Journal of Molecular Structure 1117 (2016) 201–207

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Synthesis mesomorphic and theoretical studies of some new unsymmetrical dimeric ethers of 6-amino-1,3-dimethyluracil and biphenyl cores

AbdulKarim-Talaq Mohammad [a, *], H.T. Srinivasa [b], Hameed Madlool Mohammed [c], S. Hariprasad [d], Guan-Yeow Yeap [e]

[a] Chemistry Department, College of Science, University of Anbar, Ramadi, Iraq
[b] Raman Research Institute, Soft Condensed Matter Group, Sadashivanagara, Bengaluru 560080, Karnataka, India
[c] Chemistry Department, College of Science for Women, University of Baghdad, Baghdad, Iraq
[d] Department of Chemistry, Central College Campus, Bangalore University, Bengaluru 560001, Karnataka, India
[e] Liquid Crystal Research Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, Minden 11800, Penang, Malaysia

ARTICLE INFO

Article history:
Received 21 November 2015
Received in revised form
12 March 2016
Accepted 15 March 2016
Available online 18 March 2016

Keywords:
Liquid crystals
Dimers
Mesophases
Heterocycles
Uracil
Theoretical studies

ABSTRACT

New sets of unsymmetric calamitic molecules with uracil unit at one end and biphenyl core at another end were synthesized. Liquid crystal property of these molecules was investigated by POM and DSC techniques. All compounds exhibit LC property depending on the spacer and terminal alkoxy chain of the molecules. First set shows smectic phase in lower members and nematic phase appeared in higher members. The second set favour nematic liquid crystalline phase with respect to spacer alkyl chain length. Molecules are escaped from the planarity as a result disturbing the layer stacking leads to nematic phase in higher analogues. Theoretical studies have been performed for all the compounds and are found to be in agreement with the results of the current studies.

1. Introduction

It has been well documented that the liquid crystalline behaviour 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 [1–6]. Liquid crystalline materials possess many applications in scientific and technological areas, in particular as display devices, organic light emitting diodes (OLEDs), anisotropic networks, photoconductors and semiconductor materials [7–9]. Dimer is one, in the classification of liquid crystals in which two rigid mesogenic units are joined by a flexible spacer [10]. The phase transition behaviour of dimer depends on the chain length especially the parity of the connecting spacer [11,12]. Recently, research based on dimers has received considerable attention owing to the fact that the dimers could behave as model compounds for the understanding of the technologically important semi-flexible main chain liquid crystal polymers and as model compounds for side group liquid crystal polymers [13–15]. On the other hand, studies on mesogenic structures containing heterocyclic rings have increased remarkably, owing to their abilities to exhibit mesogenic behaviour either similar to or superior to the linear phenyl analogs [16–21]. Further, the presence of heteroatoms (O, S and N) has lead to significant changes in the corresponding liquid crystalline phases and/or in the physical properties of the observed phases because the heteroatoms are 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 [22–24]. With respect to the nucleic acid bases, the cholesteric mesophase has been observed only in adenine and thymine with cholesterol moiety [25,26].

Due to our interest, we are continuing our investigations on preparation and characterization of heterocycle-based thermotropic liquid crystals. Moreover, recently, we have reported

---

* Corresponding author.
E-mail address: drmohamadtalaq@gmail.com (A.-T. Mohammad).

http://dx.doi.org/10.1016/j.molstruc.2016.03.052

mesogenic compounds possessing a biphenyl ester moiety with a 6-amino-1,3-dimethyluracil unit [27]. Here, we wish to access two more homologous series of compounds synthesis, characterization and evaluation for their liquid crystals properties belong to unsymmetric dimer series of 5-(4-(5-(4′-(alkyloxy)biphenyl-4-yloxy)alkyloxy)benzylideneamino)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione containing 6-amino-1,3-dimethyluracil at one end and with alkoxyphenyl terminal at the other end possessing chains of varying central methylene spacer lengths (n = 6 and 8).

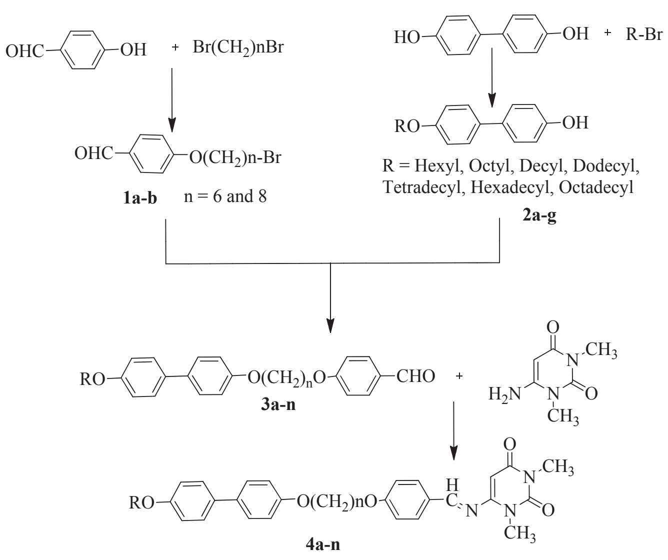
The physical properties of the title compounds were studied by Fourier-Transform Infra-Red (FT-IR) Spectroscopy and high resolution nuclear magnetic resonance (NMR) techniques. The phase transition temperatures and enthalpy values of the title compounds were measured by differential scanning calorimetry (DSC) and the textures of the mesophases were studied using polarizing optical microscope (POM).

2. Results and discussion

2.1. Synthesis and characterization

The synthetic route for the target compounds **4a**–**4n** is shown in Scheme 1. Spectroscopic methods such as FT-IR and NMR (^{1}H and ^{13}C) were employed to elucidate the structures of compounds **4a**–**n**. Molecular structure characterizations were in good agreement with software predictions. Compounds **4a**–**g** having methylene spacer length n = 6 and terminal alkyl chain varies from n = 6–18, whereas compounds **4h**–**n** have methylene spacer length n = 8 with varying terminal alkyl chain from n = 6–18.

FT-IR spectra of compounds **4a**–**n** exhibit absorption bands that can be assigned to the stretching of aliphatic C-H within the frequency range 2995–2868 cm^{-1}. The C=O stretch frequency appears between the range of 1777–1760 cm^{-1}. The band which appears at the frequency 1628-1618 cm^{-1} is attributed to the stretching of C=N. The ether group of spacer chain and terminal chain gave rise to strong absorptions at 1255-1250 cm^{-1}. The FT-IR spectroscopic study was further supported by the application of ^{1}H NMR and ^{13}C NMR in an effort to elucidate the molecular structures. The NMR spectra obtained indicate that all members of the homologous series exhibit similar trend in ^{1}H-^{1}H splitting and chemical shifts. The NMR resonances with respect to the diagnostic peaks are discussed based on the representative compound **4a** (with -C_6H_{12}- methylene spacer and -C_6H_{13} terminal chain). ^{1}H NMR assignment of compound **4a** has been carried out with aid of two dimensional ^{1}H-^{1}H COSY experiment. A singlet at 6.83 ppm is attributed to the vinyl proton of the hetero uracil ring. The presence of the azomethine protons (−CH=N−) appears as singlet at 8.84 ppm. The absorption of 12 aromatic protons from two different distinguishable positions at the aromatic rings gave rise to a multiplet between 6.87 and 8.60 ppm. Another three triplets were detected at 4.17 ppm, 4.05 ppm and 3.91 ppm were assigned to the ethoxy protons adjacent to the methylene protons in spacer chain and terminal alkoxy chain respectively. Two singlets at 3.42 ppm and 3.12 ppm were assigned to methyl groups attached to nitrogen atom in 6-amino-1,3-dimethyluracil ring. A triplet was observed at the high-field of 0.81 ppm, which can be assigned to the methyl protons of the terminal hexyl group in compound **4a**.



Scheme 1. Synthetic route for **4a**–**n**.

2.2. Phase transitions and mesomorphic behaviours

Phase transition temperatures and optical textures were analysed by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The transition temperatures (°C) and respective enthalpies (kJ mol^{-1}) obtained from the DSC thermograms are given in Table 1. All the synthesized molecules **4a**–**n** tended to exhibit enantiotropic liquid crystal properties. The solid samples were sandwiched between untreated glass plate and a cover slip and subjected to heating followed by cooling scans at the rate of 5 °C/min for textural observations through POM. In the first set of compounds **4a**–**g**, SmA phase was observed in compounds **4a**–**d**, whereas compounds **4e**–**g** shows nematic phase. The representative DSC scans of **4c** as shown in Fig 1. For example compound **4c** show transitions at 143.30 °C (22.08) and 160.31 °C (1.23) on heating scan which corresponds to Cr-to-SmA-to-Iso phase sequence. In the cooling scan reverse transitions were

Table 1
The heating/cooling phase transition temperatures (°C) and the associated enthalpies (kJ mol^{-1}) for target compounds **4a**–**n**.

Compound	n	R	Heating/Cooling scans
4a	6	C_6H_{13}	Cr 112.2 (22.84) SmA130.1 (4.20) Iso Cr 98.5 (−19.32) SmA 118.7 (−2.11) Iso
4b	6	C_8H_{17}	Cr 119.6 (25.10) SmA 136.3 (3.80) Iso Cr 111.4 (−21.45) SmA 126.2 (−6.78) Iso
4c	6	$C_{10}H_{21}$	Cr 143.3 (22.08) SmA 160.3 (1.23) Iso Cr 141 (−23.22) SmA 154 (−1.78) Iso
4d	6	$C_{12}H_{25}$	Cr 159.2 (27.08) SmA 176.5 (2.44) Iso Cr 154.4 (−18.56) SmA 170.9 (3.30) Iso
4e	6	$C_{14}H_{29}$	Cr 171.1 (15.60) N 190.5 (4.67) Iso Cr 167.8 (−21.45) N 183 (−5.44) Iso
4f	6	$C_{16}H_{33}$	Cr 185.1 (29.18) N 202.3 (5.98) Iso Cr 178.8 (−27.06) N 195.8 (−6.04) Iso
4g	6	$C_{18}H_{37}$	Cr 197.7 (21.55) N 211.8 (7.89) Iso Cr 189.9 (−18.90) N 204.7 (−8.78) Iso
4h	8	C_6H_{13}	Cr 116.2 (25.76) SmA 130.2 (8.35) Iso Cr 104.7 (−23.54) SmA 121.1 (−3.45) Iso
4i	8	C_8H_{17}	Cr 138.9 (24.90) N 161.2 (2.09) Iso Cr 133.1 (−17.67) N 155.9 (−1.30) Iso
4j	8	$C_{10}H_{21}$	Cr 148.2 (19.00) N 173.1 (2.98) Iso Cr 142.1 (−26.40) N 167.5 (−2.49) Iso
4k	8	$C_{12}H_{25}$	Cr 173 (25.06) N 190.1 (3.50) Iso Cr 166.9 (−19.17) N 182 (−3.88) Iso
4l	8	$C_{14}H_{29}$	Cr 188.2 (19.34) N 206.2 (5.66) Iso Cr 181.2 (−25.00) N 198.4 (−4.79) Iso
4m	8	$C_{16}H_{33}$	Cr 194.1 (17.70) N 215.6 (7.82) Iso Cr 187.2 (−20.60) N 208.6 (−6.49) Iso
4n	8	$C_{18}H_{37}$	Cr 210 (18.33) N 232.1 (9.08) Iso Cr 205.8 (−18.0) N 226 (−7.20) Iso

Cr = Crystal; SmA = Smectic A phase; N = Nematic phase; Iso = Isotropic phase.