

Chapter-4

Synthesis and mesomorphic properties of

- (i) 1,3-Phenylene bis[4-(4-n-alkoxybenzoyloxy)benzoates]
(Series-4.I)
- (ii) 1,3-Phenylene bis[4-(4-n-alkoxybenzoyloxy)2-fluorobenzoates]
(Series-4.II)
- (iii) 1,3-Phenylene bis[4-(4-n-alkoxybenzoyloxy)3-fluorobenzoates]
(Series-4.III)
- (iv) 1,3-Phenylene bis[4-(2-fluoro-4-n-alkoxybenzoyloxy)benzoates]
(Series-4.IV)
- (v) 1,3-Phenylene bis[4-(3-fluoro-4-n-alkoxybenzoyloxy)benzoates]
(Series-4.V)
- (vi) 1,3-Phenylene bis[4-(2-fluoro-4-n-alkoxybenzoyloxy)2-fluoro-
benzoates] (Series-4.VI)
- (vii) 1,3-Phenylene bis[4-(3-fluoro-4-n-alkoxybenzoyloxy)2-fluoro-
benzoates] (Series-4.VII)
- (viii) 1,3-Phenylene bis[4-(2-fluoro-4-n-alkoxybenzoyloxy)3-fluoro-
benzoates] (Series-4.VIII)
- (ix) 1,3-Phenylene bis[4-(3-fluoro-4-n-alkoxybenzoyloxy)3-fluoro-
benzoates] (Series-4.IX)
- (x) 1,3-Phenylene bis[4-(4-n-alkylbenzoyloxy)2-fluorobenzoates]
(Series-4.X)
- (xi) 1,3-Phenylene bis[4-(4-n-tetradecylbenzoyloxy)3-fluorobenzoate]
(Compound 4.K.1)
- (xii) 1,3-Phenylene bis[4-(4-n-alkoxybenzoyloxy)3-chlorobenzoates]
(Series-4.XI)

A brief account of the mesomorphic properties of bent-core compounds containing five phenyl rings

Since the discovery of ferroelectricity in calamitic liquid crystals by Meyer *et al.* [5] there has been remarkable progress in not only the synthesis of new compounds exhibiting ferroelectric properties but also in application devices using this property. Ferroelectric properties have been observed in pure compounds exhibiting a chiral smectic C (SmC^*) phase or by doping the smectic C liquid crystal with a suitable chiral substance. In both of these cases chiral molecules are involved. However, molecular chirality is not a necessary condition for realizing ferroelectric liquid crystals. Ferroelectricity may be observed in compounds with polar structure in which the direction of polarization is reversed by the application of an electric field. Polar order may be realized in the mesophases of compounds composed of achiral bent-core or banana-shaped molecules because they cannot rotate easily about their long molecular axis.

In the last couple of years, there has been a number of reports on the electro-optical switching behaviour of banana-shaped compounds [20, 28, 29, 30, 54]. One of the phases for which electro-optical behaviour has been studied extensively is the antiferroelectric B_2 phase [20, 28]. The new sub-field of thermotropic liquid crystals composed of bent-core molecules has provided a wealth of new and exciting mesophases in a short span of time. During the last few years, a large number of such five-ring compounds have been synthesized with a view to understand the relationship between molecular structure and the nature of the mesophase/s they exhibit [13, 32, 41, 43, 50, 52, 53, 55, 56, 59, 70, 89, 90, 92, 93, 94, 99, 100, 101, 102, 103, 104, 105, 106]. In addition, compounds with six and seven aromatic rings in the core have also been examined. Most of the compounds described in the review [32] contain five aromatic rings with azomethine linkage group and are derivatives of resorcinol, which has been widely used as the central unit. However, the synthesis and characterization of mesophases obtained for complete homologous series of five-ring bent-core compounds appear to be limited [32, 43, 52, 59, 89, 101]. There are a number of five-ring bent-core compounds in which the central phenyl ring is substituted by different groups [32, 41, 53, 94, 101] and the influence of these on the mesomorphic properties has been studied. In addition, there are numerous studies on the effect of different lateral substituents on the arms of the five-ring bent-core molecules on the mesomorphic properties [38, 41, 50, 51, 52, 53, 56, 68, 69, 70, 99, 100, 101]. Amongst these, a lateral fluorine substituent *ortho* to the terminal *n*-alkoxy chain induces interesting electro-optical switching properties to the mesophases. For

example, Bedel *et al.* [38, 52] reported ferroelectric switching behaviour for the higher homologues of few series of five-ring Schiff's base esters. Later, Nadasi *et al.* [41] found ferroelectric properties in achiral five-ring Schiff's base esters with lateral fluorine substituents both on the central phenyl ring as well as the outer phenyl rings. Recently, Rauch *et al.* [91] reported a ferroelectric phase for 3,4'-biphenylene-bis[4-(3-fluoro-4-n-octyloxy-phenyliminomethyl)benzoate], which again contains fluorine substituent *ortho* to the terminal n-alkoxy chain. In addition, the compounds containing branched alkyl chains [54, 90] as well as the compounds containing vinylic end group and alkyl chains [92] show ferroelectric properties. Recently, Dantlgraber *et al.* [93] reported ferroelectric properties in compounds containing siloxane unit at one end of the arm and an n-alkoxy chain at the other end.

All these observations indicate that coupling and decoupling of chains between the layers play a role in determining the nature of the mesophases. In calamitic liquid crystals, the permeation of molecules between the layers is possible only for synclitic ordering of molecules like the arrangement in SmC^* phase. Since this is thermodynamically (entropically) favoured, this is a commonly observed mesophase in most of the chiral compounds. In contrast, the interlayer fluctuations are forbidden in anticlinic tilted antiferroelectric (SmC_A^*) phases as explained by Nadasi *et al.* [41] and hence these are not very common. Thus, the high temperature phase is ferroelectric and the antiferroelectric phase appears at a lower temperature for a given compound in calamitic liquid crystals. In case of bent-core molecules the same argument is valid by assuming each smectic layer as a connected pair of anticlinically arranged rods. Then, the interlayer fluctuations are favourable for antiferroelectric phases and not for ferroelectric phases, which means the antiferroelectric phases are stable as observed experimentally [32]. A schematic representation of the arrangement of molecules in these two phases is shown in figure 4.1.

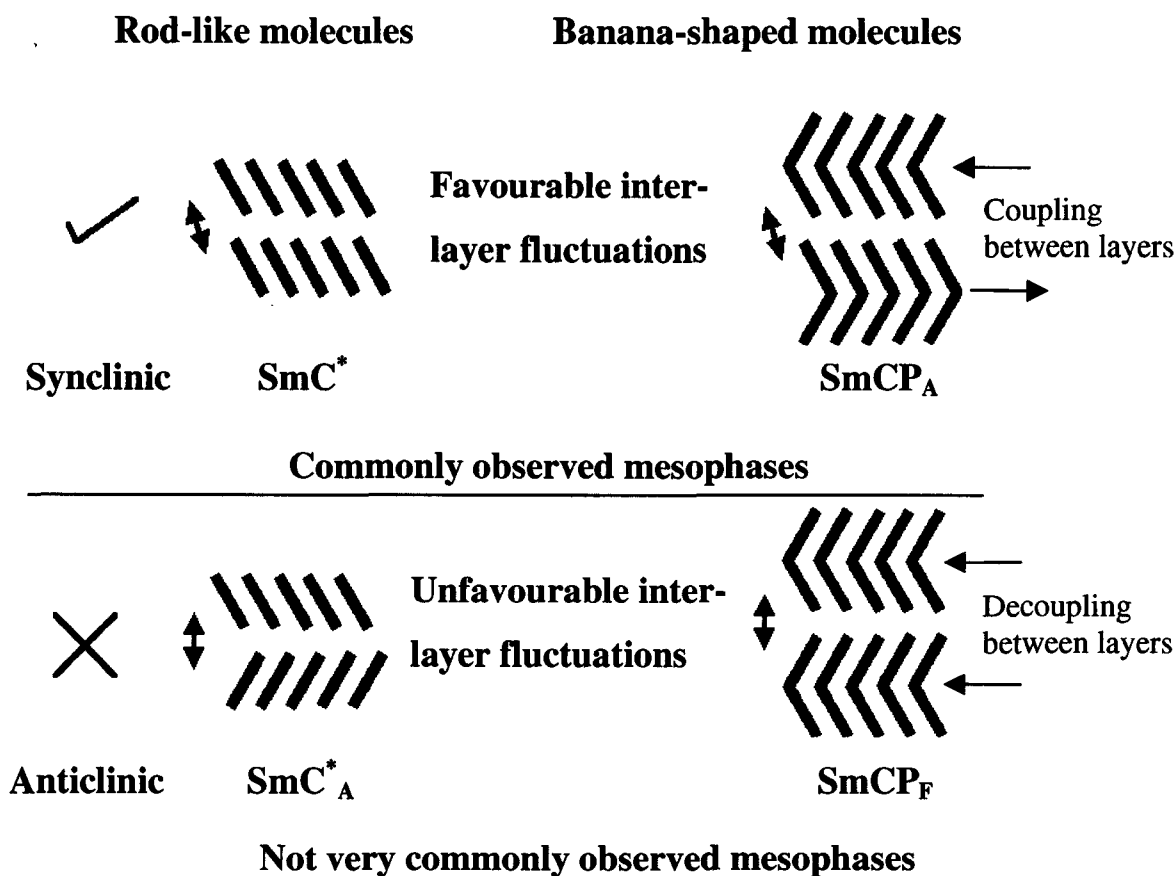


Fig. 4.1. A schematic representation of arrangement of rod-like and banana-shaped molecules in ferro- and antiferro-electric phases, the demonstration of coupling and decoupling between the layers which are responsible for the stability of different mesophases. Nadasi *et al.* [41]

In order to generate a ferroelectric phase, the molecular design should be such that a decoupling between the layers is induced. The introduction of suitable lateral substituents into bent-core compounds has a bearing on the mesophases induced [32, 36, 38, 48, 51, 60, 61, 66].

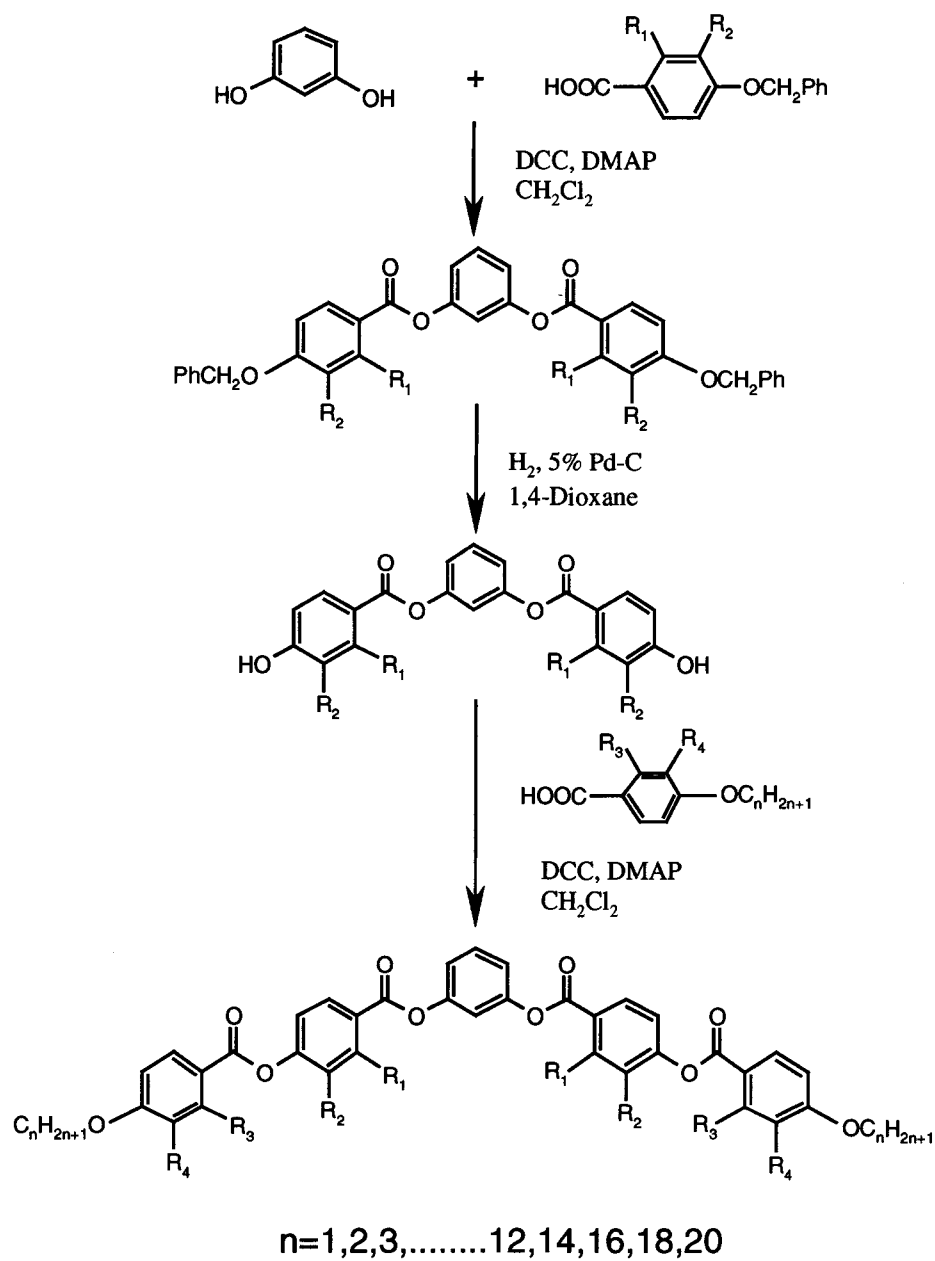
However, there has not been any systematic evaluation of the influence of a lateral substituent on the liquid crystalline properties of compounds composed of banana-shaped molecules. It is for this reason that we decided to examine a system in detail and the results of the investigations are reported in this chapter.

Results and discussion

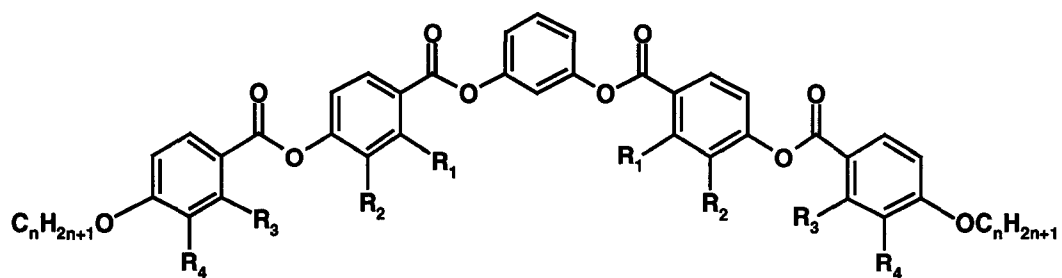
We chose a five-ring ester system derived from resorcinol which does not contain the relatively unstable azomethine linking group. We have systematically substituted the phenyl rings of the arms of the bent-core molecules with fluorine and examined the mesomorphic properties.

As a result, several homologous series of compounds substituted laterally by fluorine on the arms of the symmetrical bent-core (BC) molecules were synthesized by following the general synthetic pathway shown in scheme 4.1. Resorcinol was obtained commercially and used without further purification. 4-Benzyloxybenzoic acid, 2-fluoro-4-benzyloxybenzoic acid, 3-fluoro-4-benzyloxybenzoic acid, 2-fluoro-4-n-alkoxybenzoic acids and 3-fluoro-4-n-alkoxybenzoic acids were prepared as already described in Chapter-2. 3-Chloro-4-benzyloxybenzoic acid was prepared by following a procedure described elsewhere [36] as follows. 2-Chlorophenylacetate was subjected to Fries' rearrangement to get 3-chloro-4-hydroxyacetophenone which was benzylated to obtain 3-chloro-4-benzyloxyacetophenone. This was further oxidized using sodium hypobromite in 1,4-dioxane to get the desired carboxylic acid. 2-Fluoro- or 3-fluoro-4-benzyloxybenzoic acid was condensed with resorcinol in dichloromethane in the presence of a dehydrating agent N, N'-dicyclohexylcarbodiimide (DCC) and a catalyst (N, N-dimethylamino)pyridine (DMAP). The resultant dibenzyloxy ester obtained was subjected to hydrogenolysis in the presence of 5% Pd-C catalyst in an hydrogen atmosphere. The target compounds were prepared by reacting the purified bis-phenol with two equivalents of 2-fluoro- or 3-fluoro-4-n-alkoxybenzoic acids as described above.

A total of one hundred and nine compounds belonging to eleven different homologous series have been studied and the general molecular structure representing these homologous series is shown in structure 4.I.

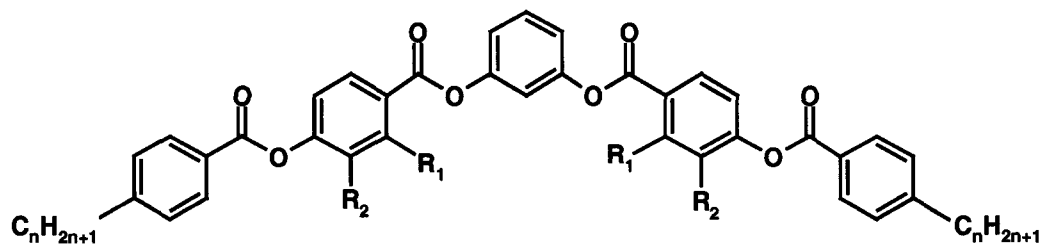


Scheme 4.1. General synthetic pathway used for obtaining the symmetrical banana-shaped mesogens derived from resorcinol.



$n=1,2,3,\dots,12,14,16,18,20$

$R_1=H, R_2=H, R_3=H, R_4=H$	Series-4.I
$R_1=F, R_2=H, R_3=H, R_4=H$	Series-4.II
$R_1=H, R_2=F, R_3=H, R_4=H$	Series-4.III
$R_1=H, R_2=H, R_3=F, R_4=H$	Series-4.IV
$R_1=H, R_2=H, R_3=H, R_4=F$	Series-4.V
$R_1=F, R_2=H, R_3=F, R_4=H$	Series-4.VI
$R_1=F, R_2=H, R_3=H, R_4=F$	Series-4.VII
$R_1=H, R_2=F, R_3=F, R_4=H$	Series-4.VIII
$R_1=H, R_2=F, R_3=H, R_4=F$	Series-4.IX
$R_1=H, R_2=Cl, R_3=H, R_4=H$	Series-4.XI



$R_1=F, R_2=H,$ Series-4.X

$n=8,9,10,11,12,14,16$

$R_1=H, R_2=F,$ Compound 4.K.1

$n=14$

Structure 4.I

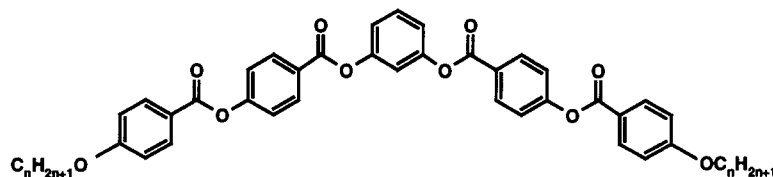
A systematic study has been carried out to examine the influence of a fluorine substituent on the mesomorphic behaviour of five-ring esters. In any such study, the starting point would be to examine the liquid crystalline properties of the unsubstituted parent compounds (series 4.I).

The transition temperatures and the associated enthalpies of the compounds of this series are summarized in table 4.1. As can be seen in this table, all the fifteen homologues are mesomorphic. On cooling the isotropic liquid of compounds 4.A.1 to 4.A.5, large batonnets appear first, which coalesce to form a fan-shaped texture. Compound 4.A.4 is enantiotropic while the remaining are monotropic. Though the texture appears similar to the focal-conic texture of the SmA phase of calamitic liquid crystals, it has not been possible to obtain a homeotropic texture even on mechanical shearing. This excludes the possibility of SmA phase. No electro-optical switching behaviour could be observed for this mesophase. Based on these observations and X-ray studies (discussed later), it has been identified as a B₆ phase. The clearing transition enthalpy value for this phase is in the range of 9-16 kJmol⁻¹ which is normally obtained for B-phases. Interestingly, the lowest homologue (compound 4.A.1) shows the banana phase (B₆) and it is monotropic. The terminal methoxy group of this compound can be considered as part of the core which stabilizes the intercalated structure which is enhanced due to its opposing dipoles. On increasing the chain length, the core-core interactions are reduced by the electro-positive alkyl chains and hence the B₆ phase gets stabilized.

Compounds 4.A.6 to 4.A.9 show a different mesophase behaviour. On cooling the isotropic liquid of these compounds, a fern-like pattern develops and coalesce to form a mosaic texture and these are typical for a B₁ phase. The rectangular lattice obtained for this phase was confirmed from XRD studies and will be described later. The clearing enthalpy value obtained varies and is about 17-18 kJmol⁻¹. Compounds 4.A.10 to 4.A.15 show another type of mesophase. Compound 4.A.10 is monotropic and the remaining are enantiotropic mesomorphic. The textural features observed for this mesophase are very similar to the well characterized B₂ phase. Based on XRD and electro-optical studies (which will be described later), this mesophase has been identified as a B₂ phase.

It is also appropriate to note here that compound 4.A.8 has been reported [32] to exhibit an enantiotropic B₁ phase with a melting point of 111°C. However, we observe only a monotropic B₁ phase. For compound 4.A.10, B₁ phase is observed on cooling only though

Table 4.1. Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kJmol^{-1}) (*in italics*) for compounds of series 4.I.



Compound	n	Cr	B ₂	B ₁	B ₆	I
4.A.1	1	. 168.5 <i>46.3</i>	-	-	(. 143.5) <i>9.3</i>	.
4.A.2	2	. 173.0 <i>49.3</i>	-	-	(. 167.5) <i>11.6</i>	.
4.A.3	3	. 175.0 <i>53.2</i>	-	-	(. 160.5) <i>12.9</i>	.
4.A.4	4	. 157.5 <i>37.6</i>	-	-	. 161.5 <i>14.9</i>	.
4.A.5	5	. 170.0 <i>82.0</i>	-	-	(. 148.5) <i>15.5</i>	.
4.A.6	6	. 138.5 <i>48.9</i>	-	. 140.5 <i>17.8</i>	-	.
4.A.7	7	. 132.5 <i>54.4</i>	-	(. 129.5) <i>17.7</i>	-	.
4.A.8	8	. 124.5 <i>66.2</i>	-	(. 123.0) <i>19.1</i>	-	.
4.A.9	9	. 115.0 <i>75.1</i>	-	(. 114.0) <i>18.3</i>	-	.
4.A.10	10	. 111.5 <i>54.6</i>	(. 110.0) <i>20.3</i>	-	-	.
4.A.11	11	. 105.0 <i>38.3</i>	. 113.5 <i>21.6</i>	-	-	.
4.A.12	12	. 106.0 <i>42.7</i>	. 116.5 <i>22.5</i>	-	-	.
4.A.13	14	. 107.0 <i>50.6</i>	. 119.5 <i>24.3</i>	-	-	.
4.A.14	16	. 110.5 <i>81.8</i>	. 121.5 <i>26.0</i>	-	-	.
4.A.15	18	. 112.0 <i>68.9</i>	. 121.5 <i>24.5</i>	-	-	.

Key: Applicable to all tables: Cr =Crystalline phase; B₁=Two-dimensional banana phase; B₂=Lamellar antiferroelectric banana phase; B₆=Intercalated smectic banana phase; B_{X1}=Banana ferroelectric lamellar phase; B_{X2}=Banana ferroelectric two- or three-dimensional phase; I=Isotropic phase; . Phase exists; - Phase does not exist; Temperature in parentheses indicate monotropic transitions.

over a very narrow range of 1°C in addition to a B₂ phase [34]. The transition temperatures of compounds **4.A.12** and **4.A.13** agree fairly well with what is reported [34] in the literature. A plot of the transition temperatures as a function of the number of carbon atoms in the terminal n-alkoxy chains for series **4.I** is shown in figure 4.2. It can be seen that the B₁-I and B₂-I transition points follow the general patterns observed previously [61].

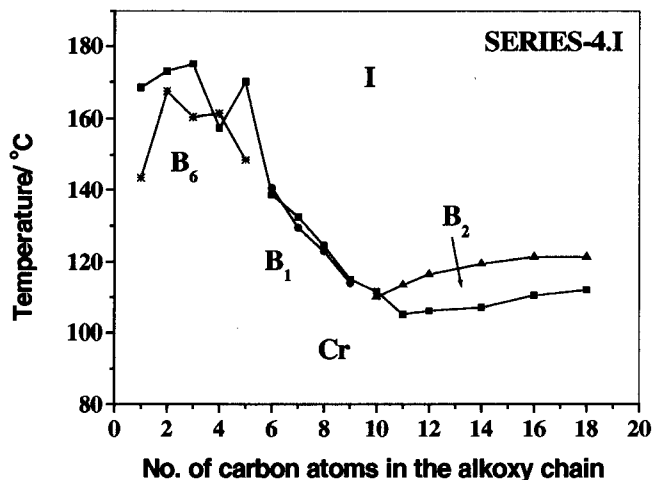
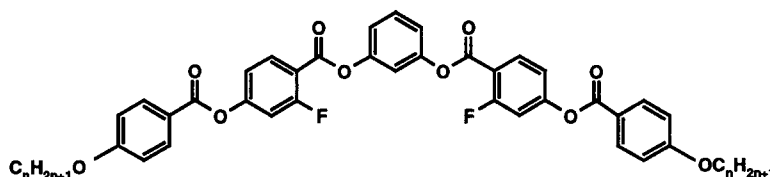


Fig. 4.2. Plot of transition temperatures as a function of the number of carbon atoms in the n-alkoxy chains obtained for series **4.I**.

In the case of compounds of series **4.II**, a fluorine substituent (R₁) is introduced *ortho* to the carboxylate group connected to the central phenyl ring. The transition temperatures together with the enthalpies of this series are given in table 4.2. It can be seen that the mesomorphic behaviour of the homologues of this series is similar to those observed for compounds of series **4.I**. While there is a general decrease in the melting as well as the clearing temperatures, the metastable phases become enantiotropic as a result of this fluorine substitution. However, a monotropic B₁ phase observed for compound **4.A.9** is totally eliminated as a result of this substitution (compound **4.B.9**). Apart from the core and the lateral substituents, the length of the terminal n-alkoxy chain also plays an important role with regard to the stability of the individual mesophases. As can be seen in series **4.I** and **4.II**, the B₆ phase occurs as a metastable phase, becomes enantiotropic on ascending the series and becomes monotropic again after certain chain length (for example, compounds **4.A.1** to **4.A.5** and **4.B.1** to **4.B.5**). One can see that for compounds **4.A.5** and **4.B.5**, the melting points are rather high as a result of which a metastable phase is seen. On increasing the chain length further, the core-core and the tail-tail interactions increase and hence the molecules exist as clusters. These arrange in a two-dimensional rectangular fashion such that the polarization

due to the clusters get annulled which helps in further stabilization of the intercalated structure. As usual, for compounds containing longer chains smectic ordering was obtained.

Table 4.2. Transition temperatures (°C) and enthalpies (kJmol⁻¹) (*in italics*) for compounds of series 4.II.



Compound	n	Cr	B ₂	B ₁	B ₆	I
4.B.1	1	. 176.0 <i>63.0</i>	-	-	(. 125.5) ^a	.
4.B.2	2	. 152.0 <i>42.9</i>	-	-	. 155.0 <i>10.8</i>	.
4.B.3	3	. 126.5 <i>26.6</i>	-	-	. 147.0 <i>11.9</i>	.
4.B.4	4	. 128.5 <i>40.4</i>	-	-	. 146.0 <i>13.3</i>	.
4.B.5	5	. 139.0 <i>64.1</i>	-	-	(. 130.0) <i>11.6</i>	.
4.B.6	6	. 108.0 <i>29.0</i>	-	. 121.5 <i>15.8</i>	-	.
4.B.7	7	. 118.5 <i>57.1</i>	-	(. 109.5) <i>15.2</i>	-	.
4.B.8	8	. 112.0 <i>58.7</i>	-	(. 101.0) <i>15.8</i>	-	.
4.B.9	9	. 97.0 <i>65.2</i>	-	-	-	.
4.B.10	10	. 96.5 <i>44.9</i>	. 98.0 <i>19.8</i>	-	-	.
4.B.11	11	. 95.0 <i>49.4</i>	. 101.0 <i>20.8</i>	-	-	.
4.B.12	12	. 93.0 <i>48.1</i>	. 105.0 <i>22.8</i>	-	-	.
4.B.13	14	. 91.0 <i>44.4</i>	. 109.0 <i>21.9</i>	-	-	.
4.B.14	16	. 94.5 <i>63.2</i>	. 110.5 <i>24.4</i>	-	-	.
4.B.15	18	. 99.5 <i>87.9</i>	. 112.5 <i>26.0</i>	-	-	.

a: enthalpy could not be determined as the sample crystallizes immediately.

A plot of the transition temperatures as a function of the number of carbon atoms in the terminal n-alkoxy chains for series **4.II** is shown in figure 4.3.

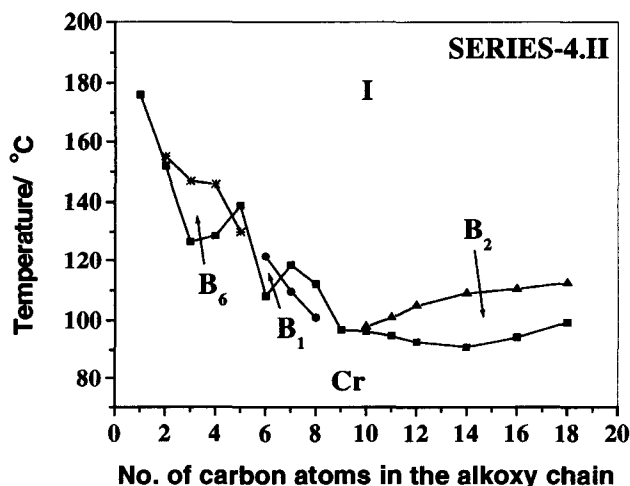


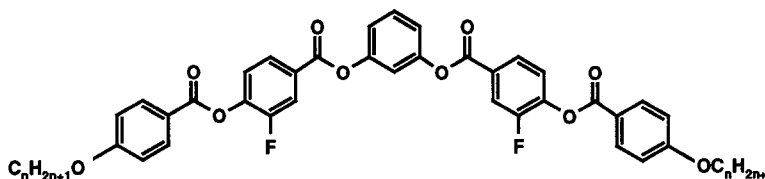
Fig. 4.3. Plot of transition temperatures as a function of the number of carbon atoms in the n-alkoxy chains obtained for series **4.II**.

When a fluorine substituent is in the *meta* position (R_2) as in series **4.III**, the mesogenic properties are completely suppressed and as a matter of fact only one compound (**4.C.2**) exhibits a monotropic B_6 phase. In table 4.3, the melting points and the associated enthalpies, the clearing temperature and the enthalpy for compound **4.C.2** are given. It is interesting to note that the melting points of these compounds are higher as compared to their analogues of series **4.II**. This suggests that the dipolar effects play a dominant role as opposed to steric factors in determining the occurrence of the mesophases in these five-ring esters.

Now, let us turn our attention to the terminal phenyl ring. When a fluorine substituent is introduced on the terminal phenyl ring ($R_3=F$, series **4.IV**), the occurrence of the mesophases in the series is similar to those observed for the homologues of series **4.II**. In other words, the intercalated mesophase B_6 , the two-dimensional rectangular columnar mesophase B_1 and the antiferroelectric mesophase B_2 are obtained on ascending the series. The homologue where the crossover from B_1 to B_2 phase takes place on ascending the series, namely compound **4.D.8**, exhibits a highly metastable B_2 phase on fast cooling and neither the temperature nor the enthalpy could be determined from DSC. The transition temperatures together with the associated enthalpies for the homologues of series **4.IV** are collected in table 4.4. From this table it is clear that the two-dimensional B_1 phase is suppressed more when compared to the intercalated B_6 phase as a result of the substitution. All the compounds which exhibit a B_6

phase show the same type of textures when the isotropic liquid is cooled slowly [13, 36, 43, 61, 89, 101]. A typical photomicrograph of the texture of the B₆ mesophase exhibited by

Table 4.3. Transition temperatures (°C) and enthalpies (kJmol⁻¹) (*in italics*) for compounds of series 4.III.



Compound	n	Cr	B ₆	I
4.C.1	3	.	137.0 <i>48.0</i>	-
4.C.2	4	.	130.0 <i>50.5</i>	(. 109.0) <i>9.4</i>
4.C.3	5	.	142.0 <i>61.3</i>	-
4.C.4	6	.	124.5 <i>50.2</i>	-
4.C.5	7	.	125.5 <i>57.7</i>	-
4.C.6	8	.	125.0 <i>52.2</i>	-
4.C.7	9	.	125.5 <i>56.4</i>	-
4.C.8	14	.	122.5 ^b <i>97.4</i>	-
4.C.9	18	.	120.0 ^b <i>113.5</i>	-

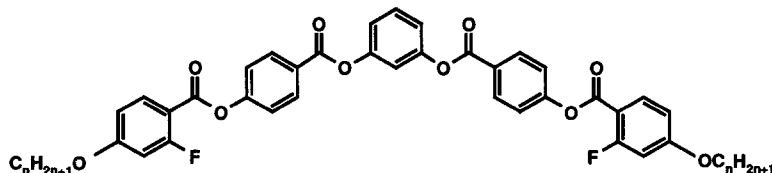
b : compound has crystal-crystal transition; enthalpy denoted is the sum of all previous transitions.

compound **4.D.4** is shown in figure 4.4a. However, the two-dimensional B₁ phase shows both spherulites and dendritic patterns as it grows from the isotropic phase [35, 36, 43, 61]. An optical photomicrograph of the growth of the B₁ mesophase of compound **4.D.5** is shown in figure 4.4b. The textures exhibited by the well studied lamellar antiferroelectric B₂ phase has been reported by a number of researchers [34, 36, 38, 60, 89]. A typical photomicrograph of the mesophase exhibited by compound **4.D.11** is shown in figure 4.4c. A plot of the transition temperatures as a function of the number of carbon atoms in the terminal chains for this series

is shown in figure 4.4d. The clearing temperature curves for these three phases are typical for such transitions as observed in a number of other series of compounds.

However, when a fluorine is substituted *ortho* to the terminal n-alkoxy chain ($R_4=F$) a very interesting phase behaviour is observed (series 4.V). The transition temperatures and the

Table 4.4. Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kJmol^{-1}) (*in italics*) for compounds of series 4.IV.



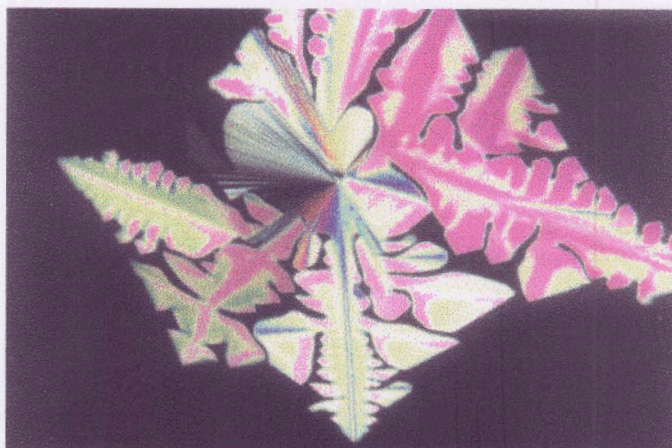
Compound	n	Cr	B ₂	B ₁	B ₆	I
4.D.1	3	. 151.0 48.0	-	-	-	.
4.D.2	4	. 133.5 38.6	-	-	(. 129.0) 11.1	.
4.D.3	5	. 148.0 64.7	-	-	(. 123.5) 12.0	.
4.D.4	6	. 117.0 34.3	-	-	. 120.0 13.3	.
4.D.5	7	. 112.0 46.0	-	(. 111.0) 15.4	-	.
4.D.6	8	. 107.0 64.5	-	(. 105.0) 15.9	-	.
4.D.7	9	. 103.5 80.1	-	(. 95.0) ^a	-	.
4.D.8	10	. 106.5 55.6	-	-	-	.
4.D.9	11	. 101.0 68.7	(. 97.0) 19.9	-	-	.
4.D.10	12	. 100.0 38.5	. 101.0 21.2	-	-	.
4.D.11	14	. 99.0 63.2	. 106.0 23.0	-	-	.
4.D.12	16	. 91.0 67.3	. 108.5 24.8	-	-	.
4.D.13	18	. 95.0 75.4	. 110.0 25.4	-	-	.

a: enthalpy could not be determined as the sample crystallizes immediately.

(a)



(b)



(c)

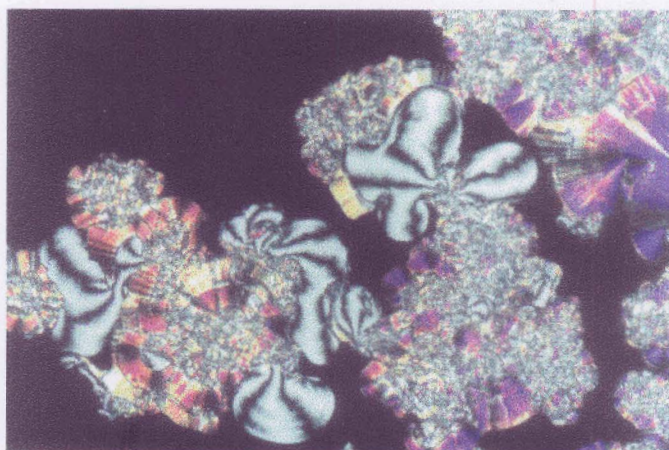


Fig. 4.4. Optical photomicrographs obtained on cooling the isotropic liquid (a) B₆ phase of compound 4.D.4, (b) B₁ phase of compound 4D5 and (c) B₂ phase of compound 4.D.11.

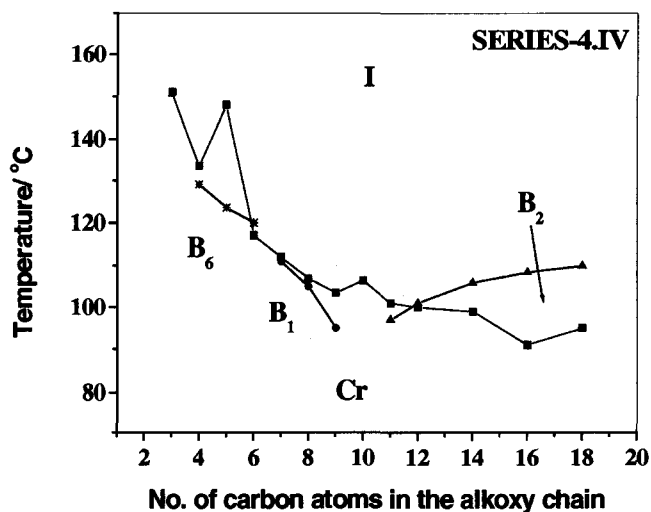
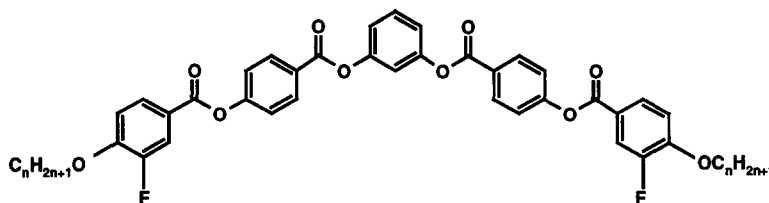


Fig. 4.4d. Plot of transition temperatures as a function of the number of carbon atoms in the n-alkoxy chains obtained for series 4.IV.

associated enthalpies for the homologues of this series 4.V are summarized in table 4.5. For compounds with chains containing less than or equal to eleven carbon atoms no mesophase is observed and this is in contrast to what is observed for homologues of series 4.IV. In other words, the intercalated B-phases namely, B₆ and B₁ are suppressed completely. Compound 4.E.5 is monotropic while compounds 4.E.6 and 4.E.7 are enantiotropic mesomorphic and all the three exhibit very similar textures. A sample of compound 4.E.7 was taken between an untreated glass slide and a cover slip and heated such that the mesophase appears. On observing the sample under a polarizing microscope an unspecified grainy texture develops. The viscosity of this mesophase is quite high and is difficult to shear. After shearing, the grainy texture is altered and the field of view becomes dark. The clearing enthalpy obtained for this mesophase is about 24 kJmol⁻¹. On cooling the isotropic liquid sufficiently, the mesophase appears dark under the field of view and the chiral domains of opposite handedness could be observed by rotating the polarizer or analyzer as shown in figure 4.23. However, by rotating the heating stage or sample, no change in the brightness or darkness in these chiral domains could be seen in uncrossed position. This indicates that the helical axis of the chiral domains is perpendicular to the substrate or which coincides with the optical axis. From these observations it was difficult to identify this mesophase with any of the well known banana phases B₁ to B₇ and hence this mesophase has been designated as B_{X1}. Recently, Dantlgraber *et al.* [93] reported a smectic ferroelectric liquid crystal, the features of which are similar to that of a B_{X1} phase.

Compounds **4.E.8** and **4.E.9** exhibit an enantiotropic mesophase and have a thermal range of 10.5°C and 9.5°C respectively. On examination of a thin film of this material under a polarizing microscope, two different types of textures could be seen. On slow cooling of the isotropic phase, reddish brown and grey coloured focal-conic domains appear and photomicrographs of this are shown in figures **4.5a**, **4.5b** and **4.5c**. In either case, shearing of the sample was quite easy indicating that the mesophase is less viscous and this resulted in an unspecified texture. The differential scanning calorimetric thermogram obtained for this compound is shown in figure **4.6**. The clearing enthalpy values for these two compounds are comparable to that obtained for compound **4.E.7**. The textural features of this mesophase also

Table 4.5. Transition temperatures (°C) and enthalpies (kJmol⁻¹) (*in italics*) for compounds of series 4.V.



Compound	n	Cr	B _{X2}	B _{X1}	I
4.E.1	7	. 130.0 ^b <i>73.3</i>	-	-	.
4.E.2	9	. 130.0 <i>47.6</i>	-	-	.
4.E.3	10	. 129.0 ^b <i>85.7</i>	-	-	.
4.E.4	11	. 129.0 ^b <i>111.0</i>	-	-	.
4.E.5	12	. 128.0 ^b <i>110.0</i>	-	(. 127.5) <i>21.8</i>	.
4.E.6	14	. 124.0 ^b <i>97.9</i>	-	. 128.5 <i>23.3</i>	.
4.E.7	16	. 121.0 ^b <i>104.9</i>	-	. 129.0 <i>24.3</i>	.
4.E.8	18	. 118.0 ^b <i>125.7</i>	. 128.5 <i>24.4</i>	-	.
4.E.9	20	. 117.5 ^b <i>95.8</i>	. 127.0 <i>24.5</i>	-	.

b : compound has crystal-crystal transition; enthalpy denoted is the sum of all previous transitions.

(a)



(b)



(c)

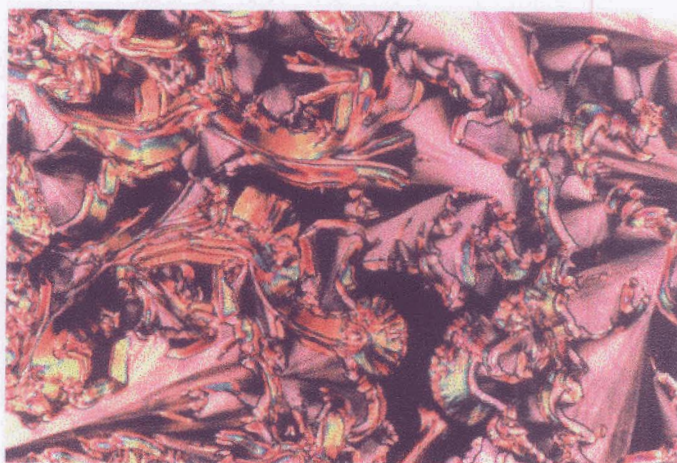


Fig. 4.5. Optical photomicrographs obtained on cooling the isotropic liquid, (a) B_{x2} phase of compound 4.E.8; (b) and (c) B_{x2} phase of compound 4.E.9.

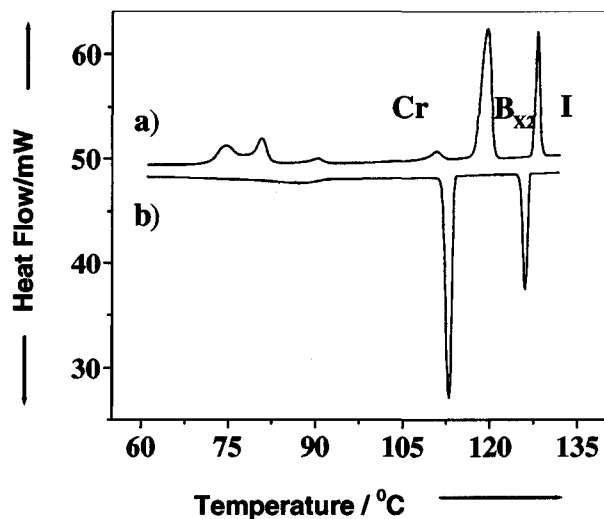


Fig. 4.6. Differential scanning calorimetric scans obtained at a rate of $5^{\circ}\text{C min}^{-1}$ for compound 4.E.9; (a) heating cycle, (b) cooling cycle.

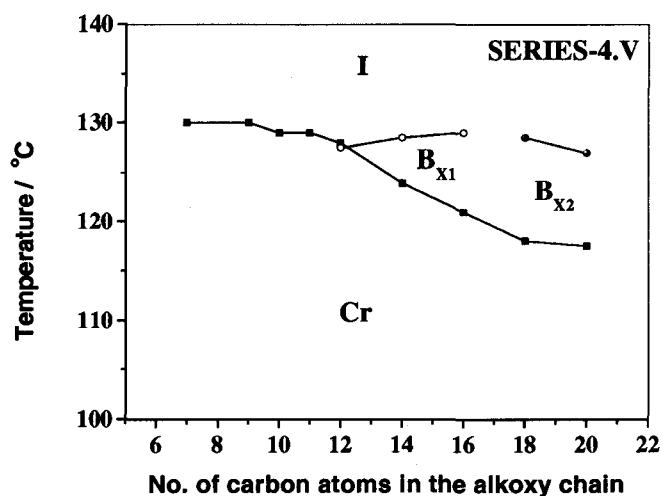


Fig. 4.7. Plot of transition temperatures as a function of the number of carbon atoms in the n-alkoxy chains obtained for series 4.V.

does not correspond to any of the other known banana phases and hence this mesophase has been designated as B_{x2}. More interestingly, compounds 4.E.5 to 4.E.7 show a lamellar ordering and the mesophase exhibits ferroelectric properties. The mesophase of compounds 4.E.8 and 4.E.9 show a two- or three-dimensional structural pattern as determined by X-ray diffraction studies and exhibit ferroelectric properties. This type of behaviour represents the first example of two different mesophase structures exhibited by homologues of the same series which show ferroelectric properties.

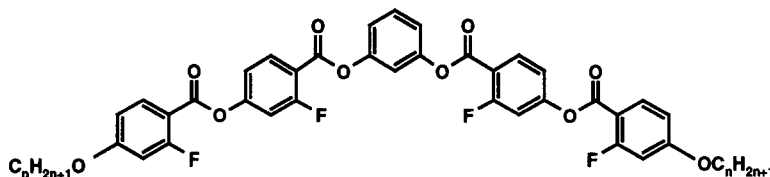
In both these phases namely B_{X1} and B_{X2} , the melting as well as the clearing temperatures are drastically increased when compared to either the parent series **4.I** or any of the other fluorine substituted mesogens in these five-ring esters. This perhaps is due to fluorine at *ortho* position influencing a change in the conformation of either the core or the terminal chains such that the packing efficiency increases. A plot of the transition temperatures as a function of the number of carbon atoms in the terminal n-alkoxy chains for compounds of series **4.V** is shown in figure **4.7**.

Now, let us examine the mesomorphic behaviour in compounds which contain a fluorine substituent in each of the phenyl rings on the arms of these bent-core materials. The transition temperatures and the associated enthalpies for fifteen compounds of series **4.VI** are summarized in table **4.6**. In this series of compounds, fluorine is substituted *ortho* to the two carboxylate groups. When compared to the unsubstituted compounds (series **4.I**), there is a general decrease of the melting points in all the homologues. More importantly, although the three mesophases viz. B_2 , B_1 and B_6 are retained in the series, the mesophases are suppressed to a large extent. For example, compound **4.F.1** is non-mesomorphic while compound **4.F.2** shows a highly metastable B_6 phase. Since the mesophase crystallizes immediately, it was not possible to determine the temperature or enthalpy for this transition. Compounds **4.F.3** to **4.F.8**, **4.F.10** and **4.F.12** are all monotropic and the remaining four compounds are enantiotropic. Compound **4.F.9** displays a highly metastable columnar B_1 phase on fast cooling the isotropic liquid as seen under a polarizing microscope and sometimes crystallizes before the mesophase could be seen. In contrast, fourteen of the monofluorosubstituted compounds (series **4.II**) are all mesomorphic. A plot of the transition temperatures as a function of the length of the n-alkoxy chain for this series is shown in figure **4.8**. The general trend observed in other homologous series of compounds is seen here also.

In the case of compounds of homologous series **4.VII**, a fluorine is substituted *ortho* to the terminal n-alkoxy chain and a fluorine *ortho* to the carboxylate group (table **4.7**). It is interesting to note that the antiferroelectric B_2 phase is replaced by a lamellar phase which shows ferroelectric properties. Compounds **4.G.1** and **4.G.2** show a monotropic B_6 phase while compounds **4.G.3** and **4.G.4** exhibit a monotropic B_1 phase and compound **4.G.5** is non-mesomorphic. Compounds **4.G.6** to **4.G.13** are all enantiotropic mesomorphic. A plot of the transition temperatures as a function of the length of the n-alkoxy chain is shown in figure **4.9**.

As in the previous case, there is a general reduction in the melting as well as clearing points when compared with those of the unsubstituted compounds (series 4.I). It is remarkable to

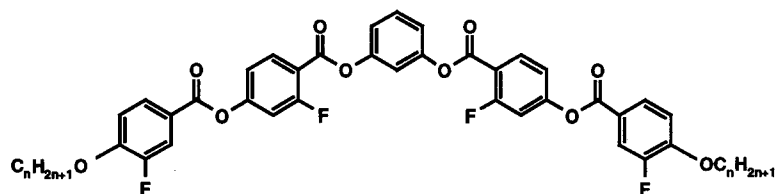
Table 4.6. Transition temperatures (°C) and enthalpies (kJmol⁻¹) (*in italics*) for compounds of series 4.VI.



Compound	n	Cr	B ₂	B ₁	B ₆	I
4.F.1	1	. 161.5 <i>59.4</i>	-	-	-	.
4.F.2	2	. 162.5 <i>59.2</i>	-	-	-	.
4.F.3	3	. 132.0 <i>48.2</i>	-	-	(. 120.0) <i>9.6</i>	.
4.F.4	4	. 130.5 <i>52.2</i>	-	-	(. 127.5) <i>11.7</i>	.
4.F.5	5	. 129.0 <i>64.9</i>	-	-	(. 115.5) <i>11.5</i>	.
4.F.6	6	. 109.0 <i>48.0</i>	-	(. 108.0) <i>13.4</i>	-	.
4.F.7	7	. 100.0 <i>46.5</i>	-	(. 96.0) <i>13.8</i>	-	.
4.F.8	8	. 95.5 <i>48.8</i>	-	(. 87.5) <i>14.0</i>	-	.
4.F.9	9	. 94.0 <i>52.1</i>	-	-	-	.
4.F.10	10	. 96.0 <i>58.0</i>	(. 81.5) [†] <i>18.7</i>	-	-	.
4.F.11	11	. 78.0 <i>23.9</i>	. 87.5 <i>21.6</i>	-	-	.
4.F.12	12	. 97.0 <i>58.4</i>	(. 92.0) <i>21.1</i>	-	-	.
4.F.13	14	. 87.0 <i>69.1</i>	. 97.5 <i>22.7</i>	-	-	.
4.F.14	16	. 93.5 <i>81.8</i>	. 101.0 <i>24.0</i>	-	-	.
4.F.15	18	. 97.0 <i>93.8</i>	. 102.5 <i>26.1</i>	-	-	.

†: temperature obtained on cooling.

Table 4.7. Transition temperatures (°C) and enthalpies (kJmol⁻¹) (*in italics*) for compounds of series 4.VII.



Compound	n	Cr	B _{X1}	B ₁	B ₆	I
4.G.1	4	. 144.0 <i>53.7</i>	-	-	(. 141.0) <i>14.3</i>	.
4.G.2	5	. 149.0 <i>74.9</i>	-	-	(. 128.0) <i>14.5</i>	.
4.G.3	6	. 129.0 <i>56.2</i>	-	(. 117.5) <i>15.5</i>	-	.
4.G.4	7	. 107.5 <i>79.2</i>	-	(. 106.0) <i>15.3</i>	-	.
4.G.5	8	. 108.0 <i>78.8</i>	-	-	-	.
4.G.6	9	. 107.0 <i>74.8</i>	. 110.5 <i>19.7</i>	-	-	.
4.G.7	10	. 105.0 <i>57.1</i>	. 113.5 <i>21.6</i>	-	-	.
4.G.8	11	. 106.0 ^b <i>92.4</i>	. 115.5 <i>22.1</i>	-	-	.
4.G.9	12	. 99.5 ^b <i>92.8</i>	. 117.5 <i>23.1</i>	-	-	.
4.G.10	14	. 103.0 ^b <i>104.5</i>	. 120.5 <i>24.2</i>	-	-	.
4.G.11	16	. 105.0 ^b <i>109.6</i>	. 122.0 <i>24.6</i>	-	-	.
4.G.12	18	. 107.0 ^b <i>131.7</i>	. 122.0 <i>25.2</i>	-	-	.
4.G.13	20	. 108.0 ^b <i>120.9</i>	. 121.0 <i>26.0</i>	-	-	.

b : compound has crystal-crystal transition; enthalpy denoted is the sum of all previous transitions.

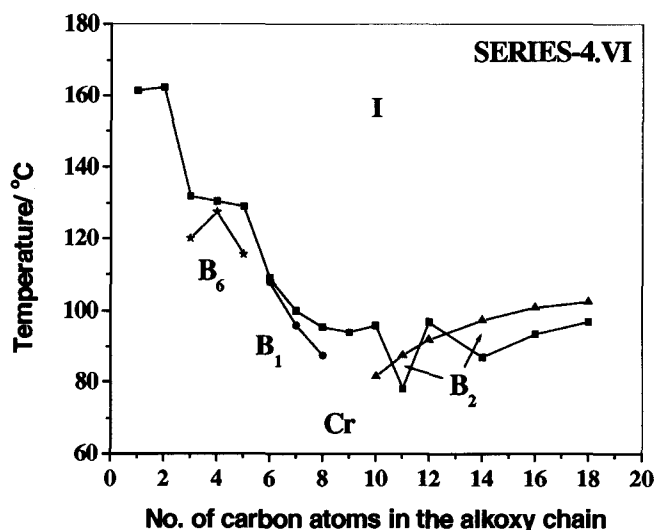


Fig. 4.8. Plot of transition temperatures as a function of the number of carbon atoms in the n-alkoxy chains obtained for series 4.VI.

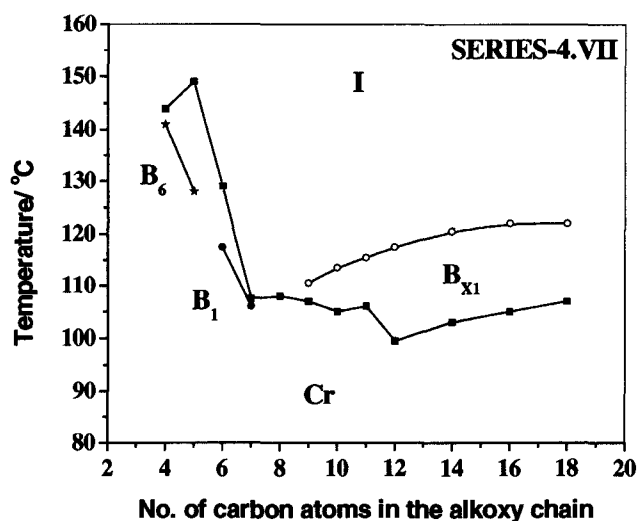
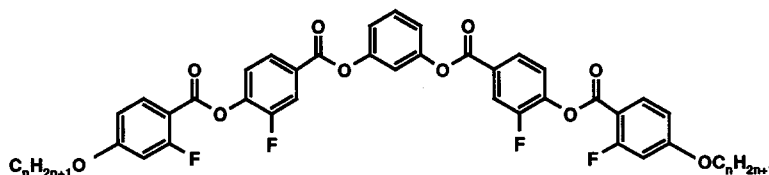


Fig. 4.9. Plot of transition temperatures as a function of the number of carbon atoms in the n-alkoxy chains obtained for series 4.VII.

note that two fluorine substituents (each arm) enhance the mesogenic character of these compounds. For example, compounds 4.E.1 to 4.E.4 which are monofluoro substituted (each arm) derivatives are non-mesomorphic while the corresponding difluorosubstituted (each arm) compounds 4.G.4, 4.G.6 to 4.G.8 are all mesomorphic. In addition, compounds 4.G.6 to 4.G.13 show a lamellar mesophase (B_{x1}) with ferroelectric characteristics as mentioned earlier (compounds 4.E.5 to 4.E.7). Also, the two- or three-dimensional ferroelectric phase obtained for compounds 4.E.8 and 4.E.9 are not observed in this series.

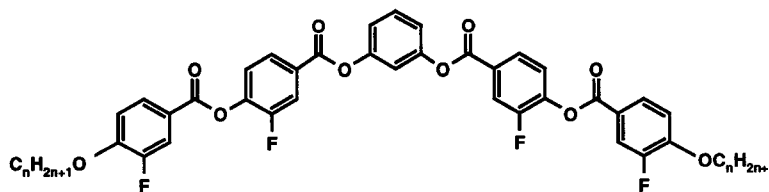
The position of fluorine substitution is really very critical for the occurrence of a particular type of mesophase. If a fluorine is substituted *meta* to the carboxylate group of the first phenyl moiety, then irrespective of the position of the fluorine substituent on the terminal phenyl group of these five-ring esters, no mesophase is observed. This behaviour is illustrated with two derivatives of each of the series **4.VIII** and **4.IX** (compounds **4.H.1**, **4.H.2** and **4.I.1**, **4.I.2** as shown in tables **4.8** and **4.9** respectively) and the latter two show fairly high melting points. This in itself is a strong proof for the dipolar effects in such compounds which play an important role in inducing mesophase/s.

Table 4.8. Melting points (°C) and enthalpies (kJmol⁻¹) (*in italics*) for compounds of series 4.VIII.



Compound	n	Cr	I	
4.H.1	6	.	114.0	.
			<i>43.8</i>	
4.H.2	14	.	113.0	.
			<i>67.8</i>	

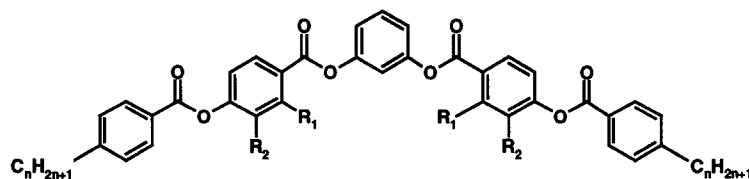
Table 4.9. Melting points (°C) and enthalpies (kJmol⁻¹) (*in italics*) for compounds of series 4.IX.



Compound	n	Cr	I	
4.I.1	6	.	160.0	.
			<i>63.1</i>	
4.I.2	14	.	152.0	.
			<i>84.9</i>	

In order to study the effect of a terminal n-alkyl chain vs n-alkoxy chain, we examined only two series of compounds. In series **4.X** for example, there is a fluorine substitution *ortho* to carboxylate group of the first phenyl moiety and a terminal n-alkyl chain. The transition temperatures and the associated enthalpies for this series of compounds are summarized in table **4.10**. As can be seen, only one mesophase type was observed and the antiferroelectric B₂ phase could be obtained for chain lengths where $n \geq 11$ and all are enantiotropic. The thermal range of the mesophase appears to get reduced when there is a terminal n-alkyl group. As discussed earlier (in series **4.II**), the n-alkoxy end groups stabilizes the intercalated B₆ and B₁ phases in addition to the antiferroelectric B₂ phase. We made only one compound **4.K.1** in which a fluorine is substituted at *meta* position on the middle phenyl ring with n-alkyl terminal chains, which is non-mesomorphic and we presume that all other homologues will also be non-mesomorphic (see series **4.III**). If the fluorine is present in *meta* position (w.r.t. the carboxylate group) of the first phenyl ring, independent of whether it is n-alkyl or

Table 4.10. Transition temperatures (°C) and enthalpies (kJmol⁻¹) (*in italics*) for compounds of series **4.X**. and a compound **4.K.1**.



Compound	R ₁	R ₂	n	Cr	B ₂	I
4.J.1	F	H	8	.	100.5 <i>49.6</i>	- .
4.J.2	F	H	9	.	104.5 <i>53.3</i>	- .
4.J.3	F	H	10	.	102.5 <i>49.2</i>	- .
4.J.4	F	H	11	.	101.5 <i>28.5</i>	. 104.0 <i>22.2</i>
4.J.5	F	H	12	.	99.5 <i>31.2</i>	. 105.5 <i>23.9</i>
4.J.6	F	H	14	.	97.5 <i>55.1</i>	. 108.5 <i>25.9</i>
4.J.7	F	H	16	.	96.5 <i>42.5</i>	. 110.5 <i>26.6</i>
4.K.1	H	F	14	.	97.0 <i>100.2</i>	- .

n-alkoxy end group, the derivatives are non-mesomorphic. A plot of the transition temperatures as a function of the length of the terminal n-alkyl chain for series **4.X** is shown in figure **4.10** and the B₂ - I transition points show the usual smooth curve trend.

From these observations, it is clear that fluorine substitution at *ortho* position to the carboxylate group of either the middle or the outer phenyl ring, the mesomorphic behaviour of the parent compounds is retained with minimal changes. However, the effect is drastic when a

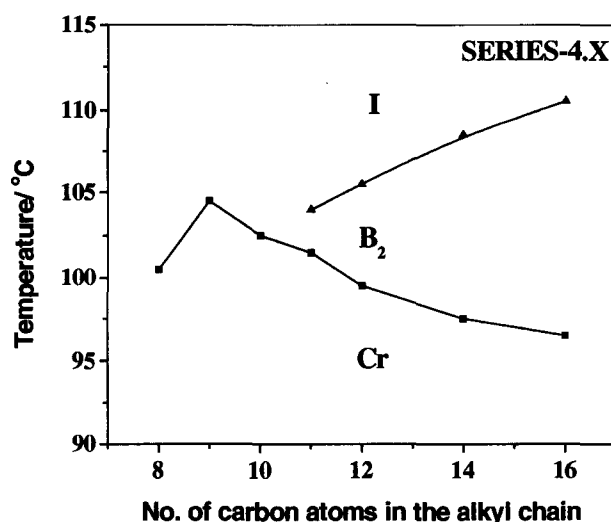
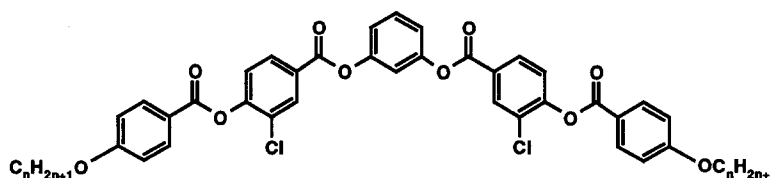


Fig. 4.10. A plot of transition temperatures as a function of the number of carbon atoms in the n-alkyl chains obtained for the compounds of series **4.X**

fluorine is substituted at *meta* position of the middle or the outer phenyl ring. In many cases (series **4.III**, **4.VIII**, **4.IX** and compound **4.K.1**), the fluorine substitution completely destroys the mesophase. In some other cases (series **4.V** and **4.VII**) the switching behaviour as well as the structure of the mesophase is completely changed when compared with the unsubstituted or the other fluorine substituted compounds.

The melting points are marginally higher for compounds of series **4.III**, when compared with the parent compounds of series **4.I**. In order to examine the influence of a larger but less polar substituent such as chlorine, a few compounds were synthesized, the melting points and the enthalpies obtained are shown in table **4.11**. Though the melting temperatures obtained are comparable to those of the unsubstituted parent compounds, no mesophase could be observed. This again clearly indicates that the dipolar effects are significant in these type of compounds for the occurrence of the mesophases.

Table 4.11. Melting points ($^{\circ}\text{C}$) and enthalpies (kJmol^{-1}) (*in italics*) for compounds of series 4.XI.



Compound	n	Cr	I
4.L.1	5	.	98.5 <i>29.6</i>
4.L.2	8	.	96.0 <i>44.5</i>
4.L.3	9	.	96.5 <i>45.7</i>
4.L.4	10	.	101.0 <i>52.6</i>
4.L.5	11	.	101.5 <i>57.5</i>
4.L.6	12	.	106.5 <i>63.7</i>
4.L.7	14	.	109.0 <i>67.1</i>
4.L.8	18	.	94.5 <i>73.1</i>

X-Ray investigations

X-Ray diffraction studies have been carried out on the mesophases of compounds of various series discussed earlier and are described below. The XRD data obtained for the mesophases of some compounds are summarized in table 4.12. Compounds belonging to series **4.I** and **4.II** exhibit B_6 , B_1 and B_2 mesophases on ascending the series. The intercalation in B_6 phase, the rectangular lattice in B_1 phase and the lamellar ordering in B_2 phase were confirmed through XRD studies. However, in series **4.III** only one homologue (compound **4.C.2**) is mesomorphic which shows a metastable B_6 phase and XRD studies could not be carried out.

In series **4.IV**, compound **4.D.4** shows two sharp reflections in the small angle region at $d_1=19.5\text{\AA}$ and $d_2=9.7\text{\AA}$ at a temperature of 118°C . These reflections are in the ratio 1:1/2 indicating a lamellar ordering for the mesophase. However, the first order reflection at $19.5\text{\AA}$

Table 4.12. The d-spacings (Å) obtained for different mesophases and the corresponding Miller indices shown in brackets for various compounds. The XRD studies have been carried out on mesophases obtained on cooling the isotropic phases.

Compound	d-spacings Å / Miller indices	Lattice parameters/ Å		Phase type
		a	b	
4.A.4	18.0 (01), 9.0 (02)	-	-	B ₆
4.A.8	24.7 (11), 21.1 (02)	30.5	42.2	B ₁
4.A.12	35.7 (01), 17.9 (02)	-	-	B ₂
4.B.3	17.2 (01), 8.6 (02)	-	-	B ₆
4.B.4	17.9 (01)	-	-	B ₆
4.B.6	20.5 (11), 19.2 (02)	24.2	38.4	B ₁
4.B.8	23.7 (11), 20.9 (02)	28.8	41.8	B ₁
4.B.12	33.0 (01), 16.5 (02)	-	-	B ₂
4.D.4	19.5 (01), 9.7 (02)	-	-	B ₆
4.D.5	21.8 (11), 20.5 (02)	25.7	41.0	B ₁
4.D.10	33.7 (01), 16.8 (02)	-	-	B ₂
4.D.11	36.3 (01), 18.5 (02), 12.3 (03)	-	-	B ₂
4.E.5	39.2 (01), 19.6 (02), 13.0 (03)	-	-	B _{X1}
4.E.6	42.3 (01), 21.3 (02), 14.2 (03)	-	-	B _{X1}
4.E.7	45.3 (01), 22.7 (02), 15.1 (03)	-	-	B _{X1}
4.E.8	46.7, 26.6, 24.7, 22.0, 17.8, 15.9, 13.1, 12.0, 10.4	-	-	B _{X2}
4.E.9	48.7, 27.7, 24.9, 18.7, 16.6, 12.4, 11.0	-	-	B _{X2}
4.F.4	17.9 (01), 9.0 (02)	-	-	B ₆
4.F.6	19.8 (11), 19.2 (02)	23.1	38.4	B ₁
4.F.12	33.0 (01), 16.5 (02)	-	-	B ₂
4.F.13	35.3 (01), 17.8 (02), 11.9 (03)	-	-	B ₂
4.F.14	37.4 (01), 12.6 (03)	-	-	B ₂
4.G.1	17.9 (01), 8.9 (02)	-	-	B ₆
4.G.4	24.6 (11), 20.0 (02)	31.2	40.0	B ₁
4.G.6	35.6 (01), 17.8 (02)	-	-	B _{X1}
4.G.9	38.7 (01), 19.4 (02)	-	-	B _{X1}
4.G.10	41.6 (01), 20.8 (02), 13.9 (03)	-	-	B _{X1}
4.J.7	39.8 (01), 19.9 (02), 13.3 (03), 10.0 (04)	-	-	B ₂

can be indexed to a reflection from (01) plane which corresponds to nearly the half molecular length by assuming a fully extended all *trans* conformation of the n-alkoxy chain. This clearly shows intercalation as well as tilting of the bent-core molecules in the mesophase. Also, a diffuse peak in the wide-angle region at 4.7 Å shows the absence of an in-plane order. From this, we have concluded that the mesophase is indeed B₆. The X-ray angular intensity profile obtained for the mesophase of compound **4.D.4** is shown in figure **4.11a**. Similar X-ray diffraction patterns were obtained for the B₆ phase of other compounds belonging to different homologous series and the data are shown in table **4.12**. Since the B₆ phase is observed for compounds with short chain lengths, the probability of the chains taking *gauche* conformations is also small. The estimated tilt angle of the molecules is of the order of 25-30° depending upon the chemical nature of the compounds.

The XRD of an unoriented sample of compound **4.D.5** shows two sharp reflections at $d_1=21.8$ Å and $d_2=20.5$ Å in the small angle region at 109°C (monotropic phase). These could be indexed as reflections from (11) and (02) planes, which form a rectangular lattice with lattice parameters $a=25.7$ Å and $b=41$ Å by assuming a tilt of the molecules. As usual, a diffuse peak in the wide-angle region at about 4.6 Å was obtained which is indicative of a liquid-like in-plane order. The X-ray angular intensity profile obtained for the mesophase of compound **4.D.5** is shown in figure **4.11b**. We have also obtained a monodomain sample for the mesophase of compound **4.G.4**. The pattern observed in the small angle region of this sample is shown in figure **4.11c**. The innermost four spots obtained are from two-dimensional (11) planes and the outer two spots are due to the intercalated layered planes (02). No electro-optical switching could be observed for this mesophase even at fairly high electric fields. Also, no homeotropic textures could be obtained even on mechanical shearing as observed under a polarizing microscope indicating that the molecules might be tilted in a rectangular lattice. From X-ray diffraction studies and textural features we have identified this mesophase to be a two-dimensional B₁ phase. Based on X-ray diffraction patterns and optical textures shown by the mesophases of compounds **4.F.6**, **4.F.7** and **4.F.8** of series **4.VI** as well as compound **4.G.3** of series **4.VII**, have all been characterized as a B₁ phase.

The mesophase of the higher homologues of series **4.IV** showed a different X-ray diffraction pattern. For example, in the small angle region, compound **4.D.11** showed lamellar reflections at $d_1=36.3$ Å, $d_2=18.5$ Å and $d_3=12.3$ Å indicating a smectic ordering for the mesophase. The

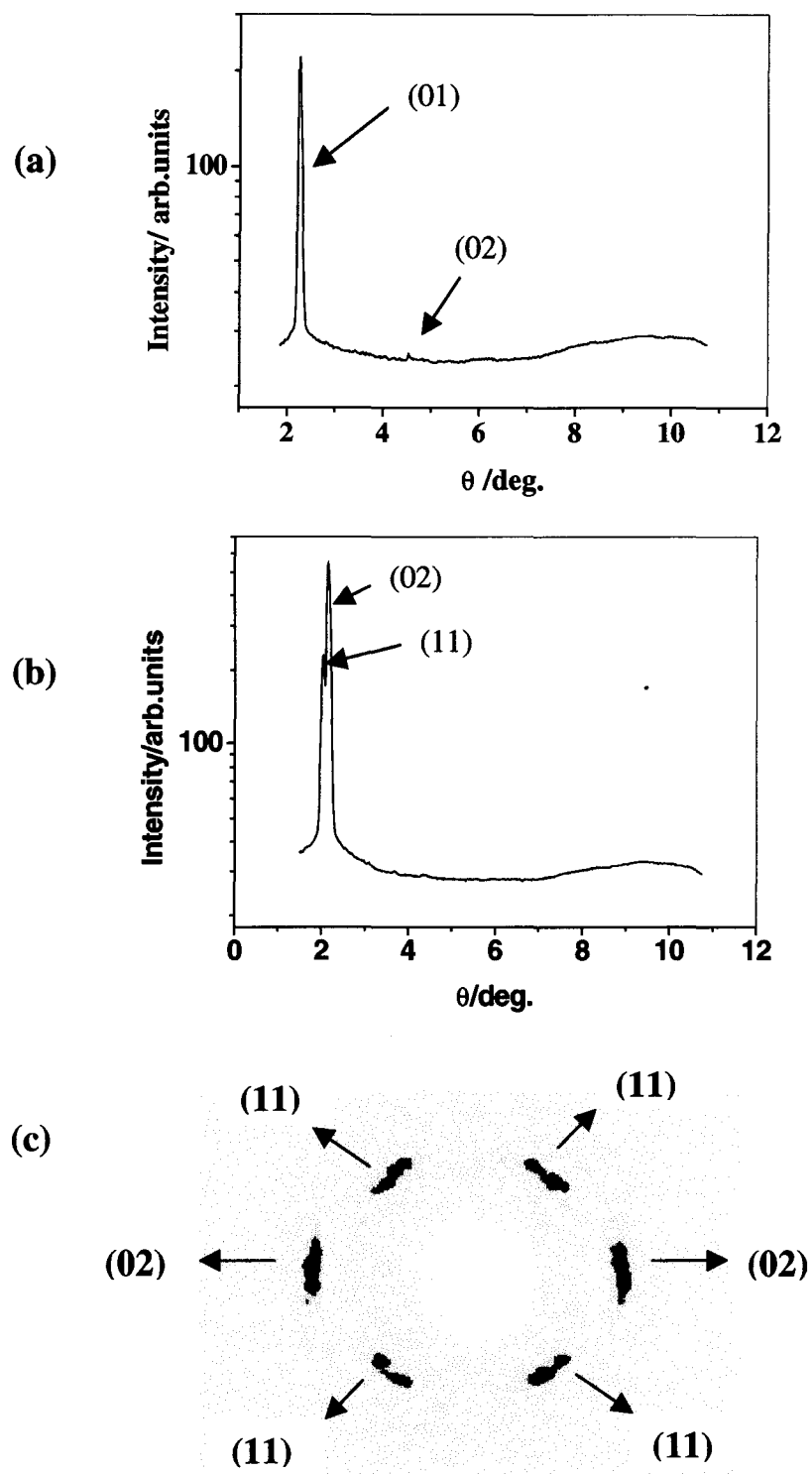


Fig. 4.11. The X-ray angular intensity profiles obtained for (a) the B_6 phase of compound 4.D.4, (b) B_1 phase of compound 4.D.5. (c) The small angle oriented pattern of the columnar B_1 phase obtained for compound 4.G.4. The inner four spots obtained are due to the two-dimensional (11) planes and the outer two spots are from the intercalated layer planes (02).

first order layer spacing is lower than the calculated molecular length suggesting that this is a tilted smectic phase with a calculated tilt angle of about 53° . As usual, a diffuse wide-angle reflection at $4.7\text{ \AA}$ could also be seen indicating a liquid-like in-plane order. The X-ray angular intensity profile obtained for the mesophase of compound **4.D.11** is shown in figure **4.12a**. The mesophase shows antiferroelectric switching behaviour and exhibits all the textural features of a B_2 phase. Hence, we have characterized this mesophase as B_2 . Similar X-ray diffraction patterns and electro-optical switching characteristics were obtained for the mesophases of compounds **4.F.10** to **4.F.15** of series **4.VI** and compounds **4.J.4** to **4.J.7** of series **4.X** and all of them have been characterized as a B_2 phase.

The two mesophases exhibited by compounds of series **4.V** show the following features. The powder X-ray diffraction pattern obtained for compound **4.E.7** showed a diffuse wide-angle peak at about $4.7\text{ \AA}$ indicating a liquid-like in-plane order. In the small angle region, three sharp reflections could be seen at $d_1=45.3\text{ \AA}$, $d_2=22.7\text{ \AA}$ and $d_3=15.1\text{ \AA}$. These reflections are in the ratio $1:1/2:1/3$ indicating of a lamellar order for the mesophase and are independent of temperature. The layer spacing determined from these measurements are lower than the calculated molecular length (assuming that all the methylene units in the n-alkoxy chain are in the fully extended all *trans* conformation) indicating that this is a tilted smectic phase with a tilt angle of 48° . Similar diffraction patterns were obtained for compounds **4.E.5** and **4.E.6** also suggesting that mesophases of all the three compounds are of the same type. A typical diffraction pattern obtained for compound **4.E.7** is shown in figure **4.12b**.

However, the diffraction patterns obtained for the mesophases of compounds **4.E.8** and **4.E.9** are completely different from those seen for the above three compounds **4.E.5**, **4.E.6** and **4.E.7**. A diffuse wide-angle peak at $4.7\text{ \AA}$ indicative of a liquid-like in-plane order was seen as usual. Compound **4.E.8** shows the following very interesting XRD pattern. The incommensurate small angle reflections obtained are at $d_1=46.7\text{ \AA}$, $d_2=26.6\text{ \AA}$, $d_3=24.7\text{ \AA}$, $d_4=22.0\text{ \AA}$, $d_5=17.8\text{ \AA}$, $d_6=15.9\text{ \AA}$, $d_7=13.1\text{ \AA}$, $d_8=12.0\text{ \AA}$ and $d_9=10.4\text{ \AA}$. Of these, d_1 , d_2 , d_5 , d_6 , d_7 , d_8 and d_9 reflections are in the ratio of $1:1/\sqrt{3}:1/\sqrt{7}:1/3:1/\sqrt{13}:1/4:1/\sqrt{21}$ respectively and these reflections can be indexed as (01), (11), (12 or 21), (03 or 30), (31 or 13), (04 or 40) and (14 or 41) respectively for a two-dimensional hexagonal columnar phase. The lattice parameter value a obtained is $53.9\text{ \AA}$. From this value, the calculated d-spacings $d_{01}=46.7\text{ \AA}$, $d_{11}=26.9\text{ \AA}$, d_{12} or $d_{21}=17.6\text{ \AA}$, d_{03} or $d_{30}=15.5\text{ \AA}$, d_{13} or $d_{31}=12.9\text{ \AA}$, d_{04} or $d_{40}=12.0\text{ \AA}$ and d_{14} or $d_{41}=10.2\text{ \AA}$ are obtained which agree well with the experimentally

observed values. The remaining two reflections obtained in the small angle region viz. $d_3=24.7 \text{ \AA}$ and $d_4=22.0 \text{ \AA}$ cannot be indexed for a two-dimensional hexagonal columnar phase. However, if one chooses a three-dimensional hexagonal columnar phase, then these two reflections can be indexed as (001) and (101) respectively with the additional lattice parameter, $c=24.7 \text{ \AA}$. Using this value, the calculated d-spacings are, $d_{001}=24.7 \text{ \AA}$ and $d_{101}=21.8 \text{ \AA}$. These values agree well the experimentally observed values. Thus, the B_{X2} phase obtained for compound **4.E.8** can be considered as a three-dimensional hexagonal columnar phase. Similarly, compound **4.E.9** shows many incommensurate small angle reflections at $d_1=48.7 \text{ \AA}$, $d_2=27.7 \text{ \AA}$, $d_3=24.9 \text{ \AA}$, $d_4=18.7 \text{ \AA}$, $d_5=16.6 \text{ \AA}$, $d_6=12.4 \text{ \AA}$ and $d_7=11.0 \text{ \AA}$. These reflections are in the ratio of $1:1/\sqrt{3}:1/2:1/\sqrt{7}:1/3:1/4$ and $1/\sqrt{21}$, which can be indexed as (01), (11), (02), (12 or 21), (03), (04) and (14 or 41) for a two-dimensional hexagonal columnar phase. The lattice parameter value obtained, $a=56.2 \text{ \AA}$. From this, the calculated d-spacings are $d_{01}=48.7 \text{ \AA}$, $d_{11}=28.0 \text{ \AA}$, $d_{02}=24.3 \text{ \AA}$, d_{12} or $d_{21}=18.4 \text{ \AA}$, $d_{03}=16.2 \text{ \AA}$, $d_{04}=12.2 \text{ \AA}$ and d_{14} or $d_{41}=10.6 \text{ \AA}$. The calculated d-spacings agree well with the experimentally observed values. However, no additional reflections could be obtained as observed in compound **4.E.8**. The small angle reflections obtained for the mesophase of compounds **4.E.8** and **4.E.9** can also be indexed for a two-dimensional rectangular lattice as given below. For compound **4.E.8**: $46.7 \text{ \AA}$ (11), $26.6 \text{ \AA}$ (02), $24.7 \text{ \AA}$ (40), $22.0 \text{ \AA}$ (41), $17.8 \text{ \AA}$ (03 or 42), $15.9 \text{ \AA}$ (33 or 52), $13.1 \text{ \AA}$ (04 or 14 or 53), $12.0 \text{ \AA}$ (44 or 80), $10.4 \text{ \AA}$ (05 or 15 or 75); $a=97.5 \text{ \AA}$ and $b=53.2 \text{ \AA}$. Similarly for compound **4.E.9**: $48.7 \text{ \AA}$ (11), $27.7 \text{ \AA}$ (02), $24.9 \text{ \AA}$ (22), $18.7 \text{ \AA}$ (42), $16.6 \text{ \AA}$ (52), $12.4 \text{ \AA}$ (44), $11.0 \text{ \AA}$ (15 or 05 or 25); $a=102.2 \text{ \AA}$ and $b=55.4 \text{ \AA}$. A partially oriented X-ray pattern was obtained in this columnar B_{X2} phase for compound **4.E.8** and is shown in figure **4.13**. However from the available data, it is too complex for any conclusions to be drawn. Further studies are required to confirm the exact structure of this B_{X2} mesophase.

As can be seen in table **4.12**, the layer thickness in the B_{X1} phase increases on increasing the chain length ($42.3 \text{ \AA}$ for compound **4.E.6** and $45.3 \text{ \AA}$ for compound **4.E.7**) as usual for any smectic phase. However, the increase in layer thickness is maintained even in the two-dimensional B_{X2} phase of compounds **4.E.8** and **4.E.9** ($46.7 \text{ \AA}$ for compound **4.E.8** and $49.7 \text{ \AA}$ for compound **4.E.9**). The X-ray diffraction pattern for the higher homologues (compounds **4.G.6** to **4.G.13**) of series **4.VII** shows lamellar ordering and the X-ray data obtained for some of these compounds are shown in table **4.12**. For all these compounds a diffuse peak maxima at about $4.7 \text{ \AA}$ in the wide-angle region is seen indicating a liquid-like in-plane order.

As we shall see later, this mesophase exhibits ferroelectric properties and we have assigned the symbol B_{X1} ($SmC_S P_F$) to the same.

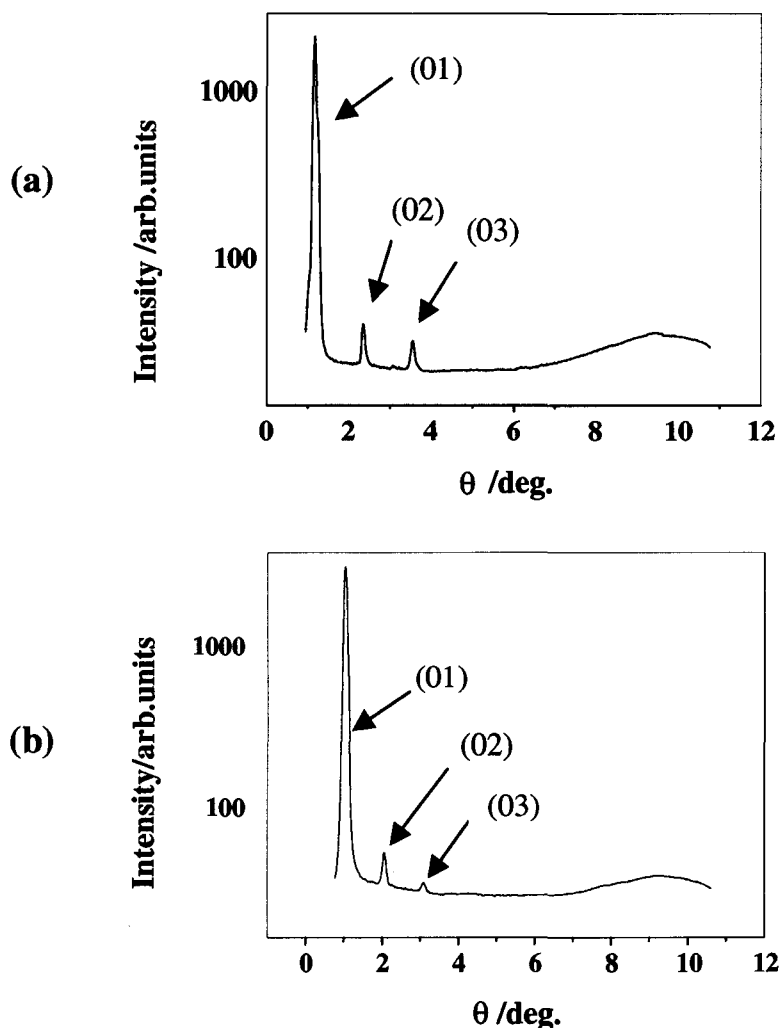


Fig. 4.12. The X-ray angular intensity profiles obtained (a) in the B_2 phase exhibited by compound 4.D.11 and (b) B_{X1} mesophase exhibited by compound 4.E.7.

The XRD data of various compounds are recorded in table 4.12, from which the following observations can be made. Depending on the position of fluorine in the presently investigated series of compounds both ferro- and antiferro-electric phases are obtained. The layer thickness varies from series to series for the homologues with the same chain length. For example, consider the unsubstituted parent compound 4.A.12 (series 4.I, $n=12$) has a layer thickness of 35.7 Å and the corresponding fluorine substituted compounds exhibit the following layer spacings. Compound 4.B.12 (series 4.II, $n=12$): 33 Å; compound 4.D.10 (series 4.IV, $n=12$): 33.7 Å; compound 4.E.5 (series 4.V, $n=12$): 39.2 Å; compound 4.F.12 (series 4.VI, $n=12$): 33 Å; compound 4.G.9 (series 4.VII, $n=12$): 38.7 Å. It is thus clear that if a fluorine is substituted at *ortho* position to the carboxylate group either on the middle or the outer phenyl

ring or on both the phenyl rings, then the layer spacings obtained are lower than the value obtained for the unsubstituted parent compounds of the corresponding homologue. However, if the fluorine is substituted at *meta* position on the outer phenyl ring then the layer spacing increases when compared to the parent compounds.

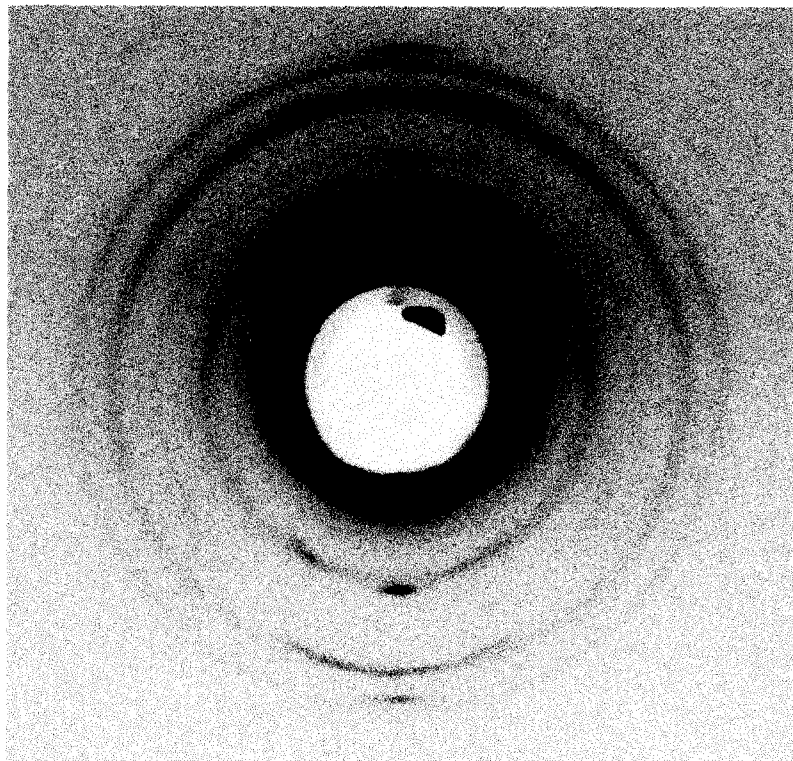


Fig. 4.13. A partially oriented X-ray pattern obtained in the B_{X2} phase of compound 4.E.8.

As reported by Bedel *et al.* [38] fluorine substitution at *ortho* position with respect to the carbonyl group of the outer phenyl ring in five-ring Schiff's base esters reduces the layer spacing of the B_2 phase when compared to the unsubstituted parent compounds. They have also speculated that this may be due to the large interlayer penetration of the terminal chains. This kind of interlayer interactions of terminal chains are entropically favourable for the antiferroelectric ordering of BC molecules in successive layers (B_2 phase) [41] as explained in figure 4.1. This also may explain the occurrence of a favourable sequence B_6 , B_1 and B_2 phases on ascending the series. However, if a fluorine is substituted at *ortho* position with respect to the terminal chain of the outer phenyl ring (which gives rise to the ferroelectric ground state), these interlayer interactions will be unfavourable, which also increases the layer spacing. Thus, the position of fluorine substitution strongly influences the electro-static interactions as well as conformational changes which result in the decrease or increase of the layer spacings (due to coupling or decoupling of layers respectively). In addition, a fluorine

substitution at *ortho* position (adjacent to aliphatic chains) increases the entropy of the chains. Thus, the unfavourable interlayer interactions destabilize the antiferroelectric phases.

Electro-optical studies

The electro-optical switching behaviour was investigated for several fluorine substituted compounds belonging to different homologous series with a view to examine the position of fluorine substituent and the change in the switching behaviour. Obviously, the starting point for any such investigations would be to consider the mesomorphic behaviour and the switching characteristics of the unsubstituted parent compounds (series **4.I**). As explained earlier, compounds **4.A.1** to **4.A.5** show a B₆ phase and compounds **4.A.6** to **4.A.9** show a B₁ phase and both of these phases do not switch. However, compounds **4.A.10** to **4.A.15** exhibit the antiferroelectric B₂ phase [34]. When a fluorine is substituted *ortho* to the carboxylate group of the middle phenyl ring (series **4.II**), the mesomorphic behaviour is similar to those of the parent compounds. The saturated polarization value obtained for compound **4.B.14** is about 560 nC cm⁻² (± 40 V for a cell thickness of 3.2 μm). However, in the case of compounds of series **4.III**, only one compound shows a monotropic B₆ phase and the remaining are non-mesomorphic.

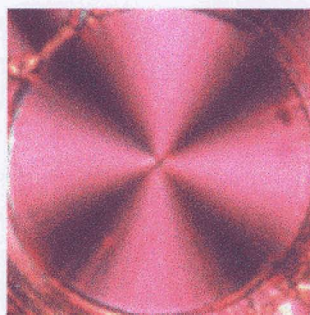
Electro-optical switching characteristics were carried out for one of the compounds of series **4.IV** where a fluorine substitution is *meta* to the terminal n-alkoxy chain. A sample of compound **4.D.12** was taken in a cell constructed for homogeneous alignment with a thickness of 8.7 μm . On cooling from the isotropic liquid under a dc electric field of about 3.5 V μm^{-1} (threshold voltage is about 2.5 V μm^{-1}), colourful spherulitic growth could be observed under a polarizing microscope. The dark brushes could be seen to make an angle with respect to the orientation directions of the crossed polarizers and by reversing the polarity of the applied electric field, the brushes rotate in the opposite direction. However, on switching off the electric field it stabilizes the ferroelectric state thus showing bistability. At a relatively higher electric field of about 7 V μm^{-1} the tristable switching is clearly seen under a polarizing microscope as shown in figure **4.14**. These observations indicate the existence of concentric circular smectic layers. The dark extinction cross (figure **4.14**) indicates the position of the director of bent-core molecules in these smectic layers which is parallel or perpendicular to the crossed polarizers. As can be seen in figure **4.14**, the field induced ferroelectric domains are chiral in which the antiferroelectric ground state must contain the anticlinic tilt of BC molecules in successive layers and hence the resultant extinction cross is parallel to the

orientation directions of the crossed polarizers. A weak birefringence in the ground state ($E=0$) is due to the anticlinic tilt of BC molecules ($\text{SmC}_\text{AP}_\text{A}$) in adjacent layers which produces a helical structure. On application of an electric field, the maximum rotation of dark brushes obtained with respect to the layer normal is about $\pm 40^\circ$ (tilt angle of the core part), which is the optical tilt angle.

To measure the spontaneous polarization of this switchable mesophase, a triangular-wave method was employed. The same sample cell was used for this experiment also. By applying a fairly high triangular voltage of about $\pm 17 \text{ V}\mu\text{m}^{-1}$ and at a frequency of 30 Hz at 95°C , two polarization current peaks were observed for each half cycle confirming the antiferroelectric ground state for this mesophase. A typical switching current response obtained in this B_2 phase of compound **4.D.12** is shown in figure **4.15**. The calculated average saturated polarization value is about 440 nC cm^{-2} .

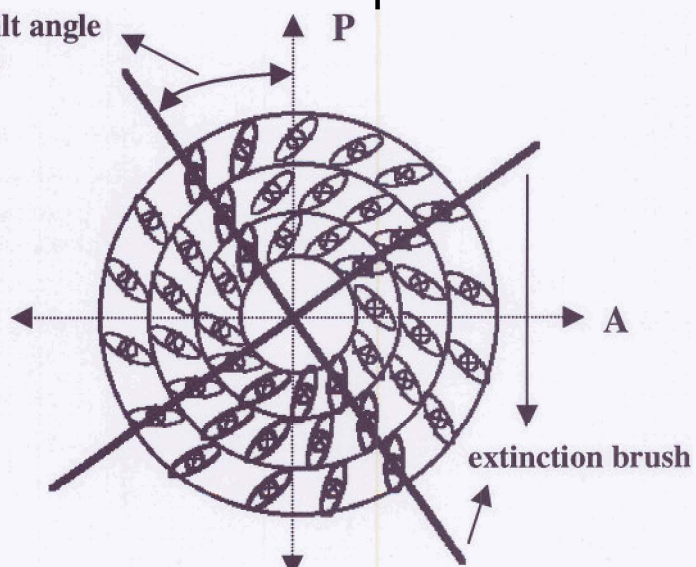
Similar antiferroelectric current response was obtained by the application of a modified triangular-wave electric field for compound **4.F.14**. The saturated polarization value for the B_2 mesophase of this compound was determined to be 635 nC cm^{-2} and the current response trace obtained is shown in figure **4.16**.

The electro-optical behaviour of the mesophases exhibited by compounds **4.E.6** and **4.E.7** were examined in cells constructed for planar alignment. A sample of compound **4.E.7** was filled in the isotropic phase and cooled slowly to the mesophase. The mesophase appeared dark on observation under a polarizing microscope. On applying a triangular voltage, at a relatively high threshold ($\pm 10 \text{ V}\mu\text{m}^{-1}$), colourful focal-conic regions appear from the dark field of view as shown in figure **4.17**. Simultaneously, a single current peak for each half cycle could be seen at a sufficiently high triangular-wave electric field ($\pm 12 \text{ V}\mu\text{m}^{-1}$) and at a low frequency of 1 Hz at 122°C . However, at a high frequency (200 Hz), a racemic ferroelectric structure is induced in which the extinction cross obtained is parallel to the directions of the crossed polarizers. A typical switching current response obtained for the mesophase of compound **4.E.7** is shown in figure **4.18a**. The saturated spontaneous polarization value, P_s was calculated by integrating the area under the peak of each half cycle and the average value was determined to be about 290 nC cm^{-2} . In order to further establish the ferroelectric behaviour in this mesophase, modified triangular-wave electric field (triple plateau) experiments were carried out as described in Chapter-2.

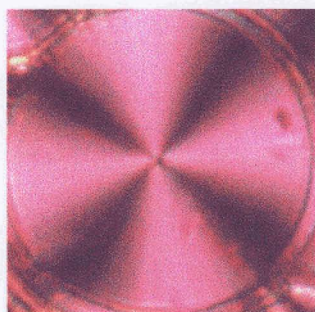
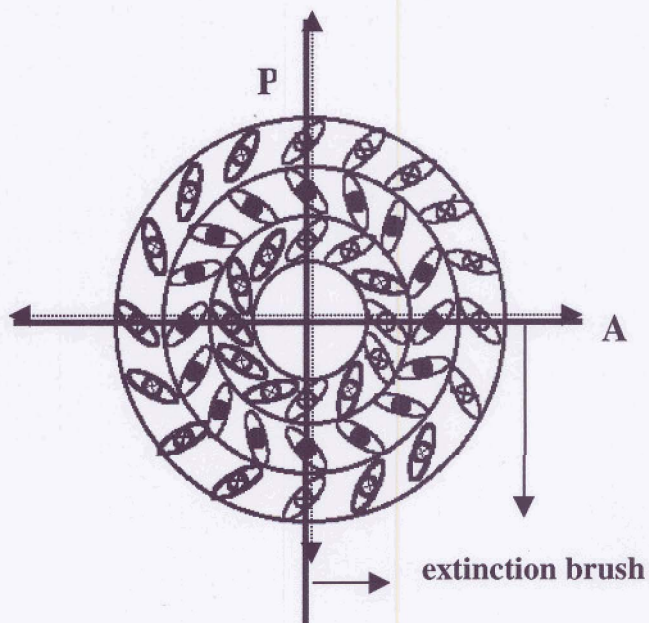


(a) $+7 \text{ V } \mu\text{m}^{-1}$; SmC_SP_F

Optical tilt angle
(+)



(b) 0 V ; SmC_AP_A



(c) $-7 \text{ V } \mu\text{m}^{-1}$; SmC_SP_F

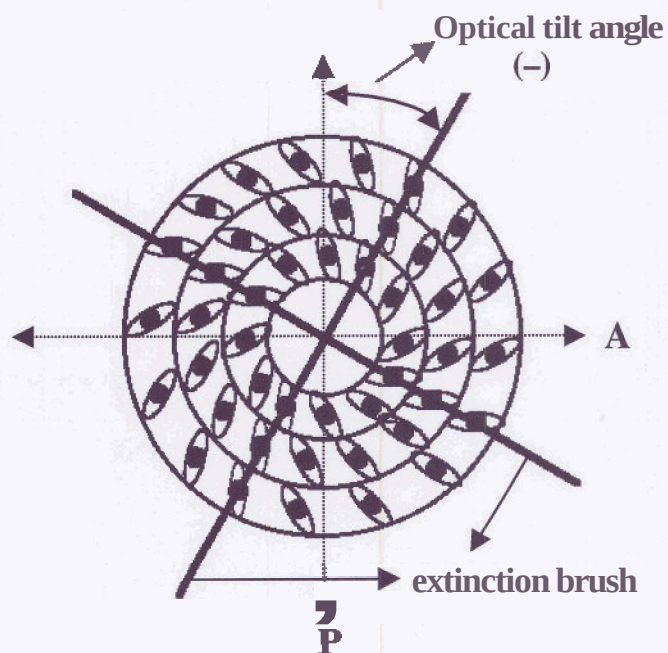


Fig. 4.14

Fig. 4.14. Optical photomicrograph of circular domains obtained for compound 4.D.12 under a dc electric field. (a) $+7 \text{ V}\mu\text{m}^{-1}$, chiral ferroelectric state ($\text{SmC}_\text{S}\text{P}_\text{F}$), (b) $0 \text{ V}\mu\text{m}^{-1}$, chiral antiferroelectric ground state ($\text{SmC}_\text{A}\text{P}_\text{A}$) and (c) $-7 \text{ V}\mu\text{m}^{-1}$, another chiral ferroelectric state ($\text{SmC}_\text{S}\text{P}_\text{F}$) demonstrating the tristable switching for an antiferroelectric phase. A schematic representation of the arrangement of molecules in domains of concentric circular smectic layers (cross-sectional area) responsible for the occurrence of dark brushes in both ferro- and antiferro-electric states by the application of an electric field between crossed polarizers is shown on the right hand side. The layer normal is along the directions of the crossed polarizers.

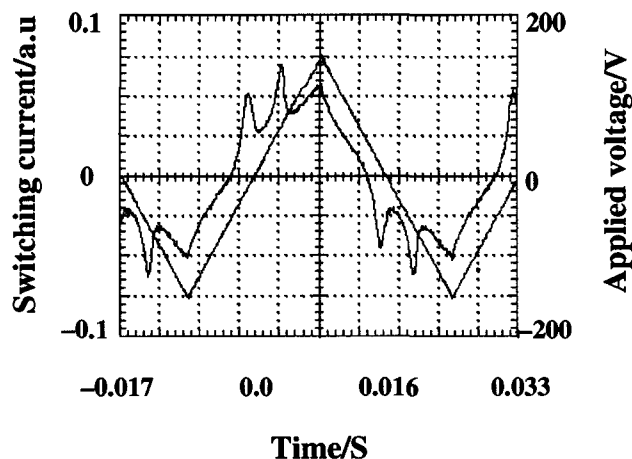


Fig. 4.15. Switching current response obtained in the mesophase of compound 4.D.12 by applying a triangular voltage ($\pm 150 \text{ V}$, 30 Hz) at 95°C . Sample thickness $8.7 \mu\text{m}$; spontaneous polarization $\approx 440 \text{ nC cm}^{-2}$.

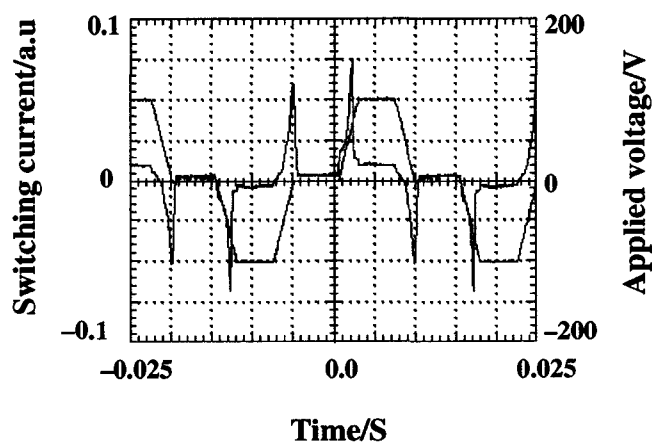


Fig. 4.16. Switching current response obtained in the mesophase of compound 4.F.14 by applying a modified triangular voltage ($\pm 100 \text{ V}$, 33 Hz) at 94°C indicating the antiferroelectric ground state. Sample thickness $6.2 \mu\text{m}$; spontaneous polarization $\approx 635 \text{ nC cm}^{-2}$.

The current response trace obtained using triple plateau for compound **4.E.7** is shown in figure **4.18b**. Similar changes in the texture at the threshold voltage as well as the switching behaviour (ferroelectric) could be observed for the mesophase of compound **4.E.6** also. The saturated spontaneous polarization value determined for the mesophase of this compound is about 300 nC cm^{-2} . The textural features shown by the compounds **4.E.5**, **4.E.6** and **4.E.7** are not comparable to the mesophase of a compound which was reported [54] as a smectic ferroelectric phase.

In the case of compound **4.E.8**, the isotropic phase was cooled slowly under a triangular-wave electric field to obtain uniformly aligned domains. Even at a relatively low threshold voltage ($\pm 7 \text{ V}\mu\text{m}^{-1}$) at 1Hz, some colourful circular domains could be seen under the microscope. At the same time, a single polarization current peak for each half cycle was observed indicating a ferroelectric type switching behaviour for the mesophase. A switching current response obtained in this mesophase is shown in figure **4.19a**. The saturated spontaneous polarization value obtained at a sufficiently high triangular voltage ($\pm 9.4 \text{ V}\mu\text{m}^{-1}$) is about 390 nC cm^{-2} . This indicates that the ferroelectric phase induced by the application of field ($-V$) is stable, because it is not winding back to a non-polar phase when the polarity of the field is reversed ($+V$).

Though the X-ray data is indicative of a two- or three-dimensional structure for the mesophase of this compound, it switches at relatively low threshold voltages. Similar ferroelectric type switching behaviour was observed for compound **4.E.9**. The spontaneous polarization value obtained for the mesophase of this compound is comparatively higher than those obtained for compounds **4.E.6** and **4.E.7** which exhibit a lamellar ferroelectric phase. Also, the textural features of the mesophase of compounds **4.E.8** and **4.E.9** are not comparable to the two-dimensional ferroelectric phase reported by Bedel *et al.* [51]. Hence we have designated this mesophase as B_{X2} . The current response trace obtained using triple plateau for the mesophase of compound **4.E.8** is shown in figure **4.19b**.

If B_{X1} and B_{X2} mesophases are antiferroelectric, then the above obtained single polarization current peak would have to split into two in the modified triangular-wave as demonstrated by Bedel *et al.*[50] for their compounds. This is an other evidence in support of the ferroelectric switching behaviour of both these mesophases. Figure **4.20** shows a schematic representation

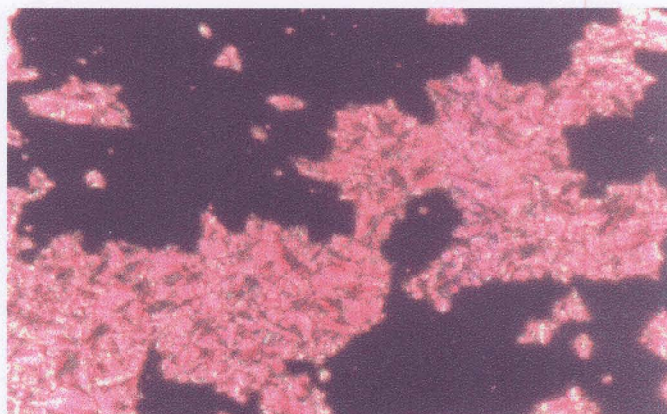


Fig. 4.17. Colourful broken fad-conic domains appearing from the dark field of view for compound 4.E.7 at the threshold voltage of $\pm 10 \text{ V}\mu\text{m}^{-1}$ at 5Hz. Temperature 122°C .

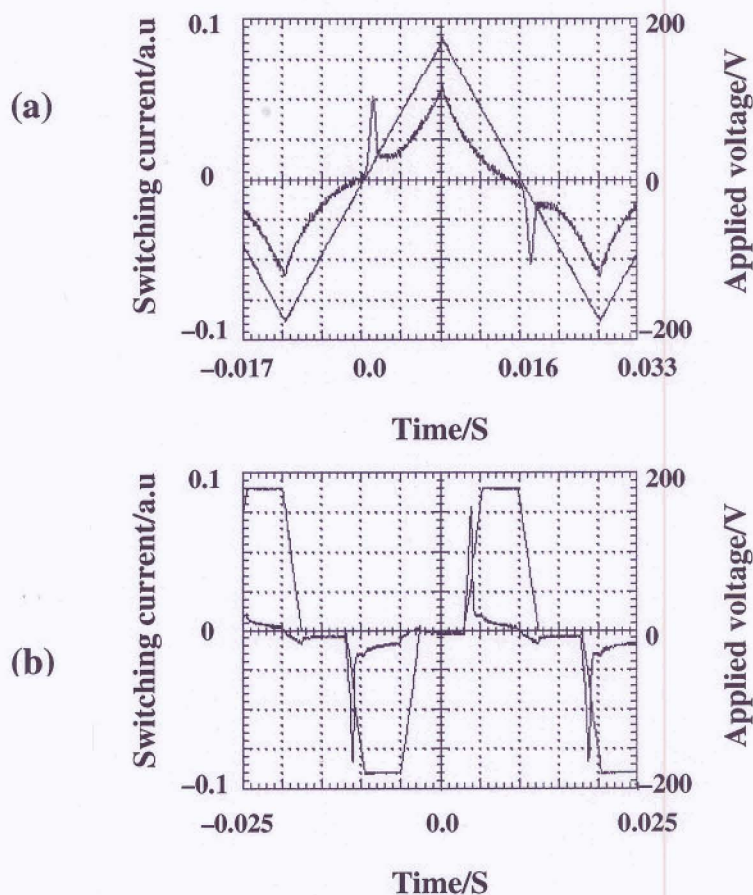


Fig. 4.18. (a) Switching current response obtained in the mesophase of compound 4.E.7 by applying a simple triangular voltage ($\pm 175 \text{ V}$, 5 Hz) at 122°C . Sample thickness $15 \mu\text{m}$; spontaneous polarization $\approx 290 \text{ nC cm}^{-2}$. (b) Current response obtained by applying a modified triangular-wave electric field of about $\pm 180 \text{ V}$ at a frequency of 33 Hz for the same compound in the same cell, confirming the ferroelectric ground state.

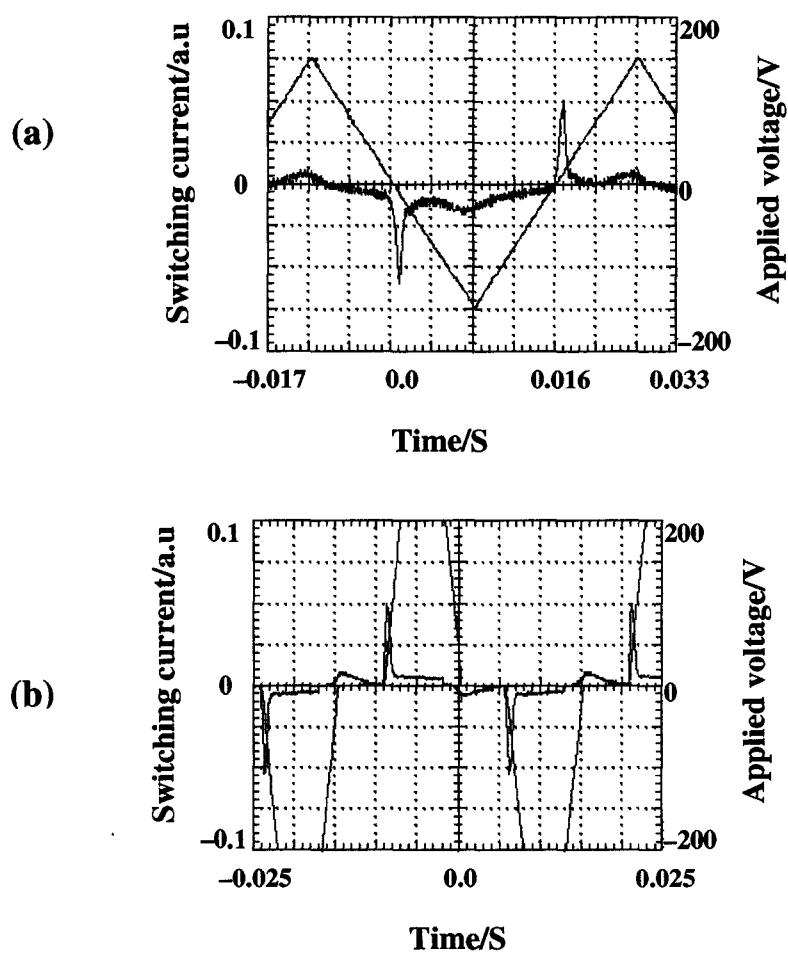


Fig. 4.19. (a) Switching current response obtained in the mesophase of compound 4.E.8 by applying a simple triangular voltage (± 150 V, 5 Hz) at 121°C . Sample thickness $16\ \mu\text{m}$; spontaneous polarization $\approx 390\ \text{nC cm}^{-2}$. (b) Current response obtained by applying a modified triangular-wave electric field of about ± 200 V at a frequency of 33 Hz for the same compound in the same cell, confirming the ferroelectric ground state.

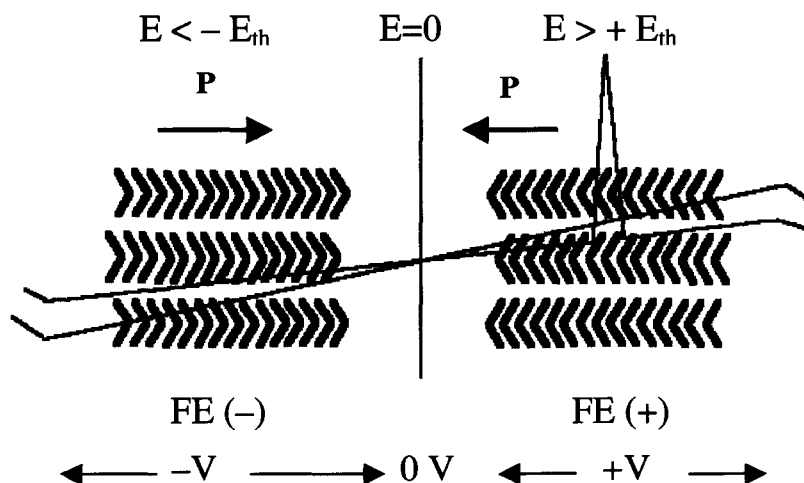


Fig. 4.20. A schematic representation of the orientation of molecules in the ferroelectric phase obtained by the application of a triangular-wave electric field which is responsible for the occurrence of a single polarization current peak.

of the orientation of molecules in the ferroelectric phase by the application of triangular-wave electric field responsible for the occurrence of a single polarization current peak.

Finally, in order to establish the bistability of the two mesophases B_{X1} and B_{X2} , we have carried out some dc field experiments. A cell was constructed using ITO coated glass plates pre-treated with polyimide for homogeneous alignment of the sample. The cell thickness was measured to be $7.9\ \mu\text{m}$. A sample of compound **4.E.7** was taken in such a cell and cooled slowly ($0.1\ ^\circ\text{C}\ \text{min}^{-1}$) from the isotropic phase under a relatively high dc electric field ($\approx 12\ \text{V}\mu\text{m}^{-1}$). Partially aligned circular domains could be observed under a microscope in which the dark brushes make an angle with respect to the orientation directions of the crossed polarizers. On reversing the polarity of the electric field, the dark brushes rotate in the opposite direction by the same amount. Interestingly, only homochiral ferroelectric domains are induced from the heterochiral ferroelectric ground state. More importantly, on switching off the field, the orientation of the brushes remain unchanged in the two different states indicating that the molecular orientation (orientation of dipoles) is retained. As a matter of fact, these bistable states remain unchanged for hours. This is ample proof of the ferroelectric ground state for the mesophase. Typical optical photomicrographs obtained for compound **4.E.7**, with and without field are shown in figure 4.21. The estimated director tilt (tilt of the core part) of the molecules from the layer normal is about $\pm 28^\circ$. After obtaining the circular domains with high electric fields, these domains switch even at lower applied voltages ($5\ \text{V}\mu\text{m}^{-1}$) supporting the ferroelectric ground state for the mesophase.

Similar experiments were carried out for the two or three-dimensional mesophase of compound **4.E.8**. In this case reddish brown circular domains were obtained (threshold $\approx 5\ \text{V}\mu\text{m}^{-1}$) and bistable switching was observed as in the case of compound **4.E.7**. On switching off the field, both the bistable states (+V and -V) which had reddish brown colour change to bluish green colour while retaining the orientation directions of the dark brushes. The bluish green colour was retained when the voltage was reduced gradually from the threshold voltage until it was switched off. The change in the birefringence may be due to a change in the order parameter (S). In the presence of an electric field, the degree of molecular orientation increases along the direction of the electric field. Hence, the order parameter as well as the birefringence increase (reddish brown). In the absence of the electric field, the molecules can relax while retaining the orientation of the dipoles. So the magnitude of order parameter and birefringence decrease (bluish green). This can be expected for the two-dimensional

mesophases. The optical photomicrographs obtained in the different states for the B_{X2} mesophase is shown in figure 4.22.

The switching behaviour of compounds of series 4.VII (compounds 4.G.6 to 4.G.13) is similar to those observed for the B_{X1} phase of compounds 4.E.6 and 4.E.7 of series 4.V. For example, on slow cooling from the isotropic liquid of a sample of compound 4.G.10, the

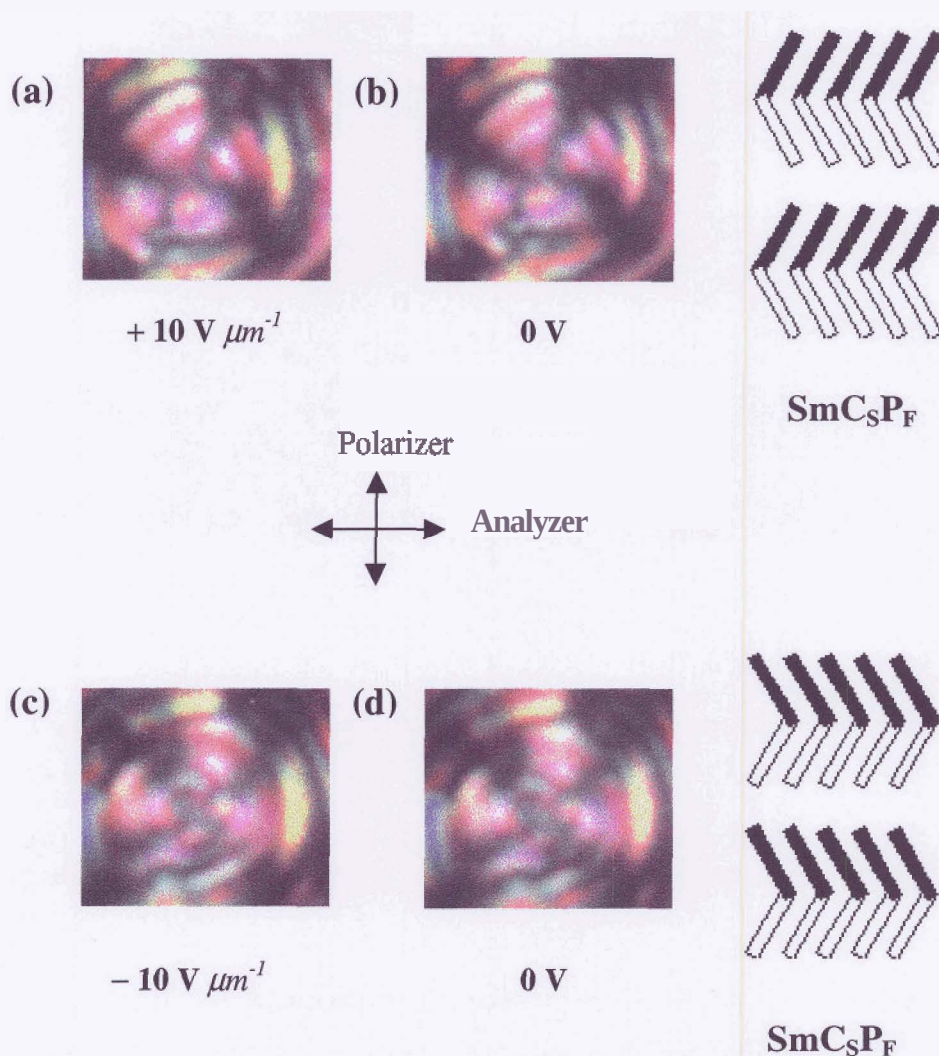


Fig. 4.21. Optical photomicrographs of circular domains obtained for compound 4.E.7 by applying a relatively high dc voltage ($12 \text{ V } \mu\text{m}^{-1}$) at 122°C . Cell thickness $7.9 \text{ } \mu\text{m}$. (a) Domain obtained at $+10 \text{ V } \mu\text{m}^{-1}$ (dark brushes oriented in the antidock-wise direction) and (b) domain obtained after turning off the electric field; notice that there is no change in the orientation of the brushes. (c) Domain obtained after the reversal of polarity of the field ($-10 \text{ V } \mu\text{m}^{-1}$); notice the rotation of the brushes in the clock-wise direction. (d) Domain obtained after switching off the field where the orientation of the brushes are retained, demonstrating the bistable states.

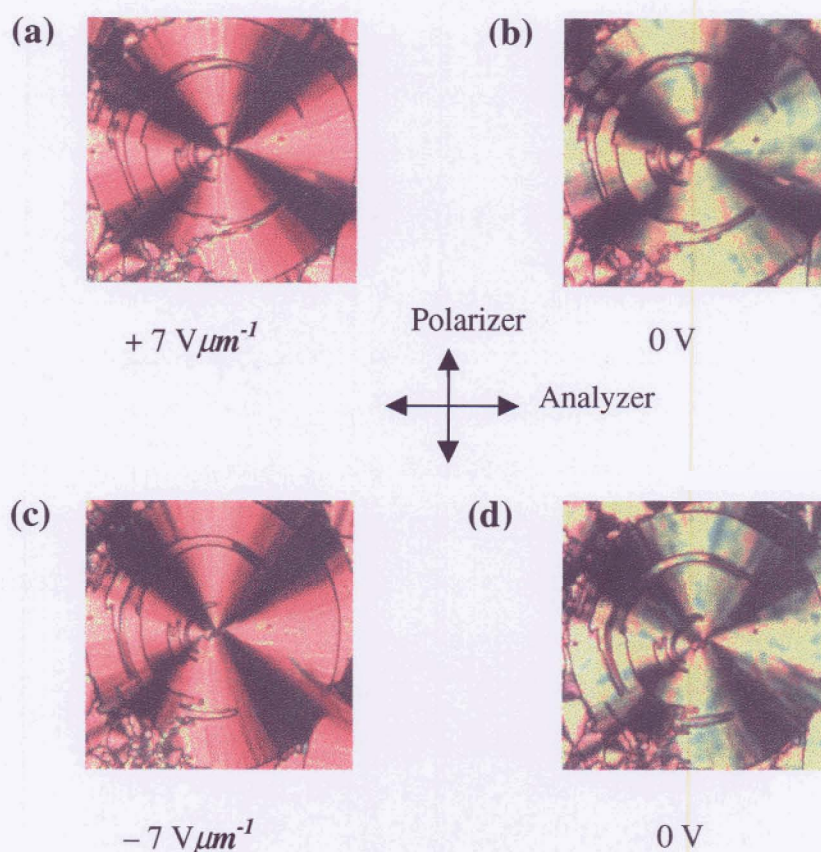


Fig. 4.22. Optical photomicrographs of circular domains obtained for compound 4.E.8 by applying a dc voltage ($7 \text{ V} \mu\text{m}^{-1}$) at 120°C . Cell thickness $8.5 \mu\text{m}$. Changes similar to that observed for compound 4.E.7 is seen for this compound also. (a) $+7 \text{ V}$, (b) 0 V , (c) -7 V and (d) 0 V . Notice that the orientation of brushes for both the cases (a), (b) and (c), (d) as also the colour changes in the presence and absence of the field clearly showing the bistability.

mesophase appears dark but the chiral domains of opposite handedness could be seen by rotating ($\approx 6^\circ$) either the polarizer or the analyzer. An optical photomicrograph showing these heterochiral domains (textures a and b) in the B_{X1} phase of compound 4.G.10 is shown in figure 4.23. On applying a triangular-wave electric field of about $\pm 11 \text{ V} \mu\text{m}^{-1}$ (threshold voltage), these domains transform to a more birefringent texture as shown in figure 4.24a. Simultaneously, a single polarization current peak was recorded for each half cycle of the triangular-wave which exists even at low frequencies ($<1 \text{ Hz}$) indicating the ferroelectric nature of the mesophase. The saturated polarization at $\pm 13 \text{ V} \mu\text{m}^{-1}$ for this ferroelectric phase was determined to be about 280 nC cm^{-2} . A typical current response trace obtained for this

mesophase is shown in figure 4.24b. It should also be mentioned that on switching off the electric field, the colourful texture relaxes in contrast to what was observed for the B_{X1} mesophase of compounds of series 4.V. In addition, when a modified triangular-wave electric field was applied to the sample, clearly *only* one polarization current peak for each half cycle was seen, indicating the ferroelectric nature of the mesophase. The modified triangular-wave current response obtained for this B_{X1} phase is shown in figure 4.24c.

In order to unambiguously establish ferroelectricity, a sample of the above compound 4.G.10 was taken in a $6\ \mu\text{m}$ thick cell prepared for homogeneous alignment. On slow cooling of the isotropic liquid under a dc electric field of $16\ \text{V}\mu\text{m}^{-1}$, partially aligned circular domains could be observed. The bistability could be clearly observed with and without fields as shown in figure 4.25. Also, the texture remains unchanged on switching off the dc electric field. The calculated optical tilt angle in the ferroelectric B_{X1} phase is about $\pm 35^\circ$.

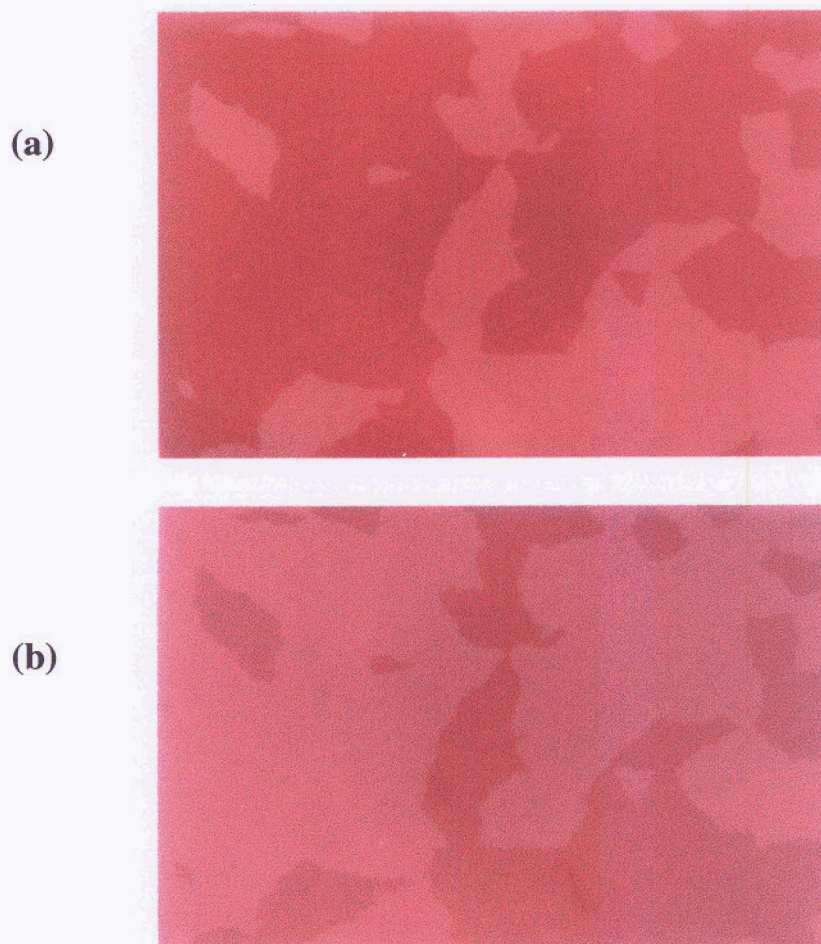
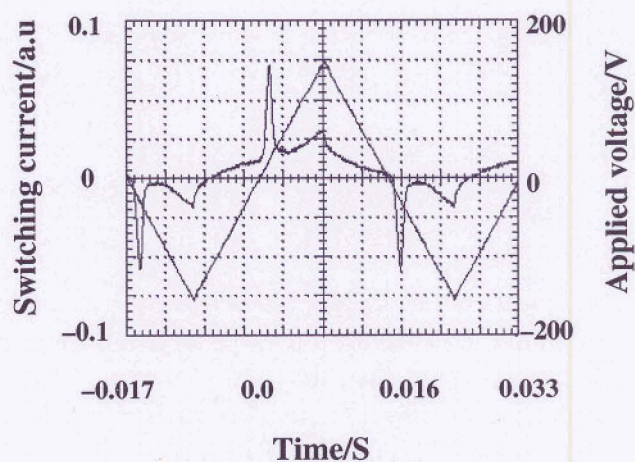


Fig. 4.23. Optical photomicrographs (a) and (b) obtained on cooling the B_{X1} phase of compound 4.G.10 showing the chiral domains of opposite handedness (by rotating the polarizer or the analyzer).

(a)



(b)



(c)

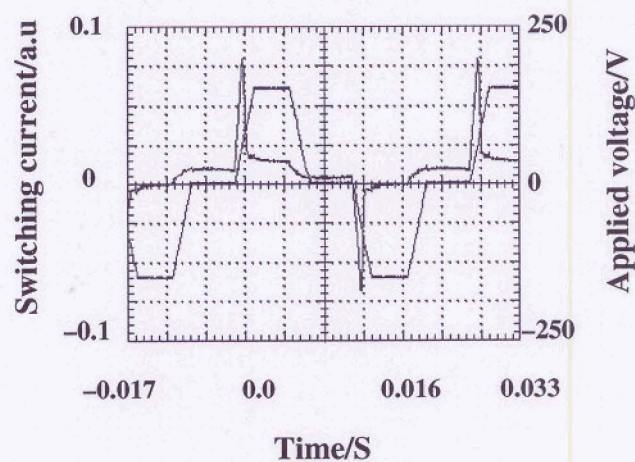


Fig. 4.24. (a) Photomicrograph obtained in the B_{x1} mesophase of compound 4.G.10 above the threshold voltage of triangular-wave electric field, (b) switching current response obtained in the same mesophase of compound 4.G.10 by applying a simple triangular voltage (± 150 V, 30 Hz) at 110°C . Sample thickness $14\ \mu\text{m}$; spontaneous polarization $\approx 280\ \text{nC cm}^{-2}$ and (c) current response obtained by applying a modified triangular-wave electric field of about ± 150 V at a frequency of 33 Hz for the same compound in the same cell.

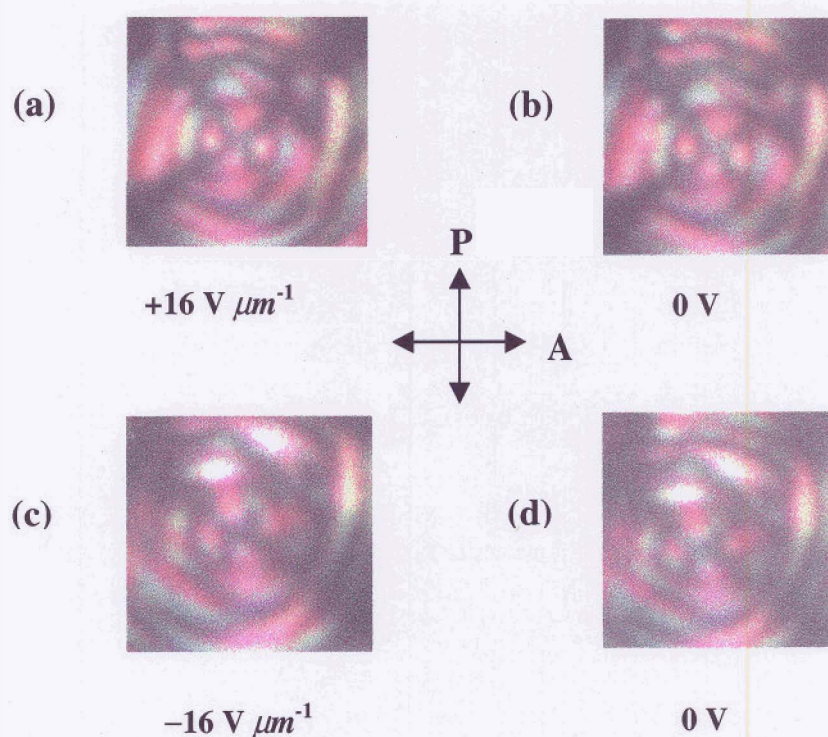


Fig. 4.25. Optical photomicrographs of circular domains obtained for compound **4.G.10** under a dc electric field of about $\pm 16 \text{ V } \mu\text{m}^{-1}$. Domains (a) and (b) obtained at $+16 \text{ V } \mu\text{m}^{-1}$ and 0 V respectively. Similarly, domains (c) and (d) obtained after the reversal of the polarity of the applied field, that is, $-16 \text{ V } \mu\text{m}^{-1}$ and 0 V respectively. Notice that there is no change in the orientation directions of the dark brushes obtained with and without the field. This demonstrates bistability for ferroelectric ground state (SmC_sP_F).

Compounds **4.F.14** and **4.G.11** were mixed as 1:1 weight per cent in the isotropic state. On cooling the isotropic liquid of this mixture under a polarizing microscope, one can clearly see that the antiferroelectric B_2 phase separates out from the dark regions of the ferroelectric B_{X1} phase as shown in figure 4.26. This further confirms that the ground state structures of these two phases are different.

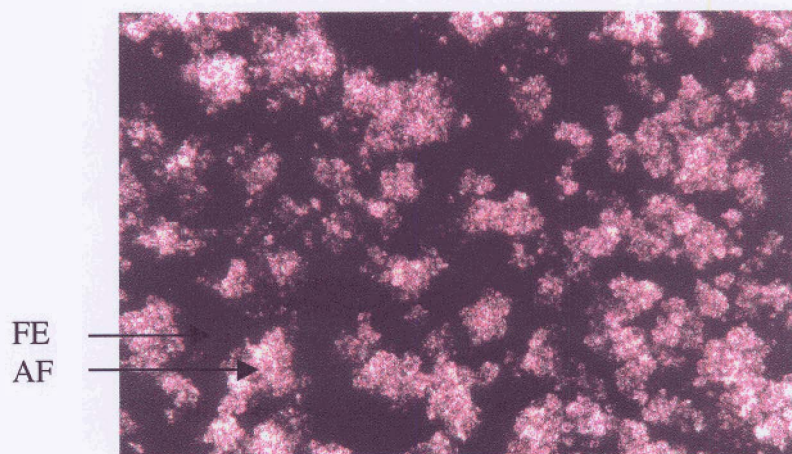


Fig. 4.26. A photomicrograph showing the phase separation between ferro- (dark regions) and antiferro-electric (bright regions) phases ON cooling the isotropic liquid of a mixture of compounds 4.F.14 and 4.G.11.

Conclusions

A systematic study of the influence of fluorine substituent on the liquid crystalline properties of five-ring esters has been carried out. It is observed that the position of the fluorine plays a major role in influencing the type of mesophase. In one series (series 4.III), the mesomorphic properties are greatly suppressed. The most interesting result is the occurrence of two different ferroelectric phases, when a fluorine is substituted *ortho* to the terminal *n*-alkoxy chain (series 4.V). The novel ferroelectric mesophases obtained have been designated as B_{X1} and B_{X2} respectively. The B_{X1} mesophase represents the first example of a compound exhibiting chiral ferroelectric domains. Also, whenever a ferroelectric phase is observed, the layer spacing is found to increase w.r.t the unsubstituted analogues. However, in the case of fluorine substituted compounds exhibiting an antiferroelectric phase, the layer spacing decreases. Surprisingly in such systems, the mesophases are destabilized if another fluorine is substituted in the *meta* position of the middle phenyl ring (series 4.IX). All these observations suggest that dipolar interactions play a significant role in influencing the occurrence of a particular type of mesophase in these five-ring esters.

Experimental

1,3-Phenylene bis(4-benzyloxybenzoate), (4.1)

This was synthesized following a procedure described for compound **3.4** (Chapter-3) but using 4-benzyloxybenzoic acid instead of 2-fluoro-4-benzyloxybenzoic acid.

Yield, 80%; m.p. 195-196°C; $\nu_{\max}$: 2920, 2854, 1730, 1600, 1456, 1270, 1115 cm^{-1} ; δ_{H} : 8.16-8.14 (d, 4H, $^3J_{8.88}$ Hz, Ar-H), 7.48-7.34 (m, 10H, Ar-H), 7.15-7.12 (m, 4H, Ar-H), 7.07-7.05 (d, 4H, $^3J_{8.88}$ Hz, Ar-H), 5.16 (s, 4H, $2 \times \text{ArCH}_2\text{O}-$). Elemental analysis: $\text{C}_{34}\text{H}_{26}\text{O}_6$ requires, C, 76.97; H, 4.94%; found, C, 76.85; H, 4.85%.

1,3-Phenylene bis(4-hydroxybenzoate), (4.2)

This was prepared following a procedure described for compound **3.5** (Chapter-3).

Yield, 92%; m.p. 237-238 °C; $\nu_{\max}$: 3350, 2924, 2850, 1705, 1598, 1460, 1245, 1128 cm^{-1} ; δ_{H} : 9.7(s, 2H, $2 \times \text{Ar}-\text{OH}$, exchangeable with D_2O), 8.08-8.05(d, 4H, $^3J_{8.84}$ Hz, Ar-H), 7.56-7.52(t, 1H, $^3J_{8.32\text{Hz}}$, Ar-H), 7.22-7.2(m, 3H, Ar-H), 7.02-6.99 (d, 4H, $^3J_{8.84}$ Hz, Ar-H). Elemental analysis: $\text{C}_{20}\text{H}_{14}\text{O}_6$ requires, C, 68.57; H, 4.03%; found, C, 69.01; H, 3.64%.

1,3-Phenylene bis(2-fluoro-4-hydroxybenzoate), (4.3)

The synthetic procedure for this compound is given in Chapter-3 (3.5).

1,3-Phenylene bis(3-fluoro-4-benzyloxybenzoate), (4.4)

This was synthesized following a procedure described for compound **3.4** (Chapter-3) using 3-fluoro-4-benzyloxybenzoic acid instead of 2-fluoro-4-benzyloxybenzoic acid.

Yield, 78%; m.p. 142-143°C; $\nu_{\max}$: 2920, 2854, 1732, 1605, 1456, 1270, 1118 cm^{-1} ; δ_{H} : 7.94-7.9 (m, 4H, Ar-H), 7.47-7.34 (m, 10H, Ar-H), 7.15-7.07 (m, 6H, Ar-H), 5.24 (s, 4H, $2 \times \text{ArCH}_2\text{O}-$).

1,3-Phenylene bis(3-fluoro-4-hydroxybenzoate), (4.5)

This was prepared following a procedure described for compound **3.5** (Chapter-3).

Yield, 89%; m.p. 198-199°C; $\nu_{\max}$: 3355, 2924, 2850, 1705, 1598, 1460, 1240, 1128 cm^{-1} ; δ_{H} : 9.89(s, 2H, $2 \times \text{Ar}-\text{OH}$, exchangeable with D_2O), 7.91-7.87(m, 4H, Ar-H), 7.56-7.52(t, 1H, $^3J_{8.3}$ Hz, Ar-H), 7.26-7.19(m, 5H, Ar-H).

1,3-Phenylene bis(3-chloro-4-benzyloxybenzoate), (4.6)

This was synthesized following a procedure described for compound **3.4** (Chapter-3) using 3-chloro-4-benzyloxybenzoic acid instead of 2-fluoro-4-benzyloxybenzoic acid.

Yield, 75%; m.p. 151-152°C; $\nu_{\max}$: 2930, 2850, 1722, 1600, 1460, 1270, 1118 cm^{-1} ; δ_{H} : 8.23-8.22 (d, 1H, $^4J_{2.12}$ Hz, Ar-H), 8.06-8.03 (dd, 2H, $^3J_{8.66}$ Hz, $^4J_{2.12}$ Hz, Ar-H), 7.48-7.33 (m, 13H, Ar-H), 7.15-7.12 (m, 2H, Ar-H), 7.06-7.04 (d, 2H, $^3J_{8.72}$ Hz, Ar-H), 5.26 (s, 4H, $2 \times \text{ArCH}_2\text{O}$ -). Elemental analysis: $\text{C}_{34}\text{H}_{24}\text{O}_6$ requires, C, 68.11; H, 4.03%; found, C, 68.08; H, 4.07%.

1,3-Phenylene bis(3-chloro-4-hydroxybenzoate), (4.7)

This was prepared following a procedure described for compound 3.5 (Chapter-3).

Yield, 86%; m.p. 232-233.5°C; $\nu_{\max}$: 3355, 2920, 2850, 1705, 1598, 1466, 1242, 1128 cm^{-1} ; $\delta_{\text{H}}(\text{DMSO}-d_6)$: 11.44 (s, 2H, $2 \times \text{Ar-OH}$, exchangeable with D_2O), 8.15-8.14 (d, 1H, $^4J_{2.08}$ Hz, Ar-H), 8.02-7.99 (dd, 2H, $^3J_{8.52}$ Hz, $^4J_{2.12}$ Hz, Ar-H), 7.58-7.54 (t, 1H, $^3J_{8.28}$ Hz, Ar-H), 7.3-7.19 (m, 6H, Ar-H). Elemental analysis: $\text{C}_{20}\text{H}_{12}\text{O}_6$ requires, C, 57.28; H, 2.88%; found, C, 56.93; H, 2.87%.

1,3-Phenylene bis[4-(4-methoxybenzoyloxy) benzoate], (4.A.1)

This was synthesized by following a procedure described for compound 3.A.1 (Chapter-3) using 1,3-Phenylene bis (4-hydroxybenzoate) and 4-methoxybenzoic acid. Yield, 70%; m.p. 168.5°C; $\nu_{\max}$: 2924, 2855, 1734, 1603, 1508, 1456, 1250, 1169 cm^{-1} ; δ_{H} : 8.30-8.27 (d, 4H, $^3J_{8.72}$ Hz, Ar-H), 8.19-8.16 (d, 4H, $^3J_{8.92}$ Hz, Ar-H), 7.52-7.48 (t, 1H, $^3J_{8.44}$ Hz, Ar-H), 7.4-7.36 (d, 4H, $^3J_{8.72}$ Hz, Ar-H), 7.21-7.17 (m, 3H, Ar-H), 7.03-6.99 (d, 4H, $^3J_{8.92}$ Hz, Ar-H), 3.91 (s, 6H, $2 \times \text{Ar-OCH}_3$). Elemental analysis: $\text{C}_{36}\text{H}_{26}\text{O}_{10}$ requires, C, 69.9; H, 4.23%; found, C, 69.73; H, 3.87%.

1,3-Phenylene bis[4-(4-ethoxybenzoyloxy) benzoate], (4.A.2)

Yield, 73%; m.p. 173°C; $\nu_{\max}$: 2924, 2855, 1732, 1607, 1512, 1458, 1267, 1161 cm^{-1} ; δ_{H} : 8.30-8.27 (d, 4H, $^3J_{8.76}$ Hz, Ar-H), 8.18-8.14 (d, 4H, $^3J_{8.92}$ Hz, Ar-H), 7.52-7.48 (t, 1H, $^3J_{8.48}$ Hz, Ar-H), 7.4-7.36 (d, 4H, $^3J_{8.76}$ Hz, Ar-H), 7.21-7.17 (m, 3H, Ar-H), 7.01-6.99 (d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.17-4.12 (q, 4H, $^3J_{7.0}$ Hz, $2 \times \text{Ar-OCH}_2$ -), 1.49-1.46 (t, 6H, $2 \times \text{Ar-OCH}_2\text{-CH}_3$). Elemental analysis: $\text{C}_{38}\text{H}_{30}\text{O}_{10}$ requires, C, 70.58; H, 4.67%; found, C, 70.28; H, 4.68%.

1,3-Phenylene bis[4-(4-n-propyloxybenzoyloxy) benzoate], (4.A.3)

Yield, 71%; m.p. 175°C; $\nu_{\max}$: 2924, 2855, 1734, 1605, 1508, 1458, 1263, 1167 cm^{-1} ; δ_{H} : 8.30-8.27 (d, 4H, $^3J_{8.76}$ Hz, Ar-H), 8.18-8.14 (d, 4H, $^3J_{8.92}$ Hz, Ar-H), 7.52-7.48 (t, 1H, $^3J_{8.4}$ Hz, Ar-H), 7.4-7.36 (d, 4H, $^3J_{8.76}$ Hz, Ar-H), 7.21-7.17 (m, 3H, Ar-H), 7.01-6.98 (d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.04-4.01 (t, 4H, $^3J_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2$ -), 1.91-1.82 (m, 4H, $2 \times \text{Ar-OCH}_2\text{-CH}_2$ -),

1.09-1.06(t, 6H, $^3J_{7.4}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$). Elemental analysis: $\text{C}_{40}\text{H}_{34}\text{O}_{10}$ requires, C, 71.2; H, 5.08%; found, C, 70.85; H, 5.01%.

1,3-Phenylene bis[4-(4-n-butyloxybenzoyloxy) benzoate], (4.A.4)

Yield, 75%; m.p. 157.5°C ; ν_{max} : 2924, 2855, 1736, 1605, 1508, 1458, 1261, 1170 cm^{-1} ; δ_{H} : 8.30-8.26(d, 4H, $^3J_{8.72}$ Hz, Ar-H), 8.18-8.14(d, 4H, $^3J_{8.9}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3J_{8.4}$ Hz, Ar-H), 7.4-7.36(d, 4H, $^3J_{8.72}$ Hz, Ar-H), 7.21-7.17(m, 3H, Ar-H), 7.01-6.97(d, 4H, $^3J_{8.9}$ Hz, Ar-H), 4.04-4.01(t, 4H, $^3J_{6.52}$ Hz, $2 \times \text{Ar}-\text{OCH}_2-$), 1.85-1.78(quin, 4H, $^3J_{6.6}$ Hz, $2 \times \text{Ar}-\text{OCH}_2-\text{CH}_2-$), 1.57-1.48(m, 4H, $2 \times -\text{CH}_2-\text{CH}_3$), 1.02-0.98(t, 6H, $^3J_{7.4}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$). Elemental analysis: $\text{C}_{42}\text{H}_{38}\text{O}_{10}$ requires, C, 71.78; H, 5.45%; found, C, 71.44; H, 5.36%.

1,3-Phenylene bis[4-(4-n-pentyloxybenzoyloxy) benzoate], (4.A.5)

Yield, 73%; m.p. 170°C ; ν_{max} : 2926, 2855, 1732, 1605, 1508, 1458, 1259, 1160 cm^{-1} ; δ_{H} : 8.29-8.27(d, 4H, $^3J_{8.68}$ Hz, Ar-H), 8.17-8.15(d, 4H, $^3J_{8.84}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3J_{8.36}$ Hz, Ar-H), 7.39-7.37(d, 4H, $^3J_{8.68}$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 7.01-6.98(d, 4H, $^3J_{8.84}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3J_{6.56}$ Hz, $2 \times \text{Ar}-\text{OCH}_2-$), 1.85-1.80(quin, 4H, $^3J_{6.66}$ Hz, $2 \times \text{Ar}-\text{OCH}_2-\text{CH}_2-$), 1.51-1.36(m, 8H, $4 \times -\text{CH}_2-$), 0.97-0.94(t, 6H, $^3J_{7.12}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$). Elemental analysis: $\text{C}_{44}\text{H}_{42}\text{O}_{10}$ requires, C, 71.31; H, 5.79%; found, C, 71.53; H, 5.72%.

1,3-Phenylene bis[4-(4-n-hexyloxybenzoyloxy) benzoate], (4.A.6)

Yield, 71%; m.p. 138.5°C ; ν_{max} : 2924, 2855, 1732, 1724, 1608, 1508, 1458, 1278, 1167 cm^{-1} ; δ_{H} : 8.29-8.26(d, 4H, $^3J_{8.72}$ Hz, Ar-H), 8.17-8.14(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3J_{8.36}$ Hz, Ar-H), 7.39-7.36(d, 4H, $^3J_{8.7}$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 7.01-6.98(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3J_{6.56}$ Hz, $2 \times \text{Ar}-\text{OCH}_2-$), 1.86-1.79(quin, 4H, $^3J_{6.62}$ Hz, $2 \times \text{Ar}-\text{OCH}_2-\text{CH}_2-$), 1.52-1.34(m, 12H, $6 \times -\text{CH}_2-$), 0.94-0.90(t, 6H, $^3J_{6.96}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$). Elemental analysis: $\text{C}_{46}\text{H}_{46}\text{O}_{10}$ requires, C, 72.8; H, 6.1%; found, C, 73.05; H, 6.07%.

1,3-Phenylene bis[4-(4-n-heptyloxybenzoyloxy) benzoate], (4.A.7)

Yield, 74%; m.p. 132.5°C ; ν_{max} : 2924, 2855, 1730, 1607, 1458, 1260, 1165 cm^{-1} ; δ_{H} : 8.29-8.27(d, 4H, $^3J_{8.76}$ Hz, Ar-H), 8.16-8.14(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3J_{8.44}$ Hz, Ar-H), 7.39-7.36(d, 4H, $^3J_{8.76}$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 7.0-6.98(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3J_{6.56}$ Hz, $2 \times \text{Ar}-\text{OCH}_2-$), 1.86-1.79(quin, 4H, $^3J_{6.6}$ Hz, $2 \times \text{Ar}-$

OCH₂-CH₂-), 1.52-1.32(m, 16H, 8 × -CH₂-), 0.92-0.88(t, 6H, ³J6.76 Hz, 2 × -CH₂-CH₃). Elemental analysis: C₄₈H₅₀O₁₀ requires, C, 73.26; H, 6.4%; found, C, 72.91; H, 6.36%.

1,3-Phenylene bis[4-(4-n-octyloxybenzoyloxy) benzoate], (4.A.8)

Yield, 72%; m.p. 124.5°C; $\nu_{\max}$: 2924, 2856, 1737, 1726, 1603, 1510, 1458, 1252, 1163 cm⁻¹; δ_{H} : 8.29-8.27(d, 4H, ³J8.72 Hz, Ar-H), 8.16-8.14(d, 4H, ³J8.92 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.44 Hz, Ar-H), 7.39-7.36(d, 4H, ³J8.72 Hz, Ar-H), 7.21-7.17(m, 3H, Ar-H), 7.0-6.98(d, 4H, ³J8.92 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.66 Hz, 2 × Ar-OCH₂-CH₂-), 1.52-1.32(m, 20H, 10 × -CH₂-), 0.91-0.88(t, 6H, ³J6.76 Hz, 2 × -CH₂-CH₃). Elemental analysis: C₅₀H₅₄O₁₀ requires, C, 73.68; H, 6.67%; found, C, 73.89; H, 6.72%.

1,3-Phenylene bis[4-(4-n-nonyloxybenzoyloxy) benzoate], (4.A.9)

Yield, 70%; m.p. 115°C; $\nu_{\max}$: 2924, 2855, 1740, 1603, 1512, 1458, 1255, 1160 cm⁻¹; δ_{H} : 8.29-8.27(d, 4H, ³J8.64 Hz, Ar-H), 8.17-8.15(d, 4H, ³J8.76 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.32 Hz, Ar-H), 7.39-7.37(d, 4H, ³J8.64 Hz, Ar-H), 7.21-7.17(m, 3H, Ar-H), 7.0-6.98(d, 4H, ³J8.76 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.52 Hz, 2 × Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-), 1.51-1.24(m, 24H, 12 × -CH₂-), 0.91-0.87(t, 6H, ³J6.56 Hz, 2 × -CH₂-CH₃). Elemental analysis: C₅₂H₅₈O₁₀ requires, C, 74.08; H, 6.93%; found, C, 73.6; H, 6.95%.

1,3-Phenylene bis[4-(4-n-decyloxybenzoyloxy) benzoate], (4.A.10)

Yield, 68%; m.p. 111.5°C; $\nu_{\max}$: 2922, 2855, 1730, 1720, 1605, 1508, 1458, 1257, 1169 cm⁻¹; δ_{H} : 8.29-8.27(d, 4H, ³J8.76 Hz, Ar-H), 8.17-8.15(d, 4H, ³J8.92 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.56 Hz, Ar-H), 7.39-7.36(d, 4H, ³J8.76 Hz, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.0-6.98(d, 4H, ³J8.92 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-), 1.51-1.28(m, 28H, 14 × -CH₂-), 0.91-0.87(t, 6H, ³J6.56 Hz, 2 × -CH₂-CH₃). Elemental analysis: C₅₄H₆₂O₁₀ requires, C, 74.45; H, 7.17%; found, C, 74.72; H, 7.23%.

1,3-Phenylene bis[4-(4-n-undecyloxybenzoyloxy) benzoate], (4.A.11)

Yield, 69%; m.p. 105°C; $\nu_{\max}$: 2922, 2855, 1735, 1722, 1602, 1508, 1458, 1253, 1163 cm⁻¹; δ_{H} : 8.29-8.27(d, 4H, ³J8.76 Hz, Ar-H), 8.17-8.15(d, 4H, ³J8.92 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.56 Hz, Ar-H), 7.39-7.36(d, 4H, ³J8.76 Hz, Ar-H), 7.20-7.18(m, 3H, Ar-H), 7.0-6.98(d, 4H, ³J8.92 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.64 Hz,

2 × Ar-OCH₂-CH₂-), 1.51-1.28(m, 32H, 16 × -CH₂-), 0.90-0.87(t, 6H, ³J6.68 Hz, 2 × -CH₂-CH₃). Elemental analysis: C₅₆H₆₆O₁₀ requires, C, 74.8; H, 7.4%; found, C, 74.96; H, 7.44%.

1,3-Phenylene bis[4-(4-n-dodecyloxybenzoyloxy) benzoate], (4.A.12)

Yield, 71%; m.p. 106°C; ν_{max}: 2922, 2853, 1736, 1722, 1603, 1508, 1458, 1253, 1163 cm⁻¹; δ_H: 8.30-8.27(d, 4H, ³J8.72 Hz, Ar-H), 8.17-8.12(d, 4H, ³J8.92 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.48 Hz, Ar-H), 7.39-7.35(d, 4H, ³J8.72 Hz, Ar-H), 7.20-7.18(m, 3H, Ar-H), 7.0-6.98(d, 4H, ³J8.92 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.64 Hz, 2 × Ar-OCH₂-CH₂-), 1.51-1.28(m, 36H, 18 × -CH₂-), 0.90-0.87(t, 6H, ³J6.6 Hz, 2 × -CH₂-CH₃). Elemental analysis: C₅₈H₇₀O₁₀ requires, C, 75.13; H, 7.6%; found, C, 75.03; H, 7.88%.

1,3-Phenylene bis[4-(4-n-tetradecyloxybenzoyloxy) benzoate], (4.A.13)

Yield, 76%; m.p. 107°C; ν_{max}: 2922, 2854, 1735, 1720, 1603, 1508, 1456, 1253, 1160 cm⁻¹; δ_H: 8.30-8.26(d, 4H, ³J8.76 Hz, Ar-H), 8.17-8.13(d, 4H, ³J8.88 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.36 Hz, Ar-H), 7.39-7.36(d, 4H, ³J8.76 Hz, Ar-H), 7.20-7.18(m, 3H, Ar-H), 7.0-6.98(d, 4H, ³J8.88 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-), 1.51-1.27(m, 44H, 22 × -CH₂-), 0.90-0.87(t, 6H, ³J6.64 Hz, 2 × -CH₂-CH₃). Elemental analysis: C₆₂H₇₈O₁₀ requires, C, 75.73; H, 7.99%; found, C, 75.95; H, 8.12%.

1,3-Phenylene bis[4-(4-n-hexadecyloxybenzoyloxy) benzoate], (4.A.14)

Yield, 75%; m.p. 110.5°C; ν_{max}: 2918, 2850, 1734, 1610, 1510, 1458, 1259, 1168 cm⁻¹; δ_H: 8.30-8.27(d, 4H, ³J8.72 Hz, Ar-H), 8.17-8.14(d, 4H, ³J8.88 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.48 Hz, Ar-H), 7.39-7.37(d, 4H, ³J8.72 Hz, Ar-H), 7.21-7.17(m, 3H, Ar-H), 7.0-6.98(d, 4H, ³J8.88 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.52 Hz, 2 × Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-), 1.51-1.26(m, 52H, 26 × -CH₂-), 0.90-0.86(t, 6H, ³J6.64 Hz, 2 × -CH₂-CH₃). Elemental analysis: C₆₆H₈₆O₁₀ requires, C, 76.26; H, 8.34%; found, C, 76.59; H, 8.55%.

1,3-Phenylene bis[4-(4-n-octadecyloxybenzoyloxy) benzoate], (4.A.15)

Yield, 72%; m.p. 112°C; ν_{max}: 2918, 2851, 1734, 1610, 1510, 1458, 1259, 1168 cm⁻¹; δ_H: 8.29-8.27(d, 4H, ³J8.68 Hz, Ar-H), 8.17-8.14(d, 4H, ³J8.88 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.4 Hz, Ar-H), 7.39-7.37(d, 4H, ³J8.68 Hz, Ar-H), 7.21-7.17(m, 3H, Ar-H), 7.0-6.98(d, 4H, ³J8.88 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.68 Hz, 2 × Ar-

OCH₂-CH₂-), 1.53-1.22(m, 60H, 30 × -CH₂-), 0.90-0.86(t, 6H, ³J6.6 Hz, 2 × -CH₂-CH₃).
Elemental analysis: C₇₀H₉₄O₁₀ requires, C, 76.74; H, 8.64%; found, C, 76.79; H, 8.88%.

1,3-Phenylene bis[4-(4-methoxybenzoyloxy) 2-fluorobenzoate], (4.B.1)

Yield, 64%; m.p. 176°C; ν_{max}: 2924, 2855, 1745, 1734, 1724, 1608, 1508, 1460, 1250, 1134 cm⁻¹; δ_H: 8.21-8.14(m, 6H, Ar-H), 7.52-7.48(t, 1H, ³J8.36 Hz, Ar-H), 7.24-7.17(m, 7H, Ar-H), 7.03-6.99(d, 4H, ³J8.92 Hz, Ar-H), 3.92(s, 6H, 2 × Ar-OCH₃).

1,3-Phenylene bis[4-(4-ethoxybenzoyloxy) 2-fluorobenzoate], (4.B.2)

Yield, 61%; m.p. 152°C; ν_{max}: 2924, 2855, 1740, 1732, 1724, 1608, 1508, 1458, 1250, 1134 cm⁻¹; δ_H: 8.21-8.12(m, 6H, Ar-H), 7.52-7.48(t, 1H, ³J8.4 Hz, Ar-H), 7.26-7.16(m, 7H, Ar-H), 7.01-6.97(d, 4H, ³J8.96 Hz, Ar-H), 4.17-4.12(q, 4H, ³J7.0 Hz, 2 × Ar-OCH₂-), 1.49-1.46(t, 6H, 2 × Ar-OCH₂-CH₃).

1,3-Phenylene bis[4-(4-n-propyloxybenzoyloxy) 2-fluorobenzoate], (4.B.3)

Yield, 64%; m.p. 126.5°C; ν_{max}: 2924, 2855, 1751, 1736, 1728, 1607, 1508, 1462, 1234, 1128 cm⁻¹; δ_H: 8.21-8.13(m, 6H, Ar-H), 7.52-7.48(t, 1H, ³J8.2 Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 7.01-6.98(d, 4H, ³J8.84 Hz, Ar-H), 4.04-4.01(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-), 1.91-1.82(m, 4H, 2 × Ar-OCH₂-CH₂-), 1.09-1.06(t, 6H, ³J7.44 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(4-n-butyloxybenzoyloxy) 2-fluorobenzoate], (4.B.4)

Yield, 65%; m.p. 128.5°C; ν_{max}: 2924, 2855, 1750, 1736, 1728, 1607, 1508, 1462, 1234, 1128 cm⁻¹; δ_H: 8.20-8.11(m, 6H, Ar-H), 7.51-7.48(t, 1H, ³J8.24 Hz, Ar-H), 7.24-7.16(m, 7H, Ar-H), 7.01-6.97(d, 4H, ³J8.84 Hz, Ar-H), 4.08-4.05(t, 4H, ³J6.52 Hz, 2 × Ar-OCH₂-), 1.85-1.78(quin, 4H, ³J6.64 Hz, 2 × Ar-OCH₂-CH₂-), 1.57-1.48(m, 4H, 2 × -CH₂-CH₃), 1.02-0.98(t, 6H, ³J7.4 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(4-n-pentyloxybenzoyloxy) 2-fluorobenzoate], (4.B.5)

Yield, 68%; m.p. 139°C; ν_{max}: 2920, 2855, 1751, 1737, 1732, 1607, 1514, 1460, 1236, 1126 cm⁻¹; δ_H: 8.20-8.12(m, 6H, Ar-H), 7.51-7.48(t, 1H, ³J8.32 Hz, Ar-H), 7.24-7.16(m, 7H, Ar-H), 7.01-6.98(d, 4H, ³J8.92 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-), 1.85-1.80(quin, 4H, ³J6.64 Hz, 2 × Ar-OCH₂-CH₂-), 1.51-1.36(m, 8H, 4 × -CH₂-), 0.97-0.94(t, 6H, ³J7.12 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(4-n-hexyloxybenzoyloxy) 2-fluorobenzoate], (4.B.6)

Yield, 66%; m.p. 108°C; $\nu_{\max}$: 2920, 2856, 1751, 1738, 1732, 1607, 1514, 1460, 1236, 1126 cm^{-1} ; δ_{H} : 8.20-8.12(m, 6H, Ar-H), 7.51-7.48(t, 1H, $^3\text{J}_{8.16}$ Hz, Ar-H), 7.24-7.17(m, 7H, Ar-H), 7.0-6.98(d, 4H, $^3\text{J}_{8.8}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.85-1.81(quin, 4H, $^3\text{J}_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.52-1.35(m, 12H, $6 \times -\text{CH}_2-$), 0.94-0.90(t, 6H, $^3\text{J}_{6.72}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(4-n-heptyloxybenzoyloxy) 2-fluorobenzoate], (4.B.7)

Yield, 68%; m.p. 118.5°C; $\nu_{\max}$: 2920, 2854, 1750, 1738, 1732, 1608, 1514, 1458, 1236, 1126 cm^{-1} ; δ_{H} : 8.20-8.13(m, 6H, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.36}$ Hz, Ar-H), 7.24-7.16(m, 7H, Ar-H), 7.0-6.98(d, 4H, $^3\text{J}_{8.92}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.85-1.81(quin, 4H, $^3\text{J}_{6.64}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.52-1.32(m, 16H, $8 \times -\text{CH}_2-$), 0.92-0.88(t, 6H, $^3\text{J}_{6.8}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(4-n-octyloxybenzoyloxy) 2-fluorobenzoate], (4.B.8)

Yield, 65%; m.p. 112°C; $\nu_{\max}$: 2924, 2854, 1749, 1738, 1724, 1608, 1512, 1458, 1236, 1130 cm^{-1} ; δ_{H} : 8.20-8.12(m, 6H, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.28}$ Hz, Ar-H), 7.24-7.16(m, 7H, Ar-H), 7.0-6.98(d, 4H, $^3\text{J}_{8.88}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.87-1.81(quin, 4H, $^3\text{J}_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.53-1.30(m, 20H, $10 \times -\text{CH}_2-$), 0.91-0.88(t, 6H, $^3\text{J}_{6.6}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(4-n-nonyloxybenzoyloxy) 2-fluorobenzoate], (4.B.9)

Yield, 69%; m.p. 97°C; $\nu_{\max}$: 2924, 2854, 1745, 1724, 1605, 1460, 1236, 1130 cm^{-1} ; δ_{H} : 8.20-8.12(m, 6H, Ar-H), 7.50-7.47(t, 1H, $^3\text{J}_{8.2}$ Hz, Ar-H), 7.23-7.16(m, 7H, Ar-H), 7.0-6.97(d, 4H, $^3\text{J}_{8.88}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.86-1.79(quin, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.48-1.30(m, 24H, $12 \times -\text{CH}_2-$), 0.91-0.87(t, 6H, $^3\text{J}_{6.6}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$); δ_{C} : 164, 163.8, 161.7, 161.5, 156.3, 151.1, 145.4, 133.4, 132.5, 129.8, 120.5, 119.4, 117.9, 115.7, 115.1, 114.5, 111.5, 111.2, 68.4, 31.8, 29.9, 29.5, 29.3, 29.2, 25.9, 22.6, 14.0.

1,3-Phenylene bis[4-(4-n-decyloxybenzoyloxy) 2-fluorobenzoate], (4.B.10)

Yield, 66%; m.p. 96.5°C; $\nu_{\max}$: 2924, 2854, 1745, 1724, 1605, 1460, 1236, 1130 cm^{-1} ; δ_{H} : 8.20-8.12(m, 6H, Ar-H), 7.50-7.47(t, 1H, $^3\text{J}_{8.2}$ Hz, Ar-H), 7.23-7.16(m, 7H, Ar-H), 7.0-6.97(d, 4H, $^3\text{J}_{8.88}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.86-1.79(quin, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.48-1.30(m, 28H, $14 \times -\text{CH}_2-$), 0.91-0.87(t, 6H, $^3\text{J}_{6.84}$ Hz, 2

$\times$ -CH₂-CH₃); δ_C : 164, 163.8, 161.7, 161.5, 156.2, 151.1, 145.4, 133.4, 132.5, 129.8, 120.5, 119.4, 117.9, 115.7, 115.1, 114.5, 111.5, 111.2, 68.4, 31.8, 29.9, 29.5, 29.3, 29.2, 29.0, 25.9, 22.6, 14.1.

1,3-Phenylene bis[4-(4-n-undecyloxybenzoyloxy) 2-fluorobenzoate], (4.B.11)

Yield, 68%; m.p. 95°C; $\nu_{\max}$: 2924, 2850, 1745, 1724, 1605, 1460, 1236, 1130 cm⁻¹; δ_H : 8.20-8.12(m, 6H, Ar-H), 7.51-7.47(t, 1H, ³J8.28 Hz, Ar-H), 7.24-7.16(m, 7H, Ar-H), 7.0-6.97(d, 4H, ³J8.88 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.52 Hz, 2 $\times$ Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.52 Hz, 2 $\times$ Ar-OCH₂-CH₂-), 1.54-1.3(m, 32H, 16 $\times$ -CH₂-), 0.9-0.87(t, 6H, ³J6.6 Hz, 2 $\times$ -CH₂-CH₃); δ_C : 164, 163.8, 161.7, 161.5, 156.2, 151.1, 145.4, 133.4, 132.5, 129.8, 120.5, 119.4, 117.9, 115.7, 115.1, 114.5, 111.5, 111.2, 68.4, 31.8, 29.9, 29.5, 29.3, 29.2, 29.0, 28.4, 25.9, 22.6, 14.1.

1,3-Phenylene bis[4-(4-n-dodecyloxybenzoyloxy) 2-fluorobenzoate], (4.B.12)

Yield, 66%; m.p. 93°C; $\nu_{\max}$: 2924, 2850, 1742, 1726, 1605, 1460, 1236, 1130 cm⁻¹; δ_H : 8.20-8.11(m, 6H, Ar-H), 7.51-7.47(t, 1H, ³J8.32 Hz, Ar-H), 7.24-7.16(m, 7H, Ar-H), 7.0-6.97(d, 4H, ³J8.96 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.52 Hz, 2 $\times$ Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.52 Hz, 2 $\times$ Ar-OCH₂-CH₂-), 1.54-1.3(m, 32H, 16 $\times$ -CH₂-), 0.9-0.87(t, 6H, ³J6.6 Hz, 2 $\times$ -CH₂-CH₃); δ_C : 164, 163.8, 161.7, 161.5, 156.2, 151.1, 145.4, 133.4, 132.5, 129.8, 120.5, 119.4, 117.9, 115.7, 115.1, 114.5, 111.5, 111.2, 68.4, 36.0, 31.8, 29.9, 29.5, 29.3, 29.2, 29.0, 28.4, 25.9, 22.6, 14.1.

1,3-Phenylene bis[4-(4-n-tetradecyloxybenzoyloxy) 2-fluorobenzoate], (4.B.13)

Yield, 69%; m.p. 91°C; $\nu_{\max}$: 2920, 2853, 1740, 1726, 1607, 1460, 1250, 1169 cm⁻¹; δ_H : 8.20-8.12(m, 6H, Ar-H), 7.51-7.47(t, 1H, ³J8.36 Hz, Ar-H), 7.24-7.16(m, 7H, Ar-H), 7.0-6.97(d, 4H, ³J8.96 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.56 Hz, 2 $\times$ Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.68 Hz, 2 $\times$ Ar-OCH₂-CH₂-), 1.54-1.4(m, 40H, 20 $\times$ -CH₂-), 0.9-0.86(t, 6H, ³J6.64 Hz, 2 $\times$ -CH₂-CH₃); δ_C : 164, 163.8, 161.7, 161.5, 156.1, 151.1, 145.4, 133.4, 132.5, 129.8, 120.5, 119.4, 117.9, 115.7, 115.0, 114.5, 111.5, 111.2, 68.4, 36.0, 31.8, 29.6, 29.5, 29.3, 29.2, 29.0, 28.4, 25.9, 22.6, 14.1.

1,3-Phenylene bis[4-(4-n-hexadecyloxybenzoyloxy) 2-fluorobenzoate], (4.B.14)

Yield, 66%; m.p. 94.5°C; $\nu_{\max}$: 2922, 2852, 1743, 1724, 1605, 1460, 1236, 1130 cm⁻¹; δ_H : 8.20-8.12(m, 6H, Ar-H), 7.51-7.47(t, 1H, ³J8.32 Hz, Ar-H), 7.24-7.16(m, 7H, Ar-H), 7.0-

6.97(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3J_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.86-1.79(quin, 4H, $^3J_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.54-1.4(m, 48H, $24 \times -\text{CH}_2-$), 0.9-0.86(t, 6H, $^3J_{6.64}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$); δ_{C} : 164, 163.8, 161.7, 161.5, 156.1, 151.1, 145.4, 133.4, 132.5, 129.8, 120.5, 119.4, 117.9, 115.7, 115.0, 114.5, 111.5, 111.2, 68.4, 36.0, 31.8, 29.6, 29.5, 29.3, 29.2, 29.0, 28.4, 25.9, 22.6, 14.1.

1,3-Phenylene bis[4-(4-n-octadecyloxybenzoyloxy) 2-fluorobenzoate], (4.B.15)

Yield, 68%; m.p. 99.5°C; ν_{max} : 2922, 2854, 1744, 1724, 1605, 1460, 1236, 1130 cm^{-1} ; δ_{H} : 8.20-8.12(m, 6H, Ar-H), 7.51-7.47(t, 1H, $^3J_{8.28}$ Hz, Ar-H), 7.23-7.16(m, 7H, Ar-H), 7.0-6.97(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3J_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.86-1.79(quin, 4H, $^3J_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.48-1.44(m, 56H, $28 \times -\text{CH}_2-$), 0.89-0.86(t, 6H, $^3J_{6.56}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$). δ_{C} : 164, 163.8, 161.7, 161.5, 156.1, 151.1, 145.4, 133.4, 132.5, 129.8, 120.5, 119.4, 117.9, 115.7, 115.0, 114.5, 111.5, 111.2, 68.4, 36.0, 31.8, 29.6, 29.5, 29.3, 29.2, 29.0, 28.4, 25.9, 22.6, 14.1.

1,3-Phenylene bis[4-(4-n-propyloxybenzoyloxy) 3-fluorobenzoate], (4.C.1)

Yield, 67%; m.p. 137°C; ν_{max} : 2924, 2855, 1736, 1730, 1605, 1512, 1460, 1236, 1124 cm^{-1} ; δ_{H} : 8.18-8.15(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 8.08-8.03(m, 4H, Ar-H), 7.53-7.42(m, 3H, Ar-H), 7.2-7.18(m, 3H, Ar-H), 7.01-6.99(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.04-4.01(t, 4H, $^3J_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.91-1.82(m, 4H, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.09-1.05(t, 6H, $^3J_{7.4}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(4-n-butyloxybenzoyloxy) 3-fluorobenzoate], (4.C.2)

Yield, 65%; m.p. 130°C; ν_{max} : 2924, 2854, 1740, 1607, 1512, 1460, 1236, 1124 cm^{-1} ; δ_{H} : 8.18-8.14(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 8.08-8.03(m, 4H, Ar-H), 7.53-7.42(m, 3H, Ar-H), 7.2-7.18(m, 3H, Ar-H), 7.01-6.98(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.08-4.05(t, 4H, $^3J_{6.48}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.85-1.78(quin, 4H, $^3J_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.57-1.48(m, 4H, $2 \times -\text{CH}_2-\text{CH}_3$), 1.02-0.98(t, 6H, $^3J_{7.36}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(4-n-pentyloxybenzoyloxy) 3-fluorobenzoate], (4.C.3)

Yield, 70%; m.p. 142°C; ν_{max} : 2924, 2854, 1742, 1606, 1514, 1458, 1257, 1124 cm^{-1} ; δ_{H} : 8.18-8.15(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 8.08-8.03(m, 4H, Ar-H), 7.53-7.42(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.98(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.08-4.05(t, 4H, $^3J_{6.48}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.87-1.80(quin, 4H, $^3J_{6.64}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.51-1.36(m, 8H, $4 \times -\text{CH}_2-$), 0.97-0.94(t, 6H, $^3J_{7.16}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(4-n-hexyloxybenzoyloxy) 3-fluorobenzoate], (4.C.4)

Yield, 68%; m.p. 124.5°C; $\nu_{\max}$: 2924, 2854, 1740, 1606, 1514, 1458, 1254, 1124 cm^{-1} ; δ_{H} : 8.18-8.15(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 8.07-8.03(m, 4H, Ar-H), 7.53-7.42(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.98(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.08-4.04(t, 4H, $^3J_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.87-1.79(quin, 4H, $^3J_{6.72}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.52-1.24(m, 12H, $6 \times -\text{CH}_2-$), 0.94-0.9(t, 6H, $^3J_{6.96}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(4-n-heptyloxybenzoyloxy) 3-fluorobenzoate], (4.C.5)

Yield, 66%; m.p. 125.5°C; $\nu_{\max}$: 2924, 2852, 1747, 1740, 1605, 1514, 1458, 1254, 1124 cm^{-1} ; δ_{H} : 8.18-8.15(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 8.07-8.03(m, 4H, Ar-H), 7.53-7.42(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.98(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.08-4.04(t, 4H, $^3J_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.87-1.79(quin, 4H, $^3J_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.52-1.32(m, 16H, $8 \times -\text{CH}_2-$), 0.92-0.89(t, 6H, $^3J_{6.8}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(4-n-octyloxybenzoyloxy) 3-fluorobenzoate], (4.C.6)

Yield, 65%; m.p. 125°C; $\nu_{\max}$: 2924, 2852, 1747, 1740, 1605, 1514, 1458, 1254, 1124 cm^{-1} ; δ_{H} : 8.18-8.15(d, 4H, $^3J_{8.96}$ Hz, Ar-H), 8.07-8.03(m, 4H, Ar-H), 7.53-7.42(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.98(d, 4H, $^3J_{8.96}$ Hz, Ar-H), 4.08-4.04(t, 4H, $^3J_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.87-1.79(quin, 4H, $^3J_{6.72}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.50-1.30(m, 20H, $10 \times -\text{CH}_2-$), 0.91-0.88(t, 6H, $^3J_{6.64}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(4-n-nonyloxybenzoyloxy) 3-fluorobenzoate], (4.C.7)

Yield, 69%; m.p. 125.5°C; $\nu_{\max}$: 2924, 2852, 1747, 1740, 1605, 1516, 1458, 1254, 1120 cm^{-1} ; δ_{H} : 8.18-8.15(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 8.07-8.03(m, 4H, Ar-H), 7.53-7.42(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.98(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3J_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.87-1.79(quin, 4H, $^3J_{6.72}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.50-1.29(m, 24H, $12 \times -\text{CH}_2-$), 0.91-0.87(t, 6H, $^3J_{6.64}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(4-n-tetradecyloxybenzoyloxy) 3-fluorobenzoate], (4.C.8)

Yield, 70%; m.p. 122.5°C; $\nu_{\max}$: 2916, 2851, 1740, 1612, 1510, 1458, 1259, 1124 cm^{-1} ; δ_{H} : 8.17-8.15(d, 4H, $^3J_{8.84}$ Hz, Ar-H), 8.07-8.03(m, 4H, Ar-H), 7.51-7.42(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.98(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3J_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.85-1.79(quin, 4H, $^3J_{7.0}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.50-1.29(m, 44H, $22 \times -\text{CH}_2-$), 0.89-0.86(t, 6H, $^3J_{6.64}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(4-n-octadecyloxybenzoyloxy) 3-fluorobenzoate], (4.C.9)

Yield, 67%; m.p. 120°C; $\nu_{\max}$: 2916, 2851, 1740, 1610, 1508, 1458, 1259, 1125 cm^{-1} ; δ_{H} : 8.17-8.15(d, 4H, $^3\text{J}8.92$ Hz, Ar-H), 8.07-8.03(m, 4H, Ar-H), 7.51-7.42(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.98(d, 4H, $^3\text{J}8.92$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3\text{J}6.56$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.85-1.79(quin, 4H, $^3\text{J}7.0$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.48-1.22(m, 60H, $30 \times -\text{CH}_2-$), 0.89-0.86(t, 6H, $^3\text{J}6.64$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-propyloxybenzoyloxy) benzoate], (4.D.1)

Yield, 70%; m.p. 151°C; $\nu_{\max}$: 2924, 2855, 1737, 1618, 1508, 1456, 1260, 1128 cm^{-1} ; δ_{H} : 8.29-8.27(d, 4H, $^3\text{J}8.64$ Hz, Ar-H), 8.08-8.04(m, 2H, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}8.36$ Hz, Ar-H), 7.4-7.38(d, 4H, $^3\text{J}8.64$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 6.81-6.78(dd, 2H, $^3\text{J}8.86$ Hz, $^4\text{J}2.24$ Hz, Ar-H), 6.73-6.69(dd, 2H, $^3\text{J}12.76$ Hz, $^4\text{J}2.24$ Hz, Ar-H), 4.02-3.99(t, 4H, $^3\text{J}6.52$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.91-1.82(m, 4H, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.09-1.05(t, 6H, $^3\text{J}7.4$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-butyloxybenzoyloxy) benzoate], (4.D.2)

Yield, 68%; m.p. 133.5°C; $\nu_{\max}$: 2924, 2855, 1737, 1618, 1508, 1456, 1260, 1128 cm^{-1} ; δ_{H} : 8.29-8.27(d, 4H, $^3\text{J}8.68$ Hz, Ar-H), 8.08-8.04(m, 2H, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}8.4$ Hz, Ar-H), 7.4-7.38(d, 4H, $^3\text{J}8.64$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 6.81-6.78(dd, 2H, $^3\text{J}8.88$ Hz, $^4\text{J}2.36$ Hz, Ar-H), 6.73-6.69(dd, 2H, $^3\text{J}12.72$ Hz, $^4\text{J}2.34$ Hz, Ar-H), 4.06-4.03(t, 4H, $^3\text{J}6.48$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.85-1.78(quin, 4H, $^3\text{J}6.6$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.55-1.47(m, 4H, $2 \times -\text{CH}_2-\text{CH}_3$), 1.02-0.98(t, 6H, $^3\text{J}7.36$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-pentyloxybenzoyloxy) benzoate], (4.D.3)

Yield, 66%; m.p. 148°C; $\nu_{\max}$: 2924, 2855, 1737, 1618, 1508, 1456, 1276, 1130 cm^{-1} ; δ_{H} : 8.29-8.27(d, 4H, $^3\text{J}8.48$ Hz, Ar-H), 8.08-8.04(m, 2H, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}8.12$ Hz, Ar-H), 7.4-7.38(d, 4H, $^3\text{J}8.48$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 6.81-6.78(dd, 2H, $^3\text{J}8.88$ Hz, $^4\text{J}2.12$ Hz, Ar-H), 6.73-6.69(dd, 2H, $^3\text{J}12.7$ Hz, $^4\text{J}2.04$ Hz, Ar-H), 4.06-4.02(t, 4H, $^3\text{J}6.52$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.85-1.80(quin, 4H, $^3\text{J}6.96$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.49-1.38(m, 8H, $4 \times -\text{CH}_2-$), 0.97-0.94(t, 6H, $^3\text{J}7.16$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-hexyloxybenzoyloxy) benzoate], (4.D.4)

Yield, 66%; m.p. 117°C; $\nu_{\max}$: 2924, 2855, 1743, 1737, 1618, 1508, 1456, 1276, 1130 cm^{-1} ; δ_{H} : 8.29-8.27(d, 4H, $^3\text{J}8.48$ Hz, Ar-H), 8.08-8.04(m, 2H, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}8.12$ Hz,

Ar-H), 7.4-7.38(d, 4H, $^3J_{8.48}$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 6.81-6.78(dd, 2H, $^3J_{8.9}$ Hz, $^4J_{2.24}$ Hz, Ar-H), 6.73-6.69(dd, 2H, $^3J_{12.7}$ Hz, $^4J_{2.08}$ Hz, Ar-H), 4.06-4.02(t, 4H, $^3J_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2\text{-}$), 1.86-1.79(quin, 4H, $^3J_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.49-1.38(m, 12H, $6 \times \text{-CH}_2\text{-}$), 0.97-0.94(t, 6H, $^3J_{7.16}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-heptyloxybenzoyloxy) benzoate], (4.D.5)

Yield, 67%; m.p. 112°C; ν_{max} : 2924, 2854, 1740, 1737, 1618, 1506, 1456, 1276, 1130 cm^{-1} ; δ_{H} : 8.29-8.27(d, 4H, $^3J_{8.68}$ Hz, Ar-H), 8.08-8.04(m, 2H, Ar-H), 7.5-7.48(t, 1H, $^3J_{8.12}$ Hz, Ar-H), 7.4-7.38(d, 4H, $^3J_{8.68}$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 6.81-6.78(dd, 2H, $^3J_{8.88}$ Hz, $^4J_{2.28}$ Hz, Ar-H), 6.73-6.69(dd, 2H, $^3J_{12.74}$ Hz, $^4J_{2.24}$ Hz, Ar-H), 4.06-4.02(t, 4H, $^3J_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2\text{-}$), 1.85-1.79(quin, 4H, $^3J_{6.96}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.49-1.33(m, 16H, $8 \times \text{-CH}_2\text{-}$), 0.93-0.89(t, 6H, $^3J_{6.52}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-octyloxybenzoyloxy) benzoate], (4.D.6)

Yield, 70%; m.p. 107°C; ν_{max} : 2922, 2854, 1743, 1736, 1626, 1506, 1458, 1269, 1139 cm^{-1} ; δ_{H} : 8.29-8.27(d, 4H, $^3J_{8.56}$ Hz, Ar-H), 8.08-8.04(m, 2H, Ar-H), 7.5-7.48(t, 1H, $^3J_{8.16}$ Hz, Ar-H), 7.4-7.38(d, 4H, $^3J_{8.6}$ Hz, Ar-H), 7.20-7.18(m, 3H, Ar-H), 6.81-6.78(dd, 2H, $^3J_{8.88}$ Hz, $^4J_{2.04}$ Hz, Ar-H), 6.73-6.69(dd, 2H, $^3J_{12.72}$ Hz, $^4J_{2.04}$ Hz, Ar-H), 4.06-4.02(t, 4H, $^3J_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2\text{-}$), 1.86-1.79(quin, 4H, $^3J_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.49-1.3(m, 20H, $10 \times \text{-CH}_2\text{-}$), 0.92-0.88(t, 6H, $^3J_{6.2}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-nonyloxybenzoyloxy) benzoate], (4.D.7)

Yield, 68%; m.p. 103.5°C; ν_{max} : 2922, 2854, 1743, 1735, 1625, 1506, 1456, 1240, 1169 cm^{-1} ; δ_{H} : 8.29-8.27(d, 4H, $^3J_{8.28}$ Hz, Ar-H), 8.08-8.04(m, 2H, Ar-H), 7.5-7.48(t, 1H, $^3J_{8.0}$ Hz, Ar-H), 7.4-7.38(d, 4H, $^3J_{8.6}$ Hz, Ar-H), 7.20-7.18(m, 3H, Ar-H), 6.80-6.78(dd, 2H, $^3J_{8.88}$ Hz, $^4J_{2.06}$ Hz, Ar-H), 6.73-6.69(dd, 2H, $^3J_{12.72}$ Hz, $^4J_{2.06}$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3J_{6.78}$ Hz, $2 \times \text{Ar-OCH}_2\text{-}$), 1.86-1.79(quin, 4H, $^3J_{6.64}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.47-1.3(m, 24H, $12 \times \text{-CH}_2\text{-}$), 0.91-0.88(t, 6H, $^3J_{6.2}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-decyloxybenzoyloxy) benzoate], (4.D.8)

Yield, 70%; m.p. 106.5°C; ν_{max} : 2922, 2854, 1743, 1735, 1625, 1506, 1458, 1238, 1169 cm^{-1} ; δ_{H} : 8.29-8.27(d, 4H, $^3J_{8.68}$ Hz, Ar-H), 8.08-8.04(m, 2H, Ar-H), 7.5-7.48(t, 1H, $^3J_{8.36}$ Hz, Ar-H), 7.4-7.38(d, 4H, $^3J_{8.68}$ Hz, Ar-H), 7.25-7.17(m, 3H, Ar-H), 6.80-6.78(dd, 2H, $^3J_{8.86}$ Hz, $^4J_{2.28}$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3J_{12.74}$ Hz, $^4J_{2.32}$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3J_{6.52}$ Hz,

2 × Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-), 1.47-1.28(m, 28H, 14 × -CH₂-), 0.90-0.87(t, 6H, ³J6.52 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(2-fluoro-4-n-undecyloxybenzoyloxy) benzoate], (4.D.9)

Yield, 73%; m.p. 101°C; $\nu_{\max}$: 2922, 2852, 1734, 1724, 1620, 1603, 1506, 1458, 1275, 1130 cm⁻¹; δ_{H} : 8.29-8.27(d, 4H, ³J8.56 Hz, Ar-H), 8.08-8.04(m, 2H, Ar-H), 7.52-7.48(t, 1H, ³J8.16 Hz, Ar-H), 7.4-7.38(d, 4H, ³J8.56 Hz, Ar-H), 7.2-7.17(m, 3H, Ar-H), 6.80-6.78(dd, 2H, ³J8.88 Hz, ⁴J2.04 Hz, Ar-H), 6.72-6.68(dd, 2H, ³J12.7 Hz, ⁴J1.96 Hz, Ar-H), 4.05-4.02(t, 4H, ³J6.48 Hz, 2 × Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-), 1.49-1.28(m, 32H, 16 × -CH₂-), 0.90-0.87(t, 6H, ³J6.32 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(2-fluoro-4-n-dodecyloxybenzoyloxy) benzoate], (4.D.10)

Yield, 71%; m.p. 100°C; $\nu_{\max}$: 2922, 2854, 1730, 1724, 1620, 1600, 1506, 1458, 1275, 1130 cm⁻¹; δ_{H} : 8.29-8.27(d, 4H, ³J8.48 Hz, Ar-H), 8.08-8.04(m, 2H, Ar-H), 7.52-7.48(t, 1H, ³J8.12 Hz, Ar-H), 7.4-7.38(d, 4H, ³J8.48 Hz, Ar-H), 7.2-7.17(m, 3H, Ar-H), 6.80-6.78(dd, 2H, ³J8.9 Hz, ⁴J1.8 Hz, Ar-H), 6.72-6.68(dd, 2H, ³J12.68 Hz, ⁴J1.72 Hz, Ar-H), 4.05-4.02(t, 4H, ³J6.48 Hz, 2 × Ar-OCH₂-), 1.86-1.79(quin, 4H, ³J6.64 Hz, 2 × Ar-OCH₂-CH₂-), 1.49-1.27(m, 36H, 18 × -CH₂-), 0.90-0.87(t, 6H, ³J6.32 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(2-fluoro-4-n-tetradecyloxybenzoyloxy) benzoate], (4.D.11)

Yield, 69%; m.p. 99°C; $\nu_{\max}$: 2922, 2854, 1730, 1725, 1620, 1600, 1508, 1456, 1275, 1132 cm⁻¹; δ_{H} : 8.29-8.27(d, 4H, ³J8.6 Hz, Ar-H), 8.08-8.04(m, 2H, Ar-H), 7.50-7.48(t, 1H, ³J8.12 Hz, Ar-H), 7.4-7.38(d, 4H, ³J8.64 Hz, Ar-H), 7.2-7.17(m, 3H, Ar-H), 6.80-6.78(dd, 2H, ³J8.9 Hz, ⁴J2.0 Hz, Ar-H), 6.72-6.68(dd, 2H, ³J12.7 Hz, ⁴J2.08 Hz, Ar-H), 4.05-4.02(t, 4H, ³J6.48 Hz, 2 × Ar-OCH₂-), 1.84-1.8(quin, 4H, ³J6.64 Hz, 2 × Ar-OCH₂-CH₂-), 1.49-1.27(m, 44H, 22 × -CH₂-), 0.90-0.86(t, 6H, ³J6.32 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(2-fluoro-4-n-hexadecyloxybenzoyloxy) benzoate], (4.D.12)

Yield, 67%; m.p. 91°C; $\nu_{\max}$: 2916, 2852, 1740, 1626, 1601, 1506, 1458, 1284, 1132 cm⁻¹; δ_{H} : 8.29-8.27(d, 4H, ³J8.6 Hz, Ar-H), 8.08-8.04(m, 2H, Ar-H), 7.50-7.48(t, 1H, ³J8.06 Hz, Ar-H), 7.4-7.38(d, 4H, ³J8.6 Hz, Ar-H), 7.2-7.18(m, 3H, Ar-H), 6.80-6.78(dd, 2H, ³J8.9 Hz, ⁴J2.04 Hz, Ar-H), 6.72-6.68(dd, 2H, ³J12.72 Hz, ⁴J2.04 Hz, Ar-H), 4.05-4.02(t, 4H, ³J6.48 Hz, 2 × Ar-OCH₂-), 1.84-1.8(quin, 4H, ³J7.04 Hz, 2 × Ar-OCH₂-CH₂-), 1.47-1.26(m, 52H, 26 × -CH₂-), 0.90-0.86(t, 6H, ³J6.32 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(2-fluoro-4-n-octadecyloxybenzoyloxy) benzoate], (4.D.13)

Yield, 70%; m.p. 95°C; $\nu_{\max}$: 2916, 2850, 1740, 1620, 1601, 1506, 1458, 1284, 1130 cm^{-1} ; δ_{H} : 8.29-8.27(d, 4H, $^3\text{J}_{8.72}$ Hz, Ar-H), 8.08-8.04(m, 2H, Ar-H), 7.50-7.48(t, 1H, $^3\text{J}_{8.06}$ Hz, Ar-H), 7.4-7.38(d, 4H, $^3\text{J}_{8.72}$ Hz, Ar-H), 7.2-7.18(m, 3H, Ar-H), 6.80-6.78(dd, 2H, $^3\text{J}_{8.88}$ Hz, $^4\text{J}_{2.04}$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3\text{J}_{12.72}$ Hz, $^4\text{J}_{2.04}$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.84-1.8(quin, 4H, $^3\text{J}_{6.96}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.47-1.26(m, 60H, $30 \times -\text{CH}_2-$), 0.90-0.86(t, 6H, $^3\text{J}_{6.64}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-heptyloxybenzoyloxy) benzoate], (4.E.1)

Yield, 65%; m.p. 130°C; $\nu_{\max}$: 2931, 2849, 1736, 1726, 1618, 1608, 1439, 1282, 1080 cm^{-1} ; δ_{H} : 8.3-8.27(d, 4H, $^3\text{J}_{8.64}$ Hz, Ar-H), 7.98-7.96(d, 2H, $^3\text{J}_{8.68}$ Hz, Ar-H), 7.92-7.89(dd, 2H, $^3\text{J}_{11.44}$ Hz, $^4\text{J}_{2.0}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.4}$ Hz, Ar-H), 7.38-7.36(d, 4H, $^3\text{J}_{8.68}$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 7.07-7.03(t, 2H, $^3\text{J}_{8.32}$ Hz, Ar-H), 4.15-4.11(t, 4H, $^3\text{J}_{6.6}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.91-1.84(quin, 4H, $^3\text{J}_{6.76}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.53-1.31(m, 16H, $8 \times -\text{CH}_2-$), 0.92-0.89(t, 6H, $^3\text{J}_{6.68}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-nonyloxybenzoyloxy) benzoate], (4.E.2)

Yield, 68%; m.p. 130°C; $\nu_{\max}$: 2931, 2849, 1736, 1724, 1618, 1608, 1439, 1282, 1080 cm^{-1} ; δ_{H} : 8.3-8.27(d, 4H, $^3\text{J}_{8.68}$ Hz, Ar-H), 7.98-7.96(d, 2H, $^3\text{J}_{8.64}$ Hz, Ar-H), 7.92-7.89(dd, 2H, $^3\text{J}_{11.4}$ Hz, $^4\text{J}_{1.96}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.28}$ Hz, Ar-H), 7.38-7.36(d, 4H, $^3\text{J}_{8.64}$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 7.07-7.03(t, 2H, $^3\text{J}_{8.32}$ Hz, Ar-H), 4.15-4.11(t, 4H, $^3\text{J}_{6.6}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.91-1.84(quin, 4H, $^3\text{J}_{6.72}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.53-1.29(m, 24H, $12 \times -\text{CH}_2-$), 0.91-0.87(t, 6H, $^3\text{J}_{6.44}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-decyloxybenzoyloxy) benzoate], (4.E.3)

Yield, 66%; m.p. 129°C; $\nu_{\max}$: 2916, 2850, 1736, 1726, 1618, 1608, 1439, 1282, 1084 cm^{-1} ; δ_{H} : 8.3-8.27(d, 4H, $^3\text{J}_{8.6}$ Hz, Ar-H), 7.98-7.96(d, 2H, $^3\text{J}_{8.52}$ Hz, Ar-H), 7.92-7.89(dd, 2H, $^3\text{J}_{11.42}$ Hz, $^4\text{J}_{1.92}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.28}$ Hz, Ar-H), 7.38-7.36(d, 4H, $^3\text{J}_{8.64}$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 7.07-7.03(t, 2H, $^3\text{J}_{8.28}$ Hz, Ar-H), 4.15-4.11(t, 4H, $^3\text{J}_{6.6}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.91-1.84(quin, 4H, $^3\text{J}_{6.72}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.53-1.29(m, 28H, $14 \times -\text{CH}_2-$), 0.91-0.87(t, 6H, $^3\text{J}_{6.44}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-undecyloxybenzoyloxy) benzoate], (4.E.4)

Yield, 69%; m.p. 129°C; $\nu_{\max}$: 2916, 2850, 1736, 1728, 1618, 1605, 1438, 1282, 1084 cm^{-1} ;
 δ_{H} : 8.3-8.27(d, 4H, $^3\text{J}_{8.56}$ Hz, Ar-H), 7.98-7.96(d, 2H, $^3\text{J}_{8.50}$ Hz, Ar-H), 7.92-7.89(dd, 2H, $^3\text{J}_{11.40}$ Hz, $^4\text{J}_{1.92}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.28}$ Hz, Ar-H), 7.38-7.36(d, 4H, $^3\text{J}_{8.66}$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 7.07-7.03(t, 2H, $^3\text{J}_{8.28}$ Hz, Ar-H), 4.15-4.11(t, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.91-1.84(quin, 4H, $^3\text{J}_{6.70}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2-$), 1.53-1.29(m, 32H, $16 \times \text{-CH}_2-$), 0.91-0.87(t, 6H, $^3\text{J}_{6.44}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-dodecyloxybenzoyloxy) benzoate], (4.E.5)

Yield, 71%; m.p. 128°C; $\nu_{\max}$: 2916, 2851, 1736, 1726, 1618, 1608, 1439, 1285, 1084 cm^{-1} ;
 δ_{H} : 8.3-8.27(d, 4H, $^3\text{J}_{8.56}$ Hz, Ar-H), 7.98-7.96(d, 2H, $^3\text{J}_{8.64}$ Hz, Ar-H), 7.92-7.89(dd, 2H, $^3\text{J}_{11.40}$ Hz, $^4\text{J}_{1.92}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.12}$ Hz, Ar-H), 7.38-7.36(d, 4H, $^3\text{J}_{8.6}$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 7.07-7.03(t, 2H, $^3\text{J}_{8.28}$ Hz, Ar-H), 4.14-4.11(t, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.91-1.84(quin, 4H, $^3\text{J}_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2-$), 1.53-1.27(m, 36H, $18 \times \text{-CH}_2-$), 0.91-0.87(t, 6H, $^3\text{J}_{6.32}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-tetradecyloxybenzoyloxy) benzoate], (4.E.6)

Yield, 70%; m.p. 124°C; $\nu_{\max}$: 2916, 2850, 1736, 1726, 1618, 1608, 1439, 1286, 1085 cm^{-1} ;
 δ_{H} : 8.3-8.27(d, 4H, $^3\text{J}_{8.68}$ Hz, Ar-H), 7.98-7.96(d, 2H, $^3\text{J}_{9.0}$ Hz, Ar-H), 7.92-7.89(dd, 2H, $^3\text{J}_{11.40}$ Hz, $^4\text{J}_{2.0}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.12}$ Hz, Ar-H), 7.38-7.36(d, 4H, $^3\text{J}_{8.68}$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 7.07-7.03(t, 2H, $^3\text{J}_{8.32}$ Hz, Ar-H), 4.15-4.11(t, 4H, $^3\text{J}_{6.6}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.89-1.84(quin, 4H, $^3\text{J}_{7.08}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2-$), 1.51-1.26(m, 44H, $22 \times \text{-CH}_2-$), 0.9-0.86(t, 6H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-hexadecyloxybenzoyloxy) benzoate], (4.E.7)

Yield, 72%; m.p. 121°C; $\nu_{\max}$: 2916, 2851, 1734, 1726, 1618, 1608, 1439, 1285, 1084 cm^{-1} ;
 δ_{H} : 8.3-8.27(d, 4H, $^3\text{J}_{8.66}$ Hz, Ar-H), 7.98-7.96(d, 2H, $^3\text{J}_{9.0}$ Hz, Ar-H), 7.92-7.89(dd, 2H, $^3\text{J}_{11.40}$ Hz, $^4\text{J}_{2.0}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.12}$ Hz, Ar-H), 7.38-7.36(d, 4H, $^3\text{J}_{8.66}$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 7.07-7.03(t, 2H, $^3\text{J}_{8.30}$ Hz, Ar-H), 4.15-4.11(t, 4H, $^3\text{J}_{6.62}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.89-1.84(quin, 4H, $^3\text{J}_{7.0}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2-$), 1.51-1.26(m, 52H, $26 \times \text{-CH}_2-$), 0.9-0.86(t, 6H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-octadecyloxybenzoyloxy) benzoate], (4.E.8)

Yield, 69%; m.p. 118°C; $\nu_{\max}$: 2914, 2849, 1741, 1734, 1726, 1618, 1608, 1439, 1283, 1084 cm^{-1} ; δ_{H} : 8.3-8.27(d, 4H, $^3\text{J}_{8.56}$ Hz, Ar-H), 7.98-7.96(d, 2H, $^3\text{J}_{8.96}$ Hz, Ar-H), 7.92-7.89(dd, 2H, $^3\text{J}_{11.40}$ Hz, $^4\text{J}_{1.96}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.06}$ Hz, Ar-H), 7.38-7.36(d, 4H, $^3\text{J}_{8.56}$ Hz, Ar-H), 7.20-7.17(m, 3H, Ar-H), 7.07-7.03(t, 2H, $^3\text{J}_{8.30}$ Hz, Ar-H), 4.15-4.11(t, 4H, $^3\text{J}_{6.6}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.89-1.84(quin, 4H, $^3\text{J}_{7.6}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2-$), 1.49-1.26(m, 60H, $30 \times \text{-CH}_2-$), 0.89-0.86(t, 6H, $^3\text{J}_{6.28}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-eicocyloxybenzoyloxy) benzoate], (4.E.9)

Yield, 70%; m.p. 117.5°C; $\nu_{\max}$: 2914, 2849, 1741, 1734, 1726, 1618, 1608, 1439, 1283, 1084 cm^{-1} ; δ_{H} : 8.3-8.27(d, 4H, $^3\text{J}_{8.64}$ Hz, Ar-H), 7.98-7.96(d, 2H, $^3\text{J}_{8.56}$ Hz, Ar-H), 7.92-7.89(dd, 2H, $^3\text{J}_{11.42}$ Hz, $^4\text{J}_{1.68}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.28}$ Hz, Ar-H), 7.38-7.36(d, 4H, $^3\text{J}_{8.6}$ Hz, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.07-7.03(t, 2H, $^3\text{J}_{8.32}$ Hz, Ar-H), 4.15-4.12(t, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.9-1.84(quin, 4H, $^3\text{J}_{6.72}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2-$), 1.51-1.26(m, 68H, $34 \times \text{-CH}_2-$), 0.9-0.86(t, 6H, $^3\text{J}_{6.24}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-methoxybenzoyloxy) 2-fluorobenzoate], (4.F.1)

Yield, 60%; m.p. 161.5°C; $\nu_{\max}(\text{KBr})$: 2962, 2874, 1740, 1728, 1620, 1575, 1437, 1276, 1130 cm^{-1} ; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.02(t, 2H, $^3\text{J}_{8.6}$ Hz, Ar-H), 7.51-7.48(t, 1H, $^3\text{J}_{8.28}$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 6.8-6.78(dd, 2H, $^3\text{J}_{8.86}$ Hz, $^4\text{J}_{2.04}$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3\text{J}_{12.76}$ Hz, $^4\text{J}_{2.08}$ Hz, Ar-H), 3.92(s, 6H, $2 \times \text{Ar-OCH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-ethoxybenzoyloxy) 2-fluorobenzoate], (4.F.2)

Yield, 58%; m.p. 162.5°C; $\nu_{\max}(\text{KBr})$: 2960, 2874, 1740, 1730, 1620, 1575, 1436, 1276, 1130 cm^{-1} ; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.02(t, 2H, $^3\text{J}_{8.56}$ Hz, Ar-H), 7.51-7.48(t, 1H, $^3\text{J}_{8.28}$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 6.8-6.78(dd, 2H, $^3\text{J}_{8.86}$ Hz, $^4\text{J}_{2.0}$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3\text{J}_{12.76}$ Hz, $^4\text{J}_{2.0}$ Hz, Ar-H), 4.14-4.09(q, 4H, $^3\text{J}_{6.96}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.48-1.45(t, 6H, $2 \times \text{Ar-OCH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-propyloxybenzoyloxy)2-fluorobenzoate],(4.F.3)

Yield, 54%; m.p. 132°C; $\nu_{\max}(\text{KBr})$: 2960, 2874, 1745, 1730, 1620, 1575, 1436, 1276, 1128 cm^{-1} ; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.01(t, 2H, $^3\text{J}_{8.6}$ Hz, Ar-H), 7.51-7.47(t, 1H, $^3\text{J}_{8.32}$ Hz, Ar-H), 7.23-7.18(m, 7H, Ar-H), 6.8-6.78(dd, 2H, $^3\text{J}_{8.86}$ Hz, $^4\text{J}_{2.12}$ Hz, Ar-H), 6.72-

6.69(dd, 2H, $^3J_{12.78}$ Hz, $^4J_{2.24}$ Hz, Ar-H), 4.02-3.99(t, 4H, $^3J_{6.52}$ Hz, $2 \times$ Ar-OCH₂-), 1.9-1.81(m, 4H, $2 \times$ Ar-OCH₂-CH₂-), 1.08-1.04(t, 6H, $^3J_{7.44}$ Hz, $2 \times$ -CH₂-CH₃).

1,3-Phenylene bis[4-(2-fluoro-4-n-butyloxybenzoyloxy) 2-fluorobenzoate], (4.F.4)

Yield, 55%; m.p. 130.5°C; $\nu_{\max}$ (KBr): 2958, 2870, 1750, 1732, 1618, 1578, 1436, 1276, 1128 cm⁻¹; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.01(t, 2H, $^3J_{8.6}$ Hz, Ar-H), 7.51-7.47(t, 1H, $^3J_{8.32}$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 6.8-6.78(dd, 2H, $^3J_{8.86}$ Hz, $^4J_{2.16}$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3J_{12.74}$ Hz, $^4J_{2.2}$ Hz, Ar-H), 4.06-4.03(t, 4H, $^3J_{6.48}$ Hz, $2 \times$ Ar-OCH₂-), 1.85-1.77(quin, 4H, $^3J_{6.6}$ Hz, $2 \times$ Ar-OCH₂-CH₂-), 1.57-1.48(m, 4H, $2 \times$ -CH₂-CH₃), 1.01-0.98(t, 6H, $^3J_{7.36}$ Hz, $2 \times$ -CH₂-CH₃).

1,3-Phenylene bis[4-(2-fluoro-4-n-pentyloxybenzoyloxy)2-fluorobenzoate], (4.F.5)

Yield, 57%; m.p. 129°C; $\nu_{\max}$: 2955, 2860, 1732, 1618, 1578, 1437, 1276, 1125 cm⁻¹; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.01(t, 2H, $^3J_{8.68}$ Hz, Ar-H), 7.51-7.47(t, 1H, $^3J_{8.28}$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 6.8-6.78(dd, 2H, $^3J_{8.86}$ Hz, $^4J_{2.04}$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3J_{12.74}$ Hz, $^4J_{2.12}$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3J_{6.52}$ Hz, $2 \times$ Ar-OCH₂-), 1.86-1.79(quin, 4H, $^3J_{6.56}$ Hz, $2 \times$ Ar-OCH₂-CH₂-), 1.49-1.36(m, 8H, $4 \times$ -CH₂-), 0.97-0.93(t, 6H, $^3J_{7.04}$ Hz, $2 \times$ -CH₂-CH₃).

1,3-Phenylene bis[4-(2-fluoro-4-n-hexyloxybenzoyloxy) 2-fluorobenzoate], (4.F.6)

Yield, 59%; m.p. 109°C; $\nu_{\max}$: 2955, 2860, 1732, 1618, 1578, 1437, 1276, 1128 cm⁻¹; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.01(t, 2H, $^3J_{8.68}$ Hz, Ar-H), 7.51-7.47(t, 1H, $^3J_{8.34}$ Hz, Ar-H), 7.23-7.18(m, 7H, Ar-H), 6.8-6.78(dd, 2H, $^3J_{8.86}$ Hz, $^4J_{2.04}$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3J_{12.74}$ Hz, $^4J_{2.12}$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3J_{6.52}$ Hz, $2 \times$ Ar-OCH₂-), 1.86-1.79(quin, 4H, $^3J_{6.56}$ Hz, $2 \times$ Ar-OCH₂-CH₂-), 1.49-1.36(m, 12H, $6 \times$ -CH₂-), 0.97-0.93(t, 6H, $^3J_{7.04}$ Hz, $2 \times$ -CH₂-CH₃).

1,3-Phenylene bis[4-(2-fluoro-4-n-heptyloxybenzoyloxy) 2-fluorobenzoate],(4.F.7)

Yield, 62%; m.p. 100°C; $\nu_{\max}$ (KBr): 2962, 2873, 1740, 1728, 1620, 1575, 1437, 1276, 1130 cm⁻¹; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.02(t, 2H, $^3J_{8.64}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3J_{8.36}$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 6.81-6.78(dd, 2H, $^3J_{8.88}$ Hz, $^4J_{2.32}$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3J_{12.76}$ Hz, $^4J_{2.32}$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3J_{6.52}$ Hz, $2 \times$ Ar-OCH₂-), 1.86-1.79(quin, 4H, $^3J_{6.64}$ Hz, $2 \times$ Ar-OCH₂-CH₂-), 1.49-1.32(m, 16H, $8 \times$ -CH₂-), 0.92-0.89(t, 6H, $^3J_{6.8}$ Hz, $2 \times$ -CH₂-CH₃).

1,3-Phenylene bis[4-(2-fluoro-4-n-octyloxybenzoyloxy) 2-fluorobenzoate], (4.F.8)

Yield, 65%; m.p. 95.5°C; $\nu_{\max}$: 2922, 2850, 1732, 1618, 1595, 1437, 1276, 1130 cm^{-1} ; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.02(t, 2H, $^3\text{J}8.68$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}8.36$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 6.81-6.78(dd, 2H, $^3\text{J}8.88$ Hz, $^4\text{J}2.32$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3\text{J}12.76$ Hz, $^4\text{J}2.36$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3\text{J}6.56$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.86-1.79(quin, 4H, $^3\text{J}6.72$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.47-1.32(m, 20H, $10 \times -\text{CH}_2-$), 0.91-0.87(t, 6H, $^3\text{J}6.68$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-nonyloxybenzoyloxy) 2-fluorobenzoate], (4.F.9)

Yield, 63%; m.p. 94°C; $\nu_{\max}$: 2922, 2850, 1732, 1618, 1595, 1436, 1276, 1130 cm^{-1} ; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.02(t, 2H, $^3\text{J}8.64$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}8.36$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 6.81-6.78(dd, 2H, $^3\text{J}8.88$ Hz, $^4\text{J}2.4$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3\text{J}12.74$ Hz, $^4\text{J}2.32$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3\text{J}6.52$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.86-1.79(quin, 4H, $^3\text{J}6.68$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.47-1.32(m, 24H, $12 \times -\text{CH}_2-$), 0.91-0.87(t, 6H, $^3\text{J}6.68$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-decyloxybenzoyloxy) 2-fluorobenzoate], (4.F.10)

Yield, 66%; m.p. 96°C; $\nu_{\max}$: 2924, 2853, 1740, 1732, 1725, 1620, 1576, 1437, 1276, 1128 cm^{-1} ; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.02(t, 2H, $^3\text{J}8.68$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}8.32$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 6.81-6.78(dd, 2H, $^3\text{J}8.88$ Hz, $^4\text{J}2.32$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3\text{J}12.76$ Hz, $^4\text{J}2.36$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3\text{J}6.52$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.86-1.79(quin, 4H, $^3\text{J}6.64$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.47-1.28(m, 28H, $14 \times -\text{CH}_2-$), 0.91-0.87(t, 6H, $^3\text{J}6.64$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-undecyloxybenzoyloxy) 2-fluorobenzoate], (4.F.11)

Yield, 65%; m.p. 78°C; $\nu_{\max}$: 2924, 2854, 1740, 1730, 1725, 1620, 1576, 1437, 1276, 1128 cm^{-1} ; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.02(t, 2H, $^3\text{J}8.64$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}8.36$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 6.81-6.78(dd, 2H, $^3\text{J}8.88$ Hz, $^4\text{J}2.36$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3\text{J}12.76$ Hz, $^4\text{J}2.32$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3\text{J}6.52$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.86-1.79(quin, 4H, $^3\text{J}6.68$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.47-1.28(m, 32H, $16 \times -\text{CH}_2-$), 0.9-0.87(t, 6H, $^3\text{J}6.68$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$); δ_{C} : 165.5, 165.4, 164.2, 162.9, 161.7, 161.6, 161.4, 155.9, 155.8, 151.1, 133.9, 133.5, 129.9, 119.5, 117.9, 115.8, 115.2, 111.6, 111.3, 111.1, 108.9, 103.2, 102.9, 69.0, 31.9, 29.6, 29.4, 28.9, 25.9, 22.7, 14.1

1,3-Phenylene bis[4-(2-fluoro-4-n-dodecyloxybenzoyloxy) 2-fluorobenzoate], (4.F.12)

Yield, 63%; m.p. 97°C; $\nu_{\max}$: 2916, 2851, 1733, 1728, 1620, 1576, 1437, 1276, 1128 cm^{-1} ; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.02(t, 2H, $^3\text{J}_{8.72}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.2}$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 6.81-6.78(dd, 2H, $^3\text{J}_{8.88}$ Hz, $^4\text{J}_{2.28}$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3\text{J}_{12.74}$ Hz, $^4\text{J}_{2.28}$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.86-1.79(quin, 4H, $^3\text{J}_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.47-1.28(m, 36H, $18 \times -\text{CH}_2-$), 0.9-0.87(t, 6H, $^3\text{J}_{6.48}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-tetradecyloxybenzoyloxy) 2-fluorobenzoate], (4.F.13)

Yield, 62%; m.p. 87°C; $\nu_{\max}$: 2916, 2850, 1740, 1728, 1620, 1576, 1437, 1276, 1128 cm^{-1} ; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.02(t, 2H, $^3\text{J}_{8.72}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.2}$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 6.81-6.78(dd, 2H, $^3\text{J}_{8.88}$ Hz, $^4\text{J}_{2.28}$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3\text{J}_{12.74}$ Hz, $^4\text{J}_{2.36}$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.84-1.8(quin, 4H, $^3\text{J}_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.47-1.28(m, 44H, $22 \times -\text{CH}_2-$), 0.9-0.86(t, 6H, $^3\text{J}_{6.6}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-hexadecyloxybenzoyloxy) 2-fluorobenzoate], (4.F.14)

Yield, 66%; m.p. 93.5°C; $\nu_{\max}(\text{KBr})$: 2920, 2851, 1743, 1730, 1615, 1574, 1437, 1276, 1130 cm^{-1} ; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.02(t, 2H, $^3\text{J}_{8.68}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.2}$ Hz, Ar-H), 7.23-7.18(m, 7H, Ar-H), 6.81-6.78(dd, 2H, $^3\text{J}_{8.88}$ Hz, $^4\text{J}_{2.32}$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3\text{J}_{12.76}$ Hz, $^4\text{J}_{2.28}$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.84-1.8(quin, 4H, $^3\text{J}_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.47-1.28(m, 52H, $26 \times -\text{CH}_2-$), 0.9-0.86(t, 6H, $^3\text{J}_{6.4}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-octadecyloxybenzoyloxy) 2-fluorobenzoate], (4.F.15)

Yield, 64%; m.p. 97°C; $\nu_{\max}$: 2914, 2851, 1734, 1728, 1618, 1574, 1462, 1292, 1130 cm^{-1} ; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 8.06-8.02(t, 2H, $^3\text{J}_{8.68}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3\text{J}_{8.0}$ Hz, Ar-H), 7.22-7.18(m, 7H, Ar-H), 6.81-6.78(dd, 2H, $^3\text{J}_{8.88}$ Hz, $^4\text{J}_{2.24}$ Hz, Ar-H), 6.72-6.68(dd, 2H, $^3\text{J}_{12.76}$ Hz, $^4\text{J}_{2.36}$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.84-1.8(quin, 4H, $^3\text{J}_{6.62}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.47-1.28(m, 60H, $30 \times -\text{CH}_2-$), 0.9-0.86(t, 6H, $^3\text{J}_{6.64}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-butyloxybenzoyloxy) 2-fluorobenzoate], (4.G.1)

Yield, 65%; m.p. 144°C; $\nu_{\max}$: 2952, 2852, 1755, 1726, 1616, 1595, 1437, 1230, 1191 cm^{-1} ;
 δ_{H} : 8.21-8.17(m, 2H, Ar-H), 7.97-7.95(d, 2H, $^3J_{8.64}$ Hz, Ar-H), 7.90-7.87(dd, 2H, $^3J_{11.4}$ Hz, $^4J_{1.88}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3J_{8.36}$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 7.07-7.03(t, 2H, $^3J_{8.28}$ Hz, Ar-H), 4.16-4.13(t, 4H, $^3J_{6.48}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.9-1.83(quin, 4H, $^3J_{6.64}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.54-1.49(m, 4H, $2 \times -\text{CH}_2-\text{CH}_3$), 1.02-0.99(t, 6H, $^3J_{7.36}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-pentyloxybenzoyloxy)2-fluorobenzoate],(4.G.2)

Yield, 65%; m.p. 149°C; $\nu_{\max}$: 2952, 2852, 1755, 1726, 1616, 1595, 1437, 1230, 1191 cm^{-1} ;
 δ_{H} : 8.21-8.17(m, 2H, Ar-H), 7.97-7.95(d, 2H, $^3J_{8.64}$ Hz, Ar-H), 7.90-7.87(dd, 2H, $^3J_{11.4}$ Hz, $^4J_{1.88}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3J_{8.36}$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 7.07-7.03(t, 2H, $^3J_{8.28}$ Hz, Ar-H), 4.16-4.13(t, 4H, $^3J_{6.48}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.9-1.83(quin, 4H, $^3J_{6.64}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.54-1.49(m, 8H, $4 \times -\text{CH}_2-\text{CH}_3$), 1.02-0.99(t, 6H, $^3J_{7.36}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-hexyloxybenzoyloxy) 2-fluorobenzoate], (4.G.3)

Yield, 64%; m.p. 129°C; $\nu_{\max}$: 2926, 2850, 1752, 1726, 1616, 1596, 1473, 1230, 1192 cm^{-1} ;
 δ_{H} : 8.21-8.17(m, 2H, Ar-H), 7.97-7.95(d, 2H, $^3J_{8.64}$ Hz, Ar-H), 7.90-7.87(dd, 2H, $^3J_{11.4}$ Hz, $^4J_{1.88}$ Hz, Ar-H), 7.52-7.48(m, 1H, Ar-H), 7.23-7.17(m, 7H, Ar-H), 7.07-7.03(t, 2H, $^3J_{8.28}$ Hz, Ar-H), 4.15-4.12(t, 4H, $^3J_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.9-1.84(quin, 4H, $^3J_{6.72}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.54-1.35(m, 12H, $6 \times -\text{CH}_2-\text{CH}_3$), 0.93-0.9(t, 6H, $^3J_{6.88}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-heptyloxybenzoyloxy)2-fluorobenzoate],(4.G.4)

Yield, 65%; m.p. 107.5°C; $\nu_{\max}$: 2924, 2855, 1753, 1728, 1624, 1598, 1462, 1234, 1192 cm^{-1} ;
 δ_{H} : 8.21-8.17(m, 2H, Ar-H), 7.97-7.95(d, 2H, $^3J_{8.64}$ Hz, Ar-H), 7.90-7.87(dd, 2H, $^3J_{11.4}$ Hz, $^4J_{1.88}$ Hz, Ar-H), 7.52-7.48(t, 1H, $^3J_{8.12}$ Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 7.07-7.03(t, 2H, $^3J_{8.24}$ Hz, Ar-H), 4.15-4.11(t, 4H, $^3J_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.91-1.84(quin, 4H, $^3J_{7.08}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.54-1.32(m, 16H, $8 \times -\text{CH}_2-\text{CH}_3$), 0.92-0.88(t, 6H, $^3J_{6.68}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-octyloxybenzoyloxy) 2-fluorobenzoate], (4.G.5)

Yield, 61%; m.p. 108°C; $\nu_{\max}$: 2924, 2854, 1753, 1728, 1624, 1599, 1462, 1234, 1192 cm^{-1} ;
 δ_{H} : 8.21-8.17(m, 2H, Ar-H), 7.97-7.95(d, 2H, $^3J_{8.64}$ Hz, Ar-H), 7.90-7.87(dd, 2H, $^3J_{11.4}$ Hz,

⁴J1.88 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.12 Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 7.07-7.03(t, 2H, ³J8.32 Hz, Ar-H), 4.15-4.11(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-), 1.91-1.84(quin, 4H, ³J6.72 Hz, 2 × Ar-OCH₂-CH₂-), 1.54-1.3(m, 20H, 10 × -CH₂-CH₃), 0.91-0.88(t, 6H, ³J6.48 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(3-fluoro-4-n-nonyloxybenzoyloxy)2-fluorobenzoate], (4.G.6)

Yield, 63%; m.p. 107°C; $\nu_{\max}$: 2924, 2854, 1750, 1728, 1624, 1599, 1460, 1234, 1192 cm⁻¹; δ_{H} : 8.21-8.17(m, 2H, Ar-H), 7.97-7.95(d, 2H, ³J8.64 Hz, Ar-H), 7.90-7.87(dd, 2H, ³J11.36 Hz, ⁴J2.04 Hz, Ar-H), 7.5-7.48(t, 1H, ³J8.12 Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 7.07-7.03(t, 2H, ³J8.32 Hz, Ar-H), 4.15-4.11(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-), 1.89-1.84(quin, 4H, ³J6.72 Hz, 2 × Ar-OCH₂-CH₂-), 1.54-1.3(m, 24H, 12 × -CH₂-CH₃), 0.9-0.87(t, 6H, ³J6.56 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(3-fluoro-4-n-decyloxybenzoyloxy) 2-fluorobenzoate], (4.G.7)

Yield, 68%; m.p. 105°C; $\nu_{\max}(\text{KBr})$: 2920, 2851, 1740, 1732, 1616, 1591, 1421, 1234, 1190 cm⁻¹; δ_{H} : 8.21-8.17(m, 2H, Ar-H), 7.97-7.95(d, 2H, ³J9.12 Hz, Ar-H), 7.90-7.87(dd, 2H, ³J11.36 Hz, ⁴J2.0 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.2 Hz, Ar-H), 7.23-7.16(m, 7H, Ar-H), 7.07-7.03(t, 2H, ³J8.28 Hz, Ar-H), 4.15-4.11(t, 4H, ³J6.6 Hz, 2 × Ar-OCH₂-), 1.89-1.84(quin, 4H, ³J7.12 Hz, 2 × Ar-OCH₂-CH₂-), 1.54-1.35(m, 28H, 14 × -CH₂-CH₃), 0.9-0.87(t, 6H, ³J6.48 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(3-fluoro-4-n-undecyloxybenzoyloxy) 2-fluorobenzoate], (4.G.8)

Yield, 66%; m.p. 106°C; $\nu_{\max}$: 2920, 2850, 1740, 1730, 1616, 1591, 1421, 1234, 1190 cm⁻¹; δ_{H} : 8.21-8.17(m, 2H, Ar-H), 7.97-7.95(d, 2H, ³J8.68 Hz, Ar-H), 7.90-7.87(dd, 2H, ³J11.34 Hz, ⁴J1.84 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.16 Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 7.07-7.03(t, 2H, ³J8.32 Hz, Ar-H), 4.15-4.11(t, 4H, ³J6.6 Hz, 2 × Ar-OCH₂-), 1.89-1.84(quin, 4H, ³J7.12 Hz, 2 × Ar-OCH₂-CH₂-), 1.54-1.35(m, 32H, 16 × -CH₂-CH₃), 0.9-0.87(t, 6H, ³J6.44 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(3-fluoro-4-n-dodecyloxybenzoyloxy) 2-fluorobenzoate], (4.G.9)

Yield, 64%; m.p. 99.5°C; $\nu_{\max}$: 2922, 2854, 1742, 1724, 1614, 1591, 1421, 1234, 1190 cm⁻¹; δ_{H} : 8.21-8.17(m, 2H, Ar-H), 7.97-7.95(d, 2H, ³J9.12 Hz, Ar-H), 7.90-7.87(dd, 2H, ³J11.36 Hz, ⁴J2.0 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.2 Hz, Ar-H), 7.25-7.17(m, 7H, Ar-H), 7.07-7.03(t, 2H, ³J8.32 Hz, Ar-H), 4.15-4.11(t, 4H, ³J6.6 Hz, 2 × Ar-OCH₂-), 1.89-1.84(quin, 4H, ³J7.16

Hz, 2 × Ar-OCH₂-CH₂-), 1.54-1.35(m, 36H, 18 × -CH₂-CH₃), 0.9-0.87(t, 6H, ³J6.44 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(3-fluoro-4-n-tetradecyloxybenzoyloxy) 2-fluorobenzoate], (4.G.10)

Yield, 67%; m.p. 103°C; $\nu_{\max}$: 2922, 2852, 1740, 1724, 1612, 1590, 1421, 1234, 1190 cm⁻¹; δ_{H} : 8.21-8.17(m, 2H, Ar-H), 7.97-7.95(d, 2H, ³J8.72 Hz, Ar-H), 7.90-7.87(dd, 2H, ³J11.36 Hz, ⁴J1.84 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.24 Hz, Ar-H), 7.25-7.17(m, 7H, Ar-H), 7.07-7.03(t, 2H, ³J8.32 Hz, Ar-H), 4.15-4.11(t, 4H, ³J6.6 Hz, 2 × Ar-OCH₂-), 1.91-1.26(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-), 1.54-1.35(m, 44H, 22 × -CH₂-CH₃), 0.9-0.87(t, 6H, ³J6.48 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(3-fluoro-4-n-hexadecyloxybenzoyloxy) 2-fluorobenzoate], (4.G.11)

Yield, 66%; m.p. 105°C; $\nu_{\max}$ (KBr): 2918, 2849, 1740, 1732, 1612, 1591, 1421, 1232, 1190 cm⁻¹; δ_{H} : 8.21-8.17(m, 2H, Ar-H), 7.97-7.95(d, 2H, ³J8.70 Hz, Ar-H), 7.90-7.87(dd, 2H, ³J11.34 Hz, ⁴J2.0 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.24 Hz, Ar-H), 7.25-7.17(m, 7H, Ar-H), 7.07-7.03(t, 2H, ³J8.30 Hz, Ar-H), 4.15-4.11(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-), 1.91-1.26(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-), 1.54-1.35(m, 52H, 26 × -CH₂-CH₃), 0.9-0.87(t, 6H, ³J6.48 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(3-fluoro-4-n-octadecyloxybenzoyloxy) 2-fluorobenzoate], (4.G.12)

Yield, 63%; m.p. 107°C; $\nu_{\max}$ (KBr): 2918, 2849, 1742, 1722, 1614, 1591, 1421, 1229, 1192 cm⁻¹; δ_{H} : 8.21-8.17(m, 2H, Ar-H), 7.97-7.95(d, 2H, ³J8.6 Hz, Ar-H), 7.90-7.87(dd, 2H, ³J11.36 Hz, ⁴J1.96 Hz, Ar-H), 7.52-7.48(t, 1H, ³J8.24 Hz, Ar-H), 7.23-7.17(m, 7H, Ar-H), 7.07-7.03(t, 2H, ³J8.36 Hz, Ar-H), 4.15-4.12(t, 4H, ³J6.52 Hz, 2 × Ar-OCH₂-), 1.91-1.84(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-), 1.5-1.45(m, 60H, 30 × -CH₂-CH₃), 0.9-0.86(t, 6H, ³J6.48 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(3-fluoro-4-n-eicocyloxybenzoyloxy) 2-fluorobenzoate], (4.G.13)

Yield, 65%; m.p. 108°C; $\nu_{\max}$ (KBr): 2918, 2849, 1742, 1722, 1614, 1591, 1421, 1229, 1192 cm⁻¹; δ_{H} : 8.20-8.16(m, 2H, Ar-H), 7.97-7.95(d, 2H, ³J8.56 Hz, Ar-H), 7.90-7.87(dd, 2H, ³J11.36 Hz, ⁴J1.96 Hz, Ar-H), 7.51-7.47(t, 1H, ³J8.24 Hz, Ar-H), 7.20-7.17(m, 7H, Ar-H), 7.07-7.03(t, 2H, ³J8.2 Hz, Ar-H), 4.15-4.12(t, 4H, ³J6.48 Hz, 2 × Ar-OCH₂-), 1.91-1.84(quin, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-CH₂-), 1.5-1.2(m, 68H, 34 × -CH₂-CH₃), 0.9-0.86(t, 6H, ³J6.32 Hz, 2 × -CH₂-CH₃).

1,3-Phenylene bis[4-(2-fluoro-4-n-hexyloxybenzoyloxy) 3-fluorobenzoate], (4.H.1)

Yield, 65%; m.p. 114°C; $\nu_{\max}$: 2925, 2850, 1745, 1726, 1615, 1598, 1476, 1230, 1192 cm^{-1} ; δ_{H} : 8.09-8.02(m, 6H, Ar-H), 7.53-7.42(m, 3H, Ar-H), 7.2-7.17(m, 3H, Ar-H), 6.8-6.78 (dd, 2H, $^3\text{J}8.9$ Hz, $^4\text{J}2.2$ Hz, Ar-H), 6.72-6.69 (dd, 2H, $^3\text{J}12.66$ Hz, $^4\text{J}2.16$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3\text{J}6.48$ Hz, $2 \times \text{Ar-OCH}_2$ -), 1.86-1.80(quin, 4H, $^3\text{J}6.64$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2$ -), 1.5-1.33(m, 12H, $6 \times \text{-CH}_2\text{-CH}_3$), 0.9-0.86(t, 6H, $^3\text{J}6.56$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(2-fluoro-4-n-tetradecyloxybenzoyloxy) 3-fluorobenzoate], (4.H.2)

Yield, 68%; m.p. 113°C; $\nu_{\max}$: 2925, 2852, 1742, 1724, 1612, 1599, 1478, 1230, 1190 cm^{-1} ; δ_{H} : 8.09-8.02(m, 6H, Ar-H), 7.53-7.42(m, 3H, Ar-H), 7.2-7.16(m, 3H, Ar-H), 6.8-6.78 (dd, 2H, $^3\text{J}8.92$ Hz, $^4\text{J}2.0$ Hz, Ar-H), 6.72-6.69 (dd, 2H, $^3\text{J}12.6$ Hz, $^4\text{J}2.06$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3\text{J}6.46$ Hz, $2 \times \text{Ar-OCH}_2$ -), 1.86-1.80(quin, 4H, $^3\text{J}6.64$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2$ -), 1.5-1.33(m, 44H, $22 \times \text{-CH}_2\text{-CH}_3$), 0.9-0.86(t, 6H, $^3\text{J}6.56$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-hexyloxybenzoyloxy) 3-fluorobenzoate], (4.I.1)

Yield, 61%; m.p. 160°C; $\nu_{\max}$: 2924, 2852, 1740, 1725, 1615, 1599, 1476, 1230, 1190 cm^{-1} ; δ_{H} : 8.0-7.96(m, 4H, Ar-H), 7.92-7.90(d, 2H, $^3\text{J}8.6$ Hz, Ar-H), 7.86-7.83(d, 2H, $^3\text{J}11.4$ Hz, Ar-H), 7.46-7.42 (t, 1H, $^3\text{J}7.64$ Hz, Ar-H), 7.38-7.34 (t, 2H, $^3\text{J}7.64$ Hz, Ar-H), 7.18-7.11(m, 3H, Ar-H), 7.0-6.96(t, 3H, $^3\text{J}8.36$ Hz, Ar-H), 4.08-4.04(t, 4H, $^3\text{J}6.52$ Hz, $2 \times \text{Ar-OCH}_2$ -), 1.84-1.80(quin, 4H, $^3\text{J}6.64$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2$ -), 1.43-1.14(m, 12H, $6 \times \text{-CH}_2\text{-CH}_3$), 0.82-0.79(t, 6H, $^3\text{J}6.04$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(3-fluoro-4-n-tetradecyloxybenzoyloxy) 3-fluorobenzoate], (4.I.2)

Yield, 68%; m.p. 152°C; $\nu_{\max}$: 2925, 2850, 1740, 1722, 1610, 1599, 1478, 1230, 1190 cm^{-1} ; δ_{H} : 8.0-7.96(m, 4H, Ar-H), 7.92-7.90(d, 2H, $^3\text{J}8.56$ Hz, Ar-H), 7.86-7.83(d, 2H, $^3\text{J}11.0$ Hz, Ar-H), 7.46-7.42 (t, 1H, $^3\text{J}7.6$ Hz, Ar-H), 7.38-7.34 (t, 2H, $^3\text{J}7.6$ Hz, Ar-H), 7.18-7.11(m, 3H, Ar-H), 7.0-6.96(t, 3H, $^3\text{J}8.3$ Hz, Ar-H), 4.08-4.04(t, 4H, $^3\text{J}6.56$ Hz, $2 \times \text{Ar-OCH}_2$ -), 1.84-1.80(quin, 4H, $^3\text{J}6.52$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2$ -), 1.43-1.14(m, 44H, $22 \times \text{-CH}_2\text{-CH}_3$), 0.82-0.79(t, 6H, $^3\text{J}6.0$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

1,3-Phenylene bis[4-(4-n-octylbenzoyloxy) 2-fluorobenzoate], (4.J.1)

Yield, 65%; m.p. 100.5°C; $\nu_{\max}$: 2924, 2854, 1744, 1722, 1607, 1458, 1236, 1128 cm^{-1} ; δ_{H} : 8.21-8.17(m, 2H, Ar-H), 8.11-8.09(d, 4H, $^3\text{J}8.08$ Hz, Ar-H), 7.52-7.48 (t, 1H, $^3\text{J}8.2$ Hz, Ar-H), 7.35-7.33(d, 4H, $^3\text{J}8.12$ Hz, Ar-H), 7.24-7.17(m, 7H, Ar-H), 2.73-2.69(t, 4H, $^3\text{J}7.48$ Hz, 2

$\times$ Ar-CH₂-), 1.67-1.63(quin, 4H, ³J6.48 Hz, 2 $\times$ Ar-CH₂-CH₂), 1.32-1.27(m, 20H, 10 $\times$ -CH₂-), 0.9-0.87(t, 6H, ³J6.52 Hz, 2 $\times$ -CH₂-CH₃).

1,3-Phenylene bis[4-(4-n-nonylbenzoyloxy) 2-fluorobenzoate], (4.J.2)

Yield, 68%; m.p. 104.5°C; $\nu_{\max}$: 2924, 2852, 1742, 1720, 1605, 1456, 1236, 1128 cm⁻¹; δ_{H} : 8.21-8.17(m, 2H, Ar-H), 8.11-8.09(d, 4H, ³J8.0 Hz, Ar-H), 7.52-7.48 (t, 1H, ³J8.2 Hz, Ar-H), 7.35-7.33(d, 4H, ³J8.1 Hz, Ar-H), 7.24-7.17(m, 7H, Ar-H), 2.73-2.69(t, 4H, ³J7.48 Hz, 2 $\times$ Ar-CH₂-), 1.67-1.63(quin, 4H, ³J6.4 Hz, 2 $\times$ Ar-CH₂-CH₂), 1.32-1.27(m, 24H, 12 $\times$ -CH₂-), 0.9-0.87(t, 6H, ³J6.52 Hz, 2 $\times$ -CH₂-CH₃).

1,3-Phenylene bis[4-(4-n-decylbenzoyloxy) 2-fluorobenzoate], (4.J.3)

Yield, 70%; m.p. 102.5°C; $\nu_{\max}$: 2925, 2852, 1742, 1720, 1605, 1456, 1236, 1130 cm⁻¹; δ_{H} : 8.21-8.16(m, 2H, Ar-H), 8.11-8.09(d, 4H, ³J8.1 Hz, Ar-H), 7.52-7.48 (t, 1H, ³J8.24 Hz, Ar-H), 7.35-7.33(d, 4H, ³J8.1 Hz, Ar-H), 7.24-7.17(m, 7H, Ar-H), 2.73-2.69(t, 4H, ³J7.45 Hz, 2 $\times$ Ar-CH₂-), 1.67-1.63(quin, 4H, ³J6.4 Hz, 2 $\times$ Ar-CH₂-CH₂), 1.32-1.27(m, 28H, 14 $\times$ -CH₂-), 0.9-0.87(t, 6H, ³J6.56 Hz, 2 $\times$ -CH₂-CH₃).

1,3-Phenylene bis[4-(4-n-undecylbenzoyloxy) 2-fluorobenzoate], (4.J.4)

Yield, 67%; m.p. 101.5°C; $\nu_{\max}$: 2924, 2852, 1743, 1732, 1610, 1458, 1244, 1138 cm⁻¹; δ_{H} : 8.21-8.16(m, 2H, Ar-H), 8.11-8.08(d, 4H, ³J8.16 Hz, Ar-H), 7.52-7.48 (t, 1H, ³J8.29 Hz, Ar-H), 7.35-7.33(d, 4H, ³J8.17 Hz, Ar-H), 7.24-7.17(m, 7H, Ar-H), 2.73-2.69(t, 4H, ³J7.56 Hz, 2 $\times$ Ar-CH₂-), 1.67-1.63(quin, 4H, ³J6.56 Hz, 2 $\times$ Ar-CH₂-CH₂), 1.32-1.27(m, 32H, 16 $\times$ -CH₂-), 0.9-0.87(t, 6H, ³J6.56 Hz, 2 $\times$ -CH₂-CH₃).

1,3-Phenylene bis[4-(4-n-dodecylbenzoyloxy) 2-fluorobenzoate], (4.J.5)

Yield, 65%; m.p. 99.5°C; $\nu_{\max}$: 2922, 2852, 1745, 1732, 1612, 1466, 1256, 1138 cm⁻¹; δ_{H} : 8.21-8.16(m, 2H, Ar-H), 8.11-8.09(d, 4H, ³J8.24 Hz, Ar-H), 7.51-7.47 (t, 1H, ³J8.36 Hz, Ar-H), 7.34-7.32(d, 4H, ³J8.24 Hz, Ar-H), 7.23-7.16(m, 7H, Ar-H), 2.72-2.68(t, 4H, ³J7.6 Hz, 2 $\times$ Ar-CH₂-), 1.7-1.6(quin, 4H, ³J6.56 Hz, 2 $\times$ Ar-CH₂-CH₂-), 1.31-1.22(m, 36H, 18 $\times$ -CH₂-), 0.89-0.86(t, 6H, ³J6.64 Hz, 2 $\times$ -CH₂-CH₃).

1,3-Phenylene bis[4-(4-n-tetradecylbenzoyloxy) 2-fluorobenzoate], (4.J.6)

Yield, 67%; m.p. 97.5°C; $\nu_{\max}$: 2920, 2851, 1742, 1730, 1612, 1470, 1248, 1140 cm⁻¹; δ_{H} : 8.21-8.16(m, 2H, Ar-H), 8.11-8.09(d, 4H, ³J8.28 Hz, Ar-H), 7.51-7.47 (t, 1H, ³J8.4 Hz, Ar-H), 7.34-7.32(d, 4H, ³J8.28 Hz, Ar-H), 7.23-7.16(m, 7H, Ar-H), 2.72-2.68(t, 4H, ³J7.56 Hz, 2

$\times$ Ar-CH₂-), 1.7-1.6(quin, 4H, ³J6.52 Hz, 2 $\times$ Ar-CH₂-CH₂-), 1.31-1.22(m, 44H, 22 $\times$ -CH₂-), 0.89-0.86(t, 6H, ³J6.6 Hz, 2 $\times$ -CH₂-CH₃).

1,3-Phenylene bis[4-(4-n-hexadecylbenzoyloxy) 2-fluorobenzoate], (4.J.7)

Yield, 68%; m.p. 96.5°C; $\nu_{\max}$: 2920, 2851, 1740, 1728, 1610, 1470, 1250, 1140 cm⁻¹; δ_{H} : 8.21-8.17(m, 2H, Ar-H), 8.12-8.09(d, 4H, ³J8.2 Hz, Ar-H), 7.52-7.48 (t, 1H, ³J8.32 Hz, Ar-H), 7.35-7.33(d, 4H, ³J8.2 Hz, Ar-H), 7.24-7.17(m, 7H, Ar-H), 2.73-2.69(t, 4H, ³J7.64 Hz, 2 $\times$ Ar-CH₂-), 1.67-1.57(quin, 4H, ³J6.72 Hz, 2 $\times$ Ar-CH₂-CH₂-), 1.42-1.05(m, 52H, 26 $\times$ -CH₂-), 0.89-0.86(t, 6H, ³J6.56 Hz, 2 $\times$ -CH₂-CH₃).

1,3-Phenylene bis[4-(4-n-tetradecylbenzoyloxy) 3-fluorobenzoate], (4.K.1)

Yield, 70%; m.p. 97°C; $\nu_{\max}$: 2920, 2852, 1740, 1610, 1458, 1259, 1128 cm⁻¹; δ_{H} : 8.14-8.12(d, 4H, ³J8.2 Hz, Ar-H), 8.08-8.04(m, 4H, Ar-H), 7.54-7.42(m, 3H, Ar-H), 7.35-7.33(d, 4H, ³J8.24 Hz, Ar-H), 7.2-7.18(m, 3H, Ar-H), 2.73-2.69(t, 4H, ³J7.68 Hz, 2 $\times$ Ar-CH₂-), 1.66-1.64(quin, 4H, ³J7.4 Hz, 2 $\times$ Ar-CH₂-CH₂-), 1.32-1.26(m, 44H, 22 $\times$ -CH₂-), 0.89-0.86(t, 6H, ³J6.52 Hz, 2 $\times$ -CH₂-CH₃).

1,3-Phenylene bis[4-(4-n-pentyloxybenzoyloxy) 3-chlorobenzoate], (4.L.1)

Yield, 70%; m.p. 98.5°C; $\nu_{\max}$: 2924, 2854, 1743, 1724, 1607, 1510, 1460, 1269, 1124 cm⁻¹; δ_{H} : 8.34-8.33(d, 2H, ⁴J2.04 Hz, Ar-H), 8.21-8.16(m, 6H, Ar-H), 7.53-7.46(m, 3H, Ar-H), 7.2-7.18(m, 3H, Ar-H), 7.01-6.99(d, 4H, ³J8.96 Hz, Ar-H), 4.08-4.05(t, 4H, ³J6.56 Hz, 2 $\times$ Ar-OCH₂-), 1.87-1.80(quin, 4H, ³J6.64 Hz, 2 $\times$ Ar-OCH₂-CH₂-), 1.51-1.36(m, 8H, 4 $\times$ -CH₂-), 0.97-0.94(t, 6H, ³J7.12 Hz, 2 $\times$ -CH₂-CH₃). Elemental analysis: C₄₄H₄₀O₁₀Cl₂ requires, C, 66.07; H, 5.04%; found, C, 66.05; H, 5.08%.

1,3-Phenylene bis[4-(4-n-octyloxybenzoyloxy) 3-chlorobenzoate], (4.L.2)

Yield, 72%; m.p. 96°C; $\nu_{\max}$: 2924, 2855, 1738, 1608, 1597, 1460, 1271, 1140 cm⁻¹; δ_{H} : 8.34-8.33(d, 2H, ⁴J2.0 Hz, Ar-H), 8.2-8.16(m, 6H, Ar-H), 7.54-7.46(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.99(d, 4H, ³J8.92 Hz, Ar-H), 4.08-4.05(t, 4H, ³J6.52 Hz, 2 $\times$ Ar-OCH₂-), 1.87-1.80(quin, 4H, ³J6.64 Hz, 2 $\times$ Ar-OCH₂-CH₂-), 1.51-1.30(m, 20H, 10 $\times$ -CH₂-), 0.91-0.88(t, 6H, ³J6.64 Hz, 2 $\times$ -CH₂-CH₃). Elemental analysis: C₅₀H₅₂O₁₀Cl₂ requires, C, 67.93; H, 5.93%; found, C, 67.57; H, 5.95%.

1,3-Phenylene bis[4-(4-n-nonyloxybenzoyloxy) 3-chlorobenzoate], (4.L.3)

Yield, 69%; m.p. 96.5°C; $\nu_{\max}$: 2924, 2855, 1743, 1728, 1605, 1599, 1460, 1269, 1142 cm^{-1} ; δ_{H} : 8.34-8.33(d, 2H, $^4J_{2.0}$ Hz, Ar-H), 8.2-8.16(m, 6H, Ar-H), 7.54-7.46(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.99(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.08-4.05(t, 4H, $^3J_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.87-1.80(quin, 4H, $^3J_{6.64}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.51-1.30(m, 24H, $12 \times -\text{CH}_2-$), 0.91-0.88(t, 6H, $^3J_{6.64}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$). Elemental analysis: $\text{C}_{52}\text{H}_{56}\text{O}_{10}\text{Cl}_2$ requires, C, 68.48; H, 6.18%; found, C, 68.57; H, 6.15%.

1,3-Phenylene bis[4-(4-n-decyloxybenzoyloxy) 3-chlorobenzoate], (4.L.4)

Yield, 70%; m.p. 101°C; $\nu_{\max}$: 2924, 2854, 1740, 1725, 1605, 1599, 1460, 1269, 1140 cm^{-1} ; δ_{H} : 8.34-8.33(d, 2H, $^4J_{2.04}$ Hz, Ar-H), 8.2-8.16(m, 6H, Ar-H), 7.54-7.46(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.99(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 4.08-4.05(t, 4H, $^3J_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.87-1.80(quin, 4H, $^3J_{6.64}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.51-1.30(m, 28H, $14 \times -\text{CH}_2-$), 0.91-0.88(t, 6H, $^3J_{6.64}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$). Elemental analysis: $\text{C}_{54}\text{H}_{60}\text{O}_{10}\text{Cl}_2$ requires, C, 68.99; H, 6.43%; found, C, 68.73; H, 6.55%.

1,3-Phenylene bis[4-(4-n-undecyloxybenzoyloxy) 3-chlorobenzoate], (4.L.5)

Yield, 68%; m.p. 101.5°C; $\nu_{\max}$: 2924, 2853, 1742, 1728, 1605, 1599, 1458, 1269, 1140 cm^{-1} ; δ_{H} : 8.34-8.33(d, 2H, $^4J_{2.04}$ Hz, Ar-H), 8.2-8.16(m, 6H, Ar-H), 7.54-7.46(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.99(d, 4H, $^3J_{8.96}$ Hz, Ar-H), 4.08-4.05(t, 4H, $^3J_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.87-1.80(quin, 4H, $^3J_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.51-1.30(m, 32H, $16 \times -\text{CH}_2-$), 0.9-0.87(t, 6H, $^3J_{6.72}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$). Elemental analysis: $\text{C}_{56}\text{H}_{64}\text{O}_{10}\text{Cl}_2$ requires, C, 69.47; H, 6.66%; found, C, 69.28; H, 6.69%.

1,3-Phenylene bis[4-(4-n-dodecyloxybenzoyloxy) 3-chlorobenzoate], (4.L.6)

Yield, 66%; m.p. 106.5°C; $\nu_{\max}$: 2924, 2854, 1740, 1725, 1605, 1599, 1456, 1269, 1142 cm^{-1} ; δ_{H} : 8.34-8.33(d, 2H, $^4J_{2.04}$ Hz, Ar-H), 8.2-8.16(m, 6H, Ar-H), 7.54-7.34(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.99(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 4.08-4.05(t, 4H, $^3J_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.87-1.80(quin, 4H, $^3J_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.51-1.32(m, 36H, $18 \times -\text{CH}_2-$), 0.9-0.87(t, 6H, $^3J_{6.56}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$). Elemental analysis: $\text{C}_{58}\text{H}_{68}\text{O}_{10}\text{Cl}_2$ requires, C, 69.93; H, 6.88%; found, C, 70.1; H, 6.93%.

1,3-Phenylene bis[4-(4-n-tetradecyloxybenzoyloxy) 3-chlorobenzoate], (4.L.7)

Yield, 69%; m.p. 109°C; $\nu_{\max}$: 2922, 2852, 1746, 1728, 1605, 1599, 1456, 1271, 1142 cm^{-1} ; δ_{H} : 8.34-8.33(d, 2H, $^4J_{2.04}$ Hz, Ar-H), 8.2-8.16(m, 6H, Ar-H), 7.54-7.34(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.99(d, 4H, $^3J_{8.96}$ Hz, Ar-H), 4.08-4.05(t, 4H, $^3J_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.87-1.80(quin, 4H, $^3J_{6.68}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.51-1.32(m, 44H, $22 \times -\text{CH}_2-$), 0.9-0.87(t, 6H, $^3J_{6.68}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$). Elemental analysis: $\text{C}_{62}\text{H}_{76}\text{O}_{10}\text{Cl}_2$ requires, C, 70.77; H, 7.28%; found, C, 71.0; H, 7.44%.

1,3-Phenylene bis[4-(4-n-octadecyloxybenzoyloxy) 3-chlorobenzoate], (4.L.8)

Yield, 71%; m.p. 94.5°C; $\nu_{\max}$: 2920, 2851, 1736, 1728, 1605, 1599, 1456, 1270, 1142 cm^{-1} ; δ_{H} : 8.34-8.33(d, 2H, $^4J_{2.0}$ Hz, Ar-H), 8.2-8.16(m, 6H, Ar-H), 7.54-7.34(m, 3H, Ar-H), 7.21-7.18(m, 3H, Ar-H), 7.01-6.99(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 4.08-4.04(t, 4H, $^3J_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2-$), 1.87-1.80(quin, 4H, $^3J_{6.72}$ Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-$), 1.51-1.32(m, 60H, $30 \times -\text{CH}_2-$), 0.9-0.86(t, 6H, $^3J_{6.6}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$). Elemental analysis: $\text{C}_{70}\text{H}_{92}\text{O}_{10}\text{Cl}_2$ requires, C, 72.2; H, 7.96%; found, C, 72.6; H, 8.16%.