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# Antiferroelectric Bent-Core Liquid Crystals for Molecular Switching Applications

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A homologous series of unsymmetrical bent-core (BC) liquid crystalline (LC) molecules were synthesized and characterized. Structural effects on mesomorphic and physiochemical properties were investigated in terms of variation in one terminal chain length with respect to constant at another terminal. The synthesis and characterization of new bent-core mesogens were exhibiting antiferroelectric switchable columnar phases. The homologues with short methylene chains (**8a** and **8b**) and longer methylene chain (**8d–8g**) molecules exhibited switchable B<sub>2</sub> mesophase and nonswitchable rectangular columnar B<sub>1</sub> phase obtained for phase middle homologue (**8c**). The spacer effect was observed in forming B<sub>2</sub> phase with various lengths of spacers. Spontaneous polarization was measured and maximum of 535 nC/cm<sup>-1</sup> observed for longer methylene chain containing compound (**8g**).

## 1. Introduction

Increasing attention has been paid to generate a new type of switchable organic molecules; several ferroelectric liquid crystals (FLCs) and antiferroelectric liquid crystals (AFLCs) were reported.<sup>1–5</sup> Symmetrical<sup>6,7</sup> and unsymmetrical dimers<sup>8,9</sup> and oligomers have gained significant roles in recent years because of the remarkable dependence on their transitional properties and formation of anti/ferroelectricity. With the dependence on molecular structure, intermolecular interactions play an important role (e.g., polar forces, charge-transfer complexes, hydrogen bonds) in the formation of the mesophase.<sup>10</sup> Niori et al.<sup>11</sup> initially demonstrated that smectic phases of achiral molecules with bent shapes can exhibit ferroelectric switching property because of the specific steric interaction in the bent shape molecules, ascribed to the C<sub>2v</sub> symmetry of packing the banana-shaped molecules into a layer. The molecules can preferably be packed in bent direction giving rise to a long-range correlation of lateral dipole moments.<sup>12</sup> Later, antiferroelectric liquid crystals were discovered and finally identified by tri-stable switching with a sharp threshold and a double hysteresis.<sup>13</sup> This has paved development in very fast electro-optic devices because of quick response of these materials used for flat-panel displays.<sup>14–17</sup> The tri-stable switching is observed by two methods, namely, electro-optic effect and switching current measurements. There are eight different bent-shaped or banana-shaped mesophases (B1–B8) of achiral molecules have been identified. In analogy to SmAP (P means polar), the phase is designated as SmCP, which can either be ferroelectric or antiferroelectric.<sup>18–22</sup> These SmCP phases are also distinguished as four types with respect to tilt direction (synclonic or anticlinic), such as SmC<sub>S</sub>P<sub>A</sub>, SmC<sub>A</sub>P<sub>A</sub>, SmC<sub>S</sub>P<sub>F</sub>, and SmC<sub>F</sub>P<sub>F</sub>.<sup>23</sup>

These bent-core materials are the origin of anti/ferroelectricity, which is attributed to efficient packing of bent molecules into smectic layers or columns. This architecture of molecules in the mesophase induced polarization along the bent direction, and such induced polarization can be reversed by application of an external electric field.<sup>24</sup> The present work illustrates new bent-core mesogens form columnar (B1 and B2) phases. They

exhibited unusual electro-optical response based on the textural features of columnar phases.

## 2. Experimental Section

**2.1. Materials.** Solvents, such as benzene, methanol, ethanol, dichloromethane, ethyl acetate, tetrahydrofuran, and acetone, were purified by the reported procedure.<sup>25</sup> Hydrobromic acid 47% (SRL), potassium hydroxide, sodium hydroxide, potassium carbonate, hydrochloric acid (Merck, India), 4-hydroxybenzoic acid, 4-hydroxybenzaldehyde, potassium iodide and triethylamine (Spectrochem, India), *N,N*-dicyclohexylcarbodiimide (DCC), palladium carbon (10%), potassium dichromate, resorcinol, benzyl chloride, and 4-(dimethylamino)pyridine (DMAP) (Aldrich) were used as received.

**2.2. Characterization Methods.** Infrared spectra were obtained on Thermo Electron Corporation Nicolet 380 FT-IR spectrometer. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Bruker AM-400 spectrometer with Me<sub>3</sub>Si as internal standard. Differential scanning calorimetry (DSC) was conducted on a Perkin-Elmer model DSC Pyris 1 system calibrated with indium and zinc standards. Polarizing microscopy was performed with a Euromex polarizing microscope equipped with a Linkem HFS 91 heating stage and a TP-93 temperature programmer. A small quantity of sample was placed between two thin glass coverslips and was heated and cooled at the rate of 5 °C min<sup>-1</sup>. Variable-temperature XRD studies were carried out on unoriented powder samples taken in Lindemann capillaries of 0.7 mm diameter. Cu Ka (1.54 Å) radiation from a 4 kW rotating anode X-ray source with a graphite crystal monochromator was used. Physical property of antiferroelectric phase for the synthesized materials was measured in antiparallel aligned cells purchased from EHC Co., Japan. Spontaneous polarization (P<sub>s</sub>) was measured by a triangular wave method.<sup>26</sup> The signals were detected with HP54502A digital oscilloscope. The voltage applied to the cell was produced by an arbitrary waveform generator (AG 1200) and amplified by a homemade power preamplifier.

**2.3. Synthesis of 4-Hydroxybenzoic Acid (2a).** 4-Hydroxybenzoic acid (6.4 g, 46 mmol) and potassium hydroxide (19 g, 138 mmol) were dissolved in dry DMF (30 mL) and stirred for 1 h at room temperature. 1-Bromohexane (7.6 g, 46 mmol) was then added dropwise to this solution, followed by addition of

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potassium iodide (0.8 g, 0.0046 mmol) in one portion. The solution was heated to 100 °C for 24 h while being stirred. The reaction mixture was filtered and washed the precipitate with DMF (3 × 20 mL). Filtrate and washings were collected and concentrated by vacuum distillation. Then the mixture was poured into water (500 mL) and neutralized with 10% hydrochloric acid solution. The resultant precipitate was filtered and recrystallized from ethanol to get the desired product (yield 65%). A similar procedure was adopted for preparation of **2b–2g**.

**2a.** mp: 82–138 °C. C<sub>13</sub>H<sub>18</sub>O<sub>3</sub>: Calcd C, 70.24; H, 8.16; O, 21.59; found C, 70.32; H, 8.19; O, 21.48. FT-IR (KBr pellet, cm<sup>-1</sup>): 2919, 2848, 1682, 1256, 945, 771. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 11.02 (s, 1H, -COOH), 8.12(d, 2H, Ar-H), 6.96(d, 2H, Ar-H), 4.01(t, 2H, -OCH<sub>2</sub>), 1.81(q, 1H, -CH<sub>2</sub>), 1.24–1.39(m, -CH<sub>2</sub>), 0.93(t, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 172.2, 163.7, 132.3, 121.4, 114.18, 68.2, 31.6, 29.0, 25.8, 22.5.

**2.4. Synthesis of 4-(4-*n*-Hexyloxybenzoyloxy)benzaldehyde (3a).** A mixture of 4-hexyloxybenzoic acid (5 g, 22 mmol), 4-hydroxybenzaldehyde (1.8 g 22 mmol), dicyclohexylcarbodiimide (DCC) (3 g, 25 mmol), and 5%/w of 4-dimethylaminopyridine (DMAP) was dissolved in methylene chloride (200 mL), and the resulting solution was stirred for 12 h at room temperature under nitrogen atmosphere. Precipitated byproduct urea was filtered from the reaction mixture, and the filtrate was evaporated. The residue was purified by silica gel column using chloroform as eluent. After recrystallization in ethanol, 4-(4-*n*-hexyloxybenzoyloxy) benzaldehyde (5.8 g; 86%) was obtained as a white powder. A similar procedure was adopted for preparation of **3b–3g**.

**3a.** mp: 71 °C. C<sub>20</sub>H<sub>22</sub>O<sub>4</sub>: Calcd C, 73.60; H, 6.79; O, 19.61; found C, 73.73; H, 6.71; O, 19.55. FT-IR (KBr pellet, cm<sup>-1</sup>): 2912, 2865, 2364, 1736, 1604, 1267, 1259. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 10.02(s, 1H, -CHO), 8.14 (d, 4H, Ar-H), 7.96(d, 2H, Ar-H), 7.4(d, 1H, Ar-H), 6.98(d, 1H, Ar-H), 4.05 (t, 2H, -OCH<sub>2</sub>), 1.71(dd, 2H, -CH<sub>2</sub>), 1.24–1.39 (m, 6H, -CH<sub>2</sub>), 0.84(t, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 191.5, 166.6, 163.7, 163.3, 154.1, 132.0, 130.8, 128.2, 122.1, 120.3, 114.6, 67.9, 31.1, 28.6, 25.7, 22.03, 13.88.

**2.5. Synthesis of 4-(4-*n*-Hexyloxybenzoyloxy) Benzoic Acid (4a).** 4-(4-*n*-Hexyloxybenzoyloxy) benzaldehyde (5 g, 15 mmol) was dissolved in acetone (20 mL), treated with Jones reagent [mixture chromium oxide (26.72 g) with concentrated sulfuric acid (23 mL)], and diluted with water to make the final volume of 100 mL. Addition of Jones reagent<sup>27</sup> was continued until red color persisted for at least 1 min. Resultant mixture was stirred at room temperature for 30 min to ensure the completion of oxidation. Excess oxidizing reagent was quenched with 2-propanol. Reaction solution was then diluted with water and repeated extraction with ether. Combined organic extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuum. Crude product was then recrystallized from ethanol to yield the desired product (4.25 g; 77%). A similar procedure was adopted for the preparation of **4b–4g**.

**4a.** mp: 102–196 °C. C<sub>20</sub>H<sub>22</sub>O<sub>5</sub>: Calcd C, 73.60; H, 6.79; O, 19.61; found C, 70.84; H, 5.89; O, 23.26. FT-IR (KBr pellet, cm<sup>-1</sup>): 2962, 2865, 1739, 1604, 1259. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 10.97(s, 1H, -COOH), 8.20–8.06 (dd, 4H, Ar-H), 7.96(d, 2H, Ar-H), 7.09(d, 2H, Ar-H), 4.05, (t, 2H, -OCH<sub>2</sub>), 1.68–1.73(m, -CH<sub>2</sub>), 1.23–1.39 (m, 6H, -CH<sub>2</sub>), 0.84(t, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 166.6, 163.7, 163.3, 154.1, 132.0, 130.8, 128.2, 122.1, 120.3, 114.6, 67.9, 31.1, 28.6, 25.3, 22.0, 13.8.

**2.6. Synthesis of Resorcinolmonobenzylether (1).** Resorcinol (11 g, 100 mmol) was dissolved in acetone (100 mL). To this solution, powdered potassium carbonate (13.8 g, 300 mmol) and potassium iodide (pinch) were added slowly. The mixture was refluxed, and benzyl chloride (11.6 mL, 100 mmol) added dropwise to the refluxing mixture over a period of 30 min. It was refluxed for 48 h, cooled, filtered, and washed with acetone; the collected filtrates were concentrated by vacuum distillation. Product thus obtained was purified by column chromatography using chloroform and hexane (3:7) mixture as eluent to yield brown color viscous liquid (12 g; 72%).

**1.** C<sub>13</sub>H<sub>10</sub>O<sub>2</sub>: Calcd C, 77.98; H, 6.04; O, 15.98; found C, 77.67; H, 6.47; O, 15.85. FT-IR (KBr pellet, cm<sup>-1</sup>): 3290, 3112, 1745, 1603, 1257. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.27 (d, 2H, Ar-H), 7.65–7.71(m, 3H, Ar-H), 7.32(t, 1H, Ar-H), 6.91–6.97 (m, 3H, Ar-H), 5.38 (s, 1H, -OH), 5.19 (s, 2H, -OCH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 163.8, 157.2, 152.6, 132.2, 130.8, 128.3, 113.2, 112.6, 106.5.

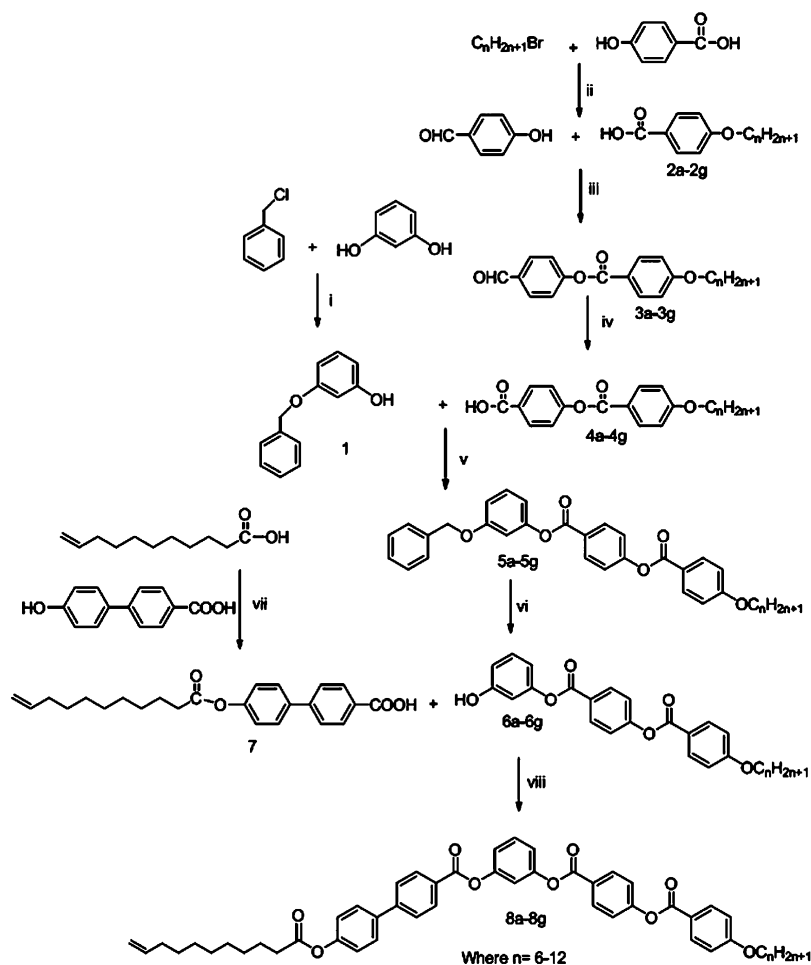
**2.7. Synthesis of 4-(4-*n*-Hexyloxybenzoyloxy) Phenylmonobenzylether 3-Benzoate (5a).** A mixture of 4-(4-*n*-alkyloxybenzoyloxy)benzoic acid (3.42 g, 10 mmol), resorcinol monobenzylether (2 g, 10 mmol) DCC (2.5 g, 12 mmol), and a catalytic amount of DMAP in dry dichloromethane (50 mL) were stirred for 12 h. The precipitated *N,N'*-9-dicyclohexylurea was filtered and washed with excess of dichloromethane, and the filtrate was concentrated in a rotary evaporator. The residue was purified by silica gel column using chloroform as eluent. The product obtained on removal of chloroform was further purified by recrystallization using mixture of chloroform and hexane (1:3) to get a 4.5 g yield (85%). A similar procedure was adopted for preparation of **5b–5g**.

**5a.** mp: 72 °C C<sub>33</sub>H<sub>32</sub>O<sub>6</sub>: Calcd C, 75.55; H, 6.15; O, 18.30; found C, 75.32; H, 6.18; O, 18.49. FT-IR (KBr pellet, cm<sup>-1</sup>): 2938, 2865, 2364, 1740, 1605, 1259. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 8.29 (d, 2H, Ar-H), 8.15 (d, 2H, Ar-H), 7.68 (d, 2H, Ar-H), 7.40–7.41 (m, 8H, Ar-H), 7.20–7.25 (m, 3H, Ar-H), 7.18 (s, 1H, Ar-H), 7.03 (d, 2H, Ar-H), 5.23 (t, 2H, -COCH<sub>2</sub>), 5.19 (s, 2H, -OCH<sub>2</sub>) 1.71 (dd, 2H, -CH<sub>2</sub>), 1.24–1.39 (m, 6H, -CH<sub>2</sub>), 0.84(t, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 166.6, 163.7, 163.3, 154.1, 151.9, 136.2, 132.0, 130.8, 130.2, 129.5, 129.1, 128.2, 122.1, 120.3, 114.6, 113.9, 111.8, 108.1, 69.5, 67.9, 31.1, 28.6, 25.7, 22.03, 13.88.

**2.8. Synthesis of 4-(4-*n*-Hexyloxybenzoyloxy)phenyl-3-hydroxybenzoate (6a).** 4-(4-*n*-Alkyloxybenzoyloxy) phenylmonobenzylether-3-benzoate (4.2 g, 8.0 mmol) was dissolved in ethyl acetate (150 mL) containing a suspension of Pd/C catalyst (10% Pd/C).<sup>28</sup> The mixture was stirred for 24 h under H<sub>2</sub> atmosphere, filtered, and concentrated under vacuum. Crude product thus obtained was purified by silica gel column chromatography using ethyl acetate–hexane (1:3) as eluent to yield 88%. A similar procedure was adopted for **6b–6g**.

**6a.** mp: 144 °C. C<sub>26</sub>H<sub>26</sub>O<sub>6</sub>: Calcd C, 71.87; H, 6.03; O, 22.09; found C, 71.62; H, 6.21; O, 22.16. FT-IR (KBr pellet, cm<sup>-1</sup>): 3640, 2938, 2865, 1741, 1608, 1258. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 8.29 (d, 2H, Ar-H), 8.15 (d, 2H, Ar-H), 7.68 (d, 2H, Ar-H), 7.42 (t, 1H, Ar-H), 7.23 (d, 2H, Ar-H), 7.00–7.06 (m, 23H, Ar-H), 5.57 (s, 1H, OH), 5.23 (t, 2H, -OCH<sub>2</sub>), 1.71 (dd, 2H, -CH<sub>2</sub>), 1.24–1.39 (m, 6H, -CH<sub>2</sub>), 0.84(t, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 166.6, 163.7, 163.3, 154.1, 151.9, 130.8, 129.1, 128.2, 122.1, 114.6, 111.8, 108.1, 69.5, 67.9, 31.1, 28.6, 25.7, 22.03, 13.88.

**2.9. Synthesis of 4-(4'-Undecyloxyphenyl)benzoic Acid (7).** 10-Undecenoic acid (10 mL, 50 mmol) was reacted with excess thionyl chloride in the presence of benzene at 50–55

Scheme 1. Synthesis of 3-(4-(*n*-(Alkyloxy)benzoyloxy)benzoyloxy)phenyl-14'-(undec-11-enoyloxy)biphenyl-4-carboxylate (8a–8g)

REAGENTS: i)  $K_2CO_3$ , KI/Acetone, ii) KOH, KI/Ethanol, iii, v, vii) DCC, DMAP/DCM, iv) Jones reagent, vi)  $Pd/C$ ,  $H_2$ /EtOAc vii)  $SOCl_2$ , TEA/THF

$^{\circ}C$  for 5 h. Then the excess  $SOCl_2$  and benzene were removed under vacuum distillation, the generated acid chlorides used in situ for the subsequent step immediately. 4-(4'-Hydroxyphenyl) benzoic acid (10.7 g, 50 mmol) and TEA (8.4 mL, 60 mmol) were dissolved in dry THF. The acid chloride was added dropwise to the reaction mixture at room temperature and stirred for 24 h. Then the mixture was filtered and solvent removed in a rotary evaporator. The residue was dissolved in ethyl acetate and washed with dilute hydrochloric acid. Then the solvent was dried in sodium sulfate and solvent removed under vacuum. The crude product was recrystallized from ethanol to get white powder (16.2 g; 65%).

**7.** mp: 143–320  $^{\circ}C$  (decomposed).  $C_{24}H_{28}O_4$ : Calcd C, 75.76; H, 7.42, O, 16.82; found C, 75.52; H, 7.71; O, 16.77. FT-IR (KBr pellet,  $cm^{-1}$ ): 2926, 2854, 1747, 1684, 1603, 1190, 1135.  $^1H$  NMR ( $CDCl_3$ , 400 MHz),  $\delta$  (ppm): 10.97(s, 1H,  $-COOH$ ), 8.10 (d, 2H, Ar-H), 7.65(d, 2H, Ar-H), 7.62 (d, 2H, Ar-H), 7.18(d, 2H, Ar-H), 5.76–5.85 (m, 1H,  $-CH$ ), 5.02 (m, 2H,  $-CH_2$ ), 2.58(t, 2H,  $-CH_2$ ), 2.04 (q, 2H,  $-CH_2$ ), 1.74–1.79(q, 2H,  $-CH_2$ ), 1.23–1.46 (m, 10H,  $-CH_2$ ).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  172.1, 168.4, 150.7, 145.2, 139.0, 137.5, 130.2, 129.6, 128.1, 121.9, 115.9, 34.0, 33.6, 29.1, 29.0, 28.7, 24.8.

**2.10. Synthesis of 4-(4-*n*-Hexyloxybenzoyloxy)-4-(4'-undecanoyloxyphenyl)phenyl-3-benzoate (8a).** To a mixture of 4-(4'-undecanoyloxyphenyl) benzoic acid (0.01 mol), 4-(4-*n*-alkyloxybenzoyloxy) phenyl-3-hydroxybenzoate (0.01 mol)

DCC (0.015 mol), and a catalytic amount of DMAP in dry dichloromethane (100 mL) were stirred for 12 h under  $N_2$  atmosphere. Precipitated *N,N'*-9-dicyclohexylurea was filtered out and washed with excess of dichloromethane, and the solvent was removed in a rotary evaporator. The residue was purified by silica gel column using chloroform as eluent. The product obtained on removal of chloroform was further purified by column chromatography using a mixture of chloroform and hexane (1:3) to get 80% yield. The similar procedure was adopted for the preparation of **8b–8g**.

**8a.** mp: 82.6–119  $^{\circ}C$ .  $C_{50}H_{52}O_9$ : Calcd C, 75.35; H, 6.58; O, 18.07; found C, 75.38; H, 6.36; O, 18.25. FT-IR (KBr pellet,  $cm^{-1}$ ): 2939, 2865, 1748, 1984, 1604, 1259.  $^1H$  NMR ( $CDCl_3$ , 500 MHz),  $\delta$  (ppm): 8.29 (d, 4H, Ar-H), 8.17 (d, 2H, Ar-H), 7.73 (d, 2H, Ar-H), 7.66 (d, 2H, Ar-H), 7.51(t, 1H, Ar-H), 7.40 (d, 2H, Ar-H), 7.27 (s, 1H, Ar-H), 7.22 (m, 3H, Ar-H), 7.01(d, 2H, Ar-H), (5.79–5.87 (m, 1H,  $-CH$ ), 4.94–5.04 (m, 2H,  $-CH_2$ ), 4.07(t, 2H,  $-OCH_2$ ), 2.61 (t, 2H,  $-OOCCH_2$ ), 2.05–2.09(q, 2H,  $-CH_2$ ), 1.76–1.87(m, 2H,  $-CH_2$ ), 1.34–1.61(m, 18H,  $-CH_2$ ), 0.93(t, 3H,  $-CH_3$ ).  $^{13}C$  NMR (500 MHz,  $CDCl_3$ ): 172.2, 164.6, 164.3, 164.1, 163.8, 155.5, 151.5, 151.4, 151.0, 145.6, 139.1, 137.4, 132.4, 131.8, 130.8, 129.8, 128.5, 128.3, 128.0, 127.2, 126.9, 122.3, 122.17, 122.15, 120.9, 119.3, 119.2, 115.8, 114.4, 114.1, 77.2, 77.0, 76.7, 68.4, 34.4, 33.7, 31.5, 29.3, 29.2, 29.1, 29.0, 28.8, 25.6, 24.9, 22.5, 14.0.

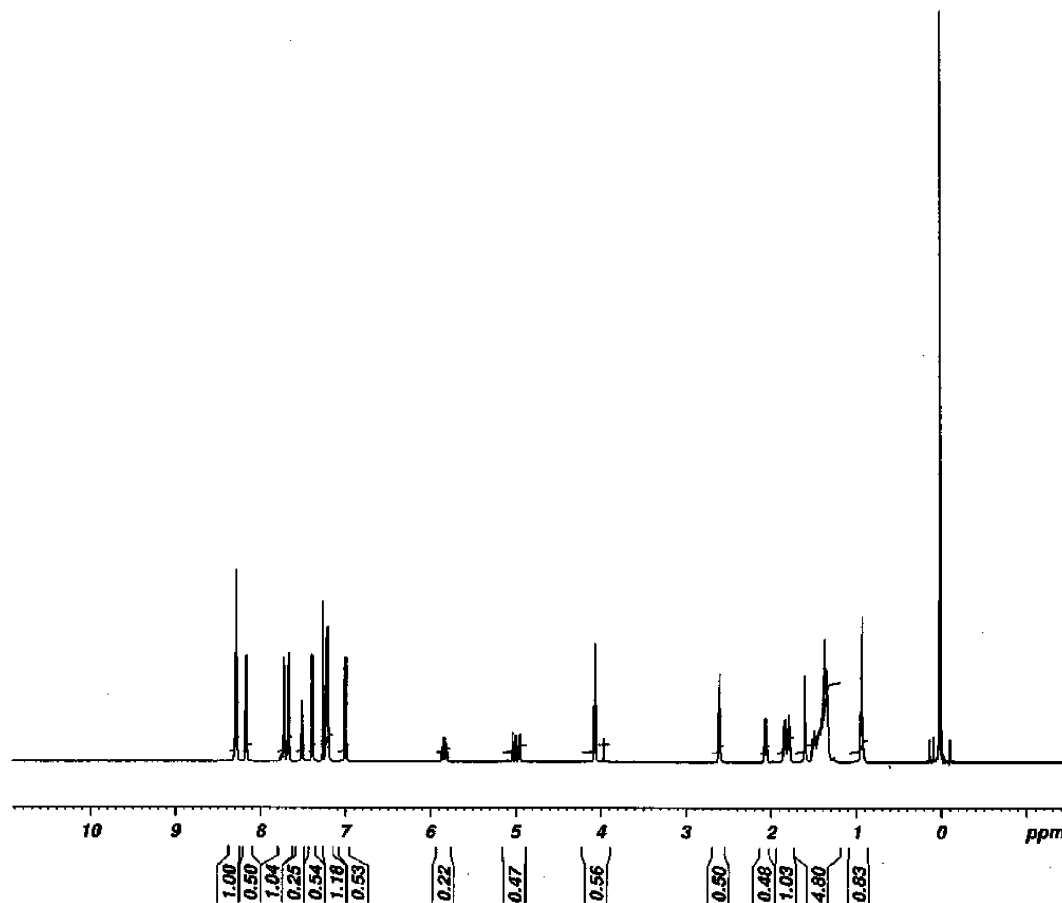


Figure 1.  $^1\text{H}$  NMR spectrum of 3-(4-(4-(octyloxy)benzoyloxy) benzoyloxy)phenyl4'-(undec-11-enoyloxy)biphenyl-4-carboxylate (**8a**).

### 3. Results and Discussion

**3.1. Synthesis.** The target bent-core liquid crystalline molecules were synthesized as shown in Scheme 1. The key intermediate 4-(4'-*n*-alkyloxybenzaldehyde) (**3**) was synthesized by the reaction between 4-hydroxybenzaldehyde and *n*-alkyloxybenzoic acid, followed by oxidation using  $\text{KMnO}_4$  in the presence of acetone and treated with resorcinol monobenzylether (**1**) yielded 4-(4-*n*-alkyloxybenzoyloxy) phenylmonobenzylether-3-benzoate (**5**). Further, the benzyl group was deprotected by palladium carbon in hydrogen atmosphere to get 4-(4-*n*-hexyloxybenzoyloxy) phenyl-3-hydroxybenzoate (**6**), which was reacted with 4-(4'-undecnoyloxyphenyl)benzoic acid (**7**) using DCC and DMAP in the presence of dichloromethane to form 4-(4-*n*-alkyloxybenzoyloxy)-4-(4'-undecnoyloxyphenyl)phenyl-3-benzoate (**8**) as a white solid, and the representative proton NMR spectrum of compound **8c** is shown in Figure 1.

**3.2. Mesomorphic Property of Intermediate.** Interesting mesophases were generated not only by the final compound but also the intermediates exhibited mesophases in accordance with literature. 4-Alkyloxybenzoic acid (**2a–2g**) shows schlieren nematic phase, but the compound of 4-(4-*n*-alkyloxybenzoyloxy) benzaldehyde (**3a–3g**) is unable to display LC phases; rather, it melts in a short range of 46–68 °C. Again, the functional group of aldehyde was converted to carboxylic acid (**4a–4g**) displays schlieren nematic phase at various temperatures with respect to terminal chain length attributed to the formation of hydrogen bonding of carboxylic group. The 4-(4-*n*-alkyloxybenzoyloxy)phenylmonobenzylether-3-benzoate (**5a–5g**) and 4-(4-*n*-alkyloxy benzoyloxy)phenyl-3-hydroxybenzoate (**6a–6g**) were lacking to depict mesophases. 4-(4'-Undecanoyloxyphenyl) benzoic acid (**7**) exhibited schlieren nematic at its melting

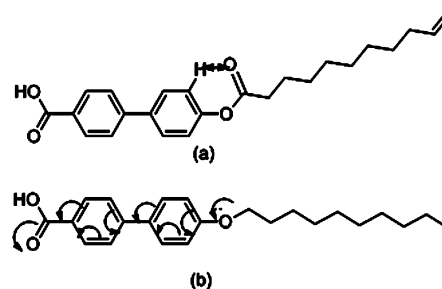


Figure 2. Electron delocalization structure of compound: (a) ester linkage and (b) ether linkage.

temperature 143 °C and exhibited nematic phase up to the decomposition temperature of 320 °C. This highly stable mesophase is attributable to ester linkage present in the compound (Figure 2). This is ascribed to the attraction between carbonyl oxygen and proton of the aromatic ring look like an extended mesogen (**3a**), additionally it restrict free mobility of mesogen and terminal spacer however, in the case of ether linked compound (**3b**), free delocalization of electron favors formation of external hydrogen bonding between the molecules.<sup>29,30</sup> Aspect ratio also changed between **3a** and **3b** could be the reason for mesophase stability of ester linkage containing compound.

**3.3. Mesomorphic Property of Bent-Core Molecules (8a–8g).** Mesomorphic properties of all the compounds were investigated using classical techniques. Transition temperatures and their associated enthalpy values obtained for the compounds are summarized in Table 1 and all the compounds demonstrated liquid crystalline property bearing enantiotropic in nature. The mesomorphic property of the series is represented schematically



Table 1. Transition Temperatures (°C) and Associated Enthalpies (J/g) for Compounds 8a–8g<sup>a</sup>

sample	methylene chain ( <i>n</i> )	DSC data (°C) <sup>b</sup>				
		Cr	mosaic	B1	B2	I
8a	6	*		102 (8.6 J/g)	*	119 (9.9 J/g)
8b	7	*		93.5 (7.4 J/g)	*	102.5 (8.1 J/g)
8c	8	*	80 <sup>c</sup>	82.6 (12.5 J/g)	*	108.3 (14.4 J/g)
8d	9	*		75 (11.2 J/g)	*	104 (12.6 J/g)
8e	10	*		73 (4.6 J/g)	*	112.5 (6.3 J/g)
8f	11	*		70.5 (6.6 J/g)	*	128.5 (8.4 J/g)
8g	12	*		65.5 (6.2 J/g)	*	126.3 (7.8 J/g)

<sup>a</sup> Cr = crystalline phase, B1, B2 = columnar phase, and I = isotropic liquids. <sup>b</sup> Transition temperatures observed by DSC. <sup>c</sup> Mesophase observed on cooling cycle only.

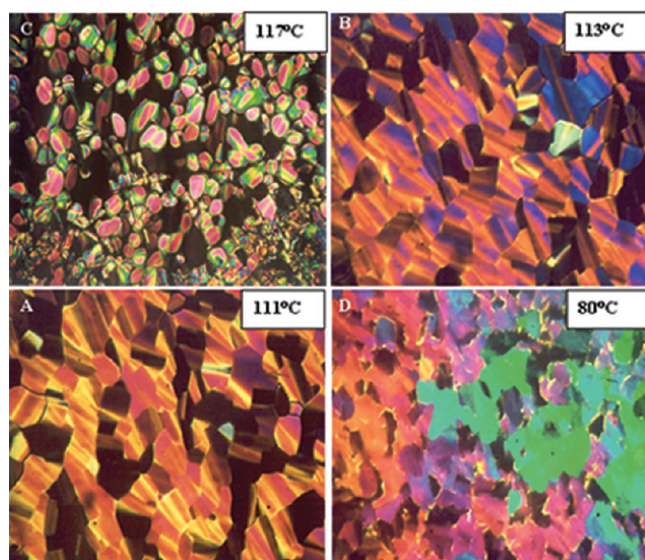


Figure 3. Optical photomicrographs of the textures observed on cooling from the isotropic state (A) at 117 °C B<sub>1</sub> phase, (B) at 113 °C B<sub>1</sub> phase, (C) at 111 °C B<sub>1</sub> phase, and (D) at 80 °C mosaic texture of compound 8c.

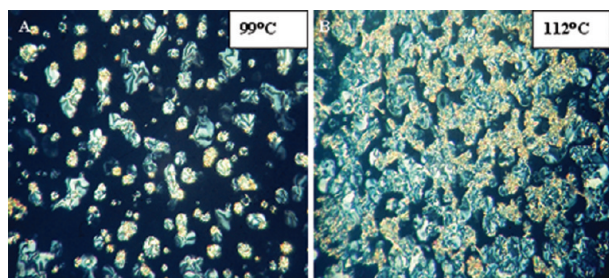


Figure 4. Optical photomicrographs of A and B at the transitions 99 and 112 °C of the compound 8b displays B<sub>2</sub> phase by cooling cycle.

in Figure 3 and 4. In this series (8a–8g), seven compounds with two different terminal lengths were studied. Herein, one arm (wing) contains constant terminal chain length but other side with variable terminal chain lengths of 6–12 units. These seven unsymmetrical compounds exposed the trend with anticipated banana-shaped LC compounds.

Among the various compounds containing shorter and longer chains (8a–8g), 8c alone exhibited B<sub>1</sub> mesophase and displayed small colored domains with some fans, in addition to schlieren

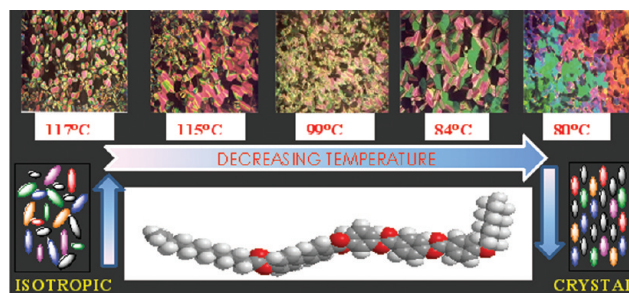


Figure 5. Representative POM photographs of 8c from isotropic to crystals.

textures and typical B<sub>1</sub> textures observed on cooling from isotropic liquid similar to available in the literature.<sup>31,32</sup> The shorter length homologue 8c exhibited columnar mesophase (B<sub>1</sub>), this phase can be detected on cooling from the isotropic state by the formation of mosaic-like texture and spherulites (Figure 5). For this B<sub>1</sub> phase, a rectangular columnar structure has been proposed. The shorter (8a and 8b) and longer (8d–8g) chain containing compounds demonstrated B<sub>2</sub> (SmCP<sub>A</sub>) mesophase with exception of compound 8c. The textures observed for these compounds on cooling from isotropic phase indicated similar with textures found for other compounds with B<sub>2</sub> phase.<sup>33</sup>

To determine the influence of unsymmetry, the compounds were compared with published series of symmetry and asymmetric compounds and revealed that it follows similar trend to terminal chain lengths one side arms having 8 carbons another side having 8, 11, and 12 carbon containing chains. These three terminals containing symmetry, as well as unsymmetry bent core compounds, show the B<sub>1</sub> phase, whereas remaining compounds depicts B<sub>2</sub> phases. This phase sequence is well agreed with this series of compounds. Apparently unsymmetry in bent-core compounds, by introducing two different mesogens and terminal chain lengths stabilize B<sub>2</sub> phase.

Representative DSC thermogram of compound 8c is shown in Figure 6. Heating and cooling thermograms of DSC were measured at a rate of 5 °C/min. Assignment of liquid crystalline phases was observed through optical textures confirmed by DSC patterns. Phase transition temperatures and change in enthalpy ( $\Delta H$ ) was measured by DSC are summarized in Table 2. The compounds 8a–8g exhibited two endo thermic and two exothermic transitions during heating and cooling process respectively, which corresponds to crystalline–liquid crystalline

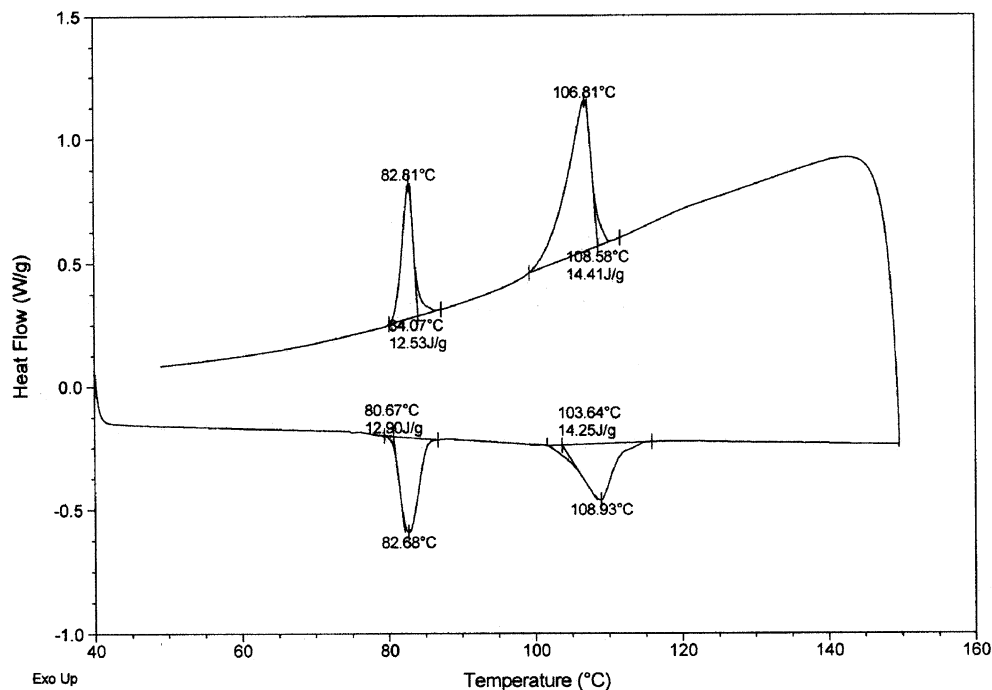


Figure 6. Photographs of DSC thermogram of compound 8a.

Table 2. Transition Temperatures (°C)  $T_m$  (Temperature of Melting) and  $T_i$  (Temperature of Isotropic State) for Compounds 8a–8e

compound	DSC (°C)			HOPM (°C)		
	$T_m$	$T_i$	$\Delta T$	$T_m$	$T_i$	$\Delta T$
8a	102	119	17	103	120	18
8b	93.5	102.5	9	94.5	103	8.5
8c	82	118.5	36.5	83	120	37
8d	75	104	29	77	105.3	28.3
8e	73	112.5	39.5	74.6	113.8	39.2
8f	70.5	128.5	58	72	130	58
8g	65.5	126.3	60.8	68	127.2	59.2

and liquid crystalline–isotropic transition temperature  $T_m$  and  $T_i$ , respectively. The  $T_m$  of the series of compounds was observed in the range of 65.5–102 °C. In this series of compounds, 8g demonstrated maximum mesophase duration ( $\Delta T$ ) 60.8 °C; on the other hand, 8b has very low mesophase duration ( $\Delta T$ ) of 9 °C. The transitions observed under POM were in accordance with DSC results. The correlation between the series of compounds and transition temperatures ( $T_m$  and  $T_i$ ) observed from DSC measurement are shown in Figure 7.

### 3.3.1. Variable-Temperature X-ray Diffraction Studies.

To ascertain the structure of two different mesophases observed by the X-ray diffraction study. The diffraction patterns were

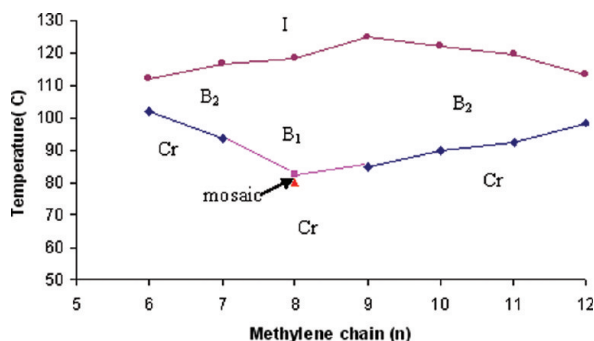


Figure 7. Plot of transition temperature as a function of spacer length on cooling.

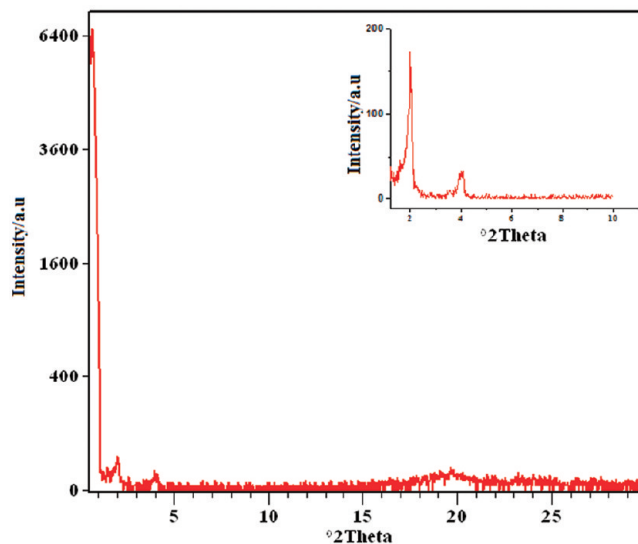


Figure 8. Variable-temperature X-ray angular intensity profiles obtained for B1 phase of compound 8c.

recorded on cooling the sample into the mesophase from isotropic phase. The diffraction pattern of an nonoriented sample of mesophase obtained at 90 °C, a diffused peak in the wide angle region with  $d$  spacing 4.5 Å indication the liquid like in-plane order. The mesophase of compound 8c gave two reflections in the small angle region with spacing at  $d_1 = 28.76$  Å and  $d_2 = 21.92$  Å, which could be indexed to 11 and 02 planes of a rectangular lattice. The XRD diffractogram obtained for the mesophase of this compound 8c is shown in Figure 8. A representative and typical diffraction pattern obtained for compound 8e at 100 °C is shown in Figure 9 (see also Table 3). The diffuse character of the wide angle peak at 4.4 Å indicates the absence of liquid like in-plane order. In the small angle region, two sharp reflections were seen with  $d$  spacing of 44.2 and 21.9 Å. These reflections are in the ratio of 1:1/2 indicating a lamellar ordering in the mesophase. The layer spacing is lower than the calculated molecular length of 45.7

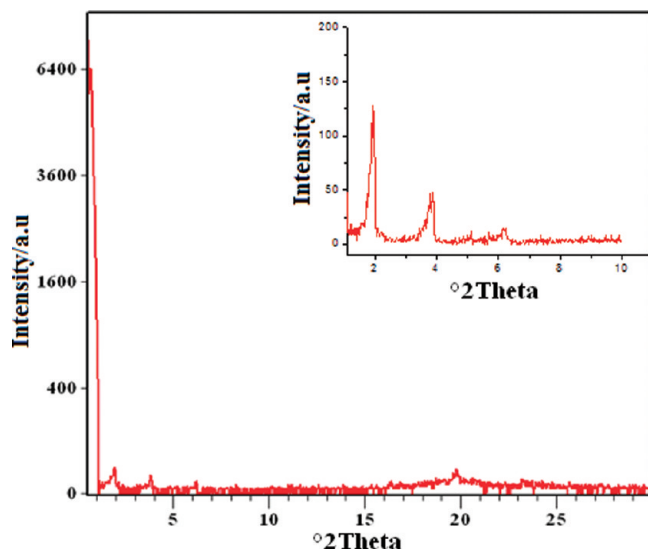


Figure 9. Variable-temperature X-ray diffractogram obtained for the B<sub>2</sub> phase of compound 8e.

Table 3. Small Angle Bragg Reflections (Å) and Their Mesophase of Compounds (8a–8e)

compound	<i>d</i> -spacing/Å	Miller indices	mesophase	<i>T</i> /°C
8a	41.88, 20.67	(01) (02)	B <sub>2</sub>	100
8b	42.56, 21.30	(01) (02)	B <sub>2</sub>	95
8c	28.76, 21.92	(11) (02)	B <sub>1</sub>	85
8d	44.18, 22.08	(01) (02)	B <sub>2</sub>	90
8e	45.84, 23.15	(01) (02)	B <sub>2</sub>	90
8f	46.60, 23.28	(01) (02)	B <sub>2</sub>	100
8g	48.32, 24.11	(01) (02)	B <sub>2</sub>	100

Å obtained from the energy minimized structure of all trans conformation.

**3.4. Electro-optical Investigations.** Electro-optical investigations were carried out on the compounds (8a–8g). Since the characteristic behavior was same, only the experimental observations made on compound 8a alone described in detail.<sup>34,35</sup> For the a.c. field experiments, a sample of compound 8a was filled into an treated ITO-coated homemade cell of uniform thickness 5 μm by capillary action, the current responds were measured across a 1 kΩ resistance. The sample was cooled slowly from the isotropic phase under a triangle wave voltage of 20 V<sub>pp</sub> and a frequency of 20 Hz. The switching current response obtained in the B<sub>2</sub> phase of compound 8a was shown in Figure 10. Regarding the electro-optical measurements, compounds 8a–8b and 8d–8g exhibited two polarization current peaks per half cycle were observed at a very low threshold voltage indicating an antiferroelectric ground state for the mesophase. The field induced transition was found to be

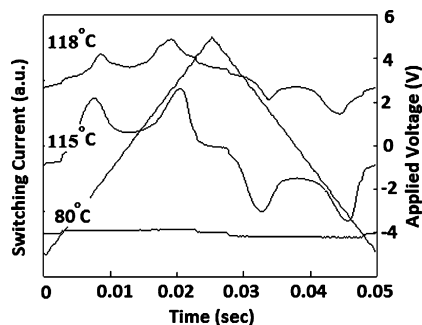


Figure 10. Switching current behavior of the compound 8a in homogeneously aligned cell with 5 μm thickness at 20 Hz of frequency and the amplitude of 20 V<sub>pp</sub>.

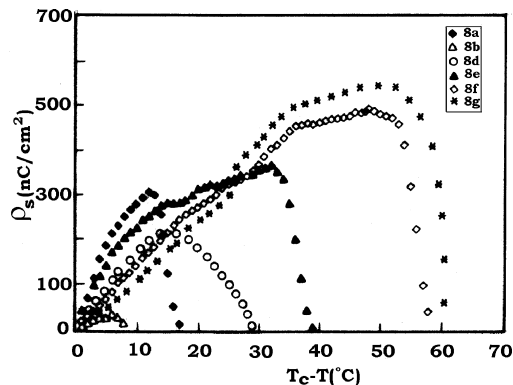


Figure 11. Magnitudes of the spontaneous polarization plotted as a function of temperature for compounds 8a–8b and 8d–8g.

reversible. Accordingly, it may be reasoned out that the presence of macroscopic polar order along the system is easily induced by cooperative interaction between the polarization and an applied electric field. The observations are quite similar to those obtained for the B<sub>2</sub> mesophase exhibited by the compounds. The compound 8c does not respond in the applied field, B<sub>1</sub> phase was further confirmed by this electro-optical observation.

The temperature dependence of magnitude of spontaneous polarization ( $P_s$ ) obtained by integrating the area under peak is shown in Figure 11. The  $P_s$  values increase rapidly in the vicinity of I–B<sub>2</sub> transition temperature and then graduate increase to reach maxima as the temperature kept on cooling. The steep drops of the  $P_s$  values at low temperature resulted from crystallization. It is evident that  $P_s$  has weak temperature dependence from the isotropic phase, but near SmCP–I transition, it evidence a steep drop and vanishes in the isotropic phase. The polarization reaches values as high as 535 nC cm<sup>−2</sup>.

#### 4. Conclusion

In summary, the synthesis and mesomorphic behavior of seven new banana-shaped compounds belonging to a homologous series, having unsymmetrical mesogen are reported. In terms of linking group and terminal chains, the two rod-like molecular arms (wings) are highly unsymmetrical. In general, shorter chain, as well as longer chain homologues of this series, exhibited a synclinic antiferroelectric polar smectic-C phase with the exception of compound 8c. The mesomorphic behavior of the series of compounds is in good agreement with general behavior of bent-core materials. Furthermore, the high polarization value via 535 nC cm<sup>−2</sup> for 8g, and very low polarization value via 31.1 nC cm<sup>−2</sup> belongs to 8b were obtained. The spontaneous polarization values increases with increasing terminal chains.

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