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## Liquid Crystals

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### Synthesis and mesomorphic properties of 3-(4-*n*-alkyloxyarylamino)methylene)chroman-2,4-diones

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## Synthesis and mesomorphic properties of 3-(4-*n*-alkyloxyarylamino)methylene)chroman-2,4-diones

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The synthesis, characterisation and mesomorphic properties of new liquid crystals are reported. The goal was to obtain amides starting from 7-decanoyloxychromone-3-carboxylic acid and 4-*n*-alkoxyanilines. However, instead of the expected amides, in each case a mixture of two isomeric *E/Z* enamionones was isolated, with a ratio 3/1. The mesophase behaviour of the five mixtures was characterised and studied using differential scanning calorimetry and polarising optical microscopy. The transitions are enantiotropic, the peaks being sharp and the mesomorphic range wide. All the compounds exhibit a smectic C phase and the derivatives with shorter chains also exhibit a nematic phase.

**Keywords:** chromone; enamionones; mesomorphic

### 1. Introduction

The design of liquid crystals including heterocyclic rings has allowed the preparation of a great variety of mesogenic compounds with interesting properties. When a heterocycle forms part of a calamitic structure, mesogenic properties are affected because of the dipole moment of the heteroatomic moiety, the loss of molecular symmetry and deviation from linearity and planarity.

A large number of different heterocyclic rings have been used (1). Flavones and isoflavone derivatives with mesomorphic properties are scarce; only a few examples have been reported (2). The basic nucleus of flavones is the 4-oxo-4*H*(1)-benzopyran heterocycle (trivial name chromone).

The synthesis of compounds with heterocycles fused to a chromone has attracted considerable interest as a consequence of their pharmacological properties. 3-formylchromone is a key precursor for this kind of compound (3).

On the other hand, some functional central bridgings have proven to be very useful in promoting mesomorphic properties, e.g. the ester and imine groups, which are some of the most commonly used. The amide group is infrequently encountered in liquid crystal derivatives (4) because, in general, it gives rise to significantly higher intermolecular interactions, which often preclude mesomorphic behaviour.

We have previously reported the synthesis and mesomorphic properties of esters derived from de 7-*n*-decanoyloxychromone-3-carboxylic acid (5). Thus, we considered it interesting to synthesise a series of amides starting from the same acid in order to study

the effect of the amide moiety on the mesomorphic properties when compared with their ester homologues and with other liquid crystalline amides already described elsewhere. However, as we report in this article, instead of the expected amides, compounds with enamionone structure were isolated. Moreover, these enamionones showed mesomorphic properties. This is the first example of mesomorphic behaviour ever reported for this type of compound.

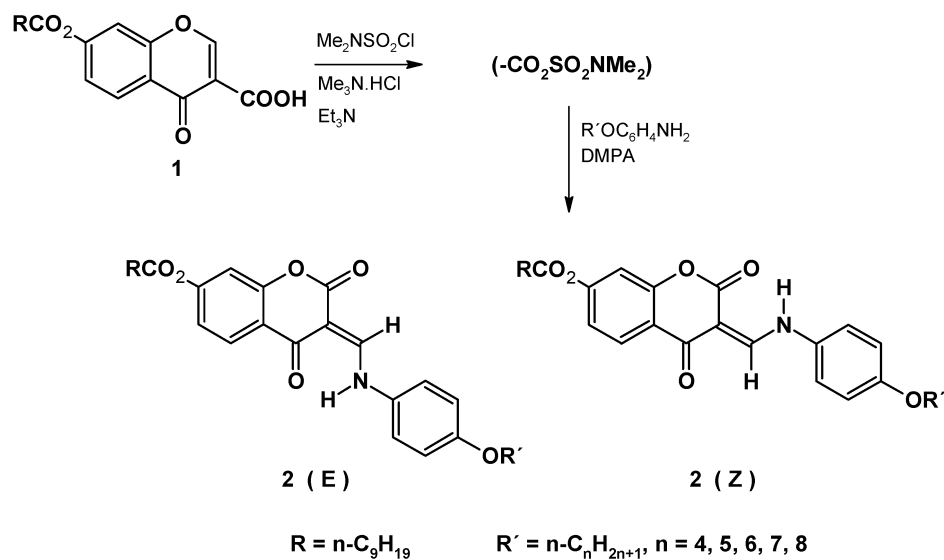
### 2. Synthesis

The synthesis of the amides was planned following the same procedure that was used to obtain the series of chromone esters, since according to our experience it is the only one that gives positive results. The acid was activated by reaction of the carboxyl group with dimethylsulfamoyl chloride (Me<sub>2</sub>NSO<sub>2</sub>Cl) and trimethylamine in MeCN. Trimethylamine was generated in situ by reaction of its hydrochloride with triethylamine. Afterwards, a solution of 4-alkyloxyarylamine and DMPA in MeCN was added (Scheme 1). Esters and amides of aliphatic and aromatic acids have been obtained with this procedure (6).

The yellow solids obtained as products showed liquid crystalline behaviour. However, the <sup>1</sup>H NMR spectra did not agree with the expected amide structure, but with a mixture of two isomeric (*E/Z*) enamionones. Efforts to separate the isomers using column chromatography were unsuccessful.

The *E/Z* ratio was determined from the <sup>1</sup>H NMR spectra (Figure 1 and Table 1) of compound 2 (*n*=4). Two low-field doublets with an approximate ratio of

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Scheme 1. Synthetic route for enaminones.

3/1 correspond to the NH proton, which couples with the hydrogen at C-11 and also forms a hydrogen bond with the oxygen at C=O. The chemical shifts are 13.8 ppm (13.3 Hz) and 11.9 ppm (14.1 Hz). The signal at 13.8 ppm corresponds to the *Z* isomer, since it is able to produce a stronger intramolecular

hydrogen bond (7). The other doublet, at 11.9 ppm, corresponds to the NH of isomer *E*. The signals at 9.0 ppm (d, 14.4 Hz) and 8.8 ppm (d, 13.7 Hz), also in a ratio of 1/3 correspond to the proton at C-11 that is cis with respect to the  $\alpha,\beta$ -unsaturated ester (*E* isomer) and to the proton at C-11 that is trans to the ester (*Z*

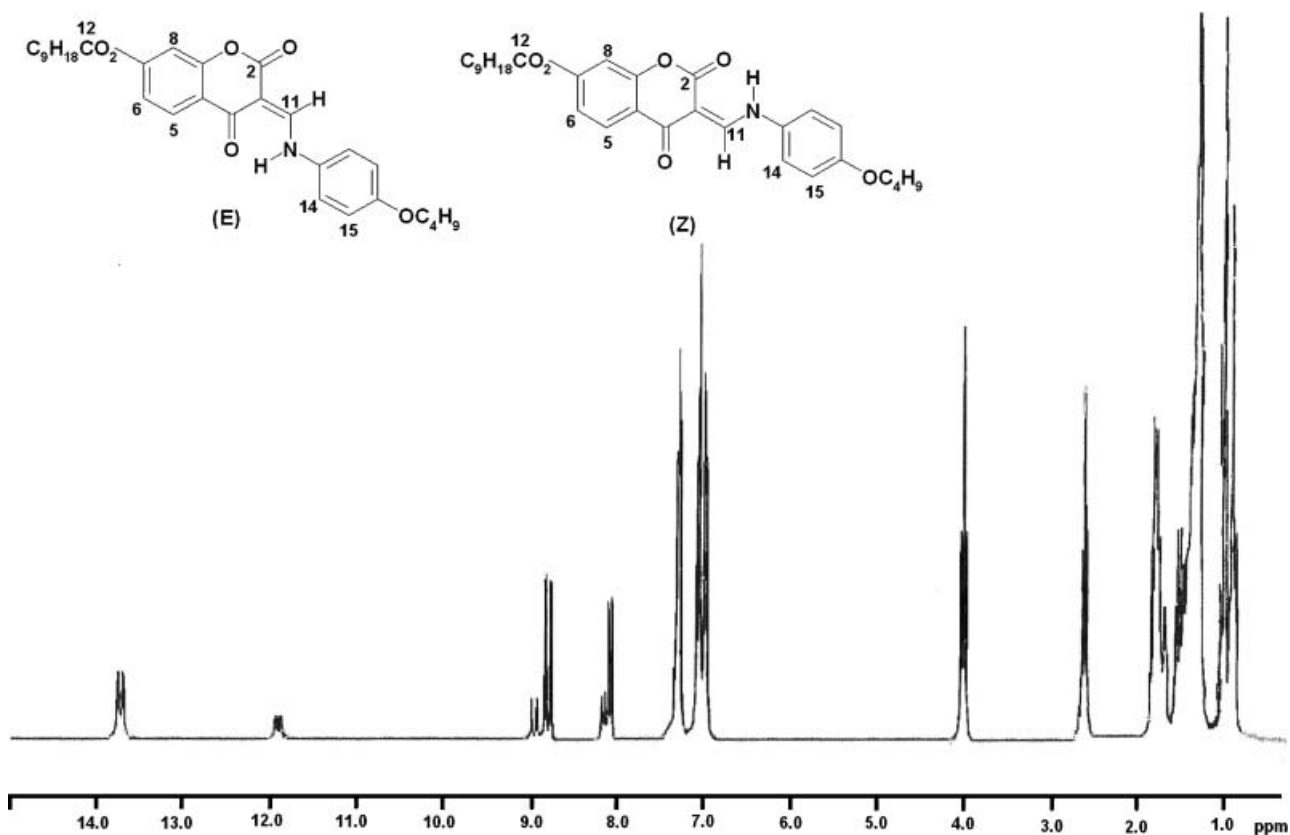
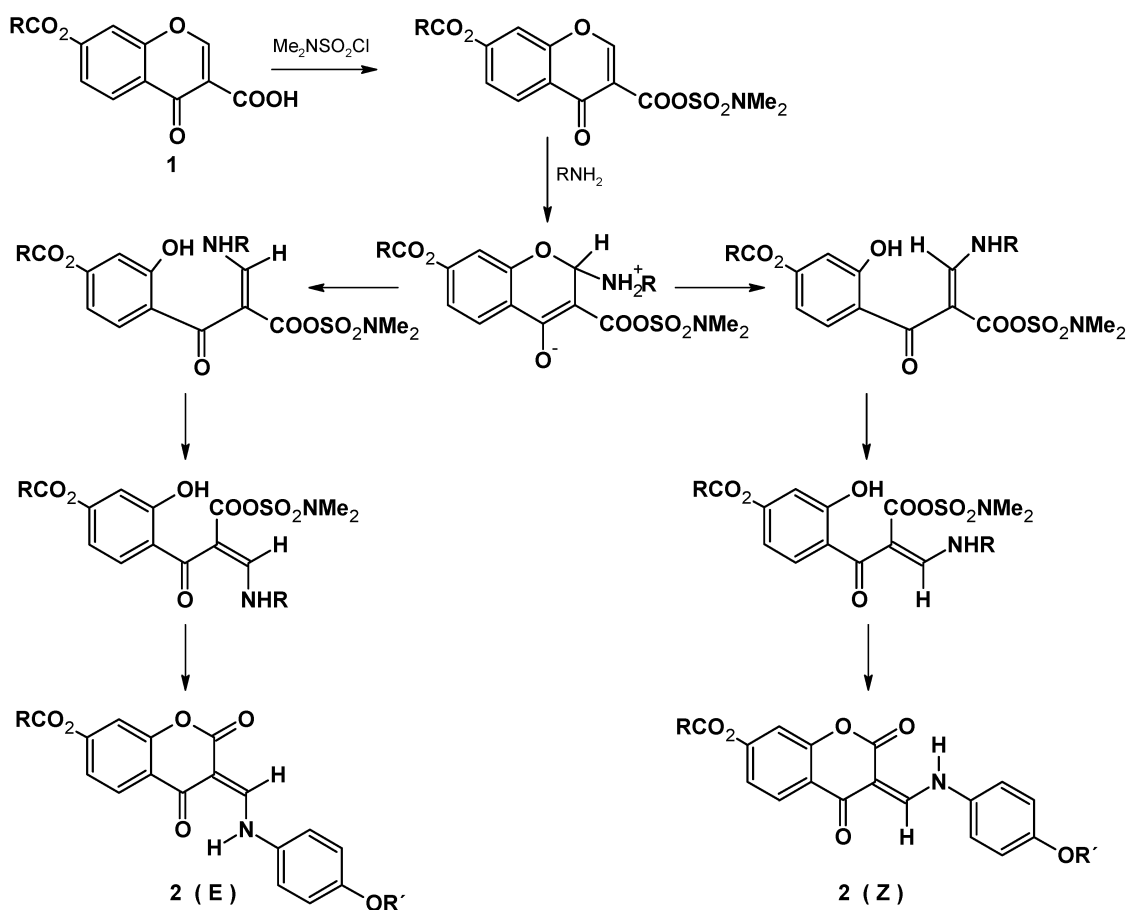
Figure 1.  $^1\text{H}$  NMR of compound 2 ( $n=4$ ).

Table 1. (a)  $^1\text{H}$  NMR and (b) IR spectral data of compounds **2** ( $n=4, 5, 6, 7, 8$ ).

(a)							
Chemical shifts ( $\delta$ ) in $\text{CDCl}_3/\text{ppm}$							
Compound <b>2</b>	NH		=CH		H-5		H-6 H-8 Ar-H
	Z	E	E	Z	E	Z	Z+E
$n=4$	13.8 (13.3)	11.9 (14.1)	9.0 (14.4)	8.8 (13.7)	8.2 (9.3)	8.1 (9.2)	6.9–7.4 m
$n=5$	13.7 (13.3)	11.9 (14.2)	8.9 (14.6)	8.8 (13.8)	8.2 (7.8)	8.1 (7.6)	6.9–7.5 m
$n=6$	13.6 (13.7)	11.8 (13.9)	8.8 (14.4)	8.7 (13.7)	8.1 (9.0)	8.0 (9.0)	6.8–7.4 m
$n=7$	13.7 (14.0)	11.9 (14.0)	8.9 (14.6)	8.8 (13.6)	8.2 (9.2)	8.1 (9.2)	6.9–7.3 m
$n=8$	13.7 (13.7)	11.9 (14.0)	8.9 (14.5)	8.8 (13.7)	8.2 (9.2)	8.1 (9.1)	6.9–7.3 m

Numbers in brackets are  $J$  values in Hz.

(b)			
IR/ $\text{cm}^{-1}$	N-H	OC=O	C=O
$n=4$	3436	1758, 1653	1608
$n=5$	3441	1752, 1655	1598
$n=6$	3426	1757, 1654	1603
$n=7$	3447	1757, 1598	1650
$n=8$	3432	1751, 1598	1649



Scheme 2. Mechanism of alternative enaminone synthesis.

Table 2. Transition temperatures and enthalpies for 3-(4-*n*-alkoxyphenylaminomethylene)-7-decanoyloxychroman-2,4-diones (**2**).

Compound <b>2</b> R=C <sub>n</sub> H <sub>2n+1</sub>	Transition	Temperature/°C	ΔH/kJ mol <sup>-1</sup>
<i>n</i> =4	Cr–SmC	131.4	39.1
	SmC–N	152.7	0.6
	N–I	184.6	1.1
<i>n</i> =5	Cr–SmC	128.8	36.5
	SmC–N	164.8	1.4
	N–I	180.4	1.5
<i>n</i> =6	Cr–SmC	122.4	36.4
	SmC–N	177.2	2.1
	N–I	183.7	2.0
<i>n</i> =7	Cr–SmC	122.8	40.5
	SmC–I	181.5	8.2
<i>n</i> =8	Cr–SmC	120.9	29.8
	SmC–I	180.2	7.6

isomer), respectively (**8**). Two doublets at 8.2 ppm (9.3 Hz) and 8.1 ppm (9.2 Hz) correspond to the proton at C-5 for isomers *E* and *Z*, respectively. In the rest of the signals, duplication was not observed because the other protons lie too far from the C=O...H–NH bridge. Consequently, they are not

affected by the *cis*–*trans* isomerism. The <sup>13</sup>C NMR spectra reveal, in the *sp*<sup>2</sup> region, more signals than should be expected for a single isomer. The yields were low, 40–50 %, because tertiary amines can decarboxylate chromone-3-carboxylic acids and chromone-3-carboxaldehydes (**9**). The synthesis of other related compounds has been reported previously. A two-step procedure starting from chromone-3-carboxaldehyde with an arylamine followed by oxidation was described (**10**).

In Scheme 2, a feasible mechanism for this result is shown. The arylamine adds at position 2 of the activated acid followed by an opening of the pyrane ring. Subsequent recyclisation furnishes the stereoisomeric mixture of enaminones **2** (*Z*) and **2** (*E*).

### 3. Results and discussion

The liquid crystalline behaviour of compounds **2** (*n*=4, 5, 6, 7, 8) was characterised and studied using differential scanning calorimetry (DSC) and polarising optical microscopy (POM). The phase transitions and thermodynamic data are summarised in Table 2.

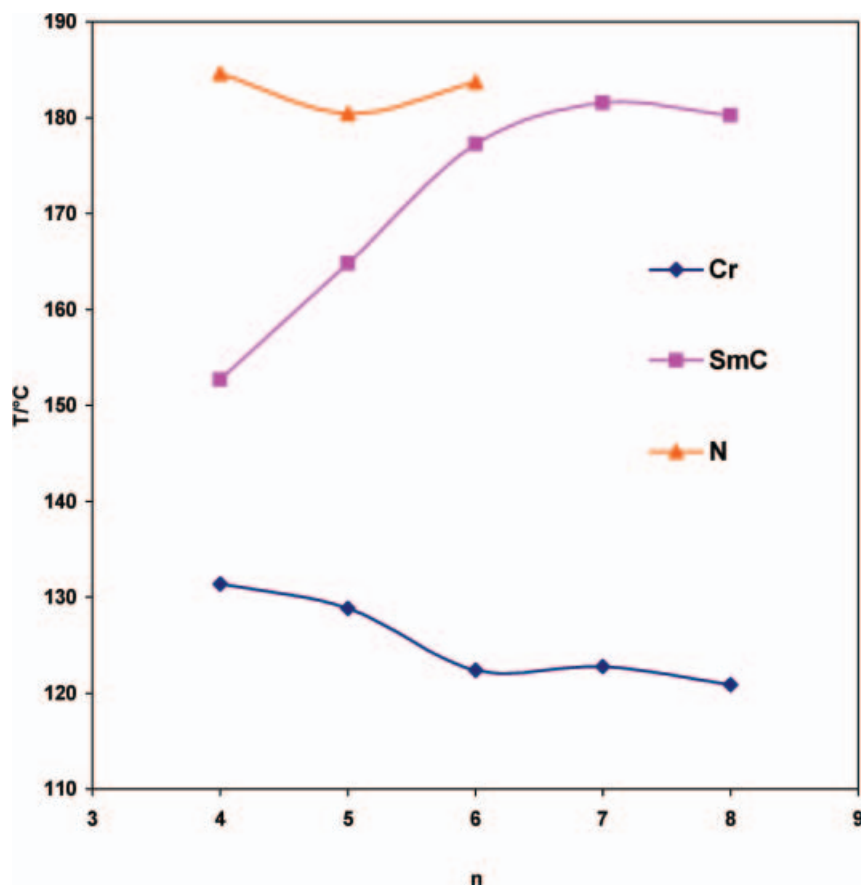


Figure 2. Mesomorphic behaviour as a function of number (*n*) of carbon atoms in the terminal alkoxy chains of compounds **2**.

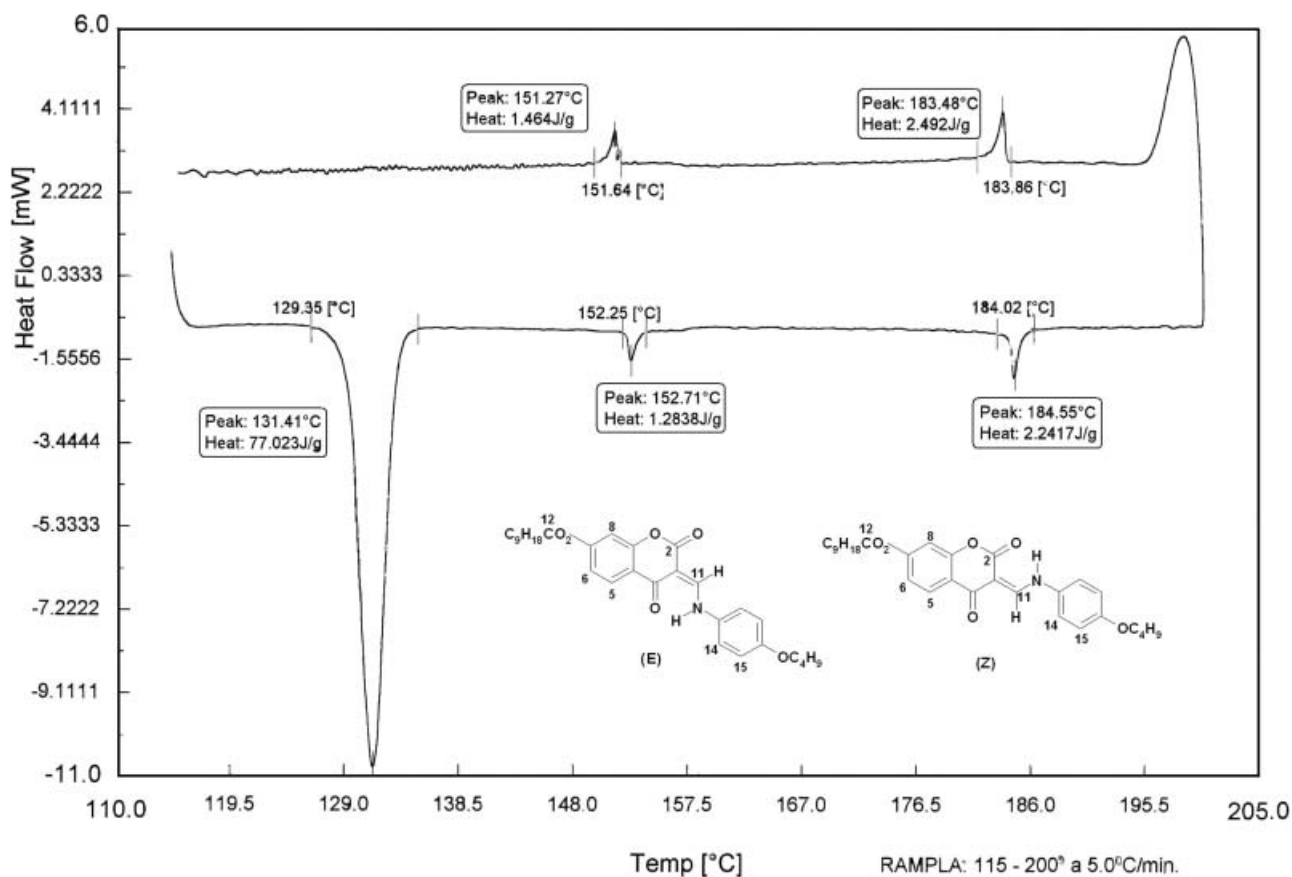


Figure 3. DSC thermograms of compound 2 ( $n=4$ ).

A graphical representation of the mesomorphic behaviour as a function of the number ( $n$ ) of carbon atoms in the lateral chain is also presented in Figure 2. All the compounds exhibited enantiotropic behaviour and all the DSC thermogram peaks are sharp (see Figure 3), the type of mesophase being dependent on the chain length. The compounds with shorter chains ( $n=4, 5, 6$ ) exhibited nematic and smectic C (SmC) phases, whereas the compounds with longer chains ( $n=7, 8$ ) exhibited only a SmC phase. The nematic and SmC phases were observed and identified on the basis of optical textures; the characteristic schlieren texture was used to identify the SmC phases and was observed on cooling the nematic phases.

The temperature ranges of the nematic phases exhibited for 2 ( $n=4, 5, 6$ ) were 31.9–6.5°C on heating, decreasing as the chain length increased. The enthalpies of the nematic–isotropic transition were in the range 1.1–2.0 kJ mol<sup>-1</sup>, and increased with increasing chain length. This increase in enthalpies indicated that the phase became more ordered as the chain length increased.

The temperatures of the smectic–nematic transition increased from 152.7°C ( $n=4$ ) to 177.2°C ( $n=6$ ) on heating. The enthalpies of the smectic–nematic

transition also increased with chain length from 0.6 ( $n=4$ ) to 2.1 kJ mol<sup>-1</sup> ( $n=6$ ). This increase in transition enthalpies was in fact parallel to the increase in the nematic–isotropic enthalpy. The results indicate that the temperature range of the nematic phase decreased (31.9–6.5°C) but that the temperature range of the SmC phase was increased (21.3–59.3°C). Nevertheless, the overall temperature range of the mesophases was relatively insensitive to the chain length, 53.2 ( $n=4$ ) to 61.3°C ( $n=6$ ).

The esters of 7- $n$ -decanoyloxochromonecarboxylic acids described in a previous report (5) exhibited smectic A and SmC mesophases. Clearing temperatures are roughly 10°C lower than the enamines presented here, although the mesomorphic range is quite similar.

#### 4. Experimental

##### Characterisation

The structures of the new compounds were confirmed by <sup>1</sup>H NMR (Bruker AC-250 P) spectra and FTIR (Nicolet Magna 550) spectra (see Table 1). The purity of the products was evaluated by thin layer chromatography and elemental analysis (Table 3).

Table 3. Elemental analysis of 3-(4-*n*-alkyloxyphenylaminomethylene)-7-decanoyloxychroman-2,4-diones (2).

Empirical formula R=C <sub>n</sub> H <sub>2n+1</sub>	C/%		H/%		N/%	
	Calculated	Found	Calculated	Found	Calculated	Found
<i>n</i> =4, C <sub>30</sub> H <sub>37</sub> NO <sub>6</sub>	71.01	70.80	7.30	7.29	2.76	2.81
<i>n</i> =5, C <sub>31</sub> H <sub>39</sub> NO <sub>6</sub>	71.40	71.03	7.48	7.47	2.69	2.74
<i>n</i> =6, C <sub>32</sub> H <sub>41</sub> NO <sub>6</sub>	71.78	71.75	7.66	7.74	2.62	2.65
<i>n</i> =7, C <sub>33</sub> H <sub>43</sub> NO <sub>6</sub>	72.13	71.82	7.83	7.76	2.55	2.59
<i>n</i> =8, C <sub>34</sub> H <sub>45</sub> NO <sub>6</sub>	72.47	72.04	7.99	7.96	2.49	2.56

The transition temperatures and enthalpies were determined by DSC using a Rheometric DSC-V calorimeter. Samples were encapsulated in aluminium pans and studied at a scanning rate of 5°C min<sup>-1</sup> during heating and cooling. The instrument was calibrated using an indium standard (155.66°C, 28.45 J g<sup>-1</sup>). Textures of the mesophases were studied with a Leitz Ortholux polarising optical microscope equipped with a Mettler FP 52 hot stage.

### Synthesis

#### 7-*n*-Decanoyloxychromone-3-carboxylic acid (1).

This compound was synthesised following the previously reported route (5).

#### 3-(4-*n*-Alkyloxyphenylaminomethylene-7-decanoyloxy)-chroman-2,4-diones (2).

The compounds were synthesised using a procedure described by Wakasugi *et al.* (6) where the reactivity of the acid is enhanced with dimethylsulfamoyl chloride in order to obtain esters and amides, with some variations in the procedure, as described below. To a magnetically stirred mixture of 7-*n*-decanoyloxychromone-3-carboxylic acid (0.20 g, 0.56 mmol) in 15 ml of dry MeCN containing dry Me<sub>3</sub>N.HCl (0.16 g, 1.67 mmol) at 0–5°C under reduced pressure, Me<sub>2</sub>NSO<sub>2</sub>Cl (0.12 ml, 1.13 mmol) was added and then Et<sub>3</sub>N (0.23 ml, 1.67 mmol). Subsequently a solution of 4-*n*-alkyloxyaniline (0.56 mmol) in 5 ml of MeCN containing DMAP (7 mg, 0.057 mmol) was added. The mixture was stirred for 3 h at the same temperature and then it was poured into an ice–water

mixture and refrigerated overnight. The solid material that separated was filtered off, washed several times with water and purified by recrystallisation from ethanol. Yield 40–50 %.

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