

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

NMR study of molecular dynamics in a mixture of two polar liquid crystals (CBOOA and DOBCA)

P. J. Sebastião^a; M. H. Godinho^a; A. C. Ribeiro^a; D. Guillon^{bc}; M. Vilfan^d

^a Centro de Física da Matéria Condensada (INIC), Lisboa, Codex, Portugal ^b Groupe des Matériaux Organiques, Institut Charles Sadron (CRM-EAHP), Strasbourg, Cedex, France ^c Institut de Physique et Chimie des Matériaux de Strasbourg, CNRS-UPL-EHICS, France ^d J. Stefan Institute, University of Ljubljana, Ljubljana, Yugoslavia

To cite this Article Sebastião, P. J. , Godinho, M. H. , Ribeiro, A. C. , Guillon, D. and Vilfan, M.(1992) 'NMR study of molecular dynamics in a mixture of two polar liquid crystals (CBOOA and DOBCA)', *Liquid Crystals*, 11: 4, 621 – 635

To link to this Article: DOI: 10.1080/02678299208029014

URL: <http://dx.doi.org/10.1080/02678299208029014>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

NMR study of molecular dynamics in a mixture of two polar liquid crystals (CBOOA and DOBCA)

by P. J. SEBASTIÃO†, M. H. GODINHO†, A. C. RIBEIRO†*,
D. GUILLON‡ and M. VILFAN§

† Centro de Física da Matéria Condensada (INIC),
Av. Prof. Gama Pinto, 2, 1699 Lisboa Codex, Portugal

‡ Groupe des Matériaux Organiques,
Institut Charles Sadron (CRM-EAHP), CNRS-ULP 6,
Rue Boussingault, 67083 Strasbourg Cedex, France and
Institut de Physique et Chimie des Matériaux de Strasbourg,
UM 380046, CNRS-UPL-EHICS, France

§ J. Stefan Institute, University of Ljubljana, Jamova 39,
61000 Ljubljana, Yugoslavia

(Received 20 February 1989; accepted 16 October 1991)

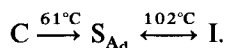
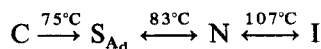
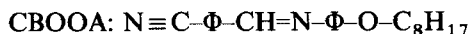
A mixture containing 70 per cent 4-cyanobenzylidene-4'-*n*-octylaniline (CBOOA) and 30 per cent 4-*n*-dodeciloxybenzylidene-4'-cyanoaniline (DOBCA) has been studied by optical microscopy, differential scanning calorimetry, X-ray diffraction and, primarily, by NMR spectroscopy. The smectic phase of the mixture is a partial bilayer smectic A phase (S_{A_d}), in which about one half of the molecules are associated in pairs through their polar cyano end groups. The molecular dynamics in the smectic A_d phase of the mixture was studied by proton spin-lattice relaxation. Self-diffusion and rotations/reorientations were found to be essential relaxation mechanisms while the contribution of the order director fluctuations seems to be very small in all frequency regions. The correlation times associated with the molecular rotational motion around the short molecular axis, τ_s , are of the order 10^{-10} s and the ratio $\tau_s/\tau_L \approx 6.2$. The translational diffusion coefficients D_{\perp} are of the order $10^{-11} \text{ m}^2 \text{ s}^{-1}$. The possible contribution to the relaxation rate of an additional relaxation mechanism associated with the dissociation and recombination of molecules in dimers within the smectic layers is also analysed.

1. Introduction

Liquid-crystalline compounds containing a strong polar end group ($\text{C}\equiv\text{N}$, for example), as well as their binary mixtures often exhibit a peculiar polymorphism due to the specific molecular organization within the smectic phases [1]. The layer spacing in different smectic phases can be either of one or two molecular lengths or an intermediate value, depending on the exact chemical architecture of the molecule and on the temperature [2]. The occurrence of reentrant phases [3], of incommensurate smectic phases [4-6] and of the so-called smectic antiphases [5, 7] has also been reported for this kind of compound. The interest in these systems is evidenced by the large number of papers concerning experimental work, theoretical aspects and microscopic models (see [8-10] and references therein).

* Author for correspondence.

In this paper, we report a study of the molecular dynamics in the smectic A phase of a binary mixture of two polar liquid crystals, namely 4-cyanobenzylidene-4'-*n*-octylaniline and 4-*n*-dodeciloxybenzylidene-4'-*n*-cyanoaniline (respectively abbreviated as CBOOA and DOBCA in what follows):



The molecules of these two compounds have very similar chemical structures. They belong to the class of polar asymmetric smectogens and are composed of a rigid aromatic core with one aliphatic chain at one end and a polar terminal group at the other. The only differences between the two compounds are the length of the aliphatic chain and the direction of the electric dipole associated with the azomethine bridge, CH=N. Both compounds exhibit a partial bilayer smectic A phase, S_{Ad} , with a layer spacing close to 1.4 times the molecular length [11, 12].

We have used optical microscopy and differential scanning calorimetry in the study of the liquid-crystalline polymorphism of a binary mixture containing 70 per cent CBOOA and 30 per cent DOBCA. The structural parameters of the partial bilayer smectic A phase, exhibited by the mixture, have been determined by low angle X-ray diffraction. The molecular dynamics in the same mesophase has been investigated using the NMR technique to determine the spin-lattice relaxation times, T_1 .

2. Experimental

The transition temperatures and the corresponding enthalpies of the binary mixture containing 70 per cent CBOOA and 30 per cent DOBCA were determined using a Perkin-Elmer 1B differential scanning calorimeter; DSC peak maximum positions were taken as the transition temperatures. These were also confirmed with an Olympus BH polarizing microscope equipped with a Mettler FP 52 hot stage. The X-ray diffraction measurements were performed using a Guinier camera equipped with a bent quartz monochromator ($\text{Cu-K}_{\alpha 1}$ radiation) and an electric oven. The sample was sealed in a 1 mm diameter capillary tube and the patterns recorded photographically. For the binary mixture studied the spin-lattice relaxation time was measured at ten frequencies between 5.6 MHz and 300 MHz in the smectic A_d phase using the $\pi-\tau-\pi/2$ pulse sequence in Bruker spectrometers SXP 4-100 MHz and CXP 300 MHz. Complementary measurements of T_1 in the rotating frame ($T_{1\rho}$) were also performed. For each frequency, measurements were performed by decreasing the temperature from the isotropic phase very slowly. The temperature of the sample was controlled to $\pm 0.3^\circ\text{C}$, and the estimated error in the absolute value was less than 1°C .

3. Results and discussion

The transition temperatures of the mixture studied were determined by DSC and optical microscopy. There is a good agreement between the values of the transition

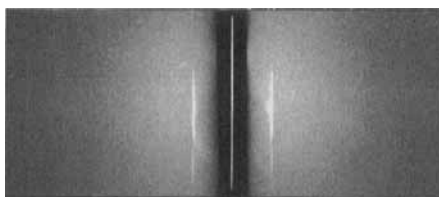


Figure 1. X-ray diffraction pattern obtained for a sample containing 70 per cent of CBOOA and 30 per cent of DOBCA.

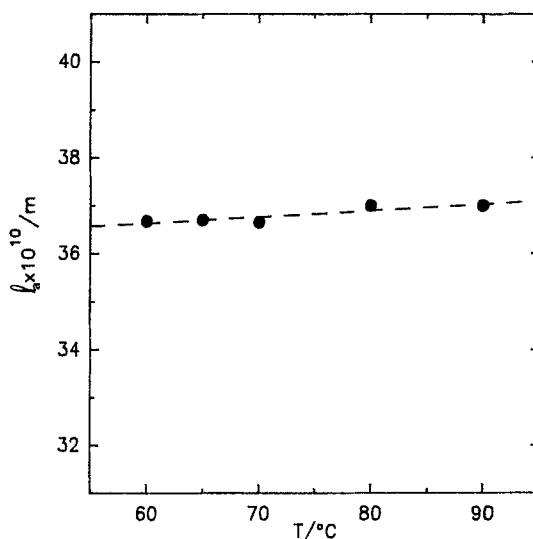
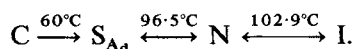


Figure 2. The layer spacing as a function of temperature in the S_{A_d} phase of the binary mixture containing 70 per cent of CBOOA and 30 per cent of DOBCA.

temperatures found by the two methods. The phase sequence exhibited by the mixture is



The range of the smectic A_d phase is much broader than in the pure CBOOA while the nematic phase, needed for the uniform orientation of the director by the magnetic field, is retained. The smectic A_d phases of both compounds show complete miscibility, as seen by the classical contact method [13] and this is expected in view of the similar chemical structure. Figure 1 displays an X-ray diffraction pattern recorded for the smectic A_d phase of the binary mixture. It contains a sharp reflection in the low angle region, whose spacing corresponds to the layer thickness, and a diffuse band in the wide angle region related to the intermolecular separation within a layer. The sharp reflection clearly indicates that mixing of the two compounds occurs at a molecular level in the sample. Knowing the molecular lengths of pure CBOOA (26.0×10^{-10} m) and pure DOBCA (30.8×10^{-10} m) in their extended chain configuration, the average molecular length l in this binary mixture can be estimated to be 27.4×10^{-10} m by

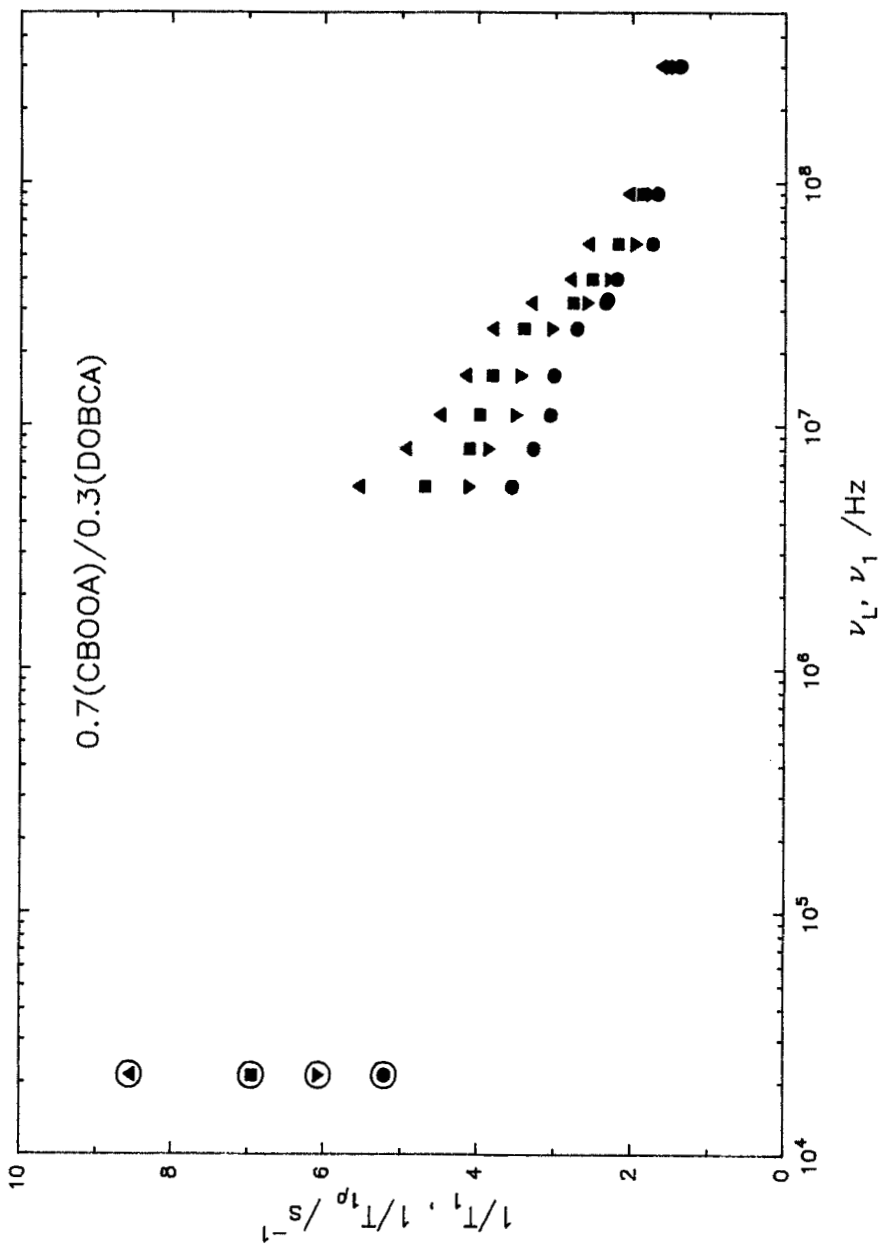


Figure 3. The frequency dependence of the proton spin-lattice relaxation rate $1/T_1$ for a sample containing 70 per cent of CBOOA and 30 per cent of DOBCA at four temperatures in the smectic A phase, and $1/T_{1\rho}$ measurements performed at the same temperatures with $\nu_1 = 21.3$ kHz, $\nu_L = 56$ MHz. ● $T = 77^\circ\text{C}$; ▼ $T = 82^\circ\text{C}$; ■ $T = 73^\circ\text{C}$; ▲ $T = 68^\circ\text{C}$; ○ $1/T_{1\rho}$.

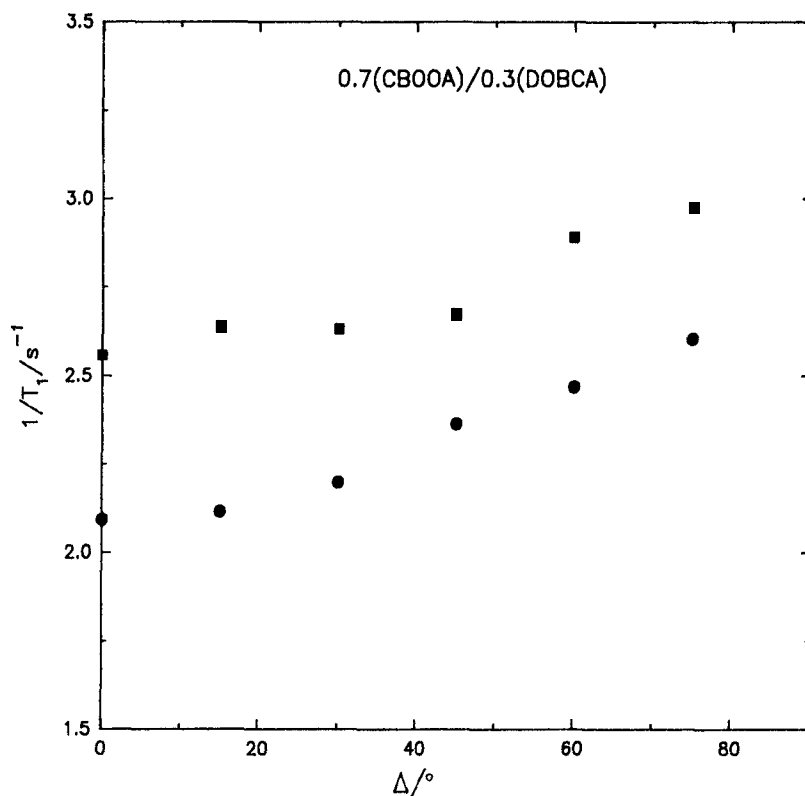


Figure 4. The angular dependence of $1/T_1$ in the smectic A phase, for a sample containing 70 per cent of CBOOA and 30 per cent of DOBCA at 77°C and 68°C ($\nu_L = 56$ MHz). ● T = 77°C; ■ T = 68°C.

taking into account the concentrations of CBOOA and DOBCA. As the layer spacing observed in the smectic A phase, ranges from 36.7×10^{-10} m to 37.0×10^{-10} m depending on the temperature (see figure 2), the ratio of the molecules associated through their cyano end group (calculated according to the model of [9]) is about 0.5 over the whole temperature range of the smectic A_d phase. This value is approximately the same as in the two pure compounds, and shows that the degree of association of the molecules does not depend on the concentration ratio in this mixture.

The NMR measurements of the proton spin-lattice relaxation rate, performed at different Larmor frequencies and four temperatures in the partial bilayer smectic phase, are shown in figure 3. This figure includes also the measurements of the relaxation rate in the rotating frame, $1/T_{1\rho}$, for $\nu_1 = 21.3$ kHz and $\nu_L = 56$ MHz. The angular dependence of $1/T_1$, which has been determined experimentally for two temperatures in the S_{A_d} phase, is presented in figure 4.

3.1. Theory

In the analysis of the experimental data in view of the molecular dynamics, three different relaxation mechanisms, so far well established for the relaxation in liquid crystals [14], are taken into account. In contrast to our previous paper on spin relaxation in partial bilayer smectic phases [15], where, as a first approximation, self-

diffusion was described by Torrey's theory [16] with a corrective factor [17] and rotational motions were derived from the isotropic case [18], the present analysis is considerably improved. The improvement concerns in particular the two mechanisms which contribute mostly to the relaxation of protons in the MHz regime, i.e. self-diffusion induced relaxation and molecular rotational motions, where now the structural details of the mesophase are taken into account.

The overall relaxation rate is described by the sum of three contributions provided the cross-over terms can be omitted

$$\left(\frac{1}{T_1}\right) = \left(\frac{1}{T_1}\right)_{\text{SD}} + \left(\frac{1}{T_1}\right)_{\text{ODF}} + \left(\frac{1}{T_1}\right)_{\text{R}}, \quad (1a)$$

$$\left(\frac{1}{T_{1\rho}}\right) = \left(\frac{1}{T_{1\rho}}\right)_{\text{SD}} + \left(\frac{1}{T_{1\rho}}\right)_{\text{ODF}} + \left(\frac{1}{T_{1\rho}}\right)_{\text{R}}, \quad (1b)$$

with the subscript SD denoting self-diffusion, ODF order director fluctuations and R local reorientations. The proton spin relaxation rates for different mechanisms in the laboratory and rotating frames $(1/T_1)$, $(1/T_{1\rho})$, are obtained from the spectral densities of the corresponding autocorrelations functions for the dipolar interaction [18]

$$\left(\frac{1}{T_1}\right)(\nu_L, \Delta) = \frac{9}{8}\gamma^4\hbar^2 [J^{(1)}(\nu_L, \Delta) + J^{(2)}(2\nu_L, \Delta)], \quad (2)$$

$$\left(\frac{1}{T_{1\rho}}\right)(\nu_1, \nu_L, \Delta) = \frac{9}{8}\gamma^4\hbar^2 \left[\frac{1}{4}J^{(0)}(2\nu_1, \Delta) + \frac{5}{2}J^{(1)}(\nu_L, \Delta) + \frac{1}{4}J^{(2)}(2\nu_L, \Delta) \right], \quad (3)$$

where $\gamma^4\hbar^2 = 5.69 \times 10^{-49} \text{ m}^6 \text{ s}^{-2}$ for protons, ν_L is the Larmor frequency, ν_1 the resonant frequency in the rotating frame and Δ the angle between the liquid crystal director and external magnetic field. The rotated spectral densities at angle Δ , can be obtained from the non-rotated ones through the expression [19]

$$J^{(k)}(\nu_L, \Delta) = \sum_{n=0}^2 f_{kn}(\Delta) J^{(n)}(\nu_L, \Delta=0^\circ), \quad (4)$$

with

$$f_{kn}(\Delta) = \frac{1}{8} \begin{bmatrix} 8 - 24 \sin^2 \Delta + 18 \sin^4 \Delta & 144(\sin^2 \Delta - \sin^4 \Delta) & 9 \sin^4 \Delta \\ 2(\sin^2 \Delta - \sin^4 \Delta) & 8 - 20 \sin^2 \Delta + 16 \sin^4 \Delta & 2 \sin^2 \Delta - \sin^4 \Delta \\ 2 \sin^4 \Delta & 16(2 \sin^2 \Delta - \sin^4 \Delta) & 8 - 8 \sin^2 \Delta + \sin^4 \Delta \end{bmatrix}. \quad (5)$$

Spectral densities for the three different types of molecular motion are as follows.

(i) The contribution of translational self-diffusion is described by the theory of Vilfan and Žumer [17], appropriate for the smectic A phase, in which the spectral densities are given by

$$J^{(k)}(\nu_L, \Delta=0^\circ) = n \frac{\tau_\perp}{d^3} R^{(k)} \left(\nu_L \tau_\perp; \frac{\langle r_\perp^2 \rangle}{d^2}; \frac{D_\parallel}{D_\perp}; \frac{l}{d}; \frac{a}{d} \right). \quad (6)$$

Here n is the spin density, τ_\perp is the average time between two successive interlayer jumps, d is the diameter of the cylindrical molecules, $\langle r_\perp^2 \rangle$ is the mean square jump distance within layers, l is the length of molecules in the monolayer smectic A phase and layer thickness otherwise, and a is the distance of closest approach between molecules

belonging to adjacent layers. D_{\perp} and D_{\parallel} are the diffusion coefficients for intra- and inter-layer diffusion. The functions $R^{(k)}$ have been calculated numerically for a number of reasonable values of the parameters involved, namely those obtained from our X-ray measurements.

(ii) The contribution of local molecular reorientations around the long and short molecular axes and of the conformational changes of the aliphatic chains is considered by taking into account the molecular shape and the structural anisotropy of the smectic mesophase. Neglecting the conformational changes, which are too fast to relax protons in the MHz regime, the local reorientations of anisotropic cylindrically symmetric molecules can cause the relaxation, for which the spectral densities are obtained following the procedure of Woessner [20] and [21–24] as

$$J^{(k)}(\nu_L) = \frac{4}{3} C_k \sum_{i=-2}^2 \frac{D_{ik}^2 D_{ik}^{2*} d_{i0}^2 d_{i0}^{2*}}{r^6} \frac{\tau_{|i|}}{1 + 4\pi^2 \nu_L^2 \tau_{|i|}^2}, \quad (7)$$

where $C_0 = 6$, $C_1 = 1$ and $C_2 = 4$ and τ_i can be expressed in terms of τ_s and τ_L , the correlation times for rotations along the short and long molecular axis, respectively:

$$\tau_0 = \tau_s, \quad \frac{1}{\tau_1} = \frac{1}{6\tau_L} + \frac{5}{6\tau_s}, \quad \frac{1}{\tau_2} = \frac{2}{3\tau_L} + \frac{1}{3\tau_s}.$$

The ratio τ_s/τ_L directly depends on the molecular anisotropy l/d [25].

D_{ik}^2 , in equation (7), is the second rank Wigner rotation matrix and d_{i0}^2 is the reduced Wigner rotation matrix. In a phase with uniaxial symmetry their expectation values can be expressed in terms of ensemble averages of the second and fourth rank Legendre polynomials of the angle θ between the director and the long molecular axis

$$S = \langle P_2 \rangle = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad \text{and} \quad \langle P_4 \rangle = \frac{1}{8} \langle 35 \cos^4 \theta - 30 \cos^2 \theta + 3 \rangle.$$

α is the angle between the intramolecular internuclear vector and the long molecular axis.

$$\overline{D_{\pm ik}^2 D_{\pm ik}^{2*}} = \frac{1}{35} \begin{bmatrix} 7 + 10S + 18\langle P_4 \rangle & 7 + 5S - 12\langle P_4 \rangle & 7 - 10S + 3\langle P_4 \rangle \\ 7 + 5S - 12\langle P_4 \rangle & \frac{1}{2}(14 + 5S + 16\langle P_4 \rangle) & 7 - 5S - 2\langle P_4 \rangle \\ 7 - 10S + 3\langle P_4 \rangle & 7 - 5S - 2\langle P_4 \rangle & \frac{1}{2}(14 + 20S + \langle P_4 \rangle) \end{bmatrix} \quad (8)$$

and

$$\left. \begin{aligned} \frac{d_{00}^2 d_{00}^{2*}}{r^6} &= \frac{(3 \cos^2 \alpha - 1)^2}{4r^6}, \\ \frac{d_{\pm 10}^2 d_{\pm 10}^{2*}}{r^6} &= \frac{3 \sin^2 2\alpha}{8r^6}, \\ \frac{d_{\pm 20}^2 d_{\pm 20}^{2*}}{r^6} &= \frac{3 \sin^4 \alpha}{8r^6}. \end{aligned} \right\} \quad (9)$$

In equation (9) the averaging refers to the different internuclear vectors along a molecule.

In the extreme narrowing limit ($\nu_L \tau_i \ll 1$) the spectral densities from expression (7) are frequency independent. The number of free parameters is reduced, the expressions become simpler and it becomes easier to understand the influence of some molecular and structural parameters on the molecular dynamics. In particular, the dependence of $(1/T_1)_R$ and $(1/T_{1\rho})_R$ on $\langle P_4 \rangle$ disappears and the remaining free parameters are the nematic order parameter S , the correlation time τ_s , the ratio τ_s/τ_L and the inter-proton coordinates in the molecular frame, α_{ij}, r_{ij} . The temperature and angular dependences of the relaxation rates $(1/T_1)_R$ and $(1/T_{1\rho})_R$ can, therefore, be written in a simplified form

$$\left(\frac{1}{T_1}\right)_R(\nu_L \tau_i \ll 1, \Delta) = f_R\left(\tau_s, \frac{\tau_s}{\tau_L}, \alpha_{ij}, r_{ij}\right) + R_S\left(\tau_s, \frac{\tau_s}{\tau_L}, S, \alpha_{ij}, r_{ij}\right) \left[\sin^2 \Delta - \frac{2}{3}\right], \quad (10)$$

$$\left(\frac{1}{T_{1\rho}}\right)_R(\nu_L \tau_i, \nu_1 \tau_i \ll 1, \Delta) = f_R\left(\tau_s, \frac{\tau_s}{\tau_L}, \alpha_{ij}, r_{ij}\right) + R_S\left(\tau_s, \frac{\tau_s}{\tau_L}, S, \alpha_{ij}, r_{ij}\right) \left[\frac{1}{3} - \frac{1}{2} \sin^2 \Delta\right], \quad (11)$$

$$f_R\left(\tau_s, \frac{\tau_s}{\tau_L}, \alpha_{ij}, r_{ij}\right) = \frac{3}{2} \gamma^4 \hbar^2 \tau_s [A^{(0)} + 2A^{(1)} + A^{(2)}], \quad (12)$$

$$R_S\left(\tau_s, \frac{\tau_s}{\tau_L}, S, \alpha_{ij}, r_{ij}\right) = \frac{9}{4} \gamma^4 \hbar^2 \tau_s S [A^{(0)} + A^{(1)} - A^{(2)}], \quad (13)$$

$$\left. \begin{aligned} A^{(0)} &= \frac{(3 \cos^2 \alpha - 1)^2}{4r^6}, \\ A^{(1)} &= \frac{3}{5 + \frac{\tau_s}{\tau_L}} \frac{3 \sin^2 2\alpha}{4r^6}, \\ A^{(2)} &= \frac{6}{2 + 4 \frac{\tau_s}{\tau_L}} \frac{3 \sin^4 \alpha}{4r^6} \end{aligned} \right\} \quad (14)$$

Equations (10)–(13) are valid for the isotropic phase as well if the value of the nematic order parameter S equals zero. Here, of course, the angular dependence of the relaxation rates disappears. The classical isotropic model [18] is obtained when the ratio τ_s/τ_L equals one (i.e. spheres). When the director is parallel to the external magnetic field ($\Delta = 0^\circ$) equation (10) can be expressed in terms of the correlation time τ_s and an effective interproton distance r_{eff} [26], or an averaged interproton distance and a corrective factor ε [27], which account for both the molecular and mesophase anisotropies. As the nematic order parameter S can be estimated from other measurements [28], equations (10)–(14) allow us to obtain both the correlation time for the rotations about the short molecular axis, τ_s , and the anisotropic ratio τ_s/τ_L from the $1/T_1$ dispersion and angular data.

For the aliphatic chains in their most extended conformation, it is reasonable to use $\alpha_{ij} = 0$, $r_{ij} = 2.44 \times 10^{-10}$ m for the protons of the benzene rings (32 per cent) and $\alpha_{ij} = 90^\circ$, $r_{ij} = 1.79 \times 10^{-10}$ m for those belonging to the chains (68 per cent), which contribute the largest part to $(1/T_1)_R$ and $(1/T_{1\rho})_R$.

(iii) The contribution of the order director fluctuations to the relaxation rate in the smectic A phase can depend on the Larmor frequency either as $\nu_L^{-1/2}$ [29], as for nematics [30], or ν_L^{-1} , if only layer undulations take place [31]. In the first case the dispersion of the spectral densities, derived for nematic liquid crystals in finite size domains [32] can be written as

$$J^{(k)}(\nu_L, \Delta) = \frac{A'}{\sqrt{\nu_L}} f_{k1}(\Delta) \left[g\left(\frac{\nu_{H,C}}{\nu_L}\right) - g\left(\frac{\nu_{L,C}}{\nu_L}\right) \right], \quad (15)$$

$$g(a) = \frac{1}{\pi} \left[\arctan(\sqrt{(2a)+1}) + \arctan(\sqrt{(2a)-1}) - \arctan\left(\frac{\sqrt{(2a)}}{a+1}\right) \right].$$

In the second case, where only smectic layer undulations are included, the spectral densities are given by [29, 31]:

$$J^{(k)}(\nu_L, \Delta) = \frac{A''}{\nu_L} f_{k1}(\Delta) \left[\frac{2}{\pi} \arctan\left(\frac{\nu_{H,C}}{\nu_L}\right) - \frac{2}{\pi} \arctan\left(\frac{\nu_{L,C}}{\nu_L}\right) \right]. \quad (16)$$

Here A' and A'' are constants describing the strength of the order director fluctuations and $\nu_{H,C}$ and $\nu_{L,C}$ are the high and low cut-off frequencies, respectively.

The temperature dependence of the resulting T_1^{-1} and $T_{1\rho}^{-1}$ results primarily from the temperature dependences of the rotational correlation time, τ_s , and the self-diffusion coefficient D_{\perp} , with activation energies E_s and E_D , respectively. The ratio τ_s/τ_L is assumed to be temperature independent to a first approximation for a modest temperature interval [25, 33].

3.2. Comparison of theory and experiment

In the analysis of the experimental data, expressions (1 a) and (1 b) together with the corresponding spectral densities for different relaxation mechanisms were fitted simultaneously to account for the frequency, temperature and angular dependences of the experimental data ($1/T_1$) and $(1/T_{1\rho})(\Delta=0^\circ)$ in the S_{A_d} phase until the best agreement between theory and experiment was obtained within reasonable limits of the fitted parameters. A non-linear least-square method was used in the fit. The fitted parameters were τ_s , E_s , τ_L , E_D , the anisotropic ratio τ_s/τ_L and A , the strength of the order director fluctuations.

In the calculation of the self-diffusion contribution [17] we used $d = 5 \times 10^{-10}$ m, $\langle r_{\perp}^2 \rangle/d^2 = 1$, $D_{\parallel}/D_{\perp} = 1$, $a/d = 0.5$ and $l/d = 7$, in agreement with the X-ray data. The values of these parameters were not critical for the fit as they can be changed appreciably without really affecting the values of the quantities varied.

The order parameter S was estimated from the results obtained for pure CBOOA [28], considering that the chemical structure of both CBOOA and DOBCA are similar and also their relative concentration in the mixture. An empirical model [34] was used to interpolate the S values for CBOOA. For the temperature range studied the values of S were between 0.74 and 0.79.

The best consistent fitted values of τ_s , τ_L , and D_{\perp} without cut-off frequencies (i.e. $\nu_{L,C} = 0$ and $\nu_{H,C} \rightarrow \infty$) in the ODF contribution, modelled by expression (15), are summarized in the table. The fitted activation energies and ratio τ_s/τ_L are $E_D = 41$ kJ mol $^{-1}$, $E_s = 29$ kJ mol $^{-1}$ and $\tau_s/\tau_L = 6.2$. For all temperatures, the factor A corresponding to the ODF mechanism, $(1/T_1 = A\nu_L^{-1/2})$, is very low, smaller than 200 s $^{-3/2}$. The frequency dependences of the experimental data and of the theoretical

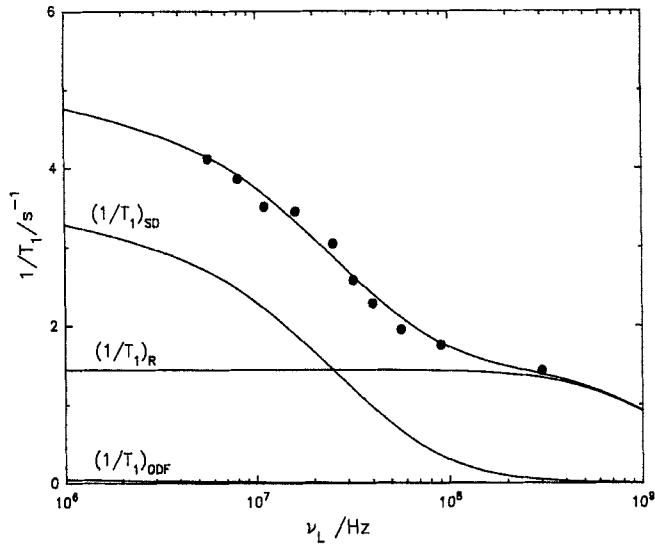


Figure 5. Fit of the calculated $1/T_1$ to the experimental results as a function of ν_L , obtained with equation (1) at 77°C as described in the text. The contributions of different relaxation mechanisms are shown. 0.7 (CBOOA)/0.3 (DOBCA); $T = 77^\circ\text{C}$.

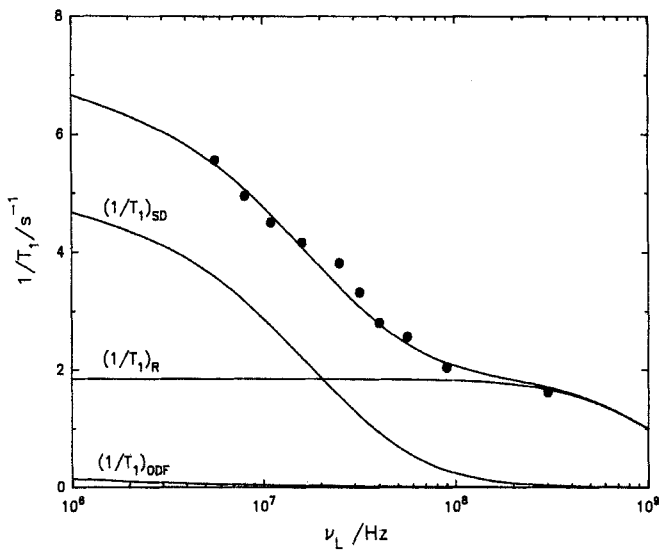


Figure 6. The fit of the calculated $1/T_1$ to the experimental results as a function of ν_L , obtained with equation (1) at 68°C as described in the text. The contributions of different relaxation mechanisms are shown. 0.7 (CBOOA)/0.3 (DOBCA); $T = 68^\circ\text{C}$.

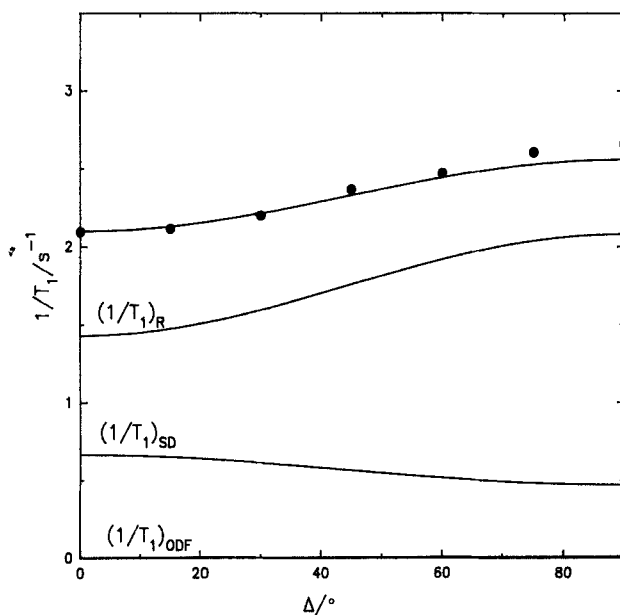


Figure 7. The fit of the calculated $1/T_1$ to the experimental results as a function of the angle Δ , obtained with equation (1) at 77°C as described in the text. The contributions of different relaxation mechanisms are shown. 0.7 (CBOOA)/0.3 (DOBCA); $T = 77^\circ\text{C}$; $\nu_L = 56\text{ MHz}$.

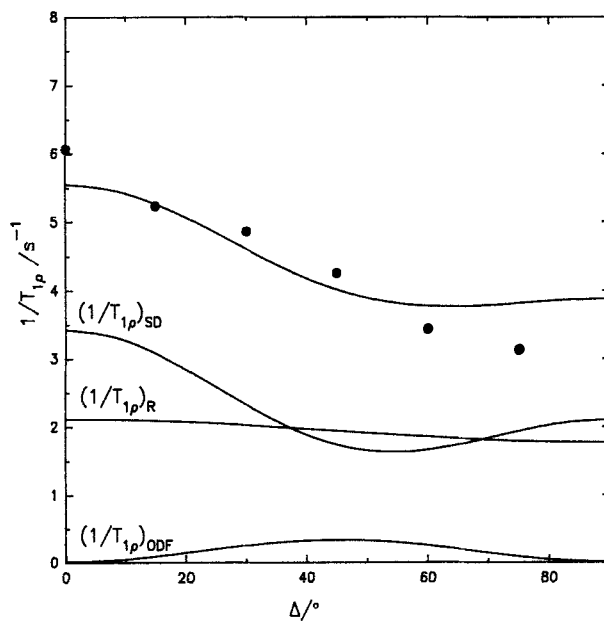


Figure 8. The fit of the calculated $1/T_{1\rho}$ to the experimental results as a function of the angle Δ , obtained with equation (1 b) at 77°C as described in the text. The contributions of different relaxation mechanisms are shown. 0.7 (CBOOA)/0.3 (DOBCA); $T = 77^\circ\text{C}$; $\nu_1 = 21.3\text{ kHz}$; $\nu_L = 56\text{ MHz}$.

curves obtained with the fitted parameters at two temperatures in the S_{Ad} phase are shown, as examples, in figures 5 and 6. Figure 7 shows the fitted curve of the angular dependence at $T=77^\circ\text{C}$. Our analysis has shown the following results:

- (i) Self-diffusion is the dominant relaxation mechanism at frequencies below 20 MHz while local rotations/reorientations are the most important contribution at higher frequencies. The values of the τ_s are of the order of 10^{-10} s and the diffusion time, τ_L , between jumps about 10 times larger, giving rise to the interlayer diffusion constant of the order of 10^{-11} $\text{m}^2 \text{s}^{-1}$. As both the self diffusion and local reorientational contributions have similar frequency dependences in the MHz regime, it should be stressed that a fit with the larger diffusion constant and accordingly slower local reorientations could not be satisfactorily obtained in view of the observed angular dependence of the relaxation rate.
- (ii) The fit of the angular dependence is strongly influenced by the ratio τ_s/τ_L . The value obtained of 6.2 is in agreement with the dimensions of the molecules [25]. However, the degree of the sample alignment in the magnetic field strongly influences the relaxation rate. In our case the sample seems to be well oriented. Still, the anisotropic ratio τ_s/τ_L could be close to 7, if we account for the free rotation/reorientation of monomers and dimers [9], and this would mean that the alignment of the sample is not complete.
- (iii) For all the frequencies and temperatures studied the contribution associated with order director fluctuations is very small and this result is in complete agreement with additional $(1/T_{1\rho})(\Delta)$ measurements performed at one temperature in the S_{Ad} phase as shown in figure 8. In fact the theoretical angular dependence of $1/T_{1\rho}$ of the ODF contribution presents a bell-shape behaviour described by

$$\left(\frac{1}{T_{1\rho}}\right)_{\text{ODF}} = \frac{A}{\sqrt{v_1}} \left[\frac{f_{01}(\Delta)}{4\sqrt{2}} + \sqrt{\left(\frac{v_1}{v_L}\right)} \left(\frac{5}{2} f_{11}(\Delta) + \frac{f_{21}(\Delta)}{4\sqrt{2}} \right) \right], \quad (17)$$

with $v_{L,C}=0$ and $v_{H,C}\rightarrow\infty$. It would give a maximum of $1/T_{1\rho}$ at $\Delta=45^\circ$, if the ODF contribution were dominant at $v_1=21.3$ kHz. This behaviour was not observed experimentally as shown in figure 8. We also fitted expression (1 b) to the $1/T_{1\rho}$ angular data at 77°C with a free constant A , but with constraints of the table for self-diffusion and rotation mechanisms. For this temperature we have obtained for the free parameter A a value of $62 \text{ s}^{-3/2}$ in complete agreement with our previous conclusions.

Parameters corresponding to the best fits obtained using equation (1) with $(1/T_{1\rho})_{\text{ODF}} = Av_L^{-1/2}$, at different temperatures in the S_{Ad} phase of a mixture containing 70 per cent of CBOOA and 30 per cent of DOBCA.

$T/^\circ\text{C}$	$\tau_s \times 10^{10}/\text{s}$	$\tau_L \times 10^9/\text{s}$	$D_\perp \times 10^{11}/\text{m}^2 \text{s}^{-1}$
82	1.9	1.72	3.63
77	2.2	2.10	2.98
73	2.4	2.47	2.53
68	2.8	3.05	2.05

In addition to the analysis described we have made a complete analysis of our results using equation (16) to describe the ODF contribution. However the use of both equations (15) and (16) gave very similar results and conclusions.

With the analysis of $1/T_1(\nu_L, T, \Delta)$ and $1/T_{1\rho}(\nu_L, \nu_1, T, \Delta)$ it was thus possible to obtain a good picture of the importance of the different relaxation mechanisms in the MHz regime in a partial bilayer smectic A phase and the values of the parameters describing the dynamic processes. We could extend our conclusions to the kHz range where the T_1 measurements are not accessible with conventional spectrometers. In fact, the $T_{1\rho}$ measurements are very suggestive, since there is only a factor of about 1.5 between $1/T_{1\rho}(\Delta=0^\circ)$ at $\nu_1=21.3$ kHz and $1/T_1$ at $\nu_L=5.6$ MHz for each temperature; this result indicates a slowing down of the relaxation rate at low frequencies as observed previously in pure DOBCA [35] and HOBCA [15]. This behaviour could also suggest the existence of a low cut-off frequency in the ODF modes close to 1 MHz as previously admitted by Vilfan *et al.* [29] for S_A phases. As an example two fits of $1/T_1(\nu_L)$ are compared in figure 9 for the mixture studied at 77°C. One using the $A\nu_L^{-1/2}$ law to describe the order director fluctuation mechanism, the other considering a low cut-off frequency in the fluctuation modes, $\nu_{L,c}=1$ MHz and $\nu_{H,c}\rightarrow\infty$. The value of $1/T_{1\rho}$ at 5×10^{-4} T is also presented as a guide. From the analysis of figure 9 we can conclude

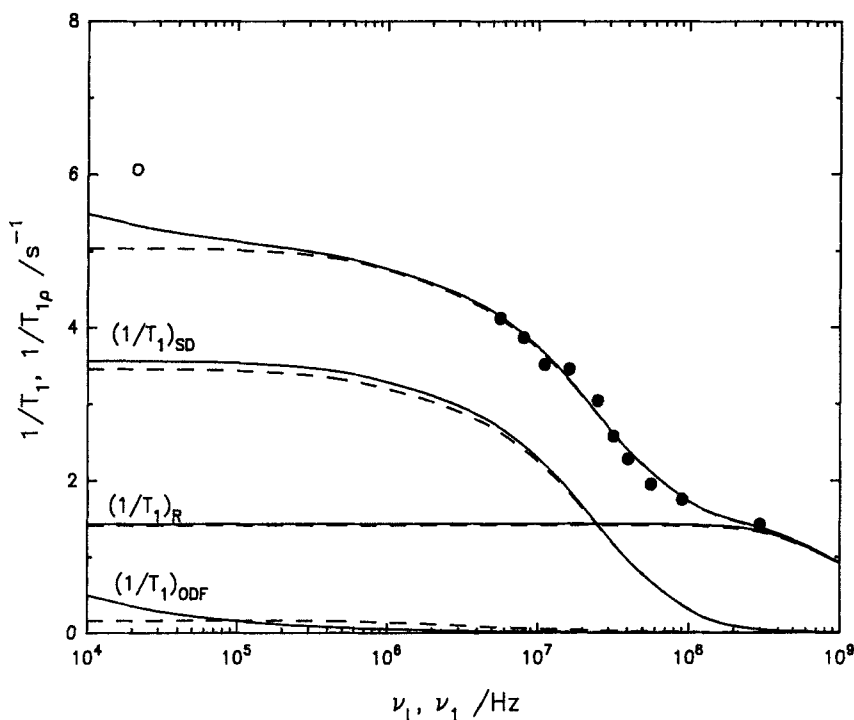


Figure 9. The fit of the calculated $1/T_1$ to the experimental results as a function of ν_L at 77°C ($1/T_{1\rho}$ is shown as a guide). The solid lines correspond to the best fit obtained using equation (1) when the ODF spectral densities (15) are taken without cut-off frequencies ($1/T_{1,ODF} = A\nu_L^{-1/2}$ ($\nu_{L,c}=0, \nu_{H,c}\rightarrow\infty$)). The dotted lines correspond to the best fit obtained using equation (1) but considering a low cut-off frequency $\nu_{L,c}=1$ MHz in the ODF model (15), $\nu_{H,c}\rightarrow\infty$. 0.7 (CBOOA)/0.3 (DOBCA); T = 77°C; ○ $1/T_{1\rho}$ ($\nu_L=56$ MHz); ● $1/T_1$.

that the two global fits with and without cut-off are essentially the same in the frequency domain explored and do not influence the values of the basis fitted parameters.

Since the diffusion contribution decreases with increasing diffusion coefficients, D_{\perp} and D_{\parallel} , we must note that they could show a significant increase if we consider the onset of an additional relaxation mechanism described by a BPP frequency dependence with a correlation time larger than 10^{-8} s, probably related with the process of dissociation and recombination of dimers within the smectic layers [9]. On the other hand, Figueirinhas *et al.* [10], in the analysis of deuterium NMR spectra in the S_{A_d} phase of cyano compounds, concluded that the correlation time associated with the process of dimerisation of molecules must be shorter than 10^{-6} s. We can thus restrain the dimer's lifetime to be larger than 10^{-8} s and shorter than 10^{-6} s.

4. Conclusions

The mesomorphic polymorphism exhibited by a mixture of two polar asymmetric mesogens has been characterized and analysed by optical microscopy, differential scanning calorimetry and X-ray diffraction. The analysis of the proton spin-lattice relaxation rate results in the S_{A_d} phase shows that the essential relaxation mechanisms in the MHz domain are rotation/reorientations and self-diffusion. Self-diffusion gives the most important contribution to the total relaxation rate at frequencies below 20 MHz. This result shows a strong modulation of the relaxation rate due to intermolecular spin interactions associated with self-diffusion of single molecules and pairs of molecules, within and between the smectic layers, as predicted by Guillon and Skoulios for the partial bilayered smectic phases [9]. The contribution of ODF to the relaxation rate is not the dominant relaxation mechanism even in the kHz domain. An additional relaxation mechanism could be associated with the dissociation and recombination of dimers within the smectic layers, as described in [9]. If present, this mechanism would be described by a BPP frequency dependent model with a correlation time larger than 10^{-8} s.

We wish to thank Dr Helena Santos (Centro de Química Estrutural-INIC) for the experimental manipulations with the CXP Spectrometer. We also acknowledge the financial support of JNICT (Project 87/460).

References

- [1] HARDOUIN, F., LEVELUT, A. M., SIGAUD, G., ACHARD, M. F., TINH, N. H., and GASPAROUX, H., 1981, *Symmetries and Broken Symmetries*, edited by N. Boccara (Idset), p. 231.
- [2] HARDOUIN, F., LEVELUT, A. M., ACHARD, M. F., and SIGAUD, G., 1983, *J. Chim. phys.*, **80**, 53.
- [3] CLADIS, P. E., 1975, *Phys. Rev. Lett.*, **35**, 48.
- [4] BROWNSEY, G. J., and LEADBETTER, A. J., 1980, *Phys. Rev. Lett.*, **44**, 1608.
- [5] PROST, J., and BAROIS, P., 1983, *J. Chim. phys.*, **80**, 65.
- [6] RATNA, B. R., SHASHIDHAR, R., and RAJA, V. N., 1985, *Phys. Rev. Lett.*, **55**, 1476.
- [7] SIGAUD, G., HARDOUIN, F., ACHARD, M. F., and LEVELUT, A. M., 1981, *J. Phys., Paris*, **42**, 107.
- [8] CLADIS, P. E., 1988, *Molec. Crystals liq. Crystals*, **165**, 85; SHASHIDHAR, R., and RATNA, B. R., 1989, *Liq. Crystals*, **5**, 421.
- [9] GUILLON, D., and SKOULIOS, A., 1983, *Molec. Crystals liq. Crystals*, **91**, 341; 1984, *J. Phys., Paris*, **45**, 607.
- [10] FIGUEIRINHAS, J. L., CRUZ, C., RIBEIRO, A. C., and TINH, N. H., 1992, *Molec. Crystals liq. Crystals* (in the press).
- [11] GUILLON, D., SEURIN, P., and SKOULIOS, A., 1979, *Molec. Crystals liq. Crystals*, **51**, 149.
- [12] SEURIN, P., GUILLON, D., and SKOULIOS, A., 1981, *Molec. Crystals liq. Crystals*, **71**, 37; SEURIN, P., 1979, Dissertation, University of Louis Pasteur, Strasbourg.

- [13] SACKMANN, H., and DEMUS, D., 1966, *Molec. Crystals liq. Crystals*, **2**, 81.
- [14] MUGELE, TH., GRAF, V., WÖLFEL, W., and NOACK, F., 1980, *Z. Naturf. (a)*, **35**, 924. NOACK, F., NOTTER, M., and WEIB, W., 1988, *Liq. Crystals*, **3**, 907. PUSIOL, D., and NOACK, F., 1988, *Proceedings of the 10th Ampère Summer School and Symposium*, Portoróz, pp. 222–225. NOACK, F., 1988, *Proceedings of the 10th Ampère Summer School and Symposium*, Portoróz, pp. 195–199.
- [15] RIBEIRO, A. C., SEBASTIÃO, P. J., and VILFAN, M., 1988, *Liq. Crystals*, **3**, 937.
- [16] TORREY, H. C., 1953, *Phys. Rev.*, **92**, 962.
- [17] VILFAN, M., and ŽUMER, S., 1980, *Phys. Rev. A*, **21**, 672.
- [18] ABRAGAM, A., 1961, *The Principles of Nuclear Magnetism* (Clarendon Press); WOLF, D., 1979, *Spin-Temperature and Nuclear Spin Relaxation in Matter* (Clarendon Press).
- [19] UKLEJA, P., PIRS, J., and DOANE, J. W., 1976, *Phys. Rev. A*, **14**, 414.
- [20] WOESSNER, D. E., 1962, *J. chem. Phys.*, **36**, 1; 1962, *Ibid.*, **37**, 647.
- [21] VILFAN, M., 1978, Ph.D. Thesis, University of Ljubljana.
- [22] BECKMANN, P. A., EMSLEY, J. W., LUCKHURST, G. R., and TURNER, D. L., 1983, *Molec. Phys.*, **50**, 699; 1986, *Ibid.*, **59**, 97.
- [23] SEBASTIÃO, P. J., 1990, Monograph, Technical University of Lisbon, I. S. T.
- [24] VOLD, R. R., and VOLD, R. G., 1988, *J. chem. Phys.*, **88**, 1443.
- [25] SHIMITZU, H., 1962, *J. chem. Phys.*, **37**, 765.
- [26] SCHWEIKERT, K. H., and NOACK, F., 1989, *Z. Naturf.*, **44**, 597.
- [27] BLINC, R., VILFAN, M., LUZAR, M., SELIGER, J., and ŽAGAR, V., 1978, *J. chem. Phys.*, **68**, 303.
- [28] CRUZ, C., FIGUEIRINHAS, J. L., RIBEIRO, A. C., and MARTINS, A. F., 1990, *Communication presented at the 10th General Conference of the Condensed Matter Division of the E. P. S.*, Lisbon.
- [29] VILFAN, M., KOGOJ, M., and BLINC, R., 1987, *J. chem. Phys.*, **86**, 1055.
- [30] PINCUS, P., 1969, *Solid St. Commun.*, **7**, 415.
- [31] BLINC, R., LUZAR, M., VILFAN, M., and BURGAR, M., 1975, *J. chem. Phys.*, **63**, 3445.
- [32] ŽUPANČIČ, I., ŽAGAR, V., ROŽMARIN, M., LEVSTIK, I., KOGOVŠEK, F., and BLINC, R., 1976, *Solid St. Commun.*, **18**, 1591.
- [33] KOHLHAMMER, K., MÜLLER, M., and KOTHE, G., 1989, *Liq. Crystals*, **5**, 1525.
- [34] HANSON, E. G., and SHEN, Y. R., 1976, *Molec. Crystals liq. Crystals*, **36**, 193.
- [35] RIBEIRO, A. C., 1987, *Molec. Crystals liq. Crystals*, **151**, 287.