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

AbdulKarim-Talaq Mohammad, H.T. Srinivasa, Hameed Madlool Mohammed, S. Hariprasad, Guan-Yeow Yeap

Uracil Liquid Crystals

Where **n** = 6 and 8. **R** = C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$
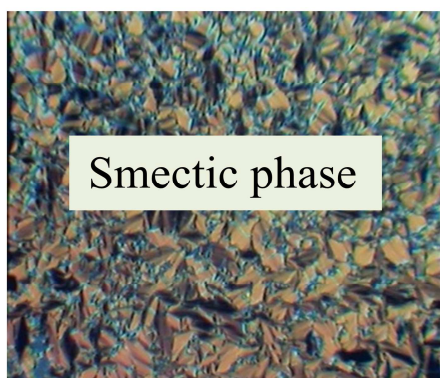
Smectic phase

Nematic phase

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

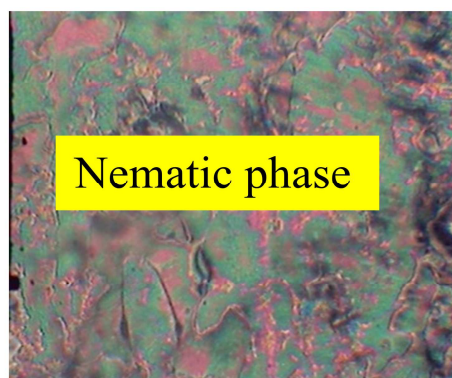AbdulKarim-Talaq Mohammad[1], Srinivasa, H. T[2], Hameed Madlool Mohammed[3], Hariprasad, S[4], Guan-Yeow Yeap[5]

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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.

Keyword: liquid crystals, dimers, mesophases, heterocycles, uracil, theoretical studies

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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 [9]. 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 behavior 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 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).

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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** has methylene spacer length n = 8 with varying terminal alkyl chain from n = 6-18.

Insert Scheme 1 is about here

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$_6$H$_{12}$- methylene spacer and -C$_6$H$_{13}$ 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

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different distinguishable positions at the aromatic rings gave rise to a multiplet between 6.87-8.60 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**.

insert Table 1 is about here

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 (ºC) 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 absered at 141 °C (-23.22) and 154 °C (-1.78) which corresponds to Iso-to SmA-to-Cr state. Compound **4c** displayed sandy texture having small focal conics as depicted in Fig 2 (a) and focal conic texture for **4d** as shown in Fig 2 (b). Compounds **4e-g** shows enantiotropic nematic phase. The difference in the mesophase behavior of **4a-d** and **4e-g** molecules can be explained by the number of aliphatic chains present at the periphery and at spacer position of the molecules. In this regard, a smaller aliphatic chain seems to be a co-ordinating in terms of achieving a good packing and may leads to SmA mesophase. In case of **4e-g** the peripheral, spacer alkyl chains and bulky of 6-amino-1,3-dimethyluracil moiety may not allow molecules to pack each other as a result nematic phase is existed.

Insert Figure 1 is about here

Notably, in the second set of compounds **4h-n,** only **4h** shows SmA phase, whereas other members showing enantiotropic nematic phase. The representative DSC scans of compound **4i** shown in Fig 1. On heating the sample **4i** melts to a nematic mesophase with Schlieren texture at 138.89 °C and then it went to isotropic liquid state at 161.23 °C. In a similar way, in cooling scan nematic mesophase re-appeared at 155.90 °C and then crystallised at 133.12 °C. The textures observed on heating scan from crystal can be observed in Figure 2 (c) for **4l** and (d) for **4n**. The SmA phase is observed in **4h** compound and nematic phase was observed in the compounds of **4i-n**, this could be the result of a lower degree of planarity from the terminal bulky 6-amino-1,3-dimethyluracil group. This lack of planarity prevents molecular packing and end up with less ordered nematic mesophase in higher members.

Insert Figure 2 is about here

However, both the set of compounds **4a-g** (spacer n = 6) and **4h-n** (spacer n = 8) shows completely irrelevant results with respect to spacer, for this kind of unexpected results we reason that, it is known that the pronounced odd even effect is relevant to a spacer in dimers and this trend is not followed by present case, because only two spacers (n = 6 and 8) were studied and also both are even members. Usually in dimers, lower members favour the nematic phase and higher members favour the smectic phase with add-even effects [34]. The present results are fully contraries than expected. The effects of the spacer length on the transition temperatures and phase behaviour observed in this series are not in accord with those observed for conventional low molar mass mesogens or dimers. The same effect is observed in present series of compounds with increasing carbon atoms in both the terminal and spacer alkyl chain. The results are found here are unusual when compare to the normal behaviour of the dimers [35].

Further, all the compounds which are showing nematic to isotropic transitions are associated with higher enthalpy values than the associated enthalpies of SmA to Isotropic transitions. This factor is completely depend on the orientation order of the molecules, means high orientation order is existed between the molecules in the

nematic phase, as a result molecules requires high enthalpy to transform another phase, same fact has been observed in this case. Moreover, this is presumably due to the rather bulky shape of the 6-amino-1,3-dimethyluracil group and this increased molecular biaxiality has been used to account for relatively high clearing entropies. Thus, the orientational order is enhanced and a higher enthalpy values for nematic to isotropic transitions would be expected [36,37]

A plot of transition temperature as a function of alkyl chain length at periphery as well as in the spacer for the sets of **4a-g** and **4h-n** is shown in Fig 3 (a) and (b). The clearing temperature for both sets of compounds shows a tendency of ascending curve along with increasing in the number of carbons at periphery and spacer chain throughout the set of compounds. The first set **4a-h** compounds have little lower transition temperature than the second set **4h-n** of compounds. A comparison of mesomorphic behaviour of these unsymmetrical sets of compounds reveals that crystal-to-mesophase average range is about 16 °C for the set **4a-g**, whereas in **4h-n** set of compounds average crystal-to-mesophase range was increased to 19 °C. The study proves that the increase of spacer and terminal chain length favour stabilization of the mesophases.

Insert Figure 3 is about here

2.3 Theoretical studies

Theoretical studies have been carried out by Hyper Chem program to get a better understanding of the relationship between the structure and type of phases. Theoretical models of compounds **4a**, **4g**, **4h** and **4h** are depicted in Figure 4 in which the length of spacer alkoxy chain varied from n = 6 and 8, respectively. Theoretically calculated data and experimental results are in agreement to the title compounds.

Insert Figure 4 is about here

As shown in Figure 4, 1,3-dimethyluracil ring and biphenyl ring which is adjacent to the spacer appeared at different positions which depended on the number of carbons at the alkoxy spacer [31-33]. The models indicated that 1,3-dimethyluracil and biphenyl core groups take different opposite terminal ends according to number of carbons at spacer change from n = 6 and 8. Non-planar geometry of 1,3-

dimethyluracil and biphenyl rings was observed in compound **4a** and this geometry tends to exhibit Smectic A. However, a more planar geometry of 1,3-dimethyluracil and biphenyl was found in compounds **4f** molecular conformation favoured arrangement of a nematic phase. Likewise, same phenomena have been observed in compounds type **4h-n** when a carbon spacer n = 8, compounds **4h** (Figure 4) show also non-planar geometry of 1,3-dimethyluracil and biphenyl rings, while compounds **4n** shown more planarity comparison with compound **4h.** Also we can revels from figure 4 the terminal alkyl chain play well to effected the planarity of 1,3-dimethyluracil and biphenyl rings

Finally, the study reveals that the variation of terminal alkyl chain and spacer chain length plays an important role in the type of phase occurred in both set of compounds.

3. Conclusions

In this article, the synthesis, mesomorphic and theoretical models of some novel dimeric liquid crystalline compounds have been studied. All title compounds exhibited liquid crystal properties. Smectic A was observed with short spacer groups, while nematic phase appears with longer spacer groups. Theoretical models presented for few compounds are in good agreement with our results.

4. Experimental

4.1. Materials

Bromoalkanes, α,ω-dibromoalkanes, 4-hydroxybenzaldehyde, 6-amino-1,3-dimethyluracil, 4,4'-dihydroxybiphenyl were obtained from Aldrich. The fine chemicals and required solvents were used directly from the bottles without further purification. Thin-layer chromatography (TLC) was performed on pre-coated silica-gel on aluminium plates.

4. 2 Measurement

The FT-IR spectra of the intermediates and title compounds were analyzed in the form of KBr pellets and the spectra were recorded in the range of 4000-400 cm^{-1} using a Perkin Elmer 2000 FT-IR spectrophotometer. The elemental microanalyses (CHN) were performed using a Perkin Elmer 2400 LS Series CHNS/O analyzer. The ^{1}H and ^{13}C NMR spectra were recorded in dimethylsulphoxide (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 shift values (δ) were referenced to internal standard tetramethylsilane (TMS). The concentration of solute molecules was 40 mg in 1.0 ml DMSO. Standard Bruker pulse programs [28] were used throughout the entire experiment. Texture observation was carried out using Carl Zeiss Axioskop 40 optical microscope equipped with Linkam LTS350 hot stage and TMS94 temperature controller. 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 °C min^{-1} on heating and cooling, respectively.

Theoretical models were obtained using Hyper Chem 8.0.8 (Hypercube Inc.) in the Liquid Crystal Institute of Kent State University, USA. Data set of the compounds was entered as two-dimensional sketches into Hyper Chem program.

4.3 Synthesis

The synthetic routes of the intermediates **1a-b**, **2a-g**, **3a-n** and title compounds **4a-n** are shown in Scheme 1. The Williamson's etherification method used for the preparation of compounds **1a-b**, **2a-g** and **3a-n.** Compounds **1a-b** were synthesised via reaction between equimolar amounts of 1,6-dibromohexane or 1,8-dibromooctane with 4-hydroxybenzaldehyde in DMF in present of K_2CO_3 at 145 °C for 4 hr [29, 30]. Compounds **2a-g** were synthesised by the reaction between 4,4'-dihydroxybiphenyl with a series of alkylbromides ranging from 6 to 18 carbons. The final compounds **3a-n** was obtained by the reaction between **1a-b** and **2a-g**.

*4.3.1 **General synthetic procedure for 4a-n***

*4.3.2. 5-[-{6-(4'-Alkyloxy)biphenyl-4-yloxy)alkyloxy)benzylideneamino}-1,3-dimethyl-pyrimidine]2,4(1H,3H)-dione (**4a-4n**)*

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The target compounds were synthesised according to method described by Majumdar *et al* [27, 30]. A mixture of compound 6-amino-1,3-dimethyluracil (128 mg, 0.827 mmol) and 4-(6-(4'-(hexyloxy)biphenyl-4-yloxy)hexyloxy)benzaldehyde **3a** (500 mg, 0.827 mmol) was refluxed in absolute ethanol in the presence of a catalytic amount of glacial acetic acid for 2 h. The Schiff base **4a** was obtained as a precipitate from the hot reaction mixture. Further, to get pure compound it was repeatedly washed with hot ethanol and dried in vacuum.

The analytical data of FT-IR, ^{1}H and ^{13}C NMR for title compounds are summarized as follows:

5-(6-(4'-(Hexyloxy)biphenyl]-4-yloxy)hexyloxy)benzylidene)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione **(4a).** Yield 73 %; Anal: found for $C_{37}H_{45}N_3O_5$ (%): C, 72.83; H, 7.24; N, 6.99. Calc. C, 72.64; H, 7.41; N, 6.87. IR: v_{max}(KBr, cm^{-1}): 2995, 2883, 1770 1620, 1580, 1251. ^{1}HNMR δ (ppm, DMSO): 8.84 (s, 1H. -CH=N-), 6.87-8.60 (m, 12H, Ar-H), 6.83 (s, 1H), 4.17 (t, 2H, J = 6.89 Hz, -OCH$_2$-), 4.05 (t, 2H, J = 6.67 Hz), 3.91 (t, 2H, J = 6.14 Hz), 3.42 (s, 3H), 3.12 (s, 3H), 1.89-1.71 (m, 16H), 0.81 (t, 3H, -CH$_3$). ^{13}C NMR δ : 176.04, 169.70, 162.00 (C=O), 161.20 (C=N), 160.94, 158.23 (Ar-C-O), 115.12-141.04 (Ar-C), 62.67 (C-O-C), 21.20 (CH$_2$), 15.11 (CH$_3$) ppm.

5-(6-(4'-(Octyloxy)biphenyl]-4-yloxy)hexyloxy)benzylidene)amino)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione **(4b).** Yield 78 %; Anal: found for $C_{39}H_{49}N_3O_5$ (%): C, 73.08; H, 7.60; N, 6.43. Calc. C, 73.21; H, 7.72; N, 6.57. IR: v_{max}(KBr, cm^{-1}): 2989, 2871, 1766 1618, 1573, 1250. ^{1}HNMR δ (ppm, DMSO): 8.76 (s, 1H, -CH=N-), 6.86-8.58 (m, 12H, Ar-H), 6.80 (s, 1H), 4.14 (t, 2H, J = 6.88 Hz, -OCH$_2$-), 4.01 (t, 2H, J = 6.20 Hz), 3.90 (t, 2H, J = 6.38 Hz), 3.41 (s, 3H), 3.11 (s, 3H), 1.87-1.74 (m, 20H), 0.85 (t, 3H, -CH$_3$). ^{13}C NMR δ : 175.30, 168.11, 162.89 (C=O), 161.59 (C=N), 161.08, 159.44 (Ar-C-O), 114.77-140.39 (Ar-C), 62.07 (C-O-C), 21.20 (CH$_2$), 14.56 (CH$_3$) ppm.

5-(6-(4'-(Decyloxy)-biphenyl]-4-yloxy)hexyloxy)benzylidene)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione **(4c).** Yield 69 %; Anal: found for $C_{41}H_{53}N_3O_5$ (%): C, 73.89; H, 8.11; N, 6.14. Calc. C, 73.73; H, 8.00; N, 6.29. IR: v_{max}(KBr, cm^{-1}): 2992, 2880, 1772 1628, 1587, 1255. ^{1}HNMR δ (ppm, DMSO): 8.82 (s, 1H, -CH=N-), 6.92-8.63 (m, 12H, Ar-H), 6.87 (s, 1H), 4.17 (t, 2H, J = 6.39 Hz), 4.07 (t, 2H, J =

6.67 Hz, -OCH$_2$-), 3.93 (t, 2H, J = 6.09 Hz), 3.49 (s, 3H), 3.15 (s, 3H), 1.87-1.73 (m, 24H), 0.88 (t, 3H, -CH$_3$). ^{13}C NMR δ : 174.95, 168.78, 162.50 (C=O), 161.06 (C=N), 161.86, 160.17 (Ar-C-O), 114.90-140.07 (Ar-C), 62.30 (C-O-C), 22.30 (CH$_2$), 14.60 (CH$_3$) ppm.

5-(6-(4'-(Dodecyloxy)-biphenyl]-4-yloxy)hexyloxy)benzylidene)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione **(4d).** Yield 75 %; Anal: found for C$_{43}$H$_{57}$N$_3$O$_5$ (%): C, 74.40; H, 8.49; N, 6.27. Calc. C, 74.21; H, 8.26; N, 6.04. IR: υ_{max}(KBr, cm^{-1}): 2990, 2884, 1775 1622, 1583, 1253. ^{1}HNMR δ (ppm, DMSO): 8.80 (s, 1H, -CH=N-), 6.95-8.65 (m, 12H, Ar-H), 6.88 (s, 1H), 4.18 (t, 2H, J = 6.28 Hz), 4.05 (t, 2H, J = 6.89 Hz, -OCH$_2$-), 3.96 (t, 2H, J = 6.19 Hz), 3.45 (s, 3H), 3.18 (s, 3H), 1.86-1.76 (m, 28H), 0.89 (t, 3H, -CH$_3$). ^{13}C NMR δ : 175.11, 167.20, 162.93 (C=O), 160.75 (C=N), 159.23, 158.30 (Ar-C-O), 114.06-140.69 (Ar-C), 61.07 (C-O-C), 21.44 (CH$_2$), 15.05 (CH$_3$) ppm.

5-(6-(4'-(Tetradecyloxy)-biphenyl]-4-yloxy)hexyloxy)benzylidene)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione **(4e).** Yield 81 %; Anal: found for C$_{45}$H$_{61}$N$_3$O$_5$ (%): C, 74.80; H, 8.31; N, 5.64. Calc. C, 74.65; H, 8.49; N, 5.80. IR: υ_{max}(KBr, cm^{-1}): 2992, 2882, 1777 1625, 1589, 1251. ^{1}HNMR δ (ppm, DMSO): 8.65 (s, 1H, -CH=N-), 6.95-8.51 (m, 12H, Ar-H), 6.86 (s, 1H), 4.19 (t, 2H, J = 6.70 Hz), 4.08 (t, 2H, J = 6.47 Hz, -OCH$_2$-), 3.94 (t, 2H, J = 6.49 Hz), 3.49 (s, 3H), 3.14 (s, 3H), 1.87-1.70 (m, 32H), 0.92 (t, 3H, -CH$_3$). ^{13}C NMR δ : 174.88, 167.84, 164.02 (C=O), 162.20 (C=N), 159.22, 158.90 (Ar-C-O), 114.00-140.27 (Ar-C), 62.04 (C-O-C), 22.15 (CH$_2$), 15.38 (CH$_3$) ppm.

5-(6-(4'-(Hexadecyloxy)-biphenyl]-4-yloxy)hexyloxy)benzylidene)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione **(4f).** Yield 76 %; Anal: found for C$_{47}$H$_{65}$N$_3$O$_5$ (%): C, 75.20; H, 8.55; N, 5.71. Calc. C, 75.06; H, 8.71; N, 5.59. IR: υ_{max}(KBr, cm^{-1}): 2986, 2872, 1774 1628, 1584, 1255. ^{1}HNMR δ (ppm, DMSO): 8.72 (s, 1H, -CH=N-), 6.85-8.40 (m, 12H, Ar-H), 6.80 (s, 1H), 4.12 (t, 2H, J = 6.09 Hz, -OCH$_2$-), 4.01 (t, 2H, J = 6.60 Hz), 3.92 (t, 2H, J = 6.70 Hz), 3.47 (s, 3H), 3.12 (s, 3H), 1.88-1.76 (m, 36H), 0.81 (t, 3H, -CH$_3$). ^{13}C NMR δ : 176.02, 168.00, 164.96 (C=O), 161.83 (C=N), 160.80, 159.30 (Ar-C-O), 115.20-140.98 (Ar-C), 61.60 (C-O-C), 22.83 (CH$_2$), 14.36 (CH$_3$) ppm.

5-(6-(4'-(Octadecyloxy)-biphenyl]-4-yloxy)hexyloxy)benzylidene)-1,3-
dimethylpyrimidine-2,4(1*H*,3*H*)-dione **(4g).** Yield 70 %; Anal: found for $C_{49}H_{69}N_3O_5$
(%): C, 75.60; H, 8.76; N, 5.50. Calc. C, 75.44; H, 8.92; N, 5.39. IR: υ_{max}(KBr, cm^{-1}):
2983, 2868, 1770 1625, 1580, 1254. ^{1}HNMR δ (ppm, DMSO): 8.76 (s, 1H, -CH=N-),
6.93-8.46 (m, 12H, Ar-H), 6.83 (s, 1H), 4.18 (t, 2H, J = 6.84 Hz), 4.06 (t, 2H, J =
6.75 Hz), 3.95 (t, 2H, J = 6.19 Hz, -OCH$_2$-), 3.48 (s, 3H), 3.11 (s, 3H), 1.89-1.77 (m,
40H), 0.80 (t, 3H, -CH$_3$). ^{13}C NMR δ : 175.69, 166.49, 164.03 (C=O), 160.10 (C=N),
160.21,159.11 (Ar-C-O), 115.00-140.31 (Ar-C), 62.09 (C-O-C), 22.30 (CH$_2$), 14.07
(CH$_3$) ppm.

5-(8-(4'-(Hexyloxy)-[biphenyl]-4-yloxy)octyloxy)benzylidene)-1,3-
dimethylpyrimidine-2,4(1*H*,3*H*)-dione **(4h).** Yield 66 %; Anal: found for $C_{39}H_{49}N_3O_5$
(%): C, 73.45; H, 7.80; N, 6.39. Calc. C, 73.21; H, 7.72; N, 6.57. IR: υ_{max}(KBr, cm^{-1}):
2980, 2871, 1769 1622, 1583, 1250. ^{1}HNMR δ (ppm, DMSO): 8.74 (s, 1H, -CH=N-),
6.90-8.51 (m, 12H, Ar-H), 6.85 (s, 1H), 4.19 (t, 2H, J = 6.93 Hz), 4.08 (t, 2H, J =
6.41 Hz, -OCH$_2$-), 3.93 (t, 2H, J = 6.63 Hz), 3.44 (s, 3H), 3.18 (s, 3H), 1.87-1.71 (m,
20H), 0.85 (t, 3H, -CH$_3$). ^{13}C NMR δ : 174.09, 165.20, 163.20 (C=O), 162.60 (C=N),
161.57, 160.29 (Ar-C-O), 114.69-141.14 (Ar-C), 62.39 (C-O-C), 21.30 (CH$_2$), 15.21
(CH$_3$) ppm.

5-(8-(4'-(Octyloxy)-[biphenyl]-4-yloxy)octyloxy)benzylidene)-1,3-
dimethylpyrimidine-2,4(1*H*,3*H*)-dione **(4i).** Yield 67 %; Anal: found for $C_{41}H_{53}N_3O_5$
(%): C, 73.88; H, 8.25; N, 6.40. Calc. C, 73.73; H, 8.00; N, 6.29. IR: υ_{max}(KBr, cm^{-1}):
2993, 2882, 1772 1620, 1584, 1253. ^{1}HNMR δ (ppm, DMSO): 8.72 (s, 1H, -CH=N-),
6.86-8.58 (m, 12H, Ar-H), 6.80 (s, 1H), 4.15 (t, 2H, J = 6.76 Hz, -OCH$_2$-), 4.02 (t,
2H, J = 6.90 Hz), 3.98 (t, 2H, J = 6.12 Hz), 3.48 (s, 3H), 3.20 (s, 3H), 1.89-1.73 (m,
24H), 0.87 (t, 3H, -CH$_3$). ^{13}C NMR δ : 175.50, 164.58, 162.99 (C=O), 162.00 (C=N),
160.46, 159.33 (Ar-C-O), 114.19-140.29 (Ar-C), 62.00 (C-O-C), 22.58 (CH$_2$), 15.44
(CH$_3$) ppm.

5-(8-(4'-(Decyloxy)-[biphenyl]-4-yloxy)octyloxy)benzylidene)-1,3-
dimethylpyrimidine-2,4(1*H*,3*H*)-dione **(4j).** Yield 73 %; Anal: found for $C_{43}H_{57}N_3O_5$
(%): C, 74.30; H, 8.08; N, 6.20. Calc. C, 74.21; H, 8.26; N, 6.04. IR: υ_{max}(KBr, cm^{-1}):

2988, 2869, 1774 1625, 1580, 1251. ^{1}HNMR δ (ppm, DMSO): 8.68 (s, 1H, -CH=N-), 6.92-8.53 (m, 12H, Ar-H), 6.86 (s, 1H), 4.18 (t, 2H, J = 6.00 Hz, -OCH$_2$-), 4.06 (t, 2H, J = 6.20 Hz), 3.94 (t, 2H, J = 6.44 Hz), 3.40 (s, 3H), 3.29 (s, 3H), 1.88-1.70 (m, 28H), 0.79 (t, 3H, -CH$_3$). ^{13}C NMR δ : 176.10, 166.90, 164.20 (C=O), 163.50 (C=N), 162.50, 160.90 (Ar-C-O), 114.88-140.00 (Ar-C), 62.61 (C-O-C), 21.95 (CH$_2$), 15.83 (CH$_3$) ppm.

5-(8-(4'-(Dodecyloxy)-[bipheny]-4-yloxy)octyloxy)benzylidene)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione **(4k).** Yield 70 %; Anal: found for C$_{45}$H$_{61}$N$_3$O$_5$ (%): C, 74.51; H, 8.60; N, 5.66. Calc. C, 74.65; H, 8.49; N, 5.80. IR: υ_{max}(KBr, cm^{-1}): 2990, 2874, 1760 1618, 1589, 1254. ^{1}HNMR δ (ppm, DMSO): 8.63 (s, 1H, -CH=N-), 6.93-8.50 (m, 12H, Ar-H), 6.84 (s, 1H), 4.12 (t, 2H, J = 6.77 Hz, -OCH$_2$-), 4.00 (t, 2H, J = 6.30 Hz), 3.89 (t, 2H, J = 6.62 Hz), 3.45 (s, 3H), 3.22 (s, 3H), 1.89-1.71 (m, 32H), 0.89 (t, 3H, -CH$_3$). ^{13}C NMR δ : 176.30, 166.09, 164.20 (C=O), 163.40 (C=N), 162.33, 161.18 (Ar-C-O), 114.21-140.48 (Ar-C), 61.20 (C-O-C), 22.07 (CH$_2$), 14.40 (CH$_3$) ppm.

5-(8-(4'-(Tetradecyloxy)-[biphenyl]-4-yloxy)octyloxy)benzylidene)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione **(4l).** Yield 65 %; Anal: found for C$_{47}$H$_{65}$N$_3$O$_5$ (%): C, 75.30; H, 8.92; N, 5.73. Calc. C, 75.06; H, 8.71; N, 5.59. IR: υ_{max}(KBr, cm^{-1}): 2987, 2870, 1769 1623, 1580, 1251. ^{1}HNMR δ (ppm, DMSO): 8.68 (s, 1H, -CH=N-), 6.90-8.62 (m, 12H, Ar-H), 6.88 (s, 1H), 4.13 (t, 2H, J = 6.50 Hz, -OCH$_2$-), 4.02 (t, 2H, J = 6.47 Hz), 3.83 (t, 2H, J = 6.20 Hz), 3.48 (s, 3H), 3.27 (s, 3H), 1.87-1.72 (m, 36H), 0.84 (t, 3H, -CH$_3$). ^{13}C NMR δ : 174.10, 165.78, 163.20 (C=O), 160.94 (C=N), 161.23, 159.03 (Ar-C-O), 114.88-140.05 (Ar-C), 61.77 (C-O-C), 22.30 (CH$_2$), 14.57 (CH$_3$) ppm.

5-(8-(4'-(Hexadecyloxy)-[biphenyl]-4-yloxy)octyloxy)benzylidene)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione **(4m).** Yield 69 %; Anal: found for C$_{49}$H$_{69}$N$_3$O$_5$ (%): C, 75.52; H, 8.82; N, 5.48. Calc. C, 75.44; H, 8.92; N, 5.39. IR: υ_{max}(KBr, cm^{-1}): 2980, 2872, 1768 1625, 1582, 1250. ^{1}HNMR δ (ppm, DMSO): 8.70 (s, 1H, -CH=N-), 6.98-8.50 (m, 12H, Ar-H), 6.86 (s, 1H), 4.18 (t, 2H, J = 6.10 Hz, -OCH$_2$-), 4.06 (t, 2H, J = 6.42 Hz), 3.92 (t, 2H, J = 6.79 Hz), 3.42 (s, 3H), 3.21 (s, 3H), 1.88-1.70 (m, 40H), 0.88 (t, 3H, -CH$_3$). ^{13}C NMR δ : 174.30, 165.60, 163.11 (C=O), 160.00 (C=N),

160.19, 159.67 (Ar-C-O), 114.07-140.29 (Ar-C), 61.30 (C-O-C), 22.80 (CH$_2$), 14.69 (CH$_3$) ppm.

5-(8-(4'-(Octadecyloxy)-[biphenyl]-4-yloxy)octyloxy)benzylidene)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione **(4n).** Yield 77 %; Anal: found for C$_{51}$H$_{73}$N$_3$O$_5$ (%): C, 75.64; H, 9.28; N, 5.08. Calc. C, 75.80; H, 9.10; N, 5.20. IR: υ_{max}(KBr, cm^{-1}): 2985, 2873, 1770 1622, 1580, 1254. ^{1}HNMR δ (ppm, DMSO): 8.73 (s, 1H, -CH=N-), 6.93-8.56 (m, 12H, Ar-H), 6.88 (s, 1H), 4.19 (t, 2H, J = 6.99 Hz, -OCH$_2$-), 4.04 (t, 2H, J = 6.79 Hz), 3.96 (t, 2H, J = 6.11 Hz), 3.48 (s, 3H), 3.24 (s, 3H), 1.89-1.72 (m, 44H), 0.90 (t, 3H, -CH$_3$). ^{13}C NMR δ : 175.00, 165.88, 162.09 (C=O), 160.60 (C=N), 160.71, 159.14 (Ar-C-O), 114.49-140.67 (Ar-C), 62.09 (C-O-C), 21.20 (CH$_2$), 14.27 (CH$_3$) ppm.

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Table 1. The heating/cooling phase transition temperatures (^{o}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
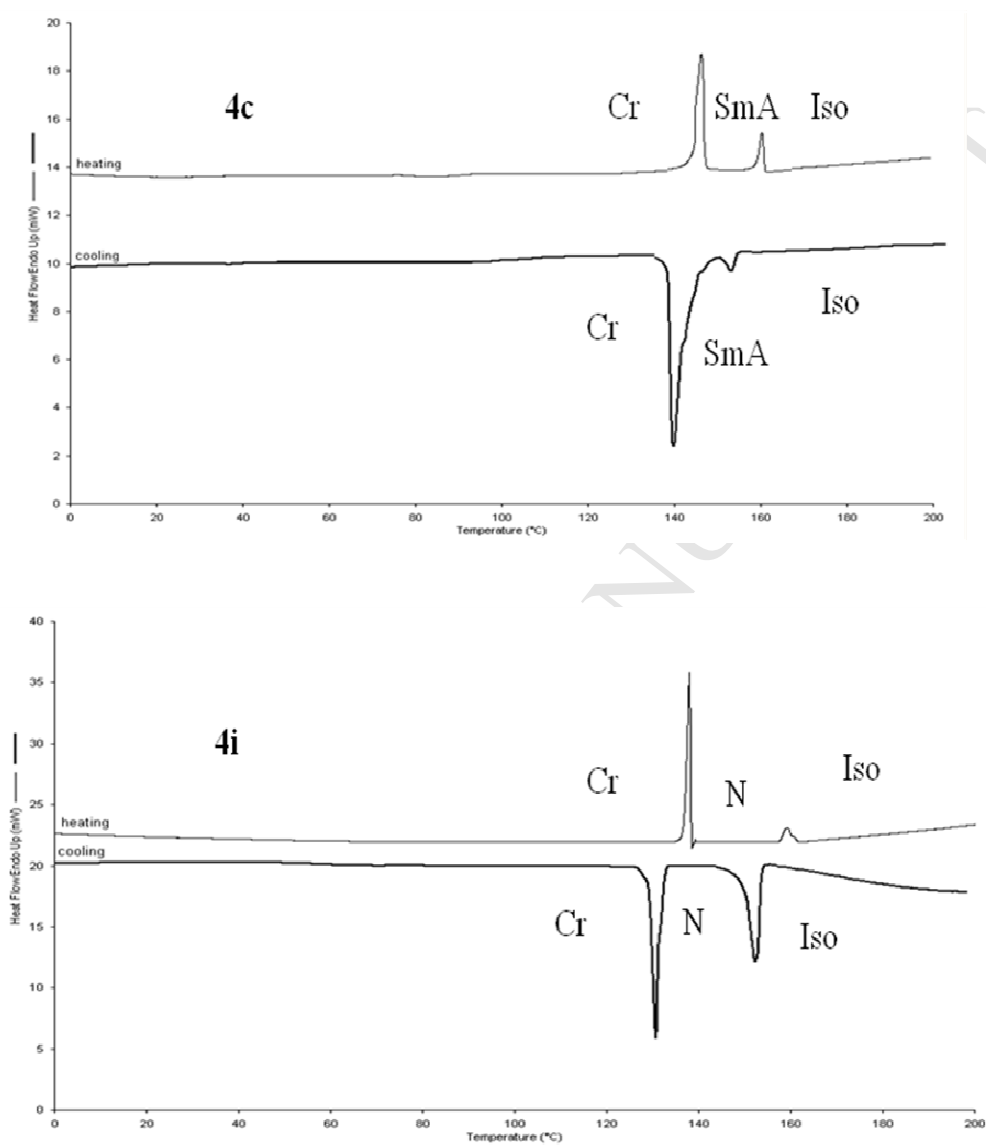
**Fig 1.** DSC scans of **4c** and **4i** on heating and cooling cycles.
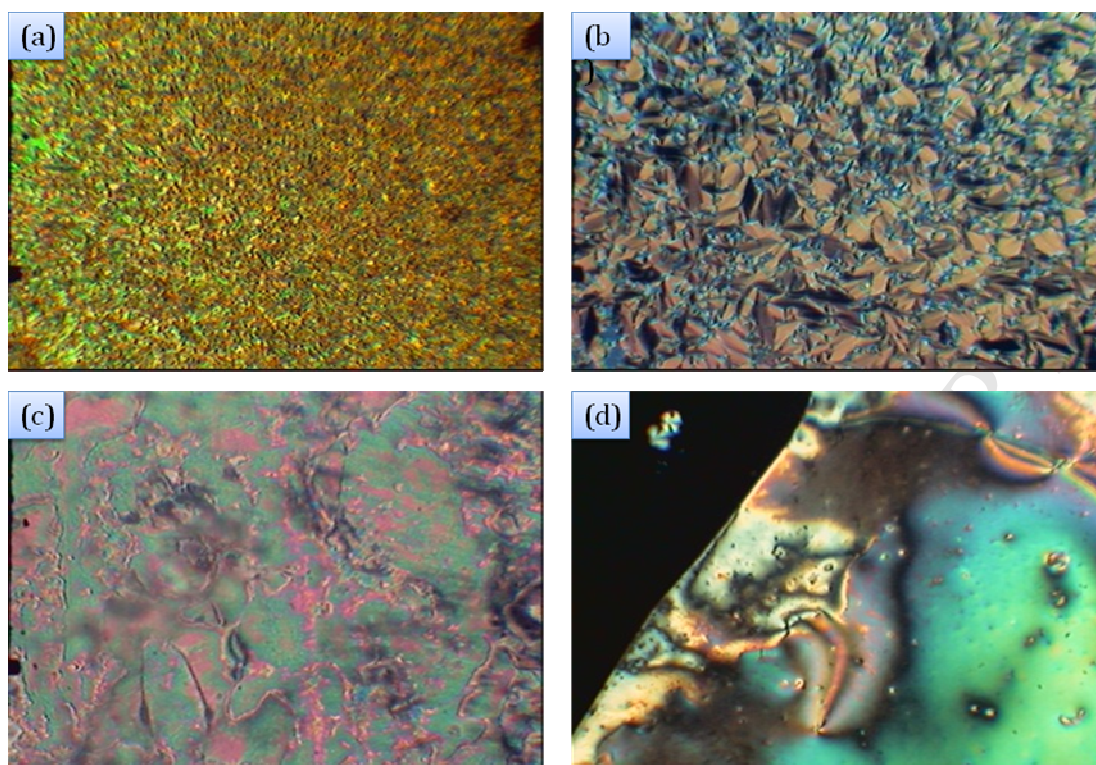
Fig 2. (a) (colour online) Optical photomicrographs of compound **4c** exhibiting SmA mesophase upon heating at 150 °C (b) **4d** upon heating displaying SmA at 165 °C (c) **4l** displaying nemaic phase upon heating at 194 °C (d) **4n** exhibiting nematic texture upon heating at 228 °C.
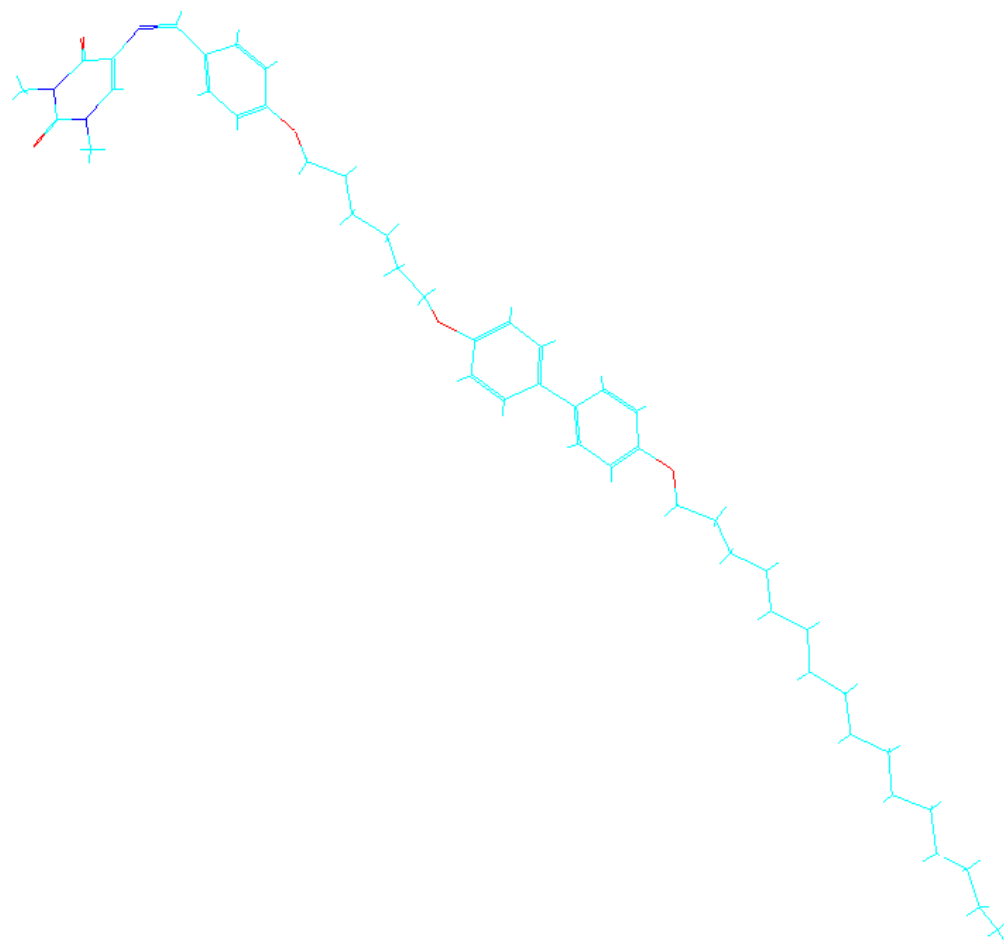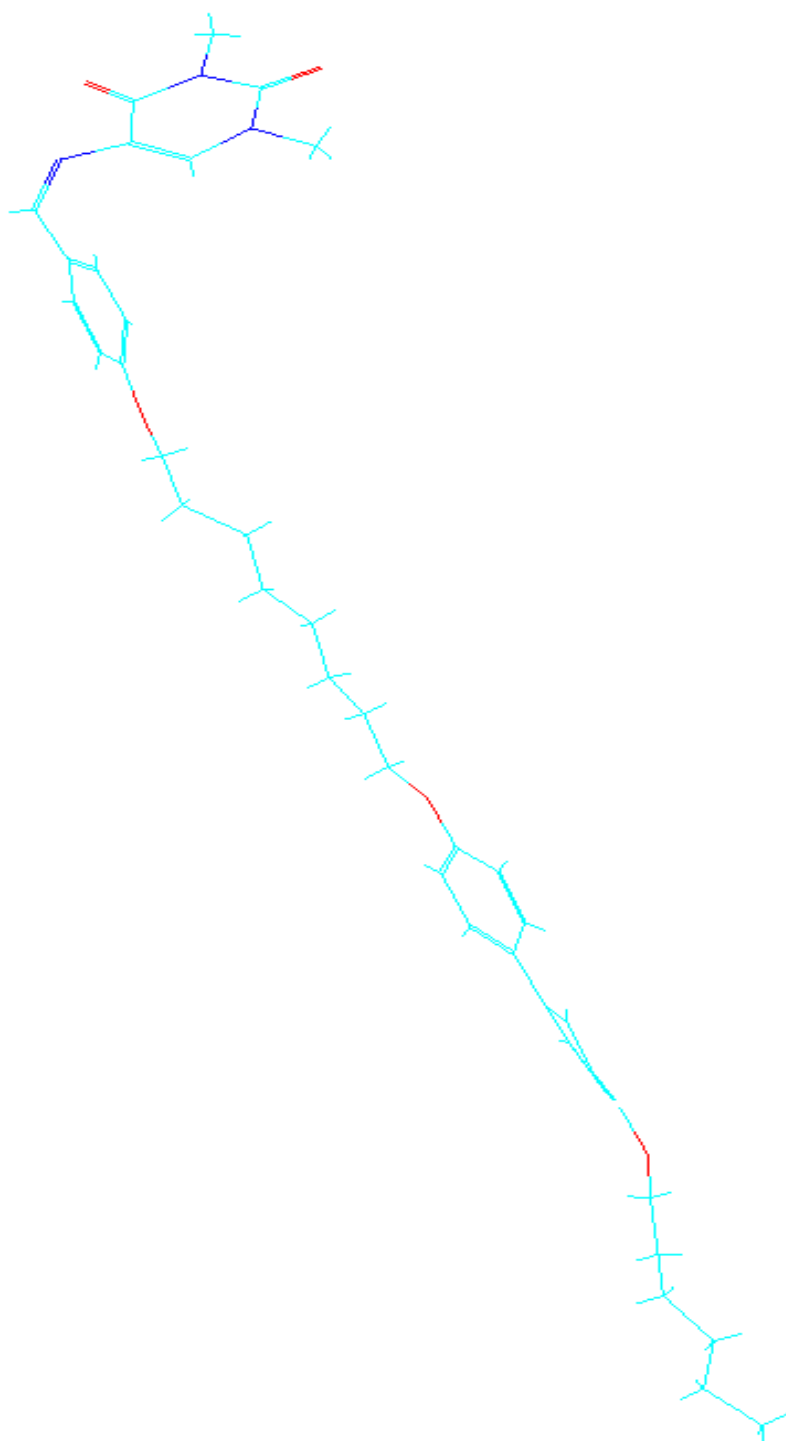

2
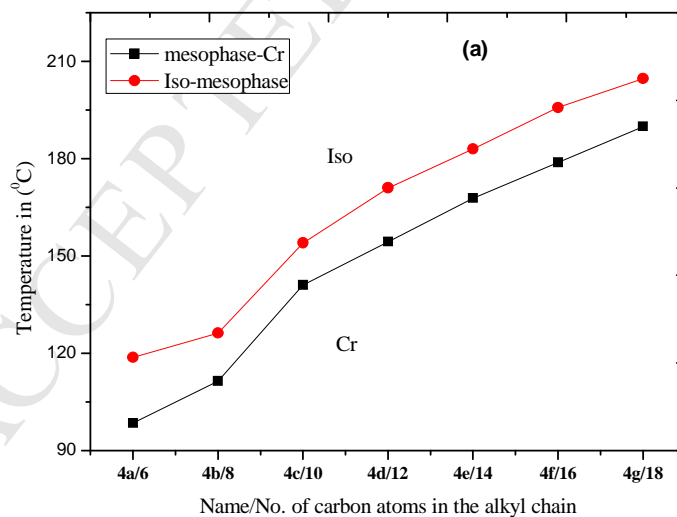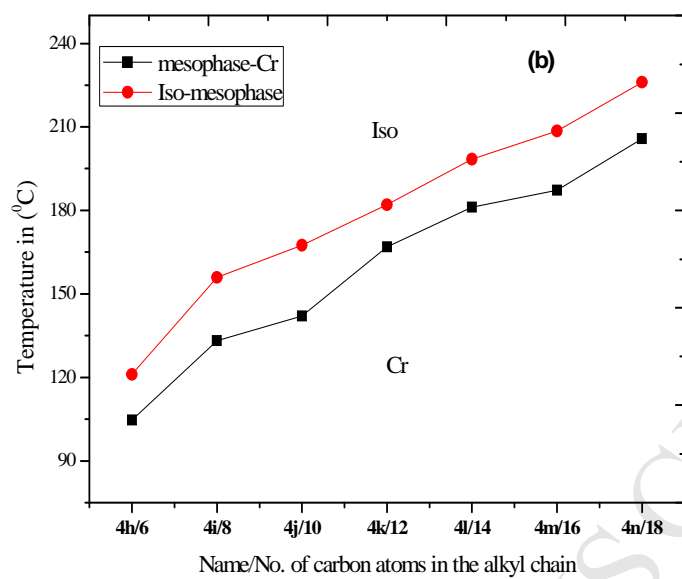
Fig 3. (colour online) Plot of cooling scan transition temperature as a function of the number of carbon atoms in the terminal chain for the sets (a) **4a-g** and (b) **4h-n**.
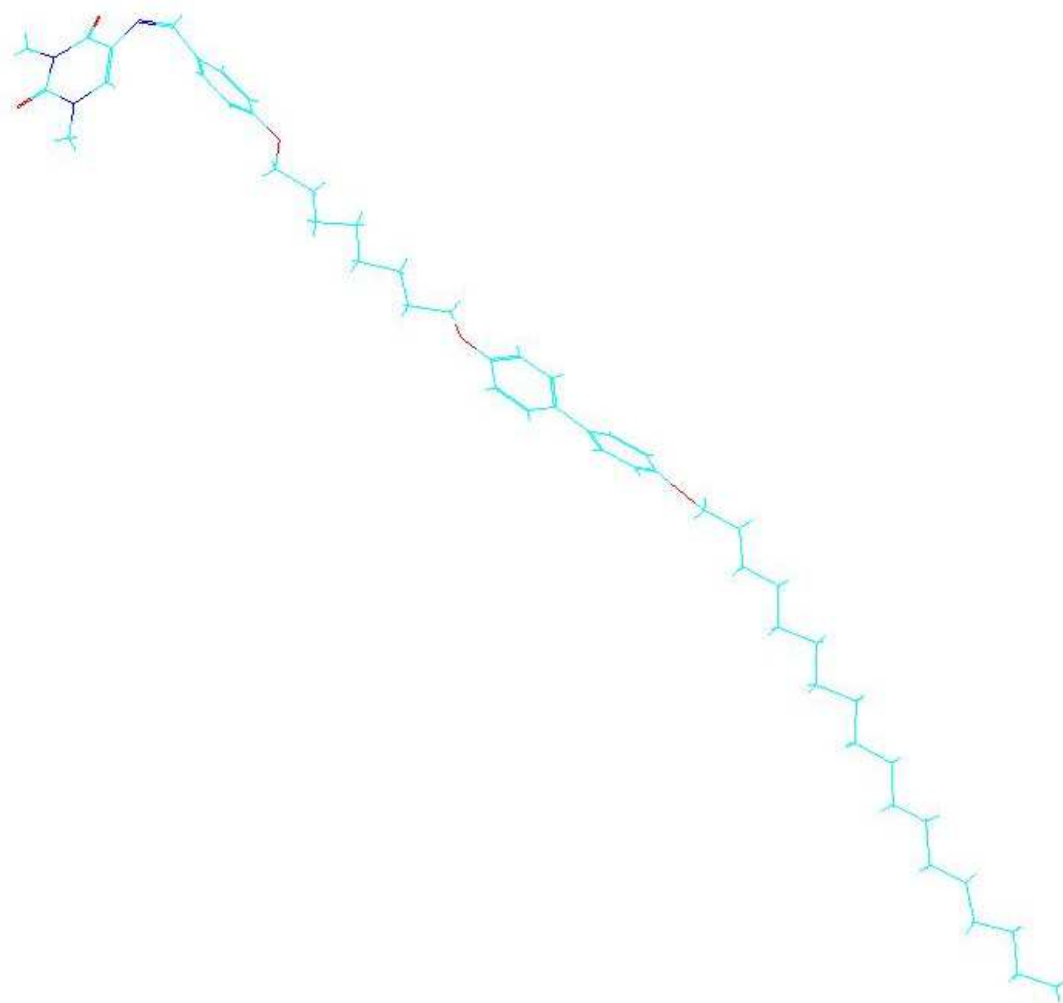
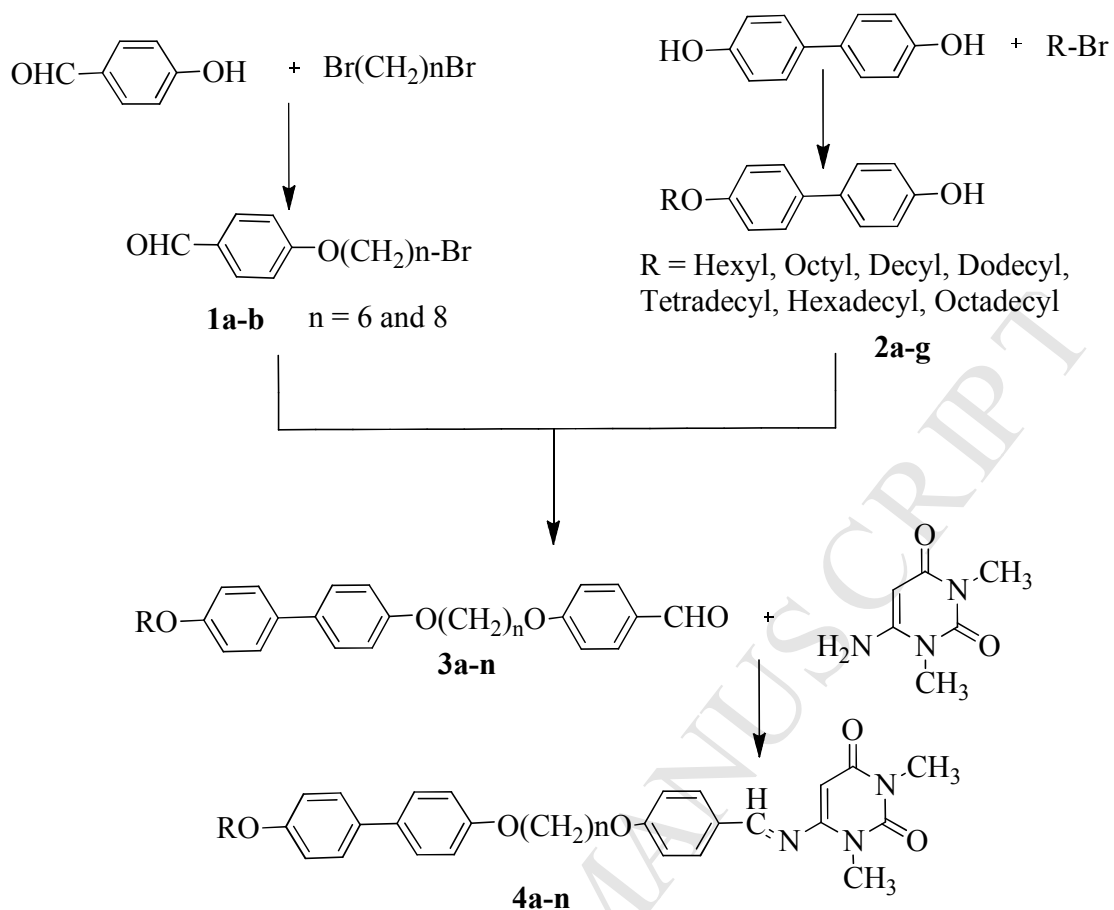HyperChem of **4a**

3
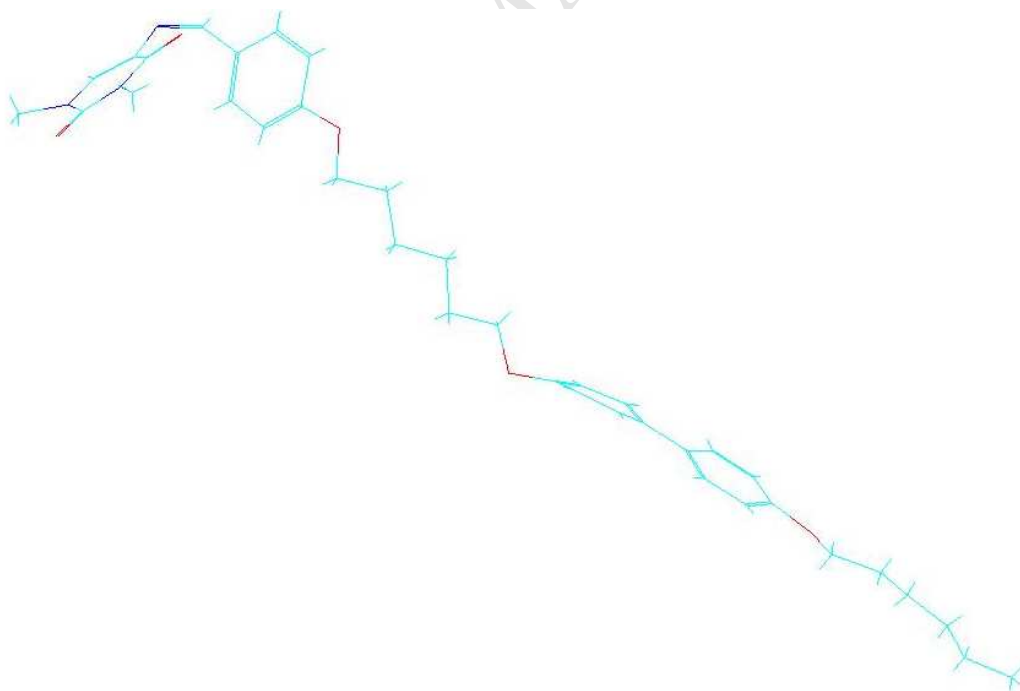
HyperChem of **4f**

HyperChem of **4h**

HyperChem of **4n**

Fig 4. (colour online) Theoretical molecular models of compound **4a, 4f, 4h,** and **4n** using HyperChem program

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

1

Highlights

● New sets of unsymmetric calamitic molecules with uracil and biphenyl core were

 synthesized.

● Liquid crystal properties are investigated by DSC and POM techniques.

 ● Theoretical studies was also studied.

 ● Smectic phase in lower members and nematic phase appeared in higher members