

Synthesis, characterization and theoretical study of a new liquid crystal compound with an oxazepine core



AbdulKarim-Talaq Mohammad^{a,*}, Guan-Yeow Yeap^b, Hasnah Osman^b

^aChemistry Department, College of Science, Anbar University, Ramadi, Iraq

^bLiquid Crystal Research Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, Minden 11800, Penang, Malaysia

HIGHLIGHTS

- A novel heterocyclic compounds based liquid crystal were synthesized and identified.
- The relationship of the core structures and the mesomorphic were investigated.
- Theoretical studies was studied.
- The SmA and N phases were observed.
- The nematic phase can only observed in long-chain derivatives.

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ABSTRACT

A novel synthesis of heterocyclic liquid crystal compounds containing a seven-membered 1,3-oxazepine with terminal alkyloxy chains has been carried out. The molecular structures of these compounds were substantiated by FT-IR NMR elemental analysis. The relationship between the structures and the mesomorphic behaviours of their derivatives were investigated. The results showed that the formation of mesophases is strongly dependent on the type of core moiety. All compounds with oxazepinediones and oxazepanediones are non-mesogenic and only exhibit Cr₁–Cr₂ upon cooling and heating. However, the SmA and N phases were observed in the 5,6-benzo [1,3] oxazepine-4,7-diones series of compounds. The study also revealed that the length of the alkyl chain has a significant effect on the liquid crystalline properties; the nematic phase can only observed in long-chain derivatives of 5,6-benzo [1,3] oxazepine-4,7-diones. Theoretical studies are in agreement with our result.

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Introduction

Liquid–crystal synthesis has been investigated due to the successful development and application of liquid crystals, particularly in the area of electro-optical display [1]. In recent decades there has been much interest in the synthesis and characterization of heterocyclic compounds because of their interesting properties, such as liquid–crystallinity and nonlinear optical properties [2–6]. Among these materials, disk-like liquid crystals are particularly worthy of attention [7–10]. Liquid crystalline materials are of great interest, especially because of their unique optical properties. The ability of liquid crystalline phases to regulate reactivity depends on a number of factors, such as the mesophase type and reactant molecular length, flexibility and polarizability [11]. For this reason,

altering the core structure is a significant factor that changes the mesomorphic properties [12]. Heterocycles are of great importance as core units in thermotropic liquid crystals because they can impart lateral and/or longitudinal dipoles combined with changes in the molecular shape [13,14]. The incorporation of heteroatoms result in considerable changes in the corresponding liquid crystalline phases and/or in the physical properties of the observed phases, as most of the heteroatoms (S, O, and N) commonly introduced are more polarizable than carbon [15]. We recently reported the synthesis and characterization of a large number of three type-ring heterocyclic oxazepine LC materials that exhibited one phase, N (nematic) phase [16–18]. This work was one of the first to report the incorporation of the oxazepine moiety in a mesogen structure and clearly demonstrated that this moiety is conducive to the formation of the tilted nematic phase. In a continuation of our work on oxazepine-based mesogen compounds, we will describe the thermal and electro-optic results obtained from the three series of compounds containing the oxazepindione moiety. The phase

* Corresponding author. Tel.: +964 7902529959, +1 330 3895376.

E-mail addresses: drmohamadtaq@gmail.com, mtalaq_gst@kent.edu (A.-T. Mohammad).

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 transform infrared (FT-IR) and high resolution nuclear magnetic resonance NMR (^1H and ^{13}C NMR).

Experimental

Maleic anhydride, succinic anhydride, phthalic anhydride, 4-hydroxybenzaldehyde, 4-hydroxyaniline, 1-bromohexane, 1-bromooctane, 1-bromodecane, 1-bromododecane, 1-bromohexadecane and 1-bromooctadecane (Aldrich), 1-bromotetradecane (Merch), were used directly without further purification. Thin-layer chromatography (TLC) was performed on silica-gel plates.

Synthesis

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

4-(4-hydroxybenzylideneamino)phenol

The imine was synthesized by mixing equimolar amounts of 4-hydroxybenzaldehyde with *p*-hydroxyaniline in absolute ethanol. The reaction mixture was refluxed for 2 h. The solution was then allowed to cool to room temperature which formed a precipitate that was filtered. The filter cake was crystallized from absolute ethanol and dried under reduced pressure.

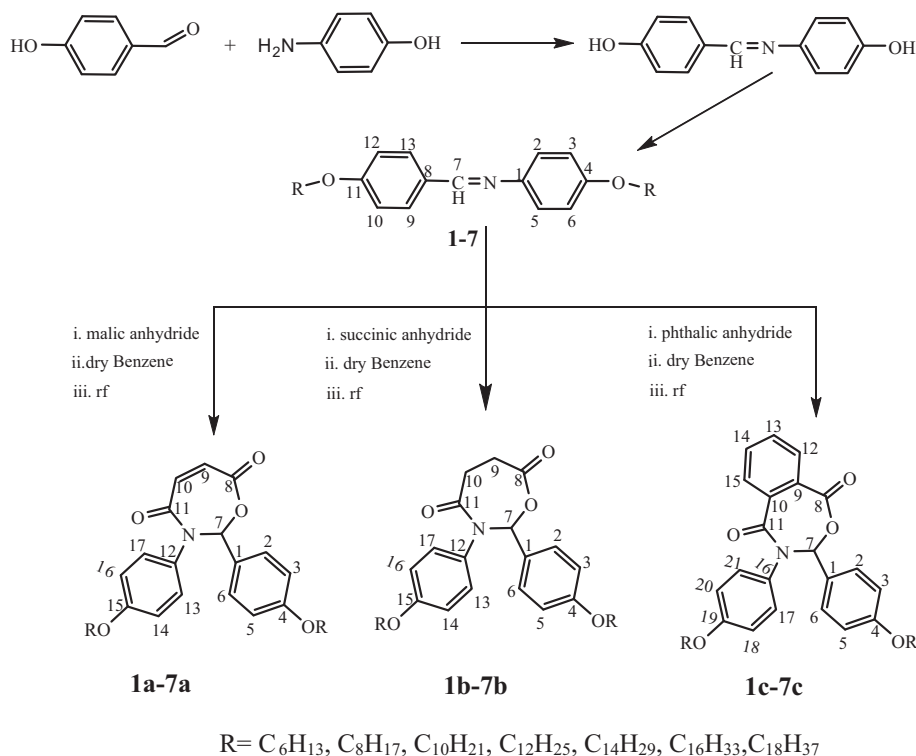
General procedure for the synthesis of 4-(alkyloxy)-*N*-(4-(alkyloxy)benzylidene)aniline (1-7)

The compounds were synthesized by the same method as described for compound 1.

A mixture containing 0.1 mol of 4-(4-hydroxybenzylideneamino)phenol, 0.25 mol of anhydrous sodium carbonate and 0.25 mol of 1-bromohexane was dissolved in 50 mL of DMF and allowed to heat for 4 h at 150 °C under continuous stirring as documented by Yeap et al. [16]. The resulting mixture was then poured into an ice-water bath (approx. 5 °C) whereupon a precipitate formed. The precipitate was filtered and washed once with KOH and water, dried and finally recrystallized from ethanol to yield compound 1 in 77% yield.

The yields, elemental analytical, select FT-IR, ^1H and ^{13}C NMR data for compounds 1-7 are summarized as follows:

- Yield 77%; m.p. 80–81 °C. Anal. found for $\text{C}_{25}\text{H}_{35}\text{NO}_2$ (%): C 78.90, H 9.18, N 3.60. Calc (%) C 78.70, H 9.25, N 3.67. IR: ν_{max} (cm^{-1}): 3055, 2980, 2951, 1620, 1610, 1580, 1250. ^1H NMR δ (ppm): 7.70 (d, H2 and H6), 7.31 (d, H3 and H5), 8.51 (s, H7), 7.19 (d, H9 and H13), 7.08 (d, H10 and H12), 4.12 (t, $\text{C}_4\text{—OCH}_2$), 4.01 (t, $\text{C}_{11}\text{—OCH}_2$), 1.87–1.21 (m, $(\text{CH}_2)_n$), 0.80 (t, CH_3). ^{13}C NMR δ (ppm): 115.11–133.12 (Ar—C), 161.11 (Ar—C—O), 164.23 (C=N), 70.03 (O— CH_2), 22.32–32.88 (CH_2)_n, 15.04 (CH_3).
- Yield 85 %; m.p. 83–84 °C. Anal. found for $\text{C}_{29}\text{H}_{43}\text{NO}$ (%): C 79.64, H 9.78, N 3.12. Calc (%) C 79.59, H 9.90, N 3.20. IR: ν_{max} (cm^{-1}): 3054, 2985, 2950, 1625, 1604, 1583, 1247. ^1H NMR δ (ppm): 7.72 (d, H2 and H6), 7.30 (d, H3 and H5), 8.47 (s, H7), 7.15 (d, H9 and H13), 7.05 (d, H10 and H12), 4.11 (t, $\text{C}_4\text{—OCH}_2$), 4.02 (t, $\text{C}_{11}\text{—OCH}_2$), 1.80–1.20 (m, $(\text{CH}_2)_n$), 0.82 (t, CH_3). ^{13}C NMR δ (ppm): 115.55–132.89 (Ar—C), 161.55 (Ar—C—O), 164.61 (C=N), 70.51 (O— CH_2), 22.81–32.02 (CH_2)_n, 15.17 (CH_3).
- Yield 72 %; m.p. 87–88 °C. Anal. found for $\text{C}_{33}\text{H}_{51}\text{NO}_2$ (%): C 80.35, H 10.33, N 2.90. Calc (%) C 80.27, H 10.41, N 2.84. IR: ν_{max} (cm^{-1}): 3052, 2982, 2952, 1628, 1607, 1580, 1252. ^1H NMR δ (ppm): 7.71 (d, H2 and H6), 7.31 (d, H3 and H5), 8.52 (s, H7), 7.14 (d, H9 and H13), 7.02 (d, H10 and H12), 4.10 (t, $\text{C}_4\text{—OCH}_2$), 4.02 (t, $\text{C}_{11}\text{—OCH}_2$), 1.82–1.26 (m, $(\text{CH}_2)_n$), 0.87 (t, CH_3). ^{13}C NMR δ (ppm): 115.80–132.06 (Ar—C), 161.01 (Ar—C—O), 164.40 (C=N), 70.77 (O— CH_2), 23.20–32.71 (CH_2)_n, 15.81 (CH_3).



Scheme 1. Synthetic route to synthesis title compounds 1a-7a, 1b-7b and 1c-7c.

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