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Occurrence of Five Different Orthogonal Smectic Phases in a Bent-Core (BC) Liquid Crystal

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Five orthogonal smectic phases ($Sm-A$, $Sm-A_b$, $Sm-AP_R$, $Sm-AP_{AR}$, and $Sm-AP_A$) were observed in a 4-cyanoresorcinol bisbenzoate with two terephthalate –based wings achiral bent-core (BC) compound. The phase behavior was investigated by polarising optical microscopy, second harmonic electro-optic response (EO_2) and dielectric spectroscopy. The field dependent biaxiality of polar and non-polar $Sm-A$ phases was studied. It is obviously of enormous scientific significance and practical interest to find five different orthogonal smectic phases in a low molecular weight bent-core (BC) compound at relatively low temperatures.

Keywords bent-core molecule; orthogonal Smectic; electro-optic effects; dielectric relaxation

1. Introduction

A considerable interest has been shown by the liquid crystalline community in the study of ferroelectricity and antiferroelectricity in liquid crystalline (LC) materials composed of achiral molecules [1–3]. In 1992, Brand *et al.* introduced a model of ferroelectricity for an orthogonal smectic phase (CP) formed by non-chiral bent-core (BC) molecules [4] and Niori *et al.* reported the first experimental evidence of ferroelectricity in 1996 [5].

Recently, many orthogonal smectics composed of BC, LC molecules showing different phase structures and phase transitions have been synthesized and investigated with a large shape biaxiality and strong polarity [6–9]. Some of the studies in this direction include an investigation of orthogonal polar smectic mesophases such as $Sm-AP_A$ [10–13], $Sm-AP_R$ [14, 15] and $Sm-AP_{AR}$ [16]. In all these achiral $Sm-A$ phases, the molecular rotation

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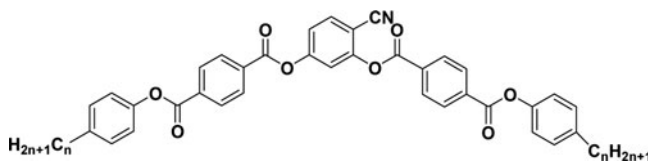


Figure 1. Molecular structure of the bent core LC compound with chain length $n = 16$

around its principal axis within a smectic layer at least to some extent is biased. Hence, the molecules are packed in the BC direction which is also the polar-axis direction in a single layer. In Sm-AP_R phase, the polarization direction from layer to layer is randomized leading to the macroscopic non-birefringent texture under crossed polarizers and in Sm-AP_A phase, the polarization direction between the adjacent layers are anti-parallel leading to an antiferroelectric phase which is biaxial. Ferroelectric phase (Sm-AP_F) with polarization direction in adjacent layers parallel to each other has also been observed [17]. The existence of non-polar biaxial Sm-A_b phase or C_M (McMillan) first suggested by de Gennes [1] was recently observed in LCs built from the non-symmetrical BC molecules and in their mixtures with calamitic molecules [18, 19].

Here we report a new BC material with symmetric terminal chain lengths which exhibits a phase sequence of three different polar orthogonal smectic phases (Sm-AP_A , Sm-AP_{AR} and Sm-AP_R) in addition to optically biaxial non-polar Sm-A_b on cooling down from the optically uniaxial Sm-A . Occurrence of these phases was confirmed by biaxiality measurements [20–23], second harmonic electro-optic response [23] and dielectric spectroscopy [24]. It is obviously of enormous to significance to find the five different mesophases at relatively lower temperature region in a low molar pure BC compound having a highly polar cyano group attached to the middle of the core.

2. Experiments

The smectic BC compound under study, 4-cyanoresorcinol bisbenzoate with two terephthalate-based wings was synthesized in Halle Germany. The molecular structure along with the phase transition temperatures and phase sequences are shown in Fig. 1. The material under investigation has symmetric terminal alkyl chains on both sides with the number of carbon atoms 16 (chain length = 16). It exhibits the following phase sequence: Cr 75°C - Sm-AP_A 90°C - Sm-AP_{AR} 98°C - Sm-AP_R 107°C - Sm-A_b 125°C - Sm-A 164°C - I on cooling from the isotropic temperature and Cr 110°C - Sm-A_b 125°C - Sm-A 162°C - I, on heating from the crystalline state. It is interesting to note that the homologue series with very similar molecular structure, with C = O bonds pointed in the same direction, exhibit only nematic phases [25].

For electro-optic measurements homeotropic alignment is obtained by two glass substrate coated with polymer AL60702 (JSR Korea). The electrodes are arranged with a separation of $\sim 80 \mu\text{m}$ for applying the in-plane electric field at a frequency of 110 Hz by etching indium tin oxide (ITO) stripes on the bottom glass substrate. The dielectric study is carried out using broadband high resolution dielectric spectrometer (Novo control GmbH, Germany) on planar (homogenous) cells. Homogeneous cell configuration was obtained by coating with polymer RN 1175 (Nissan chemicals, Japan). Sample thickness is adjusted using appropriate spacers and interference technique is used to measure the cell thickness.

3. Results and Discussions

3.1. Biaxiality Measurements

Biaxiality measurements were performed using a tilting optical compensator. The effect of applied field on different Sm-A phases was studied in a $5.5 \mu\text{m}$ homeotropic cell under crossed polarizers with an angle of 45° between the electric field and the polarizer axes. Magnitude of biaxiality measured as a function of voltage for different phases with a reduction in temperature is shown in Fig. 2.

On cooling the cell from the optically uniaxial Sm-A to 125°C , it first transforms to an optically biaxial Sm- A_b phase. By the application of electric field ($0.4 \text{ V}/\mu\text{m}$) the initial low-biaxiality ($\delta n = 1.61 \times 10^{-4}$) with a Schlieren texture becomes ordered and on a further increase in the field ($8.75 \text{ V}/\mu\text{m}$) the magnitude of biaxiality increases to $\delta n = 0.0094$ at 118°C . On further cooling this optically biaxial phase (Sm- A_b) turns to optically uniaxial Sm- AP_R phase at 107°C . The initial uniaxial state goes to biaxial state ($\delta n = 0.0056$) only at a higher field ($8.75 \text{ V}/\mu\text{m}$). It shows an increasing trend of biaxiality by the application of higher electric field. The device containing the sample turns to Sm- AP_{AR} phase at 98°C , the macroscopically uniaxial state ($\delta n = 0$) goes to biaxial antiferroelectric state ($\delta n = 0.0019$ at $1.5 \text{ V}/\mu\text{m}$) and then to ferroelectric ordered saturated state ($\delta n = 0.0140$, at $6.25 \text{ V}/\mu\text{m}$) through uniaxial order ($\delta n = 0$ at $2.75 \text{ V}/\mu\text{m}$). At 90°C , the initial Schlieren texture of Sm- AP_A phase ($\delta n = 0.0026$, at $0 \text{ V}/\mu\text{m}$) goes to the ordered biaxial antiferroelectric structure ($\delta n = 0.0073$, at $1.25 \text{ V}/\mu\text{m}$) and on further application of field; it turns to ordered ferroelectric saturated state ($\delta n = 0.0168$, at $5.25 \text{ V}/\mu\text{m}$) through an optically uniaxial state ($\delta n = 0$, at $3.5 \text{ V}/\mu\text{m}$). At a particular temperature (78°C), δn value of both antiferroelectric and ferroelectric states are similar. From Fig. 2 it is clearly seen that the magnitude of field dependent biaxiality of all smectic phases gradually increases with a reduction in temperature.

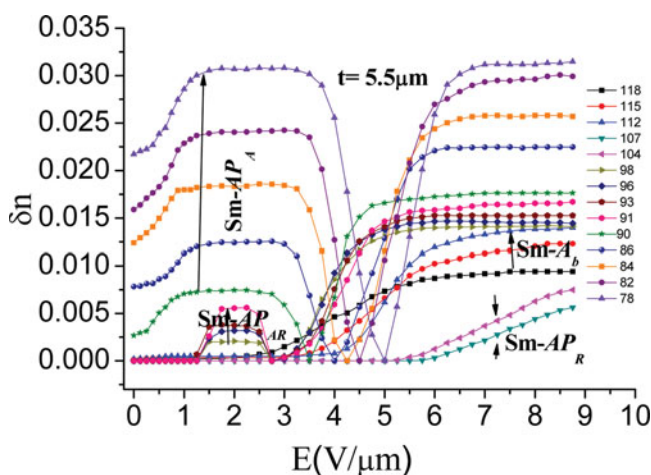


Figure 2. The field dependent biaxiality measurement of orthogonal smectic LC phases, Sm- A_b (118°C – 112°C), Sm- AP_R (106°C – 103°C), Sm- AP_{AR} (100°C – 91°C) and Sm- AP_A (88°C – 78°C), on cooling down from the uniaxial Sm-A phase. Measurements are carried out on a $5.5 \mu\text{m}$ homeotropic cell under an in-plane electric field. The various phases are marked on the left and right. The curves for various colors may not all be clear in the Figure.

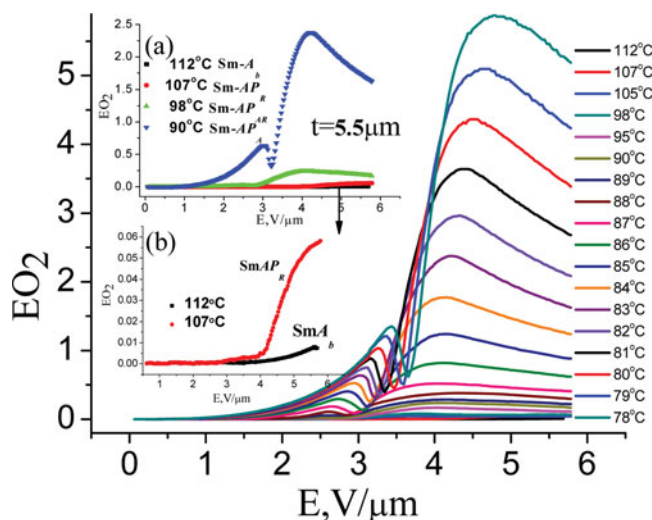


Figure 3. The 2nd harmonic electro-optic response (EO_2) of orthogonal smectic phases observed in BCLC compound (PAL29) with a reduction in temperature from the isotropic phase. The inset figure (a) shows the Sm- A_b at 112°C (■), Sm- AP_R at 107°C (°), Sm- AP_{AR} at 98°C (°73;) and Sm- AP_A at 90°C (▼). The inset figure (b) shows the EO_2 response only in Sm- A_b phase at 112°C (■) and red filled circle SmAPR.

3.2. Second Harmonic Electro-optic Response

The second harmonic electro-optic response (EO_2) was recorded [23] by applying a square-wave ac voltage at a $f = 80$ Hz across the in-plane electrodes having electrode distance $\sim 80 \mu\text{m}$. The magnitude of EO_2 response is proportional to the $\sin^2\theta$, where, $\theta = \pi nd/\lambda$. If $\theta \ll 1$, the linear dependence of $\delta n(\mathbf{E})$ on \mathbf{E} would give a quadratic dependence of EO_2 on \mathbf{E} (i.e., $EO_2 \propto E^2$) due to $EO_2 \propto \theta^2$. Figure 3 shows the temperature dependent EO_2 response while the sample is cooled from the SmA phase.

The plot in Fig. 3 reveals the presence of all orthogonal phases (Sm- A_b , Sm- AP_R , Sm- AP_{AR} and Sm- AP_A) and it is in good agreement with the biaxiality measurement results. The inset figure (a) of Fig. 3 shows the phases Sm- A_b at 112°C, Sm- AP_R , at 107°C Sm- AP_{AR} at 98°C and Sm- AP_A at 90°C. As the magnitude of EO_2 response is very small for Sm- A_b and Sm- AP_R when compared to the other Sm- AP_{AR} and Sm- AP_A phases, the field dependent EO_2 response of both Sm- A_b and Sm- AP_R are repeated on an extended scale separately in inset figure (b) of Fig. 3. The EO_2 response from the material under study is fitted to the equation $EO_2 = k.E^\gamma$ to determine the exponent γ . In Sm- AP_R and Sm- AP_{AR} , $\gamma = 2$ for the lower values of \mathbf{E} , which implies the linear dependence of $\delta n(\mathbf{E})$ on \mathbf{E} due to the polar interaction with \mathbf{E} . When we consider Sm- AP_A phase, γ shows a cross over behavior (2.5 to 3.5) due to the combination of polar and dielectric interactions. In optically biaxial Sm- A_b , the fitting result shows $\gamma = 4.2$, which assumes that this phase is non-polar in nature.

3.3. Dielectric Measurements

The dielectric relaxation measurement over a frequency range 1Hz to 1MHz was performed in a homogeneous cell having $7.3 \mu\text{m}$ thickness. Low resistance ($20 \Omega/\square$) indium tin oxide (ITO) glass substrates were used to make cells for the study. The measurement was carried

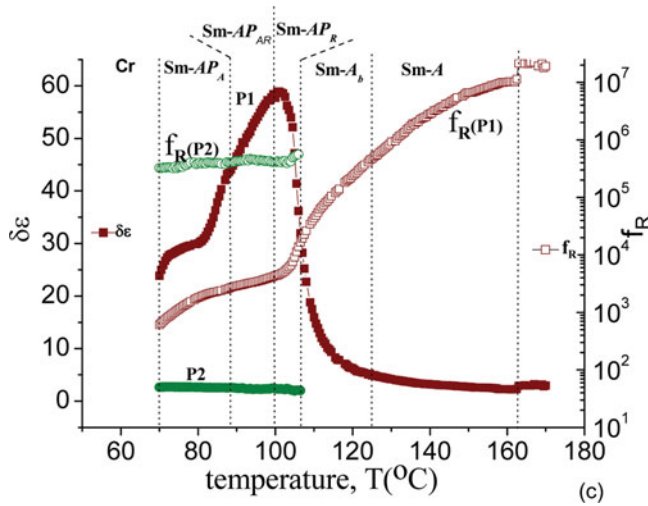


Figure 4. Dielectric relaxation strength ($\delta\epsilon$) and the relaxation frequency (f_R) as a function of temperature measured in a planar cell configuration.

out over a temperature range of 170°C – 70°C (varied in steps of 0.5°C) and the dielectric spectrum is fitted to the Havriliak-Negami equation,

$$\epsilon^*(\omega) = \epsilon' - i\epsilon'' = \epsilon_\infty + \sum_{j=1}^n \frac{\delta\epsilon_j}{[1 + (i\omega\tau_j)^{\alpha_j}]^{\beta_j}} - \frac{i\sigma_{dc}}{\epsilon_0\omega} \quad (1)$$

where, ϵ_∞ is the high frequency dielectric permittivity, j varying from 1 to n (number of relaxation process), ω is the angular frequency, ϵ_0 is the permittivity in free space, τ_j is the relaxation time of the j^{th} relaxation process, $\delta\epsilon_j$ is the dielectric relaxation strength and α_j and β_j are the symmetric and asymmetric broadening parameters of the j^{th} process. The fitting parameters of the dominant process, e.g. dielectric strength, $\delta\epsilon$ (amplitude) and the relaxation frequency, f_R are shown in Fig. 4 (see [26]).

While cooling down from the isotropic phase, the relaxation processes, P1 is moving towards the lower frequency part. In polar phases, the high frequency relaxation mode is due to the non collective motion of polar molecules and the low frequency relaxation mode is due to the collective movement of dipole moments. It is clearly seen in Fig. 4 that, the dielectric amplitude $\Delta\epsilon$ increases with a reduction in temperature and reaches maximum at the Sm-AP_R to Sm-AP_{AR} phase transition.

4. Conclusions and Perspectives

In summary, the occurrence of five different orthogonal smectic phases (Sm-A , Sm-A_b , Sm-AP_R , Sm-AP_{AR} , and Sm-AP_A) by field dependent biaxiality measurements were confirmed by the second harmonic electro-optic response and the dielectric spectroscopy. The Sm-A_b phase exhibits very small values of biaxiality when compared to all other orthogonal smectic phases observed. Biaxiality measurement results are in agreement with the second harmonic electro-optic response measurement results. The dielectric study reveals an increasing trend of dielectric amplitude with a reduction in temperature and it reaches the summit at Sm-AP_R to Sm-AP_{AR} phase transition region.

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