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Proton spin-lattice relaxation study of a partial bilayer smectic A phase

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Proton spin–lattice relaxation study of a partial bilayer smectic A phase

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Measurements of proton spin–lattice relaxation rates for the partial bilayer smectic A phase of 4-((4′-*n*-hexadecyloxybenzylidene)-amino) benzonitrile obtained at different Larmor frequencies and temperatures show that the essential relaxation mechanisms in the MHz frequency region are translational self-diffusion and local molecular reorientations similar to those in monolayer smectics. The values of the diffusion constant obtained from the fit of the theory to the experimental data show a range from $2{\cdot}6 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$ at 95°C to $1{\cdot}7 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$ at 75°C. A dynamic process specific to the partial bilayer smectic A phase seems to influence relaxation below 10 MHz. It can be associated either with the dimerization of molecules in the layers or with a higher value of the low cut-off frequency of order director fluctuations than that found in monolayer smectic A phases.

1. Introduction

Since the first proton spin–lattice relaxation study of the smectic A phase performed in 1969 by Doane and Visintainer [1], intensive investigations of the relaxation phenomena have been carried out in smectic liquid crystals [2–15]. It is now well understood that the relaxation mechanisms for protons in the smectic A phase are basically the same as in the nematic phase, i.e. molecular translational diffusion, local molecular reorientations and order director fluctuations. However, a detailed theoretical study shows that their contributions to the total relaxation rate can exhibit a frequency dependence somewhat different from that in nematics. For example, order director fluctuations, which give a relaxation rate proportional to $\omega_L^{-1/2}$ in the nematic phase, exhibit a levelling-off in the smectic A phase at low frequencies which is due to the onset of smectic order [14]. Or, in the case when order director fluctuations are only layer undulations of smectic layers, the relaxation rate is proportional to ω_L^{-1} instead of $\omega_L^{-1/2}$ [2]. In addition the translational diffusion relaxation mechanism should exhibit the details of the diffusion process associated with the structure of the smectic phase [8] at very low frequencies, while at higher frequencies it is well described by Torrey's theory [16] for viscous liquids. As for the relative importance of different relaxation mechanisms, it is nowadays generally accepted on the basis of the spin–lattice relaxation measurements in a wide frequency range from 10^3–10^9 Hz [7] that local molecular reorientations and

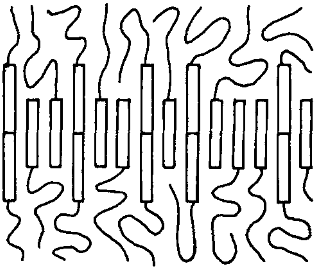
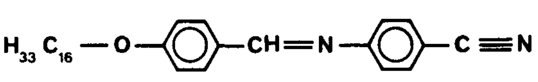


Figure 1. Structural model proposed by Guillon and Skoulios for the partial bilayer smectic A phases.

translational self-diffusion relax protons predominantly in the MHz frequency regime while order director fluctuations become important at Larmor frequencies in the kHz regime. Their contribution in the MHz regime is masked by the other two relaxation mechanisms [7, 7 (a)].

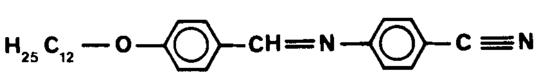
In this paper we present the results of a proton spin–lattice relaxation study of a smectic A phase with partial bilayers. The layer thickness in the smectic A phase of this type is larger than the length of a single molecule but smaller than two molecular lengths. Such mesophases are formed by mesogens with a highly polar cyano group at one end of the aromatic core and a single paraffinic tail at the other end [17]. They are of particular interest because of the phenomenon of reentrance of the nematic or the smectic A phase [18]. During the intense research of this peculiar polymorphism exhibited by the cyano mesogens, several models were proposed to account for the partial bilayer behaviour [19–21]. According to a model proposed by Guillon and Skoulios [21], the partial smectic bilayers consist both of single molecules and of pairs of molecules with associated cyano groups. The monomer and dimer units are distributed randomly in the layers but remain perpendicular to the layer (see figure 1). In such systems, in addition to the molecular motions known from liquid crystals with monolayer smectic A phases, the dissociation and formation of dimers is expected to take place and provide a strong modulation of intermolecular proton interactions.

In order to obtain an insight into the dynamics of molecules packed into a partial bilayer we have studied the proton spin–lattice relaxation rate T_1^{-1} in the liquid crystal 4-((4′-*n*-hexadecyloxybenzylidene)-amino) benzonitrile (16CN).



$$\mathrm{Cr} \xrightarrow{72^\circ\mathrm{C}} \mathrm{S_A} \xleftrightarrow{104^\circ\mathrm{C}} \mathrm{I}$$

Its smectic layer thickness is about 49·5 Å which exceeds the length l of a single molecule by the factor 1·37 [22]. The results are compared to those obtained previously for a similar liquid crystal 4-((4′-*n*-dodecyloxybenzylidene)-amino) benzonitrile (12CN) with the same core but with a different chain length [15].



$$\mathrm{Cr} \xrightarrow{62{\cdot}2^\circ\mathrm{C}} \mathrm{S_A} \xleftrightarrow{103^\circ\mathrm{C}} \mathrm{I}$$

2. Experimental

The proton spin–lattice relaxation times in 16CN have been measured by means of standard pulse sequences in the whole temperature region of the smectic A phase for ten frequencies between 5·6 and 90 MHz using a Bruker SXP-4/100 MHz spectrometer. All of the data were obtained on cooling the sample slowly from the isotropic phase into the smectic A phase in the magnetic field. The temperature of the sample was controlled to within ± 0·3°C.

The temperature dependence of the proton relaxation time T_1 is shown in figure 2. T_1 increases with increasing temperature in the smectic A phase and then slightly but abruptly drops at the smectic A–isotropic transition, for all Larmor frequencies. Such behaviour has been observed in some monolayer smectic A phases as well (TBBA [2], DOBAMBC [11]), while in some others like 4-chloro-4′-*n*-hexyloxybenzylidene aniline (6Cl) [13] the relaxation time decreases with increasing temperature.

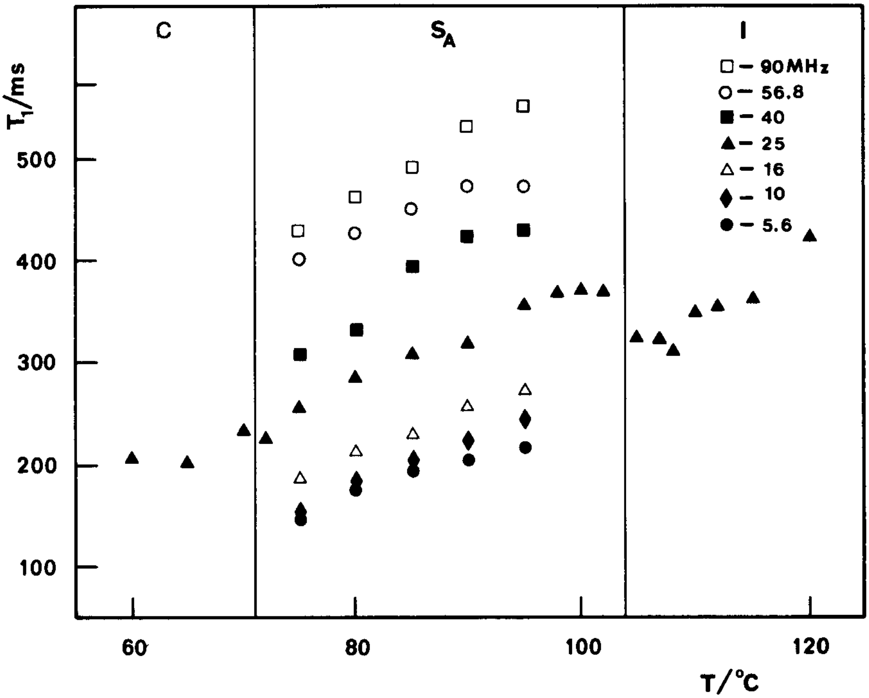


Figure 2. Temperature dependence of the proton spin–lattice relaxation time T_1 in the S_A and isotropic phase of 16CN.

The dependence of the proton relaxation rate T_1^{-1} on Larmor frequency ω_L at three different temperatures is illustrated in figure 3. Close to $\nu_L = 10$ MHz a levelling-off of the relaxation rate takes place. It is only slightly observable at higher temperatures but it is enhanced considerably in the lower temperature range of the smectic A phase (see figure 3). In order to be sure that it is not due to a different degree of orientation of the smectic A phase in low magnetic fields, the measurements of T_1^{-1} at 5·6 MHz were performed both upon cooling in the magnetic fields of 0·133 T and 1·33 T. No difference in T_1^{-1} exceeding the experimental error could be observed. The homologue of 16CN, 12CN, exhibits a similar slowing down of the increase of the relaxation rate in the region below 10 MHz as shown in figure 4. Preliminary measurements of the proton relaxation time in the rotating frame suggest, in view of the

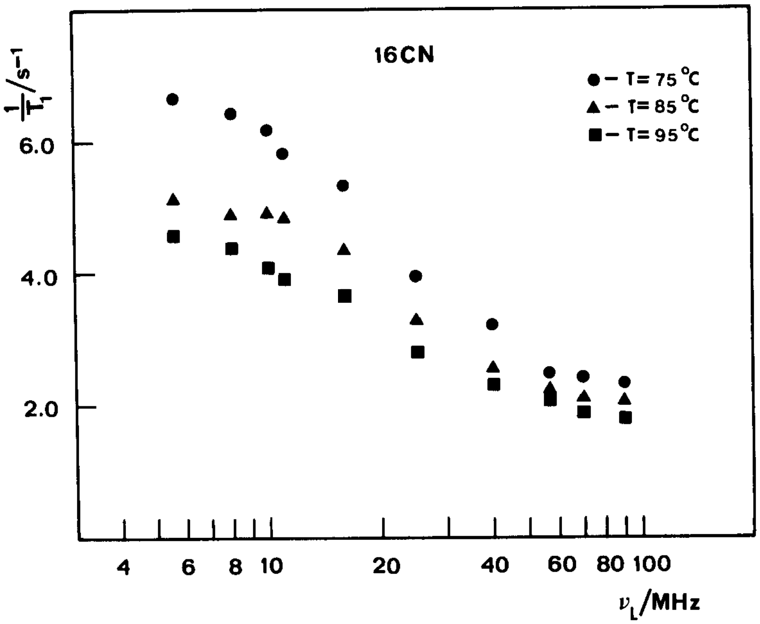


Figure 3. Frequency dependence of the proton spin-lattice relaxation rate $1/T_1$ (ν_L) for three temperatures in the S_A phase of 16CN.

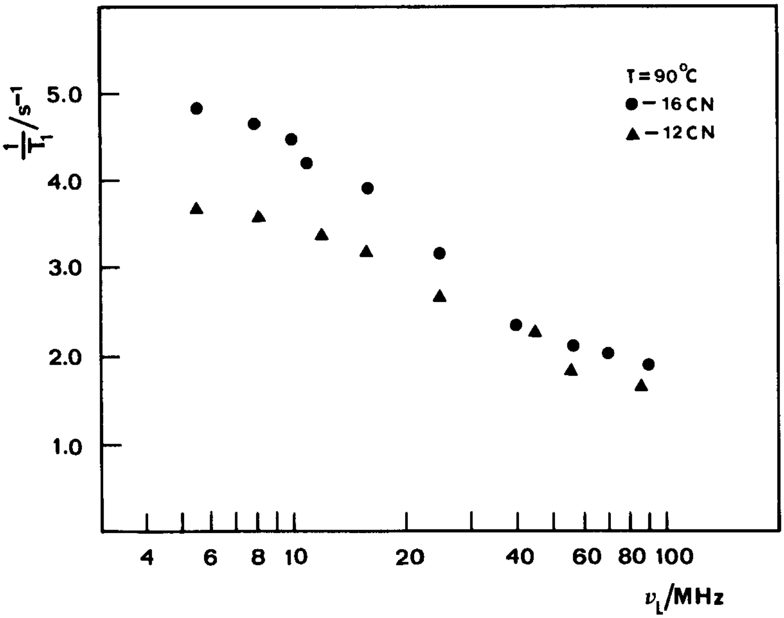


Figure 4. Frequency dependence of the proton spin-lattice relaxation rate $1/T_1$ (ν_L) in the S_A phases of 16CN and 12CN at 90°C.

relatively long $T_{1\varrho}$ values, that there is no considerable increase of the relaxation rate even in the kHz regime.

In addition to the temperature and frequency dependences, the angular dependence of the proton relaxation rate has been determined. It is shown in figure 5 for

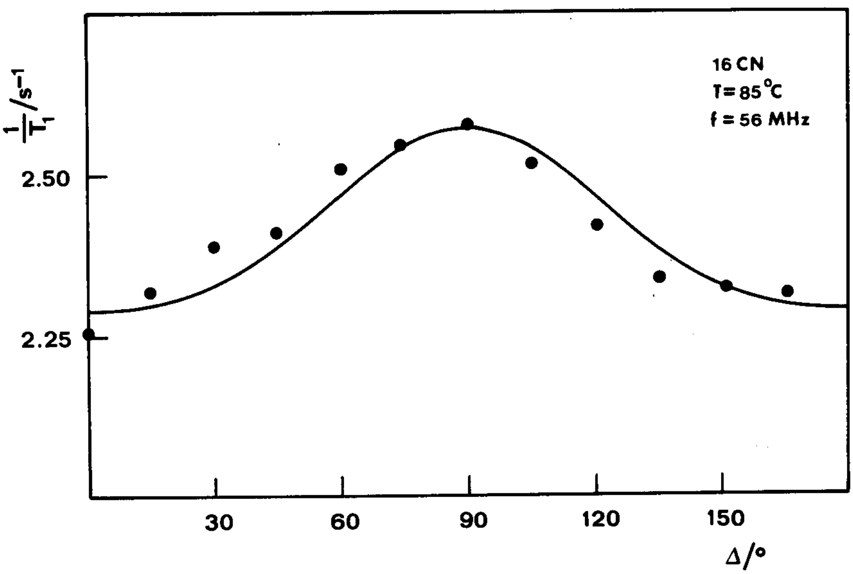


Figure 5. Experimentally determined angular dependence of the proton T_1^{-1} in the S_A phase of 16CN at $\nu_L = 56$ MHz and $T = 85$°C. The solid curve is only a guide to the eye.

the protons of 16CN at $T = 85$°C and $\nu_L = 56$ MHz. T_1^{-1} exhibits an increase of about 15 per cent when the angle Δ between the magnetic field and the normal to the smectic layers is changed from 0° to 90°. This angular dependence indicates that the sample of 16CN in the smectic A phase is at least partly, if not completely, uniformly oriented.

3. Analysis of experimental data and discussion

In order to see which molecular motions influence the proton spin–lattice relaxation in partial smectic bilayers, the dispersion of T_1^{-1} should be analysed with a view of the various relaxation mechanisms. We assume that the frequency dependences of the contributions of different relaxation mechanisms to T_1^{-1} are approximately the same for smectic phases with partial bilayers as for monolayer smectic phases, though we are aware that the details can differ considerably (for example, the decay times and cut-off frequencies of order director fluctuation modes or the details of the process of translational self-diffusion).

The analysis of the dispersion data has been performed by fitting the equation

$$T_1^{-1} = (T_1^{-1})_{SD} + (T_1^{-1})_{ODF} + (T_1^{-1})_R, \qquad (1)$$

with the experimental T_1^{-1} data until the best agreement was obtained. In equation (1) $(T_1^{-1})_{SD}$ denotes the contribution of molecular translational self-diffusion for which an analytical expression given by Torrey [16] is used. However, the reduction factor 1·4, proposed by Vilfan and Zümer [8], is taken in account. $(T_1^{-1})_R$ denotes the contribution of fast local molecular reorientations which are expected to contribute with a frequency independent term. $(T_1^{-1})_R$ is described in its simplest form by the well-known expression [23]

$$(T_1^{-1}) = 3/2\gamma^4\hbar^2 r^{-6}\tau_R, \qquad (2)$$

which gives the relaxation rate due to isotropic rotation of spin pairs in the fast motion limit with a correlation time τ_R and r denotes the intramolecular inter-proton distance. $(T_1^{-1})_{ODF}$ is the term due to order director fluctuations whose contribution to the total relaxation rate is given by

$$(T_1^{-1})_{ODF} = A/\sqrt{\nu_L}. \tag{3}$$

The theoretical expressions were fitted to the experimental data by varying the parameters: $D_\perp$, which is the translational diffusion constant within the smectic layer, $d_\perp$, which is the distance of closest approach between two spins on neighbouring molecules and which is approximately equal to the diameter of the molecule, a frequency independent term $(T_1^{-1})_R$, and the strength A of the order director fluctuations contribution. The results of the best fits at two temperatures are displayed, as examples, in figures 6 (*a*) and 6 (*b*). These figures also show the contributions of the proposed relaxation mechanisms to the overall relaxation. The values of the parameters obtained from the best fit at each temperature are summarized in the table below.

As we show in the table, the values obtained for the molecular self-diffusion constant within the smectic layer decrease from $2{\cdot}6 \times 10^{-11}\,\mathrm{m^2/s}$ at 95°C to $1{\cdot}7 \times 10^{-11}\,\mathrm{m^2/s}$ at 75°C. They are quite insensitive to the choice of the other parameters and are in good agreement with data reported in the literature for other smectic A compounds [24]. At all temperatures the best fit was obtained with $d_\perp = (5 \pm 0{\cdot}2)$ Å. The frequency-independent contribution $(T_1^{-1})_R$, which is ascribed to the fast local reorientations of the molecule as a whole or to motions of separate molecular segments, is between 1 and $2\,\mathrm{s^{-1}}$. An approximate estimate of the rotational correlation time τ_R can be obtained by using equation (2). By taking $r = 1{\cdot}79$ Å for the protons belonging to the chain and $r = 2{\cdot}44$ Å for the protons linked to the benzene ring we have obtained values of τ_R between $6{\cdot}1 \times 10^{-11}$ s and $9{\cdot}3 \times 10^{-11}$ s. The constant A is determined with low accuracy because of the very small contribution which order director fluctuations yield in the MHz regime. A is about $500\,\mathrm{s^{-3/2}}$.

The values of the parameters, which have been obtained in the analysis of the T_1^{-1} dispersion data, account well for the measured temperature and angular dependences of T_1^{-1}. The relaxation rate due to the fast molecular rotations is, in the frequency-independent region, basically proportional to the rotational correlation time τ_R, and the contribution of molecular self-diffusion to $\tau_{\perp D}$ given by $d_\perp^2/4D_\perp$, if the condition $\omega_L\tau_{\perp D} \ll 1$ is fulfilled. In our case, the fitted values of τ_R are of the order 10^{-11} s and $\tau_{\perp D} \approx 10^{-9}$ s, which means that the relaxation rate should decrease with increasing temperature in the same way as τ_R or $\tau_{\perp D}$; this is indeed observed experimentally (see figure 2).

The angular dependence shown in figure 5 has been measured at 56 MHz where local molecular reorientations represent the dominant contribution to the relaxation

Parameters associated with the best fits obtained with equation (1) at different temperatures in the S_A phase of 16CN.

T/°C	$D_\perp \times 10^{11}/\mathrm{m^2\,s^{-1}}$	$(1/T_1)_R/\mathrm{s^{-1}}$	$\tau_R \times 10^{11}$/s
95	2·6	1·29	6·1
90	2·4	1·37	6·4
85	2·1	1·60	7·5
80	1·9	1·76	8·3
75	1·7	1·98	9·3

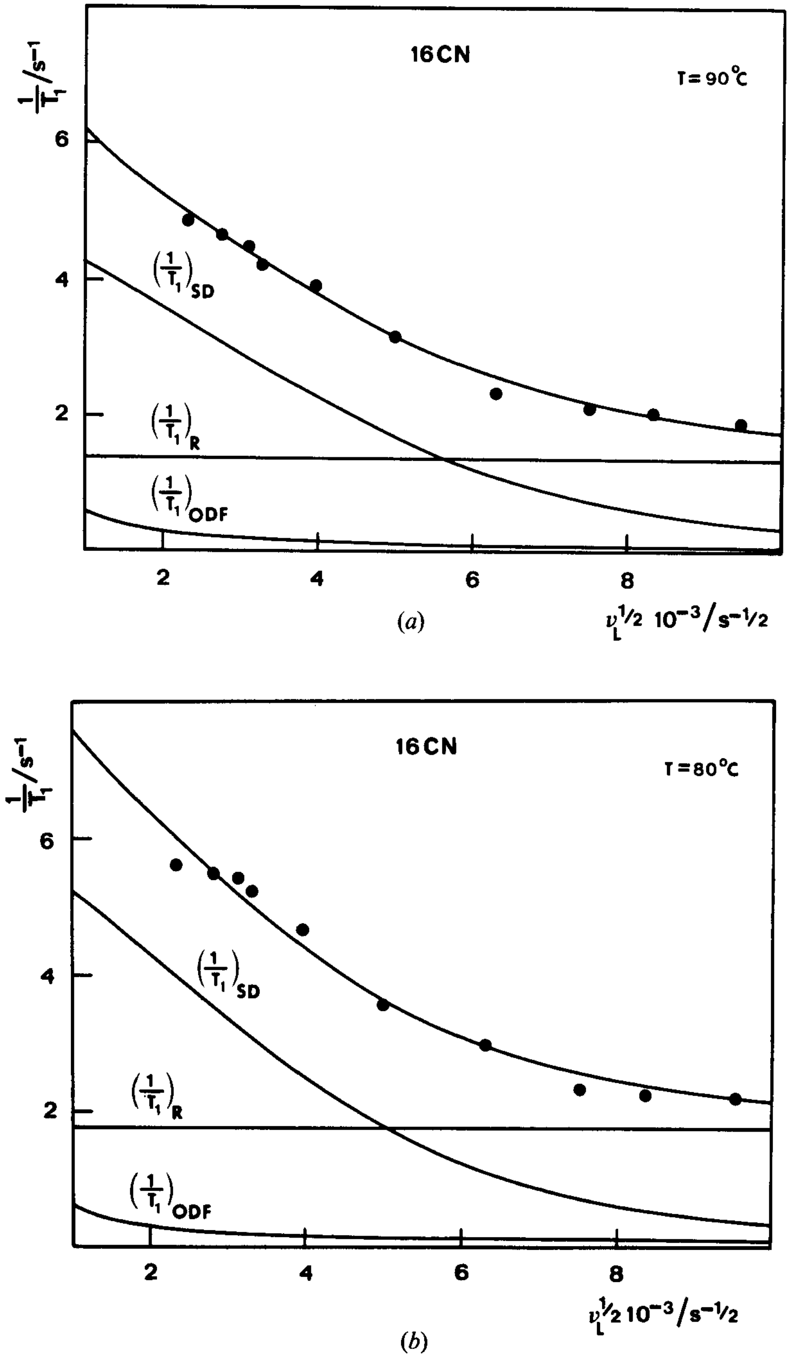


Figure 6. (*a*) Experimental $1/T_1$ as a function of $\nu_L^{1/2}$ for $T = 90°C$ in the S_A phase of 16CN. The solid line is the theoretical dispersion curve calculated from equation (1) and with the parameters described in the text. The contributions of different relaxation mechanisms are shown. (*b*) Experimental $1/T_1$ as a function of $\nu_L^{1/2}$ for $T = 80°C$ in the S_A phase of 16CN. The solid line is the theoretical dispersion calculated from equation (1) and with the parameters described in the text. The contributions of different relaxation mechanisms are shown.

rate. This mechanism can cause under certain circumstances, i.e. when the correlation times for rotations around the short and long molecular axes are not equal, an angular dependence of the type which has been observed experimentally.

Comparing the agreement between the theory and experiment in the proton T_1^{-1} dispersion it should be stressed, however, that the relaxation mechanisms considered provide a far better fit to the experimental data at higher temperatures (95°C and 90°C) than at lower temperatures. They do not account for the slowing down of the increase of the relaxation rate below 10 MHz, which is obviously present at lower temperatures. This discrepancy can be improved considerably by taking into account either the onset of an additional relaxation mechanism (i) or a lower cut-off frequency in the contribution of ODF (ii).

(i) It is possible to improve the agreement between theory and experimental data at low frequencies and low temperatures, if, in addition to the standard relaxation mechanisms, another is added with a BPP-type frequency dependence [23] as a first approximation and with a correlation time of about 4×10^{-9} s. The motion associated with this relaxation mechanism has a correlation time which is larger than the usual local reorientational times of molecules in the smectic A phases [25]. It can possibly be ascribed to the process of dimerization of molecules within the smectic layers.

(ii) The second possibility for the explanation of the slowing down at low frequencies is the inclusion of a low cut-off frequency in the order director fluctuations mechanism. In the nematic phase the low cut-off frequency excludes the fluctuations modes with wavelengths larger than the dimension of a uniformly oriented domain. The relaxation rate $(T_1^{-1})_{\mathrm{ODF}}$ is then given by [26]

$$T^{-1}_{1_{\mathrm{ODF}}} = \frac{A}{(\pi\sqrt{\nu_{\mathrm{L}}})}\left[1/2\ln\frac{a^2 + a\sqrt{2} + 1}{a^2 - a\sqrt{2} + 1} + \arctan(a\sqrt{2} + 1) + \arctan(a\sqrt{2} - 1)\right], \tag{4}$$

where $a = (\nu_{\mathrm{L}}/\nu_{\mathrm{L,c}})^{1/2}$, and $\nu_{\mathrm{L,c}}$ is the low cut-off frequency. In the smectic A phase a similar effect, i.e. the levelling off of the ODF relaxation rate at low frequencies, is produced by the onset of the smectic order itself [14]. It is estimated to take place close to 1 MHz for smectics with viscosity coefficients about 1 poise and accordingly higher if the viscosity is lower. It can be described formally, to a good accuracy, by equation (4) as well. The introduction of a cut-off frequency $\nu_{\mathrm{L,c}}$ of approximately 8 MHz in the fit of the proton dispersion data of 16CN and a simultaneous increase of A do improve the agreement between theory and experiment considerably.

In conclusion we may say that the proton spin-lattice relaxation mechanisms in a partial bilayer smectic A phase as studied in 16CN and its homologue 12CN [15] are, in the MHz regime, predominantly the same as in monolayer smectics, i.e. translational self-diffusion and local molecular reorientations. The specific properties of the bilayer phase seem to influence the relaxation below 10 MHz. It is not possible to conclude at present whether this is the process of dimerization and monomerization of the molecules within the layers or a low cut-off frequency of the order director fluctuation modes. The low cut-off frequency should be, in this case, considerably higher than in monolayers where it has been found to be about 10 kHz [7]. Dispersion data at frequencies below 1 MHz would be necessary to decide between these two possibilities.

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