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## Nematogenic and smectogenic liquid crystals from new heterocyclic isoflavone derivatives: Synthesis, characterization and X-ray diffraction studies

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## Abstract

A new series of liquid crystals comprising eight heterocyclic isoflavone esters, 7-alkanoyloxy-3-[4'-(3-methylbutyloxyphenyl)]-4H-1-benzopyran-4-ones exhibiting enantiotropic nematic (N) and smectic C (SmC) phases were synthesized and investigated. The mesomorphic properties of all derivatives were investigated by means of differential calorimetry and polarized optical microscopy. Wide angle X-ray diffraction technique was employed to investigate the molecular packing associated with the intermolecular interaction as well as the correlation between the thermal behaviour of these compounds with their anisotropy properties within a mesophase.

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It has been well documented that the study of liquid crystalline materials is very important for the continual development and understanding of the field of molecular engineering [1,2]. The design and synthesis of thermotropic liquid crystals (LCs), especially noteworthy in case of conventional calamitic (rod-like) LCs, discotic (disc-like) mesogens, and to some extents, polymeric LCs have attracted much interest from both fundamental research and practical application points of view, thus emerged as an area of active research [3–5]. Research focused on modifying existing molecules, particularly natural products, has shown to be a viable approach leading to new compounds showing liquid crystalline properties [6]. Our present interest on new natural product-based heterocyclic mesogens is focused on isoflavone derivatives. Isoflavones are water-soluble chemicals found in many plants. They comprise a class of often naturally occurring organic compounds related to the flavonoids and their derivatives constitute the largest of compounds among the natural isoflavonoids [7,8]. The mesogenicity of several isoflavone derivatives as potential mesogens and their ability to form calamitic LCs of which many were polymorphic, exhibiting wide thermomorphic ranges have been studied and reported in recent years [9,10]. The introduction of heterocyclic rings within the central core and the linking groups between the middle and the terminal fragments have claimed to be responsible for the liquid crystalline behaviour of classical calamitic mesogens leading to various mesomorphism.

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 $\begin{array}{l} {\rm R}'={\rm C} \ _{n}{\rm H}_{2n+1} \ ; \ {\rm R}={\rm OCH} \ _{2}{\rm CH}_{2}{\rm CH(CH} \ _{3}){\rm CH}_{3} \\ {\rm Compounds} \ : {\rm 4} \ (n=3), \ {\rm 5} \ (n=5), \ {\rm 6} \ (n=7), \ {\rm 7} \ (n=9), \ {\rm 8} \ (n=11), \ {\rm 9} \ (n=13), \ {\rm 10} \ (n=15), \ {\rm 11} \ (n=17) \\ \end{array}$ 

Scheme 1. Reactions and reagents. (a) KOH (2 equiv), 1-bromo-3-methylbutane (1.1 equiv), refluxing in methanol, 18 h; (b) resorcinol (1.1 equiv) in BF<sub>3</sub>/Et<sub>2</sub>O, N<sub>2</sub>, 70–75 °C, 4 h; (c) BF<sub>3</sub>/Et<sub>2</sub>O (4 equiv) in DMF, N<sub>2</sub>, 55 °C, 1 h; then in MeSO<sub>2</sub>Cl (3 equiv), N<sub>2</sub>, 85 °C, 1.5 h; (d) acid chlorides, R'COCl (1.1 equiv) (R' =  $C_nH_{2n+1}$ ; n = 3, 5, 7, 9, 11, 13, 15, 17); triethylamine (catalytic), stirred in dry DMF/CH<sub>2</sub>Cl<sub>2</sub>, N<sub>2</sub>, rt, 6 h.

However, the study on the relationship between the difference in phase behaviour of this type of compounds and their molecular structure particularly on the correlation study between the molecular anisotropy and to the mesogenic behaviour of these compounds using X-ray diffraction was not well documented. As such, we are prompted to carry out a comprehensive study on isoflavone-cored mesogens covering both aspects. In this paper, we describe the synthesis, characterization and mesomorphic properties of a new series of calamitic isoflavone ester, 7-alkanoyloxy-3-[4'-(3-methylbutyloxyphenyl)]-4H-1-benzopyran-4-ones, **4–11** with various alkanoyloxy chain lengths in odd-parity. The synthetic routes toward the formation of the intermediates and title compounds are shown in Scheme 1 and their structures were elucidated *via* elemental analysis, FT-IR and NMR spectroscopic techniques [11].

The mesomorphic behaviour of compounds 4-11 was characterized and studied using differential scanning calorimetry (DSC) and polarized optical microscope (POM). Their phase transition temperatures and associated enthalpies were collated in Table 1. All derivatives exhibited enantiotropic mesophases regardless of the alkyl chain length. Derivatives with short alkyloxy chains, 4 (n = 3) and 5 (n = 5) are nematogenic. Observation under crossed

Table 1 Phase transition temperatures and enthalpy change for compounds **4–11** during heating.

Compound	Phase transition	Temperature (°C)	Enthalpy change (kJ mol <sup>-1</sup> )
4	Cr–N	124.0	32.4
	N–I	140.0	0.8
5	Cr–N	126.0	29.6
	N–I	132.0	0.9
6	Cr–SmC	119.0	24.8
	SmC–I	133.0	5.0
7	Cr–SmC	109.0	27.8
	SmC–I	135.0	6.7
8	Cr–SmC	135.0	35.5
	SmC–I	139.0	7.1
9	Cr–SmC	100.0	29.0
	SmC–I	129.0	7.5
10	Cr–SmC	96.0	27.6
	SmC–I	131.0	7.9
11	Cr–SmC	94.0	31.9
	SmC–I	123.0	7.7

Cr, crystal; N, nematic; SmC, smectic C; I, isotropic.



Fig. 1. (a) Compound **5** displaying marble texture of the N phase upon heating. (b) Schlieren texture co-exists with broken focal-conic fans of SmC phase exhibited by compound **6**.

polarizers of compound **5** showed marble texture (Fig. 1a) The N phase for these homologues is thermally stable with mesomorphic ranges of 16 °C and 6 °C, respectively at high clearing temperatures (exceeding 130.0 °C).

However, the N phase is not detectable in other derivatives of which the number of carbon atoms in the odd-parity terminal chains,  $n \ge 7$ . This observation can be rationalized in terms of the presence of long terminal alkyl chains which become interwined that leads to tilted and disordered lamellar packing as commonly found in SmC phase [12]. SmC phase exhibited by compounds **6–11** (n = 7, 9, 11, 13, 15 and 17) can be characterized by the formation of batonnets that coalesce to form the less crisp, broken fan-shaped textures. A typical morphology of these compounds can be shown by compound **6** in Fig. 1b of which the Schlieren texture co-exists with some fan-shaped domains which are due to inhomogeneity in alignment of the sample.

It can be generalized that the clearing temperatures are found to increase with the length of the alkyloxy chains in odd parity. This may probably be attributed to an enhanced dispersive interaction or van der Waals interaction between the terminal alkyloxy chains. However, the melting temperatures of compounds **9–11** is found to be lower than those of compounds **4–8** which could probably be due to the repulsive (steric) forces leading to larger intermolecular distance, a consequence of deviation from linearity of the terminal alkyloxy chains in compounds **9–11**. Although the molecular structures of compounds **4–8** may be fully stretched, the long molecular axis of compounds **9–11** could be distorted from linearity. Furthermore, the flexibility of long alkyloxy chains tends to disrupt molecular packing thus facilitating molecular tilting and stabilizes the SmC phase formation when coupled with enhanced intermolecular forces of attraction associated with the ester and ether linkages of the terminal chains. Hence, the molecules are assumed to be able to pack effectively in a lamellar manner and in space leading to higher sustainability of SmC phase [13]. This is indicated by a rather broad thermal mesomorphic range ( $\leq 20.0$  °C), high clearing temperatures (>100 °C) and large isotropic transition enthalpies (>6 kJ/mol) for all derivatives.

The powder X-ray diffraction measurements were performed on compound **6** to confirm the structure of SmC phase [12]. As can be seen in Fig. 2, the layer spacing values, *d*, of compound **6** in SmC phase are almost independent on temperature. Upon cooling, the layer spacing decreased from 27.5 Å at 130.0 °C and reached a minimum at 27.4 Å around 110.0 °C, then it increased slightly and reached a maximum of 27.7 Å upon crystallization at 75.0 °C. The layer spacing of compound **6** was 0.8–1.1 Å shorter than that of its effective molecular length, *l* (28.5 Å) estimated



Fig. 2. Layer spacing of compound 6 during a transition from SmC phase to crystal phase upon cooling.

using CCDC Mercury 1.4.2 version. The observation in layer spacing reflected the conformations of molecules in crystal and SmC phase, respectively. The molecules thus assumed to be almost fully stretched in crystal phase but are slightly tilted in SmC phase. However, the tilt angle in SmC phase cannot be determined due to a first order transition, a transition that involved a discontinuity in entropy, which is the first derivative of the Gibbs energy function [14,15].

In conclusion, all the target compounds exhibited stable, enantiotropic liquid crystalline nematic and smectic C phases. The mesophases were found to be side chain dependent; compounds **4** (n = 3) and **5** (n = 5) were nematogenic whilst compounds **6–11** (n = 7, 9, 11, 13, 15, 17) were smectogenic. The planarity and enhanced polarity of the oxygen atoms of the ester and ether linkages as well as the heterocyclic central moiety may be attributed to the stability of the mesophases.

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- [11] Analytical and spectroscopic data for the representative compound **7**: Yield 60%, anal: calcd. for  $C_{30}H_{38}O_5$ , C 75.27, H 8.00, found, C 75.28, H 8.80%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.32 (d, 1H, J = 8.7, Ar–H), 7.97 (s, 1H, Ar–H), 7.49 (d, 2H, J = 8.7, Ar–H), 7.28 (d, 1H, J = 2.1, Ar–H), 7.14–7.16 (dd, 1H, J = 8.7, J = 2.1, Ar–H), 6.97 (d, 2H, J = 8.7, Ar–H), 4.01–4.04 (t, 2H, OCH<sub>2</sub>), 2.59–2.63 (t, 2H, CH<sub>2</sub>COO), 1.81–1.89 (m, 1H, OCH<sub>2</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>3</sub>), 1.70–1.80 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.62–1.69 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>3</sub>), 1.29–1.43 (m, 10H, (CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>COO), 0.97 (d, 6H, (OCH<sub>2</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>3</sub>)) 0.87–0.91 (t, 3H, COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  176.22, 159.69, 157.06, 154.93, 152.95, 130.47, 128.21, 125.62, 123.97, 122.64, 119.85, 115.00, 111.27 (C<sub>arom</sub>), 171.90 (COO), 66.84 (OCH<sub>2</sub>), 25.45 (CH), 23.08–38.35 (CH<sub>2</sub>), 23.00, 14.52 (CH<sub>3</sub>).
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