

Synthesis and comparative studies of phase transition behaviour of new dimeric liquid crystals consisting of dimethyluracil and biphenyl cores



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ABSTRACT

A new homologous series of mesogens containing 6-amino-1,3-dimethyluracil moiety have been synthesized. The structures of the compounds were characterised by elemental analysis, FT-IR, ¹H and ¹³C NMR spectroscopic techniques. Their mesomorphic properties were studied by polarising optical microscopy attached to a heating stage. Microscopy data were supported with transition temperatures and enthalpy change values obtained from the differential scanning calorimetry analysis. The studies have shown that the mesomorphic properties of the compounds are dependent on the lengths of alkoxy-spacers. Compounds **4a–f** with a shorter alkoxy-spacer chain (n = 6) exhibited smectic A phase, while compounds **4g–r** with a alkoxy-spacer chain (n = 8 or 10) displayed nematic phase.

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1. Introduction

Liquid crystals play an important role in today's world of science and technology, due to their technological applications, particularly as optical imaging liquid crystal displays, organic light emitting diodes (OLED's), anisotropic networks and semiconductor materials [1–3]. The mesomorphic behaviour of organic compounds depends on the structure of the molecules and can be varied by modifying its molecular structure including linking, terminal and core groups [4].

The simplest molecules consist of two liquid crystalline/non-liquid crystalline units connected by a flexible spacer usually in the sense of linearity, and are known as LC dimers [5,6]. A wide range of low molar mass dimeric molecular architectures are known to exhibit interesting LC properties when compared to the conventional monomer low molar mass LCs [7]. Moreover, the studies directed toward the dimers are enormous due to their LC favorable chemical structure, size/type of the core, connecting groups and terminal/spacer alkyl chains [8,9].

In recent years, many mesomorphic compounds containing differing heterocyclic units have been synthesized, with the interest in such structures growing constantly [10–12]. This is not only because of the greater possibilities with heterocyclics in the design of new mesogenic

molecules, but also due to fact that the insertion of heteroatoms strongly influences the formation of mesomorphic phases. The inclusion effect of heteroatoms (S, O and N) alters the geometric shape of the molecule considerably, thereby influencing the polarity, polarisability and sometime type of mesophase, phase transition temperatures, dielectric- and other properties of the mesogens [13].

Nucleic acids are biologically very important for the sustenance of life on earth, occurring in both RNA and DNA. The heterocyclic base moieties present in nucleic acids are well-known. These bases present in the nucleic acids are expected to be applicable to the design of molecular assemblies with diverse liquid-crystalline properties, since each nucleobase specifically forms a base pair with its predetermined partner. Some attempts to prepare thermotropic liquid crystals of nucleobase derivatives were unsuccessful [14–16]; but there are several reported examples of lyotropic liquid crystals derived from DNA and nucleotides [17,18].

This article reports on our on-going research on the synthesis and characterization of heterocyclic based liquid crystalline materials [19–23]. The present work expands our understanding of the structure-liquid crystalline property relationship of these materials. Specifically we focus on a new series of mesogenic compounds containing 1,3-dimethyluracil core system having alkoxy-spacer [–O–(CH₂)_n–O–] with an even number of carbon atoms ranging from C₆H₁₀ to C₁₀H₂₄. A pendant biphenyl moiety is connected to this core by an alkyl chain varying in length from n = 6–16 carbons.

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2. Experimental

2.1. Materials

A series of α,ω -dibromoalkanes, 4-hydroxybenzaldehyde, 6-amino-1,3-dimethyluracil, 4'-hydroxybiphenyl-4-carboxylic acid, hexanol, octanol, decanol, dodecanol, tetradecanol, hexadecanol were purchased from Sigma-Aldrich. The chemicals were used directly as received without further purification. Thin-layer chromatography (TLC) was performed on pre-coated silica-gel on aluminum plates using 2:8 ratio of ethyl acetate and petroleum ether as an eluent.

2.2. Measurements

Elemental (CHN) microanalyses were performed using a Perkin Elmer 2400 LS Series CHNS/O analyzer. FT-IR spectra were obtained using KBr pellets and the spectra were recorded in the range of 4000–400 cm^{-1} using a Perkin Elmer 2000-FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in dimethylsulphoxide ($\text{DMSO}-d_6$) at 25 $^\circ\text{C}$ on a Bruker 400 MHz UltrashieldTM FT-NMR spectrometer equipped with a 5 mm BBI inverse gradient probe. Chemicals shift was referenced to internal tetramethylsilane (TMS). The concentration of solute molecules was 50 mg in 1.0 ml 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 $^\circ\text{C}/\text{min}^{-1}$ 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.

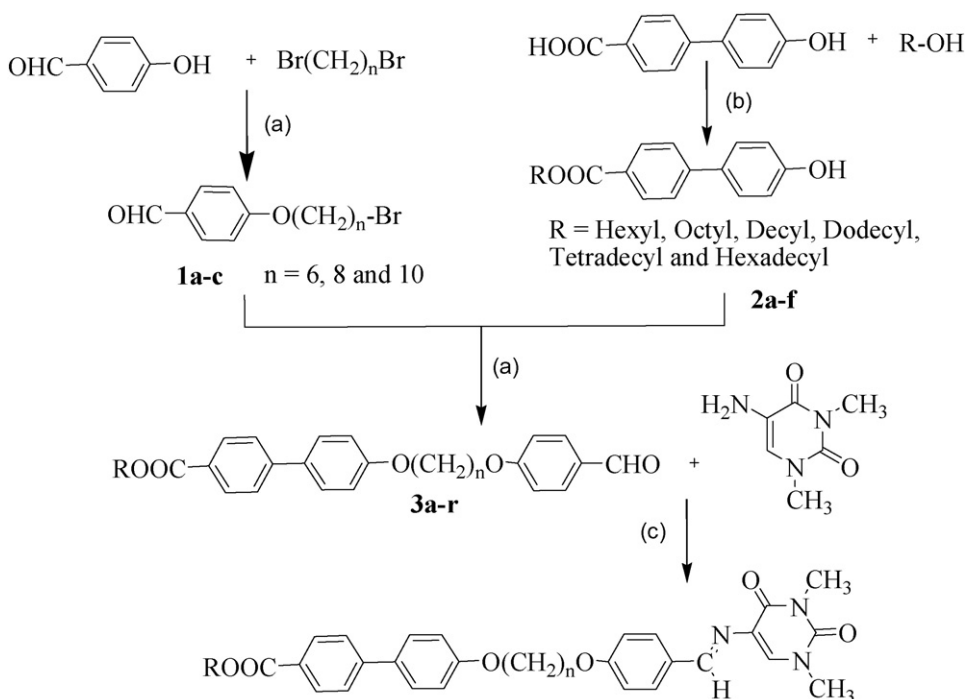
Molecular models were obtained using HyperChem 8.0.8 (Hypercube Inc.) in the Liquid Crystal Institute of Kent State University, USA.

Data sets of the compounds were entered as two-dimensional sketches into the HyperChem program.

2.3. Synthesis and characterization of 4a–r

The synthetic approach to the intermediates **1a–c**, **2a–f**, **3a–r** and title compounds **4a–r** are illustrated in Scheme 1. Refluxing 4-hydroxybenzaldehyde and anhydrous Na_2CO_3 with 1,6-dibromohexane/1,8-dibromohexane/1,10-dibromohexanes in DMF solvent gave the corresponding compounds **1a–c** [25,26]. The esters **4'-hydroxybiphenyl-4-carboxyalkanoates 2a–f** were synthesized employing the esterification reaction between 4-hydroxyphenyl-4-benzoic acid and hexyl to hexadecyl alcohols at 120 $^\circ\text{C}$ in the presence of 1 ml of sulphuric acid as dehydrating agent. Intermediates **3a–r** were synthesized via the Williamson etherification between **1a–c** and **2a–f** in DMF solvent using anhydrous Na_2CO_3 as a catalyst. The new dimeric target compounds **4a–r** were synthesized by the reaction of alkyl-4'-(n-(4-formylphenoxy)alkyloxy)biphenyl-4-carboxylate **3a–r** with 6-amino-1,3-dimethyluracil by refluxing in ethanol at 98 $^\circ\text{C}$ with catalytic quantity of glacial acetic acid. Complete FT-IR, ^1H and ^{13}C NMR assignments of compounds **4a–r** were obtained and substantiated with the aid of DEPT and two-dimensional ^1H - ^1H correlation spectroscopy (COSY, NOESY), ^1H - ^{13}C heteronuclear multiple quantum correlation (HMQC) and ^1H - ^{13}C heteronuclear multiple bond correlation (HMBC) spectroscopies.

In the FT-IR spectrum of compound **4a**, the bands assignable to the C–H stretching at 2982–2875 cm^{-1} can be ascribed to the alkyl spacer and the alkyl ester group attached to one of the terminals of the dimer. The strong band observed at 1752 cm^{-1} is assigned to carbonyl group C=O. On the other hand, the C=N gave a band at 1625 cm^{-1} with medium intensity. The band at 1256 cm^{-1} is due to the ether C–O stretching in the fingerprint region. The FT-IR spectra of compounds **4b–r** exhibited similar diagnostic bands as those observed in compound **4a**.



4a–r, where $n = -\text{C}_6\text{H}_{12}-, -\text{C}_8\text{H}_{16}- \text{ and } -\text{C}_{10}\text{H}_{20}-$

$\text{R} = \text{C}_6\text{H}_{13}, \text{C}_8\text{H}_{17}, \text{C}_{10}\text{H}_{21}, \text{C}_{12}\text{H}_{25}, \text{C}_{14}\text{H}_{29} \text{ and } \text{C}_{16}\text{H}_{33}$

Scheme 1. Synthetic route and reagents for the formation of **4a–r**. (a) DMF, anhydrous Na_2CO_3 , reflux, 12 h. (b) Conc H_2SO_4 , 120 $^\circ\text{C}$, (c) ethanol, 98 $^\circ\text{C}$, 6 h, catalytic acetic acid.

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