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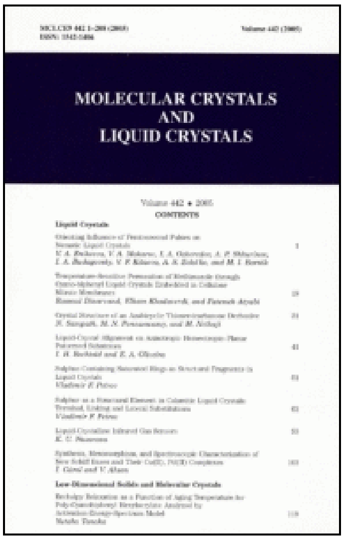

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Synthesis and Characterization of Symmetrical Eight Aromatic Ring Containing Bent-Shaped Material Derived from Benzophenone

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Synthesis and Characterization of Symmetrical Eight Aromatic Ring Containing Bent-Shaped Material Derived from Benzophenone

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A new family of symmetrical eight aromatic ring-containing bent-shaped mesogens in which the central elbow is a ketone has been synthesized and characterized. The effect of the side chain on the mesomorphism has been studied. All the bent derivatives were found to exhibit mesomorphism. The higher homologues of the series exhibit the B1 phase and the lower homologues of the series show the B6 phase.

Keywords B1 phase; B6 phase; bent-shaped; eight aromatic rings; HRXRD; mesogen

Introduction

Liquid-crystalline compounds have found wide application in scientific and technological areas, especially as flat panel displays [1], light-emitting diodes (OLED) [2], anisotropic networks [3], and photoconductor and semiconduction materials [4]. Among numerous liquid-crystalline compounds of different shapes synthesized so far by different research groups, bent-shaped liquid-crystalline compounds are the most popular [5]. In 1996, Niori *et al.* [6] reported on ferroelectricity in a smectic phase formed by banana-shaped Schiff's base derivatives, first synthesized by Matsunaga *et al.* [7]. The distinct molecular structure, unconventional mesomorphic properties, occurrence of a spontaneous symmetry breaking in some cases, and special switching behavior of some of their mesophases immediately attracted great interest [8,9].

These types of materials form several new liquid-crystalline phases designated by levels B1–B8 and some exhibit interesting ferro- and antiferroelectric properties, although the molecules are achiral. With the exception of B3 and B4, all the Bn mesophases represent a lamellar organization without in-plane order. B2, B6, and B8 can be considered as the analogues of a "monolayer-smectic," "intercalated-smectic," and "bilayer-smectic," respectively. B5 represents an antiferroelectric response. B1 and B7 correspond to more complex two-dimensional structures.

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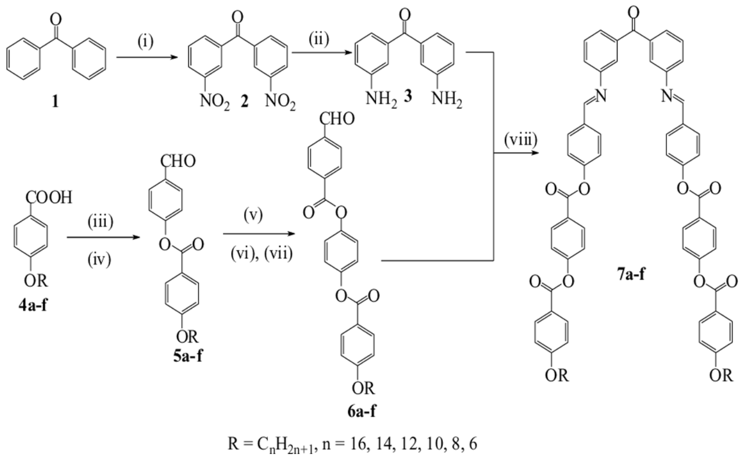
In the bent-core molecule, the bending angle is the most important structural feature for the formation of a polar-order mesophase. Depending on the chemical structure of the molecule, the bending angle can be varied in the range 105–140° in order to show the typical properties of the bent-shaped molecules [10]. Molecules with a bending angle outside this limit in most cases show nonpolar mesophases [11]. Another interesting factor that influences the mesophase behavior of the bent-core molecule is the number of phenyl rings in the bent-shaped molecules. Most of the bent-core molecules discovered so far contain five aromatic rings with a bending angle around 120° [12]. There are examples of modification of the bending angle using five-member heterocyclic units or introducing substitution at the central core. There are also limited examples of bent-core molecules with three [13], four [13], six [14], seven [15], and nine aromatic rings [16]. For the past few years we have synthesized several bent-shaped materials with unusual shapes [17] and studied their structure–property relationships. In continuation of our earlier efforts, we have undertaken a study to synthesize a homologous series of banana-shaped materials containing eight aromatic rings with a deviation of bending angle from the usual bending angle of bent-core materials. Liquid crystals with a total of eight rings will possess high molar masses.

Liquid crystal displays [LCDs] derived from high-molecular-mass liquid crystals are known to possess a number of advantages; for example simple and minimal fabrication cost, flexibility, high brightness, small switching time, etc., over low-molar-mass LCDs. These materials can be used in switchable windows, infrared shutters, angular discriminating filters, thermo-optic and electro-optic switches etc. [18–22]. Herein we report our results on the synthesis and characterization of liquid-crystalline properties of the newly synthesized compounds with polarizing optical microscopy (POM), differential scanning colorimetry (DSC), and high-resolution X-ray diffraction (HRXRD) experiments.

Experimental

The methodology used for the synthesis of banana-shaped materials **7a-f** is depicted in Scheme 1. Benzophenone was first converted into its dinitro derivative (**2**), which was then reduced to the diamine derivative (**3**). Compounds **6a-f** were prepared by Jones oxidation of ester aldehydes **5a-f** followed by esterification with 4-hydroxy benzaldehyde. The diamino derivative **3** was then heated under reflux with 4-(4-formylbenzoyloxy)phenyl 4-(alkyloxy)benzoates in absolute ethanol in the presence of a catalytic amount of glacial acetic acid to afford the homologous series **7a-f**.

All the chemicals were procured from either Sigma Aldrich Chemicals Pvt. Ltd. or Spectrochem, Mumbai, India. Silica gel [(60–120 mesh) was used for chromatographic separation. Silica gel G (E-Merck, India) was used for thin-layer chromatography (TLC). Petroleum ether refers to the fraction boiling between 60°C and 80°C. Infrared (IR) spectra were recorded on a Perkin-Elmer L 120-000A spectrometer (ν_{max} in cm^{-1}) on KBr disks. ^{1}H nuclear magnetic resonance(NMR) (300 MHz, 400 MHz, 500 MHz) spectra were recorded on a Bruker DPX-300, DPX-400, DPX-500 spectrometer in $CDCl_3$ (chemical shift in δ) with trimethyl siloxane (TMS) as internal standard. Carbon, hydrogen, nitrogen (CHN) analyses were recorded on a 2400 series II CHN analyzer (Perkin Elmer). The liquid-crystalline properties were established by thermal microscopy (Nikon polarizing microscope LV100POL attached with an Instec hot and



Scheme 1. Reaction conditions and reagents: (i) Conc. H_2SO_4, fuming HNO_3, heat, 60°C, 2 h; (ii) ethyl acctate, $SnCl_2$, $2H_2O$, conc. HCl(cat) reflux, 4 h; (iii) $SOCl_2$, reflux, 1 h; (iv) 4-hydroxybenzaldehyde, DCM, aq K_2CO_3, Bu_4NHSO_4, 12 h; (v) Jone's reagent, acctone, r.t.; (vi) $SOCl_2$, reflux, 1 h; (vii) 4-hydroxy benzaldehyde, DCM, aq K_2CO_3, Bu_4NHSO_4, 4 h; (viii) Dry alcohol, Cat. AcOH, reflux, 4 h.

cold stage HCS302, with STC200 temperature controller configured for HCS302) and the phase transitions were confirmed by DSC (Perkin-Elmer Diamond DSC system).

General Procedure for the Preparation of Compounds 2 and 3

3,3′-Dinitrobenzophenone **2** and 3,3′-diaminobenzophenone **3** were prepared according to our earlier published procedure [10].

General Procedure for the Formation of Aldehydes 6a-f

A mixture of 4-(4-(hexadecyloxy)benzoyloxy)benzoic acid (500 mg, 0.99 mmol) and $SOCl_2$ was stirred at 100°C for 3 h. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (20 mL). A solution of 4-hydroxybenzaldehyde (121 mg, 0.99 mmol) in CH_2Cl_2 (20 mL) and tetrabutyl ammonium hydrogen sulfate (catalytic amount) was added to the stirred solution of acid chloride. To this reaction mixture an aqueous solution of K_2CO_3 (274 mg, 1.98 mmol) was added slowly. After stirring for 4 h at room temperature, the solution was washed with 5% HCl (2 × 20 mL) and then with 5% aqueous NaOH (2 × 20 mL). The organic layer was dried (Na_2SO_4) and the solvent evaporated under reduced pressure. The residue was purified by column chromatography over silica gel using petroleum. ether-ethyl acetate (9:1) as an eluent to give aldehyde **6a**. The aldehydes **6b-f** were prepared accordingly.

Compound 6a. White solid, yield 93%, IR (KBr, cm^{-1}): ν_{max}: 2,916, 1,743, 1,703, 1,604. ^1H NMR ($CDCl_3$, 400 MHz): $\delta_H = 10.03$ (s, 1H), 8.27 (dd, 2H, $J = 2.0$ Hz, 6.8 Hz), 8.14 (dd, 2H, $J = 2.0$ Hz, 7.2 Hz), 7.98 (dd, 2H, $J = 1.6$ Hz, 6.8 Hz), 7.38–7.44 (m, 4H), 6.98 (dd, 2H, $J = 2.0$ Hz, 7.2 Hz), 4.04 (t, 2H, $J = 6.4$ Hz), 1.81 (quint, 2H, $J = 7.2$ Hz), 1.22–1.58 (m, 26H), 0.86 (t, 3H, $J = 6.8$ Hz). Anal. Calcd. for $C_{37}H_{46}O_6$: C, 75.74; H, 7.90%. Found: C, 75.90; H, 7.68%.

Compound 6b. White solid, yield 95%, IR (KBr, cm^{-1}): ν_{max}: 2,917, 1,735, 1,702, 1,603. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 10.03$ (s, 1H), 8.27 (dd, 2H, $J = 2.0$ Hz, 6.8 Hz), 8.13 (dd, 2H, $J = 2.0$ Hz, 7.2 Hz), 7.97 (dd, 2H, $J = 2.0$ Hz, 6.8 Hz), 7.37–7.44 (m, 4H), 6.97 (dd, 2H, $J = 2.0$ Hz, 7.2 Hz), 4.04 (t, 2H, $J = 6.4$ Hz), 1.79 (quint, 2H, $J = 6.8$ Hz), 1.27–1.58 (m, 22H), 0.87 (t, 3H, $J = 6.8$ Hz). Anal. Calcd. for $C_{35}H_{42}O_6$: C, 75.24; H, 7.58%. Found: C, 75.48; H, 7.71%.

Compound 6c was prepared according to earlier published procedure [26].

Compound 6d. White solid, yield 90%, IR (KBr, cm^{-1}): ν_{max}: 2,917, 1,741, 1,705, 1,605. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 9.96$ (s, 1H), 8.19 (dd, 2H, $J = 2.0$ Hz, 7.2 Hz), 8.06 (dd, 2H, $J = 2.0$ Hz, 7.2 Hz), 7.90 (dd, 2H, $J = 2.0$ Hz, 6.8 Hz), 7.30–7.37 (m, 4H), 6.90 (d, 2H, $J = 9.2$ Hz), 3.97 (t, 2H, $J = 6.4$ Hz), 1.72 (quint, 2H, $J = 6.4$ Hz), 1.15–1.56 (m, 14H), 0.80 (t, 3H, $J = 7.2$ Hz). Anal. Calcd. for $C_{31}H_{34}O_6$: C, 74.08; H, 6.82%. Found: C, 74.24; H, 7.03%.

Compound 6e. White solid, yield 92%, IR (KBr, cm^{-1}): ν_{max}: 2,920, 1,743, 1,706, 1,606. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 10.04$ (s, 1H), 8.27 (d, 2H, $J = 8.8$ Hz), 8.14 (d, 2H, $J = 8.8$ Hz), 7.97 (d, 2H, $J = 8.4$ Hz), 7.41 (d, 2H, $J = 8.4$ Hz), 7.38 (d, 2H, $J = 8.8$ Hz), 6.98 (d, 2H, $J = 8.8$ Hz), 4.04 (t, 2H, $J = 6.8$ Hz), 1.79 (quint, 2H, $J = 6.4$ Hz), 1.25–1.63 (m, 10H), 0.88 (t, 3H, $J = 6.8$ Hz). Anal. Calcd. for $C_{29}H_{30}O_6$: C, 73.40; H, 6.37%. Found: C, 73.57; H, 6.53%.

Compound 6f. White solid, yield 95%, IR (KBr, cm^{-1}): ν_{max}: 2,920, 1,734, 1,703, 1,605. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 10.03$ (s, 1H), 8.27 (d, 2H, $J = 8.8$ Hz), 8.14 (d, 2H, $J = 8.4$ Hz), 7.97 (d, 2H, $J = 8.8$ Hz), 7.41 (d, 2H, $J = 8.4$ Hz), 7.38 (d, 2H, $J = 8.4$ Hz), 6.98 (d, 2H, $J = 8.8$ Hz), 4.04 (t, 2H, $J = 6.4$ Hz), 1.81 (quint, 2H, $J = 6.8$ Hz), 1.27–1.57 (m, 6H), 0.87 (t, 3H, $J = 6.8$ Hz). Anal. Calcd. for $C_{27}H_{26}O_6$: C, 72.63; H, 5.87%. Found: C, 72.85; H, 5.81%.

General Procedure for the Preparation of Compound 7A-E

3,3 ′ -Diaminobenzophenone **3** (0.05 g, 0.02 mmol) was heated under reflux with 4-(4-formylbenzoyloxy)phenyl 4-(hexyloxy)benzoates **6a** (0.28 g, 0.047 mmol) in absolute ethanol in the presence of a catalytic amount of glacial acetic acid to afford the desired product **7a**. All the other compounds were prepared according to a similar procedure as mentioned above.

Compound 7a. Yellow solid, yield 97%, IR (KBr, cm^{-1}): ν_{max}: 2,919, 1,744, 1,734, 1,663, 1,628, 1,603. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta_H = 8.52$ (s, 2H), 8.28 (d, 4H, $J = 8.7$ Hz), 8.14 (d, 4H, $J = 8.8$ Hz), 7.99 (d, 4H, $J = 8.6$ Hz), 7.70 (d, 2H, $J = 7.5$ Hz), 7.67 (s, 2H), 7.52 (t, 2H, $J = 7.6$ Hz), 7.46 (d, 2H, $J = 7.8$ Hz), 7.36–7.40 (m, 8H), 6.98 (d, 4H, $J = 8.9$ Hz), 4.04 (t, 4H, $J = 6.5$ Hz), 1.80 (quint, 4H, $J = 6.6$ Hz), 1.26–1.50 (m, 52H), 0.87 (t, 6H, $J = 7.0$ Hz).^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta_C = 196.2$, 164.3, 164.1, 163.9, 160.3, 155.6, 153.5, 152.0, 138.6, 133.7, 132.4, 131.9, 131.3, 130.2, 129.2, 127.7, 126.5, 125.5, 122.6, 122.3, 122.2, 121.9, 120.9, 114.4, 68.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.0, 26.0, 22.7, 14.1. Anal. Calcd. for $C_{87}H_{100}N_2O_{11}$: C, 77.42; H, 7.47; N, 2.08%. Found: C, 77.59; H, 7.63; N, 2.13%.

Compound 7b. Yellow solid, yield 98% IR (KBr, cm^{-1}): ν_{max}: 2,919, 1,743, 1,664, 1,628, 1,603. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta_H = 8.52$ (s, 2H), 8.28 (d, 4H,

$J = 8.6$ Hz), 8.14 (d, 4H, $J = 8.8$ Hz), 7.99 (d, 4H, $J = 8.6$ Hz), 7.70 (d, 2H, $J = 7.5$ Hz), 7.67 (s, 2H), 7.52 (t, 2H, $J = 7.8$ Hz), 7.46 (d, 2H, $J = 8.0$ Hz), 7.36 (t, 8H, $J = 8.4$ Hz), 6.98 (d, 4H, $J = 8.9$ Hz), 4.04 (t, 4H, $J = 6.5$ Hz), 1.80 (quint, 4H, $J = 6.6$ Hz), 1.27–1.56 (m, 44H), 0.87 (t, 6H, $J = 7.1$ Hz).^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta_C = 191.0$, 164.3, 164.1, 163.9, 160.3, 155.6, 153.5, 152.0, 138.6, 133.7, 132.4, 131.9, 131.3, 130.3, 129.2, 127.7, 126.5, 125.5, 122.3, 122.2, 121.9, 120.9, 114.4, 68.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.0, 25.9, 22.7, 14.1. Anal. Calcd. for $C_{83}H_{92}N_2O_{11}$: C, 77.06; H, 7.17; N, 2.17%. Found: C, 77.29; H, 7.45; N, 2.11%.

Compound 7c. Yellow solid, yield 95%, IR (KBr, cm^{-1}): ν_{max}: 2920, 1743, 1734, 1664, 1628, 1603. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta_H = 8.52$ (s, 2H), 8.28 (d, 4H, $J = 9.2$ Hz), 8.14 (d, 4H, $J = 8.9$ Hz), 7.99 (d, 4H, $J = 8.8$ Hz), 7.70 (d, 2H, $J = 7.6$ Hz), 7.67 (s, 2H), 7.52 (t, 2H, $J = 7.8$ Hz), 7.46 (d, 2H, $J = 7.8$ Hz), 7.36–7.40 (m, 8H), 6.98 (d, 4H, $J = 8.9$ Hz), 4.04 (t, 4H, $J = 6.5$ Hz), 1.80 (quint, 4H, $J = 6.5$ Hz), 1.27–1.49 (m, 36H), 0.87 (t, 6H, $J = 7.1$ Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta_C = 196.2$, 164.3, 164.1, 163.9, 160.3, 155.6, 153.5, 152.0, 138.6, 133.7, 132.5, 131.9, 130.3, 129.2, 127.7, 126.5, 125.5, 122.3, 122.2, 121.9, 120.9, 114.4, 68.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.1, 26.0, 22.7, 14.1. Anal. Calcd. for $C_{79}H_{84}N_2O_{11}$: C, 76.67; H, 6.84; N, 2.26%. Found: C, 76.94; H, 7.03; N, 2.35%.

Compound 7d. Yellow solid, yield 92%, IR (KBr, cm^{-1}): ν_{max}: 2,920, 2,850, 1,743, 1,734, 1,628, 1,603.^{1}H NMR ($CDCl_3$, 400 MHz): 8.52 (s, 2H), 8.28 (d, 4H, $J = 8.8$ Hz), 8.14 (d, 4H, $J = 8.8$ Hz), 7.99 (d, 4H, $J = 8.4$ Hz), 7.70 (d, 2H, $J = 7.6$ Hz), 7.68 (s, 2H), 7.52 (t, 2H, $J = 7.6$ Hz), 7.46 (d, 2H, $J = 8.0$ Hz), 7.36–7.43 (m, 8H), 6.98 (d, 4H, $J = 8.8$ Hz), 4.04 (t, 4H, $J = 6.4$ Hz), 1.79 (quint, 4H, $J = 6.4$ Hz), 1.28–1.62 (m, 28H), 0.87 (t, 6H, $J = 6.8$ Hz).^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta_C = 196.1$, 164.3, 164.1, 163.9, 160.3, 155.6, 155.5, 152.0, 138.6, 133.7, 132.4, 131.9, 130.3, 129.2, 127.7, 126.6, 125.5, 122.3, 122.2, 121.9, 120.9, 114.4, 68.4, 31.9, 29.6, 29.4, 29.3, 29.1, 26.0, 22.7, 14.1. Anal. Calcd. for $C_{75}H_{76}N_2O_{11}$: C, 76.25; H, 6.48; N, 2.37%. Found: C, 76.49; H, 6.63; N, 2.54%.

Compound 7e. Yellow solid, yield 98%, IR (KBr, cm^{-1}): ν_{max}: 2,923, 1,734, 1,655, 1,627, 1,603. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta_H = 8.52$ (s, 2H), 8.28 (d, 4H, $J = 8.6$ Hz), 8.14 (d,4H, $J = 8.9$ Hz), 7.99 (d, 4H, $J = 8.6$ Hz), 7.70 (d, 2H, $J = 7.6$ Hz), 7.68 (s, 2H), 7.52 (t, 2H, $J = 7.6$ Hz), 7.46 (d, 2H, $J = 8.4$ Hz), 7.36 (t, 8H, $J = 8.4$ Hz), 6.98 (d, 4H, $J = 8.9$ Hz), 4.04 (t, 4H, $J = 6.6$ Hz), 1.80 (quint, 4H, $J = 6.6$ Hz), 1.30–1.48 (m, 20H), 0.88 (t, 6H, $J = 7.0$ Hz).^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta_C = 196.1$, 164.3, 164.0, 163.8, 160.2, 155.5, 153.6, 153.5, 152.0, 138.6, 133.7, 132.4, 131.9, 130.3, 129.2, 127.6, 126.5, 125.5, 122.3, 122.2, 121.9, 120.9, 114.4, 68.4, 31.8, 29.3, 29.2, 29.0, 26.0, 22.6, 14.1. Anal. Calcd. for $C_{71}H_{68}N_2O_{11}$: C, 75.78; H, 6.09; N, 2.49%. Found: C, 75.90; H, 6.26; N, 2.53%.

Compound 7f. Yellow solid, yield 90%, IR (KBr, cm^{-1}): ν_{max}: 2,929, 1,736, 1,659, 1,627, 1,603. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta_H = 8.52$ (s, 2H), 8.28 (d, 4H, $J = 8.6$ Hz), 8.14 (d, 4H, $J = 8.9$ Hz), 7.99 (d, 4H, $J = 8.6$ Hz), 7.70 (d, 2H, $J = 7.6$ Hz), 7.67 (s, 2H), 7.52 (t, 2H, $J = 7.8$ Hz), 7.46 (d, 2H, $J = 7.8$ Hz), 7.36–7.39 (m, 8H), 6.98 (d, 4H, $J = 8.9$ Hz), 4.04 (t, 4H, $J = 6.5$ Hz), 1.81 (quint, 4H, $J = 6.6$ Hz), 1.34–1.50 (m, 12H), 0.91 (t, 6H, $J = 7.0$ Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta_C = 196.2$, 164.3, 164.1, 163.9, 160.3, 155.6, 153.5, 152.1, 138.6, 133.7, 132.4, 131.9, 130.3, 129.2, 127.7, 126.5, 125.5, 122.3, 122.2, 121.9, 120.9, 114.4, 68.4, 31.6, 29.1, 25.7, 22.6, 14.0. Anal. Calcd. for $C_{67}H_{60}N_2O_{11}$: C, 75.26; H, 5.66; N, 2.62%. Found: C, 75.40; H, 5.77; N, 2.81%.

Results and Discussion

The mesomorphism of all the compounds was investigated using polarizing microscopy and differential scanning calorimetry. The DSC scans of each of these compounds were run by raising their temperatures well above the clearing point. The thermal behavior was found to be reproducible and all the compounds were thermally stable. The transition temperatures and associated transition enthalpies obtained from the DSC thermograms are summarized in Table 1. The peak temperatures were given in°C and the numbers in the parentheses indicate the transition enthalpy (ΔH) in kJ mol^{-1}. As can be seen from Table 1, all six compounds synthesized were found to be liquid crystalline. All compounds except **7c** were found to be enantiotropic in nature.

In the DSC scan, compounds **7a, 7d,** and **7e** exhibited some solid–solid phase transitions in addition to crystal–liquid-crystalline phase transitions and liquid-crystalline phase–isotropic phase transitions. These types of transitions were observed only in the DSC scan of those compounds in heating cycles. All the compounds exhibited only one liquid-crystalline phase transition in both heating and cooling cycles. The melting points as well the clearing temperatures decreased as the chain length of R increased (compound **7b** does not follow the sequence). On

Table 1. Phase transition temperatures (°C) and associated enthalpies (ΔH, KJ mol^{-1}) of compounds **7a–f**

Compound 7a:

$$\mathrm{Cr} \xrightarrow[(38.9)]{119.3} \mathrm{Cr}_1 \xrightarrow[(10.0)]{148.7} \mathrm{B1} \xrightarrow[(13.3)]{190.5} \mathrm{I} \xrightarrow[(12.8)]{188.8} \mathrm{B1} \xrightarrow[(47.6)]{123.3} \mathrm{Cr}$$

Compound 7b:

$$\mathrm{Cr} \xrightarrow[(3.7)]{78.4} \mathrm{B1} \xrightarrow[(2.5)]{176.9} \mathrm{I} \xrightarrow[(2.2)]{175.0} \mathrm{B1} \xrightarrow[(6.3)]{69.0} \mathrm{Cr}$$

Compound 7c:

$$\mathrm{Cr} \xrightarrow[(3.6)]{126.6} \mathrm{B1} \xrightarrow[(8.3)]{196.2} \mathrm{I} \xrightarrow[(9.9)]{194.7} \mathrm{B1} \longrightarrow \text{No crystallisation peak found in DSC}$$

Compound 7d:

$$\mathrm{Cr} \xrightarrow[(61.8)]{132.4} \mathrm{Cr}_1 \xrightarrow[(17.1)]{145.3} \mathrm{B1} \xrightarrow[(18.6)]{216.7} \mathrm{I} \xrightarrow[(17.5)]{214.4} \mathrm{B1} \xrightarrow[(22.2)]{96.9} \mathrm{Cr}$$

Compound 7e:

$$\mathrm{Cr} \xrightarrow[(9.1)]{146.9} \mathrm{Cr}_1 \xrightarrow[(13.3)]{153.9} \mathrm{B6} \xrightarrow[(15.3)]{233.3} \mathrm{I} \xrightarrow[(12.5)]{230.2} \mathrm{B6} \xrightarrow[(22.9)]{99.4} \mathrm{Cr}$$

Compound 7f:

$$\mathrm{Cr} \xrightarrow[(41.7)]{163.3} \mathrm{B6} \xrightarrow[(13.9)]{244.4} \mathrm{I} \xrightarrow[(8.6)]{237.7} \mathrm{B6} \xrightarrow[(7.9)]{105.9} \mathrm{Cr}$$

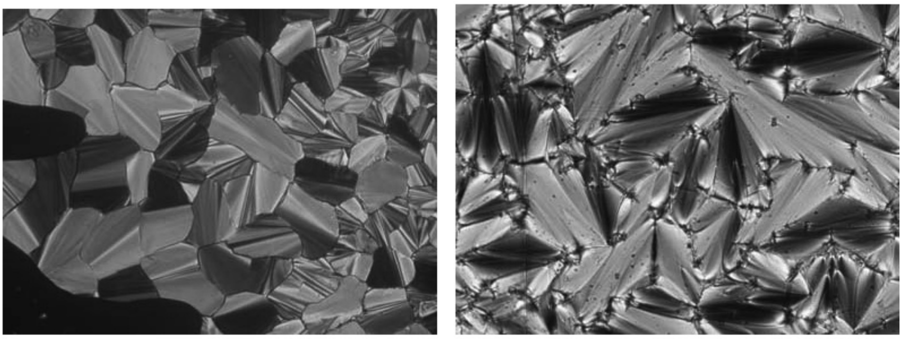
cooling from the isotropic liquid state, small batonnets were formed, which rapidly turned into branched lancets (Fig. 1a) and finally coalesced into a mosaic-like texture (Fig. 1b) with some spherulitic domains for compound **7b**. Compounds **7a, 7c,** and **7d** exhibited a similar type of POM pictogram on cooling from the isotropic liquid.

On cooling from the isotropic liquid state, compound **7e** showed the formation of batonnets that coalesced to a fan texture (Fig. 1c). This mesophase could never be aligned homeotropically; thus, the possibility of an SmA phase as typical for calamitic molecules can be excluded.

In order to determine the structure of the mesophases by XRD, measurements were carried out in the mesophase temperature ranges of compounds **7c** and **7f**. The XRD pattern of the mesophase obtained from compound **7c** at 150°C is shown in Fig. 2. In the small-angle region two sharp reflection peaks were obtained at $d_1 = 35.48\,\text{Å}$ and $d_2 = 30.98\,\text{Å}$, these reflections can be identified as a B1 phase according to the literature report [23].

The XRD pattern of the mesophase obtained from compound **7f** at 160°C is shown in Fig. 3. Compound **7f** in the mesophase exhibited only one sharp reflection peak at $d = 27.25\,\text{Å}$. In addition, both compounds exhibited a diffuse peak in the wide-angle region, indicating a liquid-like corelation within the molecules. For this compound, the layer spacing was close to the half length (calculated from molecular modeling) of the molecules. This d-value suggests an intercalated structure.

(a) branched lancets of **7b** at 174°C.



(b) mosaic-like texture of **7b** at 153°C.

(c) fanlike-texture of **7e** at 193°C.

Figure 1. (a) branched lancets of **7b** at 174°C. (b) mosaic-like texture of 7b at 153°C. (c) Fanlike-texture of **7e** at 193°C.

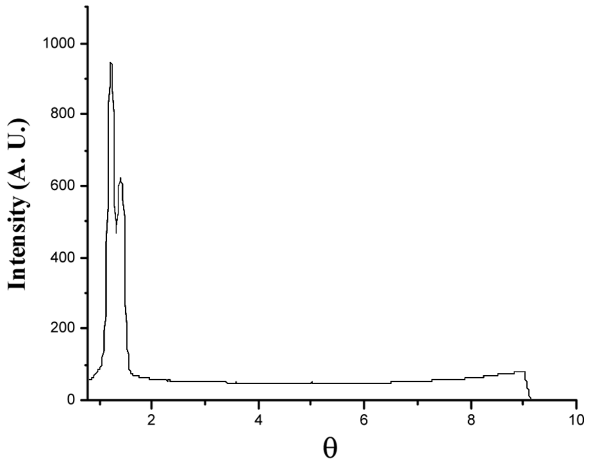


Figure 2. X-ray diffraction diagram of compound *7c* at 150°C.

Microscopic observations as well as the X-ray data are in agreement with the results obtained for intercalated SmC phases of other banana-shaped compounds, designated as B6 [23].

Yelamaggad *et al.* [24] reported "peelable banana"-shaped materials containing seven aromatic rings in which the shape biaxiality of a rod-like mesogen is enhanced by covalently linking the mesogen to a bent-core molecule through a flexible polymethylene spacer. These compounds exhibited biaxial smectic and nematic phases. Shen *et al.* [15] synthesized a series of achiral seven aromatic ring-containing bent-shaped materials devoid of Schiff's base units and observed three types of mesophases: rectangular columnar phase, designated as B1; intercalated fluid smectic phase, S_{intercal}, and a nematic phase. Due to the high molar mass, not only the melting points but also the clearing temperatures were rather high. Recently, Gorecka *et al.* [16] reported a hexagonal columnar phase for nine aromatic ring-containing

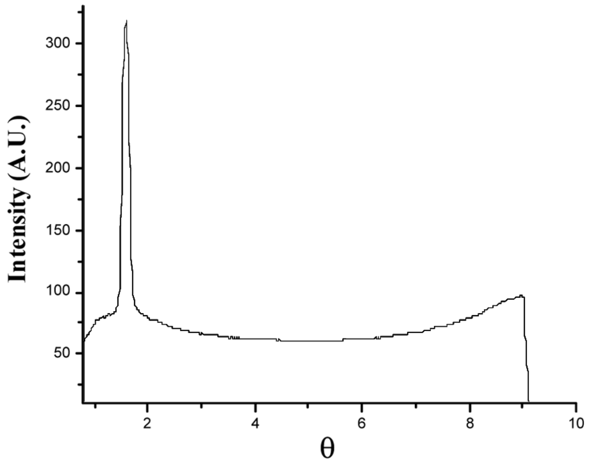


Figure 3. X-ray diffraction diagram of compound *7f* at 160°C.

polycatenar bent-core molecules. Lasac *et al.* [25] reported a six aromatic ring-containing bent-shaped mesogen with a 4,4′ -dihydroxybenzophenone core. They reported that the dicatenar compound displayed only the SmC phase, where as while tetracatenar and polycatenar molecules displayed hexagonal columnar phases. Recently we reported six aromatic ring-containing bent-shaped material with a 3,3′-benzophenone core[17c]. The higher homologues of the series exhibit B2 phase whereas lower homologues of the series did not exhibit any mesomorphism.

To conclude, we have mainly focused on eight aromatic ring-containing bent-shaped materials with a 3,3′-benzophenone core. All the compounds exhibited mesomorphism. Four of the six bent-shaped materials exhibited a B1 phase and rest of the materials exhibited a B6 phase. To the best of our knowledge, this is the first report of eight aromatic ring-containing bent-core materials. In general, an increase in the number of aromatic rings in the bent-core increases melting temperature and leads to nonmesomorphic behavior, so the observation of mesomorphism in all the synthesized bent-core materials is quite interesting. Moreover, the bending angle clearly deviates from the usual bending angle of bent-core materials, but we did not observe any other phase besides the general phases expected from the bent-core materials. We feel that our synthesized compounds are novel due to variations in the aforesaid two parameters.

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