

Chapter 2

Synthesis and mesomorphic properties of

[S]-[+]-1-methylheptyl-4-[4'-(*trans*-4''-n-alkoxycinnamoyloxy)benzoyloxy]benzoates

and

[S]-[+]-1-methylheptyl-4-[4'-(*trans*-4''-n-alkoxy- α -methylcinnamoyloxy)benzoyloxy]benzoates

Chapter 2

A brief account of mesomorphic properties of chiral di- and tri- esters containing two and three phenyl rings

The liquid crystalline properties of organic compounds are highly sensitive to changes in the chemical structure, and considerable effort has been devoted to the systematic study of closely related compounds in order to establish empirical relationship between structural and other parameters and the thermal stabilities of the various types of mesophases which may be observed.' In the past few years, much attention has been devoted to the preparation and study of homologous series of chiral organic compounds which show mesogenic behaviour.

Many organic compounds exhibiting liquid crystalline properties contain two phenyl rings with substituents in the para positions. On moving from two ring mesogens with one linking unit to three ring mesogens with two linking units, mesophase thermal stabilities are greatly enhanced. In a three ring system when two rings are linked by a unit which preserves conjugative interaction and molecular rigidity, e.g., $-\text{CH}=\text{N}-$, $-\text{CH}=\text{CH}-$, etc., the second linking unit can be more flexible, e.g., $-\text{CH}_2-\text{CH}_2-$, $-\text{O}-\text{CH}_2-$ etc. This implies that if a considerable portion of a lath-like molecule is rigid and packs parallel to similar portions of neighbouring molecules, more flexible parts of the molecules may be constrained to lie in line with more rigid part. However, a combination of a rigid and a flexible linking unit in three ring mesogens gives less thermally stable mesophases than those that occur with two rigid linking units.^{2,3}

Since the discovery of ferroelectricity in the chiral smectic C (S_C^*) phase by Meyer et al.⁴ in 1975 and the proposal of electro-optical devices using ferroelectric liquid crystals by Clark and Lagerwall⁵ in 1980, extensive studies have been carried out on ferroelectric

liquid crystal materials and their use in applications. One of the most important features of ferroelectric liquid crystal (FLC) devices is fast bistable switching.

Since the discovery of tristable switching and a subsequent identification of antiferroelectric ($S_{C_A}^*$), ferroelectric ($S_{C_\gamma}^*$) and chiral C_α ($S_{C_\alpha}^*$) smectic phases in 4-(1-methylheptyloxycarbonyl)phenyl-4'-octyloxybiphenyl-4-carboxylate (MHPOBC),⁶⁻⁹ much research has been carried out on basic and application aspects.¹⁰⁻¹² However, there remain several unresolved problems such as the origin of the appearance of the antiferroelectric and ferroelectric phases especially from the standpoint of molecular structure. Although liquid crystal molecules are treated as rigid rods in most theoretical approaches until now, the molecular conformations and the intermolecular interactions are thought to be the key to understanding the origin of these phases and the transitions between them.

The changes in the mesomorphic properties on extension of the core in a molecule is illustrated by considering the two series of compounds 2.A and 2.B.¹³ A comparison between the two series shows that because of the longer core of the molecules of series 2.B, both the melting points and the clearing temperatures are higher and the temperature ranges of mesophases are widened. All the homologues of series 2.B ($n=1$ to $n=10$) show enantiotropic mesophases. The lower homologues ($n=1$ to $n=3$) exhibit only a cholesteric (N^*) phase. However, this phase exists over a wide range of temperature (about 125°C) for these homologues. For the homologue when $n = 4$, a smectic A (S_A) phase is observed in addition to the cholesteric phase. In series 2.A, the cholesteric phase is exhibited by only two homologues ($n=6$ and $n=7$). The smectic A phase is observed for compounds with $n=8$ in both series and their range of temperatures are different. The n-decyloxy compound ($n=10$) of series 2.A has a thermal range for the ferroelectric smectic C (S_C^*)

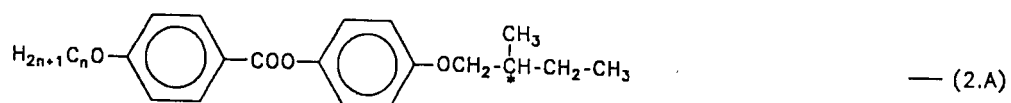
phase equal to 7.5°C, whereas the corresponding homologue of series 2.B has a range of 36.5°C. Thus, the temperature range of S_C^* phase has indeed been widened by increasing the core length of the molecule.

Similar conclusions can be drawn by considering series 2.C and 2.D.¹⁴ There is no cholesteric phase in these two series of compounds. It can be seen that the additional benzyloxy group in 2.D has increased the clearing temperature by about 110°C and the S_C^* - S_A transition temperature by about 93°C in the n-decyloxy homologue. In series 2.D the additional phenyl ring induced a thermally more stable ferroelectric phase below the S_A phase. The effect of introduction of a methyl group at a-position of a cinnamic acid ester will be discussed later.

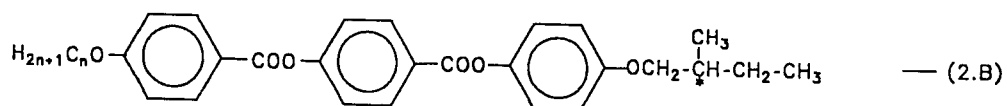
Results and discussion

In an effort to obtain $S_{C_A}^*$, $S_{C_\gamma}^*$ and S_C^* phases with relatively wide temperature ranges and study their properties upon changes in molecular structure, a number of compounds were investigated. In this chapter, we discuss the synthesis and properties of [S]-[+]-1-methylheptyl-4-[4'-(*trans*-4''-n-alkoxycinnamoyloxy)benzyloxy]benzoates, series (2.E) and [S]-[+]-1-methylheptyl-4-[4'-(*trans*-4''-n-alkoxy- α -methylcinnamoyloxy) benzyloxy] benzoates, series (2.F). The transition temperatures along with the enthalpies for both the homologous series of compounds are given in tables 2.1 and 2.2 respectively.

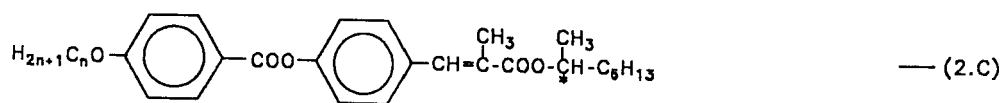
The synthesis of these two series of liquid crystalline compounds was carried out as outlined in a scheme shown in figure 2.1. The *trans*-4-n-alkoxycinnamic acids were prepared following a procedure described by Gray and Jones.¹⁵ The *trans*-4-n-alkoxy- α -methylcinnamic acids were prepared according to the method described by Johnson.¹⁶



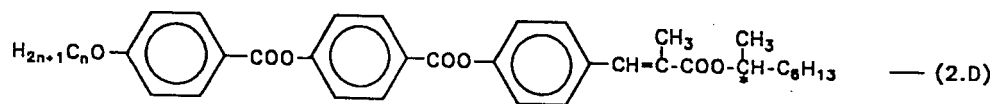
$n = 10, C 44.0 S_C^* 51.5 S_A 63.5 I$



$n = 10, C 92.0 S_C^* 128.5 S_A 168.0 N^* 190.0 I$



$n = 10, C 20.6 (S_C^* 14.7) S_A 38.2 I$



$n = 10, C 62.6 S_C^* 109.5 S_A 149.3 I$

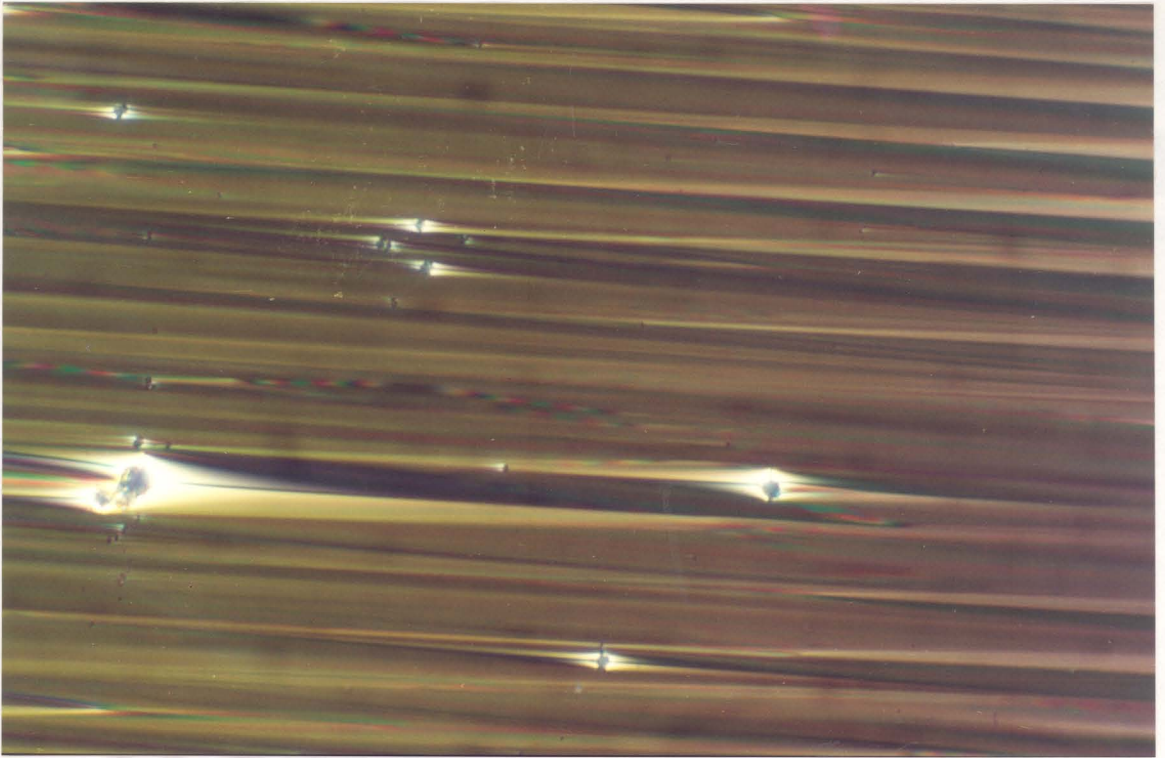


Plate 2.a. Photomicrograph of sample (2.E.5) showing S_A (aligned) phase at 148.0°C.

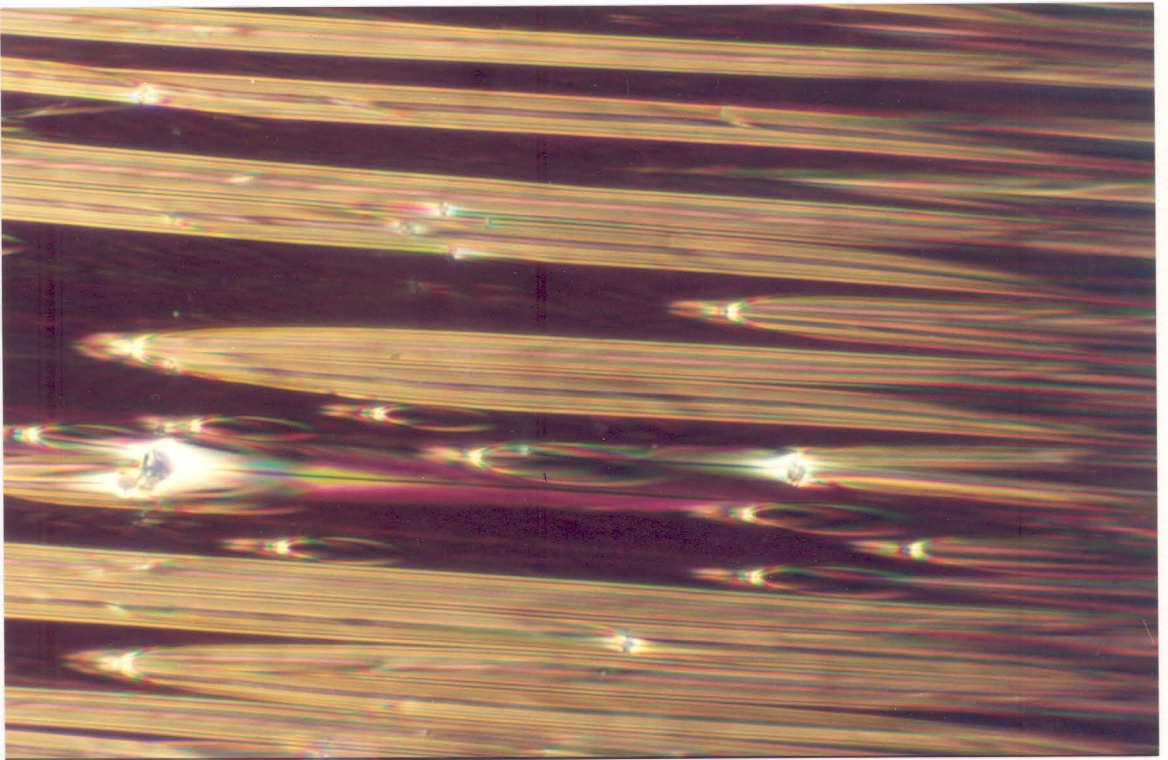


Plate 2.b. Photomicrograph of sample (2.E.5) showing $S_{C\alpha}^*$ (aligned) phase at 145.8°C.

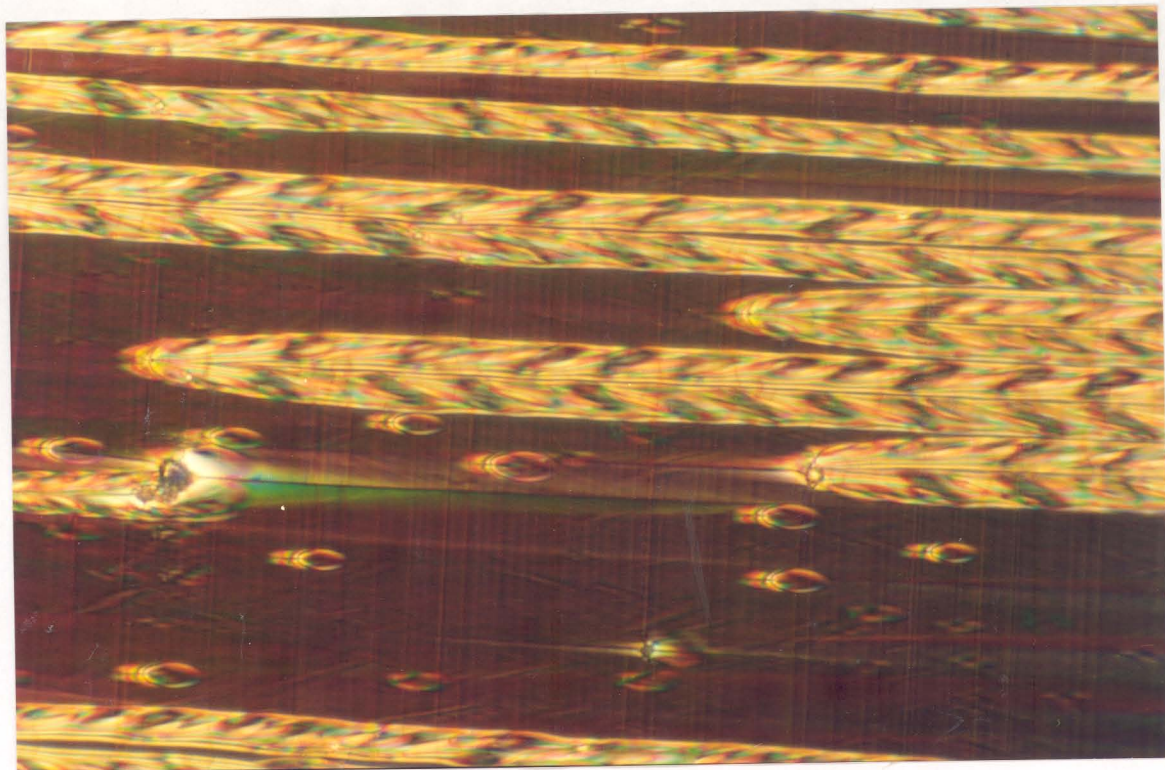


Plate 2.c. Photomicrograph of sample (2.E.5) showing S_C^* (aligned) phase at 137.0°C.

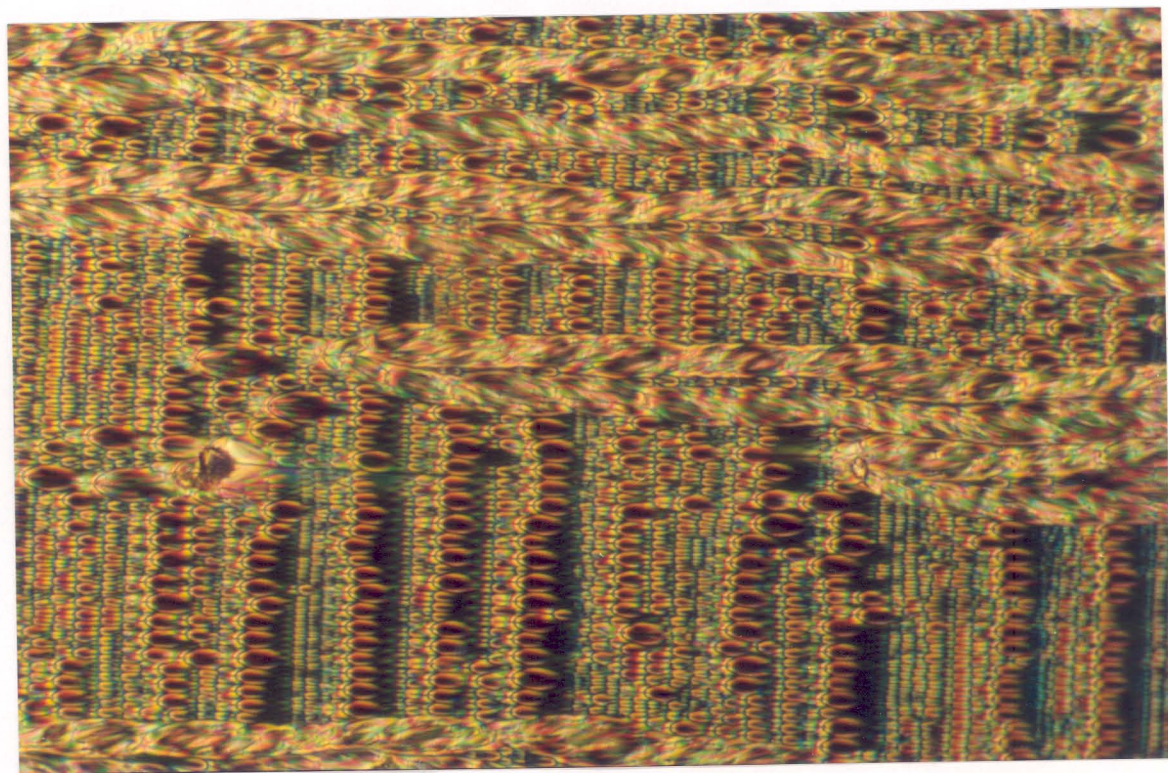
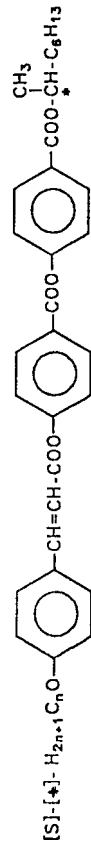


Plate 2.d. Photomicrograph of sample (2.E.5) showing $S_{C_A}^*$ (aligned) phase at 120.0°C.

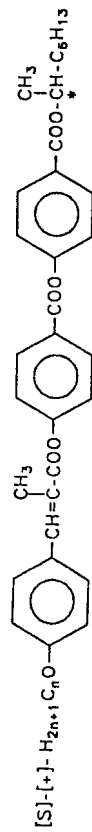
Table Phase sequence, transition temperatures (°C) and enthalpies (Jg⁻¹) of



Co n u n o r	n	C	S _{C_A} *	S _{C_γ} *	S _{C*}	S _{C_α} *	S _A	I
2.E.1	6	107.2 57.8	-	-	118.0 0.054	-	171.4 87	.
2.E.2	7	92.5 52.4	117.0 0.011	110.0 0.021	131.7 0.011	133. 0.05	172.0 7.9	
2.Σ.3	8	79.5 66.8	124.0 0.005	126.0 0.03	140.0 [†]	142.0 0.13	168.5 7.1	
2.Σ.4	9	81.0 40.5	121.5 0.022	124.0 0.039	141.5 0.021	145.5 0.35	161.0 5.9	64.5 64
2.Σ.5	10	86.0 53.1	121.0 0.012	123.5 0.063	145.8 [†]	148.5 0.79	161.0 5.9	
2.Σ.6	11	87.0 50.8	109.0 0.01	112.0 0.023	145.0 [†]	147.3 0.89	161.0 5.9	57.0 55
2.Σ.7	12	88.0 51.3	110.5 0.02	112.5 0.04	144.0 [†]	145.8 0.96	161.0 5.9	54.5 43
2.Σ.8	14	85.5 65.5	93.5 0.015	96.0 0.03	142.0 [†]	143.7 0.99	151.0 3.4	
2.Σ.9	10	83.0 44.5	-	-	141.0 1.7	-	151.0 3.4	47.0 24

† : The enthalpy could not be measured

Table 2.2. Phase sequence, transition temperatures ($^{\circ}\text{C}$) and enthalpies (Jg^{-1}) of



Compound number	n	C	$S_{C_X}^*$	$S_{C_Y}^*$	$S_{C_Z}^*$	$S_{C_{\alpha}}^*$	S_A	I
2.F.1	8	. 58.5 51.3	-	-	-	-	. 119.5 8.7	. .
2.F.2	9	. 57.5 66.1	-	-	(. 52.5) 0.005	. 59.6 0.13	. 115.5 7.4	. .
2.F.3	10	. 62.5 61.9	(. 59.5) 0.04	. 69.5 0.015	-	. 73.5 0.03	. 114.0 8.8	. .
2.F.4	11	. 60.7 48.3	-	-	. 84.2 0.008	. 88.0 0.013	. 113.7 7.9	. .
2.F.5	12	. 57.0 75.6	(. 40.0) 0.04	. 62.1 0.4	. 90.6 0.023	. 93.0 0.03	. 113.0 7.8	. .
2.F.6	14	. 64.2 56.8	-	-	. 94.0 0.21	-	. 110.0 5.9	. .

† : The enthalpy could not be measured

[S]-[+]-1-Methylheptyl-4-hydroxybenzoate (2.7) was obtained by hydrogenolysis of [S]-[+]-1-methylheptyl-4-benzyloxybenzoate (2.6) with 5% palladium on charcoal (5% Pd-C), which was obtained by an esterification reaction of 4-benzyloxybenzoic acid (BBA) (2.5) and [S]-[+]-2-octanol with N,N'-dicyclohexylcarbodiimide (DCC). [S]-[+]-1-Methylheptyl-4-(4'-hydroxybenzoyloxy)benzoate (2.9) was obtained by a similar sequence of reactions. The benzylation reaction was carried out using sodium ethoxide as a base in ethanol solution. Hydrogenolysis was performed in ethanol or ethylacetate solutions using 5% Pd-C at room temperature. All the esterification reactions were carried out by condensing the appropriate carboxylic acids with phenols in dichloromethane at room temperature.

The phase behaviour of chiral compounds of series 2.E is summarised in table 2.1. These compounds exhibit S_A phase over the entire series. The clearing temperature decreases with increasing length of the n-alkoxy chain with no odd-even effect. The $S_{C^*_\alpha}$ phase precedes the other helical smectics from compound 2.E.2 to 2.E.8 (n=7 to n=14). The temperature range of this phase is rather narrow. The S_{C^*} phase appears for compound 2.E.2 (n=7) and becomes dominant for compound 2.E.9 (n=16). The $S_{C^*_A}$ phase appears from compound 2.E.2 (n=7) and persists **upto** compound 2.E.8 (n=14). The temperature range of this phase also decreases with increasing n-alkoxy chain length. No direct transition from S_{C^*} to $S_{C^*_A}$ phase could be observed in this series of pure chiral compounds. The two phases are always separated by one or two intermediate ferrielectric ($S_{C^*_\gamma}$) phases. The ferrielectric phase could be easily identified under the microscope as this mesophase fluctuates dynamically in homeotropic regions.¹⁷ The photomicrograph of this texture is shown in Plate 2.e. Compound 2.E.9 (n=16) exhibits only S_A and S_{C^*} phases

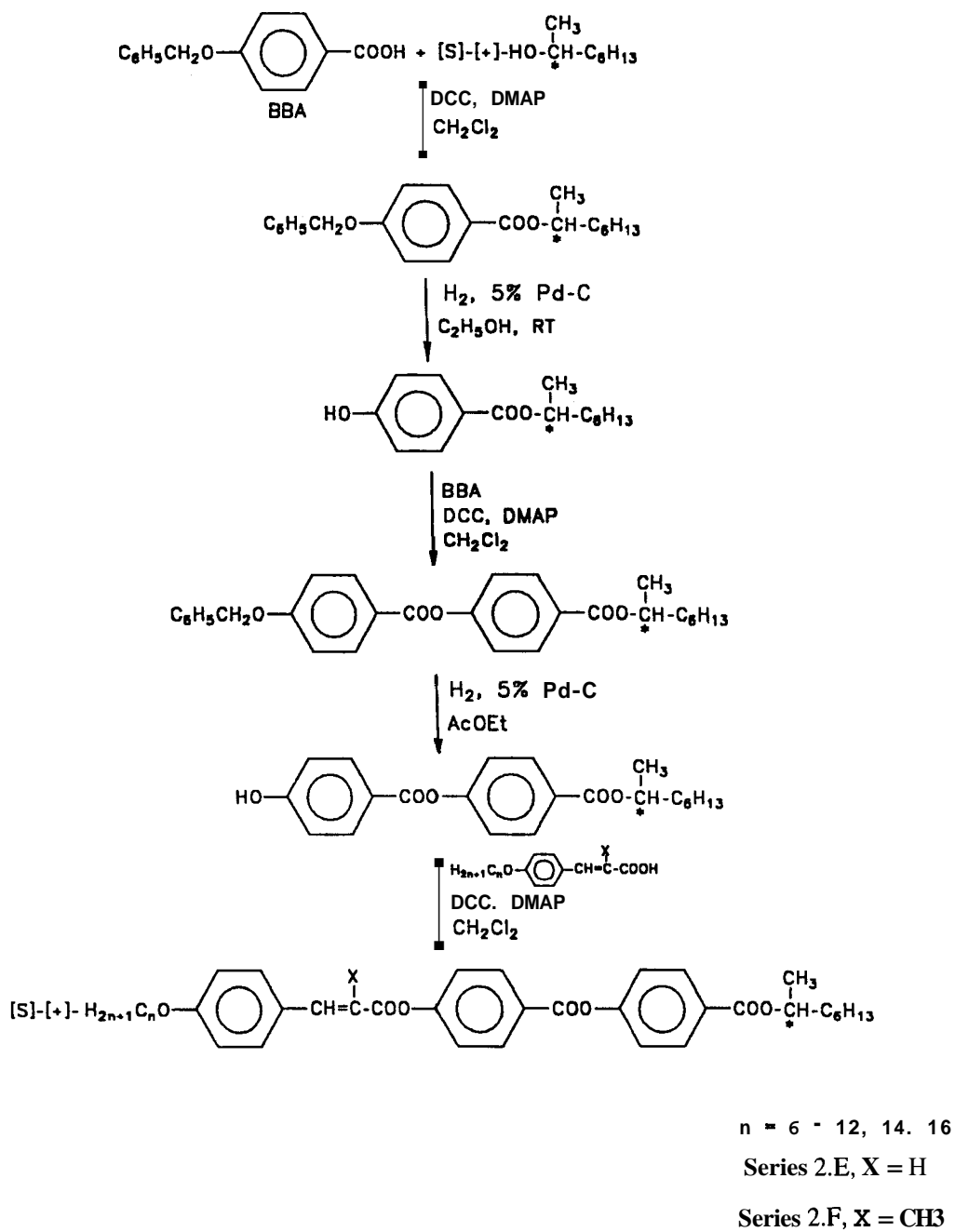


Figure 2.1. Synthetic scheme for the preparation of the compounds of series 2.E and 2.F.

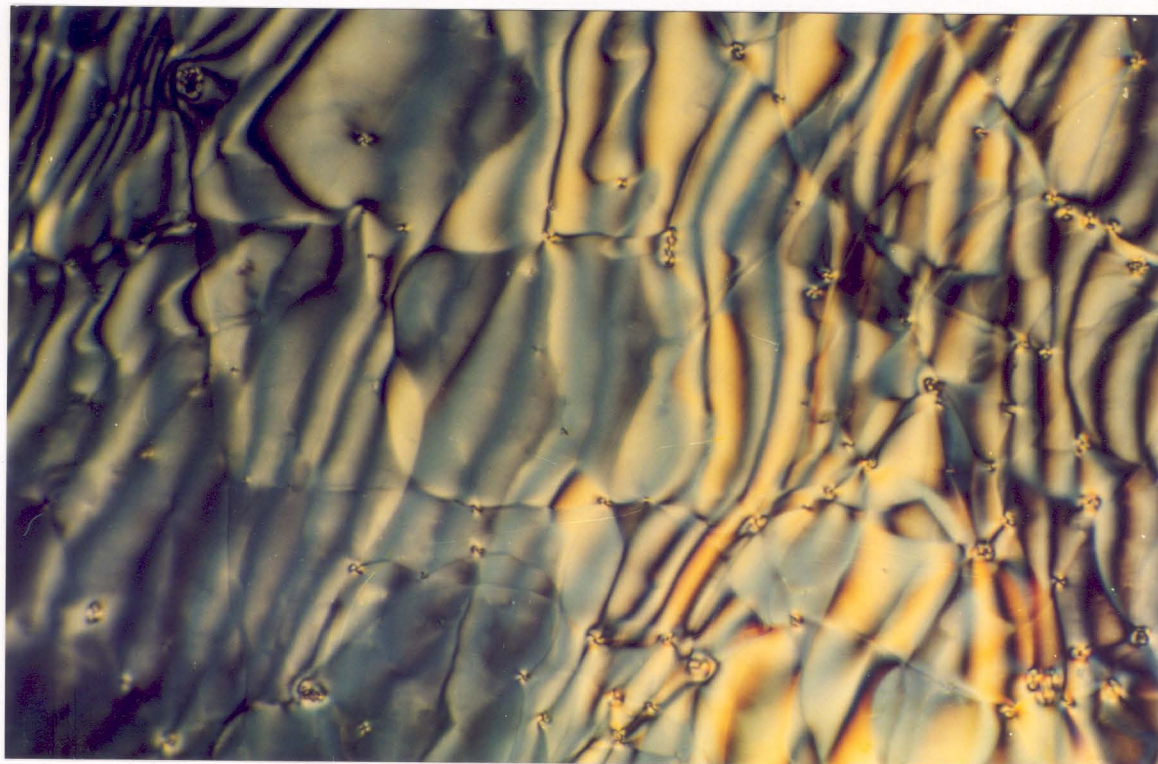


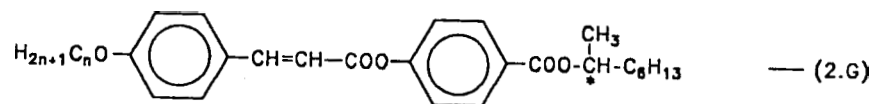
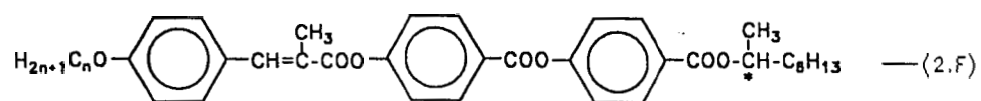
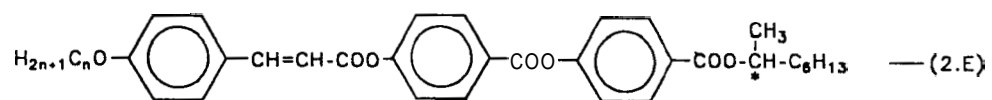
Plate 2.e. Texture of the S_C^* phase of compound 2.E.5 at 123.0°C in homeotropic region.

and does not show any $S_{C_A}^*$ phase. Hence the synthesis of the other higher homologues of this series was not pursued any further. In this homologous series, compound 2.E.3 has the widest range of antiferroelectric phase (44.5°C) and the lowest melting point (79.5°C).

As can be seen in table 2.2, compounds of series 2.F exhibit the following phases. Compound 2.F.1 shows only S_A phase and compounds 2.F.2 and 2.F.4 show S_A , $S_{C_\alpha}^*$ and S_C^* phases. A monotropic S_C^* phase was observed for compound 2.F.2. Compound 2.F.3 shows S_A , $S_{C_\alpha}^*$, $S_{C_\gamma}^*$, $S_{C_X}^*$ phases on cooling from isotropic liquid. Similar kind of phase sequence has been observed by Faye *et al.*¹⁸ in some fluoro substituted tribenzoates. Compound 2.F.5 shows S_A , $S_{C_\alpha}^*$, S_C^* , $S_{C_\gamma}^*$ and $S_{C_X}^*$ phases on cooling the isotropic liquid, where $S_{C_X}^*$ is an unidentified smectic phase. Compound 2.F.6 shows only S_A and S_C^* phases. Amongst all the compounds of this series melting point is highest for compound 2.F.6 (64.2°C) and least for compound 2.F.5 (57.0°C).

As mentioned above, all the fifteen compounds in tables 2.1 and 2.2 exhibit smectic A phase. However, only six compounds (2.E.3 to 2.E.9) of series 2.E show antiferroelectric phase. The range of S_A phase follows a descending order on increasing n-alkoxy chain length.

Heppke *et al.*¹⁹ have synthesised lower homologues of series 2.G. The n-octyloxy homologue of this series can be compared with [S]-[+]-1-methylheptyl-4-[4'-(*trans*-4''-n-octyloxy)cinnamoyloxy]benzoyloxy]benzoate (2.E.3). The compound 2.E.3 has an additional benzoyloxy group compared to the n-octyloxy homologue of series 2.G. This results in an enhancement of the mesophase transition temperatures to a considerable extent and all the phases are enantiotropic. The thermal stabilities of S_A , S_C^* , $S_{C_A}^*$ phases



2.G.1 $n = 8$, C 40.1 ($S_{c_A}^*$ 30.9 $S_{c_Y}^*$ 33.4) S_{c^*} 46.4 S_A 57.8 I

2.G.2 $n = 16$, C 42.3 S_{c^*} 53.5 TGB_A 56.2 I

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increased by about **90 °C**. A $S_{C\alpha}^*$ phase with a thermal range of **4 °C** has also been induced in compound **2.E.3**.

Nguyen *et al.*²⁰ have synthesised two higher homologues of series 2.G. The n-hexadecyloxy homologue of this series shows TGB_A phase at higher temperature and S_C^* phase at lower temperature. It can be compared with [S]-[+]-1-methylheptyl-4-[4'-(*trans*-4''-n-hexadecyloxycinnamoyloxy)benzoyloxy]benzoate (**2.E.9**). This compound (**2.E.9**) has an additional benzoyloxy group as compared to the n-hexadecyloxy homologue of series **2.G**. This results in an enhancement of the S_C^* phase transition temperature to a considerable extent. The thermal stability of S_C^* phase increases by about **90 °C**. However, this compound does not exhibit TGB_A phase, but exhibits S_A phase.

A comparison of transition temperatures of [S]-[+]-1-methylheptyl-4-[4'-(*trans*-4''-n-decyloxy- α -methylcinnamoyloxy)benzoyloxy]benzoate (**2.F.3**) and the compound without the methyl group at α -position (**2.E.5**) may be made. The α -methyl group has a pronounced effect on the types as well as transition temperatures of the mesophases when compared with those of the unsubstituted compounds. The melting points and clearing temperatures are reduced by about **25-30 °C** and **35-40 °C** respectively. The $S_{C_A}^*$ phase is eliminated in the α -methyl substituted compounds and an unidentified smectic phase is injected. The α -methyl group fills the space within the molecule without any substantial broadening. This thickening effect is considerably enhanced due to steric interaction between the methyl group and the *ortho* ring protons.

A plot of the number of the carbon atoms in the alkoxy chain *versus* the transition temperatures of series **2.E** and series **2.F** are shown in figures **2.2** and **2.3** respectively. It is seen that $I - S_A$ transition temperatures decrease gradually on increasing the carbon

chain length. A slow rise is seen for the $S_A - S_C^*$ transition temperatures. The $S_{C_\gamma}^* - S_{C_A}^*$ transition temperatures also show a general increase and then show a decreasing trend with increasing n-alkoxy chain length. The mesophase textures were observed for compound 2.E.5 using a homogeneously aligned sample sandwiched between a glass slide and a cover slip, under a polarising microscope. For the S_A phase a black region with some focal-conics was observed as shown in Plate 2.a. However, for the $S_{C_\alpha}^*$ phase thin, dark and clear bands parallel to the rubbing direction was obtained (Plate 2.b). When the transition to the S_C^* phase takes place a rope-like texture as shown in Plate 2.c was observed. The textures obtained on transition from S_C^* phase to $S_{C_\gamma}^*$ phase was not clear. The transition to the $S_{C_A}^*$ phase could be clearly seen as stripes grow perpendicular to the rubbing direction and a typical texture is shown in Plate 2.d. The photomicrographs of these smectic mesophases are similar to those observed by Goodby *et al.*²¹ and Nguyen *et al.*¹⁷

The above assignment of the different smectic phases relies mainly on the miscibility diagram between compound 2.E.3 and a well known compound [S]-[+]-MHPOBC. An isobaric binary phase diagram obtained is shown in figure 2.4. In this diagram complete miscibility of the different phases can be seen. The mixtures were made as weight/weight ratio and mixed well in their isotropic states. An isobaric phase diagram between compound 2.E.8 and the n-tetradecyloxy homologue of series 2.G is shown in figure 2.5. Complete miscibility of the S_C^* phase can be seen in this diagram.

A comparison of the molecular structures of the two series 2.D and 2.F indicates that the α -methyl group lies at the end of the core in the former while it is at the middle of the core in the latter. All the transition temperatures are higher in series 2.D than the

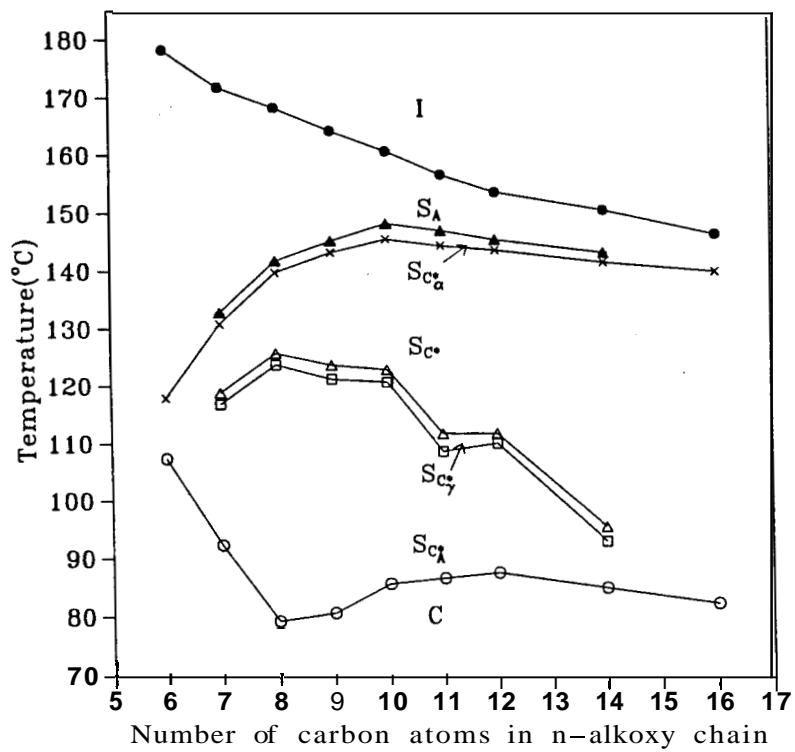


Figure 2.2. A plot of transition temperatures as a function of n-alkoxy chain length for series 2.E.

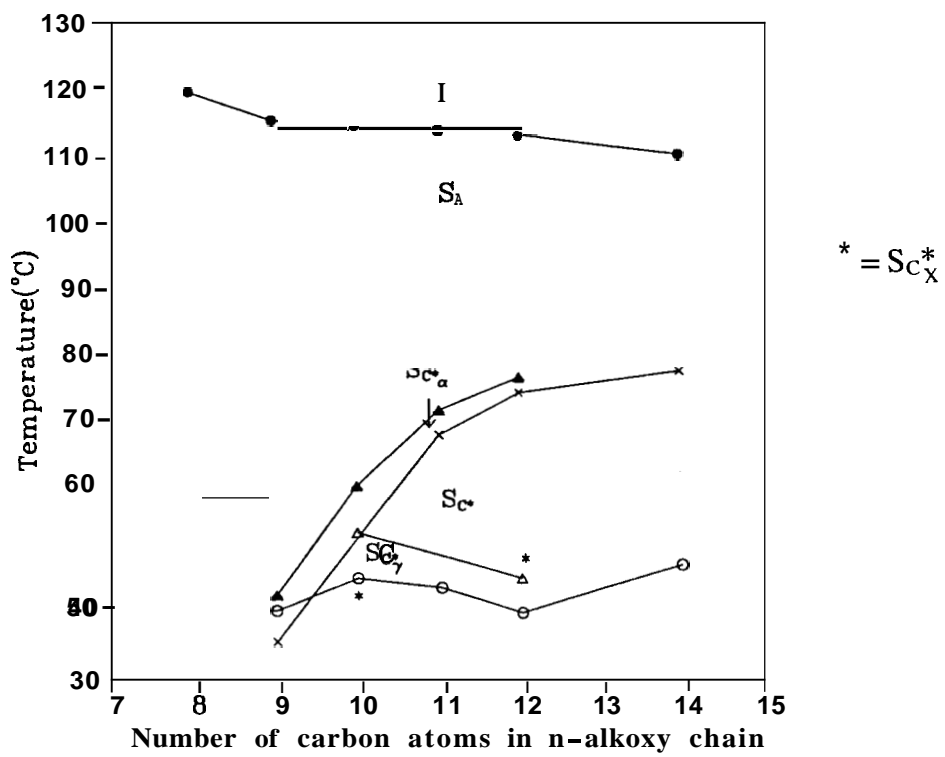


Figure 2.3. A plot of transition temperatures as a function of n-alkoxy chain length for series 2.F.

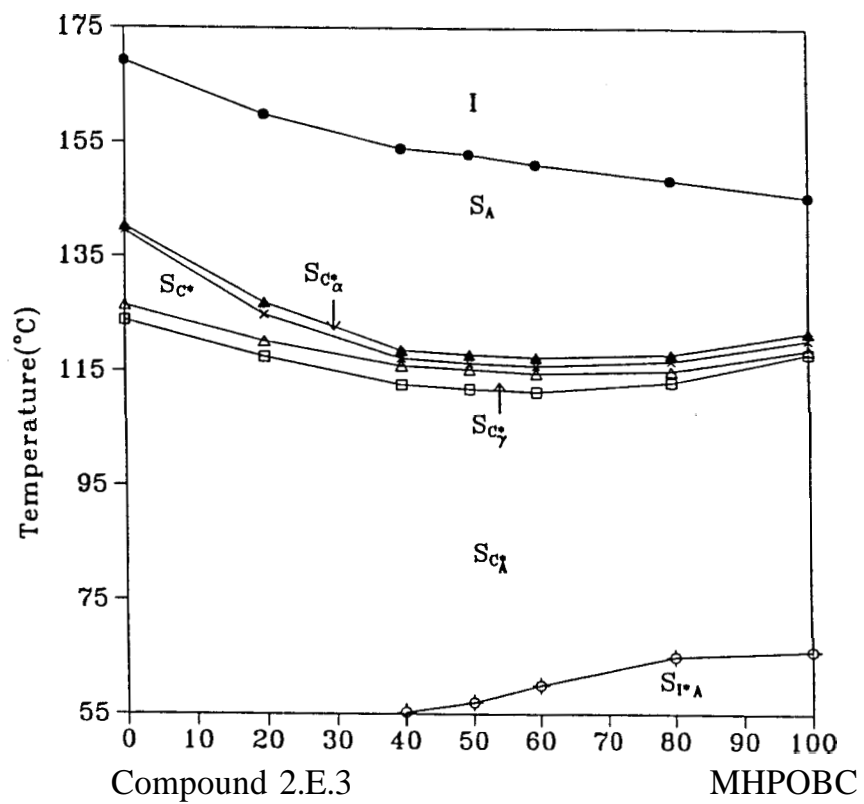


Figure 24. Isobaric binary phase diagram between compound **2.E.3** on the left and MHPOBC on the right.

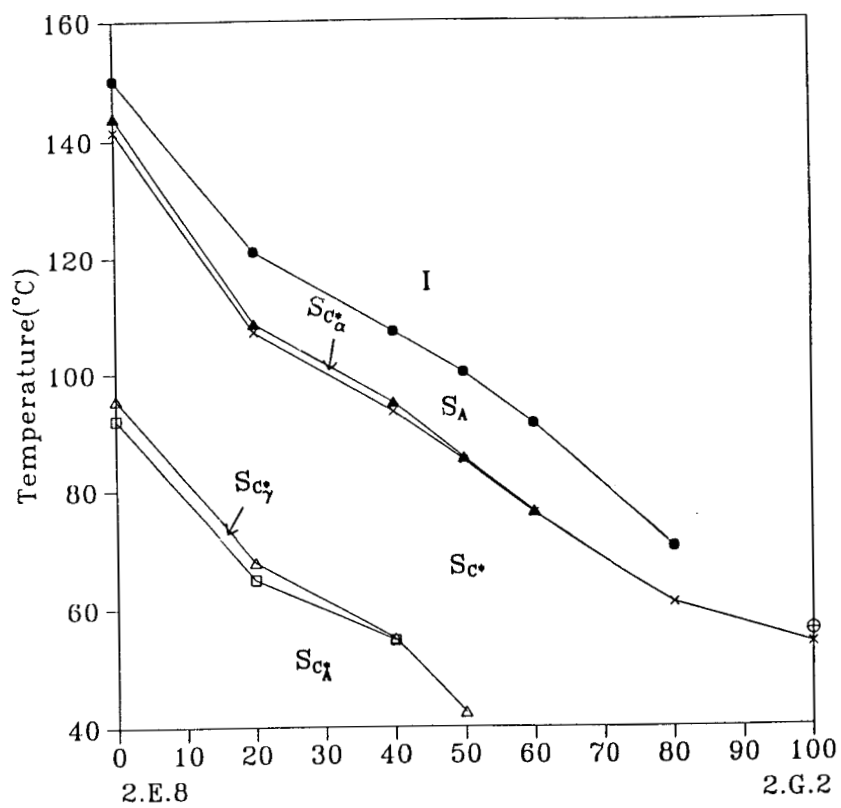


Figure 2.5. Isobaric binary phase diagram between compound 2.E.8 on the left and compound 2.G.2 on the right

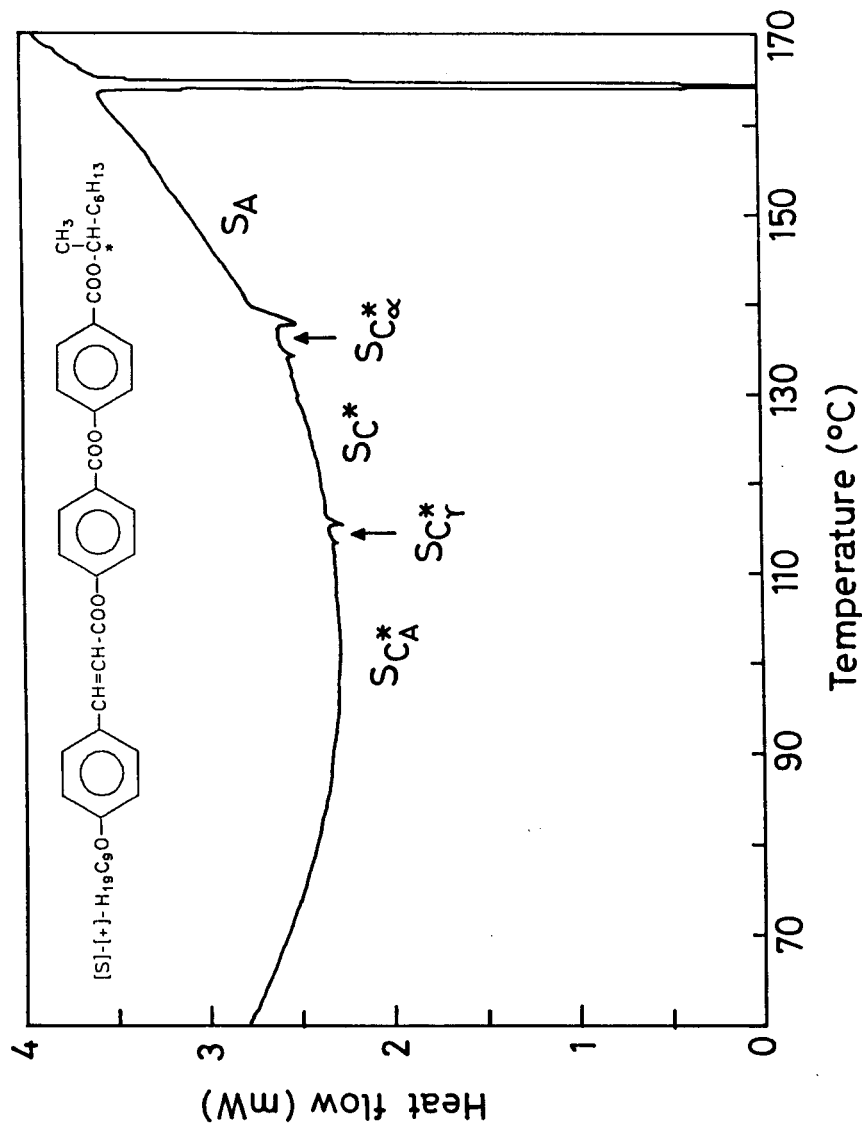
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corresponding temperatures of the homologues of series 2.F. The S_A -I transition temperatures are higher by about 35°C. Within the homologous series 2.F, the thermal range of S_C^* phase increases with increasing carbon chain from about 23.5°C for compound 2.F.4 to about 29.3°C for compound 2.F.6.

Figures 2.6 and 2.7 show the current response to an applied triangular wave in the different phases of the compounds 2.E.5 and 2.F.3 respectively. The oscilloscope traces which are characteristic of the patterns reported for each of these phases are more clear in compound 2.F.3 than in compound 2.E.5. In particular, the second peak observed in the $S_{C_\alpha}^*$ phase is quite strong in compound 2.F.3, the reason for which is not obvious; perhaps the absence of S_C^* phase between $S_{C_\alpha}^*$ and $S_{C_\gamma}^*$ phases could be responsible for this.

Figure 2.8 is a plot of the temperature dependence of polarisation for the compound 2.E.5, showing a smooth variation across the different transitions. This is to be expected as the measurements were done using a field which was above the helix unwinding field.

Plots of optical tilt angle and pitch as a function of reduced temperature for compound 2.E.5 are shown in figures 2.9(a) and 2.9(b). The tilt angle is seen to have appreciable temperature dependence, which is in contrast to the temperature independent tilt observed in another compound exhibiting $S_{C_\alpha}^*$ - S_C^* transition. But it must be mentioned that in the latter case it was observed that the value of polarisation abruptly increases at the transition, a feature not observed in the present case. The reason for these could be the strength of the transition. However, since the structure of the $S_{C_\alpha}^*$ is not yet very clear, it is difficult to comment on this. The helical pitch too has a strong temperature dependence and also has a large magnitude.



The dsc thermogram of compound 2.E.4.

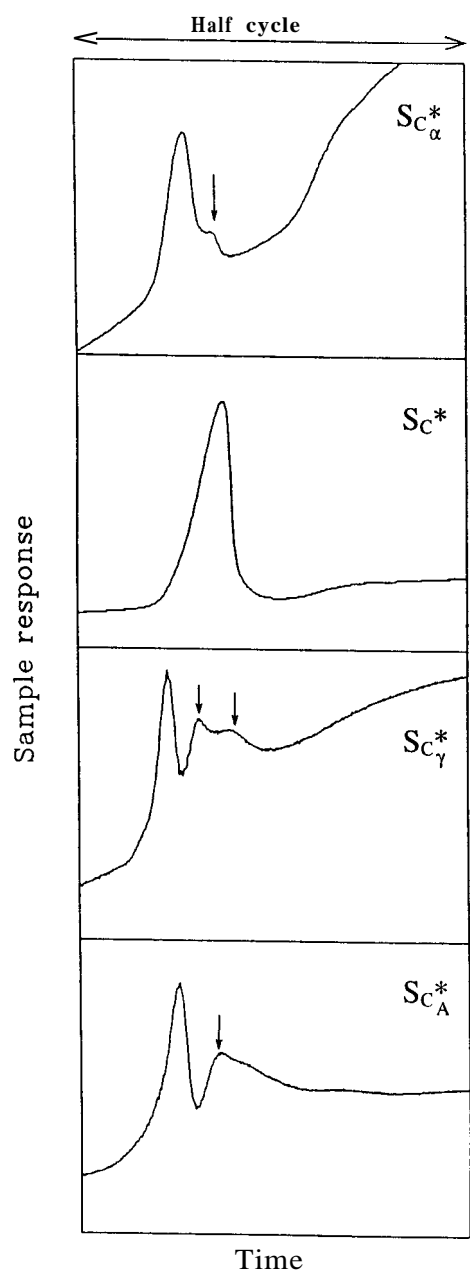


Figure 2.6. Current response patterns in the $S_{C\alpha}^*$, S_C^* , $S_{C\gamma}^*$ and S_{CA}^* phases of compound 2.E.5.

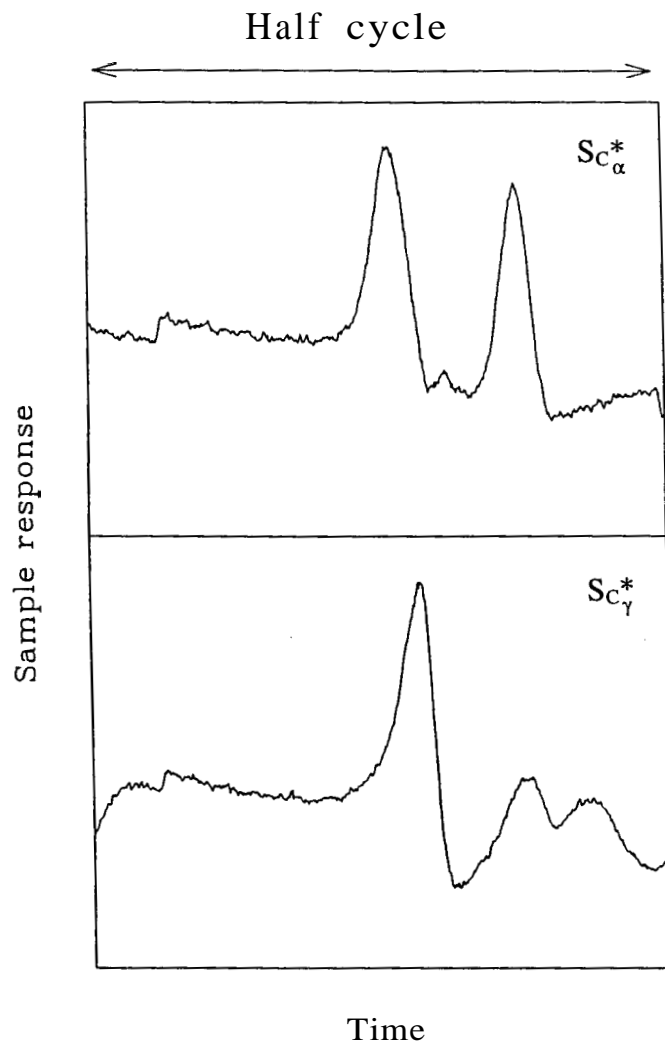


Figure 2.7. Oscilloscope traces obtained by applying triangular wave field to the sample (2.F.3). Notice that the strength of the second peak is comparable to the usual peak in the $S_{C_{\alpha}}^*$ phase.

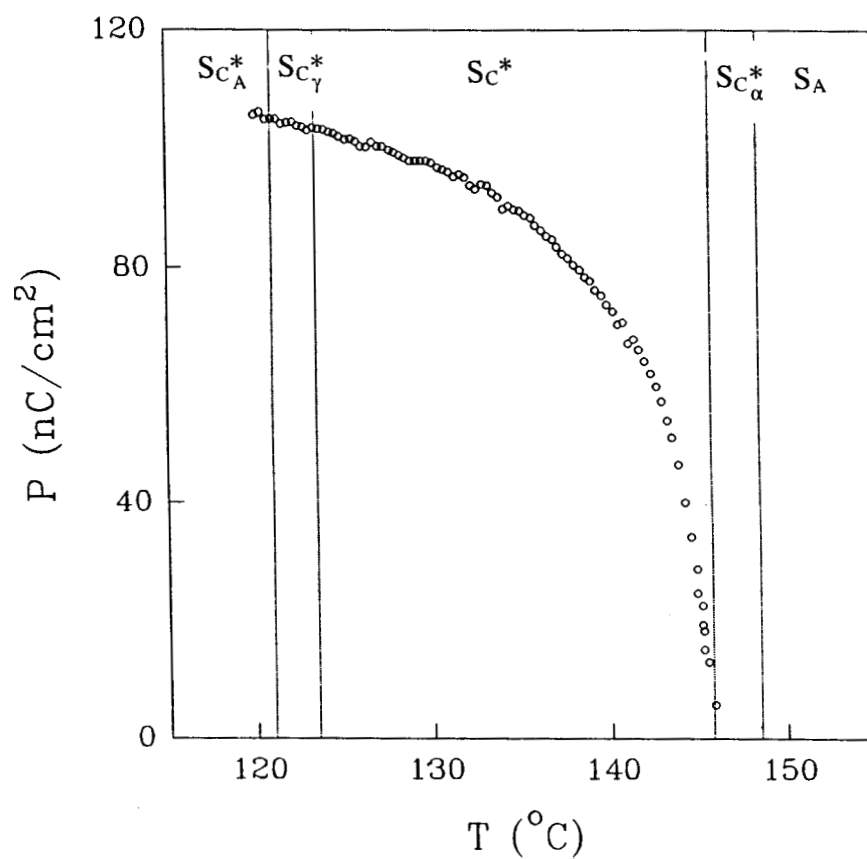
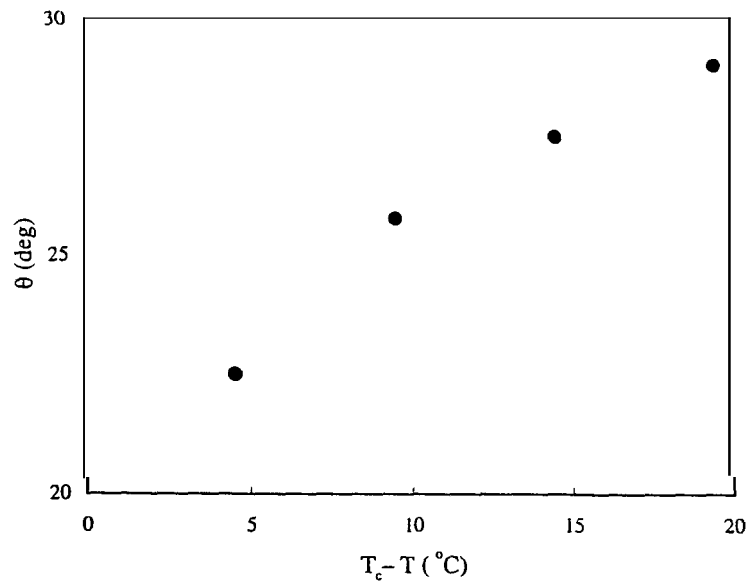
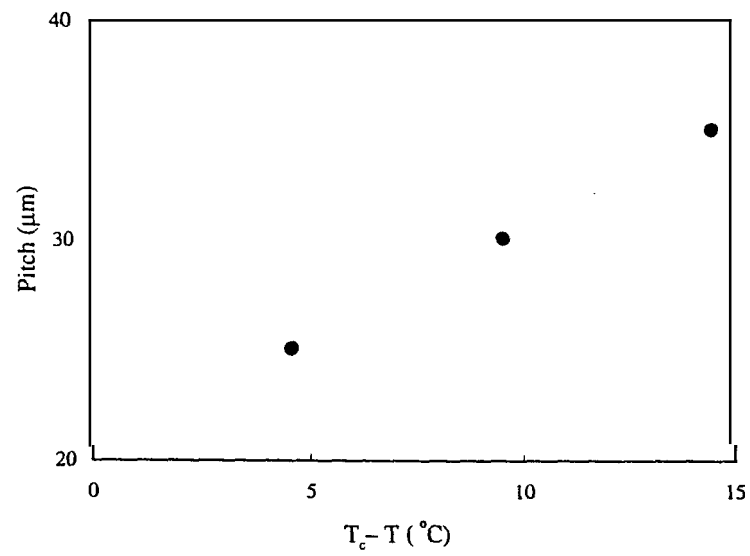


Figure 2.8. Polarisation versus temperature plot for compound 2.E.5.



a



b

Figure 2.9. Plot of reduced temperature ($T_c - T$) versus (a) optical tilt angle and (b) pitch.

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Experimental

General methods of investigation

Anhydrous solvents used were prepared from commercial solvents following the standard procedures. All solid starting materials were crystallised before use. The melting and boiling points reported herein are all corrected and are in degree celsius. Analytical tlc was carried out using silica gel supplied by BDH India Ltd. and the spots rendered visible by brief exposure to iodine vapour. Readymade tlc aluminum cards coated with silica gel with a fluorescent indicator manufactured by Fluka AG, Switzerland, were also used. The spots on these plates were rendered visible by exposing them to a DESAGA HP-UVIS lamp at 254 and/or 366 nm. Silica gel (60-120 mesh, ACME, India) was used for column chromatography. Infrared absorption spectra were recorded on a Shimadzu IR-435 spectrophotometer, as nujol mull unless otherwise stated. The proton magnetic resonance spectra were taken on a Bruker WP80 SY FT NMR spectrometer using tetramethylsilane as an internal reference standard. The chemical shifts are quoted as “ δ ” (parts per million) downfield from the reference. CDCl_3 was used as a solvent for all the compounds unless otherwise stated. Elemental analyses were carried out on a CARLO-ERBA 1106 elemental analyser. Specific rotations were measured either on a ROUSSEL JOUAN digital polarimeter TYPE 71 or on an Optical Activity AA-1000 polarimeter at 589 nm sodium line. The transition temperatures were measured under a Leitz Laborlux 12 POL polarising microscope equipped with a Mettler FP52 heating stage and a FP52 controller, by sandwiching samples between a glass slide and a cover slip. Simultaneously the mesophase textures were also observed. The enthalpies of transitions were determined from thermograms obtained on a Perkin-Elmer, Model DSC-4 or DSC-7 differential

scanning calorimeter and are reported in J/g. The heating and cooling rates were 5°C/min. and 3°C/min. respectively. The calorimeters were calibrated using pure indium as a standard.

All experiments have been conducted using samples sandwiched between ITO-coated glass plates. Mylar spacers were used to define the thickness of the cell (typically = 10 μm for the polarisation and tilt angle measurements and = 50 μm for pitch experiments). For spontaneous polarisation (P_S) measurements the triangular wave method^{22,23} was employed. To identify/confirm the presence of antiferroelectric and/or the "sub-phases" a low frequency (0.97 Hz) probing field had to be used. However, the measurements as a function of temperature were carried out at a higher frequency (9.7 Hz) to avoid conductivity problems associated with low frequency large magnitude fields. The tilt angle (θ) of the molecules with respect to the smectic layer normal was calculated from the difference in the extinction positions of the sample between crossed polarisers under a near-DC (0.1 Hz) switching field. The field has to be high enough to unwind the helical structure. This would result in an unwound C^* structure. The pitch values were determined by the optical diffraction method.²⁴

4-n-Hexyloxybenzaldehyde, (2.1)

This was prepared following a procedure of Gray and Jones.¹⁵ Thus, a solution of sodium ethoxide was prepared by dissolving sodium (2.3 g, 0.1 g atom) in absolute ethanol (100 ml). 4-Hydroxybenzaldehyde (12.2 g, 100 mmol) was added to it. This mixture was stirred and refluxed for thirty minutes. 1-Bromohexane (19.7 g, 110 mmol) was then added to it. The refluxing and stirring was continued for a further period of six hours. Ethanol was removed by distillation under reduced pressure, the residue was poured into ice cold water. This was acidified with hydrochloric acid, extracted with ether (3X300 ml), the combined ethereal extracts was washed with 10% aqueous sodium hydroxide (3X100 ml), water (3X100 ml) and dried (Na₂SO₄). Removal of the solvent afforded a liquid which was distilled under reduced pressure to give pure 4-n-hexyloxybenzaldehyde (15.3 g, 70%); b.p 142-145°C/2 mm of Hg (Reported²⁵ b.p 177-180°C/10 mm of Hg).

The physical data of the cognate preparations of other 4-n-alkoxybenzaldehydes are given in table 2.3.

***trans*-4-n-Hexyloxycinnamic acid, (2.2)**

This was prepared following the procedure of Gray and Jones.¹⁵ Thus, a mixture of 4-n-hexyloxybenzaldehyde (12.3 g, 60 mmol), malonic acid (12.5 g, 120 mmol), pyridine (25 ml) and a few drops of piperidine was heated at 100°C in an oil bath for three hours. The mixture was then poured into ice and concentrated hydrochloric acid. The precipitate so obtained was filtered, washed with water and dried. This was recrystallised from acetic acid until the melting point was constant (13.3 g, 90%); m.p. 152.0°C (Reported¹⁵ m.p. 153.0°C).

The physical data of the cognate preparations of the other *trans*-4-n-alkoxycinnamic acids are given in table 2.4.

Table 2.3. Physical constants of 4-n-alkoxybenzaldehydes

Compound number	n	Observed b.p. °C/mm	Reported b.p. °C/mm	Reference
1	7	137-139/14	143-146/15	25
2	8	155-157/2	141-144/10.1	25
3	9	172-175/11	163-166/10.5	25
4	10	135-140/10.1	185/14	15
5	11	180-183/11	185/11	26
6	12	160-163/11	194/18	15
7	14	170/10.4	-	-
8	16	233-237/13	230/13	15

Table 2.4 Physical constants of *trans*-4-n-alkoxycinnamic acids

Compound number	n	Observed m.p. °C	Reported m.p. °C	Reference
1	7	148.0	148.0	15
2	8	147.0	146.0	15
3	9	138.0	138.5	15
4	10	136.0	136.0	15
5	11	127.0	127.0	23
6	12	132.0	132.0	15
7	14	125.0	-	-
8	16	117.5	118.0	15

***trans*-4-*n*-Octyloxy- α -methylcinnamic acid, (2.3)**

This was prepared following a procedure described by Johnson.¹⁶ Thus, a mixture of **4-*n*-octyloxybenzaldehyde** (14.0 g, 60.0 mmol), propionic anhydride (9.56 g, 75.0 mmol) and potassium propionate (6.72 g, 60.0 mmol) was heated in an oil bath at 130°C for thirty hours. The warm reaction mixture was poured into a stirred mixture of concentrated hydrochloric acid and ice-cold water. The pale brown semi-solid hardened after about thirty minutes. It was filtered off, washed with water, dried and recrystallised from petroleum ether (14.0 g, 81%); m.p. 82.0°C (Reported²⁷ m.p. 83.0°C).

The physical data of the cognate preparations of other ***trans*-4-*n*-alkoxy- α -methylcinnamic acids** are given in table 2.5.

Table 2.5. Physical constants of ***trans*-4-*n*-alkoxy- α -methylcinnamic acids**

Compound number	n	Observed m.p. °C	Reported m.p. °C	Reference
1	9	84.5	82.5	27
2	10	79.0	79.5	27
3	11	88.0	88.2	27
4	12	85.5	86.0	27
5	14	90.5	-	-

Ethyl-4-benzyloxybenzoate, (2.4)

A solution of sodium ethoxide was prepared by dissolving sodium (4.6 g, 0.2 g atom) in absolute ethanol (150 ml). Ethyl-4-hydroxybenzoate (33.2 g, 200 mmol) was added to

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it. The resulting reaction mixture was stirred and **refluxed** for thirty minutes. Benzylchloride (27.8 g, 220 mmol) was then added to it. The stirring and refluxing was continued for a further period of twelve hours. Excess ethanol was distilled off, the residue poured into cold water and extracted with ether (3X100 ml). The combined ethereal solution was washed with 10% aqueous sodium hydroxide (2X75 ml) and water (2X60 ml). The ethereal solution was dried (Na_2SO_4) and the solvent removed. The solid residue was crystallised from ethanol (40.0 g, 78%); **m.p.** 46.0°C (Reported ²⁸ **m.p.** 46.0°C).

4-Benzyloxybenzoic acid, (2.5)

A mixture of **ethyl-4-benzyloxybenzoate** (30.0 g, 120 mmol), potassium hydroxide (8.6 g, 150 mmol), water (20 ml) and ethanol (50 ml) was **refluxed** for six hours. Ethanol was removed by distillation and the residue poured into cold water. This was acidified by adding cold, concentrated hydrochloric acid. The white precipitate so obtained was filtered off, washed with water and dried. This was **crystallised** from ethanol (25.0 g, 90%); **m.p.** 191-192°C (Reported ²⁹ **m.p.** 188.0°C)

[S]-[+]-1-Methylheptyl-4-benzyloxybenzoate, (2.6)

This was prepared following a esterification procedure of Hassner and Alexanian.³⁰ Thus, a mixture of 4-benzyloxybenzoic acid (4.0 g, 17.54 mmol), [S]-[+]-octan-2-ol (2.3 g, 17.54 mmol), 4-N,N'-dimethylaminopyridine (DMAP) (1.3 g, 10.5 mmol) and dichloromethane (80 ml) was stirred for five minutes. To the mixture, was added DCC (5.4 g, 26.7 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

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dichloromethane (100 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. [S]-[+]-1-**Methylheptyl-4-benzyloxybenzoate** was obtained as a viscous liquid (5.18 g, 87%); $[\alpha]_{\text{D}}^{25} = 21.8^\circ$ (5.5 mg/ml in CH_2Cl_2); ν_{max} (neat): 3000, 1710, 1610, 1580, 1280, 1050 cm^{-1} ; δ : 0.63-2.39(14H, m, 2XCH₃, 4XCH₂), 4.15(1H, m, COOCH), 5.12(2H, s, ArCH₂OAr), 6.9 and 8.02(4H, AB q, J=8 Hz, ArH), 7.4(5H, s, ArH);

Elemental analysis: Found, C, 78.11; H, 8.31% $\text{C}_{22}\text{H}_{28}\text{O}_3$ requires
C, 77.64; H, 8.23%.

[S]-[+]-1-Methylheptyl-4-hydroxybenzoate, (2.7)

A mixture of [S]-[+]-1-methylheptyl-4-benzyloxybenzoate (5.0 g, 14.7 mmol) dissolved in ethanol (40 ml) and 5% Pd-C catalyst (2.0 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 afforded a viscous liquid (3.0 g, 82.0%); $[\alpha]_{\text{D}}^{25} = 39.7^\circ$ (5.1 mg/ml in CH_2Cl_2); ν_{max} (neat): 3310, 2950, 1740, 1690, 1600, 1510, 1450, 1275 and 1050 cm^{-1} ; δ : 0.75-2.0(16H, m, 2XCH₃, 5XCH₂), 4.2(1H, m, COOCH), 6.9 and 7.25(4H, AB q, J=9.0 Hz, ArH), 7.2(1H, s, ArOH);

Elemental analysis: Found, C, 71.86; H, 8.81% $\text{C}_{15}\text{H}_{22}\text{O}_3$ requires
C, 72.0; H, 8.80%.

[S]-[+]-1-Methylheptyl-4-(4'-benzyloxybenzoyloxy)benzoate, (2.8)

A mixture of 4-benzyloxybenzoic acid (2.64 g, 11.6 mmol), [S]-[+]-1-methylheptyl-4-hydroxybenzoate (2.9 g, 11.6 mmol), DCC (2.36 g, 11.6 mmol), DMAP (0.14 g, 1.16 mmol) and dry dichloromethane was stirred for two hours at room temperature. N,N'-Dicyclohexylurea formed was filtered off and the filtrate was diluted with dichloromethane (50 ml). The combined organic solution was washed successively with water (2X30 ml), 5% aqueous acetic acid (3X50 ml), water (3X50 ml) and dried (Na₂SO₄). 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 (4.8 g, 87%); m.p. 111.1°C; $[\alpha]_D^{25} = 25.7^\circ$ (4.5 mg/ml in CH₂Cl₂); ν_{\max} : 2950, 2850, 1720, 1620, 1600, 1480, 1280 and 1050 cm⁻¹; δ : 0.94-2.28(16H, m, 2XCH₃, 5XCH₂), 4.35(1H, m, COOCH), 5.18(2H, s, ArCH₂OAr), 7.0 and 8.13(4H, AB q, J=7.6 Hz, ArH), 7.2 and 8.18(4H, AB q, J=7.6 Hz, ArH), 7.4(5H, s, ArH);

Elemental analysis: Found, C, 76.26; H, 7.12% C₂₉H₃₂O₅ requires
C, 76.48; H, 7.03%.

[S]-[+]-1-Methylheptyl-4'-hydroxybenzoyloxy)benzoate, (2.9)

Hydrogenolysis of compound 2.8 was carried out in ethylacetate solution as described for compound 2.7. Yield 81.0%; m.p. 82.6°C; $[\alpha]_D^{25} = 33.2^\circ$ (6.2 mg/ml in CH₂Cl₂); ν_{\max} : 3310, 2950, 1740, 1690, 1600, 1510, 1450, 1275 and 1050 cm⁻¹; δ : 0.75-2.0(16H, m, 2XCH₃, 5XCH₂), 4.1(1H, m, COOCH), 6.92 and 8.04(4H, AB q, J=8.3 Hz, ArH), 7.16 and 8.08(4H, AB q, J=9.6 Hz, ArH), 7.33(1H, s, ArOH);

Elemental analysis: Found, C, 72.28; H, 7.24% C₂₂H₂₆O₅ requires
C, 72.31; H, 7.12%.

[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-decyloxycinnamoyloxy)benzoyloxy]benzoate, (2.E.5)

This was prepared using a procedure described for compound 2.8. Yield, 87%; m.p. 86°C; $[\alpha]_D^{25} = 19.27^\circ$ (5.5 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (35H, m, 3XCH₃, 13XCH₂), 4.1(2H, t, J=6.6 Hz, ArOCH₂), 5.0-5.34(1H, m, COOCH), 6.42 and 7.84 (AB q, 2H, J=18.6 Hz, CH=CH-COO-), 6.88 and 7.45 (4H, AB q, J=9.0 Hz, ArH), 7.32 and 8.16 (4H, AB q, J=9.5 Hz, ArH), 7.4 and 8.3 (4H, AB q, J=9.0 Hz, ArH);

Elemental analysis: Found, C, 74.7; H, 8.08% $\text{C}_{41}\text{H}_{52}\text{O}_7$ requires
C, 75.0; H, 7.92%.

The physical data of the cognate preparations of the other [S]-[+]-1-methylheptyl-4-[4'-(*trans*-4''-n-alkoxycinnamoyloxy)benzoyloxy]benzoates are given below.

[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-hexyloxycinnamoyloxy)benzoyloxy]benzoate, (2.E.1)

Yield, 79%; m.p. 107.2°C; $[\alpha]_D^{25} = 18.5^\circ$ (4.8 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0(27H, m, 3XCH₃, 9XCH₂), 4.1(2H, t, J=6.6 Hz, ArOCH₂), 5.0-5.34(1H, m, COOCH), 6.42 and 7.84 (AB q, 2H, J=18.6 Hz, CH=CH-COO-), 6.88 and 7.45 (4H, AB q, J=9.0 Hz, ArH), 7.32 and 8.16 (4H, AB q, J=9.5 Hz, ArH), 7.4 and 8.3 (4H, AB q, J=9.0 Hz, ArH);

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Elemental analysis: Found, C, 77.62; H, 7.45% $C_{37}H_{44}O_7$ requires
C, 77.99; H, 7.3%.

[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-heptyloxycinnamoyloxy)benzo- yloxy]benzoate, (2.E.2)

Yield, 80%; m.p. 92.5°C; $[\alpha]_D^{25} = 19.10^\circ$ (5.2 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0(29H, m, 3XCH₃, 10XCH₂), 4.1(2H, t, J=6.6 Hz, ArOCH₂), 5.0-5.34(1H, m, COOCH), 6.42 and 7.84 (AB q, 2H, J=18.6 Hz, CH=CH-COO-), 6.88 and 7.45 (4H, AB q, J=9.0 Hz, ArH), 7.32 and 8.16 (4H, AB q, J=9.5 Hz, ArH), 7.4 and 8.3 (4H, AB q, J=9.0 Hz, ArH);

Elemental analysis: Found, C, 74.42; H, 7.58% $C_{38}H_{46}O_7$ requires
C, 74.26; H, 7.49%.

[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-octyloxycinnamoyloxy)benzoyl- oxy]benzoate, (2.E.3)

Yield, 76%; m.p. 79.5°C; $[\alpha]_D^{25} = 18.5^\circ$ (5.0 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0(31H, m, 3XCH₃, 11XCH₂), 4.1(2H, t, J=6.6 Hz, ArOCH₂), 5.0-5.34(1H, m, COOCH), 6.42 and 7.84 (AB q, 2H, J=18.6 Hz, CH=CH-COO-), 6.88 and 7.45 (4H, AB q, J=9.0 Hz, ArH), 7.32 and 8.16 (4H, AB q, J=9.5 Hz, ArH), 7.4 and 8.3 (4H, AB q, J=9.0 Hz, ArH);

Elemental analysis: Found, C, 74.87; H, 7.87% $C_{39}H_{48}O_7$ requires
C, 74.52; H, 7.64%.

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[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-nonyloxy)cinnamoyloxy]benzoyloxy]benzoate, (2.E.4)

Yield, 73%; m.p. 81.0°C; $[\alpha]_D^{25} = 18.9^\circ$ (5.9 mg/ml in CH_2Cl_2); ν : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0(33H, m, 3XCH₃, 12XCH₂), 4.1(2H, t, J=6.6 Hz, ArOCH₂), 5.0-5.34(1H, m, COOCH), 6.42 and 7.84 (AB q, 2H, J=18.6 Hz, CH=CH-COO-), 6.88 and 7.45 (4H, AB q, J=9.0 Hz, ArH), 7.32 and 8.16 (4H, AB q, J=9.5 Hz, ArH), 7.4 and 8.3 (4H, AB q, J=9.0 Hz, ArH);

Elemental analysis: Found, C, 74.71; H, 7.99% $\text{C}_{40}\text{H}_{50}\text{O}_7$ requires
C, 74.76; H, 7.78%.

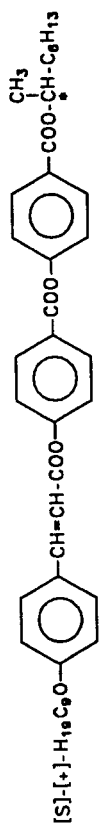
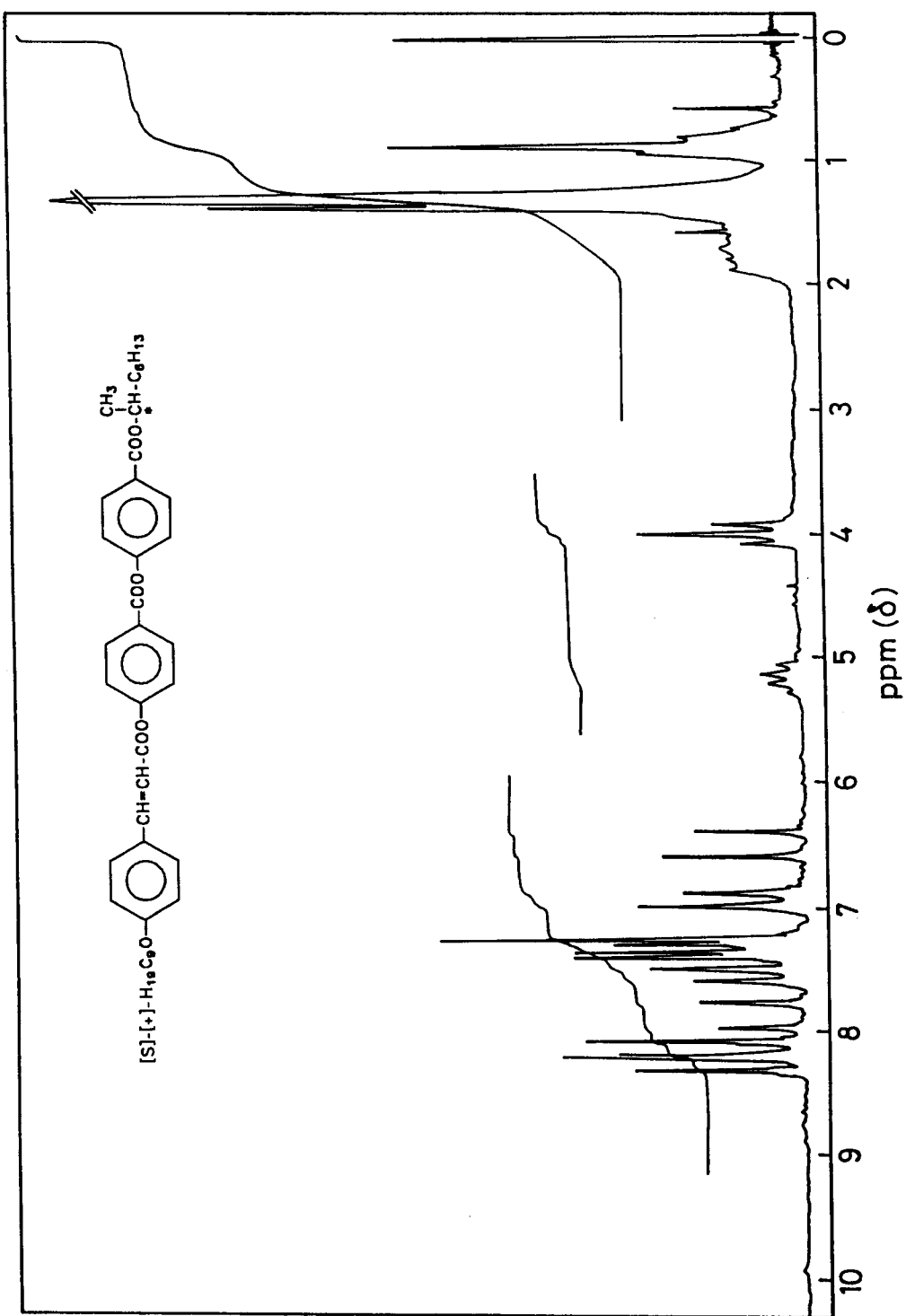
[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-undecyloxy)cinnamoyloxy]benzoyloxy]benzoate, (2.E.6)

Yield, 81%; m.p. 87.0°C; $[\alpha]_D^{25} = 18.2^\circ$ (6.9 mg/ml in CH_2Cl_2); ν : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0(37H, m, 3XCH₃, 14XCH₂), 4.1(2H, t, J=6.6 Hz, ArOCH₂), 5.0-5.34(1H, m, COOCH), 6.42 and 7.84 (AB q, 2H, J=18.6 Hz, CH=CH-COO-), 6.88 and 7.45 (4H, AB q, J=9.0 Hz, ArH), 7.32 and 8.16 (4H, AB q, J=9.5 Hz, ArH), 7.4 and 8.3 (4H, AB q, J=9.0 Hz, ArH);

Elemental analysis: Found, C, 74.89; H, 8.19% $\text{C}_{42}\text{H}_{54}\text{O}_7$ requires
C, 75.22; H, 8.05%.

[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-dodecyloxy)cinnamoyloxy]benzoyloxy]benzoate, (2.E.7)

Yield, 80%; m.p. 88.0°C; $[\alpha]_D^{25} = 20.2^\circ$ (5.3 mg/ml in CH_2Cl_2); ν : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0(39H, m, 3XCH₃, 15XCH₂),



¹H NMR spectrum for compound 2.E.4.

4.1(2H, t, J=6.6 Hz, ArOCH₂), 5.0-5.34(1H, m, COOCH), 6.42 and 7.84 (AB q, 2H, J=18.6 Hz, CH=CH-COO-), 6.88 and 7.45 (4H, AB q, J=9.0 Hz, ArH), 7.32 and 8.16 (4H, AB q, J=9.5 Hz, ArH), 7.4 and 8.3 (4H, AB q, J=9.0 Hz, ArH);

Elemental analysis: Found, C, 75.57; H, 8.38% C₄₃H₅₆O₇ requires
C, 75.43; H, 8.18%.

[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-tetradecyloxycinnamoyloxy)benzoyloxy]benzoate, (2.E.8)

Yield, 82%; m.p. 85.5°C; $[\alpha]_D^{25} = 17.9^\circ$ (5.4 mg/ml in CH₂Cl₂); ν_{\max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm⁻¹; 6: 0.7-2.0(43H, m, 3XCH₃, 17XCH₂), 4.1(2H, t, J=6.6 Hz, ArOCH₂), 5.0-5.34(1H, m, COOCH), 6.42 and 7.84 (AB q, 2H, J=18.6 Hz, CH=CH-COO-), 6.88 and 7.45 (4H, AB q, J=9.0 Hz, ArH), 7.32 and 8.16 (4H, AB q, J=9.5 Hz, ArH), 7.4 and 8.3 (4H, AB q, J=9.0 Hz, ArH);

Elemental analysis: Found, C, 75.83; H, 8.43% C₄₅H₆₀O₇ requires
C, 75.84; H, 8.42%.

[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-hexadecyloxycinnamoyloxy)benzoyloxy]benzoate, (2.E.9)

Yield, 76%; m.p. 83.0°C; $[\alpha]_D^{25} = 18.1^\circ$ (5.6 mg/ml in CH₂Cl₂); ν_{\max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm⁻¹; 6: 0.7-2.0(47H, m, 3XCH₃, 19XCH₂), 4.1(2H, t, J=6.6 Hz, ArOCH₂), 5.0-5.34(1H, m, COOCH), 6.42 and 7.84 (AB q, 2H, J=18.6 Hz, CH=CH-COO-), 6.88 and 7.45 (4H, AB q, J=9.0 Hz, ArH), 7.32 and 8.16 (4H, AB q, J=9.5 Hz, ArH), 7.4 and 8.3 (4H, AB q, J=9.0 Hz, ArH);

Elemental analysis: Found, C, 76.64; H, 8.87% C₄₇H₆₄O₇ requires
C, 76.21; H, 8.64%.

[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-decyloxy- α -methylcinnamoyloxy)benzoyloxy]benzoate, (2.F.3)

This was prepared according to the procedure described for compound 2.8. Yield, 87%; m.p. 62.5°C; $[\alpha]_D^{25} = 21.37^\circ$ (4.9 mg/ml in CH₂Cl₂); ν_{\max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm⁻¹; δ : 0.75-1.95(35H, m, 3XCH₃, 13XCH₂), 2.27(3H, d, J=1.1 Hz, C=C(CH₃)), 4.0(2H, t, J=6.5 Hz, ArOCH₂), 5.14(1H, m, COOCH), 6.85 and 7.45(4H, AB q, J=9.0 Hz, ArH), 7.32 and 8.16 (4H, AB q, J=9.5 Hz, ArH), 7.4 and 8.3 (4H, AB q, J=9.0 Hz, ArH), 7.87(1H, s, CH=C-);

Elemental analysis: Found, C, 74.90; H, 8.29% C₄₂H₅₄O₇ requires
C, 75.22; H, 8.05%.

The physical data of the cognate preparations of the other [S]-[+]-1-methylheptyl-4-[4'-(*trans*-4''-n-alkoxy- α -methylcinnamoyloxy)benzoyloxy]benzoates are given below.

[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-octyloxy- α -methylcinnamoyloxy)benzoyloxy]benzoate, (2.F.1)

Yield, 80%; m.p. 58.5°C; $[\alpha]_D^{25} = 21.0^\circ$ (6.0 mg/ml in CH₂Cl₂); ν_{\max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm⁻¹; δ : 0.75-1.95(31H, m, 3XCH₃, 11XCH₂), 2.27(3H, d, J=1.1 Hz, C=C(CH₃)), 4.0(2H, t, J=6.5 Hz, ArOCH₂), 5.0-5.36(1H, m, COOCH), 6.85 and 7.45(4H, AB q, J=9.0 Hz, ArH), 7.32 and 8.16 (4H, AB q, J=9.5 Hz, ArH), 7.4 and 8.3 (4H, AB q, J=9.0 Hz, ArH), 7.87(1H, s, CH=C-);

Elemental analysis: Found, C, 75.14; H, 7.96% C₄₀H₅₀O₇ requires
C, 74.76; H, 7.78%.

[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-nonyloxy- α -methylcinnamoyl-oxo)benzoyloxy]benzoate, (2.F.2)

Yield, 78%; m.p. 57.5 °C; $[\alpha]_D^{25} = 22.0^\circ$ (4.8 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.75-1.95(33H, m, 3XCH₃, 12XCH₂), 2.27(3H, d, J=1.1 Hz, C=C(CH₃)), 4.0(2H, t, J=6.5 Hz, ArOCH₂), 5.0-5.36(1H, m, COOCH), 6.85 and 7.45(4H, AB q, J=9.0 Hz, ArH), 7.32 and 8.16 (4H, AB q, J=9.5 Hz, ArH), 7.4 and 8.3 (4H, AB q, J=9.0 Hz, ArH), 7.87(1H, s, CH=C-);

Elemental analysis: Found, C, 74.89; H, 8.11% C₄₁H₅₂O₇ requires
C, 74.99; H, 7.92%.

[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-undecyloxy- α -methylcinnamoyl-oxo)benzoyloxy]benzoate, (2.F.4)

Yield, 79%; m.p. 60.7°C; $[\alpha]_D^{25} = 20.7^\circ$ (6.1 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.75-1.95(37H, m, 3XCH₃, 14XCH₂), 2.27(3H, d, J=1.1 Hz, C=C(CH₃)), 4.0(2H, t, J=6.5 Hz, ArOCH₂), 5.0-5.36(1H, m, COOCH), 6.85 and 7.45(4H, AB q, J=9.0 Hz, ArH), 7.32 and 8.16 (4H, AB q, J=9.5 Hz, ArH), 7.4 and 8.3 (4H, AB q, J=9.0 Hz, ArH), 7.87(1H, s, CH=C-);

Elemental analysis: Found, C, 75.07; H, 8.32% C₄₃H₅₆O₇ requires
C, 75.43; H, 8.18%.

[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-dodecyloxy- α -methylcinnamoyl-oxo)benzoyloxy]benzoate, (2.F.5)

Yield, 81%; m.p. 57.0°C; $[\alpha]_D^{25} = 22.4^\circ$ (3.8 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.75-1.95(m, 39H, 3XCH₃, 15XCH₂),

2.27(d, 3H, $J=1.1$ Hz, $C=C(CH_3)$), 4.0(2H, t, $J=6.5$ Hz, $ArOCH_2$), 5.0-5.36(m, 1H, $COOCH$), 6.85 and 7.45(4H, AB q, $J=9.0$ Hz, ArH), 7.32 and 8.16 (4H, AB q, $J=9.5$ Hz, ArH), 7.4 and 8.3 (4H, AB q, $J=9.0$ Hz, ArH), 7.87(1H, s, $CH=C-$);

Elemental analysis: Found, C, 75.64; H, 8.51% $C_{44}H_{58}O_7$ requires
C, 75.64; H, 8.30%.

[S]-[+]-1-Methylheptyl-4-[4'-(*trans*-4''-n-tetradecyloxy- α -methylcinnamoyloxy)benzoyloxy]benzoate, (2.F.6)

Yield, 82%; m.p. 64.2°C; $[\alpha]_D^{25} = 20.6^\circ$ (4.0 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; **6**: 0.75-1.95(m, 43H, 3X CH_3 , 17X CH_2), 2.27(d, 3H, $J=1.1$ Hz, $C=C(CH_3)$), 4.0(2H, t, $J=6.5$ Hz, $ArOCH_2$), 5.0-5.36(m, 1H, $COOCH$), 6.85 and 7.45(4H, AB q, $J=9.0$ Hz, ArH), 7.32 and 8.16 (4H, AB q, $J=9.5$ Hz, ArH), 7.4 and 8.3 (4H, AB q, $J=9.0$ Hz, ArH), 7.87(1H, s, $CH=C-$);

Elemental analysis: Found, C, 76.14; H, 8.73% $C_{46}H_{62}O_7$ requires
C, 76.03; H, 8.54%.

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