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Synthesis and mesomorphic properties of some biphenyl–phenyl triesters as potential longitudinal ferroelectrics†

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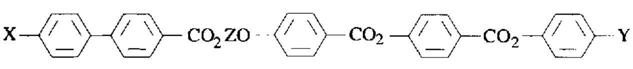
A homologous series of 'fraternal twin' molecules consisting of relatively short and relatively long mesogenic units connected by a flexible spacer group and flexible chains as the terminal groups was synthesized in an attempt to form a non-chiral longitudinal ferroelectric smectic phase. The shorter of the two mesogenic units consisted of a 4-alkyl/alkoxy substituted biphenyl ester; the longer a terbenzoate group. Mesomorphic properties were determined by hot-stage polarizing microscopy and DSC. Several smectic phases were observed as well as nematic phases. Characterization of the smectic phases by microscopic textures is discussed.

1. Introduction

It has been suggested that non-chiral ferroelectric smectic phases can be formed when molecules have the appropriate structures [1, 2]. Consider molecules which consist of four or more segments. Suppose that three of these segments are sufficiently different in their structures either in their polarity or in their shape so that when they pack (microphase), they separate into at least three separate layers. Then conceivably, each smectic layer will be polar and consist of three different layers. If, in addition, the two ends of the molecule are sufficiently similar so that they belong to the same layer then these molecules could stack in a polar fashion forming longitudinal ferroelectric liquid crystalline phases. In this paper, we describe our first attempt to synthesize compounds that have this structure and such phases.

We chose to synthesize a series of triesters of the type **1**:



1

a $Z = (CH_2)_7$, $X = R$, RO, **b** $Z = (CH_2)_2$, $X = C_7$, **c** $Z = (CH_2CH_2)_2O$, $X = C_7$.

The structure **1** with $Y = C_9H_{17}$ consists of two very different, rather rigid aromatic segments with similar alkyl tails, connected to each other with another alkyl spacer. Because these mesogens are so different, it is possible that they will pack separately from each other, forming a polar layer as shown in figure 1 (*a*). Provided such polar layers are formed, they potentially have parallel ferroelectric ordering (as in figure 1 (*a*)) or antiferroelectric ordering (as in figure 1 (*b*)). Differences between the two tails of the mesogen (which are deliberately small in **1**) will tend to favour antiferroelectric ordering, while dipolar interactions and elastic interactions will tend to favour ferroelectric ordering. It is also possible that non-polar layers form either randomly up and down mesogens in each layer (see figure 1 (*c*)), or

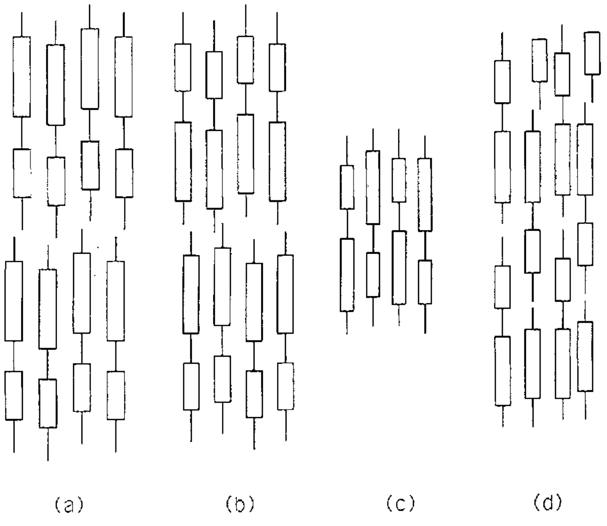


Figure 1. Schematic of the possible uniaxial smectic phases with no in plane order for the molecule **1** (*a*) Ferroelectric (the hypothesized S_{A_P}) phase, (*b*) an anti-ferroelectric S_{A2} phase with twice the period, (*c*) a paraelectric S_A phase and (*d*) an interleaved S_A phase.

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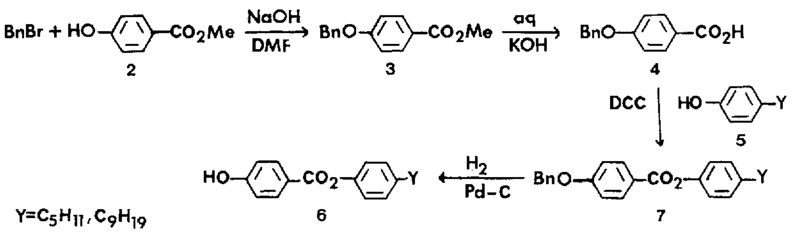
as interleaved mesogens (see figure 1 (*d*)). Randomly up and down mesogens are not favoured by sufficiently different rigid segments. Interleaved mesogens are discouraged by a sufficiently large difference (for example, in length) between the total tail and the flexible spacer. The compound **1** was designed to favour the ferroelectric ordering.

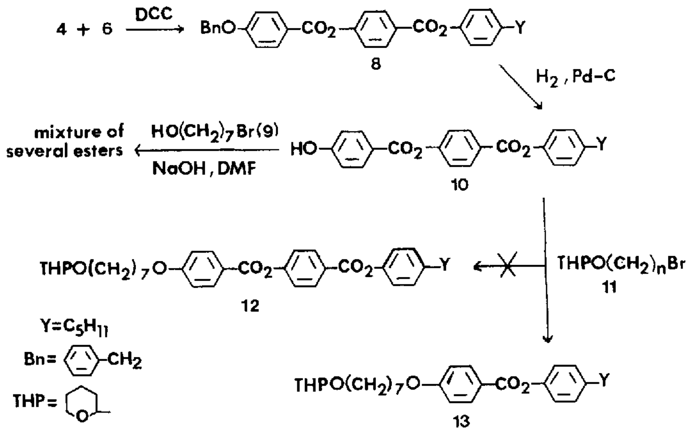
2. Synthesis

Our synthesis of the triesters **1** began with the preparation of the hydroxy ester intermediate **6** according to the literature methods [3, 4] as shown in scheme 1. The initial approach was to esterify this phenol with the protected hydroxybenzoic acid **4** to obtain the ester **8** (see scheme 2) followed by hydrogenolysis to the hydroxy-diester **10**. However, treatment of this diester with the bromo alcohol **9** gave a mixture of several esters resulting from transesterification. An attempt to use the THP protected alcohol **11** gave some of the ester **13** resulting from ester exchange but none of the desired diester **12**. In these initial attempts, $Y = C_5$ since the phenol **5** was available in our laboratories. Ester exchange was avoided by first preparing the protected acid **17** (see scheme 3), esterifying to obtain the diester **16** and removal of the protecting group to give the alcohol **18**. Esterification with the biphenyl acid or acid chloride **19** gave the desired ester **1 a**. Longer reaction times were needed to obtain high yields with the biphenyl than with the phenyl esters. This is also true for the preparation of the acid chloride. In this synthesis, $Y = C_9$ since this is the preferred chain length and the synthesis of the phenol had by now been accomplished.

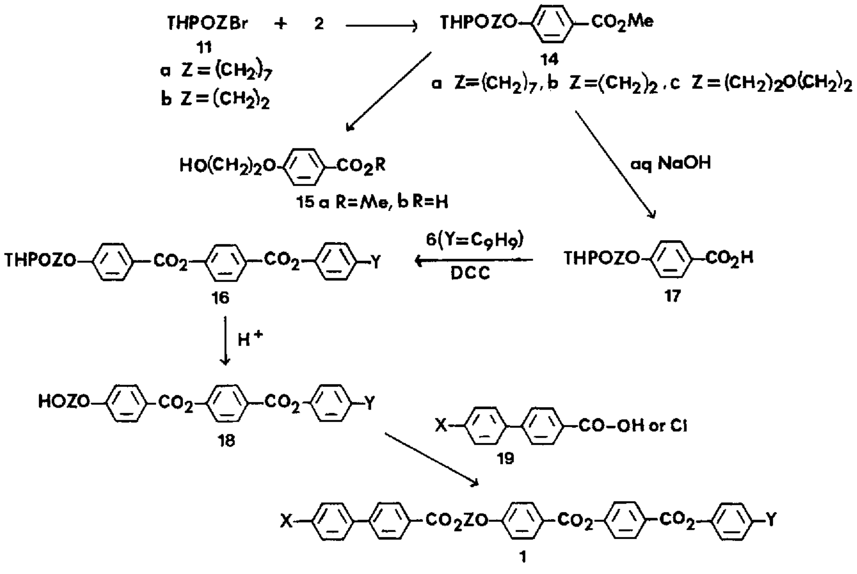
The THP protected acid **17 c** was prepared by first synthesizing the ester **14 b**, removing the THP group to obtain the alcohol **15 a**, alkylating again with the bromide **11 b** to obtain the ester **14 c** and then hydrolysing to the acid (see scheme 3). In the synthesis of the ester **14 c**, the material isolated showed only one spot by TLC and an NMR spectrum supported this structure with possibly some impurity present. Since the acid **17 c** was easier to recrystallize than the ester, the ester **14 c** was hydrolysed without purification. This, however, yielded a mixture of two similar acids which was not detected until the acid was esterified to the diester **16**. Two esters were isolated when this material was purified by flash chromatography. NMR showed that these contained two different spacers: $Z = (CH_2)_2$ (**16 b**) and $(CH_2CH_2)_2O$ (**16 c**) indicating that the alcohol **15 a** had not been completely alkylated. This was confirmed by the isolation of the acid **15 b** as first crop crystals in the recrystallization of



Scheme 1.



Scheme 2.

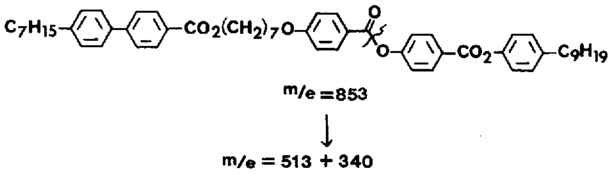


Scheme 3.

the crude product from the hydrolysis of the ester **14c**. Both of the esters were purified and showed mesomorphic properties. Removal of the THP group followed by esterification with the acid **19** gave separately the triesters **1b** and **1c**.

All compounds were purified by recrystallization and/or by flash chromatography followed by recrystallization until melting points were constant. At least one hot filtration through hard (Whatman 50) filter paper was used to remove insoluble materials. Various methods (TLC, GC, IR and NMR) were used to detect impurities. The purity of materials having mesomorphic properties was also checked by the sharpness of their clearing temperatures which was $\leqslant 0{\cdot}3^{\circ}C$. In our experience, this range is very sensitive to impurities having similar structures but different clearing temperatures, with a short range usually indicating a high purity. This method, however, apparently does not always work if the clearing temperatures are similar as shown by our inability to detect the ester **16b** in **16c**. The difference in structures in these molecules is so small in comparison to the size of the molecule, that the clearing temperatures are essentially the same.

Structural characterization of all compounds was accomplished using IR and NMR. Elemental analyses were obtained for a few pertinent compounds and a mass spectrum for **1a** $X = R = C_7$. No parent peak was observed, but a major fragment at $m/e = 513$ provided support for structure **1a** via the fragmentation pattern shown in scheme 4. The $m/e = 340$ fragment was not seen but degraded to smaller fragments.



Scheme 4.

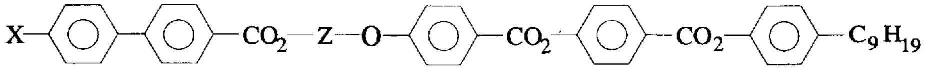
3. Mesomorphic properties

Transition temperatures as determined by hot stage polarizing microscopy are given in table 1. Many of the intermediates synthesized also showed mesomorphic properties. These data are recorded in the experimental section.

Both melting and clearing temperatures were near or above 100°. Compounds with $Z = (CH_2)_7$ showed little variation in these temperatures when the chain length of $X = R$ was changed. The analogues with $Z = (CH_2)_2$ or $(CH_2CH_2)_2O$ had lower clearing temperatures but comparable melting temperatures of those found with $Z = (CH_2)_7$.

Crystal-to-crystal changes were observed in all but two of these compounds. These occurred after cooling the sample below its crystallization temperature (Cr_1) and then reheating (Cr_2) with conversion to Cr_2 usually occurring below the crystallization temperature. These crystals (Cr_2) then melted to the lowest mesophase on further heating. For the homologues with $X = C_5H_{11}$ and C_7H_{15}, two different melting temperatures were observed. With the C_5 homologue, the smectic C was

Table 1. Transition temperatures (°C) for the



X	Z	Cr_2[a]	Cr_1[b]	S[c]	S_C	Transitional	S_A	N	I
C_7H_{15}	$(CH_2)_2$	104·6	105·7	116·5 116·8			138·2		139·9–140·0
C_3H_7	$(CH_2)_7$	89·0					111·5–113·0	171·7	193·2–193·5
C_5H_{11}	$(CH_2)_7$	85·2	~75		(97·5–98·4) 99·3–99·9 (Cr_2)	(99·1)	124·2–126·1(Cr_1)	181·7–181·8	188·5 188·7
C_7H_{15}	$(CH_2)_7$	94·9	70·3		(118·0–120·0)[d] 110·3–110·6(Cr_2)	(124·7–126·3)	127·4 128·8(Cr_1)		184·4–184·7
C_9H_{19}	$(CH_2)_7$	97·3	82·8		119·7–121·0(Cr_1)	137·7–138·2	140·3, 144·9[d]		185·2–185·5
$C_{12}H_{25}$	$(CH_2)_7$	96·7	78·4		120·1–121·7(Cr_1)[e] 109·1–109·7(Cr_2)		158·9–159·1		182·9–183·2
$C_5H_{11}O$	$(CH_2)_7$	93·9	87·5				123·5–124·7(Cr_1) 100–105(Cr_2)	188·5 188·7	196·6–197·1
$C_{10}H_{21}O$	$(CH_2)_7$	100·1	99·1[f]		116·5–117·1(Cr_3)[f] 117·5(Cr_2)	147·1	150·4		192·8–193·2
C_7H_{15}	$(CH_2)_2O(CH_2)_2$	97·8					110·7–111·5		177·4–177·6

[a] Crystallization temperature obtained by cooling the melt at 2° min^{-1}.

[b] Crystal-to-crystal change observed by cooling below Cr_2 and reheating 2° min^{-1}.

[c] S = unidentified smectic, S_C = smectic C, S_A = smectic A, N = nematic and I = isotropic liquid, 'transitional' is discussed in the text and parenthesis indicate a monotropic phase which occurs below the melting temperature.

[d] The two crystal forms observed in this homologue showed two slightly different melting temperatures.

[e] Observation of the smectic C schlieren texture shows the S_C–S_A transition at 140·3, whereas the broken fan texture converts to the S_A fan texture at a higher temperature. More discussion is given in the text.

[f] The crystal changes differed from the other analogues in that on cooling Cr_2 converted to Cr_1 at 99·1° and then to Cr_3 at 88°. Reheating Cr_2 and Cr_3 gave two different melting temperatures.

enantiotropic with respect to both crystal forms, whereas with the C_7 homologue, the smectic C phase was enantiotropic when melting occurred from Cr_2 and monotropic when melting occurred from Cr_1.

All these triesters showed an enantiotropic smectic A phase. With a shorter $X = R$ or RO chain, a nematic phase was also observed. When $Z = (CH_2)_2$, a more highly ordered smectic phase occurred below the smectic A phase that showed a focal conic texture similar to that for a smectic B phase but no homeotropic texture. Not enough material was available to do an X-ray identification of this phase. When $Z = (CH_2)_7$ and $X = C_5$–C_9 or $C_{10}O$, a texture which looked similar but not identical to that of a smectic C phase was observed below the smectic A phase. Continued cooling eventually gave a typical smectic C texture. This transitional texture was also observed on reheating the smectic C texture. It was not observed when $X = C_{12}O$ which showed a typical smectic A to C transition.

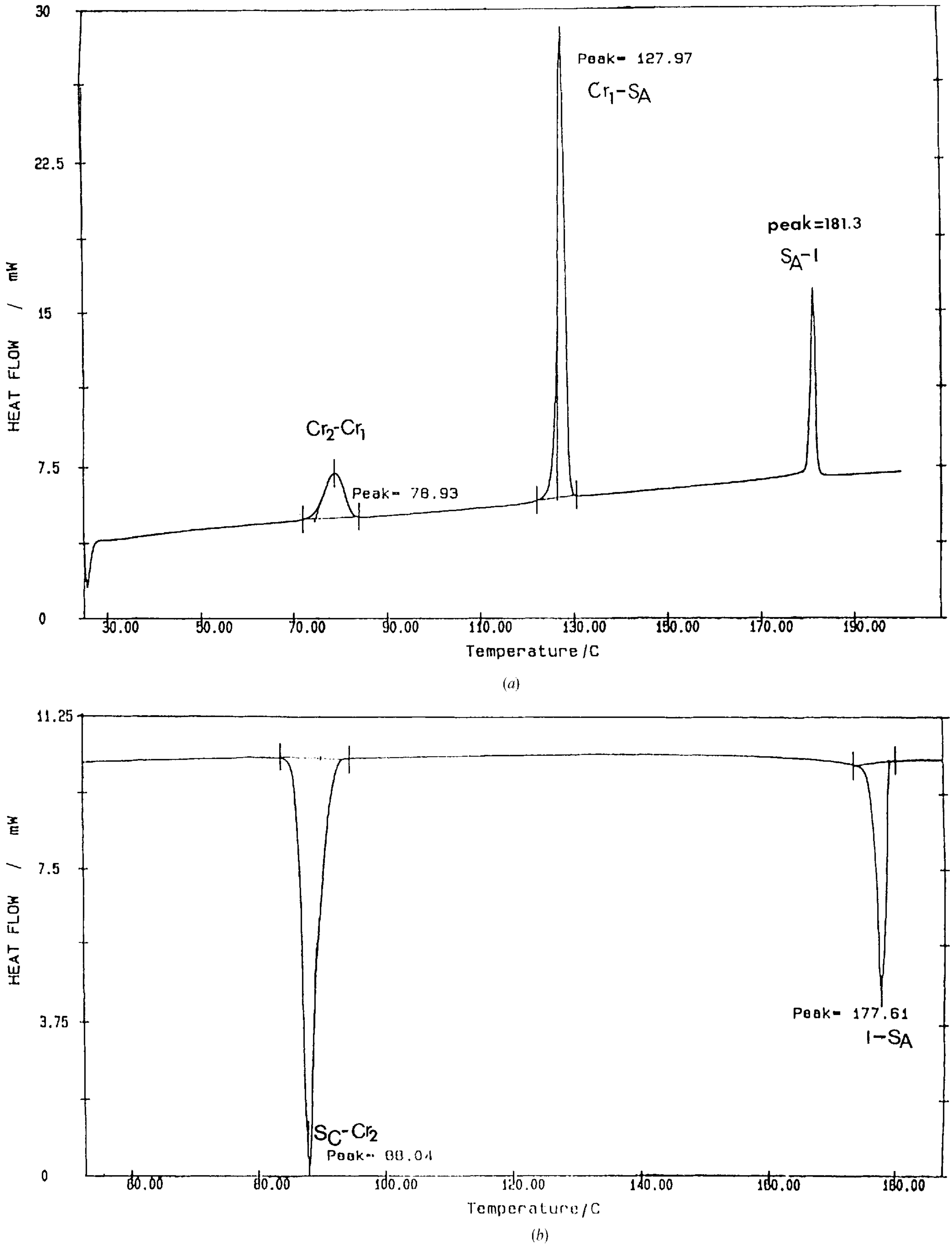
In a typical smectic A–C transition, cooling the focal conic fans of the smectic A phase causes these fans to quickly convert to the broken fans of the smectic C phase. Breakup of the fan texture continues to occur as the tilt angle increases. Cooling the black homeotropic texture of the smectic A phase quickly gives the grey schlieren texture of the smectic C phase at nearly the same temperature as the broken fans form. This texture is characterized by the presence of threads with disclination points at their intersection which show four armed crosses. Continued cooling leads to wave after wave of different shades of grey until there is no longer a change in the tilt angle. The black uniaxial conoscopic cross observed in the homeotropic texture of the smectic A phase quickly separates and converts to the faint biaxial cross on cooling into the smectic C phase.

In these triesters, breakup of the smectic A fans occurred immediately on cooling, but did not continue with further cooling. This change began at a higher temperature than did the appearance of the schlieren texture. In between these two points, the black homeotropic texture became lighter on cooling, giving a grey texture showing boundaries but no schlieren texture. On further cooling, the threads and disclination points of the schlieren texture gradually formed. Once the schlieren texture was formed, no further changes occurred on cooling. Both the schlieren and fan textures were typical of those observed for the tilted smectic C phase. The temperature range for this transitional texture is recorded in table 1 under the column headed 'transitional.'

DSC scans for the triester with $X = C_7H_{15}$ and $Z = (CH_2)_7$ showed three peaks in the heating scan: 78·93° (crystal to crystal) 127·97° (melting) and 181·3° (clearing). No peak was observed for the S_C–S_A transition either on heating (see figure 2 (*a*)) or cooling (see figure 2 (*b*)) suggesting the presence of a second order transition. Thermal data obtained from DSC scans for several homologues are given in table 2.

Since schlieren textures can occur in other smectic phases than the smectic C phase, additional microscopic studies were done to determine if this phase with the schlieren texture was indeed a tilted smectic phase. Observation of the schlieren crosses, while the polarizer and analyser were rotated simultaneously, showed a rotation in the crosses as well. Some rotated in the same direction as the polarizers whereas others rotated in the opposite direction, but always with the magnitude of the rotation remaining the same. This observation is consistent with the fourfold crosses being disclinations in a S_C director, provided there are both charge $+1$ and charge -1 disclinations. That is, the molecules are tilted relative to the layers and there are points around which the tilt direction rotates by 360° as we go around the defect, with the rotation of this tilt either parallel or antiparallel of the rotation of space.

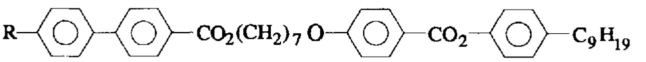
In order to confirm that the director was actually tilted, changes in the director pattern as the sample was tilted relative to the direction of propagation of light were also observed. One such experiment is illustrated in figure 3, together with the tilt pattern which explains it. With the polarizers oriented at + or −45°, the slide was moved until a fourfold cross was in the centre of the field with the dark lines oriented approximately parallel to the polarizers. This is consistent with the director tilted in the plane parallel to one of the polarizers along these dark lines. Additionally, it was observed that when the sample was tilted (rotated around an axis in the plane of the sample as shown in figure 3) that the bright upper quadrant between approximately − and +45° became brighter while the lower quadrant grew darker, becoming essentially completely dark when the sample was tilted by approximately 5°. There was little change in the appearance of the two remaining quadrants. As the phase shift between the two polarizations of light on traversing this sample is small (the light is white, not coloured through crossed polarizers), we concluded that the effective birefringence of the upper quadrant increased with increasing tilt and that of the lower decreased while those of the other quadrants remained the same. This implies that a principle axis of the optical dielectric tensor is tilted parallel to the tilt of the slide in the upper quadrant and antiparallel thereto in the lower quadrant. Generally, in liquid crystals, the principal axes of the optical dielectric tensor are closely related to the average directors of the core. This supports the director pattern shown in figure 3 and is inconsistent with an untilted director.


HEAT FLOW / mW
30
22.5
15
7.5
0
Peak= 127.97
Cr_1-S_A
peak=181.3
S_A-I
Cr_2-Cr_1
Peak= 78.93
30.00
50.00
70.00
90.00
110.00
130.00
150.00
170.00
190.00
Temperature /C
HEAT FLOW / mW
11.25
7.5
3.75
0
Peak= 177.61
I-S_A
S_C-Cr_2
Peak= 88.04
60.00
80.00
100.00
120.00
140.00
160.00
180.00
Temperature /C

(*a*)

(*b*)

Table 2. DSCdata for the



R	Transition[a]	T/°C	ΔH/kJ mol^{-1}
C_7	Cr_2–Cr_1[b]	78·93	12·36
	Cr_1–S_C	127·97	46·50
	S_A–I	180·98	12·09
	I–S_A	177·61	−32·81
	S_C–Cr	88·04	−11·42
C_9	Cr–S_C	120·25	45·53
	S_A–I	182·20	17·59
	I–S_A	179·44	−37·98
	S_C–Cr	95·46	−16·22
C_{12}	Cr–S_C	121·02	48·78
	S_A–I	180·53	18·53
	I–S_A	177·37	−40·63
	S_C–Cr	93·83	−16·44

[a] Cr = crystal, S_C = smectic C, S_A = smectic A and I = isotropic liquid.

[b] Transition not always observed.

Similar experiments have been done in other configurations and analysed in the same manner to give smectic C director patterns. Of course, there are a number of other possible smectic phases which would have such crosses in their schlieren textures but the different signs of the changes on either side of the defect when the sample is tilted is consistent only with a tilted phase. Since the dark quadrant is completely dark when the sample is tilted by 5°, we conclude that the tilt is about 5°. However, these results are consistent with either an ordinary smectic C phase with C_{2h} symmetry or a polar smectic C_p phase with C_s symmetry (or other phases with $C2$ or $C1$ symmetry) in which there are additional symmetries broken, for example, the top and bottom of the layers are distinguishable. That we do not have such a phase is argued by the fact that the transition appears to be 'typically' second order, i.e. shows the same second order behaviour in a number of homologues and the transition between a ($D_{\infty h}$) smectic A can be 'typically' second order by Landau analysis to only the smectic C phase among the tilted phases. Of course, if the smectic A phase is a ferroelectric ($C_{\infty h}$) smectic A_p phase then a typically second order transition would be expected to be only a smectic C_p phase. Thus, the major possibilities for this transition would be a smectic A to C or a smectic A_p to smectic C_p transition. The observance of typical focal conic textures in the smectic A and C phases which would require gradients of polarization in such polar phases supports the former rather than the latter. A large polarization would give a large energy cost—in the absence of Debye–Hückel screening in an effectively infinite elastic constant and the presence thereof of large elastic constants [5] which would be expected to change the textures.

Additionally, when the sample was highly tilted, the pattern observed resembled that of the 'transitional' pattern. Thus, this texture seems to be the result of the director tilting slowly and the slide not being completely flat giving a texture that was difficult to characterize. On cooling, the fuzzy light–dark boundaries seen in the transitional texture become sharper but remain in the same location as the temperature is decreased, while the remainder of the typical smectic C schlieren pattern appears. This is also consistent with the occurrence of additional tilting giving the more clearly identifiable features of the smectic C schlieren texture.

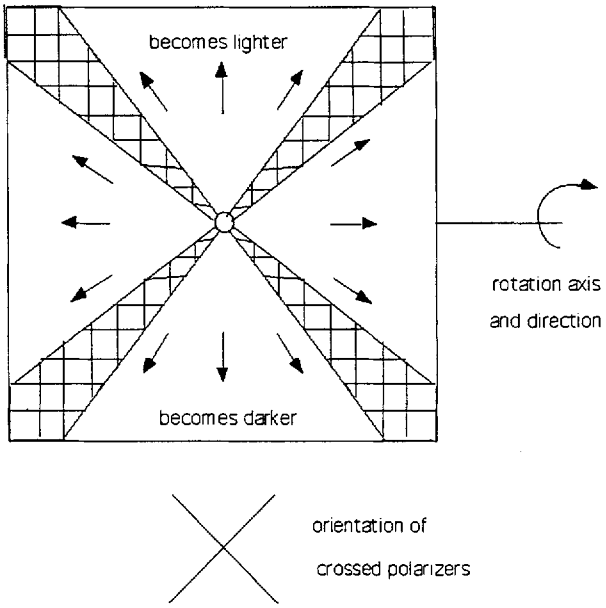


Figure 3. Figure showing the charge +1 dislocation characterized as discussed in the text. Cross-hatched region shows the dark portion of the fourfold cross as observed when the sample is untilted. The polarizers were at 45° to the horizontal or vertical as shown below the figure. The slide was rotated in the horizontal plan. The arrows show the hypothesized smectic C director configuration, consistent with the experimental observations discussed in the text, with the arrow showing the projection of the molecular axis onto the plane of the slide and the head of the arrow on the side of the molecule which is closest to the observer (points out of the paper).

Figure 2. DSC scans for compound **1** with $X = C_7H_{15}$ $Z = (CH_2)_7$ and $Y = C_9H_{19}$. (*a*) Heating at 10°$^{-1}$min^{-1} and (*b*) cooling at 10°$^{-1}$min^{-1}.

This smectic A–C transition has been studied more extensively by X-ray crystallography which shows an increasing layer spacing in the temperature range for the smectic A–C transition which is difficult to reconcile with these conclusions. Results of these studies will be reported elsewhere.

4. Experimental

4.1. *Materials and analysis*

The THP ethers **11** were prepared using the method described earlier [6]. The synthesis and properties for both the ether with $n=2$ and 7 were reported earlier [7, 8]. Purification of the crude ethers was by immediate distillation. Although these could be used in subsequent reactions, further purification was possible by flash chromatography on silica gel using a 50 per cent CH_2Cl_2 in hexane solution containing 1 per cent Et_3N as the solvent. The ether containing fractions were detected by GC. These purified THP ethers seemed to be more stable but as a precaution, were stored under N_2 at 5° until needed. Amberlite IR-120 (plus) ion exchange resin was used to remove the THP group from the diester **16**. The NaH (80 per cent in oil) was washed with hexane immediately before using to remove the oil. DMF was dried over Linde molecular sieves 4 Å and THF distilled over LAH prior to use. Anhydrous Na_2SO_4 was used to dry all organic extracts. TLC data were obtained using Anal-Tech silica gel GHLF uniplates with UV light and I_2 as detectors. Flash chromatography was done using Mallincrodt silica gel (230–400 mesh) under N_2 (4–15 psi) by the method previously described [9]. A Waters Delta Prep 3000 Instrument with a Burdick–Jackson silica gel column was used to obtain HPLC data. Gas–liquid chromatography was done using a Hewlett–Packard 5890 Series 2 instrument equipped with a 5 mm methyl silicone gum column using a temperature gradient of 50–225° and a flow rate of He of 20° min^{-1}. All compounds were purified by recrystallization and/or flash chromatography until they showed only one spot by TLC, no impurities in their NMR spectrum and constant melting points with a temperature range $\leqslant 3°$. A Thomas–Hoover melting point apparatus was used to determine melting points (°C) for all non-mesogenic materials; all of which are corrected. Melting points are not provided for mesomorphic materials since the more accurate microscopic transition temperatures are given. All temperatures are given as °C.

IR spectra (cm^{-1}) were run either as a film or in mineral oil on a Nicolet Magna FT–IR Spectrometer 550. NMR spectra were obtained in $CDCl_3$ (unless otherwise noted) using a Varian Gemini 200 instrument with TMS as the internal standard. Chemical shift values are in δ and coupling constants in Hz. Aromatic protons were differentiated as 'be' for benzene ring and 'biph' for biphenyl, using the same numbering system as used in the nomenclature for these compounds. When necessary, 2-D NMR was used to confirm peak assignments. Elemental analyses were obtained from Oneida Research Services, Inc., Whitesboro, NY. The mass spectrum was run on a Kratos KOMPACT MALDI-III using a Sun SPARC classic data base and a matrix of the sample in 2,5-dihydroxybenzoic acid (10 mg ml^{-1}) in H_2O/MeCN (2:3) with the instrument internally calibrated using gramicidin S.

Transition temperatures (°C) were determined using a Leitz Laborlux 12 POL polarizing microscope fitted with a modified and calibrated Mettler FP-2 heating stage at a heating rate of 2° min^{-1} and a Bertrand lens for conoscopic studies. Crystallization temperatures were obtained by cooling the melt at 2° min^{-1} until crystals formed to insure that all mesophases had been observed before this temperature. These crystals were reheated to obtain the melting temperature and to confirm that these were not mesophases. Whenever possible, mesophases were identified by their typical textures as reported earlier [10, 11]. Abbreviations used are Cr = crystals, I = isotropic liquid, N = nematic and S_A and S_C are for smectics A and C respectively. Transition temperatures were determined for all rod-like molecules including most of the intermediates. DSC scans were run at 5–10° min^{-1} using a Perkin–Elmer DSC-7 instrument.

4.2. *Synthesis*

4.2.1. *4′-Alkylphenyl-4-benzyloxybenzoate 7 $R = C_5H_{11}$*

The synthesis of this homologue was reported earlier [4]. We used the typical carbodiimide esterification method to prepare our compound [12] except the reaction time was longer (refluxed 6·5 h, stirred at RT 17 h). The crude product was purified by flash chromatography using 30 per cent CH_2Cl_2 (20 per cent would probably work better) in hexane as the eluting solvent followed by recrystallization from MeCN giving a yield of 61·4 per cent. Transition temperatures were 120·9–125·7° (Cr–I) and 102·9° (I–Cr) (lit. [4] m.p. 124°) and TLC ($CHCl_3$) $R_f = 0{\cdot}73$. IR and NMR data agreed with published data.

4.2.1.1. $R = C_9H_{19}$

This homologue was prepared in the same manner without chromatographic purification in a yield of 85·3 per cent after recrystallization from abs EtOH. Transition temperatures were 114·1–116·3° (Cr–I) and 99·2° (I–Cr).

4.2.2. *4′-Alkylphenyl-4-hydroxybenzoate 6 $R = C_5H_{11}$*

Hydrogenolysis of the benzyl ether **7** in HOAC to this phenol, was reported earlier [4]. We used a different solvent as described below for the C_9 homologue. The phenol **6** was isolated in a 50·9 per cent yield (recovery of 49·1 per cent of the starting material indicated the reaction time was too short) after flash chromatography (CH_2Cl_2) followed by recrystallization from CCl_4. m.p. 134·5° (softens, microscopic studies suggest the presence of two crystal forms) 142° (lit. [4] m.p. = 142°).

4.2.2.1. *$R = C_9H_{19}$*

A solution of the benzyl ether **7** ($R = C_9H_{19}$) (10·8 g, 25·0 mmol) in THF (200 ml) containing two drops of concentrated H_2SO_4 and 10 per cent Pd-C (1·09 g) was hydrogenated at 50 lb in^{-2} at 30° for 18 h and then filtered through Celite. The filtrate was rotovaped to give 8·4 g (>100 per cent) of the crude phenol. Recrystallization of this material from hexane gave 7·99 g (93·9 per cent) of the purified phenol **6** ($R = C_9H_{19}$): Transition temperatures 124·6–125·5° (Cr–I) and 122·7–122·3° (I–Cr) and NMR 8·09 (d, 2, $J=8{\cdot}59$, ArH *ortho* to CO_2), 7·22 (d, 2, $J=8{\cdot}51$, ArH *ortho* to R), 7·09 (d, 2, $J=8{\cdot}14$, ArH *ortho* to OCO), 6·87 (d, 2, $J=8{\cdot}62$, ArH *ortho* to OH), 5·99 (s, 1, OH), 2·61 (t, 2, $J=7{\cdot}70$, $ArCH_2$), 1·61 (quint, 2, $J=7{\cdot}14$, $ArCH_2\underline{CH_2}$, 1·26 (br, s, 12, $6CH_2$) and 0·88 (t, 3, $J=6{\cdot}27$, CH_3).

4.2.3. *4″-Pentylphenyl-4-(4′-benzyloxybenzoyloxy) benzoate **8** ($R = C_5H_{11}$)*

This ester was prepared by esterification of the acid **4** with the phenol **6** using the standard carbodiimide procedure [11] but with a reflux time of 11 h. followed by stirring at RT for 18 h. The crude material was purified by flash chromatography using 50–100 per cent CH_2Cl_2 in hexane followed by recrystallization from THF to give 5·39 g (83·2 per cent) of the purified ester **8** ($R = C_5H_{11}$): TLC ($CHCl_3$) $R_f=0{\cdot}69$; IR 1740 (str, CO_2Ar) and 1600, 1500 (str, Ar); NMR 8·27 (d, 2, $J=8{\cdot}79$, ArH_2) 8·17 (d, 2, $J=8{\cdot}88$, $ArH_{2'}$), 7·50–7·41 (m, 5, C_6H_5), 7·35 (d, 2, $J=8{\cdot}71$, ArH_3), 7·23 (d, 2, $J=7{\cdot}98$, $ArH_{3''}$), 7·12 (d, 2, $J=7{\cdot}69$, $ArH_{2''}$), 7·07 (d, 2, $J=8{\cdot}83$, $ArH_{3'}$), 5·17 (s, 2, OCH_2), 2·63 (t, 2, $J=7{\cdot}65$, $ArCH_2$), 1·64 (quint, 2, $J=5{\cdot}94$, $ArCH_2\underline{CH_2}$), 1·45–1·25 (m, 4, $2CH_2$) and 0·90 (t, 3, $J=6{\cdot}44$, CH_3) and transition temperatures 154·1–156·6° (Cr–N), 220·6–220·7° (N–I), 148·7–148·9° (S_A–N) and 123·4° (S_A–Cr).

4.2.4. *4-Hydroxybenzoic acid, 4′-(4″-Pentylphenoxycarbonyl)phenyl esters **10** ($R = C_5H_{11}$)*

The same hydrogenolysis procedure as used for the benzyl ether **7** was used except no acid was added to the solvent to avoid ester cleavage. The crude product was recrystallized from hexane to give the phenol **10** ($R = C_5H_{11}$) in a 70·3 per cent yield: TLC ($CHCl_3$) $R_f=0{\cdot}18$; IR 3400 (str, OH), 1720, 1700 (str, CO_2R) and 1600, 1590, 1520 (str, Ar); NMR 8·27(d, 2, $J=8{\cdot}67$, ArH_2), 8·10 (d, 2, $J=8{\cdot}88$, $ArH_{2'}$) 7·35 (d, 2, $J=8{\cdot}67$, ArH_3), 7·23 (d, 2, $J=9{\cdot}04$, $ArH_{3''}$), 7·12 (d, 2, $J=8{\cdot}62$, $ArH_{2''}$), 6·87 (d, 2, $J=8{\cdot}79$, $ArH_{3'}$), 6·21, (s, 1, OH), 2·62 (t, 2, $J=7{\cdot}65$, $ArCH_2$), 1·74–1·52 (m, 2, $ArCH_2\underline{CH_2}$) 1·45–1·23 (m, 4, $2CH_2$) and 0·89 (t, 3, $J=6{\cdot}39$, CH_3) and transition temperatures 170·3–173·3° (Cr–N), 216° (N–I, polymerizes) and 152·2° (N–Cr).

4.2.5. *(4′-Pentylphenyl)-4-[7-(tetrahydropyran-2-yloxy)-heptyloxy]benzoate **13** ($R = C_5H_{11}$)*

Sodium hydride was slowly added to a stirred solution of the phenol **10** ($R = C_5H_{11}$) at RT followed by a dropwise addition of the bromide **11**. This reaction mixture was stirred at RT for 33 h, poured into H_2O and the insoluble solid removed by filtration, washed with H_2O and dried (422 mg). An attempt was made to dissolve this material in $CHCl_3$ and extract with H_2O, but an emulsion formed which was difficult to separate. From this emulsion, 240 mg of material was isolated which showed many spots by TLC ($CHCl_3$) major spots $R_f=0{\cdot}24$, 0·46 and 0·61. This material was flash chromatographed to give 190 mg of a light yellow solid showing a primary spot with $R_f=0{\cdot}29$ and two fainter spots. A NMR spectrum suggested that this material was primarily the ester **13**: IR 1729·4 (str CO_2Ar), 1617·6 (str, Ar) and 1512 (str, Ar); NMR 8·11 (d, 2, $J=8{\cdot}95$, ArH *ortho* to CO_2Ar), 7·20 (d, 2, $J=8{\cdot}67$, ArH *ortho* to R), 7·07 (d, 2, $J=8{\cdot}67$, ArH *ortho* to OCOAr), 6·94 (d, 2, $J=8{\cdot}95$, ArH *ortho* to OR), 4·58–4·51 (m, 1, CH), 4·02 (t, 2, $J=6{\cdot}50$, $ArOCH_2$), 3·94–3·63 (m, 2, OCH_2), 3·56–3·30 (m, 2, OCH_2), 2·60 (t, 2, $J=7{\cdot}65$, $ArCH_2$), 1·84–1·22 (m, 22, C_3H_6, C_5H_{10} and $THPH_{3-5}$) and 0·88 (t, 3, $J=6{\cdot}55$, CH_3). Microscopic studies showed a small amount of impurity, no mesophases and transition temperatures 39·2–43·1° (Cr–I) and 26·0° (I–Cr).

4.2.6. *4-[7-Tetrahydropyran-2-yloxy)]heptyloxybenzoic acid methyl ester **14a***

Sodium hydride (1·87 g, 0·06 mol) was slowly added to a stirred solution of the phenol **2** (9·5 g, 0·06 mol) in anhydrous DMF (77 ml) at RT. Stirring was continued for 35 min giving a clear liquid. To this was added dropwise a solution of the bromide **11a** (17·43 g, 0·06 mol) in anhyd DMF (10 ml), the reaction mixture stirred at 80° for 24 h, cooled to RT and the DMF removed *in vacuo*. The remaining material was dissolved in H_2O and extracted with $CHCl_3$. The organic layer was washed with 5 per cent aq KOH and H_2O, dried, filtered and the filtrate rotovapoured to give 21·0 g (96·1 per cent) of the crude ether. Purification of this material by recrystallization from abs ETOH gave 17·1 g (78·4 per cent) of the ether **14a**: m.p. 60–63°; TLC ($CHCl_3$) $R_f=0{\cdot}23$; IR 1724 (str, CO_2R) and 1613, 1510 cm^{-1} (str, Ar) and NMR 7·98 (d, 2, $J=8{\cdot}63$, ArH *ortho* to CO_2Me), 6·90 (d, 2, $J=8{\cdot}63$, ArH *ortho* to OR), 4·58 (t, 1, $J=$

2·06, CH), 4·00 (t, 2, $J=6{\cdot}47$, $ArOCH_2$), 3·88 (s, 3, CO_2Me), 3·85–3·67 (m, 2, OCH_2), 3·58–3·31 (m, 2, OCH_2), 1·81 (quint, 2, $J=5{\cdot}46$, $ArOCH_2\underline{CH_2}$) and 1·75–1·33 (m, 14, C_4H_8 and $THPH_{3-5}$).

The *ether* ***14b*** was prepared in the same manner in a crude yield of 85·9 per cent. Purification was by flash chromatography using 80–100 per cent CH_2Cl_2 to give this ether as a yellow liquid (53·0 per cent). NMR data differed only in the aliphatic region: 4·71 (t, 1, $J=3{\cdot}40$, CH), 4·27–4·18 (m consisting of q or 2t, 2, $ArOCH_2$), 4·18–3·99 (m, 1–2, OCH_2), 3·96–3·75 (m with s; 5–6; CH_3, $THPOCH_2$, OCH_2), 3·60–3·47 (m, 1) and 1·94–1·45 (m, 6, $THPH_{3-5}$). GLC showed the following peaks: $t_R=3{\cdot}27$ (0·71 per cent **11a**), 4·06 (2·2 per cent), 6·12 (9·25 per cent, **15a**) and 8·73 (86·76 per cent, **14b**).

4.2.7. *4-[(2-Hydroxyethyl)oxy]benzoate* ***15a***

To a stirred mixture of ion exchange resin (1·40 g) in MeOH (200 ml) was added dropwise a solution of the ether **14b** (12·10 g), 0·04 mol) in MeOH (200 ml). This solution was heated at 45° for 2 h, stirred at RT for 2 h and then filtered. The filtrate was rotovapoured to give 9·67 g of the crude product. Recrystallization of this material from benzene gave 6·81 g (80·7 per cent) of the purified alcohol **14**: m.p. 65–68·5° (lit. [13] m.p. = 65–66°); TLC ($CHCl_3$) $R_f=0{\cdot}11$; IR 3300 (str, OH), 1730 (str, CO_2R), 1620 (str, Ar) and 1510 (med, Ar); NMR 7·99 (d, 2, $J=9{\cdot}12$, ArH *ortho* to CO_2), 6·93 (d, 2, $J=8{\cdot}95$, ArH *ortho* to O*R*), 4·14 (t, 2, $J=4{\cdot}21$, $ArOCH_2$), 3·99 (t, 2, $J=4{\cdot}20$, $\underline{CH_2}OH$), 3·89 (s, 3, CH_3) and 2·27 (br, s, 1, OH) and GLC $t_R=6{\cdot}12$ (100 per cent).

4.2.8. *4-[7-(Tetrahydropyran-2-yloxy)]ethoxyethoxybenzoic acid methyl ester* ***14c***

The alcohol **15** was alkylated with the bromide **11b** in the same manner as the phenol **2** giving the crude ether **14c** as a yellow liquid in a 78·8 per cent yield: TLC $R_f=0{\cdot}13$. A NMR spectrum showed that this material contained an impurity. Since it was felt that purification would be easier by recrystallizing the acid, this material was not purified (see discussion in the text).

4.2.9. *4-[7-(Tetrahydropyran-2yloxy)]heptyloxybenzoic acid* ***17a***

To a stirred solution of the ester **14a** (16·8 g, 0·05 mol) in abs EtOH (89 ml) at RT was added a solution of NaOH (6·0 g, 0·15 mol) in H_2O (71 ml). This reaction mixture was refluxed for 5 h, stirred at RT for 17 h and rotovapoured. Water was added to the remaining material. This mixture was extracted with Et_2O, the layers separated and the aqueous layer added to a solution of dilute NH_4Cl. The solid gel-like precipitate was removed by filtration, washed with H_2O and dried to give the crude acid (> 100 per cent). This material was extracted with hot abs EtOH, the insoluble solid removed by filtration (7·0 g, water soluble), H_2O added to the filtrate and the precipitate removed by filtration, washed with H_2O and dried to give 9·05 g of the desired acid. Additional material (5·91 g) was obtained from the filtrate by adding 3 M HCl. Both crops were combined and recrystallized from hexane to give 11·78 g (72·9 per cent) of the purified acid **17a**: m.p. 73·0–76·5°; TLC ($CHCl_3$)$R_f=0{\cdot}03$, IR 3000–2200 (br, acid), 1690 (str, CO_2H) and 1603, 1515 cm^{-1} (str, med Ar); NMR ($CDCl_3$) 8·05 (d, 2, $J=8{\cdot}87$, ArH *ortho* to CO_2H), 6·92 (d, 2, $J=8{\cdot}91$, ArH *ortho* to O*R*), 4·64–4·55 (t or m, 1, CH), 4·02 (t, 2, $J=6{\cdot}45$, 2, $ArOCH_2$), 3·96–3·67 (m, 2, OCH_2), 3·59–3·31 (m, 2, OCH_2) and 1·92–1·32 (m, 16, $THPH_{3-5}$ and C_5H_{10}); transition temperatures 78·9–80·0° (Cr–I), 76·7° (N–I), 74·2–74·1° (N–Cr) and analysis calculated for $C_{19}H_{28}O_5$: C 67·83, H 8·39; Found C 67·93 H 8·38 per cent.

The ester **14c** was hydrolysed in the same manner to the acid **17c** except the reflux time was 17·5 h followed by stirring at RT for 5 h. The aqueous extract was acidified with concd HCl to give 4·64 g of the crude acid **17c**. This material was recrystallized from EtOAc to give 4·03 g of the 'purified' acid. This acid was also isolated as the first crop in the EtOAc recrystallization: m.p. 165° (lit [14] m.p. = 177°); IR 3300–2500 (br, CO_2H), 1683 (str, CO_2H), 1611 (str, Ar), 1510 cm^{-1} (med, Ar); NMR ($CDCl_3$/DMSO) 7·98 (d, 2, $J=8{\cdot}79$, ArH *ortho* to CO_2H), 6·94 (d, 2, $J=8{\cdot}96$, ArH *ortho* to O*R*), 4·13 (t, 2, $J=4{\cdot}76$, $ArOCH_2$), 3·94 (t, 2, $J=4{\cdot}68$, $\underline{CH_2}OH$). Later esterification indicated that *c.* 31·3 per cent of this material was the alcohol acid **15b** and the remainder the desired acid **17c** (54·2 per cent yield). Transition temperatures 80·1–83·5° (Cr_c–I) and 77·2° (I–Cr).

4.2.10. *4″-(Nonylphenyl-4-[4′-(7-(tetrahydropyran-2-yloxy))heptyloxybenzyloxybenzoyloxy]-benzoate* ***16a*** *($R = C_9H_{19}$)*

The standard carbodiimide method [11] with the acid **17a** and the phenol **6** ($R = C_9H_{19}$) was used but with a reflux time of 18 h. The crude product (99·9 per cent) was recrystallized from abs EtOH (We now believe that flash chromatography with 90 per cent CH_2Cl_2 in hexane followed by recrystallization from abs EtOH would have been a better approach) to give 13·5 g (92·9 per cent) of the purified diester **16a**: TLC ($CHCl_3$) $R_f=0{\cdot}16$; IR 1740, 1734, 1732 (str, CO_2Ar) and 1610, 1514 (med, Ar); NMR 8·28 (d, 2, $J=8{\cdot}80$, ArH_2), 8·16 (d, 2, $J=8{\cdot}91$, $ArH_{2'}$), 7·36 (d, 2, $J=8{\cdot}71$, ArH_3), 7·24 (d, 2, $J=10{\cdot}01$, $ArH_{3''}$), 7·12 (d, 2, $J=8{\cdot}51$, $ArH_{2''}$), 6·99 (d, 2, $J=8{\cdot}95$, $ArH_{3'}$), 4·58 (t or m, 1, CH), 4·05 (t, 2, $J=6{\cdot}47$, $ArOCH_2$), 3·96–3·69 (m, 2, OCH_2), 3·59–3·33 (m, 2, OCH_2), 2·63 (t, 2, $J=7{\cdot}65$, $ArCH_2$), 2·00–1·19 (m, 30, $THPH_{3-5}$,

C_5H_{10} and C_7H_{14}) and 0·89 (t, 3, J=6·41, CH_3) and transition temperatures 72·9–73·7° (Cr–S_c), 106·3 (Cr–N), 130·0–130·1 (N–I) and 46·9 (S_c–Cr).

The mixture of the acids **17 b** and **c** was treated in the same manner except the reaction mixture was extracted only with H_2O. Purification of the product by flash chromatography using 90–100 per cent CH_2Cl_2 in hexane followed by recrystallization from abs EtOH gave what was initially thought to be the ester **16 c**, but later shown to contain at least 26·8 wt % of the ester **16 b**: TLC ($CHCl_3$) R_f=0·03, IR 1744 (str, CO_2R), 1739 (str, CO_2Ar) and 1611, 1510 (str, Ar); NMR($CDCl_3$) 8·28 (d, J=8·51, 2, ArH_2), 8·16 (d, 2, J=8·71, $ArH_{2'}$), 7·36 (d, 2, J=8·22, ArH_3), 7·24 (d, 2, J=9·24, $ArH_{3''}$), 7·12 (d, 2, J=8·14, $ArH_{2''}$), 7·03 (d, 2, J=8·51, $ArH_{3'}$), 4·66 (t, 1, J=?, CH), 4·25 (t, 2, J=4·58, $ArOCH_2$), 4·08–3·83 (m or 2t, 4, 2 OCH_2CH_2O), 3·78 (t, 2, J=4·56, $THPOCH_2$), 3·72–3·60 (m, 1, $THPH_{6eq}$), 3·60–3·46 (m, 1, $THPH_{6ax}$), 2·63 (t, 2, J=7·59, $ArCH_2$), 1·91–1·46 (m, 8, $ArCH_2\underline{CH_2}$ and $THPH_{3-5}$), 1·28 (br, s, 12, C_6H_{12}), 0·89 (t, 3, J= 6·15, CH_3) and transition temperatures 57·6–58·0° (Cr–S_A), 96·7–96·8° (S_A–N), 124·1–124·4° (N–I), 48·1–46·1° (S_A–Cr_2), 49·9 (Cr_2–Cr_1 on reheating). HPLC (10 per cent EtOAc–CH_2Cl_2) later confirmed the presence of two esters: 78·4 per cent **16 c** and 19·75 per cent **16 b**.

4.2.11. *4''-Nonylphenyl-4-[4'-(7-hydroxy)heptyloxybenzyloxybenzoyloxy)benzoate **18 a***

A solution of the THP ether **16 a** (12·61 g, 0·02 mol) in MeOH (120 ml) and THF (240 ml) containing ion exchange resin (2·48 g) was stirred and heated near the reflux temperature for 18 h and then refluxed for 3 h. The cooled reaction mixture was filtered and the filtrate rotovapoured to give 11·05 g (>100 per cent) of the crude alcohol. Recrystallization of this material from abs EtOH gave 10·8 g (98·5 per cent) of the purified alcohol **18 a**: TLC ($CHCl_3$) R_f=0·17, IR 3427, 3388 (med–str, OH) 1743, 1730 (str, CO_2Ar), 1611 cm^{-1} (med, Ar); NMR ($CDCl_3$) 8·28 (d, 2, J=8·80, ArH_2), 8·16 (d, 2, J=8·92, $ArH_{2'}$), 7·36 (d, 2, J=8·75, ArH_3), 7·24 (d, 2, J=9·81, $ArH_{3''}$), 7·12 (d, 2, J=8·47, $ArH_{2''}$), 6·99 (d, 2, J=9·00, $ArH_{3'}$), 4·06 (t, 2, J=6·50, $ArOCH_2$), 3·66 (t, 2, J=6·43, $HO\underline{CH_2}$) 2·63 (t, 2, J=7·65, $ArCH_2$) 1·84 (quint, 2, J=7·33, $ArOCH_2\underline{CH_2}$), 1·72–1·20 (m, 22, C_4H_8 and C_7H_{14}) and 0·88 (t, 3, J=6·36, CH_3).

The THP ether **16 c** was treated in a similar manner. The reaction mixture was stirred at 35–40° for 24 h, an additional (0·5 g) resin added and refluxed for 7 h. Purification of the crude product by flash chromatography using 4 per cent EtOAc in CH_2Cl_2 gave two major fractions: fraction 1 (360 mg, 26·9 per cent of the total product); TLC ($CHCl_3$) R_f=0·08; IR 3350 (wk–med, OH), 1744, 1738 (str, CO_2Ar), 1611, 1513 (str, Ar); NMR 8·20 (d, 2, J=8·71, ArH_2), 8·10 (d, 2, J=8·95, $ArH_{2'}$), 7·28 (d, 2, J=8·67, ArH_3), 7·16 (d, 2, J=8·87, $ArH_{3''}$), 7·04 (d, 2, J=8·42, $ArH_{2''}$), 6·95 (d, 2, J=8·96, $ArH_{3'}$), 4·11 (t, 2, J=3·56, $ArOCH_2$), 3·95 (t, 2, J=3·38, $\underline{CH_2}OH$), 2·55 (t, 2, J=7·50, $ArCH_2$), 1·55–1·20 (m, 2, $ArCH_2\underline{CH_2}$), 1·40–0·50 (m, 12, C_6H_{12}), 0·81 (t, 3, J= 5·68, CH_3) indicates this is **18 b** with transition temperatures 132·0–133, 6° (Cr–S_c), 133·1–134·40 (S_c–S_A), 192·5–192·7° (S_A–N), 193·4–195·1° dec (N–I) and 124·2° (N–Cr) and fraction 2 (984 mg, 66·5 per cent yield of **18 c**) TLC ($CHCl_3$) R_f=0·05, IR (same as fraction 1); NMR 8·28 (d, 2, J=8·63, ArH_2), 8·17 (d, 2, J=8·83, $ArH_{2'}$), 7·36 (d, 2, J=8·80, ArH_3), 7·24 (d, 2, J=9·32, $ArH_{3''}$), 7·12 (d, 2, J=8·42, $ArH_{2''}$), 7·03 (d, 2, J=8·87, $ArH_{3'}$), 4·25 (t, 2, J=4·60, $ArOCH_2$), 3·92 (t, 2, J=4·56, $ArOCH_2\underline{CH_2}$), 3·80 (t, 2, J=4·13, $\underline{CH_2}$ CH_2OH), 3·70 (t, 2, J=4·29, $\underline{CH_2}OH$), 2·63 (t, 2, J=7·51, $ArCH_2$), 1·80 (br s, 1, OH), 1·63 (quint, 2, $ArCH_2\underline{CH_2}$), 1·27 (s, 12, C_6H_{12}) 0·88 (t, 3, J=6·41, CH_3) indicating that this fraction is **18 c** with transition temperatures ~60° (Cr_2–Cr_1), ~82° (Cr_1–S_c), 129·2–130·5° (S_c–S_A), 149·5° (S_A–N), 162·1–162·5° (N–I), 60° (S_c–Cr_1) and 50° (Cr_1–Cr_2).

4.2.12. *Synthesis of the esters **1**, 4'-alkyl/alkoxy-l,1'-biphenyl-4-carboxylate, 7-[4-((4-[(4-nonylphenoxy)carbonyl]phenoxy)carbonyl)phenolheptyl ester*

Both the DCC [11] and acid chloride [11] methods were tried with the latter giving higher yields. Best results were achieved by refluxing the reaction mixture for 48 h. Purification was done using flash chromatography with 30–60 per cent CH_2Cl_2 in hexane followed by recrystallization from CH_3CN/EtOAc. The biphenyl acid chloride was prepared by refluxing the acid **18** (Y= OH) with $SOCl_2$ for 24 h followed by removal of the $SOCl_2$. This crude acid chloride was used without purification.

Examples of characterization data for these esters are as follows: IR 1730, 1715 (str, esters), 1611, 1513 (wk, Ar). NMR spectra for $X=C_5H_{11}$, $Z=(CH_2)_7$, $Y=C_9H_{19}$: 8·28 (d, 2, J=8·67, $beH_{3'}$), 8·16 (d, 2, J=8·95, beH_3), 8·10 (d, 2, J=8·51, $biphH_3$), 7·66 (d, 2, J=8·30, $biphH_2$), 7·55 (d, 2, 8·26, $biphH_{2'}$), 7·36 (d, 2, J=8·67, $beH_{2'}$), 7·29 (d, 2, J=8·26, $biphH_{3'}$), 7·24 (d, 2, J=8·95, $beH_{3''}$), 7·12 (d, 2, J=8·55, $beH_{2''}$), 6·99 (d, 2, J=8·91, beH_2), 4·36 (t, 2, J=6·56, CO_2CH_2), 4·07 (t, 2, J=6·36, $beOCH_2$), 2·66 (t, 2, 6·96, $biphCH_2$), 2·62 (t, 2, J=5·78, $beCH_2$), 1·96–1·73 (m, 4, $CO_2CH_2\underline{CH_2}$ and $OCH_2\underline{CH_2}$), 1·73–1·43 (m, 8, $2ArCH_2\underline{CH_2}$, $CO_2(CH_2)_2$ $\underline{CH_2}$ and $O(CH_2)_2\underline{CH_2}$), 1·43–1·15 (m, 18, $biphC_2H_4$, $CO_2(CH_2)_3\underline{CH_2}$, beC_6H_{12}), 0·91 (t, 3, J=6·68, $biphCH_3$) and 0·89 (t, 3, J=6·76, $beCH_3$); $X=C_7H_{15}$, $Z=(CH_2)_2$ and $Y=C_9H_{19}$ differed only in the following CH_2 proton shifts: 4·74 (t, 2, J=4·52, CO_2CH_2), 4·43 (t, 2, J=4·62, beOCH_2), 1·78 1·61 (m, 4, be$CH_2\underline{CH_2}$) and 0·88 (t, 6, J=6·37, $2CH_3$); $R = C_7H_{15}$, $Z = (CH_2CH_2)_2O$ and $Y = C_9H_{19}$ differed from $Z = (CH_2)_2$ in the following CH_2 proton shifts: 4·54 (t, 2, J=4·62, CO_2CH_2), 4·26 (t, 2, J=4·40, beOCH_2), 3·97 (t, 4, J=4·44, $CO_2CH_2\underline{CH_2}O$, be$OCH_2\underline{CH_2}O$), 2·74–2·57 (m, 4, be$CH_2$) and $X = C_5H_{11}O$, $Z = (CH_2)_7$ and $Y = C_9H_{19}$: 8·28 (d, 2, J=8·51, be$H_{3'}$), 8·16 (d, 2, J=8·83, beH_3), 8·09 (d, 2, J=8·43, biphH_3), 7·62 (d, 2, J=8·14, biphH_2), 7·56 (d, 2, J=8·71, biph$H_{2'}$), 7·36 (d, 2, J=8·70, be$H_{2'}$), 7·24 (d, 2, J=8·84, be$H_{3''}$), 7·12 (d, 2, 8·34, be$H_{2''}$), 6·99 (d, 4, J=8·71, biph$H_{3'}$ and beH_2), 4·36 (t, 2, J=6·59, CO_2CH_2), 4·07 (t, 2, J=6·04, beOCH_2), 4·01 (t, 2, J=6·45, biphOCH_2), 2·63 (t, 2, J=7·51, beCH_2), 1·98–1·70 (m, 6, Oβ–CH_2), 1·70–1·14 (m, 24, remaining CH_2,s), 0·95 (t, 3, J=6·82, biphCH_3) and 0·89 (t, 3, J=6·95, beCH_3).

Additional characterization data for **1** ($X = C_7H_{15}$, $Z = (CH_2)_7$, $Y = C_9H_{19}$): the mass spectrum showed no parent peak at 852, but major fragments at 708, 513 (M-340 acylium ion), 247, 137 and 24; ^{13}C NMR 166·58, 164·61, 164·29, 163·71, 155·23, 148·71, 145·51, 143·16, 140·58, 137·22, 132·39, 131·72, 129·99, 129·31, 128·97, 128·82, 127·05, 126·75, 122·01, 121·25, 120·98, 114·36, 77·62, 76·98, 76·35, 68·21, 64·92, 35·60, 35·36, 31·87, 31·78, 31·44, 29·49, 29·27, 29·16, 28·98, 26·66, 25·97, 25·90, 22·64, 14·09 and 0·03. HPLC (CH_2Cl_2–hexane) showed a purity >99·8 per cent. Analysis calculated for $C_{56}H_{68}O_7$: C, 78·84; H, 8·03; Found C, 78·38; H, 78·19.

5. Conclusions

A variety of triesters of the type **1** were synthesized. All showed smectic A phases with various combinations of nematic and smectic C phases. Analogues with mid-chain lengths (C_5–C_9) showed an unusual transition from the smectic A to the smectic C phase. Textures in this region were similar to known smectic C textures. Extensive microscopic studies showed that this transitional texture is one resulting from a phase in which the optical axis is tilted relative to the smectic layers (which have previously formed.)

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