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# Ferroelectric response in an achiral non-symmetric bent liquid crystal: $C_{12}C_{10}$

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#### ABSTRACT

An achiral Non-Symmetric Bent Liquid Crystal (BLC) with a Oxadiazole based hetero cyclic central moiety, abbreviated as  $C_{12}C_{10}$  viz., dodecyl[4-{5-(4'-decyloxy)biphenyl-4-yl}-1,2,4-oxadiazol-3-yl]benzoate, exhibiting FerroElectric (FE) response is reported. Product is confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analysis. Characterization of BLC phases is carried out by Polarized Optical Microscopy (POM), Differential Scanning Calorimetry (DSC), Spontaneous Polarization ( $P_S$ ) and Low Frequency (10 Hz– 10 MHz) Dielectric Relaxation studies.  $C_{12}C_{10}$  exhibits enantiotropic LC SmA, FE B<sub>2</sub>, SmG, SmE phase variance. I–SmA, B<sub>2</sub>–SmG and SmG–SmE transitions are of first order nature. FE B<sub>2</sub> phases exhibits a moderate  $P_S$  of ~80 nC cm<sup>-2</sup>. B<sub>2</sub> phase exhibits Curie–Weiss behavior to confirm FE nature. Off-centered low frequency (KHz) dispersion infers a scissor mode and a high frequency (MHz) mode to reflect the distinct time-scale response. Dielectric Dispersion is relatively susceptible in lower frequency KHz region. Arrhenius shift in Relaxation Frequency ( $f_R$ ) infers higher activation energy ( $E_a$ ) in non-FE phases for HF mode and lower value for KHz mode. Trends of  $f_R$ , dielectric strength  $\Delta_{e}$ ,  $\alpha$ -parameter and  $E_a$  are discussed in view of the data reported in other LC compounds.

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# 1. Introduction

Liquid Crystals (LC) represent [1] a class of self organized systems that exhibit exotic crystalline phase structures and interesting [2] field-response for their utility in devices. LC systems [3] attract both of the fundamental [4] and application aspects [5,6] of scientific importance. LC phase structures are found to exhibit [7] isotropic fluidity and anisotropic crystalline properties simultaneously, and are called as 'Mesophases'. The information regarding response of LC phase structure is utilized in many of the modern [8] appliances like thermography, Electro-Optical (EO) displays, medical diagnostic tools etc. The physical response in LCs is understood as an interaction [9] of the structural assembly with the external field. Specific combinations of flow and anisotropy aspects of LCs renders them viable [10] in flat panel displays. A systematic classification of LC phase structures based on the temperature variation is initially carried out by the study of microscopic optical textures [11] exhibited by them. As such, the

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http://dx.doi.org/10.1016/j.physb.2014.06.004 0921-4526/© 2014 Elsevier B.V. All rights reserved. relevant data provides information regarding the underlying order parameter that stabilized an LC phase, i.e., Nematic, Cholesteric and Smectic phases. These LC materials are known for their better EO performance [1,7,12,13] due to the large birefringence. The advent of ferroelectricity in the tilted chiral Smectic (SmC\* phase) versions [14] rendered them more viable in EO devices. A SmC\* phase confined in surface stabilized geometry [15] leads for their being harnessed with faster ( $\mu$  s) response [15–18]. However, the conventional Nematic phase based devices are known to operate at milli second speed. The synthetic path adopted for the preparation of chiral LCs (exhibiting SmC\*) is prohibitively costly. Hence, LC researchers followed the path of supra-molecular design of BLCs [19], which are found to exhibit FE response.

The achiral bent mesogens (BLCs) initially reported [19–21] are found to exhibit ferroelectric (FE) and Antiferroelectric (AF) switching in their Smectic phases. Vorlander reported [22,23] several bent-core LCs, which are found [24,25] to exhibit lower thermal stability for the FE mesophases than those of the calamitic mesogens. Eight different phases, designated as B<sub>1</sub>, B<sub>2</sub>, .....B<sub>8</sub> (where "B" stands for bent, banana, bow or boomerang) are identified [26] by Tschierske. Detailed classification schemes for the BLCs are presented by Takezoe [27] and Lubensky [28] that







paved the way for a better understanding of their field response. Reports [29–98] for BLC characterization speak out eight different BLC phases structures. However, only two of the phase structures viz.,  $B_2$  and  $B_5$  are found [27] to exhibit FE response. The organization of bent-core molecules in Smectic layers would be interesting, particularly when such arrangements lead to a biased response to the field, i.e., by polarization ( $P_S$ ) switching.

An overview of the reports [20,29–98] of FE response in BLCs also reveals that a central moiety is usually docked (Template 1) to two lateral moieties which are symmetrically configured on either of the sides. Each of the lateral moiety contains aromatic cores (with or without substituted) and flexible end chains (with a number of methyline units –CH<sub>2</sub>). Recently, many shape persistant BLC are also reported [99–109]. However, they are reported to be incapable of exhibiting FE response. Heterocyclic central moieties are also used [99–109] to design bent LC molecules. However, the BLCs reported so far with oxadiazole central moiety are found to exhibit Nematic, biaxial Nematic and Columnar (hexagonal) LC phases only.

From geometry point of view, BLCs so far reported [29–98] may also be classified as symmetric or non-symmetric depending on the constitution and configuration of aromatic cores and/or substitutions on (i) central miety, (ii) lateral moieties, (iii) end chains (of lateral moieties). It is noticed that non-symmetric BLCs can also be designed [99–109] by selecting a heterocyclic 5–membered ring as central moiety, viz., by an oxadiazole moiety. A meticulous review of BLC literature reveals [99–109] the fact that nonsymmetric molecular frame promotes the occurrence of FE B<sub>2</sub> and B<sub>5</sub> phases. Further, the FE phase stability needs to be shunted down towards device operating room temperature (RT) range for their viability in devices. Enhancement of magnitude for  $P_{\rm S}$  would be advantageous for their utility in storage devices.

Our earlier effort [110] to synthesize non-symmetric BLCs, viz.,  $C_8C_m$  series with 3,5-substututed 2,4-oxadiazole as central moiety, and distinct lateral moieties with differing order of aromaticity and length of end chains resulted in the realization of FE BLC phases down to 52 °C. It is noticed that non-symmetric (NS) nature can be imparted to the BLC molecular frame in  $C_8C_m$  series of BLCs in two ways. Involving a biphenyl moiety (two aromatic cores) on one side





Template 1. General molecular structure of Bent Liquid Crystal.

and a benzoate moiety on the other side of lateral moieties leads to non-symmetric nature of BLC molecular frame. The non-symmetric nature is further enhanced by increasing the chain length (i.e., from m=8 to 16) on one side of lateral moieties, while keeping the invariant chain length (with n=8) on the other side.

In the wake of the requirement to realize an ambient FE BLC phase structure through the design of non-symmetric molecular frame, we present the typical design of an NS BLC and followed by the usual characterization of it. The NS feature of BLC frame owes to the possession of greater chain length on the side (of lateral moiety) with less number of aromatic cores. Symbolically, the present BLC molecule is abbreviated as  $C_{12}C_{10}$ , in distinction with that  $C_8C_m$  (varied from m=8 to 16) series [110] of BLCs. The characterization of LC phases exhibited by  $C_{12}C_{10}$  is carried out by POM, DSC,  $P_S$  studies and LF (10 KHz–10 MHz) dielectric studies.

The paper is organized in 3–sections. Introduction to LCs and utility of FE achiral BLCs is presented in Section 1. Stepwise synthesis followed by and product confirmation and details of experimental techniques used for the characterization of LC phases are detailed in Section 2. The experimental results are discussed in Section 3.

# 2. Synthesis and experimental methods

2.1. Synthesis and spectroscopic characterization of dodecyl  $4-(5-(4'-(decyloxy)biphenyl-4-yl)-1,2,4-oxadiazol-3-yl)benzoate, C_{12}C_{10}$  BLC.

Synthetic route followed for the preparation of  $C_{12}C_{10}$  BLC is presented in Scheme 1 in four (i–iv) steps.

#### Step-i:

Octyl 4-cyanobenzoate (2)

To a solution of p-cyano benzoic acid (10 g, 0.067 mol), dry dichloromethane (100 mL) was added along with DCC (15.10 g, 0.074 mol) and DMAP (0.411 g, 0.003 mol) under Nitrogen atmosphere. The contents were stirred thoroughly. The process of stirring is continued followed by the addition of Octan-1-ol (10.61 g, 0.0815 mol of 1). Now, the reaction mixture was further stirred for 16 h. Reaction mixture was filtered and the filtrate was concentrated to get the crude product. Crude product was purified by column chromatography using silica gel (60–120). Compound, when eluted in EtOAc and petroleum ether, was found to give a product of Octyl 4-cyanobenzoate (2) appearing as a white solid approximately  $\sim$  13.8 g, to vouch 78.3% yield. <sup>1</sup>H NMR (with CDCl<sub>3</sub> as standard) study is carried out for the confirmation.

Elemental analysis: calculated for C<sub>16</sub>H<sub>21</sub>NO<sub>2</sub> (259.34), C 74.10, H 8.16, N 5.40%; found C 74.08, H 8.21, N 5.38%

Octyl 4-(N'-hydroxycarbamimidoyl)benzoate (3)

To the solution of Octyl 4-cyanobenzoate (13.8 g, 0.535 mol) taken in ethanol (80 mL), hydroxylamine hydrochloride (4.1 g, 0.0589 mol) was added and the mixture was thoroughly stirred. In presence of sodium hydroxide (2.36 g, 0.0589) and water (5 mL), the above mixture was heated under reflux for 3 h. Reaction mixture was cooled in a freezer for 24 h. The cold solution with the contents is filtered. The white crystalline substance was collected and then dried. The product was recrystallized using hexane, which was found to weigh to  $\sim$  10 g, while the yield is found to be 64.5%. Corresponding <sup>1</sup>H NMR (with CDCl<sub>3</sub>) is carried out to confirmation.

Elemental analysis: calculated for  $C_{16}H_{24}N_2O_3$  (292.37) C 65.73, H 8.27, N 9.58%; found C 65.55, H 8. 24, N 9.55% Octyl 4-(5-(4-bromophenyl)-1,2,4-oxadiazol-3-yl)benzoate (5) Octyl 4-(N'-hydroxycarbamimidoyl) benzoate (10 g, 0.034 mol



Scheme 1. Synthetic route for the preparation of  $C_{12}C_{10}$ .

of 3) was dissolved in dry pyridine (50 mL). The reaction mixture was cooled to 0 °C followed by the addition *p*-bromobenzoyl chloride (7.5 g 0.0342 of 4). The mixture was heated under reflux for 5 h. The cooled reaction mixture was poured into ice cold water (300 mL). The crude product was filtered. It was purified by re-crystallization in hot ethanol. The yield (12.3 g of 5) is found to be  $\sim$ 78.64%. It's <sup>1</sup>H NMR (CDCl<sub>3</sub>) analysis is carried out to confirm the product.

Elemental analysis: calculated for C23H25BrN2O3 (457.36)

C 60.40, H 5.51, N 6.13%, found C 60.20, H 5.36, N 6.17%. Step-ii

General procedure for synthesis of substituted Decyloxy Bromo Benzene (8):

Substituted Bromo-phenol (4.82 mmol of 6) is added to dry Acetonitrile (10 Vol) and the solution is stirred thoroughly. Further,  $K_2CO_3$  (7.2 mmol) and Decyl bromide (5.3 mmol of **7**)

are also added, and the reaction mixture was heated at 80 °C for 8 h. Acetonitrile was removed and residue was taken with EtOAc. In the water mixture, the organic layer was separated. A water wash is administered followed by the treatment in brine solution. It is dried over anhydrous sodium sulfate. The corresponding product, i.e., Decyloxy bromo benzene (8) was taken as such for next step without further purification. 1-bromo-4-(decyloxy) benzene (8)

Yield 86.35%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\partial$  (ppm) 7.36 (d, J=6.84 Hz, 2H), 6.77 (d, 6.84 Hz, 2H), 3.91(t, J=6.51 Hz, 2H), 1.75 (quintet, 2H), 1.27–1.44 (m, 14H), 0.88 (t, J=6.45 Hz).

Elemental analysis: calculated for  $C_{16}H_{25}BrO$  (313.27) C 61.34, H 8.04. Found: C 61.28, H 8.10.

Procedure for the synthesis of Boronate ester (9)

To 1-bromo-4-(decyloxy) benzene (i.e., 4.37 mmol of 8) solution, 1, 4 Dioxane (20 vol) was added along with Bis

pinacolato-diboran (17.51 mmol) and potassium acetate (21.85 mmol). The reactants were stirred for 5 mt and Nitrogen was purged out continuously for about 15 min. The  $pd(dppf)Cl_2$  (0.21 mmol) was added and the resulting reaction mixture was heated at 100 °C for about 16 h. Reaction mixture was cooled and filtered through a pad of Celite. The filtrate was concentrated. The residue was purified by column chromatography by using Silica gel (60–120) and product was eluted at 1–2% of EtoAc in hexane.

4,4,5,5-tetramethyl-2-(4-(decyloxy)phenyl)-1,3,2-dioxaborolane, (9)

Yield 70.80%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.87 (d, J=8.58 Hz, 2H), 7.56 (d, J=8.58 Hz, 2H), 4.09 (t, J=6.70 Hz, 2H), 1.57–1.64 (m, 2H), 1.16–1.28 (m, 25H), 0.89 (t, J=6.86 Hz, 3H). Elemental analysis: calculated for C<sub>22</sub>H<sub>37</sub>BO<sub>3</sub> (360.33) C 73.33, H 10.35 Found C 73.02, H 10.21.

Step-iii

Procedure for the synthesis of Octyl 4-(5-(4'-(Decyloxy)biphenyl-4-yl)-1,2,4-oxadiazol-3-yl)benzoates, (10)

A biphenyl moiety is realized in one of the lateral moieties of proposed BLC through the Suzuki [111] coupling reaction as presented in the synthetic route of preparation for the C<sub>12</sub>C<sub>10</sub>. To a solution of Octyl 4-(5-(4-bromophenyl)-1,2,4oxadiazol-3-yl) benzoate, (0.091 mmol of 5), the 4,4,5,5tetramethyl-2-(4-(decyloxy)phenyl)-1,3,2-dioxaborolanes (1.36 mmol of 9) is added and stirred by adding 1,2-DME (10 Vol) and aqueous Na<sub>2</sub>CO<sub>3</sub> (2.00 mmol) solution. Nitrogen was purged out for 15 min, followed by the addition of Pd (pph<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.018 mmol). The reaction was refluxed for 16 h under Nitrogen atmosphere. Reaction mixture was concentrated and residue was taken in Dichloromethane. It was given a wash with water and brine solution. The product (10) was dried over anhydrous sodium sulfate and concentrated. Crude product was purified by column chromatography (SiO<sub>2</sub> 230-400) and the product was eluted in 40% Dichloromethane mixed with petroleum ether. The product (10) obtained was re-crystallized from dichloro methane and methanol mixture. The synthetic yield is observed to be a color less (white) solid.

Octyl 4-[(5-(4'-(decyloxy)biphenyl-4-yl)-1,2,4-oxadiazol-3-yl)] benzoate, (10)

Yield 41.27%, <sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>:  $\partial$  (ppm) 8.25–8.29 (m, 4H), 8.19 (d, J=8.52 Hz, 2H), 7.75 (d, J=8.48 Hz, 2H), 7.61 (d, J=8.72 Hz, 2H), 7.02 (d, J=8.76 Hz, 2H), 4.36 (t, J=6.64 Hz, 2H), 4.02 (t, J=6.56 Hz, 2H), 1.79–1.84 (m, 4H), 1.27–1.56 (m, 31H), 0.89 (quintet, 6H).

Elemental analysis: calculated for C<sub>39</sub>H<sub>50</sub>N<sub>2</sub>O<sub>4</sub> (610.82) C 76.69, H 8.25, N 4.59 Found C 76.34, H 7.97, N 4.35.

# Step-iv

Synthesis of Dodecyl 4-(5-(4'-(decyloxy)biphenyl-4-yl)-1,2,4-oxadiazol-3-yl)benzoate (12)

To a stirred solution of octyl 4-(5-(4'-(decyloxy)biphenyl-4-yl)-1,2,4-oxadiazol-3-yl)benzoate 10 (0.25 g, 0.409 mmol), Methanol, water and THF was added in 1:1:2 (40 vol) ratio along with KOH (0.045 g, 0.818 mmol) at 0 °C and stirred. The reaction mixture was stirred for 16 h. THF was removed and the reaction mixture was cooled to 0 °C. Reaction mixture was acidified with 1.5 N HCl solution. Solid separated was filtered and given water wash and dried. The residue was taken in dry dichloromethane (10 vol) and was added to DCC (0.126 g, 0.614 mmol) and DMAP (0.075 g, 0.614 mmol) under Nitrogen atmosphere, followed by the addition of Dodecanol (11), (0.114 g, 0.614 mmol). The reaction mixture was stirred for 16 h. Solid separated was filtered. Filtrate was concentrated to get the crude product. Crude product was purified by column chromatography using silica gel (230–400 mesh). Compound was eluted in 40% DCM and petroleum ether. Purified compound was re-crystalized from DCM/Methanol mixture to procure dodecyl 4-(5-(4'-(decyloxy)biphenyl-4-yl)-1,2,4-oxa-diazol-3-yl)benzoate (12) as white solid (0.2 g, 74.07%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

The <sup>1</sup>H NMR spectra exhibited by  $C_{12}C_{10}$  (12) is presented in Fig. 1.

 $\partial$  (ppm) 0.92 (t, *J*=6.64 Hz, 6H), 1.29–1.39 (m, 29H) 1.44–1.52 (m, 4H), 1.78–1.85 (m, 2H), 4.03 (t, *J*=6.56 Hz, 2H), 4.37 (t, *J*=6.68 Hz, 2H), 7.03 (d, *J*=8.76 Hz, 2H), 7.62 (d, *J*=8.72 Hz, 2H), 7.76 (d, *J*=8.4 Hz, 2H), 8.20 (d, *J*=8.4 Hz, 2H), 8.27 (d, *J*=8.28 Hz, 4H)

<sup>13</sup>C NMR (CDCl<sub>3</sub>)

The  ${}^{13}C$  NMR spectra exhibited by  $C_{12}C_{10}$  (12) is presented in Fig. 2.

*a* 14.04, 22.61, 25.97, 28.63, 29.18, 29.22, 29.25, 29.27, 29.33, 29.46, 29.51, 29.56, 31.83, 65.44, 68.10, 114.96, 121.97, 127.04, 127.40, 128.21, 128.60, 129.94, 130.94, 131.66, 132.73, 145.28, 159.58, 165.98, 168.24, 175.95;

Elemental analysis: calculated for C<sub>43</sub>H<sub>58</sub>N<sub>2</sub>O<sub>4</sub> (666.93) C 77.44, H 8.77, N 4.20 Found C 73.29, H 7.75, N 4.10.

# 2.2. Experimental techniques for the LC phase characterization

<sup>1</sup>H NMR study of  $C_{12}C_{10}$  is carried out with a Bruker 400 MHz spectrometer using deuterated Chloroform as solvent and Tetramethyl Silane as internal standard (procured from Sigma-Aldrich). Polarized Optical Microscopy (POM) is carried out using an SD-Tech instrument in conjunction with an Instec HCS-402 Hot stage in conjunction with an STC-200 Temperature Controller which



**Fig. 1.** <sup>1</sup>H NMR spectra for  $C_{12}C_{10}$ .



works with an accuracy of  $\pm 0.1$  K. Calorimetry is carried out with a Schimadzu DSC-60 instrument operated at scan rate of 5  $^{\circ}$ C m<sup>-1</sup>. P<sub>S</sub> studies were carried out with Device Tech., (USA made 5 µm spaced) pre-treated transparent conductive (ITO) coated glass cells by field reversal method [112]. A Tektronix, DPO-3052, 500 MHz Digital Memory Oscilloscope and an AF (Tektronix, AFG-3021B) generator triggered with a triangular ac output (10  $V_{p-p}$  at 10 Hz) are used for  $P_S$  study. A triangular wave of 20–30  $V_{p-p}$  is used as input signal for the estimation of  $P_{\rm S}$ . The area under the output wave (averaged in one cycle) is mechanically measured as  $P_{s}$ . The Ps measurements are carried out by calibrating the setup with standard [113] FE substance FLC-9. LF dielectric investigations are carried out with the help of a Wayne Kerr Impedance Analyzer (20 Hz-10 MHz) and the BLC filled cells which were used for  $P_{\rm S}$  study. Instec (USA) pretreated (polymer buffed) cells of (5 µm spaced) made up of ITO coated transparent glass plates are used during the POM, P<sub>S</sub> measurements and LF dielectric investigations. Hysteresis behavior in FE B<sub>2</sub> Phase is studied through the capacitance measurements of LC filled cells, while impedance analyzer is operated in meter mode corresponding to the 1  $V_{p-p}$  oscillating signal at 100 KHz. Field variation is realized through the Bias-ON configuration of the Impedance Analyzer, i.e., bias field superposed over the 1  $V_{\rm p-p}$  triggering input. Since the LC cells are of 5  $\mu$ m spacing, the field is taken as bias field multiplied by  $0.2 \times 10^6 V \,\mu m^{-1}$ . Lead capacitance determined using AR Benzene (Fischer) is found to be 2 pF. The empty cell is found to exhibit (Fig. 3) temperature (or frequency) invariant (~48.87 pF) dielectric response over the frequency range of 10 Hz-10 MHz.



Fig. 3. Temperature and frequency variations of capacitance (C) for empty cell.

#### 3. Results and discussion

Owing to the fact that the observed number of H-atoms and C-atoms (Step–4 of Section 2.1 and Figs. 1 and 2) in the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra along with elemental composition agree with the expected number of H-atoms and C-atoms in the targeted (Scheme 1) BLC compound, viz.,  $C_{12}C_{10}$ ; the synthesis of the final product is argued to be successful. It is also confirmed that the product is free from impurities at spectroscopic level.

# 3.1. Polarized optical microscopy:

 $C_{12}C_{10}$  material is introduced into the 5 µm spaced (Device Tech made) cell when the material is at 3 °C above its clearing temperature (i.e., when  $C_{12}C_{10}$  is in isotropic liquid state) by capillary action. C12C10 is filled into Device Tech cells to ensure the homogeneously aligned state to the sample. The LC filled cell is placed in Instec hot stage for the Polarized Optical Microscopy (POM) studies. The POM is set in crossed polar configuration. With the help of an Instec temperature controller, the sample is heated by operating it in programmable mode. The textures exhibited by sample are observed through the oculars of the microscope. These POM textures are projected on to a TV monitor through a CCD camera setup. Microscope textures exhibited by sample are recorded both in heating and cooling scans. All the textures exhibited by  $C_{12}C_{10}$  (both in heating and cooling runs) in different BLC phases during the heating/cooling scans are found to be one or other forms of focal conic fan textures (or its modifications). This observation infers that C12C10 is exhibiting layered Smectic LC phases in the thermal range, i.e., from room temperature to the isotropic liquid state (i.e., up to clearing temperature). Similar trend of textural observations are also held in the cooling scan of POM. Observation of any textural change at a specific temperature is considered as the phase transition temperature. Hence, this specific temperature at which the textural change occurs is recorded as phase transition temperature  $(T_c)$  through the POM technique.  $C_{12}C_{10}$  is found exhibit arched focal conic fan texture at RT (30 °C) initially. But, in cooling scan, SmA is observed to grow as focal conic batonnet (Plate 1) texture from isotropic liquid. Broken focal conic texture is observed (Plate 2) in SmX phase (tentatively labeled, which is later confirmed as FE  $B_2$  (by the  $P_s$  observation in the ongoing Section 3.4). Twined mosaic texture is observed (Plate 3) for the SmG phase. The arced focal conic fan texture is observed (Plate 4) for SmE phase. The microscopic texture reported [114,115] for the SmE phase in calamatic LCs is found to be analogous to the arced focal conic fan texture (Plate 4) exhibited



Plate 1. Focal conic fan texture of SmA phase in  $C_{12}C_{10}$  at 175  $^\circ C$  .

**Plate 2.** Broken focal conic fan texture of  $B_2$  phase in  $C_{12}C_{10}$  at 99.2 °C.



Plate 3. Colored mosaic texture of SmG phase exhibited in  $C_{12}C_{10}$  at 56.9 °C .



Plate 4. Arced focal conic texture of SmE phase in  $C_{12}C_{10}$  at 40.8 °C .

by SmE phase in  $C_{12}C_{10}$ . Further, SmE phase in  $C_{12}C_{10}$  is not found to respond to P<sub>S</sub> switching. Hence, it is confirmed that SmE phase is a non FE phase. The arched foal conic texture of SmE is found to change (at 56.3 °C) into mosaic texture with reduced area and undulated edges of fans with an intertwined geometry in the adjacent domains. The textural appearance of this phase seems to be made-up of intertwined or interspersed focal conic domains.

Similar mosaic textures are also reported [11] in literature for SmG phase.

#### 3.2. Identification of SmX as $B_2$

On heating of SmG phase, the sample undergoes a textural change at 82.7 °C and grows into a larger area bearing texture with relatively more bright surface with increased discontinuities at the boundaries. Since, the texture resembles that of focal conic fans, this phase is tentatively labeled as SmX phase. SmX phase exhibited by  $C_{12}C_{10}$  in the heating run is subsequently relabeled as B<sub>2</sub> phase owing to its FE switching behavior (as presented in the ongoing Section 3.5). Further, heating of SmX phase in  $C_{12}C_{10}$  its leads to the formation (  $\sim\!157~^\circ\!C)$  of smooth, clear and fine edged focal conic fan texture, which resembles characteristic [11] focal conic fan texture of SmA phase. Further heating leads to the change of texture to dark brown appearance. This appearance is identified as isotropic liquid phase. It is found that  $C_{12}C_{10}$  exhibits SmA, SmX (relabeled as B<sub>2</sub> due to the P<sub>S</sub> switching), SmG and SmE phases in the cooling scan also. Thus, the observed LC phase variance exhibited by C12C10; i.e., SmA, B2, SmG, SmE is confirmed as enantiotropic in nature. The phase transition temperatures recorded through POM in heating and cooling runs are presented in Table 1. The thermal spans of LC phases observed for  $C_{12}C_{10}$  in heating scan are found to slightly differ from those observed in cooling scan. However, the hierarchy of occurrence is found to remain invariant.

#### 3.3. Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) experiments are carried out for  $C_{12}C_{10}$  in both of the heating and cooling scans at a rate of 5  $^{\circ}$ C m<sup>-1</sup>. The phase transition temperatures are determined from the peaks (or valley) of thermograms. The DSC thermograms recorded for  $C_{12}C_{10}$  are presented in Fig. 4. The three peaks observed in heating scan (Fig. 4) are identified as SmE to SmG, SmG to SmX (or B<sub>2</sub>), SmA to Isotropic phase transitions. The DSC thermogram is not exhibiting any peak in vicinity of 157 °C, i.e., corresponding to the SmX to SmA transition. Hence, the SmA-SmX (B<sub>2</sub>) transition is inferred as second ordered nature. The remaining LC phase transitions, viz., Iso-SmA, SmX-SmG and SmG-SmE are argued to be of first order nature due to the fact that they involve finite heat  $(\Delta H)$  of transition. The  $\Delta H$  values (enclosed in square braces) recorded during the heating and cooling scans of DSC and the phase transition temperatures  $T_{\rm C}$  are presented in Table 1. The phase transition temperatures determined by DSC are found to agree with those by POM studies. The observed first ordered nature for the I-SmA, SmX-SmG and SmG-SmE transitions reflects upon the considerable structural changes across the transitions.

#### 3.4. Spontaneous polarization studies

Spontaneous polarization  $P_{S}(T)$  in the FE B<sub>2</sub> phase exhibited by  $C_{12}C_{10}$  is determined by field reversal method. As the LC system transits (Fig. 5) into SmX phase with the decreasing temperature of SmA phase, the output wave (superposed over the input triangular wave) is observed to develop a peak. The temperature at which output wave develops a peak is identified as SmA-B<sub>2</sub> phase transition temperature. The value of SmA–SmX(B<sub>2</sub>) transition temperature is found to agree with the observed (Table 1) from POM and DSC. The area under the output wave represents the  $P_{\rm S}$  exhibited by the sample at the temperature of interest in SmX phase. Hence, SmX phase is confirmed to exhibit FE switching. SmX phase hence forth is re-labeled as B<sub>2</sub> phase.



Table 1	
Data of phases, transition temperatures $T_{\rm C}$ (in	°C) and Enthalpy ( $\Delta H$ in J gm <sup>-1</sup> ) by POM, DSC, $P_{\rm S}$ and LF dielectrics.

BLC molecule	Method		Details of phases, transition temperatures ( $T_c$ in $^\circ C$ ) and enthalpy ( $\Delta H$ in J/g)	(Δ <i>T</i> ) <sub>FE</sub> / °C
C <sub>12</sub> C <sub>10</sub>	РОМ	Heating	RT(30 °C) SmE−59.3 → SmG −82.7 → $B_2$ −157.1 → SmA−178.4 → Iso	74.4
		Cooling	RT(30 °C) SmE $\leftarrow$ 50.2-SmG $\leftarrow$ 59.1-B <sub>2</sub> $\leftarrow$ 157- SmA $\leftarrow$ 178.3-Iso	97.9
	DSC	Heating	RT(30 °C) SmE-59.2 → SmG-82.81 → $B_2$ -157.07 → SmA-178.31 → Iso.	74.26
			[65.79] [8.32]	
		Cooling	RT(30 °C) SmE ← 50.3 – SmG ← 59.1 – $B_2$ ← 157.07 – SmA ← 178.3 – Iso.	97.9
		-	[2.41] [7.99]	
	Ps	Cooling	$SmG \leftarrow 59.1 - B_2 \leftarrow 157 - SmA$	97.9
	LF-Dielectrics capacitance loss factor	Cooling	$SmE \leftarrow 49 - SmG \leftarrow 59.1 - B_2 \leftarrow 157 - SmA \leftarrow 178.4 - Iso.$	97.9

Values in [] indicate enthalpy.



**Fig. 4.** DSC thermogram for  $C_{12}C_{10}$ .

At different temperatures, the output wave is recorded and recalled as to determine the area under the peak (estimated automatically by the memory scope). The area (averaged over 1 cycle) under peak estimated electronically (by CRO itself) reflects upon  $P_{\rm S}$  value.

The observed variation of  $P_{\rm S}$  with temperature  $P_{\rm S}(T)$  in  $C_{12}C_{10}$  in its FE B<sub>2</sub> phase is (in Fig. 6) is found to exhibit a saturation value of  $\sim$ 80 nC cm<sup>-2</sup>. The P<sub>s</sub> value in FE B<sub>2</sub> phase exhibited by C<sub>12</sub>C<sub>10</sub>, when compared to the  $P_{\rm S}$  reported [110] for  $C_8C_{\rm m}$  series of BLCs possessing analogous molecular frame (i.e., for C<sub>8</sub>C<sub>m</sub>) is found to be less by 20%. The relatively lower  $P_S$  value of  $C_{12}C_{10}$  is argued due to the NS symmetric design features. As discussed in the final part of introduction part, the inclusion of twelve methyline (-CH<sub>2</sub>) units on the side of benzoate moiety leads to the reduction of nonsymmetric nature of molecular frame, i.e., in comparison with  $C_8C_{10}$  of  $C_8C_m$  series. This might have lead to the reduction in  $P_{s}$ . As such, decreasing NS nature frame is predicted to cause a reduced  $P_S$  value in NS type of BLCs. The  $P_S$  observed in  $C_{12}C_{10}$ seems to be an intermediate value in comparison with the  $P_{\rm S}$ exhibited [112] by chiral LC phases (SmC\*). P<sub>S</sub> value in B<sub>2</sub> phase of  $C_{12}C_{10}$  is also found to fall in the lower range of values reported [29-98] in  $B_2$  and  $B_5$  phases of NS BLCs.

The growth of  $P_S(T)$  observed in the B<sub>2</sub> phase of C<sub>12</sub>C<sub>10</sub> is found to be rather asymptotically fast in comparison with that  $P_S(T)$ reported [112,113] in SmC\* phase. The relatively fast growth of  $P_S$ value is attributed to the distinct nature of growth of polarization in the supra-molecular BLC phase structures.

Spontaneous polarization  $P_s$  in FE phases represents the order parameter  $\theta$ . The order parameter in the case of FE LC phase structures is attributed with secondary nature, especially in SmC\* phase. The Tilt angle plays the primary order parameter, while Ps plays the role of secondary order parameter in chiral center based SmC\* phase structures. Growth of order parameter [116] with the relevant thermodynamic variable (say temperature *T*) provides information regarding the strength of microscopic interactions and their range of operation. However, in case of achiral FE B<sub>2</sub> or FE B<sub>5</sub> LC phase structures, Ps represents a unique order parameter. Hence, Normalized Order parameter  $\theta_N$  and universal dimension-less temperature scale ( $T^U$ ) are estimated from the observed dispersion of  $P_s(T)$  from the relations given by

$$\theta_{\rm N} = P_{\rm i}(T)/P_{\rm sat} \tag{1}$$

where,  $P_i(T)$  is the observed  $P_s$  at the temperature of interest in B<sub>2</sub> phase and

 $P_{\text{sat}}$  is the maximum  $P_{\text{s}}$  observed for  $C_{12}C_{10}$  in its  $B_2$  phase, i.e., 83.09 nC cm<sup>-2</sup>.

$$T^{\rm U} = [T_{\rm M} - T_{\rm i}] / [\Delta T]_{\rm B2} \tag{2}$$

where,  $T_M$  is the melting transition temperature for the B<sub>2</sub> phase in C<sub>12</sub>C<sub>10</sub> i.e., 157 °C.

 $T_i$  is the temperature of interest and [ $\Delta T$ ] B<sub>2</sub> is the thermal stability of B<sub>2</sub> phase, i.e., 98 °C.

Growth of  $\theta_N$  with  $T^U$  is also presented in Fig. 6. The data of dispersal of  $\theta_N$  with  $T^U$  is fitted to a relation [Ref] given by

$$\theta_{\rm N} \propto [T^{\rm U}]^{\beta_2} \tag{3}$$

where, critical exponent [116] reflects the characteristic nature of growth of relevant order parameter. Data of  $\theta_N$  ( $T^U$ ) fitted to the relation-3 yielded the order parameter exponent  $\beta_2$  with a value of 0.075  $\pm$  0.001. The exponent is found to deviate much from the critical field expected value. The solid line generated out of the non-linear least square fitting procedure is also superposed over the dispersal of data in fig. 6. The goodness of the fit is demonstrated through the estimated p-value of 0.975 during the  $\chi^{-2}$ -test.

# 3.5. Low frequency dielectric studies

# 3.5.1. Phase transitions by capacitance C(T) and loss factor $tan\Delta(T)$ :

The  $C_{12}C_{10}$  cell is connected to the impedance analyzer. Impedance analyzer is operated at a fixed frequency of 100 kHz and triggered by  $1\,V_{\mathrm{p}-\mathrm{p}}$  oscillating signal under the bias-off condition. The Impedance Analyzer is operated in LCR meter mode, and the output panel readings of capacitance C(T) and loss factor  $Tan \Delta(T)$  exhibited by sample (at the temperature of interest) are recorded in all BLC phases of C<sub>12</sub>C<sub>10</sub> in the cooling run. The Instec temperature controller is programmed to go to 3 °C above  $(\sim 182 \text{ °C})$  the clearing temperature of  $C_{12}C_{10}$ . The instrument is programmed to cool down at a rate of 0.02 °C up to room temperature ( $\sim$ 25 °C). The readings of capacitance C(T) and loss factor  $Tan\Delta(T)$  are recorded. The observed temperature variation for capacitance C(T) and loss factor  $Tan\Delta(T)$  are presented in Fig. 7. The peaks in capacitance C and the valleys in loss factor Tan∆ are identified as phase transition temperatures (as denoted by inset arrows). The observed values of phase transition temperatures



**Fig. 5.**  $P_S$  profile for by  $C_{12}C_{10}$  in FE  $B_2$  phase at 150 °C.



**Fig. 6.** Temperature variation of  $P_{S}(T)$  FE B<sub>2</sub> phase in C<sub>12</sub>C<sub>10</sub>.



Fig. 7. Temperature variation of capacitance C(T) and Loss Factor  $Tan \Delta(T)$  for  $C_{12}C_{10}.$ 

exhibited by  $C_{12}C_{10}$  during the LF dielectric study (in cooling run) are presented in Table 1. The phase transition temperatures determined by LF dielectric method are found to agree with the values determined by POM, DSC and P<sub>S</sub> techniques. Increasing trend of capacitance in the vicinity of a phase transition infers the increasing dipolar correlation pertaining to the on-coming phase structure. It is noticeable that the SmA to B<sub>2</sub> transition could not be



Fig. 8. Field variation of capacitance C(E) i.e., hysteresis behavior for  $C_{12}C_{10}$ .

detected by DSC, due to its second order nature. However, it could be evinced by the present LF dielectric method. Hence, the LF dielectric method is argued to be capable of detecting even the second (continuous) order transitions involving the marginal structural changes.

#### 3.5.2. Low frequency dielectric hysteresis behavior

Variation of capacitance with applied electric field (Bias-on configuration) is studied in the  $C_{12}C_{10}$  in its FE B<sub>2</sub> phase at 150 °C. Capacitance (C) as a measure of E-field response is measured. DC field is blocked by a capacitor. Hence, E-field response exhibited by the  $C_{12}C_{10}$  in the FE B<sub>2</sub> phase is effectively measured by operating the Impedance analyzer in bias field ON configuration. Thus, a known dc field of 0 to  $\pm 40$  V may be superposed over the 1 V<sub>p-p</sub> input oscillating signal at a fixed frequency of 100 kHz. Hysteresis behavior is studied over a cycle of field. Thus, the bias field is varied over a cycle, i.e., in the intervals of 0-40 V; 40-0 V; 0 to -40 V and -40 to 0 V. Field intensity is given as V cm<sup>-1</sup>. In the present case of 5  $\mu$ m spaced cells filled with  $C_{12}C_{10}$  the field intensity is read in  $0.2 \times 10^6 \, V \, m^{-1}$  as labeled in Fig. 8. The observed capacitance variation with the applied field is presented in Fig. 8. It is observed that for the higher applied fields, the increasing trend seems to result in a higher capacitance value, than that resulted during the decreasing trend of field (in both of the positive and negative half cycles). For convenience of reading, color contrast (red/green) is adopted during the variation of applied field in Fig. 8. It is also found interesting to notice the occurrence of cross-over of the field, especially in the case of negative half cycle. This is suggestive of a



**Fig. 9.** Frequency variation of capacitance  $C(\omega)$  and Loss Factor Tan $\Delta$  for  $C_{12}C_{10}$  in SmA phase at different temperatures.

possible V-shaped switching in FE  $B_2$  phase in  $C_{12}C_{10}$ . The observed hysteresis behavior reinstates the FE nature of the  $B_2$  phase and its possible utility in a storage device.

#### 3.5.3. Low frequency relaxation behavior:

The low frequency (10 Hz–10 MHz) dielectric dispersion is measured as variation in capacitance C and loss factor Tan $\Delta$  at different specified temperatures in different LC phases during the cooling scan of  $C_{12}C_{10}$  (for the bias-off configuration). The capacitance  $C(\omega)$  and loss factor Tan $\Delta(\omega)$  are recorded (from panel–1 and –2 respectively) at the temperature of interest in all LC phases exhibited by  $C_{12}C_{10}$ . The variation of  $C(\omega)$  and Tan $\Delta(\omega)$ is presented in Fig. 9 (in SmA as representative). In the wake of the temperature invariant (Fig. 3) capacitance exhibited by the empty cell (~48.87 pF) the relative permittivity  $\varepsilon'$  (or  $\varepsilon_r$ ) is estimated by

$$\varepsilon'(\omega) = C/48.87 = \varepsilon_{\rm r}(\omega) \tag{4}$$

The dielectric loss  $\varepsilon''(\omega)$  is estimated by

$$(\omega) = \varepsilon_{\Gamma} * \operatorname{Tan} \Delta$$



Fig. 10. Cole-Cole plots for SmA, FE B<sub>2</sub>, SmG and SmE phases of C<sub>12</sub>C<sub>10</sub>.

(5)

However, by the dielectric dispersion in LCs is given [117,118] by

$$\varepsilon^*(\omega) = \varepsilon_{\infty} - \{(\Delta \varepsilon)/(1 + [j\omega\tau]^{1-a})\}$$
(6)

Where,

 $\Delta \epsilon = [\epsilon_0 - \epsilon_\infty]$  is the dielectric strength, estimated by extrapolating  $\epsilon''$  on to the  $\epsilon_r$  axis.

- $\tau$  = the Relaxation time given by  $1/f_{\rm R}$
- $\omega = 2\pi f$  and

 $\alpha$  = the distribution parameter reflecting upon the degrees of freedom exhibited by the phase in any LC phase structure.

The observed  $\text{Tan}\Delta(\omega)$  or  $\varepsilon''(\omega)$  recorded at any specific temperature in all the LC phases exhibited by  $C_{12}C_{10}$  is found to be accompanied by two peaks. The frequency corresponding to the peak value of  $\varepsilon''_{\text{max}}$  (or  $\text{Tan}\Delta_{\text{max}}$ ) is identified as the relaxation frequency  $f_{\text{R}}$ . The dielectric loss  $\varepsilon''$  recorded at the temperature of interest in all the LC phases of  $C_{12}C_{10}$  is found to exhibit two peaks to infer a low frequency (KHz) relaxation process and a higher frequency (MHz) relaxation process. In the wake of the observed temperature invariant (Fig. 3) behavior of capacitance C(T), Tan $\Delta$ 



Fig. 11. Arrhenius plots of LF and HF relaxations in C<sub>12</sub>C<sub>10</sub>.

(T) or  $\varepsilon''(T)$  exhibited by  $C_{12}C_{10}$ , the peaks in Tan $\Delta$  (or  $\varepsilon''$ ) in LC phases of  $C_{12}C_{10}$  and their shift with temperatures are attributed to the contributions of BLC material. A careful observation of variation in  $\varepsilon''(\omega)$  with frequency also reveals the non-symmetric response of LC phases, i.e., about the  $\varepsilon''_{max}$ . The non-symmetric response of loss  $\varepsilon''$  (or Tan $\Delta$  about its maximum value) with the increasing frequency in turn suggests for an off-centered dielectric dispersion [117,118] in the BLC phases. In order to analyze the observed LF dielectric response and to investigate the two distinct (time scale wise) modes of relaxation behavior, the data of  $\varepsilon''$  and  $\varepsilon_r$  viz., the LF dielectric dispersion (i.e., in all LC phases exhibited by C<sub>12</sub>C<sub>10</sub> for both LF and HF relaxations) is presented as Cole–Cole plots in Fig. 10. The data of LF dielectric parameters corresponding to the LF and HF relaxation modes, viz., Relaxation frequency  $f_{\rm R}$ , loss maximum  $e''_{max}$ , dielectric strength  $\Delta e$ , distribution parameter- $\alpha$  and activation energy ( $E_a$ ) are estimated from the Cole-Cole plots and reduced temperature plots (Fig. 11). The data of LF dielectric parameters for  $C_{12}C_{10}$  is presented in Table 2. The range of f<sub>R</sub> corresponding to low frequency relaxation mode is found to coincide with that reported [119] for scissor mode in other BLCs. The scissor mode of vibration is found to be sluggish. The scissor mode of vibration is attributed to the co-operative reorientation mechanism of the two lateral moieties (with flexible chains) together to the field. Hence, LF relaxation is argued rather sluggish and manifests in KHz region. The high frequency mode is attributed to the reorientation mechanism of longitudinal dipole moment  $\mu_{I}$  (configured on the central moiety) to the applied field. As it spreads less space, it is expected to be relatively fast. Hence, observed relaxations and their time scale agrees with the expected values. The  $\epsilon_o$  and  $\epsilon_\infty$  are determined from Cole–Cole plots as extrapolated values of Cole–Cole arc of  $\varepsilon''$  which intersects with  $\varepsilon_r$  axis. The point of intersection towards the LF side is read as  $\varepsilon_0$ and that at HF side is read as  $\varepsilon_\infty.$  An overview of the Cole–Cole plots in both of the LF and HF relaxations reveals a greater temperature shift of  $\varepsilon_r$  in the LF end (i.e., through  $\varepsilon_0$ ) in all the BLC phases. The observed large temperature shift of  $\varepsilon_0$  speaks out the relative dielectric susceptibility  $\Delta \varepsilon = [\varepsilon_0 - \varepsilon_\infty]$  of BLC phase

#### Table 2

Data of relaxation frequency  $f_{R}$ , Loss Maximum  $\varepsilon''_{max}$ , dielectric strength  $\Delta \varepsilon$ ,  $\alpha$ - parameter and activation energy  $E_a$  in BLC phases of  $C_{12}C_{10}$ .

	Phase variance	Temp °C	Low frequency relaxation				High frequency relaxation			
SmA {0.864} [0.041]         178         1.8732         177.76         364         0.0348         6.4810         0.5999         1.42         0.314           170         1.9321         173.005         362         0.0522         6.4812         0.5463         1.228         0.279           166         1.9570         171.82         361         0.0696         6.4990         0.5466         1.207         0.261           164         1.9746         170.62         348         0.087         6.5016         0.5464         1.186         0.243           162         1.9821         170.30         341         0.1044         6.5210         0.5461         1.164         0.209           B2 {0.053} [0.077]         156.6         1.7064         150.48         300         0.1218         6.5390         0.5461         1.164         0.209           B2 {0.053} [0.077]         156.6         1.7064         150.48         300         0.1218         6.1351         1.252         1.6         0.0696           136.5         1.7304         124.97         265.5         0.1218         6.196         1.2568         1.34         0.1566           165.5         1.661         0.677         63.747         1			f <sub>R</sub> (KHz)	${m arepsilon''}_{ m max}$	$\Delta \boldsymbol{\varepsilon} \!=\! [\boldsymbol{\varepsilon}_{0} \!-\! \boldsymbol{\varepsilon}_{\infty}]$	α	f <sub>R</sub> (MHz)	${\varepsilon''}_{\max}$	$\Delta \boldsymbol{\varepsilon} \!=\! [\boldsymbol{\varepsilon}_{0} \!-\! \boldsymbol{\varepsilon}_{\infty}]$	α
170       1.9321       173.005       362       0.0522       6.4812       0.5463       1.228       0.279         166       1.9570       171.82       361       0.0696       6.4990       0.5466       1.207       0.261         164       1.9746       170.62       348       0.087       6.5016       0.5464       1.186       0.243         162       1.9821       170.30       341       0.1044       6.5210       0.5452       1.175       0.226         158       1.9935       166.45       340       0.1218       6.5390       0.5461       1.164       0.209         B <sub>2</sub> {0.053} [0.077]       156.6       1.7064       150.48       300       0.1218       6.5390       0.5461       1.164       0.209         B <sub>2</sub> {0.053} [0.077]       156.6       1.7064       150.48       300       0.1218       6.1551       1.2568       1.34       0.1566         116.5       1.7483       98.32       218.5       0.1044       6.2571       1.2636       1.25       0.174         96.5       1.7662       28.03       105.7       0.6966       6.4563       1.284       1.07       0.208         61.5       1.9935       25.19	SmA {0.864} [0.041]	178	1.8732	177.76	364	0.0348	6.4810	0.5999	1.42	0.314
166         1.9570         171.82         361         0.0696         6. 4990         0.5466         1.207         0.261           164         1.9746         170.62         348         0.087         6.5016         0.5464         1.186         0.243           162         1.9821         170.30         341         0.1044         6.5210         0.5452         1.175         0.226           158         1.9935         166.45         340         0.1218         6.5390         0.5461         1.164         0.209           B2 {0.053} [0.077]         156.6         1.7064         150.48         300         0.1392         6.1351         1.2522         1.6         0.0696           136.5         1.7304         124.97         265.5         0.1218         6.196         1.2668         1.34         0.1566           116.5         1.7483         98.32         218.5         0.1044         6.2571         1.2636         1.25         0.174           96.5         1.7607         63.747         168.6         0.087         6.3252         1.2749         1.16         0.191           76.5         1.7662         28.03         105.7         0.0696         6.4563         1.284         1		170	1.9321	173.005	362	0.0522	6.4812	0.5463	1.228	0.279
164         1.9746         170.62         348         0.087         6.5016         0.5464         1.186         0.243           162         1.9821         170.30         341         0.1044         6.5210         0.5452         1.175         0.226           158         1.9935         166.45         340         0.1218         6.5390         0.5461         1.164         0.209           B2 (0.053) [0.077]         156.6         1.7064         150.48         300         0.1392         6.1351         1.2522         1.6         0.0696           136.5         1.7304         124.97         265.5         0.1218         6.196         1.2568         1.34         0.1566           116.5         1.7483         98.32         218.5         0.1044         6.2571         1.2636         1.25         0.174           96.5         1.7607         63.747         168.6         0.087         6.3252         1.2749         1.16         0.191           76.5         1.7662         28.03         105.7         0.0696         6.4563         1.284         1.07         0.208           61.5         1.9935         25.19         55.8         0.0522         6.5402         1.285         0.9		166	1.9570	171.82	361	0.0696	6. 4990	0.5466	1.207	0.261
162       1.9821       170.30       341       0.1044       6.5210       0.5452       1.175       0.226         158       1.9935       166.45       340       0.1218       6.5390       0.5461       1.164       0.209         B2 {0.053} [0.077]       156.6       1.7064       150.48       300       0.1392       6.1351       1.2522       1.6       0.0696         136.5       1.7304       124.97       265.5       0.1218       6.196       1.2568       1.34       0.1566         116.5       1.7483       98.32       218.5       0.1044       6.2571       1.2636       1.25       0.174         96.5       1.7607       63.747       168.6       0.087       6.3252       1.2749       1.16       0.191         76.5       1.7662       28.03       105.7       0.0696       6.4563       1.284       1.07       0.208         61.5       1.9935       25.19       55.8       0.0522       6.5402       1.285       0.98       0.226         SmG {0.623} [0.065]       58       1.4172       14.027       20.86       0.2436       6.0782       0.1268       0.50       0.1566         56       1.5326       11.01       <		164	1.9746	170.62	348	0.087	6.5016	0.5464	1.186	0.243
158         1.9935         166.45         340         0.1218         6.5390         0.5461         1.164         0.209           B2 [0.053] [0.077]         156.6         1.7064         150.48         300         0.1392         6.1351         1.2522         1.6         0.0696           136.5         1.7304         124.97         265.5         0.1218         6.196         1.2568         1.34         0.1566           116.5         1.7483         98.32         218.5         0.1044         6.2571         1.2636         1.25         0.174           96.5         1.7607         63.747         168.6         0.087         6.3252         1.2749         1.16         0.191           76.5         1.7662         28.03         105.7         0.0696         6.4563         1.284         1.07         0.208           61.5         1.9935         25.19         55.8         0.0522         6.5402         1.285         0.98         0.226           SmG {0.623} [0.065]         58         1.4172         14.027         20.86         0.2436         6.0782         0.1268         0.50         0.1566           56         1.5326         11.01         20.07         0.261         6.087		162	1.9821	170.30	341	0.1044	6.5210	0.5452	1.175	0.226
B2 {0.053} [0.077]         156.6         1.7064         150.48         300         0.1392         6.1351         1.2522         1.6         0.0696           136.5         1.7304         124.97         265.5         0.1218         6.196         1.2568         1.34         0.1566           116.5         1.7483         98.32         218.5         0.1044         6.2571         1.2636         1.25         0.174           96.5         1.7607         63.747         168.6         0.087         6.3252         1.2749         1.16         0.191           76.5         1.7662         28.03         105.7         0.0696         6.4563         1.284         1.07         0.208           61.5         1.9935         25.19         55.8         0.0522         6.5402         1.285         0.98         0.226           SmG {0.623} [0.065]         58         1.4172         14.027         20.86         0.2436         6.0782         0.1268         0.50         0.1566           56         1.5326         11.01         20.07         0.261         6.087         0.1172         0.451         0.174           55         1.553         9.99         19.56         0.2784         6.0958		158	1.9935	166.45	340	0.1218	6.5390	0.5461	1.164	0.209
136.5       1.7304       124.97       265.5       0.1218       6.196       1.2568       1.34       0.1566         116.5       1.7483       98.32       218.5       0.1044       6.2571       1.2636       1.25       0.174         96.5       1.7607       63.747       168.6       0.087       6.3252       1.2749       1.16       0.191         76.5       1.7662       28.03       105.7       0.0696       6.4563       1.284       1.07       0.208         61.5       1.9935       25.19       55.8       0.0522       6.5402       1.285       0.98       0.226         SmG {0.623} [0.065]       58       1.4172       14.027       20.86       0.2436       6.0782       0.1268       0.50       0.1566         56       1.5326       11.01       20.07       0.261       6.087       0.1172       0.451       0.174         55       1.553       9.99       19.56       0.2264       6.0958       0.11029       0.43       0.2088         54       1.5868       8.567       14.05       0.3366       6.1966       0.1003       0.4       0.2268	B <sub>2</sub> {0.053} [0.077]	156.6	1.7064	150.48	300	0.1392	6.1351	1.2522	1.6	0.0696
116.5         1.7483         98.32         218.5         0.1044         6.2571         1.2636         1.25         0.174           96.5         1.7607         63.747         168.6         0.087         6.3252         1.2749         1.16         0.191           76.5         1.7662         28.03         105.7         0.0696         6.4563         1.284         1.07         0.208           61.5         1.9935         25.19         55.8         0.0522         6.5402         1.285         0.98         0.226           SmG {0.623} [0.065]         58         1.4172         14.027         20.86         0.2436         6.0782         0.1268         0.50         0.1566           56         1.5326         11.01         20.07         0.261         6.087         0.1172         0.451         0.174           55         1.553         9.99         19.56         0.2386         0.11029         0.431         0.208           54         1.5868         8.567         14.05         0.3306         6.1046         0.1003         0.4         0.2268		136.5	1.7304	124.97	265.5	0.1218	6.196	1.2568	1.34	0.1566
96.5         1.7607         63.747         168.6         0.087         6.3252         1.2749         1.16         0.191           76.5         1.7662         28.03         105.7         0.0696         6.4563         1.284         1.07         0.208           61.5         1.9935         25.19         55.8         0.0522         6.5402         1.285         0.98         0.226           SmG {0.623} [0.065]         58         1.4172         14.027         20.86         0.2436         6.0782         0.1268         0.50         0.1566           56         1.5326         11.01         20.07         0.261         6.087         0.1172         0.451         0.174           55         1.553         9.99         19.56         0.2386         6.1062         0.1003         0.43         0.2088           54         1.5868         8.567         14.05         0.3306         6.1046         0.1003         0.43         0.2088		116.5	1.7483	98.32	218.5	0.1044	6.2571	1.2636	1.25	0.174
76.5         1.7662         28.03         105.7         0.0696         6.4563         1.284         1.07         0.208           61.5         1.9935         25.19         55.8         0.0522         6.5402         1.285         0.98         0.226           SmG {0.623} [0.065]         58         1.4172         14.027         20.86         0.2436         6.0782         0.1268         0.50         0.1566           56         1.5326         11.01         20.07         0.261         6.087         0.1172         0.451         0.174           55         1.553         9.99         19.56         0.2784         6.0958         0.11029         0.43         0.2088           54         1.5868         8.567         14.05         0.3306         6.1046         0.1003         0.4         0.2268		96.5	1.7607	63.747	168.6	0.087	6.3252	1.2749	1.16	0.191
61.5         1.9935         25.19         55.8         0.0522         6.5402         1.285         0.98         0.226           SmG {0.623} [0.065]         58         1.4172         14.027         20.86         0.2436         6.0782         0.1268         0.50         0.1566           56         1.5326         11.01         20.07         0.261         6.087         0.1172         0.451         0.174           55         1.553         9.99         19.56         0.2784         6.0958         0.11029         0.43         0.2083           54         1.5868         8.567         14.05         0.3306         6.1046         0.1003         0.4         0.2261		76.5	1.7662	28.03	105.7	0.0696	6.4563	1.284	1.07	0.208
SmG {0.623} [0.065]         58         1.4172         14.027         20.86         0.2436         6.0782         0.1268         0.50         0.1566           56         1.5326         11.01         20.07         0.261         6.087         0.1172         0.451         0.174           55         1.553         9.99         19.56         0.2784         6.0958         0.11029         0.43         0.2088           54         1.5868         8.567         14.05         0.3306         6.1046         0.1003         0.4         0.2263		61.5	1.9935	25.19	55.8	0.0522	6.5402	1.285	0.98	0.226
56         1.5326         11.01         20.07         0.261         6.087         0.1172         0.451         0.174           55         1.553         9.99         19.56         0.2784         6.0958         0.11029         0.43         0.2088           54         1.5868         8.567         14.05         0.3306         6.1046         0.1003         0.4         0.2263	SmG {0.623} [0.065]	58	1.4172	14.027	20.86	0.2436	6.0782	0.1268	0.50	0.1566
55         1.553         9.99         19.56         0.2784         6.0958         0.11029         0.43         0.2088           54         1.5868         8.567         14.05         0.3306         6.1046         0.1003         0.4         0.2263		56	1.5326	11.01	20.07	0.261	6.087	0.1172	0.451	0.174
54 1 5868 8 567 14 05 0 3306 6 1046 0 1003 0 4 0 2262		55	1.553	9.99	19.56	0.2784	6.0958	0.11029	0.43	0.2088
1.500 0.507 1.500 0.500 0.1040 0.1005 0.4 0.2202		54	1.5868	8.567	14.05	0.3306	6.1046	0.1003	0.4	0.2262
52 1.7609 6.8643 13.33 0.3654 6.1135 0.08659 0.36 0.261		52	1.7609	6.8643	13.33	0.3654	6.1135	0.08659	0.36	0.261
SmE {0.038} [0.014]         48         1.5303         15.99         12         0.1392         5.9652         0.07970         0.33         0.0348	SmE {0.038} [0.014]	48	1.5303	15.99	12	0.1392	5.9652	0.07970	0.33	0.0348
45 1.541 13.66 10 0.174 6.0541 0.07894 0.32 0.0696		45	1.541	13.66	10	0.174	6.0541	0.07894	0.32	0.0696
40 1.560 10.25 8.7 0.2088 6.0598 0.07766 0.319 0.087		40	1.560	10.25	8.7	0.2088	6.0598	0.07766	0.319	0.087
35 1.575 7.125 7.8 0.2262 6.0664 0.07741 0.317 0.1218		35	1.575	7.125	7.8	0.2262	6.0664	0.07741	0.317	0.1218
33         1.5892         6.00         6.6         0.2436         6.0805         0.07613         0.315         0.3654		33	1.5892	6.00	6.6	0.2436	6.0805	0.07613	0.315	0.3654

structure in the LF kHz region.

Values in {} indicate LF activation energy and values in [] indicate HF activation energy in eV.



**Fig. 12.** Temperature variation of LF dielectric strength  $\Delta \epsilon(T)$  in FE B<sub>2</sub> phase.

An overview of LF dielectric data (Table 2) for C<sub>12</sub>C<sub>10</sub> reveals that the  $f_{\rm R}$  follows a shift with a temperature in all the LC phases. This shift in  $f_{\rm R}$  is suggestive of Arrhenius behavior in both of the LF and HF relaxations. The potential barrier experienced by an LC phase structure during its orientation (to the applied field) is estimated by drawing (Fig. 11) the corresponding reduced temperature plots. The activation energies (Table 2) observed for LC phases of  $C_{12}C_{10}$  are found to agree with the range of  $f_R$  reported [97,110,119] in other LCs. The LF activation energy ( $E_a$ ) in  $C_{12}C_{10}$ seems to be higher than that in its HF relaxation process in the SmA, SmG and SmE phases. Further, these phases are found not to exhibit FE switching. Thus, the non-FE bent LC phases are found to exhibit higher  $E_a$  during their LF mode of relaxation in  $C_{12}C_{10}$ . Loss maximum ( $\varepsilon''_{max}$ ), dielectric strength ( $\Delta \varepsilon$ ) and the  $\alpha$ -parameter are also found to shift with temperature. In contrast to the lower values involved with HF relaxation, the loss maximum ( $\varepsilon''_{max}$ ) and dielectric strength ( $\Delta \varepsilon$ ) are found to assume higher values during the LF relaxations. The larger value of loss ( $\varepsilon''_{max}$ ) and dielectric strength ( $\Delta \varepsilon$ ) regarding the LF relaxation implies a large of operational range and strength of the scissor relaxation mode. The variation of  $\alpha$ -value with temperature reflects upon the increasing degrees of freedom, which in turn infers the relative fixation of molecular dipole in the LC phase structure.

#### 3.5.4. FE Curie behavior in $B_2$ phase

The variation of dielectric strength  $\Delta \varepsilon$  with temperature in FE B<sub>2</sub> phase exhibited by  $C_{12}C_{10}$  is presented in Fig. 12. The data of  $\Delta \varepsilon(T)$  in the FE B<sub>2</sub> phase is fitted to the Curie–Weiss [120] relation given by

$$\Delta T \propto 1/[\Delta \varepsilon]^{\gamma} \tag{7}$$

The LF data of  $\Delta \varepsilon(T)$  in FE B<sub>2</sub> phase is fitted to the Eq. 7 is found to yield an exponent ( $\gamma$ ) value equal to 0.9995  $\pm$  0.00004. The value of exponent ( $\gamma$ ) is found to be close to unity to reflect upon the Curie– Weiss behavior exhibited by FE B<sub>2</sub> phase.

# 4. Conclusions

In NS BLCs like  $C_{12}C_{10}$ , it may be concluded that

- Using a Hetereocyclic central moiety, FE LC phases can be realized.
- Non-symmetric molecular frame promotes extended stability for FE LC phases.
- Non-symmetric frame in BLCs leads to a sluggish lowfrequency scissor mode and a fast HF relaxation mode.

- Order parameter P<sub>S</sub> in FE phases of BLCs exhibits rapid asymptotic behavior.
- LF dielectric response predominates in kHz region.
- FE B<sub>2</sub> phase NS BLCs exhibits higher activation energies during their LF mode.
- FE B<sub>2</sub> phase in NS BLCs follows Curie–Weiss behavior.

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# Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.physb.2014.06.004.

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