Chapter 3

Synthesis and mesomorphic properties of

[S]-[+]-1-methylheptyl-4-[4′-(6″-n-alkoxypyridine-3-carbonyloxy) benzoyloxy]benzoates

and

[S]-[+]-4-(1-methylheptyloxy)phenyl-4′-(6″-n-alkoxypyridine-3-carbonyloxy)benzoates

Chapter 3

A brief survey of the mesomorphic properties of compounds containing pyridyl moiety

In recent years the great scientific and practical interest in liquid crystals has generated an increasing requirement for compounds with specific properties. Therefore chemists are still searching for new structural units and structural variations in order to find compounds which are capable of meeting the specific requirements.

Since the discovery of antiferroelectric smectic ($S_{C_A^*}$) phase in MHPOBC by Chandani *et al.*[1] in 1989, considerable attention has been paid to the study of such materials with characteristic tristable switching useful in display devices.[2-8] As a consequence, a number of these types of materials have been synthesised and an attempt to correlate the molecular structure of the liquid crystals to the appearance of the $S_{C_A^*}$ phase has been carried out.[9] A recent review by Fukuda *et al.*[10] mentions more than 300 compounds exhibiting $S_{C_A^*}$ phase.

Goodby and his co-workers have demonstrated that the formation of the $S_{C_A^*}$ phase in chiral liquid crystalline systems depends strongly on the chirality of the molecules.[11-15] That is, the chiral materials with the $S_{C_A^*}$ phase generally occurs in compounds containing optically active octan-2-ol, 2-methyloctanoic acid, 1,1,1-trifluorooctan-2-ol etc.[1,16-18] where the chiral centre is relatively close to the central rigid-core of the molecule. In addition, the peripheral alkyl chain length on the external side of the chiral centre is relatively long. The antiferroelectric liquid crystals so far synthesised may be classified as those exhibiting four types of phase sequences.[19]

1. $S_{C_A^*}$ - $S_{C_\gamma^*}$ - S_C^*- $S_{C_\alpha^*}$ - S_A - Iso.
2. $S_{C_A^*}$ - S_C^* - S_A - Iso.
3. $S_{C_A^*}$ - S_A - Iso.
4. $S_{C_A^*}$ - Iso.

The phase sequence 1 has been observed in MHPOBC with extremely high optical purity.[1,6] The $S_{C_\gamma^*}$ and $S_{C_\alpha^*}$ phases in MHPOBC disappear by slightly decreasing the optical purity, resulting in the phase sequence 2.[18] The $S_{C_\alpha^*}$ phase is supposedly a biaxial S_A phase.[20,21]

A large number of liquid crystals contain phenyl, naphthyl and substituted biphenyl moieties in their core. Mesomorphic compounds with heterocyclic nuclei are still not numerous, although they are of interest because of greater possibilities in the variations of direction and magnitude of their permanent dipole moments and as a consequence of that in the variation of sign and magnitude of their dielectric anisotropy.

It has been observed that compounds containing pyridyl and pyrimidyl rings differ from those containing phenyl and other heterocyclic rings in that they appear to favour smectic behaviour and also that they have the lower crystal thermal stabilities, although it is normally considered that crystal thermal stability changes are unpredictable.[22]

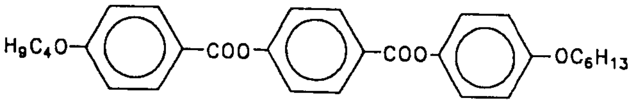
The changes in the mesomorphic properties on insertion of a hetero atom such as nitrogen into the core is illustrated by considering the two compounds **3.A** and 3.B.[23] The comparison shows that for compound 3.B, both melting and clearing temperatures are lower and the total temperature range of the mesophase is reduced. This compound exhibits smectic phases in addition to the nematic phase, whereas compound **3.A** shows thermally stable nematic phase only.

The position of the nitrogen in a ring also plays an important role in the formation of mesophases. For example consider the pairs of compounds 3.C, 3.D [24] and 3.E, 3.F.[25] In compound 3.C the nitrogen atom is at position-2 with respect to the carbon atom which is attached to the ester group and at position-3 in compound 3.D. Compound 3.C shows smectic phase in addition to the nematic phase, whereas compound 3.D shows only a nematic phase. In compound 3.E the nitrogen atom is at position-3 with respect to the carbon atom which is attached to the phenyl ring and at position-2 in compound 3.F. Compound 3.E shows only a smectic phase, where as compound 3.F shows smectic as well as nematic phases.

We can conclude from the above results that the trends shown in mesomorphic behaviour in compounds of this type cannot be interpreted simply in terms of changes in molecular diameter, net dipole moment or angle of twist between the rings due to difference between ortho-proton : ortho-proton and ortho-proton : hetero atom lone pair of electron interactions.

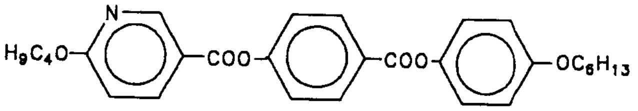
Chemically hetero atom in pyridine or related systems is known to behave similarly in many respects like an aromatic nitro group.[26] The hetero atom has a high electronegativity and make the ring deactivated relative to benzene. Electron withdrawal is most pronounced from positions 2 and 4, because of conjugative interactions with the hetero atom; but from the above results one cannot compare the nature of the mesophases directly.

It appears, however, that the use of a pyridyl ring as an aromatic component of aryl esters causes mesomorphic behaviour different to that of conventional aryl esters containing disubstituted phenyl rings. With a view to examine the influence of a pyridyl



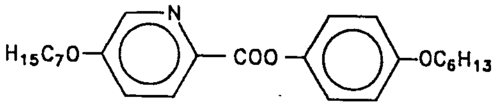
— 3.A

C 91.0 N 215.0 I



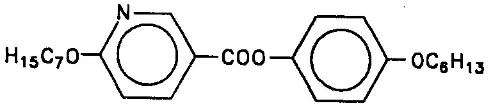
— 3.B

C 74.0 S_C 120.0 S_A 134.0 N 193.0 I



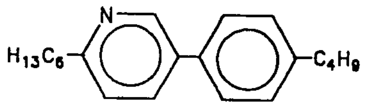
— 3.C

C 60.0 S_{C^*} 66.5 N 85.2 I



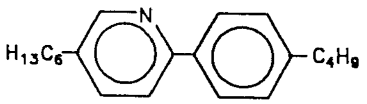
— 3.D

C 44.5 N 51.0 I



— 3.E

C 48.0 S 85.0 I



— 3.F

C 50.0 S 54.0 N 61.0 I

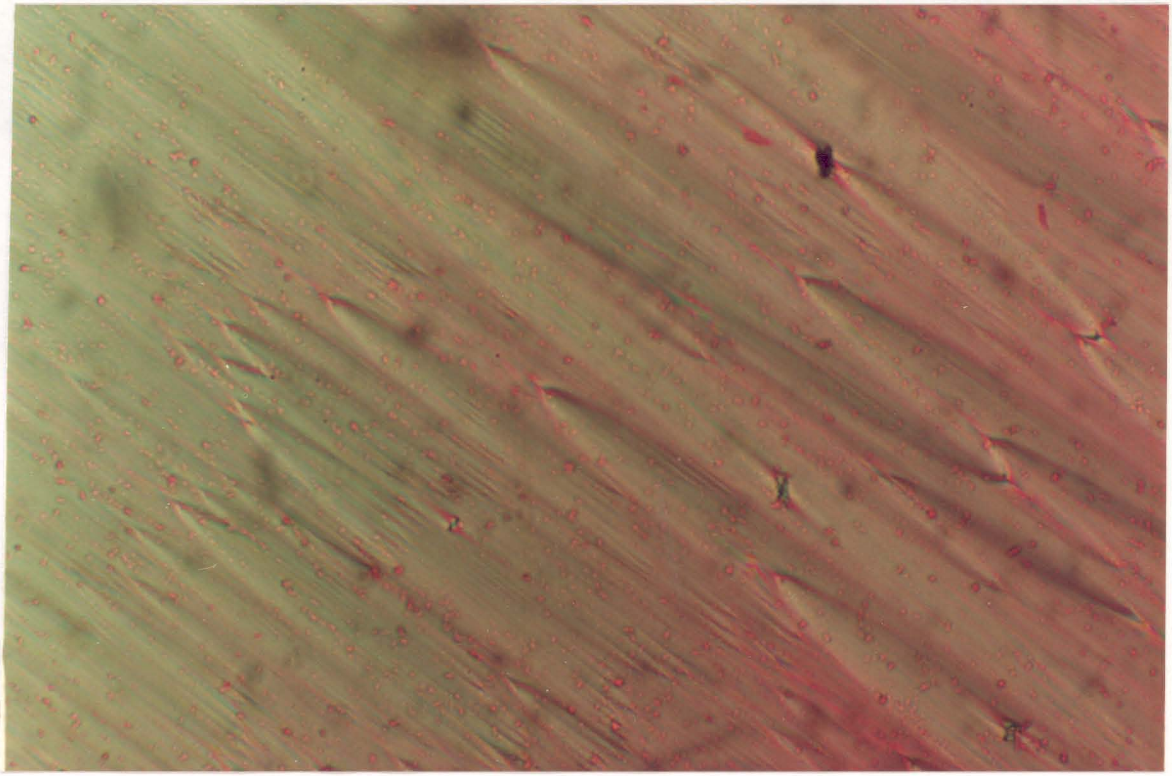


Plate 3.a. Photomicrograph of sample (3.G.5) showing S_A (aligned) phase at 100.0°C.

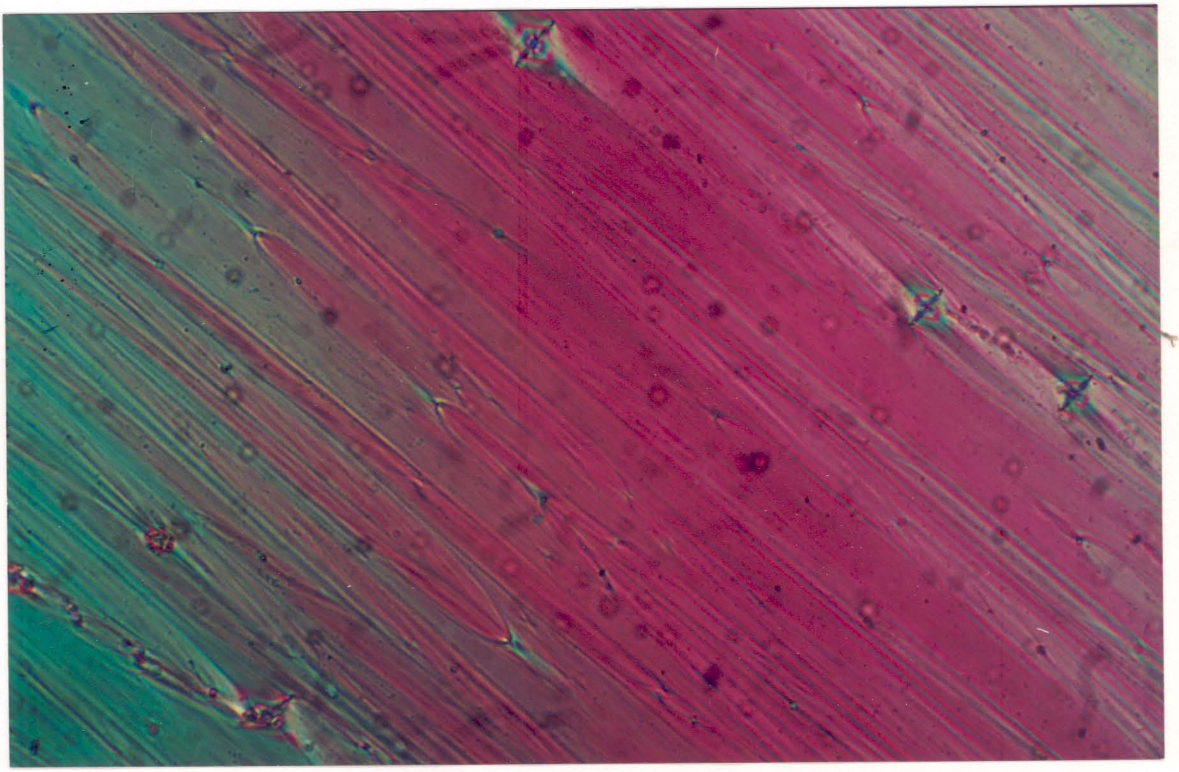


Plate 3.b. Photomicrograph of sample (3.G.5) showing $S_{C_\alpha}^*$ (aligned) phase at 87.0°C.

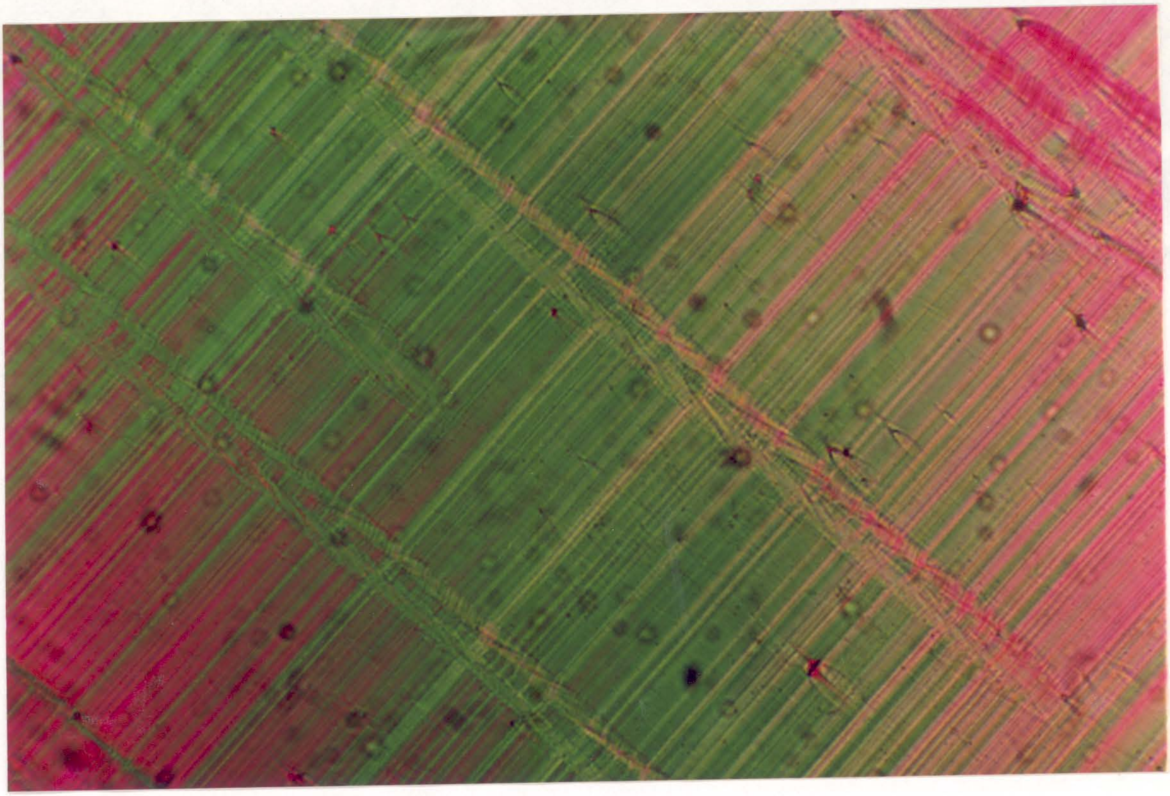


Plate 3.c. Photomicrograph of sample (3.G.5) showing S_C^* (aligned) phase at 83.0°C.

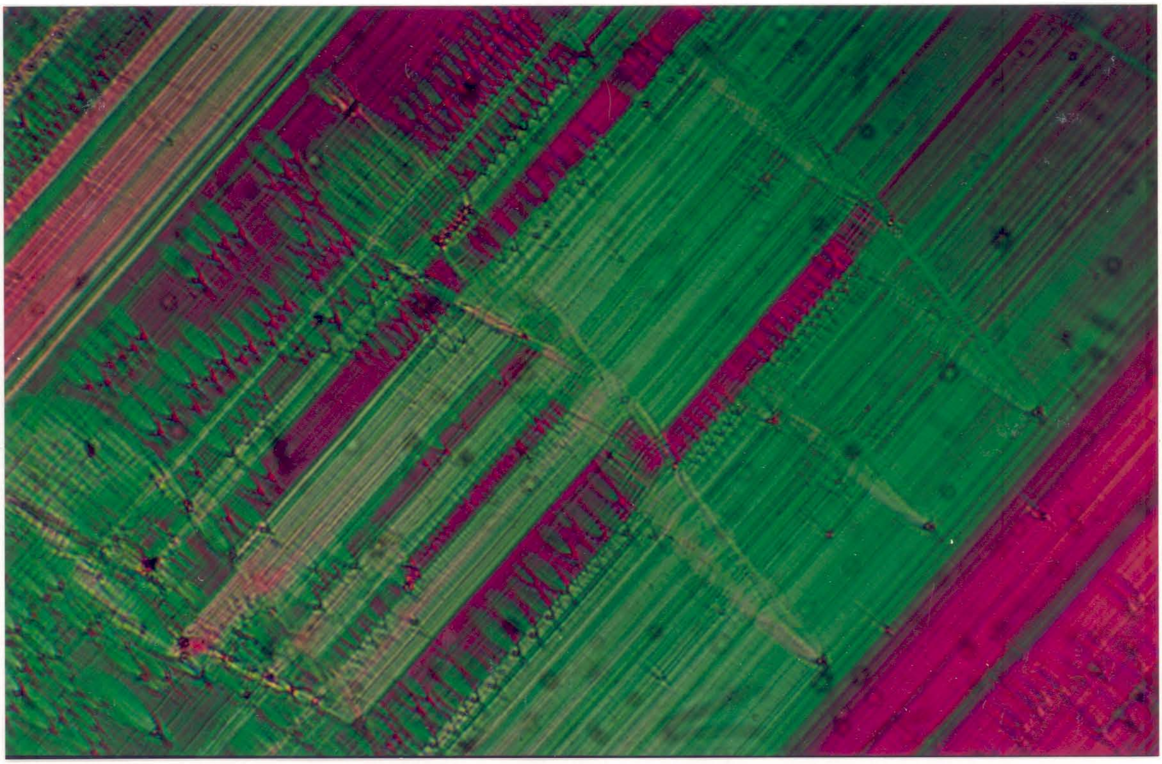


Plate 3.d. Photomicrograph of sample (3.G.5) showing $S_{C_A}^*$ (aligned) phase at 75.0°C.

moiety two homologous series of compounds have been synthesised and their mesomorphic behaviour investigated. We also present thermodynamic data obtained from these two series of structurally related compounds. An attempt is also made to relate the changes observed in mesophase thermal stability to these changes in molecular structure. These changes have been accomplished by replacing a phenyl ring in a known liquid crystalline compound by a pyridyl ring.

The direction and magnitude of dipole moment of an aromatic fluoro-group can be compared with the nitrogen in pyridine containing systems. The direction of electron flow in aromatic fluoro compounds is the same as that of the lone pair of electrons on the nitrogen atom. The size of the fluoro group is comparable with hydrogen and increase in breadth of the molecule by a fluoro substituent is negligible and these aspects will be discussed later.

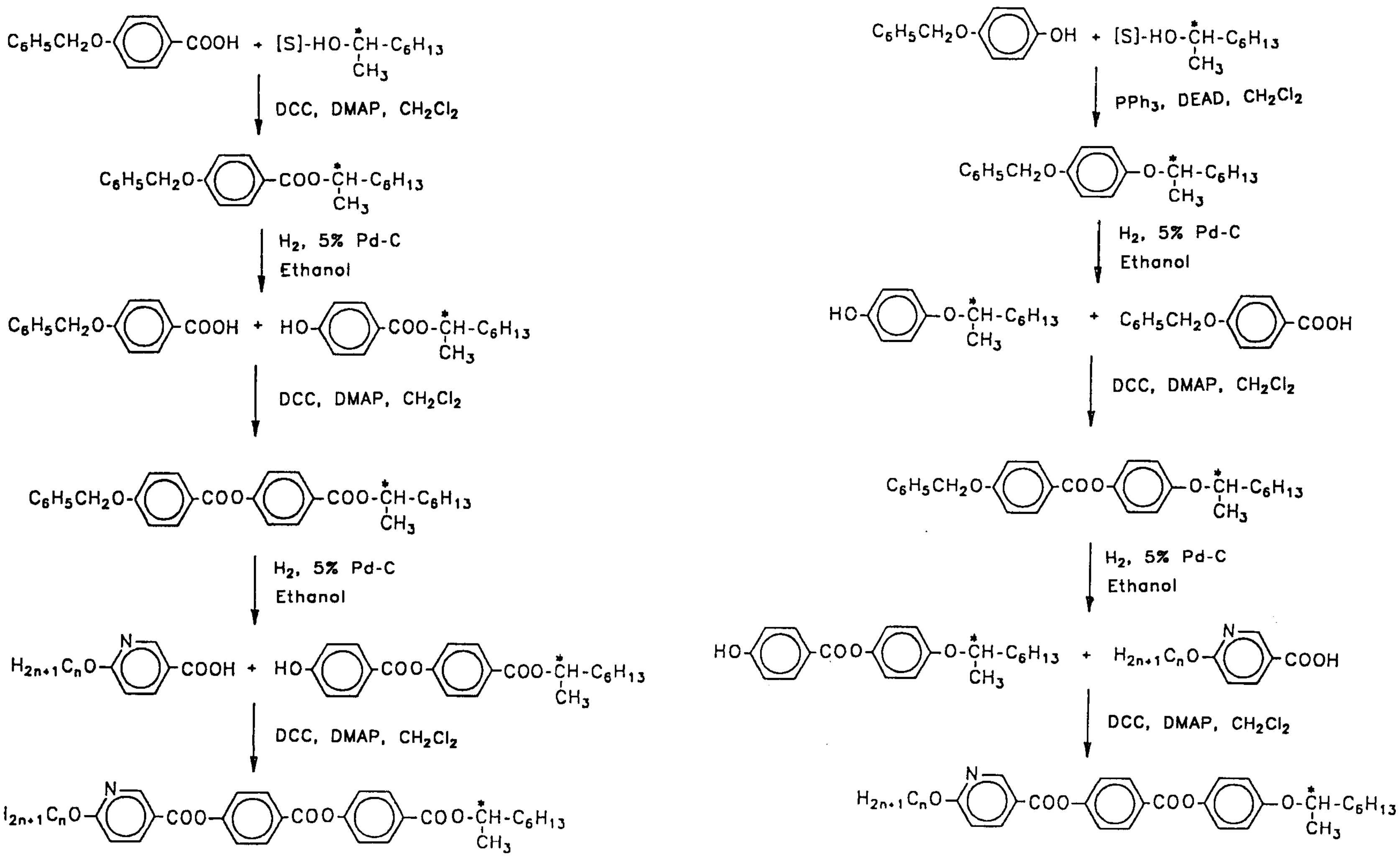
Results and discussion

As already mentioned, the advantage of substituting a pyridyl ring for a phenyl ring is that a permanent dipole moment is introduced into the molecule without increasing the molecular breadth. At the same time, the axial molecular electronic polarisability increases owing to the delocalisation of the lone pair of electrons of the hetero atom.[27]

Based on this empirical hypothesis, we have designed and synthesised new optically active compounds using [+] or [-]-octan-2-ol, as the chiral building block. Thus, two homologous series of compounds viz., [S]-[+]-1-methylheptyl-4[4′-(6″-n-alkoxypyridine-3-carbonyloxy)benzoyloxy]benzoates *(3.G)* and [S]-[+]-4-(1-methylheptlyoxy) phenyl-4'-(6″-n-alkoxypyridine-3-carbonyloxy)benzoates **(3.H)** were prepared for this study. In this study, we examine the influence of the terminal linking group on the stabilisation of tilted smectic phases.

The synthesis of these two series of liquid crystalline compounds was carried out as outlined in a scheme shown in figure 3.1. 6-n-Alkoxypyridine-3-carboxylic acids were prepared following a procedure described by Pavluchenko et *al.*[28] The benzyloxybenzoic acid (2.5) was prepared by a etherification reaction between benzylchloride and ethyl-4-hydroxybenzoate, followed by saponification and acidification. Its esterification with [S]-[+]-octan-2-ol was accomplished in the presence of a dehydrating agent such as DCC and DMAP as a catalyst as described in chapter 2. Etherification reaction of 4-benzyloxyphenol with [R]-[-]-octan-2-ol was performed following a procedure described by Mitsunobu and Eguchi [29] and inversion in absolute configuration was observed after the reaction. The deprotection of the phenolic group was achieved through a 5% palladium on charcoal catalysed hydrogenolysis reaction. The phenol (3.7) was esterified with the acid 2.5 (chapter2) and the same procedure was repeated in order to lengthen the molecule by one phenyl ring. The final compounds were obtained by a similar esterification reaction.

The mesophases were observed in thin films by sandwiching the sample between a glass slide and a cover slip. On cooling the isotropic liquid of compound 3.G.5, the homeotropic and focal-conic texture of a S_A phase was observed. The $S_{C_\alpha}^*$ phase was hardly detectable by microscopic observation because its texture is similar to that of the S_A phase. The ferroelectric phase appears with a striated fan shaped or pseudo-homeotropic texture. On cooling further produces a transition to the ferrielectric phase which exhibits a typical texture as shown in Plate 2.e (chapter 2). In homeotropic regions of the cell, the texture constantly moves, probably due to the changes in helical pitch. As



Series 3.G.

Series 3.H

Figure 3.1. Synthetic scheme for the preparation of the compounds of series 3.G and 3.H.

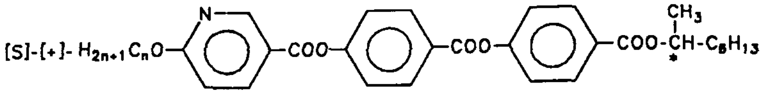
the temperature is decreased further, the antiferroelectric phase appears which looks like a ferroelectric phase only.

A planar alignment of the sample allowed to distinguish antiferroelectric phase from ferroelectric phase, but not the ferrielectric phase. It also reveals an intermediate phase $S_{C_{\alpha}}^{*}$ between S_A and S_C* phases. In $S_{C_{\alpha}}^{*}$ phase, the homogeneous coloured regions of the S_A phase becomes striated with thin, dark and clear bands parallel to the rubbing direction. The textures of S_A and $S_{C_{\alpha}}^{*}$ phases are shown in Plates 3.a and 3.b respectively. At the transition to the S_C* phase, little perpendicular lines appear as shown in Plate 3.c. The transition to the $S_{C_{A}}^{*}$ phase was detected as a clear change of the texture. The new texture appears with large stripes growing perpendicular to the rubbing direction and a photomicrograph of this is shown in Plate 3.d.

All the compounds of both the series are mesomorphic. The transition temperatures along with their enthalpies are given in tables 3.1 and 3.2 respectively. Slight differences in transition temperatures were obtained for series 3.G between optically measured and those obtained on a DSC. These have been attributed as partly due to instrumental factors and difficulties in distinguishing some transitions. However, the transition temperatures given in table (3.1) are those obtained from DSC thermograms. The sub-phases could be detected at the highest sensitivity available on the DSC-7 instrument.

Figures 3.2 and 3.3 show the phase behaviour as a function of n-alkoxy chain length for the series 3.G and 3.H respectively. The clearing temperatures decrease gradually with no odd-even effect. The S_A phase exists in both series of compounds. As can be seen the temperature range of existence of this phase decreases with increasing chain length, while the thermal stability of S_C* phase increases with increasing chain length.

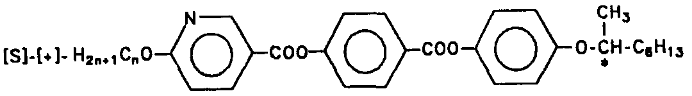
Table 3.1. Phase sequences, transition temperatures (°C) and enthalpies (Jg^{-1}) of



Compound number	n	C		$S_{C_A^*}$		$S_{C_\gamma^*}$		S_{C^*}		$S_{C_\alpha^*}$		S_A		I
3.G.1	6	.	76.5 *63.7*	-		-		-		-		.	112.5 *8.2*	
3.G.2	7	.	80.3 *68.3*	-		-		(.	56.2) *0.027*	(.	57.4) *0.022*	.	107.5 *7.2*	.
3.G.3	8	.	72.2 *64.0*	(.	68.8) *0.01*	(.	71.0) *0.013*	.	73.0 *0.014*		76.5 *0.016*	.	106.0 *8.1*	.
3.G.4	9	.	70.2 *63.2*	(.	66.7) *0.01*	.	71.1 *0.013*	.	80.2 *0.022*		84.0 *0.075*	.	103.0 *7.4*	.
3.G.5	10	.	67.2 *74.5*	.	76.8 *0.027*		78.8 *0.029*	.	85.5 *0.023*		87.5 *0.06*	.	102.5 *7.4*	.
3.G.6	11	.	71.6 *84.9*	(.	60.1) *0.076*	(.	66.4) *0.01*	.	89.4 *0.34*		90.1'	.	100.5 *7.0*	.
3.G.7	12	.	75.0 *84.6*	(.	64.6) *0.015*	(.	70.7) *0.022*	.	91.0 *0.51*		-	.	99.0 *6.9*	.

† : The enthalpy could not be measured

Table 3.2. Phase sequences, transition temperatures (°C) and enthalpies (Jg^{-1}) of



Compound number	n	C		Sc*		SA		I
3.H.1	7		89.3 *45.4*	-			100.0 *6.7*	
3.H.2	8	.	76.2 *59.2*	-		.	108.0 *7.4*	.
3.H.3	9	.	52.7 *54.6*	.	80.5 *0.04*	.	100.5 *7.1*	.
3.H.4	10	.	56.7 *62.1*	.	86.1 *0.08*	.	101.3 *7.9*	.
3.H.5	11	.	65.7 *74.7*	.	91.6 *0.16*	.	100.6 *8.0*	.
3.H.6	12	.	65.8 *69.3*	.	94.0 *0.25*	.	100.5 *8.1*	.

† : The enthalpy could not be measured

As can be seen in figure 3.2, the compounds of series 3.G show the following phases on increasing the alkoxy chain length. Compound 3.G.1 exhibits only a S_A phase. Compound 3.G.2 exhibits S_A, $S_{C_\alpha}^*$ and S_C^* phases. Compounds 3.G.3 to 3.G.5 show S_A, $S_{C_\alpha}^*$, S_C^*, $S_{C_\gamma}^*$ and $S_{C_A}^*$ phases. Compounds 3.G.6 and 3.G.7 exhibit S_A, S_C^*, $S_{C_\gamma}^*$ and $S_{C_A}^*$ phases in that sequence. The $S_{C_\gamma}^*$ phase is enantiotropic in compounds 3.G.4 and 3.G.5, while in all other compounds it is metastable. The $S_{C_A}^*$ phase is also monotropic in all compounds except in compound 3.G.5. Compound 3.G.5 is the best among all; it exhibits five mesophases at relatively low temperatures and all these are enantiotropic. The temperature range of $S_{C_\alpha}^*$ phase is considerable (2.0°C). As can be seen, the $S_{C_\gamma}^*$ and $S_{C_\alpha}^*$ phases show very strong odd-even effect for the higher homologues of this series.

As shown in figure 3.3, compounds 3.H.I and 3.H.2 show only S_A phase. The remaining homologues of the series 3.H exhibit S_C^* phase in addition to the S_A phase. The thermal stability of S_C^* phase increases with increasing n-alkoxy chain length.

Faye *et al.*[30] have synthesised analogous series of compounds 3.1. The mesomorphic behaviour of these compounds can be compared with those of series 3.G. In the compounds of series 3.G, one of the phenyl rings is replaced by a pyridyl ring. The resulting compounds have low melting and clearing temperatures. Ferroelectric, ferrielectric and antiferroelectric phases are injected into this series at relatively shorter n-alkoxy chain lengths. Ferrielectric and antiferroelectric phases become thermally metastable except in compound 3.G.5. In series 3.1, for longer alkoxy chains all these phases are enantiotropic and thermally more stable.

We can conclude the same, when we compare the series 3.G and 3.J.[30] One of the phenyl rings of compounds of series 3.1 [30] was replaced by a fluoro substituted phenyl

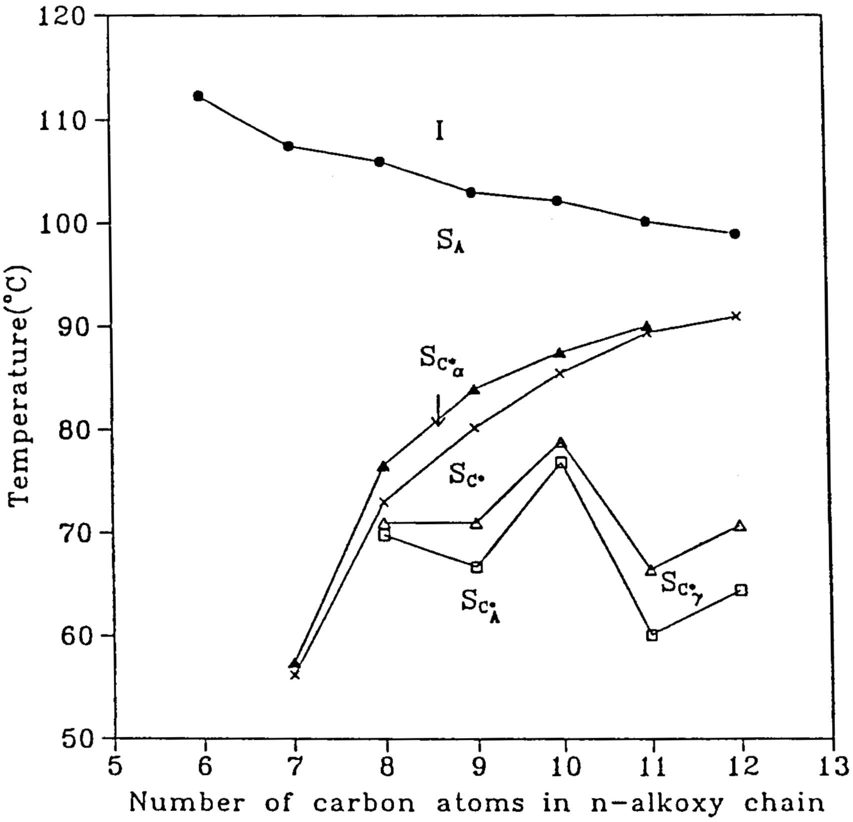


Figure 3.2. A plot of transition temperatures as a function of n-alkoxy chain length for series 3.G.

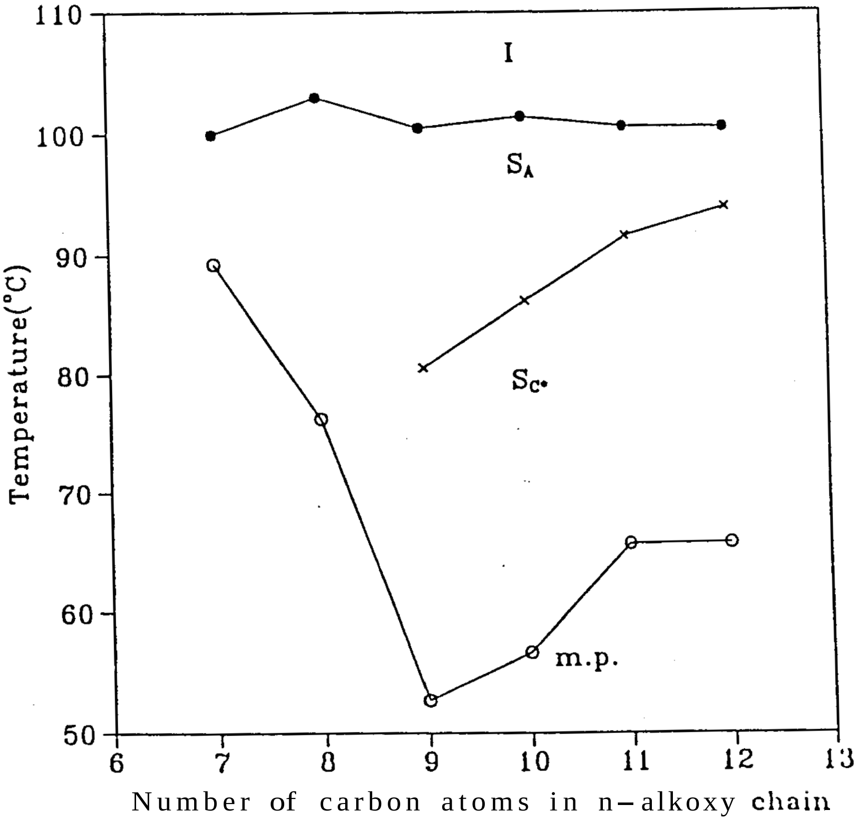
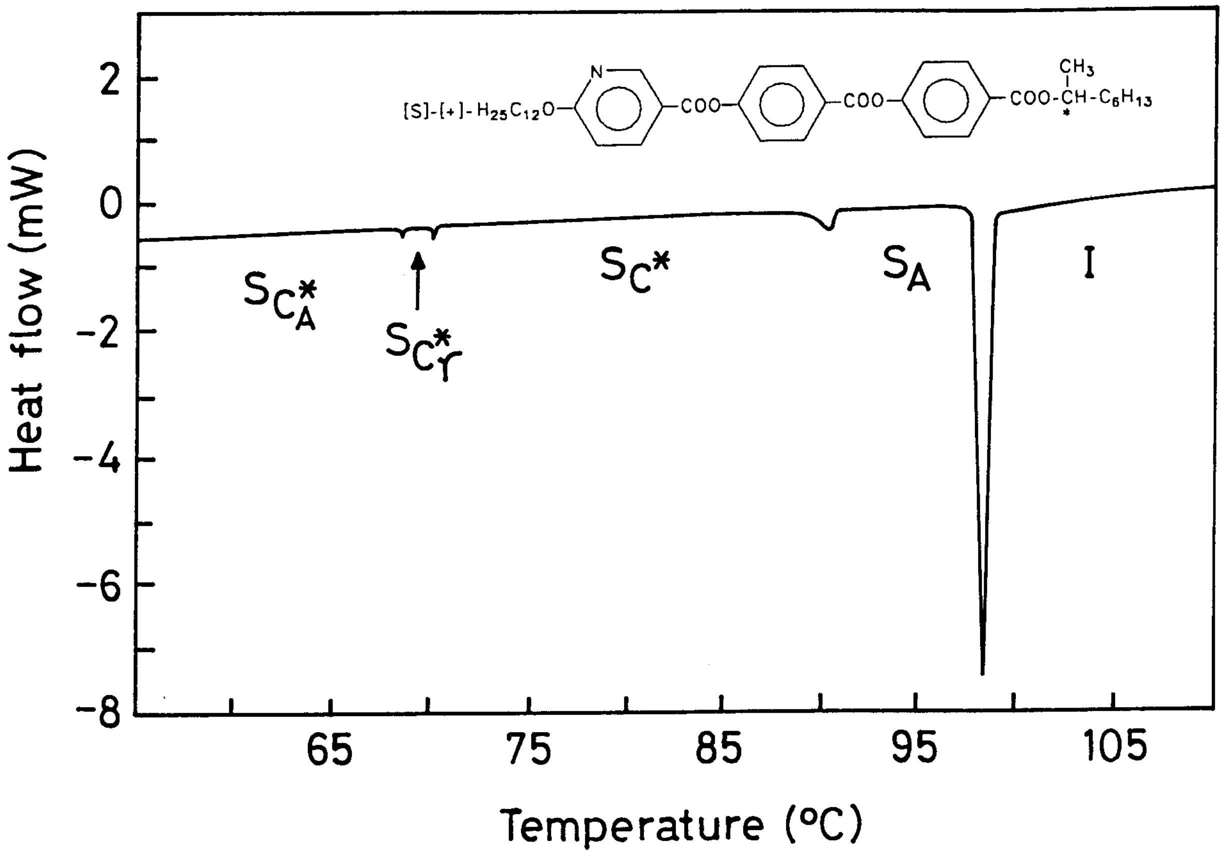


Figure 3.3. A plot of transition temperatures as a function of n-alkoxy chain length for series **3.H.**



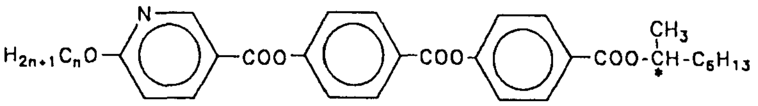
The dsc thermogram of compound 3.G.7.

ring. Compounds of series 3.5 show enantiotropic ferroelectric, ferrielectric and antiferroelectric phases.

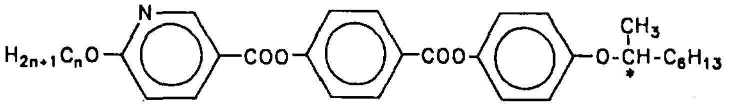
A comparison of the three series of compounds 3.G, 3.1 and 3.5 indicates, that there is not much difference between the three series. All of them display the same rich polymorphism, but the phase temperature ranges of series 3.G are lower when compared with the other two series. The clearing temperatures decrease in the order of 3.1 > 3.J > 3.G. This can probably be attributed to the lone pair of electrons on nitrogen in the pyridyl moiety which increases the polarity of the molecules.

Nabor *et al.*[31] have synthesised analogous series of compounds 3.K containing a thioester group. The transition temperatures and mesophases of these can be compared with compounds of series 3.H. Compounds of series 3.H differ from series 3.K as follows. In series 3.H the fluoro substituted phenyl ring is replaced by a pyridine ring and one of the ester linkage group is replaced by a thioester linkage. Series 3.H shows S_A phase for shorter alkoxy chain lengths and S_A, S_C^* phases for longer alkoxy chains. However, homologues of series 3.K show blue phase and cholesteric phase for shorter alkoxy chain lengths and S_A and S_C^* phases for longer alkoxy chain lengths.

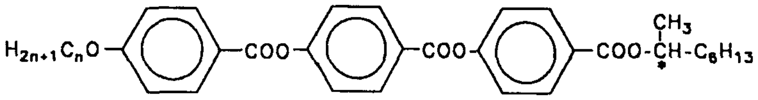
The most striking result in the present study concern the compounds of series 3.G and 3.H, which differ in the terminal linking group. While there is a ester functionality between chiral carbon and the core in series 3.G, there is an ether linkage in series 3.H. Compounds of series 3.G exhibit S_A, $S_{C_\alpha^*}$, S_C^*, $S_{C_\gamma^*}$ and $S_{C_A^*}$ phases, but compounds of series 3.H show only S_A and S_C^* phases. These results show that the ester linking group at the end of the core seems to play an important role in influencing the formation of S_C^*, $S_{C_A^*}$ and other sub-phases.



—3.G

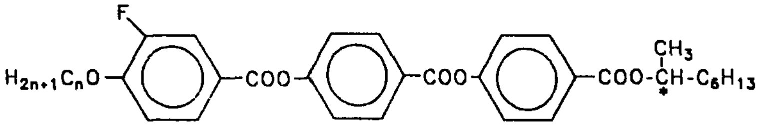


—3.H



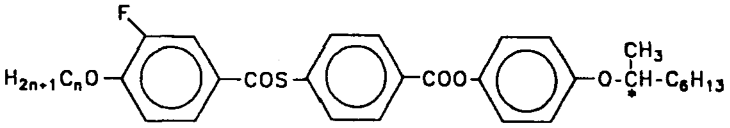
—3.I

n =10, C 90.3 $S_{C_A^*}$ 99.2 $S_{C_\gamma^*}$ 102.7 S_{C^*} 114.0 $S_{C_\alpha^*}$ 115.3 S_A 135.5 I



—3.J

n =10, C 89.3 $S_{C_A^*}$ 101.8 $S_{C_\gamma^*}$ 103.4 S_{C^*} 112.8 $S_{C_\alpha^*}$ 113.3 S_A 127.1 I



—3.K

n =7, C 68.4 S_{C^*} 118.3 S_A 126.1 N* 129.5 BP 129.8 I

n =10, C 69.4 S_{C^*} 119.5 S_A 125.2 N* 126.8 I

Optical purity studies

In order to confirm the presence of the ferrielectric and antiferroelectric phases of compounds of series 3.G, miscibility studies were carried out between compound 3.G.5 and [S]-[+]-MHPOBC. An isobaric binary phase diagram was obtained and this is shown in figure 3.4. The mixtures were made as weight/weight ratio and mixed thoroughly in their isotropic states. The phase diagram shows continuous miscibility across the whole composition range for all the different phases which confirms the optical observations.

Polarisation

Figure 3.5 shows the temperature dependence of spontaneous polarisation (P) for compound 3.H.4. The behaviour is typical for a compound exhibiting S_A - S_C^* transition. Figure 3.6 shows the current response to an applied triangular wave in the different phases of compound 3.G.5. These oscilloscope-traces are similar to the ones reported for each of these phases. In particular, the second peak observed in the $S_{C\alpha}^*$ phase is quite conspicuous. In addition to the regular features obtained in the $S_{C\gamma}^*$ and S_{CA}^* phases, we also noticed a strong back-flow effect, which was observed in some earlier reports also.[10]

Figure 3.7 shows the thermal variation of spontaneouslfield-induced polarisation for compound 3.G.5. The magnitude of polarisation varies smoothly across S_C^* - $S_{C\gamma}^*$ and $S_{C\gamma}^*$ - S_{CA}^* transitions. This is to be expected as the measurements were done at a relatively high frequency of 9.7 Hz and a field which was above the helix unwinding field. **A** remarkable feature to be noticed is that the transition from $S_{C\alpha}^*$ to S_C^* phase manifests as a step in the polarisation variation. To our knowledge, this is the first instance where such a feature is observed across S_C^* - $S_{C\alpha}^*$ transition.

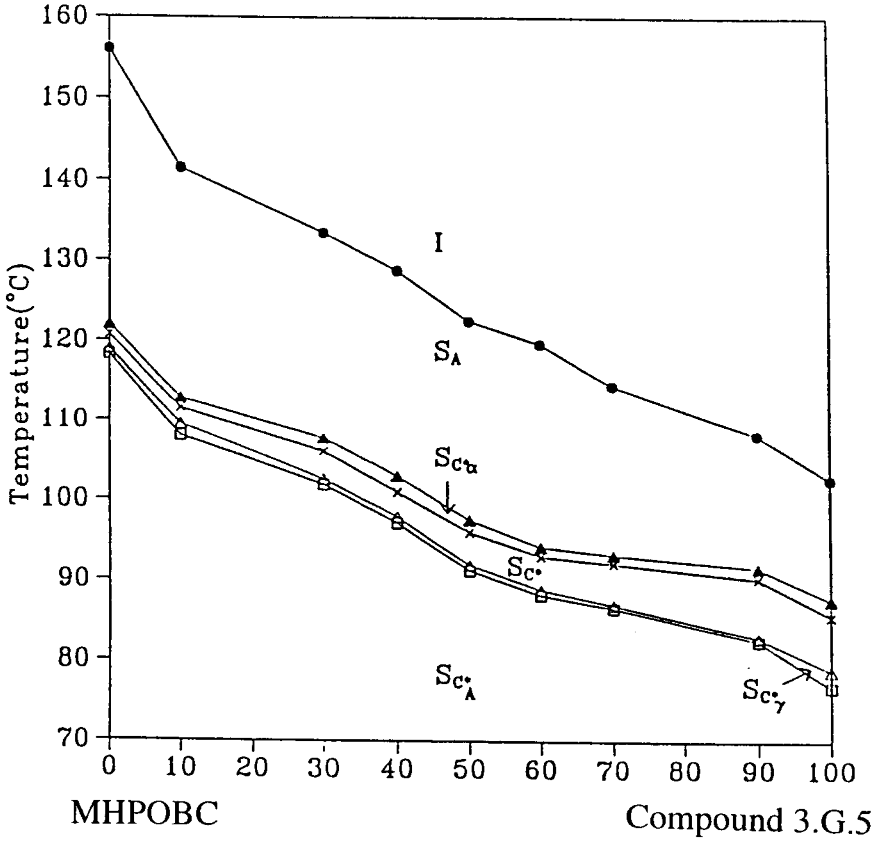


Figure 3.4. Miscibility phase diagram (weight/weight ratio) between compound ***3.G.5*** on the right and MHPOBC on the left.

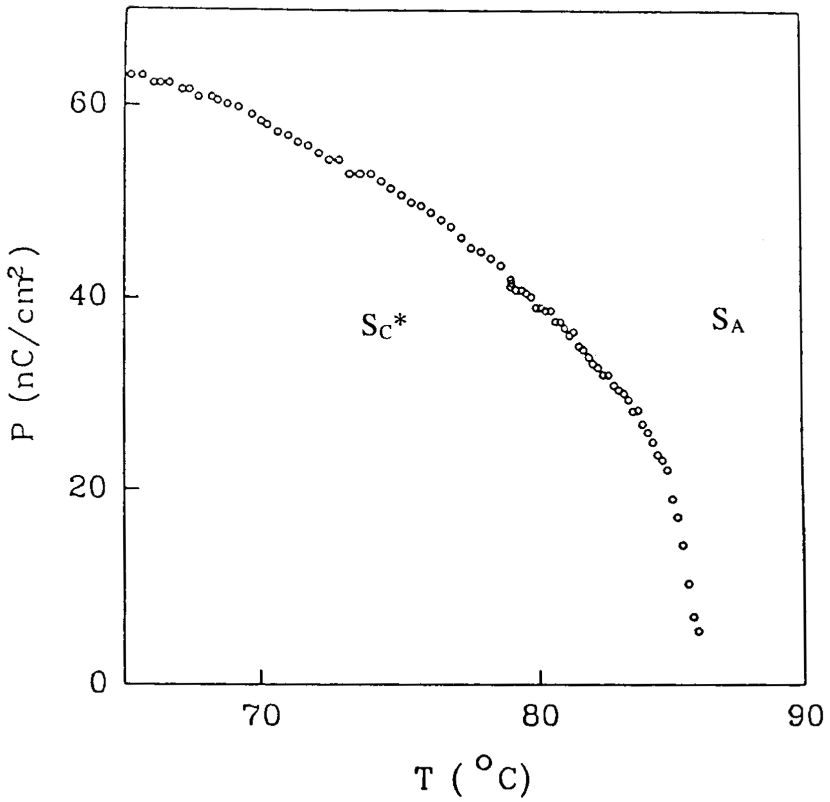


Figure 3.5. Thermal variation of polarisation for compound **3.H.4.**

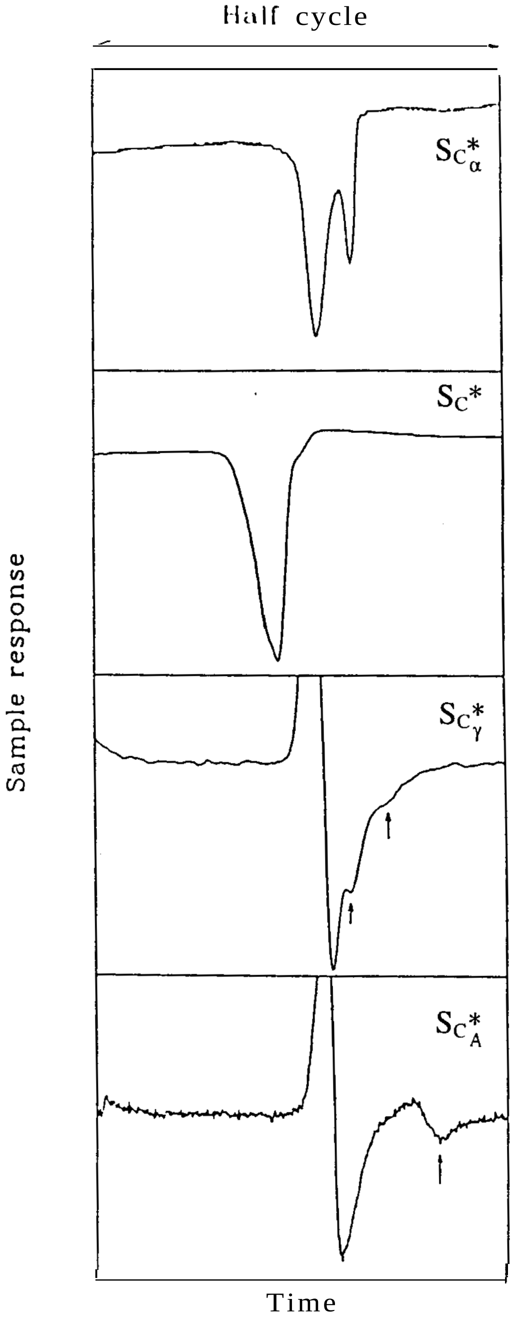


Figure 3.6. Raw oscilloscope traces in the Sc^*_α , Sc^*, Sc^*_γ , Sc^*_A phases of compound 3.G.5. The arrows point to the subsidiary peaks.

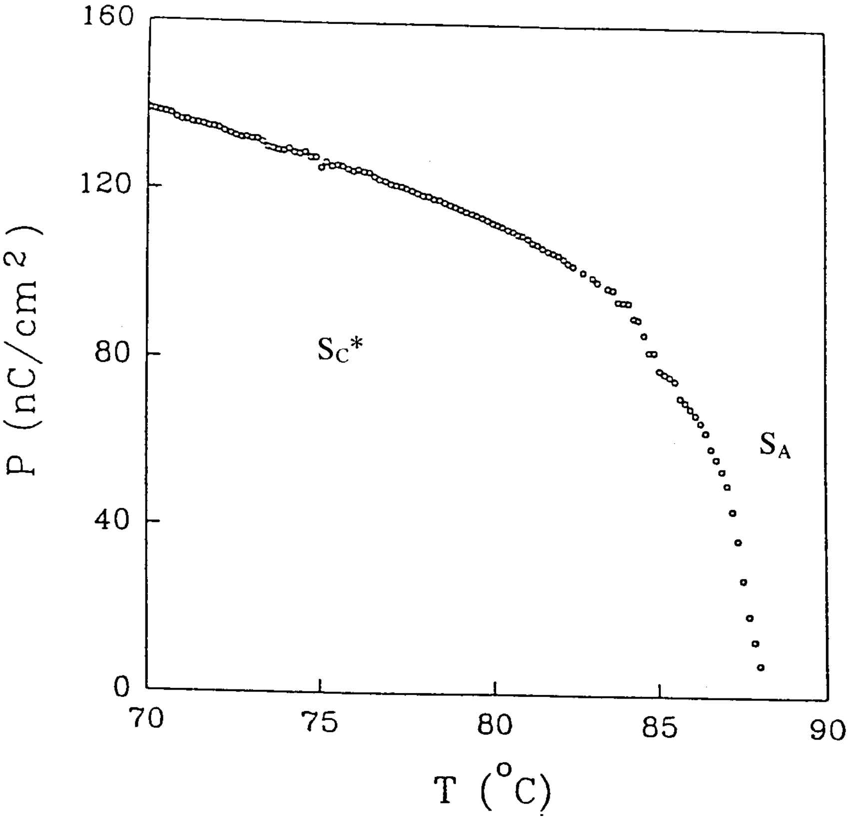


Figure 3.7. Variation of spontaneous/induced polarisation as a function of temperature for compound 3.G.5. Notice the step in P at the $S_{C_\alpha}^*$ - S_C^* transition.

Tilt angle and Pitch

Plots of optical tilt angle as a function of reduced temperature for compounds 3.H.4 and 3.G.5 are shown in figures 3.8 (a) and 3.8 (b) respectively. Although the value of the tilt angle far away from the transition is observed to be very similar in both the compounds, the temperature variations are different. This could be because in compound 3.H.4 there is a direct S_A- S_C* transition while in compound 3.G.5 the $S_{C_\alpha}^*$ phase intervenes. Similar behaviour was observed in the pitch versus reduced temperature plots also (shown in figures 3.9 (a) and 3.9 (b)). The pitch values were determined by the optical diffraction method.[34]

Dielectric Constant

Dielectric measurements were carried out by using an impedance analyser.[35] Figure 3.10 shows the variation of the transverse dielectric constant $\varepsilon_\perp$ as a function of temperature at a frequency of 105 Hz for compound 3.G.5. One observes clear changes at the S_A - $S_{C_\alpha}^*$, $S_{C_\alpha}^*$ - S_C* and S_C*- $S_{C_\gamma}^*$ transitions. The sharp increase observed at the $S_{C_\alpha}^*$ - S_C* transition could be due to the presence of Goldstone mode in the S_C* phase. With the application of a DC bias field of 1.25 V/µm the value in the S_C* phase decreases (figure 3.11). The decrease becomes substantial if the frequency of the probing field is increased (figure 3.12). Both these observations confirm that the main contribution in the S_C* phase is due to the Goldstone mode.

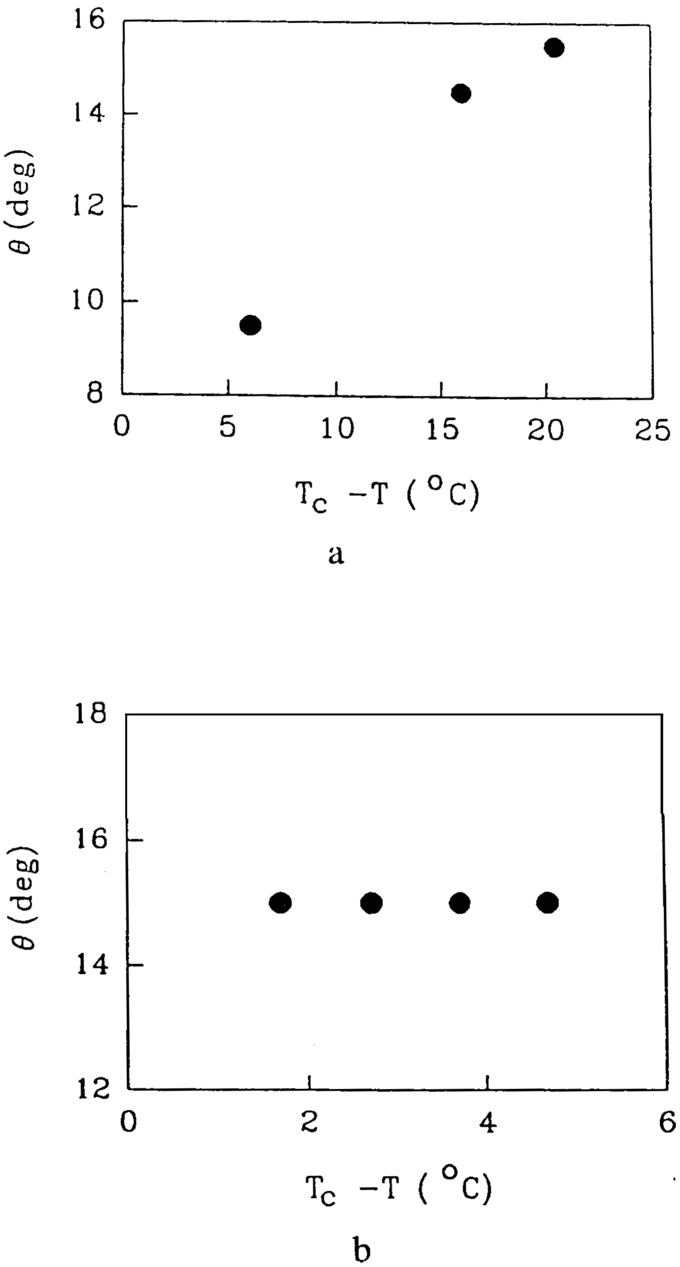


Figure 3.8. Plot of tilt angle versus reduced temperature for (a) compound **3.H.4** and (b) compound ***3.G.5.***

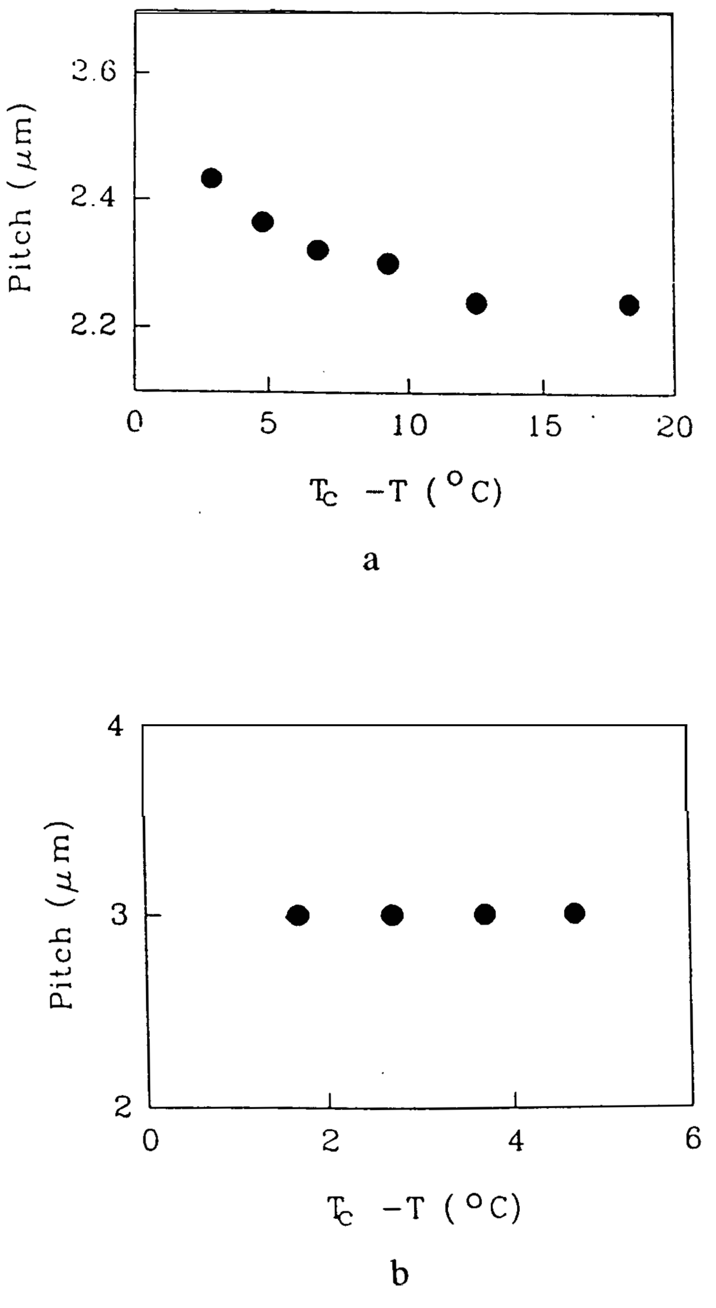
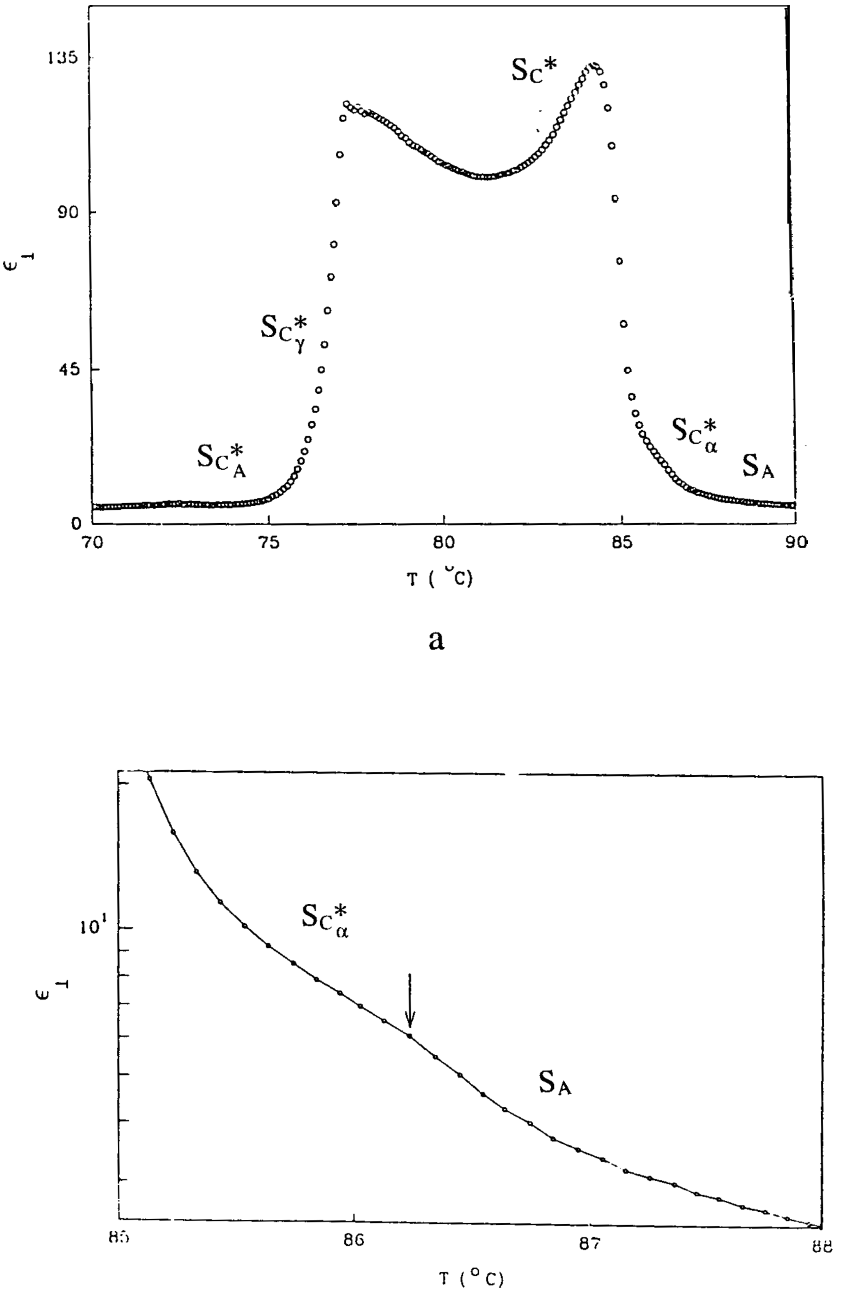


Figure 3.9. Plot of helical pitch versus reduced temperature for compound 3.H.4 and (b) compound ***3.G.5.***



a

b

Figure 3.10.(a) Temperature dependence of the transverse dielectric constant ($\varepsilon_{\perp}$) for compound 3.G.5. Probing frequency f = 105 Hz with zero DC bias, (b) enlarged view of (a) near the S_A - $S_{C_\alpha}^*$ transition.

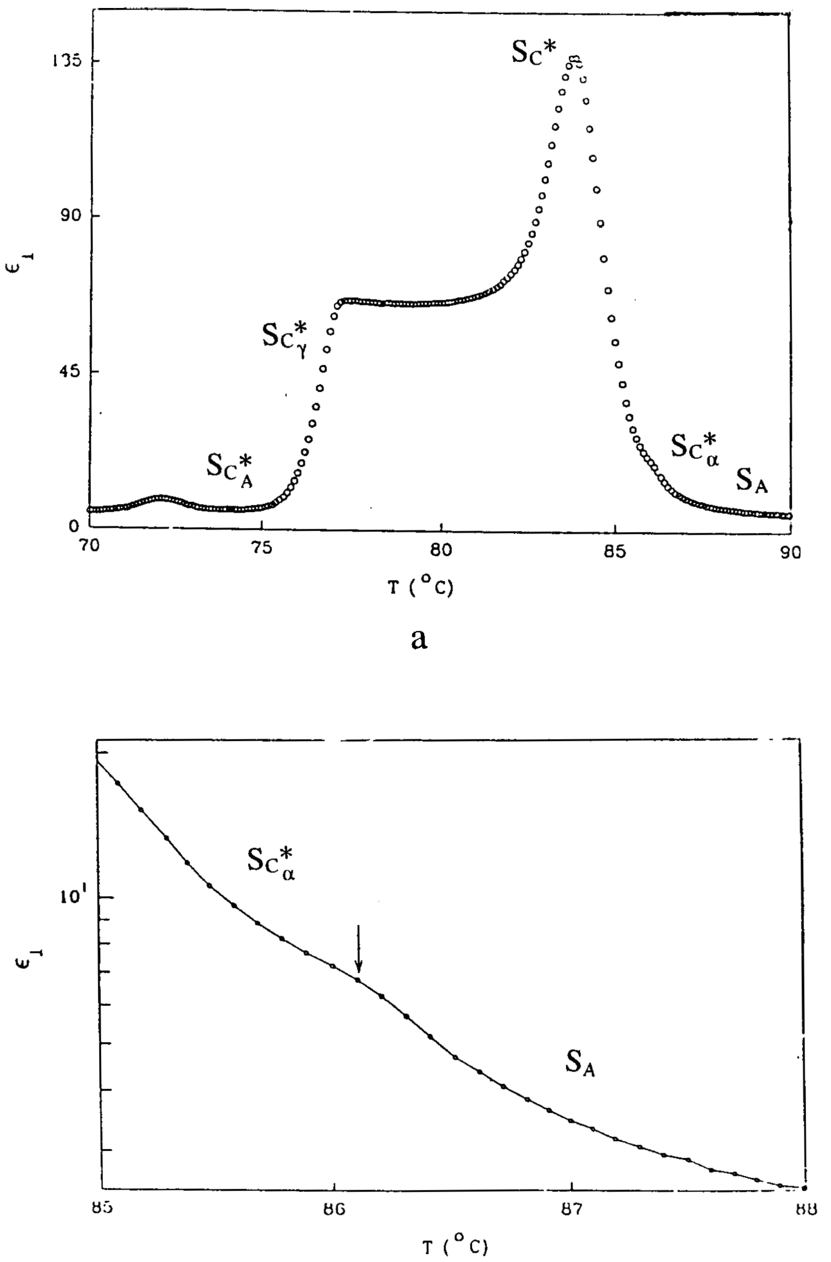


Figure 3.11. (a) Static dielectric constant ($\varepsilon_\perp$) as a function of temperature for compound 3.G.5. Probing frequency f = 105 Hz with a DC bias of 1.25 V/μm. (b) Enlarged view of (a) in the vicinity of the S_A - Sc^*_α transition.

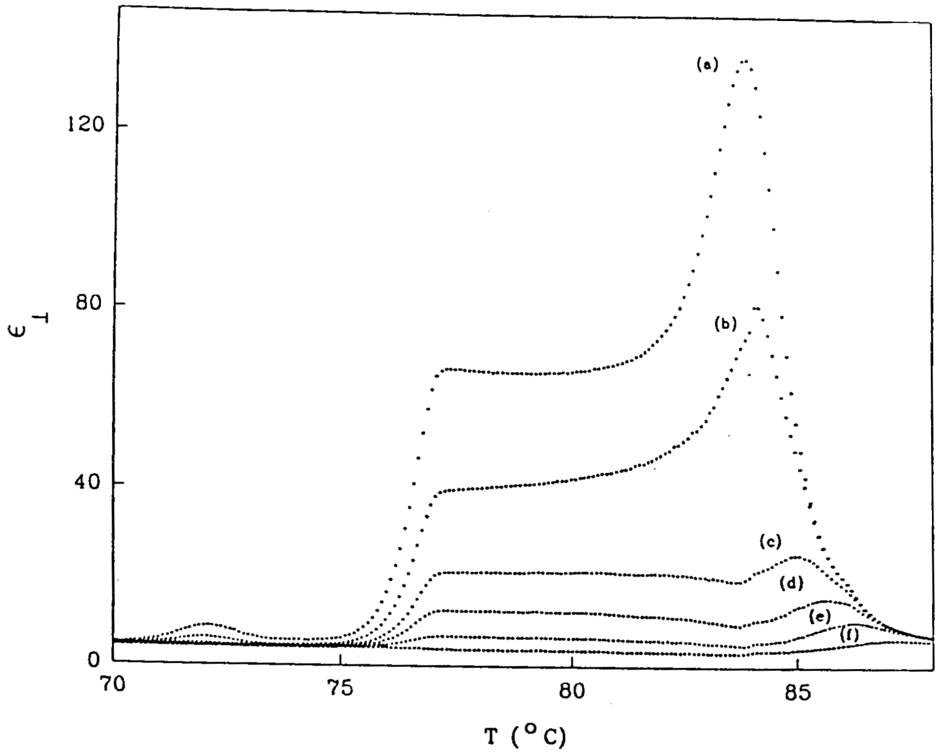


Figure 3.12. Influence of the magnitude of probing frequency on the thermal variation of $\varepsilon_\perp$ for compound 3.G.5. DC bias used = 1.25 V/μm. The frequencies are (a) 0.105 (b) 1.0 (c) 5.0 (d) 10.0 (e) 20.0 (f) 50.0 KHz.

Experimental

Coumalic acid, (3.1)

Fuming sulphuric acid (20-30%, 50 ml) was added dropwise to a mixture of malic acid (200 g, 1400 m mol.) and concentrated sulphuric acid (170 ml) within an hour. This solution was heated on a water bath for two to three hours with occasional shaking. The reaction mixture was cooled to room temperature, poured into 800 g of crushed ice with stirring and left at room temperature for about twenty-four hours. The product was filtered, washed with ice-cold water (3X50 ml), dried on a water bath and crystallised from methanol (50.0 g, 23.8%); m.p. 206-208°C (Reported [36] m.p. 206-208°C).

Methylcoumalate, (3.2)

Coumalic acid (50.0 g, 354.6 mmol.) was added in portions to concentrated sulphuric acid (138 ml) within twenty-five minutes. The reaction temperature was maintained around 25-30°C by immersion of the flask in an ice-bath. Methanol (70 ml) was added to the reaction mixture and heated on a water bath for an hour. This was cooled to room temperature and poured into water. To this was added anhydrous Na_2CO_3 (220 g) in small portions with stirring. The precipitated ester was filtered and dissolved in $CHCl_3$, washed with water (5X300 ml), dried (Na_2SO_4) and the solvent removed (18.0 g, 32.75%); m.p. 68-70°C (Reported [36] m.p. 74°C).

6-Hydroxypyridine-3-carboxylic acid, (3.3)

Methylcoumalate (18 g, 11.6 mmol) was added in portions within fifteen minutes to cold (15-20°C) ammonium hydroxide (46.8 ml) and stirred for fifty minutes. The reaction mixture was poured into hot 17% NaOH solution (240 ml) and heated to boil for about ten minutes, then cooled to room temperature, acidified with concentrated HCI (100 ml), the solid material so obtained was filtered off and washed with cold water. This was dissolved in $NaHCO_3$ solution, charcolised, filtered, cooled and acidified. The solid so obtained was filtered off, washed with cold water and dried (9.0 g, 61.4%); m.p. >300°C (decomposes), (Reported[37] m.p. >300°C).

6-Chloropyridine-3-carboxylic acid, (3.4)

A mixture of 6-hydroxypyridine-3-carboxylic acid (15.0 g, 107.9 mmol) and phosphorus pentachloride (PCl_5)(22.5 g, 108 mmol) was cooled to 10-15°C. Phosphorus oxychloride ($POCl_3$)(125 ml) was added dropwise at that temperature, then heated to reflux for about four hours. Excess $POCl_3$ was removed by distillation under reduced pressure. The residue so obtained was poured into ice cold water and the solid filtered. This solid was crystallised from water (13.0 g, 76.7%); m.p. 194-196°C (Reported[38] 195-197°C).

6-n-Hexyloxypyridine-3-carboxylic acid, (3.5)

This was prepared following a reaction described by Pavluchenko *et al.*[28] Thus, a solution of sodium hexoxide was prepared by dissolving sodium (6.0 g, 0.26 g atom) in n-hexan-1-ol (200 ml). To this 6-chloropyridine-3-carboxylic acid (2.3 g, 14.65 mmol) in dimethylformamide (DMF)(100 ml) was added and refluxed for about ten hours. Excess n-hexan-1-ol and DMF were removed by distillation under reduced pressure. The reaction mixture was acidified with 10% HCI. The solid so obtained was filtered off, washed with cold water, dried and crystallised from petroleum ether (b.p 40-60°C) (2.0 g, 62%); m.p.

93.2°C (Reported [28] m.p. 93.2°C); ν_{max}: 3100, 2500, 1780, 1640, 1580, 1480, 1240 and 1050 cm^{-1}.

The transition temperatures of the 6-n-alkoxypyridine-3-carboxylic acids are given in table 3.3.

Table 3.3. Transition temperatures of 6-n-alkoxypyridine-3-carboxylic acids

Compound number	n	C		S_C		N		I
1	6	.	93.2.	-		(.	90.6)	.
2	7	.	88.5	-			89.5	
3	8	.	88.0	.	87.3		94.2	.
4	9	.	86.8	.	90.7		92.5	
5	10	.	87.2	.	95.1	-		
6	11	.	88.5	.	95.5	-		
7	12	.	84.4	.	96.6	-		

[S]-[+]-4-(1-Methylheptyloxyphenyl)benzylether, (3.6)

This was prepared following a procedure of Mitsunobu and Eguchi [29] Thus, diethylazodicarboxylate (DEAD) (4.76 g, 27.3 mmol) was added dropwise to a cold stirred solution of 4-benzyloxyphenol (5.0 g, 25 mmol), [R]-[-]-octan-2-ol (3.25 g, 24.9 mmol), triphenyl phosphine (7.0 g, 26.3 mmol) and dichloromethane (56.0 ml) for one hour. The reaction mixture was stirred at room temperature for four hours and the solid formed during the reaction was filtered off. The residue obtained on removal of solvent from the filtrate was chromatographed on silica gel and eluted with a 3:1 mixture of chloroform and petroleum ether (b.p. 60-80°C). On removal of solvent from the eluate, the desired compound was obtained as a viscous liquid (5.3 g, 76%); $[\alpha]_D^{25} = 6.6^\circ$ (4.6 mg/ml in CH_2Cl_2); ν_{max} (neat): 2990, 1500, 1480, 1380, 1240 and 1050 cm^{-1}; 6: 0.7-2.0(16H, m, 2XCH_3, 5XCH_2), 4.2(1H, m, ArOCH), 5.1(2H, s, ArCH_2O), 6.83(5H, s, ArH), 7.29(4H, s, ArH);

Elemental analysis: Found, C, 80.75; H, 8.72% $C_{21}H_{28}O_2$ requires
C, 80.76; H, 8.97%.

[S]-[+]-4-(1-Methylheptyloxy)phenol, (3.7)

A mixture of [S]-[+]-4-(1-methylheptyloxyphenyl)benzylether (7.0 g, 22.43 mmol), ethanol (40 ml) and 5% Pd-C catalyst (3.0 g) was stirred in an atmosphere of hydrogen till the calculated quantity of hydrogen was absorbed. The reaction mixture was then filtered and ethanol removed by distillation under reduced pressure. The residual liquid was chromatographed on silica gel and eluted with chloroform and ethylacetate (9:1) mixture. Removal of the solvent from the eluate gave a viscous liquid (4.2 g, 84.3%); $[\alpha]_D^{25} = 7.6^\circ$ (5.2 mg/ml in CH_2Cl_2); ν_{max} (neat): 3600, 3000, 1500, 1480, 1240 and 1050 cm^{-1}; 6: 0.7-2.0(16H, m, 2XCH_3, 5XCH), 4.2(1H, m, ArOCH), 6.78(4H, s, ArH), 7.2(1H, s, ArOH);

Elemental analysis: Found, C, 75.83; H, 9.84% $C_{14}H_{22}O_2$ requires
C, 75.67; H, 9.90%.

[S]-[+]-4-(1-Methylheptyloxy)phenyl-4′-benzyloxybenzoate,(3.8)

This was prepared following a procedure described by Hassner and Alexanian.[39] Thus, a mixture of 4-benzyloxybenzoic acid (2.64 g, 11.6 mmol), [S]-[+]- 4-(1-methylheptyloxy)phenol (2.57 g, 11.6 mmol), DCC (2.36 g, 11.6 mmol), DMAP (0.14 g, 11.6 mmol) and dry dichloromethane (20 ml)was stirred for two hours at room temperature. The N,N′-dicyclohexylurea formed was filtered off and the filtrate was washed successively with water (2X30 ml), 5%aqueous acetic acid (3X50 ml), water (3X50 ml) and dried (Na_2SO_4). The residue obtained on removal of solvent was chromatographed on silica gel and eluted with chloroform. Removal of solvent from the eluate afforded a white solid which was crystallised from ethanol (4.35g, 87%); m.p. 118.8"C; $[\alpha]_D^{25}$ = 6.0 ° (4.1 mg/ml in CH_2Cl_2; v„: 2950, 1740, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; *6:* 0.94-2.28 (16H, m, $2XCH_3$, $5XCH_2$), 4.35(1H, m, ArOCH), 5.18(2H, s, $ArCH_2OAr$), 6.87 and 8.06(4H, AB q, J=7.5 Hz, ArH), 6.83(5H, s, ArH), 7.29(4H, s, ArH);

Elemental analysis:	Found,	C, 77.45; H, 7.62%	$C_{28}H_{32}O_4$ requires
		C, 77.77; H, 7.40%.	

[S]-[+]-4-(1-Methylheptyloxy)phenyl-4′-hydroxybenzoate, (3.9)

This was prepared following a procedure described for compound 3.7. Yield, 81.0%; m.p. 107.0°C; $[\alpha]_D^{25}$ = 7.1 ° (5.2 mg/ml in CH_2Cl_2); v„: 3310, 2950, 1740, 1690, 1600, 1510, 1450, 1275 and 1050 cm^{-1}; *6:* 0.75-2.0(16H, m, $2XCH_3$, $5XCH_2$), 4.1(1H, m, ArOCH), 6.5-8.1(7H, m, ArH) 7.2(1H, s, ArOH);

Elemental analysis:	Found,	C, 73.02; H, 7.32%	$C_{21}H_{26}O_4$ requires
		C, 73.39; H, 7.57%.	

[S]-[+]-1-Methylheptyl-4-[4′-(6″-n-hexyloxypyridine-3-carbonyloxy) benzoyloxy]benzoate, (3.G.1)

This was prepared following a procedure described for compound 3.8. Yield, 236 mg, 87%; m.p. 76.4 °C; $[\alpha]_D^{25}$ = 22.75 ° (4.4 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1720, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0 (27H, m, 3XCH_3, 9XCH_2), 4.38(2H, t, J=7.8 Hz, ArOCH_2), 5.18(1H, m, COOCH), 6.82(1H, dd, J=9.7 Hz, ArH), 7.32 and 8.15(4H, AB q, J=8.4 Hz, ArH), 7.4 and 8.3(4H, AB q, J=8.5 Hz, ArH), 8.17 (1H, dd, J=9.4 Hz, ArH), 9.0(1H, dd, J=1.9 Hz, ArH);

Elemental analysis: Found, C, 70.67; H, 7.27; N, 2.37% $C_{34}H_{41}NO_7$ requires C, 71.08; H, 7.14; N, 2.43%.

The physical data of the cognate preparations of the other [S]-[+]-1-methylheptyl-4-[4′-(6″-n-alkoxypyridine-3-carbonyloxy)benzoyloxy]benzoates are given below.

[S]-[+]-1-Methylheptyl-4-[4′-(6″-n-heptyloxypyridine-3-carbonyloxy) benzoyloxy]benzoate, (3.G.2)

Yield, 84%; m.p. 80.3 °C; $[\alpha]_D^{25}$ = 23.3 ° (4.1 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1720, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(29H, m, 3XCH_3, 10XCH_2), 4.38(2H, t, J=7.8 Hz, ArOCH_2), 5.18(1H, m, COOCH), 6.82(1H, dd, J=9.7 Hz, ArH), 7.32 and 8.15(4H, AB q, J=8.4 Hz, ArH), 7.4 and 8.3(4H, AB q, J=8.5 Hz, ArH), 8.17(1H, dd, J=9.4 Hz, ArH), 9.0(1H, dd, J=1.9 Hz, ArH);

Elemental analysis: Found, C, 71.17; H, 7.29; N, 2.05% $C_{35}H_{43}NO_7$ requires C, 71.42; H, 7.31; N, 2.38%.

[S]-[+]-1-Methylheptyl-4-[4′-(6″-n-octyloxypyridine-3-carbonyloxy) benzoyloxy]benzoate, (3.G.3)

Yield, 82%; m.p. 71.9 °C; $[\alpha]_D^{25}$ = 21.24 ° (6.2 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1720, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(31H, m, 3XCH_3, 11XCH_2), 4.38(2H, t, J=7.8 Hz, ArOCH_2), 5.18(1H, m, COOCH), 6.82(1H, dd, J=9.7 Hz, ArH), 7.32 and

8.15(4H, AB q, J=8.4 Hz,ArH), 7.4 and 8.3(4H, AB q, J=8.5 Hz, ArH), 8.17(1H, dd, J=9.4 Hz, ArH), 9.0(1H, dd, J=1.9 Hz, ArH);

Elemental analysis: Found, C, 71.79; H, 7.72; N, 2.17% $C_{36}H_{45}NO_7$ requires
C, 71.76; H, 7.47; N, 2.32%.

[S]-[+]-1-Methylheptyl-4-[4′-(6″-n-nonyloxypyridine-3-carbonyloxy) benzoyloxy]benzoate, (3.G.4)

Yield, 80%; m.p. 70.2 °C; $[\alpha]_D^{25}$ = 21.46 ° (4.4 mg/ml in CH_2Cl_2); v; 2950, 1740, 1720, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(33H, m, $3XCH_3$, $12XCH_2$), 4.38(2H, t, J=7.8 Hz, $ArOCH_2$), 5.18(1H, m, COOCH), 6.82(1H, dd, J=9.7 Hz, ArH), 7.32 and 8.15(4H, AB q, J=8.4 Hz, ArH), 7.4 and 8.3(4H, AB q, J=8.5 Hz, ArH), 8.17(1H, dd, J=9.4 Hz, ArH), 9.0(1H, dd, J=1.9 Hz, ArH);

Elemental analysis: Found, C, 71.86; H, 7.93; N, 2.12% $C_{37}H_{47}NO_7$ requires
C, 72.07; H, 7.62; N, 2.27%.

[S]-[+]-1-Methylheptyl-4-[4′-(6″-n-decyloxypyridine-3-carbonyloxy) benzoyloxy]benzoate, (3.G.5)

Yield, 83%; m.p. 66.9 °C; $[\alpha]_D^{25}$ = 19.35 ° (4.3 mg/ml in CH_2Cl_2); v; 2950, 1740, 1720, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(35H, m, $3XCH_3$, $13XCH_2$), 4.38(2H, t, J=7.8 Hz, $ArOCH_2$), 5.18(1H, m, COOCH), 6.82(1H, dd, J=9.7 Hz, ArH), 7.32 and 8.15(4H, AB q, J=8.4 Hz, ArH), 7.4 and 8.3(4H, AB q, J=8.5 Hz, ArH), 8.17(1H, dd, J=9.4 Hz, ArH), 9.0(1H, dd, J=1.9 Hz, ArH);

Elemental analysis: Found, C, 71.97; H, 7.92; N, 2.08% $C_{38}H_{49}NO_7$ requires
C, 72.38; H, 7.77; N, 2.22%.

[S]-[+]-1-Methylheptyl-4-[4′-(6″-n-undecyloxypyridine-3-carbonyloxy) benzoyloxy]benzoate, (3.G.6)

Yield, 82%; m.p. 71.6 °C; $[\alpha]_D^{25}$ = 19.62 ° (4.6 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1720, 1605, 1490, 1270 and 1050 cm^{-1}; *6:* 0.7-2.0(37H, m, 3XCH$_3$, 14XCH$_2$), 4.38(2H, t, J=7.8 Hz, ArOCH$_2$), 5.18(1H, m, COOCH), 6.82(1H, dd, J=9.7 Hz, ArH), 7.32 and 8.15(4H, AB q, J=8.4 Hz, ArH), 7.4 and 8.3(4H, AB q, J=8.5 Hz, ArH), 8.17(1H, dd, J=9.4 Hz, ArH), 9.0(1H, dd, J=1.9 Hz, ArH);

Elemental analysis: Found, C, 72.33; H, 8.17; N, 2.09% $C_{39}H_{51}NO_7$ requires C, 72.67; H, 7.91; N, 2.17%.

[S]-[+]-1-Methylheptyl-4-[4′-(6″-n-dodecyloxypyridine-3-carbonyloxy) benzoyloxy]benzoate, (3.G.7)

Yield, 80%; m.p. 74.3 °C; $[\alpha]_D^{25}$ = 19.02 ° (3.7 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1720, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(39H, m, 3XCH$_3$, 15XCH$_2$), 4.38(2H, t, J=7.8 Hz, ArOCH$_2$), 5.18(1H, m, COOCH), 6.82(1H, dd, J=9.7 Hz, ArH), 7.32 and 8.15(4H, AB q, J=8.4 Hz, ArH), 7.4 and 8.3(4H, AB q, J=8.5 Hz, ArH), 8.17(1H, dd, J=9.4 Hz, ArH), 9.0(1H, dd, J=1.9 Hz, ArH);

Elemental analysis: Found, C, 72.65; H, 8.31; N, 1.99% $C_{40}H_{53}NO_7$ requires C, 72.94; H, 8.05; N, 2.12%.

[S]-[+]-4-(1-Methylheptyloxy)phenyl-4′-(6″-n-heptyloxypyridine-3-carbonyloxy)benzoate, (3.H.1)

This was prepared following a procedure described for compound 3.8. Yield, 87% m.p. 89.3 "C; $[\alpha]_D^{25}$ = 4.08 ° (4.0 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1720, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(29H, m, 3XCH_3, 10XCH_2), 5.0-5.34(3H, m, ArOCH and ArOCH_2), 6.82(1H, dd, J=9.7 Hz, ArH), 7.32 and 8.15(4H, AB q, J=8.4 Hz, ArH), 7.4 and 8.3(4H, J=8.5 Hz, ArH), 8.17(1H, dd, J=9.4 Hz, ArH), 9.0(1H, dd, J=2.0 Hz, ArH);

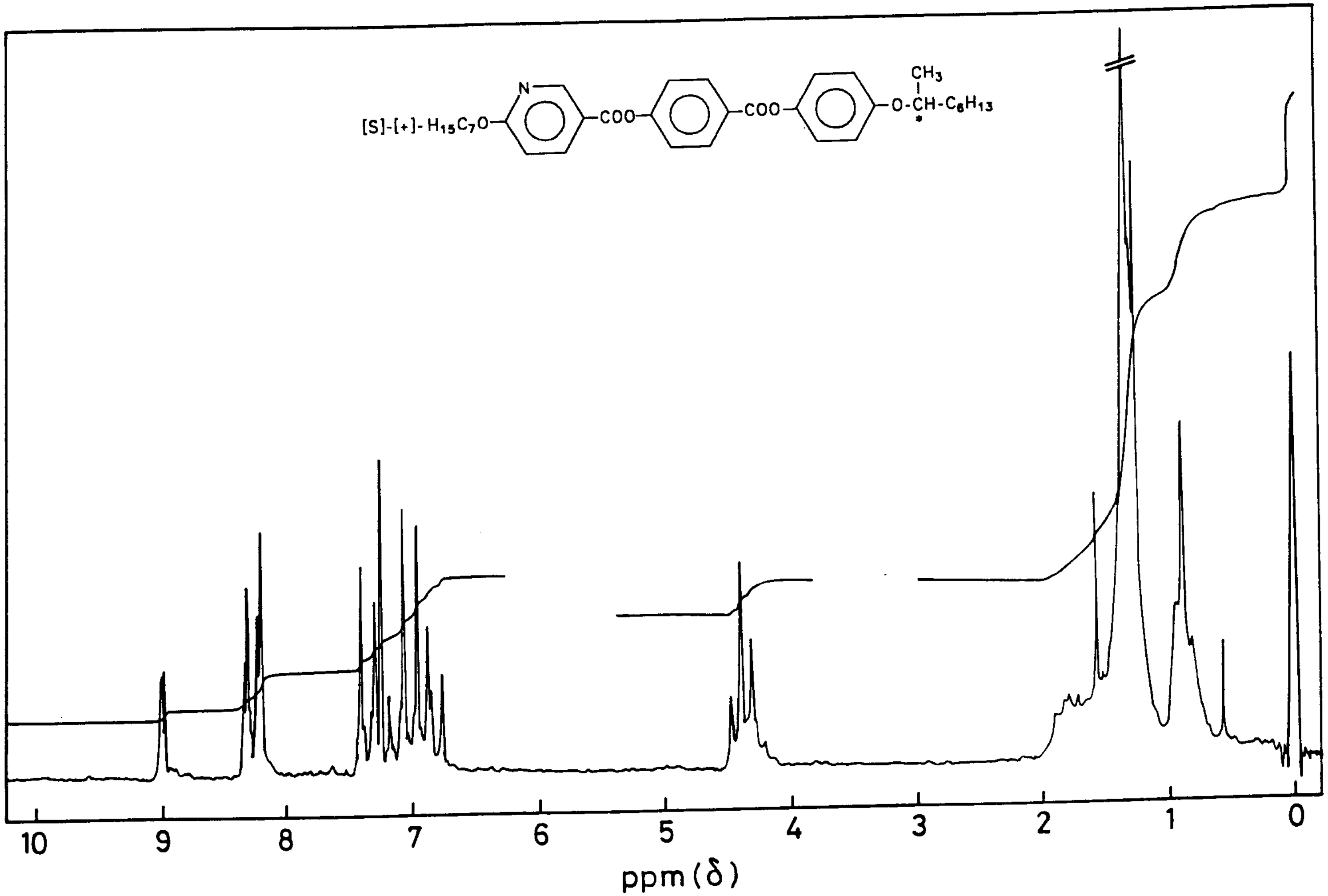
Elemental analysis: Found, C, 72.53; H, 7.85; N, 2.34% $C_{34}H_{43}NO_6$ requires C, 72.85; H, 7.67; N, 2.44%.

The physical data of the cognate preparations of the other [S]-[+]-4-(1-methylheptyloxy) phenyl-4′-(6″-n-alkoxypyridine-3-carbonyloxy)benzoates are given below.

[S]-[+]-4-(1-Methylheptyloxy)phenyl-4′-(6″-n-octyloxypyridine-3-carbonyloxy)benzoate, (3.H.2)

Yield, 80%; m.p. 76.2 °C; $[\alpha]_D^{25}$ = 3.72 ° (4.3 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1720, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(31H, m, 3XCH_3, 11XCH_2), 5.0-5.34(3H, m, ArOCH and ArOCH_2), 6.82(1H, dd, J=9.7 Hz, ArH), 7.32 and 8.15(4H, AB q, J=8.4 Hz, ArH), 7.4 and 8.3(4H, J=8.5 Hz, ArH), 8.17(1H, dd, J=9.4 Hz, ArH), 9.0(1H, dd, J=2.0 Hz, ArH);

Elemental analysis: Found, C, 73.43; H, 8.02; N, 2.46% $C_{35}H_{45}NO_6$ requires C, 73.17; H, 7.83; N, 2.43%.



^{1}H NMR spectrum for compound 3.H.

[S]-[+]-4-(1-Methylheptyloxy)phenyl-4′-(6″-n-nonyloxypyridine-3-carbonyloxy)benzoate, (3.H.3)

Yield, 84%; m.p. 52.7 °C; $[\alpha]_D^{25}$ = 3.55 ° (5.6 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1720, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(33H, m, $3XCH_3$, $12XCH_2$), 5.0-5.34(3H, m, ArOCH and $ArOCH_2$), 6.82(1H, dd, J=9.7 Hz, ArH), 7.32 and 8.15(4H, AB q, J=8.4 Hz, ArH), 7.4 and 8.3(4H, J=8.5 Hz, ArH), 8.17(1H, dd, J=9.4 Hz, ArH), 9.0(1H, dd, J=2.0 Hz, ArH);

Elemental analysis: Found, C, 73.71; H, 8.22; N, 2.32% $C_{36}H_{47}NO_6$ requires C, 73.46; H, 7.99; N, 2.38%.

[S]-[+]-4-(1-Methylheptyloxy)phenyl-4′-(6″-n-decyloxypyridine-3-carbonyloxy)benzoate, (3.H.4)

Yield, 81%; m.p. 56.7 °C; $[\alpha]_D^{25}$ = 1.71 ° (7.0 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1720, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(35H, m, $3XCH_3$, $13XCH_2$), 5.0-5.34(3H, m, ArOCH and $ArOCH_2$), 6.82(1H, dd, J=9.7 Hz, ArH), 7.32 and 8.15(4H, AB q, J=8.4 Hz, ArH), 7.4 and 8.3(4H, J=8.5 Hz, ArH), 8.17(1H, dd, J=9.4 Hz, ArH), 9.0(1H, dd, J=2.0 Hz, ArH);

Elemental analysis: Found, C, 73.47; H, 8.50; N, 2.28% $C_{37}H_{49}NO_6$ requires C, 73.75; H, 8.13; N, 2.32%.

[S]-[+]-4-(1-Methylheptyloxy)phenyl-4′-(6″-n-undecyloxypyridine-3-carbonyloxy)benzoate, (3.H.5)

Yield, 78%; m.p. 65.7 °C; $[\alpha]_D^{25}$ = 1.48 ° (4.0 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1720, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(37H, m, $3XCH_3$, $14XCH_2$), 5.0-

5.34(3H, m, ArOCH and $ArOCH_2$), 6.82(1H, dd, J=9.7 Hz, ArH), 7.32 and 8.15(4H, AB q, J=8.4 Hz, ArH), 7.4 and 8.3(4H, J=8.5 Hz, ArH), 8.17(1H, dd, J=9.4 Hz, ArH), 9.0(1H, dd, J=2.0 Hz, ArH);

Elemental analysis: Found, C, 73.81; H, 8.48; N, 2.04% $C_{38}H_{51}NO_6$ requires C, 74.02; H, 8.27; N, 2.27%.

[S]-[+]-4-(1-Methylheptyloxy)phenyl-4′-(6″-n-dodecyloxypyridine-3-carbonyloxy)benzoate, (3.H.6)

Yield, 85%; m.p. 65.8 °C; $[\alpha]_D^{25}$ = 2.11 ° (4.7 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1720, 1605, 1490, 1270 and 1050 cm^{-1}; δ: 0.7-2.0(39H, m, $3XCH_3$, $15XCH_2$), 5.0-5.34(3H, m, ArOCH and $ArOCH_2$), 6.82(1H, dd, J=9.7 Hz, ArH), 7.32 and 8.15(4H, AB q, J=8.4 Hz, ArH), 7.4 and 8.3(4H, J=8.5 Hz, ArH), 8.17(1H, dd, J=9.4 Hz, ArH), 9.0(1H, dd, J=2.0 Hz, ArH);

Elemental analysis: Found, C, 74.62; H, 8.82; N, 2.23% $C_{39}H_{53}NO_6$ requires C, 74.28; H, 8.41; N, 2.22%.

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