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# Synthesis and mesomorphic characterization of azoesters with a coumarin ring†

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We have synthesized a homologous series of azoesters consisting of a coumaryl moiety as the end group. Eleven derivatives of this series exhibit mesomorphism. The nematic mesophase is exhibited from ethyl homologue onward, while the smectic phase commences at the pentyl derivative and is exhibited along with the nematic phase up to the hexadecyl derivative. The N–I transition temperatures curves show the usual odd–even effect. All the compounds in this series are thermally stable and exhibit a wide mesomorphic range of nearly 120°C. Their thermal stabilities and other characteristics are discussed.

## 1. Introduction

The liquid crystalline properties of organic compounds are highly sensitive to changes in chemical structure. Considerable effort has been devoted to the systematic study of mesomorphism in homocyclic compounds [1–3]. However, heterocyclic moieties are comparatively less explored. The mesogenicity of coumarin derivatives has been studied by only a few researchers [4, 5]. The type of mesophase in coumarin derivatives depends on the chemical structure of groups substituted at different positions. Substitution by an ester group tends to produce the smectic A phase, while a cyano group causes the appearance of the nematic as well as smectic A mesophases [5]. We thought it interesting to incorporate the azo group into the system, to evaluate its effect on the coumarin skeleton.

Azobenzene derivatives were among the first ten discovered liquid crystalline compounds [6, 7]. The series, namely 4-*n*-alkoxy-4′-alkylazobenzenes with short alkyl chains, was first described by Steinstrasser and Pohl [8]. It was followed by series of papers on similar compounds by de Jeu [9], Demus *et al.* [10], Dabrowski *et al.* [11] and Dave *et al.* [12]. Azobenzene derivatives have become particularly interesting because of the photoresponsive behaviour of the photochromic group. Moreover they are rich in polymesomorphism and have been successfully applied in non-linear optics [13].

## 2. Experimental

The synthetic route for the present series is shown in the scheme. 4-Hydroxyphenylazo-4′-benzoic acid [14], 4-*n*-alkoxyphenylazo-4′-benzoic acids [15], 4-*n*-alkoxyphenylazo-4′-benzoyl chlorides and 4-methyl-7-hydroxycoumarin [16] were synthesized by reported methods.

4-Methyl-7-coumaryl 4-(4-*n*-alkoxyphenylazo)benzoates were synthesised by the following method: 0.01 mol of 4-methyl-7-hydroxycoumarin was dissolved in 10 ml of dry pyridine and the solution was added slowly to 0.01 mol of the respective cold 4-*n*-alkoxyphenylazo-4′-benzoyl chloride. The mixture was heated under reflux on a water bath for one hour and was allowed to stand overnight. It was acidified with 1:1 cold aqueous HCl to precipitate the esters which were filtered and washed with water. The final product was crystallized several times from *n*-propyl alcohol until constant transition temperatures were obtained. The transition temperatures and elemental analysis are recorded in tables 1 and 2, respectively.

FTIR (Nujol, KBr pellets, $cm^{-1}$): $n$-$OC_6H_{13}$ 2923, 2359, 1733, 1598, 1253, 1076, 861, 580, 547; $n$-$OC_{12}H_{25}$: 2923, 2359, 1731, 1603, 1079, 1020, 888, 549. $^1H$ NMR ($CDCl_3$, 100 MHz, $\delta$ ppm, standard TMS): $n$-$OC_{12}H_{25}$ 0.9 (t, 3H, $-CH_3$), 1.27 (bs, 20H, $10 \times -CH_2$), 2.44 (s, 3H, $-CH_3$ of coumarin ring), 4.05 (t, 2H, $-OCH_2$), 6.27 (s, 1H, alicyclic proton), 6.8–7.6 (m, 5H at $C_2$, $C_6$, $C''_5$, $C''_6$ and $C''_8$), 8.0 (d, 4H at $C_3$, $C_5$, $C'_2$ and $C'_6$), 8.4 (d, 2H at $C'_3$ and $C'_5$).

All the compounds were analysed by elemental analysis using a Coleman USA-CHN analyser; they were in conformity with the theoretical values. Transition temperatures and textures of mesophases were studied

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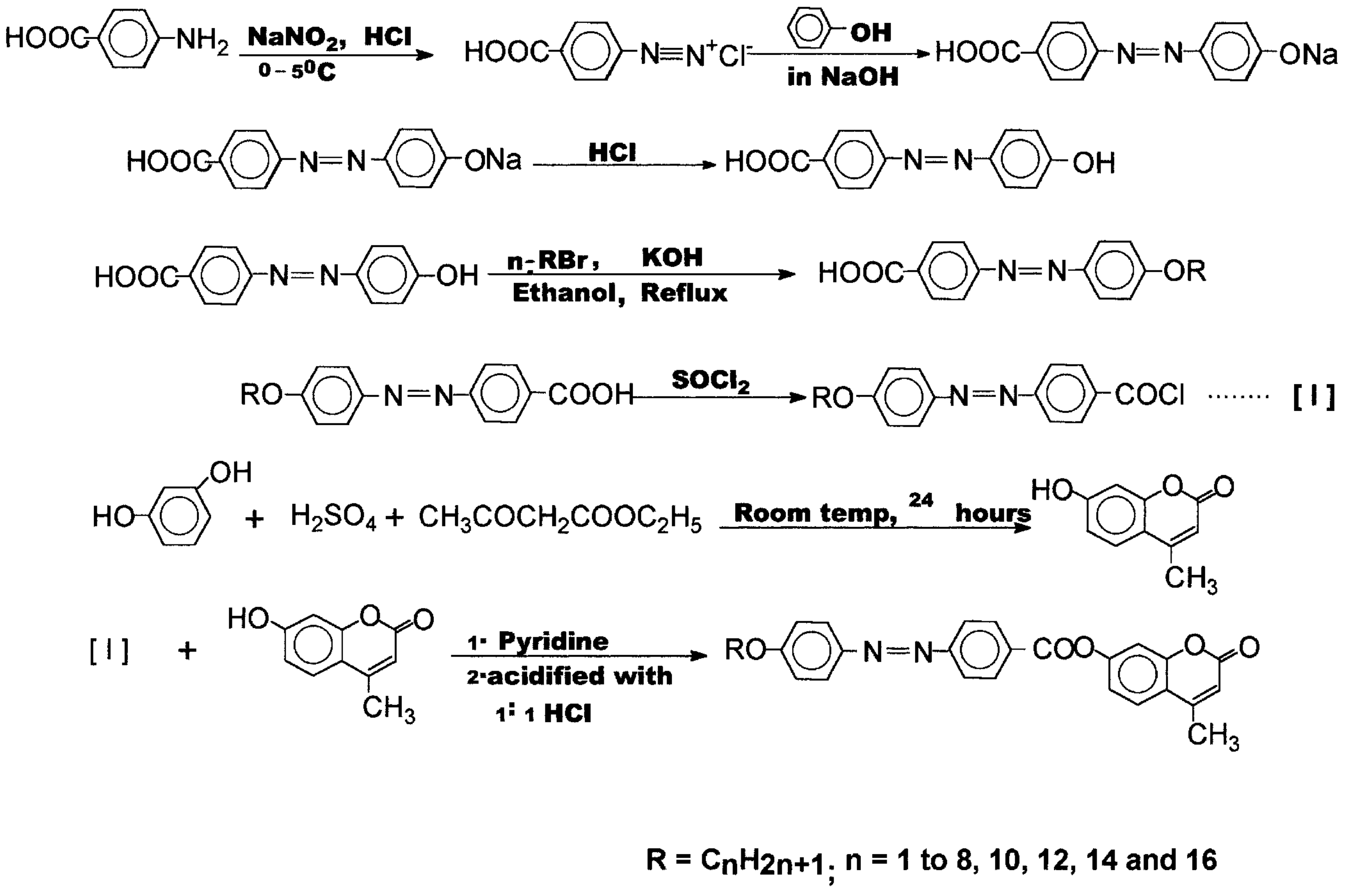


Scheme. Synthetic route to series A compounds.

Table 1. Transition temperatures (°C) 4-methyl-7-coumaryl 4-(4-*n*-alkoxyphenylazo) benzoates.

| | Transition | | | |
|---|---|---|---|---|
| *n*-Alkoxy group | Smectic B | Smectic C | Nematic | Isotropic |
| Methoxy | — | — | — | 230 |
| Ethoxy | — | — | 195 | 245 |
| Propoxy | — | — | 158 | 228 |
| Butoxy | — | — | 182 | 230 |
| Pentoxy | — | 114 | 136 | 208 |
| Hexyloxy | — | 106 | 151 | 216 |
| Heptyloxy | — | 114 | 158 | 202 |
| Octyloxy | (105)[a] | 130 | 163 | 205 |
| Decyloxy | (115)[a] | 122 | 169 | 195 |
| Dodecyloxy | — | 131 | 170 | 188 |
| Tetradecyloxy | — | 122 | 166 | 185 |
| Hexadeyloxy | — | 109 | 162 | 190 |

[a] Values in parentheses show monotropic transitions.

by using a Leitz Laborlux polarizing microscope provided with a Kofler heating stage. Differential scanning calorimetry of the representative *n*-octyloxy homologue was carried out using a Mettler DSC 20.

The analytical spectroscopic data of a few representative compounds were obtained on a Perkin-Elmer FTIR, a JEOL FX 100 spectrophotometer (for NMR) and a Perkin-Elmer fluorescence spectrophotometer.

Table 2. Elemental analysis for 4-methyl-7-caumaryl 4-(4-*n*-alkoxyphenylazo)benzoates

| *n*-Alkoxy group | % Required C | H | N | % Found C | H | N |
|---|---|---|---|---|---|---|
| Methoxy | 69.56 | 4.34 | 6.76 | 69.68 | 4.31 | 6.81 |
| Ethoxy | 70.09 | 4.67 | 6.54 | 70.02 | 4.65 | 6.58 |
| Propoxy | 70.58 | 4.97 | 6.33 | 70.66 | 4.95 | 6.37 |
| Butoxy | 71.05 | 5.26 | 6.14 | 70.98 | 5.30 | 6.05 |
| Pentoxy | 71.48 | 5.53 | 5.95 | 71.50 | 5.60 | 5.90 |
| Hexyloxy | 71.90 | 5.78 | 5.78 | 71.78 | 5.83 | 5.75 |
| Heptyloxy | 72.28 | 6.02 | 5.62 | 72.40 | 5.96 | 5.61 |
| Octyloxy | 72.65 | 6.25 | 5.46 | 72.57 | 6.09 | 5.51 |
| Decyloxy | 73.33 | 6.66 | 5.18 | 73.38 | 6.36 | 5.23 |
| Dodecyloxy | 73.94 | 7.04 | 4.92 | 73.91 | 7.28 | 4.97 |
| Tetradecyloxy | 74.49 | 7.38 | 4.69 | 74.50 | 7.42 | 4.72 |
| Hexadecyloxy | 75.00 | 7.69 | 4.48 | 74.88 | 7.77 | 4.39 |

## 3. Results and discussion

Twelve compounds of this series were synthesized and their mesogenic properties studied. All the homologues are mesogenic, except the methyl derivative, which is non-mesogenic in nature. The nematic phase is exhibited from the ethyl homologue onward; the smectic C phase is seen at the pentyl derivative and is exhibited along with nematic phase up to the last hexadecyl homologue studied. In this series, two homologues, octyl and decyl, exhibit an additional monotropic SmB phase.

### 3.1. *Thermal properties*

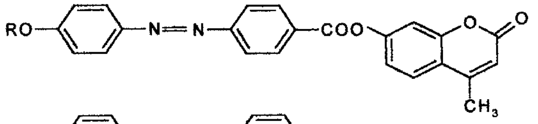
Figure 1 shows the plot of transition temperature versus the number of carbon atoms in the *n*-alkoxy chain. The Sm–N curve rises from the pentyl derivative, forming a smooth curve up to the dodecyl homologue; it then falls slightly in the last two homologues. The N–I transition points fall on two odd–even curves; the upper even curve falls smoothly with a slight rise at the hexadecyl homologue, while the lower odd curve falls forming an arc between the propyl and pentyl derivatives. The $C_{16}$ compound exhibits a diverging instead of a covering trend in both Cr–N and N–I transitions. It is generally seen that the crystal–mesomorphic transition shows no regular trend; however, with the increase in length of the *n*-alkoxy chain in the $C_{16}$ homologue, the polarizibility of the molecules increases, thereby causing higher N–I transitions [17]. The SmC–SmB (monotropic) curve shows a rising tendency from the octyl to decyl homologues. The higher homologues do not show a SmB phase even on careful supercooling of their melts. Although the coumarin moiety has a breadth-increasing effect in the series, it has well balanced lateral and terminal cohesive forces, which contribute to enhanced mesomorphic properties in this series.

In the present series, it was observed that the entropy change at 105°C (figure 2) was too high for a smectic A–C transition but was comparable to smectic A–B or smectic C–B transitions [18]. This observation can be attributed to the polar ordering of the molecules within the smectic strata.

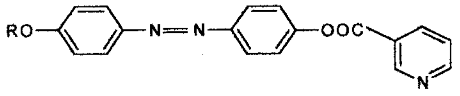
Table 3 summarizes the average thermal stabilities of the present series (A) and three other homologous series (I, II, III) taken for comparative study:

A 4-methyl-7-coumaryl 4-(4-*n*-alkoxyphenylazo)benzoates,
I 4-(4-*n*-alkoxyphenylazo)phenyl 3-nicotinates [19],
II 4-(4-*n*-alkoxybenzoyloxy)phenylazo-5′-thiazoles [20],
III 2-methyl-6-(4-*n*-alkoxybenzoyloxy)benzopyran-4-[H] [21].

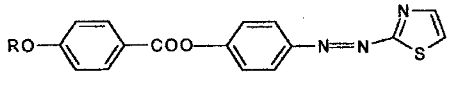
Their molecular geometry is given below:



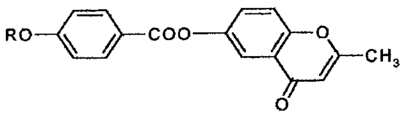
A



I



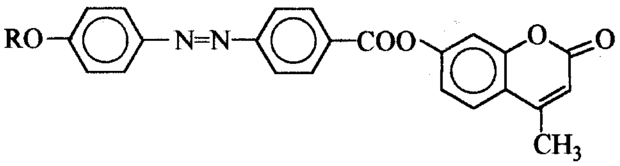
II



III

Table 3. Average Thermal Stabilities (°C)

| Transition | Series A | I | II | III |
|---|---|---|---|---|
| NI | 210.1<br>($C_1$–$C_{16}$) | 208.5<br>($C_1$–$C_4$) | 129.0<br>($C_1$–$C_{14}$) | 67.5<br>($C_{10}$) |
| Sm–N or Sm–I | 159.3<br>($C_5$–$C_{16}$) | — | 115.0<br>($C_{10}$–$C_{16}$) | 67.66<br>($C_{12}$–$C_{16}$) |
| Commencement of smectic phase | $C_5$ | — | $C_7$ | $C_6$ |



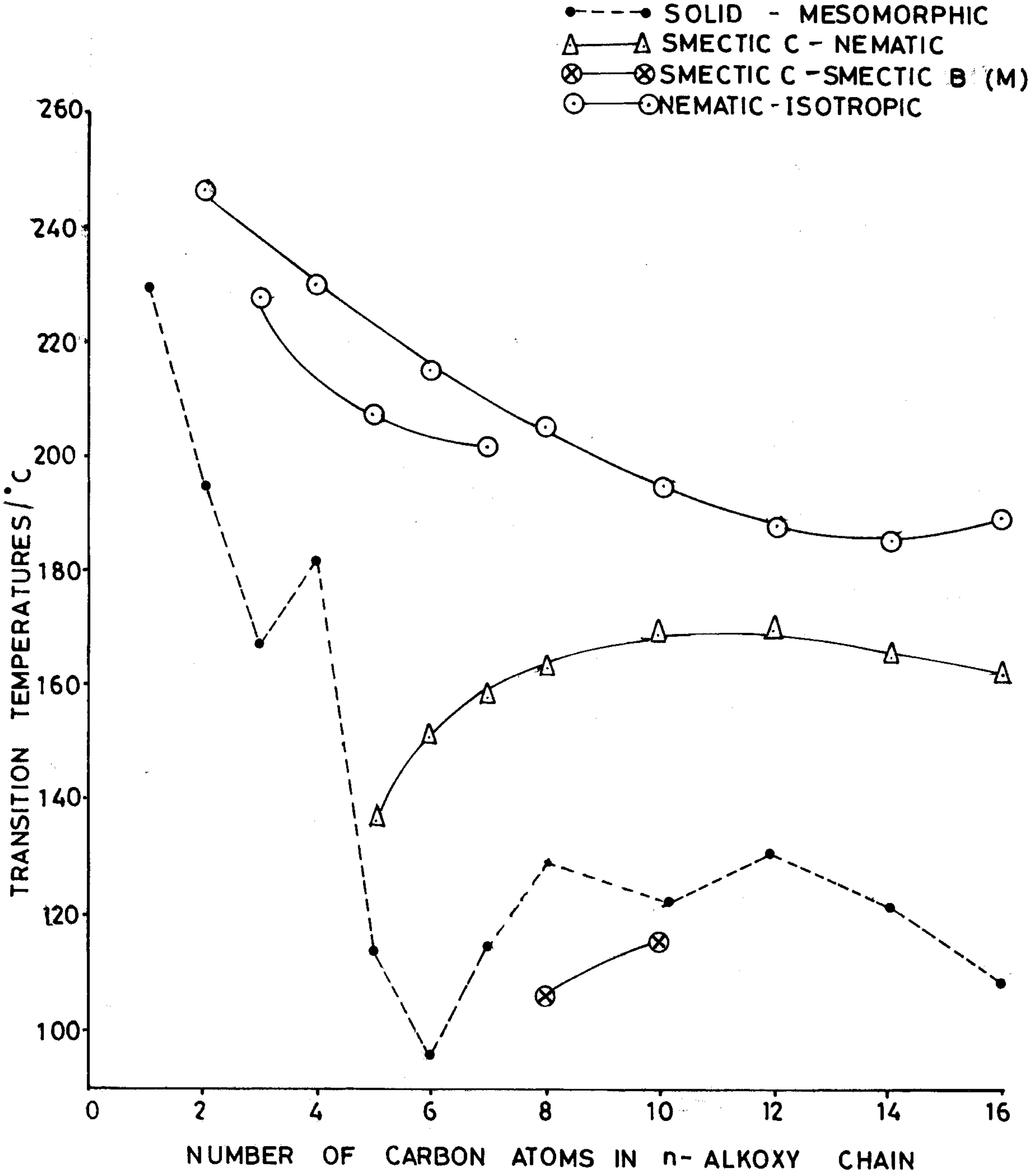


Figure 1. Transition temperatures versus the number of carbon atoms in the *n*-alkoxy chain for the 4-methyl-7-coumaryl 4-(4-*n*-alkoxyphenylazo)benzoates.

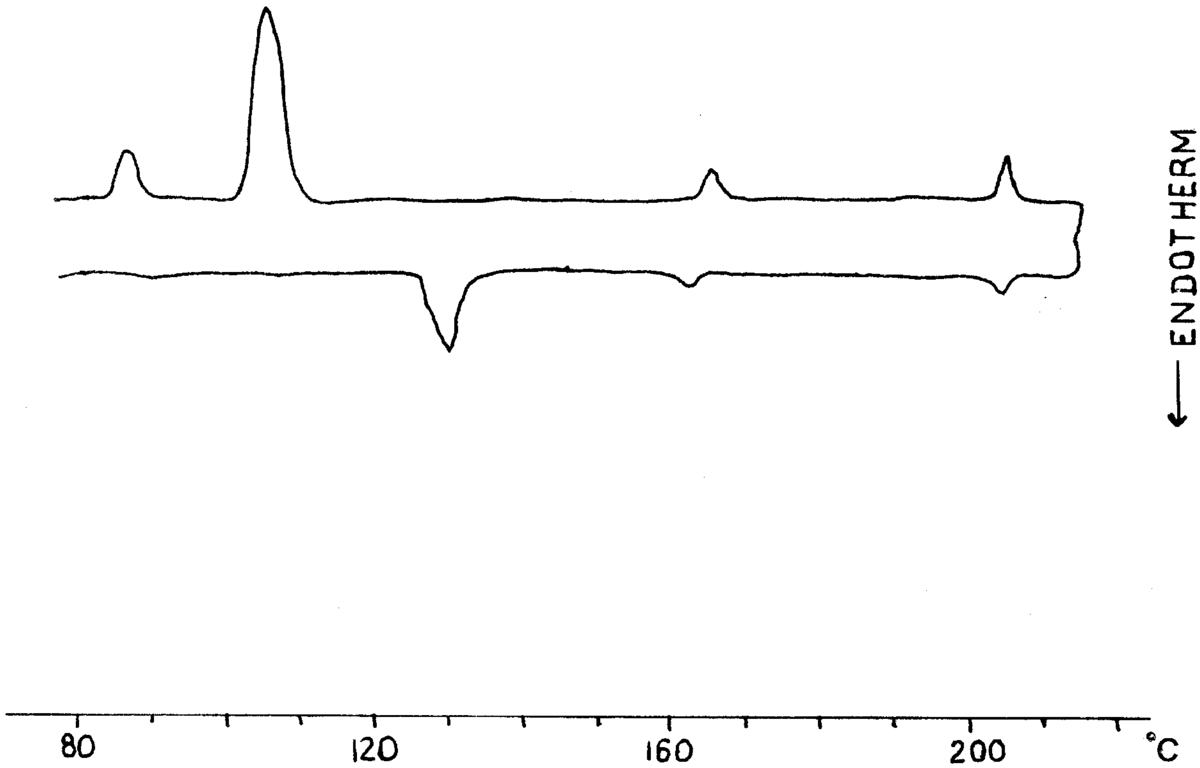


Figure 2. DSC thermogram for the *n*-octyloxy homologue. Heating rate was 10°C min$^{-1}$. The enthalpy values obtained for different transitions were 10.78 J g$^{-1}$ (Cr–SmC), 0.572 J g$^{-1}$ (SmC–N), 1.021 J g$^{-1}$ (N–I) and 36.74 J g$^{-1}$ (SmC–SmB; monotropic).

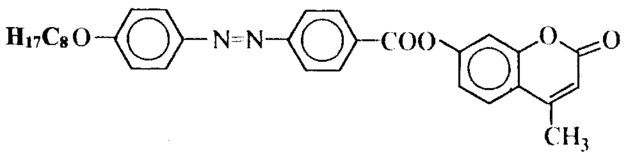
A comparison of the molecular geometry of the above series shows that series A has a coumarin ring, while series I and II have pyridine and thiazole rings, respectively. It is seen that the average N–I and Sm–I thermal stabilities of series A is the highest and the commencement of the smectic phase in this series is also earlier, at the $C_5$ derivative. The enhanced mesomorphic properties of coumarin derivatives have been explained by the asymmetric and large dipole moment of the coumarin skeleton which is perpendicular to the molecular axis [5]. The coumarin ring increases the molecular polarizability which aids the formation of smectic phases and gives rise to higher N–I and Sm–I thermal stabilities compared with those of series I and II.

The molecules of series A are longer than those of series III, due to the addition of a phenyl ring and an $-N{=}N-$ central linkage. Moreover series III has a flavone ring in place of a coumarin ring. Consequently, both the positions of $-C{=}O$ and $-O-$ in the heterocyclic ring skeleton [4] sensitively affect the molecular packings in the mesophase. All the above factors contribute to the enhanced mesogenic properties of series A compared with those of III.

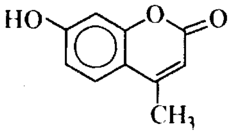
### 3.2. *Fluorescence study*

Aromatic rings with their π-electrons can act in conjugation with electron-donating groups (auxochromes like $-NH_2$, $R$HN–, $R_1R_2$N–, –O–, –OH, –O$R$, etc.) and electron-accepting groups (like –CN, –C=C–, –CO–, etc.) to produce strong absorption in the UV or visible regions, which may give rise to fluorescence. Since the derivatives of the present series contain –N=N– and –CO– groups in their molecular structure, compounds HC and 8BC were studied for their fluorescent properties (figure 3) on the Perkin-Elmer fluorescence spectrophotometer at room temperature, in the solid state. Emission spectra were recorded for the compounds. In the compound HC, the fluorescent emission peak is observed at 720 nm whereas in the 8BC homologue, it is observed at 630 nm. Here HC absorbs at a higher wavelength because of the presence of the auxochromic –OH group on an aromatic ring, which extends the conjugation; however this conjugation is withdrawn when this –OH group is esterified in the 8BC homologue, due to the electron withdrawing effect of the acyl (Ar–CO) group (figure 3). Thus esterification of the –OH group and the presence of a –N=N– linkage results in a shift to 630 nm in the 8BC homologue.

**8BC** -



**HC** -



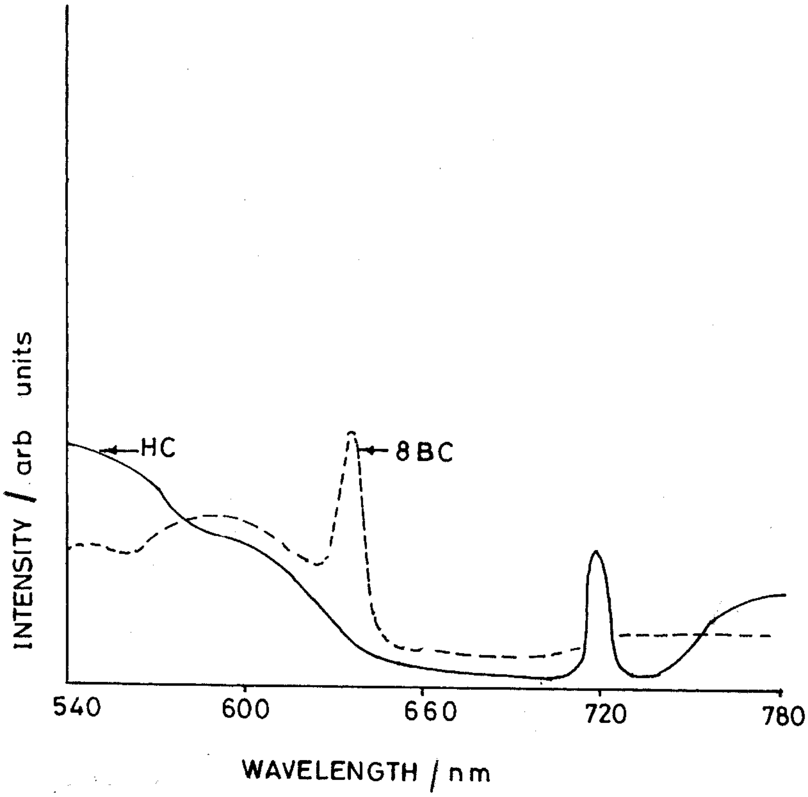


Figure 3. Fluorescence spectra for 7-hydroxy-4-methylcoumarin (HC) and for the *n*-octyloxy homologue (8BC).

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