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# A Deuterium Nuclear Magnetic Resonance Investigation of Field Induced Director Dynamics in a Nematic Slab Subject to Magnetic and Pulsed Electric Fields

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Deuterium nuclear magnetic resonance (NMR) spectroscopy has been used to investigate the field-induced director dynamics in a nematic liquid crystal, 4-pentyl-$d_2$-4′-cyanobiphenyl (5CB-$d_2$) deuteriated in the α-position of the pentyl chain, confined between two glass plates. The NMR spectra have been measured as a function of time after turning an electric field on and off. It is demonstrated that the field-induced director dynamics in the nematic liquid crystal cells can be successfully time-resolved. In addition, it is found that the doublet NMR spectra become powder-like during the turn-on and turn-off processes. It is shown that the rotational viscosity and the diamagnetic anisotropy of 5CB-$d_2$ can be determined from the time-resolved NMR spectra by assuming uniform alignment of the director.

*Keywords:* director dynamics; rotational viscosity; diamagnetic anisotropy; deuterium nuclear magnetic resonance

## INTRODUCTION

Nuclear magnetic resonance (NMR) has been widely used in the study of liquid crystals. The effect of an electric field on the NMR spectra of a nematic was first demonstrated using proton NMR [1]. Recently, deuterium NMR has been widely used in the investigation of liquid crystals in particular because the deuterium NMR spectra of specifically or fully deuteriated materials are simple compared to the proton NMR spectra [1-4]. The quadrupolar splitting from deuterons observed in the liquid crystal phase is related to the orientational order parameter and so deuterium NMR has been widely used for the study of the orientational order of liquid crystals and their phase transitions [2]. The quadrupolar splitting is also related to the angle made by the director with the magnetic field. Hence, deuterium NMR spectroscopy is expected to be a powerful method with which to investigate the director orientation and distribution, for example, in a nematic liquid crystal slab (capacitance [5] or optical [6] methods have often been used for this purpose but these methods give only the spatial average of the director distribution). However, the director distribution in a thin nematic slab has not yet been studied with deuterium NMR spectroscopy. It is well-known that director distributions in nematic slabs are affected by the substrate surface as well as by externally applied fields. Precise information concerning the director distribution is important both scientifically and technologically, from it the interaction between substrate surfaces and nematogenic molecules could be understood and the design of nematic displays could be improved.

In this paper, we describe our experiments using deuterium NMR spectroscopy to investigate the field-induced director dynamics in 5CB-$d_2$ slabs, that is, the time dependence of the director orientation during and after the application of an electric field. The director dynamics in thin nematic slabs are, in principle, complex because of the influence of the substrate surfaces. To avoid such complexity and to elucidate the director dynamics in the bulk nematic slabs, we have carried out deuterium NMR experiments in slabs ~100μm thick. Information on the field-induced director dynamics in such thick slabs is important to help understand the influence of the substrate surfaces on that in thin nematic slabs.

## EXPERIMENT

Sample preparation

The nematogen chosen for our study was 5CB-$d_2$, which was specifically deuteriated in the $\alpha$-position of the pentyl chain of 4-pentyl-4'-cyanobiphenyl (5CB); the diamagnetic anisotropy ($\Delta\tilde{\chi}$) and dielectric anisotropy ($\Delta\tilde{\varepsilon}$) are both positive. A cell was prepared in which 5CB-$d_2$ was contained between two glass plates coated with transparent $In_2O_3$ electrodes separated by 100 μm mylar spacers. The transparent electrodes were coated with polyimide and the surface of the polyimide was rubbed unidirectionally in a parallel manner for a uniform planar director orientation. A JEOL Lambda 300 NMR spectrometer (B=7.05T) was used to record the NMR spectra. The nematic cell was set so that the glass plates were parallel to the magnetic field and an electric field was applied normal to the surface of the glass plates (see Fig. 1). When the electric field was turned on, the director moved towards the electric field in a plane defined by **E** and **B**. After the electric field was turned off, the director moved until it was aligned parallel to the magnetic field. All of the measurements were made at 293 K.

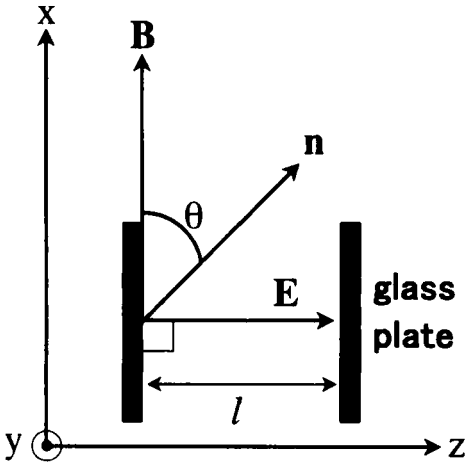


FIGURE 1 The sample geometry and definition of the angle θ between the director and the magnetic field. The cell thickness is denoted by *l*. The magnetic field (**B**), electric field (**E**) and director (**n**) are in the xz plane.

DNMR pulse sequences

Figures 2(a) and 2(b) show schematically the pulse sequences for the observation of the turn-on and turn-off processes, respectively. To obtain a good signal-to-noise ratio, the deuterium NMR spectrum was obtained by repeating these pulse sequences more than 10 thousand times. The 90° pulse is 6μs and the delay between successive pulses after the acquisition of a free-induction decay (FID) is 100 ms, these were obtained using a quadrupplar echo sequence.

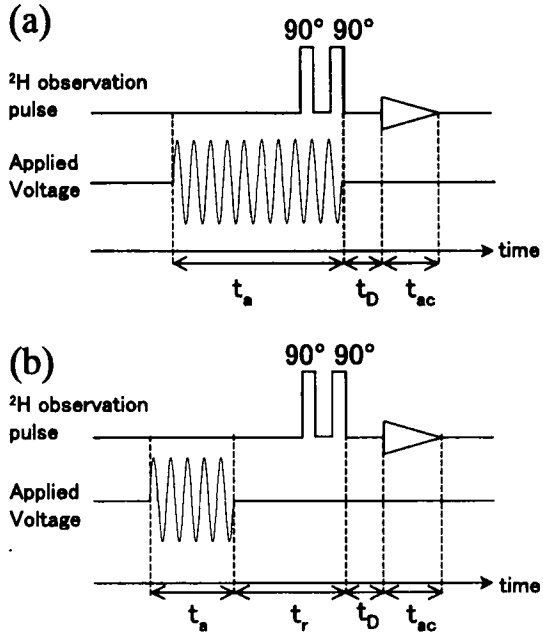


FIGURE 2 The pulse sequences for the observation of (a) the turn-on and (b) the turn-off processes. The triangular symbols in the $^2H$ observation pulse sequences denote data acquisition. $t_a$ is the time during which the external voltage is applied, $t_r$ is the time allowed for director relaxation, $t_D$ (~ 4 μs) is the dead time of the receiver coil, and $t_{ac}$ (~ 54 ms) is the acquisition time for the free-induction decay. The acquired free-induction decay corresponds to that collected just after the second 90° pulse. For the turn-on process, $t_a$ was changed over the range 0 to 100 ms. For the turn-off process, $t_a$ was 50 ms and $t_r$ was varied in the range 0 to 10 ms.

To observe the turn-on process, the deuterium NMR spectrum was measured after the application of a sinusoidal voltage (70.7 $V_{rms}$) to the cell for a time $t_a$ (see Fig. 2(a)). The applied voltage had a frequency 10 kHz; this was used in order to achieve a time resolution of 0.1 ms. Deuterium NMR spectra, which reflect the director dynamics, were observed by changing $t_a$ from 0 to 100 ms. $t_D$ is the dead time of the receiver coil and $t_{ac}$ is the acquisition time for the free-induction decay.

To observe the turn-off process, the deuterium NMR spectrum was measured after the applied voltage was turned off (see Fig. 2(b)). First, the sinusoidal voltage (65.0 $V_{rms}$) was applied to the cell for a time $t_a$ in order to make $\theta=40°$. Then, the sinusoidal voltage was turned off, so that the director began to relax from $\theta=40°$ to parallel to the magnetic field. The relaxation of the director distribution was observed in the time range $0 \leq t_r \leq 10$ ms. The reason for choosing the observation of the relaxation from $\theta=40°$ is that the pathway for the director realignment is unique. In the relaxation process from $\theta=90°$ to 0°, the spectra expected during this realignment process should be much more complex due to the degeneracy of the realignment pathway of the director from $\theta=90°$ [3]. We have observed this more complex behaviour in the relaxation process from 90° for a 5CB-$d_2$ sample but we will not be concerned with it in this paper.

## RESULTS AND DISCUSSION

Deuterium NMR spectra obtained during the turn-on and turn-off processes are shown in Figs. 3(a) and 3(b), respectively. In the turn-on process, the quadrupolar splitting decreases initially, passes through zero, and then increases with time. In the turn-off process, on the other hand, the quadrupolar splitting only increases because the director relaxes from $\theta=40°$. It can be seen from Figs. 3(a) and 3(b) that some line broadening and additional broad components are present in certain of the spectra, as well as the main quadrupolar splitting. This may be due to variation in the sample thickness (the unevenness in thickness is estimated to be possibly 5 to 10 %), which would cause a difference in the electric field response of the director at different parts of the cell. The initial director profile at t=0 ms is obtained by turning on an electric field (of 65.0 $V_{rms}$) for 50 ms which produces the same kind of spectrum as, for example, for the turn-on at 10 to 15 ms (see Fig.3(a)). Following the turn-off, the directors at

different initial orientations relax back at the same speeds merging together after ~2ms. The line broadening contains information concerning the director distribution because the deuterium NMR spectra result from a sum of signals from all director orientations in a liquid crystal cell. However, we shall not deal with this aspect of the spectra here but use only the main quadrupolar splitting for the analysis of the field-induced director dynamics. We note that analogous line broadening has been observed in the proton NMR spectra of the nematic phase of a side chain thermotropic polyacrylate under the influence of an electric field [4]. However, no information about the director distribution was obtained because proton NMR spectra are usually far more complex than deuterium NMR spectra. In contrast the director orientation can easily be 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 director distribution that causes the line broadening in the deuterium NMR spectra shown in Fig. 3 then the time dependence of the director orientation is easily determined. The deuterium NMR spectrum of a monodomain nematic with the director parallel to the magnetic field contains a quadrupolar splitting given by

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

Here $q_{CD}$ is the deuterium quadrupolar coupling constant and $S_{CD}$ is the orientational order parameter of the C-D bond direction. When a sufficiently strong electric field is applied, the director begins to align in the direction of the electric field because the dielectric anisotropy is positive for 5CB. In this case, the quadrupolar splitting is given by [7]

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

where θ is the angle between the magnetic field **B** and the director, as shown in Fig. 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 $\Delta\tilde{\nu}_0$.

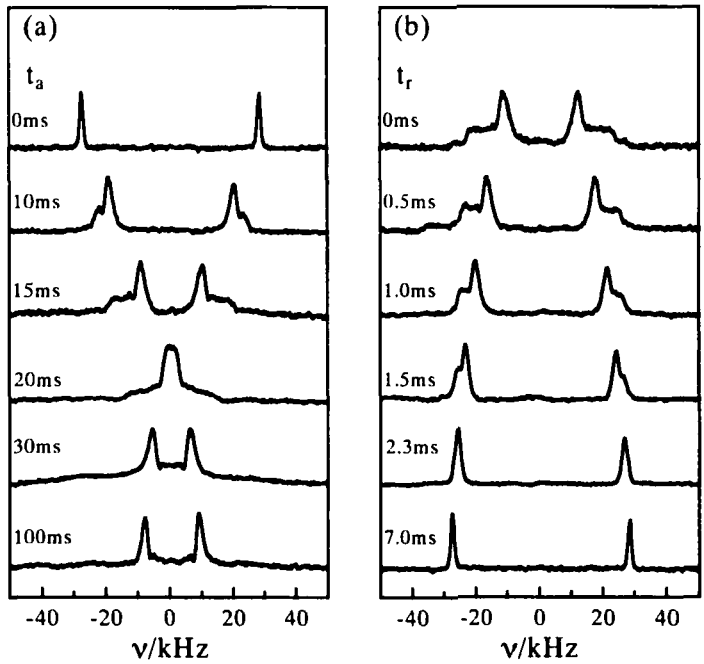


FIGURE 3 The deuterium NMR spectra for the turn-on (a) and turn-off (b) processes recorded at 293 K. In the turn-on process, the spectra were measured by changing the application time for the voltage ($t_a$). In the turn-off process, the spectra were measured at a time $t_r$ after the voltage was turned off.

According to continuum theory [8], we should consider the one-dimensional distortion of the director across the cell (see Fig. 1) because the deuterium NMR spectra show a powder-like pattern, which indicates the presence of a range of director orientations. However, all of the deuterium NMR spectra appear to be dominated by a single doublet which allows us to determine the director orientation associated with an essentially monodomain region of the sample. In this analysis, we therefore treat the director as being uniformly aligned and use the quadrupolar splitting measured for this doublet to calculate the angle between the director and the magnetic

field. In a real experiment it is difficult to set the electric field exactly perpendicular to the magnetic field (as shown in Fig.1) and so we consider here the more general experimental geometry given in Fig. 4 in which the electric field makes an angle $\alpha$ with the magnetic field. The rate of change of the director orientation is given, for the turn-on process, by the torque-balance equation [9] which for a monodomain is

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

where $\mu_0$ is the magnetic permeability and $\varepsilon_0$ is the dielectric permittivity of a vacuum.

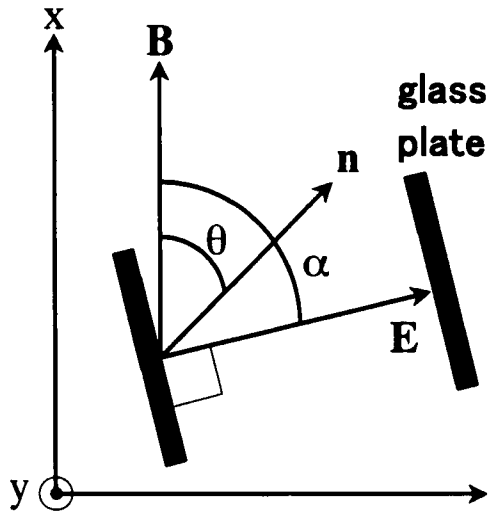


FIGURE 4 The general experimental geometry used for the continuum analysis. The director and electric field make the angles θ and α, respectively, with the magnetic field.

The solution of Eq. (3) is obtained analytically as

$$\tan(\theta(t) - \theta_\infty) = \tan(\theta_0 - \theta_\infty) \exp\left(-\frac{t}{\tau}\right) , \qquad (4)$$

where $\theta_\infty$ is the limiting value of $\theta(t)$ when t is infinity, $\tau$ is the relaxation time, and $\theta_0$ is the initial angle. The limiting value $\theta_\infty$ is given by

$$\cos 2\theta_\infty = \frac{\frac{\Delta\tilde{\chi}B^2}{2\mu_0} + \frac{\varepsilon_0\Delta\tilde{\varepsilon}E^2}{2}\cos 2\alpha}{\sqrt{\left(\frac{\Delta\tilde{\chi}B^2}{2\mu_0}\right)^2 + \left(\frac{\varepsilon_0\Delta\tilde{\varepsilon}E^2}{2}\right)^2 + 2\frac{\Delta\tilde{\chi}B^2}{2\mu_0}\frac{\varepsilon_0\Delta\tilde{\varepsilon}E^2}{2}\cos 2\alpha}} . \quad (5)$$

For the special case in which the electric field is perpendicular to the magnetic field, $\alpha$=90°, Eq. (5) reduces to

$$\cos 2\theta_\infty = \frac{\frac{\Delta\tilde{\chi}B^2}{2\mu_0} - \frac{\varepsilon_0\Delta\tilde{\varepsilon}E^2}{2}}{\sqrt{\left(\frac{\Delta\tilde{\chi}B^2}{2\mu_0} - \frac{\varepsilon_0\Delta\tilde{\varepsilon}E^2}{2}\right)^2}} = \frac{\frac{\Delta\tilde{\chi}B^2}{2\mu_0} - \frac{\varepsilon_0\Delta\tilde{\varepsilon}E^2}{2}}{\left|\frac{\Delta\tilde{\chi}B^2}{2\mu_0} - \frac{\varepsilon_0\Delta\tilde{\varepsilon}E^2}{2}\right|} . \quad (6)$$

If the magnetic torque is larger than the electric torque, $\frac{\Delta\tilde{\chi}B^2}{2\mu_0} - \frac{\varepsilon_0\Delta\tilde{\varepsilon}E^2}{2} > 0$, $\cos 2\theta_\infty = 1$ and therefore the limiting value of the angle $\theta_\infty$ is 0°. However, if the magnetic torque is smaller than the electric field, $\frac{\Delta\tilde{\chi}B^2}{2\mu_0} - \frac{\varepsilon_0\Delta\tilde{\varepsilon}E^2}{2} < 0$, $\cos 2\theta_\infty = -1$ and therefore the limiting value of the angle $\theta_\infty$ is 90°. This indicates that the director tends to align parallel to the magnetic field when the magnetic torque is larger than the electric torque or parallel to the electric field when the electric torque is larger. The relaxation times for the turn-on ($\tau_a$) and turn-off ($\tau_r$) processes are then

$$\tau_a = \frac{\gamma_1}{\sqrt{\left(\frac{\Delta\tilde{\chi}B^2}{\mu_0}\right)^2 + \left(\varepsilon_0\Delta\tilde{\varepsilon}E^2\right)^2 + 2\frac{\Delta\tilde{\chi}B^2}{\mu_0}\varepsilon_0\Delta\tilde{\varepsilon}E^2\cos 2\alpha}} \quad (7)$$

and

$$\tau_r = \frac{\gamma_1}{\Delta\tilde{\chi}\frac{B^2}{\mu_0}}, \tag{8}$$

respectively. It is evident from Eqs. (5) (7) and (8) that $\gamma_1$, $\Delta\tilde{\chi}$ and $\alpha$ can be determined by measuring $\tau_a$, $\tau_r$ and $\theta_\infty$ for given values of **E** and **B** if $\Delta\tilde{\varepsilon}$ is known.

We show in Fig. 5(a) the temporal variation in the director orientation determined from the deuterium NMR spectra using Eq. (2) for the turn-on process, in which we have substituted the experimental value $\Delta\tilde{\nu}_0 = 56.2$ kHz. We see in Fig. 5(a) that the director rotates and then aligns at the limiting angle $\theta_\infty$ of 68°.

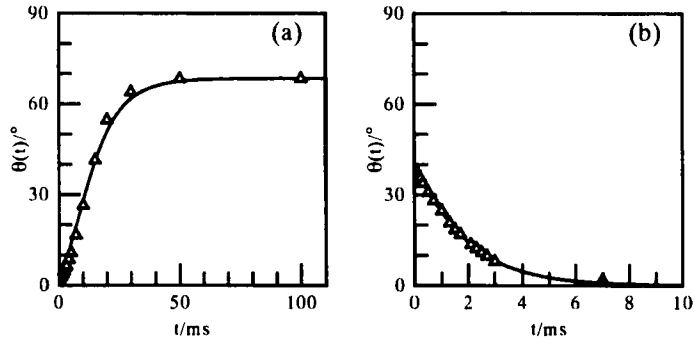


FIGURE 5 The time dependence of θ(t) for the turn-on (a) and turn-off (b) processes. For the turn-on process, the director aligns in the direction of the limiting value ($\theta_\infty$=68°) with time. For the turn-off process, θ relaxes back from $\theta_0$=40° to $\theta_\infty$=0°. The solid lines are the best fits to Eq.(4). The time constants obtained from this fitting are $\tau_a$=10.1 ms for the turn-on and $\tau_r$=1.76 ms for the turn-off.

In the turn-off process, the time-dependence of the director orientation can be obtained in the same way and is shown in Fig. 5(b). The director rotates back parallel to the magnetic field and the time taken for the alignment process is much faster in the turn-off process than in the turn-on process, this is clearly apparent from the very different timescales in Figs. 5(a) and 5(b). The large difference in the relaxation times for the turn-on and turn-off processes follows from Eqs. (7) and (8) and originates from the very different magnitudes of

the resultant torque on the director in the two cases.

The values of $\tau_a$ and $\tau_r$ are determined, from the fitted lines in Fig. 5, to be 10.1 ± 0.31 ms and 1.76 ± 0.01 ms, respectively. Using Eqs. (5), (6) and (7) and $\Delta\tilde{\varepsilon}$ =10.0 [10], the values of $\gamma_1$, $\Delta\tilde{\chi}$ and $\alpha$ are calculated to be 0.137 ± 0.001 Pa s, (1.98 ± 0.01)×10$^{-6}$ and 87.0° ± 0.1°, respectively. We note that our values of $\gamma_1$ and $\Delta\tilde{\chi}$ are in good agreement with those reported in the literature [11-13], in which the values of $\gamma_1$ and $\Delta\tilde{\chi}$ are 0.10 Pa s and 2.28×10$^{-6}$, respectively. Analogous information concerning the director dynamics could be obtained by other methods, such as capacitance [5] and transmitted light [6] measurements. However, it is difficult to determine both the rotational viscosity and the diamagnetic anisotropy at the same time. On the other hand, using deuterium NMR measurements, the rotational viscosity and diamagnetic anisotropy are both determined using the simple relation between the relaxation times for the turn-on and turn-off processes. In addition, deuterium NMR spectroscopy presents the possibility of being able to explore the spatial distribution of the director in nematic cells as a function of time during the turn-on and turn-off processes.

## CONCLUSION

Deuterium NMR spectroscopy has been employed to investigate the field-induced director dynamics in nematic slabs, 100 μm thick, and time-resolved NMR spectra have been obtained with a good signal-to-noise ratio. We have followed the director dynamics from the time dependence of the quadrupolar splittings based on the assumption that the director is uniformly aligned. From the relaxation times, we have determined the rotational viscosity coefficient and the diamagnetic anisotropy of 5CB to be 0.137 Pa s and 1.98 × 10$^{-6}$, respectively. Both of these quantities are found to be in good agreement with the literature values. We have also found that the deuterium NMR spectra of 5CB-$d_2$ slabs exhibit powder-like features during the turn-on and turn-off processes. The spatial director distributions associated with the powder-like pattern could be obtained by numerically solving the torque balance equations for the surface and the bulk of the nematic sample and then fitting these solutions to the deuterium NMR spectra. The present results indicate that deuterium NMR spectroscopy is a valuable technique with which to investigate director dynamics in thin nematic slabs.

## *References*

[1] J. C. Rowell, W. D. Phillips, L. R. Melby and M. Panar, *J. Chem. Phys.* **43,** 3442 (1965).
[2] G. R. Luckhurst, *J. Chem. Soc., Faraday Trans. 2,* **84,** 961 (1988).
[3] A. F. Martins, P. Esnault and F. Volino, *Phys. Rev. Lett.,* **57,** 1745 (1986).
[4] M. Winkler, D. Geschke and P. Holstein, *Liq. Cryst.,* **17,** 283 (1994).
[5] Hp. Schad, *J. Appl. Phys.,* **54,** 4994 (1983).
[6] Hp. Schad, G. Baur and G. Meier, *J. Chem. Phys.,* **71,** 3174 (1979).
[7] S. M. Fan, G. R. Luckhurst and S. J. Picken, *J. Chem. Phys.,* **101,** 3255 (1994).
[8] F. C. Frank, *Disc. Faraday Soc.,* **25,** 19 (1958).
[9] G. Labrunie and J. Robert, *J. Appl. Phys.,* **44,** 4869 (1973).
[10] see for example, P. J. Collings and M. Hird, *Introduction to Liquid Crystals, Chemistry and Physics* (Taylor & Francis Ltd. 1997), p197.
[11] D. A. Dunmur and W. H. Miller, *J. Physique,* **40,** 361 (1979).
[12] B. Bahadur, *Liquid Crystals-Applications and Uses Vol.1* (World Scientific Pub. Co., 1990), P.156.
[13] K. Skarp, S. T. Lagerwall and B. Stebler, *Mol. Cryst. Liq. Cryst.,* **60,** 215 (1980).