Chapter 4

Synthesis and mesomorphic properties of [R]-[-]-1-methylheptyl-4′-(3″-chloro-4″-n-alkoxybenzoyloxy) biphenyl-4-carboxylates

A brief account of the mesomorphic properties of compounds exhibiting twist grain boundary phases

The discovery of the first liquid crystalline material in 1888 [1,2] also heralded an age of fascination with chirality and optical activity in ordered fluids. The cholesteric mesophase, which was the first liquid crystal to be found, exhibits form optical activity by virtue of a helical arrangement of its constituent molecules. One hundred years later the discovery of a new helical smectic liquid crystal, the smectic-A* (TGB_A) phase was discovered.[3] In this phase the lath-like molecules are arranged in layers with their long axes on average normal to the layer planes. Parallel to the layers there is a helical ordering of the molecules. This phase may be described by a model in which grain boundaries of screw dislocations rotate blocks of layers with respect to each other.

The formation of such a helical structure in the plane of layers is difficult to conceive without disruption of the layer planes. However, Renn and Lubensky [4] predicted that the formation of a helix would be possible if a lattice of screw dislocations is incorporated into the structure of a normal smectic A phase. The helical twist is effected by a small rotation of blocks of the smectic A phase about an axis perpendicular to the director. **A** shift in registry between the individual blocks is produced by the inclusion of screw dislocations. A periodic array of such defects was predicted to form grain boundaries. Hence the twisted smectic A phase has become known as the twist grain boundary (TGB_A) phase. This novel helical smectic A* phase is a liquid crystal analogue of the Abrikosov phase of type II superconductors.[5] Initially, Renn and Lubensky suggested that under certain circumstances the twist grain boundary phase could mediate the cholesteric to smectic A transition. Later they expanded their model to incorporate the cholesteric to smectic C* (S_C*) transition, the phase predicted to be formed in this case was called the TGB_C phase. Two forms of this phase are expected, one where the molecules are simply inclined to the layer planes with no interlayer twist (TGB_C), and other where they are allowed to form helical structures normal to the layer planes in addition to the helices formed by the screw dislocations (TGB_C*).[6]

Goodby et *al.*[3,7] made the first experimental observation of such a phase existing with the synthesis of some phenyl propiolates (4.A). However, these materials were found to exhibit a direct isotropic liquid to TGB_A phase transition and no cholesteric - TGB_A - smectic A phase sequence was observed. Subsequent investigations revealed that a new class of chiral compounds gave some examples of the N*- TGB_A-S_A phase sequence [8-10] predicted by Renn and Lubensky.[4]

The materials showing TGB_A phase are generally highly chiral and their racemic versions exhibit only the ordinary S_A phase. The molecular chirality is thought to play a critical role in the twist of the smectic layers in one of two ways. In one case, the smectic layers remain fairly well defined over a certain distance beyond which the effective twist occurs. The twist is then incorporated into the system by successive blocks of well-defined smectic layers with respect to the layer plane, separated by defect regions.[4] Clearly, in this model the twist is confined within the defect region which is referred to as TGB. In another model, the smectic layers are still constrained parallel to each other as before, but the twist continuously develops within each smectic block as if the system possesses a sort of cholesteric phase with layer ordering. Accordingly, this structure would not be optically the same as the TGB phase, but would be similar to the cholesteric phase with enhanced orientational order.

The early structural studies carried out by Goodby *et al.*[3,7] on chiral 1-methylheptyl-4′-[(4″-n-alkoxyphenyl)propioloyloxy]biphenyl-4-carboxylates (4.B) revealed that TGB_A phase was formed only when certain criteria were satisfied.[11,12] These are (i) the presence of a short temperature range of S_A phase and a S_A-S_C* phase transition close to the clearing point, thus allowing pretransitional fluctuations to stabilise the resulting TGB_A phase; (ii) the transition from the cholesteric or liquid phase must approach second order; and (iii) the system must have strong chirality so as to be able to induce a twist through the S_A phase. The layered structure was evident by X-ray diffraction studies and the structure revealed by optical studies in the range of the visible wavelength shares common features with cholesteric liquid crystals.[3]

Racemic modifications of optically active compounds have been used in the past to aid the identification of mesophases in chiral materials.[3,7,10,13] A racemic mixture can be obtained if the isotropic liquids of the [R] and [S] enantiomers are allowed to make a sharp contact between glass plates and then allowed to cool to their liquid crystalline phases. At the junction of the two materials there is the formation of a racemic modification and moving away from the contact eventually gives the texture of either of the pure enantiomers, depending on the direction selected. Thus, a concentration gradient can be observed under the microscope and the phase changes that occur with varying concentration can be studied as a function of temperature. For compounds exhibiting a TGB_A phase the racemic modification exhibits a smectic A phase and a platelet texture away from the racemic modification.[14]

The fluoro-substituent is favoured as a lateral group in liquid crystal research for a variety of reasons, for example its small van der Waals radius [15] and its high polarity, *etc.*[16]

These properties frequently have well established effects on thermal stability [17] and other related properties.[18]

However, very little work has been carried out on the influence of molecular structure on the formation and stability of the TGB_A phase other than increasing the terminal n-alkoxy substituent chain length. We planned to investigate the influence of a lateral chloro-substituent present at position 3 in 4-n-alkoxybenzoates on the formation of TGB_A phase and properties of the smectic C* phase.

In this chapter we examine the properties of chiral carboxylates with particular reference to the effect of molecular chirality on the stabilisation of TGB_A phase. For instance, it is thought that the occurrence of a TGB_A phase is critically dependent on the nature of core of a liquid crystal molecule. In order to investigate this effect we have prepared a series of compounds, 4.F and compare it with those of series 4.A, in which the aliphatic chain attached to the asymmetric centre is common and the two differ in the nature of substituent at *ortho* to the n-alkoxy chain.

The novel TGB_A phase was observed in a newly synthesised family of ferroelectric materials, viz. [R]-[-] and [S]-[+]-1-methylheptyl-4′-(3″-chloro-4″-n-alkoxybenzoyloxy) biphenyl-4-carboxylates (4.F). These materials were prepared by the synthetic pathway shown in figure 4.1.

These materials were prepared by the esterification of a number of 3-chloro-4-n-alkoxybenzoic acids with [R]-[-] or [S]-[+]-1-methylheptyl-4′-hydroxybiphenyl-4-carboxylate. The 3-chloro-4-n-alkoxybenzoic acid portion of the target compounds was prepared starting from *ortho*-chlorophenol, which was acetylated with acetylchloride in the presence of pyridine. The resulting acetate (4.6), was then converted to the 3-chloro-

3-hydroxyacetophenone (4.7), by Fries rearrangement [19] using anhydrous aluminum chloride. The hydroxy compound was alkylated with a suitable n-alkylbromide in the presence of anhydrous potassium carbonate. Sodium hypobromite oxidation of the resulting n-alkoxyacetophenone gave the corresponding carboxylic acid. The biphenyl portion of the target materials was prepared starting from 4-methoxybiphenyl (4.1). This compound was acetylated using $AlCl_3$ in carbondisulphide and then demethylated with aqueous 48% HBr to give 4-hydroxy-4'-acetylbiphenyl (4.3), which was protected with benzylchloride as a benzylether (4.4). The 4-benzyloxy-4'-acetylbiphenyl was oxidised to the corresponding carboxylic acid (4.5) by using sodium hypobromite. This carboxylic acid was esterified with [R]-[-] or [S]-[+]-octan-2-ol in the presence of DCC and DMAP. The resulting ester (4.10) was debenzylated by hydrogenolysis reaction using 5% Pd-C.

Results and discussion

The transition temperatures with their enthalpies for the compounds of series 4.F are summarised in table 4.1. A plot of transition temperatures versus n-alkoxy chain length is shown in figure 4.2. From table 4.1, it can be seen that all the compounds are mesomorphic and they do not exhibit a cholesteric phase. The melting and clearing temperatures are relatively low. Clearing temperatures of all the compounds are below 100°C. The phase behaviour of the homologous series was studied by a variety of different techniques. The n-decyloxy homologue (4.F.1) shows only a metastable S_A phase. The phase sequence for the higher homologues of the series is TGB_A, S_A and S_C* on cooling from isotropic liquid. The evidence for the helical nature of the TGB_A phase formed was obtained by a simple experiment in which the compound was sandwiched between clean glass plates and heated to the isotropic liquid and allowed to cool into the TGB_A phase.

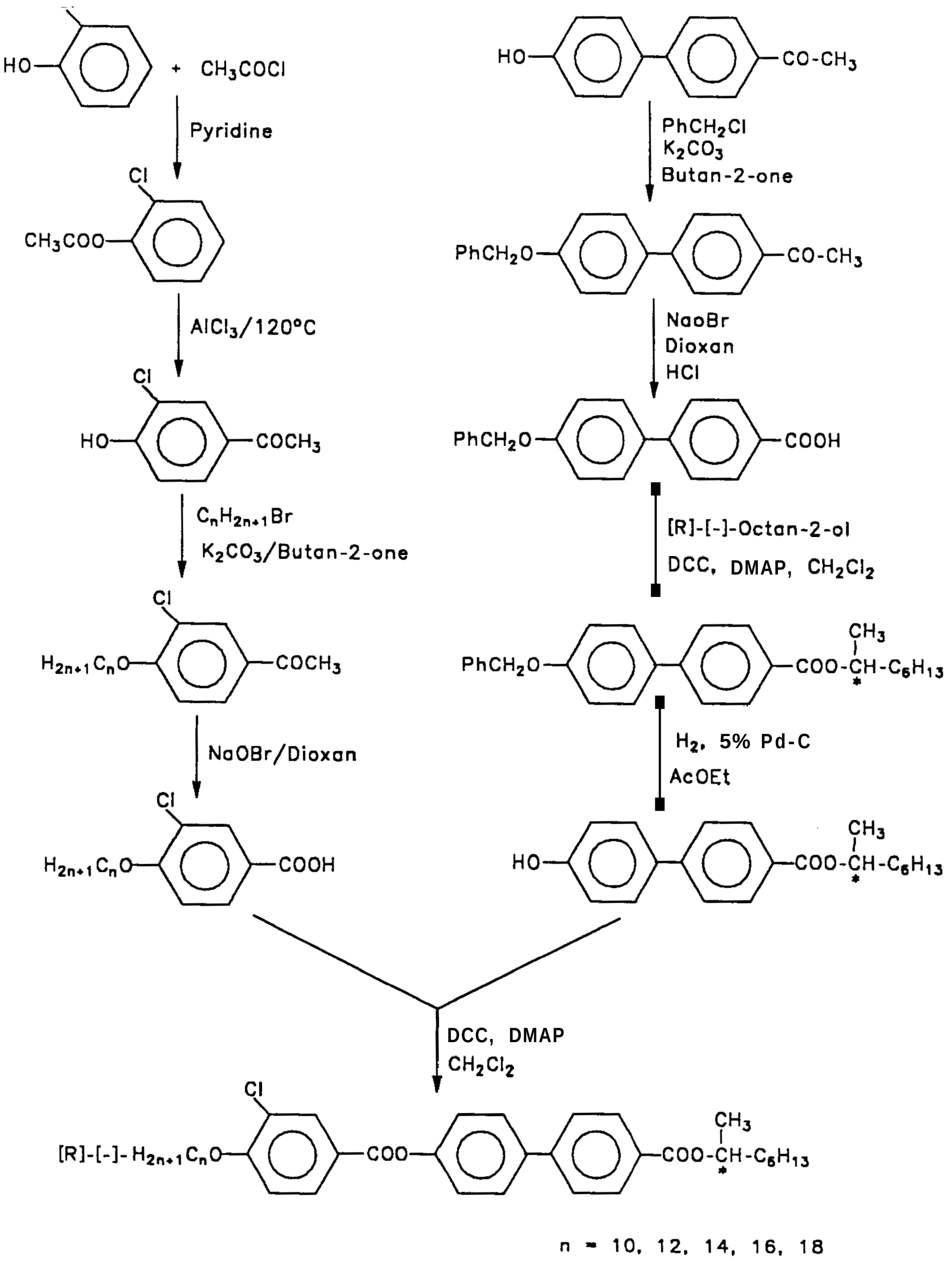
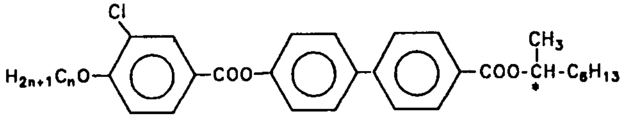


Figure 4.1. Synthetic scheme for the preparation of the compounds of series 4.F.

Table Phase sequence, transition temperatures (^{o}C) and enthalpies (kJ mole^{-1}) of



Compound number	n	C		S_C*		S_A		TGB_A		I
4.F.1	10	.	97.0 *33.4*	–		(.	86.0) *8.7*	–		.
4.F.2	12	.	50.3 *22.7*	.	77. 9 *0.32*	.	$80.4^{\dagger}$	.	83.6 *2.1*	.
4.F.3	14	.	42.0 *22.5*	.	76.5 *0.33*	.	$77.0^{\dagger}$	.	81.8 *2.3*	.
4.F.4	16	.	41.0 *44.6*	.	70.9 *0.21*	.	$75.0^{\dagger}$	.	79.0 *2.5*	.
4.F.5	18	.	43.4 *47.3*	.	71.0 *0.23*	.	$77.2^{\dagger}$	.	79.0 *2.6*	.
4.F.6	14	.	39.0 *24.8*	.	75.3 *0.34*	.	$72.8^{\dagger}$	.	80.5 *2.3*	.

† : The enthalpy could not be measured

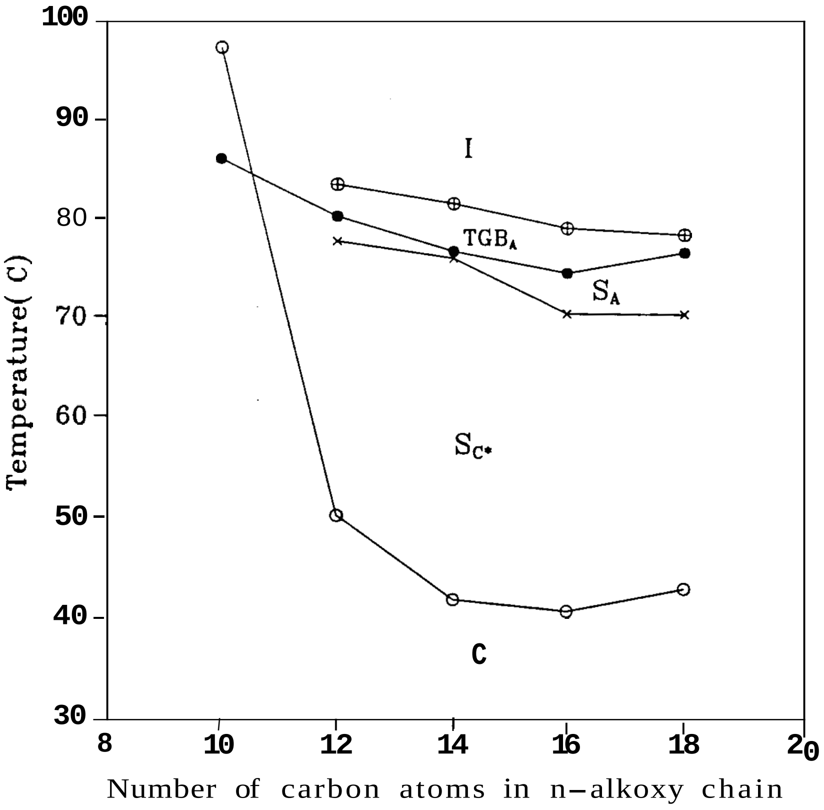


Figure 4.2. **A** plot of transition temperatures as a function of n-alkoxy chain length for series 4.F.

The mesophase was found to form in two distinct ways i.e. one a platelet texture and the other a Grandjean plane texture. The platelet texture of TGB$_A$ phase in some ways resemblss the platelet texture of blue phase I and the Grandjean plane texture appears iridescent and similar in nature to that of the cholesteric phase. As the plane texture nucleates and grows bands within the texture can be seen. These bands are possibly related to integral multiples of the pitch of the helix of the phase. Subsequent cooling produces a transition to a smectic A phase and on further cooling to S$_C$* phase.

Enantiomeric purity

Mixtures were made by accurate weighing of the desired amount of [R]-[-] and [S]-[+] enantiomers and mixed well in their isotropic states. The binary mixtures were analysed by polarised-light microscopy. The miscibility phase diagram of the compounds 4.F.3 and 4.F.6 is shown in figure 4.3. The clearing point rises as the optical purity of the binary mixture decreases. Two wing like regions of the TGB$_A$ phase appear between compositions of 0 and 5% wt./wt. of either [R] or [S] enantiomers. The temperature ranges for these TGB$_A$ wings differ considerably. The wings in the phase diagram indicates the sensitive nature of the TGB$_A$ phase to optical purity. Figure 4.3 shows that the S$_A$ and S$_C$* phases of the two compounds are continuously miscible.

The racemate displays different mesogenic behaviour to that shown by the enantiomers and here the TGB$_A$-S$_A$-S$_C$* phase sequence was replaced by a S$_A$-S$_C$ phase sequence. The phase thermal stabilities of the racemate is slightly higher than the phase shown by the pure enantiomers. A photomicrograph of the contact preparation between [R]-[-] and [S]-[+] enantiomers of n-tetradecyloxy homologue is shown in Plate 4.a.

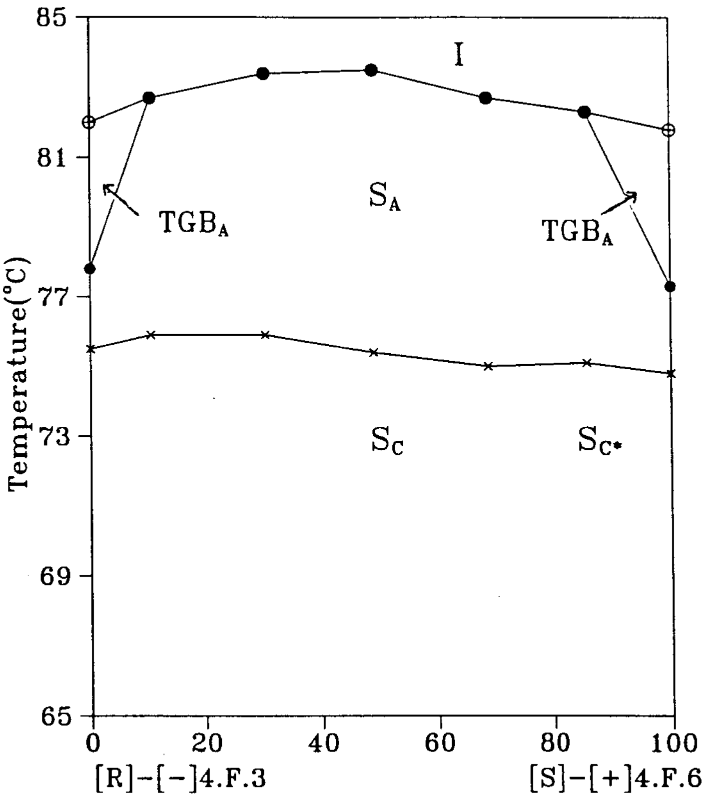


Figure 4.3. Binary phase diagram for mixtures of [R]- and [S]-1-methylheptyl-4-(3''-chloro, 4''-n-tetradecyloxybenzoyloxy)biphenyl-4-carboxylates.

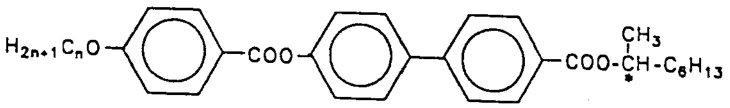
Cano-wedge [20] cells were employed to investigate further the TGB_A -S_A transition in compound 4.F.3, the surface orienting coating coupled with the separation of the glass plates giving improved textures of the mesophase. On heating, at the transition from the S_A to TGB_A, the focal-conic fans of the S_A texture develop transition lines and this gives way to the TGB_A phase, which is characterised by zones of filaments and Grandjean plane disclination lines. Rotation of the upper polariser of the microscope clearly showed a colour dispersion for white light caused by the helicity and hence the optically active nature of the phase. The presence of Grandjean disclination lines confirms the presence of a helical structure in TGB_A phase. However, the absence of any effect that is related to helicity or optical activity in the smectic **A** phase confirms the structure of this phase as being non-helical and consequently proves the occurrence of a TGB_A to S_A transition.

The photomicrographs were taken for compound 4.F.3 between crossed polarisers at various temperatures. The growth of the helical TGB_A phase from the isotropic liquid results in iridescent textures, similar to the cholesteric texture developed in a homeotropic geometry. On further cooling of the sample, textures characteristic of the TGB_A state were fully developed. In homogeneous regions, the TGB_A phase exhibits multiple connected platelets, related to integral multiples of the helical pitch of the phase as shown in Plate 4.b. On further cooling, the focal conic-fans which are characteristic of S_A phase are developed from the TGB_A phase. One of the most interesting features is the texture with filaments, shown in Plate 4.c, which grow in homeotropic region when the sample is heated from the S_A phase into the TGB_A state.

Goodby and his coworkers synthesised two homologous series 4.A,[21] 4.B[3,7,14] and Nguyen *et al.*[22] have synthesised the homologous series 4.C. The compounds of all these three series show rich polymesomorphism. The n-tetradecyloxy homologue of series 4.A shows the phase sequence from isotropic liquid as S_A, S_C*, $S^*_{C_\gamma}$ and $S^*_{C_A}$ phases. However, the corresponding homologues of series 4.B and 4.C exhibit TGB_A, S_A and S_C* phase sequence. A comparison of the molecular structure shows that the compounds of series 4.A differ from series 4.B and 4.C by a triple bond. As a result thermal stabilities of the mesophases are reduced and the phase sequence is also altered. Compounds of series 4.B differ from 4.C in the position of the triple bond. In series 4.B this is between the phenyl ring and a ester bridging group while it is between the two phenyl rings in series 4.C. As a result compounds of series 4.B have higher thermal stabilities of the mesophases.

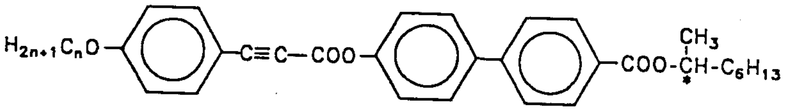
Consider the three homologous series 4.B, 4.D.a and 4.D.b.[23] In series 4.D.a and 4.D.b a phenyl hydrogen is replaced by a fluorine atom and these are positional isomers. The clearing temperatures of these two series of compounds are lower than the corresponding parent series 4.B. It is interesting to note that when the fluorine substituent is at position 3 with respect to the n-tetradecyloxy chain in series 4.D.b, the higher homologues exhibit the same phase sequence as the compounds of series 4.B. They also exhibit a S_A phase below TGB_A phase on cooling and then transform to S_C* phase on lowering the temperature further. However, when the fluorine substituent is at position 2 with respect to the n-tetradecyloxy chain as in series 4.D.a., only metastable S_A and S_C* phases are observed. Hence it may be inferred that the appearance of the TGB_A phase in 4.D.b could be that the polarity and polarisability is comparable to the compounds of the parent series 4.B.

Navailles *et al.*[24] have synthesised two homologous series 4.E.a and 4.E.b. Both series have the fluoro substituent on phenyl ring and are positional isomers. Compounds



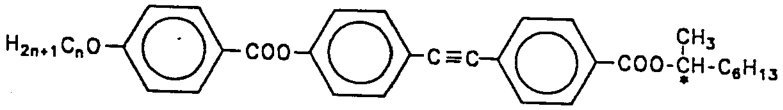
— 4.A

n = 10, C 65.2 (J* 47.8) $\mathrm{S}_{\mathrm{C}^*_\mathrm{A}}$ 69.0 $\mathrm{S}_{\mathrm{C}^*_\gamma}$ 75.9 $\mathrm{S}_{\mathrm{C}^*}$ 105.4 S_A 124.5 I



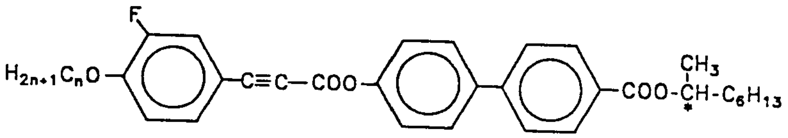
— 4.B

n = 14, C 78.3 $\mathrm{S}_{\mathrm{C}^*_\mathrm{A}}$ 42.5 $\mathrm{S}_{\mathrm{C}^*_\gamma}$ 53.4 $\mathrm{S}_{\mathrm{C}^*}$ 89.7 TGB_A 93.8 I



— 4.C

n = 18, C 79.0 $\mathrm{S}_{\mathrm{C}^*}$ 103.0 TGB_A 110 I



— 4.D.a

n = 14, C 80.3 ($\mathrm{S}_{\mathrm{C}^*}$ 75.3) I

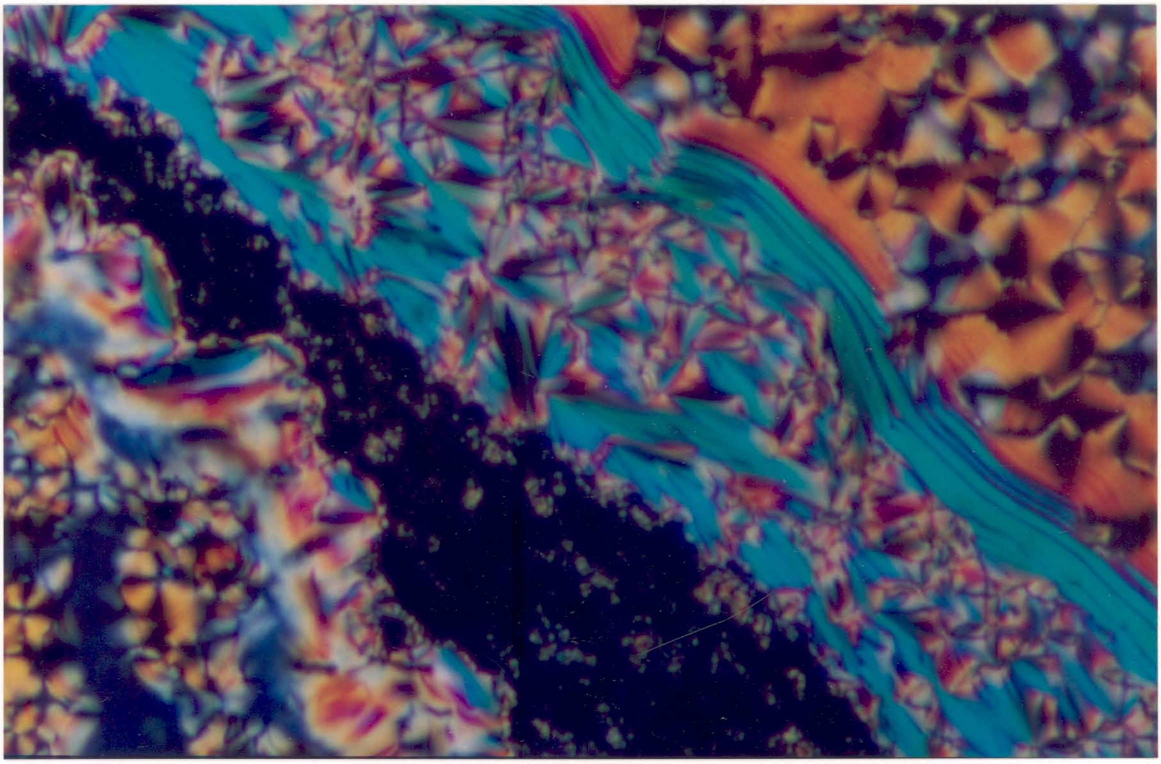


Plate 4.a. Photomicrograph of a contact preparation between4.F.3 and 4.F.6. The materials are both in their TGB_A phases at 79.8°C. In the central region of the contact, the pitch is compensated and becomes a S_A phase.

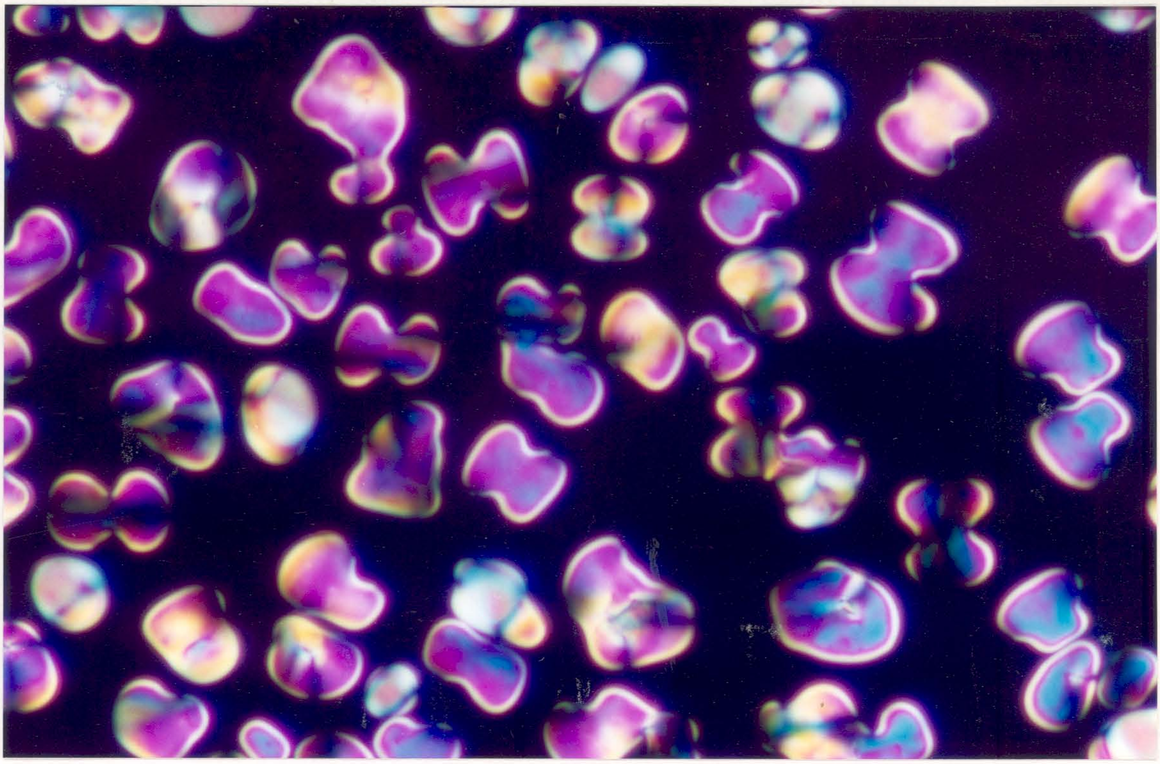


Plate 4.b. Photomicrograph of sample (4.F.3) showing TGB$_A$ phase at 79.0°C.

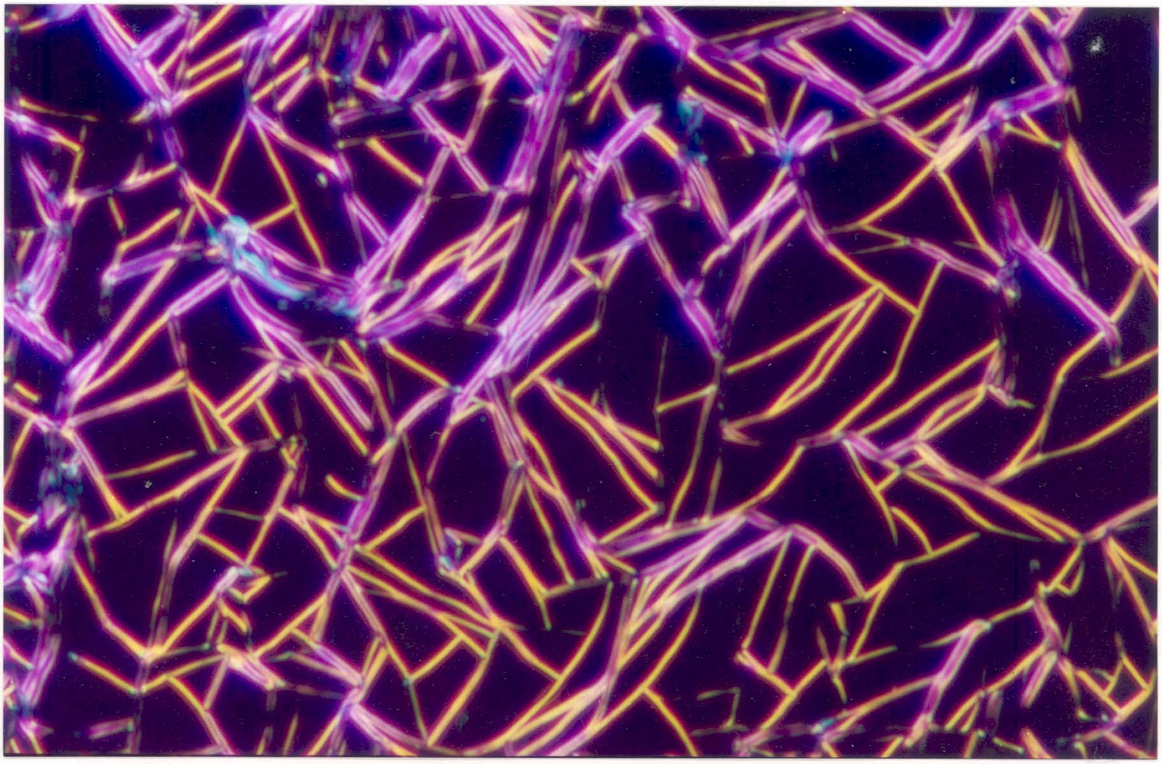


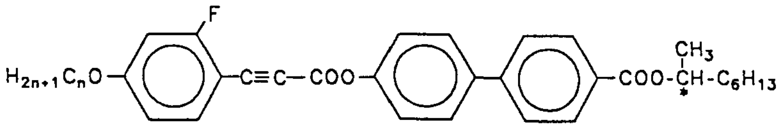
Plate 4.c. Photomicrograph of sample (4.F.3) showing TGB$_A$ phase (from homeotropic region of S$_A$ phase) at 77.0°C.

of series 4.C are the parent compounds for both the series. All these three series exhibit the TGB_A phase. Both the series 4.E.a and 4.E.b differ from series 4.D.a and 4.D.b in the position of the triple bond. From the above observations we can conclude that the existence of TGB_A phase is sensitive to the nature of the molecular core. When we substitute a hydrogen *ortho* to n-alkoxy group by chloro group, the homologous series 4.F is obtained. The n-tetradecyloxy homologue of this series shows S_A and TGB_A phases above S_C* phase on heating and it does not show ferrielectric and antiferroelectric phases like the corresponding homologue of series 4.A. All the phase transition temperatures for compounds of series 4.F are relatively lower than those for series 4.A.

Compare the two homologous series 4.D.a and 4.F. The two differ by the nature of a lateral substituent and a triple bond. Series 4.F has a chloro group in the position of fluoro group present in series 4.D.a and it does not have a triple bond. Compounds of 4.D.a show only S_A and S_C* phases, whereas compounds of series 4.F show TGB_A phase in addition to the S_A and S_C* phases. Hence, the polarisability and polarity of the molecule seem to play an important role in exhibiting the TGB_A phase.

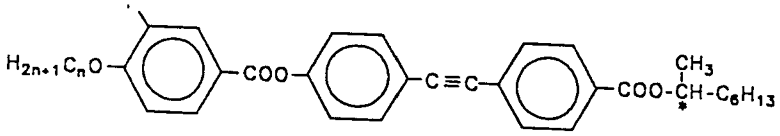
In collaboration with the Bordeaux group, the helical pitch in S_C* phase was measured for compound 4.F.3 by a method previously reported.[25, 26] Prismatic samples oriented in the Grandjean-Cano wedge with a weak angle (<0.25 deg.) was used. **A** planar alignment is necessary in the TGB mesophase whereas a pseudo homeotropic alignment is needed in the S_C* phase. The helical pitch obtained as a function of temperature is shown in figure 4.4.

As can be seen, in the TGB_A phase, the pitch is rather large and is about 0.5 μm near the isotropic phase producing selective reflection of dark red light. On cooling the pitch



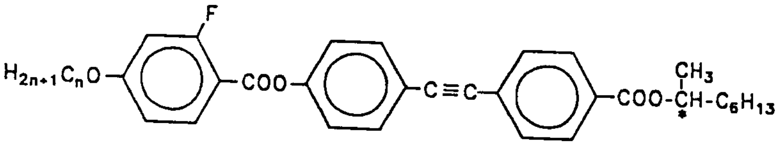
4.D.b

n = 14, C 48.9 S_{C^*} 72.6 S_A 80.8 TGB_A 85.8 I



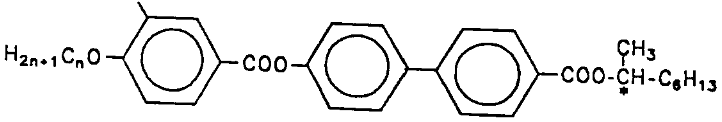
4.E.a

n = 14, C 66.5 S_{C^*} 94.9 TGB_A 104.9 I



4.E.b

n = 14, C 66.4 S_{C^*} 98.5 TGB_A 112.5 I



4.F

value increases and reaches a maximum value of 1.5 μm at 79.0°C. **A** high viscosity of the sample hinders the pitch divergence and hence accurate measurements have not been possible in this phase at lower temperatures.

In the S_C* phase, the pitch is very short viz., 0.24 μm at low temperature (42.0°C) giving selective reflection of red light (with $\lambda = 2np$). This increases upto a maximum of 0.3 μm at 72.0°C (violet, $\lambda = np$). **As** one approaches the TGB_A phase on heating, the pitch abruptly decreases to 0.15 μm producing red, orange and blue reflected light. In this compound no smectic **A** phase is seen.

To summarise, it can be said that in the three phenyl ring systems, the appearance of the TGB_A, antiferroelectric, ferroelectric phases seem to depend on the subtle changes that are made on the molecular structure. Specifically the introduction of a chloro group at the *ortho* position to the n-alkoxy chain (series 4.F) result in compounds which exhibit the TGB_A phase at the expense of the ferrielectric and antiferroelectric phases.

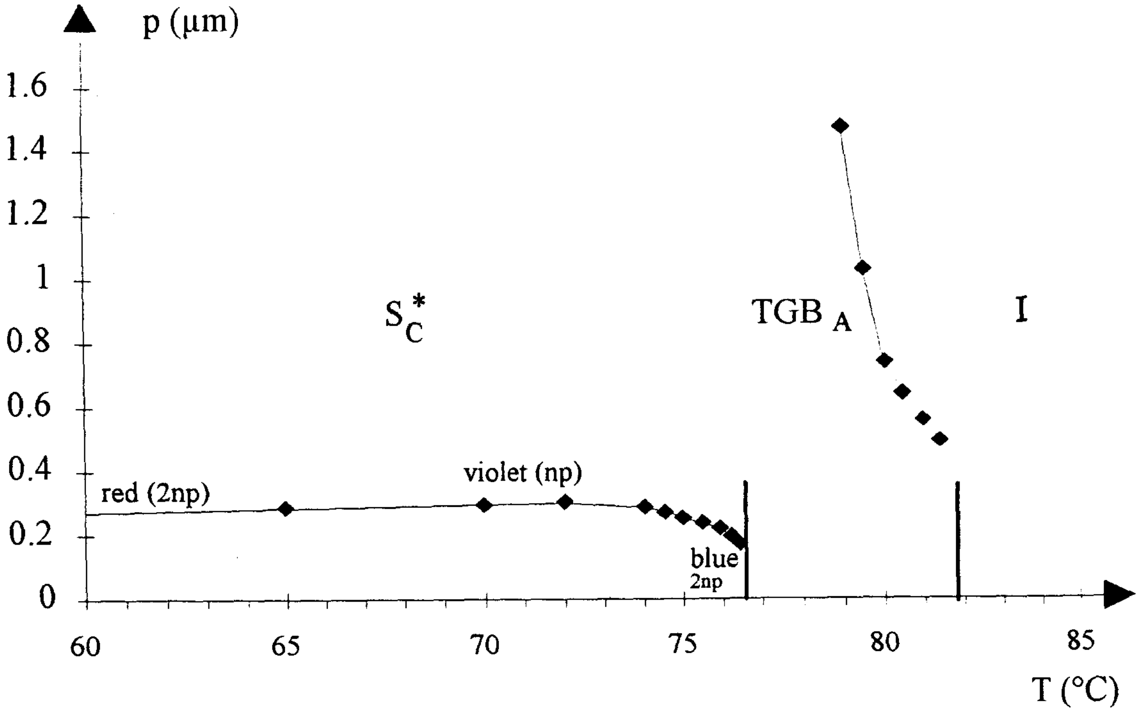


Figure 4.4. Plot of helical pitch versus reduced temperature for compound 4 **F.3** in S_C* **phase.**

Experimental

4-Methoxybiphenyl (4.1)

4-Hydroxybiphenyl (51.0 g, 300 mmol) was placed in a 500 ml three-necked flask equipped with a pressure equalising separatory funnel, a mechanical stirrer and a reflux condenser. **A** solution of sodium hydroxide (12.8 g, 320 mmol) in water (128 ml) and ethyl alcohol (100 ml) was added to it. This mixture was stirred and dimethylsulphate (37.8 g, 300 mmol) was added dropwise to it over a period of one hour. Then the reaction mixture was refluxed for one and half hours. When the solution became clear, this was cooled ,the solid product so obtained was filtered off, washed with water, dried and recrystallised from ethanol(54.2 g, 80%); m.p. 89.0°C (Reported [27] m.p. 91.O°C)

4-Methoxy-4′-acetylbiphenyl (4.2)

In a 500 ml three-necked flask fitted with a mechanical stirrer, a pressure equalising separatory funnel and a reflux condenser connected to a water trap through anhydrous calcium chloride guard tube, was placed a mixture of 4-methoxybiphenyl (18.4 g, 100 mmol), anhydrous aluminum chloride (18.7 g, 140 mmol) and carbon disulphide (175 ml). This was cooled in an ice-bath and while stirring freshly distilled acetyl chloride **(7.8** g, 100 mmol) was added dropwise to it. After the addition was complete the reaction mixture was stirred at 35.0°C for five hours and then refluxed for one hour. After the removal of carbon disulphide, the residue was poured into a mixture of ice and concentrated hydrochloric acid. The solid formed was filtered and boiled with ether (50.0 ml) for fifteen minutes and the ethereal solution was decanted off. The ether insoluble portion was crystallised from isopropanol(14.7 g, 65%); m.p. 157.0^{0}C (Reported [28] m.p.156.5°C).

4-Hydroxy-4′-acetylbiphenyl (4.3)

A mixture of 4-methoxy-4′-acetylbiphenyl (10.0 g, 44.0 mmol), hydrobromic acid (48%, 75 ml)and acetic acid (125 ml) was refluxed for sixteen hours. It was then poured into ice-cold water and the precipitate formed was filtered, washed with water and dried. The crude product so obtained was crystallised from ethanol (8.9 g, 95%); m.p. 146-147°C (Reported [29] m.p. 146-147°C).

4-Benzyloxy-4′-acetylbiphenyl (4.4)

A mixture of 4-hydroxy-4′-acetylbiphenyl (4.24 g, 20 mmol), benzylchloride (3.03 g, 24 mmol), potassium carbonate(8.28 g, 60 mmol) and dry acetone(100 ml) was refluxed for forty-eight hours. Then the acetone was distilled off from the reaction mixture and the residue poured into a mixture of ice and concentrated hydrochloric acid and extracted with chloroform (3X100 ml). The combined chloroform solution was washed with water (3X100 ml) and dried (Na_2SO_4). The solvent was removed and the residue was chromatographed. The required material so obtained was crystallised from t-butanol (4.2g, 70%); m.p. 162-165.0^{0}C.

4-Benzyloxybiphenyl-4'-carboxylic acid (4.5)

A solution of sodium hypobromite was prepared by adding bromine (6.4 g, 40 mmol) to a solution of sodium hydroxide (3.2 g, 80 mmol) in water (40 ml) at -5°C. This was added to a vigorously stirred solution of 4-benzyloxy-4′-acetylbiphenyl (3.0 g, 10 mmol) in 1, 4-dioxane (20 ml). The addition was carried out at 30-35°C during thirty minutes.

Stirring was continued and the temperature was raised to 60°C and held there for one hour to ensure completion of the reaction. Enough aqueous sodium metabisulphite was added to destroy the excess of hypobromite. Water (50 ml) was added and about 40 ml of the liquid was distilled. The residual portion was cooled and acidified with concentrated hydrochloric acid. The white precipitate so obtained was filtered off, washed thoroughly with water and dried. This was crystallised from acetic acid (2.3 g, 76.6%); m.p. 267°C (decomposes).

2-Chlorophenylacetate (4.6)

To an ice-cold solution of 2-chlorophenol (32.1 g, 250 mmol) in pyridine (75 ml), acetyl chloride (19.6 g, 250 mmol) was added dropwise over a period of one hour. This mixture was stirred at room temperature for four hours and poured into a mixture of ice and concentrated hydrochloric acid. This was extracted with chloroform (2X150 ml) and the combined chloroform extracts was washed with water (3X200 ml). The chloroform solution was dried (Na_2SO_4) and the solvent removed. The crude product so obtained was distilled under reduced pressure(37.7 g, 88%); b.p. 65°C/2-3 mm of Hg (Reported [27] b.p. 103°C/15 mm of Hg).

3-Chloro-4-hydroxyacetophenone (4.7)

This compound was prepared using a Fries rearrangement.[19] Thus, a mixture of 2-chlorophenylacetate (37.6 g, 200 mmol) and anhydrous aluminum chloride (58.8 g, 400 mmol) was heated for two hours at 120°C in an oil bath. It was then poured into a mixture of ice and concentrated hydrochloric acid. The precipitate formed was filtered, washed with water until the washings were neutral and dried. The crude product so obtained was crystallised from toluene(24.0 g, 64%); m.p. 99.0°C (Reported [27] m.p. 100.0-100.5°C); ν_{max}: 3350,2960, 1700, 1600, 1510, 1450, 1275 and 1050 cm^{-1}.

3-Chloro-4-n-tetradecyloxyacetophenone (4.8)

A mixture of 3-chloro-4-hydroxyacetophenone (2 g, 11.7 mmol), 1-bromotetradecane (2.85 g, 12.9 mmol), anhydrous potassium carbonate(4.85 g, 35.1 mmol) and dry butan-2-one (35 ml) was refluxed for twenty-four hours. Then, butan-2-one was distilled off from the reaction mixture and the residue poured into a mixture of ice and concentrated hydrochloric acid and extracted with chloroform(3X50 ml). The combined chloroform solution was washed with water (3X30 ml) and dried ($CaCl_2$). The solvent was removed and the residue was chromatographed. The required material so obtained was crystallised from t-butanol(3.0 g. 71%); m.p. 74.2°C; ν_{max}: 3000, 1710, 1610, 1580, 1280, 1050 cm^{-1}.

The physical data of the cognate preparations of other 3-chloro-4-n-alkoxyacetophenones are given in table 4.2.

Table 4.2. Melting points of 3-chloro-4-n-alkoxyacetophenones

Compound number	n	Observed m.p (°C)
1	10	55.8
2	12	62.1
3	16	68.2
4	18	79.8

3-Chloro-4-n-tetradecyloxybenzoic acid (4.9)

A solution of sodium hypobromite was prepared by adding bromine (4.36 g, 27.2 mmol) to a solution of sodium hydroxide (3.81 g, 95.5 mmol) in water (25 ml) at -5°C. This was added to a vigorously stirred solution of 3-chloro-4-n-tetradecyloxyacetophenone (2.0 g, 5.4 mmol) in 1, 4-dioxane (20 ml). The addition was carried out at 30-35°C during thirty minutes, then the temperature was raised to 60°C and held there for one hour. Enough aqueous sodium metabisulphite was added to destroy the excess of hypobromite. Water (30 ml) was added and about 30 ml of the liquid was distilled. The residual portion was cooled and acidified with concentrated hydrochloric acid. The white precipitate obtained was filtered, washed thoroughly with water and dried. This was crystallised from isopropanol(1.4 g, 70.2%); m.p. 104°C; ν_{max}: 3600, 3000, 1710, 1610, 1580, 1280, 1050 cm^{-1}.

The physical data of the cognate preparations of other **3-chloro-4-n-alkoxybenzoic** acids are given in table 4.3.

Table 4.3. Melting points of 3-chloro-4-n-alkoxybenzoic acids

Compound number	n	Observed m.p (°C)	Reported m.p (°C)	Reference
1	10	99.0 -100.0	105.0	28
2	12	100.5-101.0	101.5	28
3	16	98.8-99.0	99.5	28
4	18	106.0-107.0	107.5	28

[R]-[-]-1-Methylheptyl-4′-benzyloxybiphenyl-4-carboxylate (4.10)

This was prepared following a esterification procedure of Hassner and Alexanian.[30] Thus, a mixture of 4′-benzyloxybiphenyl-4-carboxylic acid(1 g, 3.28 mmol),R-[-]-octan-2-ol(0.42g, 3.28 mrnol), DMAP (0.25g, 1.96 mmol) and dichloromethane (16.0 ml) was stirred for five minutes. To the mixture, was added DCC (1.3 g, 6.3 mmol) and stirring was continued for six hours at room temperature. The solid N,N′-dicyclohexylurea formed was filtered off and the filtrate was diluted with dichloromethane(50 ml). The solution was washed with 5% aqueous acetic acid(2X30 ml), water(3X30 ml) and dried (Na_2SO_4). After the solvent was removed, the residue was purified by column chromatography on silica gel using chloroform as eluent (3.5 g, 87%); m.p. 104.6-105.7°C; $[\alpha]_D^{25}$ = - 36.9 ° (5.1 mg/ml in CH_2Cl_2);,,ν 3000, 1710, 1610. 1580, 1280, 1050 cm^{-1}; 6: 0.63-2.39(16H, m, $2XCH_3$, $5XCH_2$), 4.15 (1H, m, COOCH). 5.12(2H, s, $ArCH_2OAr$), 6.95 and 7.6(4H, AB q, J=9 Hz, ArH), 7.4(5H, s, ArH), 7.75 and 8.2(4H, AB q, J=8.9 Hz, ArH);

Elemental analysis: Found, C, 80.68; H, 7.64% $C_{28}H_{32}O_3$ requires
C, 80.78; H, 7.69%.

[S]-[+]-1-Methylheptyl-4′-benzyloxybiphenyl-4-carboxylate (4.11)

This was prepared following a procedure similar to the one described above for compound 4.10, but using [S]-[+]-octan-2-ol (4.10). Yield, 84%; m.p.104-106°C: $[\alpha]_D^{25}$ = 36.9 ° (4.6 mg/ml in CH_2Cl_2); ν_{max}: 3000, 1710, 1610, 1580, 1280. 1050 cm^{-1}; δ: 0.63-2.39(16H, m. 2XCH3. $5XCH_2$), 4.15 (1H. m, COOCH), 5.12(2H. s, $ArCH_2OAr$), 6.95 and 7.6(4H. AB q, J=9 Hz. ArH), 7.7(5H. s, ArH), 7.75 and 8.2(4H. AB q, J=8.9 Hz. ArH);

Elemental analysis: Found, C, S0.56; H, 7.71% $C_{28}H_{32}O_3$ requires
C, 80.78; H. 7.69%.

[R]-[-]-1-Methylheptyl-4″-hydroxybiphenyl-4-carboxylate (4.12)

A mixture of [R]-[-]-1-methylheptyl-4′-benzyloxybiphenyl-4-carboxylate(3.0 g, 7.21 mmol) in 1,4-dioxane(20 ml) and 5% Pd-C catalyst(1.2 g) was stirred in an atmosphere of hydrogen till the calculated quantity of hydrogen was absorbed. The reaction mixture was then filtered off and 1,4-dioxane removed by distillation under reduced pressure. The residual solid was chromatographed on silica gel and eluted with chloroform and ethylacetate (9:1) mixture. Removal of the solvent from the eluate afforded a white crystalline solid(1.9 g, 81.5%); m.p. 84-86°C (Reported [23] m.p. 84-86°C); $[\alpha]_D^{25}$ = - 43.5 ° (3.2 mg/ml in CH_2Cl_2); ν_{max}: 3350. 2960, 1740, 1690, 1600, 1510, 1450, 1275 and 1050 cm^{-1}; 6: 0.75-2.0(16H, m, 2XCH_3, 5XCH_2) 4.2(1H, m, COOCH), 6.95 and 7.6(4H, AB q, J=9 Hz, ArH), 7.5(1H, s, ArOH), 7.55 and 8.2(4H, AB q, J=8.7 Hz, ArH);

Elemental analysis: Found, C, 77.41; H, 7.96% $C_{21}H_{26}O_3$ requires
C, 77.3; H, 7.97%.

[S]-[+]-1-Methylheptyl-4′-hydroxybiphenyl-4-carboxylate (4.13)

This was prepared following a procedure similar to the one described above (4.12). Yield, 80%; m.p. 86-88°C (Reported [23] m.p. 87-89°C); $[\alpha]_D^{25}$ = 43.2 ° (5.1 mg/ml in CH_2Cl_2); ν_{max}: 3350, 2960, 1740, 1690, 1600, 1510, 1450, 1275 and 1050 cm^{-1}; 6: 0.75-2.0(16H, m, 2XCH_3, 5XCH_2), 4.2(1H, m, COOCH), 6.95 and 7.6(4H, AB q. J=9 Hz, ArH), 7.5(1H, s, ArOH), 7.55 and 8.2(4H, AB q, J=8.7 Hz, ArH);

Elemental analysis: Found. C, 77.21; H. 7.7470 $C_{21}H_{26}O_3$ requires
C, 77.3; H, 7.97%.

[R]-[-]-1-Methylheptyl-4′-(3″-chloro-4″-n-tetradecyloxybenzoyloxy) biphenyl-4-carboxylate (4.F.3)

This was prepared following a procedure similar to the one described above (4.10). Yield, 70.5%; m.p. 42.0°C; $[\alpha]_D^{25}$ = - 19.23 ° (2.6 mg/ml in CH_2Cl_2); ν: 2950, 1740, 1730, 1710, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(43H, m, $3XCH_3$, $17XCH_2$), 4.09(2H, t, J=6.6 Hz, $ArOCH_2$), 5.03(1H, m, COOCH), 7.01(1H, dd, J=8 Hz, ArH), 7.32(1H, dd, J=7.4 Hz, ArH), 7.38(1H, dd. J=7.5 Hz, ArH), 7.58 and 8.13(4H, AB q, J=9.3 Hz, ArH), 7.6 and 8.23(4H, AB q, J=9 Hz, ArH);

Elemental analysis: Found, C, 74.53; H, 8.67% $C_{42}H_{57}ClO_5$ requires
C, 74.5; H, 8.42%.

The physical data of the cognate preparations of the other [R]-[-]-1-methylheptyl-4′-(3″-chloro-4″-n-alkoxybenzoyloxy)biphenyl-4-carboxylates are given below.

[R]-[-]-1-Methylheptyl-4′-(3″-chloro-4″-n-decyloxybenzoyloxy)biphenyl-4-carboxylate (4.F.1)

Yield, 71%; m.p. 97.0°C; $[\alpha]_D^{25}$ = - 20.8 ° (3.6 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1730, 1710, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(35H, m, $3XCH_3$, $13XCH_2$), 4.13(2H, t, J=6.6 Hz, $ArOCH_2$), 5.03(1H, m, COOCH), 7.01(1H, dd, J=S Hz, ArH), 7.32(1H, dd, J=7.4 Hz, ArH), 7.38(1H, dd. J=7.5 Hz, ArH), 7.58 and 8.13(4H, AB q, J=9.3 Hz, ArH), 7.6 and 8.23(4H, AB q, J=9 Hz, ArH);

Elemental analysis: Found. C, 73.5; H. 8.11% $C_{38}H_{49}ClO_5$ requires
C, 73.48; H, 7.89%.

[R]-[-]-1-Methylheptyl-4′-(3″-chloro-4″-n-dodecyloxybenzoyloxy)biphenyl-4-carboxylate (4.F.2)

Yield, 74%; m.p. 50.3°C; $[\alpha]_D^{25}$ = - 19.42 ° (2.8 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1730, 1710, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(39H, m. $3XCH_3$, $15XCH_2$), 4.13(2H, t, J=6.6 Hz, $ArOCH_2$), 5.03(1H, m, COOCH), 7.01(1H, dd, J=8 Hz, ArH), 7.32(1H, dd, J=7.4 Hz, ArH), 7.38(1H, dd, J=7.5 Hz, ArH), 7.58 and 8.13(4H, AB q, J=9.3 Hz, ArH), 7.6 and 8.23(4H, AB q, J=9 Hz, ArH);

Elemental analysis: Found, C, 73.61; H, 8.31% $C_{40}H_{53}ClO_5$ requires C, 74.06; H, 8.17%.

[R]-[-]-1-Methylheptyl-4′-(3″-chloro-4″-n-hexadecyloxybenzoyloxy) biphenyl-4-carboxylate (4.F.4)

Yield, 80%; m.p. 41.0°C; $[\alpha]_D^{25}$ = - 20.17 ° (4.6 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1730, 1710, 1605, 1490, 1270 and 1050 cm^{-1}; 6: 0.7-2.0(47H, m, $3XCH_3$, $19XCH_2$), 4.13(2H, t, J=6.6 Hz, $ArOCH_2$), 5.03(1H, m, COOCH), 7.01(1H, dd, J=8 Hz, ArH), 7.32(1H, dd, J=7.4 Hz, ArH), 7.38(1H, dd, J=7.5 Hz, ArH), 7.58 and 8.13(4H, AB q, J=9.3 Hz, ArH), 7.6 and 8.23(4H, AB q, J=9 Hz, ArH);

Elemental analysis: Found, C, 74.55; H, 8.83% $C_{44}H_{61}ClO_5$ requires C, 74.96; H, 8.65%.

[R]-[-]-1-Methylheptyl-4′-(3″-chloro-4″-n-octadecyloxybenzoyloxy) biphenyl-4-carboxylate (4.F.5)

Yield. 82%; m.p. 43.4°C; $[\alpha]_D^{25}$ = - 16.6 ° (3.2 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1730, 1710. 1605, 1490. 1270 and 1050 cm^{-1}; 6: 0.7-2.0(51H, m, $3XCH_3$, $21XCH_2$), 4.13(2H, t, J=6.6 Hz, $ArOCH_2$), 5.03(1H, m, COOCH), 7.01(1H, dd, J=8 Hz, ArH), 7.32(1H, dd, J=7.4 Hz, ArH), 7.38(1H, dd, J=7.5 Hz, ArH), 7.58 and 8.13(4H, AB q, J=9.3 Hz, ArH), 7.6 and 8.23(4H, AB q, J=9 Hz, ArH);

Elemental analysis: Found, C, 75.13; H, 9.05% $C_{46}H_{65}ClO_5$ requires
C, 75.35; H, 8.87%.

[S]-[+]-1-Methylheptyl-4′-(3″-chloro-4″-n-tetradecyloxybenzoyloxy) biphenyl-4-carboxylate (4.F.6)

Yield, 84%; m.p. 39.0°C; $[\alpha]_D^{25}$ = 22.4 ° (2.6 mg/ml in CH_2Cl_2); ν 2950, 1740, 1730, 1710, 1605, 1490, 1270 and 1050 cm^{-1}; δ: 0.7-2.0(43H, m, $3XCH_3$, $17XCH_2$), 4.13(2H, t, J=6.6 Hz, $ArOCH_2$), 5.03(1H, m, COOCH), 7.01(1H, dd, J=8 Hz, ArH), 7.32(1H, dd, J=7.4 Hz, ArH), 7.38(1H, dd, J=7.5 Hz, ArH), 7.58 and 8.13(4H, AB q, J=9.3 Hz, ArH), 7.6 and 8.23(4H, AB q, J=9 Hz, ArH);

Elemental analysis: Found, C, 74.11; H, 8.59% $C_{42}H_{57}ClO_5$ requires
C, 74.5; H, 8.42%.

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