

Experimental evidence of an optical shuttering action in cholesteric phase of a double hydrogen bonded ferroelectric liquid crystal

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A novel series of double hydrogen bonded liquid crystals have been isolated. Hydrogen bond was formed between non mesogen chiral ingredient levo tartaric acid (LTA) and mesogenic undecyloxy benzoic acids (11BA). Thermal and electrical properties exhibited by levo tartaric acid and undecyloxy benzoic acid (LTA+11BA) were discussed. Interesting feature of the present investigation was observation of an optical shuttering action in LTA+11BA hydrogen bonded complex on application of a stipulated applied dc bias voltage. By enhancement of the dc bias voltage the mesogen behaves like an optical shutter, thus this hydrogen bonded complex mesogen acts as an effective light modulator. It was noticed that this action of shuttering was reversible, in the sense that when applied bias voltage was removed the original texture was restored. Experimental results relating to textures, optical tilt, dielectric studies and optical shuttering action were presented. This optical shutter property of the mesogen can be exploited for commercial and display device applications.

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1. Introduction

'Liquid Crystal' (LC) materials refer to the fourth state of matter that possess dual property of crystals and liquids. Their anisotropic physical properties (characteristic of its crystalline nature) and the inherent surface alignment (to the substrate) tendency (characteristic of its fluidity) are extensively exploited [1-3] to design LC based Electro-Optic devices. Their overall shape [4] being cylindrical, renders them readily viable for surface alignment. In the field of supra-molecular LCs, especially in the field of hydrogen bonded LCs, the influence of soft-covalent interaction for the thermal stability of phases of device interest is widely [2-14] studied.

The configuration and spread of the hydrogen bonding interaction with regard to the long molecular dipole moment in the calamitic LCs along with the corresponding molecular dipole models are argued [5,7,8] to originate the distinct properties in the family of hydrogen bonded liquid crystals (HBLC). However, as an integrated overview, for the microscopic interactions among molecular dipoles as contributed by the underlying chemical moieties configured on the molecular body (or frame) would be of immense utility in devices. The field of 'Systematic Studies' in the area of LCs is expected to further reveal the truth of microscopic interactions. The growth of order (and crystalline nature) is logically expected to increase with decreasing temperature in these LC materials in their condensed version of matter.

In the case of HBLCs the molecular frame possesses [10, 18-22] additional soft-covalent interaction. Further, in case of non-ferroelectric and ferroelectric HBLCs, the

observed [13, 21] variation in device relevant properties like thermal stability, spontaneous polarization, tilt angle, switching times etc., are addressed through dipolar and refined dipolar models to vouch the fact that soft-covalent interaction extends rather inclined to the long molecular dipole moment. Further, the presence of additional interaction in the form of anisotropic dipole moment along the molecular body is believed to be the origin of the orientational disorder leading to tilted phases.

With our previous experience [23-30], in designing, synthesizing and characterizing various types of liquid crystals, a successful attempt has been made in characterizing a novel series of inter hydrogen bonded liquid crystal

In the present communication a homologous series of HBLC is designed in such a way that the molecule possesses double hydrogen bonding with chiral ingredient levo tartaric acid moiety. Thermal and electrical characterizations of undecyloxy benzoic acid and levo tartaric acid complex (LTA+11BA) pertaining to the present series are discussed in detail.

2. Experimental

Optical textural observations are made with a Nikon polarizing microscope equipped with Nikon digital CCD camera system with 5 mega pixels and 2560*1920 pixel resolutions. The liquid crystalline textures are processed, analyzed and stored with the aid of ACT-2U imaging software system. The temperature control of the liquid crystal cell is equipped by Instec HCS402-STC 200 temperature controller (Instec, USA) to a temperature

resolution of $\pm 0.1^\circ\text{C}$. This unit is interfaced to computer by IEEE -STC 200 to control and monitor the temperature. The liquid crystal sample is filled by capillary action in its isotropic state into a commercially available (Instec, USA) polyamide buffer cell with 4 micron spacer. Optical extinction technique is used for the determination of tilt angle. The transition temperatures and corresponding enthalpy values are obtained by DSC (Shimadzu DSC-60). FTIR spectra has been recorded (ABB FTIR MB3000) and analyzed with the MB3000 software. Light intensity measurements were made with photo transistor (TSL 252) where the sample is placed under crossed polarizers of the Nikon polarizing microscope. The p-n-alkoxy benzoic acids (nABA) and levo tartaric acid were supplied by Sigma Aldrich, Germany and all the solvents used are E.Merk grade.

2.1 Synthesis of HBLC

The present intermolecular hydrogen bonded mesogen is synthesized by the addition of two moles of undecyloxy benzoic acids (11BA) with one mole of levo tartaric acid (LTA) in N,N-Dimethyl formamide (DMF) respectively. Further it has been subjected to constant stirring for 10 hours at ambient temperature of 30°C till a white precipitate in a dense solution is formed. The white crystalline crude complexes so obtained by removing excess DMF are then recrystallized with Dimethyl Sulfoxide (DMSO) and the yield varied from 85% to 95%. The general molecular structure of the present homologous series of p-n-alkoxy benzoic acids with levo tartaric acid is depicted in the figure 1, where n represents the alkoxy carbon number.

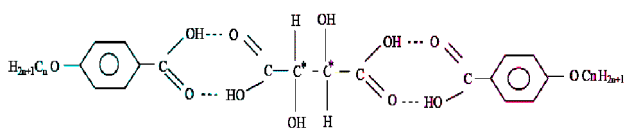


Fig. 1. General molecular diagram of LTA+nBA homologous series.

3. Results

Levo tartaric acid and undecyloxy benzoic acid complex (LTA+11BA) isolated are white crystalline solids and are stable at room temperature. It is insoluble in water and sparingly soluble in common organic solvents such as methanol, ethanol, and benzene and dichloro methane. However it shows a high degree of solubility in coordinating solvents like dimethyl sulfoxide (DMSO) and pyridine. It melts at specific temperatures below 140°C . Further it shows high thermal and chemical stability when

subjected to repeated thermal scans performed during polarizing microscopic studies (POM) and differential scanning calorimetric (DSC) studies.

3.1 Infrared Spectroscopy (FTIR)

IR spectra of free p-n-alkoxy benzoic acid, levo tartaric acid and their intermolecular hydrogen bonded complexes are recorded in the solid state (KBr) at room temperature.

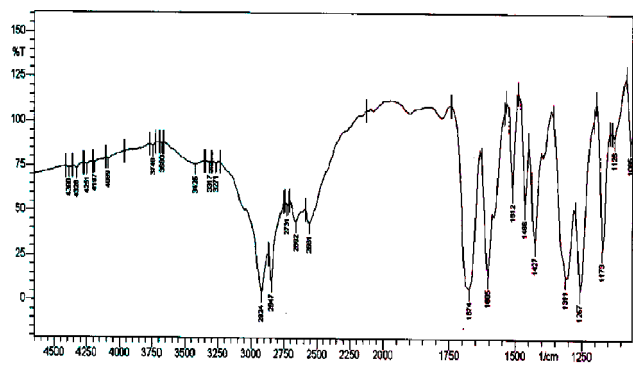


Fig. 2. FTIR spectrum of LTA+11BA hydrogen bonded complex.

Fig. 2 illustrates the FTIR spectra of the hydrogen bonded complex of LTA+11BA in solid state at room temperature. The solid state spectra of free alkoxy benzoic acid is reported [21] to have two sharp bands at 1685 cm^{-1} and 1695 cm^{-1} due to the frequency $\nu(\text{C}=\text{O})$ mode. The doubling feature of this stretching mode confirms the dimeric nature of alkoxy benzoic acid at room temperature [21]. Further in the present LTA+11BA hydrogen bonded complex a band appearing at 2924 cm^{-1} is assigned to $\nu(\text{O}-\text{H})$ mode of the carboxylic acid group.

The doubling nature of $\nu(\text{C}=\text{O})$ mode may be attributed to the dimeric nature of acid group at room temperature [21] Corresponding spectrum of solution state (chloroform) show a strong intense band suggesting the existence of monomeric form of benzoic acid. A noteworthy feature in the spectra of LTA+11BA complex is the appearance of a broad band at 1674 cm^{-1} and non appearance of the doubling nature of $\nu(\text{C}=\text{O})$ mode of benzoic acid moiety. This clearly suggests that the dimeric nature of the benzoic acid dissociates and prefers to exist in a monomeric form upon complexation.

3.2 Phase identification

The observed phase variants, transition temperatures and corresponding enthalpy values obtained by DSC in cooling and heating cycles for the LTA+11BA complex are presented in table 1.

Table 1. Transition temperatures obtained by various techniques. Enthalpy values (J/g) are given in parenthesis.

Complex	Phase variance	Technique	Crystal Melt	Ch	C*	G*	Crystal	
LTA+11BA	ChC*G*	DSC (h)	97.84 (47.68)	140.21 (2.33)	129.37 (2.47)	#		
		DSC (c)		136.78 (2.96)	125.5 (2.12)	84.84 (8.55)	72.54 (12.81)	
		POM (c)		137.1	126.2	85.3	72.9	
		Dielectric Studies (c)	10 KHz		134.9	128.2	87.3	69.0
			100 KHz		135	128.4	87.3	68.9

Monotropic transition, (c) cooling run, (h) heating run

3.3 LTA+nBA homologous series

The levo tartaric acid and alkoxy benzoic acid homologous complex is found to exhibit characteristic textures [31], viz., Cholesteric (finger print texture), Smectic C* (schlieren texture) and Smectic G* (multi colored mosaic texture) respectively. The phase sequence of the levo tartaric acid and undecyloxy benzoic acid (LTA+11BA) hydrogen bonded complex in the cooling run can be shown as:



3.4 DSC studies

DSC thermograms are recorded in heating and cooling cycles. The liquid crystal sample is crimped in an aluminum cell and heated with a scan rate of 10°C/min and hold at its isotropic temperature for one minute so as to attain thermal stability. The cooling run is performed with an identical scan rate of 10°C/min. DSC thermo gram of LTA+11BA is illustrated as figure 3.

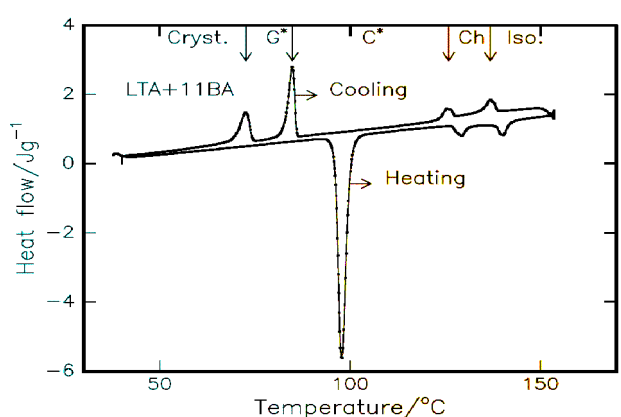


Fig. 3. DSC thermo gram of LTA+11BA complex recorded with a scan rate of 10°C/min.

The respective equilibrium transition temperatures and corresponding enthalpy values of the mesogens are listed separately in table 1. POM studies are in good agreement with the DSC results.

4. Discussion

4.1 Phase diagrams

The phase diagrams of pure p-n-alkoxy benzoic acids and the present homologous series (nBA+LTA) are constructed and reported [30] through optical polarizing microscopic studies by the phase transition temperatures observed in the cooling run of the mesogens of the present homologous series. The phase diagram of pure p-n-alkoxy benzoic acids is reported [24] to exhibit three phases namely, Nematic, smectic C* and smectic G*.

4.2 Optical tilt angle studies

For the hydrogen bonded LTA+11BA complex, optical tilt angle has been experimentally measured by optical extinction method [32] in the smectic C* phases.

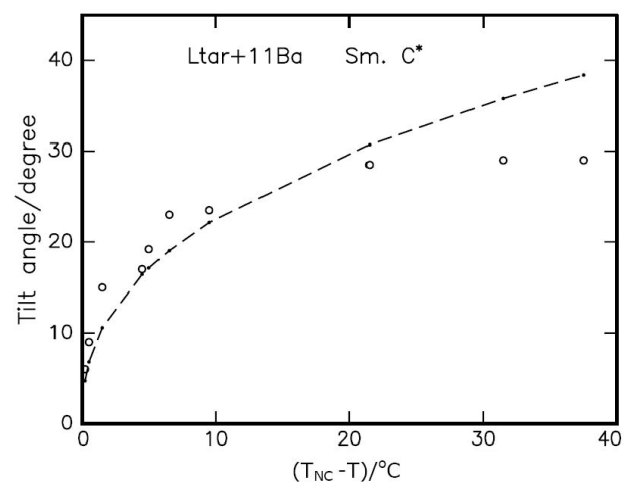


Fig. 4. Temperature dependence of optical tilt in smectic C* phase. Solid line denotes the fit.

From the Fig. 4 it is observed that the tilt angle increases with decreasing temperature and attains a saturation value of 29°. The large magnitudes of the tilt angle are attributed [22] to the direction of the soft covalent hydrogen bond interaction which spreads along molecular long axis with finite inclination.

Tilt angle is a primary order parameter [32,33] in tilted phases namely smectic C^* . The temperature variation is estimated by fitting the observed data of $\theta(T)$ to the relation

$$\theta(T) \propto (T - T_C)^\beta \quad (1)$$

The critical exponent β value estimated by fitting the data of $\theta(T)$ to the above equation (1) is found to be 0.50 to agree with the Mean Field [34] prediction. The dotted line in the figure 4 depicts the fitted data. Further, the agreement of β with Mean Field value infers the long-range interaction of transverse dipole moment for the stabilization of tilted smectic C^* phase.

4.3 Dielectric studies

Dielectric studies enable to detect a second order transition which goes unobserved in the DSC study. Variation of capacitance and dielectric loss with temperature is performed for LTA+11BA of the present homologous series. The mesogen filled in a commercially available 4 micron polyamide buffed cell (Instec) and is excited with a frequency of 10 kHz and 100 kHz respectively. Silver leads are drawn from the cell for electrical contacts. Simultaneous textural observations are made to co-relate the phase exhibited by the mesogen to the dielectric data. Thus the textural transition temperatures and dielectric spectrum are studied together. The dielectric spectrum of undecyloxy benzoic acid complex (LTA+11BA), as depicted in Fig. 5, is discussed below.

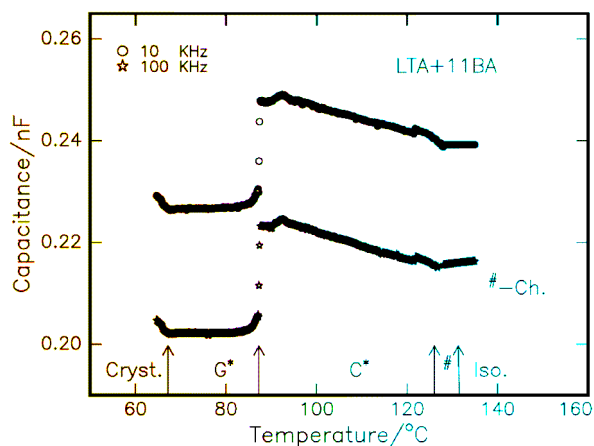


Fig. 5. Temperature dependence of capacitance at 10 KHz and 100 KHz.

From Fig. 5 the following points can be inferred.

- As the temperature is decreased from isotropic, a small knick is observed at 134.9°C indicating the onset of the cholesteric phase. Cholesteric finger print texture is observed indicating the onset of the phase.
- On further decrement of the temperature the stabilization of the Cholesteric phase is evidenced where

the capacitance started increasing without any sudden anomaly in the dielectric spectrum.

- At 128.2°C a small anomaly in the magnitude of the capacitance indicates the onset of smectic C^* phase. Schlieren texture is observed with the onset of this phase.
- In the entire region of smectic C^* phase a linear increment in the magnitude of the capacitance is observed indicating the growth and stabilization of the phase.
- Smectic G^* phase is observed as a sudden steep fall in the magnitude of capacitance at 87.3°C indicates the transition from smectic C^* to smectic G^* phase. A multi colored mosaic texture is observed indicating the onset of smectic G^* phase
- Further decrement in temperature showed an unaltered variation of the capacitance indicating the stabilization of smectic G^* phase.
- A sudden variation in the magnitude of the capacitance at 69.9°C is attributed to the transition from the mesogenic phase to crystal. The formation of the crystal is also evidenced through optical textural studies. Similar variations are observed in dielectric loss spectrum. The transition temperatures obtained by this technique are in good agreement with POM and DSC studies and are tabulated in table 1.

4.4 Dielectric relaxation

Dielectric dispersion i.e. frequency variation of dielectric loss exhibited by LTA +11BA is studied at different temperatures in smectic C^* phases in the frequency range of 5 Hz to 13 MHz respectively. An impedance analyzer (HP4192A) is operated with 1V_{P-P} oscillating signal with zero bias field. Relative permittivity $\epsilon'_r(\omega)$ and dielectric loss $\epsilon''(\omega)$ are calculated by the following equations

$$\begin{aligned} * \epsilon'_r(\omega) &= \epsilon'_r(\omega) - j\epsilon''(\omega) \\ \epsilon'_r(\omega) &= [C_{LC} - C_{leads}] / [C_{empty} - C_{leads}] \\ * \epsilon''(\omega) &= \text{Tan}\delta(\omega) \epsilon'_r(\omega) \end{aligned}$$

To detect the possible relaxation in the HBFLC complex, the mesogen is scanned in the frequency range of 5 Hz to 13 MHz at different temperatures corresponding to smectic C^* phases. LTA+11BA mesogen exhibits a relaxation mechanism namely Goldstone Mode (GM).

4.5 Goldstone mode

Goldstone mode in smectic C^* phase of LTA+11BA complex is studied and analyzed. As reported [22] in HBFLC, Goldstone mode is observed at lower frequencies namely at around 950 Hz in LTA+11BA complex. The variation of the capacitance with corresponding dielectric loss at various temperature which are referred as Cole-Cole plots, in smectic C^* for the LTA+11BA are shown in figure 6 and is interpreted as due to collective response originated due to the excitation of the coupled transverse dipole moment situated around the chiral centers over the layers in the form of polarization helix. This relaxation is identified [35] as Goldstone mode.

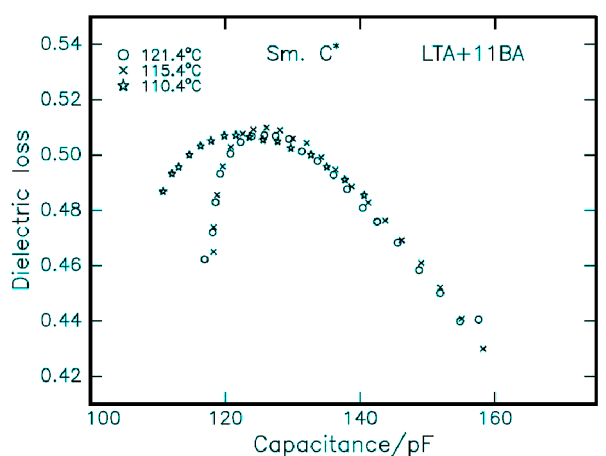


Fig. 6. Cole-Cole plots in smectic C* phase at various temperatures.

The order of f_r relevant to the GM in the present compounds is found to be comparable to that reported [36,22] in other FLCs and HBFLC compounds. It is further observed that GM relaxation is suppressed under different applied fields as depicted in Fig. 7. Thus this experimental evidence confirms that GM originates from the helix spread over the smectic layers of respective phase.

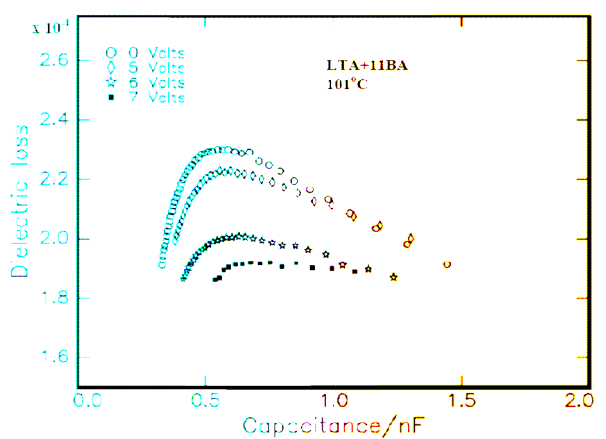


Fig. 7. Suppression of the helix under various applied external bias in the Goldstone mode of smectic C* phase.

4.6 Field induced transition (FiT)

It is reported [29, 35-43] that when a mesogen is subjected to an applied external field in cholesteric, nematic or smectic C* phase there can be a phase transition which is referred as field induced transition (FiT).

The present hydrogen bonded complex is subjected to various strengths of external dc bias voltage derived from HP 4192A impedance analyzer, to investigate the occurrence of FiT.

4.7 Optical shutter action in LTA+11BA

LTA+11BA compound in its cholesteric phase when an applied dc bias voltage exceeds a particular threshold value, the phase of the compound is observed to prefer homeotropic like alignment with light being optically extinct which is referred as optical shutter. Plates 1 to 4 depict the cholesteric texture under the influence of various applied fields, further, it is interesting to note that immediately after withdrawing the bias voltage from any of the induced transition the original texture of the cholesteric phase is retained. Thus this process is reversible with bias voltage. In the entire thermal span of cholesteric phase (~136°C to ~125°C) this is observed. While in the other phases preceding and succeeding cholesteric phase no such transition is found. Thus the field induced transitions can be represented as

$$E_0 \rightarrow \text{Optical shutter } (E_1)$$

A quantitative approach has been developed to study the effect of applied electric field on hydrogen bonded LTA+11BA with optical textural studies and dielectric studies. The cholesteric phase with a bias voltage (both polarities) less than or equal to ± 3.75 volts/micron is referred as E_0 where there is no change in the texture of the smectic phase as depicted in plate 1. As the voltage is increased in steps of 1.25 volts/micron the intensity of the light from the texture drops as can be seen from plates 2 and 3.

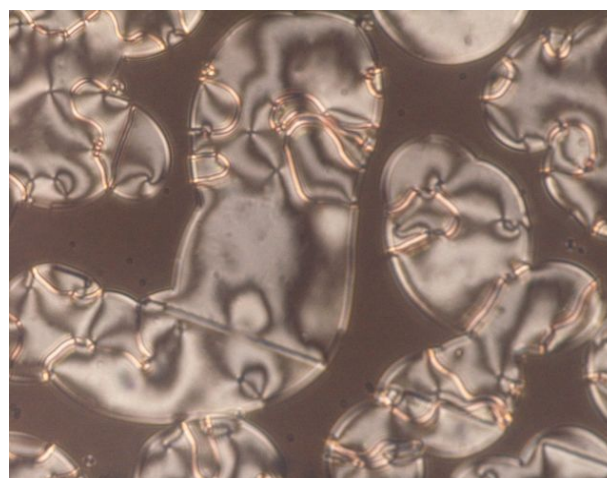


Plate 1. Cholesteric phase with applied external bias voltage of 1.25 volts/micron

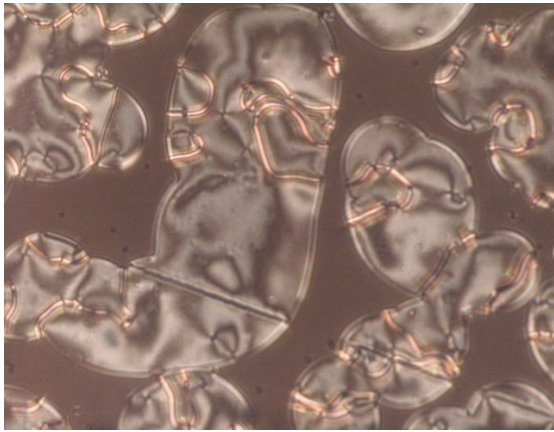


Plate 2. Cholesteric phase with applied external bias voltage of 2.50 volts/micron

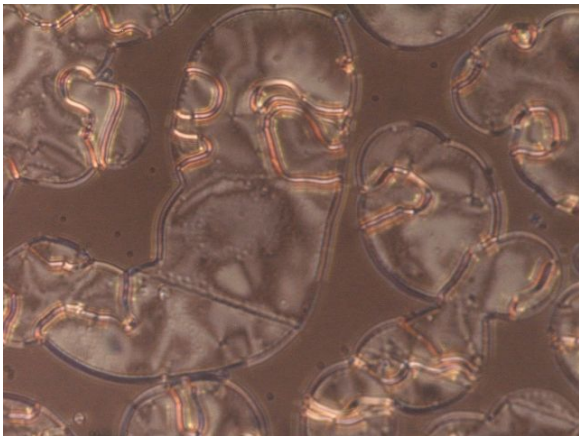


Plate 3. Cholesteric phase with applied external bias voltage of 3.75 volts/micron

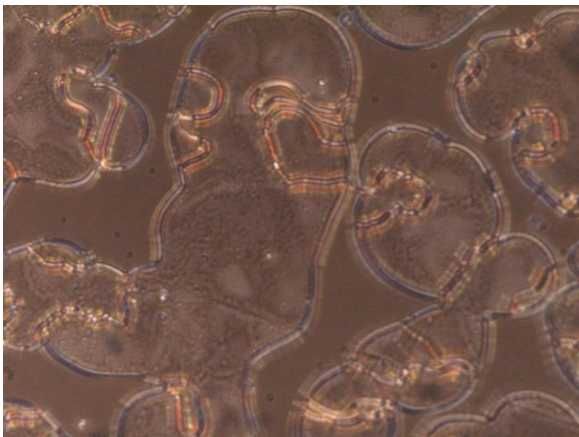


Plate 4. Cholesteric phase with applied external bias voltage of 5.00 volts/micron

An important observation is that when a dc bias voltage of ± 5.0 volts/micron is applied, the optical extinction is observed with the optical texture of the compound suddenly disappears, this new phase is designated as optical shutter (E_1) which is depicted as

plate 4. One of the possible reasons for this interesting phenomenon may be the realignment of the molecules to form a homeotropic like alignment.

To substantiate the above results dielectric studies were performed. The variation of the capacitance with respect to various external bias voltages is studied in cholesteric phase. Such a variation for LTA+11BA compound is shown in figure 9. Figures 8 and 9 are depicted below.

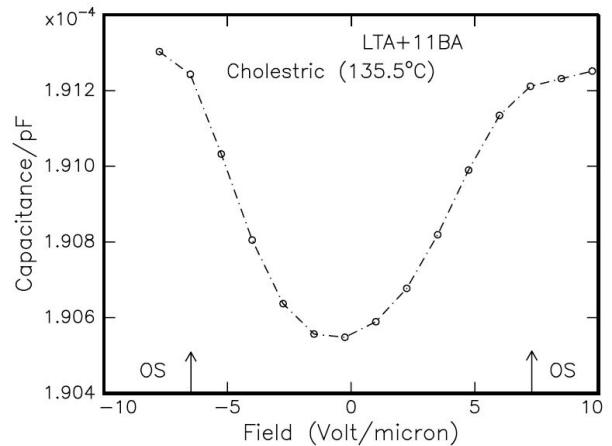


Fig. 8. Field dependence of capacitance in the cholesteric phase of LTA+11BA

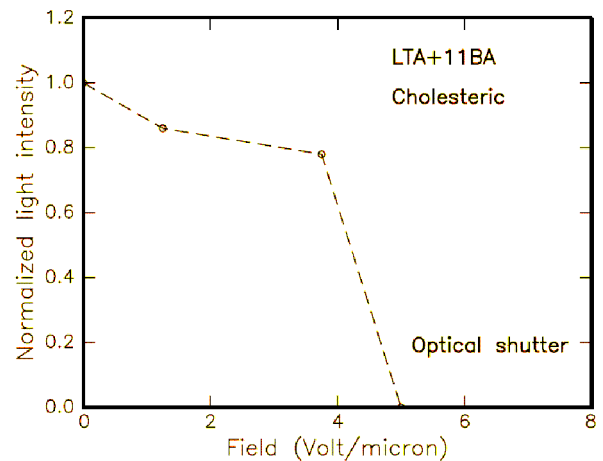


Fig. 9. Intensity profile of the cholesteric phase under various applied external bias voltages.

The plot depicts a symmetric variation of the capacitance with respect to both positive and negative applied bias voltages. From the figure 8, it can be inferred that

- Capacitance variation is identical for both the polarities inferring no influence of polarity.
- Field induced transition i.e. $E_0 - E_1$ (optical shutter), are not sudden and abrupt but smooth and uniform.

- c) Frequency has no influence on the threshold values of the FiT.
- d) Equilibrium states for the low and the high field are found to be distinct.

4.8 Intensity profile of the optical texture in FiT

The sample LTA+11BA is filled in a commercially available buffer cell (Instec) and silver leads are drawn for contact. The intensity profile in various phases has been experimentally analyzed by applying external bias voltage of both polarities drawn from impedance analyzer (HP 4192A) and the intensity of the light from the liquid crystal sample is measured by a photo diode (TSL 252). As the external bias voltage is incremented in small steps, this in turn induced various FiT at different magnitudes of the applied voltage. The variation of the intensity of the texture is noted at each step of the applied bias voltage and plotted as shown in figure 9. It is not surprising to note that the magnitude of the light is almost unaltered in any of the induced transitions except in E_0 , and E_1 respectively. During the transition from E_0 and E_1 there is a steep sudden decrement of the intensity of light manifesting the distortion of the helix. In the this phase of FiT, which is referred as optical shutter, the optical profile is completely vanished. Thus the liquid crystal behaved as an optical shutter (plates 1- 4). Hence this HBLC may be used as a light modulator.

4.9 Molecular modeling of field induced transitions

A qualitative approach for the observed optical shutter phenomenon is described below. In the literature it is reported [44-48] the distortion and unwinding of the helicoidal structure with applied field in the liquid crystal mesogen. The untwisting of the helical structure of a hydrogen bonded liquid crystal (HBLC) in a thin plane layer exposed to an external action (temperature or field) and its dependence on the molecular adhesive forces at the layer boundaries are responsible for field induced transitions. If the helical pitch is not infinite a non zero average polarization exists locally. When subjected to a weak electric fields the helix distorts [41] giving rise to small change in transmitted light as observed when the cell is placed under crossed polarizer. At much stronger fields there is a sudden transition such that the azimuthal orientation of the director is spatially uniform and all layers polarization is parallel to the applied field.

For very long pitch the liquid crystal behavior at small electric fields is expected to be different. The tilt plane of the molecules lies parallel to plane of the cell under these circumstances a continuous variation of the director orientation with field ($E=0$) begins. In this region the director profile is undisturbed. At the next level i.e. $E=1$, the electric field is sufficient to overcome the elasticity possessed by the molecules. Molecules in adjacent layer undergo unequal azimuthal rotations resulting in a locally averaged nonzero polarization that couples to the electric field. At much higher fields ($E=1$) the distortion is more and it helps in rapid switching which is analogous to short

helical pitch materials. The role of the anchoring energy is considerable at low fields, as the field increases the molecules get loosely bounded by the substrate surface. In other words the liquid crystal behaves as a light modulator. At high fields the extinction of the light is observed and this state may be referred as optical shutter. The parameters like helical pitch, anchoring energy and light modulation vary with applied field and govern the utility of the liquid crystal in display applications.

It has been experimentally observed from the helix studies that the magnitude of helical pitch decreases as one proceeds from the E_0 to E_1 and finally vanishes in E_1 phase. Thus it can be concluded that pitch in various field induced phases orient depending on the strength of the applied bias. It is no surprise that the molecules prefer an alignment which resembles the homeotropic alignment, when the bias strength is increased to a maximum value and thus the molecules inhibit the light and act as a total optical shutter. The possible reasons for this field induced transitions can be the various surface anchoring energy [49] possessed by the liquid crystalline molecules.

5. Conclusions

A novel series of alternate double hydrogen bonded ferroelectric complexes have been isolated and characterized. Optical shuttering action has been detected in a compound and theoretical modeling has been proposed for the same.

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