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New fluorescent mesogens with benzopyran-4[H] one heterocyclic moiety

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We have reported on isoflavone derivatives as potential mesogens. Few mesogens of chromone and flavone derivatives are found in the literature. Chromones are fluorescent in character. In the present study, a homologous series of 2-methyl-6-(4′-*n* alkoxybenzoyloxy)benzopyran-4[H] one, was synthesized by condensing 2-methyl-6-hydroxybenzopyran-4[H] one with thirteen different 4′-*n*-alkoxybenzoyl chlorides. The lower members of the series are not mesogenic in character. The decyloxy to hexadecyloxy derivatives do exhibit liquid crystalline mesophases. The decyloxy member exhibited only the monotropic nematic phase. The dodecyloxy to hexadecyloxy of benzopyran-4[H] one derivatives exhibit smectic mesophases. DSC studies served the dual purpose of confirming the microscopic transition temperatures. The synthesized compounds are characterized by elemental analysis and spectroscopy. The thermal stabilities of the homologous series were compared with those of corresponding flavones and isoflavones.

1. Introduction

Chromones are benzopyran derivatives and these comprise a varied class of natural products. Moreover chromone derivatives give fluorescence in dilute alkali and acidic media [1]. Mesogens with benzopyran are rare [2–4]. Tadashiro *et al.* [5], have reported flavone derivatives showing mesogenic behaviour. Over the last few years, we have been trying to understand the effect of the benzopyran moiety [6, 7] on liquid crystallinity. Recently, we have reported potential mesogens with 3-phenyl-4[H]-4 one benzopyran (isoflavone) derivatives [7]. Therefore it was thought of interest to synthesize the substituted benzopyran-4[H] on (chromone) derivatives and study the mesogenic behaviour as well as its fluorescent properties.

2. Experimental

Microanalysis of the compounds were performed on a Coleman carbon–hydrogen analyser, and IR spectra were recorded on a Shimadzu IR-408. NMR spectra were recorded on a Perkin–Elmer R-32 spectrometer. Liquid crystalline properties were investigated on a Leitz Labourlux II polarizing microscope with heating stage. DSC were investigated on a Mettler TA-4000 system.

4-Hydroxybenzoic acid (BDH), the appropriate alkyl halide (BDH), hydroquinone (Sisco chem), $AlCl_3$ (Sisco chem) and acetic anhydride (BDH) were used in the synthesis. The synthetic route is illustrated in figure 1. The 4-*n*-alkoxybenzoic acids [8], 4-*n*-alkoxybenzoyl chloride [8], hydroquinone diacetate, 2,5-dihydroxyacetophenone and 2-methyl-6-hydroxybenzopyran-4-[H] one [9] were prepared according to reported methods.

The general preparation of 2-methyl-6-(4′-*n*-alkoxybenzoyloxy)benzopyran-4[H] one is as follows: 2-methyl-6-hydroxybenzopyran-4[H] one (0·02 mol) was dissolved in 5 ml of dry pyridine and a cold solution of 4-*n*-alkoxybenzoyl chloride in 5 ml of dry pyridine was added slowly to it with constant stirring in an ice bath. The mixture was allowed to stand overnight at room temperature. It was acidified with 1:1 dilute hydrochloric acid. The precipitates were filtered off, washed with cold solution of alkali, followed by cold water and recrystallized from ethanol.

Elemental analysis of all compounds was found to be satisfactory. Spectral analysis of 2-methyl-6-(4′-*n*-alkoxybenzoyloxy)benzopyran-4[H] one is given in the following form: (i) The IR (KBr) spectra of the compounds showed the characteristics frequency of an ester at $1740\,cm^{-1}$ and carbonyl group at $1640\,cm^{-1}$. Other signals observed were at 2975, 1605, 1445 and $1090\,cm^{-1}$. (ii) The NMR spectrum (90 MHz $CDCl_3$) of compound **10** exhibited signals at δ 1·35 (s, 19 H, alkoxy

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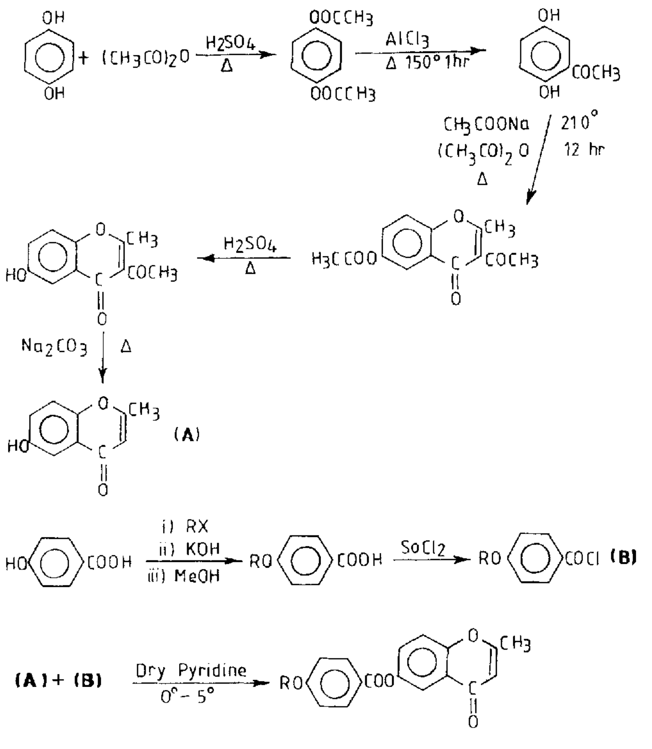


Figure 1.

chain at C_6), 2·4 (s, 3 H C_2–CH_3), 4·1 (t, 2 H, alkoxy chain attached at C_6), 6·9 (d, $J = 9$ Hz, 2 H, C_3' and C_5'), 7·45 (m, 2 H, C_7, C_8), 7·9 (d, $J = 3$ Hz, 1 H, C_5) and 8·15 (d, $J = 9$ Hz, 2 H, C_2' and C_6').

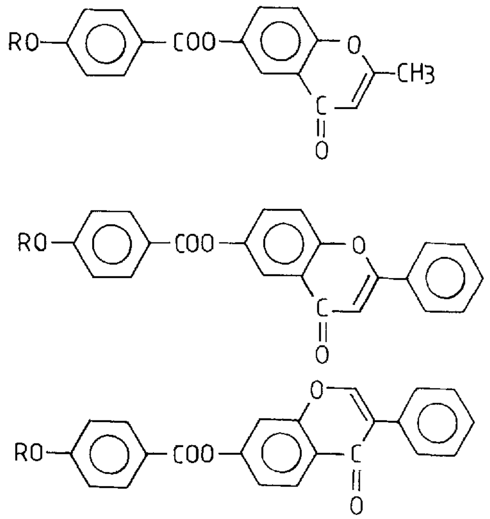
3. Results and discussions

The transition temperatures of the compounds synthesized are compiled in table 1. A few transitions were obtained by DSC with a view to confirm the observation under the microscope. The temperature dependence against the number of carbons atoms on the terminal chain is shown in figure 2.

The first nine members of the series were non-mesogenic. Mesophase behaviour is exhibited from the *n*-decyloxy to *n*-hexadecyloxy derivatives. The *n*-decyloxy member exhibits a monotropic nematic mesophase, whereas the *n*-dodecyloxy to *n*-hexadecyloxy derivatives exhibit enantiotropic smectic mesophases.

The transition temperatures increase with increasing number of carbon atoms in the alkoxy chain showing smectic and nematic mesophases. The mesomorphic behaviour exhibited by this system is of interest in understanding the effect of different structural aspects on the mesomorphism keeping in view the molecular geometry of benzopyran moiety. The smectic thermal stability of series **I** was compared with that of the reported series **A** [5] and **B** [7], in table 2

Series



(1)

(A)

(B)

The similarity in the structure of series **I** with series **A** and **B** lies in the fact that all of them have a heterocyclic moiety fused to the benzene ring. The difference in the structure of series **I** and **A** is a methylene group in the place of a phenyl ring; the phenyl ring increases the molecular polarizability and length relative to that of the methylene group.

The average nematic thermal stability of series **I** is less than that of series **A** and **B**. In the series **I** the nematic

Table 1. The transition temperatures of the 2-methyl-6-(4′-*n*-alkoxybenzoyloxy)benzopyran-4[H] one.

		Transition temperature/°C		
Compound	*R*	Smectic	Nematic	Isotropic
1	Methyl	—	—	174·4
2	Ethyl	—	—	160·3
3	Propyl	—	—	153·3
4	Butyl	—	—	119·4
5	Pentyl	—	—	106·3
6	Hexyl	—	—	105·2
7	Heptyl	—	—	83·2
8	Octyl	—	—	81·2
9	Nonyl	—	—	82·5
1-	Decyl	—	(69·5)	73·0
11	Dodecyl	53·3	—	85·2
12	Tetradecyl	59·0	—	90·6
13	Hexadecyl	87·7	—	119·1

Parentheses denote a monotopic transition.

DSC of compound **10**.

Compound	Heating rate K min^{-1}	H/J g^{-1}	S/J g^{-1} K^{-1}	Mean
10	10	1·12761	0·00329229	0·00329229

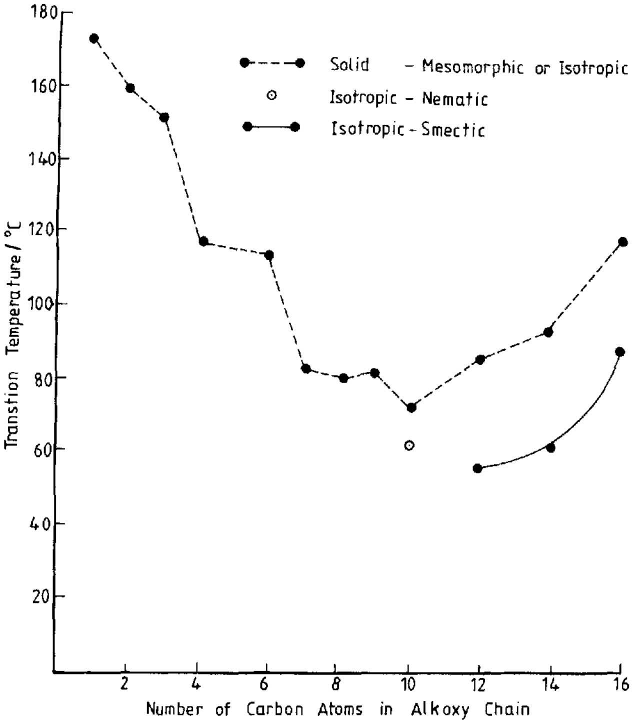


Figure 2. The temperature dependence against the number of carbon atoms *n* in the terminal alkoxy chain of series **I**.

mesophase is only exhibited by the *n*-decyloxy derivative whilst for series **A** and **B** the nematic mesophase is exhibited by each homologue. This is due to phenyl rings which are more polarizable and longer than the methylene group. The increase in polarizability and length induces mesomorphism with higher thermal stabilities [10]

The smectic thermal stabilities of series **I** are lower relative to series **B** because the phenyl ring is substituted. However, the phenyl ring adjacent to the keto group affects the smectic mesophase of series **A** whilst series **I** with a methylene group has a higher smectic thermal stability.

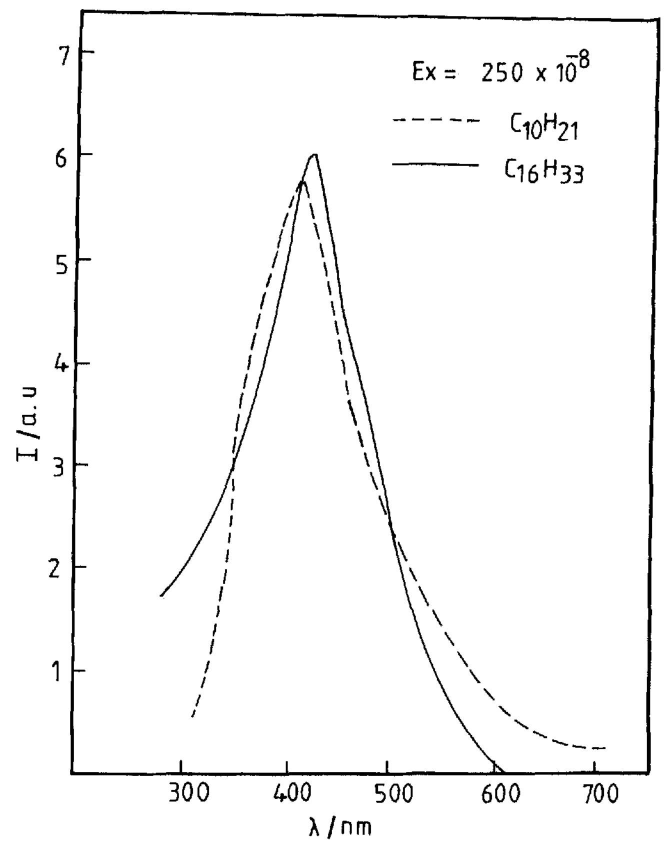
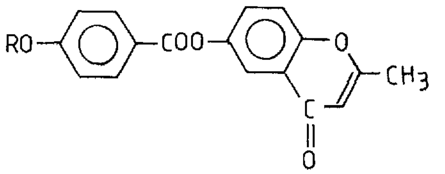


Figure 3. Emission spectrum of homologues **10** and **13**.

From the structure of the compounds of series **I**, it is seen that a lone pair of electrons is present on the oxygen of the chromone ring and that of the ester linkage. These non-bonding electrons have a perturbing effect [11]. The presence of the hydrogen bond which is formed with the non-bonding electrons on the oxygen in the chromone ring increases its strength compared to that of the ester linkage which ultimately reduces the perturbing effect in the system. This reduction in perturbance increases the fluorescence [12]. This is responsible for the 360 nm band observed in the case of excitation at 310 × 10^{-7} of the decyl homologue **10** and hexadecyl homologue **13** (see table 1).

Table 2. Average thermal stabilities of series **I**, **A** and **B**.

Phase	Series **I**	Series **A**	Series **B**
Nematic–isotropic	67·50 C_{10} only	184° C_1–C_9	210·88° C_1–C_9
Smectic–isotropic	67·66° C_{12}, C_{14}, C_{16}	— —	137° C_{12}, C_{14}, C_{16}
Commencement of the smectic phase	C_{12}	—	C_6



where *R* = (**10**) $C_{10}H_{21}$
(**13**) $C_{16}H_{33}$

It is observed from the trend in series **I** that a considerable drop in the intensity of the band at 360 nm of the two emission peaks present at 360 and 430 nm (see figure 3).

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