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A Deuterium Nuclear Magnetic Resonance Investigation of the Director Distribution in a Thin Nematic Liquid Crystal Slab

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The director distribution in a thin nematic liquid crystal (NLC), 4-pentyl-d_2-4′-cyanobiphenyl (5CB-d_2) deuteriated in the α-position of the pentyl chain, confined between two glass plates, with untreated and treated anchoring conditions, has been investigated using a deuterium nuclear magnetic resonance (NMR).

The NMR spectra have been measured as a function of the applied electric field. In the absence of surface forces it is found that the director aligns parallel to the magnetic field at relatively low values of the electric field as $\Delta\widetilde{\chi}$ is positive for 5CB. Then as the electric field is increased the director remains parallel to the magnetic field until some critical value of the electric field, at which point the director is aligned parallel to the electric field and hence perpendicular to the magnetic field, since $\Delta\widetilde{\varepsilon}$ is positive for 5CB. In the presence of surface forces with increasing electric field the quadrupolar splitting decreases, passes through zero and then increases again to a value which is essentially half of that at zero electric field. That is, the director orientation changes more or less continuously from being parallel to the magnetic field to being orthogonal to it, as the electric field grows.

Keywords: nematic liquid crystal; director distribution; surface anchoring; deuterium nuclear magnetic resonance; continuum theory

1. INTRODUCTION

There is considerable interest in the director distribution in the bulk and at the surfaces of a nematic liquid crystal (NLC) cell, in both basic science and technology [1,2]. It is well known that the director distribution in the bulk of a LC cell is affected by the substrate surface, as well as by externally applied fields, such as electric and magnetic fields. The nematic phase is especially sensitive to external agents, in particular, to surface forces. Macroscopically, the surface effects are manifested in the director orientation in the bulk.

It is important in investigating the director distribution affected by the surface anchoring in an NLC slab to understand the director distribution directly from observation of the NLC slab. Optical methods to measure the director distribution in a NLC cell are reported in the literatures [3,4]. Nuclear magnetic resonance (NMR) spectroscopy is one of the best methods to investigate the director distribution because the spectrum observed is the sum of spectra from each director orientation. Although various magnetic nuclei have been employed in NMR studies of liquid crystals, deuterium has probably been the most informative for non-rigid molecules [5]. Recently deuterium NMR is used to investigate the director distribution in 5CB confined in micro tubes [6]. However there are a few reports on the applications of a proton NMR [7,8] to thin liquid crystal layers.

In this study we have used deuterium nuclear magnetic resonance to investigate the director distribution in 5CB, confined between two glass plates and subject to both magnetic and electric fields.

2. THEORETICAL FRAMEWORK

Deuterium has a nuclear spin of one and so possesses a quadrupole moment, which interacts with the electric field gradient at the nucleus, to give a quadrupolar interaction tensor. This does not influence the number of lines in the deuterium NMR spectrum for a normal liquid because the rapid and random molecular motion averages the quadrupolar interaction to zero. The NMR spectrum of a single deuteron therefore contains a single line composed of a pair of degenerate transitions. In a uniform, orientationally ordered phase, provided the molecular motion is still fast, the degeneracy of the transitions is removed and the spectrum contains two lines of equal intensity, as indicated schematically in Fig.1. The separation, $\Delta\tilde{\nu}$, between the quadrupolar split lines is related to the components of the Saupe ordering matrix and the quadrupolar tensor, $\mathbf{q}$. However, for aliphatic deuterons the quadrupolar tensor is, to a good approximation,

cylindrically symmetric about the C-D bond direction, and then the quadrupolar splitting is given by [9]

$$\tilde{\nu} = (3/2) q_{CD} S_{CD} = \Delta\tilde{\nu}_o , \qquad (1)$$

where S_{CD} is the orientational order parameter for the C-D axis and q_{CD} is quadrupolar coupling constant. Typical deuterium NMR spectra in the isotropic and nematic phases for a single deuteron in a C-D bond are shown in Fig.1 (a) and (b).

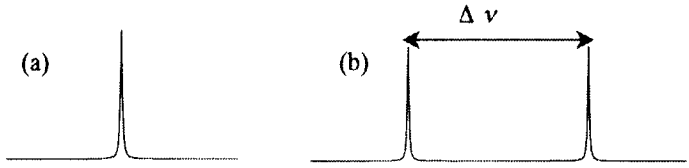

Figure 1. A typical deuterium NMR spectrum of a single deuteron in an isotropic phase (a) and a partially ordered system (b)

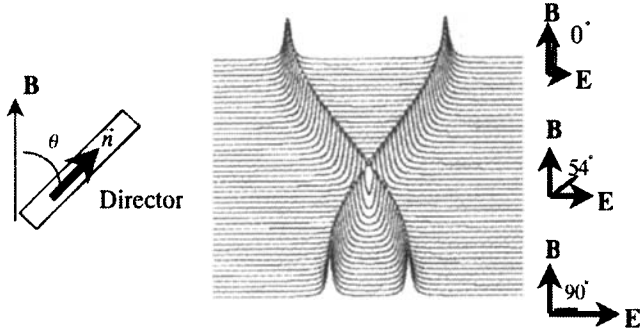

Figure 2. Angular dependence of deuterium NMR spectrum, θ is the angle between the director and the magnetic field. The value of the angle θ is increased from 0 to 90^0 in steps of 2 degrees.

In this analysis the director is taken to be parallel to the magnetic field. However, when the angle the director makes with the magnetic field changes, the splitting will also change in a well-defined angular way. The value of the splitting at any angle θ the director makes with the magnetic field is now given by multiplying $\Delta\tilde{\nu}$ from Eq.(1) by a $P_2(\cos\theta)$ angular factor so we have

$$\Delta\tilde{\nu} = \Delta\tilde{\nu}_o P_2(\cos\theta) = \Delta\tilde{\nu}_o (3\cos^2\theta - 1)/2 , \qquad (2)$$

where θ is the angle between the director and the field. Equation (2) shows that with increasing θ the quadrupolar splitting decreases, passes through zero and then increases again to a value which at θ=90° is half

that at theta=0 as illustrated in Fig.2. When the angle theta is 54.74° - the so called magic angle - the angular factor $P_2(\cos\theta)$ is zero and hence the quadrupolar splitting is zero. This is clearly shown in Fig.2.

Deuterium NMR could provide a very good method for investigating the director distribution in a thin NLC cell subject to an electric field because of the sensitivity of the NMR spectrum to the director orientation as given by Eq.(2) and illustrated in Fig.2. By varying the intensity of the electric field, the total balance of the magnetic field, the electric field, the surface force and the elastic torque can be controlled. In other words the application of an electric field makes it possible to investigate the director distribution in a thin NLC cell even in the presence of the strong magnetic field of the NMR spectrometer.

We now consider the total free energy, G, of the system in order to understand the director distribution in a thin nematic cell subject to both magnetic and electric fields. Here G contains four terms associated with elastic distortions, G_d, surface anchoring, G_s, and with interactions of the cell with the two fields, G_m and G_e; that is,

$$G=\int (G_d + G_m + G_e)dz + G_s \,, \tag{3}$$

where the integral is over the z coordinate (corresponding to the direction normal to the glass plates). The coordinate system defined by our experiments and used in the calculations is shown in Fig.3, in which the magnetic and electric fields are applied parallel and normal to the glass plates, respectively.

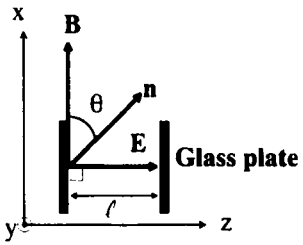

Figure 3. The geometry of the coordinate system used in our calculations

Because of the large difference in the magnitudes of the electric and magnetic susceptibilities of liquid crystals, the field energy terms have different forms. In the case of the magnetic field, the diamagnetic susceptibility is small ($\tilde{\chi} \sim 10^{-6}$) so that the cell does not significantly perturb the applied field. In the case of the electric field, both the

permittivity and the permittivity anisotropy are large so that the electric field and the displacement can be significantly altered by the presence of the cell [10]. The orientation dependent free energy associated with the magnetic field can be written as

$$G_m = -\Delta\tilde{\chi}/(2\mu_0)(\boldsymbol{B}\cdot\boldsymbol{n})^2, \tag{4}$$

where μ_0 is the permeability of free space, $\boldsymbol{B}=\mu_0\boldsymbol{H}$, and $\Delta\tilde{\chi}$ is the anisotropy of the diamagnetic susceptibility of the material. The free energy due to the electric field is of the form

$$G_e=-\varepsilon_o\Delta\tilde{\varepsilon}\,(\boldsymbol{E}\cdot\boldsymbol{n})^2/2, \tag{5}$$

where ε_0 is the permittivity of free space. The application of a voltage across the bulk results in an electric displacement $\boldsymbol{D}$,

$$D_\alpha = \varepsilon_o\tilde{\varepsilon}_\perp E_\alpha + \varepsilon_o(\tilde{\varepsilon} - \tilde{\varepsilon}_\perp)n_\alpha n_\beta E_\beta, \tag{6}$$

where $\tilde{\varepsilon}_{\parallel}$ and $\tilde{\varepsilon}_\perp$ are the principal values of the bulk dielectric susceptibility tensor, parallel and normal to the director. Assuming that $\boldsymbol{D}$ and $\boldsymbol{E}$ vary only in the z direction, and neglecting the effects of space charge, $\nabla\cdot\boldsymbol{D}=0$ implies that D_z is a constant across the bulk. D_z can be found from Eq.(6) as

$$D_z = \left[\varepsilon_o\tilde{\varepsilon}_\perp E_\alpha + \varepsilon_o\Delta\tilde{\varepsilon}\sin^2\theta(z)\right]E(z), \tag{7}$$

The surface anchoring energy, G_S, may be expressed as [1]

$$G_S=-(A/2)(\boldsymbol{n}\cdot\boldsymbol{e})^2. \tag{8}$$

Here A is a surface anchoring strength and $\boldsymbol{e}$ is the easy direction or the anchoring direction.

From Fig 3, the director $\boldsymbol{n}$, electric field $\boldsymbol{E}$, and magnetic field $\boldsymbol{B}$ can be written as

$$\boldsymbol{n}=(\cos\theta(z),\ 0,\ \sin\theta(z)), \tag{9}$$

$$\boldsymbol{E}=(0,\ 0,\ E(z)), \tag{10}$$

$$\boldsymbol{B}=(B,\ 0,\ 0). \tag{11}$$

The normal Euler-Lagrange approach to minimize the total free energy, including the unified surface anchoring energy, leads to the basic equations from which to calculate the director distribution $\theta(z)$ [see Eqs. (18), (19), (22), and (23) in Ref. 11]. They can be expressed as

$$f(\theta(z))\frac{d^2\theta(z)}{dz^2} + \frac{1}{2}\frac{df(\theta(z))}{dz}\left(\frac{d\theta(z)}{dz}\right)^2 = \left[\frac{\Delta\tilde{\chi}}{2\mu_o}B^2 - \frac{\varepsilon_o\Delta\tilde{\varepsilon}}{2}E^2(z)\right]\sin 2\theta(z), \tag{12}$$

$$f(\theta(z))\frac{d\theta(z)}{dz}\bigg|_{z=0} = \frac{A^-}{2}\sin 2(\theta^{o-} - \theta_{0-}), \tag{13}$$

$$f(\theta(z))\frac{d\theta(z)}{dz}\bigg|_{z=l} = -\frac{A^+}{2}\sin 2(\theta^{o+} - \theta_{o-}), \tag{14}$$

$$\frac{d}{dz}\left[\varepsilon_o \tilde{\varepsilon}_\perp + \varepsilon_o \Delta\tilde{\varepsilon} \sin^2\theta(z)\right] E(z) = 0, \; V = \int_0^{\ell} E(z)dz, \tag{15}$$

where $f(\theta(z)) = k_{11}\cos^2\theta(z) + k_{33}\sin^2\theta(z)$, and k_{11} and k_{33} are the splay and bend elastic constants of the NLC, respectively. ℓ is the bulk thickness, V is the voltage applied to the NLC cell, and θ^{0-} and θ^{0+} are the pretilt angles of the surface directors at z=0 and z= ℓ, respectively. θ_{0-} and θ_{0+} are the pretilt angles of the easy axis at z=0 and z= ℓ, respectively. A^- and A^+ are surface anchoring strengths at z=0 and z= ℓ, respectively. In our case we set $\theta^0 = \theta^{0-}$, $\theta_0 = \theta_{0-} = -\theta_{0+}$ and $A = A^- = A^+$. Torque balance equations at both surfaces, Eqs. (13)-(14), give boundary conditions to solve the torque balance equation in the bulk, Eq. (12), and the perturbation of the electric field, Eq.(15). Numerical solution of Eqs. (12)-(15) gives the voltage dependence of the director distribution across the NLC bulk.

3. EXPERIMENTAL

The deuterium NMR experimental setup is shown schematically in Fig.4. A JEOL Lambda 300 spectrometer (B=7.05T) was used in our experiments. The NLC cell was set so that the glass surfaces

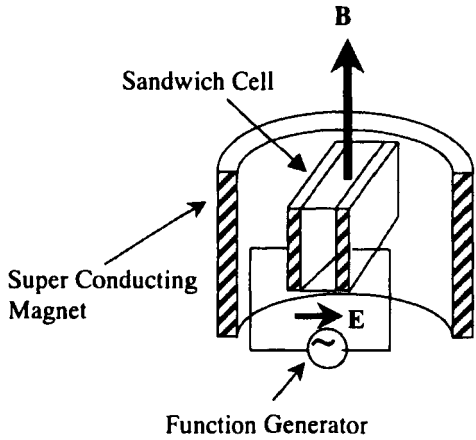

Figure 4. Deuterium NMR experimental setup

were parallel to the magnetic field. In our experiment the projection of the easy axis onto the glass surface is parallel to the magnetic. The electric field of 1kHz was applied normal to the glass surface. This

frequency is sufficient to overcome the effects of mobile ionic conduction. By changing the intensity of the electric field, the director orientation rotates in a plane defined by ***B*** and ***E***. The NLC used in our study was 5CB-d2, which was specifically deuteriated in the α-position of the alkyl chain (Fig. 5); the diamagnetic anisotropy ($\Delta\chi$) and dielectric anisotropy ($\Delta\varepsilon$) are both positive.

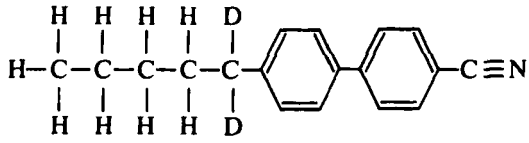

Figure 5. Structure of 5CB-d_2 used in the deuterium NMR spectroscopy

Three thin NLC sandwich cells of different thickness and anchoring strength were used. The glass plates of the cells are coated with a thin layer of transparent In_2O_3 to act as electrodes. The glass surface of the thickest cell, 100μm thickness, was untreated to give zero anchoring strength. The surfaces of the second cell, of 55.7μm thickness, were rubbed unidirectionally in a parallel manner to produce a homogeneous director orientation. The surface anchoring strength was measured using a saturation voltage method [12] and was found to be $A = 7.5\times 10^{-5}$J/m^2. This corresponds to the so-called weak anchoring condition. The surfaces of the third cell, of 55.5μm thickness, was coated with a thin polyimide film and also rubbed unidirectionally in a parallel manner to produce a homogeneous director orientation. The surface anchoring strength was found to be $A = 6.4\times 10^{-4}$J/m^2. This corresponds to the so-called strong anchoring condition. All the deuterium NMR measurements were carried out at a constant temperature of 298K.

4. RESULTS AND DISCUSSION

The deuterium NMR spectra measured as a function of the applied electric field for the NLC cell with a thickness of 100μm are shown in Fig.6. The voltage dependence of the quadrupolar splitting for the case of no surface forces shows that the director aligns parallel to the magnetic field. Then as the electric field is increased the director remains parallel to the magnetic field until at some critical value of the

electric field strength, at which point the director alignment is changed to parallel to the electric field and hence perpendicular to the magnetic field. This voltage dependence of the quadrupolar splitting can be understood from considering Eq.(12) only since the surface anchoring strength (Eqs.(13)-(14)) is zero in this case and director deformation due to surface effects can be ignored. It means that there is no director deformation in the bulk and the director distributes as being a monodomain in the bulk. That is, the left side of Eq.(12) can be set to be zero and Eq.(12) gives two kids of solutions. One is that the director orients parallel to the magnetic field. This gives a spectrum with maximum splitting. The other is the director orientation parallel to the electric field and this gives a spectrum with half the value of the splitting at zero electric field. However, as seen in Fig. 6, two doublets appear at V=62V. The simultaneous appearance of the two doublets is

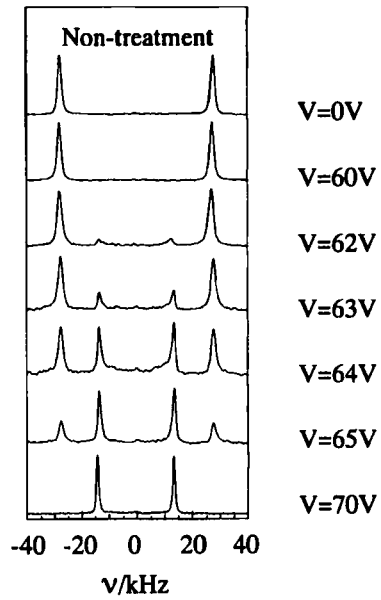

Figure 6. Voltage dependence of the deuterium NMR spectra at 298K for the 100 μm cell with untreated glass surfaces.

due to the inhomogeneity of the thickness of the liquid crystal film. The exact thickness of the nominal 100μm cell is uncertain, as we do not have a method of accurately measuring the thickness and its variation over the entire cell; we are, therefore, using the nominal value of the spacer given by the supplier. If the thickness variation over the entire cell is say from 100μm to 105μm, the electric field strength over the entire bulk has a gradient sufficiently large to give the two doublets shown in Fig.6 in the voltage range 62 to 65V.

The deuterium NMR spectra measured for the NLC cell (55.7 μm thick) with weak anchoring condition are shown in Fig.7(a). The voltage dependence of the quadrupolar splitting shows that with

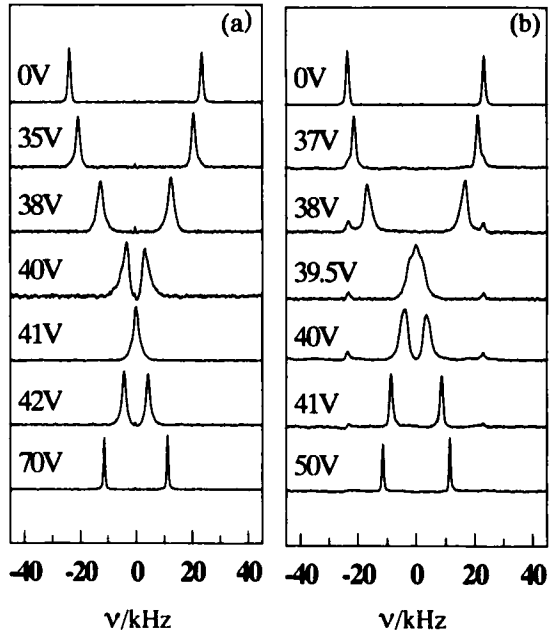

Figure 7 The deuterium NMR spectra measured at 298K for two NLC cells (a) 55.7 μm cell with weak anchoring condition and (b) 55.5 μm with strong anchoring condition.

increasing electric field strength the spacing between the lines is reduced, passes through zero and then increases again to a value which is essentially half of that at zero electric field. It would seem that the director orientation changes more or less continuously from being parallel to the magnetic field to being orthogonal to it, as the electric field grows. This change of the quadrupolar splitting follows the pattern illustrated in Fig.(2) on the basis of Eq.(2). Also as the electric field is increased, the lines appear to broaden leading to a decrease in the signal-to-noise ratio. For higher electric fields, however, the lines sharpen up again resulting in an improved signal-to-noise ratio. Thus the experimental results indicate a change in the director orientation with increasing field and a slight broadening of the director distribution in the bulk.

The deuterium NMR spectra measured for the NLC cell with a strong anchoring condition are shown in Fig.7 (b). The trend of the voltage dependence of the quadrupolar splitting is similar to that for the weak anchoring cell as shown in Fig.7 (a). However, there is one significant deference between the spectra for the NLC cells with weak and strong anchoring conditions. In the case of the strong cell we observe, for voltages ranging from 38 to 41V, another doublet of lower intensity but with large quadrupolar splitting which of similar value to the splitting at V=0. It would seem that, because of the strong anchoring condition, the director near the substrate surface orients more or less parallel to the magnetic field even in the presence of relatively high electric field.

The voltage dependence of the deuterium NMR spectra shown in Figs.7 (a) and (b) reflects the director distribution throughout the sample, which is determined by the unified surface anchoring, elastic, magnetic, and electric energies. The director distribution is obtained theoretically via the numerical solution of Eqs. (12)-(15) as a function of the electric field. The deuterium NMR spectra can then be simulated by using these director distributions. The overall NMR spectrum is obtained by dividing the nematic slab into very thin layers, calculating the expected spectrum for each layer from the director distribution and then adding together all these individual spectra. Rigorous simulations of the director distribution and deuterium NMR spectra are now under progress.

5. CONCLUSION

Deuterium NMR has been employed to investigate the director distribution in a thin NLC cell. The dependence of the quadrupolar

splitting on the electric field strength have been measured for three kinds of cells: one with no surface forces, the second with weak and the third with strong anchoring forces. No surface forces shows, at a certain critical value of the electric field strength, a sudden change of director orientation from being parallel to the magnetic field to being parallel to the electric field. This behaviour was explained according to Eq.(12) when the left side is set equal to zero. For the cell with weak anchoring forces, the director orientation changes continuously from being parallel to the magnetic field to being orthogonal to it. The cell with strong anchoring forces showed not only a continuous change in the director orientation as in the weak anchoring cell but also the appearance of a doublet due to the presence of a small, but significant, fraction of the NLC cell in which the director is still aligning more or less parallel to surface of the glass plates. We have interpreted these results in terms of changes in the director distribution due to the presence of surface anchoring, elastic as well as electric and magnetic energies (Eqs. (12)-(14)). The director orientation changes continuously from being parallel to the magnetic field to being orthogonal to it, as the electric field grows, for the cell with weak and strong anchoring forces. Our experimental results clearly show that deuterium NMR is a very valuable technique with which to investigate the director distribution in thin liquid crystal cells. The exact prediction of the deuterium NMR spectra is now under progress.

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References

[1] B. Jérôme, *Rep. Prog. Phys.* **54,** 391(1991).
[2] L.M. Blinov and V.G. Chigrinov, *Electrooptic Effects in Liquid Crystal Materials* (Springer-Verlag, New York, 1994), p.118.
[3] F. Yang and J.R. Sambles, *Mol. Cryst. Liq. Cryst.* **250,** 143(1994).
[4] H. Toriumi, T. Akahane, M. Kimura, T. Tadokoro, and K. Akao, Proceedings of the Fourth International Display Workshops (Nagoya, Japan), 49(1997).
[5] see, for example, *NMR of Liquid Crystals,* ed. J.W. Emsley (Reidel, Dordrecht, 1–985).
[6] G.P. Crawford, R.J. Ondris-Crawford and J.W. Doane, *Phys. Rev. E* **53,** 3647(1996).
[7] J.C. Rowell, W.D. Phillips, L.R. Melby and M. Panar, *J. Chem. Phys.* **43,** 3442(1965).
[8] M. Winkler, D. Geschke and P. Holstein, *Liq. Cryst.* **17,** 283(1994).
[9] G.R. Luckhurst, J. Chem. Soc., *Faraday Trans. 2,* **84,** 961(1988).
[10] H.J. Deuling, E. Guyon and P. Pieranski, *Solid State Commu.* **15,** 277(1974).
[11] A. Sugimura, G.R. Luckhurst and Z. Ou-Yang, *Phys. Rev. E* **52,** 681(1995).
[12] A. Sugimura, T. Miyamoto, M. Tsuji, and M. Kuze, *Appl. Phys. Lett.* **72,** 329(1998).