

Research Article

Synthesis and phase transition studies of new dimer compounds connected to a 1,3-dimethylbarbituric acid core

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Abstract: A series of dimeric unsymmetrical liquid crystals derived from heterocyclic 1,3-dimethylbarbituric acid exhibiting smectic A and nematic phase are reported. All compounds were prepared by the condensation of 4'-(R-(4formylphenoxy)butoxy)biphenyl-4-carboxylate with 1,3-dimethylbarbituric acid in ethanol. The mesomorphic properties were investigated by DSC and POM, where the type of phase depends on the length of spacer alkoxy chains and the length of the terminal chain. While the SmA phase was observed upon the heating and cooling run when the spacer alkoxy chains carbon numbers increased (n = 6), the N phase was observed when the length of spacer alkoxy chains increased (n = 8 and 10).

Key words: Mesogen, Schiff's base, pyrimidine, 1,3-dimethylbarbituric acid

1. Introduction

Liquid crystal dimers have often been regarded as a model for the semiflexible main-chain liquid crystalline polymers, which are known to possess great application value.¹ Dimeric liquid crystals are attractive because they exhibit different properties from the corresponding low molecular mass mesogens. For example, the transition properties of dimeric liquid crystals are known to depend on the length and parity of the flexible spacer. Many kinds of dimeric and trimeric mesogenic molecules have been reported.^{2,3} In order to understand further the physical and chemical properties of the polymers, extensive research into liquid crystal oligomers has been carried out only to discover that these materials also exhibit unique liquid crystal properties, which are not observed in conventional liquid crystals.^{1–5} Liquid crystal dimers, with 2 mesogenic groups connected by 1 flexible spacer, are the shortest of all oligomers. Various mesogenic groups, such as heterocyclic benzoxazole, have been introduced into the system of dimers.⁶

In the mesophase, the presence of a heterocyclic ring in either of the 2 mesogenic groups within the dimers can induce a different kind of intermolecular interaction; hence it would be interesting if further research could be carried out on this subject.^{7,8} These significant findings on dimers have prompted researchers to synthesize its longer counterpart with 3 mesogenic groups connected by 2 spacers, which are known as trimers or trimesogens.⁹

In this paper we report our continued research on the synthesis of heterocycles containing liquid crystalline materials.¹⁰⁻¹² To understand the structure of the liquid crystalline property relationship we synthesized and

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characterized a series of unsymmetrical liquid crystals dimers, with these new mesogenic compounds containing 1,3-dimethylbarbituric acid moieties with an ether spacer with even parity ranging from C_6H_{10} to $C_{10}H_{24}$. This is connected to biphenyl with a terminal ester moiety ranking from 6 to 16 carbons.

2. Experimental

2.1. Characterization

FT-IR analyses were performed on a PerkinElmer 2000-FT-IR spectrophotometer in the form of KBr pellets and the spectra were recorded in the range of 4000–400 cm⁻¹. The ¹H and ¹³C NMR spectra were recorded in dimethylsulfoxide (DMSO-d₆) for the title compounds at 298 K on a Bruker 400 MHz Ultrashied FT-NMR spectrometer equipped with a 5-mm BBI inverse gradient probe. Chemicals shift was referenced to internal tetramethylsilane (TMS). The concentration of solute molecules was 50 mg in 1.0 mL of DMSO. Standard Bruker pulse programs¹³ were used throughout the experiment. The elemental (CHN) microanalyses were performed using a PerkinElmer 2400 LS Series CHNS/O analyzer. Melting points were recorded by Gallenkamp digital melting point.

Phase transition temperatures and associated enthalpy values were determined using a differential scanning calorimeter (Elmer Pyris 1 DSC) operated at a scanning rate of ± 5 °C min⁻¹ on heating and cooling, respectively. Texture observation was carried out using a Carl Zeiss Axioskop 40 optical microscope equipped with Linkam LTS350 hot stage and TMS94 temperature controller.

2.2. Materials

The series of hexanol, octanol, decanol, dodecanol, tetradecanol, hexadecanol, α, ω -dibromoalkanes, 4-hydroxybenzaldehyde, 4'-hydroxybiphenyl-4-carboxylic acid, and 1,3-dimethylbarbituric acid were purchased from Aldrich. The chemicals were used directly from the bottles without further purification. Thin-layer chromatography (TLC) was performed on silica-gel plates.

2.3. Synthesis

The liquid crystal dimers were synthesized according to the synthetic routes given in the Scheme. Compound 1 was synthesized via a condensation reaction between 4-hydroxybenzaldehyde with 1,6-dibromohexane, 1,8-dibromohexane, and 1,10-dibromohexane.¹⁴ Compounds 2a–f resulted from the reaction between hydroxybip-henyl-4-carboxyliacid and various alcohols ranging from $C_6 H_{14} O$ to $C_{16} H_{34} O$. Compounds 3a–r were prepared from the Williamson ether synthetic reactions between compounds 1a–c and compounds 2a–f. Compounds 3a–r were subsequently reacted with 1,3-dimethylbarbituric acid to yield the desired compounds 4a–r.

2.3.1. Synthesis of compounds 4a-r

The title compounds were synthesized according to the method described by Majumdar et al.¹⁵ A mixture of compound 1,3-dimethylbarbituric acid (0.156 g, 0.001 mol) and hexyl 4'-(6-(4-formylphenoxy)hexyloxy)biphenyl-4-carboxylate **3a** (0.502 g, 0.001 mol) was refluxed in absolute ethanol for 3 h. The product, **4a**, was obtained as a precipitate from the hot reaction mixture. It was repeatedly washed with hot ethanol and dried in a vacuum.



Scheme. Synthetic route towards the formation of intermediates and title compounds 4a-r.

The analytical, FT-IR, and ¹H and ¹³C NMR data for the title compounds are summarized as follows:

4a Yield 82% mp 110.14 °C. Anal: found for $C_{38}H_{44}N_2O_7$ (%): C, 71.40; H, 6.80; N, 4.28. Calc (%), C, 71.23; H, 6.92; N, 4.37. IR: v_{max} (KBr) (cm⁻¹): 2980, 2864, 1760, 1650, 1588, 1250. ¹H NMR δ (ppm) (DMSO): 8.61 (s, 1H), 6.90–8.52 (6d, C₆H₅–, 12H), 4.12 (t, 2H, J = 6.69 Hz), 4.03 (t, 2H, J = 6.27 Hz), 3.52 (t, 2H, J = 6.09 Hz), 3.28 (s, 3H), 3.14 (s, 3H), 0.82 (t, 3H). ¹³C NMR δ (ppm): 174.21, 165.71, 164.89 (C=O), 161.20 (Ar–C–O), 160.07 (C=C), 115.48–141.00 (Ar–C), 60.52 (C–O–C), 22.49 (CH₂), 15.04 (CH₃).

4b Yield 85% mp 121.01 °C. Anal: found for C₄₀H₄₈N₂O₇ (%): C, 71.60; H, 7.39; N, 4.10. Calc (%), C, 71.83; H, 7.23; N, 4.19. IR: v_{max} (KBr) (cm⁻¹): 2983, 2860, 1767, 1655, 1583, 1252. ¹H NMR δ (ppm) (DMSO): 8.60 (s, 1H), 6.94–8.57 (6d, C₆H₅–, 12H), 4.15 (t, 2H, J = 6.90 Hz), 4.00 (t, 2H, J = 6.67 Hz),

3.50 (t, 2H, J = 6.25 Hz), 3.25 (s, 3H), 3.10 (s, 3H), 0.85 (t, 3H). ¹³ C NMR δ (ppm): 174.00, 164.30, 163.08 (C=O), 161.85 (Ar–C–O), 160.74 (C=C), 114.52–140.75 (Ar–C), 61.18 (C–O–C), 22.64 (CH₂), 14.82 (CH₃).

4c Yield 77% mp 126.60 °C. Anal: found for C₄₂H₅₂N₂O₇ (%): C, 72.50; H, 7.67; N, 4.14. Calc (%), C, 72.39; H, 7.52; N, 4.02. IR: v_{max} (KBr) (cm⁻¹): 2988, 2865, 1760, 1660, 1580, 1256. ¹H NMR δ (ppm) (DMSO): 8.67 (s, 1H), 6.98–8.60 (6d, C₆H₅–, 12H), 4.10 (t, 2H, J = 6.34 Hz), 4.02 (t, 2H, J = 6.20 Hz), 3.41 (t, 2H, J = 6.60 Hz), 3.21 (s, 3H), 3.09 (s, 3H), 0.89 (t, 3H). ¹³C NMR δ (ppm): 175.22, 165.70, 163.87 (C=O), 162.59 (Ar–C–O), 159.69 (C=C), 115.03–140.38 (Ar–C), 60.90 (C–O–C), 21.84 (CH₂), 15.05 (CH₃).

4d Yield 70% mp 134.33 °C. Anal: found for $C_{44}H_{56}N_2O_7$ (%): C, 72.76; H, 7.90; N, 3.69. Calc (%), C, C, 72.90; H, 7.79; N, 3.86. IR: v_{max} (KBr) (cm⁻¹): 2982, 2860, 1768, 1665, 1582, 1255. ¹H NMR δ (ppm) (DMSO): 8.63 (s, 1H), 6.95–8.58 (6d, C_6H_5 –, 12H), 4.17 (t, 2H, J = 6.80 Hz), 4.08 (t, 2H, J = 6.75 Hz), 3.46 (t, 2H, J = 6.08 Hz), 3.28 (s, 3H), 3.10 (s, 3H), 0.83 (t, 3H). ¹³C NMR δ (ppm): 174.67, 164.27, 162.50 (C=O), 161.15 (Ar–C–O), 159.05 (C=C), 115.78–141.16 (Ar–C), 61.25 (C–O–C), 22.15 (CH₂), 14.10 (CH₃).

4e Yield 70% mp 140.19 °C. Anal: found for $C_{46}H_{60}N_2O_7$ (%): C, 73.29; H, 8.16; N, 3.56. Calc (%), C, 73.37; H, 8.03; N, 3.72. IR: v_{max} (KBr) (cm⁻¹): 2975, 2864, 1770 1663, 1587, 1252. ¹H NMR δ (ppm) (DMSO): 8.60 (s, 1H), 6.91–8.60 (6d, C_6H_5 –, 12H), 4.18 (t, 2H, J = 6.49 Hz), 4.04 (t, 2H, J = 6.78 Hz), 3.40 (t, 2H, J = 6.48 Hz), 3.22 (s, 3H), 3.07 (s, 3H), 0.80 (t, 3H). ¹³C NMR δ (ppm): 175.11, 165.30, 163.20 (C=O), 162.08 (Ar–C–O), 160.43 (C=C), 114.33–140.59 (Ar–C), 62.76 (C–O–C), 22.64 (CH₂), 15.30 (CH₃).

4f Yield 85% mp 152.50 °C. Anal: found for C₄₈H₆₄N₂O₇ (%): C, 73.60; H, 8.13; N, 3.40. Calc (%), C, 73.81; H, 8.26; N, 3.59. IR: v_{max} (KBr) (cm⁻¹): 2984, 2869, 1761 1658, 1583, 1255. ¹H NMR δ (ppm) (DMSO): 8.66 (s, 1H), 6.95–8.70 (6d, C₆H₅–, 12H), 4.11 (t, 2H, J = 6.79 Hz), 4.01 (t, 2H, J = 6.05 Hz), 3.46 (t, 2H, J = 6.48 Hz), 3.25 (s, 3H), 3.09 (s, 3H), 0.89 (t, 3H). ¹³C NMR δ (ppm): 174.89, 164.59, 163.63 (C=O), 162.94 (Ar–C–O), 161.16 (C=C), 115.13–140.84 (Ar–C), 61.20 (C–O–C), 21.85 (CH₂), 14.77 (CH₃).

4g Yield 83% mp 119.70 °C. Anal: found for C₄₀H₄₈N₂O₇ (%): C, 71.98; H, 7.10; N, 4.30. Calc C, 71.83; H, 7.23; N, 4.19. IR: v_{max} (KBr) (cm⁻¹): 2988, 2864, 1761, 1660, 1586, 1250. ¹H NMR δ (ppm) (DMSO): 8.70 (s, 1H), 6.90–8.52 (6d, C₆H₅–, 12H), 4.12 (t, 2H, J = 6.08 Hz), 4.04 (t, 2H, J = 6.50 Hz), 3.43 (t, 2H, J = 6.90 Hz), 3.23 (s, 3H), 3.08 (s, 3H), 0.80 (t, 3H). ¹³C NMR δ (ppm): 175.07, 163.28, 162.04 (C=O), 161.20 (Ar–C–O), 160.40 (C=C), 114.19–140.87 (Ar–C), 60.47 (C–O–C), 22.64 (CH₂), 15.75 (CH₃).

4h Yield 83% mp 127.33 °C. Anal: found for $C_{42}H_{52}N_2O_7$ (%): C, 72.50; H, 7.34; N, 4.16. Calc C, 72.39; H, 7.52; N, 4.02. IR: v_{max} (KBr) (cm⁻¹): 2980, 2867, 1770, 1669, 1585, 1254. ¹H NMR δ (ppm) (DMSO): 8.64 (s, 1H), 6.91–8.40 (6d, C_6H_5 –, 12H), 4.10 (t, 2H, J = 6.70 Hz), 4.02 (t, 2H, J = 6.16 Hz), 3.42 (t, 2H, J = 6.68 Hz), 3.26 (s, 3H), 3.11 (s, 3H), 0.85 (t, 3H). ¹³C NMR δ (ppm): 174.50, 162.17, 161.49 (C=O), 160.21 (Ar–C–O), 159.11 (C=C), 114.06–139.14 (Ar–C), 60.07 (C–O–C), 21.00 (CH₂), 14.49 (CH₃).

4i Yield 83% mp 143.89 °C. Anal: found for $C_{44}H_{56}N_2O_7$ (%): C, 72.71; H, 7.94; N, 3.66. Calc C, 72.90; H, 7.79; N, 3.86. IR: v_{max} (KBr) (cm⁻¹): 2989, 2864, 1763, 1650, 1581, 1257. ¹H NMR δ (ppm) (DMSO): 8.68 (s, 1H), 6.93–8.46 (6d, C_6H_5 –, 12H), 4.14 (t, 2H, J = 6.22 Hz), 4.07 (t, 2H, J = 6.74 Hz), 3.40 (t, 2H, J = 6.89 Hz), 3.20 (s, 3H), 3.03 (s, 3H), 0.85 (t, 3H). ¹³C NMR δ (ppm): 174.96, 163.50, 161.78 (C=O), 161.38 (Ar–C–O), 159.88 (C=C), 115.20–140.67 (Ar–C), 61.30 (C–O–C), 22.19 (CH₂), 15.78 (CH₃).

4j Yield 75% mp 140.12 °C. Anal: found for $C_{46}H_{60}N_2O_7$ (%): C, 73.50; H, 8.14; N, 3.63. Calc C, 73.37; H, 8.03; N, 3.72. IR: v_{max} (KBr) (cm⁻¹): 2980, 2870, 1766, 1660, 1580, 1252. ¹H NMR δ (ppm)

(DMSO): 8.70 (s, 1H), 6.95–8.44 (6d, C₆H₅–, 12H), 4.19 (t, 2H, J = 6.67 Hz), 4.01 (t, 2H, J = 6.05 Hz), 3.45 (t, 2H, J = 6.22 Hz), 3.18 (s, 3H), 3.06 (s, 3H), 0.89 (t, 3H). ¹³ C NMR δ (ppm): 175.07, 163.96, 162.03 (C=O), 161.77 (Ar–C–O), 160.14 (C=C), 115.05–140.47 (Ar–C), 60.37 (C–O–C), 22.67 (CH₂), 14.20 (CH₃).

4k Yield 79% mp 148.65 °C. Anal: found for $C_{48}H_{64}N_2O_7$ (%): C, 73.98; H, 8.14; N, 3.43. Calc C, 73.81; H, 8.26; N, 3.59. IR: v_{max} (KBr) (cm⁻¹): 2990, 2878, 1774, 1657, 1589, 1250. ¹H NMR δ (ppm) (DMSO): 8.80 (s, 1H), 6.98–8.53 (6d, C_6H_5 –, 12H), 4.17 (t, 2H, J = 6.89 Hz), 4.08 (t, 2H, J = 6.70 Hz), 3.40 (t, 2H, J = 6.64 Hz), 3.11 (s, 3H), 3.02 (s, 3H), 0.80 (t, 3H). ¹³C NMR δ (ppm): 176.21, 165.36, 163.61 (C=O), 162.17 (Ar–C–O), 160.85 (C=C), 115.47–140.50 (Ar–C), 61.93 (C–O–C), 22.06 (CH₂), 15.10 (CH₃).

41 Yield 84% mp 149.50 °C. Anal: found for $C_{50}H_{68}N_2O_7$ (%): C, 74.40; H, 8.56; N, 3.24. Calc C, 74.22; H, 8.47; N, 3.46. IR: v_{max} (KBr) (cm⁻¹): 2986, 2864, 1762, 1661, 1581, 1254. ¹H NMR δ (ppm) (DMSO): 8.85 (s, 1H), 6.93–8.59 (6d, C_6H_5 –, 12H), 4.14 (t, 2H, J = 6.70 Hz), 4.02 (t, 2H, J = 6.43 Hz), 3.45 (t, 2H, J = 6.39 Hz), 3.15 (s, 3H), 3.08 (s, 3H), 0.89 (t, 3H). ¹³C NMR δ (ppm): 175.14, 164.20, 162.77 (C=O), 161.05 (Ar–C–O), 160.14 (C=C), 114.02–140.38 (Ar–C), 60.16 (C–O–C), 21.69 (CH₂), 14.06 (CH₃).

4m Yield 80% mp 130.01 °C. Anal: found for C₄₂H₅₂N₂O₇ (%): C, 72.50; H, 7.29; N, 4.19. Calc C, 72.39; H, 7.52; N, 4.02. IR: v_{max} (KBr) (cm⁻¹): 2976, 2865, 1773, 1660, 1584, 1250. ¹H NMR δ (ppm) (DMSO): 8.82 (s, 1H), 6.91–8.55 (6d, C₆H₅–, 12H), 4.11 (t, 2H, J = 6.20 Hz), 4.06 (t, 2H, J = 6.80 Hz), 3.46 (t, 2H, J = 6.85 Hz), 3.12 (s, 3H), 3.04 (s, 3H), 0.80 (t, 3H). ¹³C NMR δ (ppm): 174.56, 164.49, 162.10 (C=O), 160.86 (Ar–C–O), 159.23 (C=C), 114.60–140.07 (Ar–C), 61.02 (C–O–C), 22.20 (CH₂), 14.69 (CH₃).

4n Yield 84% mp 142.14 °C. Anal: found for $C_{44}H_{56}N_2O_7$ (%): C, 72.73; H, 7.51; N, 3.98. Calc C, 72.90; H, 7.79; N, 3.86. IR: v_{max} (KBr) (cm⁻¹): 2984, 2872, 1770, 1653, 1578, 1257. ¹H NMR δ (ppm) (DMSO): 8.88 (s, 1H), 6.97–8.60 (6d, C_6H_5 –, 12H), 4.19 (t, 2H, J = 6.84 Hz), 4.08 (t, 2H, J = 6.29 Hz), 3.49 (t, 2H, J = 6.94 Hz), 3.15 (s, 3H), 3.08 (s, 3H), 0.78 (t, 3H). ¹³C NMR δ (ppm): 175.08, 164.27, 162.84 (C=O), 160.15 (Ar–C–O), 160.97 (C=C), 115.20–141.30 (Ar–C), 62.11 (C–O–C), 22.67 (CH₂), 15.38 (CH₃).

4o Yield 79% mp 157.20 °C. Anal: found for $C_{46}H_{60}N_2O_7$ (%): C, 73.52; H, 8.20; N, 3.91. Calc C, 73.37; H, 8.03; N, 3.72. IR: v_{max} (KBr) (cm⁻¹): 2993, 2876, 1764, 1661, 1582, 1252. ¹HNMR δ (ppm) (DMSO): 8.83 (s, 1H), 6.94–8.66 (6d, C_6H_5 –, 12H), 4.12 (t, 2H, J = 6.39 Hz), 4.00 (t, 2H, J = 6.49 Hz), 3.45 (t, 2H, J = 6.31 Hz), 3.18 (s, 3H), 3.04 (s, 3H), 0.82 (t, 3H). ¹³C NMR δ (ppm): 173.48, 165.05, 162.20 (C=O), 161.06 (Ar–C–O), 160.21 (C=C), 114.50–140.67 (Ar–C), 60.80 (C–O–C), 21.05 (CH₂), 14.95 (CH₃).

4p Yield 77% mp 165.00 °C. Anal: found for $C_{48}H_{64}N_2O_7$ (%): C, 73.64; H, 8.40; N, 3.38. Calc C, 73.81; H, 8.26; N, 3.59. IR: v_{max} (KBr) (cm⁻¹): 2980, 2867, 1772, 1653, 1585, 1250. ¹H NMR δ (ppm) (DMSO): 8.85 (s, 1H), 6.90–8.40 (6d, C_6H_5 –, 12H), 4.11 (t, 2H, J = 6.74 Hz), 3.97 (t, 2H, J = 6.85 Hz), 3.40 (t, 2H, J = 6.63 Hz), 3.12 (s, 3H), 3.00 (s, 3H), 0.74 (t, 3H). ¹³C NMR δ (ppm): 173.87, 164.96, 162.82 (C=O), 161.47 (Ar–C–O), 159.89 (C=C), 114.02–140.33 (Ar–C), 60.41 (C–O–C), 22.32 (CH₂), 15.02 (CH₃).

4q Yield 89% mp 172.60 °C. Anal: found for $C_{50}H_{68}N_2O_7$ (%): C, 74.06; H, 8.62; N, 3.25. Calc C, 74.22; H, 8.47; N, 3.46. IR: v_{max} (KBr) (cm⁻¹): 2986, 2871, 1765, 1660, 1580, 1250. ¹H NMR δ (ppm) (DMSO): 8.80 (s, 1H), 6.99–8.57 (6d, C_6H_5 –, 12H), 4.19 (t, 2H, J = 6.07 Hz), 4.03 (t, 2H, J = 6.39 Hz), 3.48 (t, 2H, J = 6.29 Hz), 3.23 (s, 3H), 3.08 (s, 3H), 0.83 (t, 3H). ¹³C NMR δ (ppm): 174.67, 165.06, 163.26 (C=O), 162.00 (Ar–C–O), 160.28 (C=C), 115.17–141.09 (Ar–C), 61.32 (C–O–C), 21.44 (CH₂), 14.92 (CH₃).

4r Yield 78% mp 183.14 °C. Anal: found for C₅₂H₇₂N₂O₇ (%): C, 74.86; H, 8.41; N, 3.50. Calc C, 74.61; H, 8.67; N, 3.35. IR: v_{max} (KBr) (cm⁻¹): 2990, 2884, 1775, 1666, 1579, 1255. ¹H NMR δ (ppm) (DMSO): 8.87 (s, 1H), 6.94–8.60 (6d, C₆H₅–, 12H), 4.14 (t, 2H, J = 6.78 Hz), 4.07 (t, 2H, J = 6.56 Hz), 3.50 (t, 2H, J = 6.48 Hz), 3.26 (s, 3H), 3.10 (s, 3H), 0.89 (t, 3H). ¹³C NMR δ (ppm): 175.09, 166.48, 164.37 (C=O), 162.87 (Ar–C–O), 160.40 (C=C), 115.07–140.97 (Ar–C), 61.86 (C–O–C), 22.83 (CH₂), 15.60 (CH₃).

3. Results and discussion

3.1. Synthesis and characterization

The condensation reaction of alkyl 4'-(R-(4-formylphenoxy)butoxy)biphenyl-4-carboxylate with 1,3-dimethylbarbituric acid in ethanol gave a good yield of the products (**4a**–**r**). The purity of the target compounds was checked by TLC. Structural identification of the title compounds was achieved by employing a combination of elemental analysis and spectroscopic techniques (FT-IR and NMR). The percentages of C, H, and N from the elemental analysis conform to the calculated values for title compounds **4a**–**r**.

The FT-IR data of compounds 4a-r are given in the synthetic procedures. The vibration band with the wave numbers of 2980 cm⁻¹ and 2864 cm⁻¹ can be assigned to an alkyl spacer and the alkyl group attached to one of the dimer terminals. The C=O bond gives rise to a band with a strong intensity at 1760 cm⁻¹. The FT-IR data for compound 4a show a band assignable to ether C–O stretching at 1250 cm⁻¹ in the fingerprint region, which indicated that the alkylation reaction has taken place.

The ¹H NMR for compound **4a** shows a triplet at δ 0.82 ppm, which can be attributed to the methyl protons of the terminal alkyl chain. The 2 singlets at the region of δ 3.28 ppm and δ 3.14 ppm can be attributed to the 2 methyl protons in the 1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione ring. The triplet assignable to the ester O-CH₂ protons can be observed at δ 4.12 ppm, while 2 triplets attributed to the methoxy protons of the spacer are evident at δ 4.03 ppm and δ 3.52 ppm. The 12 aromatic protons of compound **4a** give rise to 6 doublets with their resonances observed at δ 6.90-8.52 ppm. The singlet observed at a low field δ 8.61 ppm was characteristic of the proton of ph-C=CH. In terms of splitting and chemical shift, the spectra of compounds **4b**-**r** are similar to that of compound **4a**.

3.2. Thermal behavior and texture observation

To characterize the liquid crystalline behavior of the new synthesized compounds 4a-4r, the phase transition temperatures together with transition enthalpy values were determined by DSC and all the data are tabulated in the Table.

Figure 1 shows the DSC thermograms of compounds $4\mathbf{k}$ as an example. The textural observations of the mesophase were carried out using a polarizing optical microscope POM, provided with a heating stage and a central processor. All title compounds $4\mathbf{a}$ - $4\mathbf{r}$ are mesomorphic regardless of the spacer alkoxy chain length and terminal chain; however, the type of mesophase is dependent on the length of spacer alkoxy chain. The mesophase was obtained during the heating and cooling process. These compounds exhibited a smectic phase or nematic phase. For compounds $4\mathbf{a}$ - $4\mathbf{f}$ (n = 6, R = 6, 8, 10, 12, 14, 16) the clearing temperatures were increased as the carbon numbers of the terminal alkyl chains and alkoxy chain increased, T = 110.14 °C < 121.01 °C < 126.60 °C < 134.33 °C < 140.19 °C < 152.50 °C (R = 6, 8, 10, 12, 14, 16, n = 6). The phases were identified as smectic A. Upon the heating run the POM showed the formation of bâtonnets that coalesced to form a focal conic fan-shaped texture characteristic of SmA phase. Moreover, upon the heating cycle on the differential scanning calorimetry (DSC) thermogram the peaks were observed at respective temperatures of 88.20 °C (Δ H

Compounds	Transition temperature °C (corresponding enthalpy changes in kJ mol ⁻¹) Heating/Cooling
4a	Cr 88.20 (2.34) SmA 110.14 (42.07) I
	Cr 67.02 (-39.51) SmA 104.78 (-5.89) I
4b	Cr 98.79 (6.22) SmA 121.01 (29.50) I
	Cr 90.11 (-19.70) SmA 113.62 (-2.19) I
4c	Cr 109.51 (3.86) SmA 126.60 (49.31) I
	Cr 104.00 (-27.10) SmA 119.00 (-8.77) I
4d	Cr 120.79 (1.06) SmA 134.33 (35.61) I
	Cr 117.78 (-49.12) N SmA 129.04 (-8.03) I
4e	Cr 123.98 (5.29) SmA 140.19 (51.73) I
	Cr 120.50 (-64.16) SmA 133.80 (-3.22) 1
4f	Cr 136.15 (6.62) SmA 152.50 (41.38) I
	Cr 135.10 (-28.20) SmA 148.11 (-0.94) 1
4g	Cr 94.67 (5.31) N 119.70 (18.44) I
	Cr 89.49 (-37.80) N 114.08 (-2.33) 1
4h	Cr 105.00 (2.77) N 127.33 (26.59) I
	C_{1} 100.40 (-29.90) N 122.00 (-7.08) 1
41	Cr 113 22 (-44 20) N 136 70 (-2 34) I
4:	C_{r} 122 04 (1 20) N 140 12 (26 10) L
4)	Cr 112.04 (1.59) N 140.12 (20.10) I Cr 119.72 (-16.57) N 133.89 (-7.07) I
4k	Cr 126 55 (1 79) N 148 65 (31 80) I
	Cr 124.11 (-15.23) N 140.93 (-4.06) I
41	Cr 133 00 (2.89) N 159 50 (19 59) I
	Cr 128.09 (-20.66) N 154.03 (-2.30) I
4m	Cr 108.78 (4.30) N 130.01 (15.04) I
	Cr 105.00 (-13.41) N 125.60 (-1.34) I
4n	Cr 119.07 (3.61) N 142.14 (17.70) I
	Cr 113.11 (-20.83) N 137.50 (-2.07) I
40	Cr 132.42 (6.72) N 157.20 (19.20) I
	Cr 127.00 (-16.92) N 149.79 (-2.49) I
4p	Cr 138.00 (0.89) N 165.00 (20.60) I
	Cr 132.11 (-15.66) N 159.93 (-2.91) I
4q	Cr 148.88 (5.01) N 172.60 (17.71) I
	Cr 146.04 (-18.30) N 168.05 (-6.70) I
4r	Cr 157.93 (1.03) N 183.14 (19.00) I
<u> </u>	Cr 154.76 (-19.32) N 178.00 (-4.44) I

Table. Phase transition temperatures (°C) and the corresponding enthalpies (J/g) of compounds 4a-r.

= 2.34), 98.79 °C ($\Delta H = 6.22$), 109.51 °C ($\Delta H = 3.86$), 120.79 °C ($\Delta H = 1.06$), 123.98 °C ($\Delta H = 5.29$), and 136.15 °C ($\Delta H = 6.62$), which are characterized to phase transition SmA-I (Figure 2a). The temperatures of the smectic phases shown by compounds **4a**–**4f** were 21.94 °C, 22.22 °C, 17.09 °C, 13.54 °C, 16.21 °C, and 16.35 °C. The enthalpies of the smectic–isotropic transition were in the range of 6.62–1.06 KJ mol⁻¹ and changed irregularly as the terminal chains increased. A typical texture described as focal–conic or Schlieren domains was identified by POM and when cooling from isotropic liquid the coexistence of fan-shaped textures was observed. The observed phase was assigned as a SmA phase. All observed liquid crystalline textures are

typical according to the literature. ^{16,17} The phase transition of I-SmA was detected by DSC through the peaks observed upon the cooling of compounds **4a**–**4f** (n = 6, R = 6, 8, 10, 12, 14, 16) at the respective temperatures of 104.78 °C (Δ H = -5.89), 113.62 °C (Δ H = -2.19), 119.00 °C (Δ H = -8.77), 129.04 °C (Δ H = -8.03), 133.80 °C (Δ H = -3.22), and 148.11 °C (Δ H = -0.94). The temperatures of the smectic phases upon cooling were 37.76 °C, 23.51 °C, 15.00 °C, 11.26 °C, 13.30 °C, and 13.01 °C. Likewise, the enthalpies of the phase transition isotropic–smectic were in the range of -8.77 to -0.94 KJ mol⁻¹ and changed irregularly as the terminal chains increased.





The mesomorphic properties of compound 4g-4l (n = 8, R = 6, 8, 10, 12, 14, 16) are also given in the Table. It can clearly be shown from the DSC differential scanning calorimetry that the clearing temperatures increased as the carbon numbers of the terminal alkyl chains and alkoxy chain increased, T = 119.70 °C < 127.33 °C < 143.89 °C < 140.12 °C < 148.65 °C < 159.50 °C (R = 6, 8, 10, 12, 14, 16, n = 8), with high enthalpy within the range of 13.80–18.44 kJ mol⁻¹. Moreover, the DSC thermogram was identified by broad peaks upon the heating run at temperatures in respective compounds 4g-4l of 94.67 °C ($\Delta H = 5.31$), 105.00 °C ($\Delta H = 2.77$), 120.89 °C ($\Delta H = 4.05$), 122.04 °C ($\Delta H = 1.39$), 126.55 °C ($\Delta H = 1.79$), and 133.00 °C ($\Delta H = 2.89$) respectively, to phase transition of N-I. In the same behavior of compound 4a-4f, the enthalpies changed irregularly as the terminal chains of the N-I transition increased at the range of 5.38–1.39 kJ mol⁻¹. The N-I phase was also characterized by POM, upon heating cycle texture showed only a Schlieren nematic phase and the texture at the clearing temperature was typical of the nematic–isotropic transition. The temperatures of the N-I phase were found to be 25.03 °C, 22.33 °C, 23.00 °C, 18.08 °C, 22.10 °C, and 26.50 °C. On the other hand, the DSC thermogram upon the cooling run of compounds 4g-4l was also characterized by broad peaks, which were assigned to the I-N phase at temperatures of 114.08 °C ($\Delta H = -2.33$), 122.00 °C

 $(\Delta H = -7.68)$, 136.70 °C ($\Delta H = -2.34$), 133.89 °C ($\Delta H = -7.07$), 140.93 °C ($\Delta H = -4.06$), and 154.03 °C ($\Delta H = -2.30$), respectively. The phase temperatures were found to be 24.59 °C, 21.60 °C, 23.48 °C, 14.17 °C, 16.82 °C, and 29.94 °C, while the enthalpies changed irregularly as the terminal chains increased. A small droplet appeared and coalesced to form the classical or marble texture upon cooling under the optical microscopy (POM), which is characteristic of a nematic phase. Figure 2b shows a nematic droplet coalesced at 157 °C upon cooling for compound **4I**.



Figure 2. (a) SmA fan-shaped texture at 90 °C upon cooling run for compound 4a; (b) Nematic droplets coalesced at 157 °C upon cooling for compound 4I.

In compounds 4m-4r (n = 10, R = 6, 8, 10, 12, 14, 16), the N-I phase was identified. Upon heating the POM revealed the texture of the nematic phase by the presence of Schlieren texture characteristics of N phase. In the same way, the DSC thermogram upon heating revealed the N-I phase at temperatures of 108.78 °C (Δ H = 4.30), 119.07 °C (Δ H = 3.61), 132.42 °C (Δ H = 6.72), 138 °C (Δ H = 0.89), 148.88 °C (Δ H = 5.01), and 157.93 °C (Δ H = 1.03). The clearing temperatures, which were also observed, increased as the carbon numbers of the terminal alkyl chains and alkoxy chain increased, whereby T = 130.01 °C, 142.14 °C, 157.20 °C, 165.00 °C, 172.60 °C, and 183.14 °C. This may be due to the excessive Van der Waals attractive forces between the terminal alkyl chains or between the alkoxy chains where the melting temperatures increased from n = 6 to 18.¹⁸ The N-I phase temperatures at the heating run were found to be 21.32 °C, 23.07 °C, 24.78 °C, 27.00 °C, 23.72 °C, and 25.21 °C.

The nematic phase (I-N) was also observed upon cooling for compounds 4m-4r. Upon the cooling run the DSC thermorgam showed a broad band, which was identified to the I-N phase at temperatures of 125.60 °C ($\Delta H = -1.34$), 137.50 °C ($\Delta H = -2.07$), 149.79 °C ($\Delta H = -2.49$), 159.93 °C ($\Delta H = -2.91$), 168.05 °C ($\Delta H = -6.70$), and 178.00 °C ($\Delta H = -4.44$), respectively. Moreover, the phase temperatures were found to be 20.60 °C, 24.39 °C, 22.79 °C, 27.82 °C, 22.01 °C, and 23.24 °C for respective compounds 4m-4r. Under optical microscopy (POM) upon the cooling run a small droplet appeared and coalesced to form the classical or marble texture, which is characteristic of a nematic phase.

From the result above it can clearly be shown that the type of phase depends on the length of spacer alkoxy chains and the length of terminal chains. The SmA phase was observed upon the heating and cooling run when the spacer alkoxy chains' carbon numbers increased (n = 6). The N phase was observed when the length of spacer alkoxy chains increased (n = 8 and 10), for compounds 4g-r. In the literature, adenine and thymine with cholesterol were prepared as thermotropic liquid crystals. In these compounds only the cholesteric phase has been observed.^{18,19} However, there were several unsuccessful studies of the formation of lyotropic liquid crystals by DNA and nucleotides^{20,21} and were done to prepare thermotropic liquid crystals of nucleobase derivatives.^{22–24}

4. Conclusion

In order to understand the effect of 1,3-dimethylbarbituric acid with the space alkoxy chain on the formation of mesophases, new mesogenic compounds were synthesized. All synthesized compounds exhibited liquid crystal properties when the spacer alkoxy chain (n = 6) the SmA phase was observed. However, the N phase appeared when the alkoxyl spacer chain increased to 8 and 10.

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