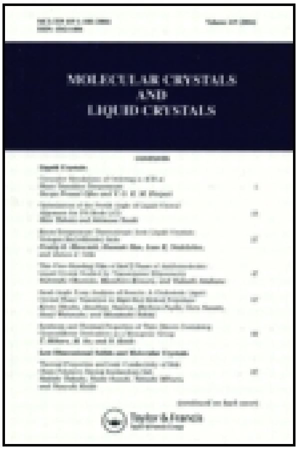

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An Unusual Sequence of Smectic Phases Formed by Members of the Homologous Series of 3-Fluoro-4-octyloxyphenyl 4-(5-Alkyl-2-thienyl)benzoates

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An Unusual Sequence of Smectic Phases Formed by Members of the Homologous Series of 3-Fluoro-4-octyloxyphenyl 4-(5-Alkyl-2-thienyl)benzoates

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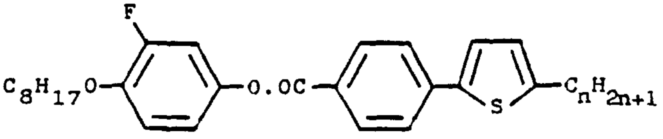
Nine 4-(5-*n*-alkyl-2-thienyl)benzoic acids have been converted into esters by reaction with 3-fluoro-4-*n*-octyloxyphenol. The liquid crystal properties of these esters have been investigated by thermal optical microscopy, differential scanning calorimetry, and X-ray diffraction. For the octyl and nonyl homologues the properties of the third smectic phase in the sequence S_A-S_C-S_3-S_E observed on cooling the isotropic liquid are unusual. The S_3 phase is orthogonal with unstructured layers corresponding with a second S_A phase.

The 4-(5-*n*-alkyl-2-thienyl)benzoic acids also form liquid crystals and, in addition to the S_C phase shown by other homologues, the octyl-decyl compounds give rise to a second, unidentified smectic phase.

Keywords: New smectic phase sequence, smectogenic thiophene esters

INTRODUCTION

Nine members (n = 4–10, 12, 14) of the homologous series of 3-fluoro-4-octyloxyphenyl 4-(5-alkyl-2-thienyl)benzoates (I) have been prepared and their liquid crystal properties investigated. The members, n = 8 and 9, give rise to an unusual sequence of four smectic mesophases on cooling the isotropic liquid. Details[1] of the investigation of these phases by optical microscopy, X-ray diffraction, and differential scanning calorimetry are given in the following discussion.



(I)

TABLE I

Transition temperatures for 3-fluoro-4-octyloxyphenyl 4-(5-alkyl-2-thienyl)benzoates

	Transition temperature (°C)[a]						
n-Alkyl group	$C\text{-}S_A(S_C,S_3)$	$N(S_A)\text{-}I$	$S_A\text{-}N$	$S_A\text{-}S_C$	$S_C\text{-}S_3(S_I)$	$S_A(S_3)\text{-}S_E$	$S_A(S_C,S_E,S_I)\text{-}C$[b]
C_4H_9	$\underline{C\text{-}S_A}$ 76	$\underline{N\text{-}I}$ 132.2	122.5				$\underline{S_A\text{-}C}$ 56.0
C_5H_{11}	77.5	137.5	135.5				65.0
C_6H_{13}	80.0	$\underline{S_A\text{-}I}$ 136.0					64.0
C_7H_{15}	76.5	139.8				$\underline{S_A\text{-}S_E}$ (54.8)[c]	$\underline{S_E\text{-}C}$ 53.0
C_8H_{17}	$\underline{C\text{-}S_3}$ 81.2	138.4		$\underline{S_A\text{-}S_C}$ 99.7	$\underline{S_C\text{-}S_3}$ 82.8	$\underline{S_3\text{-}S_E}$ (51.7)	50.0
C_9H_{19}	$\underline{C\text{-}S_C}$ 85.0	138.3		117.0	(65.4)	(51.1)	51.1
$C_{10}H_{21}$	80.5	137.0		125.7			$\underline{S_C\text{-}C}$ 50.0
$C_{12}H_{25}$	79.0	134.8		129.5	$\underline{S_C\text{-}S_I}$ (62.5)		$\underline{S_I\text{-}C}$ 59.8
$C_{14}H_{29}$	79.5	131.5		127.6			$\underline{S_C\text{-}C}$ 71.5

[a] Symbols have their usual meaning: C, crystal; I, isotropic liquid; N, nematic; S_A, smectic A, etc. Thus $C\text{-}S_A$ represents the temperature (m.p,) at which a transition from the crystalline solid to the smectic A phase occurs.

[b] Temperature of crystallisation (at a cooling rate of approximately 4°/min).

[c] Values in parenthesis are for monotropic transitions.

RESULTS AND DISCUSSION

The liquid crystal transition temperatures of nine members of the homologous series of esters (I) are listed in Table I, and shown plotted against *n*, the number of carbon atoms in the alkyl chain, in Figure 1.

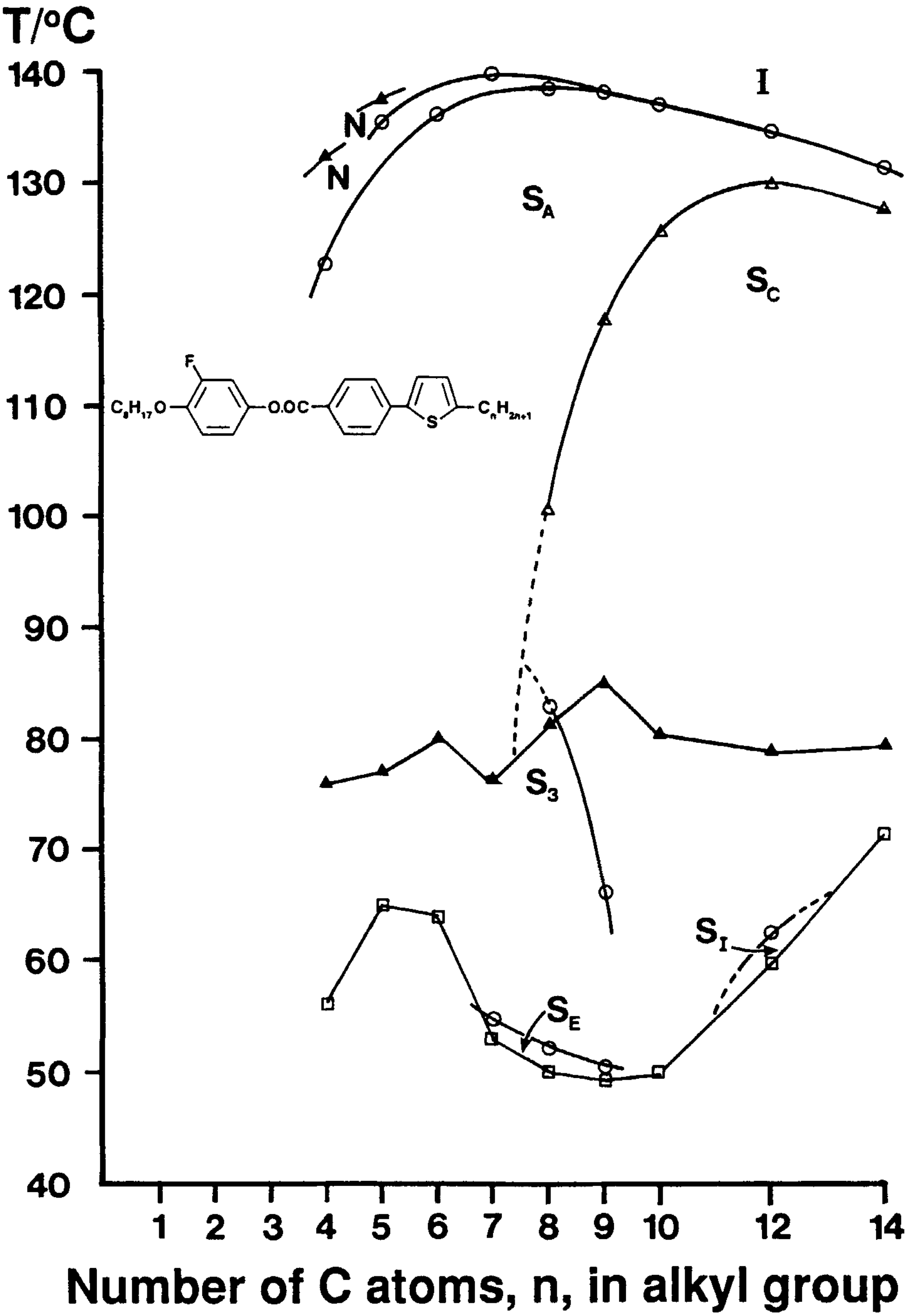


FIGURE 1 3-Fluoro-4-*n*-octyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates: transition temperatures v. *n*, the number of carbon atoms in the alkyl chain.

On cooling from the isotropic liquid, only the early homologues, $n = 4$ and 5, give rise initially to a nematic phase. This is followed by an S_A phase, which is also formed directly from the isotropic liquid for the remaining members, $n = 8$, 9, 10, 12, and 14. It is reasonable to infer that the points for the N-I transition temperatures fit odd-n and even-n curves which rise with increasing n and become coincident with the uppermost of the two similar curves that may be drawn through the points for the S_A-N or S_A-I transition temperatures. The S_A-I transition temperatures reach maxima at $n = 7$ and 8, and then decrease for the remaining members. The homologues $n = 8$, 9, 10, 12, and 14 also show an S_C phase and the points for the S_C-S_A transition temperatures lie on a curve which rises steeply to reach a maximum at $n = 12$ and then falls for $n = 14$.

The homologues $n = 7$, 8, 9, 10, 12, and 14 show different behavior on cooling the S_A or S_C phases until crystallization occurs. The S_A phase of the homologue $n = 7$ gives an S_E phase, whereas the S_C phases of the homologues $n = 8$ and $n = 9$ give rise to an additional, unidentified (S_3) phase before the S_E phase is formed. The homologues $n = 10$ and $n = 14$ pass directly to the crystal from the S_C phase, whereas for the compound $n = 12$ a transition to an S_I phase is observed before crystallization occurs. Assignment of this phase as S_I rather than S_F is based on the existence of a schlieren texture which is difficult to bring into optical focus.[2a]

Investigation of the S_3 Phase of the Homologues $n = 8$ and 9 of (I)

(a) Optical microscopy. Phase type assignments were made by observation during thermal optical microscopy of the textural changes occurring during the sequence of transitions shown below.

On cooling the isotropic liquid, at transition (1) bâtonnets form and give rise to well-defined focal conic fans interspersed with homeotropic areas, typical of an S_A phase (Plate 1, $n = 9$). After transition (2) the fans become broken and a schlieren texture, expected for an S_C phase, develops in the formerly homeotropic regions (Plate 2, $n = 9$). The S_3 phase is formed after transition (3). In the S_3 phase, the fans almost completely recover their previous well-defined nature and are accompanied by a return to homeotropy as the schlieren areas disappear. Some lateral imperfections are retained on some of the fans, but these become less prominent on rapid cooling to just above transition temperature (4) (Plate 3, $n = 9$). After transition (4) the fans become crossed by permanent concentric arcs accompanied

$$n=8 \quad I \xrightarrow[(1)]{138.4^{\circ}C} S_A \xrightarrow[(2)]{99.7^{\circ}C} S_C \xrightarrow[(3)]{82.8^{\circ}C} S_3 \xrightarrow[(4)]{51.7^{\circ}C} S_E \xrightarrow[(5)]{50^{\circ}C} C$$

$$n=9 \quad I \xrightarrow[(1)]{138.3^{\circ}C} S_A \xrightarrow[(2)]{117.0^{\circ}C} S_C \xrightarrow[(3)]{65.4^{\circ}C} S_3 \xrightarrow[(4)]{51.1^{\circ}C} S_E \xrightarrow[(5)]{51.1^{\circ}C} C$$

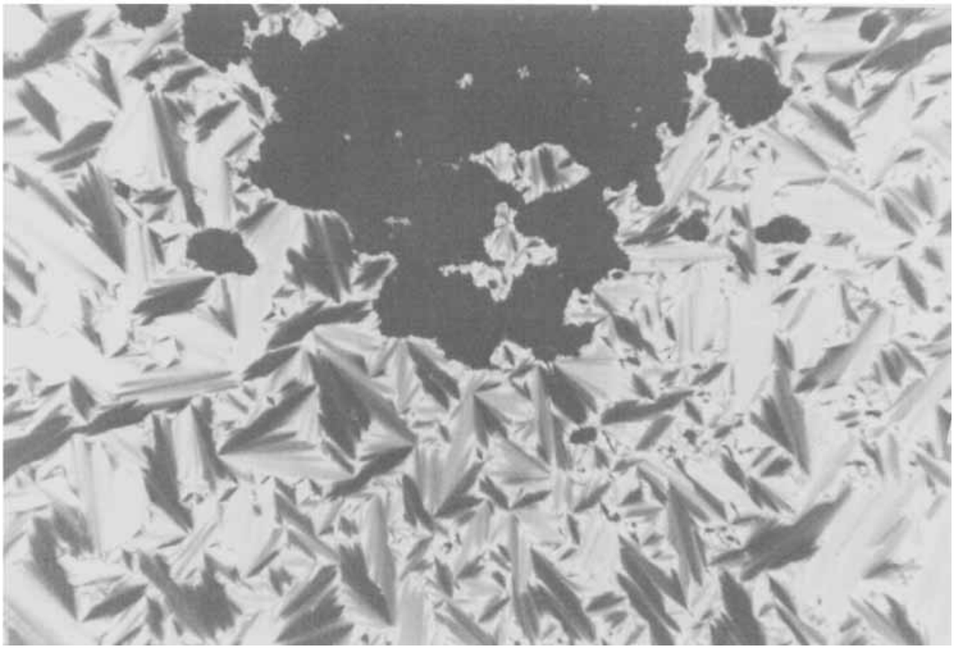


PLATE 1 S_A phase of (I), $n = 9$. See Color Plate XXII.

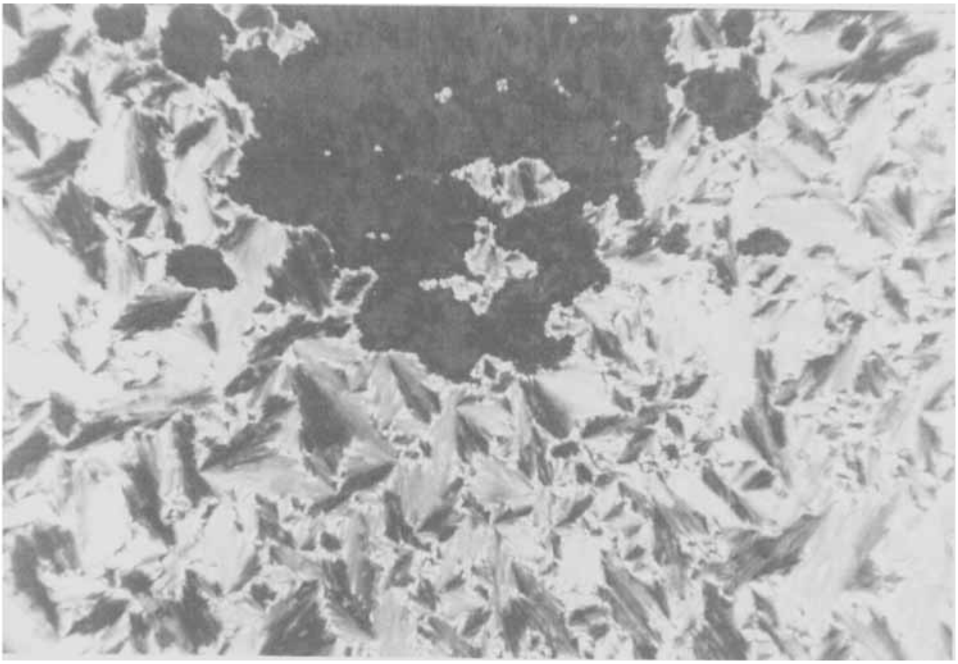


PLATE 2 S_C phase of (I), $n = 9$. See Color Plate XXIII.

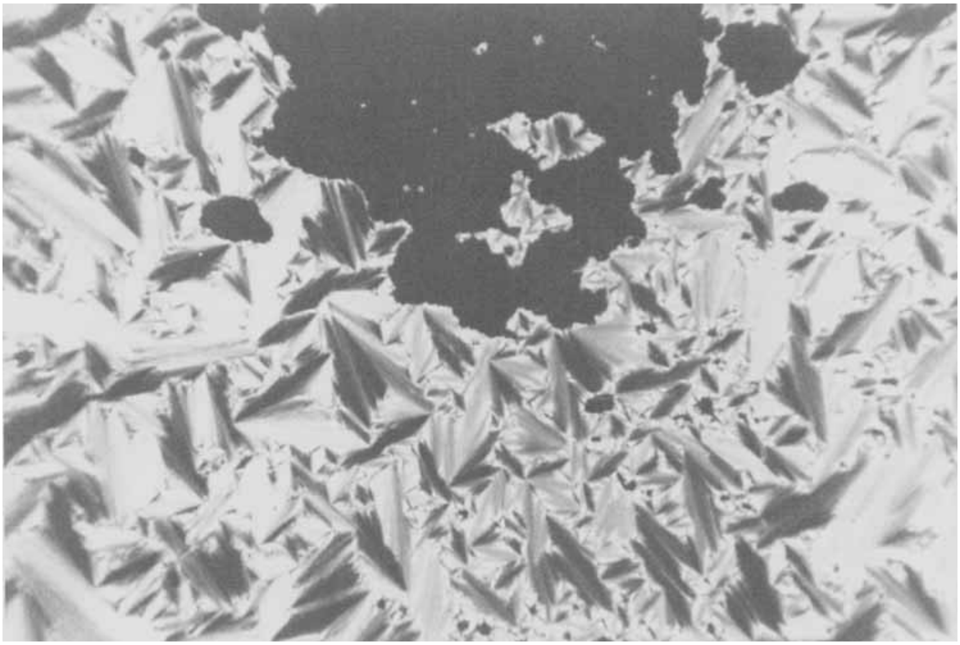


PLATE 3 S_3 phase of (I), $n = 9$ just before S_3-S_E transition. See Color Plate XXIV.

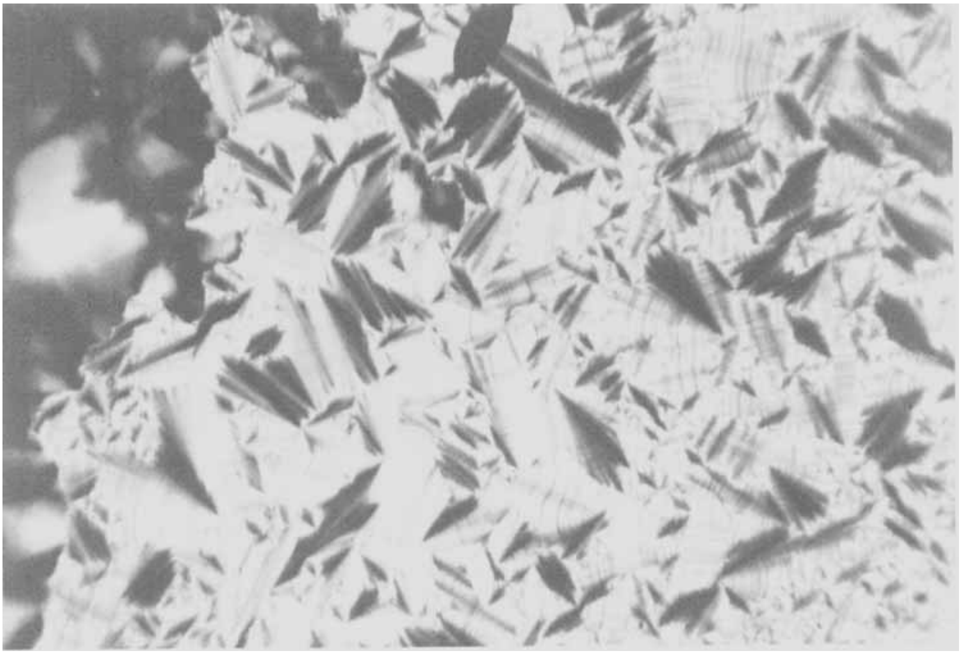


PLATE 4 S_E phase of (I), $n = 8$. See Color Plate XXV.

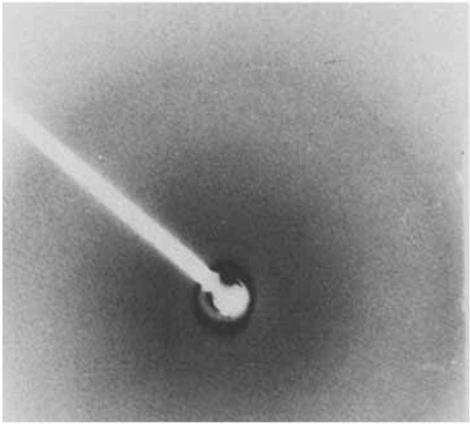


PLATE 5 X-Ray powder photograph of S_A phase of (I), $n = 8$.

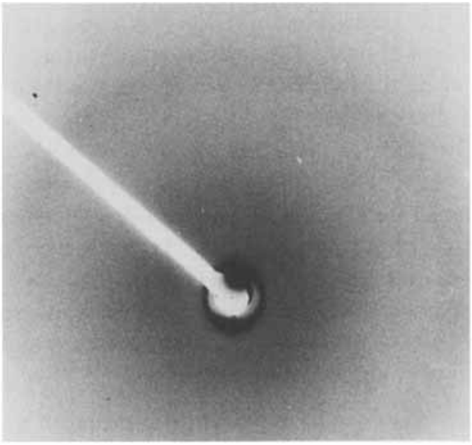


PLATE 6 X-Ray powder photograph of S_C phase of (I), $n = 8$.

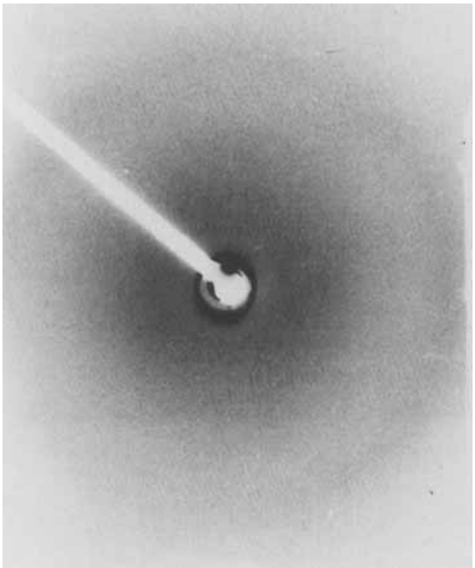


PLATE 7 X-Ray powder photograph of S_3 phase of (I), $n = 8$.

by the appearance of overlapping translucent platelets in the formerly homeotropic areas, behavior characteristic of an S_E phase (Plate 4, $n = 8$). Crystallization (5) follows very soon after this transition ($n = 8$) or is concurrent with it ($n = 9$).

The esters $n = 8$ and $n = 9$ show rather different characteristics in the S_C phase. For the compound $n = 8$, the schlieren is only very weakly developed and the focal conic fans retain a more or less fixed appearance throughout the temperature range of the S_C phase. In contrast, as the compound $n = 9$ is cooled, the schlieren shows continuous changes, reaching a stage of maximum development towards the middle of the temperature range of the S_C phase before gradually losing its identity as the transition to the S_3 phase approaches. These changes are accompanied by continuous reorganization activity within the fine structure of the focal conic fans.

These observations suggest that the tilt angle of the molecules in the S_C layers of the compound $n = 9$ may be subject to greater variation and may attain a larger value than that for the homologue $n = 8$.

(b) X-Ray diffraction. Essentially because the schlieren areas of the S_C phase revert back to homeotropy at transition (3) we initially assigned the S_3 phase as a smectic B phase, although the focal conic fans of the S_3 phase do not possess the characteristic smooth appearance of S_B fans.[2b]

However, X-ray diffraction studies indicate the absence of an ordered S_B phase. The S_A, S_C, and S_3 phases all give virtually identical X-ray powder photographs with a diffuse outer ring (Plates 5, 6, and 7, respectively, for the ester $n = 8$). Throughout the temperature range of the S_3 phase the X-ray photographs show

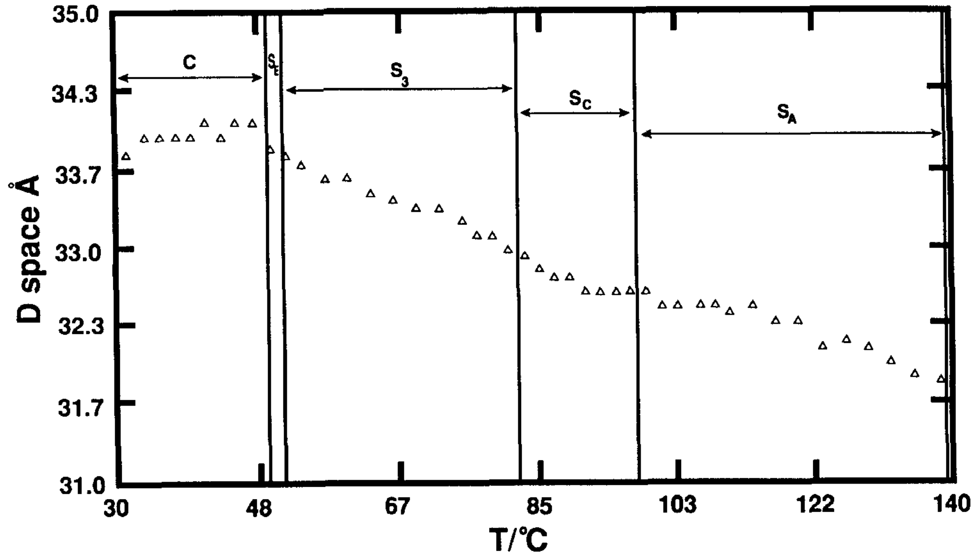


FIGURE 2 Layer spacing v. temperature for (I), $n = 8$.

no indication of the fairly sharp outer ring which is a consequence of the ordered arrangement of molecules in S_B layers.[3] An X-ray photograph of the S_E phase could not be obtained due to crystallization of the sample during exposure to X-rays.

X-Ray diffractometer studies have enabled measurements of the smectic layer spacing as a function of temperature to be made. The results for the homologue $n = 8$ are shown in Figure 2.†

The molecular length of the homologue $n = 8$ in its extended conformation, obtained using CHEMX[4] and from model building, is of the order of 34.7 Å. Our measurements of layer spacings, including those for the orthogonal S_E phase, are all less than this and are in fact lower in the S_A phase than in the tilted S_C phase, so some interdigitation of the alkyl chains seems likely throughout the smectic range. The increase in layer spacing with decreasing temperature could of course represent a decrease in tilt angle and/or interdigitation of the chains, making any measurement of tilt angle problematic. However, if it is assumed that the interdigitation is similar in the S_E and S_C phases then this leads to a tilt angle of about 23° in the S_C phase.

It is of interest to note that throughout the smectic range, the spacing increases in a fairly uniform manner as the sample of the homologue $n = 8$ is cooled. This differs from the behavior of other related compounds we have studied which normally show a gradual decrease in layer spacing following the transition from an S_A to an S_C phase, followed by an increase as the transition from the S_C to a lower temperature smectic phase is approached. In particular, for compounds having an S_C followed by an S_B phase, a sudden jump in layer spacing occurs as the tilt angle

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† Note added in proof. The homologue $n = 9$ gives similar results.

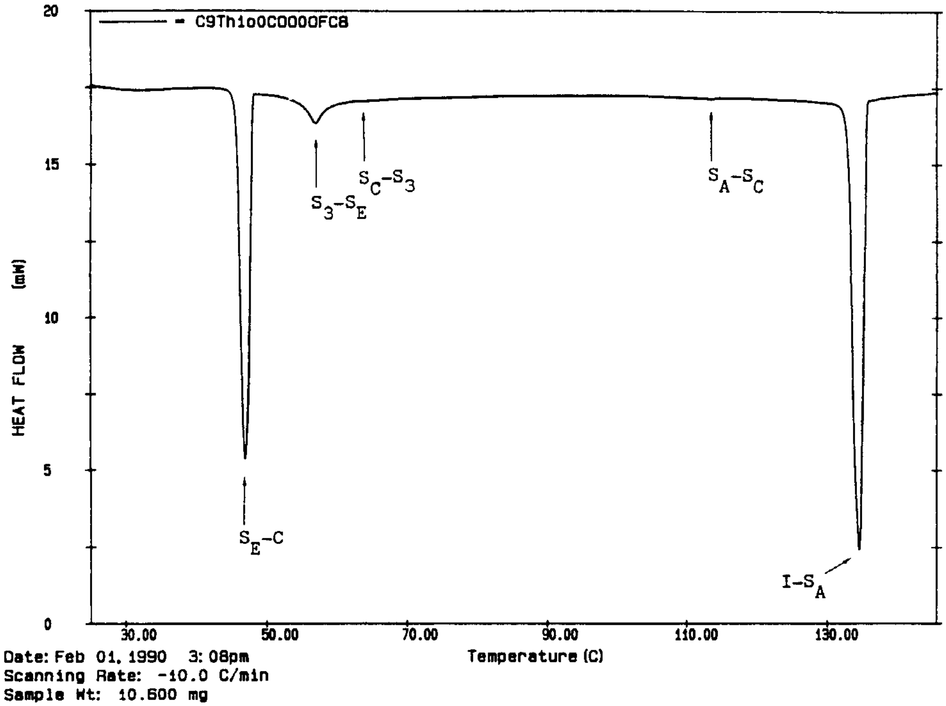


FIGURE 3 DSC thermogram (cooling cycle) for (I), $n = 9$.

of the molecules returns to zero. Clearly no such change is observed at the transition from the S_C to the S_3 phase of the homologue $n = 8$, further evidence of the absence of an S_B phase.

(c) Differential scanning calorimetry. The DSC thermograms for the cooling cycle from the isotropic liquid for the esters $n = 8$ and $n = 9$ are shown in Figures 3, 4, and 5.

For the compound $n = 9$, the positions of the I-S_A, S_A-S_C, S_C-S_3, S_3-S_E, and S_E-C transitions are indicated on the full thermogram (Figure 3) with the corresponding expanded scale thermogram showing the S_A-S_C, S_C-S_3, and S_3-S_E transitions only (Figure 4). Very small enthalpies are associated with both the S_A-S_C and S_C-S_3 transitions. Thus, it is clear that the S_C-S_3 transition is not a first order transition as would be expected if a transition to an ordered S_B phase was involved.

This conclusion is reaffirmed by examination of the DSC thermogram for the compound $n = 8$ (Figure 5). In this case, the S_A-S_C and S_C-S_3 transitions are associated with such low enthalpies that they cannot be detected at all, even on rescaling the heat flow axis. The low enthalpies associated with transitions to and from the S_C phase support the supposition that the S_C phase of the ester $n = 8$ has a very small tilt angle.

The nine 4-(5-*n*-alkyl-2-thienyl)benzoic acids, from which the esters (I) are derived, also form liquid crystals. The liquid crystal transition temperatures for these

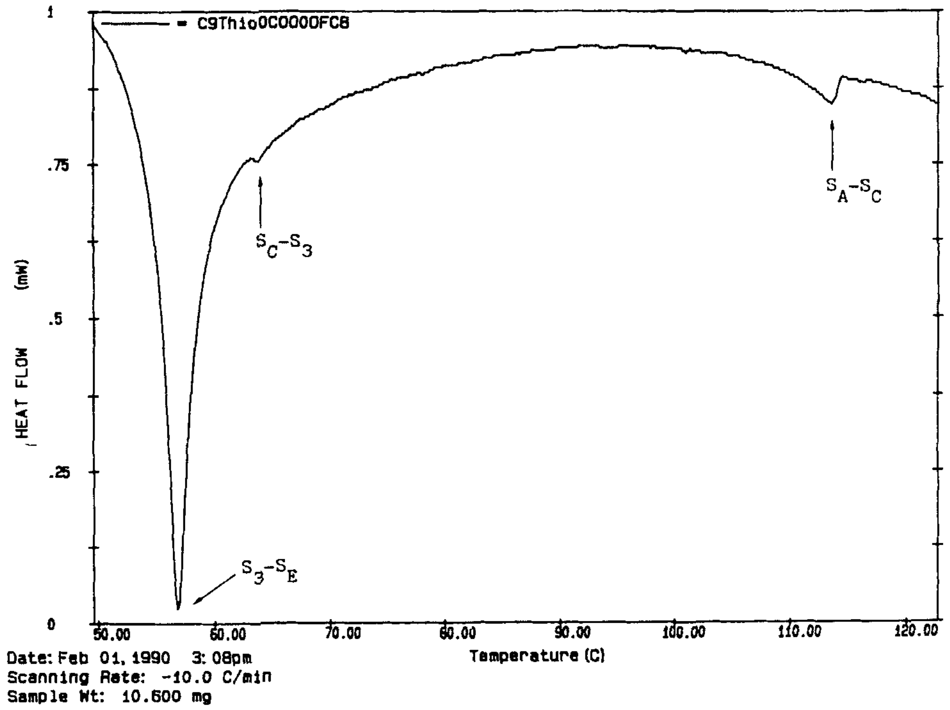


FIGURE 4 DSC thermogram (expanded scale cooling cycle) for (I), $n = 9$.

compounds are given in the experimental section, and are shown plotted against n, the number of carbon atoms in the alkyl chain, in Figure 6. Although the plot is generally as expected, nevertheless it may be significant that the octyl-decyl compounds also give rise to a second smectic (S_X) phase in addition to the S_C phase shown by other homologues. Work to identify the S_X phase is being undertaken and the synthesis of related compounds is in progress.

CONCLUSION

It is clear from the X-ray diffraction and DSC studies that the S_3 phase has unstructured layers. The optical texture changes from homeotropic to schlieren to homeotropic again indicate a change in the arrangement of molecules in the layers from orthogonal to tilted to orthogonal in the phase sequence S_A-S_C-S_3. The conclusion that the S_3 phase is a second S_A phase is unescapable in view of the closely similar structural characteristics of the two phases.

Further investigations on this and on related series are in progress.

EXPERIMENTAL

The esters were prepared by standard methods illustrated in the synthetic scheme. The identities of certain intermediates and final products were established by con-

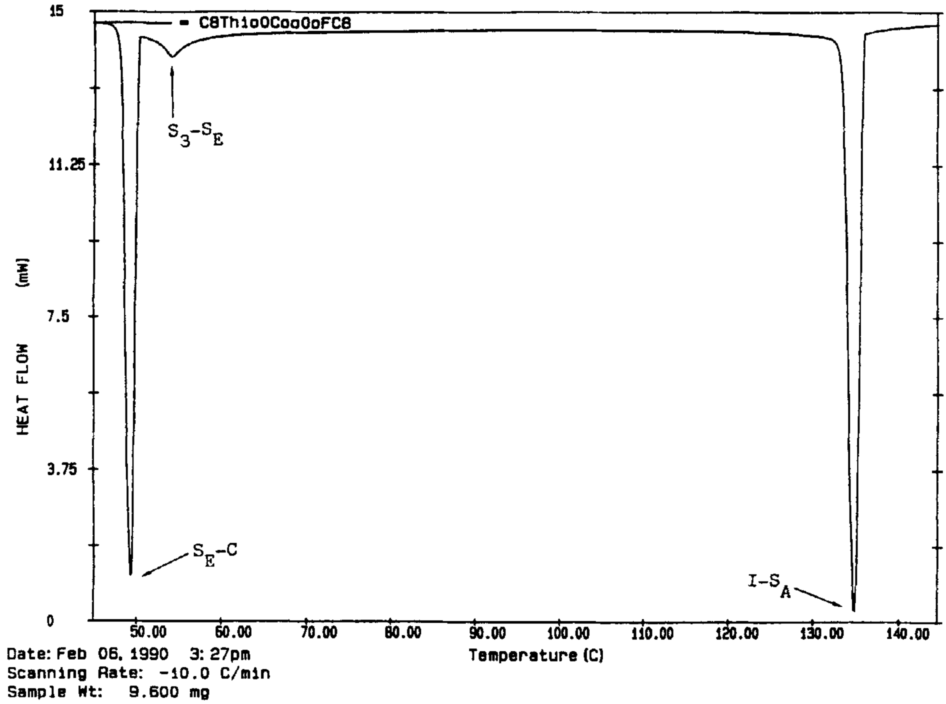


FIGURE 5 DSC thermogram (cooling cycle) for (I), *n* = 8.

sideration of their i.r., mass, ^1H, or ^{13}C n.m.r. spectra. By HPLC the purity of the esters was established as 99.5% or better. Thermal optical microscopy was carried out with a Vickers M75 polarizing microscope in conjunction with a Mettler FP 52 hot stage and FP 5 control unit. X-ray studies were carried out on powder samples contained in 0.3 mm Lindemann glass tubes. Filtered CuK_α radiation was used. Thermal analysis was carried out with a Perkin Elmer DSC 7 differential scanning calorimeter.

Preparation of Materials

The 3-fluoro-4-*n*-octyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates (I) were prepared as summarized in the synthetic scheme.

Step 1 was accomplished by diazotization of ethyl 4-aminobenzoate (24.8 g, 0.15 mol) in a mixture of water (75 ml) and concentrated hydrochloric acid (20 ml) in the usual manner. The quantity of sodium nitrite (5.2 g, 0.075 mol) in water (12 ml) added was only one half of that necessary to effect complete diazotization, and sodium acetate (21.0 g, 0.26 mol) in water (40 ml) was then slowly added to the cold solution. After stirring for 45 min the precipitated crude product was filtered off and purified by recrystallization from toluene-light petroleum (b.p. 60–80°C) affording the 4,4′-diethoxycarbonyldiazoaminobenzene, 15.6 g (61%) as yellow crystals, m.p. 157–158°C (Lit.[5] m.p. 152–154°C).

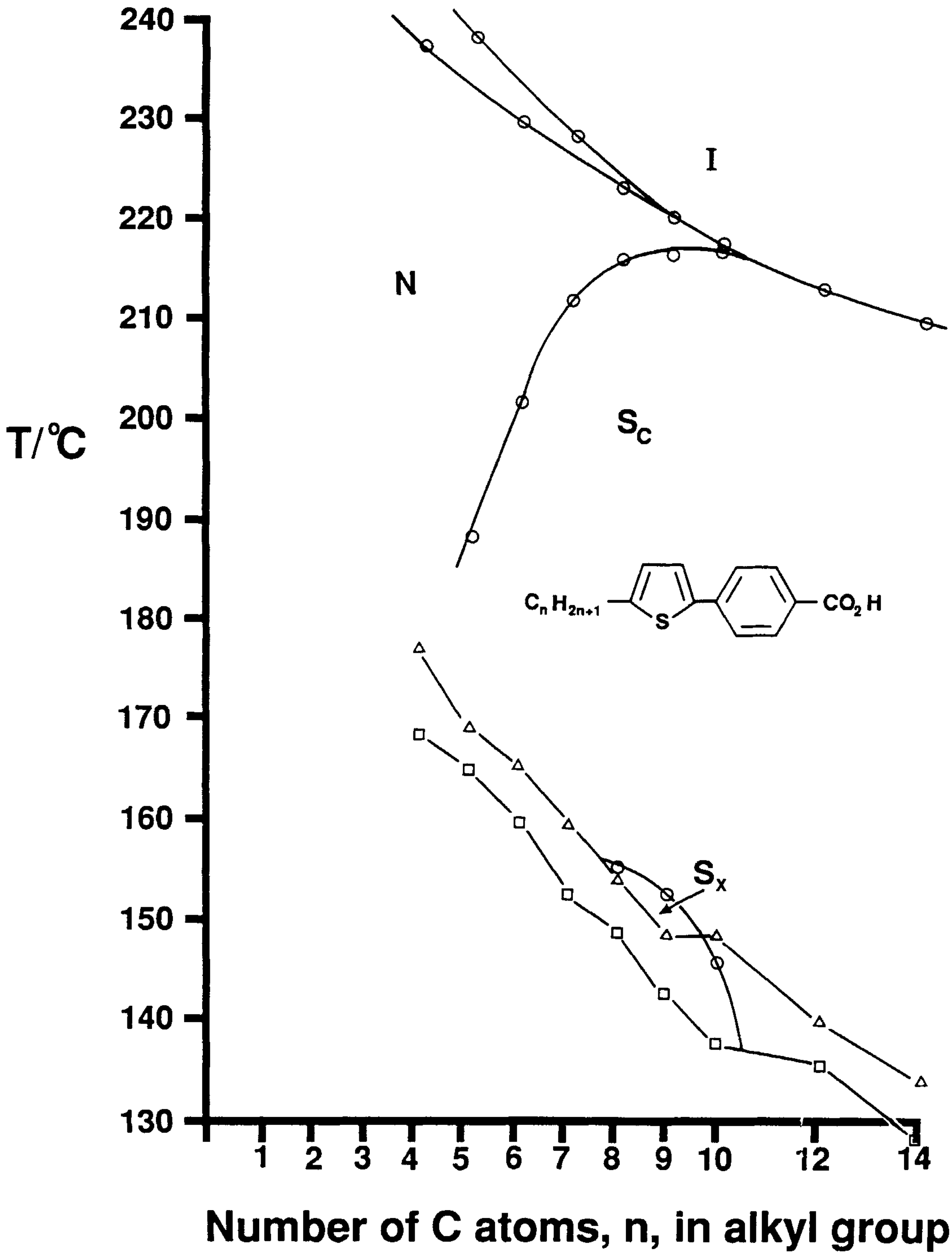


FIGURE 6 4-(5-*n*-Alkyl-2-thienyl)benzoic acids: transition temperatures v. *n*, the number of carbon atoms in the alkyl chain.

In step 2, a solution of 4,4′-diethoxycarbonyldiazoaminobenzene (8 g, 0.023 mol) and isopentyl nitrite (4.7 ml) in thiophene (120 ml) was stirred at room temperature for 72 h, during which time the color changed from yellow to dark red. The reaction mixture was then poured into water, stirred vigorously and the organic layer separated. After removal of the thiophene the dark red oil was purified by column chromatography on neutral alumina eluted with chloroform, and then subjected to short path vacuum distillation. The resulting pale yellow oil, b.p. 145°C/0.05 mm, solidified on cooling and was recrystallized from light petroleum (b.p. 60–80°C) to give the ethyl 4-(2-thienyl)benzoate, 5.08 g (95%), as colorless crystals, m.p. 64–65°C (Lit.[6] m.p. 62–63°C); ν_{max} (KBr) 3094, 2998, 2978, 2935, 1699 (C=O), 1604, 1463, 1279, 862, 774, 727 cm^{-1}; δ_H ($CDCl_3$) 1.38 (3H, t, CH_3), 4.35 (2H, q, CH_2), 6.95–8.05 (7H, m, ArH).

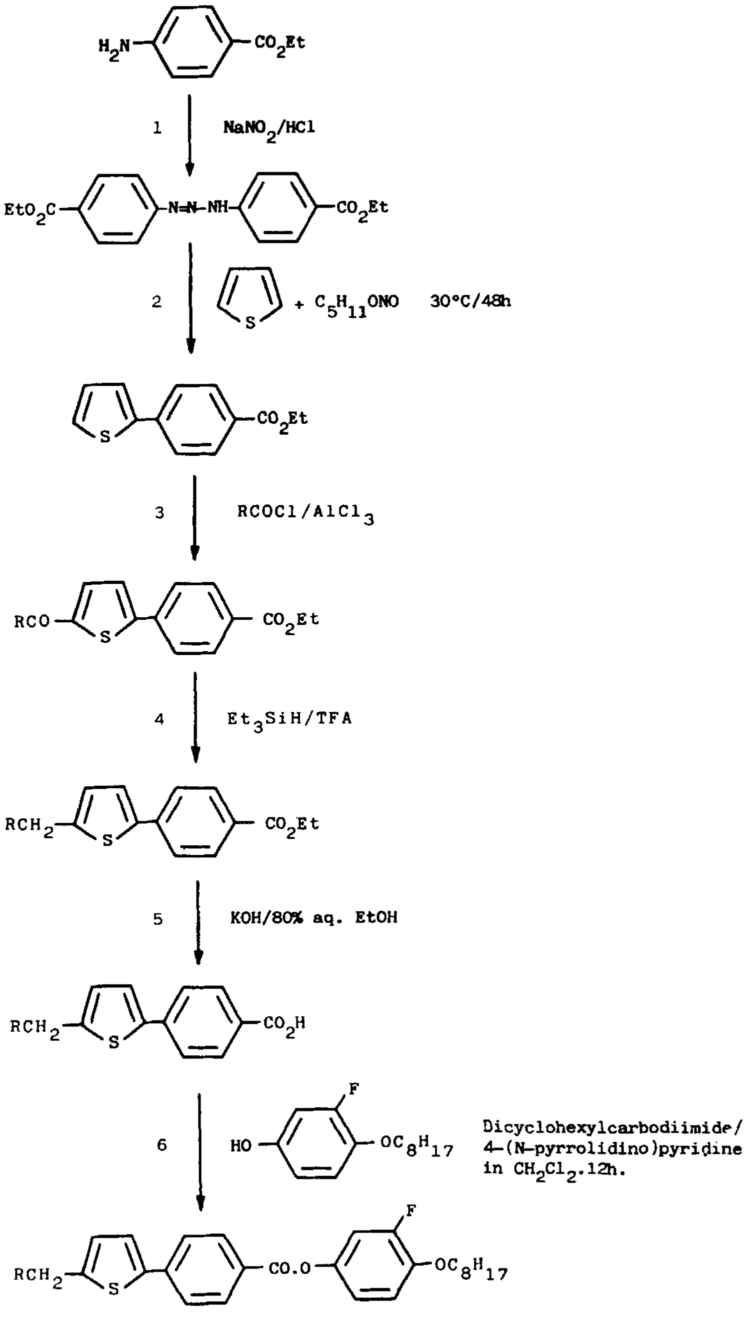
Friedel-Crafts acylation (step 3) of ethyl 4-(2-thienyl)benzoate was carried out by the addition of tin(IV) chloride (3.65 g, 0.014 mol) to a stirred solution of the ester (0.028 mol) and the appropriate acid chloride (0.028 mol) in dichloromethane (40 ml) at 5°C. The reaction mixture was then stirred at room temperature for 6 h. After work-up the crude ketones were recrystallized from chloroform-light petroleum (b.p. 60–80°C) to give the *ethyl 4-(5-n-alkanoyl-2-thienyl)benzoates* as colorless crystalline solids (52–73%), m.p.s. (°C): C_3H_7CO, 151.5–152; C_4H_9CO, 125.5–126; $C_5H_{11}CO$, 124–125; $C_6H_{13}CO$, 109.5–110.5; $C_7H_{15}CO$, 95.5–96°; $C_8H_{17}CO$, 124.5–125.5; $C_9H_{19}CO$, 127–127.5; $C_{11}H_{23}CO$, 99.5–100; $C_{13}H_{27}CO$, 102–103.

The following data, which are typical of the series, refer to the *n*-octanoyl homologue; ν_{max} (KBr) 2952, 2922, 2849, 1715 (C=O), 1660 (C=O) 1604, 1468, 1449, 1187, 799, 766 cm^{-1}; δ_H ($CDCl_3$) 0.73–1.05 (3H, t, CH_3), 1.13–2.12 (13H, m, 5 CH_2, CH_3), 2.91 (2H, t, CH_2CO), 4.45 (2H, q, CO_2CH_2), 7.43 (1H, d, ArH), 7.63–7.89 (3H, m, ArH), 8.14 (2H, d, ArH).

Reduction[7] of the ethyl 4-(5-*n*-alkanoyl-2-thienyl)benzoates (step 4) was carried out by the dropwise addition of triethylsilane (3.64 g, 0.031 mol) to a stirred solution of the appropriate ketone (0.013 mol) in trifluoroacetic acid (9.77 g, 0.086 mol) cooled to 5°C. The reaction mixture was maintained below 30°C throughout the addition, and then stirred at room temperature for 12 h, water (45 ml) added, and the resulting white solid extracted into ether. The ether solution was washed with 4M-aqueous sodium hydroxide, and the solvent removed. The residue was recrystallized from light petroleum (b.p. 60–80°C) affording the *ethyl 4-(5-n-alkyl-2-thienyl)benzoates* as colorless crystals (83–93%), m.p.s. (°C): C_4H_9, 72.5–73.5; C_5H_{11}, 66.5–67.5; C_6H_{13}, 72.5–73.5; C_7H_{15}, 79–79.5; C_8H_{17}, 87–87.5; C_9H_{19}, 86–87; $C_{10}H_{21}$, 80–80.5; $C_{12}H_{25}$, 74–74.5; $C_{14}H_{29}$, 89.5–90.5.

The following data refer to the *n*-octyl homologue and are representative of the series: ν_{max} (KBr) 2955, 2920, 2847, 1711 (C=O), 1605, 1466, 1278, 1183, 1110, 850, 800, 767 cm^{-1}; δ_H ($CDCl_3$) 0.76–1.05 (3H, t, CH_3); 1.10–1.99 (15H, m, 6 CH_2, CH_3), 2.83 (2H, t, $ArCH_2$), 4.38 (2H, q, CO_2CH_2), 6.75, 7.22 (2H, δ, 2,5-disubstituted thiophene), 7.58, 8.02 (4H, dd, ArH).

The ethyl 4-(5-*n*-alkyl-2-thienyl)benzoates (0.006 mol) were hydrolyzed (step 5) by heating under reflux with potassium hydroxide (3 g, 0.054 mol) in 80% aqueous



SYNTHETIC ROUTE to 3-fluoro-4-*n*-octyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates.

ethanol (30 ml) for 2 h. In each case the reaction mixture was cooled, diluted with water (30 ml) and acidified with concentrated hydrochloric acid. The precipitated crude acids were recrystallized in turn from ethanol and from glacial acetic acid:water affording the *4-(5-n-alkyl-2-thienyl)benzoic acids* as white crystalline solids (85–91% after one recrystallization) with the following transition temperatures (°C): C_4H_9, *C-N* 172, *N-I* 238; C_5H_{11}, $C\text{-}S_C$ 168, $S_C\text{-}N$ 187, *N-I* 237; C_6H_{13}, $C\text{-}S_C$ 165, $S_C\text{-}N$ 200, *N-I* 229; C_7H_{15}, $C\text{-}S_C$ 159.5, $S_C\text{-}N$ 210.5, *N-I* 227; C_8H_{17}, $C\text{-}S_X$ 153.5, $S_X\text{-}S_C$ 154, $S_C\text{-}N$ 214.5, *N-I* 222; C_9H_{19}, $C\text{-}S_X$ 148, $S_X\text{-}S_C$ 151.5, $S_C\text{-}N$ 215.5, *N-I* 218.5; $C_{10}H_{21}$, $C\text{-}S_C$ 148, $S_X\text{-}S_C$ (144.5), $S_C\text{-}N$ 215.5, *N-I* 216.5; $C_{12}H_{25}$, $C\text{-}S_C$ 139, $S_C\text{-}I$ 212; $C_{14}H_{29}$, $C\text{-}S_C$ 134, $S_C\text{-}I$ 212.

The following spectroscopic data, typical of the series, refer to the *n*-octyl homologue: ν_{max} (KBr) 3250-2550(OH), 2954, 2923, 2849, 1683 (C=O), 1604, 1468, 1427, 1296, 952, 853, 810, 769 cm^{-1}; δ_H ($CDCl_3$/DMSO) 0.70–1.01 (3H, t, CH_3), 1.05–1.98 (12H, m, 6 CH_2), 2.82 (2H, t, $ArCH_2$), 6.83, 7.41, (2H, d, 2,5-disubstituted thiophene), 7.56, 8.00 (4H, dd, ArH), no OH signal observed.

The *3-fluoro-4-n-octyloxyphenyl 4-(5-n-alkyl-2-thienyl)benzoates* were prepared (step 6) by the addition of dicyclohexylcarbodiimide (0.34 g, 0.017 mol) to the appropriate 4-(5-*n*-alkyl-2-thienyl)benzoic acid and 3-fluoro-4-octyloxyphenol[8] (0.4 g, 0.0017 mol) in dichloromethane (50 ml). After stirring at room temperature for 30 min, 4-(N-pyrrolidino)pyridine (0.01 g) was added to catalyze the reaction, whereafter stirring was continued for 10–12 h at room temperature. Insoluble material was removed by hot filtration and the solvent removed. The residue was purified by column chromatography on silica gel, eluting with 2:1 light petroleum (b.p. 40–60°): chloroform. The esters were then recrystallized from ethanol until the *N-I* transition temperatures remained constant. The yields after one crystallization were 55–75%. M.p.s. and liquid crystal transition temperatures are listed in Table I.

The following data for 3-fluoro-4-*n*-octyloxyphenyl 4-(5-*n*-octyl-2-thienyl)benzoate are typical of the series: m/z 539 (M^+, 1.9%), 538 (4.9), 301 (7.4), 300 (24.7), 299 (100), 200 (2.5), 172 (15.3), 171 (5.0), 128 (2.1); ν_{max} (KBr) 2954, 2918, 2848, 1739 (C=O), 1604, 1525, 1471, 1277, 1215, 804, 761 cm^{-1}; δ_H ($CDCl_3$) 0.68–1.02 (6H, t, $2CH_3$), 1.09–1.98 (24H, m, $12CH_2$), 2.82 (2H, t, $ArCH_2$), 4.0 (2H, t, $ArOCH_2$), 6.72–7.35 (5H, m, ArH), 7.61, 8.11 (4H, dd, ArH).

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