# Experimental Investigation on Pretilt Angle in Binary Liquid Crystal Composed of Highly Polar Molecules

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We report the measurement of dielectric constants, birefringence, and pretilt angle in binary mixtures of nematic liquid crystals (CP7B and CCN-47). CP7B has a strong longitudinal dipole moment and exhibits a large positive dielectric anisotropy ($\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp > 0$) and CCN-47 has a strong transverse dipole moment and exhibits a large negative dielectric anisotropy. In the mixtures, $\varepsilon_\parallel$ increases with increasing CP7B concentration, whereas $\varepsilon_\perp$ remains almost constant. We show that the pretilt angle increases with $\Delta\varepsilon$ and birefringence ($\Delta n = n_e - n_o$) much rapidly than reported earlier. It is suggested that this effect may arise due the presence of strong permanent dipole moments in the molecules.
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## 1. Introduction

The uniform alignment of liquid crystal (LC) molecules on a substrate treated with an alignment layer is important both from the technological and fundamental points of view.[1,2] There are several techniques for obtaining a uniform orientation of nematic LC director $\hat{n}$, which is the unit vector along the average orientation of the long axes of the molecules. Among all techniques, the most familiar and widely used technique is the rubbing of the substrate treated with a suitable polyimide. The rubbing provides not only a uniform alignment but also a certain pretilt angle $\theta_p$, i.e., the acute angle between the rubbing direction and $\hat{n}$ at the boundary surface. The performance of LC display devices is strongly affected by $\theta_p$. For example, a twisted nematic (TN) display made of low $\theta_p$ gives rise to undesirable light scattering because of the introduction of a reverse twist structure and the associated boundaries between two twisted structures. On the other hand, displays made of high $\theta_p$ show disturbing interference colors and have a low multiplexing capacity. Therefore, the dependence of $\theta_p$ on various factors should be known to realize optimized display performance. The important factors that determine $\theta_p$ are the chemical structures and physical properties of the LCs as well as the alignment layers. There have been several reports on the effect of the chemical structure of the alignment layer and rubbing strength on $\theta_p$.[3–7] Some studies have also been carried out to understand the effect of molecular structure, physical properties such as dielectric anisotropy ($\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$), birefringence ($\Delta n = n_e - n_o$), and the anchoring energies of the LCs on $\theta_p$.[3–5] The subscripts in the dielectric constant refer to the field direction with respect to $\hat{n}$, and those in $n$ represent extraordinary and ordinary refractive indices, respectively.

In most of these studies, several mixtures of nematic LCs made of rodlike molecules have been used. Recently, we have measured $\theta_p$ in a discotic nematic LC and found that $\theta_p$ in such a negative material is low.[7] More recently, we have also shown that a LC made of banana-shaped molecules with negative dielectric anisotropy in the nematic phase exhibits a very low $\theta_p$ (less than 1°)[8] on a rubbed polyimide surface designed to give a high $\theta_p$. These findings motivated us to carry out systematic investigations on the relationship among pretilt angle, molecular dipole, dielectric constants, and birefringence in calamitic LCs. For this purpose we chose several binary mixtures composed of two highly polar molecules. The first compound has a strong longitudinal dipole moment and exhibits a large positive dielectric anisotropy and the second one has a strong transverse dipole moment and exhibits a large negative dielectric anisotropy. In this paper, we report the measurement of the parallel ($\varepsilon_\parallel$) and perpendicular ($\varepsilon_\perp$) components of dielectric constant, birefringence, and pretilt angle as a function of the mixing ratio of the binary mixtures and show the effect of dielectric anisotropy, and birefringence on $\theta_p$.

## 2. Experiments

To realize the effect of a strong dipole moment on $\theta_p$, we have chosen two highly polar compounds. The chemical structures of the compounds are shown in Fig. 1. The compound *p*-cyanophenyl *p-n*-heptylbenzoate (CP7B) exhibits the following sequence of phase transitions: Cry 41.2 N 53.7 I. The nematic phase can be super cooled down to the ambient temperature. The compound 4′-butyl-4-heptyl-bicyclohexyl-4-carbonitrile (CCN-47) exhibits the following sequence of phase transitions: Cry 25.6 SmA 28.2 N 57.3 I. Both compounds were obtained from Merck and used without further purification. Glass plates with indium tin oxide (ITO) were spin-coated with polyimide (Nissan SE 7492) and cured at 180 °C for 30 min for the homogeneous alignment of the director. After curing, the plates were rubbed and assembled such that the rubbing directions were set antiparallel. The rubbing strength was kept fixed for all the cells. The sample was introduced into the cells in the
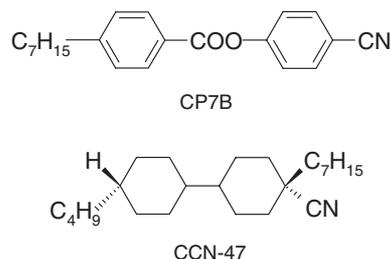


Fig. 1. Chemical structures of compounds used.

Table I. Nematic to isotropic phase transition temperatures in mixtures used.

|  | CP7B (wt %) | CCN-47 (wt %) | N–I transition temperature (°C) |
|---|---|---|---|
| Mixture-1 | 100 | 0 | 53.7 |
| Mixture-2 | 75 | 25 | 43.6 |
| Mixture-3 | 50 | 50 | 32.5 |
| Mixture-4 | 25 | 75 | 37.9 |
| Mixture-5 | 0 | 100 | 57.3 |

Table II. Pretilt angle, dielectric constant, dielectric anisotropy, and birefringence in the mixtures used.

|  | $\theta_p$ | $\varepsilon_\parallel$ | $\varepsilon_\perp$ | $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$ | $\Delta n$ |
|---|---|---|---|---|---|
| Mixture-1 | 8.5 | 29 | 9 | 20 | 0.148 |
| Mixture-2 | 6.9 | 18.1 | 10 | 8.1 | 0.117 |
| Mixture-3 | 5.1 | 14.1 | 9.1 | 5 | 0.073 |
| Mixture-4 | 5.1 | 9.4 | 8.8 | 0.6 | 0.064 |
| Mixture-5 | 2.1 | 4.0 | 9.7 | −5.7 | 0.032 |

isotropic phase and cooled slowly to the nematic phase. For homeotropic alignment, glass plates were spin-coated with polyimide (JSR JALS 204) and cured under the same condition. The temperature of the sample was controlled within an accuracy of 0.1 °C. Texture observation was carried out using a polarizing microscope. All the measurements were made while cooling the sample from the isotropic phase.

We employed a conventional crystal rotation method (CRM) for measuring the pretilt angle, which is generally used for uniaxial nematic LCs made of rodlike molecules.[9] A He–Ne laser (632.8 nm) was used to illuminate a 100-μm-thick cell and the transmitted intensity was measured as a function of the incidence angle from −45 to +45° about the axis perpendicular to the light beam and the rubbing direction. The transmitted intensity was fitted to a theoretical equation [eq. (2) in ref. 9] and $\theta_p$ was obtained as a fit parameter. The birefringence of the sample was measured at a wavelength of 550 nm using a polarizing spectrophotometer (ORC TFM-120AFT-PC) at various mixtures in the nematic phase. To determine the birefringence, the transmittance spectra were fitted to a well-known dispersion equation for nonabsorbing birefringent media where the dispersion of the refractive indices was taken care of. The dielectric measurements were conducted using an impedance analyzer (Yokogawa-Hewlett-Packard 4194A) for homogeneous and homeotropic cells. A typical cell thickness of ∼5 μm was used for measuring the birefringence and the dielectric constants. The nematic to isotropic (N–I) transition temperatures of the binary mixtures are shown in Table I. We could not measure the nematic to crystal transition temperatures because for most of the mixtures they were close or below the ambient temperature. Since we found that $\theta_p$s in all the mixtures were independent of temperature (see later), all the experiments were carried out at a fixed temperature of 30 °C and the dielectric constants were measured at a fixed frequency of 3981 Hz.

## 3. Results and Discussion

The physical properties of the pure compounds and binary mixtures are summarized in Table II. The variations in $\varepsilon_\parallel$ and $\varepsilon_\perp$ are shown in Fig. 2 as a function of the wt % of CP7B. Note that $\varepsilon_\parallel$ increases practically linearly with increasing wt % of CP7B in the mixture, whereas $\varepsilon_\perp$ remains almost constant. The increase in $\varepsilon_\parallel$ with increasing wt % of CP7B is expected as the concentration of molecules with longitudinal dipole moment increases in the mixtures. In the mixtures, the wt % of CCN-47 decreases with increasing concentration of CP7B (see Table I); hence $\varepsilon_\perp$ is expected to



Fig. 2. Variations in parallel ($\varepsilon_\parallel$) and perpendicular ($\varepsilon_\perp$) components of dielectric constant as functions of wt % of CP7B. Solid lines are drawn as guides to the eyes.
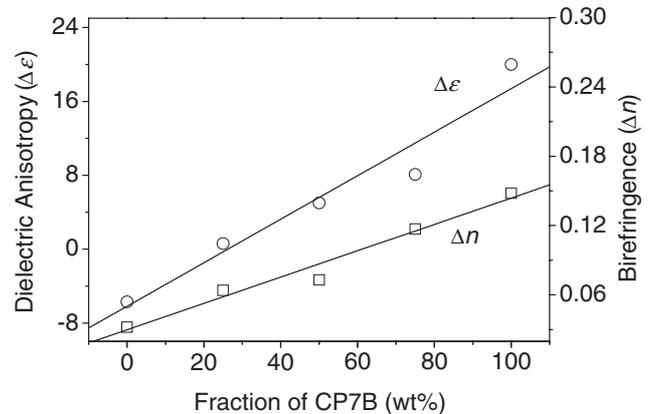


Fig. 3. Variations in dielectric anisotropy ($\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$) and birefringence ($\Delta n = n_e - n_o$) as functions of wt % of CP7B. Note the change of sign in $\Delta\varepsilon$ nearly at 25 wt % of CP7B. Solid lines represent linear fits to the data points.

decrease. However, with increasing concentration of CP7B, a transverse component of the dipole moment also contributes to the increase in $\varepsilon_\perp$ as CP7B has also a COO group at the transverse position and as a result $\varepsilon_\perp$ remains almost constant in the mixtures (see Fig. 2).

The variation in dielectric anisotropy as well as birefringence as a function of the wt % of CP7B is shown in Fig. 3. We use a least-squares method to fit the experimental data and notice that both quantities vary linearly. We also notice that the dielectric anisotropy changes sign nearly at 25 wt % of CP7B. In Fig. 4, the variation in $\theta_p$ is shown as a function of $\varepsilon_\parallel$ in the mixtures. Note that initially $\theta_p$ increases with $\varepsilon_\parallel$ and tends to saturate further. A similar observation was
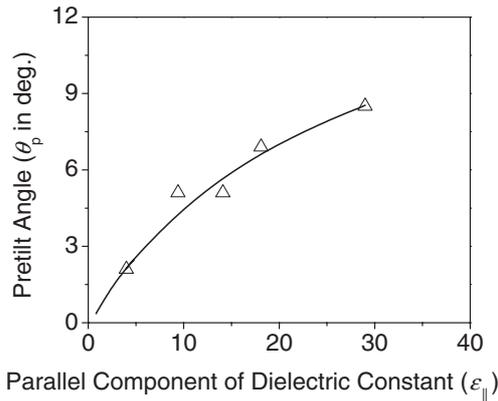
Fig. 4.   Variations in pretilt angle as function of parallel component of dielectric constant ($\varepsilon_\parallel$). A solid line is drawn as a guide to the eyes.



Fig. 6.   Variations in pretilt angle as function of birefringence. Open circles correspond to data of our binary mixtures and data corresponding to the open squares are obtained from ref. 4. Solid lines represent linear fits to the data points.
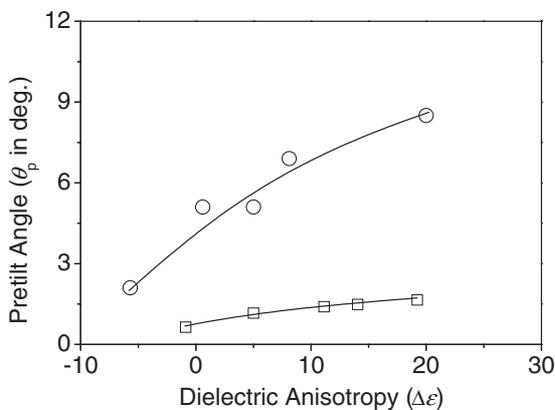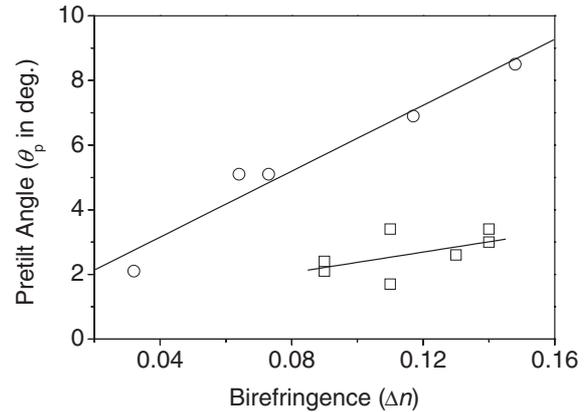


Fig. 5.   Variations in pretilt angle as function of dielectric anisotropy ($\Delta\varepsilon$). Open circles represent the data points corresponding to our binary mixtures. Data corresponding to the open squares are collected from ref. 11. Solid lines are drawn as guides to the eye.

reported by Sawada *et al.*[10] in several multicomponent mixtures of nematic LCs. They suggested that this effect was due to the dipole–dipole interaction between the nematic LC and the alignment film. The generation of the pretilt angle in nematic LCs with negative dielectric anisotropy and cyano mixtures on a rubbed polyimide surface was studied by Seo *et al.*[5] They reported that $\theta_p$ is independent of the perpendicular component of the dielectric constant in systems with positive dielectric anisotropy. The variation in $\theta_p$ as a function of $\Delta\varepsilon$ is shown in Fig. 5. We observe that $\theta_p$ increases with increasing dielectric anisotropy and tends to saturate further at higher values of the dielectric anisotropy of the mixtures. A similar observation was reported by Becker *et al.*[11] They have measured $\theta_p$ using a magneto-optical null method on several mixtures, namely, ZLI-1085, ZLI-1957/5, ZLI-1132, RQTN-605, and ROTN-403. It has also been shown by Nishikawa *et al.*[4] that $\theta_p$ increases linearly with $\Delta\varepsilon$. However, in their experiments, the exact composition of LCs was unknown.

Summarizing all these data including the present ones, we can suggest that $\theta_p$ is affected by the interaction between the strong permanent and induced electric dipole moments in the LC molecules and the dielectric anisotropy of the polymer, as mentioned by Becker *et al.*[11] We compare our pretilt

angle data (open circles) with their reported values (open squares) against $\Delta\varepsilon$ in Fig. 5. In our binary systems, the relative slope of $\theta_p/\Delta\varepsilon$ is much larger. We can interpret that this effect is enhanced due to the presence of strong dipole moments in the molecules used. In Fig. 6, we show $\theta_p$ as a function of $\Delta n$ (open circles). We use a least-squares method to fit the experimental data and notice that $\theta_p$ increases linearly with $\Delta n$. A similar observation (open squares) was also reported by Nishikawa *et al.*[4] in multi-component mixtures obtained from Merck. We find that the slope, i.e., $\theta_p/\Delta n$ is much larger in our binary mixtures. Nakayama *et al.*[12] reported that $\theta_p$ of a nematic LC increases with increasing $\Delta n$, suggesting the importance of the $\pi$–$\pi^*$ interaction or the dispersion force between the nematic LC and the alignment film. In our systems, both two LC molecules possess strong dipole moments, so that the polarizability anisotropy and hence the birefringence increases more rapidly. Thus we believe that the dispersion force is also enhanced causing relatively larger slope of $\theta_p/\Delta n$ in our mixtures.

Finally, we want to comment on the temperature dependence of $\theta_p$. As mentioned at the end of the introduction, no essential temperature dependence of $\theta_p$ was observed. For instance, $\theta_p$s were 5.08° (30 °C), 5.14° (25 °C) and 4.93° (22 °C) for Mixture-3 with an N–I transition temperature of 32.5 °C. The anisotropic physical properties, e.g., birefringence and dielectric anisotropy among others show a strong temperature dependence particularly near the N–I transition temperature. This is because of the change of the order parameter of the director orientation. For example, by increasing the temperature of the sample in the nematic phase, the distribution of the long axis of the molecules becomes broader, resulting in decreasing anisotropy. However, the average alignment direction of the molecules, i.e., the director, remains almost unaffected even if the order parameter changes, provided that the temperature dependence of the orientational change at both surfaces is neglected. The temperature dependence of pretilt angles was reported by Toda *et al.*[13] They reported a tendency wherein $\theta_p$ decreases with increasing temperature; however, they failed to explain the temperature dependence of $\theta_p$ using that of the order parameter and tentatively ascribed the

temperature dependence of $\theta_p$ to the surface orientational change. In any event, the temperature dependence of the pretilt angle is not so large when its value is smaller than $10°$, although considerable temperature dependence emerges for large pretilt angles. Recently, we have also reported that the pretilt angle for a banana nematic LC is very small and does not change with temperature in the entire nematic range.[8] In this way, the use of data at $30°C$ in this study does not pose any serious problem in grasping the important relationship between $\theta_p$ and dielectric anisotropy and birefringence.

## 4.  Conclusions

In conclusion, the effects of dielectric anisotropy and birefringence on pretilt angle in binary mixtures of two highly polar compounds, namely, CP7B and CCN-47 have been investigated. It is found that the pretilt angle strongly depends on the dielectric anisotropy as well as the birefringence. The variation in pretilt angle with birefringence is almost linear, whereas it shows a saturating tendency with dielectric anisotropy at a higher concentration of CP7B. The much larger pretilt angle in our mixtures is attributed to the strong dipole–dipole interaction, the $\pi–\pi^*$

interaction or the dispersion force between the nematic LC and the alignment film.

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