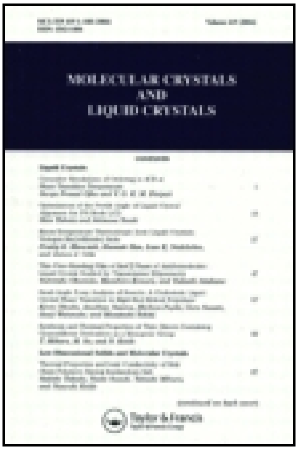

Molecular Crystals and Liquid Crystals

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

Field-Induced Director Dynamics in the Nematic Phase of 4-Octyl-4″-Cyanobiphenyl. A Deuterium Nmr Investigation

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To cite this article: Geoffrey R. Luckhurst, Bakir A. Timimi, Tetsuo Miyamoto & Akihiko Sugimura (2003): Field-Induced Director Dynamics in the Nematic Phase of 4-Octyl-4″-Cyanobiphenyl. A Deuterium Nmr Investigation, Molecular Crystals and Liquid Crystals, 394:1, 77-91

To link to this article: http://dx.doi.org/10.1080/15421400390193684

Mol. Cryst. Liq. Cryst., Vol. 394, pp. 77–91, 2003
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ISSN 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390193693

FIELD-INDUCED DIRECTOR DYNAMICS IN THE NEMATIC PHASE OF 4-OCTYL-4′-CYANOBIPHENYL. A DEUTERIUM NMR INVESTIGATION

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The response times of liquid crystal display devices are determined by a range of factors but the most important of these is usually the rotational viscosity coefficient, γ_1. In order to understand the relationship between molecular structure and viscosity it is of considerable interest to measure this viscosity coefficient for a variety of nematogens. Here we report the determination of γ_1 for 4-octyl-4′-cyanobiphenyl-d_2 at two temperatures using deuterium NMR spectroscopy. In these experiments the time taken for the alignment of the director can be changed by a field, either magnetic or electric. To do this the liquid crystal film was enclosed in a cell which allows the application of an electric field within the NMR spectrometer. The rate of director relaxation was followed by recording the deuterium NMR spectrum as a function of time during the process of turning the electric field on or off. We have carried out the experiments for a geometry in which the director orientation with respect to the magnetic field of the spectrometer does not exceed 45°. The alignment of the director throughout the relaxation process was observed to be uniform. The director relaxation was found to follow closely the predictions of the torque-balance equation given by the Leslie-Eriksen theory. The relaxation times for the turn-on and turn-off processes were determined from this equation and

This work was supported by a Scientific Grant in Aid from the Japan Society for the Promotion of Science (JSPS) and was carried out as an Anglo-Japanese research project of the International Exchange Programme supported by the Royal Society and JSPS.

found to be of the order of 1–2 ms. A knowledge of the anisotropic electric and magnetic susceptibilities then allows the determination of the rotational viscosity coefficient.

Keywords: rotational viscosity; deuterium NMR; nematic phase; director relaxation

INTRODUCTION

To obtain liquid crystal display devices with fast switching times requires the control of a range of physical properties of the liquid crystal. Paramount among these properties is the rotational viscosity coefficient, γ_1 [1–3]. Low values of γ_1 promote fast switching times and hence the design of mesogenic molecules which give such desirable low values of the viscosity coefficient is very important. However, our understanding of the relationship between molecular structure and viscosity is not well-developed. It is, therefore, of considerable interest to measure the viscosity coefficient for a range of nematogens in order to gain a better understanding of the molecular factors controlling γ_1. In principle the rotational viscosity coefficient can be determined from the measurement of the relaxation time for the nematic director when the director orientation is changed by a field, either electric or magnetic. In our experiments we enclose a liquid crystal film in a cell which allows the application of an electric field within the NMR spectrometer so that we can study the director dynamics in the presence of the electric and magnetic fields. We can then follow the rate of director relaxation during the process of turning the electric field on (where the dynamics is now affected by both the electric and magnetic fields) or turning it off (where the director relaxation is now only affected by the magnetic field) [4–5]. The physical properties of the liquid crystal that determine the characteristic director relaxation time are the dielectric permittivity anisotropy, $\Delta\varepsilon$, the anisotropy in the diamagnetic susceptibility, $\Delta\chi$, as well as the rotational viscosity coefficient, γ_1. For a uniformly aligned director (i.e. a monodomain) subject to both electric and magnetic fields, the rate of director relaxation is given by [4,7]:

$$\gamma_1\left(\frac{d\theta}{dt}\right) = -\left(\frac{\Delta\chi}{2\mu_0}\right)B^2\sin 2\theta + \left(\frac{\varepsilon_0\Delta\varepsilon}{2}\right)E^2\sin 2(\alpha-\theta), \tag{1}$$

where θ is the angle between the director and the magnetic field, $\mathbf{B}$, and α is the angle between the electric field, $\mathbf{E}$, (which is normal to the glass surface) and the magnetic field, $\mathbf{B}$ (see Fig. 1 for the experimental geometry). This torque-balance equation ignores surface anchoring effects which is a reasonable assumption for an untreated glass surface and a thick sample.

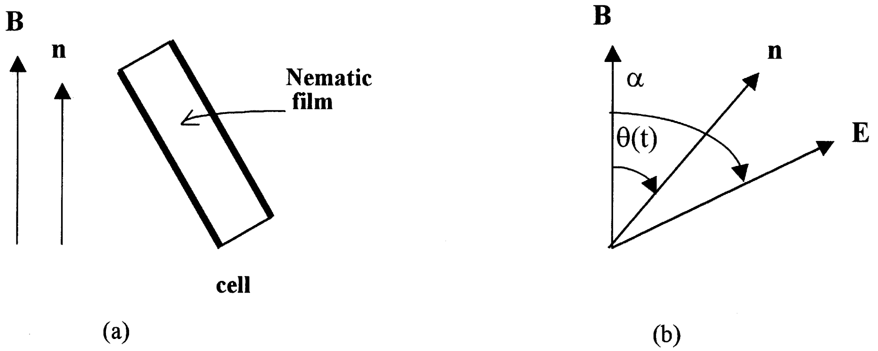

FIGURE 1 The experimental geometry: the cell is inclined at an angle relative to **B** (a) before the electric field is switched on and (b) the coordinates after the electric field is switched on.

The solution to Eq. (1) is obtained analytically as [4]:

$$\tan(\theta(\mathrm{t}) - \theta_\infty) = \tan(\theta_0 - \theta_\infty)\exp(-\mathrm{t}/\tau). \tag{2}$$

Here τ is the relaxation time characterising the dynamic process, $\theta(\mathrm{t})$ is the angle the director makes with **B** at time t, θ_0 is the initial angle (at t= 0) and θ_∞ is the final angle (t = ∞). The relaxation time depends on the rotational viscosity coefficient, γ_1, and on the values of $\Delta\varepsilon$ and $\Delta\chi$. For the turn-on and the turn-off processes the expressions for the relaxation times are, respectively [4]:

$$\tau_{\mathrm{on}} = \frac{\gamma_1}{2(U_m^2 + U_e^2 + 2U_mU_e\cos 2\alpha)^{1/2}}, \tag{3}$$

$$\tau_{\mathrm{off}} = \frac{\gamma_1}{2U_m}. \tag{4}$$

In these equations U_m and U_e are given by:

$$U_m = \frac{\Delta\chi}{2\mu_0}B^2 \quad \text{and } U_e = \frac{\varepsilon_0\Delta\varepsilon}{2}E^2.$$

Equation (3) can be recast in terms of the magnetic field-induced relaxation time τ_m and electric field-induced relaxation time, τ_e, in the following form [7]

$$\tau_{\mathrm{on}} = \frac{1}{(\tau_m^{-2} + 2\tau_m^{-1}\tau_e^{-1}\cos 2\alpha + \tau_e^{-2})^{1/2}}, \tag{5}$$

where

$$\tau_e = \frac{\gamma_1}{2U_e} \quad \text{and } \tau_m = \frac{\gamma_1}{2U_m}(\equiv \tau_{\mathrm{off}}). \tag{6}$$

Equation (3), or (5), shows that, for the same values of E and B, $\tau_{\rm on}$ increases as α increases and reaches a maximum at $\alpha = 90°$ [although when $\alpha = 90°$ the director motion is then non-uniform because of the degeneracy of the route the director could follow during relaxation and so strictly Eq. (3) cannot be applied]. Figure 2 shows an illustration of Eq. (3) for different values of the viscosity coefficient and for certain fixed values of E and B.

A further useful relationship is obtained from Eqs. (3) and (4) after some rearrangement

$$\frac{U_m}{U_e} = \frac{\mathrm{B}^2}{\mu_0\varepsilon_0 E^2}\left(\frac{\Delta\chi}{\Delta\varepsilon}\right) = \frac{1}{(R^2 - 2R\cos 2\theta_\infty + 1)^{1/2}}, \tag{7}$$

where

$$R = \tau_{\rm off}/\tau_{\rm on}. \tag{8}$$

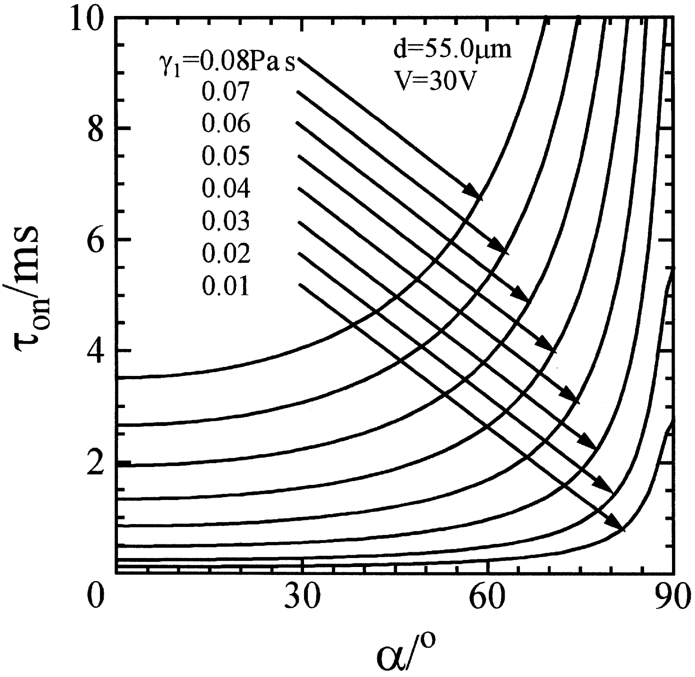

FIGURE 2 The variation of $\tau_{\rm on}$ with α calculated for a field of 30 V applied to a cell of 55.0 μm thickness (E = 0.545 MVm^{-1}) and for a magnetic flux density of 7.05T. The separate curves are for various values of the rotational viscosity coefficient, γ_1.

Another relationship which gives the ratio of the electric to the magnetic torque terms can be obtained from the torque-balance equation for a monodomain at equilibrium (from Eq. (1))

$$-\left(\frac{\Delta\chi}{2\mu_0}\right)B^2\sin 2\theta_\infty + \left(\frac{\varepsilon_0\Delta\varepsilon}{2}\right)E^2\sin 2(\alpha-\theta_\infty) = 0. \tag{9}$$

Equation (9) can be rearranged to give

$$\frac{U_m}{U_e} = \frac{\sin 2(\alpha-\theta_\infty)}{\sin 2\theta_\infty}. \tag{10}$$

The ratio R (see Eq. (8)) can also be expressed [7] by an equation similar to (10)

$$R = \left|\frac{\sin 2\alpha}{\sin 2(\alpha-\theta_\infty)}\right|. \tag{11}$$

Therefore, by measuring the two relaxation times at the same temperature to obtain R, and if we know either $\Delta\chi$ or $\Delta\varepsilon$ we can determine the value of the rotational viscosity coefficient, γ_1, from Eq. (3) or (4). Also by determining R at one temperature and determining one of the relaxation times at other temperatures we can determine γ_1 at the other temperatures, provided we know either $\Delta\chi$ or $\Delta\varepsilon$ at these temperatures and that θ_∞ is constant for a given value α. This is equivalent to the ratio $(\Delta\chi/\Delta\varepsilon)$ being temperature independent.

In order to measure the relaxation time, τ, we need, according to Eq. (2), to follow the time dependence of the angle θ(t). Here we have used deuterium NMR spectroscopy to monitor the time dependence of θ(t) utilising the simple dependence of the liquid crystal deuterium NMR spectrum for the nematic on the angle between the director and the magnetic field, **B**. For a uniformly aligned nematic containing a group of equivalent deuterons, the deuterium NMR spectrum consists, provided any dipolar couplings are negligible, of a single quadrupolar doublet. One of the advantages of using NMR spectroscopy in investigating director dynamics is that the quadrupolar splitting $\Delta\nu$ depends on the angle of orientation of the director, θ, with respect to **B** according to

$$\Delta\nu(\theta) = \Delta\nu_0\left(\frac{3\cos^2\theta - 1}{2}\right), \tag{12}$$

where $\Delta\nu_0$ is the splitting when the director is parallel to **B**. The angular variation of $\Delta\nu(\theta)$ for a monodomain director is shown in Figure 3 for a few values of θ. Thus, when monitoring the dynamics of relaxation of the nematic director we should obtain a series of simple doublets with splittings, $\Delta\nu$(t), at different times, t. From Eq. (12) we obtain as a result a series of values of θ(t) at different times. If these values of θ(t) fit the

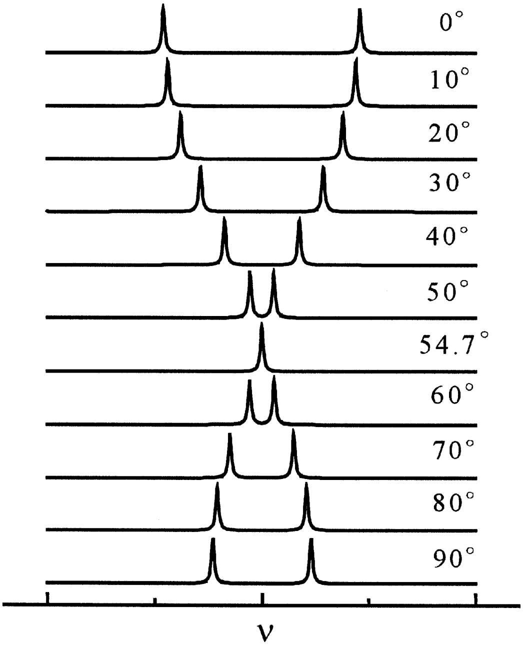

FIGURE 3 The anticipated variation of the quadrupolar splitting with the angle θ between the director and the magnetic field for a monodomain sample.

theory (i.e. Eq. (2)) then this will give us the value of the field-induced relaxation time, τ.

EXPERIMENTAL

The nematic liquid crystal used in this work is 4-α,α-d$_2$-octyl-4′-cyanobiphenyl (8CB-d$_2$) with the octyl chain deuteriated in the α position. This liquid crystal has a nematic and a smectic A phase ($T_{NI} = 312.1\,K$ and $T_{SmAN} = 304.7\,K$; there is also a small (<0.5°C) NI biphasic region). The method of preparing this specifically deuteriated liquid crystal has been described before [8]. The liquid crystal was contained in a flat cell 56.8 μm thick in which the indium/tin oxide covered surface was not rubbed or treated in any other way. The detailed construction of the cell has been described elsewhere [9]. The inclined geometry employed in this work is shown in Figure 1a. The procedure for the adjustment of the angle α (see Fig. 1b) has been described elsewhere [10]. The relaxation dynamics were carried out at two temperatures: 306.3 K $\{(T_{NI} - T) = 5.8\,K\}$ and 308.3 K $\{(T_{NI} - T) = 3.8\,K\}$. Two turn-on [using $V = 50\,V$, i.e.

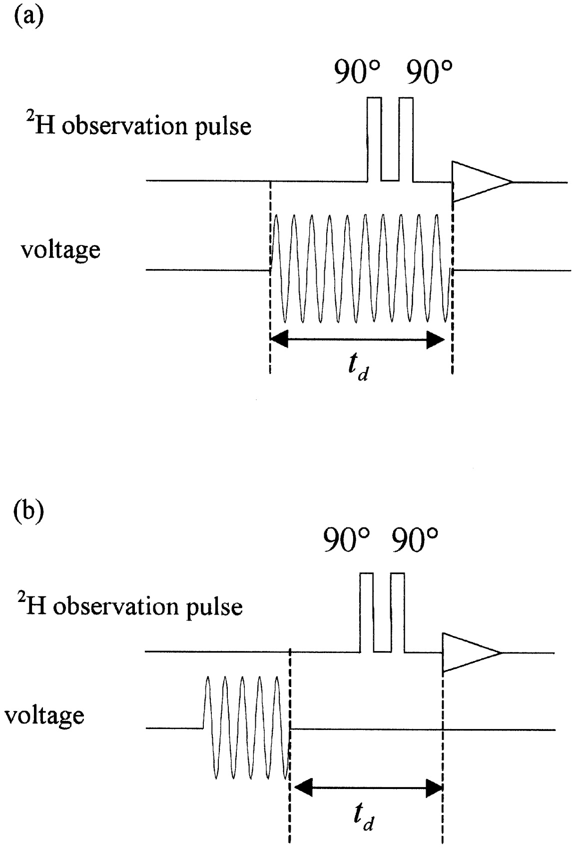

FIGURE 4 The pulse trains for (a) the turn-on relaxation measurement: see text and (b) the turn-off relaxation measurement: see text.

$E = 0.88\,\mathrm{MVm^{-1}}$, one at $T = 306.3\,\mathrm{K}$ and the other at $T = 308.3\,\mathrm{K}$] and two turn-off [using $V = 70\,\mathrm{V}(E = 1.23\,\mathrm{MVm^{-1}})$ and $V = 50\,\mathrm{V}(E = 0.88\,\mathrm{MVm^{-1}})$ both at $T = 306.3\,\mathrm{K}$] measurements were carried out. All voltages and so field values are RMS values. The spectra were recorded using a JEOL Lambda 300 spectrometer which has a magnetic flux density of 7.05 T. In our experiment we have used a sinusoidal electric field of 10 kHz frequency which was supplied via a Function Generator (Wave Factory type WF 1493). At this frequency the director behaves as if it experiences a constant electric field [11]. The electric field was switched on or off by a triggering pulse generated by the NMR spectrometer. A standard quadrupolar echo sequence was used to collect the spectra. The two 90° pulses were of 6 μs duration and the delay between pulses was ~40 μs. The electric field and

NMR pulse sequences used in the turn-on and turn-off processes are shown in Figures 4a and 4b, respectively. 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_d, a single NMR spectrum is acquired. Then about ~0.5 ms after the delay time t_d, the electric field is switched off for a sufficiently long time (50 ms) to allow the director to relax to $\theta = 0°$. This process is repeated a few thousands times to obtain a spectrum with a good signal-to-noise ratio.

In the turn-off experiment, first **E** is switched on for a sufficiently long time (~100 ms) to align the director along a direction close to the direction of **E** (this establishes the initial angle the director makes with **B**). The electric field is then switched off and after a delay time, t_d, a single NMR spectrum is acquired (corresponding to a turn-off spectrum at time t_d). The electric field remains switched off for a total of 50 ms before it is switched on again and the process repeated. Normally this process is repeated a few thousand times in order to obtain a spectrum with a good S/N.

The turn-on and turn-off dynamic measurements were carried out for many values of t_d extending from ~0.3 ms to several milliseconds.

RESULTS AND DISCUSSION

(1) Turn-on Dynamics at 308.3 K and 306.3 K

Typical deuterium NMR spectra measured at different times during the turn-on process at 308.3 K and 306.3 K are shown in Figures 5 and 6, respectively for $E = 0.88\,\mathrm{MVm}^{-1}$. The director orientation reaches its maximum value of $\theta_\infty = 33°$ after 4 to 5 ms. The values of $\theta(t)$ are plotted against t in Figures 7 and 8 for T = 308.3 K and 306.3 K, respectively. The solid lines are the fitted lines calculated according to Eq. (2) with the following parameters:

$$T = 308.3\,\mathrm{K}\text{: } \tau_{on} = 0.98\,\mathrm{ms}, \theta_\infty = 33.0°$$
$$T = 306.3\,\mathrm{K}\text{: } \tau_{on} = 1.25\,\mathrm{ms}, \theta_\infty = 32.4°$$

The fit to the experimental turn-on data is seen to be very good at both temperatures.

(2) Turn-off Dynamics at 306.3 K

Typical deuterium NMR spectra measured at different times during the turn-off relaxation process at 306.3 K and for two values of the electric field strength namely $0.88\,\mathrm{MVm}^{-1}$ and $1.23\,\mathrm{MVm}^{-1}$ are shown in Figures 9 and 10, respectively. The difference between the two sets of measurements is

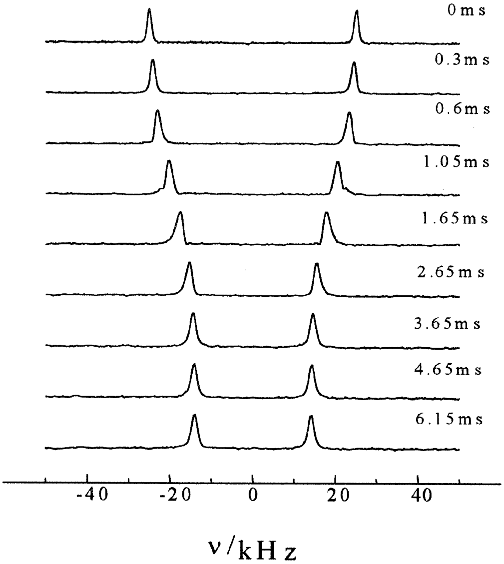

FIGURE 5 Typical spectra for the turn-on dynamics of 8CB-d_2 at different times at 308.3 K.

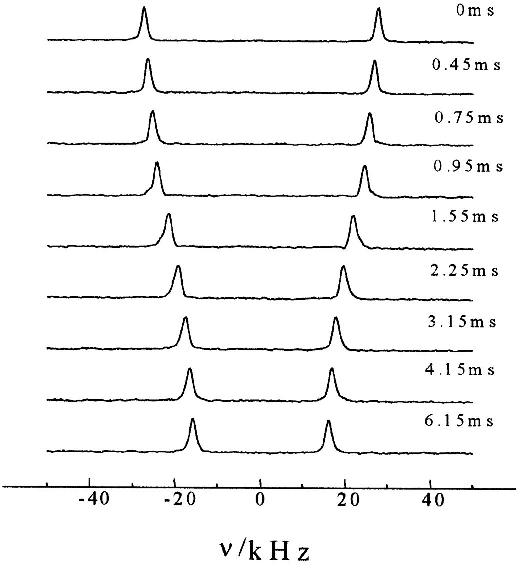

FIGURE 6 Typical spectra for the turn-on dynamics of 8CB-d_2 at different times at 306.3 K.

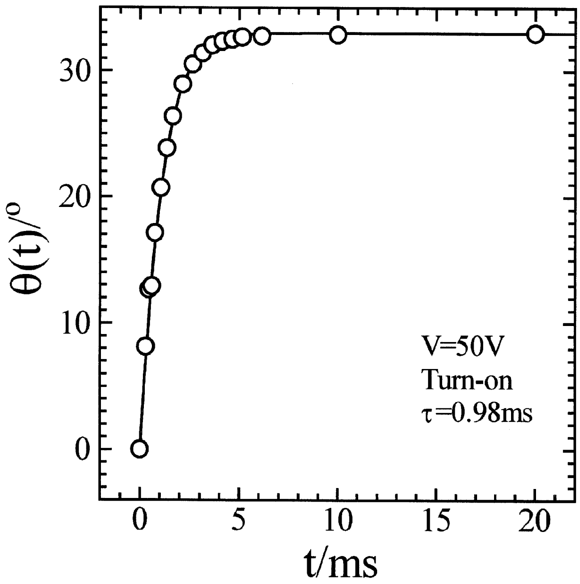

FIGURE 7 Turn-on director relaxation for 8CB-d_2 at T = 308.3 K. Experiment ○; solid line: best fit to Eq. (2).

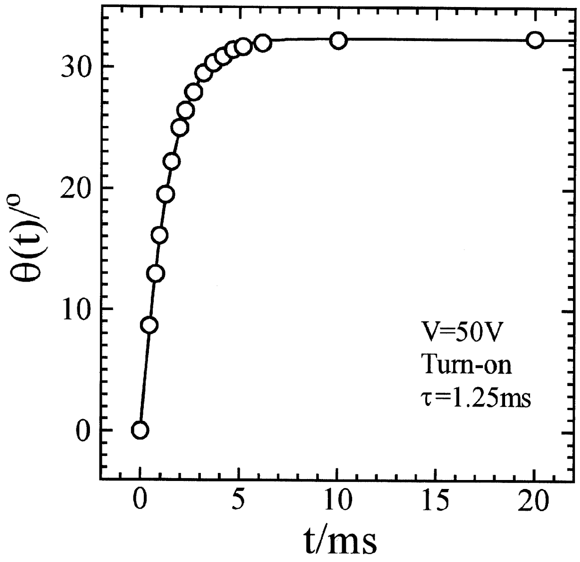

FIGURE 8 Turn-on director relaxation for 8CB-d_2 at T = 306.8 K. Experiment: ○; solid line: best fit to Eq. (2).

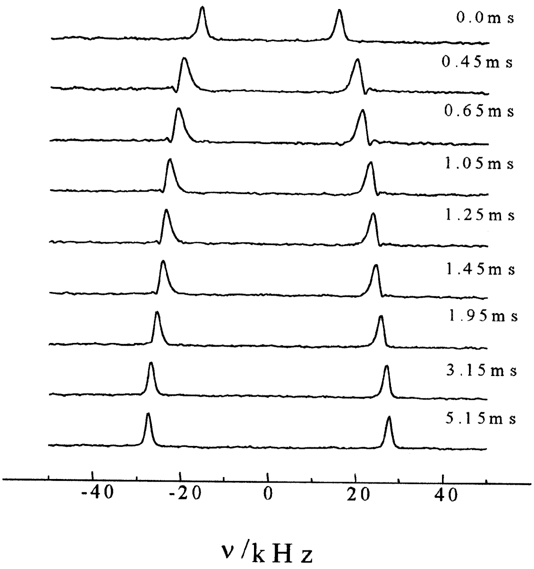

FIGURE 9 Typical spectra for the turn-off dynamics of 8CB-d_2 at different times for E = 0.88 MVm^{-1} and at T = 306.3 K.

only in the value of the starting angle θ_0, thus for $E = 0.88\,MVm^{-1}$, $\theta_0 = 33°$ while for $E = 1.23\,MVm^{-1}$, $\theta_0 = 42°$. There are some small but noticeable oscillatory features in the spectra for times up to 1.5 ms (especially so in Fig. 10). The origin of those oscillations has been investigated and they are due to the fact that for very fast director relaxation the quadrupolar splitting changes during the acquisition of the free induction decay [12]. However, for our system this does not seriously affect the main splitting which is used in the calculation of the director orientation and hence the relaxation time, τ. Figures 11 and 12 show the experimental $\theta(t)$ data for the two values of E. The solid line was calculated using Eq. (2) and the following values: $\tau_{off} = 1.90\,ms$ for both, $\theta_0 = 33°$ in Figure 11 and $\theta_0 = 42°$ in Figure 12.

We found that at 308.3 K the oscillations in the spectra were severe which prevented us from obtaining accurate values for the director orientation during the entire alignment process.

(3) The Evaluation of γ_1

First we consider evaluating γ_1 at 306.3 K where we have measured the two relaxation times, τ_{on} and τ_{off}. From the ratio $R = \tau_{on}/\tau_{off}$, the value of 33.0° is found for θ_∞ and from the known values of the electric and magnetic

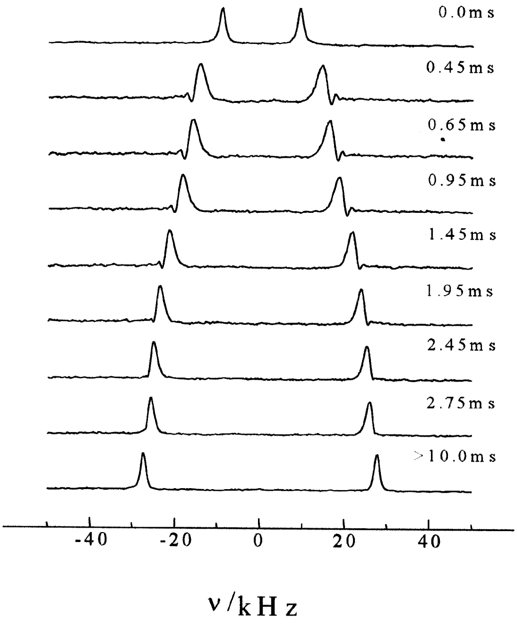

FIGURE 10 Typical spectra for the turn-off dynamics of 8CB-d_2 at different times for $E = 1.23\,\mathrm{MVm}^{-1}$ and at $T = 306.3\,\mathrm{K}$.

fields we obtain from Eq. (7) the ratio $(\Delta\chi/\Delta\varepsilon)$. To proceed further we need the value of either $\Delta\chi$ or $\Delta\varepsilon$. For 8CB, the values of $\Delta\varepsilon$ at different temperatures are available from the measurement of the dielectric permittivities by Dunmur *et al.* [13]. From the value of $\Delta\varepsilon$ at 306.3 K and the determined value of $\Delta\chi/\Delta\varepsilon$, we obtain $\Delta\chi$. Finally, by applying Eq. (4) we obtain the value of the rotational viscosity coefficient, γ_1, at this temperature. The value of γ_1 and the other parameters used are given in Table 1. We also give in Table 1 the value of γ_1 at 308.3 K. At 308.3 K we have determined only τ_{on}. To obtain a value for γ_1 we have used the fact that the ratio $(\Delta\chi/\Delta\varepsilon)$ is temperature independent which follows from the observation that θ_∞ is essentially the same at the two temperatures (see Eq. (10)). This is also consistent with the results we obtained for 5CB where τ_{on} and τ_{off} were measured at different temperatures and both R and hence $(\Delta\chi/\Delta\varepsilon)$ were found to be temperature independent [7].

In (Table 2) we compare our values of γ_1 with those given by Martins [14]. We see, for example, from Table 2, that at $(T_{\mathrm{NI}} - T) = 3.8\,\mathrm{K}$, our value for γ_1 is lower by $\sim 22\%$ than that given by Martins [14]. The reason for this difference is not clear to us at the moment but could be caused by a number of factors: differences in the value of the temperature, of the

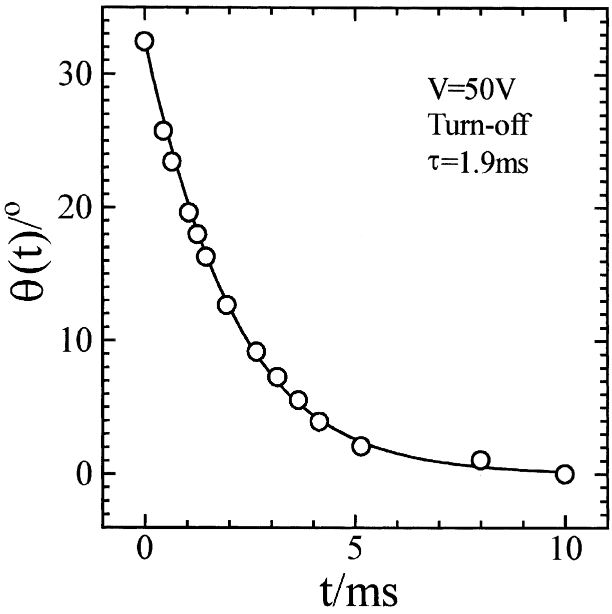

FIGURE 11 Turn-off director relaxation for 8CB-d_2 at 306.3 K. Experiment ○: E = 0.88 Mvm^{-1}; solid line: best fit to Eq. (2).

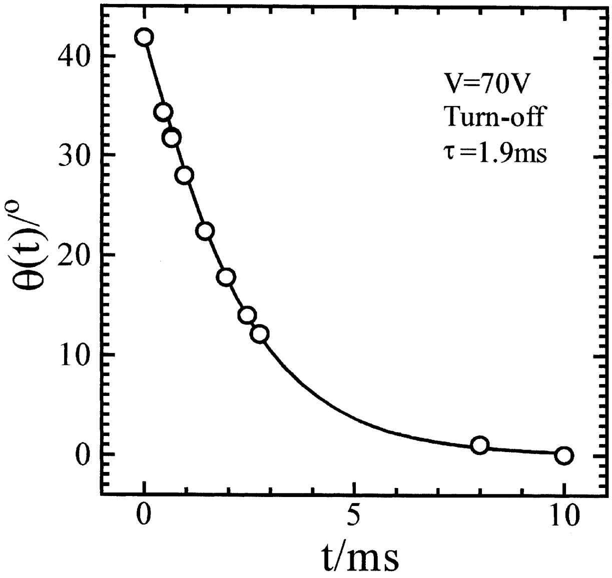

FIGURE 12 Turn-off director relaxation for 8CB-d_2 at 306.3 K. Experiment ○: E = 1.23 MVm^{-1} solid line: best fit to Eq. (2).

TABLE 1 The Experimental Conditions and Values of the Relaxation Times, Rotational Viscosity Coefficient and Other Parameters

T/K	306.3	308.3
$(T_{NI} - T)$/K	5.8	3.8
τ_{on}/ms	1.25	0.98
$\theta_{\infty}/^{\circ}$	33.0	33.0
$\tau_{off}(1)^{d}$/ms	1.90	1.49[a]
$\theta_0/^{\circ}(1)^{d}$	33.	–
$\tau_{off}(2)^{d}$/ms	1.90	1.49[a]
$\theta_0/^{\circ}(2)^{d}$	42.0	–
$\alpha/^{\circ}$	52.2	52.2
$\Delta\varepsilon^{b}$	8.2	7.95
$\Delta\chi \times 10^6$	1.00	0.97[c]
$(\Delta\chi/\Delta\varepsilon) \times 10^6$	0.121	0.121[c]
γ_1/Pas	0.075	0.057

[a] Calculated by considering $\tau_{off}/\tau_{on} = 1.52$ to be temperature independent [7].

[b] Data from ref. [12].

[c] Calculated by assuming the ratio $(\Delta\chi/\Delta\varepsilon)$ to be temperature independent.

[d] (1) Refer to turn-off at $\theta_0 = 33^{\circ}$ and (2) to turn-off at $\theta_0 = 42^{\circ}$.

TABLE 2 Values of the Rotational Viscosity Coefficient at Different Temperatures: Comparison with the Results Found by Martins [14]

$(T_{NI} - T)$/K	5.8	4.8	3.8	2.8	
γ_1/Pas		0.084	0.073	0.062	Martins [14]
γ_1/Pas	0.075		0.057		This work

transition temperatures of the samples used as well as differences in the accuracy of the experimental techniques employed.

As a matter of general interest, the viscosity coefficients for 8CB at the same value of the shifted temperature $(T_{NI} - T)$ appear to be higher than those for 5CB by about 50% [7]; this is presumably associated with the longer alkyl chain (chain entanglement) and the existence of the smectic phase in 8CB (pretransitional effects).

CONCLUSIONS

We have used deuterium NMR spectroscopy to study the dynamics of the field-induced director relaxation of 8CB-d_2 in the nematic phase at 306.3 K and 308.3 K when an electric field is switched on and off. During the relaxation process the director was observed to move as a monodomain. The director relaxation was found to follow strictly the predictions of the torque-balance equation. Two relaxation times were measured at 306.3 K: τ_{on} when the electric field is turned on (in the presence of the magnetic field of the spectrometer) and τ_{off} when the electric field is turned off. We also measured τ_{on} at 308.3 K. From these measurements and the literature data for $\Delta\varepsilon$ we have calculated the values of the rotational viscosity coefficient at 306.3 K and 308.3 K as well as the values of the diamagnetic susceptibility at these two temperatures. The values of the rotational viscosity coefficient for 8CB appear to be higher by about 50% than those for 5CB at the same shifted temperature possibly because of the longer flexible chain which could give rise to a greater degree of chain entanglement and the pretransitional effects associated with the existence of the smectic phase in 8CB.

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