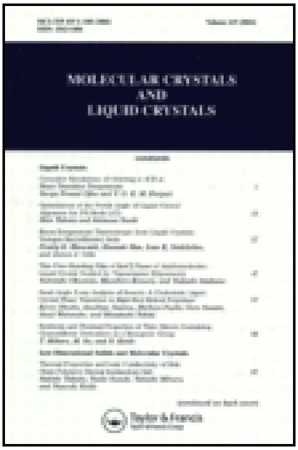

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Field-Induced Director Alignment for 4-nonyl-4′-cyano-biphenyl Near the Smectic A - Nematic Transition

D. Kamada [a], K. Okumoto [a], A. Sugimura [a], G. R. Luckhurst [b], B. A. Timimi [b] & H. Zimmermann [c]

[a] Department of Information Systems Engineering, Osaka Sangyo University, Daito-Shi, Osaka, Japan

[b] School of Chemistry and Southampton Liquid Crystal Institute, University of Southampton, Southampton, United Kingdom

[c] Max-Planck-Institut für Medizinische Forschung, Department of Biophysics, Heidelberg, Germany

To cite this article: D. Kamada, K. Okumoto, A. Sugimura, G. R. Luckhurst, B. A. Timimi & H. Zimmermann (2005): Field-Induced Director Alignment for 4-nonyl-4′-cyano-biphenyl Near the Smectic A - Nematic Transition, Molecular Crystals and Liquid Crystals, 441:1, 131-141

To link to this article: http://dx.doi.org/10.1080/154214091009626

Mol. Cryst. Liq. Cryst., Vol. 441, pp. 131–141, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/154214091009626

Taylor & Francis
Taylor & Francis Group

Field-Induced Director Alignment for 4-nonyl-4′-cyanobiphenyl Near the Smectic A – Nematic Transition

D. Kamada
K. Okumoto
A. Sugimura
Department of Information Systems Engineering, Osaka Sangyo University, Daito-Shi, Osaka, Japan

G. R. Luckhurst
B. A. Timimi
School of Chemistry and Southampton Liquid Crystal Institute, University of Southampton, Southampton, United Kingdom

H. Zimmermann
Max-Planck-Institut für Medizinische Forschung, Department of Biophysics, Heidelberg, Germany

Deuterium NMR spectroscopy has been used to investigate the director dynamics of deuteriated 4-α,α-d_2-nonyl-4′-cyanobiphenyl, where the director was aligned by an electric field. The electric field direction made an angle of 47° with the magnetic field in order to provide a unique alignment pathway; accordingly the director is expected to rotate as a monodomain. The time dependence of the director orientation was investigated at different temperatures. At each temperature in the nematic phase, all of the deuterium NMR spectra indicate that the director was uniformly oriented as a monodomain. It was found that the relaxation time in the smectic A phase is about 1,000,000 times as large as that in the nematic phase. This also results in a strong pretransitional growth of the relaxation time as the transition to the smectic A phase is approached.

Keywords: deuterium NMR; director dynamics; liquid crystal; 9CB

This work was supported by a Grant-in-aid for Scientific Research ((B) Project Number: 15360176) from the Japan Society for the Promotion of Science (JSPS).

Address correspondence to A. Sugimura, Department of Information Systems Engineering, Osaka Sangyo University, 3-1-1 Nakagaito, Daito-Shi, Osaka 574-8530, Japan. E-mail: sugimura@ise.osaka-sandai.ac.jp

1. INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy has been intensively used in liquid crystal research. Recently, deuterium NMR has been widely employed in the investigation of liquid crystals in particular because the deuterium NMR spectra of specifically or fully deuteriated materials are simple, especially when compared to their proton analogues [1]. Since the quadrupolar splitting is related to the angle made by the director with the magnetic field, deuterium NMR spectroscopy is found to be a powerful method with which to investigate the static [2,3] and dynamic [4–10] director orientation in a thin nematic film. Thus 4-pentyl-4′-cyanobiphenyl (5CB), and also 4-octyl-4′-cyanobiphenyl (8CB) [11–14], have been widely studied with deuterium NMR spectroscopy. In order to ensure that the results found for 5CB and 8CB are not specific to these mesogens it is clearly desirable to study other compounds. We have, therefore, undertaken an analogous investigation of the director dynamics in the smectic A (SmA) and nematic phases of the mesogen 4-nonyl-4′ -cyanobiphenyl (9CB).

Although the molecular structure of 9CB differs by only a single methylene group from that of 8CB its behaviour is expected to be quite different. Thus the smectic A-nematic transition for 8CB is essentially continuous whereas it is first order for 9CB, in accord with its shorter nematic range [15].

We have used deuterium NMR spectroscopy to investigate the director dynamics of chain deuteriated 4-α,α-d_2-nonyl-4′-cyanobiphenyl (9CB-d_2) in the nematic and smectic A phases, where the director was aligned by an electric field [2,11]. The electric field direction made an angle 47° with the magnetic field of the NMR spectrometer in order to provide a unique reorientation pathway. Accordingly the director is expected to rotate as a monodomain. The sample was confined between two glass plates coated with ITO whose surfaces were not treated in any way. The time dependence of the director orientation was investigated at different temperatures from 46.0 to 46.7°C in the smectic A phase to 46.7 to 49.3°C in the nematic phase. This will allow us to compare the field-induced dynamics in these two very different liquid crystal phases. Preliminary studies of 8CB have revealed that the rate of director alignment in the smectic A phase [13] is significantly larger than that in the nematic phase [14], as might be expected from the introduction of translational order. Similar differences have been found for the smectic A phase formed by the re-entrant mixture of 4-hexyloxy- and 4-octyloxy-4′-cyanobiphenyls where the rotational viscosity in the SmA phase is about 600 Pa s [16]. This compares with values of about 0.06 Pa s for the nematic phase of comparable mesogens. The rotational viscosity coefficient has also been obtained by computer simulation of model systems. Thus, for the Gay-Berne potential model parameterised to make it more realistic [17] the rotational viscosity coefficient simulated at constant volume [18] for the nematic phase is found to be essentially the same as in the smectic A phase [18], in marked contrast to experimental results for 8CB and re-entrant mixtures.

The layout of our paper is as follows. In the next section we describe the NMR experiments. The results of these are given in section 3 where they are discussed in the context of the Leslie-Ericksen hydrodynamic theory for the director dynamics. Our investigation is summarized in section 4, where we also give our conclusions.

2. EXPERIMENTAL

The liquid crystal used in this work is the α-chain deuteriated 4-α,α-d$_2$-nonyl-4′-cyanobiphenyl (9CB-d$_2$). The transition temperatures of this liquid crystal are smectic A to nematic transition $T_{SmAN} = 46.7°C$ and nematic to isotropic transition $T_{NI} = 49.3°C$. There is also a narrow (<0.5°C) biphasic region at both transitions which indicates the presence of a small concentration of impurity. The liquid crystal was contained in a sandwich cell of 97.4 μm thickness in which the indium/tin oxide covered surface had not been rubbed or further treated in any other way. The inclined geometry employed in this work is shown in Figure 1. The procedure for the adjustment of the angle α, between

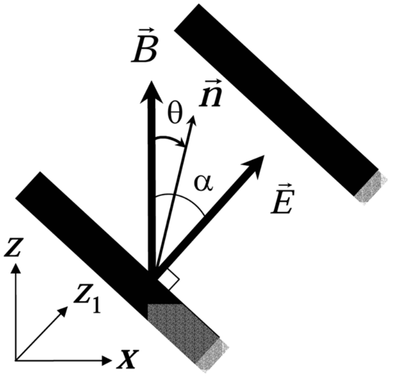

FIGURE 1 The geometry used for the experiment. The z-axis is parallel to the magnetic field and the z_1-axis is normal to the glass plate. The magnetic field, $\boldsymbol{B}$, electric field, $\boldsymbol{E}$, and director, $\boldsymbol{n}$, are in the xz -plane. The director and electric field make the angles θ and α, respectively, with the magnetic field.

the electric and magnetic field, (see Fig. 1) is described elsewhere; this angle was held constant for all of the experiments [6]. The alignment dynamics were carried out at a selection of temperatures in the smectic A and nematic phases. Turn-on [using $V = 95\,V_{RMS}$, i.e., $E = 0.97\,MVm^{-1}$] measurements, in which the electric field was switched on, were performed. The spectra were recorded using a JEOL Lambda 300 spectrometer, which has a magnetic flux density of 7.05 T. In our experiments we used a sinusoidal electric field with a 5 kHz frequency which was supplied via a function generator. A standard quadrupolar echo sequence was used to collect the spectra. The 90° pulse was of 6 μs duration and the delay between pulses was $\sim$40 μs. The electric field and NMR pulse sequences used in the turn-on process are shown in Figure 3 of Ref. 6. In the turn-on experiment the electric field is first switched on by the triggering pulse from the NMR spectrometer then after a delay time, t, a single NMR spectrum is acquired. The turn-on measurements were carried out for values of t of several milliseconds in the nematic phase and of several hours in the smectic A phase. A detailed description of the alignment experiments in the SmA of 8CB is given in Ref. [13].

3. RESULTS AND DISCUSSION

Deuterium NMR spectra, obtained during the turn-on process for the nematic phase at 47°C, are shown in Figure 2. Following the application of the electric field, the quadrupolar splitting decreases and then saturates with time after about 5 ms because the director moves from being parallel to the magnetic field to being at 28.8° to it. The recorded spectra in the initial time region for the turn-on process are seen to contain weak oscillatory spectral features, these are associated with the director motion during the acquisition time for the FID. The origin of the oscillatory spectral features is understood [7] but they are not of importance for this investigation. The time-resolved director orientation is readily determined from our experimental results because of the simple relation between the quadrupolar splitting and the director orientation, as we shall now discuss. If we neglect the narrow director distribution that causes the slight broadening of the spectral lines, then an appropriate form of the time dependence of the director orientation can be determined relatively easily. This is a good assumption since there is no elastic deformation in the nematic slab used in our experiments. The deuterium NMR spectrum originating from a group of equivalent deuterons, with negligible dipolar interactions, in a monodomain nematic sample with the director parallel to the magnetic field consists of a doublet whose separation

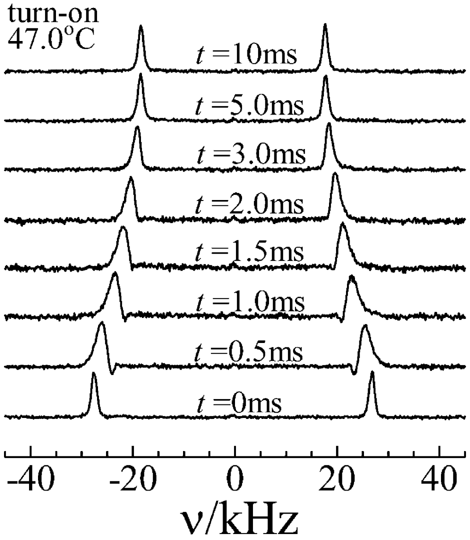

FIGURE 2 The deuterium NMR spectra for the turn-on process recorded for 9CB-d_2 in the nematic phase at 47.0°C.

(the quadrupolar splitting) is denoted by $\Delta\tilde{\nu}_0$. This quadrupolar splitting is given by

$$\Delta\tilde{\nu}_0 = \frac{3}{2} q_{\mathrm{CD}} S_{\mathrm{CD}}, \tag{1}$$

where q_{CD} is the deuterium quadrupolar coupling constant and S_{CD} is the orientational order parameter of the C–D bond. When a sufficiently strong electric field is applied, the director begins to align in the direction of the electric field provided the dielectric anisotropy is positive, as in the case of 9CB. Now, the quadrupolar splitting is given by [19]

$$\Delta\tilde{\nu}(\theta) = \Delta\tilde{\nu}_0 \frac{3\cos^2\theta - 1}{2}, \tag{2}$$

where θ is the angle between the magnetic field, $\boldsymbol{B}$, and the director, as shown in Figure 1. Thus, the value of the angle, θ, can be determined directly from Eq. (2) by measuring the quadrupolar splittings, $\Delta\tilde{\nu}(\theta)$ and $\Delta\tilde{\nu}_0$.

According to the Leslie-Ericksen theory for the nematic phase [20], we should consider the one-dimensional distortion of the director across the cell (see Fig. 1). All of the deuterium NMR spectra in our study are dominated by a single doublet with relatively narrow lines which allows us to determine the director orientation. In this analysis, therefore, we can treat the director as being uniformly aligned and use the quadrupolar splitting measured for this doublet to determine the angle between the director and the magnetic field. The rate of change of the director orientation is given, for the turn-on process, by the torque-balance equation [21]. For a monodomain nematic [9] this is

$$\gamma_1 \frac{d\theta(t)}{dt} = -\frac{\Delta\tilde{\chi}}{2\,\mu_0} B^2 \sin 2\theta(t) + \frac{\varepsilon_0 \Delta\tilde{\varepsilon}}{2} E^2 \sin 2(\alpha - \theta(t)), \tag{3}$$

where γ_1 is the rotational viscosity coefficient, μ_0 is the magnetic permeability and ε_0 the dielectric permittivity of a vacuum. The solution of Eq. (3) is obtained analytically as [9]

$$\theta(t) = \theta_\infty + \tan^{-1}[\tan(\theta_0 - \theta_\infty)\exp(-t/\tau_{\mathrm{ON}})], \tag{4}$$

where θ_∞ is the limiting value of $\theta(t)$ when t tends to infinity, τ_{ON} is the relaxation time, and θ_0 is the initial angle. The relaxation time, τ_{ON}, is given by

$$\tau_{\mathrm{ON}} = \frac{\gamma_1/(\varepsilon_0 \Delta\tilde{\varepsilon} E^2)}{\sqrt{1 + 2\rho\cos 2\alpha + \rho^2}}, \tag{5}$$

where

$$\rho = \mu_0 \varepsilon_0 \left(\frac{E}{B}\right)^2 \left(\frac{\Delta\tilde{\varepsilon}}{\Delta\tilde{\chi}}\right). \tag{6}$$

In this equation α and $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$ are temperature independent parameters [6]. That is γ_1 and $\Delta\tilde{\varepsilon}$ are the only parameters to determine the temperature dependence of τ_{ON}.

Figure 3 shows the time variation in the ratio of the quadrupolar splittings, $\Delta\tilde{\nu}(t)/\Delta\tilde{\nu}_0$, determined from the time-resolved deuterium NMR spectra shown in Figure 2 for the turn-on process; to obtain this ratio we have used the experimental value for $\Delta\tilde{\nu}_0$ of 54.6 kHz (see Fig. 2). We can see in Figure 3 for the turn-on process that the director rotates from the initial angle $\theta_0 = 0^\circ$ for $\Delta\tilde{\nu}_0 = 54.6\,\mathrm{kHz}$ and then aligns at the limiting angle, θ_∞, of 28.8° for $\Delta\tilde{\nu}_\infty = 36.0\,\mathrm{kHz}$ (see Eq. (2)), the limiting value of $\Delta\tilde{\nu}(t)$ as t tends to infinity. The value of the relaxation time, τ_{ON}, was obtained by fitting the ratio of the quadrupolar splittings as a function of time for the turn-on process. The solid line in Figure 3 shows the best-fit giving the value of τ_{ON} as 0.88 ms. We have chosen to fit the time dependence of the quadrupolar splittings ratio rather than that for the director orientation

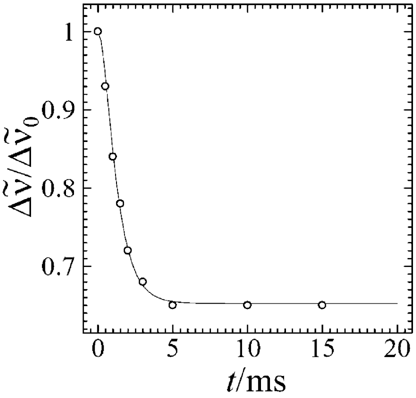

FIGURE 3 The time dependence of the ratio, $\Delta\tilde{\nu}/\Delta\tilde{\nu}_0$, for the turn-on process determined from the deuterium NMR spectra of 9CB-d$_2$ shown in Figure 2 in which the experimental value $\Delta\tilde{\nu}_0 = 54.6\,\text{kHz}$ has been used. The solid line is the best fit to Eq. (2), where $\theta(t)$ is given by Eq. with $\theta_0 = 0^\circ$ and $\theta_\infty = 28.8^\circ$. The relaxation time obtained from this fitting is $\tau_{\text{ON}} = 0.88\,\text{ms}$.

calculable from it because the splittings constitute the primary experimental data and the absolute error associated with each point is more or less constant. It is clearly apparent from the good agreement of the experimental values with the calculated line, as shown in Figure 3, that the relaxation process of the director in the monodomain nematic phase is in keeping with the predictions of the torque-balance equation (see Eq. (4)).

We now turn to the field-induced alignment of the director in the smectic A phase. Typical NMR spectra, recorded as a function of time, during the alignment of the SmA director at 46.5°C are shown in Figure 4. Here, we see that the spectrum, before switching the electric field on, consists of two sharp lines with a quadrupolar splitting, $\Delta\tilde{\nu}_0 = 60.1\,\text{kHz}$. After switching the electric field on, the quadrupolar splitting decreases and then tends to saturate with time after 140 h. This occurs because the director moves from being parallel to the magnetic field to being at an angle, $\theta_\infty = 26.1^\circ$, to it. After 15 min the lines are clearly seen to have broadened. This broadening of the spectral lines is associated with a distribution of director orientations which is present during the period of spectral acquisition; this is typically about 5 min. At $t = 1\,\text{h}$ a second quadrupolar splitting (inner doublet with a smaller splitting in Fig. 4) is observed which corresponds to the director orientation of $\theta_\infty = 26.1^\circ$. This second pair of lines indicates the presence of two smectic domains with slightly different

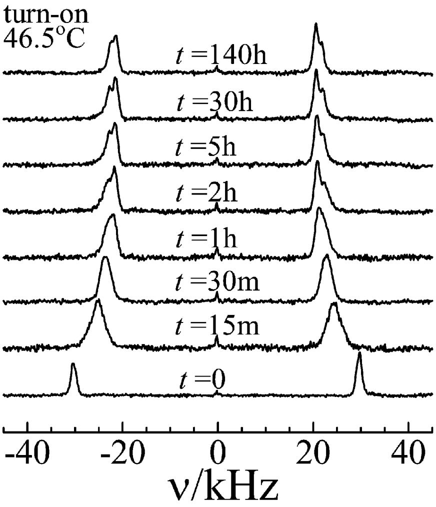

FIGURE 4 The deuterium NMR spectra for the turn-on process recorded for the smectic A phase of 9CB-d_2 at 46.5℃.

orientations; similar behaviour has been observed during the alignment of the smectic A phase of 8CB [13]. The spectrum also shows that the width of the director distribution has decreased with time (that is, as the director orientation tends to $\theta_\infty = 26.1°$). The time variation in the ratio of the quadrupolar splittings, $\Delta\tilde{\nu}(t)/\Delta\tilde{\nu}_0$, determined from the time-resolved deuterium NMR spectra (see Fig. 4) is shown in Figure 5.

Now we should discuss the rate of change of the director orientation for a monodomain smectic A. However, the hydrodynamic theory needed to discuss the director dynamics for the smectic A phase has not been developed so far. Although it has been argued [16,22] that the field-induced director alignment in the smectic A phase might, under certain conditions, be the same as for the nematic phase (see Eq. (4)). This is found to be true for the re-entrant mixture [16] but not for 8CB [22]. None the less we have attempted to fit our data for the smectic A of 9CB to Eq. (4) for a nematic. The results for the time dependence of the ratio, $\Delta\tilde{\nu}(t)/\Delta\tilde{\nu}_0$, are shown in Figure 5 and the solid line gives the best fit to Eq. (4). Although the agreement is reasonable we have also adopted an empirical approach and assumed that the relaxation process of a monodomain director within the smectic A phase follows an exponential decay according to

$$\Delta\tilde{\nu}(t)/\Delta\tilde{\nu}_0 = (1 - \Delta\tilde{\nu}_\infty/\Delta\tilde{\nu}_0)\exp(-t/\tau_{\mathrm{ON}}) + \Delta\tilde{\nu}_\infty/\Delta\tilde{\nu}_0. \tag{7}$$

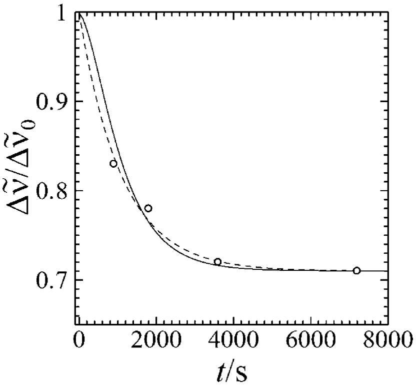

FIGURE 5 The time dependence of the ratio, $\Delta\tilde{\nu}/\Delta\tilde{\nu}_0$, for the turn-on process determined from the deuterium NMR spectra of 9CB-d_2 shown in Figure 4 at 46.5°C, in which the experimental value $\Delta\tilde{\nu}_0 = 60.1\,\text{kHz}$ has been used. For the turn-on process, the director aligns towards the limiting value, $\theta_\infty = 26.1°$. The solid line is the best fit to Eq. (4) and the dashed line to the empirical equation $\Delta\tilde{\nu}/\Delta\tilde{\nu}_0 = 0.29\exp[-t(\text{s})/1100] + 0.71$. The time constant obtained from this empirical equation is $\tau_{\text{ON}} = 1100\,\text{s}$.

We shall, however, assume that the relaxation time is given, to a reasonable approximation, by the theoretical expression for the nematic phase (see Eq. (5)). The value of the relaxation time occurring in Eq. (7) was obtained by fitting the ratio of the quadrupolar splittings as a function of time for the turn-on process. The dashed line in Figure 5 shows the best fit to Eq. (7), this is slightly better than that for the theoretical expression for a nematic. The relaxation time, τ_{ON}, found from this fit is 1100 s. This is a significantly larger value than $\tau_{\text{ON}} = 0.88\,\text{ms}$ measured at 47°C for the nematic phase. This dramatic increase in the relaxation time is to be expected as a result of the introduction of long range translational order on entering the smectic A phase from the nematic. The relaxation time for the turn-on process, τ_{ON}, obtained in this way, at different temperatures in the smectic A and nematic phases are shown in Figure 6 as a function of temperature. As is clearly apparent the relaxation time in the smectic A phase is about 1,000,000 times as large as that in the nematic phase. We can also see that in the nematic phase there is a strong growth in τ_{ON} as the transition to the smectic A phase is approached. We now discuss this pretransitional behaviour. The temperature dependence of $\Delta\tilde{\varepsilon}$ for 9CB [23], given in the inserted figure of Figure 6, shows only a small change in the dielectric anisotropy near the smectic A to nematic phase transition. Accordingly

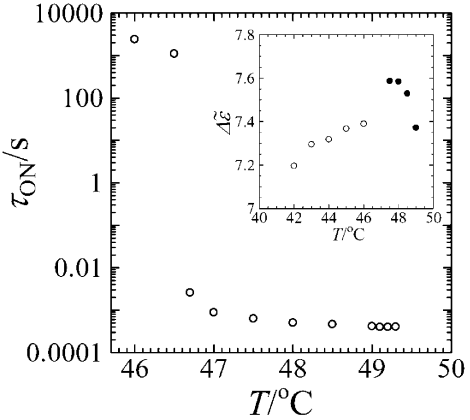

FIGURE 6 The relaxation time, τ_{ON}, for the turn-on process as a function of temperature. The insert figure shows the temperature dependence of the dielectric anisotropy for 9CB [23].

if we assume that Eq. (5) for the relaxation time is also valid for the smectic phase, it seems that the change in τ_{ON} near the transition is due to a strong growth in the rotational viscosity on going from the nematic to the smectic A phase. This pretransitional variation is expected to be strong because the rotational viscosity is so different for the two phases.

4. CONCLUSIONS

We have used deuterium NMR spectroscopy to study the electric field-induced director alignment process for 9CB-d_2 in the smectic A and nematic phases at different temperatures. During the alignment process the director was found to remain essentially as a monodomain. The director alignment for the smectic A and nematic phases was found to follow an exponential decay and the Leslie-Ericksen prediction, respectively. These gave the temperature dependence of the relaxation time for the smectic A and nematic phases. It was found that the relaxation time in the smectic phase is about 1,000,000 times larger than in the nematic phase, in agreement with previous studies but not with a computer simulation study. It also seems that the pretransitional change of the relaxation time near the transition to the nematic phase is not due to the temperature dependence of $\Delta\tilde{\varepsilon}$, but is due to a strong change of the rotational viscosity caused by the huge difference in this property for the two phases.

REFERENCES

[1] Luckhurst, G. R. (1988). *J. Chem. Soc. Faraday Trans. 2*, *84*, 961.

[2] Luckhurst, G. R., Sugimura, A., & Timimi, B. A. (2000). *Mol. Cryst. Liq. Cryst.*, *347*, 53.

[3] Luckhurst, G. R., Miyamoto, T., Sugimura, A., Takashiro, T., & Timimi, B. A. (2001). *J. Chem. Phys.*, *114*, 10493.

[4] Dunn, C. J., Luckhurst, G. R., Miyamoto, T., Sugimura, A., & Timimi, B. A. (2000). *Mol. Cryst. Liq. Cryst.*, *347*, 167.

[5] Luckhurst, G. R., Miyamoto, T., Sugimura, A., Takashiro, T., & Timimi, B. A. (2001). *Thin Solid Films*, *393*, 399.

[6] Luckhurst, G. R., Miyamoto, T., Sugimura, A., & Timimi, B. A. (2002). *J. Chem. Phys.*, *117*, 5899.

[7] Kantola, A. M., Luckhurst, G. R., Sugimura, A., & Timimi, B. A. (2003). *Mol. Cryst. Liq. Cryst.*, *402*, 353.

[8] Luckhurst, G. R., Miyamoto, T., Sugimura, A., & Timimi, B. A. (2002). *J. Chem. Phys.*, *116*, 5099.

[9] Asaka, D., Dunn, C. J., Luckhurst, G. R., Miyamoto, T., Sugimura, A., & Timimi, B. A. (2005). *Current App. Phys., 5*, in the press.

[10] Luckhurst, G. R., Miyamoto, T., Sugimura, A., Timimi, B. A., & Zimmermann, H. (2004). *J. Chem. Phys.*, *121*, 1928.

[11] Luckhurst, G. R., Sugimura, A., & Timimi, B. A. (2000). *Mol. Cryst. Liq. Cryst.*, *347*, 147.

[12] Luckhurst, G. R., Nakatsuji, M., Okumoto, K., Sugimura, A., Timimi, B. A., & Zimmermann, H. (2003). *Mol. Cryst. Liq. Cryst.*, *398*, 235.

[13] Luckhurst, G. R., Miyamoto, T., Sugimura, A., & Timimi, B. A. (2003). *Mol. Cryst. Liq. Cryst.*, *402*, 103.

[14] Luckhurst, G. R., Miyamoto, T., Sugimura, A., & Timimi, B. A. (2003). *Mol. Cryst. Liq. Cryst.*, *394*, 77.

[15] McMillan, W. L. (1972). *Phys. Rev. Lett.*, *A6*, 936.

[16] Dong, R. Y. (1981). *Mol. Cryst. Liq. Cryst. Lett.*, *72*, 59.

[17] Luckhurst, G. R. & Simmonds, P. S. J. (1993). *Mol. Phys.*, *80*, 233.

[18] Sarman, S. (1998). *J. Chem. Phys.*, *108*, 7909.

[19] Fan, S. M., Luckhurst, G. R., & Picken, S. J. (1994). *J. Chem. Phys.*, *101*, 3255.

[20] See, for example, Stewart, I. W. (2004). *The Static and Dynamic Continuum Theory of Liquid Crystals*, Taylor & Francis, 133.

[21] Labrunie, G. & Robert, J. (1973). *J. Appl. Phys.*, *44*, 4869. See, for example, Collings, P. J. & Hird, M. (1997). *Introduction to Liquid Crystals, Chemistry and Physics*, Taylor & Francis, 197.

[22] Bras, W., Emsley, J. W., Levine, Y. K., Luckhurst, G. R., Seddon, J. M., & Timimi, B. A. (2004). *J. Chem. Phys.*, *121*, 4397.

[23] Dunmur, D. A., Manterfield, M. R., Miller, W. H., & Dunleavy, J. K. (1978). *Mol. Cryst. Liq. Cryst.*, *45*, 127.