**Liquid Crystals**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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**To cite this Article** Kaspar, M. , Hamplova, V. , Pakhomov, S. A. , Bubnov, A. M. , Guittard, F. , Sverenyak, H. , Stibor, I. , Vanek, P. and Glogarova, M.(1998) 'New series of ferroelectric liquid crystals with four ester groups', Liquid Crystals, 24: 4, 599 — 605

**To link to this Article: DOI:** 10.1080/026782998207073

**URL:** http://dx.doi.org/10.1080/026782998207073

Liquid Crystals, 1998, Vol. 24, No. 4, 599–605

# New series of ferroelectric liquid crystals with four ester groups

by M. KAŠPAR, V. HAMPLOVÁ*, S. A. PAKHOMOV†, A. M. BUBNOV,
F. GUITTARD‡, H. SVERENYÁK, I. STIBOR†, P. VANĚK
and M. GLOGAROVÁ

Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2,
180 40 Prague 8, Czech Republic
†Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic
‡University of Nice—Sophia Antipolis, B.P. No. 71, F-06108 Nice, France

(*Received 23 April 1997; in final form 27 October 1997; accepted 11 November 1997*)

Three series of ferroelectric liquid crystals have been synthesized, having three ester groups in the mesogenic core and one ester group in the chiral chain. The ester groups introduced into the core decrease the temperature of crystallization, which results in a broad temperature range ferroelectric smectic C phase in homologues with a long non-chiral chain. These phases exhibit a high spontaneous polarization and relatively short pitch of the helical structure.

## 1. Introduction

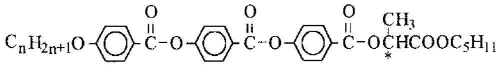
Ferroelectric liquid crystals (FLCs) have attracted attention for a long time due to the possible use of the materials in various devices. For applications, materials possessing the ferroelectric SmC* phase at low temperatures are preferable. We assume that a decreased temperature limit of the SmC* phase can be obtained by modifying the mesogenic core through introducing several ester linkages or by inserting lateral substituents. This work is devoted to a study of the influence of ester groups on the mesomorphic and ferroelectric properties. Here we report new series of FLCs with a flexible core, a chiral unit derived from (*S*)-lactic acid and four ester groups. Compounds of this structure are not very frequently studied, probably because of problems during their synthesis. The most commonly used condensation agent DCC may cause partial re-esterification of ester products during synthesis and the isolation of final products is consequently difficult. Materials with rigid cores (containing rings connected without a linkage group) are more often and more easily prepared, e.g. derivatives of 4,4′-dihydroxybiphenyl or 4′-hydroxyxantoic acid. These mesogens possess an almost similar magnitude of the molecular dipole moment, playing an important role in the formation of the SmC* phase and the value of its spontaneous polarization.

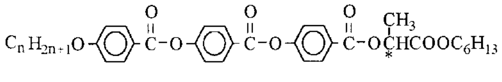
It is known that introduction of the ester group in the α-position in a chain next to the benzene ring increases slightly both melting and clearing points compared with the alkoxy substituted parent compounds [1], the SmC phase being found for homologues with chains shorter than for the alkoxy series. On the other hand, inserting the ester group into the core results in decreasing both melting and clearing points [2, 3]. Inserting the ester group in any position decreases the value of the spontaneous polarization [2].

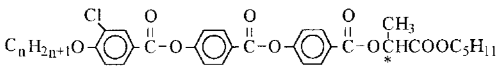
Beilstein's database reports several compounds with three aromatic rings in the core, containing three ester linkages, e.g. diphenyl terephtalates, phenyl 4-benzoyloxybenzoates, etc. [4–10]. Some of them do not exhibit mesomorphic behaviour [6]. The ferroelectric SmC* phase has already been found in similar substances with a lactate based chiral group and possessing either only two 4-substituted phenyl benzoates units in the core [11, 12] or three ring cores containing the thioester group [13]. In the latter case the chiral unit is joined to the mesogenic core by an ether link.

## 2. Synthesis

We have prepared three series of compounds:







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*Author for correspondence.

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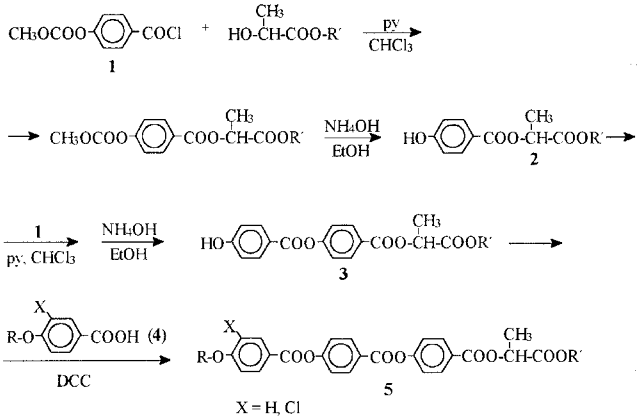
All chiral chains have the (*S*)-configuration. The synthesis was carried out according to the following scheme:



Scheme

### 2.1. *Synthesis of protected 4-(methoxycarbonyloxy)benzoyl chloride, **1** [14]*

2-Hydroxybenzoic acid (69 g, 0·5 mol) was added to a solution of 1·5 mol of sodium hydroxide in 1·5 l of water/ice mixture while stirring. Then methyl chloroformate (80 g, 0·85 mol) was slowly added to the resulting solution, which was maintained at 0°C. The reaction mixture was stirred for a further 4 h and acidified to pH 4–5 by adding concentrated HCl. The precipitate was filtered off and recrystallized from ethanol. The yield of white crystals (m.p. 85°C) was 90 g (92%). Thionyl chloride (80 ml) was mixed with 4-methoxycarbonyloxybenzoic acid (40 g, 0·21 mol) and 1 ml of dimethylformamide and the solution was heated under reflux for 2 h. The excess of thionyl chloride was removed by evaporation. The yield of crude acyl chloride **1** was 41 g.

NMR: 3·95 (3H, s, $OCH_3$), 7·37 (2H, d, $J = 8{\cdot}9$ Hz, H–Ar *meta* to –COCl), 8·18 (2H, d, $J = 8{\cdot}9$ Hz, H–Ar *ortho* to –COCl).

### 2.2. *Synthesis of n-alkyl 2(S)-(4-hydroxybenzoyloxy)propanoates, **2***

A solution of 41 g of acid chloride **1** in 100 ml of dichloromethane was slowly added to a solution of 0·23 mol of (-)-*n*-alkyl L-lactate in 100 ml of dichloromethane and 80 ml of pyridine. The reaction mixture was stirred for one day at room temperature. It was then washed with an aqueous solution of HCl (200 ml, 10%), evaporated to dryness, and 100 ml of ethanol and 100 ml of aqueous ammonia (27%) were added. The mixture was stirred at room temperature for 1 h. After the reaction, the solution was poured into water (200 ml), acidified with glacial acetic acid and shaken with diethyl ether. The organic layer was washed with water and dried over anhydrous sodium sulphate. The ether was removed by evaporation and the product distilled under reduced pressure (b.p. 190–195°C/1 torr), $[\alpha]_D^{25} = +23{\cdot}5°$ ($c = 0{\cdot}2$, EtOH). The yield was 0·16 mol (69%). These data and the NMR data below are for alkyl = *n*-pentyl.

NMR for *n*-pentyl 2-(*S*)-(4-hydroxybenzoyloxy)-propanoate: 0·88 (3H, t, $J = 6$ Hz, $C\underline{H}_3CH_2$), 1·2–1·3 (4H, m, $CH_2$), 1·6–1·7 (5H, wide doublet of $C\underline{H}_3C^*H$ ($J = 7$ Hz) and $OCH_2C\underline{H}_2$), 4·18 (2H, td, $J_1 = 6{\cdot}6$ Hz, $J_2 = 3{\cdot}3$ Hz, $OCH_2$), 5·29 (1H, q, $J = 7$ Hz, C*H), 6·80 (2H, d, $J = 8{\cdot}7$ Hz, H–Ar *ortho* to OH), 7·12 (1H, br., OH), 7·89 (2H, d, $J = 8{\cdot}7$ Hz, H–Ar *meta* to OH).

### 2.3. *Synthesis of compounds **3***

Compounds **3** were prepared in a similar way (without distillation) to that for compounds **2** from 0·16 mol of **2** and 31·4 g (0·16 mol) of **1**. The yield ($R'$ = pentyl) was 72% of a yellow liquid, $[\alpha]_D^{25} = +14{\cdot}0°$ ($c = 0{\cdot}2$, $CH_2Cl_2$).

NMR: 0·91 (3H, t, $J = 7$ Hz, $CH_3$), 1·25–1·3 (4H, m, $CH_2$), 1·6–1·7 (5H, wide doublet of $C\underline{H}_3C^*H$, 1·64, $J = 7$ Hz + $OCH_2C\underline{H}_2$), 4·18 (2H, m, $OCH_2$), 5·30 (1H, m, C*H), 6·90 (2H, d, $J = 8{\cdot}7$ Hz, H–Ar *ortho* to –OH), 7·28 (2H, d, $J = 8{\cdot}8$ Hz, H–Ar *meta* to –COO–C*H), 8·02 (2H, d, $J = 8{\cdot}7$ Hz, H–Ar *meta* to –OH), 8·12 (2H, d, $J = 8{\cdot}7$ Hz, H–Ar *ortho* to –COO–C*H).

### 2.4. *Synthesis of 4-alkoxy-3-chlorobenzoic acid (**4**, X = Cl)*

A mixture of 0·275 mol of 3-chloro-4-hydroxybenzoic acid hemihydrate (m.p. 169°C), 100 ml of ethanol, 300 ml of toluene and 1 g of *p*-toluenesulphonic acid was heated under reflux for three days with azeotropic elimination of water. The solution was neutralized, washed with water and dried. The solvents were evaporated under reduced pressure. The crude ethyl 3-chloro-4-hydroxybenzoate, obtained in 55% yield, was used in the next stage without additional purification.

NMR: 1·38 (3H, t, $J = 7$ Hz, $CH_3$), 4·35 (2H, q, $J = 7$ Hz, $CH_2$), 6·00 (1H, br., OH), 7·05 (1H, d, $J = 8{\cdot}6$ Hz, H–Ar *ortho* to OH), 7·89 (1H, dd, $J_1 = 8{\cdot}7$ Hz, $J_2 = 2{\cdot}1$ Hz, H–Ar *para* to Cl), 8·05 (1H, d, $J = 2{\cdot}1$ Hz, H–Ar *ortho* to Cl).

The preparation of 4-alkoxy-3-chlorobenzoic acids **4** was carried out using the standard Williamson reaction followed by hydrolysis with NaOH. The crude products prepared from 0·15 mol of ethyl 3-chloro-4-hydroxybenzoate were crystallized from 200 ml of ethanol. Yields were around 40%.

NMR for 3-chloro-4-*n*-decyloxybenzoic acid: 0·89 (3H, t, $J = 6{\cdot}8$ Hz, $CH_3$), 1·22–1·45 (12H, m, $CH_2$), 1·51 (2H, m, $OCH_2CH_2C\underline{H}_2$), 1·88 (2H, quint., $J = 8$ Hz, $OCH_2C\underline{H}_2$), 4·11 (2H, t, $J = 6{\cdot}5$ Hz, $OCH_2$), 6·96 (1H, d, $J = 8{\cdot}6$ Hz, H–Ar *ortho* to –O–Alk), 7·99 (1H, dd, $J_1 = 8{\cdot}6$ Hz, $J_2 = 2{\cdot}1$ Hz, H–Ar *para* to Cl), 8·13 (1H, d, $J = 2{\cdot}1$ Hz, H–Ar *ortho* to Cl).

### 2.5. *Synthesis of the final products,* **5**

*N*,*N*′-dicyclohexylcarbodiimide (15 mmol, 3·1 g) was added with stirring to a solution of 10 mmol of the mesogenic phenol **3**, 10 mmol of 4-alkoxybenzoic acid or 4-alkoxy-3-chlorobenzoic acid **4** and 0·2 g of 4-pyrrolidinopyridine in 100 ml of dichloromethane; stirring was continued for 12 h at room temperature. The precipitate (dicyclohexylurea) was removed by filtration. The filtrate was evaporated and the crude product chromatographed on silica gel (Kieselgel 60, Merck Darmstadt) using $CH_2Cl_2$ as eluent. This separation was not efficient enough to remove other esters as products of re-esterification reactions and so at the last stage the product was purified by preparative HPLC (Separon 7 μm column, 25 × 250, Tessek) using a mixture of 99·9% toluene and 0·1% methanol as the mobile phase. After crystallization from methanol the product purity was determined by analytical high pressure liquid chromatography which was carried out with an Ecom HPLC chromatograph using a silica gel column (Separon 7 μm, 3 × 150, Tessek) with a mixture of 99·9% toluene and 0·1% methanol as eluent, and detection of the eluting products by a UV–VIS detector ($\lambda = 290$ nm). Highly pure compounds (99·5–100% according to HPLC) were obtained and they gave satisfactory elemental analyses (see table 1). All new compounds were identified by $^1H$ NMR. For compound **5** ($R = n\text{-}C_9H_{19}$, $R' = n\text{-}C_5H_{11}$, $X = H$) the specific rotation was $[\alpha]_D^{25} = +9{\cdot}0°$ ($c = 0{\cdot}2$, $CHCl_3$).

NMR for compound **5**, $R = n\text{-}C_9H_{19}$, $R' = n\text{-}C_5H_{11}$, $X = H$: 0·9 (6H, m, $CH_3CH_2$), 1·2–1·56 (12H, m, $CH_2$), 1·56–1·72 (5H, d, $CH_3C*H$, 1·68, $J = 7{\cdot}1$ Hz + $COOCH_2CH_2$), 1·84 (2H, quint., $J = 7$ Hz, Ar–$OCH_2CH_2$), 4·06 (2H, t, $J = 6{\cdot}5$ Hz, Ar–$OCH_2$), 4·18 (2H, dt, $J_1 = 6{\cdot}5$ Hz, $J_2 = 2{\cdot}1$ Hz, $COOCH_2$), 5·35 (1H, q, $J = 7{\cdot}1$ Hz, C*H), 7·00 (2H, d, $J = 9$ Hz, H–Ar *ortho* to –O–Alkyl), 7·34 (2H, d, $J = 8{\cdot}7$ Hz, H–Ar *meta* to –COO–C*H), 7·39 (2H, d, $J = 8{\cdot}7$ Hz, H–Ar *ortho* to –OOC–Ar–O–Alkyl), 8·18 (4H, 2d, $J = 8{\cdot}5$ Hz, H–Ar *meta* to –O–Alk and *ortho* to –COO–C*H), 8·29 (2H, d, $J = 8{\cdot}7$ Hz, H–Ar *meta* to –OOC–Ar–O–R).

NMR for compound **5**, $R = n\text{-}C_{10}H_{21}$, $R' = n\text{-}C_5H_{11}$, $X = Cl$: 0·89 (6H, m, $CH_3CH_2$), 1·24–1·46 (16H, m, $CH_2$), 1·53 (2H, m, $CH_2$), 1·65 (5H, m, $COOCH_2CH_2$ + $CH_3C*H$, 1·65, d, $J = 7$ Hz), 1·90 (2H, quint., $J = 7$ Hz, Ar–$OCH_2CH_2$), 4·18 (4H, m, $COOCH_2$ + $ArOCH_2$), 5·35 (1H, q, $J = 7$ Hz, C*H), 7·02 (1H, d, $J = 8{\cdot}8$ Hz, H–Ar *ortho* to –O–Alkyl), 7·34 (2H, d, $J = 8{\cdot}7$ Hz, H–Ar *meta* to –COO–C*H), 7·39 (2H, d, $J = 8{\cdot}7$ Hz, H–Ar *ortho* to –OOC–Ar–O–Alkyl), 8·09 (1H, dd, $J_1 = 8{\cdot}6$ Hz, $J_2 = 2{\cdot}1$ Hz, H–Ar *para* to Cl), 8·19 (2H, d, $J = 8{\cdot}7$ Hz, H–Ar *ortho* to –COO–C*H), 8·23 (1H, d, $J = 2{\cdot}1$ Hz, H–Ar *ortho* to Cl), 8·30 (2H, d, $J = 8{\cdot}7$ Hz, H–Ar *meta* to –OOC–Ar–O–R).

## 3. Experimental results

All synthesized materials were studied by DSC (Perkin-Elmer 7). Microscopic observations and measurements of basic characteristics were carried out on planar samples (in the book shelf geometry) filled into glass cells 25 μm thick. The inner surfaces of the glass plates were provided with transparent ITO electrodes and

Table 1. HPLC data and elemental analysis data for the newly prepared compound.

| | | Elemental analysis/% | | | | | |
|---|---|---|---|---|---|---|---|
| | | Calculated | | | Found | | |
| Compound | HPLC purity/% | C | H | Cl | C | H | Cl |
| 6AL | 99·7 | 69·52 | 6·67 | | 69·52 | 6·84 | |
| 7AL | 99·7 | 69·89 | 6·84 | | 70·12 | 6·87 | |
| 8AL | 100·0 | 70·23 | 7·01 | | 70·23 | 6·84 | |
| 9AL | 100·0 | 70·57 | 7·17 | | 70·27 | 7·31 | |
| 10AL | 99·5 | 70·89 | 7·32 | | 70·93 | 7·49 | |
| 12AL | 99·6 | 71·49 | 7·61 | | 71·50 | 7·59 | |
| 6HL | 99·5 | 69·89 | 6·84 | | 69·84 | 6·59 | |
| 7HL | 100·0 | 70·23 | 7·01 | | 70·24 | 7·09 | |
| 8HL | 99·6 | 70·57 | 7·17 | | 70·53 | 7·37 | |
| 9HL | 99·5 | 70·89 | 7·32 | | 70·90 | 7·27 | |
| 10HL | 99·5 | 71·19 | 7·47 | | 71·08 | 7·39 | |
| 12HL | 99·6 | 71·77 | 7·74 | | 71·80 | 7·80 | |
| 14HL | 99·5 | 72·31 | 8·00 | | 72·52 | 8·19 | |
| 16HL | 99·7 | 72·79 | 8·23 | | 72·44 | 8·05 | |
| 10ALCl | 99·6 | 67·38 | 6·81 | 5·10 | 67·39 | 7·00 | 5·13 |
| 12ALCl | 99·5 | 68·08 | 7·11 | 4·90 | 68·45 | 7·22 | 4·98 |

polyimide layers rubbed for better uniaxial sample alignment. To improve sample alignment further, an electric field of 10–20 Hz and intensity about 40 kV cm$^{-1}$ was applied for 10–60 min.

### 3.1. *Mesomorphic properties*

The sequences of phases were determined from texture observations made on planar samples in the polarizing microscope. The phase transition temperatures and the enthalpies were evaluated from DSC studies, except the temperatures of recrystallization, which were determined by microscopic observation. Typical DSC plots for each homologous series are shown in figure 1. Mesomorphic properties of all newly synthesized compounds from the three homologous series *n*AL, *n*HL and *n*ALCl are collected in table 2. The phase transition temperatures and enthalpies were determined on cooling because the

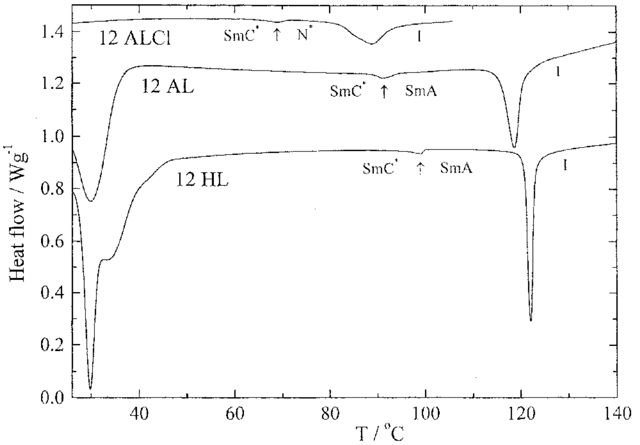


Figure 1. Typical DSC plots on cooling (rate 10 K min$^{-1}$) for each homologous series.

Table 2. Transition temperatures (°C) from DSC, measured on cooling (5 K min$^{-1}$), melting points (m.p. in °C) and transition enthalpies in kJ mol$^{-1}$ (in square brackets) for homologous series *n*AL, *n*HL, and *n*ALCl. Monotropic transitions are in round brackets; ● the phase exists, —the phase does not exist.

| Compound | m.p. | | | SmC* | | SmA | | N* | | I |
|---|---|---|---|---|---|---|---|---|---|---|
| 6AL | 67·7<br>[37·0] | Cr | 40 | — | | ● | 131·0<br>[2·8] | — | | ● |
| 7AL | 64·2<br>[27·0] | Cr | 50 | — | | ● | 126·9<br>[3·1] | — | | ● |
| 8AL | 67·6<br>[27·0] | Cr | 41 | — | | ● | 130·2<br>[3·2] | — | | ● |
| 9AL | 69·1<br>[33·6] | Cr | 48 | ● | (66·0) | ● | 122·4<br>[2·9] | — | | ● |
| 10AL | 54·4<br>[27·0] | Cr | 35 | ● | 79·0<br>[≈0·01] | ● | 134·3<br>[4·6] | — | | ● |
| 12AL | 67·3<br>[33·0] | Cr | 44 | ● | 92·5<br>[0·3] | ● | 120·7<br>[5·1] | — | | ● |
| 6HL | 50·7<br>[29·0] | Cr | < −33 | — | | ● | 139·9<br>[3·6] | — | | ● |
| 7HL | 67·3<br>[39·0] | Cr | 32 | — | | ● | 125·6<br>[2·9] | — | | ● |
| 8HL | 55·2<br>[27·0] | Cr | 33 | ● | (39·0) | ● | 129·2<br>[4·2] | — | | ● |
| 9HL | 50·5<br>[28·0] | Cr | 41 | ● | 67·2<br>[0·4] | ● | 134·6<br>[4·2] | — | | ● |
| 10HL | 55·5<br>[20·0] | Cr | 30 | ● | 82·3<br>[≈0·03] | ● | 130·6<br>[3·3] | — | | ● |
| 12HL | 56·4<br>[29·0] | Cr | 44 | ● | 99·9<br>[0·3] | ● | 122·9<br>[4·6] | — | | ● |
| 14HL | 54·9<br>[28·0] | Cr | 43 | ● | 104·2<br>[0·3] | ● | 122·6<br>[4·3] | | | ● |
| 16HL | 49·5<br>[45·0] | Cr | 44 | ● | 108·3<br>[0·1] | ● | 125·6<br>[5·3] | — | | ● |
| 10ALCl | 52·2<br>[22·0] | Cr | 36 | ● | 73·4<br>[0·2] | — | | ● | 95·5<br>[2·2] | ● |
| 12ALCl | 37·4<br>[15·0] | Cr | 24 | ● | 70·8<br>[0·1] | — | | ● | 93·0<br>[2·8] | ● |

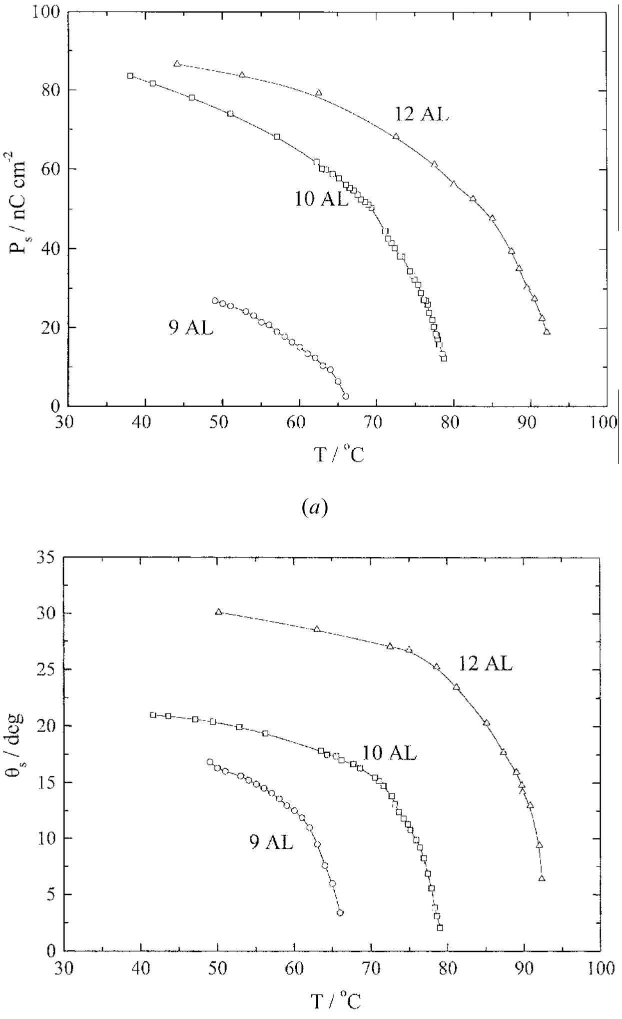
SmA–SmC* phase transition, which has a very low enthalpy, can then be more easily detected. With 9AL and 8HL the SmA–SmC* phase transition could not be detected from DSC at all, so the phase transition temperature was determined from the change of texture observed in the polarizing microscope. At this phase transition, chiralization lines accompanying occurrence of the helicoidal SmC* structure appear on cooling.

The SmA phase occurs for all the synthesized compounds from the series *n*AL and *n*HL, and the N* phase exists only in the *n*ALCl series. The ferroelectric SmC* phase was not found for compounds with short aliphatic chains, i.e. for $n=6,7,8$ and $n=6,7$ for the *n*AL and *n*HL series, respectively (see table 2). The transitions from the isotropic phase, as well as the N*–SmC* transitions observed with the *n*ALCl series, are first order and characterized by a phase coexistence region. The SmA–SmC* transition seems to be of second order or weakly first order. For both *n*AL and *n*HL series, with increasing *n* a considerable increase in the SmA–SmC* phase transition temperature occurred, as well as an extension of the temperature range of the SmC* phase.

### 3.2. *Spontaneous polarization and tilt angle*

In the ferroelectric SmC* phases the temperature dependence of the spontaneous polarization ($\mathbf{P}_S$) and the tilt angle ($\theta_S$) of the molecules from the smectic layer normal were measured. The values of $\mathbf{P}_S$ were determined from the $\mathbf{P}(\mathbf{E})$ hysteresis loops detected during $\mathbf{P}_S$ switching in an a.c. electric field $\mathbf{E}$ of frequency 60 Hz. The $\theta_S$ values were calculated from the difference between the extinction positions observed in a planar sample between crossed polarizers under opposite d.c. unwinding fields. Well aligned samples have to be used for $\theta_S$ measurements. For 8HL, $\mathbf{P}_S$ and $\theta_S$ could not be measured for the ferroelectric SmC* phase, as this monotropic phase is metastable and crystallizes under the measuring electric field.

The temperature dependences of $\mathbf{P}_S$ and $\theta_S$ are shown in figures 2(*a*) and 2(*b*) for *n*AL, figures 3(*a*) and 3(*b*) for *n*HL, and figures 4(*a*) and 4(*b*) for *n*ALCl. For *n*AL and *n*HL one can see that $\theta_S$ exhibits a saturation at low temperatures, but $\mathbf{P}_S$ still increases on cooling. Generally, $\mathbf{P}_S$ and $\theta_S$ increase with increasing *n* for both *n*AL and *n*HL series with the exception of very long chain homologues. The behaviour of $\mathbf{P}_S$ and $\theta_S$ in the SmC* phase of *n*ALCl is different because of the different origin of the transition to this phase. The values of $\theta_S$ are temperature independent and nearly the same for the 10ALCl and 12ALCl; the values of $\mathbf{P}_S$ increase on cooling about 25 K below the transition, then become constant, being higher for 10ALCl than for 12ALCl. Incomplete switching may be responsible for this saturation.



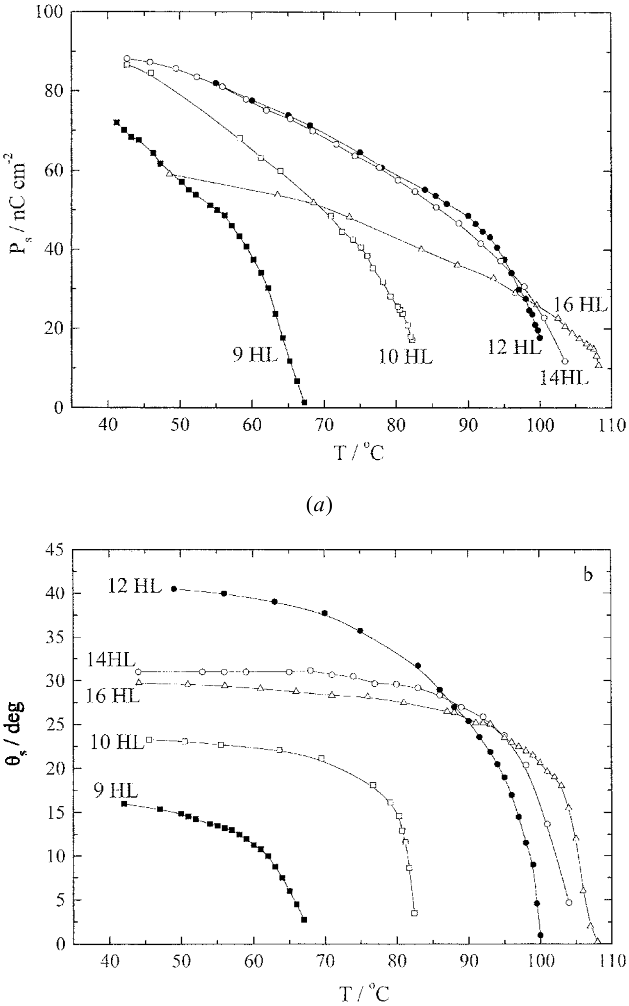
(*b*)

Figure 2. Temperature dependence of (*a*) spontaneous polarization and (*b*) spontaneous tilt angle for the *n*AL series.

### 3.3. *Helicoidal pitch*

The helicoidal pitch *p* was determined from the diffraction of He–Ne laser light at dechiralization lines. The samples were not treated by an aligning electric field, so they exhibited the fan-shaped texture. For this reason a full diffraction ring was usually observed, instead of the diffraction spots which correspond to a fully aligned sample.

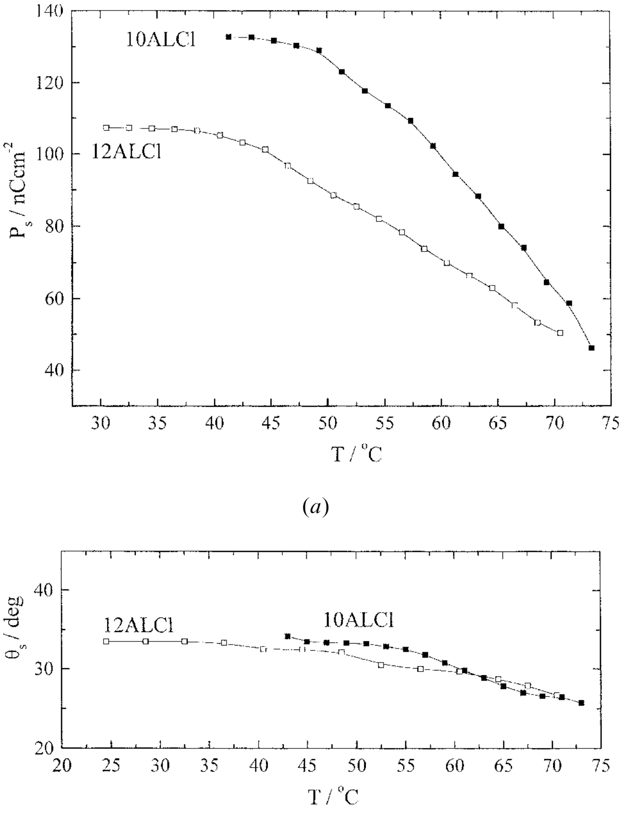
The temperature dependences of the pitch are shown in figures 5–7 for the series *n*AL, *n*HL, and *n*ALCl, respectively. The pitch is temperature independent except for a narrow temperature range below the phase transition, where, with some compounds, an increase of *p* is observed on cooling. A similar increase or a slight



(*a*)

(*b*)

Figure 3. Temperature dependence of (*a*) spontaneous polarization and (*b*) spontaneous tilt angle for the *n*HL series.



(*a*)

(*b*)

Figure 4. Temperature dependence of (*a*) spontaneous polarization and (*b*) spontaneous tilt angle for the *n*ALCl series.

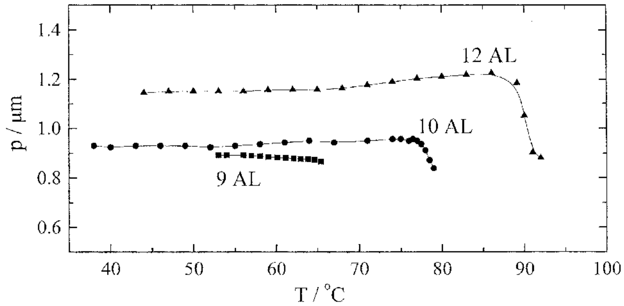


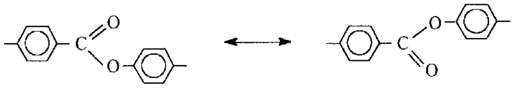
Figure 5. Temperature dependence of the helicoidal pitch for the *n*AL series.

maximum just below the SmA–SmC* phase transition is frequently observed. The origin of this effect has been explained on the basis of higher order interactions between polarization and tilt angle [15]. Temperature dependences of $p$ might also be suppressed by surface anchoring, which probably occurred for some of the samples studied. On the other hand, a temperature independent pitch occurs typically in materials with N*–SmC* phase transition.

For the *n*AL series, a slight increase of $p$ with increased $n$ was found, but for the *n*HL series no systematic relation between $p$ and $n$ was found.

## 4. Discussion

All the compounds studied contain three ester groups in the mesogenic core; these are situated next to benzene rings. This structure results in a lower rigidity of the core, because of the possibility of rotation about C–C and C–O bonds:



By this rotation, the π-electron system can stay in the plane of conjugation so that the energy of the molecular π-orbital is not increased and barriers to rotation are low. The higher rotation volume of the molecule

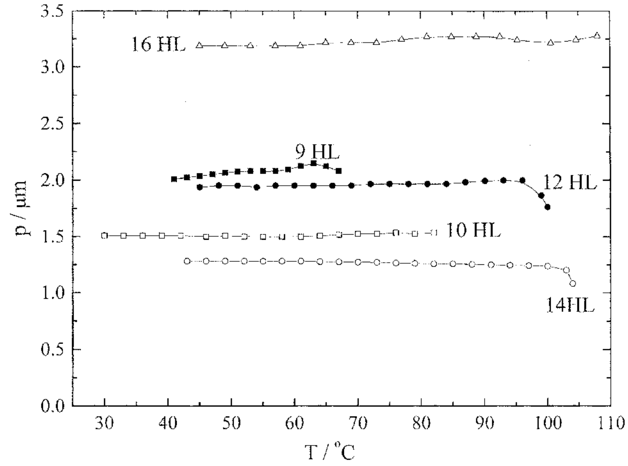


Figure 6. Temperature dependence of the helicoidal pitch for the *n*HL series.

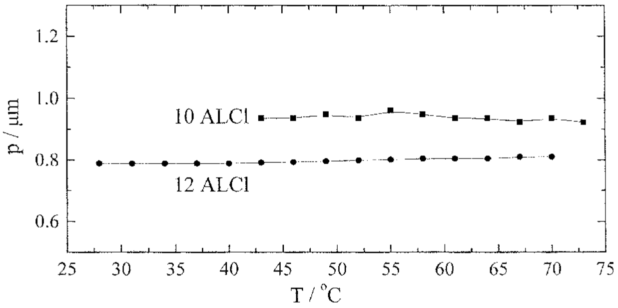


Figure 7. Temperature dependence of the helicoidal pitch for the *n*ALCl series.

enables disordering, which is probably present in the SmC* phase, but freezes out in the crystalline phase. Accordingly, the introduction of the ester group into the core may decrease the temperature of crystallization and, in this way, extend the SmC* phase range. This hypothesis seems to be confirmed by comparing related compounds possessing none, one or two ester groups in the core [2, 3, 16]. This shows that in some cases addition of each ester group can decrease the crystallization temperature by several tens of degrees.

With the series of compounds referred to in table 2, the alkyl chain length between 7 and 16 carbon atoms does not influence significantly the temperatures of either the SmC*–Cr or I–SmA phase transitions. These transition temperatures seem to be determined predominantly by core properties, probably by 'core–core' interactions. On the other hand, the alkyl chain length strongly influences the SmA–SmC* transition temperature. With an increasing number of carbon atoms in the chain, this temperature monotonously increases and so the temperature range of the SmC* phase is broadened (see table 2). Extrapolation to the shortest chain homologues ($n=6$ and 7) shows that for these compounds the SmA–SmC* transition temperature is shifted below the temperature of crystallization, which is nearly chain length independent (cf. table 2).

## 5. Conclusions

The new series of ferroelectric liquid crystals reported here afford ferroelectric phases existing over very broad temperature ranges down to rather low temperatures. They exhibit high spontaneous polarization and a relatively short pitch. These compounds can serve as chiral dopants for mixtures for the construction of displays. Ferroelectric mixtures for display application based on some of the reported compounds are now under study and will be reported elsewhere.

The work was supported by the Grants Nos. 202/96/1687 and 106/97/0337 from the Grant Agency of the Czech Republic and by the Grant COPERNICUS No. CP940168.

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