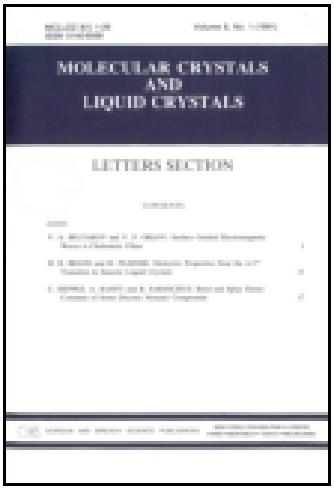

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Synthesis and Mesomorphic Behavior of New Mesogenic Compounds Possessing a Biphenyl Ester Moiety with a 6-Amino-1,3-Dimethyluracil

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*A series of mesogenic compounds consisting of 6-amino-1,3-dimethyluracil and 4′-(alkyloxy)biphenyl-4-carboxylate interlinked by iminophenylcarboxylate was synthesised. The molecular structures of these compounds were substantiated by FT-IR, 1H NMR and ^{13}C NMR along with elemental analysis. The mesomorphic properties were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The result indicated that the compounds exhibited mesophase except in compounds **3a** and **3g**, when n = 6 and 18. Focal-conic or Schlieren domains to the smectic A (SmA) phases were found in compounds when the alkyl chain $C_{n-1}H_{2n-1}$ (n = 8, 10 and 12).*

Keywords 6-amino-1,3-dimethyluracil; Synthesis; Smectic A; nematic; Liquid crystal

1. Introduction

It has been documented that compounds containing two unsaturated rings with terminal substituents or multiple substituents are low-mass molecules capable of exhibiting mesomorphic properties [1]. The understanding of the structural property relationship is elemental to molecular modifications for the synthesis of new mesogens with desirable properties and future applications [2]. Therefore, liquid crystals can be classified as monomers and oligomers, depending on the number of mesogenic cores linked by the flexible spacers. The simplest oligomer is known as the dimer in which two mesogenic units are linked by a single flexible spacer [3–6]. Also, previous findings on the dimers and trimmers have suggested that the oligomeric members can act as model compounds for the semiflexible main chain liquid crystalline polymers [7]. A striking similarity between the oligomeric and polymeric derivatives, which has received great attention from researchers, is the odd–even effect which refers to the spacer parity-dependent mesomorphic properties [8]. Because of higher degree of structure linearity, the members with even spacers possess higher phase transition temperatures in comparison to the odd members, which are less linear [7,8]. On the other hand, the heterocyclic unit is of great importance as a core particularly in thermotropic liquid crystals, which is due to their ability

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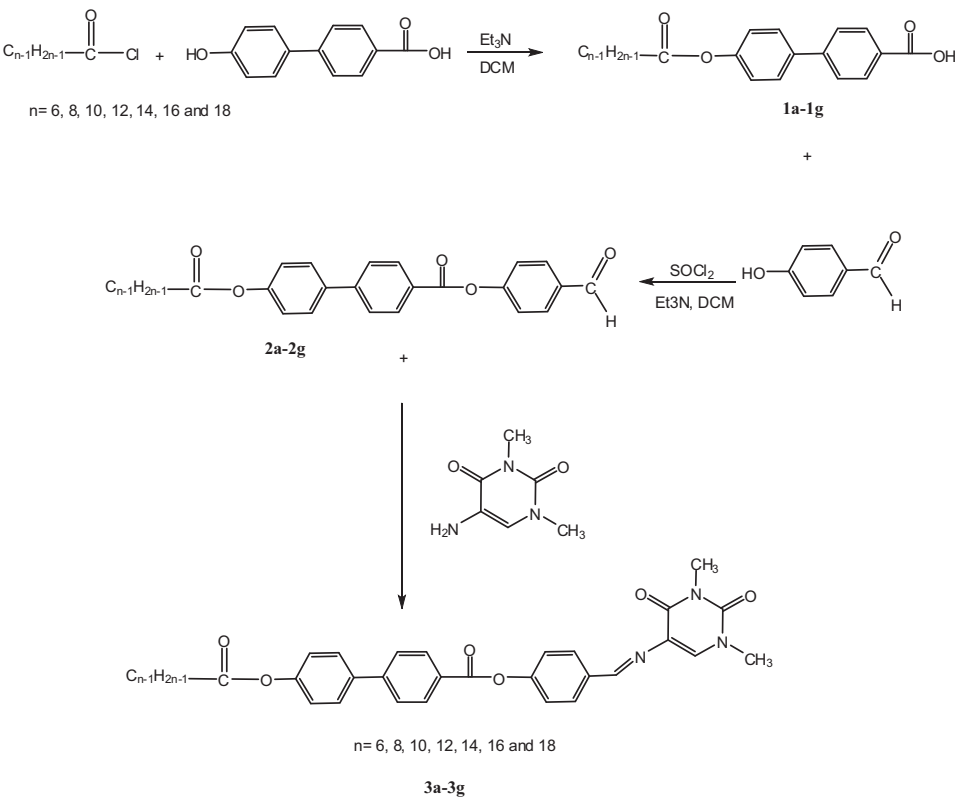
to impart lateral and/or longitudinal dipoles coupled with the changes in molecular shape [9–18]. An extensive study conducted in our laborotory on oligomers compounds and heterocyclic compounds, revealed that compounds exhibit liquid crystal properties [19–22]. In order to accomplish the research on the mesomorphic properties of dimer with heterocyclic 6-amino-1,3-dimethyluracil, we herein reported the facile synthesis and properties of the homologous series of dimer, 4-((1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylimino)methyl)phenyl-4′-(alkyloxy)biphenyl-4-carboxylate and its synthetic route is shown in Scheme 1. The phase transition temperatures and enthalpy values of the title compounds were measured by differential scanning calorimetry (DSC) and the textures of the mesophases were studied using a polarizing optical microscope (POM). The physical properties of the title compounds were studied by Fourier transformed infrared (FT-IR) and high resolution nuclear magnetic resonance NMR (^{1}H and ^{13}C NMR).

2. Experimental

2.1. Materials

All reagents 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.



Scheme 1. The synthetic routes toward synthesis of target compounds **3a–3g.**

2.2. Synthesis

The synthetic route to word the synthesis of intermediates **1a–1g, 2a–2g** and title compound **3a–3g** illustrated in Scheme 1. Compounds **1a–1g** were synthesised via a condensation reaction between 4′-hydroxybiphenyl-4-carboxylic acid with acid chloride such as hexanoyl chloride [16–17].

*2.2.1. Synthesis of the Intermediate Compounds **2a–2g**.* Compounds **2a–2g** resulted by added an excess of thionyl chloride (25 ml) to the 4'-(alkanoyloxy)biphenyl-4-carboxylic acid (5 mmol), the mixture was heated under reflux for 3 h. The hot solution was then evaporated to dryness, and the resulting solid was dissolved in dry dichloromethane (40 ml). To this, 4-hydrozybenxaldehyde (5 mmol) dissolved in 5 ml of DMF was added. The mixture was stirred and heated under reflux for 5 h under nitrogen gas. Finally, the reaction mixture was filtered and dichloromethane removed from the filtrate by evaporation; the DMF solvent in the wet residue was removed by filtration using a Buchner funnel. The remaining starting material was easily removed together with the DMF solvent. The solid **2a–2g** thus obtained was recrystallized several times with methanol whereupon the pure compound was formed.

The analytical, FT-IR, ^{1}H NMR and ^{13}C NMR for compounds **2a–2g** are summarized as follows:

2a: 4-formylphenyl 4'-(hexanoyloxy)biphenyl-4-carboxylate. Yield 71% m.p. 180–181°C. Anal: found for $C_{26}H_{24}O_5$ (%): C, 74.72; H, 5.99. Calc (%), C, 74.98; H, 5.81. IR: (KBr) υ_{max} (cm^{-1}): 2994, 2862, 1760, 1580, 1543. ^{1}HNMR δ (ppm) (DMSO): 10.69 (s, 1H), 6.87-8.63 (6d, C_6H_5-), 2.53 (t, 2H, $J = 6.90$ Hz), 0.88 (t, 3H). ^{13}C NMR δ (ppm): 186.20, 179.05, 173.11 (C=O), 114.00-153.20 (Ar-C), 23.23 (CH_2), 15.20 (CH_3).

2b: 4-formylphenyl 4′-(octanoyloxy)biphenyl-4-carboxylate. Yield 60% m.p. 183–184°C. Anal: found for $C_{28}H_{28}O_5$ (%): C, 75.86; H, 6.24. Calc (%), C, 75.65; H, 6.35. IR: (KBr) υ_{max} (cm^{-1}): 2988, 2873, 1766, 1574, 1550. ^{1}HNMR δ (ppm) (DMSO): 10.50 (s, 1H), 6.90-8.60 (6d, C_6H_5-), 2.40 (t, 2H, $J = 6.79$ Hz), 0.90 (t, 3H). ^{13}C NMR δ (ppm): 188.50, 179.78, 175.20 (C=O), 115.20-152.40 (Ar-C), 22.10 (CH_2), 14.60 (CH_3).

2c: 4-formylphenyl 4′-(decanoyloxy)biphenyl-4-carboxylate. Yield 63% m.p. 184–185°C. Anal: found for $C_{30}H_{32}O_5$ (%): C, 76.08; H, 6.61. Calc (%), C, 76.25; H, 6.83. IR: (KBr) υ_{max} (cm^{-1}): 2993, 2889, 1762, 1571, 1542. ^{1}HNMR δ (ppm) (DMSO): 10.62 (s, 1H), 6.96-8.47 (6d, C_6H_5-), 2.41 (t, 2H, $J = 6.83$ Hz), 0.91 (t, 3H). ^{13}C NMR δ (ppm): 187.93, 179.42, 174.17 (C=O), 115.78-153.04 (Ar-C), 22.50 (CH_2), 15.20 (CH_3).

2d: 4-formylphenyl 4′-(dodecanoyloxy)biphenyl-4-carboxylate. Yield 60% m.p. 181–182°C. Anal: found for $C_{32}H_{36}O_5$ (%): C, 76.90; H, 7.08 Calc (%), C, 76.77; H, 7.25. IR: (KBr) υ_{max} (cm^{-1}): 2990, 2887, 1771, 1569, 1552. ^{1}HNMR δ (ppm) (DMSO): 10.80 (s, 1H), 7.05-8.58 (6d, C_6H_5-), 2.39 (t, 2H, $J = 6.46$ Hz), 0.90 (t, 3H). ^{13}C NMR δ (ppm): 188.20, 178.10, 172.39 (C=O), 115.20-154.11 (Ar-C), 22.89 (CH_2), 14.89 (CH_3).

2e: 4-formylphenyl 4′-(tetradecanoyloxy)biphenyl-4-carboxylate. Yield 63% m.p. 186–187°C. Anal: found for $C_{34}H_{40}O_5$ (%): C, 77.39; H, 7.51. Calc (%), C, 77.24; H, 7.63. IR: (KBr) υ_{max} (cm^{-1}): 2986, 2885, 1768, 1562, 1554. ^{1}HNMR δ (ppm) (DMSO): 10.68 (s, 1H), 7.10-8.56 (6d, C_6H_5-), 2.33 (t, 2H, $J = 6.75$ Hz), 0.91 (t, 3H). ^{13}C NMR δ (ppm): 187.46, 177.89, 172.57 (C=O), 114.33-154.31 (Ar-C), 23.30 (CH_2), 15.22 (CH_3).

2f: 4-formylphenyl 4′-(palmitoyloxy)biphenyl-4-carboxylate. Yield 68% m.p. 189–190°C. Anal: found for $C_{36}H_{44}O_5$ (%): C, 77.82; H, 7.81. Calc (%) C, 77.66; H, 7.97. IR: (KBr) υ_{max} (cm^{-1}): 2983, 2889, 1771, 1560, 1552. ^{1}HNMR δ (ppm) (DMSO): 10.85 (s, 1H), 7.13-8.40 (6d, C_6H_5-), 2.35 (t, 2H, $J = 6.75$ Hz), 0.88 (t, 3H). ^{13}C NMR δ (ppm): 186.40, 176.56, 173.30 (C=O), 115.01-154.40 (Ar-C), 22.89 (CH_2), 14.70 (CH_3).

2g: 4-formylphenyl 4′-(stearoyloxy)biphenyl-4-carboxylate. Yield 65% m.p. 192–193°C. Anal: found for $C_{38}H_{48}O_5$ (%): C, 78.22; H, 8.10. Calc (%) C, 78.05; H, 8.27. IR: (KBr) υ_{max} (cm^{-1}): 2989, 2890, 1774, 1563, 1550. ^{1}HNMR δ (ppm) (DMSO): 10.64 (s, 1H), 7.11-8.43 (6d, C_6H_5-), 2.33 (t, 2H, $J = 6.39$ Hz), 0.90 (t, 3H). ^{13}C NMR δ (ppm): 187.70, 175.60, 173.30 (C=O), 115.72-154.09 (Ar-C), 22.23 (CH_2), 15.10 (CH_3).

*2.2.2. Synthesis of the title compounds **3a–3g**.* The title compounds were synthesised according to the method described by Majumdar *et al* [23]. An equimolar amounts of 6-amino-1,3-dimethyluracil with the 4-formylphenyl 4′-(alkanoyloxy)biphenyl-4-carboxylate, both dissolved in absolute ethanol was refluxed in the presence of a catalytic amount of glacial acetic acid for 3 h to synthesised target compounds **3a–3g**. The Schiff base **3a** as an example was obtained as a precipitate from the hot reaction mixture. It was repeatedly washed with hot ethanol and dried in a vacuum.

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

3a: 4-((1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylimino)methyl)phenyl 4'-(hexanoyloxy)biphenyl-4-carboxylate. Yield 64% m.p. 140.33°C. Anal: found for $C_{32}H_{31}N_3O_6$ (%): C, 69.20; H, 5.80; N, 7.35. Calc (%), C, 69.43; H, 5.64; N, 7.59. IR: (KBr) υ_{max} (cm^{-1}): 2990, 2882, 1742, 1620, 1598, 1557, 1252. ^{1}HNMR δ (ppm) (DMSO): 9.87 (s, 1H), 8.52 (s, 1H), 7.00-8.50 (6d, C_6H_5-), 3.53 (s, 3H), 3.25 (s, 3H), 2.41 (t, 2H, $J =$ 6.70 Hz), 0.90 (t, 3H). ^{13}C NMR δ (ppm): 178.00, 169.33, 168.32, 162.31 (C=O), 160.90 (C=N), 157.16 (Ar-C-O), 115.02-141.47 (Ar-C), 22.62 (CH_2), 14.33 (CH_3).

3b: 4-((1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylimino)methyl)phenyl 4'-(octanoyloxy)biphenyl-4-carboxylate. Yield 68% m.p. 148.11°C. Anal: found for $C_{34}H_{35}N_3O_6$ (%): C, 70.47; H, 6.20; N, 7.03. Calc (%), 70.21; H, 6.07; N, 7.22. IR: (KBr) υ_{max} (cm^{-1}): 2983, 2871, 1750 1617, 1593, 1558, 1250. ^{1}HNMR δ (ppm) (DMSO): 9.82 (s, 1H), 8.60 (s, 1H), 7.03-8.55 (6d, C_6H_5-), 3.56 (s, 3H), 3.26 (s, 3H), 2.40 (t, 2H, $J =$ 6.89 Hz), 0.94 (t, 3H). ^{13}C NMR δ (ppm): 176.48, 167.35, 166.90, 164.85 (C=O), 161.67 (C=N), 155.89 (Ar-C-O), 114.23-142.01 (Ar-C), 21.39 (CH_2), 15.89 (CH_3).

3c: 4-((1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylimino)methyl)phenyl 4'-(decanoyloxy)biphenyl-4-carboxylate. Yield 58% m.p. 153.00°C. Anal: found for $C_{36}H_{39}N_3O_6$ (%): C, 70.71; H, 6.63; N, 6.74; Calc (%), C, 70.92; H, 6.45; N, 6.89. IR: (KBr) υ_{max} (cm^{-1}): 2988, 2880, 1748 1622, 1592, 1560 1251. ^{1}HNMR δ (ppm) (DMSO): 9.84 (s, 1H), 8.55 (s, 1H), 7.02-8.51 (6d, C_6H_5-), 3.50 (s, 3H), 3.24 (s, 3H), 2.43 (t, 2H, $J =$ 6.70 Hz), 0.92 (t, 3H). ^{13}C NMR δ (ppm): 177.56, 169.00, 166.96, 163.29 (C=O), 160.86 (C=N), 158.89 (Ar-C-O), 115.01-140.78 (Ar-C), 22.07 (CH_2), 15.57 (CH_3).

3d: 4-((1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylimino)methyl)phenyl 4'-(dodecanoyloxy)biphenyl-4-carboxylate. Yield 65% m.p. 160.29°C. Anal: found for $C_{38}H_{43}N_3O_6$ (%): C, 71.30; H, 6.93; N, 6.29. Calc (%), C, 71.56; H, 6.80; N, 6.59. IR: (KBr) υ_{max} (cm^{-1}): 2984, 2883, 1747 1621, 1585, 1552, 1250. ^{1}HNMR δ (ppm) (DMSO): 9.85 (s, 1H), 8.52 (s, 1H), 7.00-8.53 (6d, C_6H_5-), 3.52 (s, 3H), 3.20 (s, 3H), 2.41 (t, 2H, $J =$ 6.88 Hz), 0.89 (t, 3H). ^{13}C NMR δ (ppm): 179.20, 169.67, 169.40, 164.78 (C=O), 162.90 (C=N), 156.14 (Ar-C-O), 115.23-141.00 (Ar-C), 22.70 (CH_2), 15.89 (CH_3).

3e: 4-((1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylimino)methyl)phenyl 4'-(tetradecanoyloxy)biphenyl-4-carboxylate. Yield 61% m.p. 178.06°C. Anal: found for $C_{40}H_{47}N_3O_6$ (%): C, 72.01; H, 7.23; N, 6.11. Calc (%), C, 72.16; H, 7.12; N, 6.31. IR: (KBr) υ_{max} (cm^{-1}): 2990, 2885, 1750 1620, 1596, 1558, 1252. ^{1}HNMR δ (ppm) (DMSO): 9.81 (s, 1H), 8.53 (s, 1H), 7.04-8.55 (6d, C_6H_5-), 3.54 (s, 3H), 3.23 (s, 3H), 2.42 (t, 2H,

J = 6.65 Hz), 0.88 (t, 3H). ^{13}C NMR δ (ppm): 178.89, 168.05, 166.56, 165.80 (C=O), 163.05 (C=N), 157.20 (Ar-C-O), 114.44-140.90 (Ar-C), 21.88 (CH_2), 14.67 (CH_3).

3f: 4-((1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylimino)methyl)phenyl 4'-(palmitoyloxy)biphenyl-4-carboxylate. Yield 67% m.p. 190.96°C. Anal: found for $C_{42}H_{51}N_3O_6$ (%):C, 72.51; H, 7.22; N, 6.28. Calc (%), C, 72.70; H, 7.41; N, 6.06. IR: (KBr) υ_{max} (cm^{-1}): 2986, 2886, 1754 1618, 1585, 1563, 1251. ^{1}HNMR δ (ppm) (DMSO): 9.85 (s, 1H), 8.56 (s, 1H), 7.03-8.54 (6d, C_6H_5-), 3.52 (s, 3H), 3.26 (s, 3H), 2.40 (t, 2H, J = 6.74 Hz), 0.90 (t, 3H). ^{13}C NMR δ (ppm): 177.33, 168.70, 165.43, 163.20 (C=O), 161.90 (C=N), 155.94 (Ar-C-O), 115.21-141.18 (Ar-C), 22.32 (CH_2), 14.87 (CH_3).

3g: 4-((1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylimino)methyl)phenyl 4'-(stearoyloxy)biphenyl-4-carboxylate. Yield 53% m.p. 196.79°C. Anal: found for $C_{44}H_{55}N_3O_6$ (%): C, 73.04; H, 7.93; N, 5.58. Calc (%), C, 73.20; H, 7.68; N, 5.82. IR: (KBr) υ_{max} (cm^{-1}): 2990, 2883, 1750 1620, 1589, 1556, 1250. ^{1}HNMR δ (ppm) (DMSO): 9.80 (s, 1H), 8.55 (s, 1H), 7.01-8.52 (6d, C_6H_5-), 3.55 (s, 3H), 3.24 (s, 3H), 2.43 (t, 2H, J = 6.85 Hz), 0.89 (t, 3H). ^{13}C NMR δ (ppm): 175.98, 167.05, 166.10, 164.06 (C=O), 160.77 (C=N), 156.00 (Ar-C-O), 115.80-141.45 (Ar-C), 21.90 (CH_2), 15.03 (CH_3).

2.3. Measurement

The molecular structure of intermediary and title compounds thus obtained were characterized using spectroscopic techniques (Fourier transform-infrared, FT-IR and ^{1}H NMR). The FT-IR spectra of the intermediates and the title compounds were analyzed in the form of KBr pellets and the spectra were recorded in the range of 4000–400 cm^{-1} using a Perkin Elmer 2000-FT-IR spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded in dimethylsulphoxide (DMSO-d_6) 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). Melting points were recorded by Gallenkamp digital melting point. The elemental (CHN) microanalyses were performed using a Perkin Elmer 2400 LS Series CHNS/O analyzer. The concentration of solute molecules was 50 mg in 1.0 ml DMSO. Standard Bruker pulse programs [24] were used throughout the entire experiment. The 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 Carl Zeiss Axioskop 40 optical microscope equipped with Linkam LTS350 hot stage and TMS94 temperature controller.

3. Results and Discussion

3.1. Phase Transition and Mesomorphic Behaviors

Mesophases were identified by microscopic texture observation using POM. The mesophases were identified according to the textures observed under POM and the classification the phase reported by literatures [25–26]. Transition temperatures and enthalpies for the title compounds under study were determined by DSC at a scanning rate of ±5°C min^{-1} (Fig. 1) show the DSC plot of compound **3d**. The phase transitions and the values associated with the enthalpy change data of the title compounds **3a–3g** are summarized in Table 1. All the compounds exhibited liquid crystal properties except in compounds **3a** and **3g**, when n = 6 and 18, and the mesomorphic behaviors were not found. The DSC

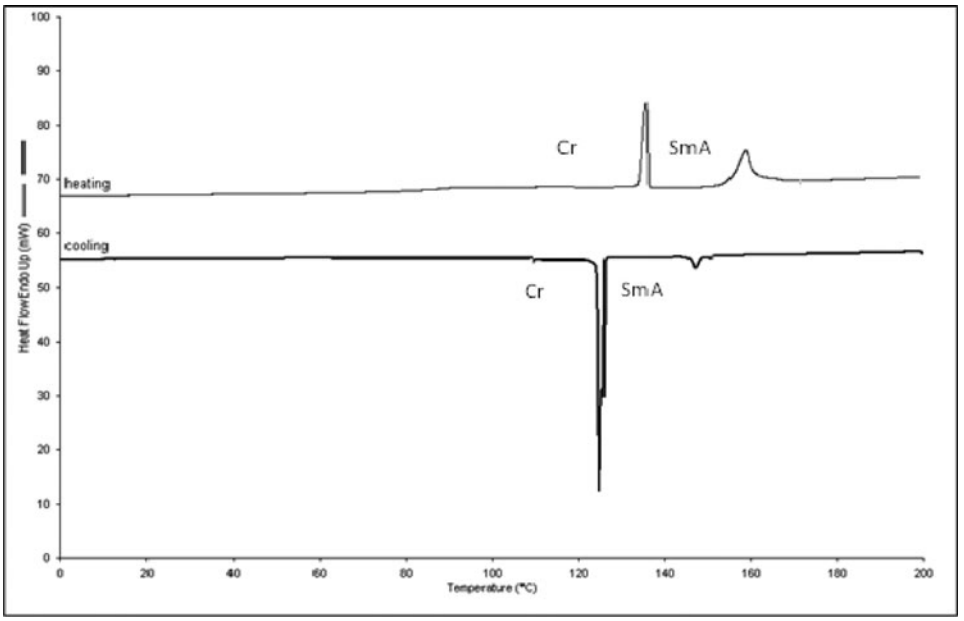


Figure 1. DSC plot on heating and cooling for compound **3d.**

results presented in Table 1 revealed only isotropic melting, during the heating process the transition of Cr-I showed at 140.33°C (80.12) and 196.79°C (23.70). On the other hand, the transition of I-Cr was also observed during the cooling process at the temperatures of 109.28°C (−67.04) and170.00°C (−32.67) on respective compounds **3a** and **3g**.

Table 1. Phase transition temperatures (°C) and the corresponding enthalpies (J/g) of compounds **3a–3g**

Compounds	Transition temperature °C (corresponding enthalpy changes in $KJmol^{-1}$) Heating/Cooling
3a	Cr 140.33 (80.12) I
	Cr 109.28 (−67.04) I
3b	Cr 121.07 (1.56) SmA 148.11 (22.70) I
	Cr 109.70 (−30.12) SmA 132.50 (−1.09) I
3c	Cr 130.66 (2.80) SmA 153.00 (28.40) I
	Cr 118.67 (−19.80) SmA 139.83 (−2.39) I
3d	Cr 137.60 (3.08) SmA 160.29 (40.57) I
	Cr 126.53 (−29.43) SmA 148.09 (−4.67) I
3e	Cr 148.10 (4.67) N 178.06 (62.33) I
	Cr 133.59 (−27.28) N 156.14 (−6.21) I
3f	Cr 166.14 (7.45) N 190.96 (40.12) I
	Cr 149.20 (−34.20) N 176.20 (−7.78) I
3g	Cr 196.79 (23.70) I
	Cr 170.00 (−32.67) I

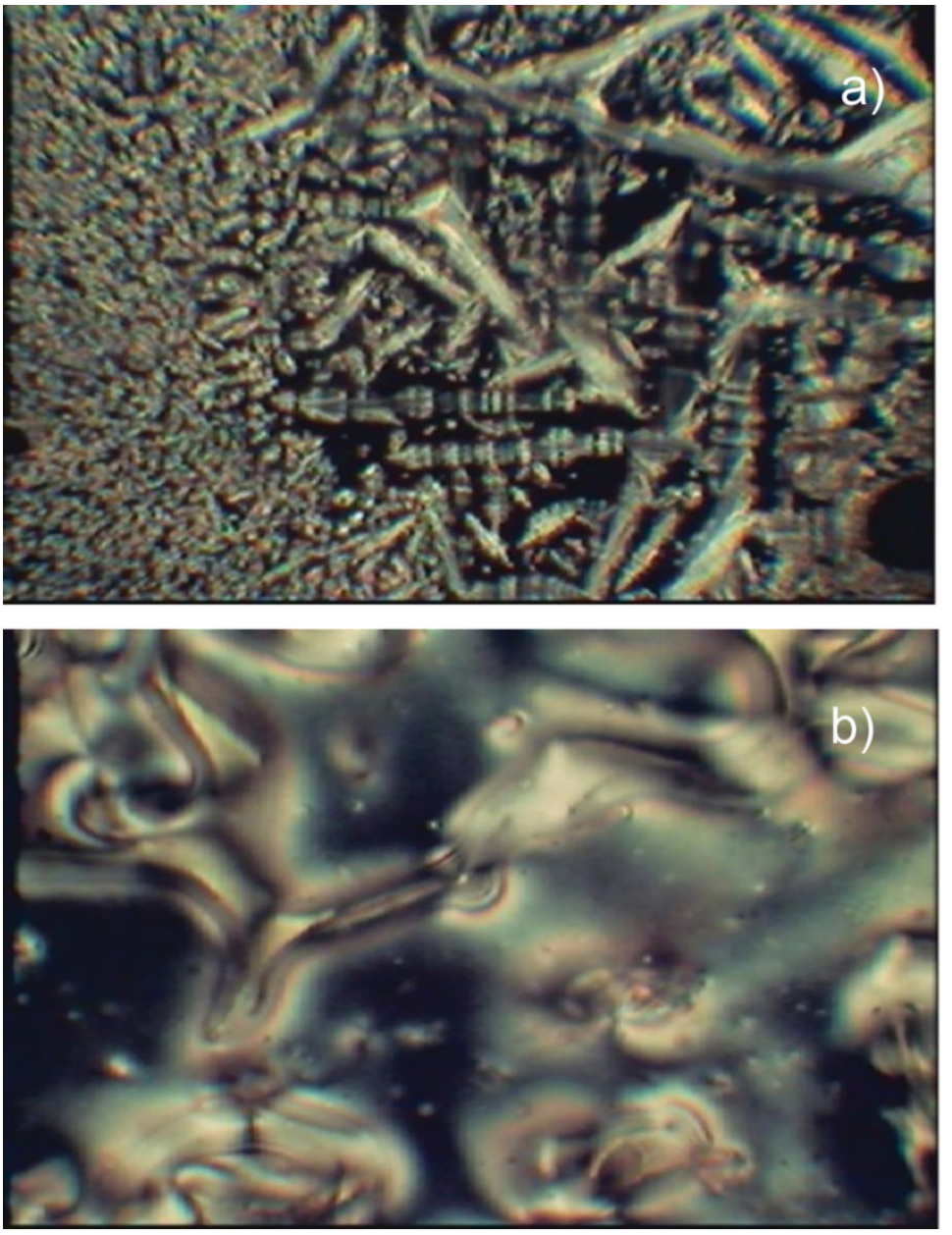


Figure 2. Optical texture of SmA phase at 141.36°C on cooling (a plate) observed in compound **3c**, and N phase at 154°C (b plate) observed in compound **3e**.

The mesogenic compounds **3b**, **3c** and **3d** exhibited liquid crystalline properties on the heating and cooling run. A polarizing optical microscope POM upon heating showed the formation of bâtonnets that coalesce to form a focal conic fan-shape texture characteristic of SmA, Figure 2(a) shown the SmA phase of compound **3c**. However, a typical texture described as focal-conic or Schlieren domains were identified by POM when cooling

from the isotropic liquid and the coexistence of fan-shaped textures were observed. The observed phase was assigned as a SmA phase. These results are also evident from the DSC thermogram, which showed the melting transition at the temperatures of 121.07°C (1.56), 130.66°C (2.80) and 137.60°C (3.08), the mesogenic region about 27.04°C, 22.34°C and 22.69°C on the heating process. During, the cooling process the melting transition was detected at the temperatures of 132.50°C (−1.09), 139.83°C (−2.39), 148.09°C (−4.67), and the mesogenic region about 22.80°C, 21.16°C and 21.56 on respective compounds **3b**–**3d**.

The N-I phase was identified, upon heating for compounds **3e** and **3f**. The POM revealed the texture of the nematic phase by the presence of the Schlieren textures characteristic of the N phase Fig. 2(b) shown the N phase of compound **3e**. In the same way the mesosphere was identified by the nematic droplet texture, brownian flashes were characteristic of the nematic phase before recrystallization. DSC curved of compounds **3d** and **3f** obtained on the first heating and cooling processes showed two endothermic or exothermic peaks, which represented a phase sequence of Cr-N-I and I-N-Cr, respectively. On heating a melting transition was observed at the respective temperatures of 148.10°C (4.67) and 166.14°C (7.45), while the clearing point appeared at 178.06°C and 190.96°C. The mesogenic region was about 29.91°C and 24.82°C. In addition, upon cooling the melting transition was observed at the 156.14°C (−6.21) and 176.20°C (−7.78), the mesogenic region was about 22.55°C and 27.00°C in respective compounds **3e** and **3f**. The clearing temperatures of the title compounds **3a–3g** increased slightly with the terminal alkyl chain. Moreover, the enthalpies in SmA-I and N-I transitions changed regularly with the terminal chain.

3.2. Physical Characterization

The FT-IR spectra of the target compounds **3a–3g** show a strong band at the range of 1742–1754 cm^{-1}, which can be assigned to the stretching vibration of carbonyl group C=O in the ester and uracil rings. Major bands observed at 2983–2990 cm^{-1} and 2880–2886 cm^{-1} indicate the presence of carbon chains in the respective compounds in which the hydrogen atoms are attached to sp3 carbons [27]. The appearance of a strong absorption bands within 1617–1622 cm^{-1} is attributable to the stretching of C=N. The presence of the diagnostic bands at the range of 1598–1585 cm^{-1} and 1552–1563 cm^{-1} is attributable to the C = C stretching of the aromatic ring [22]. The absorption bands observed in the frequency range of 1250 1252 cm^{-1} can be assigned to the stretching of the C−O of the ether linkage [28].

A complete assignment for the title compounds can be described based on respective compounds shown in Scheme 1. The ^{1}H NMR spectra of the title compounds **3a–3g** showed a singlet that integrates as one hydrogen at the chemical shift $\delta = 9.80$–9.87 ppm that corresponds to the proton attached to the carbon C in C=N bond. This can be further substantiated by the direct bond heteronuclear correlation with C within the frequency range of $\delta = 160.77$–163.05 ppm. Another singlet at the chemical shift $\delta = 8.52$ 8.60 ppm assigned to the proton in the dimethyl uracil ring. Moreover, the resonances for the C_6H_4 appear as six doublets in the downfield region of $\delta = 7.00$–7.04 ppm and $\delta = 8.50$ 8.55 ppm corresponding to the respective phenyl protons in compounds **3a–3g**. The extensive coupling in this aromatic core produces complex spectra with overlapping peaks from the various protons making specific assignment of each peak difficult. What is important to note is that the total intensity represented by the peaks in this region match the total number of aromatic protons, as expected. The ^{1}H NMR spectra of the title compounds **3a–3g** showed a two singlet which integrates as one hydrogen for each at the chemical shifts

δ = 3.50–3.56 ppm and δ = 3.20–3.26 ppm which corresponds to the methyl protons attached to the N in dimethyl uracil ring. Moreover, the ^{1}H NMR spectra also show the resonance owing to the aliphatic protons. These signals are assigned with the aid of the COSY experiment. There are two triplet signals due to the presence of methylene protons $CH_2 = COO$ and CH_3 of the ester linking group, at the respective chemical shift ranges of δ = 2.40–2.43 ppm and 0.88–0.94 ppm.

The structures of the title compounds are further substantiated by the ^{13}C NMR spectroscopic data. The ^{13}C NMR spectra of compounds **3a–3g** indicate that the diagnostic peaks observed within the range of δ = 175.98–179.20 ppm δ = 167.05–169.67 ppm δ = 165.43-169.40 ppm and δ = 162.31 165.80 ppm can be attributed to the presence of carbonyl groups (C=O). The signal of C in C=N can be assigned within the range of δ = 160.77 163.05 ppm. Moreover, the aromatic carbons give rise to different peaks within the frequency range of δ = 114.23–115.80 ppm and δ = 140.78–142.01. At a high field, a signal at δ = 14.33–15.89 ppm can be assigned to methyl carbons in ester chain.

4. Conclusions

In this paper, we have synthesised some dimethyluracil-based oligomers with a Schiff base linkage. All the compounds except **3a** and **3g** showed liquid crystalline properties. Compound **3b**–**3d** demonstrates the smectic A phase, while compounds **3e** and **3f** showed nematic phases. For compounds **3a**–**3g**, the temperatures of the clearing points increased as the length of the terminal alkyl chain increased.

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