **68,** 9.

[4] NAKAI, T., MIYAJIMA, S., TAKANISHI, Y., YOSHIDA, S., and FUKUDA, A., 1999, *J. phys. Chem. B*, **103,** 406; MIYACHI, K., TAKANISHI, Y., ISHIKAWA, K., TAKEZOE, H., and FUKUDA, A., 1997, *Phys. Rev. E*, **55,** 1632.

[5] OUCHI, Y., YOSHIOKA, Y., ISHII, H., SEKI, K., KITAMURA, M., NOYORI, R., TAKANISHI, Y., and NISHIYAMA, I., 1995, *J. mater. Chem.*, **5,** 2297.

[6] JIN, B., LING, Z., TAKANISHI, Y., ISHIKAWA, K., TAKEZOE, H., FUKUDA, A., KAKIMOTO, M., and KITAZUME, T., 1996, *Phys. Rev. E*, **53,** R4295.

[7] DONG, R. Y., 1997, *Nuclear Magnetic Resonance of Liquid Crystals* (New York: Springer-Verlag).

[8] WIMPERIS, S., 1990, *J. magn. Reson.*, **83,** 590.

[9] DONG, R., FRIESEN, L., and RICHARDS, G. M., 1994, *Mol. Phys.*, **81,** 1017.

[10] CATALANO, D., CHIELLINI, E., CHIEZZI, L., FODOR-CSORBA, K., GALLI, G., GACS-BAITZ, E., HOLLY, S., and VERACINI, C. A. *Mol. Cryst. liq. Cryst.* (in the press).

[11] DONG, R. Y., BATES, G. S., and SHEN, X., 1999, *Mol. Cryst. liq. Cryst.*, **331,** 143.

[12] NORDIO, P. L., and BUSOLIN, P., 1997, *J. chem. Phys.*, **55,** 5485; NORDIO, P. L., RIGATTI, G., and SEGRE, U., 1972, *J. chem. Phys.*, **56,** 2117.

[13] TARRONI, R., and ZANNONI, C., 1991, *J. chem. Phys.*, **95,** 4550.

[14] BECKMANN, P. A., EMSLEY, J. W., LUCKHURST, G. R., and TURNER, D. L., 1986, *Mol. Phys.*, **54,** 97.

[15] WOESSNER, D. E., 1962, *J. chem. Phys.*, **36,** 1.

[16] PRESS, W. H., FLANNERY, B. P., TEUKOLSKY, S. A., and VETTERLING, W. T., 1986, *Numerical Recipes* (Cambridge: Cambridge University Press).

[17] CALUCCI, L., GEPPI, M., VERRACINI, C. A., and DONG, R. Y., 1998, *Chem. Phys. Lett.*, **296,** 357.

[18] SCHÖNFELD, A., KREMER, F., and ZENTEL, R., 1993, *Liq. Cryst.*, **13,** 403; GESTBLOM, B., MAKRENEK, M., HASSE, W., and WRÒBEL, S., 1993, *Liq. Cryst.*, **14,** 1069.