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## Liquid Crystals

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### Synthesis of some chiral liquid crystals and study of the effect of intramolecular hydrogen bonding on the phase behaviour

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# Synthesis of some chiral liquid crystals and study of the effect of intramolecular hydrogen bonding on the phase behaviour

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The synthesis of three new series of chiral Schiff's bases containing benzilideneaniline and 2-hydroxybenzilideneaniline moieties as mesogenic cores is presented. Differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction measurements were used to study the phase transition temperatures and behaviour. The results reveal that most of these materials show chiral smectic mesomorphism.

## 1. Introduction

Since the ferroelectric liquid crystal (DOBAMBC) was prepared by Meyer *et al.* in 1975 [1] and a bistable, fast switching, electro-optical device which uses the FLC was demonstrated a few years later by Clark and Lagerwall [2], numerous FLC compounds have been prepared for fast electro-optical applications and scientific research [3, 4].

Generally speaking, the properties of liquid crystals depend on the structure of liquid crystal molecules, so the study of the relationship between molecular structure and the properties of liquid crystals is very important and interesting. In this paper, three new series of chiral liquid crystals are reported (see the scheme).

In our previous paper [5], the influence of different chiral groups (series I) on the phase behaviour of the liquid crystals was discussed, the results showing that the compound **Ib** with the *S*-2-chloro-3-methylbutanoyl as the chiral terminal group has the widest phase range. So, in series II and series III, we chose (*S*)-2-chloro-3-methylbutanoyl as the chiral terminal group. The difference is that in series II the mesogenic core was benzilideneaniline, but in series III was 2-hydroxybenzilideneaniline which has an intramolecular hydrogen bond, and as a result the compounds possess greater mesophase stability.

The mesomorphic behaviour of the resulting chiral liquid crystals has been studied by optical microscopy and differential scanning calorimetry (DSC). X-ray diffraction

was used to study some of these chiral liquid crystals (**Ic**, **II10**, **III8**, **III10**, **III12**). An example of the X-ray diffraction of compound **III12** is presented.

## 2. Results and discussion

The mesophases were identified according to their textures which were observed by optical microscopy, using the classification systems reported by Sackmann and Demus [6], and Gray and Goodby [7]. The transition temperatures, enthalpies and the mesomorphic properties of series II and series III are given in tables 1 and 2.

The variation of the transition temperatures with increasing alkoxy chain length for series III is shown in figure 1.

The results show that most of the compounds are liquid crystalline. In series II, the compounds with  $n = 1$  and  $n = 2$  exhibit monotropic N\* phases with typical schlieren textures. The compounds with  $n = 3, 4$  and  $5$  were not liquid crystalline. For the compounds **II6** and **II7**, upon cooling, a chiral N phase appeared with a schlieren texture: on further cooling this schlieren texture changed to two different mosaic textures which were identified as S<sub>B</sub> and CrG phases according to their texture and phase sequence. For compound **II8**, the phase behaviour becomes complicated. The chiral smectic C mesophase showed focal-conics, the S<sub>A</sub> phase exhibited a simple fan-shaped texture, and the N\* phase appeared with oily streak texture. Upon cooling, a S<sub>B</sub> phase with a mosaic texture could also be observed. In series III, only compound **III2** had two monotropic phases under polarized microscopy; a

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Table 1. Transition temperatures, enthalpies and derived entropies for the compounds in series **II**.

<i>n</i>	Transition†	<i>T</i> /°C	$\Delta H$ /kJ mol <sup>-1</sup>	$\Delta S$ /J mol K <sup>-1</sup>
<b>1</b>	Cr-I	83.0	23.70	66.53
	I-N*	55.9	-0.34	-1.03
	N*-Cr	43.5	-19.93	-62.91
<b>2</b>	Cr-I	86.5	17.54	48.80
	I-N*	82.3	-0.64	-1.74
	N*-Cr	64.1	-14.13	-41.90
<b>3</b>	Cr-I	74.7	27.13	77.99
<b>4</b>	Cr-I	88.0	27.10	75.03
<b>5</b>	Cr-I	84.9	28.65	80.01
<b>6</b>	Cr <sub>1</sub> -Cr <sub>2</sub>	60.4	7.32	21.94
	Cr <sub>2</sub> -I	79.0	21.66	61.50
	I-N*	79.0	-0.63	-1.78
	N*-S <sub>B</sub>	70.8	-9.09	-26.42
	S <sub>B</sub> -CrG	64.5	-0.99	-2.93
<b>7</b>	CrG-Cr	60.3	-5.96	-17.89
	Cr <sub>1</sub> -Cr <sub>2</sub>	59.7	7.57	22.75
	Cr <sub>2</sub> -I	76.3	24.02	68.73
	I-N*	75.9	-0.74	-2.11
	N*-S <sub>B</sub>	66.6	-7.88	-23.20
<b>8</b>	S <sub>B</sub> -CrG	54.8	-1.38	-4.22
	CrG-Cr	52.2	-4.84	-14.87
	Cr <sub>1</sub> -Cr <sub>2</sub>	62.9	9.19	27.43
	Cr <sub>2</sub> -S <sub>C</sub> <sup>*</sup>	69.2	15.22	44.44
	S <sub>C</sub> <sup>*</sup> -S <sub>A</sub>	71.4	0.92	2.92
	S <sub>A</sub> -N*	74.5	0.69	2.17
	N*-I	80.9	1.05	2.97
	I-N*	80.0	-1.13	-3.21
	N*-S <sub>A</sub>	73.3	very small	
	S <sub>A</sub> -S <sub>C</sub> <sup>*</sup>	70.2	-1.15	-3.32
<b>10</b>	S <sub>C</sub> <sup>*</sup> -S <sub>B</sub>	64.5	-6.51	-19.30
	S <sub>B</sub> -Cr	59.4	-10.52	-31.60
	Cr-S <sub>A</sub>	82.3	39.45	111.01
	S <sub>A</sub> -I	83.5	very small	
	I-N*	82.6	-2.92	-8.21
	N*-S <sub>A</sub>	80.4	very small	
<b>12</b>	S <sub>A</sub> -S <sub>C</sub> <sup>*</sup>	73.7	-0.49	-1.40
	S <sub>C</sub> <sup>*</sup> -Cr	67.0	-22.31	-65.59
	Cr-S <sub>A</sub>	77.6	60.70	173.08
	S <sub>A</sub> -I	82.8	24.28	68.20
	I-S <sub>A</sub>	81.7	-3.36	-9.39
	S <sub>A</sub> -Cr	70.3	-37.8	-110.10

†Cr, crystal; S<sub>B</sub>, smectic B; S<sub>A</sub>, smectic A; S<sub>C</sub><sup>\*</sup>, chiral smectic C; CrG, crystal G; I, isotropic.

cholesteric phase and a S<sub>A</sub> phase with a very narrow temperature range. From *n* = 4 onwards, compounds possessed at least S<sub>C</sub><sup>\*</sup> and S<sub>A</sub> phases. It is interesting to observe that the compound with *n* = 6 upon heating showed a S<sub>C</sub><sup>\*</sup> phase with a broken fan-shaped texture in which many stripes grow along the blade, and the S<sub>A</sub> phase with a simple fan-shaped texture. On cooling, the compound with *n* = 6 not only exhibited S<sub>A</sub> and S<sub>C</sub><sup>\*</sup> phases but also gave a short range non-fluid mosaic texture which is tentatively identified as smectic B. Figure 2 illustrates the typical textural changes for compound

Table 2. The phase changes and associated transition temperatures, enthalpies and entropies for the series **III** compounds.

<i>n</i>	Transition	<i>T</i> /°C	$\Delta H$ /kJ mol <sup>-1</sup>	$\Delta S$ /J mol K <sup>-1</sup>
<b>2</b>	Cr-I	118.2	34.93	89.24
	I-Ch	100.6	-0.70	-1.87
	Ch-S <sub>A</sub>	95.8	-1.18	-3.20
<b>4</b>	S <sub>A</sub> -Cr	94.1	-26.57	-72.34
	Cr-S <sub>A</sub>	90.7	23.62	64.90
	S <sub>A</sub> -I	100.9	3.31	8.84
<b>6</b>	I-S <sub>A</sub>	99.3	-3.21	-8.63
	S <sub>A</sub> -S <sub>C</sub> <sup>*</sup>	83.7	-1.05	-2.95
	S <sub>C</sub> <sup>*</sup> -Cr	69.0	-19.96	-58.34
	Cr-S <sub>C</sub> <sup>*</sup>	76.5	25.86	74.32
	S <sub>C</sub> <sup>*</sup> -S <sub>A</sub>	90.7	0.81	2.22
<b>8</b>	S <sub>A</sub> -I	103.6	3.88	10.28
	I-S <sub>A</sub>	101.8	-3.36	-8.96
	S <sub>A</sub> -S <sub>C</sub> <sup>*</sup>	89.6	-0.51	-1.41
	S <sub>C</sub> <sup>*</sup> -S <sub>B</sub>	59.2	-3.34	-10.05
	S <sub>B</sub> -Cr	51.3	-13.62	-41.98
	Cr-S <sub>C</sub> <sup>*</sup>	76.0	25.79	73.85
	S <sub>C</sub> <sup>*</sup> -S <sub>A</sub>	90.3	0.52	1.42
	S <sub>A</sub> -I	106.5	4.28	11.27
<b>10</b>	I-S <sub>A</sub>	104.6	-3.95	-10.44
	S <sub>A</sub> -S <sub>C</sub> <sup>*</sup>	89.5	-0.48	-1.33
	S <sub>C</sub> <sup>*</sup> -Cr†	43.0		
	Cr-S <sub>C</sub> <sup>*</sup>	76.1	39.69	113.63
	S <sub>C</sub> <sup>*</sup> -S <sub>A</sub>	90.1	0.14	0.38
	S <sub>A</sub> -I	108.1	4.66	12.11
<b>12</b>	I-S <sub>A</sub>	106.4	-4.44	-11.69
	S <sub>A</sub> -S <sub>C</sub> <sup>*</sup>	87.2	-0.31	-0.85
	S <sub>C</sub> <sup>*</sup> -Cr†	43.0		
	Cr-S <sub>C</sub> <sup>*</sup>	80.0	44.89	127.10
	S <sub>C</sub> <sup>*</sup> -S <sub>A</sub>	90.0	0.18	0.49
	S <sub>A</sub> -I	108.6	5.20	13.61
	I-S <sub>A</sub>	106.7	-4.93	-12.97
	S <sub>A</sub> -S <sub>C</sub> <sup>*</sup>	82.8	-0.18	-0.49
	S <sub>C</sub> <sup>*</sup> -Cr	43.6	-28.07	-88.60

Cr, crystal; Ch, cholesteric; S<sub>A</sub>, smectic A; S<sub>B</sub>, smectic B; S<sub>C</sub><sup>\*</sup>, smectic C; I, isotropic.

†Values from optical polarized microscopy.

**III 6.** Figure 2 (a) shows the simple fan-shaped texture, figure 2 (b) the broken fan-shaped texture and figure 2 (c) the mosaic texture.

The N\*, S<sub>A</sub> and S<sub>C</sub><sup>\*</sup> phases of the compounds were also confirmed by X-ray diffraction.

As an example, figure 3 presents the temperature-dependent X-ray diffractograms obtained from a powder sample of compound **III 12** at 90°C, 75°C and 60°C.

A weak, broad reflection at the wide angle (associated with the lateral packings) and a sharp reflection at a low angle (associated with the smectic layers) are shown by the data. Curve (a) presents a diffuse reflection at about 5.26 Å, which corresponds to the lateral spacing of two mesogenic groups. A sharp first order reflection at 33.3 Å and a second-order reflection at 16.22 Å are seen which

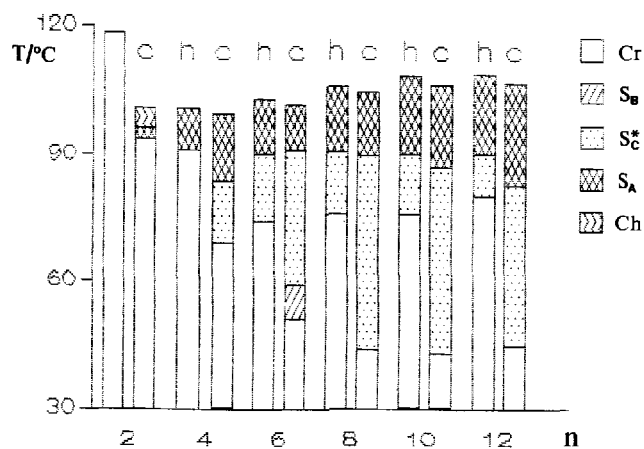


Figure 1. Transition temperatures as a function of alkoxy chain length,  $n$ , for the compounds of series III. h: heating; c: cooling.

correspond to the smectic layers. The optical texture of compound III 12 reveals a simple fan-shaped texture in this temperature range. Both results are consistent with a smectic A texture. When the temperature was lowered from 90°C to 75°C, the layer spacing of the first order reflection decreased from 33.34 Å to 32.76 Å (see curve (b)). On further cooling from 75°C to 60°C, the layer spacing of the first order reflection continued to decrease from 32.76 Å to 32.13 Å (see curve (c)). This presents strong evidence for the formation of the tilted chiral smectic phase. These results are also in agreement with the optical microscopic observation which reveals a broken fan texture. The data obtained indicate that in the  $S_C^*$  phase the layer thickness decreases gradually as the temperature decreases.

Comparing compounds II 2, 4, 6, 8, 10 and 12 with III 2, 4, 6, 8, 10 and 12, we can see that their phase sequences are very different. According to the equation of Shaefer [8] [ $E = \Delta\delta + 0.4 \pm 0.2$ ,  $\Delta\delta = \Delta\delta_{OH} - \Delta\delta_{OH^{phenol}}$ , in  $CHCl_3$ ] and the NMR signals for the OH protons of series III (see table 4)] we calculated the energy of the intramolecular hydrogen bond. The calculated energy for the hydrogen bond for the compounds III 2, 4, 6, 8, 10 and 12 is  $41.4 \pm 0.8 \text{ kJ mol}^{-1}$  between the OH group and the imine linkage. The strong hydrogen bond forces this part of the molecule to arrange itself in a coplanar way. We think this strong intramolecular hydrogen bond not only plays a decisive role in the molecular geometry of these compounds and enhances the extent of the conjugation but also enhances the intermolecular attraction of the molecules. These factors make it easy for the molecules to array parallel and form a layer structure and these factors also give rise to the greater mesomorphic stability [9] of series III.



(a)



(b)



(c)

Figure 2. Mesomorphic texture of compound III 6. (a)  $S_A$  at 95°C (cooling); (b)  $S_C^*$  at 70°C (cooling); (c)  $S_B$  at 55°C (cooling).

Fig. 2.

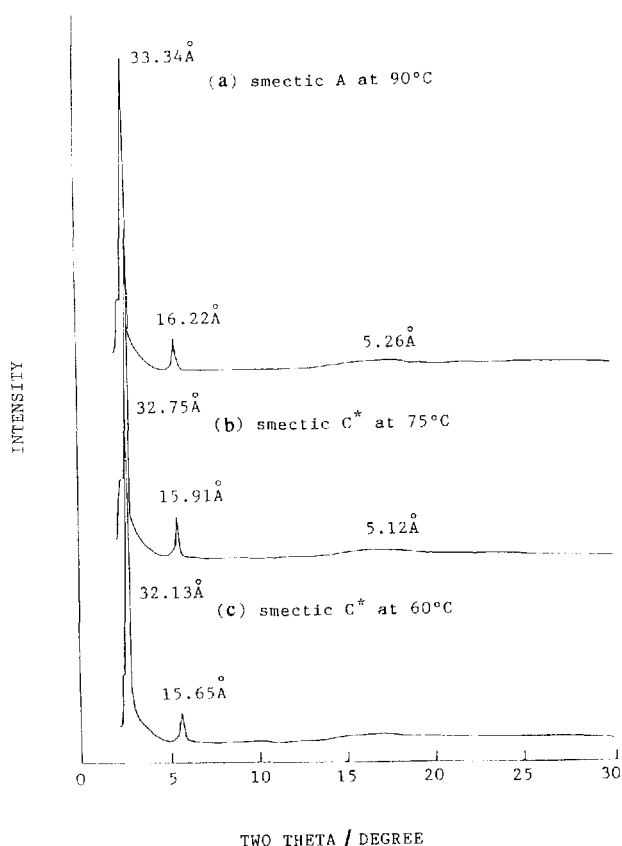


Figure 3. Temperature-dependent WAXD diagrams for the compound **III 12**, at (a) 90°C, (b) 75°C, (c) 60°C (on the cooling).

### 3. Experimental

#### 3.1. Techniques

The transition temperatures and enthalpies were determined using a Perkin–Elmer DSC-7 differential scanning calorimeter calibrated by measuring the known melting point and heat of fusion of indium (429.6 K, 28.46 J g<sup>-1</sup>). The heating and cooling rate was 5°C min<sup>-1</sup>. The mesophase textures were observed by sandwiching samples between a slide and cover glass under a Zeiss Jena optical polarizing microscope equipped with a HunJiang (P.R.C.) hot stage. Infrared spectra for all the compounds were obtained using a Nicolet 5DX FT-IR spectrometer. Elemental analyses were measured with a Perkin–Elmer 240C microanalyser. <sup>1</sup>H NMR spectra were measured with a Unity 400-NMR instrument operating at 400 MHz in CDCl<sub>3</sub>. The purities of all products were further checked by thin layer chromatography.

#### 3.2. Synthesis

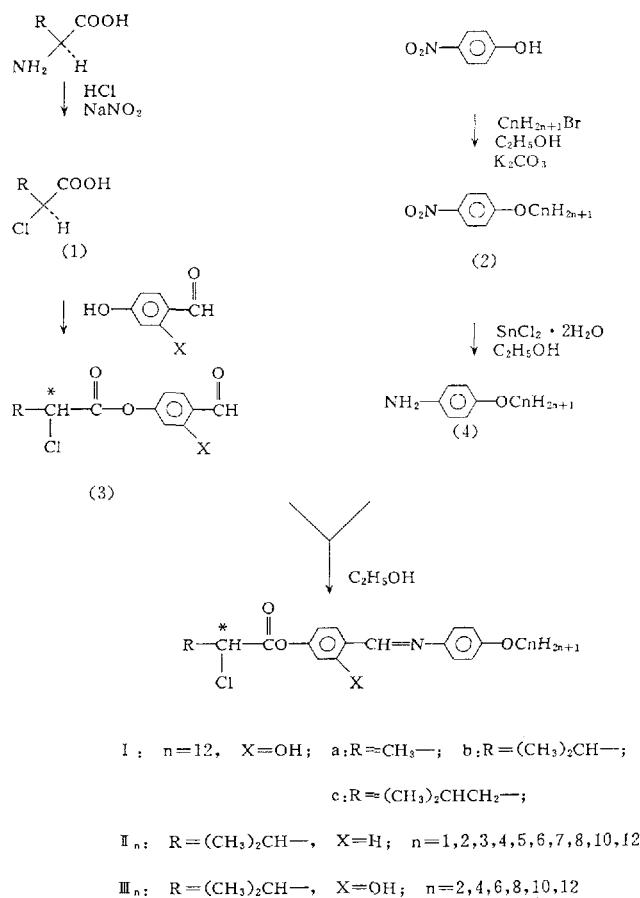
The LC compounds were prepared as shown in the scheme.

The *S*-2-chloro-3-methylbutanoic acid (**1**) was prepared by means of nucleophilic substitution of the amino group by the chlorine atom via the diazonium salt as reported by Fu *et al.* [10]. The substitution takes place with retention of the asymmetric centre configuration [11].

The *p*-nitroalkoxybenzenes (**2**) were prepared by etherification of *p*-nitrophenol and the appropriate bromoalkane according to the method of Nozdu *et al.* [12].

The chiral aldehyde (**3b**) was obtained by esterification of (**1**) with 2,4-dihydroxy benzaldehyde using the procedure of Chen and Jones [13] as follows.

A solution of *S*-2-chloro-3-methylbutanoic acid (7.4 g, 54.2 mmol), 2,4-dihydroxybenzaldehyde (8.5 g, 61.6 mmol), DCCD (12.5 g, 60.7 mmol) and a small amount of 4-*N,N*-dimethylpyridine in 60 ml CH<sub>2</sub>Cl<sub>2</sub> was stirred at room temperature for 48 h. The white insoluble product (DCU) was removed by filtration. The solution was washed with 2 M HCl, 5 per cent NaHCO<sub>3</sub> (aq) and NaCl solution, and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the residue was purified by column chromatography on silica (cyclohexane:ethyl acetate = 6:1 as eluent). 11.0 g product in oil form was

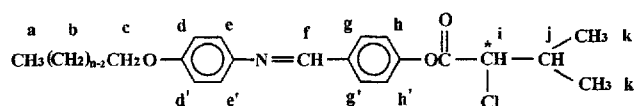


Scheme.



Table 3. Elemental analyses, yields, and the most relevant IR data for the compounds of series II.

<i>n</i>	Yield/per cent	C/per cent		H/per cent		N/per cent		$\nu_{C=O}/\text{cm}^{-1}$	$\nu_{C=N}/\text{cm}^{-1}$
		Calc.	Found	Calc.	Found	Calc.	Found		
1	74	65.99	66.10	5.70	5.73	4.05	3.60	1764.2	1628.7
2	75	66.76	66.38	6.11	5.94	3.89	3.40	1764.1	1630.5
3	66	67.47	67.35	6.43	6.27	3.75	3.62	1764.1	1629.5
4	75	68.13	68.35	6.71	6.93	3.61	3.53	1764.1	1625.8
5	68	68.74	68.26	6.97	7.12	3.49	3.28	1766.3	1627.6
6	62	69.30	69.25	7.22	7.52	3.37	3.18	1764.1	1630.5
7	72	69.83	69.60	7.50	7.46	3.26	2.97	1770.0	1623.5
8	63	70.35	70.53	7.67	7.53	3.16	2.69	1757.0	1623.4
10	70	71.26	70.96	8.06	8.13	2.97	2.69	1761.7	1622.3
12	63	72.07	71.83	8.80	8.79	2.80	2.80	1757.0	1623.4

Table 4. 400 MHz data of compounds of series II in CDC13: coupling constants *J*(Hz) and shifts  $\delta$ (ppm).

<i>n</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>dd'</i>	<i>ee'</i>	<i>f</i>	<i>gg'</i>	<i>hh'</i>	<i>i</i>	<i>j</i>	<i>kk'</i>
1	—	—	3.84 (s)	6.94 (d) <i>J</i> = 8.8	7.94 (d) <i>J</i> = 8.8	8.48 (s)	7.26 (d) <i>J</i> = 8.8	7.23 (d) <i>J</i> = 8.8	4.36 (d) <i>J</i> = 6.4	2.48 (m)	1.17 (d) <i>J</i> = 6.8
2	1.44 (t) <i>J</i> = 6.8	—	4.06 (q) <i>J</i> = 6.8	6.94 (d) <i>J</i> = 8.4	7.94 (d) <i>J</i> = 8.4	8.48 (s)	7.26 (d) <i>J</i> = 8.8	7.23 (d) <i>J</i> = 8.8	4.36 (d) <i>J</i> = 6.4	2.48 (m)	1.17 (d) <i>J</i> = 7.2
5	0.95 (t) <i>J</i> = 6.8	1.83 1.42 (m)	3.98 (t) <i>J</i> = 6.4	6.94 (d) <i>J</i> = 8.4	7.93 (d) <i>J</i> = 8.4	8.48 (s)	7.25 (d) <i>J</i> = 8.4	7.23 (d) <i>J</i> = 8.4	4.38 (d) <i>J</i> = 6.4	2.48 (m)	1.17 (d) <i>J</i> = 6.8
6	0.91 (t) <i>J</i> = 6.8	1.83 1.33 (m)	3.97 (t) <i>J</i> = 6.8	6.93 (d) <i>J</i> = 8.8	7.93 (d) <i>J</i> = 8.8	8.47 (s)	7.25 (d) <i>J</i> = 8.4	7.23 (d) <i>J</i> = 8.4	4.35 (d) <i>J</i> = 6.8	2.49 (m)	1.17 (d) <i>J</i> = 6.8
7	0.90 (t) <i>J</i> = 7.2	1.81 1.32 (m)	3.97 (t) <i>J</i> = 6.8	6.92 (d) <i>J</i> = 8.4	7.94 (d) <i>J</i> = 8.4	8.47 (s)	7.26 (d) <i>J</i> = 8.4	7.23 (d) <i>J</i> = 8.4	4.35 (d) <i>J</i> = 6.8	2.48 (m)	1.17 (d) <i>J</i> = 7.2
8	0.90 (t) <i>J</i> = 7.2	1.81 1.30 (m)	3.98 (t) <i>J</i> = 6.4	6.92 (d) <i>J</i> = 8.4	7.94 (d) <i>J</i> = 8.4	8.48 (s)	7.26 (d) <i>J</i> = 8.8	7.23 (d) <i>J</i> = 8.8	4.36 (d) <i>J</i> = 6.0	2.49 (m)	1.17 (d) <i>J</i> = 6.8
10	0.89 (t) <i>J</i> = 7.2	1.83 1.28 (m)	3.97 (t) <i>J</i> = 6.8	6.93 (d) <i>J</i> = 8.8	7.93 (d) <i>J</i> = 8.8	8.47 (s)	7.26 (d) <i>J</i> = 8.4	7.23 (d) <i>J</i> = 8.4	4.35 (d) <i>J</i> = 6.8	2.49 (m)	1.17 (d) <i>J</i> = 6.4
12	0.88 (t) <i>J</i> = 7.2	1.81 1.28 (m)	3.97 (t) <i>J</i> = 6.4	6.93 (d) <i>J</i> = 8.8	7.93 (d) <i>J</i> = 8.8	8.47 (s)	7.26 (d) <i>J</i> = 7.8	7.23 (d) <i>J</i> = 7.8	4.35 (d) <i>J</i> = 6.4	2.49 (m)	1.17 (d) <i>J</i> = 6.0

s, singlet; d, doublet; t, triplet; m, multiplet; q, quartlet.

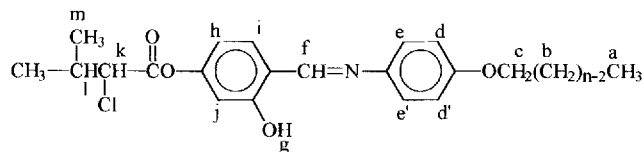
obtained. Yield 80 per cent. The oil solidified on standing at r.t. for several days but it had no sharp melting point.  $[\alpha]_D^{16} = 1.62$  ( $c = 1.55$ ,  $C_2H_5OH$ ). IR: 1771.1 ( $-COO-$ ), 1666.3 ( $-CH=O$ )  $\text{cm}^{-1}$ . Elemental analysis for  $C_{12}H_{13}ClO_4$ : found (calculated); C, 55.96 (56.14); H, 5.01 (5.10), per cent  $^1H$  NMR:  $\delta$  11.253 (1 H, s,  $-CH=O$ ), 9.884 (1 H, s,  $-OH$ ), 7.613 (1 H, d, ArH,  $J = 8.0$  Hz), 6.824 (1 H, d, ArH,  $J = 8.0$  Hz), 6.781 (1 H, s, ArH), 4.330 (1 H, d,  $-CHCl-$ ,  $J = 6.8$  Hz), 2.459 (1 H, m,  $-CH(CH_3)_2$ ), 1.153 (6 H, d,  $-CH(CH_3)_2$ ,  $J = 6.4$  Hz).

The chiral aldehyde **3a** was prepared according to the same procedure of **3b**. Yield 53.3 per cent,  $[\alpha]_D^{16} = +2.95$  ( $c = 9.5$ ,  $C_2H_5OH$ ). IR: 1770.0 ( $-COO-$ ),

Table 5. Yields and the relevant IR data for the liquid crystal of series II.

<i>n</i>	Yield† /per cent	IR	
		$\nu_{C=O}/\text{cm}^{-1}$	$\nu_{C=N}/\text{cm}^{-1}$
2	70.7	1754.3	1621.9
4	67.3	1756.7	1622.3
6	60.0	1758.0	1621.8
8	64.2	1759.2	1620.1
10	65.5	1761.7	1622.3
12	56.5	1757.0	1623.4

†The condensation of **3b** and appropriate **4**.

Table 6. The 400 MHz NMR data of compounds of series III in CDCl<sub>3</sub>: coupling constants *J*(Hz) and shifts  $\delta$  (ppm).

<i>n</i>	<i>d'e'hij</i>								
	<i>a</i>	<i>b</i>	<i>c</i>	ArH	<i>f</i>	<i>g</i>	<i>k</i>	<i>l</i>	<i>m</i>
2	1.44 (t) <i>J</i> = 7.2		4.06 (q) <i>J</i> = 7.2	6.70–7.40 (m)	8.60 (s)	13.85 (s)	4.36 (d) <i>J</i> = 7.2	2.47 (m)	1.16 (d) <i>J</i> = 6.8
4	0.99 (t) <i>J</i> = 7.2	1.48–1.82 (m)	3.99 (t) <i>J</i> = 6.4	6.70–7.39 (m)	8.60 (s)	13.86 (s)	4.33 (d) <i>J</i> = 6.8	2.48 (m)	1.16 (d) <i>J</i> = 6.8
6	0.92 (t) <i>J</i> = 7.2	1.35–1.80 (m)	3.98 (t) <i>J</i> = 6.4	6.73–7.40 (m)	8.60 (s)	13.87 (s)	4.34 (d) <i>J</i> = 6.4	2.41 (m)	1.16 (d) <i>J</i> = 6.4
8	0.89 (t) <i>J</i> = 7.2	1.29–1.81 (m)	3.96 (t) <i>J</i> = 6.4	6.70–7.40 (m)	8.60 (s)	13.88 (s)	4.34 (d) <i>J</i> = 6.4	2.49 (m)	1.16 (d) <i>J</i> = 7.2
10	0.89 (t) <i>J</i> = 7.2	1.28–1.83 (m)	3.98 (t) <i>J</i> = 6.4	6.73–7.40 (m)	8.60 (s)	13.87 (s)	4.34 (d) <i>J</i> = 6.4	2.48 (m)	1.16 (d) <i>J</i> = 6.4
12	0.88 (t) <i>J</i> = 7.2	1.26–1.82 (m)	3.98 (t) <i>J</i> = 7.2	6.70–7.40 (m)	8.60 (s)	13.87 (s)	4.34 (d) <i>J</i> = 7.2	2.46 (m)	1.16 (d) <i>J</i> = 7.2

1702.5 (–CH=O) cm<sup>-1</sup>. Elemental analysis for C<sub>12</sub>H<sub>13</sub>ClO<sub>3</sub>: found (calculated): C, 59.62 (59.88); H, 5.38 (5.41) per cent.

The alkoxyanilines **4** were obtained by the reduction of **2** using the Bellamy method [14]. It was then used without further purification.

The liquid crystals **5** were prepared by the condensation of **3** and the appropriate **4** according to the following procedure.

A solution of chiral benzaldehyde (5 mmol) and *p*-alkoxyaniline 5 mmol in 20 ml ethanol was stirred at r.t. for 2 h. The yellow precipitate was filtered off and crystallized three times from ethanol.

Tables 3–6 give some physical data for these compounds.

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