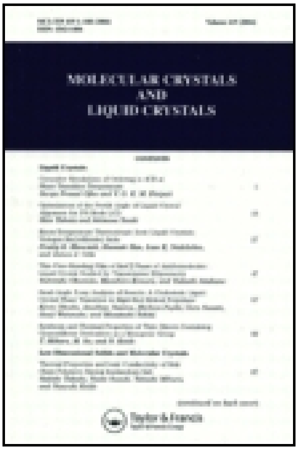

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Synthesis and Characterization of Unsymmetrical Five-Ring Achrial Banana-Shaped Compounds With a B2 Phase

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Synthesis and Characterization of Unsymmetrical Five-Ring Achrial Banana-Shaped Compounds With a B2 Phase

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Two series of unsymmetrical banana-shaped materials have been prepared with laterally substituted hydroxy and nitro groups. All the compounds exhibit liquid crystalline properties. The syntheses and liquid crystalline properties of these compounds are discussed.

Keywords: B2 phase; lamellar reflection; lateral substitution; unsymmetrical bent shaped

INTRODUCTION

Liquid crystalline phases exhibited by compounds composed of bent core (BC) molecules, which form the basis for a new sub field, are being investigated with renewed interest. This is not only because of their unique feature of showing chiral form of layered (smectic) [1,2] or two-dimensional (columnar) [3,4] liquid crystalline phases exhibiting spontaneous polarization, but also due to the formation of super helical structures [5] though the materials themselves are achiral. In general, the mesophases formed by these compounds are termed as "Banana" phases designated as B1–B8, which have been identified, based on their textural appearances and X-ray diffraction pattern. The B3 and B4 phases are crystalline mesophases, while the others are genuine liquid crystals. The most commonly encountered phases are B1, B2, B7, which have, therefore, been investigated extensively. Synthesis of both symmetrical and nonsymmetrical bent core compounds with different chemical architecture

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is of topical interest for understanding the relationship between chemical structure and mesophase behavior. Introduction of lateral substituents on the arms of BC molecules for modifying mesomorphic properties has been carried out [6–10] on a number of different systems. The influence of lateral substituents on the mesophase behavior in banana-shaped molecules is much more pronounced than that in calamatic molecules. The introduction of substituents on the central core can cause a change of the conformation, e.g., a change of the bending angle, which dictates whether conventional phase of rod-like molecules or "banana phases" are formed. Systematic studies performed on the parent series of five-ring banana-shaped mesogens has been made to investigate the sensitivity of such compounds to lateral substitutents attached to the central ring assuming the following common structure (Fig. 1).

Groups like cyano, methyl, or methoxy at the top of the bent molecules in position R_5 prevent the existence of any mesophases [11]. In contrast, the introduction of small groups like methyl or nitro into the obtuse angle of the molecules, i.e., in position R_2, results in high mesophase stability [12,13]. One chlorine atom in R_4 position results into substances having a B2 Phase [14]. The additional introduction of a second chlorine atom at R_6 position causes a change of the type of mesophase from the B-phase to nematic and smectic phases [15]. This surprising behavior has been explained by considering the conformation of the molecules. Nuclear Magnetic Resonance (NMR) investigation in the liquid crystalline state has revealed that the bending angle between two halves of the bent molecules is changed by substitutents which are situated near the connecting groups. Thus, the bending angle of about 120°, expected for the 1,3-phenyl unit was found for the parent molecule which are unsubstituted at the central ring. This bending angle is increased by the 4-chlorine atom to 134°, and by two chlorine atoms at 4,6-position is about 165°. In the latter case, the molecule exhibits a rather rod-like conformation. Therefore,

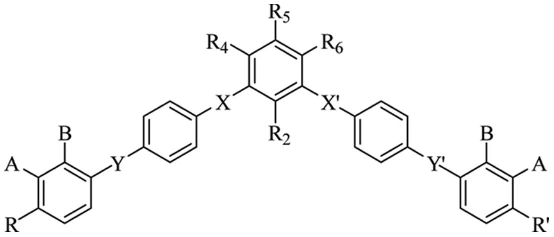


FIGURE 1 General structure of a bent-shaped molecule.

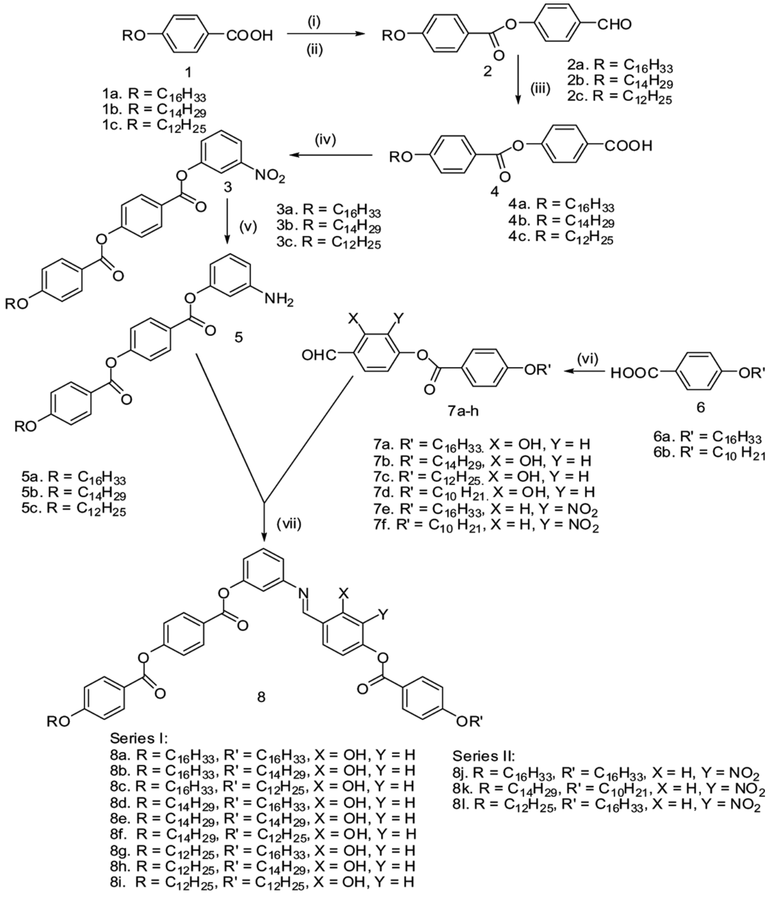
the existence of phases which are typical for calamitic mesogens is not surprising. Generally, the substituents attached to the central aromatic unit make it possible to vary the bending angle in a delicate manner. Thus, the phase sequences SmA-SmC-B2 and N-SmA-SmC-B2 were found with 4-cyano substituted resorcinol derivatives [16]. On the other hand, lateral substituents on the central core, middle rings, or terminal rings, of five-ring banana-shaped materials can change the packing of the molecules if the substituents are bulky, or influence the polar properties of the molecules. It is also well known that by increasing the number of aromatic rings along the bent core, the thermal stabilities as well as thermal ranges of the mesophases are increased. The phase sequence as a function of carbon atom on ascending a homologous series is well understood [17,18]. Symmetrical bent core molecules comprising an angular central core substituted with two identical linear rod-like mesogenic segments generally exhibit higher transition temperatures. To reduce the temperatures and to perhaps bridge the gap between bent core and rod-like liquid crystal, nonsymmetrical bent core molecules have been designed and synthesized. In these materials, either the two halves of the molecules or the linking functional groups attached to angular central core are different [19–21]. In continuation to our study on the synthesis and characterization of liquid crystalline molecule [22–23] here in we report the synthesis and evaluation of the mesomorphic behavior of nonsymmetric five ring achiral banana shaped liquid crystals consisting of two chemically nonidentical rod-like anisometric segments.

EXPERIMENTAL

All the chemicals were procured from either Sigma Aldrich Chemicals Pvt. Ltd. or Spectrochem, India. Silica gel [(60–120 mesh) was used for chromatographic separation. Silica gel G [E-Merck (India)] was used for TLC. Petroleum ether refers to the fraction boiling between 60°C and 80°C. IR spectra were recorded on a Perkin-Elmer L 120–000A spectrometer (λ_{max} in cm^{-1}) on KBr disks. UV absorption spectra were recorded in $CHCl_3$ on a Shimadzu UV-2401PC spectrophotometer (λ_{max} in nm). ^1H NMR (400 MHz) spectra were recorded on a Bruker DPX-500 spectrometer in $CDCl_3$ (chemical shift in δ) with TMS as internal standard. The liquid crystalline properties were established by thermal microscopy (Nikon polarizing microscope LV100POL attached with Instec hot and cold stage HCS302, with STC200 temperature controller configured for HCS302 and the phase transitions were confirmed by differential scanning calorimetry (Perkin–Elmer Diamond DSC Pyris1 system).

SYNTHESIS

The aforesaid series of unsymmetrical banana-shaped materials were prepared by acid catalyzed condensation of the key intermediate, namely, 4-formyl-3-hydroxyphenyl 4(n-alkyloxy)-benzoate (**7a–d**) or 4-formyl-3-nitrophenyl 4(n-alkyloxy)-benzoate (**7e–h**) with 4-[(3-aminophenoxy)carbonyl]phenyl 4-(n-alkyloxy)benzoate (**5a–c**) in ethanol as depicted in Scheme 1. The intermediates (**7a–f**) were obtained by



SCHEME 1 Reagents and conditions: (i) $SOCl_2$ reflux, 4 hrs, (ii) p-hydroxy benzaldehyde, CH_2Cl_2, DMAP, NEt_3, rt 4 hr, (iii) Jone's Oxidation, (iv) *m*-nitrophenol, CH_2Cl_2, DCC, DMAP, (v) H_2 Pd-C, Ethylacetate, (vi) 2,4-dihydroxy benzaldehyde or 4-hydroxy-3-nitrobenzaldehyde, CH_2Cl_2, DCC, DMAP, (vii) dehydrated alcohol, AcOH (cat), reflux, 4 h.

esterification of 4-(n-alkyloxy)benzoicacid with 2,4-dihydroxybenzaldehyde or 3-nitro-4-hydroxybenzaldehyde in dry dichloromethane in the presence of dicyclohexylcarbodiimide (DCC), and a catalytic amount of DMAP. Amines (**5a–c**) were prepared in five steps starting from 4-(n-alkyloxy)benzoic acid **(1a–c**). The compounds were characterized from their IR, and ^{1}H-NMR spectra.

General Procedure for the Esterfication to Prepare 4-Formyl-3-hydroxyphenyl 4(N-alkyloxy)-benzoate (7a–d) or 4-Formyl-2-nitrophenyl 4(N-alkyloxy)-benzoate (7e,f)

These were prepared according to the reported procedure [24].

General Procedure for the Preparation of 4-[(3-Aminophenoxy)carbonyl]phenyl 4-(N-alkyloxy) benzoate 5a–c

These were prepared according to published procedure [25].

General Procedure for the Schiff's Base Formation 8a–l

A mixture of 4-[(3-aminophenoxy)carbonyl]phenyl 4-(n-hexadecaloxy)-benzoate **5a** (0.1 g, 0.17 mmol) and 4-formyl-3-hydroxyphenyl 4(n-hexyloxy)-benzoate **7a** (0.08 g, 0.17 mmol) was refluxed in absolute ethanol (10 mL) in the presence of a catalytic amount of glacial acetic acid for 1 h. The schiff's base **8a** was precipitated out from reaction mixture. It was collected, washed repeatedly with hot ethanol, dried in vacuum. Similarly the other derivatives **8b–l** were prepared.

Compound 8a: IR (KBr): $\nu = 3450, 2915, 1735, 1717, 1608\,\text{cm}^{-1}$, ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 13.34$ (s, 1H, O**H**), 8.64 (s, 1H, C**H**=N), 8.26 (d, 2H, $J = 8.4$ Hz, Ar**H**), 8.10–8.14 (m, 4H, Ar**H**), 7.45 (t, 1H, $J = 8.0$ Hz, Ar**H**), 7.41 (d, 1H, $J = 8.0$ Hz, Ar**H**), 7.35 (d, 2H, $J = 8.4$ Hz, Ar**H**), 7.14–7.20 (m, 3H, Ar**H**), 6.94–6.98 (m, 4H, Ar**H**), 6.87 (d, 1H, $J = 2.0$ Hz, Ar**H**), 6.81 (dd, 1H, $J = 2.0$ Hz, 8.0 Hz, Ar**H**), 4.01–4.05 (m, 4H, OC**H₂**), 0.81–1.84 (m, 62H, aliphatic hydrogen are overlapped). Anal. Calcd. for $C_{66}H_{87}NO_9$; C, 76.34; H, 8.44; N, 1.35%. Found: C, 76.54; H, 8.60; N, 1.48%.

Compound 8b: IR (KBr): ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 13.34$ (s, 1H, O**H**), 8.66 (s, 1H, C**H**=N), 8.28 (dd, 2H, $J = 2$ Hz, 6.8 Hz, Ar**H**), 8.11–8.15 (m, 4H, Ar**H**), 7.47 (t, 1H, $J = 8.0$ Hz, Ar**H**), 7.43 (d, 1H, $J = 8.5$ Hz, Ar**H**), 7.37 (dd, 2H, $J = 2$ Hz, 6.8 Hz, Ar**H**), 7.16–7.22 (m, 3H, Ar**H**), 6.96–7.00 (m, 4H, Ar**H**), 6.89 (d, 1H,

$J = 2.2$ Hz, Ar**H**), 6.83 (dd, 1H, $J = 2.2$ Hz, 8.5 Hz, Ar**H**), 4.03–4.07 (m, 4H, OC$\mathbf{H_2}$), 0.81–1.81 (m, 58H, aliphatic hydrogens are overlapped). ^{13}C NMR (CDCl$_3$, 125 MHz): 164.7, 164.6, 164.2, 164.1, 163.0, 155.9, 152.1, 150.0, 133.8, 132.8, 132.7, 132.2, 130.6, 127.0, 122.5, 121.6, 121.3, 114.9, 114.8, 114.7, 113.6, 68.8, 32.3, 30.1, 30.0, 30.0, 29.9, 29.7, 29.5, 26.3, 23.1, 14.5.

Anal. Calcd. for $C_{64}H_{83}NO_9$; C, 76.08; H, 8.28; N, 1.39%. Found: C, 76.36; H, 8.48; N, 1.49%.

Compound 8c: IR (KBr): $\nu = 3454$, 2919, 1740, 1714, 1607 cm^{-1}, ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta_H = 13.31$ (s, 1H, O**H**), 8.65 (s, 1H, C**H**=N), 8.26 (dd, 2H, $J = 2$ Hz, 7.0 Hz, Ar**H**), 8.10–8.14 (m, 4H, Ar**H**), 7.45 (t, 1H, $J = 8.0$ Hz, Ar**H**), 7.41 (d, 1H, $J = 8.4$ Hz, Ar**H**), 7.35 (dd, 2H, $J = 2$ Hz, 6.8 Hz, Ar**H**), 7.16–7.21 (m, 3H, Ar**H**), 6.96–7.05 (m, 4H, Ar**H**), 6.88 (d, 1H, $J = 2.2$ Hz, Ar**H**), 6.83 (dd, $J = 2.2$ Hz, 8.4 Hz, 1H, Ar**H**), 4.03–4.07 (m, 4H, OC$\mathbf{H_2}$), 0.81–1.80 (m, 54H, aliphatic hydrogens are overlapped). Anal. Calcd. for $C_{62}H_{79}NO_9$; C, 75.81; H, 8.11; N, 1.43%. Found: C, 76.03; H, 8.22; N, 1.50%.

Compound 8d: IR (KBr): $\nu = 3455$, 2918, 1739, 1719, 1609 cm^{-1}, ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta_H = 13.34$ (s, 1H, O**H**), 8.64 (s, 1H, C**H**=N), 8.27 (d, 2H, $J = 8.0$ Hz, Ar**H**,), 8.11–8.15 (m, 4H, Ar**H**), 7.45 (t, 1H, $J = 8.0$ Hz, Ar**H**), 7.41 (d, 1H, $J = 8.4$ Hz, Ar**H**), 7.36 (d, 2H, $J = 8.0$ Hz, Ar**H**), 7.14–7.21 (m, 3H, Ar**H**), 6.94–6.98 (m, 4H, Ar**H**), 6.87 (d, 1H, $J = 2.0$ Hz, Ar**H**), 6.81 (dd, 1H, $J = 2.0$ Hz, Hz, 8.4 Hz, Ar**H**), 4.01–4.05 (m, 4H, OC$\mathbf{H_2}$), 0.85–1.82 (m, 58H, aliphatic hydrogen's are overlapped). Anal. Calcd. for $C_{64}H_{83}NO_9$; C, 76.08; H, 8.28; N, 1.39%. Found: C, 76.31; H, 8.40; N, 1.43%.

Compound 8e: IR (KBr): $\nu = 3444$, 2917, 1733, 1605 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta_H = 13.38$ (s, 1H, O**H**), 8.64 (s, 1H, C**H**=N), 8.26 (d, 2H, $J = 8.8$ Hz, Ar**H**), 8.10–8.15 (m, 4H, Ar**H**), 7.45 (t, 1H, $J = 8.0$ Hz, Ar**H**), 7.41 (d, 1H, $J = 8.4$ Hz, Ar**H**), 7.35 (d, 2H, $J = 8.8$ Hz, Ar**H**), 7.13–7.20 (m, 3H, Ar**H**), 6.94–6.98 (m, 4H, Ar**H**), 6.87 (d, 1H, $J = 2.0$ Hz, Ar**H**), 6.80 (dd, 1H, $J = 2.0$ Hz, 8.4 Hz, Ar**H**), 4.01–4.05 (m, 4H, OC$\mathbf{H_2}$), 0.84–1.82 (m, 54H, aliphatic hydrogen's are overlapped). Anal. Calcd. for $C_{62}H_{79}NO_9$; C, 75.81; H, 8.11; N, 1.43%. Found: C, 76.00; H, 8.40; N, 1.48%.

Compound 8f: IR (KBr): $\nu = 3450$, 2919, 1734, 1719, 1604 cm^{-1}, ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta_H = 13.33$ (s, 1H, O**H**), 8.64 (s, 1H, C**H**=N), 8.26 (d, 2H, $J = 8.8$ Hz, Ar**H**), 8.10–8.14 (m, 4H, Ar**H**), 7.45 (t, 1H, $J = 8.0$ Hz, Ar**H**), 7.41 (d, 1H, $J = 8.4$ Hz, Ar**H**), 7.35 (d, 2H, $J = 8.8$ Hz, Ar**H**), 7.13–7.20 (m, 3H, Ar**H**), 6.94–6.98 (m, 4H, Ar**H**), 6.87 (d, 1H, $J = 2.0$ Hz, Ar**H**), 6.80 (dd, 1H, $J = 2.0$ Hz, Hz, 8.4 Hz, Ar**H**), 4.01–4.05 (m, 4H, OC$\mathbf{H_2}$), 0.80–1.83 (m, 50H, aliphatic hydrogen's are overlapped). Anal. Calcd. for $C_{60}H_{75}NO_9$; C, 75.52; H, 7.92; N, 1.47%. Found: C, 75.62; H, 8.08; N, 1.53%.

Compound 8g: IR (KBr): $\nu = 3448, 2916, 1731, 1717, 1603\,cm^{-1}$, ^{1}H NMR ($CDCl_3$, 400 MHz): ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 13.30$ (s, 1H, O**H**), 8.66 (s, 1H, C**H**=N), 8.28 (dd, 2H, $J = 2.0$ Hz, 6.8 Hz, Ar**H**), 8.12–8.17 (m, 4H, Ar**H**), 7.47 (t, 1H, $J = 8.0$ Hz, Ar**H**), 7.43 (d, 1H, $J = 8.4$ Hz, Ar**H**), 7.37 (dd, 2H, $J = 2.0$ Hz, 6.8 Hz, Ar**H**), 7.15–7.22 (m, 3H, Ar**H**), 6.96–7.00 (m, 4H, Ar**H**), 6.89 (d, 1H, $J = 2.2$ Hz, Ar**H**), 6.83 (dd, 1H, $J = 2.2$ Hz, 8.4 Hz, Ar**H**), 4.01–4.03 (m, 4H, OC$\mathbf{H_2}$), 0.86–1.85 (m, 54H, aliphatic hydrogen's are overlapped). Anal. Calcd. for $C_{62}H_{79}NO_9$; C, 75.81; H, 8.11; N, 1.43%. Found: C, 76.03; H, 8.37; N, 1.49%.

Compound 8h: IR (KBr): $\nu = 3455, 2919, 1739, 1719, 1608\,cm^{-1}$; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 13.34$ (s, 1H, O**H**), 8.64 (s, 1H, C**H**=N), 8.26 (d, 2H, $J = 8.8$ Hz, Ar**H**), 8.10–8.15 (m, 4H, Ar**H**), 7.45 (t, 1H, $J = 8.0$ Hz, Ar**H**), 7.41 (d, 1H, $J = 8.4$ Hz, Ar**H**), 7.35 (d, 2H, $J = 8.8$ Hz, Ar**H**), 7.13–7.20 (m, 3H, Ar**H**), 6.94–6.98 (m, 4H, Ar**H**), 6.87 (d, 1H, $J = 2.4$ Hz, Ar**H**), 6.80 (dd, 1H, $J = 2.4$ Hz, Hz, 8.4 Hz, Ar**H**), 4.01–4.03 (m, 4H, OC$\mathbf{H_2}$) 0.84–1.80 (m, 50H, aliphatic hydrogen's overlapped). Anal. Calcd. for $C_{60}H_{75}NO_9$; C, 75.52; H, 7.92; N, 1.47%. Found: C, 75.70; H, 8.12; N, 1.56%.

Compound 8i: IR (KBr): $\nu = 3463, 2919, 1731,1605\,cm^{-1}$; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 13.35$ (s, 1H, O**H**), 8.66 (s, 1H, C**H**=N), 8.28 (dd, 2H, $J = 2.0$ Hz, 6.8 Hz, Ar**H**), 8.12–8.16 (m, 4H, Ar**H**), 7.47 (t, 1H, $J = 8.0$ Hz, Ar**H**), 7.43 (d, 1H, $J = 8.4$ Hz, Ar**H**), 7.37 (dd, 2H, $J = 2$ Hz., 6.8 Hz, Ar**H**), 7.15–7.18 (m, 3H, Ar**H**), 6.96–7.00 (m, 4H, Ar**H**), 6.89 (d, 1H, $J = 2.0$ Hz, Ar**H**), 6.83 (dd, 1H, $J = 2.0$ Hz, 8.4 Hz, Ar**H**), 4.02–4.07 (m, 4H, OC$\mathbf{H_2}$), 0.86–1.83 (m, 46H, aliphatic hydrogen's are overlapped). Anal. Calcd. for $C_{58}H_{71}NO_9$; C, 75.21; H, 7.73; N, 1.51%. Found: C, 75.50; H, 7.90; N, 1.59%.

Compound 8j: IR (KBr): $\nu = 2918, 1744, 1720, 1608\,cm^{-1}$, ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 8.61$ (d, 1H, $J = 1.9$ Hz, Ar**H**), 8.54 (s, 1H, C**H**=N), 8.27 (d, 2H, $J = 8.3$ Hz, Ar**H**), 8.11–8.14 (m, 4H, Ar**H**), 7.47–7.51 (m, 2H, Ar**H**), 7.35 (d, 2H, $J = 8.3$ Hz, Ar**H**), 7.14–7.19 (m, 3H, Ar**H**), 6.97–6.97 (m, 5H, Ar**H**), 4.01 (t, 4H, $J = 6.3$ Hz, OC$\mathbf{H_2}$), 0.86–1.84 (m, 62H, aliphatic hydrogen's are overlapped). Anal. Calcd. for $C_{66}H_{86}N_2O_{10}$; C, 74.27; H, 8.12; N, 2.62%. Found: C, 74.45; H, 8.40; N, 2.80%.

Compound 8k: IR (KBr): $\nu = 2920, 1743, 1724, 1604\,cm^{-1}$, ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 8.63$ (d, 1H, $J = 2$ Hz, Ar**H**), 8.54 (s, 1H, C**H**=N), 8.27 (d, 2H, $J = 8.4$ Hz, Ar**H**), 8.12–8.15 (m, 4H, Ar**H**), 7.47–7.51 (m, 2H, Ar**H**), 7.36 (d, 2H, $J = 8.4$ Hz, Ar**H**), 7.14–7.18 (m, 3H, Ar**H**), 6.97–6.99 (m, 5H, Ar**H**), 4.02 (t, 4H, $J = 6.3$ Hz, OC$\mathbf{H_2}$), 0.87–1.83 (m, 46 H, aliphatic hydrogen's are overlapped). Anal. Calcd. for $C_{58}H_{70}N_2O_{10}$; C, 72.93; H, 7.39; N, 2.93%. Found: C, 73.10; H, 7.49; N, 3.00%.

Compound 8l: IR (KBr): $\nu = 2916$, 1743, 1720, 1605 cm^{-1}, ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 8.63$ (d, 1H, $J = 2$ Hz, Ar**H**), 8.55 (s, 1H, C**H**=N), 8.28 (d, 2H, $J = 8.7$ Hz, Ar**H**), 8.11–8.15 (m, 4H, Ar**H**), 7.46–7.52 (m, 2H, Ar**H**), 7.36–7.41 (m, 2H, Ar**H**), 7.15–7.18 (m, 3H, Ar**H**), 6.96–7.00 (m, 5H, Ar**H**), 4.04 (t, 4H, $J = 6.6$ Hz, OC$\mathbf{H_2}$), 0.86–1.85 (m, 54 H, aliphatic hydrogen's are overlapped). Anal. Calcd. for $C_{62}H_{78}N_2O_{10}$; C, 73.63; H, 7.77; N, 2.77%. Found: C, 73.90; H, 7.90; N, 2.85%.

RESULTS AND DISCUSSION

The mesomorphic properties of all the compounds were investigated using classical techniques. The transition temperatures and the associated enthalpy values obtained for compound of series I and II are summarized in Table 1.

TABLE 1 Summarized Results of the DSC Data

Compound	Phase transition temperature °C (enthalpy KJ mol^{-1})
8a	Cr 107.7 (72.9) B2 136.6 (21.3) I I 135.0 (21.1) B2 83.9 (60.4) Cr
8b	Cr 101.1 (55.8) B2 135.8 (18.7) I I 133.7 (19.2) B2 69.5 (32.5) Cr
8c	Cr 99.9 (40.1) B2 134.7 (20.2) I I 132.8 (20.4) B2 66.1 (37.7) Cr
8d	Cr 104.7 (80.5) B2 136.5 (25.8) I I 132.8 (23.4) B2 68.3 (30.9) Cr
8e	Cr 105.6 (64.4) B2 136.5 (10.0) I I 126.0 (10.3) B2 59.8 (20.7) Cr
8f	Cr 101.8 (38.3) B2 133.8 (7.2) I I 127.9 (10.3) B2 56.7 (6.5) Cr
8g	Cr 102.3 (68.7) B2 134.9 (22.3) I I 133.1 (21.9) B2 70.5 (33.3) Cr
8h	Cr 102.1 (52.2) B2 134.7 (19.0) I I 132.6 (19.5) B2 68.9 (31.1) Cr
8i	Cr 103.0 (40.7) B2 134.1 (14.3) I I 132.1 (14.3) B2 68.9 (32.5) Cr
8j	Cr 76.9 (3.6) B2 90.8 (8.3) I I 91.5 (13.7) B2 48.3 (19.1) Cr
8k	Cr 107.7 (72.9) B2 136.6 (21.3) I I 96.73 (10.72) B2 47.75 (2.39) Cr
81	Cr 73.5 (21.7) B2 97.4 (15.3) I I 95.4 (13.7) B2 48.1 (3.0) Cr

Seemingly, the salicylaldimines (series I) and Schiff base (series II) analogues display virtually the same transitional behavior with the obvious exception that the transition (melting and the clearing) temperatures are higher for the former due to the presence of intramolecular H-bonding. All the compounds of series I and II showed two transitions in both heating and cooling cycles (Figs. 2 and 3).

The first one corresponds to crystal to liquid crystalline phase transition, and the second one corresponds to the liquid crystalline phase to isotropic phase transition. The clearing enthalpy values for this mesophase are in the range 10–25 KJmol^{-1}. In the case of compounds **8a**, **8b**, **8c**, the melting and clearing temperatures decrease slightly as the number of -CH_2 (methylene) group in the end alkoxy chain decreases. This trend was found more or less similar to the other compounds of series I. On the other hand, such a trend was not observed for the compounds of series II. The enthalpy change occurred during the phase transition is sufficiently larger for compounds of the series I than that of the series II. This may be due to the presence of

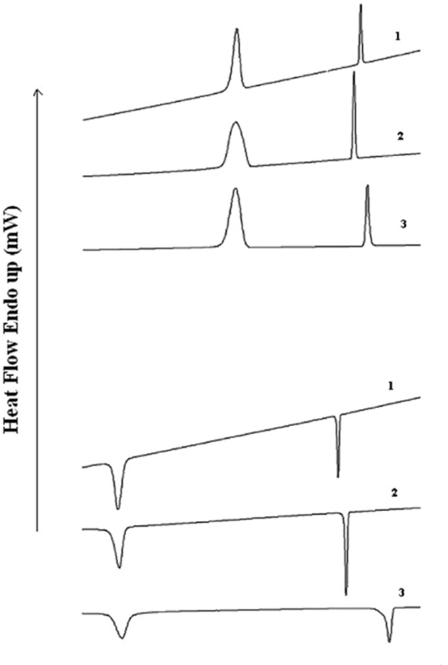


FIGURE 2 DSC thermogram of compound 1. 8i, 2. 8g, 3. 8d, of series I.

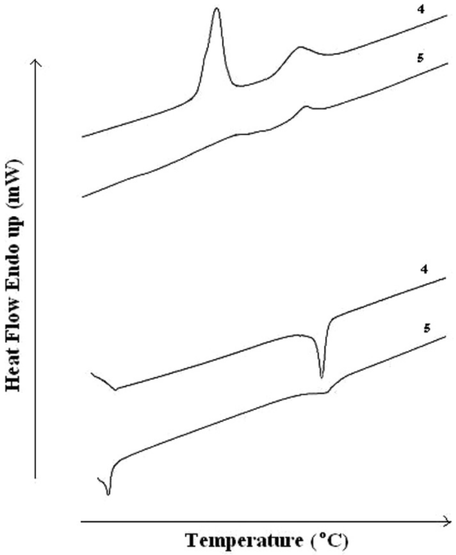


FIGURE 3 DSC thermogram of 4. 8k, 5. 8j, series II.

intramolecular H-bonding. It is also interesting to note that the melting points are not very high, and the clearing temperatures are close to about 140°C for series I and 100°C for series II, unlike many other five ring banana shaped material. Any sample of both the series when placed in a thin cell with a cell gap of $d = 5 \pm 0.2\,\mu m$ μm with homogeneous planar boundary conditions a stripe-like texture appears from the isotropic melt, which on further cooling grows slowly and fills up the whole field of view with circular domains (Figs. 4 and 5). This is a typical texture of B2 the phase. On very slow cooling from the isotropic phase B2 phase is stabilized to almost 85–65°C for salicylaldimines series I and to 48–45°C for series II, which was further confirmed by different scanning calorimetry (DSC) study.

In order to evaluate the molecular arrangement within the layer, X-ray diffraction (XRD) was performed on compound 8i. XRD was carried out on a Philips powder diffractometer (PAN analytical model no. pw 3015) operating on X'pert pro software, equipped with a temperature controller permitting low as well as high temperature operation as needed (with CuKα radiation of $\lambda = 1.5418$). The diffraction pattern of an unoriented sample of the mesophase of compound **8i** showed a diffuse peak in the wide angle region with $d = 4.6\,\text{Å}$ indicating liquid-like in-plane order.

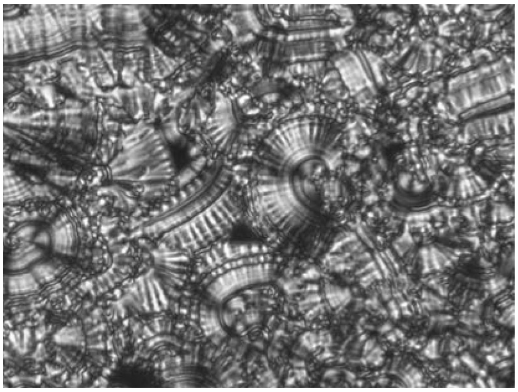


FIGURE 4 Compound 8i in thin cell at 126.9°C.

In addition, three orders of lamellar reflection (in the ratio 1:$\frac{1}{2}$:1/3) in the small angle region could be clearly seen (Fig. 6). The molecular length L ~ 51.1 Å was calculated by molecular modeling, assuming the molecules have fully stretched conformation. As the first order reflection is found to be at $2\theta = 2.5205°$ (d = 35.05 Å) which is sufficiently smaller than the molecular length L, so the molecules are assumed to be tilted within the layers. From XRD as well as textural characterization, this mesophase may be identified as B2 phase. Sadashiva et al. [26] showed excellent B2 → N transition by introducing a fluorine atom into one of the arms of a homologous

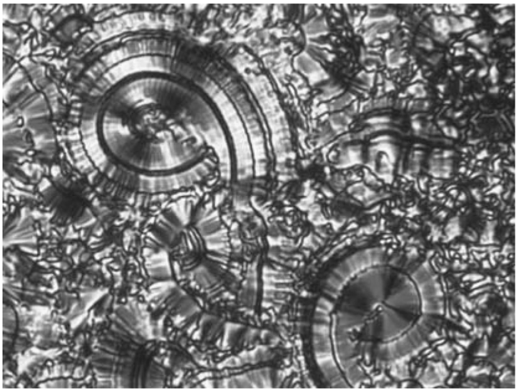


FIGURE 5 Compound 8i in thin cell at 130.5°C.

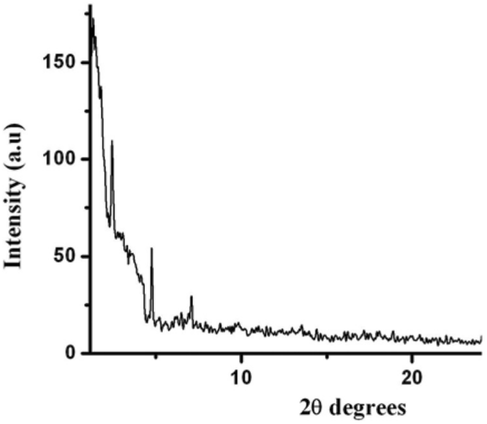


FIGURE 6 XRD diagram of compound 8i at 120°C.

series of symmetric bent core compounds with 2,7-dihydroxy naphthalene as central core but corresponding analogous derivative from 1,3-dihydroxy benzene did not show any mesophase. They also showed $SmA_{db} \rightarrow SmA_d$ phase transition by introducing fluorine into similar position of a homologous series of unsymmetrical bent core molecule with 3-hydroxy benzoic acid as a central core [27]. On the other hand, they observed a B7 phase transition by introducing a cyano or a nitro group on the central phenyl ring [28]. The occurrence of calamitic phases in conjunction with the B phases are very much common for five-ring banana-shaped materials with a lateral substitution. This may be due to the deviation of the bend angle between the two arms of the bent core molecules. In our case, we observed only the B-phase instead of lateral substitution in one of the arms of the bent-shape molecule. Thus the occurrence of only a B2 phase over a wide temperature range for all the compounds of series I and II is quite significant in our case. There are several examples of the introduction of hydroxy group in one of the arm of banana-shape material to stabilize the phases. However, to our knowledge, there is no report of the introduction of a nitro group into one of the arms of either symmetrical or unsymmetrical five-ring banana-shaped materials. In conclusion, we have achieved the synthesis of two new series of unsymmetrical bent shaped compounds with lateral hydroxy and nitro groups. These compounds exhibit only a B_2 phase over a wide temperature range, as observed by optical microscopy and DSC.

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