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Liquid Crystals

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Synthesis and ferroelectric properties of laterally substituted fluoro liquid crystals derived from 4-mercaptobenzoic acid

M. F. Nabor^a; H. T. Nguyen^a; C. Destrade^a; J. P. Marcerou^a; R. J. Twieg^b

^a Centre de Recherche Paul Pascal, Pessac, France ^b IBM Almaden Research Center, San Jose, California, U.S.A.

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Synthesis and ferroelectric properties of laterally substituted fluoro liquid crystals derived from 4-mercaptobenzoic acid

by M. F. NABOR, H. T. NGUYEN*, C. DESTRADE
and J. P. MARCEROU

Centre de Recherche Paul Pascal, Château Brivazac,
F-33600 Pessac, France

and R. J. TWIEG

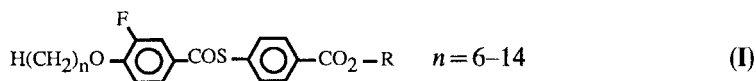
IBM Almaden Research Center, San Jose, California 95120, U.S.A.

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Several new ferroelectric liquid crystals with thiobenzoate mesogenic cores have been synthesized and the influence of a single fluorine atom ortho to the alkyloxy tail on the mesomorphic properties of some two and three benzene ring core compounds has been studied. The two benzene ring derivatives do not display the ferroelectric smectic C phase but the three phenyl ring compounds exhibit a wide temperature range S_C^* phase. The transition temperatures and enthalpies of transition for these compounds have been determined; the spontaneous polarization, response time and tilt angle have also been measured and are discussed as a function of the structure near to the chiral centre.

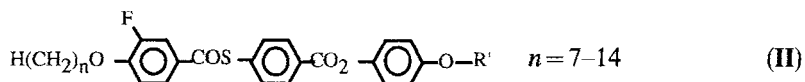
1. Introduction

Intensive research has occurred on ferroelectric liquid crystals whose existence was predicted by Meyer *et al.* [1] and whose potential for electrooptical application has been demonstrated by Clark and Lagerwall [2] and others [3]. For practical applications, the liquid crystals have to be chemically and thermally stable and show a fast response time (a high spontaneous polarization and/or a low viscosity) and a wide S_C^* phase temperature range including room temperature. Towards this goal various liquid crystals have been synthesized and many studies on the influence of the molecular structure on ferroelectricity have been reported. Numerous ferroelectric liquid crystals with phenyl benzoate cores have been described [4-9]; the phenyl thiobenzoate core is well-known to promote the stability of tilted smectic phases but less often used for preparing ferroelectric liquid crystals [10-13]. Recently some ferroelectric materials derived from 4-mercaptobenzoic acid have been reported [14] with interesting results. Additionally we have now studied the influence of fluorine on the mesomorphic properties by preparing two new series having the general formula:



* Author for correspondence.

Here the chiral tail R is derived from a chiral secondary alcohol, either 2-butanol $R = C^*H(CH_3)-C_2H_5$ (A) or 2-octanol $R = C^*H(CH_3)-C_6H_{13}$ (B). In addition to this study of the mesomorphic properties of the two benzene ring compounds we have investigated several three benzene ring derivatives. The general formula is

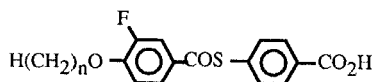


wherein R' derived from the ethyl ester (C), isopropyl ester (D) of lactic acid or 2-octanol (B).

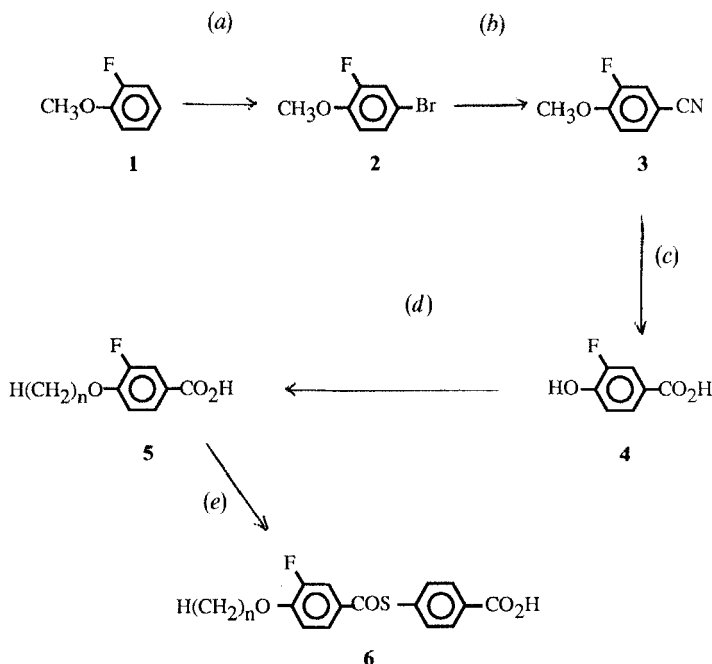
2. Results and discussion

2.1. Synthesis

For the synthesis of these new materials, the intermediate thiobenzoate acids

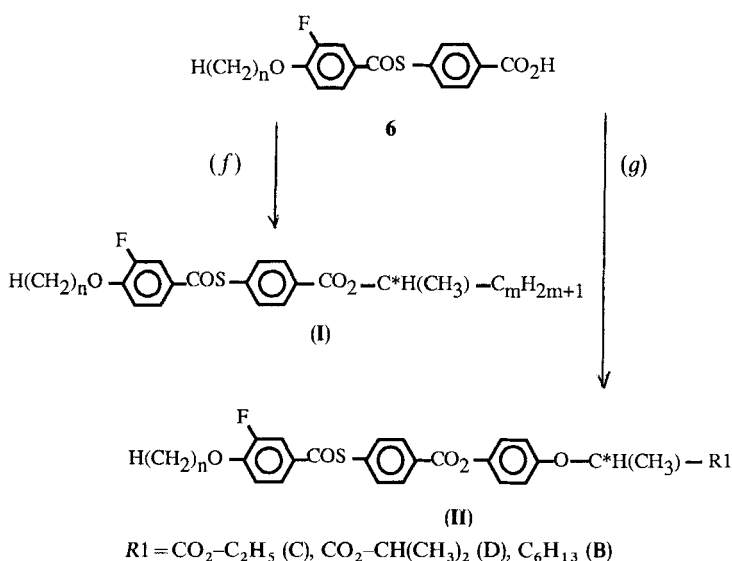


were prepared according to scheme 1.



Scheme 1. (a) Br_2 , CHCl_3 , (b) DMF , CuCN , (c) HBr , AcOH , (d) $\text{H}(\text{CH}_2)_n\text{Br}$, EtOH , KOH , (e) $(\text{COCl})_2$, CH_2Cl_2 , DMF ; 4- $\text{HS}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$, Et_3N , CH_2Cl_2 .

The two final series **I** and **II** were synthesized by esterification of the appropriate benzoic acid with different chiral alcohols. Series **I** was obtained by the Mitsunobu reaction [15] with inversion of configuration of the chiral carbon and series **II** was prepared with DCC and catalyzed by DMAP as described in scheme 2.



Scheme 2. (f) DEAD, Ph_3P , CH_2Cl_2 , $\text{HO}-\text{C}^*\text{H}(\text{CH}_3)-\text{C}_m\text{H}_{2m+1}$; $m=2$ (IA), $m=6$ (IB). (g) DCC, DMAP, $4\text{-HO}-\text{C}_6\text{H}_4-\text{OCH}(\text{CH}_3)\text{R1}$ (7).

All of the final compounds were purified by chromatography on silica gel with toluene as eluent and were recrystallized from absolute ethanol. Most of the compounds prepared are mesogenic. Phase transitions were studied by polarizing microscopy (Mettler FP 5) and DSC (Perkin-Elmer 7).

2.2. Results

The liquid crystal transition temperatures and enthalpies of transition for these new materials are presented in tables 1-4.

2.2.1. Optical microscopy studies

Series I. Most of the IB compounds derived from 2-octanol do not display any mesomorphic properties except for $n=12$ and $n=13$. Only the compounds IA derived from 2-butanol exhibit a monotropic S_A phase (except $n=7$). It is well-known that the two benzene ring compounds with a chiral 2-octanol chain rarely exhibit in general the ferroelectric S_C phase but some of the $\text{H}(\text{CH}_2)_n\text{O}-\text{C}_6\text{H}_4-\text{COS}-\text{C}_6\text{H}_4-\text{COO}-\text{CH}(\text{CH}_3)-(\text{CH}_2)_m\text{H}$ compounds [14] display a monotropic S_C^* phase and a couple a stable S_C^* phase. In this case, the instability of the S_C^* phase is further enhanced by the presence of fluorine in the meta position. Therefore these fluorinated compounds are not interesting as far as mesomorphic properties are concerned but they can be used in mixtures because the transition temperatures are very low.

Series II. The compounds with three benzene ring cores have a higher polymorphism than the two benzene core derivatives as they exhibit chiral smectic C, smectic A, cholesteric phase, and even a blue phase with short chain derivatives. As usual, the length of the alkyloxy chain governs the polymorphism of these compounds. The two series IIC and IID with chiral chains derived from ethyl and isopropyl esters of lactic acid have the same polymorphism. The N^* and S_A phases are observed in all

compounds. The first two members $n=7$ and $n=8$ do not display a chiral smectic C phase, this phase is monotropic for $n=9$ and enantiotropic for $n=10$. We can note a destabilization of N^* and S_A phases when n increases. The melting temperature is around 70°C for these two series but it is higher for the **IID** series. On the other hand the other transition temperatures are lower for **IID** because of steric hindrance of the isopropyl group which favours the cholesteric phase rather than the smectics. Consequently the S_C^* phase temperature range is higher for **IIC** than **IID**. We also find a stabilization for the S_C^* phase in **IIC**, less important in **IID**, when n increases. For example with $n=14$:



Table 1. Transition temperatures ($^\circ\text{C}$) and enthalpies [kJ mol^{-1}] of compounds **I**.

n	m	Configuration	C	S_A	I
6	2	S	• 51.6 [29.39]	• (36.8) [4.06]	•
7	2	S	• 63 [33.04]	—	•
7	6	S	• 48 [33.08]	—	•
8	2	S	• 45.5 [31.92]	• (27.1) [3.12]	•
8	6	S	• 32.8 [29.08]	—	•
9	2	S	• 45.5 [34.64]	• (25.8) [2.98]	•
9	6	S	• 36.5 [41.02]	—	•
10	2	S	• 28 [31.96]	• (26.6) [3.17]	•
10	6	S	• 34 [35.88]	—	•
11	2	S	• 30 [34.58]	• (27.8) [3.36]	•
11	6	R	• 37 [41.78]	—	•
12	2	S	• 32 [32.14]	• (30) [3.50]	•
12	6	R	• 37 [43.63]	• (14.9) [3.79]	•
13	2	S	• 36 [36.60]	• (32) [3.80]	•
13	6	S	• 37.4 [47.10]	• (14.5) [4.34]	•
14	2	S	• 34 [49.17]	• (33) [3.97]	•

Table 2. Transition temperatures ($^{\circ}\text{C}$) and enthalpies [kJ mol^{-1}] of compounds **IIc**.

n	C	S_C^*	S_A	N^*	I
7	• 77 [26·65]	—	• 111·1 [0·80]	• 117·9 [0·23]	•
8	• 72·5 [24·85]	—	• 110·5 [0·91]	• 116·7 [0·53]	•
9	• 70·4 [42·94]	• (69·3) [0·06]	• 105·7 [0·44]	• 111·6 [0·65]	•
10	• 56·8 [35·38]	• 75·7 [0·17]	• 104·1 [0·23]	• 109·7 [0·65]	•
11	• 68·1 [43·76]	• 82·4 [0·08]	• 102·1 [0·37]	• 106·8 [0·61]	•
12	• 57·9 [27·44]	• 85·7 [0·09]	• 102·3 [0·28]	• 106·4 [0·81]	•
13	• 65·4 [36·38]	• 86·6 [0·05]	• 101·5 [0·50]	• 104·5 [0·86]	•
14	• 65·3 [27·96]	• 88·2 [0·07]	• 101·2 [0·37]	• 103·8 [0·50]	•

Table 3. Transition temperatures ($^{\circ}\text{C}$) and enthalpies [kJ mol^{-1}] of compounds **IIId**.

n	C	S_C^*	S_A	N^*	I
7	• 74 [29·38]	—	• 103·8 [0·89]	• 111·9 [0·56]	•
8	• 71·6 [20·92]	—	• 102·5 [0·84]	• 110·6 [0·71]	•
9	• 77·3 [18·84]	• (68·3) [0·41]	• 98·2 [0·41]	• 105·8 [0·35]	•
10	• 58·8 [28·58]	• 73·4	• 96·1 [0·44]	• 104·1 [0·97]	•
11	• 69·5 [45·77]	• 77·3	• 93·1 [0·33]	• 101·1 [0·52]	•
12	• 73·4 [29·90]	• 81·3	• 94·7 [0·17]	• 101·2 [0·75]	•
13	• 73 [27·47]	• 81·2	• 92·7 [0·22]	• 97·9 [0·75]	•
14	• 73·1 [31·28]	• 81·4	• 91·8 [0·17]	• 96·5 [0·80]	•

Table 4. Transition temperatures ($^{\circ}\text{C}$) and enthalpies [kJ mol^{-1}] of compounds **IIB**.

<i>n</i>	C	S_C^*	S_A	N*	BP	I
7	● 68.4 [24-71]	● 118.3	● 126.1 [0.61]	● 129.5 [0.84]	● 129.8	●
8	● 62.4 [27-40]	● 120	● 125.8 [0.36]	● 128.4 [1.19]	● 129.1	●
9	● 73.8 [39-32]	● 118.3 [0.12]	● 125	● 127 [1.38]	—	●
10	● 69.4 [39-24]	● 119.5 [0.12]	● 125.2 [1.97]†	● 126.8	—	●
11	● 71 [39-13]	● 120 [0.17]	● 122.5 [3.31]†	● 124.5	—	●
12	● 67.5 [38-44]	● 121.8 [0.15]	● 123.1 [3.05]†	● 124.1	—	●
13	● 62.1 [36.06]	● 120.2	● 121.4 [4.34]†	● 122.1	—	●
14	● 63 [41.31]	● 120.8	● 121.3 [4.91]†	—	—	●

† The sum of two or three transition enthalpies.

Chiral smectic C temperature range:

$$\text{IIC } \Delta T(S_C^*) = 22.9^{\circ}\text{C},$$

$$\text{IID } \Delta T(S_C^*) = 8.3^{\circ}\text{C}.$$

The polymorphism of the series **IIB** is most important. All of the compounds show a chiral smectic C phase and $n=7$ and $n=8$ even exhibit the blue phase. The S_C^* phase is stable over a temperature range of about 60°C . We note a destabilization of the S_A and N* phases when n increases until the N* phase vanishes and a range of temperature for the S_A phase of about 1°C for $n=14$. As in the other series the melting transitions are around 70°C , but all of the transition temperatures are higher.

2.2.2. Calorimetric studies

This study was performed with a Perkin–Elmer DSC 7.

Series I. Generally the transition enthalpies are larger for the **I B** series ($m=6$) than for the **IA** series ($m=2$). For example the melting enthalpy of **IA** derivatives is about 30 kJ mol^{-1} while it is approximately 40 kJ mol^{-1} for **IB** compounds. The same ratio is found with the S_A –I transition enthalpy: 3 kJ mol^{-1} and 4 kJ mol^{-1} respectively for **IA** and **IB** series.

Series II. The three series **IIC**, **D** and **B** display the same polymorphism C – S_C^* – S_A – N^* –**I** and we have four different transition enthalpies. The melting enthalpy varies between 20 to 45 kJ mol^{-1} and the average value is 35 kJ mol^{-1} . The N^* –**I** transition enthalpy is found to be between 0.23 and 1.38 kJ mol^{-1} and increases with the chain length. The S_A – N^* transition enthalpy is about 0.8 kJ mol^{-1} for the first members of the **IIC** and **IID** series. It decreases with the chain length to 0.2 at 0.3 kJ mol^{-1} . This behaviour is also observed for the first three **IIB** compounds but from $n=10$ to $n=13$

the two transitions N^*-I and S_A-N^* are very close and enthalpies for each cannot be resolved. The $S_C^*-S_A$ transition enthalpy is very weak and not detected for the **IIB** series. It varies between 0.05 to 0.17 kJ mol⁻¹ for the other two series.

2.2.3. Electrooptical properties

We have studied the electrooptical properties of these compounds in the surface stabilized ferroelectric liquid crystal configuration, including the temperature dependence of the response time, polarization and tilt angle.

The liquid crystal was sandwiched between two glass plates (70 × 160 mm) coated with tin oxide (30 Ω cm⁻², Balzers). The planar geometry was obtained by coating both substrates with a thin layer (300 ± 50 Å) of polyvinyl alcohol. The polyvinyl alcohol was rubbed in one direction with a velvet cloth after curing. The liquid crystal was introduced by capillary action in the isotropic phase between the two electrodes and slowly cooled (1° min⁻¹) down to the S_C^* phase. The thickness is around 3 μm (checked by the Newton colours method). The value of the spontaneous polarization was obtained by measuring the transient current induced by switching the dipole when the electric field was reversed. The tilt angle was determined by rotating the sample to obtain optical extinction between crossed polarizer and analyser on application of a DC field of opposite polarity. The response time can be defined as

$$\tau = \frac{\int ip(t) dt}{2ip(\tau_m)},$$

where $ip(t)$ is the polarization current and τ_m is the time between the field reversal and the maximum of the current peak. This response time was independent of the preparation [16]. Here the recurrence frequency is 3 kHz and the applied field corresponding to the saturation of polarization is around 20 V. The polarization, the response time and the tilt angle θ have been measured as a function of temperature.

IIC series. The spontaneous polarization (see figure 1) increases when n decreases. For instance when $T_{S_C^*S_A} - T$ is around 20°C the polarization is approximately the same for $n=14$ and $n=12$ $P_S=62$ nC cm⁻² while for $n=10$, $P_S=96$ nC cm⁻². This relationship is reversed for the response time (see figure 2): which is smaller for $n=10$ than for $n=14$, because it is inversely proportional to the spontaneous polarization. For $T_{S_C^*S_A} - T$ around 20°C $\tau=15$ μs for $n=10$ while for $n=12$ and $n=14$ τ is larger than 20 μs. The relevant value of θ (see figure 7) is around 22.5° for these compounds which is an ideal value for applications.

IID series. We observe the same phenomenon as for **IIC**, but the values of both the polarization (see figure 3) and the response time (see figure 4) are larger. For $n=10$ and $T_{S_C^*S_A} - T$ around 20°C $P_S=175$ nC cm⁻². The response time is around 30 μs. The tilt angle θ (see figure 7) has the same behaviour as for the series **IID** and **IIC**.

IIB series. In contrast to the other compounds here we can study the spontaneous polarization (see figure 5) over a wide range of temperature and we find for $n=10$ and $T_{S_C^*S_A} - T=57^\circ\text{C}$, $P_S=147$ nC cm⁻². The response time (see figure 6) was still smaller for this series than for the others: for $n=10$ and $T_{S_C^*S_A} - T$ around 60°C it was less than 20 μs. For this series (see figure 7) when $n=10$ θ has a high value, $T_{S_C^*S_A} - T=12^\circ\text{C}$, $\theta=25.5^\circ$ and $T_{S_C^*S_A} - T=57^\circ\text{C}$, $\theta=31.5^\circ$.

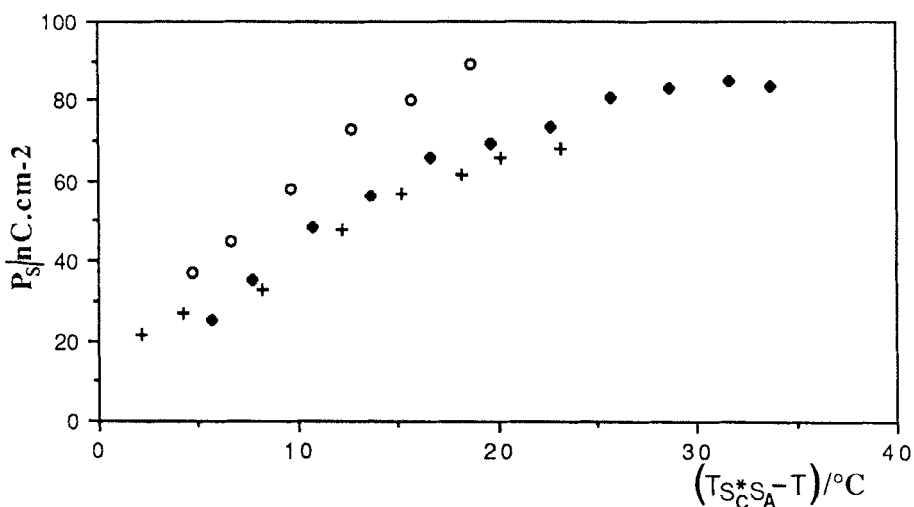


Figure 1. Polarization P_S versus $T_{S_C^*S_A} - T$ for three compounds of IIC ((\circ) $n=10$, (\blacklozenge) $n=12$, ($+$) $n=14$).

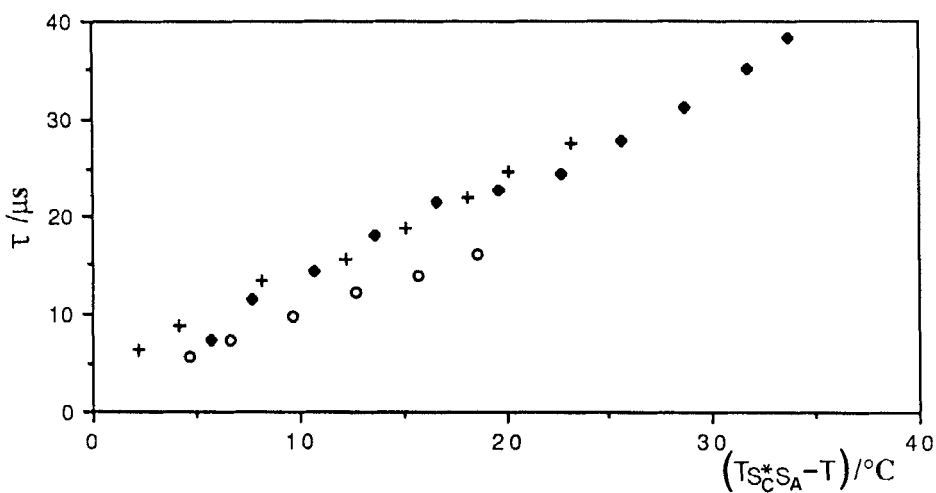


Figure 2. Response time τ versus $T_{S_C^*S_A} - T$ for three compounds of IIC ((\circ) $n=10$, (\blacklozenge) $n=12$, ($+$) $n=14$).

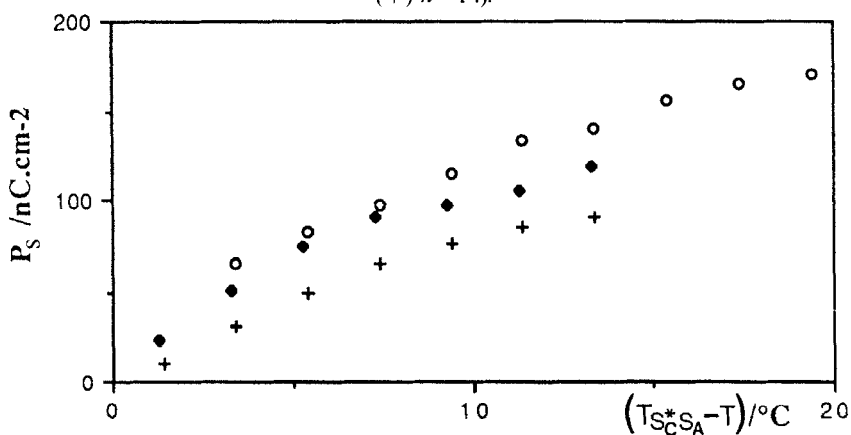


Figure 3. Polarization P_S versus $T_{S_C^*S_A} - T$ for three compounds of IID ((\circ) $n=10$, (\blacklozenge) $n=12$, ($+$) $n=14$).

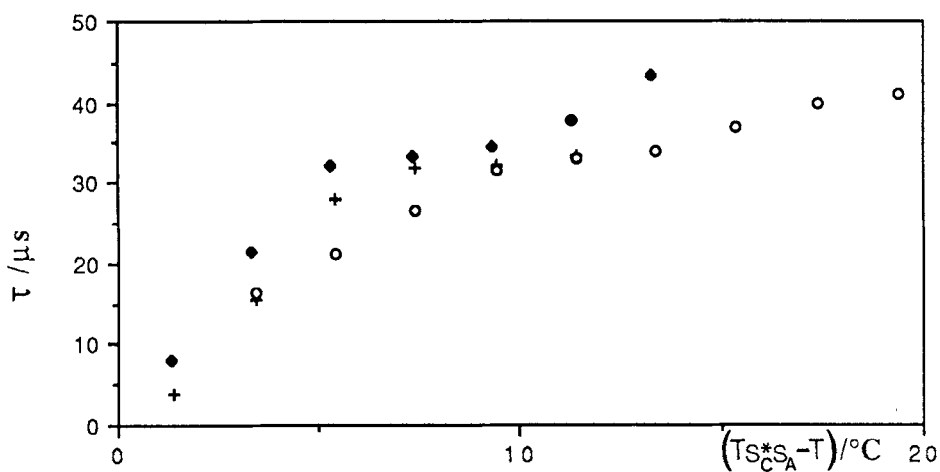


Figure 4. Response time τ versus $T_{S_C^*S_A} - T$ for three compounds of IID ((○), $n=10$, (◆) $n=12$, (+) $n=14$).

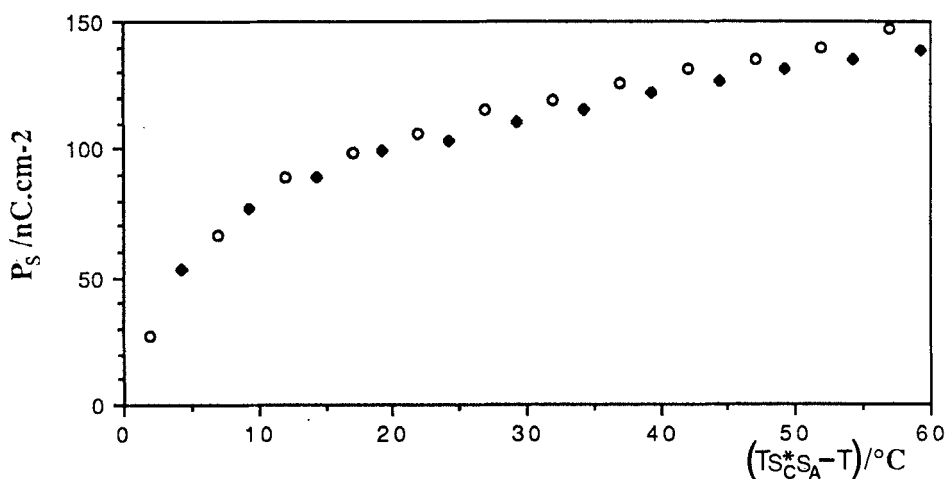


Figure 5. Polarization P_S versus $T_{S_C^*S_A} - T$ for two compounds of IIB ((○) $n=10$, (◆) $n=12$).

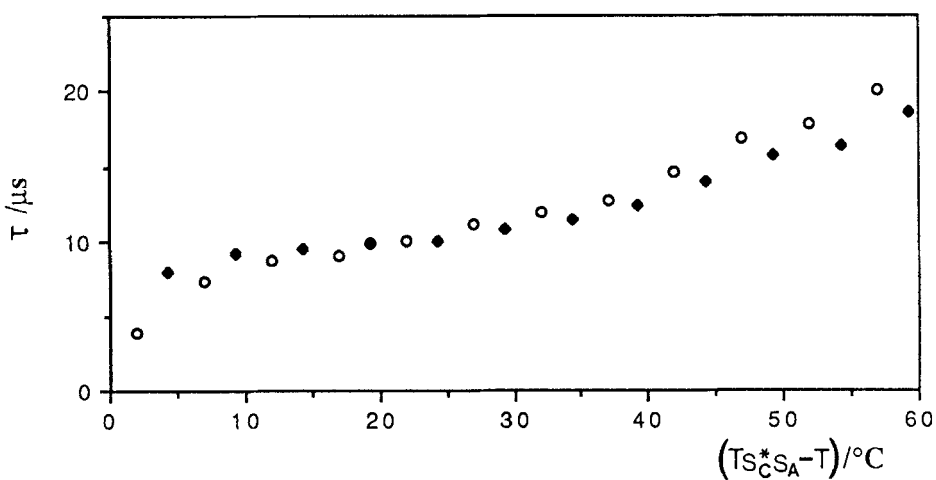


Figure 6. Response time τ versus $T_{S_C^*S_A} - T$ for two compounds of IIB ((○) $n=10$, (◆) $n=12$).

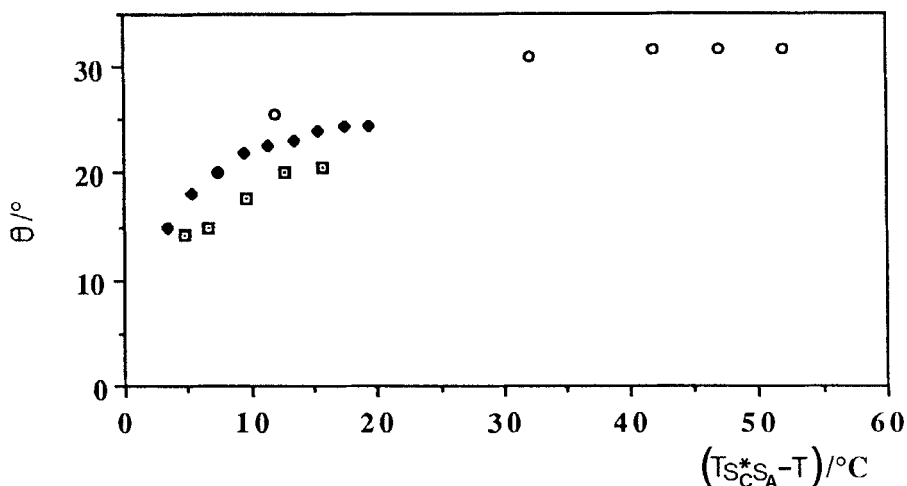
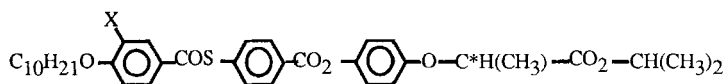


Figure 7. Tilt angle θ versus $T_{S_C^* S_A} - T$ for (\square) IIC, (\blacklozenge) IID and (\circ) IIB compounds with $n = 10$.

3. Discussion

The thiobenzoate core has the well-established property of providing tilted phases which are thermally more stable than their benzoate analogues. On the other hand, the presence of fluorine in the meta position in the core (ortho to the alkyloxy chain) decreases the transition temperatures and sometimes, for two benzene ring compounds, depresses the mesomorphic properties [17, 18]. This influence of fluorine is confirmed in series I even with the thiobenzoate core. So, we only observe the monotropic S_A phase in the IA series with a short chiral chain (chiral 2-butanol) but with the long one (chiral 2-octanol), the existence of the mesophase is only observed with very long alkyloxy chains at low temperature $< 20^\circ\text{C}$ (series IB).

The influence of fluorine on the mesomorphic properties is more useful and interesting with the three benzene ring compounds (series II). We observe a decrease of all transition temperatures, even the melting point, in comparison with the hydrogen derivatives. For example the two compounds



$$X = \text{H} \quad C \ 95.5^\circ\text{C} \ (S_C^* \ 76^\circ\text{C}) \ S_A \ 123^\circ\text{C} \ N^* \ 127.8^\circ\text{C} \ \text{I},$$

$$X = \text{F} \quad C \ 56.8^\circ\text{C} \ S_C^* \ 75.5^\circ\text{C} \ S_A \ 104.1^\circ\text{C} \ N^* \ 109.7^\circ\text{C} \ \text{I},$$

display the ferroelectric S_C at the same temperature (76°C) but the S_C^* of the latter is enantiotropic with a low melting point while the former is monotropic. Furthermore, in series II we also study the influence of the chiral chains on the mesomorphic and physical properties [19]. The difference between the IIC and IID series is the steric hindrance induced by the presence of the additional methyl group (ethyl versus isopropyl) in the latter. We observe the same polymorphism in these two series but the isopropyl group favours more the cholesteric phase rather than the other smectic phases. So, for the S_C^* temperature range, the IID series is less interesting than the IIC

series. On the other hand, the steric hindrance could block the rotation around the chiral carbon and could give rise to the spontaneous polarization enhancement which is discussed in the next paragraph.

The **IIB** series is the most interesting because all of the compounds display not only the ferroelectric smectic C phase with a wide temperature range but also high spontaneous polarization and low response time. The highest spontaneous polarization 175 nC cm^{-2} in series **II** is observed with the compound **IID** ($n = 10$) because the steric hindrance of the isopropyl group inhibits the rotation around the link of the chiral carbon. But the steric hindrance and additional ester functionality in the lactic ester series simultaneously may influence the viscosity. For this reason, even with high spontaneous polarization, the response time of compounds **IID** is still higher than **IIC**. We have reported in the last paragraph that the S_C^* temperature range of **IIC** compounds is not very wide but they have low response times. Furthermore their tilt angles versus $T_{S_C^*SA} - T$ show a shallow variation and they increase above 22.5° , which is the ideal value for application devices. This tilt angle of **IIB** compounds increases quickly and reaches up to 30° .

It is evident that among the three series **IIC**, **IID** and **IIB** that there are no single compounds which have at the same time, a wide temperature S_C^* range, low response time and tilt angle close to 22.5° . For this reason, we have to make several mixtures with appropriate compounds.

4. Experimental

The infrared spectra were recorded using a Perkin–Elmer 783 spectrophotometer and the NMR spectra with a Bruker 270 MHz.

Compounds 2 and 3 were prepared following a method previously described [20]. All compounds give satisfactory elemental analyses.

4.1. 3-Fluoro-4-hydroxybenzoic acid: 4

A solution of 4-cyano-2-fluoroanisole (30 g, 0.198 mol), 400 ml of 48 per cent hydrobromic acid and 200 ml of acetic acid was heated under reflux for 16 h. After cooling, 200 ml of water was added to the solution which was put in a refrigerator for 3 h. The solid was filtered off, washed with cold water and air dried. Yield: 25 g (80 per cent); mp = 159°C ([17] $159\text{--}160.5^\circ\text{C}$).

IR (nujol, cm^{-1}): 3500, 2920, 2700, 1780, 1600, 1530, 1400.

4.2. 3-Fluoro-4-nonyloxybenzoic acid: 5 ($n = 9$)

To a stirred solution of potassium hydroxide (5.6 g) in 10 ml of water, was added 100 ml of ethanol, 3-fluoro-4-hydroxybenzoic acid (8 g, 0.051 mol) and 1-bromononane (15 g, 0.072 mol) was added dropwise in 50 ml of ethanol. The solution was heated under reflux for 3.5 h. Then potassium hydroxide (5 g) in 5 ml of water was added to the cooled solution and the mixture was heated under reflux for a further 2 h. The solvent was evaporated and the mixture was acidified with 10 ml of concentrated hydrochloric acid, 50 g crushed ice and 50 ml of water. The solid was filtered off and recrystallized from absolute ethanol. Yield: 9.5 g (62 per cent).

Transition temperatures: C 111.9°C N 116°C I ([21] C 112°C (S 109°C) N 116.5°C I).

IR (nujol, cm^{-1}): 2900, 2750, 1760, 1610, 1580, 1510, 1460, 1410, 1320, 1300, 1210, 1140, 1090, 770.

NMR (CDCl_3 , δ) 0.9 (t, 3 H, CH_3), 1.1–1.7 (m, 14 H, 7 CH_2), 4.1 (t, 2 H, CH_2O), 7–8.2 (m, 3 H, Ar).

4.3. 4-(3'-Fluoro-4'-nonyloxybenzoylthioxy) benzoic acid: **6** ($n=9$)

To a solution of 4-mercaptobenzoic acid (3.39 g, 0.022 mol) in 100 ml of dichloromethane, was added triethylamine (2.22 g, 0.022 mol) over a period of 1–2 min. The solution was stirred in an ice-water bath and 3-fluoro-4-nonyloxybenzoyl chloride (obtained from **5** ($n=9$) with an excess of oxalyl chloride) (6.1 g, 0.02 mol) in 10 ml of dichloromethane was added over a period of 1 min. The mixture was stirred for 30 min in the ice bath and then for 1 h at room temperature. To the mixture was added 300 ml of ethyl acetate and 300 ml of 10 per cent aqueous hydrochloric acid. The mixture was heated and transferred to a separating funnel. The phases were separated and the organic phase was dried with anhydrous sodium sulphate, concentrated and the solution put in a refrigerator. The solid was filtered off, washed with cold ethyl acetate and air dried. Yield: 4 g (47 per cent).

Transition temperatures: C 149°C S_C 207°C N > 220°C I.

NMR (CDCl₃, δ) 0.9 (t, 3 H, CH₃ of C₉H₁₉), 1.1–2.1 (m, 14 H, 7 CH₂), 4.1 (t, 2 H, CH₂O), 6.9–8.4 (m, 7 H, Ar).

4.4. (R)-1-Methylpropyl 4-(3'-fluoro-4'-nonyloxybenzoylthioxy)benzoate: **IA** ($n=9$)

To a solution of **6** ($n=9$) (1 g, 2.39 mmol), (S)-2-butanol (0.194 g, 2.62 mmol), triphenylphosphine (0.885 g, 3.37 mmol) and 10 ml of dichloromethane was added dropwise diethylazodicarboxylate (DEAD) (0.588 g, 3.37 mmol) over 1 min. The resulting solution was stirred overnight. The mixture was evaporated, chromatographed on silica gel with toluene as eluent, and recrystallized from absolute ethanol. Yield: 500 mg (45 per cent).

Transition temperatures: C 45.5°C (S_A 25.8°C) I.

IR (nujol, cm⁻¹): 2900, 2860, 1710, 1670, 1280, 1160, 1110, 970.

NMR (CDCl₃, δ): 0.85 (t, 3 H, CH₃ of C₉H₁₉), 0.95 (t, 3 H, CH₃ of C₂H₅), 1.2–2 (m, 19 H, 8 CH₂ and CH₃ of CH(CH₃)), 4.1 (t, 2 H, CH₂O), 5.1 (m, 1 H, CH), 7–8.1 (m, 7 H, Ar).

4.5. 4-[(1'-Ethoxycarbonyl)ethoxy] phenol: **7C**

To a cooled solution of 4-benzyloxyphenol (15.2 g, 0.076 mol), (L)-ethyl lactate (12 g, 0.09 mol), triphenylphosphine (30 g, 0.11 mol) and 300 ml of dichloromethane was added dropwise DEAD (20 g, 0.11 mol) over 1 min. The mixture was stirred for 4 h. The solution was filtered off, evaporated and chromatographed on silica gel [14].

Hydrogenation of the benzyl ether intermediate was carried out in a solution of 95 per cent ethanol with Pd/C as catalyst at atmospheric pressure. The mixture was filtered through silica gel and evaporated. Yield: 10 g (58 per cent).

NMR (CDCl₃, δ): 1.2 (t, 3 H, CH₃ of C₂H₅), 1.65 (d, 3 H, CH₃ of CHCH₃), 4.25 (q, 2 H, CH₂CO₂), 5.3 (q, 1 H, CH), 6.9–7.5 (m, 4 H, Ar).

4.6. (R)-4-[(1'-Ethoxycarbonyl)ethoxy]phenyl-4'-(3'-fluoro-4'-nonyloxybenzoylthioxy)benzoate: **IIc** ($n=9$)

To a solution of the phenol **7C** (300 mg, 1.4 mmol) in 5 ml of dichloromethane was added DCC (280 mg, 1.4 mmol), **6** ($n=9$) (600 mg, 1.4 mmol) and DMAP (20 mg). The resulting solution was stirred at room temperature overnight. The solution was filtered, evaporated and chromatographed on silica gel with toluene as eluent. Fractions containing the pure product were combined, concentrated, and recrystallized from absolute ethanol. Yield: 500 mg (60 per cent).

Transition temperatures: C 70.4°C S_C* 75.7°C S_A 104.7°C N* 109.7°C I.

NMR (CDCl_3 , δ): 0.8 (t, 3 H, CH_3 of C_9H_{19}), 1–1.9 (m, 20 H, 7 CH_2 ; CH_3 of CHCH_3 and CH_3 of C_2H_5), 4.1 (t, 2 H, CH_2O), 4.25 (m, 1 H, CH_2CO_2), 5.3 (q, 1 H, $\text{CH}(\text{CH}_3)$), 6.9–8.2 (m, 11 H, Ar).

5. Conclusion

The fluorine on the two benzene ring cores destabilizes the liquid crystal phases and reduces the clearing temperature of three benzene ring core derivatives. Furthermore in the latter the $S_C^* - S_A$ transition temperature is not very different from the hydrogen analogues. The three series with three benzene ring cores display ferroelectric smectic C phases, particularly the **IIB** series with a wide temperature range (60°C). In spite of the larger core the response time of the **IIB** compounds is low, less than 10 μs at $T_{S_C^* - S_A} - T = 20^\circ\text{C}$. A study of the properties of mixtures from these materials is in progress.

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