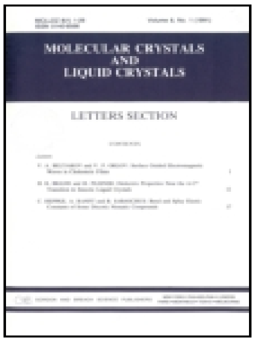

Molecular Crystals and Liquid Crystals

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Smectogenic and nematogenic liquid crystals of a new series of heterocyclic derivatives bearing an ester terminal chain: Synthesis, characterization, and theoretical study

Abdulkarim-Talaq Mohammad[a], Guan-Yeow Yeap[b], and Hasnah Osman[b]

[a]Chemistry Department, College of Science, University of Anbar, Ramadi, Iraq; [b]Liquid Crystal Research Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, Minden, Penang, Malaysia

ABSTRACT

The synthesis and mesomorphic properties of novel ester derivatives of three series heterocyclic 1,3-oxazepinediones and the 1,3-oxazepandione moiety (a–c) are described. All structures were elucidated by physical measurements and the bonding characteristics of the resulting compounds were substantiated by Fourier transform infrared spectroscopy spectroscopy. Their molecular structures are supported by the ^{1}H and ^{13}C NMR spectra along with two-dimensional COSY, HMQC, and HMBC.A structure-property relationship has been established and mesogenic properties were found to be dependent on the type of rings within the molecular core. Compounds**1a–7a** not mesogenic exhibited Cr-I upon heating and cooling, while the series compounds **1b–7b** were not mesogenic and only exhibited the transition of Cr$_1$-Cr$_2$ upon cooling and heating. In compounds **1c–7c**, the SmA observed in compounds **1c**–**3c** with short terminal alkyl chains during heating and cooling. However, the nematic phases were formed in compounds **4c–7c**. The nematic phase presence increases with the length of the terminal alkyl chain. Theoretical studies are presented in this study and are in agreement with our results.

KEYWORDS
Ester; nematogenic; oxazepinediones; smectogenic; synthesis

1. Introduction

The modification and synthesis of the liquid crystals (LCs) of heterocyclic compounds, especially those of conventional calamitic (rod-like) LCs, discotic (disc-like) mesogens, have attracted much interest from both fundamental research and practical application. Research focused on modifying existing molecules, particularly natural products, has shown to be a viable approach towards new compounds showing liquid crystalline properties [1–3]. We recently reported the synthesis and characterization of a number of oxazepine-ring heterocyclic LC materials that exhibited the nematic phase [4–6]. However, no interesting research has previously been conducted on mesogens incorporating an oxazepine ring. Oxazepine derivatives constitute one of the largest and most important classes of molecules that have contributed to a wide range of biological activities, especially anticonvulsant activity [7–10]. It is well documented that the LC phases depend largely on the mesogenic core structure: its geometry, polarisability, molecular conformation and length-to-breath ratio, as well as the number and position of permanent dipole moments in the core. Therefore, this type of oxazepine core

CONTACT Abdulkarim-Talaq Mohammad drmohamadtalaq@gmail.com; mtalaq_gst@kent.edu

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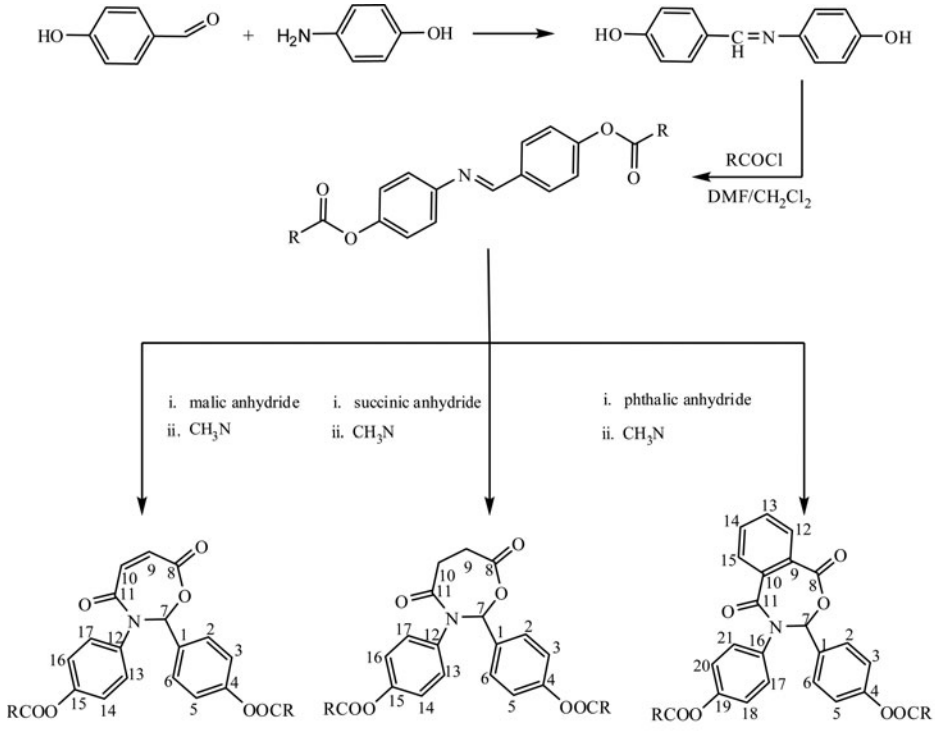

1a-7a **1b-7b** **1c-7c**

R= C_5H_{11}, C_7H_{15}, C_9H19, $C_{11}H_{23}$, $C_{13}H_{27}$, $C_{15}H_{31}$,$C_{17}H_{35}$

Scheme 1. Synthetic rout of the target compounds 1a–7a, 1b–7b, and 1c–7c.

structure has been regarded as one of the most significant factors that gives rise to mesomorphic properties [11, 12]. Recently, a large number of heterocyclic rings have been introduced into these compounds as mesogenic cores [13–25]. In a continuation of our work on heterocyclic oxazepines, this article will describe the mesomorphic properties of three series of compounds which incorporate 1,3-oxazepinediones and the 1,3-oxazepandione moiety (a–c). The structures of this compound series are shown in Scheme 1. The main aim of this work is to establish the effect of a target compound whose ester terminal chain is increased, and the thermal and physical properties of the oxazepine core. The physical properties of the title compounds were studied by Fourier transform infrared spectroscopy (FTIR) and high resolution nuclear magnetic resonance (NMR) (^{1}H and ^{13}C, homonuclear ^{1}H-^{1}H COSY, heteronuclear ^{1}H-^{13}C HMQC, and ^{1}H and ^{13}C HMBC correlation studies). 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).

2. Experimental

2.1. Material

Hexanoic acid, octanoic acid, decanoic acid, and dodecanoic acid (Merck). Tetradecanoic acid, hexadecanoic acid, octadecanoic acid, maleic anhydride, succinic anhydride, phthalic anhydride, N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), 4-hydroxybenzaldehyde, and 4-hydroxyaniline (Aldrich). All reagents were used directly without further purification. Thin-layer chromatography was performed using aluminium-backed silica gel plates (Merck 60F254), and examined under UV light. Column chromatography was performed under gravity using Merck 60 mesh silica gel.

2.2. Equipment

Elemental microanalysis (CHN) was performed using a Perkin Elmer 2400 LS Series CHNS/O analyzer. FTIR measurements on intermediates and title compounds were performed by the use of KBr pellets and the spectra recorded in the range of 4000–400 cm^{-1} using a Perkin Elmer 2000-FTIR spectrophotometer. NMR spectra were recorded in deuterated dimethyl sulfoxide (DMSO-d$_6$) at 298 K on a Bruker 400 MHz Ultrashied FT-NMR spectrometer equipped with a 5 mm BBI inverse gradient probe. Chemical shifts were referenced to an internal tetramethylsilane (TMS) standard. The concentration of solute was 50 mg in 1.0 ml of (DMSO-d$_6$). Standard Bruker pulse programs [26] were used throughout the entire experiment. The mesomorphic textures were studied using a Carl Zeiss Axioskop 40 polarizing microscope equipped with a Mettler FP5 hot stage. The heating and cooling temperatures were monitored by a Linkam TMS94 temperature controller. Phase transition temperatures and enthalpies were determined by Elmer Pyris 1 DSC at a heating and cooling rate of $\pm$ 5°C min^{-1}, respectively.

Computer modeling procedures used in this study were performed using Hyperchem 8.0.8 (Hypercube Inc.) in the LC institute of Kent state University, USA. The compounds in the data set were entered as two-dimensional sketches into Hyperchem. Full optimization geometry were performed using the semiempirical method AM1 running on Hyperchem.

2.3. Synthesis

The syntheses of the intermediates **1–7** and the target compounds **1a–7a**, **1b–7b**, and **1c–7c**, were carried out using the experimental procedure illustrated in Scheme 1. Representative syntheses are described below.

2.3.1. 4-(4-(Hexanoyloxy)benzylideneamino)phenyl hexanoate

The recrystallized 4-(4-hydroxybenzylideneamino)phenol 21.308 g (0.1 mol), hexanoic acid (0.25 mol), and DMAP 12.21 g (0.5 mol) were dissolved in 60 ml of DCM and stirred at 0°C and DCC 20.6 g (0.1 mol, dissolved in 20 ml of DCM) was added dropwise, while stirring at 0°C for 1 hr and then stirred at room temperature for another 5 hr. Finally, the mixture was filtered and excess solvent was removed from the filtrate by evaporation. The solid was recrystallized from absolute ethanol. The subsequent members of the homologous series were prepared and purified using the same method. Yield 53%. Anal. found for $C_{25}H_{31}NO_4$, C 73.47, H 7.53, N 3.49. Calc (%) C 73.32, H 7.63, N 3.42. IR:υ_{max} (cm^{-1}): 2960, 2930, 1768, 1618, 1600, 1590. ^{1}H NMR δ (ppm): 8.41 (1H, s), 7.83 (2H, d), 7.52 (2H, d), 7.42 (2H, d), 7.29 (2H, d), 2.63–2.76 (4H, CH_2COO), 1.72–1.86 (4H, m, CH_2), 0.95 (6H, t, CH_3); ^{13}C NMR δ (ppm): 15.57 (CH_3), 20.45 (CH_2), 35.44, 35.80 (CH_2CO), 116.43, 121.75, 123.44, 125.12, 133.12, 147.20 (Ar-C), 160.68, 164.11 (Ar-C-O), 172.08, 174.32 (COO).

2.3.2. Synthesis of compounds 1a–7a, 1b–7b, and 1c–7c

The title compounds were synthesized according to the method described by Tang *et al.* [27]. The synthetic method will be described as for compound **1a**. Compound **1a** was obtained from reaction of 0.098 g (0.001 mol) of maleic anhydride and 0.409 g (0.001 mol) of 4-(4-(hexanoyloxy)benzylideneamino)phenyl hexanoate in CH_3N at 80°C for 1 hr. The reaction was monitored by TLC and the solvent was distilled off in vacuo. The solid product thus obtained was filtered and recrystallized. The analytical, FTIR, ^1H and ^{13}C NMR for compounds **1a–7b**, **1b–7b**, and **1c–7c** are summarized as follows:

1a: (*Z*)-2,3-bis(4-hexanoate)phenyl)-1,3-oxazepine-4,7-diones, Yield 72% m.p. 140–141°C. Anal: found for $C_{29}H_{33}NO_7$ (%): C 68.71, H 6.74, N 2.62. Calc (%), C 68.62, H 6.55, N 2.76. IR: (KBr) υ_{max} (cm^{-1}): 3033, 2957, 2931, 1768, 1642, 1602, 1588. ^{1}HNMR δ (ppm) (DMSO): 9.61 (1H, s), 8.23 (2H, d, $J = 8.82$ Hz), 7.82 (2H, d, $J = 8.35$ Hz), 7.66 (2H, d, $J = 8.50$ Hz), 7.31 (2H, d, $J = 8.82$ Hz), 6.63 (1H, d, $J = 12.41$ Hz), 6.30 (1H, d, $J = 12.57$ Hz), 2.71–2.86 (4H, CH_2COO), 1.69–1.76 (4H, m, CH_2), 0.89 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.30 (CH_3), 21.47 (CH_2), 36.90, 37.47 (CH_2CO), 90.15 (C-N), 115.67, 120.12, 122.01, 124.12, 136.40, 145.01(Ar-C), 159.43, 162.67 (Ar-C-O), 166.23, 167.78 (C=O). 174.25, 176.00 (COO).

2a: (*Z*)-2,3-bis(4-octanoate)phenyl)-1,3-oxazepine-4,7-diones, Yield 62% m.p. 144–145°C. Anal: found for $C_{33}H_{41}NO_7$ (%): C 70.21, H 7.26, N 2.53. Calc (%), C 70.32, H 7.33, N 2.48. IR: (KBr) υ_{max} (cm^{-1}): 3028, 2965, 2929, 1770, 1635, 1601, 1589. ^{1}HNMR δ (ppm) (DMSO): 9.57 (1H, s), 8.21 (2H, d, $J = 8.77$ Hz), 7.84 (2H, d, $J = 8.40$ Hz), 7.64 (2H, d, $J = 8.49$ Hz), 7.30 (2H, d, $J = 8.80$ Hz), 6.60 (1H, d, $J = 12.49$ Hz), 6.33 (1H, d, $J = 12.50$ Hz), 2.73–2.88 (4H, CH_2COO), 1.70–1.83 (4H, m, CH_2), 0.88 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.78 (CH_3), 20.35 (CH_2), 35.26, 37.19 (CH_2CO), 90.48 (C-N), 115.90, 120.62, 122.81, 124.90, 136.00, 145.34 (Ar-C), 160.28, 163.17 (Ar-C-O), 166.45, 167.00 (C=O), 174.00, 176.47 (COO).

3a: (*Z*)-2,3-bis(4-decyloate)phenyl)-1,3-oxazepine-4,7-diones, Yield 70% m.p. 148–149°C. Anal: found for $C_{37}H_{49}NO_7$ (%): C 71.83, H 7.90, N 2.18. Calc (%), C 71.70, H 7.97, N 2.26. IR: (KBr) υ_{max} (cm^{-1}): 3030, 2963, 2929, 1774, 1638, 1600, 1582. ^{1}HNMR δ (ppm) (DMSO): 9.50 (1H, s), 8.29 (2H, d, $J = 8.71$ Hz), 7.88 (2H, d, $J = 8.49$ Hz), 7.63 (2H, d, $J = 8.48$ Hz), 7.35 (2H, d, $J = 8.87$ Hz), 6.64 (1H, d, $J = 12.60$ Hz), 6.32 (1H, d, $J = 12.47$ Hz), 2.71–2.86 (4H, CH_2COO), 1.68–1.80 (4H, m, CH_2), 0.90 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.42 (CH_3), 20.89 (CH_2), 36.01, 37.89 (CH_2CO), 89.77 (C-N), 116.07, 122.31, 123.09, 125.57, 136.24, 146.04 (Ar-C), 159.46, 162.67 (Ar-C-O), 165.47, 166.29 (C=O), 173.53, 175.89 (COO).

4a: (*Z*)-2,3-bis(4-dodecyloate)phenyl)-1,3-oxazepine-4,7-diones, Yield 74% m.p. 153–154°C. Anal: found for $C_{41}H_{57}NO_7$ (%):C 72.67, H 8.62, N 2.01. Calc (%), C 72.86, H 8.50, N 2.07. IR: (KBr) υ_{max} (cm^{-1}): 3034, 2960, 2928, 1770, 1630, 1605, 1589. ^{1}HNMR δ (ppm) (DMSO): 9.62 (1H, s), 8.33 (2H, d, $J = 8.62$ Hz), 7.89 (d, $J = 8.45$ Hz, 2H), 7.60 (d, $J = 8.53$ Hz, 2H), 7.32 (2H, d, $J = 8.82$ Hz), 6.62 (1H, d, $J = 12.55$ Hz), 6.29 (1H, d, $J = 12.43$ Hz), 2.70–2.84 (4H, CH_2COO), 1.70–1.85 (4H, m, CH_2), 0.88 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.38 (CH_3), 22.03 (CH_2), 35.99, 37.52 (CH_2CO), 90.03 (C-N), 116.57, 122.76, 123.20, 125.22, 136.00, 146.04 (Ar-C), 160.71, 164.03 (Ar-C-O), 168.12, 169.45 (C=O), 172.98, 174.90 (COO).

5a: (*Z*)-2,3-bis(4-tetracyloate)phenyl)-1,3-oxazepine-4,7-diones, Yield 69% m.p. 155–156°C. Anal: found for $C_{45}H_{65}NO_7$ (%): C 73.63, H 8.99, N 1.83. Calc (%), C 73.84, H 8.95, N 1.91. IR: (KBr) υ_{max} (cm^{-1}): 3031, 2966, 2935, 1764, 1633, 1602, 1585. ^{1}HNMR δ (ppm) (DMSO): 9.60 (1H, s), 8.35 (2H, d, $J = 8.66$ Hz), 7.81 (2H, d, $J = 8.52$ Hz), 7.63 (2H, d, $J = 8.50$ Hz), 7.34 (2H, d, $J = 8.73$ Hz), 6.60 (1H, d, $J = 12.64$ Hz), 6.28 (1H, d, $J = 12.42$ Hz), 2.64–2.82 (4H, CH_2COO), 1.62–1.81 (4H, m, CH_2), 0.89 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.30 (CH_3), 21.78 (CH_2), 35.80, 37.38 (CH_2CO), 90.19 (C-N), 116.00, 121.22, 122.30, 125.29, 136.48, 146.00 (Ar-C), 160.71, 164.58 (Ar-C-O), 167.41, 168.96 (C=O), 172.47, 174.28 (COO).

6a: (*Z*)-2,3-bis(4-hexacyloate)phenyl)-1,3-oxazepine-4,7-diones, Yield 72% m.p. 159–160°C. Anal: found for $C_{49}H_{73}NO_7$ (%): C 74.85, H 9.27, N 1.64. Calc (%), C 74.68, H 9.34, N 1.78. IR: (KBr) υ_{max} (cm^{-1}): 3035, 2958, 2931, 1765, 1636, 1600, 1584. ^{1}HNMR δ (ppm) (DMSO): 9.69 (1H, s), 8.27 (2H, d, $J = 8.77$ Hz), 7.84 (2H, d, $J = 8.58$ Hz), 7.60 (2H, d, $J = 8.42$ Hz), 7.28 (2H, d, $J = 8.81$ Hz), 6.61 (1H, d, $J = 12.35$ Hz), 6.28 (1H, d, $J = 12.57$ Hz), 2.72–2.88 (4H, CH_2COO), 1.65–1.73 (4H, m, CH_2), 0.93 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.79 (CH_3), 20.00 (CH_2), 35.27, 37.37 (CH_2CO), 90.00 (C-N), 114.88, 120.10, 121.18, 124.71, 135.70, 146.08 (Ar-C), 160.21, 164.04 (Ar-C-O), 165.88, 168.05 (C=O), 174.90, 176.57 (COO).

7a: (*Z*)-2,3-bis(4-octadecyloate)phenyl)-1,3-oxazepine-4,7-diones, Yield 62% m.p. 163–164°C. Anal: found for $C_{53}H_{81}NO_7$ (%): C 75.29, H 9.82, N 1.60. Calc, (%) C 75.40, H 9.67, N 1.66. IR: (KBr) υ_{max} (cm^{-1}): 3033, 2958, 2930, 1760, 1630, 1602, 1580. ^{1}HNMR δ (ppm) (DMSO): 9.64 (1H, s), 8.30 (2H, d, $J = 8.74$ Hz), 7.82 (2H, d, $J = 8.57$ Hz), 7.67 (2H, d, $J = 8.50$ Hz), 7.32 (2H, d, $J = 8.89$ Hz), 6.60 (1H, d, $J = 12.47$ Hz), 6.27 (1H, d, $J = 12.60$ Hz), 2.70–2.87 (4H, CH_2COO), 1.70–1.82 (4H, m, CH_2), 0.91 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.42 (CH_3), 21.34 (CH_2), 34.03, 36.93 (CH_2CO), 90.66 (C-N), 115.04, 121.78, 122.01, 125.32, 136.11, 146.00 (Ar-C), 158.89, 164.57 (Ar-C-O), 167.25, 169.41 (C=O), 172.26, 175.00 (COO).

1b: (*Z*)-2,3-bis(4-hexanoate)phenyl)-1,3-oxazepane-4,7-diones, Yield 60% m.p. 135–136°C. Anal: found for $C_{29}H_{35}NO_7$ (%):C 68.52, H 6.77, N 2.69. Calc (%), C 68.35, H 6.92, N 2.75. IR: (KBr) υ_{max} (cm^{-1}): 3020, 2966, 2927, 1760, 1633, 1600, 1579. ^{1}HNMR δ (ppm) (DMSO): 9.50 (1H, s), 8.37 (2H, d, $J = 8.80$ Hz), 7.79 (2H, d, $J = 8.47$ Hz), 7.61 (2H, d, $J = 8.59$ Hz), 7.28 (2H, d, $J = 8.92$ Hz), 2.20 (1H, t, $J = 7.30$ Hz), 2.43 (1H, t, $J = 7.03$ Hz), 2.80–2.95 (4H, CH_2COO), 1.63–1.70 (4H, m, CH_2), 0.89 (6H, t, CH_3). ^{13}C NMR δ (ppm): 14.00 (CH_3), 20.03 (CH_2), 34.00, 36.56 (CH_2CO), 90.34 (C-N), 116.67, 121.89, 122.49, 125.02, 136.34, 146.00 (Ar-C), 161.09, 163.20 (Ar-C-O), 165.36, 167.86 (C=O), 169.00, 171.23 (COO).

2b: (*Z*)-2,3-bis(4-octanoate)phenyl)-1,3-oxazepane-4,7-diones, Yield 66% m.p. 140–141°C. Anal: found for $C_{33}H_{43}NO_7$ (%): C 70.21, H 7.49, N 2.57. Calc (%),C 70.06, H 7.66, N 2.48. IR: (KBr) υ_{max} (cm^{-1}): 3018, 2962, 2922, 1768, 1629, 1604, 1583. ^{1}HNMR δ (ppm) (DMSO): 9.59 (1H, s), 8.39 (2H, d, $J = 8.84$ Hz), 7.77 (2H, d, $J = 8.50$ Hz), 7.60 (2H, d, $J = 8.52$ Hz), 7.23 (2H, d, $J = 8.86$ Hz), 2.21 (1H, t, $J = 7.35$ Hz), 2.40 (1H, t, $J = 7.09$ Hz), 2.83–2.98 (4H, CH_2COO), 1.61–1.71 (4H, m, CH_2), 0.88 (6H, t, CH_3). ^{13}C NMR δ (ppm): 14.73 (CH_3), 20.57 (CH_2), 33.51, 35.35 (CH_2CO), 90.22 (C-N), 116.04, 122.25, 123.12, 126.00, 135.31, 146.60 (Ar-C), 160.65, 163.07 (Ar-C-O), 166.24, 168.37 (C=O), 170.47, 173.76 (COO).

3b: (*Z*)-2,3-bis(4-decyloate)phenyl)-1,3-oxazepane-4,7-diones, Yield 62% m.p. 144–145°C. Anal: found for $C_{37}H_{51}NO_7$ (%): C 71.26, H 8.40, N 2.13. Calc (%),C 71.47, H 8.27, N 2.25. IR: (KBr) υ_{max} (cm^{-1}): 3014, 2952, 2928, 1764, 1626, 1600, 1587. ^{1}HNMR δ (ppm) (DMSO): 9.50 (1H, s), 8.34 (2H, d, $J = 8.78$ Hz), 7.74 (2H, d, $J = 8.63$ Hz), 7.59 (2H, d, $J = 8.62$ Hz), 7.26 (2H, d, $J = 8.81$ Hz), 2.23 (1H, t, $J = 7.27$ Hz), 2.46 (1H, t, $J = 7.03$ Hz), 2.85–2.97 (4H, CH_2COO), 1.64–1.76 (4H, m, CH_2), 0.93 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.38 (CH_3), 21.82 (CH_2), 34.13, 36.03 (CH_2CO), 90.38 (C-N), 116.87, 121.02, 122.30, 126.50, 134.51, 146.21 (Ar-C), 159.79, 162.62 (Ar-C-O), 166.90, 168.12 (C=O), 172.41, 174.80 (COO).

4b: (*Z*)-2,3-bis(4-dodecyloate)phenyl)-1,3-oxazepane-4,7-diones, Yield 76% m.p. 149–150°C. Anal: found for $C_{41}H_{59}NO_7$ (%): C 72.88, H 8.64, N 2.19. Calc (%), C 72.64, H 8.77, N 2.07. IR: (KBr) υ_{max} (cm^{-1}): 3022, 2964, 2932, 1770, 1629, 1603, 1584. ^{1}HNMR δ (ppm)

(DMSO): 9.63 (1H, s), 8.38 (2H, d, *J* = 8.84 Hz), 7.78 (2H, d, *J* = 8.60 Hz), 7.62 (2H, d, *J* = 8.61 Hz), 7.31 (2H, d, *J* = 8.87 Hz), 2.25 (1H, t, *J* = 7.32 Hz), 2.48 (1H, t, *J* = 7.13 Hz), 2.87–2.99 (4H, CH_2COO), 1.68–1.79 (4H, m, CH_2), 0.92 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.02 (CH_3), 20.48 (CH_2), 33.93, 35.64 (CH_2CO), 90.71 (C-N), 116.20, 121.45, 122.21, 126.03, 134.47, 146.11 (Ar-C), 159.35, 162.22 (Ar-C-O), 167.15, 169.78 (C=O), 172.89, 174.58 2c (COO).

5b: (*Z*)-2,3-bis(4-tetracyloate)phenyl)-1,3-oxazepane-4,7-diones, Yield 76% m.p. 152–153°C. Anal: found for $C_{45}H_{67}NO_7$ (%): C 73.76, H 9.11, N 1.98. Calc (%),C 73.63, H 9.20, N 1.91. IR: (KBr) υ_{max} (cm^{-1}): 3030, 2961, 2929, 1766, 1635, 1600, 1589. ^{1}HNMR δ (ppm) (DMSO): 9.62 (1H, s), 8.35 (2H, d, *J* = 8.87 Hz), 7.76 (2H, d, *J* = 8.67 Hz), 7.61 (2H, d, *J* = 8.53 Hz), 7.29 (2H, d, *J* = 8.89 Hz), 2.22 (1H, t, *J* = 7.30 Hz), 2.45 (1H, t, *J* = 7.07 Hz), 2.86–2.94 (4H, CH_2COO), 1.65–1.73 (4H, m, CH_2), 0.87 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.94 (CH_3), 21.03 (CH_2), 32.16, 34.28 (CH_2CO), 90.69 (C-N), 116.78, 122.21, 122.94, 126.19, 134.90, 146.60 (Ar-C), 158.49, 161.03 (Ar-C-O), 166.58, 168.02 (C=O), 173.01, 174.90 (COO).

6b: (*Z*)-2,3-bis(4-hexacyloate)phenyl)-1,3-oxazepane-4,7-diones, Yield 64% m.p. 157–158°C. Anal: found for $C_{49}H_{75}NO_7$ (%): C74.36, H 9.40, N 1.89. Calc (%), C 74.49, H 9.57, N 1.77. IR: (KBr) υ_{max} (cm^{-1}): 3034, 2960, 2937, 1770, 1629, 1604, 1588. ^{1}HNMR δ (ppm) (DMSO): 9.58 (1H, s), 8.33 (2H, d, *J* = 8.82 Hz), 7.70 (2H, d, *J* = 8.62 Hz), 7.60 (2H, d, *J* = 8.50 Hz), 7.33 (2H, d, *J* = 8.83 Hz), 2.21 (1H, t, *J* = 7.29 Hz), 2.46 (1H, t, *J* = 7.09 Hz), 2.84–2.96 (4H, CH_2COO), 1.69–1.75 (4H, m, CH_2), 0.85 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.07 (CH_3), 20.38 (CH_2), 32.76, 34.05 (CH_2CO), 90.18 (C-N), 116.17, 121.70, 122.03, 125.73, 134.00, 146.14 (Ar-C), 158.88, 160.27 (Ar-C-O), 165.40, 167.89 (C=O), 174.41, 176.23 (COO).

7b: (*Z*)-2,3-bis(4-octadecyloate)phenyl)-1,3-oxazepane-4,7-diones, Yield 64% m.p. 160–161°C. Anal: found for $C_{53}H_{83}NO_7$ (%): C 75.40, H 9.71, N 1.59. Calc (%), C 75.22, H 9.89, N 1.66. IR: (KBr) υ_{max} (cm^{-1}): 3030, 2959, 2933, 1769, 1630, 1600, 1581. ^{1}HNMR δ (ppm) (DMSO): 9.63 (1H, s), 8.36 (2H, d, *J* = 8.89 Hz), 7.74 (2H, d, *J* = 8.61 Hz), 7.61 (2H, d, *J* = 8.43 Hz), 7.31 (2H, d, *J* = 8.80 Hz), 2.23 (1H, t, *J* = 7.39 Hz), 2.48 (1H, t, *J* = 7.11 Hz), 2.85–2.98 (4H, CH_2COO), 1.71–1.79 (4H, m, CH_2), 0.88 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.88 (CH_3), 21.08 (CH_2), 32.80, 34.69 (CH_2CO), 90.06 (C-N), 116.00, 121.31, 122.67, 125.23, 134.58, 146.63 (Ar-C), 158.11, 160.68 (Ar-C-O), 163.90, 165.03 (C=O), 173.89, 175.14 (COO).

1c: 3, 4-bis(4-hexanoate)phenyl)-[*e*][1,3]oxazepine-1,5-diones, Yield 64% m.p. 140–141°C. Anal: found for $C_{33}H_{35}NO_7$ (%): C 71.20, H 6.19, N 2.69. Calc (%), C 71.08, H 6.33, N 2.51. IR: (KBr) υ_{max} (cm^{-1}): 3010, 2940, 2931, 1759, 1628, 1604, 1587. ^{1}HNMR δ (ppm) (DMSO): 9.70 (1H, s), 8.22 (2H, d, *J* = 8.60 Hz), 7.50 (2H, d, *J* = 8.44 Hz), 7.41 (2H, d, *J* = 8.27 Hz), 7.18 (2H, d, *J* = 8.92 Hz), 8.41 (1H, d, *J* = 8.06 Hz), 7.68 (1H, t, *J* = 7.91 Hz), 7.72 (1H, t, *J* = 8.20 Hz), 7.32 (1H, d, *J* = 8.09 Hz), 2.85–2.98 (4H, CH_2COO), 1.68–1.74 (4H, m, CH_2), 0.91 (6H, t, CH_3). ^{13}C NMR δ (ppm): 14.31 (CH_3), 20.84 (CH_2), 33.01, 35.79 (CH_2CO), 89.78 (C-N), 116.70, 122.01, 123.01, 125.88, 134.20, 146.10 (Ar-C), 160.19, 162.23 (Ar-C-O), 166.61, 168.92 (C=O), 175.01, 177.13 (COO),.

2c: 3, 4-bis(4-octanoate)phenyl)-[*e*][1,3]oxazepine-1,5-diones, Yield 70% m.p. 144–145°C. Anal: found for $C_{37}H_{43}NO_7$ (%): C 72.55, H 7.16, N 2.17. Calc (%), C 72.41, H 7.06, N 2.28. IR: (KBr) υ_{max} (cm^{-1}): 3014, 2945, 2930, 1766, 1625, 1601, 1582. ^{1}HNMR δ (ppm) (DMSO): 9.72 (1H, s), 8.21 (2H, d, *J* = 8.62 Hz), 7.53 (2H, d, *J* = 8.66 Hz), 7.40 (2H, d, *J* = 8.30 Hz), 7.15 (2H, d, *J* = 8.99 Hz), 8.47 (1H, d, *J* = 8.22 Hz), 7.65 (1H, t, *J* = 7.90 Hz), 7.75 (1H, t, *J* = 8.19 Hz), 7.31 (1H, d, *J* = 8.14 Hz), 2.81–2.95 (4H, CH_2COO), 1.65–1.77 (4H, m, CH_2), 0.90 (6H, t, CH_3). ^{13}C NMR δ (ppm): 14.28 (CH_3), 21.57 (CH_2), 32.48, 34.18 (CH_2CO), 89.22 (C-N), 116.94, 122.40, 123.14, 125.30, 134.32, 146.00 (Ar-C), 160.00, 162.87 (Ar-C-O), 166.20, 168.05 (C=O), 175.00, 177.68 (COO),

3c: 3, 4-bis(4-decyloate)phenyl)-[*e*][1,3]oxazepine-1,5-diones, Yield 60% m.p. 147–148°C. Anal: found for $C_{41}H_{51}NO_7$ (%): C 73.40, H 7.78, N 2.20. Calc (%), C 73.52, H 7.67, N 2.09. IR: (KBr) υ_{max} (cm^{-1}): 3020, 2949, 2927, 1768, 1620, 1600, 1589. ^{1}HNMR δ (ppm) (DMSO): 9.70 (1H, s), 8.25 (2H, d, J = 8.70 Hz), 7.55 (2H, d, J = 8.70 Hz), 7.42 (2H, d, J = 8.23 Hz), 7.19 (2H, d, J = 8.70 Hz), 8.42 (1H, d, J = 8.14 Hz), 7.60 (1H, t, J = 7.88 Hz), 7.74 (1H, t, J = 8.11 Hz), 7.30 (1H, d, J = 8.20 Hz), 2.85–2.99 (4H, CH_2COO), 1.67–1.76 (4H, m, CH_2), 0.92 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.06 (CH_3), 20.16 (CH_2), 32.94, 34.88 (CH_2CO), 90.02 (C-N), 116.45, 121.87, 122.62, 125.10, 134.00, 146.17 (Ar-C), 160.78, 162.09 (Ar-C-O), 165.31, 166.51 (C=O), 175.41, 177.45 (COO).

4c: 3, 4-bis(4-dodecyloate)phenyl)-[*e*][1,3]oxazepine-1,5-diones, Yield 71% m.p. 150–151°C. Anal: found for $C_{45}H_{59}NO_7$ (%): C 74.66, H 8.08, N 1.81. Calc (%),C 74.45, H 8.19, N 1.93. IR: (KBr) υ_{max} (cm^{-1}): 3025, 2943, 2930, 1770, 1626, 1601, 1584. ^{1}HNMR δ (ppm) (DMSO): 9.74 (1H, s), 8.26 (2H, d, J = 8.65 Hz), 7.53 (2H, d, J = 8.63 Hz), 7.48 (2H, d, J = 8.41 Hz), 7.14 (2H, d, J = 8.55 Hz), 8.40 (1H, d, J = 8.20 Hz), 7.63 (1H, t, J = 7.81 Hz), 7.73 (1H, t, J = 8.06 Hz), 7.34 (1H, d, J = 8.31 Hz), 2.84–2.96 (4H, CH_2COO), 1.64–1.75 (4H, m, CH_2), 0.90 (6H, t, CH_3). ^{13}C NMR δ (ppm): 14.38 (CH_3), 21.61 (CH_2), 32.72, 34.26 (CH_2CO), 90.77 (C-N), 115.66, 121.20, 122.01, 125.00, 134.58, 146.14 (Ar-C), 160.25, 162.38 (Ar-C-O), 164.00, 165.21 (C=O), 174.54, 176.15 (COO).

5c: 3, 4-bis(4-tetracyloate)phenyl)-[*e*][1,3]oxazepine-1,5-diones, Yield 75% m.p. 162–163°C. Anal: found for $C_{49}H_{67}NO_7$ (%): C 75.14, H 8.79, N 1.66. Calc (%), C 75.25, H 8.64, N 1.79. IR: (KBr) υ_{max} (cm^{-1}): 3022, 2940, 2933, 1768, 1623, 1600, 1580. ^{1}HNMR δ (ppm) (DMSO): 9.73 (1H, s), 8.24 (2H, d, J = 8.62 Hz), 7.51 (2H, d, J = 8.73 Hz), 7.44 (2H, d, J = 8.55 Hz), 7.11 (2H, d, J = 8.68 Hz), 8.45 (1H, d, J = 8.33 Hz), 7.66 (1H, t, J = 7.74 Hz), 7.70 (1H, t, J = 8.19 Hz), 7.36 (1H, d, J = 8.45 Hz), 2.80–2.92 (4H, CH_2COO), 1.61–1.73 (4H, m, CH_2), 0.86 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.35 (CH_3), 20.50 (CH_2), 33.08, 34.83 (CH_2CO), 90.27 (C-N), 116.27, 122.24, 123.45, 125.78, 134.41, 146.20 (Ar-C), 161.17, 163.07 (Ar-C-O), 163.57, 165.65 (C=O), 174.03, 176.97 (COO).

6c: 3, 4-bis(4-hexacyloate)phenyl)-[*e*][1,3]oxazepine-1,5-diones, Yield 78% m.p. 165–166°C. Anal: found for $C_{53}H_{75}NO_7$ (%): C 75.83, H 9.21, N 1.50. Calc (%), C 75.95, H 9.02, N 1.67. IR: (KBr) υ_{max} (cm^{-1}): 3016, 2944, 2930, 1765, 1626, 1602, 1579. ^{1}HNMR δ (ppm) (DMSO): 9.74 (1H, s), 8.29 (2H, d, J = 8.51 Hz), 7.50 (2H, d, J = 8.70 Hz), 7.49 (2H, d, J = 8.29 Hz), 7.13 (2H, d, J = 8.61 Hz), 8.48 (1H, d, J = 8.30 Hz), 7.65 (1H, t, J = 7.90 Hz), 7.78 (1H, t, J = 8.13 Hz), 7.31 (1H, d, J = 8.45 Hz), 2.82–2.96 (4H, CH_2COO), 1.64–1.77 (4H, m, CH_2), 0.88 (6H, t, CH_3). ^{13}C NMR δ (ppm): 14.39 (CH_3), 21.89 (CH_2), 32.72, 34.90 (CH_2CO), 90.89 (C-N), 115.59, 121.00, 121.19, 124.39, 134.83, 146.09 (Ar-C), 160.42, 162.61 (Ar-C-O), 164.71, 166.28 (C=O), 174.00, 176.10 (COO).

7c: 3, 4-bis(4octacyloate)phenyl)-[*e*][1,3]oxazepine-1,5-diones, Yield 68% m.p. 169–170°C. Anal: found for $C_{57}H_{83}NO_7$ (%): C 76.40, H 9.48, N 1.65. Calc (%), C 76.56, H 9.35, N 1.57. IR: (KBr) υ_{max} (cm^{-1}): 3019, 2940, 2934, 1763, 1620, 1601, 1584. ^{1}HNMR δ (ppm) (DMSO): 9.71 (1H, s), 8.28 (2H, d, J = 8.62 Hz), 7.54 (2H, d, J = 8.65 Hz), 7.46 (2H, d, J = 8.34 Hz), 7.16 (2H, d, J = 8.55 Hz), 8.43 (1H, d, J = 8.41 Hz), 7.60 (1H, t, J = 7.94 Hz), 7.76 (1H, t, J = 8.09 Hz), 7.34 (1H, d, J = 8.40 Hz), 2.85–2.98 (4H, CH_2COO), 1.66–1.78 (4H, m, CH_2), 0.90 (6H, t, CH_3). ^{13}C NMR δ (ppm): 15.40 (CH_3), 20.60 (CH_2), 32.14, 34.51 (CH_2CO), 90.01 (C-N), 116.30, 122.40, 123.20, 125.00, 134.19, 146.20 (Ar-C), 160.79, 162.36 (Ar-C-O), 164.19, 166.80 (C=O), 174.80, 176.06 (COO).

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

Compounds	Transition temperature°C (corresponding enthalpy changes in KJmol^{-1}) Heating/cooling
1a	Cr 140.56 (81.02) I
	Cr 94.34 (−62.18) I
2a	Cr 144.35 (56.78) I
	Cr 98.06 (−31.22) I
3a	Cr 148.75 (69.42) I
	Cr 102.26 (−29.67) I
4a	Cr 153.92 (27.10) I
	Cr 148.40 (−14.81) I
5a	Cr 155.48 (31.46) I
	Cr 138.00 (−33.71) I
6a	Cr 159.68 (74.06) I
	Cr 143.58 (−19.77) I
7a	Cr 163.47 (29.00) I
	Cr$_1$ 151.26 (−19.69) I
1b	Cr$_1$ 78.20 (46.39) Cr$_2$ 135.86 (67.49) I
	Cr$_1$ 84.06 (−17.49) Cr$_2$ 131.38 (−56.08) I
2b	Cr$_1$ 67.79 (78.06) Cr$_2$ 140.53 (64.36) I
	Cr$_1$ 72.11 (−46.17) Cr$_2$ 129.50 (−48.20) I
3b	Cr$_1$ 60.40 (65.38) Cr$_2$ 144.38 (40.94) I
	Cr$_1$ 59.16 (−39.78) Cr$_2$ 98.10 (−66.27) I
4b	Cr$_1$ 90.30 (33.54) Cr$_2$ 149.35 (49.80) I
	Cr$_1$ 64.79(−31.26) Cr$_2$ 90.00 (−28.28) I
5b	Cr$_1$ 85.20 (59.41) Cr$_2$ 152.87 (78.31) I
	Cr$_1$ 80.00 (−47.21) Cr$_2$ 104.63 (−22.50) I
6b	Cr$_1$ 96.30 (28.07) Cr$_2$ 157.39 (19.83) I
	Cr$_1$ 74.25 (−17.95) Cr$_2$ 122.40 (−28.70) I
7b	Cr$_1$ 80.14 (32.41) Cr$_2$ 160.88 (66.81) I
	Cr$_1$ 59.05 (−40.37) Cr$_2$ 119.20 (−81.50) I
1c	Cr$_1$ 60.44 (19.20) Cr$_2$ 127.31(30.19) SmA 140.88 (1.23) I
	Cr$_1$ 74.16 (−43.11) Cr$_2$ 120.11 (−25.30) SmA 133.03 (−2.10) I
2c	Cr$_1$ 66.12 (33.78) Cr$_2$ 132.70 (23.50) SmA 144.76 (4.30) I
	Cr$_1$ 80.63 (−28.67) Cr$_2$ 119.38 (−14.22) SmA 136.59 (−3.67) I
3c	Cr$_1$ 61.70 (49.02) Cr$_2$ 128.17 (70.16) SmA 147.54 (1.27) I
	Cr$_1$ 52.18 (−16.70) Cr$_2$ 125.60 (−40.18) SmA 138.61 (−4.53) I
4c	Cr$_1$ 82.19 (29.70) Cr$_2$ 137.10 (55.90) N 150.86 (0.85) I
	Cr$_1$ 77.30 (−20.62) Cr$_2$ 122.36 (−18.36) N 139.30 (−2.56) I
5c	Cr$_1$ 76.26 (14.32) Cr$_2$ 146.23 (16.51) N 162.91 (2.30)I
	Cr$_1$ 86.93 (−21.83) Cr$_2$ 140.01 (−36.22) N 155.14 (−1.78) I
6c	Cr$_1$ 93.16 (18.30) Cr$_2$ 150.16 (29.11) N 165.48 (3.67) I
	Cr$_1$ 80.52 (−15.90) Cr$_2$ 139.60 (−24.06) N 150.74 (−2.46) I
7c	Cr$_1$ 98.14 (30.11) Cr$_2$ 154.20 (21.28) N 169.63 (0.78) I
	Cr$_1$ 87.49 (−22.96) Cr$_2$ 145.30 (−16.60) N 158.00 (−1.66) I

3. Results and discussion

3.1. The phase transition and mesomorphic behavior of compounds 1a–7a, 1b–7b, and 1c–7c

The traces peak appears in DSC, assigned to the phase transition, and peak temperatures were consistent with those deduced from the POM experiments. The identification of the phases and determination of phase transition temperatures were achieved by POM equipped with a hot stage. Types of mesophase are assigned according to the textures observed under POM and compared with those reported in the literature [28, 29]. The phase transition temperatures for the title compounds **1a**–**7a**, **1b**–**7b**, and **1c**–**7c** are tabulated in Table 1. From this database, it can clearly be shown that compounds **1a**–**7a** are not liquid crystalline and hence only exhibit melting points as revealed by POM and DSC. DSC thermograms of compounds **1a**–**7a** during the heating and cooling process showed only one peak which can be ascribed to the direct isotropization process (Cr-I). The same phenomenon is observed when these compounds were cooled down to within the I–Cr transition. From this series of compounds (**1a–7a**), it can be generalized that melting points increase as the length of the terminal alkyl chain increases (Table 1).

To study and investigate the effects of the type of oxazepinedione core on liquid crystalline behavior, the series compound **1b–7b** were synthesized. All these compounds (**1b–7b**) are nonmesogenic, and upon heating the phase sequence of Cr_1-Cr_2-I observed by DSC thermogram was shown by the presence of two peaks. The peak which is observed at respective temperatures of 78.20°C ($\Delta H = 46.39$), 135.86°C ($\Delta H = 67.49$), 67.79°C ($\Delta H = 78.06$), 140.53°C ($\Delta H = 64.36$), 60.40°C ($\Delta H = 65.38$), 144.38°C ($\Delta H = 40.94$), and 90.30°C ($\Delta H = 33.54$), is assigned to the phase transitions Cr_1-Cr_2 in respective compound **1b–7b**. While the phase transition of Cr_2-I is characterized by the peak which is observed at the temperatures of 149.35°C ($\Delta H = 49.80$), 85.20°C ($\Delta H = 59.41$), 152.87°C ($\Delta H = 78.31$), 96.30°C ($\Delta H = 28.07$), 157.39°C ($\Delta H = 19.83$) and 80.14°C ($\Delta H = 32.41$), and 160.88°C ($\Delta H = 66.81$) in respective compound **1b–7b**.

The two peaks observed from the DSC thermogram upon the cooling process can be characterized as the I-Cr_2-Cr_1 phase sequence as shown in Table 1. The result observed in this series of compounds is very typical and closely related to our previous study [4–6]. It is shown that the melting points increase with an increase in alkyl chain length. This observation is similar to the phenomenon observed for the analogues with the alkyl (N-R) linkages [5].

The mesophases are observed in all compounds **1c–7c**. In general, compounds **1c**, **2c**, and **3c**, all of which have short terminal alkyl chains, exhibited smectic A phases during the heating and cooling process. The formation of a focal-conic fan shaped texture upon the heating process in optical microscopy observations can be assigned to the smectic A phases (Fig. 1a). On the other hand, the DSC thermogram also confirms the formation of a liquid crystalline phase. In compound **1c**, the DSC curves obtained on first heating showed three peaks; the peak observed at 60.44°C with an enthalpy value (ΔH) of 19.20 kJ mol^{-1} is characteristic of Cr_1-Cr_2, while the peak at 127.31°C ($\Delta H = 30.19$ kJ mol^{-1}) is characteristic of mesophase transition Cr_2-SmA. The peak observed at 140.88°C ($\Delta H = 1.23$ kJ mol^{-1}) is characteristic of the SmA-I phase. These phenomena are also observed in compounds **2c** and **3c** (Table 1). Likewise, upon the cooling process, the SmA phase observed for compounds **1c**, **2c**, and **3c** can be characterized by the formation of batonets that coalesce to form a focal conic fan-shaped texture (as shown by optical microscopy observations). The peaks of mesophase (I-SmA) appear at 133.03°C ($\Delta H = -2.10$ kJ mol^{-1}), 136.59°C ($\Delta H = -3.67$ kJ mol^{-1}), and 138.61°C ($\Delta H = -4.53$ KJ mol^{-1}) for respective compounds **1c**, **2c**, and **3c**.

On the other hand, upon the heating and cooling process, compounds **4c–7c** with longer terminal alkyl chains exhibited the nematic phase. Under polarized optical microscopy, the presence of schlieren texture (due to an imperfection of planarity) is characteristic of the nematic phase. Figure 1b shows the nematic phase of compound **7c** at 161.67°C of the heating process. While upon the cooling of the isotropic liquid, small droplets appeared and coalesced to form the classical schlieren or marble texture which is characteristic of a nematic phase (Fig. 1c). The peaks of the mesophase are detected upon the DSC heating process at a temperature of 150.86°C ($\Delta H = 0.85$ kJ mol^{-1}), 162.91°C ($\Delta H = 2.30$ kJ mol^{-1}), 165.48°C ($\Delta H = 3.67$ kJ mol^{-1}), and 169.63°C ($\Delta H = 0.78$ kJ mol^{-1}) with mesophase range (13.76°C, 16.68°C, 15.32°C, and 15.43°C) in respective compounds **4c–7c**. The same phenomena are observed when the compounds are cooled down wherein the I-N phase occurred at 139.30°C ($\Delta H = -2.56$ kJ mol^{-1}), 155.14°C ($\Delta H = -1.78$ kJ mol^{-1}), 150.74°C ($\Delta H = -2.46$ kJ mol^{-1}), and

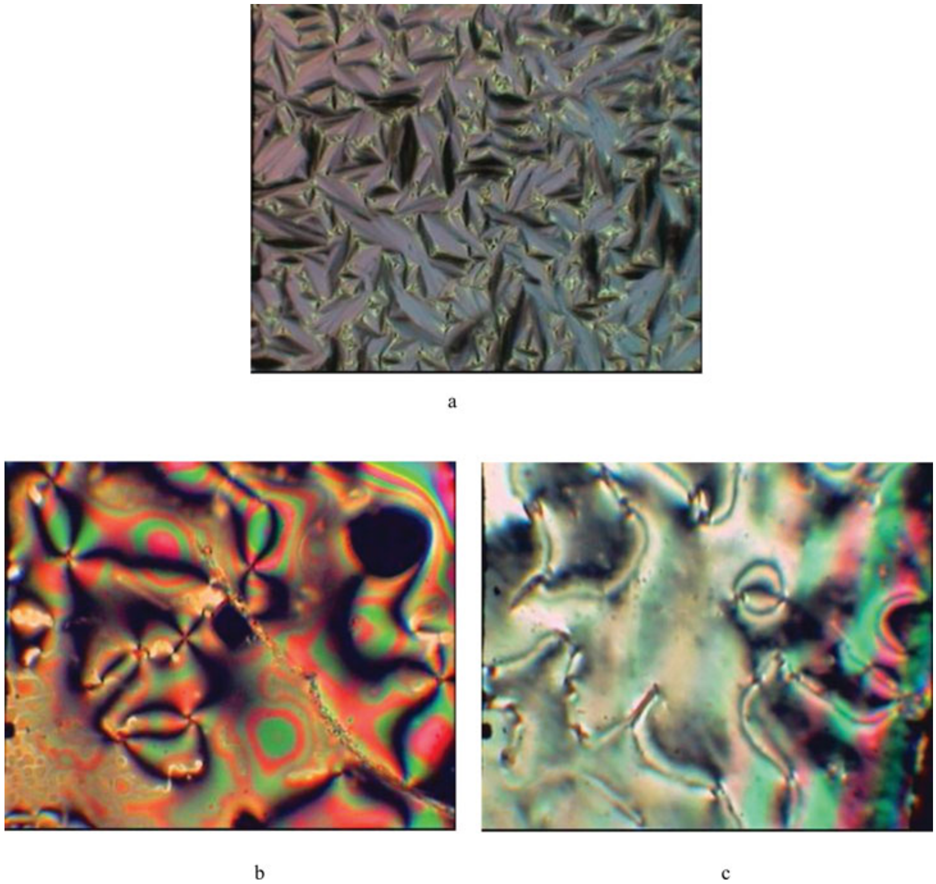

Figure 1. . Photomicrographs of (a) SmA phase shown by 3c at 140.24°C upon cooling; (b) Schlieren texture N phase shown by **7c** 161.67°C upon heating; (c) N phase shown by **7c** at 150.33°C upon cooling.

158.00°C ($\Delta H = -1.66$ kJ mol^{-1}), with a mesophase range (16.94°C, 15.13°C, 11.14°C, and 12.17°C, respectively (Table 1). The DSC of compound **7c** is shown as an example in Fig. 2b. A remarkable feature can be inferred from Fig. 3in which the **1c–7c** compounds upon cooling and heating exhibited well distinguished transition temperatures associated with Cr_1-Cr_2, Cr_2-SmA, SmA-I, I-SmA, SmA-Cr_2, Cr_2-Cr_1, Cr_1-Cr_2, N-I, I-N, N-Cr_2, and Cr_2-Cr_1 [30–33].

Theoretical studies have been carried out in order to understand the effect of the length of the ester linkage in terminal chains with types of oxazepindione ring on the structure and on the formation of mesophases. The data are also in agreement with these experimental results. The presence of a benzene ring adjacent to the seven-membered ring (compounds type c) affords the molecules more flexibility compared with compounds of types a– c (Fig. 4) [5].

3.2. Characterization

The molecular formula for the title compounds were determined by elemental analysis. Molecular structures were characterized by FTIR, ^{1}H and ^{13}C NMR techniques. Reported chemical shifts for 1,3-oxazepines, including the ^{1}H-^{13}C correlation spectra, were used as a reference [4, 5, 34–36] when making assignment related to the chemical shifts of the synthesized compounds.

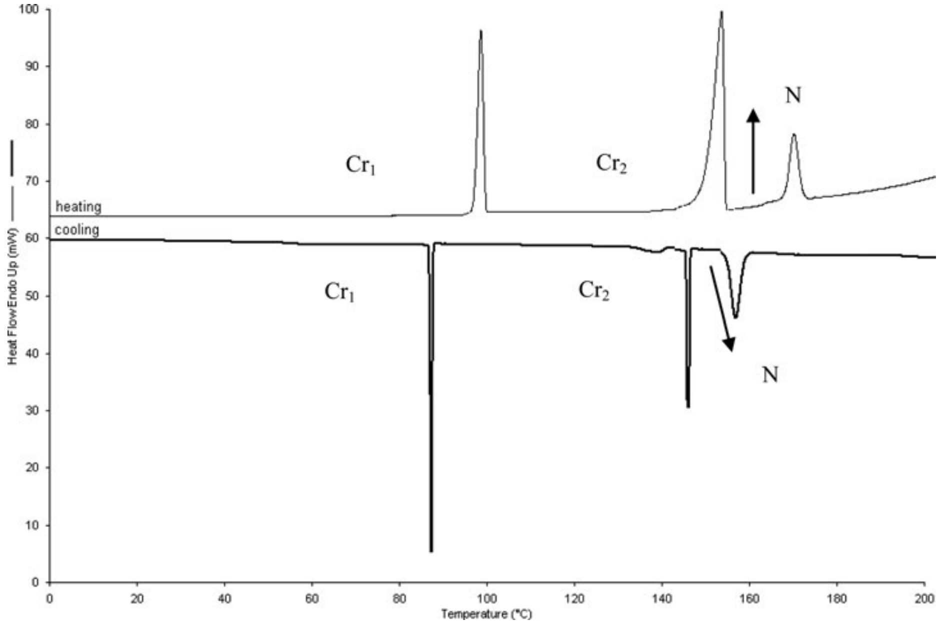

Figure 2. DSC plot on heating and cooling for select compounds 7c.

The FTIR spectra of the title compounds **1a–7b, 1b–7b**, and **1c–7c** exhibit bands that can be assigned to the stretching of aliphatic C-H bands within the frequency range 2922–3035 cm^{-1}. The band appearing with the frequency range 1759–1774 cm^{-1} can be ascribed to the stretching of the carbonyl ester (C=O). Whilst the stretching of the C=O lactone and lactam appears at 1620–1642 cm^{-1}. The band which appears at the frequency 1600–1604 cm^{-1} and 1579–1589 cm^{-1} can be attributed to the C=C of the benzene ring.

A complete structural assignment of compounds has been carried out with the aid of DEPT and two-dimensional ^{1}H-^{1}H COSY, HMQC, and HMBC experiments. A complete assignment of the title compounds **1a–7b**, **1b–7b**, and **1c–7c** have been carried out based on the numbering scheme as shown in Scheme 1. Inspection of the ^{1}H NMR spectra for compounds **1a–7a** shows that the new signals for the heterocyclic ring which appear as a double of doublets within the range of $\delta = 6.27–6.33$ ppm and $\delta = 6.60–6.64$ ppm can be assigned to protons H9 and H10, respectively. Whilst appearing as two triplets in the title compound and **1b–7b** at $\delta = 2.20–2.25$ ppm and $\delta = 2.40–2.48$ ppm. These signals are also assigned with the aid of a COSY experiment through the correlation between H9 and H10. The signal due to

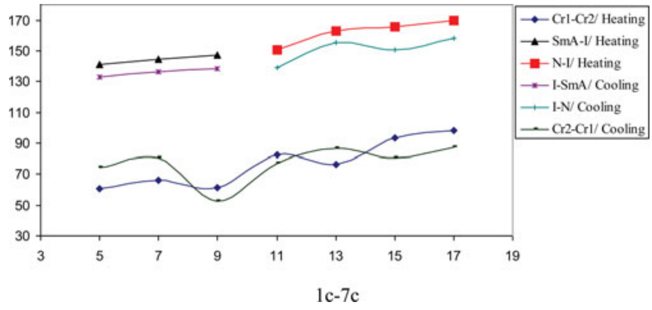

Figure 3. The dependence of phase transition temperatures, T on the number of methylene in the flexible alkyl chain compounds 1c–7c.

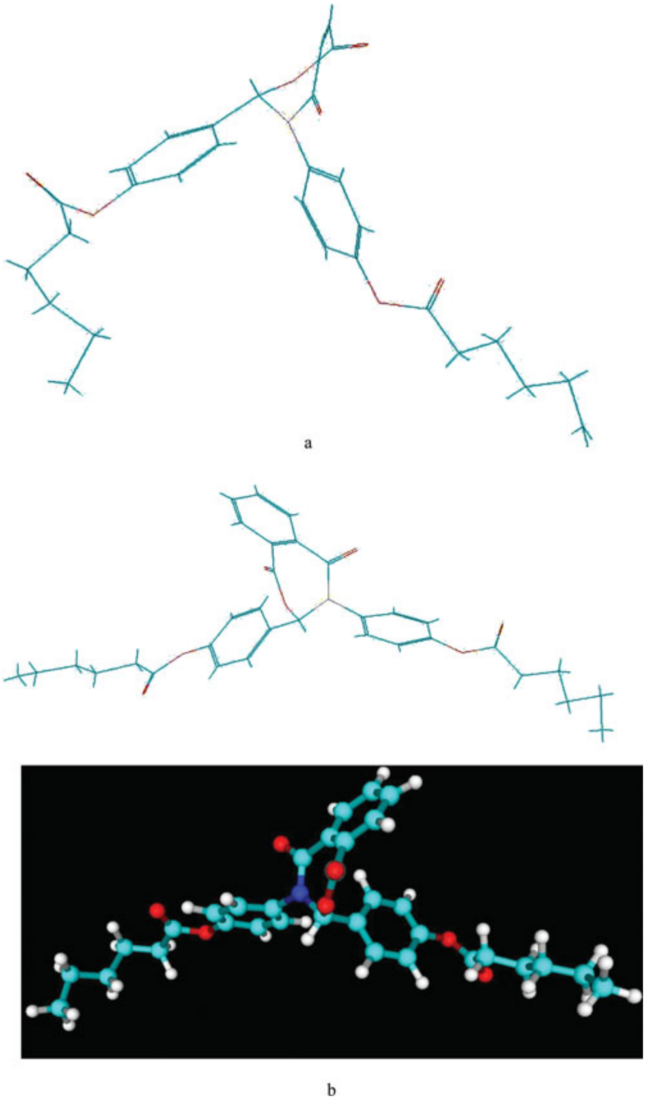

Figure 4. Molecular models of (a) compound 1a; (b) compound 1c using HyperChem program.

proton H7 appears at $\delta = 9.50–9.69$ ppm and $\delta = 9.50–9.63$ ppm relating to compounds of types **a** and **b**. These can be further substantiated by the direct bond heteronuclear correlation with C7 within the frequency range of $\delta = 89.77–90.66$ ppm and $\delta = 90.06–90.71$ ppm. It is an indication of intermolecular cyclization of compounds **1a–7b** and **1b–7b**. The resonances at $\delta = 7.28–8.30$ ppm can be ascribed to the presence of aromatic protons (C_{ph}-H) in type compound type **a**, and these aromatic protons are equivalent. These signals are also assigned with the aid of a COSY experiment through the correlation between H2 (or H6), H4 (or H6) also H13 (or H17) and H14 (or H16). In the same way the COSY reveals that the aromatic protons in compound series **b** H2 (or H6) which are assigned at the range $\delta = 8.33–8.39$ ppm are correlated with the aromatic proton H5 which is assigned as $\delta = 7.59–7.62$ ppm. Likewise, the aromatic protons H13 (or H17) which appear at $\delta = 7.70–7.79$ ppm relate to aromatic protons H14 (or H16), which are assigned to the $\delta = 7.28–7.33$ ppm range.

In the ^{1}H NMR spectra of title compounds **1c–7c** the characteristic resonance signal of aromatic protons is in the range of $\delta = 7.30$–8.29 ppm and these aromatic protons (H12, H13, H14, and H15) are nonequivalent. The same ^{1}H NMR spectra of title compounds **1a–7b**, **1b–7b**, and **1c–7c** also show the resonance owing to the aliphatic protons. These signals are assigned with the aid of the COSY experiment. A triplet at the range of $\delta = 0.85$–0.93 ppm can be assigned to the methyl protons of both terminal alkyl chains. The two subsequent sets of methylene protons at each terminal alkyl chain give rise to two separate sets of multiplets within the range $\delta = 1.61$–1.85 ppm. Two peaks attributable to the presence of methylene protons attached to the ester linking groups (CH_2–COO) are observed within the range $\delta =$ 2.64–2.99 ppm.

The ^{13}C NMR signals are identified by DEPT135 prior to HMQC and HMBC. The resonance due to the aromatic carbons of compounds **1a–7a** give rise to different peaks in the range $\delta = 114.88$–164.75 ppm, while in the $\delta = 116.00$–163.20 ppm range for title compounds **1b–7b**. These signals are based on its correlation with H2 (or H6) and H3 (or H5) in respective compounds **1a–7a** and **1b–7b**. The HMBC spectra of compounds **1c–7c** also show cross peaks between C1 atom with H3 (or H5) atom, C4 atom with H2 (or H6), C16 atom with H18 (or H20) atom, C19 atom with H17 (or H21), C12 atom with H15 atom and C14 atom with H12 atom within the range $\delta = 115.66$–163.07 ppm. The carbonyl (C=O) chemical shift at $\delta = 163.57$–167.25 ppm and $\delta = 165.21$–169.78 ppm are assigned via correlation with H9 and H10 protons in respective compounds **1a–7a** and **1b–7b**, while assigned via correlation with H12 and H15 in title compounds **1c–7c**. The correlation between H7 and C7 is used to assign the chemical shift of the heterocyclic ring at the range of $\delta = 89.77$–90.89 ppm. The observation of signals at $\delta = 174.00$–177.68 ppm can be assigned to the carbons of both ester linking groups (COO). The methylene carbons of terminal alkyl chains are observed at $\delta = 20.00$–22.03 ppm. The peaks assignable to the two methylene carbons attached to the ester linkages are observed at the range of $\delta = 32.14$–36.01 ppm and $\delta = 34.05$–37.89 ppm. A signal due to the methyl carbons of both terminal alkyl chains is observed at $\delta = 14.00$–15.94 ppm.

4. Conclusion

In order to understand the effect of the length of ester linked terminal chains with types of oxazepindione rings on the formation of mesophases, three series of heterocyclic oxazepindione compounds at the core position have been synthesized and their mesomorphic properties analyzed with respect to phase transition temperature and chemical structure. The result indicated that the formation of mesophases depends on the type of oxazepinedione ring and the length of the terminal alkyl chains. Compounds **1a–7a** exhibited Cr-I upon the heating and cooling process, while compounds **1b–7b** were also not mesogenic and only exhibited the transition of Cr_1-Cr_2 upon cooling and heating. The SmA was observed in compounds **1c–3c** which had short terminal alkyl chains during heating and cooling. However, the nematic phases were formed in compounds **4b–7b**. The presence of the nematic (N) phase increases when the length of the terminal alkyl chain increases.

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