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X-ray diffraction studies of the liquid crystal phases of certain 4-*n*-alkoxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates

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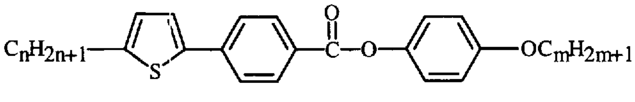
The *n*-butyl, *n*-octyl, *n*-decyl and *n*-dodecyl homologues of each of the 4-*n*-pentyloxyphenyl, 4-*n*-hexyloxyphenyl and 4-*n*-heptyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates have been prepared. All the homologues give rise to liquid crystal phases and their transition temperatures are reported. Phase identification was not straightforward, especially when distinguishing between some of the higher order smectic phases, and required a combination of thermal optical microscopy and X-ray diffraction studies, including powder photographs and detailed measurements of smectic layer spacings.

1. Introduction

This paper describes an investigation of the liquid crystal phases of members of the homologous series, (**1**), of three-ring esters derived from the 4-(5-*n*-alkyl-2-thienyl)benzoic acids and 4-*n*-alkoxyphenols. Homologous series of three-ring esters have been previously reported [1–3]. In the cases where the thiophene ring is terminal and directly attached to the ester function, the compounds are often highly smectogenic. Recently we have reported [4–6] the unusual smectic polymorphism shown by some homologues of the 3-fluoro-4-*n*-alkoxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates, which have a phase sequence S_A–S_C–S_A. In these three-ring esters, a benzene ring has been transposed with the ester linkage, so altering the core structure. The homologues in the present investigation retain this same linkage, but are not fluorinated.

Positive identification of mesophase type was generally possible from thermal optical microscopy, but in some of the homologues studied it was necessary to provide additional information from X-ray diffraction investigations



(**1**)

2. Results and discussion

Four compounds of each of three homologous series of esters (**1**; $m = 5, 6, 7$, $n = 4, 8, 10, 12$) were investigated using a combination of thermal optical microscopy and X-ray diffraction techniques. The results of these investigations have enabled the phase sequences of the compounds to be determined. The liquid crystal transition temperatures for the homologues studied are presented in table 1 and are plotted against *n*, the number of carbon atoms in the *n*-alkyl chain for each series in figures 1, 2 and 3

2.1. *Optical microscopy*

It was found that the corresponding homologues from each of the three series investigated show very similar phase behaviour. The butyl, octyl and decyl homologues all give rise to a nematic phase on cooling from the isotropic liquid. In the case of the butyl homologues, this crystallizes directly on further cooling without the formation of smectic phases.

The dodecyl homologues do not give rise to a nematic phase, but with the exception of the octyl homologue of the pentyloxy series, (**1**; $m = 5$, $n = 8$), which does not have an S_C phase, the octyl, decyl and dodecyl homologues of all three series form S_A, S_C and S_B phases which are readily assigned from their microscopic textures.

The lower temperature smectic phases formed by these compounds are not so clearly identifiable. For the

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Table 1. Transition temperatures for the 4-*n*-alkoxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates.

		Transition temperature/°C (*a*)									
n-Alkoxy group	*n*-Alkyl group	Cr–N Cr–S_B†	N–I	S_A–N S_A–I†	S_B–S_A	S_C–S_A	S_B–S_C	E–S_B	G–S_B H–S_B†	H–G	N–Cr (*b*) E–Cr† H–Cr‡
$C_5H_{11}O$	C_4H_9	96·0	153·9								81·9
	C_8H_{17}	88·9†	147·3	137·6	99·7			(84·3) (*c*)			23·0†
	$C_{10}H_{21}$	90·1†	143·2	141·1		119·6	102·8		(81·5)†		23·0‡
	$C_{12}H_{25}$	95·8†		140·4†		123·9	103·8		(93·4)	(83·2)	23·0‡
$C_6H_{13}O$	C_4H_9	90·7	156·0								76·9
	C_8H_{17}	86·1†	148·9	138·6		120·7	99·7	(75·9)			23·0†
	$C_{10}H_{21}$	89·5†	145·3	142·7†		131·5	99·4		(70·0)†		23·0‡
	$C_{12}H_{25}$	95·8†		142·1†		134·0	103·1		(86·5)†		23·0‡
$C_7H_{15}O$	C_4H_9	86·5	150·1								73·6
	C_8H_{17}	91·7†	146·2	138·8		125·6	97·8	(73·3)			23·0†
	$C_{10}H_{21}$	94·2†	143·1	141·7		135·7	100·5		(65·5)†		23·0‡
	$C_{12}H_{25}$	97·4†		140·4†		137·1	102·5		(82·0)†		23·0‡

(*a*) Symbols have their usual meaning: Cr, crystal; I, isotropic liquid; N, nematic; S_A, smectic A, etc. Thus Cr–N represents the temperature (m.p) at which a transition from the crystalline solid to the nematic phase occurs. Crystal smectic phases are denoted by the code letter, for example, H, G etc.

(*b*) Temperature of crystallization (at a cooling rate of approximately 3°C min^{-1}).

(*c*) Values in parentheses are for monotropic transitions.

pentyloxy series, (**1**; $m = 5$), the dodecyl homologue, on further cooling of the S_B phase, undergoes a phase transition marked by the gradual appearance of a cloudy grey micro-texture of the schlieren-mosaic or mosaic type, together with arced fans, most probably a smectic crystal G phase. This homologue, together with the other smectogenic homologues, shows transitions to other smectic crystal phases, which, from their optical textures, are probably either E or H phases, before crystallization occurs on cooling to near room temperature.

The lowest temperature smectic phase of the octyl homologues of all three series we tentatively assigned as smectic crystal E. In the case of the pentyloxy compound (**1**; $m = 5$, $n = 8$), this has a texture showing polygonal platelets crossed with fine hatching in the formerly homeotropic areas of the S_B phase. These congeal to a mottled platelet texture with superimposed hatching and the focal-conic fans become crossed with very fine permanent parallel arcs across their backs. On cooling the S_B phases of the octyl homologues of the hexyloxy and heptyloxy series (**1**; $m = 6$ and 7, $n = 8$), the homeotropic areas change to a grey mosaic texture. The fan areas become faintly arced in the hexyloxy homologue and finely banded in the heptyloxy homologue. The formation of such a weakly coloured mosaic texture is also characteristic of a transition from an S_B to a smectic crystal G phase, although in such cases the fans are normally broken [7]. Hence, the possibility of a G phase rather than an E phase cannot be totally discounted for these homologues.

On cooling the S_B phases of the decyl and dodecyl homologues of all three series of esters, a transition occurs in which most of the focal-conic fans develop discontinuous arcs across their backs and the homeotropic areas change to a grey mosaic texture with fine cross hatching. In each case therefore, these phases were tentatively assigned as smectic crystal H phases.

2.2. *X-ray diffraction*

X-ray diffraction studies were carried out on the compounds to attempt to verify the phase assignments made from the optical microscopy observations and to monitor how the smectic layer spacing changes with temperature. X-ray powder photographs of the lower temperature phases confirmed the correct assignment of all S_B and smectic crystal G phases, including those from the dodecyl homologue of the pentyloxy series, (**1**; $m = 5$, $n = 12$). The S_B and G photographs are both characterized by a single sharp outer ring, indicative of the ordered arrangement of molecules in the layers of these phases [8]. The phases assigned as either smectic crystal E or H all gave, as expected, additional sharp outer rings [8], but since the samples were unaligned it was not possible to distinguish between these phases from the photographs. However, the possibility of the octyl homologues of the hexyloxy and heptyloxy series (**1**; $m = 6, 7$, $n = 8$) having a G phase could be safely discounted.

The smectic layer spacings as a function of temperature and phase type were measured using an X-ray diffractometer and the results are summarized in tables 2, 3, and 4. It can be seen that in all cases the theoretical molecular

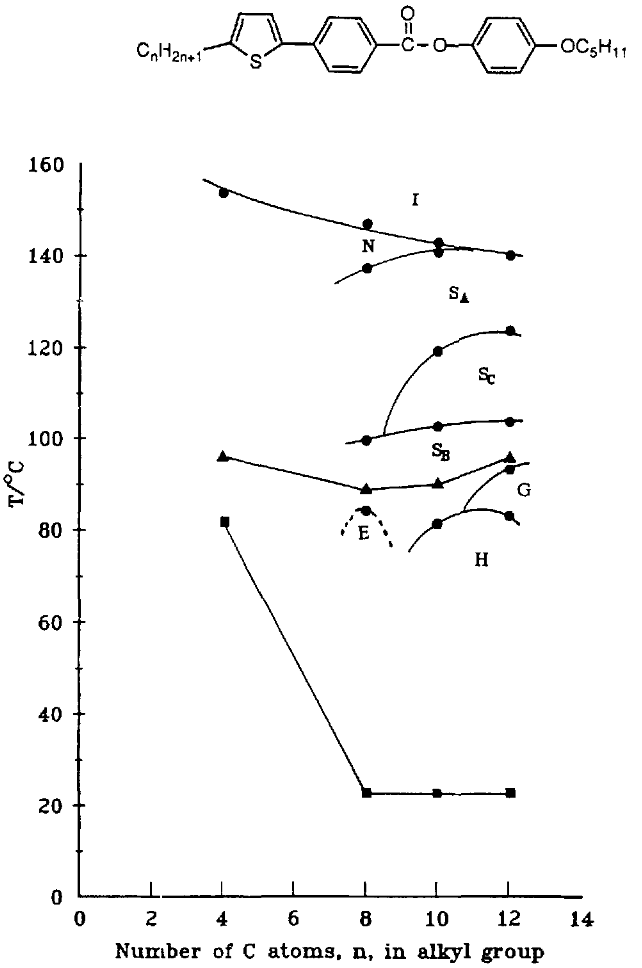


Figure 1. 4-*n*-Pentyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates: transition temperatures against *n*, the number of carbon atoms in the alkyl group. (▲) indicates mp, (●) mesophase–mesophase transition, and (■) recrystallization at a cooling rate of approximately 3°C min^{-1}.

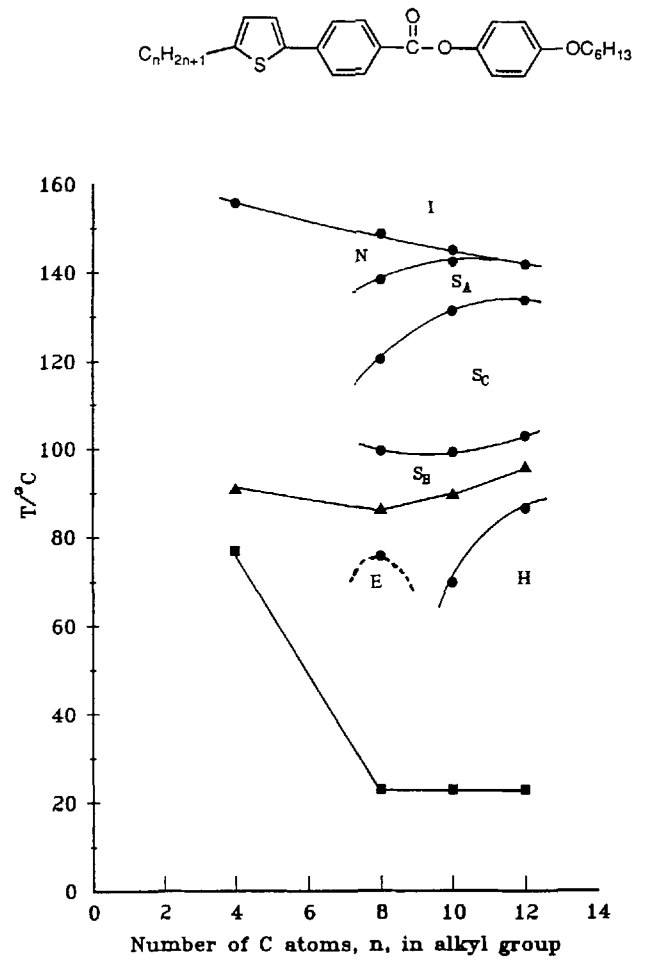


Figure 2. 4-*n*-Hexyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates: transition temperatures against *n*, the number of carbon atoms in the alkyl group. (▲) indicates mp, (●) mesophase–mesophase transition, and (■) recrystallization at a cooling rate of approximately 3°C min^{-1}.

length is greater than the measured smectic layer spacing, even in the orthogonal smectic phases. Hence it would appear that in all phases there is some interdigitation of the alkyl chains across the layer boundaries. It is of interest to note that the layer spacing in the S_A phase is always significantly less than for the S_B phase, since although the average molecular director is perpendicular to the layer planes, it is usual for the molecules in an S_A phase to be randomly tilted within the layers [9].

The behaviour of the layer spacing following the transition from S_B to either smectic crystal E or H helps to confirm the actual phase type. In cases where an E phase was expected, it can be seen that the layer spacing does not change after the transition, so confirming the orthogonal nature of the E phase. In cases where an H phase was expected, this is generally confirmed, as the spacing decreases after the transition, indicating a tilted H phase. The one exception is at the transition from the S_B phase of the decyl homologue of the heptyloxy compound (**1**; $m = 7$, $n = 10$). Here no change was observed, but on the basis of the microscopic evidence it would seem highly likely that an H phase is formed as the optical texture previously observed is identical to that of the H phase of the dodecyl homologue in this series. Thus it is reasonable to conclude that in the decyl homologue, (**1**; $m = 7$, $n = 10$), the tilt, although present, is too small to be detected. We were unable to obtain satisfactory independent confirmation of the assignment of this phase as smectic crystal H by miscibility studies with appropriate standard materials.

Detailed measurements of the layer spacings are shown for some of the compounds in figures 4–7. These clearly show the decrease in layer spacing normally observed at the S_B to H transition, but indicate that when an E phase

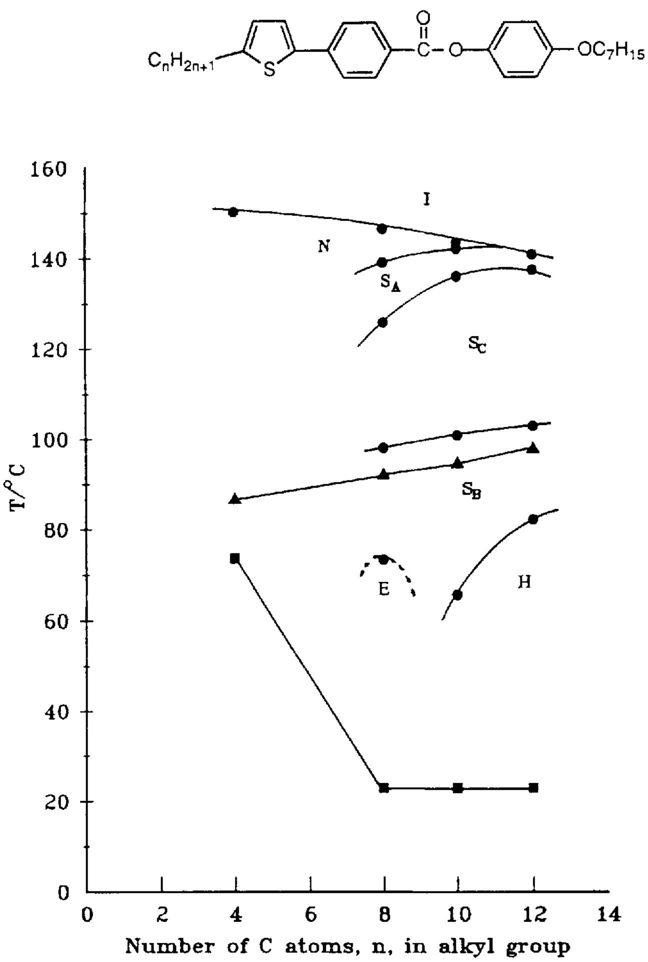


Figure 3. 4-*n*-Heptyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates: transition temperatures against *n*, the number of carbon atoms in the alkyl group. (▲) indicates mp, (●) mesophase–mesophase transition, and (■) recrystallization at a cooling rate of approximately 3°C min^{-1}.

is formed from the S_B phase, there is no significant change in the spacing.

For the higher temperature phases, the measurements show that as the S_A phases are cooled, the spacing generally increases slightly and during the S_C phase it decreases from the S_A value to a minimum and then shows a slight increase as cooling continues, indicating that in both of these phases the degree of molecular tilt varies with temperature.

3. Conclusions

This study shows the benefits of using X-ray diffraction studies for difficult phase assignments. Unlike the 4′-*n*-alkylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylate series [3], these homologues exhibit a mixture of tilted and orthogonal phases. They do not show any indication of the S_A–S_C–S_A phase behaviour exhibited by some homologues of the related fluorinated series [4–6] and, in general, have additional phase types and are mesomorphic over a wider temperature range. Measurements of layer spacings show that where an S_A phase is followed by an S_C phase, the steady increase in layer spacing observed with the fluorinated compounds does not occur. Thus, the steady increase in layer spacing may be related to the re-entrant S_A behaviour of the fluoro-analogues.

Table 2. X-ray diffractometer data for the 4-*n*-pentyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates.

n-Alkyl group	Theoretical molecular length*l*/Å	Average layer spacing *d*/Å					
		S_A	S_C	S_B	G	E	H
C_8H_{17}	31·3	28·7	—	29·8	—	29·8	—
$C_{10}H_{21}$	33·7	29·2	29·1	30·2	—	—	29·8
$C_{12}H_{25}$	36·3	30·3	30·1	31·7	31·4	—	30·9

Table 3. X-ray diffractometer data for the 4-*n*-heptyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates.

n-Alkyl group	Theoretical molecular length *l*/Å	Average layer spacing *d*/Å				
		S_A	S_C	S_B	E	H
C_8H_{17}	32·5	30·2	30·1	31·7	31·7	—
$C_{10}H_{21}$	34·9	31·2	30·9	33·1	—	32·8
$C_{12}H_{25}$	37·4	31·4	31·1	33·2	—	32·8

Table 4. X-ray diffractometer data for the 4-*n*-heptyloxyphenyl 4-(5-*n*-alkyl-2-thienyl) benzoates.

n-Alkyl group	Theoretical molecular length *l*/Å	Average layer spacing *d*/Å				
		S_A	S_C	S_B	E	H
C_8H_{17}	33·7	29·4	28·0	30·9	30·9	—
$C_{10}H_{21}$	36·2	30·0	29·7	31·9	—	31·9
$C_{12}H_{25}$	38·6	32·0	30·8	33·9	—	33·7

Comparison of the mesophase thermal stability of the esters (**1**) with their laterally fluorinated derivatives, the 3-fluoro-4-*n*-alkoxyphenyl 4-(5-*n*-alkyl-2-thienyl)-benzoates [4–6], reveals that the introduction of the lateral fluoro-substituent, which is directed away from the central core, eliminates the short nematic phase, but causes only a very small reduction (less than 2°C) in smectic thermal stability of the esters (**1**). For (**1**), relevant average values (for $n = 8$ and 10) of $T_{N\text{-}I}$ and $T_{S_A\text{-}N}$ for comparison are 147·1° and 140·7° ($m = 6$), and 144·7° and 140·3°C ($m = 7$), respectively. Corresponding values for the analogous fluoro-substituted esters are $T_{S_A\text{-}I}$ 139·5° ($m = 6$) and 138·6°C ($m = 7$).

Data suitable for meaningful comparisons with other related systems are not available. Esters derived from the

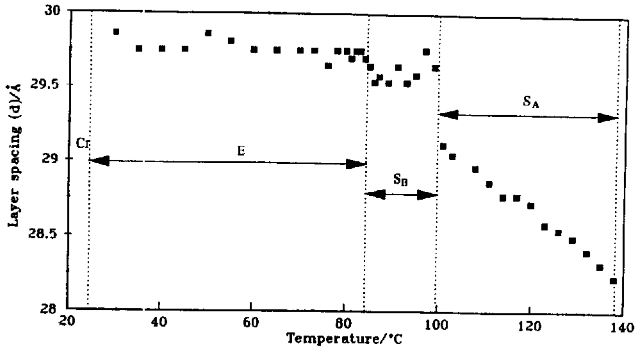


Figure 4. 4-*n*-Pentyloxyphenyl 4-(5-*n*-octyl-2-thienyl)benzoate: temperature variation of the smectic layer spacing.

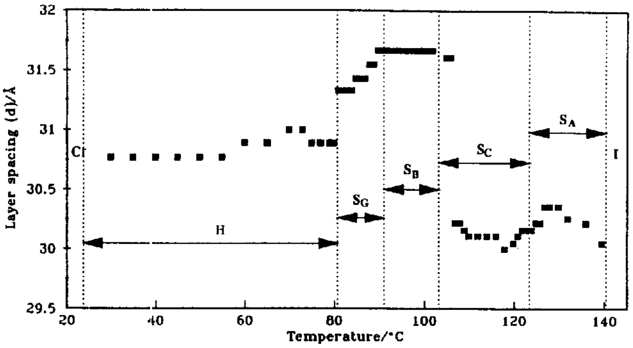


Figure 5. 4-*n*-Pentyloxyphenyl 4-(5-*n*-dodecyl-2-thienyl)benzoate: temperature variation of the smectic layer spacing.

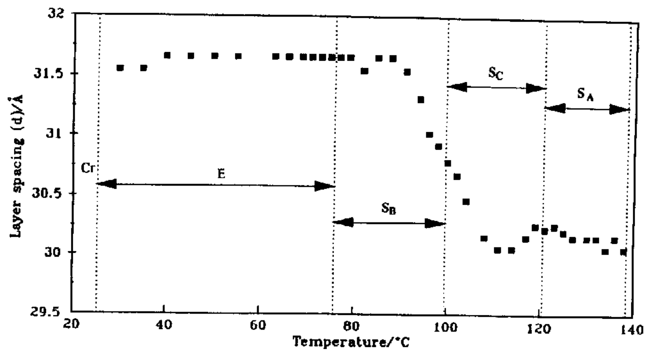


Figure 6. 4-*n*-Hexyloxyphenyl 4-(5-*n*-octyl-2-thienyl)benzoate: temperature variation of the smectic layer spacing.

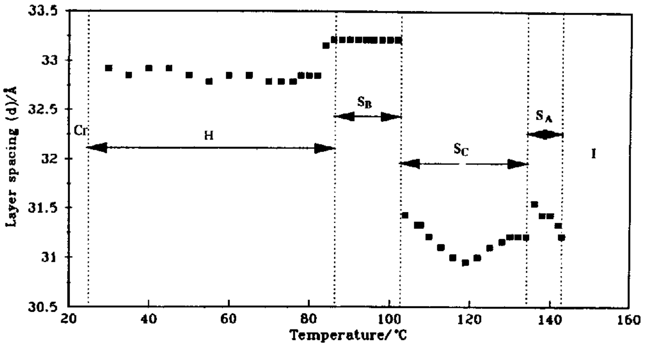


Figure 7. 4-*n*-Hexyloxyphenyl 4-(5-*n*-dodecyl-2-thienyl)benzoate: temperature variation of the smectic layer spacing.

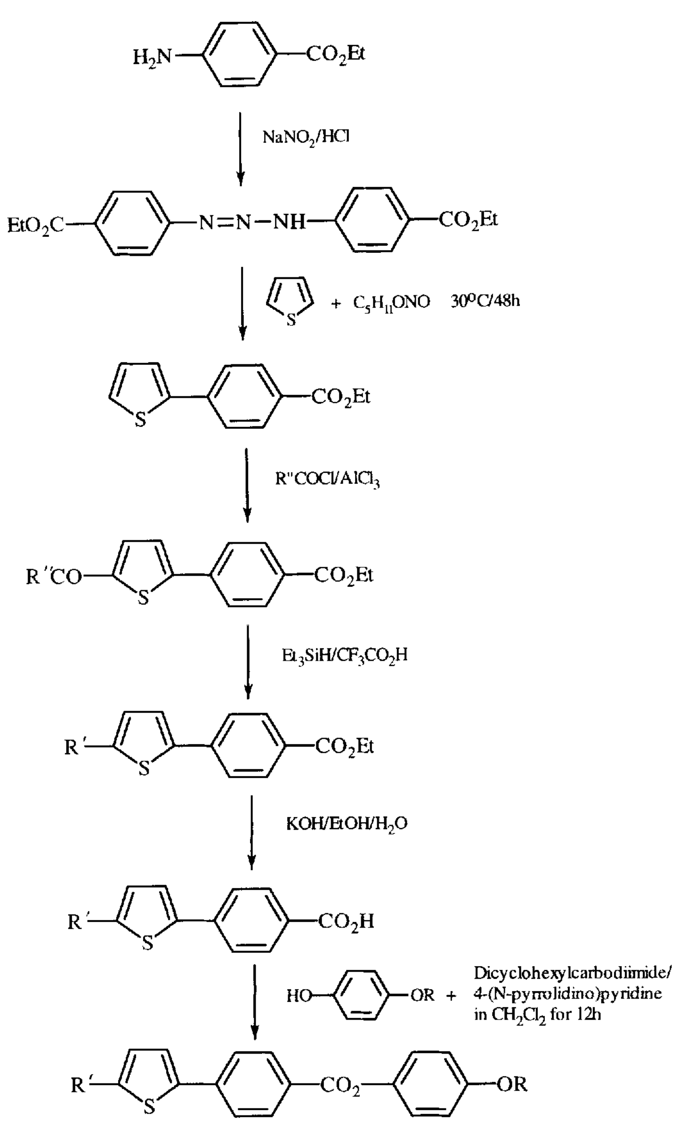
4-*n*-alkylbiphenyl-4-carboxylic acids and 4-*n*-alkoxyphenols are cited in a patent [10]. However, transition temperatures for the 4-*n*-pentyloxy-, -hexyloxy- and -heptyloxy-phenyl 4′-*n*-alkylbiphenyl-4-carboxylates corresponding with the homologues of the 4-(5-*n*-alkyl-2-thienyl)benzoates studied in the present work are not reported, nor does the patent identify the types of smectic phases shown by the alkylbiphenyl-4-carboxylates. Accordingly we intend to investigate a range of these esters and report in more detail on their liquid crystal behaviour in a future publication.

4. Experimental

4.1. *Analysis*

The esters were prepared by standard methods illustrated in the synthetic route. Structural confirmation of the structures of the intermediates and the products was obtained by ^{1}H NMR spectroscopy (either Hitachi Perkin–Elmer R24-b 60 MHz spectrometer or Jeol FX60Q 270 MHz spectrometer) with tetramethylsilane as internal standard and by infrared spectroscopy (Perkin–Elmer 157 grating spectrophotometer). Mass spectra were determined with an A.E.I. MS 902S spectrometer equipped with a Mass Spectroscopy Services 200 console and an INCOS 2300 data system. By hplc, the purity of the esters was established as 99·5 per cent or better. The hplc studies were carried out on a Hewlett Packard 1090 system, fitted with an RP18 column. The eluent used was initially a mixture of 80 per cent methanol : 20 per cent water, which over 10 min moved to 100 per cent methanol. A diode array detector was used and the spectra were integrated over the relevant absorption range.

Thermal optical microscopy was carried out with a Vickers M75 polarizing microscope in conjunction with a Mettler FP52 hot stage and FP5 control unit. X-ray photographic studies were carried out on heated powder samples contained in 0·3 mm Lindemann glass tubes and diffractometer investigations were made on a Hilton Brooks modified Philips PW1050 powder diffractometer linked to an IBM PC.XT computer. Samples were placed on an uncovered glass slide, positioned on a temperature controlled heating block. All the X-ray studies used filtered CuK$_\alpha$ radiation and sample temperatures were accurate to + / − 0·2°C. Quoted spacings from X-ray investigations are accurate to + / − 0·1 Å. The calculated molecular length of the molecules in their extended conformation was obtained using CHEMX [11].



Synthetic route to 4-*n*-alkoxyphenyl 4-(5-*n* alkyl-2-thienyl)-benzoates.

4.2. *Preparation of materials*

The 4-*n*-alkoxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates (**1**) were obtained as summarized in the synthetic route.

The esters (**1**) were prepared [5] utilizing *N*,*N'*-dicyclohexylcarbodiimide, by the reaction between appropriate 4-(5-*n*-alkyl-2-thienyl)benzoic acids, the preparation of which we have previously reported [5], and 4-*n*-alkoxyphenols, which were obtained from hydroquinone either by our earlier method [12], or, in much better yield (58–65 per cent), by the method given by Bellas and co-workers [13].

The following data for 4-*n*-pentyloxyphenyl 4-(5-*n*-dodecyl-2-thienyl)benzoate are typical of the members of the homologous series: Found: C, 76·25, H, 8·61 per cent; *m*/*z* 534 (5·9 per cent), 355 (100). $C_{34}H_{46}O_3S$ requires C, 76·36, H, 8·67 per cent; *M*, 534; ν_{max} (KBr) 2953, 2920, 2848, 1739 ($C{=}O_{str}$), 1605, 1512, 1471, 1280, 1213, 872, 806, 760 cm^{-1}; δ_H ($CDCl_3$) 0·72–1·99 (32 H, m, alkyl CH_2, CH_3), 2·82 (2 H, t, $ArCH_2$), 3·93 (2 H, t, $ArOCH_2$), 6·71–7·25 (6 H, m, ArH), 7·59 and 8·11 (4 H, d, ArH) ppm.

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