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Synthesis and Anisotropic Properties of Novel Asymmetric Diones Fused With 1,3-Oxazepine and Oxazepane Rings

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Novel synthesis of heterocyclic liquid crystal compounds containing seven-membered 1,3-oxazepine-4,7-diones, 5,6-dihydro-1,3-oxazepane-4,7-diones, and 5,6-benzo[e] [1,3]oxazepine-4,7-diones rings at para position has been carried out from the reaction of maleic, succinic, and phthalic anhydrides with N-(4-(tetradecyloxy)benzylidene) alkylamine. The various lengths of the even-parity alkyl chains C_nH_{2n+1} , in which n ranges from 6 to 18, were employed in the present study. The molecular structures of these compounds were substantiated by Fourier transformed infrared and nuclear magnetic resonance along with elemental analysis. The correlation between the structures and the mesomorphic behaviors of N-(4-(tetradecyloxy)benzylidene)alkylamines and their derivatives was investigated. Present work shows that the formation of mesophases is strongly dependent on the type of core moiety. Although the imines possessing the alkyl chain C_nH_{2n+1} (n = 6-14) exhibit smectic A (SmA) phases, the nemactogenic properties can only be observed in the series of 3,4-dihydrobenzo[e][1,3]oxazepine-1,5-diones.

Keywords 5,6-Benzo[e][1,3]oxazepine-4,7-diones; 5,6-dihydro-1,3-oxazepane-4,7-diones; liquid crystal; N-(4-(tetradecyloxy)benzylidene)alkylamine; nematic; 1,3-oxazepine-4,7-diones; smectic A; synthesis

1. Introduction

It has well been claimed that the liquid crystalline behavior of an organic compound is dependent on its molecular architecture in which a slight change in its molecular geometry gives rise to a considerable change in its mesomorphic properties [1–5]. In general, the mesomorphic behavior of an organic compound can be varied by changing the linking, terminal, and central core systems [6]. In recent years, interest in mesogenic structures containing heterocyclic rings has increased remarkably owing to their abilities to exhibit mesogenic behavior either similar to or superior to the linear phenyl analogs [7–15].

The heterocyclic compounds are of great importance as core units in thermotropic liquid crystals due to their abilities to impart lateral and/or longitudinal dipoles. Moreover, the presence of heteroatoms (O, S, and N) could lead to significant changes in

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the corresponding liquid crystalline phases and/or in the physical properties of the observed phases. Since most of the heteroatoms thus introduced are claimed to be more polarizable than carbon, therefore, a large dipole may eventually be introduced into a liquid crystal structure in comparison with the analogous phenyl-based mesogens [16–18]. The direction of the dipole moments of the core parts of the liquid crystal molecules is known to be important especially in determining the molecular alignment in mesophase [19]. This information propels us to consider the 1,3-oxazepine-diones, which possess seven-membered heterocyclic ring system. Since the modification of oxazepine core as liquid crystalline compounds was not well documented, therefore, we report the novel compounds of 3-alkyl-2-(4-(tetradecyloxy)phenyl)-1,3-oxazepine-4,7-dione, 3-alkyl-2-(4-(tetradecyloxy)phenyl)-5,6-dihydro-1,3-oxazepane-4,7-diones, and 3-alkyl-2-(4-(tetradecyloxy)phenyl)-5,6-benzo[e][1,3]oxazepine-4,7-diones. The physical properties of the title compounds were studied by Fourier transformed infrared (FT-IR) and highresolution nuclear magnetic resonance (NMR) (1 H and 13 C NMR). 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 by using a polarizing optical microscope (POM).

2. Experimental

2.1. Synthesis

The synthetic routes toward formation of all the title compounds are depicted in Scheme 1. The synthesis of each compound in all the series was identical.

2.1.1. Synthesis of 4-(Tetradecyloxy)benzaldehyde. A mixture containing 0.1 mol of 4-hydroxybenzeldehyde, 0.25 mol anhydrous sodium carbonate, and 0.1 mol 1-bromotetradecane in 50 mL of DMF was allowed to heat for 4 h at 150° C under continuous stirring as documented by Catanescu et al. [20]. The resulting mixture was then poured into an ice water bath (approximately 5°C) whereupon a precipitate formed. The precipitate was filtered and washed once with KOH and water, dried, and finally recrystallized from ethanol.

2.1.2. General Procedure for the Synthesis of N-(4-(Tetradecyloxy)-Benzylidene) alkylamine (1–7). The imines were synthesized by the same method. The synthetic method will be described on the basis of compound 1.

A mixture containing equimolar amounts of hexylamine and 4-(tetradecyloxy) benzaldehyde in absolute ethanol was refluxed for 14 h. The reaction mixture was allowed to cool to 0°C overnight. It was filtered and washed with 2% HCl and cold water before being dried at room temperature. The solid thus obtained was recrystallized twice from absolute ethanol. The analytical data, FT-IR, and ¹H and ¹³C NMR for compounds **1–7** are summarized as follows.

1: Yield 81% m.p. 60°C–61°C. Anal.: found for C₂₇H₄₇NO (%): C 80.69, H 11.67, N 3.58. Calc. (%) C 80.74, H 11.79, N 3.49. IR: υ_{max} (KBr) (cm⁻¹) 3060, 2991, 2960, 1638, 1600, 1593, 1250; ¹H NMR δ (CDCl₃): 8.02 (s, H7), 7.54 (d, J = 8.8 Hz, H2 and H6), 6.93 (d, J = 8.6 Hz, H3 and H5), 4.04 (t, C₄-OCH₂), 3.58 (t, N-CH₂), 1.85–1.23 (m, OCH₂–((CH₂)₂–CH₂)₁₃) and NCH₂–(CH₂–CH_n), 0.91 (t, CH₃); ¹³C NMR δ (CDCl₃): 162.07 (C=N), 158.11 (Ar–C–O), 132.05–116.11 (Ar-C), 71.03 (O–CH₂),



 $R = C_6H_{13}, C_8H_{17}, C_{10}H_{21}, C_{12}H_{25}, C_{14}H_{29}, C_{16}H_{33}, C_{18}H_{37}$



R= C6H13, C8H17, C10H21, C12H25, C14H29, C16H33, C18H37

Scheme 1. The reaction scheme for intermediates and title compounds with numbering atom.

60.83 (N–CH₂), 32.88–21.56 (OCH₂–((CH₂)₂–CH₂)₁₃) and NCH₂–(CH₂–CH_n), 14.93 (CH₃).

2: Yield 79% m.p. 64°C–65°C. Anal.: found for $C_{29}H_{51}NO$ (%): C 81.08, H 11.84, N, 3.15. Calc. (%) C 81.05, H 11.96, N 3.26. IR: υ_{max} (KBr) (cm⁻¹): 3044, 2990, 2958, 1640, 1598, 1581, 1258; ¹H NMR δ (CDCl₃): 8.02 (s, H7), 7.53 (d, J = 8.8 Hz, H2 and H6), 6.94 (d, J = 8.6 Hz, H3 and H5), 4.03 (t, C₄–OCH₂), 3.60 (t, N–CH₂), 1.86–1.22 (m, OCH₂–((CH₂)₂–CH₂)₁₃) and NCH₂–(CH₂–CH_n), 0.90 (t, CH₃); ¹³C NMR

 δ (CDCl₃): 162.02 (C=N), 158.15 (Ar–C–O), 132.04–116.13 (Ar–C), 71.07 (O–CH₂), 60.75 (N–CH₂), 32.85–21.57 (OCH₂–((CH₂)₂–CH₂)₁₃) and NCH₂–(CH₂–CH_n), 14.92 (CH₃).

3: Yield 77% m.p. 68°C–69°C. Anal.: found for $C_{31}H_{55}NO$ (%): C 81.29, H 12.07, N 3.04. Calc. (%) C 81.34, H 12.11, N 3.06. IR: υ_{max} (KBr) (cm⁻¹): 3010, 2986, 2938, 1629, 1581, 1510, 1249; ¹H NMR δ (CDCl₃): 8.04 (s, H7), 7.55 (d, J = 8.9 Hz, H2 and H6), 6.94 (d, J = 8.7 Hz, H3 and H5), 4.05 (t, C₄–OCH₂), 3.57 (t, N–CH₂), 1.86–1.21 (m, OCH₂–((CH₂)₂-CH₂)₁₃) and NCH₂–(CH₂–CH_n), 0.88 (t, CH₃); ¹³C NMR δ (CDCl₃): 161.95 (C=N), 158.20 (Ar–C–O), 132.09–116.15 (Ar–C), 71.09 (O–CH₂), 61.01 (N–CH₂), 32.86–21.60 (OCH₂–((CH₂)₂–CH₂)₁₃) and NCH₂–(CH₂–(CH₂–CH_n), 14.93 (CH₃).

4: Yield 69% m.p. 74°C–75°C. Anal.: found for C₃₃H₅₉NO (%): C 81.69, H 12.17, N 2.81. Calc. (%) C 81.58, H 12.24, N 2.88. IR: υ_{max} (KBr) (cm⁻¹): 3030, 2992, 2951, 1640, 1594, 1522, 1250; ¹H NMR δ (ppm) (CDCl₃): 8.03 (s, H7), 7.54 (d, J = 8.8 Hz, H2 and H6), 6.93 (d, J = 8.6 Hz, H3 and H5), 4.04 (t, C₄–OCH₂), 3.58 (t, N–CH₂), 1.87–1.23 (m, OCH₂–((CH₂)₂–CH₂)₁₃) and NCH₂–(CH₂–CH_n), 0.89 (t, CH₃); ¹³C NMR (ppm) δ (CDCl₃): 161.87 (C=N), 158.28 (Ar–C–O), 132.11–116.20 (Ar–C), 71.12 (O–CH₂), 60.92 (N–CH₂), 32.85–21.58 (OCH₂–((CH₂)₂–CH₂)₁₃) and NCH₂–(CH₂–CH_n), 14.93 (CH₃).

5: Yield 61% m.p. 78°C–79°C. Anal.: found for $C_{35}H_{63}NO$ (%): C 81.91, H 12.46, N 2.61. Calc (%) C 81.80, H 12.36, N 2.73. IR: v_{max} (KBr) (cm⁻¹): 3061, 2988, 2960, 1635, 1600, 1582, 1255; ¹HNMR δ (ppm) (CDCl₃): 8.06 (s, H7), 7.54 (d, J = 8.8 Hz, H2 and H6), 6.95 (d, J = 8.6 Hz, H3 and H5), 4.05 (t, C₄–OCH₂), 3.61 (t, N–CH₂), 1.88–1.25 (m, OCH₂–((CH₂)₂–CH₂)₁₃) and NCH₂–(CH₂–CH_n), 0.91 (t, CH₃); ¹³C NMR δ (ppm) (CDCl₃): 161.95 (C=N), 158.29 (Ar–C–O), 132.05–116.14 (Ar–C), 71.04 (O–CH₂), 61.21 (N–CH₂), 32.86–21.60 (OCH₂–((CH₂)₂–CH₂)₁₃) and NCH₂–(CH₂)₁₃) and NCH₂–(CH₂–CH_n), 14.95 (CH₃).

6: Yield 58% m.p. 77°C–78°C. Anal.: found for $C_{37}H_{67}NO$ (%): C 82.03, H 12.48, N 2.60. Calc (%) C 82.00, H 12.46, N 2.58. IR: v_{max} (KBr) (cm⁻¹): 3056, 2985, 2953, 1631, 1588, 1542, 1248; ¹H NMR δ (ppm) (CDCl₃): 8.05 (s, H7), 7.52 (d, J = 8.8 Hz, H2 and H6), 6.94 (d, J = 8.6 Hz, H3 and H5), 4.04 (t, C₄–OCH₂), 3.60 (t, N–CH₂), 1.89–1.25 (m, OCH₂–((CH₂)₂–CH₂)₁₃) and NCH₂–(CH₂–CH_n), 0.90 (t, CH₃); ¹³C NMR δ (ppm) (CDCl₃): 162.11 (C=N), 158.28 (Ar–C–O), 132.04–116.15 (Ar-C), 71.03 (O–CH₂), 61.16 (N–CH₂), 32.12–21.60 (OCH₂–((CH₂)₂–CH₂)₁₃) and NCH₂–(CH₂–CH_n), 14.93 (CH₃).

7: Yield 61% m.p. 82°C–83°C. Anal.: found for $C_{39}H_{71}NO$ (%): C 82.23, H 12.50, N 2.54. Calc (%) C 82.18, H, 12.56, N 2.46. IR: υ_{max} (KBr) (cm⁻¹): 3017, 2990, 2959, 1638, 1591, 1572, 1250. ¹HNMR δ (ppm) (CDCl₃): 8.06 (s, H7), 7.55 (d, J = 8.8 Hz, H2 and H6), 6.95 (d, J = 8.6 Hz, H3 and H5), 4.04 (t, C₄–OCH₂), 3.61 (t, N–CH₂), 1.88–1.24 (m, OCH₂–((CH₂)₂–CH₂)₁₃) and NCH₂–(CH₂–CH_n), 0.91 (t, CH₃); ¹³C NMR δ (ppm) (CDCl₃): 162.05 (C=N), 158.29 (Ar–C–O), 132.05–116.18 (Ar-C), 71.08 (O–CH₂), 61.76 (N–CH₂), 31.98–21.59 (OCH₂–((CH₂)₂–CH₂)₁₃) and NCH₂–(CH₂–CH_n), 14.93 (CH₃).

2.1.3. Synthesis of Compounds 1a-7a, 1b-7b, and 1c-7c. The title compounds were synthesized by the same method. The synthetic method will be described on the basis of compound 1a.

A solution containing maleic anhydride (0.01 mol) in dry benzene (10 mL) was added dropwise to a hot dry benzene solution (20 mL) containing compound $\mathbf{1}$ (0.01 mol) in a

round bottom flask equipped with a double-surface condenser fitted with calcium chloride guard tube. The reaction mixture was refluxed for 4 h. The reaction was monitored by thin layer chromatography (TLC) and the solvent was distilled off in vacuo. The solid product thus obtained was filtered and washed with distilled cool water. Resulting solid was recrystallized twice from 1,4-dioxane. The analytical data, FT-IR, and ¹H and ¹³C NMR for compounds **1a–7b**, **1b–7b**, and **1c–7c** are summarized as follows.

1a: Yield 61% m.p. 78°C–79°C. Anal.: found for C₃₁H₄₉NO₄ (%): C 74.61, H 9.85, N 2.74. Calc. (%) C 74.51, H 9.88, N 2.80. IR: v_{max} (KBr) (cm⁻¹): 2960, 2928, 2864, 2830, 1730, 1600, 1570, 1246. ¹HNMR δ (ppm) [dimethyl sulfoxide (DMSO)]: 9.85 (s, H7), 7.83 (d, J = 8.1 Hz, H2 and H6), 7.11 (d, J = 8.3 Hz, H3 and H5), 6.41 (d, J = 12.6 Hz, H10), 6.22 (d, J = 12.4 Hz, H9), 4.05 (t, C₄–OCH₂), 3.15 (t, N–CH₂), 1.75–1.24 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂– (CH₂–CH_n)⁺), 0.87 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 166.29 (C11), 166.05 (C8), 164.37 (C4), 132.62 (C9), 132.57 (C2 and C6), 130.87 (C10), 115.80 (C3 and C5), 90.06 (C7), 68.89 (O–CH₂), 39.70 (N–CH₂), 14.66 (CH₃).

2a: Yield 62% m.p. 81°C–82°C. Anal.: found for $C_{33}H_{53}NO_4$ (%): C 75.07, H 10.37, N 2.71. Calc. (%) C 75.10, H 10.12, N 2.65. IR: υ_{max} (KBr) (cm⁻¹): 2958, 2924, 2859, 2807, 1728, 1604, 1582, 1244. ¹HNMR δ (ppm) (DMSO): 9.85 (s, H7), 7.82 (d, J = 8.1 Hz, H2 and H6), 7.10 (d, J = 8.3 Hz, H3 and H5), 6.40 (d, J = 12.5 Hz, H10), 6.23 (d, J = 12.5, Hz H9), 4.04 (t, C₄–OCH₂), 3.15 (t, N–CH₂), 1.74–1.23 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂– (CH₂–CH_n)⁺), 0.86 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 166.24 (C11), 166.04 (C8), 164.37 (C4), 132.62 (C9), 132.56 (C2 and C6), 130.90 (C10), 115.79 (C3 and C5), 90.12 (C7), 68.90 (O–CH₂), 39.70 (N–CH₂), 14.61 (CH₃).

3a: Yield 66% m.p. 84°C–85°C. Anal.: found for C₃₅H₅₇NO₄ (%): C 75.72, H 10.59, N 2.62. Calc. (%) C 75.63, H 10.34, N 2.52. IR: υ_{max} (KBr) (cm⁻¹): 2960, 2935, 2863, 2809, 1698, 1597, 1581, 1250. ¹H NMR δ (ppm) (DMSO): 9.87 (s, H7), 7.85 (d, J = 8.2 Hz, H2 and H6), 7.12 (d, J = 8.3 Hz, H3 and H5) 6.40 (d, J = 12.5 Hz, H10), 6.26 (d, J = 12.5 Hz, H9), 4.04 (t, C₄–OCH₂), 3.16 (t, N–CH₂), 1.76–1.23 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.86 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 166.22 (C11), 166.06 (C8), 164.50 (C4), 132.64 (C9), 132.59 (C2 and C6), 130.88 (C10), 115.71 (C3 and C5), 90.06 (C7), 68.88 (O-CH₂), 39.74 (N-CH₂), 14.62 (CH₃).

4a: Yield 64% m.p. 90°C–91°C. Anal.: found for $C_{37}H_{61}NO_4$ (%): C 76.15, H 10.51, N, 2.60. Calc. (%) C 76.11, H 10.53, N 2.40. IR: υ_{max} (KBr) (cm⁻¹): 2950, 2919, 2854, 2810, 1685, 1604, 1582, 1252. ¹H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.82 (d, J = 8.1 Hz, H2 and H6), 7.11 (d, J = 8.3 Hz, H3 and H5), 6.42 (d, J = 12.5 Hz, H10), 6.21 (d, J = 12.4 Hz, H9), 4.03 (t, C₄-OCH₂), 3.14 (t, N–CH₂), 1.75–1.22 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.85 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 166.25 (C11), 166.05 (C8), 164.32 (C4), 132.64 (C9), 132.57 (C2 and C6), 130.89 (C10), 115.90 (C3 and C5), 90.05 (C7), 68.89 (O–CH₂), 39.73 (N–CH₂), 14.59 (CH₃).

5a: Yield 63% m.p. 98°C–99°C. Anal.: found for $C_{39}H_{65}NO_4$ (%): C 76.62, H 10.72, N 2.47. Calc. (%) C 76.55, H 10.71, N 2.29. IR: υ_{max} (KBr) (cm⁻¹): 2958, 2917, 2849, 2798, 1709, 1602, 1583, 1250. ¹HNMR δ (ppm) (DMSO): 9.84 (s, H7), 7.81 (d, J = 8.1 Hz, H2 and H6), 7.12 (d, J = 8.4 Hz, H3 and H5), 6.39 (d, J = 12.5 Hz, H10), 6.20 (d, J = 12.3 Hz, H9), 4.04 (t, C₄–OCH₂), 3.15 (t, N–CH₂), 1.73–1.22 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.86 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 166.23 (C11), 166.09 (C8), 164.61 (C4), 132.65 (C9), 132.55 (C2 and C6), 130.88 (C10), 116.05 (C3 and C5), 90.00 (C7), 68.90 (O-CH₂), 39.73 (N–CH₂), 14.65 (CH₃).

6a: Yield 58% m.p. 114°C–115°C. Anal.: found for $C_{41}H_{69}NO_4$ (%): C 76.84, H 10.82, N 2.13. Calc. (%) C 76.94, H 10.87, N 2.19. IR: v_{max} (KBr) (cm⁻¹): 2952, 2916, 2860,

2829, 1710, 1601, 1581, 1254. ¹H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.80 (d, J = 8.1 Hz, H2 and H6), 7.10 (d, J = 8.3 Hz, H3 and H5), 6.40 (d, J = 12.5 Hz, H10), 6.23 (d, J = 12.4 Hz, H9), 4.05 (t, C₄-OCH₂), 3.15 (t, N-CH₂), 1.72–1.22 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂– (CH₂–CH_n)⁺), 0.85 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 166.24 (C11), 166.10 (C8), 164.41 (C4), 132.66 (C9), 132.56 (C2 and C6), 130.90 (C10), 116.09 (C3 and C5), 90.05 (C7), 68.92 (O–CH₂), 39.74 (N–CH₂), 14.68 (CH₃).

7a: Yield 51% m.p. 119°C–120°C. Anal: found for $C_{43}H_{73}NO_4$ (%): C 77.24, H 11.10, N 2.18. Calc (%) C 77.31, H, 11.01, N 2.10. IR: v_{max} (KBr) (cm⁻¹): 2956, 2917, 2864, 2831, 1732, 1600, 1582, 1251. ¹H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.85 (d, J = 8.1 Hz, H2 and H6), 7.43 (d, J = 8.5 Hz, H3 and H5), 6.41 (d, J = 12.6 Hz, H10), 6.24 (d, J = 12.5 Hz, H9), 4.05 (t, C_4 –OCH₂), 3.16 (t, N–CH₂), 1.71–1.21 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂– (CH₂–CH_n)⁺), 0.85 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 166.25 (C11), 166.11 (C8), 164.61 (C4), 132.64 (C9), 132.57 (C2 and C6), 130.89 (C10), 115.84 (C3 and C5), 90.06 (C7), 68.90 (O–CH₂), 39.73 (N–CH₂), 14.68 (CH₃).

1b: Yield 64% m.p. 85°C–86°C. Anal.: found for C₃₁H₅₁NO₄ (%): C 74.17, H 10.22, N 2.81. Calc. (%) C 74.21, H 10.25, N 2.79. IR: v_{max} (KBr) (cm⁻¹): 2959, 2914, 2860, 2829, 1718, 1603, 1580, 1249. ¹H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.86 (d, J = 8.6 Hz, H2 and H6), 7.12 (d, J = 8.6 Hz, H3 and H5), 4.06 (t, C₄–OCH₂), 3.01 (t, N–CH₂), 2.41 (t, J = 7.1 Hz, H10), 2.27 (t, J = 7.0 Hz, H9), 1.70–1.21 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂– (CH₂–CH_n)⁺), 0.86 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 174.52 (C11), 171.12 (C8), 164.32 (C4), 132.76 (C2 and C6), 115.72 (C3 and C5), 90.10 (C7), 68.88 (O–CH₂), 39.35 (N–CH₂), 29.33 (C9), 27.81 (C10), 14.70 (CH₃).

2b: Yield 67% m.p. 91°C–92°C. Anal.: found for $C_{33}H_{55}NO_4$ (%): C 74.90, H 10.59, N 2.72. Calc. (%) C 74.81, H 10.46, N 2.64. IR: υ_{max} (KBr) (cm⁻¹): 2965, 2925, 2849, 2801, 1720, 1605, 1583, 1250. ¹H NMR δ (ppm) (DMSO): 9.86 (s, H7), 7.87 (d, J = 8.6 Hz, H2 and H6), 7.13 (d, J = 8.6 Hz, H3 and H5), 4.07 (t, C₄–OCH₂), 3.01 (t, N–CH₂), 2.40 (t, J = 7.1 Hz, H10), 2.27 (t, J = 7.0 Hz, H9), 1.71–1.22 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.87 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 174.50 (C11), 171.11 (C8), 164.33 (C4), 132.77 (C2 and C6), 115.71 (C3 and C5), 90.11 (C7), 68.89 (O–CH₂), 39.33 (N–CH₂), 29.32 (C9), 27.82 (C10), 14.72 (CH₃).

3b: Yield 63% m.p. 110°C–111°C. Anal.: found for C₃₅H₅₉NO₄ (%): C 75.28, H 10.50, N 2.48. Calc. (%) C 75.36, H 10.66, N 2.51. IR: v_{max} (KBr) (cm⁻¹): 2979, 2934, 2862, 2830, 1721, 1603, 1580, 1255. ¹H NMR δ (ppm) (DMSO): 9.86 (s, H7), 7.86 (d, J = 8.6 Hz, H2 and H6), 7.11 (d, J = 8.6 Hz, H3 and H5), 4.07 (t, C₄–OCH₂), 3.02 (t, N–CH₂), 1.71–1.23 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 2.40 (t, J = 7.1 Hz, H10), 2.28 (t, J = 7.0 Hz, H9), 0.86 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 174.52 (C11), 171.12 (C8), 164.34 (C4), 132.75 (C2 and C6), 115.70 (C3 and C5), 90.10 (C7), 68.90 (O–CH₂), 39.36 (N–CH₂), 29.32 (C9), 27.80 (C10), 14.72 (CH₃).

4b: Yield 56% m.p. 114°C–115°C. Anal.: found for C₃₇H₆₃NO₄ (%): C 75.90, H 10.80, N 2.30. Calc. (%) C 75.85, H 10.84, N 2.39. IR: v_{max} (KBr) (cm⁻¹): 2959, 2914, 2860, 2829, 1718, 1601, 1587, 1250. ¹H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.88 (d, J = 8.6 Hz, H2 and H6), 7.12 (d, J = 8.6 Hz, H3 and H5), 4.06 (t, C₄–OCH₂), 3.01 (t, N–CH₂), 2.41 (t, J = 7.1 Hz, H10), 2.27 (t, J = 7.0 Hz, H9), 1.72–1.22 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.86 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 174.51 (C11), 171.11 (C8), 164.32 (C4), 115.72 (C3 and C5), 132.77 (C2 and C6), 90.12 (C7), 68.91 (O–CH₂), 39.33 (N–CH₂), 29.31 (C9), 27.82 (C10), 14.73 (CH₃).

5b: Yield 55% m.p. 120°C–121°C. Anal.: found for $C_{39}H_{67}NO_4$ (%): C 76.28, H 11.15, N 2.19. Calc. (%) C 76.30, H 11.00, N 2.28. IR: υ_{max} (KBr) (cm⁻¹): 2959, 2914, 2860,

2829, 1725, 1600, 1582, 1252. ¹H NMR δ (ppm) (DMSO): 9.84 (s, H7), 7.85 (d, J = 8.6 Hz, H2 and H6), 7.10 (d, J = 8.6 Hz, H3 and H5), 4.06 (t, C₄-OCH₂), 3.02 (t, N-CH₂), 2.42 (t, J = 7.1 Hz, H10), 2.26 (t, J = 7.0 Hz, H9), 1.71–1.22 (OCH₂-(CH₂)₂-(CH₂)₁₃* and NCH₂- (CH₂-CH_n)⁺), 0.86 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 174.50 (C11), 171.13 (C8), 164.33 (C4), 132.76 (C2 and C6), 115.71 (C3 and C5), 90.11 (C7), 68.92 (O-CH₂), 39.37 (N-CH₂), 29.33 (C9), 27.82 (C10), 14.75 (CH₃).

6b: Yield 55% m.p. 123° C- 124° C. Anal.: found for C₄₁H₇₁NO₄ (%): C 76.66, H 11.19, N 2.30. Calc. (%) C 76.70, H 11.15, N 2.18. IR: v_{max} (KBr) (cm⁻¹): 2961, 2922, 2852, 2817, 1730, 1603, 1584, 1252. ¹H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.86 (d, J = 8.6 Hz, H2 and H6), 7.11 (d, J = 8.6 Hz, H3 and H5), 4.05 (t, C₄-OCH₂), 3.00 (t, N-CH₂), 2.41 (t, J = 7.1 Hz H10), 2.25 (t, J = 7.0 Hz, H9), 1.72–1.23 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.86 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 174.52 (C11), 171.12 (C8), 164.34 (C4), 132.76 (C2 and C6), 115.72 (C3 and C5), 90.12 (C7), 68.90 (O-CH₂), 39.36 (N-CH₂), 29.33 (C9), 27.80 (C10), 14.78 (CH₃).

7b: Yield 48% m.p. 130°C–131°C. Anal.: found for $C_{43}H_{75}NO_4$ (%): C 77.36, H 11.07, N 2.38. Calc. (%) C 77.08, H 11.28, N 2.09. IR: v_{max} (KBr) (cm⁻¹): 2953, 2915, 2859, 2824, 1719, 1602, 1579, 1254. ¹H NMR δ (ppm) (DMSO): 9.86 (s, H7), 7.88 (d, J = 8.6 Hz, H2 and H6), 7.13 (d, J = 8.6 Hz, H3 and H5 4.06 (t, C_4 –OCH₂), 3.01 (t, N–CH₂),), 2.41 (t, J = 7.1 Hz, H10), 2.26 (t, J = 7.0 Hz, H9), 1.71–1.22 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.85 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 174.52 (C11), 171.11 (C8), 164.34 (C4), 132.77 (C2 and C6), 115.72 (C3 and C5), 90.12 (C7), 68.90 (O–CH₂), 39.36 (N–CH₂), 29.34 (C9), 27.81 (C10), 14.79 (CH₃).

1c: Yield 51% m.p. 85°C–86°C. Anal.: found for C₃₅H₅₁NO₄ (%): C 76.52, H 9.28, N 2.60. Calc. (%) C 76.46, H 9.35, N, 2.55. IR: v_{max} (KBr) (cm⁻¹): 2961, 2930, 2853, 2802, 1704, 1607, 1582, 1262. ¹H NMR δ (ppm) (DMSO): 9.84 (s, H7), 7.84 (d, J = 7.5 Hz, H12), 7.74 (d, J = 7.7 Hz, H15), 7.51 (t, J = 7.2 Hz, H13), 7.47 (t, J = 7.4 Hz, H14), 7.35 (d, J = 8.3 Hz, H2 and H6), 7.09 (d, J = 8.2 Hz, H3 and H5), 4.06 (t, C₄–OCH₂), 3.14 (t, N–CH₂), 1.74–1.22 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.85 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 168.84 (C11), 167.45 (C8), 164.14 (C4), 135.22 (C14), 129.97 (C12), 128.41 (C13), 125.45 (C2 and C6), 122.35 (C15), 115.00 (C3 and C5), 89.98 (C7), 68.03 (O–CH₂), 39.03 (N–CH₂), 14.56 (CH₃).

2c: Yield 50% m.p. 126°C–127°C. Anal.: found for $C_{37}H_{55}NO_4$ (%): C 77.98, H 9.48, N 2.34. Calc. (%) C 77.91, H 9.59, N 2.42. IR: υ_{max} (KBr) (cm⁻¹): 2948, 2924, 2854, 2831, 1700, 1605, 1580, 1261. ¹H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.85 (d, J = 7.5 Hz, H12), 7.74 (d, J = 7.7 Hz, H15), 7.50 (t, J = 7.2 Hz, H13), 7.48 (t, J = 7.4 Hz, H14), 7.36 (d, J = 8.3 Hz, H2 and H6), 7.10 (d, J = 8.2 Hz, H3 and H5), 4.06 (t, C₄–OCH₂), 3.15 (t, N–CH₂), 1.74–1.21 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.86 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 168.85 (C11), 167.44 (C8), 163.12 (C4), 135.23 (C14), 129.97 (C12), 128.40 (C13), 125.44 (C2 and C6), 122.34 (C15), 115.01 (C3 and C5), 89.97 (C7), 68.05 (O–CH₂), 39.05 (N–CH₂), 14.55 (CH₃).

3c: Yield 43% m.p. 125°C–126°C. Anal.: found for C₃₉H₅₉NO₄ (%): C 77.40, H 9.71, N 2.22. Calc. (%) C 77.31, H 9.82, N 2.31. IR: υ_{max} (KBr) (cm⁻¹): 2950, 2918, 2857, 2821, 1706, 1600, 1577, 1259. ¹H NMR δ (ppm) (DMSO): 9.86 (s, H7), 7.86 (d, J = 7.6 Hz, H12), 7.75 (d, J = 7.7 Hz, H15), 7.52 (t, J = 7.2 Hz, H13), 7.49 (t, J = 7.4 Hz, H14), 7.39 (d, J = 8.3 Hz, H2 and H6), 7.11 (d, J = 8.2 Hz, H3 and H5), 4.07 (t, C₄–OCH₂), 3.15 (t, N–CH₂), 1.73–1.23 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.85 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 168.85 (C11), 167.45 (C8), 163.22 (C4), 135.22

(C14), 129.98 (C12), 128.44 (C13), 125.46 (C2 and C6), 122.32 (C15), 115.04 (C3 and C5), 89.98 (C7), 68.05 (O-CH₂), 39.04 (N-CH₂), 14.55 (CH₃).

4c: Yield 47% m.p. 132° C– 133° C. Anal.: found for C₄₁H₆₃NO₄ (%): C 77.60, H 10.12, N 2.30. Calc. (%) C 77.68, H 10.02, N 2.21. IR: υ_{max} (KBr) (cm⁻¹): 2952, 2922, 2864, 2811, 1727, 1601, 1583, 1260. ¹H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.85 (d, *J* = 7.5 Hz, H12), 7.74 (d, *J* = 7.7 Hz, H15), 7.52 (t, *J* = 7.2 Hz, H13), 7.48 (t, *J* = 7.4 Hz, H14), 7.39 (d, *J* = 8.3 Hz, H2 and H6), 7.11 (d, *J* = 8.2 Hz, H3 and H5), 4.08 (t, C₄–OCH₂), 3.15 (t, N–CH₂), 1.72–1.22 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.87 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 168.84 (C11), 167.43 (C8), 163.13 (C4), 135.24 (C14), 129.99 (C12), 128.43 (C13), 125.45 (C2 and C6), 122.36 (C15), 115.03 (C3 and C5), 89.99 (C7), 68.08 (O–CH₂), 39.04 (N–CH₂), 14.56 (CH₃).

5c: Yield 44% m.p. 128°C–129°C. Anal.: found for C₄₃H₆₇NO₄ (%): C 78.14, H 10.25, N 2.08. Calc. (%) C 78.02, H 10.20, N 2.12. IR: υ_{max} (KBr) (cm⁻¹): 2956, 2925, 2848, 2804, 1725, 1604, 1579, 1258. ¹H NMR δ (ppm) (DMSO): 9.86 (s, H7), 7.88 (d, *J* = 7.6 Hz H12), 7.74 (d, *J* = 7.7 Hz, H15), 7.52 (t, *J* = 7.2 Hz, H13), 7.49 (t, *J* = 7.4 Hz, H14), 7.40 (d, *J* = 8.4 Hz, H2 and H6), 7.14 (d, *J* = 8.2 Hz, H3 and H5), 4.09 (t, C₄–OCH₂), 3.17 (t, N–CH₂), 1.74–1.23 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.88 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 168.84 (C11), 167.44 (C8), 163.12 (C4), 135.23 (C14), 129.98 (C12), 128.44 (C13), 125.44 (C2 and C6), 122.36 (C15), 115.07 (C3 and C5), 90.08 (C7), 68.08 (O–CH₂), 39.05 (N–CH₂), 14.57 (CH₃).

6c: Yield 57% m.p. 129°C–130°C. Anal.: found for C₄₅H₇₁NO₄ (%): C 78.58, H 10.63, N 2.29. Calc. (%) C 78.33, H 10.37, N 2.03. IR: υ_{max} (KBr) (cm⁻¹): 2957, 2921, 2855, 2813, 1728, 1600, 1581, 1260. ¹H NMR δ (ppm) (DMSO): 9.86 (s, H7), 7.86 (d, *J* = 7.6 Hz, H12), 7.73 (d, *J* = 7.7 Hz, H15), 7.53 (t, *J* = 7.2 Hz, H13), 7.48 (t, *J* = 7.4 Hz, H14), 7.38 (d, *J* = 8.3 Hz, H2 and H6), 7.11 (d, *J* = 8.2 Hz, H3 and H5), 4.08 (t, C₄–OCH₂), 3.16 (t, N–CH₂), 1.73–1.23 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.86 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 168.95 (C11), 167.45 (C8), 163.11 (C4), 135.22 (C14), 129.98 (C12), 128.45 (C13), 125.46 (C2 and C6), 123.37 (C15), 115.07 (C3 and C5), 90.08 (C7), 68.06 (O–CH₂), 39.08 (N–CH₂), 14.56 (CH₃).

7c: Yield 51% m.p. 148°C–149°C. Anal.: found for C₄₇H₇₅NO₄ (%): C 78.56, H 10.60, N 1.98. Calc. (%) C 78.61, H 10.53, N 1.95. IR: υ_{max} (KBr) (cm⁻¹): 2961, 2929, 2849, 2816, 1710, 1603, 1580, 1261. ¹H NMR δ (ppm) (DMSO): 9.85 (s, H7), 7.87 (d, J = 7.5Hz, H12), 7.75 (d, J = 7.7 Hz, H15), 7.50 (t, J = 7.2 Hz, H13), 7.49 (t, J = 7.4 Hz, H14), 7.40 (d, J = 8.3 Hz, H2 and H6), 7.15 (d, J = 8.2 Hz, H3 and H5), 4.08 (t, C₄–OCH₂), 3.16 (t, N–CH₂), 1.73–1.24 (OCH₂–(CH₂)₂–(CH₂)₁₃* and NCH₂–(CH₂–CH_n)⁺), 0.87 (t, CH₃); ¹³C NMR δ (ppm) (DMSO): 169.16 (C11), 167.44 (C8), 163.12 (C4), 135.24 (C14), 129.97 (C12), 128.45 (C13), 125.45 (C2 and C6), 123.37 (C15), 115.08 (C3 and C5), 90.07 (C7), 68.07 (O–CH₂), 39.11 (N–CH₂), 14.57 (CH₃).

2.2. Reagents and Techniques

Hexylamine, octylamine, decylamine, dodecylamine, 4-hydroxybenzeldehyde, and anhydrides (maleic, succinic, and phthalic) were obtained from Aldrich. While tetradecylamine, hexadecylamine, and octadecylamine were purchased from Acros, 1-bromotetradecane was obtained from Merck. They were used without further purification.

The elemental (CHN) microanalyses were performed using a Perkin Elmer 2400 LS Series CHNS/O analyzer. Melting points were recorded by Gallenkamp digital melting point. The measurements were carried out through the scanning at room temperature. FT-IR measurements on intermediates and title compounds were performed on samples in the KBr pellets and the spectra were recorded in the range of 4000–400 cm⁻¹ using a Perkin Elmer 2000-FT-IR spectrophotometer. The ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ (for **1–7**) and DMSO (for **1a–7b**, **1b–7b**, and **1c–7c**) at 298 K on a Bruker 400 MHz Ultrashied FT-NMR spectrometer equipped with a 5-mm BBI inverse gradient probe. Chemicals shifts were referenced to internal tetramethylsilane (TMS). The concentration of solute molecules was 50 mg in 1.0 mL DMSO. Standard Bruker pulse programs [21] were used throughout the entire experiment.

The phase transition temperatures and enthalpy values were measured by Perkin Elmer Pyris 1 DSC at heating and cooling rates of 5° C min⁻¹, respectively.

The textures were observed using a Carl Zeiss Axioskop 40 polarizing microscope equipped with a Mettler FP5 hot stage and TMS94 temperature controller. The samples studied by optical microscopy were prepared in thin film sandwiched between glass slide and cover.

3. Results and Discussion

3.1. Mesomorphic Properties of Intermediates 1–7 and Title Compounds 1a–7a, 1b–7b, and 1c–7c

The textures illustrated by intermediates 1–7 and title compounds 1a–7a, 1b–7b, and 1c–7c under POM have been ascertained by comparing them with relevant photomicrograph from literature [22, 23]. The transition temperatures and associated enthalpies for 1–7, 1a–7a, 1b–7b, and 1c–7c upon heating and cooling are listed in Table 1. It can be inferred from Table 1 that the imines 1–5 exhibit monotropic behaviors. In addition, the temperatures with respect to the crystal-isotropic (Cr-Iso) transition upon heating run in these compounds are found to be higher than the temperature associated with the isotropic-mesophase (Iso-M) transition in which the compounds undergo supercooling [24]. The observation under polarized light within the mesomorphic region shows the presence of fan-shaped texture characteristic of the smectic A (SmA) phase upon cooling from the isotropic liquid (Fig. 1). The mesomorphic temperature ranges for compounds 1–5 are 9.92°C, 7.64°C, 9.24°C, 7.47°C, and 7.90°C, respectively. However, only isotropization and crystallization are observed upon heating (at 77.14°C and 82.54°C, respectively) and cooling (at 42°C and 61.71°C, respectively) runs in compounds **6** and **7**.

In compounds **1a–7a**, it is noteworthy that liquid crystal phases were not observed in **1a**, **2a**, and **3a**, but they exhibit the Cr-Iso transition on heating at 78.32°C, 81.00°C, and 84.11°C, respectively. A reverse process of Iso-Cr was observed on cooling at respective temperatures of 67.34°C, 74.45°C, and 77.27°C. Moreover, the **4a**, **5a**, **6a**, and **7a** are not mesogenic and inclined to the Cr₁-Cr₂-Iso transition upon heating run. Moreover, the Iso-Cr₂-Cr₁ transition is also observed on cooling run. The texture observed under POM is indicative of the presence of subphases within the crystal phase (Cr₁-Cr₂), which resembled the phenomena reported in literature [2, 25].

For the series of compounds **1b–7b**, the DSC and POM analyses reveal that the new compounds thus synthesized are not mesogenic and exhibit only Cr_1-Cr_2 -Iso and Iso- Cr_2 - Cr_1 transitions upon heating and cooling runs. This can be substantiated by the DSC, as shown for compound **6b** (Fig. 2). The high values of the enthalpy of the phase transition obtained from DSC substantiate the crystallization and the Cr_1-Cr_2 transition. The changes in crystalline structure for **6a**, as observed under polarized light, show a transition from the texture consisting huge number of slender threads (Cr_1) to colored plates (Cr_2) when the

	Transition temperature (°C) (corresponding enthalpy
Compounds	changes in KJ mol ⁻¹) heating/cooling
1	Cr 60 43 (23 16) I
1	Cr 43.20 (-10.82) Sm 4.53.12 (-3.51) J
2	Cr 64 16 (36 05) I
4	Cr 51 41 (-33 72) SmA 50 05(-2 04) I
3	Cr 68 31 (47 55) I
5	Cr 53.07 (-64.32) SmA 62.31 (-0.91) J
4	Cr 74 11 (29 64) I
•	Cr 56 95 (-49 23) SmA 64 42 (-8 54) I
5	Cr 78 00 (26 54) I
C C	Cr 60.71 (-19.62) SmA 68.61 (-2.64) I
6	Cr 77.14 (45.31) I
-	Cr 57.42 (-28.41) I
7	Cr 82.54 (33.89) I
	Cr 61.71 (-19.65) I
1a	Cr 78.32 (58.12) I
	Cr 67.34 (-38.46) I
2a	Cr 81.00 (64.75) I
	Cr 74.45 (-42.87) I
3a	Cr 84.11 (81.23) I
	Cr 77.27 (-37.79) I
4 a	Cr ₁ 60.19(4.56) Cr ₂ 90.54 (75.70) I
	Cr ₁ 48.55(-14.81) Cr ₂ 59.68 (-49.51) I
5a	Cr ₁ 68.31(33.61) Cr ₂ 98.67 (65.31) I
	Cr ₁ 52.61(-29.84) Cr ₂ 70.41 (-41.35) I
6a	Cr ₁ 88.28(48.27) Cr ₂ 114.23 (19.75) I
	Cr ₁ 48.81(-11.13) Cr ₂ 86.31 (-37.66) I
7a	Cr ₁ 63.49(25.51) Cr ₂ 119.14 (8.26) I
	Cr ₁ 40.59(-21.62) Cr ₂ 84.03 (-26.45) I
1b	Cr ₁ 41.35(38.69) Cr ₂ 85.14 (70.31) I
	Cr ₁ 37.56(-25.62) Cr ₂ 64.42 (-44.52) I
2b	Cr ₁ 58.47(39.78) Cr ₂ 91.23 (56.29) I
	$Cr_1 43.67(-21.56) Cr_2 61.54 (-39.42) I$
3b	$Cr_1 63.45(28.46) Cr_2 109.32 (63.26) I$
47	Cr_1 38.79(-29.83) Cr_2 65.65 (-33.45) 1
4b	$Cr_1 88.28(48.27) Cr_2 114.23 (19.75) I$
~ 1	$Cr_1 48.81(-11.13) Cr_2 86.31 (-37.66) I$
50	Cr_1 /9.32(42.51) Cr_2 119.62 (57.81) 1
a	$Cr_1 68.43(-39.76) Cr_2 79.44 (-17.31) I$
00	$Cr_1 \delta / .51(51.42) Cr_2 125 (45.01) I$
71.	$Cr_1 \ 50.45(-28.45) \ Cr_2 \ 91.04 \ (-42.86) \ I$
/0	Cr_1 90.14(18.20) Cr_2 129.10 (33.89) 1 Cr_2 (0.50(-21.62) Cr_2 84.02 (-26.45) L
	$Cr_1 00.59(-21.62) Cr_2 84.03 (-26.45) I$

Table 1. Phase transition temperatures (°C) and the corresponding enthalpies (J g⁻¹) ofintermediates 1–7 and title compounds 1a–7a, 1b–7b, and 1c–7c

Compounds	Transition temperature (°C) (corresponding enthalpy changes in KJ mol ⁻¹) heating/cooling
1c	Cr ₁ 74.39(26.23) Cr ₂ 130.01 (37.87) I
	Cr ₁ 58.35(-30.46) Cr ₂ 117.57 (-40.34) N 126.21 (0.72) I
2c	Cr ₁ 77.46(22.67) Cr ₂ 126.61 (28.56) I
	Cr ₁ 51.74(-32.89) Cr ₂ 112.92 (-25.22) N 122.45 (0.82) I
3c	Cr ₁ 78.41(18.65) Cr ₂ 125.41 (22.34) I
	Cr ₁ 60.26(-37.56) Cr ₂ 113.67 (-19.78) N 121.44 (1.53) I
4c	Cr ₁ 76.33(7.57) Cr ₂ 132.92(17.24) I
	Cr ₁ 58.57(-39.43) Cr ₂ 117.12 (-3.83) N 125.67 (5.42) I
5c	Cr ₁ 81.41(14.32) Cr ₂ 128.12 (21.31) I
	Cr ₁ 69.62(-30.82) Cr ₂ 114.32 (-25.31) N 121.23 (0.91) I
6c	Cr ₁ 82.30(60.83) Cr ₂ 129.36 (15.41) I
	Cr ₁ 72.32(-5.95) Cr ₂ 120.45 (-10.64) N 125.36 (1.34) I
7c	Cr ₁ 86.98(13.09) Cr ₂ 148.35 (18.67) I
	$Cr_1 68.35(-18.17) Cr_2 132.45 (-53.54) N 142.45 (1.02) I$

Table 1. Phase transition temperatures (°C) and the corresponding enthalpies (J g⁻¹) of intermediates 1–7 and title compounds 1a–7a, 1b–7b, and 1c–7c (*Continued*)

temperature was increased from 94°C to 110°C. This phenomenon can be rationalized by the minor change of molecular rearrangement within the crystal phase.

All compounds from the series of **1c–7c** upon cooling exhibit a nematic (N) phase. On cooling from the isotropic liquid, the presence of Schlieren texture characteristics of N phase was observed. The photomicrograph for compound **7c** is shown as an example in Fig. 1. Inspection from the DSC data further suggests that the temperature ranges of mesophase upon cooling are found to be relatively narrow (8.6° C, 9.5° C, 7.8° C, 8.5° C, 6.9° C, 4.9° C, and 10.0° C for **1c**, **2c**, **3c**, **4c**, **5c**, **6c**, and **7c**, respectively). The narrow ranges of mesomorphic temperatures indicate that the molecules **1c–7c** are not kinetically stable within this anisotropic region [26]. A thermogram associated with the thermal properties of compound **7c** is shown in Fig. 2.

3.2. Structure–Mesomorphic Property Relationship

From Fig. 3(a), it is apparent that the temperatures associated with the Cr-I and SmA-I transitions for the intermediates are dependent on the carbon number. These temperatures increase when the length of the terminal alkyl chain is increased from 6 to 18. A drastic change is observed when the carbon number varied from 12 to 14 upon the cooling run.

All the compounds **1a–7a** and **1b–7b** are not mesogenic despite knowing that upon heating and cooling, the transitions of Cr_1-Cr_2 and its reverse process occurred within the crystalline state. Figure 3(b) shows that the isotropization (Cr_2 -I) temperatures for **4a–7a** ascended from 90.54°C (**4a**) to 119.14°C (**7a**). The opposite trend was observed when these compounds were cooled down from isotropic liquid.

The thermal behavior as observed in compounds 1a-7a was not found in 1b-7b (Fig. 3(c)) and this can be explained in terms of the saturation of the seven-membered ring. Compounds 1a-7a with a C=C double bond in the seven-membered ring led to a more ordered arrangement within the lattice system in comparison to compounds 1b-7b.



Figure 1. Optical texture of SmA phase at 64.52° C (top plate) observed in compound **5** and N phase at 137.23° C (bottom plate) observed in compound **7**c.

A remarkable feature can be inferred from Fig. 3(d) in which the monotropic 1c-7c upon cooling exhibited well-distinguished transition temperatures associated with I-N, N-Cr₁, and Cr₁-Cr₂. The transition temperatures for each of the compounds 1c-7c differ in



Figure 2. DSC thermograms of compounds 6b and 7c.

the following order:

$$I - N > N - Cr_1 > Cr_1 - Cr_2.$$

The ability of compounds **1c–7c** to exhibit nematogenic properties can probably be attributed to the presence of the additional aromatic ring fused with the seven-membered ring resulting in a more rigid core system in comparison to compounds **1a–7a** and **1b–7b**.

3.3. FT-IR, ¹H NMR, and ¹³C NMR Spectral Studies

The infrared spectra of the title compounds **1a–7a**, **1b–7b**, and **1c–7c** show a strong band at the range of 1685–1732 cm⁻¹, which can be assigned to the stretching vibration of carbonyl group C=O in the seven-membered rings. The absorption bands observed in the frequency range of 1244–1262 cm⁻¹ can be assigned to the stretching of the C₄–O of the ether linkage [27]. The presence of the diagnostic bands at the range of 1597–1607 cm⁻¹ and 1570–1587



Figure 3. The dependence of phase transition temperatures T on the number of methylene in the terminal alkyl chain of (a) compounds 1–7, (b) compounds 4a–7a, (c) compounds 1b–7b, and (d) compounds 1c–7c.



Figure 3. (Continued)

 cm^{-1} is attributable to the C=C stretching of the aromatic ring [28]. Other major bands observed at 2914–2979 cm^{-1} and 2798–2864 cm^{-1} indicate the presence of carbon chains in the respective compounds in which the hydrogen atoms are attached to sp³ carbons [29].

A complete ¹H NMR assignment for the title compounds can be described on the basis of respective compounds, as shown in Scheme 1, in which three types of compounds have been differentiated by **a**, **b**, and **c**. The ¹H NMR spectra of title compounds **1a–7a**, **1b–7b**, and **1c–7c** showed a singlet that integrates as one hydrogen at the chemical shift $\delta = 9.84-9.87$ ppm that corresponds to the proton attached to the carbon C7 in heterocyclic ring. The presence of two doublets in the downfield region of $\delta = 6.21-6.26$ ppm and $\delta = 6.39-6.41$ ppm for compounds **1a–7a** can be attributed to H9 and H10 of heterocyclic ring. However, the ¹H NMR spectra of compounds **1b–7b** indicate that the H9 and H10 protons from the heterocyclic ring appear as two triplets at the range of $\delta = 2.25-2.28$ ppm and $\delta = 2.40-2.42$ ppm, respectively. Moreover, the resonances for the C₆H₅– appear as two doublets in downfield region of $\delta = 7.80-7.85$ ppm and $\delta = 7.10-7.43$ ppm corresponding to the respective phenyl protons H2 (or H6) and H3 (or H5) in compounds **1a–7a**. The phenyl protons H2 (or H6) and H3 (or H5) from compounds **1b–7b** appear as doublet at the ranges

of $\delta = 7.85-7.88$ ppm and 7.10–7.13 ppm, respectively. The ¹H NMR data for compounds **1c–7c** show diagnostic signals within the range of $\delta = 7.10-7.88$ ppm assignable to the aromatic protons. As for ¹H NMR spectra of compounds **1a–7a**, **1b–7b**, and **1c–7c**, there are three triplet signals due to the presence of methylene protons, C₄–OCH₂ of the ether linking group, methylene protons, and N–CH₂, and CH₃ protons in both chains at the respective chemical shift ranges of $\delta = 4.03-4.09$ ppm, 3.00–3.17 ppm, and 0.85–0.88 ppm. Two sets of multiplets at $\delta = 1.21-1.76$ ppm can be assigned to protons OCH₂–((CH₂)₂–CH₂)₁₃ and NCH₂–(CH₂–CH_n).

The structures of the title compounds are further substantiated by the ¹³C NMR data. The resonances due to the carbonyl group (C8 and C11) of heterocyclic rings in the title compounds **1a–7a**, **1b–7b**, and **1c–7c** are located in the downfield ($\delta = 166.04-166.29$ ppm, 171.11–174.52 ppm, and 167.43–168.95 ppm, respectively). The signal that appears within the range of $\delta = 89.97-90.12$ ppm can be attributed to the C7 in the heterocyclic rings. The ¹³C NMR spectra of compounds **1a–7a**, **1b–7b**, and **1c–7c** indicate that the aromatic carbons give rise to different signals within the frequency range of $\delta = 115.00-164.61$ ppm. Signals at $\delta = 132.62-132.66$ ppm and $\delta = 130.87-130.90$ ppm indicate the presence of C9 and C10 in heterocyclic ring in compounds **1a–7a**. However, the resonance due to the C9 and C10 in compounds **1b–7b** can be located at the respective chemical shift of $\delta =$ 29.31–29.34 ppm and 27.80–27.82 ppm.

The ¹³C NMR spectra of title compounds confirm that the signal at $\delta = 68.03-68.92$ ppm attributed to the presence of C₄O-CH₂ group from the ether linkage. Similarly, the presence of N-CH₂ can be confirmed by the signal observable at the range of $\delta = 39.03-39.74$ ppm. Signals ascribed to the methylene carbons of the terminal alkyloxy chain (CH₂)₂-(CH₂)₁₃ and alkyl group NCH₂-(CH₂-CH_n) can be assigned within the range of $\delta = 22.90-32.39$ ppm. At a high field, a signal at $\delta = 14.55-14.79$ ppm can be assigned to methyl carbons.

4. Conclusion

Three series of heterocyclic-based liquid crystalline compounds with the heterocyclic ring at the core position have been synthesized using new methodology and their mesomorphic properties were analyzed with respect to phase transition temperature and chemical structure. The intermediate compounds were found to exhibit SmA upon cooling. However, the types of compounds from **a** and **b** series were not mesogenic and only exhibit Cr_1-Cr_2 upon cooling and heating. The compounds in **c** series were found to show monotropic N phase upon cooling.

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