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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)]-4*H*-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.

Keywords: Heterocyclic; Isoflavone; Enantiotropic; Mesophase

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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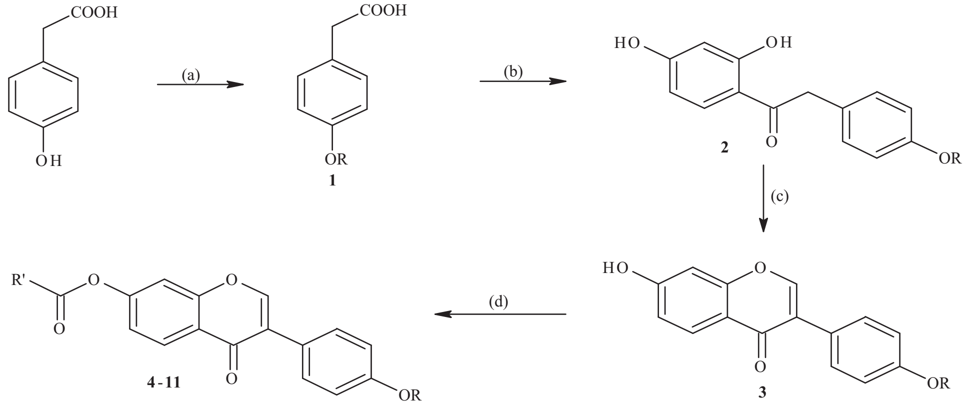

R' = C_nH_{2n+1} ; R = $OCH_2CH_2CH(CH_3)CH_3$
Compounds : **4** (*n*=3), **5** (*n*=5), **6** (*n*=7), **7** (*n*=9), **8** (*n*=11), **9** (*n*=13), **10** (*n*=15), **11** (*n*=17)

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_3/Et_2O, N_2, 70–75 °C, 4 h; (c) BF_3/Et_2O (4 equiv) in DMF, N_2, 55 °C,1 h; then in $MeSO_2Cl$ (3 equiv), N_2, 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_2Cl_2, N_2, 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)]-4*H*-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^{-1})
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.