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Three armed star mesogens based on 1,3,5-benzenetricarboxylic acid: Synthesis and mesophase characterization

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ABSTRACT

A series of star mesogens based on 1,3,5-benzenetricarboxylic acid central core, side arms containing two phenyl rings, linked through azomethine groups and hexamethylene spacers, which connect the central core and side arms were synthesized via divergent approach. The mesogens synthesized and their intermediates were structurally well characterized, using FT-IR, ¹HNMR, ¹³CNMR spectroscopy and elemental analysis techniques. The mesophase characterization was carried out using a hot stage-polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) techniques. Enantiotropic mesophases were observed for all the mesogens synthesized. An increase in the terminal chain length stabilized the smectic phase. Nematic phase was observed for the mesogens with short terminal chain length, whereas smectic polymorphism was observed on increasing the terminal chain length. XRD results suggested a tripod-like assembly of molecules in the mesophase.

Key words: Thermotropic liquid crystals, 1,3,5-benzene tricarboxylic acid, Three armed mesogens, Nematic, Smectic

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1. Introduction

The contemporary concept of designing thermotropic liquid crystals emphasizes on; shape anisometry, nanosegregation and non-linear core units [1]. Conventionally, liquid crystals were designed with rod [2-4] or disc [5, 6] shaped cores. The challenge posed by banana or bent-core mesogens has in turn motivated researchers to focus on non-conventional mesogens, deviating from linear core, typical for calamitic mesogens [7]. Thus, topologically, different molecular shapes, such as; bent-core [8], multiarm or stars [9], cones [10], shuttlecocks [11], rings [12], dendrimers [13] etc, have made inroad in liquid crystal research. These non-linear mesogens resulted in new mesophase morphologies which have paved the way for novel applications. In view of the major developments in the area of dendrons and dendrimers (multi-arm), star mesogens are gaining popularity. It is important to note that, the open chain oligomers have been shown to exhibit interesting mesophase sequence and also serve as model compounds for liquid crystalline polymers [14]. Thus, star mesogens based on tri-functional groups, such as 1,3,5-benzenetricarboxylic acid, are classified as cyclic trimers [15]. Recently, Lehmann [16] named these cyclic trimers as 'Hekates'.

From the literature [17, 18], it is found that studies on mesogens, based on 1,3,5benzenetricarboxylic acid are relatively less and they are suitable examples of star mesogens. Aggregation behavior, charge carrier mobility and nanoscale properties of 1,3,5benzenetricarboxylic acid core, based star mesogens with C_3 symmetry, have been reported recently [19-21]. The flexible spacers used to connect the central core and side arms would make the molecule to assemble in different ways in liquid crystalline phases, which causes the appearance of the different mesophase sequences. Yet, the studies on the spacercontaining arms are less reported. In this context, a series of spacer-containing star mesogens, are hereby reported, following their synthesis with a view to investigate the structureproperty relationships.

2. Experimental

2.1 Materials

1,3,5-benzenetricarbonyltrichloride, 4-hydroxybenzaldehyde, 4-butoxybenzaldehyde, 4-hexyloxybenzaldehyde, 4-nitrophenol, 6-chlorohexanol, n-bromooctane, n-bromodecane, n-bromododecane, n-bromotetradecane, n-bromohexadecane and palladium on charcoal (Pd/C, 10%) were purchased from Aldrich and used without further purification. N,N'-Dimethylformamide, tetrahydrofuran, ethanol and methanol (all obtained from SD Fine chemicals) were purified by standard procedures. Dichloromethane, ethyl acetate, diethyl ether, n–hexane, 2-butanone, acetone, potassium hydroxide (pellets), Celite-540, anhydrous potassium carbonate, anhydrous sodium sulphate were obtained from Merck (India) and used as such. Triethylamine (SD Fine chemicals) was distilled before use.

2.2 Measurements

The FT-IR spectra of samples were recorded on a Thermo–Mattson FT–IR spectrometer by the KBr pellet method. ¹H-NMR and ¹³C-NMR spectra of the compounds were recorded using JEOL GSX 500 NMR spectrometer; the samples were dissolved in CDCl₃ and TMS was used as an internal standard. Elemental analyses of the samples were recorded using Elemental Analyzer for CHNS, Model-Euro EA 3000, Euro Vector S.P.A.

Optical polarizing microphotographs were taken using Olympus BX50 polarizing microscope equipped with a Linkam THMS heating stage and a TMS 94 temperature programmer with a C7070 digital camera. The samples were placed between two 12 mm diameter cover slips and were heated with a programmed heating rate.

Differential scanning calorimetry calibrated for enthalpy and temperature was performed using TA Instruments Q-10 series. The experiments were carried out in nitrogen atmosphere at a heating rate of 10°C/min. Each sample (~5 mg) was subjected to two heating and two cooling cylces and data obtained from the 2nd heating and 2nd cooling cycles were

considered for discussion. Samples were crimpled in aluminium pans in order to ensure good thermal contact between the sample and the pan.

Small-angle X-ray scattering spectra were measured with an evacuated high performance SAXS instrument "SAXSess" (Anton Paar KG, Graz, Austria). The "SAXSess" was attached to a conventional X-ray generator (Philips, Holland) equipped with a sealed X-ray tube (a Cu anode target type, producing Cu*Ka* X-ray radiation with a wavelength of 0.154 nm), operating at 40 kV and 50 mA. The samples were measured as past cell method. The scattered X-ray intensities were detected with a 2D-imaging plate detection system Cyclone (Packard, A Packard Bioscience Company) with a spatial resolution of 50×50 µm per pixel and at sample-to-detector distance of 265 mm. A measuring time of 30 sec yielded sufficient measuring statistics. Scattering data that were read off from the imaging plate and were first corrected for the absorption of the X-rays in the sample and later transformed to the *q*-scale $(q = 4\pi/\lambda \cdot \sin \theta/2; \text{ program SAXS Quant; Anton Paar KG, Graz, Austria). The SAXS measurements were further corrected for the empty cell.$

2.3 Synthesis

2.3.1. 6-(4-nitrophenoxy)hexan-1-ol (1).

In a 500 mL two necked flask, 12.5 g (90 mmol) of K₂CO₃ and 11.8 g (85 mmol) of 4-nitrophenol were measured and dissolved in 200 mL of DMF. The solution was stirred and heated to 90°C, followed by the drop-wise addition of 100 mL DMF solution containing 12.3 g (90 mmol) of 6-chlorohexanol. The temperature of the mixture was maintained at 90°C for 4 h. Then, the reaction mixture was allowed to cool to room temperature and subsequently poured into 1L of distilled water in order to obtain a precipitate. The precipitate was filtered, washed with distilled water and dried under vacuum. The product was recrystallised in 1:3 ratio of ethyl acetate-hexane mixed solvent. The solid product was pale yellow in color.

Yield: 74%. Melting point: 66-67°C. IR (KBr, cm⁻¹): 3522 (-OH_{str}), 2950 and 2860 (-CH_{2str}), 1596 and 1504 (C=C_{str} aromatic), 1463 (-CH_{ben}), 1336 (-NO_{2str}), 1260 and 1108 (C–O–C_{str}). ¹H-NMR ppm (CDCl₃): δ 8.13 (d, 2H), 6.89 (d, 2H), 4.00 (t, 2H), 3.63 (t, 2H), 1.90 (bs, -OH), 1.79 (m, 2H), 1.56 (m, 2H), 1.45 (m, 4H). ¹³C-NMR ppm (CDCl₃): δ 164.30, 141.32, 125.95, 114.47, 68.82, 62.74, 32.63, 28.99, 25.81, 25.55. Elemental analysis: calcd. (%) for C₁₂H₁₇NO₄: C 60.23, H 7.16, N 5.85; Found: C 60.01, H 6.97, N 5.63.

2.3.2. Tris[(4-nitrophenoxy)hexyl]benzene-1,3,5-tricarboxylate (2).

55 mmol (1) and 5.5 g (55 mmol) of triethylamine were dissolved in 200 mL of 2butanone. To this solution, a 100 mL of 2-butanone solution containing 4.8 g (18.3 mmol) of 1,3,5-benzenetricarbonyltrichloride was added drop wise at 0°C and the reaction mixture was stirred for 3 h at room temperature. Then the triethylamine salt was filtered off and then the solvent was evaporated. The solid product obtained was recrystallized in 1:3 ratio of acetonemethanol mixed solvent. The solid product obtained was pale yellow in color.

Yield: 55%. m.p.: 71-73°C. IR (KBr, cm⁻¹): 3064 (CH_{str} aromatic), 2954 and 2874 (-CH_{2str}), 1724 (C=O_{str} ester), 1597 and 1504 (C=C_{str} aromatic), 1448 (-CH_{ben}), 1340 (-NO_{2str}), 1260 and 1109 (C–O–C _{str} of ester). ¹H-NMR ppm (CDCl₃): δ 8.81 (s, 3H), 8.16 (d, 6H), 6.90 (d, 6H), 4.39 (t, 6H), 4.05 (t, 6H), 1.84 (m, 6H), 1.63 (m, 6H), 1.55 (m, 12H). ¹³C-NMR ppm (CDCl₃): δ 165.15, 164.20, 141.39, 134.53, 131.48, 126.00, 114.46, 68.68, 65.76, 28.92, 28.63, 25.80, 25.73. Elemental analysis: calcd (%) for C₄₅H₅₁N₃O₁₅: C 61.84, H 5.88, N 4.80; Found: C 61.61, H 5.72, N 4.58.

2.3.3. Synthesis of Tris[(4-aminophenoxy)hexyl]benzene-1,3,5-tricarboxylate (3).

9.92 mmol of the compound (2) was reduced under hydrogen atmosphere in the presence of 10% Pd-charcoal catalyst in a 100 mL of 1:1 mixture of ethanol and tetrahydrofuran at room temperature for 48 h. Pd/C catalyst was removed by filtering the reaction mixture through Celite-540 filtering aid and evaporation of the solvents, yielded the

product. The product was recrystallised in 1:3 mixture of ethyl acetate and hexane. The solid product was reddish brown in color.

Yield: 92%. m.p.: 78-80°C. IR (KBr, cm⁻¹): 3467 and 3387 (-NH_{2str} free amine), 2934 and 2860 (-CH_{2str}), 1724 (C=O_{str} ester), 1634 (-NH_{ben}), 1513 (C=C_{str} aromatic), 1472 (-CH_{ben}), 1239 (C–O–C_{str} of ester). ¹H-NMR ppm (CDCl₃): δ 8.82 (s, 3H), 6.72 (d, 6H), 6.61 (d, 6H), 4.37 (t, 6H), 3.88 (t, 6H), 1.83 (m, 6H), 1.76 (m, 6H), 1.51 (m, 12H). ¹³C-NMR ppm (CDCl₃): δ 165.20, 152.30, 139.82, 134.02, 131.55, 116.51, 115.70, 68.50, 65.80, 29.40, 28.70, 25.88. Elemental analysis: calcd (%) for C₄₅H₅₇N₃O₉: C 68.94, H 7.32, N 5.36; Found: C 68.78, H 7.21, N 5.14.

2.3.4. Synthesis of 4-Alkoxybenzaldehydes 4(c-g).

Synthetic procedures and analytical data of 4-Alkoxybenzaldehydes 4(c-g) are given in supporting information. **4a** and **4b** were purchased from Aldrich, India.

2.3.5. Tris-{[(4-alkoxyphenyl)methylidene]aminophenoxyalkyl}benzene-1,3,5-tricarboxylate 5 (a-g)).

In a typical experiment, 1.0 mmol of amine (3) and 3.0 mmol of 4alkoxybenzaldehydes (4a-4g) were taken in a 100 mL conical flask. 3 mL ethanol was added to the conical flask and the reactants were thoroughly mixed and the flask kept in the microwave oven (power 80W) for 8 minutes. For every 1.5 minutes, the flask was taken out and the contents were mixed thoroughly and the process was repeated. The flask was allowed to cool to room temperature and the solid product obtained was washed with methanol and recrystallised in 2-butanone. All the products obtained were solid and all were pale brown in color.

2.3.5.1. Tris-{[(4-butoxyphenyl)methylidene]aminophenoxyhexyl}benzene-1,3,5-tricarboxy late (5a).

Yield: 60%. m.p.: 134°C. IR (KBr, cm⁻¹): 2936 and 2866 (-CH_{2str}), 1729 (C=O_{str} ester), 1611 and 1509 (C=C _{str} aromatic), 1472 (-CH_{ben}), 1245 (C–O–C _{str} of ester), 1166 (C–O–C _{str}). ¹H-NMR ppm (CDCl₃): δ 8.84 (s, 3H), 8.35 (s, -CH=N), 7.78 (d, 6H), 7.13 (d, 6H), 6.94 (d, 6H), 6.89 (d, 6H), 4.38 (t, 6H), 4.00 (t, 6H), 3.96 (t, 6H), 1.81 (m, 18H), 1.52 (m, 18H), 0.98 (t, 9H). ¹³C-NMR ppm (CDCl₃): δ 165.18, 161.69, 157.98, 157.50, 145.25, 134.54, 131.55, 130.30, 129.35, 122.12, 115.01, 114.72, 68.07, 67.93, 65.79, 31.32, 29.32, 28.71, 25.90, 19.32, 13.96. Elemental analysis: calcd (%) for C₇₈H₉₃N₃O₁₂: C 74.08, H 7.41, N 3.32; Found: C 74.34, H 7.36, N 3.37.

2.3.5.2. Tris-{[(4-hexyloxyphenyl)methylidene]aminophenoxyhexyl}benzene-1,3,5-tricarbo xylate (5b).

Yield: 60%. m.p.: 135° C. IR (KBr, cm⁻¹): 2935 and 2860 (-CH_{2str}), 1728 (C=O_{str} ester), 1611 and 1507 (C=C_{str} aromatic), 1466 (-CH_{ben}), 1242 and 1109 (C–O–C _{str} of ester). ¹H-NMR ppm (CDCl₃): δ 8.84 (s, 3H), 8.37 (s, -CH=N), 7.78 (d, 6H), 7.13 (d, 6H), 6.93 (d, 6H), 6.84 (d, 6H), 4.39 (t, 6H), 3.99 (t, 6H), 3.96 (t, 6H), 1.81 (m, 18H), 1.54 (m, 6H), 1.45 (m, 6H), 1.31 (m, 18H), 0.90 (t, 9H). ¹³C-NMR ppm (CDCl₃): δ 165.19, 161.46, 157.96, 157.50, 145.20, 134.55, 131.53, 130.30, 129.37, 122.13, 114.99, 114.72, 68.25, 68.07, 65.81, 31.67, 29.32, 29.25, 28.71, 25.90, 25.79, 22.70, 14.14. Elemental analysis: calcd (%) for C₈₄H₁₀₅ N₃O₁₂: C 74.79, H 7.84, N 3.11; Found: C 74. 45, H 7.76, N 3.07.

2.3.5.3. *Tris-{[(4-octyloxyphenyl)methylidene]aminophenoxyhexyl}benzene-1,3,5-tricarbo xylate (5c).*

Yield: 60%. m.p.: 133°C. IR (KBr, cm⁻¹): 2923 and 2856 (-CH_{2str}), 1729 (C=O_{str} ester), 1610 and 1509 (C=C_{str} aromatic), 1468 (-CH_{ben}), 1245 and 1109 (C–O–C _{str} of ester). ¹H-NMR ppm (CDCl₃): δ 8.84 (s, 3H), 8.35 (s, -CH=N), 7.78 (d, 6H), 7.13 (d, 6H), 6.94 (d, 6H), 6.89 (d, 6H), 4.38 (t, 6H),4.00 (t, 6H),3.96 (t, 6H), 1.82 (m, 18H), 1.54 (m, 6H), 1.45 (m, 6H), 1.31 (m, 30H), 0.88 (t, 9H). ¹³C-NMR ppm (CDCl₃): δ 165.20, 161.46, 157.98,

157.50, 145.20, 134.59, 131.53, 130.35, 129.37, 122.18, 114.99, 114.69, 68.25, 68.07, 65.81, 32.00, 29.46, 29.34, 29.29, 28.71, 26.12, 25.92, 22.77, 14.23. Elemental analysis: calcd (%) for $C_{90}H_{117}N_3O_{12}$: C 75.43, H 8.23, N 2.93; Found: C 75.12, H 8.13, N 2.90.

2.3.5.4. Tris-{[(4-decyloxyphenyl)methylidene]aminophenoxyhexyl}benzene-1,3,5-tricarboxylate (5d).

Yield: 60%. m.p.: 131°C. IR (KBr, cm⁻¹): 2928 and 2858 (-CH_{2str}), 1730 (C=O_{str} ester), 1612 and 1509 (C=C_{str} aromatic), 1468 (-CH_{ben}), 1244 (C–O–C _{str} of ester), 1163 (C–O–C_{str}). ¹H-NMR ppm (CDCl₃): δ 8.84 (s, 3H), 8.35 (s, -CH=N), 7.78 (d, 6H), 7.13 (d, 6H), 6.94 (d, 6H), 6.89 (d, 6H), 4.38 (t, 6H),4.00 (t, 6H),3.96 (t, 6H), 1.82 (m, 18H), 1.54 (m, 6H), 1.45 (m, 6H), 1.29 (m, 42H), 0.88 (t, 9H). ¹³C-NMR ppm (CDCl₃): δ 165.20, 161.46, 157.98, 157.50, 145.20, 134.59, 131.53, 130.35, 129.37, 122.18, 115.01, 114.73, 68.25, 68.07, 65.81, 32.00, 29.65, 29.54, 29.46, 29.34, 29.29, 28.71, 26.12, 25.92, 22.77, 14.23. Elemental analysis: calcd (%) for C₉₆H₁₂₉N₃O₁₂: C 76.00, H 8.57, N 2.76; Found: C 75.61, H 8.82, N 2.71.

2.3.5.5. Tris-{[(4-dodecyloxyphenyl)methylidene]aminophenoxyhexyl}benzene-1,3,5-tricarbo xylate (5e).

Yield: 60%. m.p.: 127°C. IR (KBr, cm⁻¹): 2921 and 2852 (-CH_{2str}), 1729 (C=O_{str} ester), 1612 and 1508 (C=C_{str} aromatic), 1466 (-CH_{ben}), 1243 (C–O–C _{str} of ester), 1163 (C–O–C_{str}). ¹H-NMR ppm (CDCl₃): δ 8.84 (s, 3H), 8.35 (s, -CH=N), 7.78 (d, 6H), 7.13 (d, 6H), 6.94 (d, 6H), 6.89 (d, 6H), 4.38 (t, 6H),4.00 (t, 6H),3.96 (t, 6H), 1.82 (m, 18H), 1.54 (m, 6H), 1.45 (m, 6H), 1.31 (m, 54H), 0.88 (t, 9H). ¹³C-NMR ppm (CDCl₃): δ 165.20, 161.46, 157.98, 157.50, 145.20, 134.59, 131.53, 130.35, 129.37, 122.18, 115.01, 114.73, 68.25, 68.07, 65.81, 32.00, 29.73, 29.54, 29.46, 29.34, 29.32, 28.71, 26.12, 25.92, 22.77, 14.23. Elemental analysis: calcd (%) for C₁₀₂H₁₄₁N₃O₁₂: C 76.50, H 8.87, N 2.62; Found: C 76.08, H 8.64, N 2.60.

2.3.5.6. Tris-{[(4-tetradecyloxyphenyl)methylidene]aminophenoxyhexyl}benzene-1,3,5-tricar boxylate (5f).

Yield: 60%. m.p.: 126°C. IR (KBr, cm⁻¹): 2920 and 2852 (-CH_{2str}), 1729 (C=O_{str} ester), 1613 and 1510 (C=C_{str} aromatic), 1467 (-CH_{ben}), 1244 (C–O–C _{str} of ester), 1163 (C–O–C_{str}). ¹H-NMR ppm (CDCl₃): δ 8.84 (s, 3H), 8.35 (s, -CH=N), 7.78 (d, 6H), 7.13 (d, 6H), 6.94 (d, 6H), 6.89 (d, 6H), 4.38 (t, 6H),4.00 (t, 6H),3.96 (t, 6H), 1.82 (m, 18H), 1.54 (m, 6H), 1.45 (m, 6H), 1.25 (m, 66H), 0.87 (t, 9H). ¹³C-NMR ppm (CDCl₃): δ 165,20, 161.46, 157.98, 157.50, 145.20, 134.59, 131.53, 130.35, 129.37, 122.18, 114.99, 114.73, 68.25, 68.07, 65.81, 32.00, 29.76, 29.54, 29.51,29.46, 29.42, 29.34, 29.29, 28.71, 26.12, 25.92, 22.77, 14.23. Elemental analysis: calcd (%) for C₁₀₈H₁₅₃N₃O₁₂: C 76.96, H 9.15, N 2.49; Found: C 76.65, H 9.02, N 2.42.

2.3.5.7. Tris-{[(4-hexadecyloxyphenyl)methylidene]aminophenoxyhexyl}benzene-1,3,5-tricar boxylate (5g).

Yield: 60%. m.p.: 128°C. IR (KBr, cm⁻¹): 2921 and 2853 (-CH_{2str}), 1729 (C=O_{str} ester), 1612 and 1509 (C=C_{str} aromatic), 1468 (-CH_{ben}), 1245 (C–O–C _{str} of ester), 1164 (C–O–C _{str}). ¹H-NMR ppm (CDCl₃): δ 8.84 (s, 3H), 8.35 (s, -CH=N), 7.78 (d, 6H), 7.13 (d, 6H), 6.94 (d, 6H), 6.89 (d, 6H), 4.38 (t, 6H),4.00 (t, 6H),3.96 (t, 6H), 1.82 (m, 18H), 1.54 (m, 6H), 1.45 (m, 6H), 1.25 (m, 78H), 0.87 (t, 9H). ¹³C-NMR ppm (CDCl₃): δ 165.20, 161.46, 157.98, 157.50, 145.20, 134.59, 131.53, 130.35, 129.37, 122.18, 114.99, 114.73, 68.25, 68.07, 65.81, 32.00, 29.81, 29.76, 29.61,29.46, 29.29, 28.71, 26.12, 25.92, 22.77, 14.23. Elemental analysis: calcd (%) for C₁₁₄H₁₆₅N₃O₁₂: C 77.37, H 9.39, N 2.37; Found: C 77.06, H 9.32, N 2.39.

3. Results and discussions

3.1 Synthesis of mesogens

Generally, trifunctional core derivatives can be obtained either by convergent or divergent protocols. Each approach has its own advantages and disadvantages. In the present work, the target mesogens were prepared by divergent approach, as shown in Scheme 1. Accordingly, the compound (1) was prepared by reacting 4-nitrophenol with 6-chlorohexenol in the basic condition. Thereafter, the compound (1) was treated with 1,3,5-benzenetricarbonyltrichloride in the presence of triethylamine to get the compound (2). The three nitro groups in compound (2) were reduced selectively to amines, under hydrogen atmosphere by using Pd/C as catalyst. Finally, the reaction between the resulting amine and the 4-alkoxybenzaldehydes (under microwave condition) yielded the target mesogens. It is noteworthy to mention that when compared to thermal condition, microwave-assisted reaction yielded the product with relatively good yield in a short time. In all, seven mesogens were synthesized by varying the length of the terminal alkoxy chains. The intermediates synthesized and target mesogens were well characterized by FT-IR, ¹H NMR and ¹³C NMR spectroscopy and elemental analysis techniques and the data for all the molecules were given in the preceding section.

3.2 HOPM and DSC studies

The mesogens synthesized were subjected to POM and DSC experiments for the identification of mesophases and their sequences. The data obtained from these techniques are in close agreement. The mesophases and thermal stability, as determined by POM and DSC, are listed in Table 1. POM observation confirmed enantiotropic and monotropic mesophases for all the mesogens. The mesogens (**5a**) and (**5b**) exhibited nematic phase enantiotropically on both the heating and cooling of the samples under POM. In the case of (**5a**), the formation of nematic phase was confirmed by observing spherical birefringent droplets that coalesced to homeotropic texture with birefringent spot. The sample on further cooling, exhibited homeotropy characteristic of S_A phase. DSC experiment confirms this

transition by showing characteristic enthalpy of phase change for N-S_A [22]. This further underwent transition to birefringent smectic shlieren texture, characteristic of S_C phase. The sample, on further cooling, changed into more birefringent schlieren texture and is subsequently assigned as S_I phase, due to the low transition enthalpy value found in the DSC experiment. Finally, the sample underwent crystallization.

The next higher homolog C6 (**5b**) also showed birefringent nematic droplets (Figure 1**A**). This texture changed into polygonal texture on cooling, which indicates a phase transition to smectic A phase (Figure 1**B**). On further cooling, the texture changed into shlieren texture of S_C phase (Figure 1**C**). This, on further cooling changed into the S_B phase at a relatively lower temperature and finally changed into liquid crystal glass with frozen fan texture. DSC confirms all these textural changes by showing five peaks of different enthalpy values in the cooling scan (Figure 2). On the other hand, in the heating scan, only one peak was observed even though POM showed nematic phase in the heating cycle. This is because Cr-N and N-I temperatures were very close to each other, which leads to the occurrence of overlap in the DSC thermogram.

On the heating cycle, the POM of next homolog (**5c**) showed enantiotropic S_A phase. This on cooling from isotropic liquid, led to the formation of battonets (Figure 1D) and their coalescence, leading to the focal conic fan texture of S_A phase. On further cooling, it changed to S_B phase where the transient stripes on the fan texture was noticed (Figure 1E). On continuous cooling, no major changes were noticed. In the DSC cooling cycle, three peaks were noticed and the peak at the lowest temperature was assigned to S_B - S_F (Figure 2). The DSC heating cycle showed two peaks that were assigned to Cr- S_A and S_A -I transition (Figure 3). The later peak was a shoulder signal to the former peak. The disappearance of the nematic phase in the mesogen is the notable feature when compared to the earlier homologs.

The C10 homolog (**5d**) also showed polymorphism on cooling the sample from isotropic phase. The appearance of fan texture on cooling the isotropic phase, suggested that the phase under observation was S_A . The fans formed in this texture were different from focal conic fans usually noted in S_A phase. Upon cooling the sample, transition bars typical for S_A - S_B was observed. The S_B phase changed into S_F phase at lower temperature. The DSC cooling curve also confirms these observations. The DSC, on heating, showed only one peak even though POM showed enantiotropic S_A phase. Due to the low mesophase stability, the melting and clearing transitions were superimposed and hence one peak was noticed.

The C12 (**5e**) isomer also showed the fan texture and it was assigned as S_A phase. Like the case of the C10 isomer (**5d**), the DSC heating curve of C12 isomer (**5e**) also showed only one peak (Figure 4). The cooling curve, on the other hand, showed two peaks with different enthalpy values (Figure 2). The high temperature peak was assigned to I-S_A, while the lower peak was attributed to S_F phase. POM investigation of C14 (**5f**) also indicated the formation of S_A and S_B when cooling the sample from isotropic phase. This was supported by DSC curve, wherein two peaks matching the POM temperature were observed (Figure2). The heating curve (DSC) showed one peak, similar to the C10 (5d) and C12 (**5e**) homologs, due to the low mesophase stability (Figure 3).

The C16 (5g) isomer, on heating, showed S_C phase as broken fan texture. This was further confirmed by noticing similar texture (broken fan) on cooling of the isotropic phase. On further cooling, S_C phase changed to S_F phase and then underwent textural change following the continuation of the cooling process. The mesophase texture, however, does not match with known smectic textures [23] and has been assigned as S_X phase. These textural changes were confirmed by observing three transitions with different enthalpy values in the DSC cooling scan (Figure 5). The DSC heating curve showed two peaks associated with Cr- S_C and S_C -I, in contrast to other homologs of the series (Figure 4).

POM and DSC studies of the series of mesogens indicated the presence of rich polymesomorphism in these compounds; most of these phases are monotropic in nature. In the DSC heating curves, majority of the mesogens of this series showed only one peak due to the overlapping of crystals to mesophase and mesophase to isotropic transitions. However, the cooling curves explicitly showed polymorphism and clearly matching with the POM textures. Thus, the tendency towards smectic phases was clearly evident from (**5a**) to (**5g**) homologs.

3.3 Variable Temperature powder X-ray diffraction

Powder X-ray diffraction technique was also used to confirm the mesophase exhibited by representative mesogen (**5g**) and to propose a model to explain the packing the molecules in mesophase. The X-ray diffraction spectrum of mesogen (**5g**) was recorded at 100 °C, 133 °C and 147 °C. The spectrum recorded at 100°C (spectrum not given) showed sharp peaks at low diffraction angle and high diffraction angle regions, which confirms the crystalline nature of the sample at 100°C. At 133°C, the diffractogram (Figure 6) exhibited a very sharp reflection at $2\theta = 0.97^{\circ}$ and a broad hump at $2\theta = 13.5^{\circ}$. The disappearance of large number of peaks and the presence of very sharp intense reflection at $2\theta = 0.97^{\circ}$ in the spectrum obtained at 133°C, indicated the lamellar ordering [24], typical of smectic phase and confirms the smectic C phase as observed by POM. The broad hump at high diffraction angle region indicates the liquid-like nature of terminal chains. On the other hand, on increasing the temperature to 147°C, the disappearance of low angle reflection and the presence of broad hump at high diffraction angle region suggest the isotropic phase of the sample. These results are highly consistent with the results obtained from POM and DSC experiments.

Reports on similar type of mesogens suggest that the possible conformation of the mesogen can be λ , tuning fork or \mathbf{C} shape. Here, the d-spacing, calculated from X-ray diffractogram, gives some directions in the proposing possible structure of the mesogen. The

calculated d-spacing was 88 Å. But, the geometry optimized space-filling model of the same mesogen indicated that the length of one arm of the mesogen is ~ 44 Å. Therefore, it is clearly evident [25] from the d/l ratio, which is equal to 2.0 that the interlayer d-spacing had contributions from two molecules. The λ or tuning fork conformation can support the d-spacing obtained, if the length of the molecule is equal to two arms length. Therefore, we propose the \mathfrak{E} or tripod-like conformation, which explains the requirement of a bilayer ordering (layer spacing (d) was contributed by two molecules) from the x-ray data. Furthermore, the volume occupied by \mathfrak{E} or tripod-like conformation, which is less than that of λ and tuning fork conformations, also favor this conformation.

4. CONCLUSIONS

A series of star mesogens, based on 1,3,5-benzenetricarboxylic acid was synthesized via divergent approach and the mesophase characteristics of these mesogens were studied using POM, DSC and XRD techniques. The stable nematic, smectic A and smectic C phases and the meta-stable higher order smectic phases were observed in the series. The notable feature of the investigation is the observation of rich polymesomorphism in all the mesogens of the series. The disappearance of nematic phase at C8 homolog and the stabilization of the smectic phases were observed when increasing the terminal chain length from C4 to C16. The sharp reflection at the small angle region of the X-ray diffractogram confirms the smectic layer ordering and the d/l ratio, calculated from X-ray data, supports the ε or tripod-like assembly of molecules in the mesophase.

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Fig. 1. POM textures of nematic droplets of (5b) at 137.3 °C (A), polygonal texture of smectic A phase of (5b) at 130.7 °C (B), schlieren texture of smectic C phase of (5b) at 125.4 °C (C), battonets formation of smectic A phase of (5c) at 136.0 °C (D) and smectic B phase of (5c) at 97.2 °C (E).



Fig. 2. DSC cooling curves of star mesogens



Fig. 3. DSC heating curves of star mesogens



Fig. 4. DSC heating curves of mesogens (5e) and (5g)





Fig. 6. VT-XRD spectrum of star mesogen (5g) at 133 °C.

		Transitions	Transition		Phases
	S.No	observed	temperature	ΔH	observed by
		by DSC	(°C)	(kJ/mole)	HOPM
	5a	I-N	139.0	03.4	Nematic
		$[N-S_A]$	116.0	04.1	Smectic A
		$[S_A-S_C]$	114.8	00.2	Smectic C
		$[S_C-S_I]$	80.0	00.8	Smectic I
	5b	I-N	135.9	03.7	Nematic
		[N-S _A]	130.1	05.9	Smectic A
		$[S_A - S_C]$	129.3	00.2	Smectic C
		$[S_C-S_B]$	88.6	01.3	Smectic B
	5c	I-S _A	133.9	20.2	Smectic A
		[SA-SB]	99.8	02.4	Smectic B
		$[S_B-S_F]$	95.3	01.6	Smectic F
	5d	I-S _A	123.5	24.4	Smectic A
		$[S_A-S_B]$	93.0	03.3	Smectic B
		$[S_C-S_F]$	87.0	01.5	Smectic F
	5e	I-S _A	136.1	06.2	Smectic A
		$[S_A-S_F]$	127.0	11.1	Smectic F
4	5f	I-S _A	131.4	32.7	Smectic A
		$[S_A - S_B]$	100.3	04.2	Smectic B
		$[S_B-S_F]$	94.4	01.7	Smectic F
	5g	I-S _C	132.6	10.6	Smectic C
	- 0	$[S_C - S_F]$	99.2	05.7	Smectic F
		$[S_F - S_X]$	73.5	07.1	Smectic X
_	[] indio	cates monotrop	oic phases.		

Table 1. POM and DSC results of star mesogens

Three armed star mesogens based on 1,3,5-benzenetricarboxylic acid: Synthesis and mesophase characterization

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Highlights

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- Star mesogens containing 1,3,5-benzenetricarboxylic acid central unit, two phenyl ring side arm core, ester and azomethine linking groups and terminal alkoxy groups were synthesized.
- The structural changes made in the mesogens such as increasing the terminal chain length causes significant effect in the mesophase sequence.
- > The increase of arm length stabilizes the smectic phases.
- Smectic polymorphism was observed on cooling.