

Chapter - 2

Synthesis and mesomorphic properties of

- (i) 2,7-Naphthylene bis [4-(4-n-alkylbenzoyloxy)benzoates]
(Series-2.I)**
- (ii) 2,7-Naphthylene bis [4-(4-n-alkylbenzoyloxy)2-fluorobenzoates]
(Series-2.II)**
- (iii) 2,7-Naphthylene bis [4-(4-n-alkylbenzoyloxy)3-fluorobenzoates]
(Series-2.III)**
- (iv) 2,7-Naphthylene bis [4-(4-n-alkoxybenzoyloxy)benzoates]
(Series-2.IV)**
- (v) 2,7-Naphthylene bis [4-(4-n-alkoxybenzoyloxy)2-fluorobenzoates]
(Series-2.V)**
- (vi) 2,7-Naphthylene bis [4-(4-n-alkoxybenzoyloxy)3-fluorobenzoates]
(Series-2.VI)**
- (vii) 2,7-Naphthylene bis [4-(2-fluoro-4-n-alkoxybenzoyloxy)benzoates]
(Series-2.VII)**
- (viii) 2,7-Naphthylene bis [4-(3-fluoro-4-n-alkoxybenzoyloxy)benzoates]
(Series-2.VIII)**

A brief introduction to the mesomorphic properties of banana-shaped compounds derived from 2,7-dihydroxynaphthalene

Ferro- and / or antiferro-electricity have been demonstrated in chiral liquid crystals for a long time. The possibility of obtaining longitudinal ferro- or antiferro-electric liquid crystals in the absence of molecular chirality have also been predicted theoretically [75, 76] which further stimulated the study of liquid crystals. The first experimental approach was by Tournilhac *et al.* [77] who reported a ferroelectric smectic liquid crystal which is formed by electrostatically favoured non-centrosymmetric arrangement of polyphilic achiral molecules. Later, Watanabe *et al.* [78] reported other examples of some main chain liquid crystal polymers which formed ferroelectric smectic liquid crystal. This was followed by the discovery [20] of ferroelectricity in banana liquid crystals. This has been attributed to the close packing of polar bent-core molecules into smectic layers which produce a layer polarization along the bent-direction and which can be reversed by reversing the polarity of the applied field. In addition, the tilt of BC molecules with respect to the layer normal further reduces the over all symmetry of the mesophase [28]. Since then many achiral compounds have been designed, synthesized and their mesomorphic properties have been investigated by several groups [28, 32] from the stand point of both a fundamental understanding of molecular arrangement within the mesophase and of their possible use in technological applications. The mesophases generated from bent-core molecules are not miscible with the known calamitic liquid crystals. Hence a new nomenclature viz. B₁, B₂,.....B₇, B₈ etc., have been adopted to differentiate these mesophases from the others. Among the B-phases, the B₂ phase is well studied because of the interesting electro-optical switching properties it exhibits.

Banana-shaped compounds containing 2,7-dihydroxynaphthalene as the angular central core have been synthesized and are very limited [32, 42, 63, 64, 65, 79]. Shen *et al.* [34] reported the first banana-shaped compound derived from 2,7-dihydroxynaphthalene viz. naphthylene-2,7-diyl bis[4-(5-hexylpyrimidin-2-yl)benzoate] without any mesomorphic properties (m.p. 215°C). However, Weissflog *et al.* [32] reported a banana-shaped compound containing 2,7-dihydroxynaphthalene central core which exhibits a B₁ phase. Recently, Watanabe *et al.* [63, 64, 65, 79] also reported banana-shaped compounds based on 2,7-dihydroxynaphthalene central unit containing Schiff's base linking groups on the arms viz. 2,7-naphthalene bis [4-(4-n-alkoxyphenyliminomethyl)benzoates]. The smectic phases obtained in this novel series of compounds have been designated as Sm1, Sm2 and Sm3 respectively. From XRD

experiments, they have shown that the highest temperature Sm1 phase is a simple smectic phase and the other two low temperature phases namely, Sm2 and Sm3 are ordered phases which are indicated by the additional reflections in the wide-angle region of the X-ray diffraction patterns. In other words, positional ordering was also observed within the smectic layers. The high temperature Sm1 phase shows the following very interesting optical textures. On cooling the isotropic liquid, several small fractal nuclei develop which coalesce to form domains. Interestingly, two types of domains exist and they are separated by boundaries. This can be easily recognized by rotating either the polarizer or analyzer from the crossed position in which transmittance of light from one domain is increased by rotating the polarizer and vice-versa. Also, the mesophase exists with a weak birefringence under a polarizing microscope. The circular dichroism (CD) experiments reveal that these are chiral domains of opposite handedness, which are spontaneously formed from the isotropic liquid. The addition of chiral dopant viz. 2,7-naphthalene bis [4-{4(2-methylbutoxy)phenyliminomethyl}benzoate] to such a medium, results in the occurrence of only one type of handedness as confirmed by circular dichroism measurements. They have also speculated that the origin of helical domains may be due to the conformational twist of bent-core molecules.

There are only two examples of achiral bent-core compounds known to exhibit liquid crystalline phases which are derived from 2,7-dihydroxynaphthalene [32, 79] and the other one is non-mesomorphic [42]. Since there were not many compounds having this central unit, we decided to synthesize several homologous series of esters using 2,7-dihydroxynaphthalene as the central angular unit and carried out a systematic examination of their mesomorphic properties.

The XRD and polarization measurements were carried out using the experimental set-up as shown in figures 2.1a and 2.1b respectively (see experimental). These two general methods have been mainly used to identify the mesophases for most of the compounds described in this thesis.

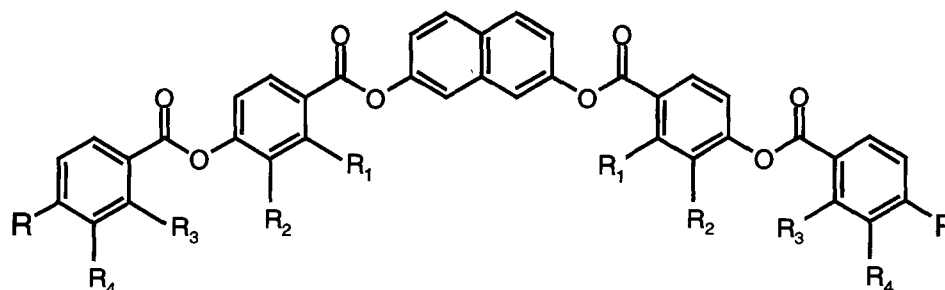
Importance of fluorine as a lateral substituent:

The effect of fluorine substituent has been extensively studied in calamitic liquid crystals for example, in order to reduce the transition temperatures and to modify the mesomorphic behaviour. In order to investigate the influence of fluorine in banana liquid crystals, we have systematically studied several homologous series which are described in this thesis. Fluorine (1.47Å) was considered as an important lateral substituent as it has a size similar to that of

hydrogen (1.2Å) and interestingly it is the most electronegative element. It has been reported that there are two important factors for the occurrence of banana phases. (i) Repartition of charges [59] and (ii) bending angle [48]. By choosing suitable polar lateral substituents, one can vary the above factors, which result in a change of mesomorphic behaviour. A fluorine substituent appears to influence greatly on the nature of mesophase exhibited by the parent compounds which sometimes results in rich polymesomorphism [41]. The synthesis and mesomorphic properties of several homologous series of compounds substituted by a fluorine in different positions of the arms of the bent-core compounds are discussed in this thesis.

Results and discussion

All the compounds are esters having the general molecular structure shown below.



$$R = C_nH_{2n+1} / OC_nH_{2n+1}$$

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

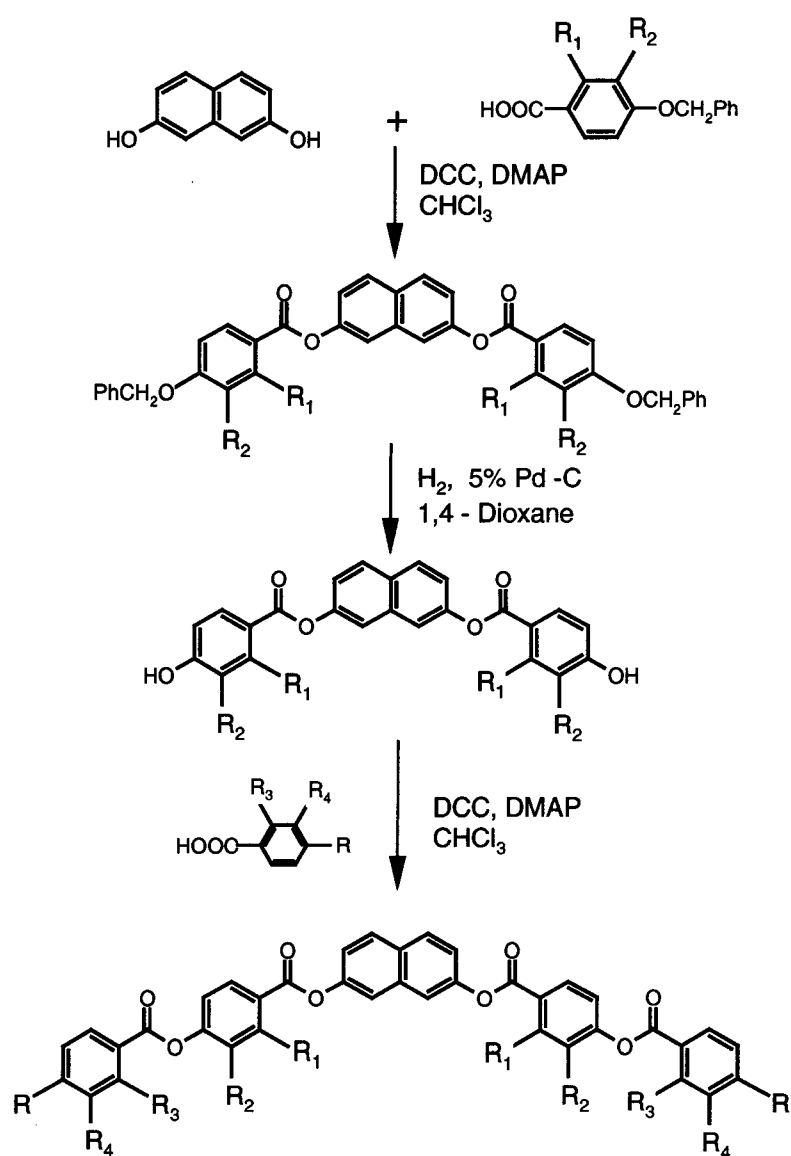
$R_1=H, R_2=H, R_3=H, R_4=H$	Series-2.I	(n-alkyl)
$R_1=F, R_2=H, R_3=H, R_4=H$	Series-2.II	(n-alkyl)
$R_1=H, R_2=F, R_3=H, R_4=H$	Series-2.III	(n-alkyl)
$R_1=H, R_2=H, R_3=H, R_4=H$	Series-2.IV	(n-alkoxy)
$R_1=F, R_2=H, R_3=H, R_4=H$	Series-2.V	(n-alkoxy)
$R_1=H, R_2=F, R_3=H, R_4=H$	Series-2.VI	(n-alkoxy)
$R_1=H, R_2=H, R_3=F, R_4=H$	Series-2.VII	(n-alkoxy)
$R_1=H, R_2=H, R_3=H, R_4=F$	Series-2.VIII	(n-alkoxy)

Structure 2.I

The bent-core compounds belonging to the eight homologous series, viz. series **2.I**, **2.II**, **2.III**, **2.IV**, **2.V**, **2.VI**, **2.VII** and **2.VIII** were prepared following a general synthetic pathway shown in scheme 2.1. The commercial 2,7-dihydroxynaphthalene obtained from Fluka, Switzerland, was purified by column chromatography and crystallized. 4-Benzyloxybenzoic

acid was prepared following a procedure described in the literature [80]. 2-Fluoro-4-hydroxybenzoic acid and 3-fluoro-4-hydroxybenzoic acid were prepared according to a procedure described earlier [81, 82]. 2-Fluoro-4-benzyloxybenzoic acid and 3-fluoro-4-benzyloxybenzoic acid were prepared from the corresponding hydroxy compounds using a procedure similar to that described for 4-benzyloxybenzoic acid. The synthetic pathway employed for the preparation of 2-fluoro-4-benzyloxybenzoic acid and 3-fluoro-4-benzyloxybenzoic acid are shown in scheme 2.2. The 4-n-alkyl- and 4-n-alkoxy-benzoic acids were prepared following a procedure described in the literature [83, 84]. The 2-Fluoro-4-n-alkoxybenzoic acids and 3-fluoro-4-n-alkoxybenzoic acids were prepared using a procedure similar to that described earlier [82, 85, 86, 87]. The synthetic route adopted to prepare these intermediates is shown in scheme 2.3. The melting points obtained for the cognate preparations of 2-fluoro-4-n-alkoxybenzoic acids and 3-fluoro-4-n-alkoxybenzoic acids are given in tables 2.A and 2.B respectively. The phenols 2.21, 2.23 and 2.25 were obtained by the esterification reaction of 2,7-dihydroxynaphthalene with 4-benzyloxybenzoic acid, 2-fluoro-4-benzyloxybenzoic acid or 3-fluoro-4-benzyloxybenzoic acid in the presence of N, N'-dicyclohexylcarbodiimide as dehydrating agent and (4-N, N-dimethylamino)pyridine as a catalyst followed by hydrogenolysis using 5% Pd-C in 1,4-dioxane at about 50°C. The bis phenols obtained 2.21, 2.23 and 2.25 respectively were condensed with two equivalents of 4-n-alkylbenzoic acids or 4-n-alkoxybenzoic acids to obtain the target compounds of series 2.I, 2.II, 2.III, 2.IV, 2.V and 2.VI. The compounds of series 2.VII and 2.VIII were obtained by condensing the bis phenol 2.21 using two equivalents of 2-fluoro-4-n-alkoxybenzoic acids or 3-fluoro-4-n-alkoxybenzoic acids respectively following the esterification reaction described above.

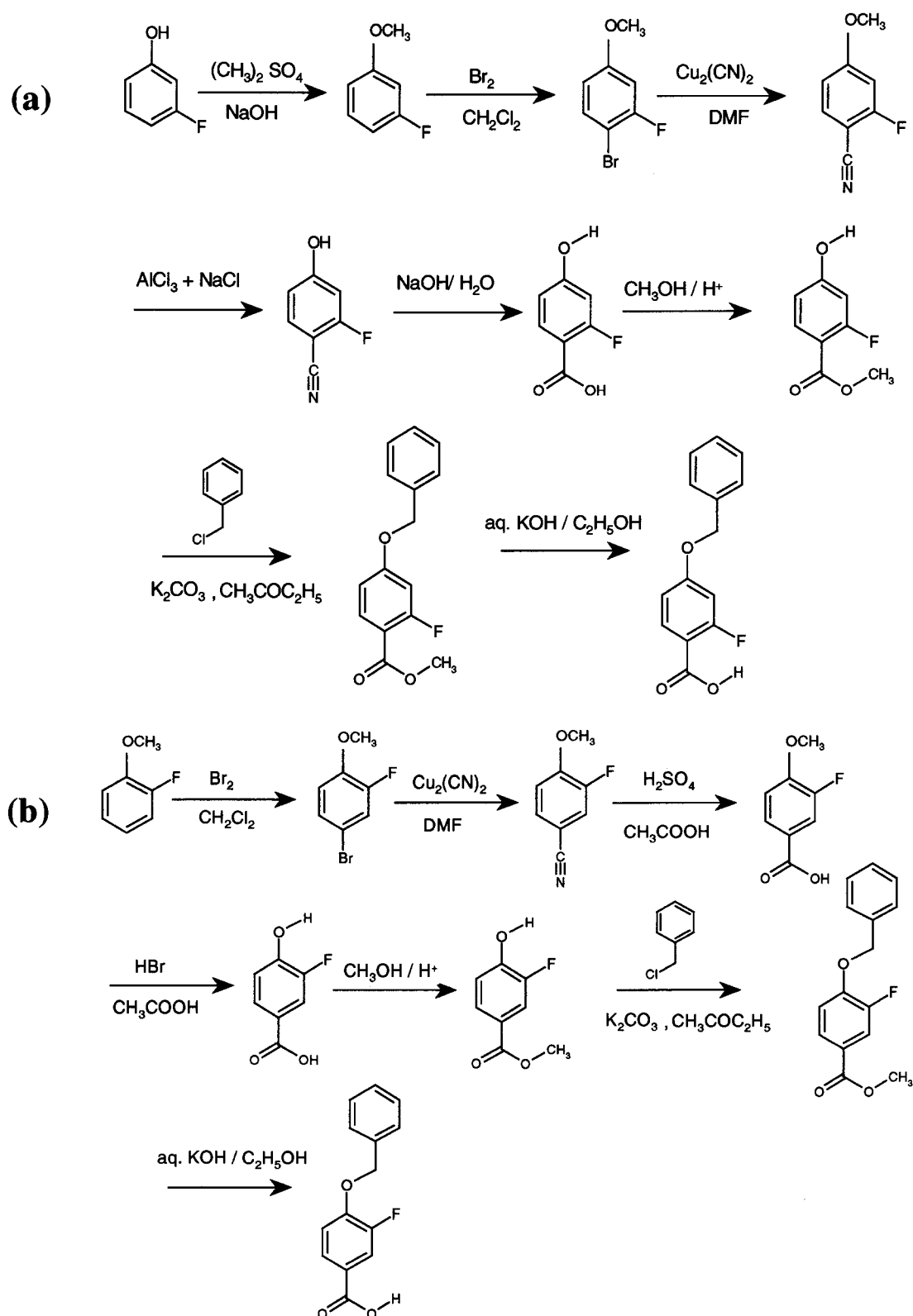
The phase transition temperatures and the associated enthalpies for the 85 compounds belonging to the eight homologous series of banana-shaped compounds viz. series 2.I, 2.II, 2.III, 2.IV, 2.V, 2.VI, 2.VII and 2.VIII are summarized in tables 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7 and 2.8 respectively. Of the 85 compounds reported 84 are mesomorphic and only one is non-mesomorphic. Most of them exhibit an antiferroelectric B_2 phase and a two-dimensional B_1 phase. Interestingly, some compounds exhibit a new smectic (B_{X1}) and two-dimensional ferroelectric (B_{X2}) phases. More interestingly, a new phase sequence (series 2.VII) such as Col_r , SmC_5P_F , Col_{hF} , Col_{rF} and Col_{obF} phases are obtained on ascending the homologous series. In addition, the first observation of a direct transition from B_6 to nematic, B_6 to SmA_C and B_1 to SmA_C phases are reported.



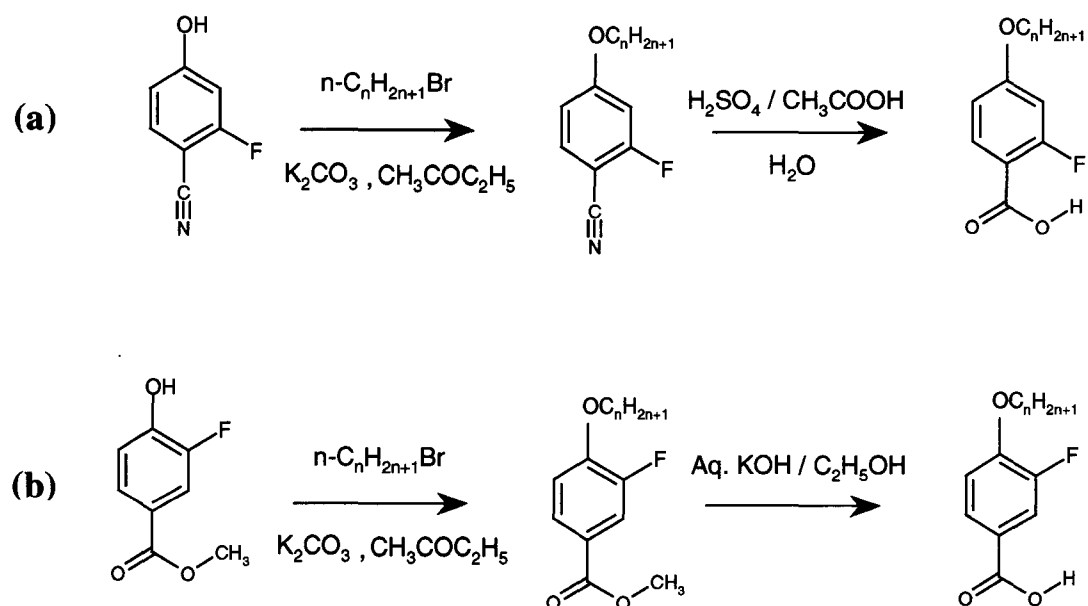
$n = 1, 2, 3, \dots, 12, 14, 16, 18$

$\text{R} = \text{C}_n\text{H}_{2n+1} / \text{OC}_n\text{H}_{2n+1}$

Scheme 2.1. General synthetic pathway used for the preparation of bent-core compounds derived from 2,7-dihydroxynaphthalene.



Scheme 2.2. Synthetic pathway employed for the preparation of (a) 2-fluoro-4-benzyloxybenzoic acid and (b) 3-fluoro-4-benzyloxybenzoic acid.



Scheme 2.3. Synthetic route used for the preparation of (a) 2-fluoro-4-n-alkoxybenzoic acids and (b) 3-fluoro-4-n-alkoxybenzoic acids.

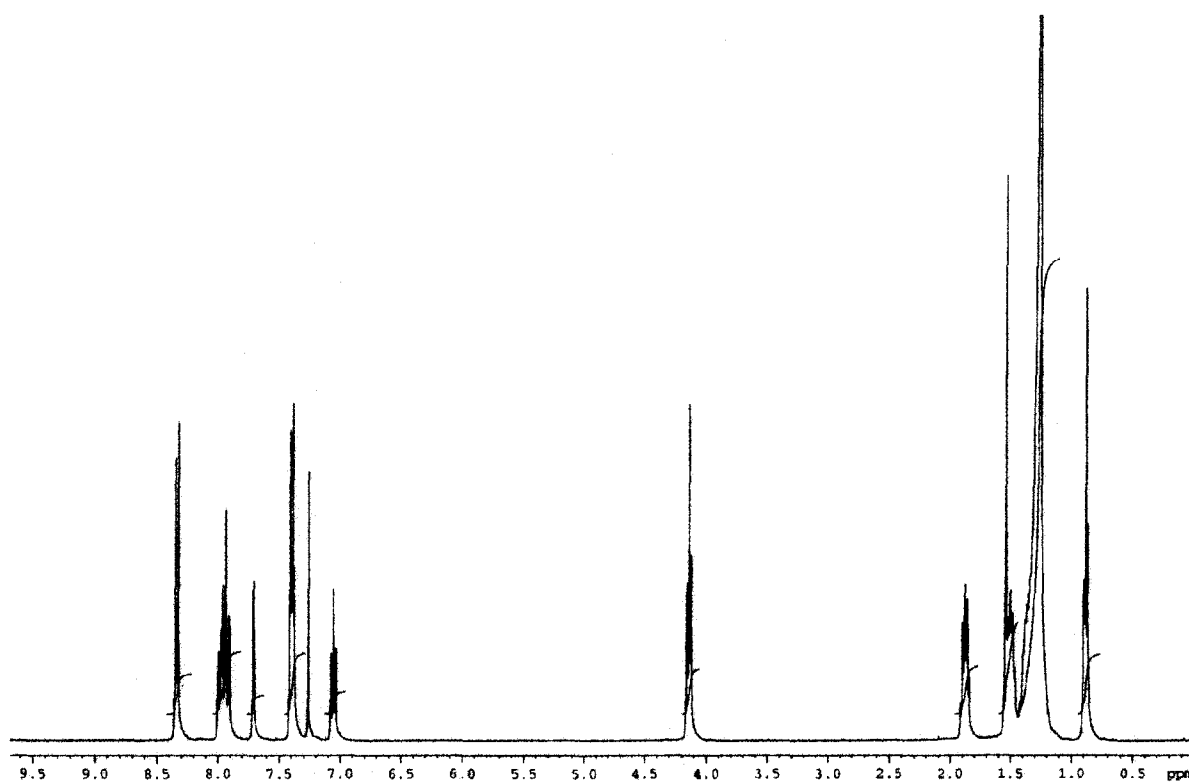


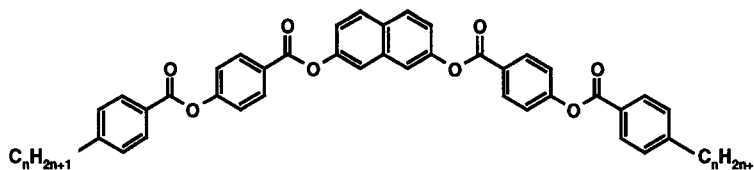
Fig. 2.2. ^1H NMR spectrum obtained for compound 2.H.7.

Mesomorphic properties of compounds of series 2.I:

The transition temperatures together with the associated enthalpies for compounds of series **2.I** are summarized in table 2.1. As can be seen in this table, compound **2.A.1** is non-mesomorphic and the remaining eleven compounds are monomesomorphic. While compounds **2.A.2** and **2.A.5** exhibit monotropic phases, compounds **2.A.3** and **2.A.4** exhibit enantiotropic phases though over a narrow range of temperature. All these four compounds show similar type of textures. On slow cooling of the isotropic liquid of these compounds, dendritic growth can be seen which coalesce to form a mosaic texture. Sometimes spherulitic growth with coloured stripes at the edges can also be seen which are features of a columnar phase. The mesophase is highly viscous, birefringent and the clearing enthalpy is rather high and is about 16-20 kJmol⁻¹. In order to confirm the nature of this mesophase, miscibility studies were carried out for one of the compounds using a standard compound namely, 1,3-phenylene bis(4-n-heptyloxybenzoyloxybenzylidene) diamine (**PBHBD**) which is known to exhibit a B₁ phase [30]. A binary phase diagram constructed as weight % of compound **PBHBD** with compound **2.A.3** is shown in figure 2.3. Although compound **2.A.3** shows a very narrow range of mesophase, it is clear from this phase diagram that the two phases are completely miscible over the entire composition range indicating that the mesophase exhibited by compound **2.A.3** is B₁. Finally, the X-ray diffraction pattern of this mesophase confirmed that it has a rectangular lattice and hence this mesophase has been identified as B₁.

However, compounds **2.A.6** to **2.A.12** show completely different textural features from that seen above. Compound **2.A.6** forms a monotropic phase, while the rest show enantiotropic phases. On slow cooling of the isotropic liquid, a fingerprint pattern develops which rapidly fills the entire field of view. A typical photomicrograph of this texture exhibited by compound **2.A.7** is shown in figure 2.4. This mesophase is less viscous when compared to a B₁ phase and hence the cover slip can be easily displaced. The clearing transition enthalpy values obtained for this mesophase is about 17-23 kJmol⁻¹. The X-ray diffraction pattern of a non-oriented sample of compound **2.A.7** showed the following features. A wide-angle diffuse peak at about 4.7 Å indicating a liquid-like in-plane order for the mesophase. In the small angle region two reflections at d₁=35 Å and d₂=17.4 Å corresponding to a lamellar ordering of the mesophase were obtained. XRD studies also indicated that this is a tilted smectic phase without in-plane order. In order to confirm the nature of the mesophase of compound **2.A.9**, miscibility studies were carried out. Compound **2.C.9** is completely miscible with a very well-known compound namely, 1,3-phenylene bis [4-(4-n-octylphenyliminomethyl)benzoate]

Table 2.1. Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kJmol^{-1}) (*in italics*) for compounds of series 2.I.



Compound	n	Cr	B ₂	B ₁	I
2.A.1	4	. 206.5 <i>62.9</i>	-	-	.
2.A.2	5	. 191.0 <i>57.2</i>	-	(. 181.5) <i>17.6</i>	.
2.A.3	6	. 175.0 <i>44.2</i>	-	. 176.5 <i>16.7</i>	.
2.A.4	7	. 172.0 <i>43.0</i>	-	. 173.5 <i>17.1</i>	.
2.A.5	8	. 168.5 <i>59.0</i>	-	(. 167.0) <i>19.6</i>	.
2.A.6	9	. 167.5 <i>51.6</i>	(. 165.0) <i>17.9</i>	-	.
2.A.7	10	. 164.5 <i>29.8</i>	. 166.5 <i>18.7</i>	-	.
2.A.8	11	. 164.5 <i>29.1</i>	. 168.5 <i>20.6</i>	-	.
2.A.9	12	. 162.5 <i>28.8</i>	. 169.0 <i>20.8</i>	-	.
2.A.10	14	. 159.0 <i>53.2</i>	. 169.5 <i>22.3</i>	-	.
2.A.11	16	. 152.0 <i>24.5</i>	. 168.5 <i>22.3</i>	-	.
2.A.12	18	. 149.0 <i>25.0</i>	. 167.0 <i>22.6</i>	-	.

Key: Applicable to all the tables: Cr=Crystalline phase; N=Nematic phase; B₁=Two-dimensional rectangular columnar phase; B₂=Lamellar antiferroelectric banana phase; B₂^{*}=Chiral antiferroelectric B₂ phase; B₆=Intercalated smectic banana phase; B_{X1}=Lamellar ferroelectric banana phase; B_{X2}=Two- or three-dimensional ferroelectric banana phase; SmA=Smectic A mesophase; SmA_C=Interdigitated smectic A mesophase; Col?=Unidentified two-dimensional columnar phase; I=Isotropic phase; . Phase exists; - Phase does not exist; Temperature in parentheses indicate monotropic transitions.

(PBOB) which exhibits a B_2 phase. The binary phase diagram obtained for the mesophases of compounds **2.C.9** and **2.A.9** is shown in figure 25 and complete miscibility can be seen over the entire concentration range. This suggests that the mesophase of compound **2.A.9** is B_2 . Finally, as we shall see later the antiferroelectric switching behaviour of this mesophase confirms that this mesophase is indeed a B_2 phase.

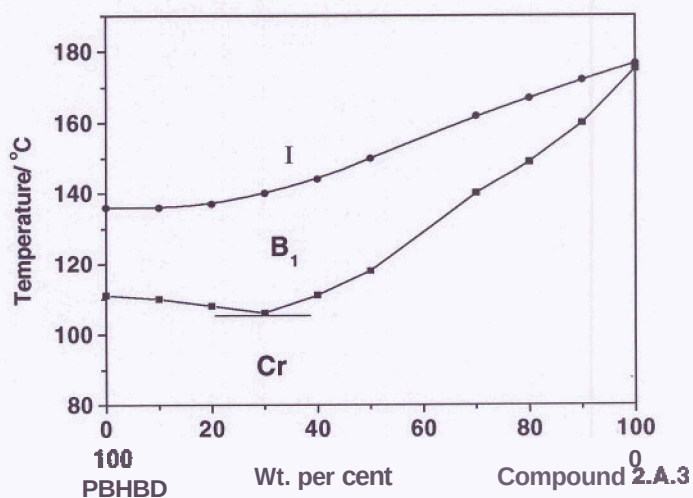


Fig. 23. Miscibility diagram of state for binary mixtures between compounds **2.A.3** and a standard PBHBD.

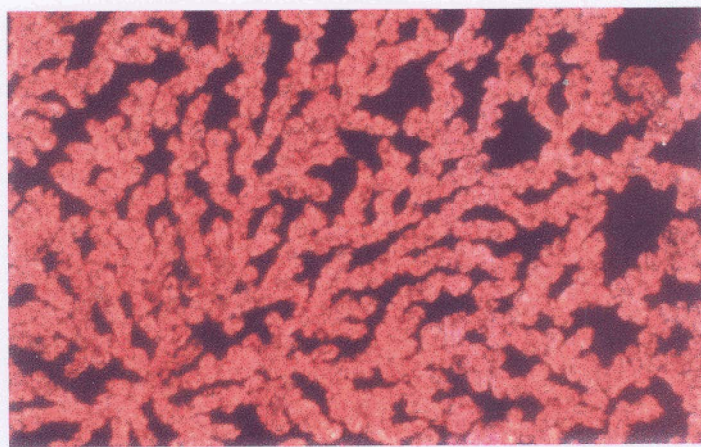


Fig. 2.4. Photomicrograph of the optical texture of B_2 phase of compound **2.A.7** growing from the isotropic liquid.

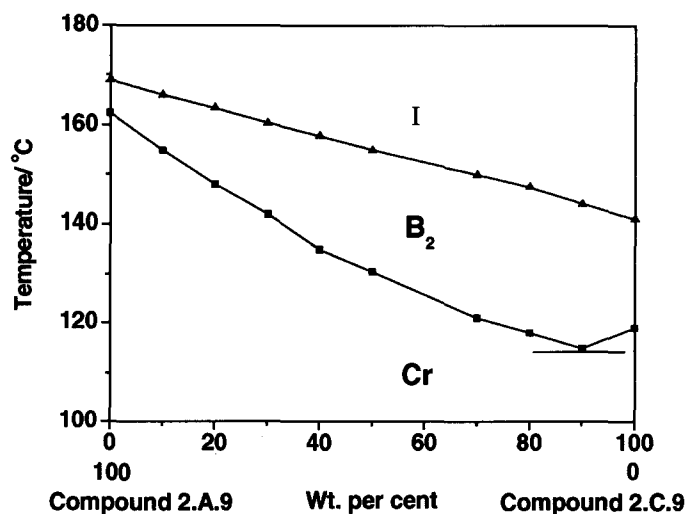


Fig. 2.5. Miscibility diagram of state for binary mixtures between compounds 2.A.9 and 2.C.9.

A plot of transition temperatures as a function of n-alkyl chain length for the compounds of series 2.I is shown in figure 2.6. As can be seen, there is a steep fall for the B₁-isotropic (I) transition temperatures as the series is ascended, the B₂-I transition temperature curve rises initially, reaches a maximum and then gradually decreases as the chain is lengthened.

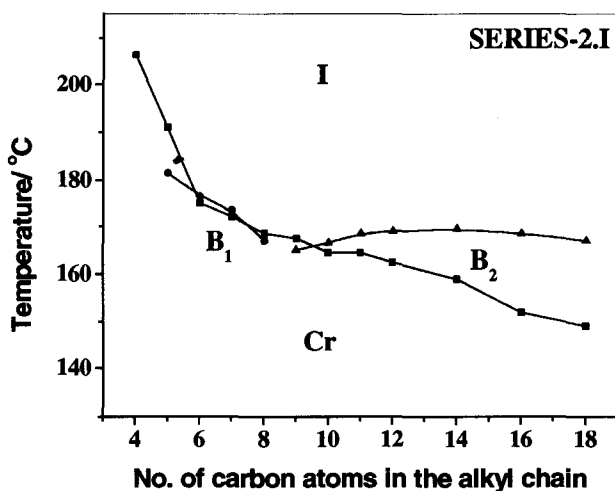


Fig. 2.6. A plot of transition temperatures as a function of n-alkyl chain length obtained for compounds of series 2.I.

Mesomorphic properties of compounds of series 2.II:

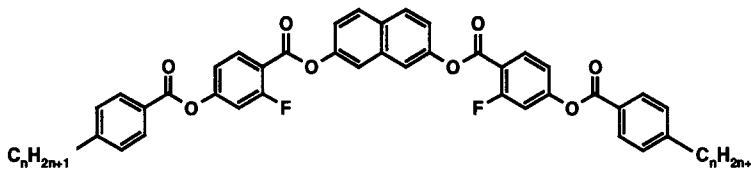
In series 2.II, a fluorine is substituted at *ortho* position with respect to the carboxylate group of the middle phenyl ring of the arms of the bent-core compound (structure 2.I).

The lowest homologue in this series (compound 2.B.1) exhibits a monotropic nematic phase. The next immediate homologue, compound 2.B.2 exhibits a metastable columnar phase in addition to a nematic phase. Cooling the isotropic liquid of compound 2.B.2 and observing under a polarizing microscope, nematic phase appears as droplets which coalesce to form a threaded texture. Observation of four- and two-brush defects under a polarizing microscope indicates the uniaxial character of the nematic phase. On further cooling the sample to a temperature of 137.5°C, fern-like pattern grows and a photomicrograph of this texture is shown in figure 2.7. This slowly fills the field of view to form a mosaic texture. This is similar to the textures exhibited by B₁ phase of compound PBHBD. The middle homologues up to 2.B.8 exhibit similar textural patterns. Miscibility studies have been carried out for the mesophase of compound 2.B.5 using compound 2.A.3 as a standard (B₁ mesophase). The binary phase diagram obtained using these two compounds is shown in figure 2.8. The complete miscibility of the two phases is further evidence for the existence of B₁ phase. In order to unambiguously prove that the phase is B₁, X-ray diffraction studies have been carried out for a non-oriented sample of one of the compounds. For example, compound 2.B.8 exhibits two sharp reflections at $d_1=25.8 \text{ \AA}$ and $d_2=21.4 \text{ \AA}$ in the small angle region. These two reflections can be indexed as (11) and (02) respectively for a two-dimensional rectangular lattice with lattice parameter values, $a=32.4 \text{ \AA}$ and $b=42.8 \text{ \AA}$. The wide-angle diffuse peak at about $4.8 \text{ \AA}$ indicates the absence of in-plane order. Neither the polarization current peak/s nor the textural changes have been observed under the electric field as expected for a B₁ phase. The interesting fact is that B₁ phase is induced as a metastable phase for compound 2.B.2, which becomes enantiotropic on ascending the series (compound 2.B.7) and becomes monotropic again after certain chain length (compound 2.B.8). This shows dependency of the alkyl chain length on the stability of the B₁ phase in addition to the core and the lateral substituents.

The higher homologues from compound 2.B.9 to 2.B.15 show different microscopic textures and X-ray diffraction pattern. The mesophase of these compounds exhibits fingerprint

textures of a B₂ phase under a polarizing microscope. The mesophase exhibited by compound **2.B.12** is completely miscible with the mesophase of compound **2.C.9** (identified as B₂) as

Table 2.2. Transition temperatures (°C) and enthalpies (kJmol⁻¹) (*in italics*) for compounds of series 2.II.



Compound	n	Cr	B ₂	B ₁	N	I
2.B.1	1	. 217.5 <i>58.8</i>	-	-	(. 201.0) <i>0.18</i>	.
2.B.2	2	. 188.5 <i>49.7</i>	-	(. 137.5) ^a	(. 170.0) <i>0.13</i>	.
2.B.3	3	. 171.0 <i>52.7</i>	-	(. 155.0) <i>10.7</i>	. 174.5 <i>0.2</i>	.
2.B.4	4	. 160.0 <i>48.0</i>	-	(. 159.0) <i>12.5</i>	-	.
2.B.5	5	. 143.0 <i>35.0</i>	-	. 162.0 <i>13.8</i>	-	.
2.B.6	6	. 150.0 <i>33.8</i>	-	. 155.5 <i>15.1</i>	-	.
2.B.7	7	. 148.0 <i>40.0</i>	-	. 151.0 <i>13.9</i>	-	.
2.B.8	8	. 154.0 <i>50.7</i>	-	(. 143.0) <i>13.8</i>	-	.
2.B.9	9	. 153.0 <i>51.5</i>	(. 147.0) <i>18.5</i>	-	-	.
2.B.10	10	. 150.0 <i>61.4</i>	(. 149.5) <i>18.9</i>	-	-	.
2.B.11	11	. 135.5 <i>41.4</i>	. 152.0 <i>21.3</i>	-	-	.
2.B.12	12	. 133.5 <i>38.9</i>	. 154.0 <i>21.6</i>	-	-	.
2.B.13	14	. 130.0 <i>53.9</i>	. 156.0 <i>22.3</i>	-	-	.
2.B.14	16	. 125.0 <i>62.5</i>	. 156.0 <i>23.4</i>	-	-	.
2.B.15	18	. 114.0 <i>58.0</i>	. 155.0 <i>23.6</i>	-	-	.

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

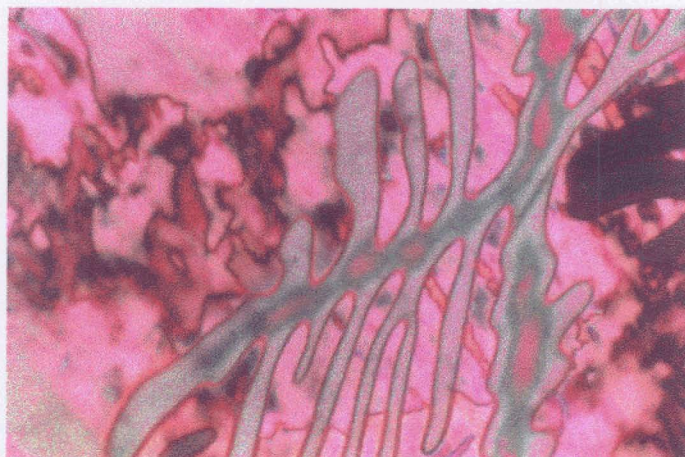


Fig. 27. Photomicrograph of the optical texture of compound 2.B.2 in which the B_1 phase is developing from the nematic phase at 137.5°C.

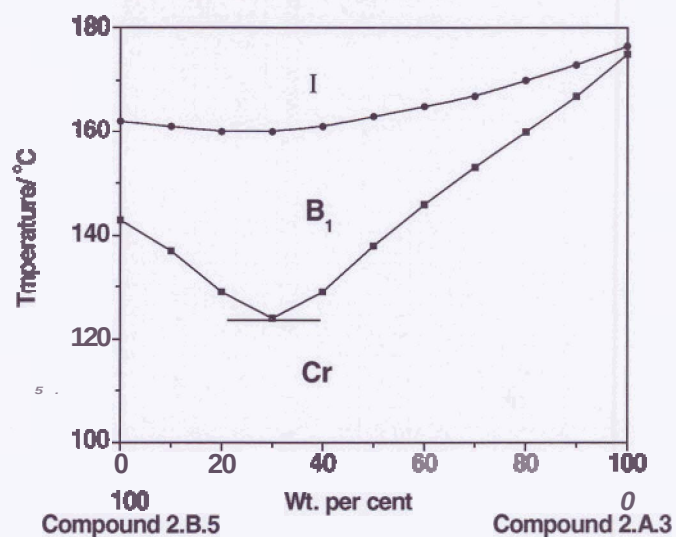


Fig. 28. Miscibility diagram of state for binary mixtures between compounds 2.B.5 and 2.A.3.

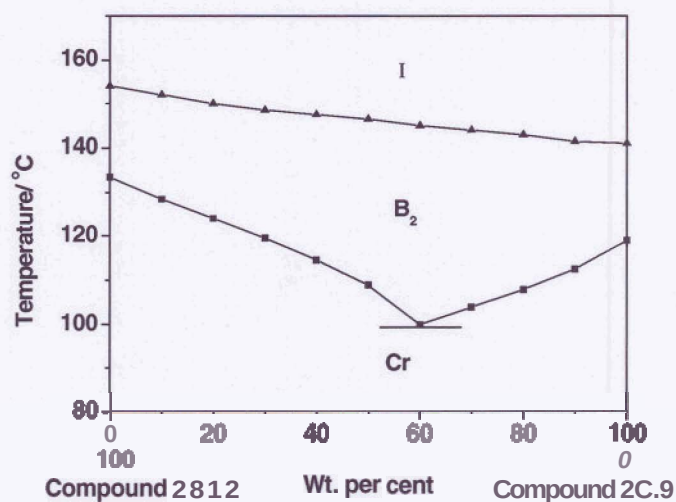


Fig. 2.9. Miscibility diagram of state for binary mixtures between compounds 2.B.12 and 2.C.9.

shown in figure 2.9 and is further evidence for a B_2 mesophase. The XRD studies suggest that this is a tilted smectic phase without in-plane order. To confirm the antiferroelectric switching behaviour of this phase triangular-wave method was employed. Compound 2.B.12 was taken between two indium tin oxide deposited conducting glass plates, with a sample thickness of $14\ \mu\text{m}$. The sample was filled in the isotropic state without any air bubbles and cooled slowly into the mesophase for obtaining good alignment. By applying a sufficiently high triangular-wave electric field of about $\pm 165\text{V}$ (threshold voltage $\pm 125\text{V}$) and at a frequency of 30 Hz at 135°C , two polarization current peaks were obtained for each half cycle confirming the antiferroelectric ground state for this mesophase. A typical switching current response obtained in this phase of compound 2.B.12 is shown in figure 2.10. The saturated spontaneous polarization value obtained by integrating the area under the peaks is about $400\ \text{nC cm}^{-2}$.

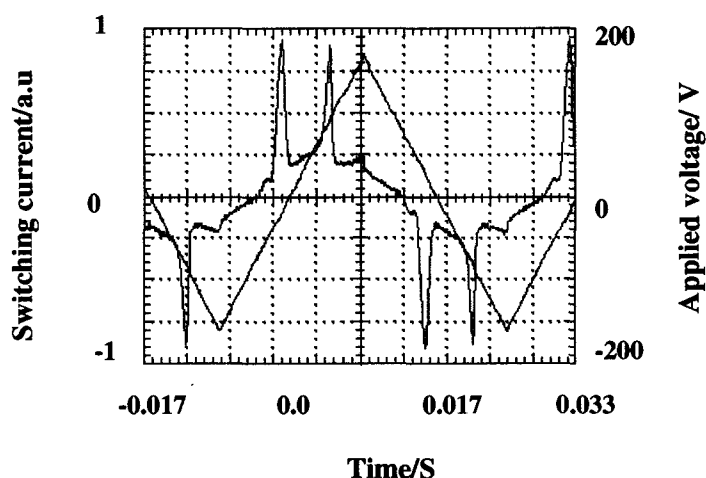


Fig. 2.10. Switching current response obtained for the mesophase of compound 2.B.12 by applying a triangular voltage ($\pm 165\text{V}$, 30 Hz) at 135°C . Sample thickness, $14\ \mu\text{m}$; spontaneous polarization $\approx 400\ \text{nC cm}^{-2}$.

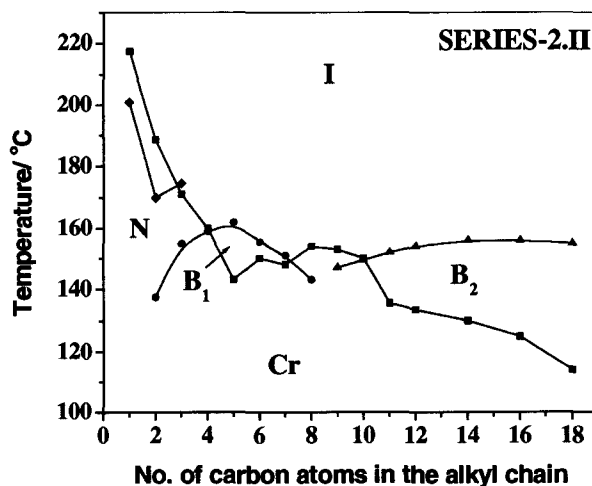


Fig. 2.11. A plot of transition temperatures as a function of n-alkyl chain length obtained for compounds of series 2.II.

A plot of transition temperatures as a function of the number of carbon atoms in the n-alkyl chain for this series is shown in figure 2.11. While there is an evidence for odd-even effect for N-I transition temperatures, the B₁-I transition temperature curve rises sharply initially, reaches a maximum and falls on ascending the series. However, the clearing temperatures for the B₂ phase lie on a smooth curve.

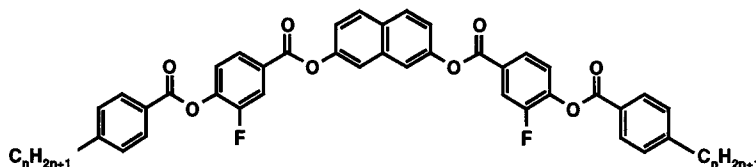
Mesomorphic properties of compounds of series 2.III:

In this series of compounds, a fluorine is substituted at *meta* position (R₂) with respect to the carboxylate group on the middle phenyl ring in the arms of the bent-core compound. The transition temperatures and the associated enthalpies for this series of compounds are summarized in table 2.3. The mesomorphic behaviour of the compounds of this series is comparable to those of series 2.II. As can be seen in table 2.3, compounds 2.C.1 and 2.C.2 show a metastable nematic phase with compound 2.C.2 showing an additional metastable B₁ phase. This metastable B₁ phase exists for compounds 2.C.3 to 2.C.5 and becomes enantiotropic for 2.C.6. Apart from the textural features, the mesophase of compound 2.C.6 is completely miscible with the mesophase of compound 2.A.3 which exhibits a B₁ phase. The binary phase diagram constructed for these two compounds is shown in figure 2.12 which indicates that the mesophase of compound 2.C.6 is indeed a B₁ phase. Finally, this was confirmed by XRD studies. Compound 2.C.6 shows the following features. A diffuse wide-angle peak at about 4.9 Å indicates the absence of in-plane order. In the small angle region, two sharp reflections at d₁=30.4 Å and d₂=22.5 Å were obtained which could be indexed as (11) and (02) reflections from a rectangular lattice with lattice parameters, a=41.2 Å and b=45 Å indicating a B₁ phase. A typical X-ray angular intensity profile obtained in the B₁ mesophase is shown in figure 2.13.

The remaining compounds from 2.C.7 to 2.C.12 exhibit the textural features of a B₂ phase. A binary phase diagram was constructed using compound 2.C.9 and a reference compound **PBOB**, which exhibits a B₂ phase and this is shown in figure 2.14. It is clear from this figure that the mesophase of compound 2.C.9 is completely miscible with the mesophase of **PBOB** over the entire composition range. This confirms that the mesophases obtained in both the compounds are of the same type. XRD studies carried out on non-oriented sample of compound 2.C.9 shows three sharp reflections at d₁=38 Å, d₂=19 Å, d₃=12.7 Å in the small angle region indicating a smectic ordering for the mesophase. The first order reflection (d₁) obtained corresponding to the layer thickness is lower than the calculated molecular length

indicating a tilt of BC molecules with respect to the layer normal. The calculated tilt angle is about 48°. The X-ray image of a non-oriented sample of the mesophase of compound **2.C.9** is shown in figure **2.15**. In order to investigate the nature of ground state structure of this

Table 2.3. Transition temperatures (°C) and enthalpies (kJmol⁻¹) (*in italics*) for compounds of series 2.III.



Compound	n	Cr	B ₂	B ₁	N	I
2.C.1	4	. 185.5 <i>50.8</i>	-	-	(. 154.0) <i>0.1</i>	.
2.C.2	5	. 154.5 <i>44.9</i>	-	(. 145.5) ^a	(. 150.5) <i>0.26</i>	.
2.C.3	6	. 173.5 <i>49.9</i>	-	(. 140.5) <i>11.3</i>	-	.
2.C.4	7	. 161.0 <i>49.5</i>	-	(. 141.5) <i>12.1</i>	-	.
2.C.5	8	. 137.0 <i>61.0</i>	-	. 137.5 <i>11.0</i>	-	.
2.C.6	9	. 133.0 <i>48.3</i>	-	. 136.5 <i>13.6</i>	-	.
2.C.7	10	. 128.5 <i>64.0</i>	. 137.5 <i>15.9</i>	-	-	.
2.C.8	11	. 121.5 <i>54.1</i>	. 140.0 <i>16.9</i>	-	-	.
2.C.9	12	. 119.0 <i>76.2</i>	. 141.0 <i>17.0</i>	-	-	.
2.C.10	14	. 116.0 <i>63.2</i>	. 143.0 <i>18.2</i>	-	-	.
2.C.11	16	. 111.5 <i>95.0</i>	. 143.5 <i>18.8</i>	-	-	.
2.C.12	18	. 111.0 <i>87.6</i>	. 142.5 <i>19.8</i>	-	-	.

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

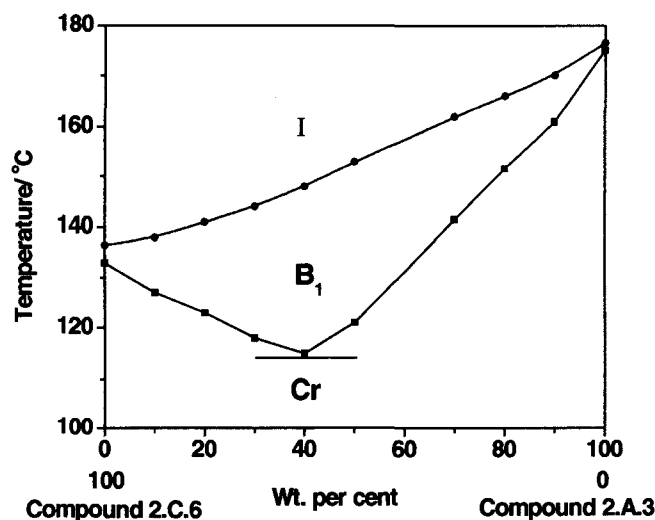


Fig. 2.12. Miscibility diagram of state for binary mixtures between compounds 2.A.3 and 2.C.6.

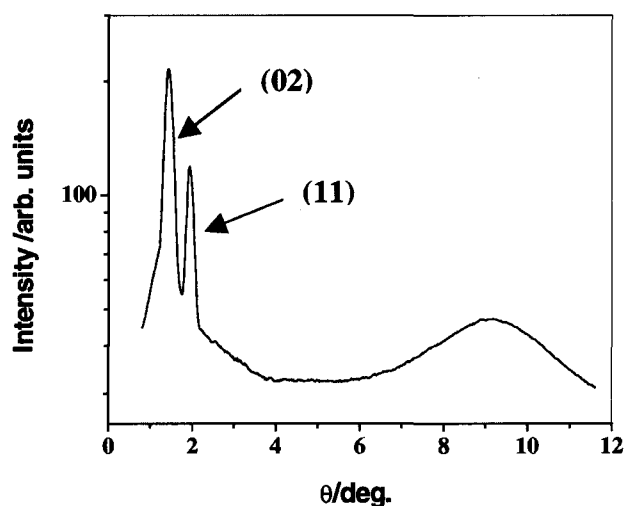


Fig. 2. 13. The X-ray angular intensity profile obtained for the B₁ phase of compound 2.C.6 at 135°C.

mesophase, dc field experiments were carried out for compound 2.C.10. The sample was taken in a homogeneously aligned and unidirectionally rubbed cell having a thickness of $5.5 \mu\text{m}$ and cooled slowly from the isotropic liquid under a dc electric field of about 40V (threshold voltage is about 25V). Colourful spherulites appeared as observed under a polarizing microscope in which the dark brushes (resulting from the equidistant circular smectic layers in which the dark brushes correspond to the direction of the optical axes of smectic layers) make an angle with respect to the directions of crossed polarizers. On reversing the polarity of the

applied field, no change in position of the dark brushes was observed. On switching off the dc electric field, circular stripes develop over the domains while retaining the position of dark brushes. These observations point towards racemic ground state structure for the mesophase. The optical photomicrographs obtained under a polarizing microscope with and without fields are shown in figure 2.16.

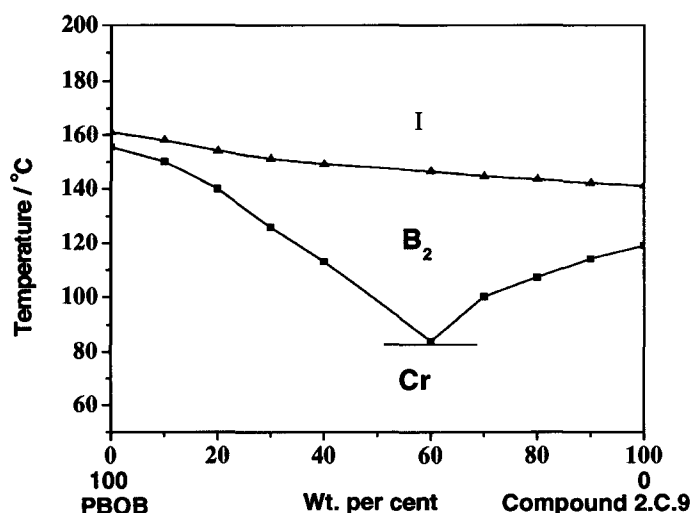


Fig. 2.14. Miscibility diagram of state for binary mixtures between compound 2.C.9 and the standard compound PBOB.

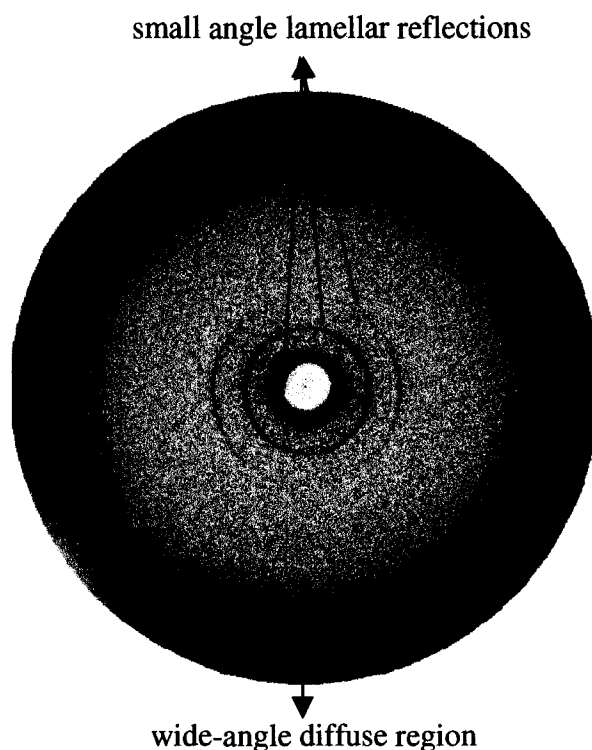


Fig. 2.15. The X-ray image of a non-oriented sample of B₂ phase obtained for compound 2.C.9 at 124°C.

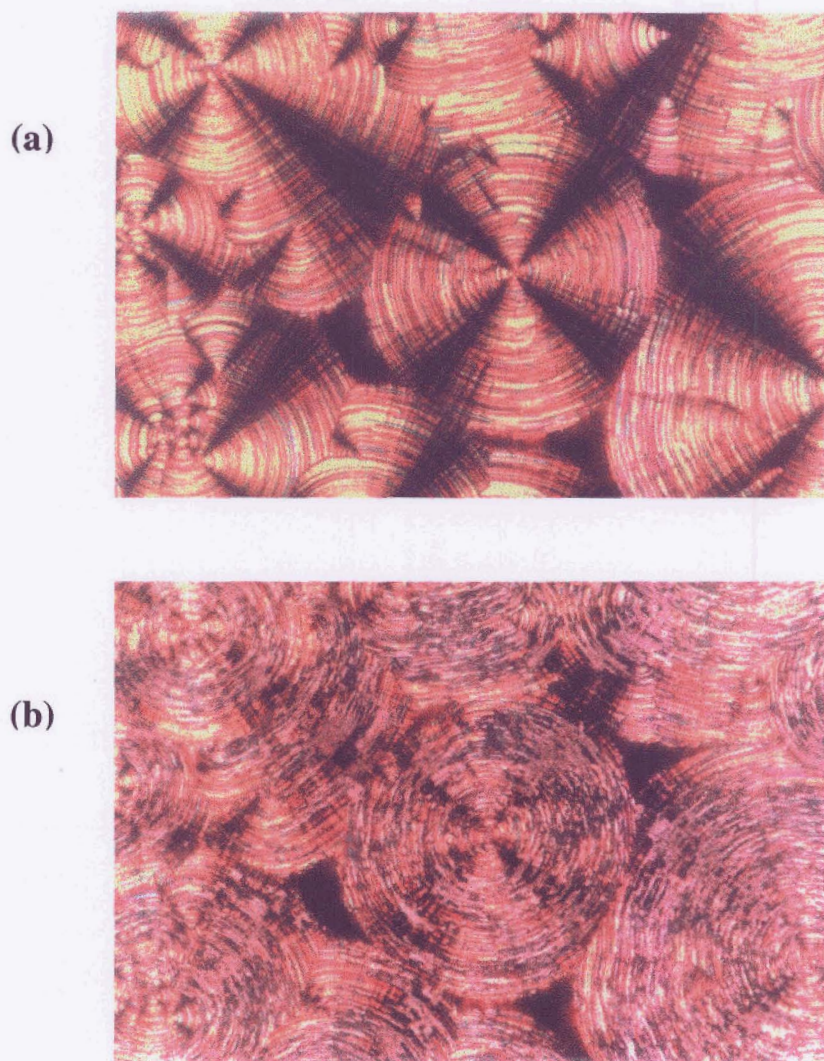


Fig. 2.16. Optical textures obtained for B₂ phase of compound 2.C.10. (a) Colourful spherulites obtained by the application of a dc electric field, $7.3 \text{ V}\mu\text{m}^{-1}$. The dark brushes obtained are independent of polarity of the applied field. (b) The racemic ground state domains obtained in the absence of electric field

A plot of transition temperatures as a function of n-alkyl chain length obtained for this series is shown in figure 2.17. As usual, the clearing temperature curves obtained for N and B₁ phases fall gradually and an odd-even effect can be seen for the B₁ phase. The transition temperatures of B₂-I fall on a smooth curve on ascending the homologous series.

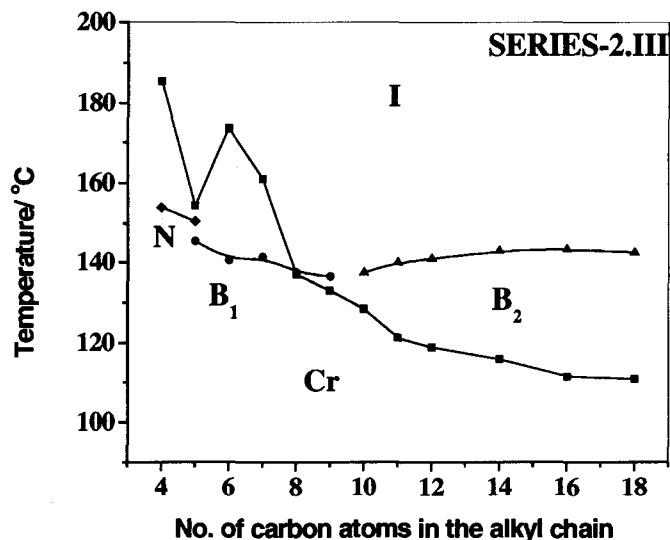


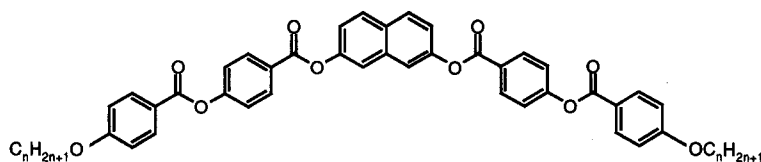
Fig. 2.17. A plot of transition temperatures as a function of n-alkyl chain length obtained for compounds of series 2.III.

Mesomorphic properties of compounds of series 2.IV:

The compounds of series 2.IV are unsubstituted esters containing n-alkoxy terminal chains and the transition temperatures as well as the associated enthalpies obtained for these are summarized in table 2.4. Only three new compounds were synthesized since a few homologues were reported earlier [32].

Compound 2.D.1 exhibits a nematic phase and a two-dimensional B₁ phase on lowering the temperature. On ascending the homologous series, the nematic phase is eliminated and only the B₁ phase gets stabilized for compounds 2.D.2, 2.D.3 and 2.D.4 [32]. However, the higher homologues, 2.D.5 and 2.D.6 exhibit chiral B₂ mesophase over a thermal range of about 50°C. On heating the solvent crystallized material, a mesophase appears resembling the texture of a B₂ phase. On cooling the isotropic phase, the mesophase appears as domains of opposite handedness. These chiral domains can be easily distinguished by rotating the polarizer from the crossed position as observed by Watanabe *et al.*[79] for Sm1 phase. The textural features, XRD studies and the switching behaviour for this mesophase are exactly similar to the one which will be described later for compound 2.E.11 of series 2.V.

Table 2.4. Transition temperatures (°C) and enthalpies (kJmol⁻¹) (*in italics*) for compounds of series 2.IV.



Compound	n	Cr	B ₂ *	B ₁	N	I	Ref.
2.D.1	4	. 197.5 <i>39.3</i>	-	. 210.0 <i>14.1</i>	. 213.0 <i>0.5</i>	.	
2.D.2	7	. 158.0 ^a	-	. 188.0 ^a	-	.	[32]
2.D.3	8	. 150.0 ^a	-	. 182.0 ^a	-	.	[32]
2.D.4	9	. 143.0 ^a	-	. 175.0 ^a	-	.	[32]
2.D.5	11	. 135.5 <i>54.4</i>	. 169.0 <i>21.4</i>	-	-	.	
2.D.6	16	. 122.0 <i>58.6</i>	. 173.0 <i>23.0</i>	-	-	.	

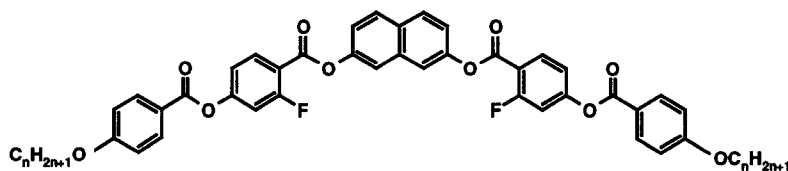
a: enthalpy values not reported.

Mesomorphic properties of compounds of series 2.V:

In this series of compounds, fluorine is substituted at *ortho* position to the carboxylate group of the middle phenyl ring (R₁) of the wings of the bent-core molecule containing terminal n-alkoxy chains. A total of 14 compounds have been synthesized and examined in detail.

Compound **2.E.1** exhibits the following features. On cooling the isotropic liquid, at 237.5°C, a nematic phase with a schlieren texture having four- and two-brush defects is formed which transforms to a threaded texture. This observation suggests a uniaxial character for the nematic phase. On cooling the nematic phase further to 188.5°C, a fan-shaped texture of the SmA phase appears. The enthalpy of this transition is rather small and is about 0.3 kJmol⁻¹. On cooling further by about one degree, additional features appeared on the existing fan-shaped texture of the SmA phase. No enthalpy change could be observed for this transition. This mesophase is designated as SmA_C (interdigitated SmA phase). On heating the SmA_C phase close to the transition (< 1°C) to the nematic phase, these unusual patterns disappear. The textural features observed in the SmA_C phase are different from the broken fan-shaped texture, which is normally seen for a SmC phase. The SmA_C phase also shows homeotropic textures

Table 2.5. Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kJmol^{-1}) (*in italics*) for compounds of series 2.V.



2.E.1 n=2 Cr 168.0 B₆ 177.0 SmA_C ≈ 188[#] SmA 189.0 N 238.0 I
48.8 5.4 0.31 0.55

Compound	n	Cr	B ₂ [*]	B ₁	B ₆	N	I
2.E.2	3	. 162.0 29.9	-	. 176.0 0.5	. 191.5 9.6	. 204.5 0.52	.
2.E.3	4	. 142.0 40.3	-	. 192.0 0.2	. 196.5 12.6	. 197.5 0.32	.
2.E.4	5	. 154.0 43.4	-	. 188.0 17.0	-	-	.
2.E.5	6	. 120.5 41.9	-	. 180.0 17.9	-	-	.
2.E.6	7	. 127.0 53.2	-	. 169.5 17.6	-	-	.
2.E.7	8	. 112.5 47.6	-	. 160.5 17.5	-	-	.
2.E.8	9	. 124.0 60.2	-	. 151.0 16.0	-	-	.
2.E.9	10	. 108.5 26.5	. 146.0 18.6	-	-	-	.
2.E.10	11	. 112.5 64.3	. 148.5 19.3	-	-	-	.
2.E.11	12	. 107.0 53.7	. 152.0 20.3	-	-	-	.
2.E.12	14	. 98.5 102.2	. 155.5 21.7	-	-	-	.
2.E.13	16	. 104.0 85.0	. 157.0 22.2	-	-	-	.
2.E.14	18	. 103.5 97.7	. 158.0 22.1	-	-	-	.

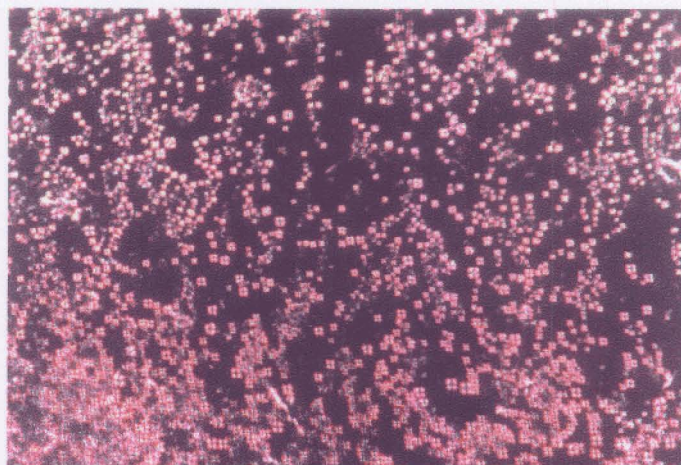
#: temperature obtained under a polarizing microscope. No transition enthalpy could be obtained in DSC.

on shearing the cover slip which excludes the possibility of a biaxial smectic A phase and a SmC phase. On cooling the SmA_C phase further to a temperature of 176°C, major changes in the texture takes place and the enthalpy of this transition is about 5 kJmol⁻¹. This mesophase is slightly viscous when compared to the higher temperature SmA_C phase. On shearing, the mesophase shows a schlieren texture with multiple brushes joining at a single point in addition to the four- and two-brush defects [88]. Based on these textural features and X-ray data, this mesophase is designated as a B₆ phase [89]. The schlieren texture in the B₆ phase can also be obtained on cooling the homeotropic regions of higher temperature SmA_C phase as shown in figure 2.18(i). The textural changes obtained in homogeneous and homeotropically aligned cells for compound 2.E.1 are shown in figure 2.18 (ii).

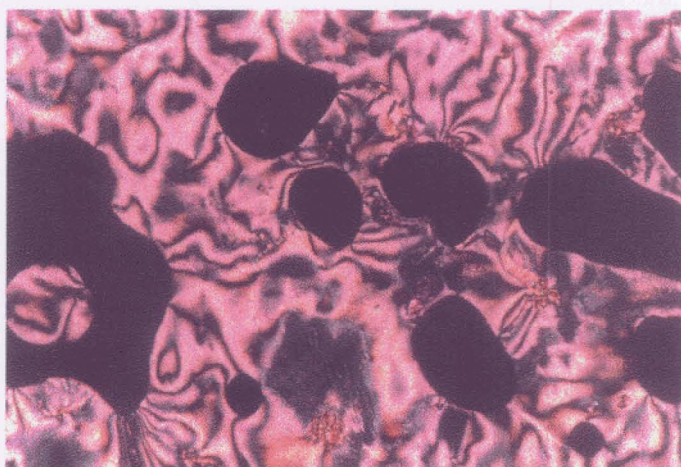
The non-oriented X-ray diffraction pattern in the SmA_C phase of this compound exhibits a very weak reflection in the small angle region at $d_1=18.1 \text{ \AA}$. The calculated full molecular length (L) is about 38 Å. The first order reflection obtained from X-ray is approximately half the calculated molecular length indicating an interdigitated structure in the SmA_C phase. A weak and broad small angle reflection suggests the disordered layer structure in the SmA_C phase. The wide-angle diffuse peak at about 4.7 Å indicates a liquid-like in-plane order. On lowering the temperature to a B₆ phase, the small angle broad reflection becomes slightly sharper and a second order reflection could also be seen. Further, no electro-optical switching could be observed in any of these phases. However, it has not been possible to carry out the X-ray diffraction studies in the SmA phase due to a narrow thermal range of temperature.

The next homologue in the series, compound 2.E.2 shows the following features. On cooling the isotropic liquid of this compound, a nematic phase appears which on further cooling to a temperature of 190°C, shows colourful batonnets which coalesce to form a fan-shaped texture. This texture is similar to the textural features observed for the usual SmA phase. However, no homeotropic textures could be obtained on shearing the sample or by surface treatment of microscopic glass slide and instead exhibits a schlieren texture [89] and hence the possibility of SmA phase can be excluded. This mesophase is quite fluid and hence a cover slip can be easily displaced. The clearing transition enthalpy is about 9.6 kJmol⁻¹. The X-ray diffraction pattern obtained in this mesophase shows two sharp reflections in the small angle region at $d_1=18.8 \text{ \AA}$ and $d_2=9.4 \text{ \AA}$, which can be indexed as (01) and (02) respectively for an intercalated B₆ phase. The wide-angle diffuse peak at 4.8Å suggests the absence of in-plane

(a)



(b)



(c)

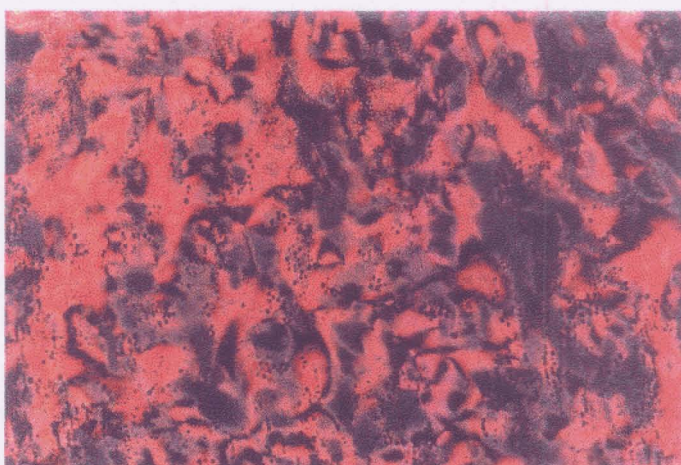
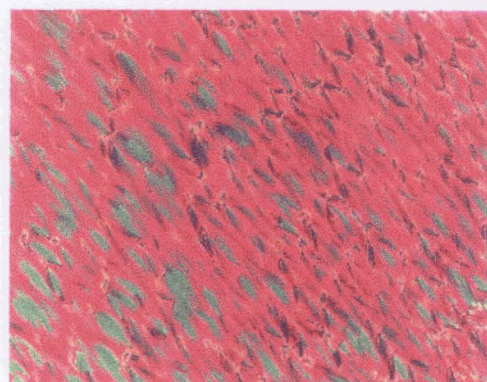


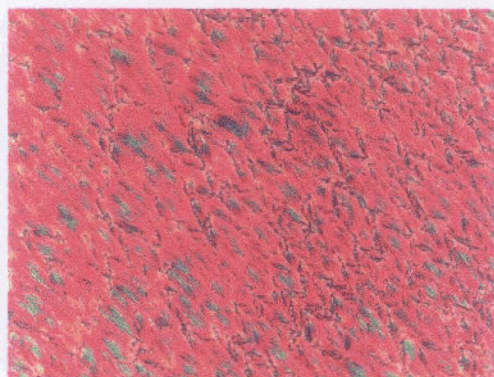
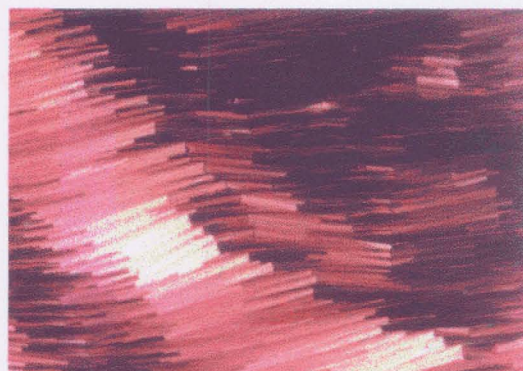
Fig. 2.18(i). Optical photomicrographs obtained for compound 2.E.1. (a) Homeotropic regions obtained in SmA_C phase, (b) appearance of schlieren texture (multiple brushes) in the B_6 mesophase upon cooling the homeotropic regions of SmA_C phase and (c) schlieren texture obtained in the B_6 phase.

Homogeneously aligned cell

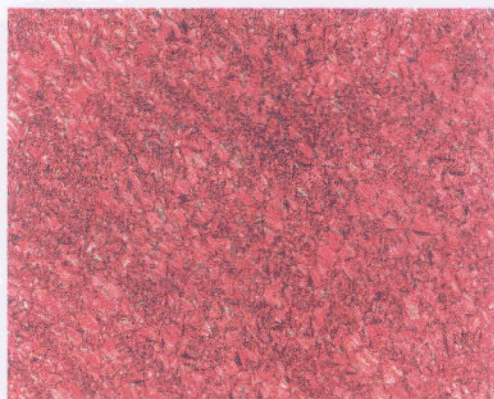
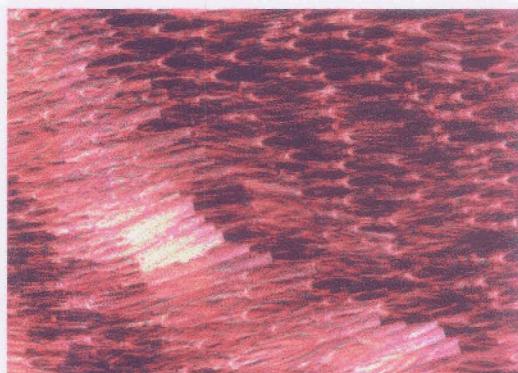
Homeotropically aligned cell



(a)



(b)



(c)

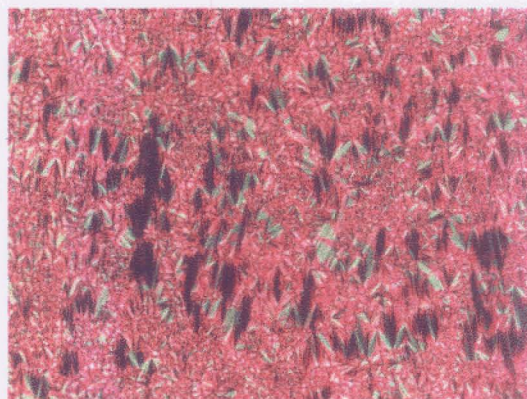


Fig. 218 (ii). The textural changes obtained in both homogeneously as well as homeotropically aligned cells for compound 2.E.1. (a) SmA phase at 188.5°C, (b) SmAc phase at 180°C and (c) B₆ phase at 170°C.



Fig.2.19. The optical photomicrograph showing B₆ phase developing from a nematic phase, compound 2.E.2, 190.5°C.

order. No switching could be observed even at a high electric field as expected for a B₆ phase. A typical photomicrograph of the texture obtained at the transition from nematic to B₆ phase is shown in figure 2.19. Perhaps, this is the first example of a compound exhibiting a direct transition from a nematic phase to an intercalated B₆ phase. On further cooling the B₆ mesophase, small changes in the texture could be observed at 175°C which is accompanied by a small enthalpy change of about 0.5 kJmol⁻¹. This indicates a minor change in the molecular arrangement. On shearing this mesophase, a mosaic texture is obtained similar to the one which is normally seen for a columnar B₁ phase. XRD studies of this mesophase show three sharp reflections in the small angle region at $d_1=18.8\text{\AA}$, $d_2=10.8\text{\AA}$ and $d_3=9.4\text{\AA}$ and without in-plane order. The first and the third order reflections are retained from the high temperature B₆ phase and the second one is an additional reflection from this mesophase and is probably from (11) plane. These reflections as such cannot be indexed for a rectangular B₁ phase. However, these reflections are in the ratio of $1: 1/\sqrt{3}:1/2$ suggesting a two-dimensional hexagonal lattice. Assuming a hexagonal lattice, these reflections can be indexed as (01), (11) and (02) respectively and the lattice parameter, $a=21.6\text{\AA}$ [$a= d(01)/\cos 30^\circ$]. However, the oriented XRD pattern shows the preferred orientation direction of the aliphatic chains. This cannot satisfy the uniaxial hexagonal symmetry. Hence, the possibility of a hexagonal columnar phase can be excluded. If one chooses a centered rectangular lattice instead of a hexagonal lattice with the same value of a , then $b=\sqrt{3}a$ (lattice parameters, $a=21.7\text{\AA}$ and $b=37.6\text{\AA}$). From this assumption, the small angle reflections obtained can be indexed as (02) or (11), (13) and (04) or (22) respectively for a rectangular lattice. Similar X-ray diffraction patterns were observed for compounds 2.E.3 and 2.E.4 and these can be indexed for a

rectangular lattice as shown in table 2.9. The X-ray data obtained for compounds 2.E.5, 2.E.6, 2.E.7 and 2.E.8 can be easily indexed for a rectangular B₁ phase and the corresponding *a* and *b* values obtained are shown in table 2.9. As can be seen in figure 2.20, on ascending the homologous series (compounds 2.E.2 to 2.E.8) the values of (02), (11) and the corresponding lattice parameters, *a*(10) and *b*(01) also increase as expected for a B₁ phase structure. Also, the difference between the values of (11) and (02) decreases on lowering the number of carbon atoms in the *n*-alkoxy chain and hence these two start overlapping for compound 2.E.5 as shown in figure 2.20.

The higher homologues viz. compounds 2.E.9 to 2.E.14 exhibit textural features similar to that reported for a Sm1 mesophase by Thisayukta *et al.*[79]. The textures obtained on heating are reminiscent of the features of a B₂ phase. However, on cooling the isotropic liquid, the mesophase appears with a weak birefringence and is highly viscous when compared with the viscosity of the same mesophase obtained on heating. The formation of the mesophase is accompanied by domains of opposite handedness which are separated by boundaries. This can be realized by rotating the polarizer or analyzer by $\pm 6^\circ$ in which the transmittance of light increases in one of the domains and vice-versa. A typical optical photomicrograph of this mesophase obtained on heating as well as on cooling for compound 2.E.11 is shown in figure 2.21. However, on rotating the sample or the heating stage, no change in the brightness or darkness of the domains could be seen in uncrossed position. This indicates that the helical axis of the chiral domains is perpendicular to the substrate. In other words, the helical axis coincides with the optical axis. A typical enthalpy value obtained for this mesophase-isotropic transition is in the range of 18-22 kJmol⁻¹. As reported by Heppke *et al.* [39], the tilting of bent-core molecules with respect to the layer normal is equally probable and hence they can build up enantiomorphic chiral structures (conglomerates). Though there are a few examples in the literature [55, 61, 79] with these features, the ground state structure and why only these BC molecules generate such a chiral structure is still a complex problem and is yet to be resolved.

The XRD studies in this mesophase show a layer structure with the tilt of molecules, without in-plane order as shown in table 2.9. Also, it can be seen that the layer spacing increases gradually but the difference in spacing between the successive homologues gets reduced on increasing the chain length. This is due to the fact that the longer chains adopt a *gauche*

Table. 2.9. The d-spacings (Å) obtained for different mesophases and the corresponding Miller indices shown in brackets for the compounds of homologous series 2.V. The XRD measurements have been carried out on mesophases obtained on cooling.

Compound	d-spacings Å / Miller indices	Lattice parameters/ Å		Phase type	T/°C
		a	b		
2.E.2	18.8 (01), 9.4 (02)	-	-	B ₆	185
	18.8 (02 or 11), 10.8 (13), 9.4(04 or 22)	21.7	37.6	B ₁ ?	170
2.E.3	19.6 (01), 9.8 (02)	-	-	B ₆	194
	19.6 (02 or 11), 11.3 (13), 9.8 (04 or 22)	22.6	39.1	B ₁ ?	160
2.E.4	20.5 (02 or 11), 11.8 (13), 10.2 (04 or 22)	23.7	41	B ₁ ?	170
2.E.5	21.8 (11), 20.9 (02), 12.2 (13), 10.6 (04)	25.6	41.8	B ₁	160
2.E.6	23.7 (11), 21.5 (02), 10.8 (04)	28.4	43.0	B ₁	150
2.E.7	24.6 (11), 22.2 (02), 11.2 (04)	29.6	44.4	B ₁	150
2.E.8	26.4 (11), 22.9 (02)	32.3	45.8	B ₁	140
2.E.9	33.3 (01), 16.6 (02), 11.1 (03)	-	-	B ₂	120
2.E.10	34.6 (01), 17.3 (02), 11.5 (03)	-	-	B ₂	120
2.E.11	35.8 (01), 17.9 (02), 11.9 (03)	-	-	B ₂	120
2.E.12	38.1 (01), 19.0 (02), 12.7 (03)	-	-	B ₂	125
2.E.13	40.2 (01), 20.1 (02), 13.4 (03)	-	-	B ₂	125
2.E.14	42.2 (01), 21.1 (02), 14.0 (03)	-	-	B ₂	125

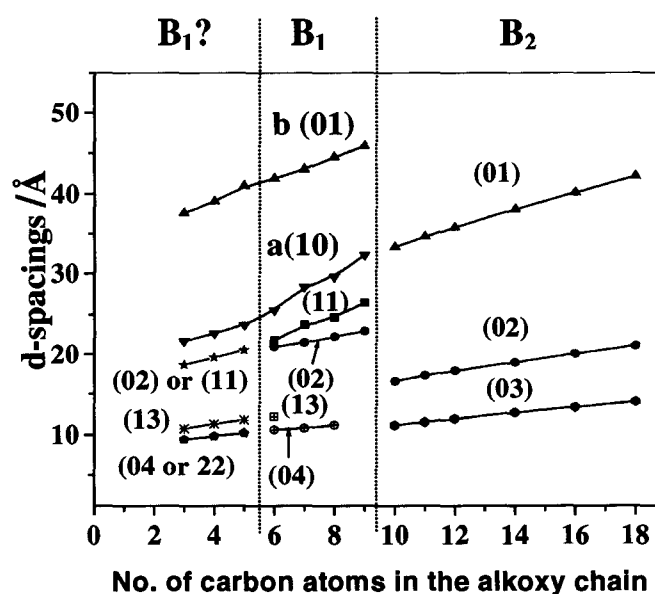


Fig. 2.20. A plot of d-spacings as a function of n-alkoxy chain length for the homologues of series 2.V, showing the changes in XRD pattern while going from one mesophase to the other.

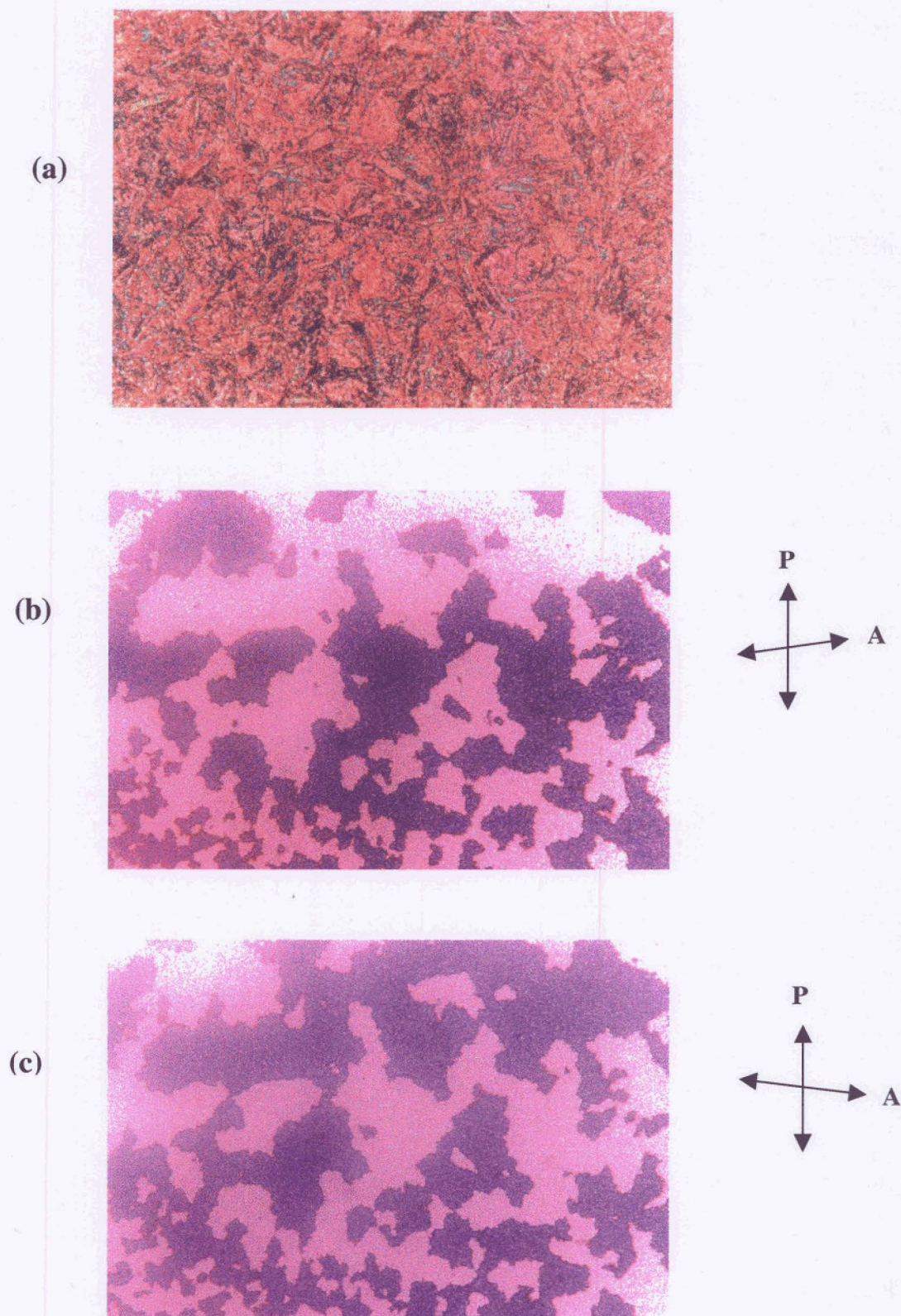


Fig. 2.21. The optical photomicrographs of a chiral B_2 mesophase of compound 2.E.11 (a) texture obtained on heating, (b) & (c) textures obtained on cooling in which chiral domains of opposite handedness can be seen by rotating the analyzer ($\pm 6^\circ$).

conformation and hence an increase in the layer spacing on ascending the series is not observed.

In order to confirm the polar ordering of BC molecules in successive layers in these enantiomorphic chiral domains and to measure the spontaneous polarization in such a medium, triangular-wave method was employed. A cell was constructed using indium tin oxide coated conducting glass plates having uniform thickness of about $10\text{ }\mu\text{m}$ and treated with polyimide for homogeneous alignment. The thickness of the cell was measured using an interferometric technique. For compound **2.E.11**, cooling the sample from the isotropic liquid under a triangular-wave electric field below threshold voltage ($\pm 50\text{V}$), weak birefringent domains of opposite handedness were seen. By applying a sufficiently high triangular voltage of about $\pm 18\text{ V}\mu\text{m}^{-1}$ and a frequency of 30 Hz, the observation of two polarization current peaks for each half cycle indicated the antiferroelectric ground state for the mesophase. A typical switching current response obtained in the mesophase of this compound is shown in figure 2.22. The calculated average saturated polarization by integrating the area under the peaks for this mesophase is about 260 nC cm^{-2} .

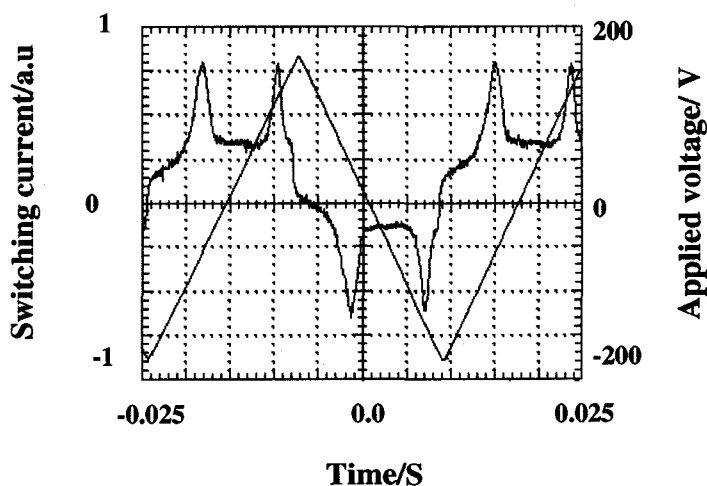


Fig. 2.22. Switching current response obtained in the mesophase of compound **2.E.11** by applying a triangular voltage ($\pm 175\text{V}$, 30 Hz) at 120°C . Sample thickness, $10\text{ }\mu\text{m}$; spontaneous polarization $\approx 260\text{ nC cm}^{-2}$.

Though the mesophase exhibits optical features, X-ray diffraction pattern and electro-optical switching behaviour seen for a B_2 phase, interestingly this mesophase always forms chiral structures (no racemic). Hence this mesophase is designated as B_2^* (chiral B_2).

As shown in figure 2.23, N-I transition temperatures decrease steeply and show an odd-even effect while the B₆-I transition temperature curve rises. However, the B₁-I transition temperature curve rises initially and then falls gradually on ascending the homologous series and all the clearing temperatures fall on a smooth curve. More interestingly, chiral B₂-I transition points lie on a smooth curve indicating the phase similarity with a B₂ phase.

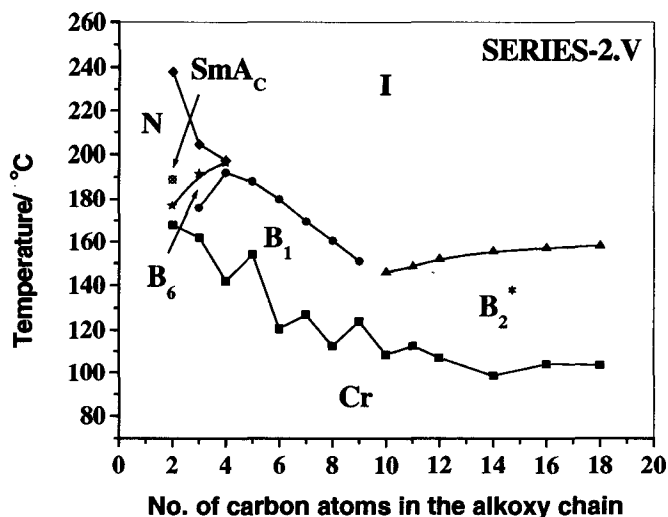


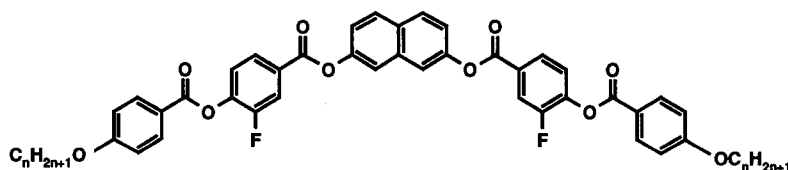
Fig. 2.23. A plot of transition temperatures as a function of n-alkoxy chain length obtained for compounds of series 2.V.

Mesomorphic properties of compounds of series 2.VI:

In this series of compounds, fluorine is substituted at *meta* position with respect to the carboxylate group of the middle phenyl ring (R₂) of the wings of the bent-core containing terminal n-alkoxy chains.

Compound 2.F.1 shows an enantiotropic nematic phase and a monotropic SmA and SmA_C phases while in compound 2.F.2 all the three phases are monotropic. The N-SmA phase transition is weakly first order and the enthalpy values are in the range of 0.2-0.4 kJmol⁻¹ while SmA to SmA_C phase transition is second order. The next higher homologue, compound 2.F.3 also exhibits a nematic and monotropic SmA, SmA_C phases. In addition, on cooling the SmA_C phase to a temperature of 148°C, a transition takes place with an enthalpy of 7.3 kJ mol⁻¹. The textural features of this phase are similar to those of a columnar phase. The XRD studies in this mesophase show two sharp reflections in the small angle region at d₁=21.3Å and d₂=19.4Å. These two reflections can be indexed as (11) and (02) respectively from a rectangular lattice with the lattice parameters, a=25.5 Å and b=38.8 Å. The wide-angle

Table 2.6. Transition temperatures (°C) and enthalpies (kJmol⁻¹) (*in italics*) for compounds of series 2.VI.



2.F.1	n=2	Cr 194.0	(SmAc $\approx$ 163.5) [#]	(SmA 165.0)	N 223.5	I
		<i>46.8</i>		<i>0.23</i>	<i>0.64</i>	
2.F.2	n=3	Cr 208.0	(SmAc $\approx$ 143.0) [#]	(SmA 145.0)	(N 191.5)	I
		<i>57.7</i>		<i>0.39</i>	<i>0.4</i>	
2.F.3	n=4	Cr 170.0	(Col? 144.5)	(B ₁ 149.0)	(SmAc $\approx$ 150.0) [#]	(SmA 151.0) N 185.0 I
		<i>54.2</i>	<i>0.65</i>	<i>7.3</i>		<i>0.4</i> <i>0.43</i>

Compound	n	Cr	B ₂	Col?	B ₁	N	I
2.F.4	5	. 182.0	-	(. 154.0) [#]	(. 156.5)	(. 169.0)	.
		<i>51.4</i>		-	<i>10.8</i>	<i>0.23</i>	
2.F.5	6	. 156.0	-	(. 145.5) [#]	. 159.0	. 163.0	.
		<i>42.9</i>		-	<i>10.8</i>	<i>0.28</i>	
2.F.6	7	. 154.0	-	(. 134.0) [#]	. 157.0	-	.
		<i>32.6</i>		-	<i>11.8</i>		
2.F.7	8	. 147.5	-		. 155.0	-	.
		<i>35.4</i>			<i>16.2</i>		
2.F.8	9	. 136.0	-		. 150.0	-	.
		<i>37.1</i>			<i>15.6</i>		
2.F.9	10	. 136.0	-		. 146.5	-	.
		<i>37.6</i>			<i>15.7</i>		
2.F.10	11	. 134.0	. 146.5		-	-	.
		<i>56.1</i>	<i>18.5</i>				
2.F.11	12	. 130.5	. 148.5		-	-	.
		<i>56.9</i>	<i>18.7</i>				
2.F.12	14	. 127.0	. 151.0		-	-	.
		<i>74.9</i>	<i>20.4</i>				
2.F.13	16	. 124.0	. 152.0		-	-	.
		<i>86.2</i>	<i>21.2</i>				
2.F.14	18	. 123.5	. 152.0		-	-	.
		<i>93.5</i>	<i>21.0</i>				

: temperature obtained under a polarizing microscope. No transition enthalpy could be obtained.

diffuse peak at 4.8 Å indicates a liquid-like ordering of the molecules in the mesophase. This has been identified as a rectangular columnar B₁ phase. A typical photomicrograph obtained at the transition from SmA_C to B₁ phase is shown in figure 2.24. On further cooling this B₁ phase to 143.5°C, a clear change in the texture is seen under a polarizing microscope with a small enthalpy change of 0.6 kJmol⁻¹ as determined from DSC thermogram. Though the basic texture of a B₁ phase remains, additional sharp lines grow in some regions of the mosaic texture as shown in figure 2.25. Since this is a highly metastable mesophase, it has not been possible to carry out XRD studies. From the microscopic observations this mesophase appears to be a highly ordered columnar phase possibly with a tilt of molecules or with a tilted lattice. On ascending the homologous series, SmA, SmA_C and nematic phases disappear and the columnar phase stabilizes for the middle homologues as shown in table 2.6. In addition, no transition enthalpy could be observed while going from B₁ phase to a low temperature columnar phase obtained for compounds 2.F.4, 2.F.5 and 2.F.6. However, these phase transitions could be clearly seen under a polarizing microscope as seen for compound 2.F.3. The B₁ to N phase transition enthalpy values obtained are about 11 kJmol⁻¹ and those for B₁ to I are about 11-16 kJmol⁻¹.

XRD studies have been carried out for all the compounds exhibiting a B₁ phase and the data are summarized in table 2.10. The increase in layer spacing for successive homologues is about 1.6 Å (0.8 Å for half molecular length) for the lower homologues (compounds 2.F.3, 2.F.4, 2.F.5 and 2.F.6), and 1.4 Å for the middle homologues (compounds 2.F.7, 2.F.8 and 2.F.9), and 1.1 Å for the higher homologues (compounds 2.F.13 and 2.F.14). This is probably due to the fact that the lower homologues normally adopt the all *trans* conformation whereas the middle homologues can have both *trans* and *gauche* conformations and the higher homologues adopt *gauche* conformations. As shown in figure 2.26, the lattice parameter value **a** rises sharply when compared with **b** which increases gradually. This suggests that the number of molecules increase in a given lattice on increasing the chain length.

Compounds from 2.F.10 to 2.F.14 show the following textural features. On cooling the isotropic liquid of a thin film of the sample, a fan-shaped texture, a schlieren texture or a fringe pattern which is normally seen for the antiferroelectric B₂ phase is obtained. The optical photomicrograph of a schlieren texture obtained in the B₂ phase of compound 2.F.12

is shown in figure 2.27. The B_2 -I transition enthalpy value obtained is in the range of 18-21 kJmol^{-1} .

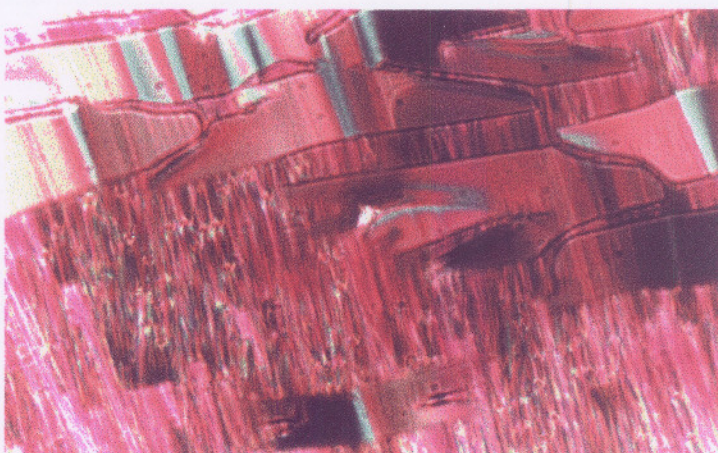


Fig. 2.24. An optical photomicrograph showing columnar B_1 phase developing from the homogeneously aligned SmA_C phase, compound 2.F.3 at 148°C .

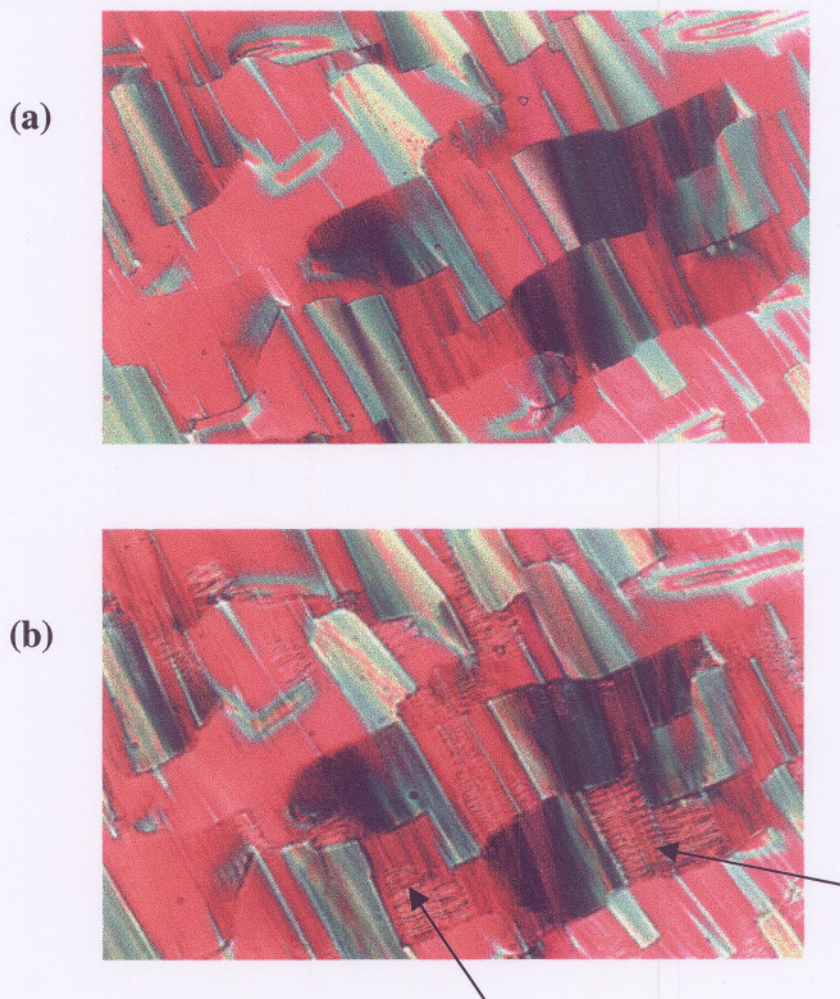


Fig. 2.25. Optical photomicrographs obtained for compound 2.F.3. (a) Completely developed B_1 phase from the homogeneously aligned SmA_C phase at 146°C . (b) Unidentified columnar phase (Col?) obtained with additional sharp lines (shown with arrow) on further cooling the B_1 phase (142.5°C).

Table.2.10. The d-spacings (Å) obtained for different mesophases and the corresponding Miller indices shown in brackets for the compounds of homologous series 2.VI. The XRD measurements have been carried out on mesophases obtained on cooling.

Compound	d-spacings Å / Miller indices	Lattice parameters/ Å		Phase type	T/°C
		a	b		
2.F.3	21.3 (11), 19.4 (02)	25.5	38.8	B ₁	147
2.F.4	22.9 ((11), 20.2 (02)	27.5	40.4	B ₁	155
2.F.5	24.5 (11), 21.0 (02)	30.2	42.0	B ₁	156
2.F.6	26.0 (11), 21.8 (02)	32.4	43.6	B ₁	154
2.F.7	27.8 (11), 22.5 (02)	35.4	45.0	B ₁	150
2.F.8	29.6 (11), 23.2 (02)	38.4	46.4	B ₁	140
2.F.9	31.3 (11), 23.9 (02)	41.4	47.8	B ₁	140
2.F.10	36.8 (01), 18.4 (02), 12.3 (03)	-	-	B ₂	140
2.F.11	37.7 (01), 18.8 (02), 12.6 (03)	-	-	B ₂	135
2.F.12	40.2 (01), 20.1 (02), 13.4 (03)	-	-	B ₂	132
2.F.13	42.6 (01), 21.3 (02), 14.2 (03)	-	-	B ₂	130
2.F.14	44.8 (01), 22.4 (02), 14.9 (03)	-	-	B ₂	130

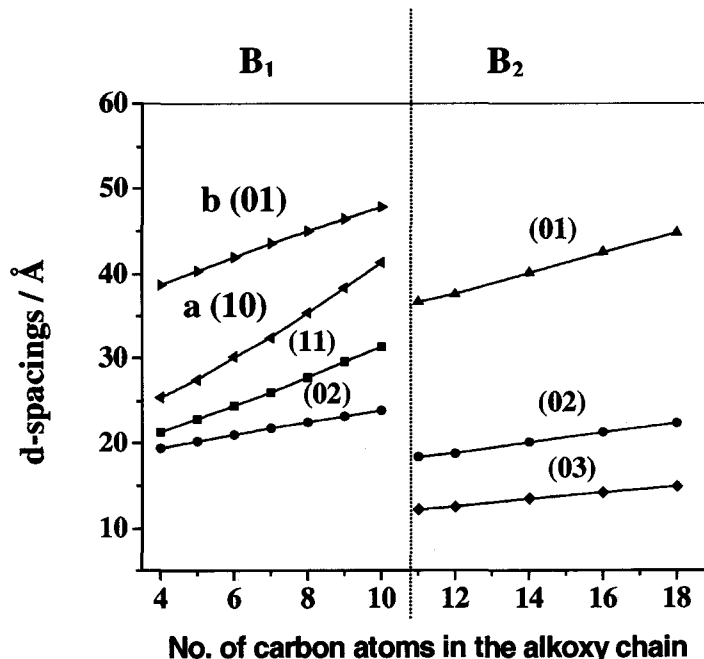


Fig. 2.26. A plot of d-spacings as a function of n-alkoxy chain length obtained for homologues of series 2.VI showing the changes in XRD pattern while going from B₁ to B₂ mesophase; a and b are lattice parameter values obtained from a rectangular B₁ phase.

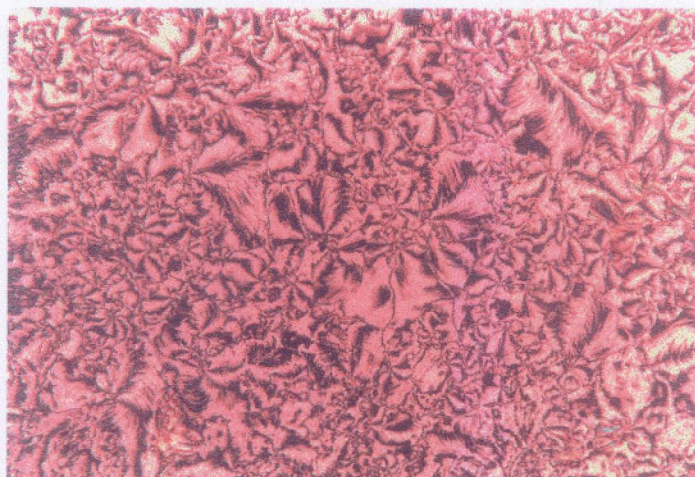


Fig. 2.27. An optical photomicrograph of the mesophase obtained on slow cooling of the isotropic phase of compound 2.F.12 at 145°C.

The X-ray diffraction studies suggest that these are tilted smectics without in-plane order as shown in table 210 and this mesophase has been identified as a B_2 phase. The layer spacing of a B_2 phase gradually increases on increasing the chain length. In order to prove the ground state antiferroelectric structure in this phase, triangular-wave method was employed. The observation of two polarization current peaks for each half cycle confirms the antiferroelectric polar ordering of BC molecules in adjacent layers. The calculated polarization value for compound 2.F.12 is about 195 nC cm^{-2} . In addition, dc field experiments for compound 2.F.12 reveal that the ground state of this B_2 phase is completely racemic as observed for compound 2.C.10 described earlier.

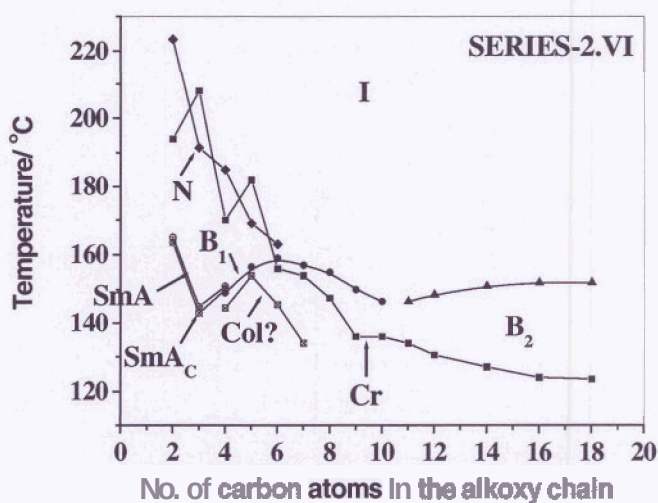


Fig. 2.28. A plot of transition temperatures as a function of *n*-alkoxy chain length obtained for compounds of series 2.VI.

A plot of transition temperatures as a function of the number of carbon atoms in the n-alkoxy chain obtained for compounds of series **2.VI** is shown in figure **2.28**. The odd-even effect for N-I transition temperatures could be clearly seen and the transition temperatures fall on ascending the series. The B₁-I transition points rise slowly, reach a maximum and then gradually decrease on increasing the chain length and all these points fall on a smooth curve. As usual, the clearing temperatures of B₂ phase fall on a smooth curve.

Mesomorphic properties of compounds of series 2.VII:

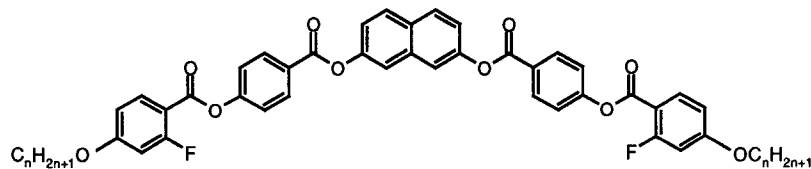
As denoted in structure **2.I**, in compounds of series **2.VII** fluorine is substituted *ortho* to the carboxylate group of the outer phenyl ring (R₃) containing the terminal n-alkoxy chains. The phase behaviour of this series of compounds is somewhat similar to those of the unsubstituted compounds, viz. series **2.IV**. The lower homologue, compound **2.G.1** exhibits an enantiotropic nematic phase and a monotropic B₁ phase while compound **2.G.2** exhibits only an enantiotropic B₁ phase without in-plane order. This was confirmed from XRD studies which showed a rectangular lattice with $d_1=23.8 \text{ \AA}$ (11), $d_2=21.5 \text{ \AA}$ (02) with lattice parameters, $a=28.6 \text{ \AA}$ and $b=43 \text{ \AA}$.

However, the higher homologues (compounds **2.G.3**, **2.G.4** and **2.G.5**) exhibit very interesting microscopic textures as well as electro-optical switching behaviour. On heating the crystal to a mesophase, they exhibit textures similar to that of a B₂ phase and on shearing the sample induces dark regions. Interestingly, on cooling the isotropic liquid to the mesophase a texture which is completely dark is obtained and on further cooling crystallization occurs with very high birefringence. The mesophase obtained on heating is less viscous and is somewhat similar to a B₂ phase while the phase obtained on cooling is more viscous and it is difficult to displace a cover slip. Even after shearing the sample, the mesophase shows only a weak birefringence. XRD studies of this mesophase suggest a simple layered structure and tilt of molecules without in-plane order. Compound **2.G.3** exhibits the small angle layer reflections at $d_1=34.2 \text{ \AA}$, $d_2=17.1 \text{ \AA}$ and $d_3=11.4 \text{ \AA}$.

To study the electro-optical switching behaviour of this mesophase and to measure the spontaneous polarization, triangular-wave method was employed. A cell of $12.7 \mu\text{m}$ thickness was constructed for planar alignment of a sample of compound **2.G.4** which was introduced in the isotropic phase and cooled slowly. After transition to the mesophase, the applied voltage was gradually increased but still the mesophase appeared dark under crossed polarizers. By the application of a high triangular-wave electric field of about $\pm 195\text{V}$ (threshold voltage is

about $\pm 175\text{V}$) at 30 Hz, only one polarization current peak was observed for each half cycle suggesting a ferroelectric switching behaviour for the mesophase. The saturated spontaneous

Table 2.7. Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kJmol^{-1}) (*in italics*) for compounds of series 2.VII.



Compound	n	Cr	B_2^*	B_1	N	I
2.G.1	4	. 182.0 <i>47.0</i>	-	(. 169.5) <i>11.0</i>	. 194.0 <i>0.41</i>	.
2.G.2	7	. 136.5 <i>40.3</i>	-	. 169.0 <i>17.2</i>	-	.
2.G.3	11	. 112.5 <i>36.6</i>	. 149.5 <i>19.6</i>	-	-	.
2.G.4	14	. 115.5 <i>22.0</i>	. 157.0 <i>21.7</i>	-	-	.
2.G.5	18	. 113.0 <i>61.4</i>	. 159.0 <i>21.8</i>	-	-	.

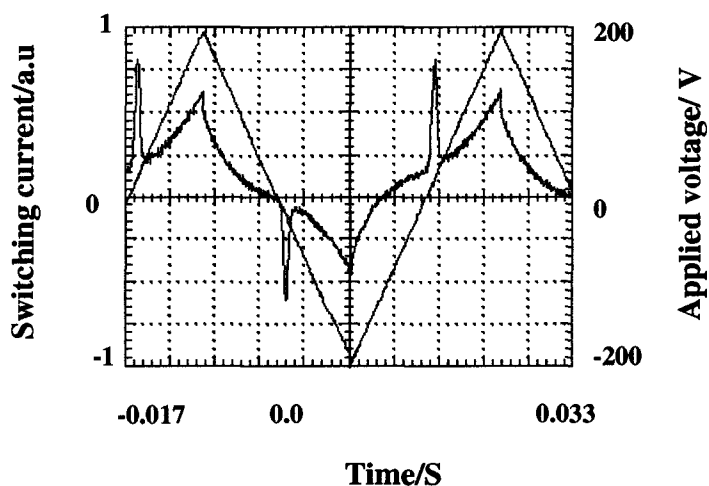


Fig. 2.29. Switching current response obtained in the mesophase of compound 2.G.4 by applying a triangular voltage ($\pm 195\text{V}$, 30Hz) at 125°C . Sample thickness, $12.7\text{ }\mu\text{m}$; spontaneous polarization $\approx 220\text{nC cm}^{-2}$.

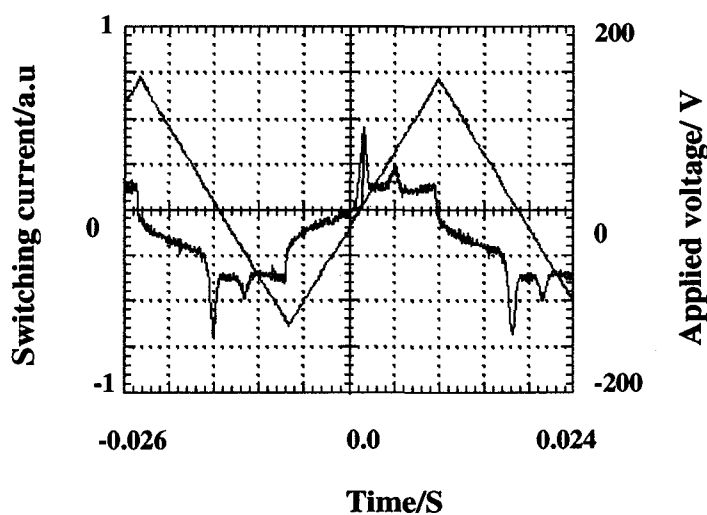


Fig. 2.30a. Switching current response obtained in the mesophase of compound 2.G.4 by applying a triangular voltage (± 130 V, 30 Hz) at 125°C . Sample thickness, $12.7\ \mu\text{m}$; spontaneous polarization $\approx 205\ \text{nC cm}^{-2}$.

polarization value obtained was about $220\ \text{nC cm}^{-2}$. The switching current response trace obtained in this mesophase is shown in figure 2.29. However, on reducing the applied voltage, the single polarization peak obtained for each half cycle splits into two, indicating the antiferroelectric ground state for the mesophase. This behaviour could also be seen at lower frequencies (< 5 Hz). The antiferroelectric type current response trace obtained in this chiral B_2 mesophase is shown in figure 2.30a. By applying a modified triangular voltage, two polarization current peaks were observed for each half period and exist in only one of the

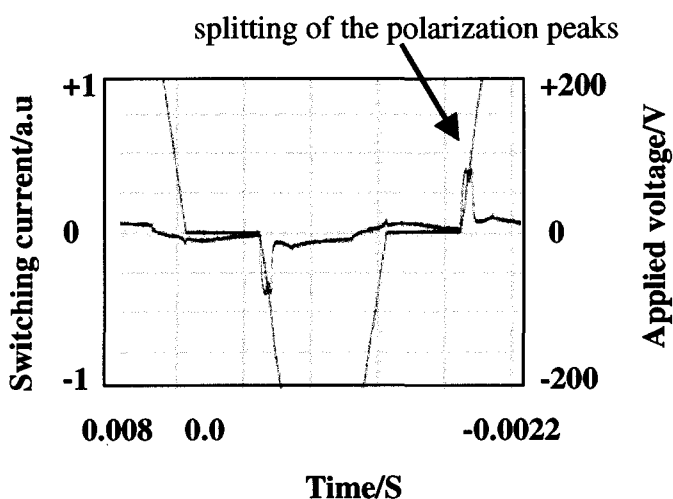


Fig. 2.30b. Switching current response obtained in the mesophase of compound 2.G.4 by applying a modified triangular voltage (± 300 V, 33 Hz) at 125°C . Sample thickness, $12.7\ \mu\text{m}$.

ferroelectric regimes as shown with an arrow in figure 2.30b. If it is antiferroelectric, then the two polarization current peaks obtained must have appeared in the two ferroelectric regimes ($-V$ to 0 and 0 to $+V$) which are separated by the antiferroelectric ground state (triple-plateau, $E=0$). This complicated switching behaviour points towards the ferroelectric ground state structure. If the mesophase is really ferroelectric, then it might exist in more than one ground state structure (for example, chiral and racemic states) which may require different voltages to switch from one state to the other. However, further studies are necessary to confirm the exact ground state structure of this mesophase.

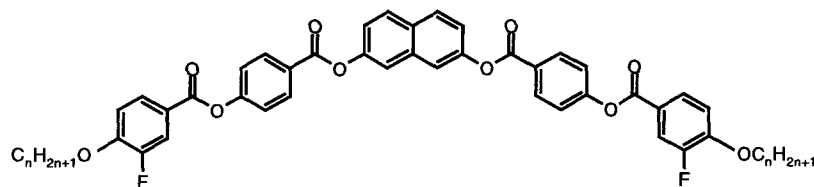
Mesomorphic properties of compounds of series 2.VIII:

In this series of compounds, fluorine is substituted at *ortho* position with respect to the terminal *n*-alkoxy chains (R_4) and the transition temperatures together with the associated enthalpies for different mesophases are summarized in table 2.8.

As can be seen, the lower homologues (compounds 2.H.1, 2.H.2 and 2.H.3) exhibit textural features similar to that of a columnar B_1 phase as observed under a polarizing microscope. Compound 2.H.3 shows the following XRD pattern. Four sharp reflections are obtained in the small angle region at $d_1=34.9$ Å, $d_2=21.3$ Å, $d_3=17.4$ Å and $d_4=13.9$ Å which can be indexed as (11), (02), (22) and (13) respectively for a rectangular lattice of a B_1 phase. From this, the lattice parameter values obtained are $a=60.9$ Å and $b=42.6$ Å. The calculated full molecular length is about 56 Å and the layer spacing obtained from XRD is 42.6 Å. This indicates that the molecules are tilted in the mesophase with a tilt angle of about 40° .

The middle homologues (compounds 2.H.4, 2.H.5 and 2.H.6) show a different phase behaviour as described below. When the isotropic liquid of compound 2.H.5 was cooled slowly and observed under a polarizing microscope, the mesophase appeared with a very weak birefringence. However, by rotating the polarizer or analyzer from the crossed position, two types of domains could be clearly seen which are separated by boundaries. These two distinct enantiomeric configurations differ in tilt direction (polar axis) of the molecules as shown in figure 2.31. Depending on the polarization directions in adjacent layers, the structure can be ferro- or antiferro-electric conglomerates. Also, depending on the tilt sense in adjacent layers the mesophase structures can be ferro- or antiferro-electric racemates. This behaviour is somewhat similar to that observed for compound 2.E.11 described earlier. The optical rotation of these enantiomorphic chiral (conglomerate) domains in this mesophase is about $\pm 7^\circ$. The

Table 2.8. Transition temperatures (°C) and enthalpies (kJ mol⁻¹) (*in italics*) for compounds of series 2.VIII.



Compound	n	Cr	Col _{obF} (B _{X2})	Col _{rF} (B _{X2})	Col _{hF} (B _{X2})	SmC ₅ P _F (B _{X1})	Col _r (B ₁)	I
2.H.1	4	.	170.0 <i>29.5</i>	-	-	-	.	207.0 <i>12.9</i>
2.H.2	7	.	164.0 <i>51.7</i>	-	-	-	.	189.5 <i>18.9</i>
2.H.3	9	.	156.0 <i>57.6</i>	-	-	-	.	183.0 <i>19.2</i>
2.H.4	10	.	156.5 <i>58.4</i>	-	-	.	183.5 <i>19.4</i>	-
2.H.5	11	.	154.5 <i>81.8</i>	-	-	.	183.5 <i>20.3</i>	-
2.H.6	12	.	155.0 <i>84.9</i>	-	-	.	184.0 <i>20.7</i>	-
2.H.7	14	.	155.5 <i>94.7</i>	-	.	184.0 <i>22.0</i>	-	-
2.H.8	16	.	152.5 <i>99.8</i>	.	184.0 <i>22.1</i>	-	-	-
2.H.9	18	.	151.0 <i>112.0</i>	.	182.5 <i>21.9</i>	-	-	-
2.H.10	20	.	149.5 <i>92.3</i>	.	180.0 <i>22.6</i>	-	-	-

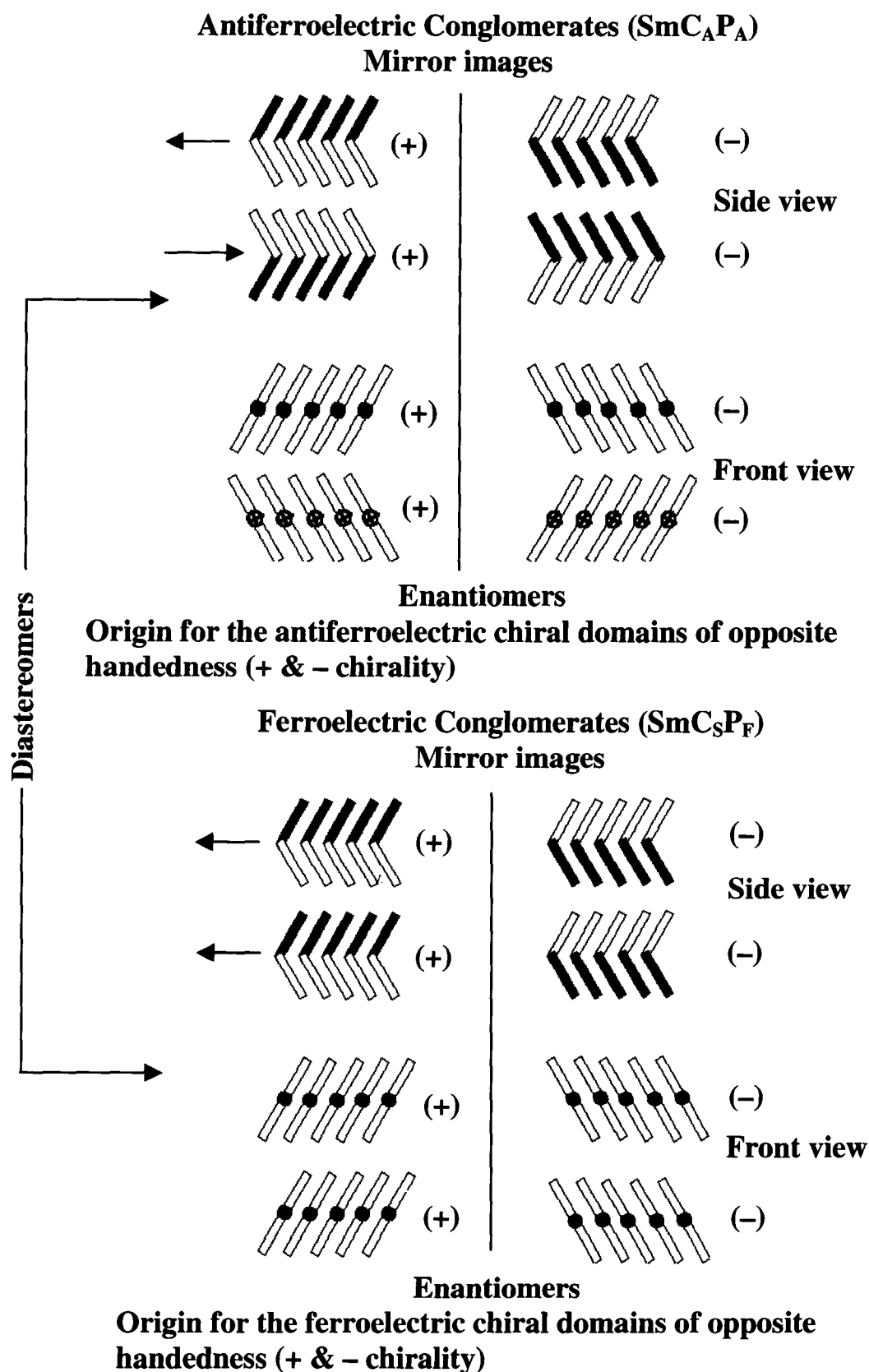
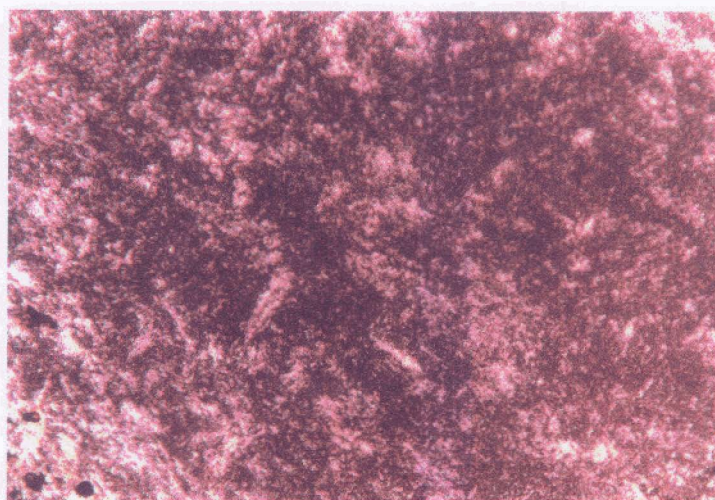
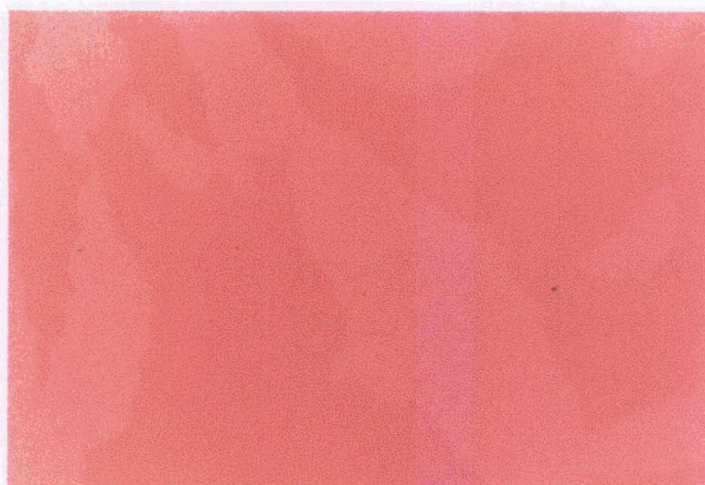


Fig. 2.31. A schematic representation of tilt of BC molecules in opposite directions (opposite polarity) with respect to the layer normal and are mirror images, which are responsible for the occurrence of chiral domains of opposite handedness. The thicker lines indicate plane above the bent-core. (After Walba *et al.* [54])

(a)



(b)



(c)

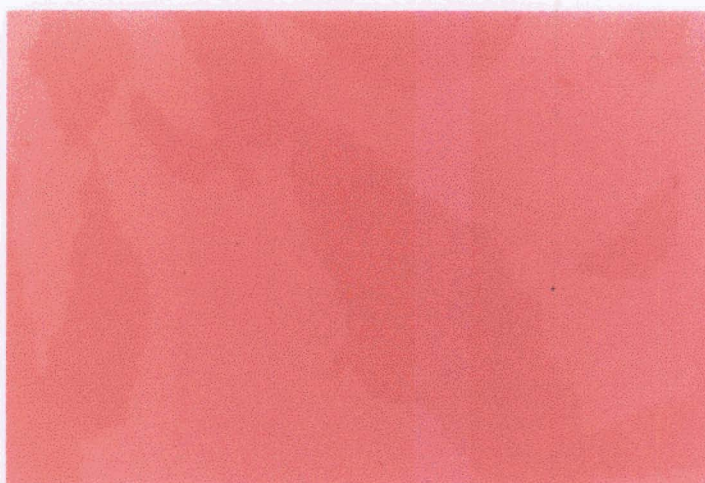


Fig. 2.32. The optical photomicrographs obtained for SmC_SP_F (B_{X1}) mesophase of compound 2.H.5. (a) Texture obtained on heating; (b) and (c) textures obtained on cooling the isotropic liquid, after rotating the analyzer by about $\pm 7^\circ$.

optical photomicrographs obtained for this mesophase on heating as well as on cooling is shown in figure 2.32. As described earlier, the helical axis in these ferroelectric chiral domains is perpendicular to the substrate or coincides with the optical axis. The mesophase to isotropic transition enthalpy values are in the range of 19-21 kJmol⁻¹ and are comparable to B₂-I transition enthalpy though the mesophase is more viscous than a B₂ phase. The XRD studies in this mesophase show three sharp reflections in the small angle region at d₁=40.5 Å, d₂=20.3 Å and d₃=13.6 Å suggesting a lamellar ordering for the mesophase. The calculated molecular length by assuming an all *trans* conformation of the methylene units of n-alkoxy chains is about 61 Å as shown in figure 2.33. This suggests a tilt of the BC molecules with respect to the layer normal and is about 48°. The wide-angle diffuse peak maxima at 4.8 Å indicates the absence of in-plane order.

In addition, this mesophase exhibits an interesting switching behaviour as described below for compound 2.H.5. A sample of this compound was taken in a homogeneously aligned cell (11 μm) and cooled slowly under a triangular-wave electric field (less than the threshold voltage) and as usual the mesophase appears with a weak birefringence and exists as conglomerates. On increasing the voltage to about ± 200 V at 40 Hz, a single polarization current peak was observed. At this high threshold voltage, colourful striped pattern appeared from the dark field of view under a polarizing microscope as shown in figure 2.34. This appears to be the unwound regions of the helical pattern and finally the whole field view becomes bright and remains so even on switching off the electric field. Either with variation in the voltage or even at low frequencies (<1Hz) only a single current peak was observed which suggests a ferroelectric ground state for the mesophase. The current was measured across a 10 kΩ resistance and the ferroelectric current response trace obtained is shown in figure 2.35. The saturated spontaneous polarization value obtained is about 290 nC cm⁻². In order to further establish the ground state structure of the ferroelectric mesophase, the modified triangular-wave electric field experiments were carried out as described by Bedel *et al.* [50]. In this method a simple triangular-wave, (-V to 0 to +V) a one step is modified as multiple steps namely triple-plateau, in order to stay for a while at fixed values, (-V, 0 or small offset v and +V separated by ramps (fig. 2.36). The time spent at +/- V (v offset) serves to stabilize the polar phases induced (or aligned) by the applied electric field. While the time at zero plateau (V=0) helps to stabilize the ground state structures such as an antiferroelectric phase. Hence there would be enough time for complete switching. This kind of voltage waveform with multiple steps helps to resolve the combined polarization current peaks if it

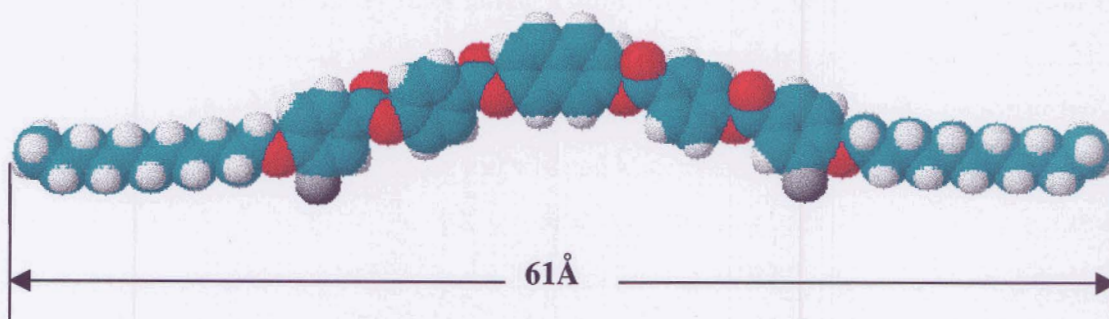


Fig. 2.33. A pictorial representation of the conformation of a molecule of compound 2.H.5 used to calculate the full molecular length.

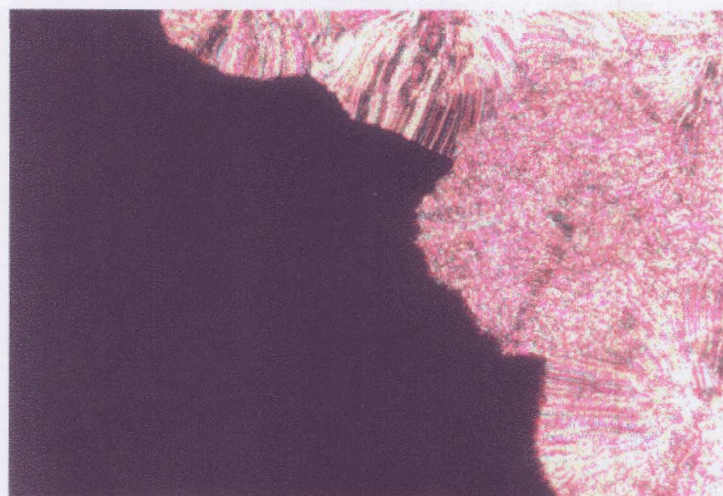


Fig. 2.34. Colourful striped pattern appearing from the dark field of view at the threshold voltage of about $\pm 18 \text{ V} \mu\text{m}^{-1}$ (40Hz) for compound 2.H.5 (B_{X1} mesophase) at 160°C .

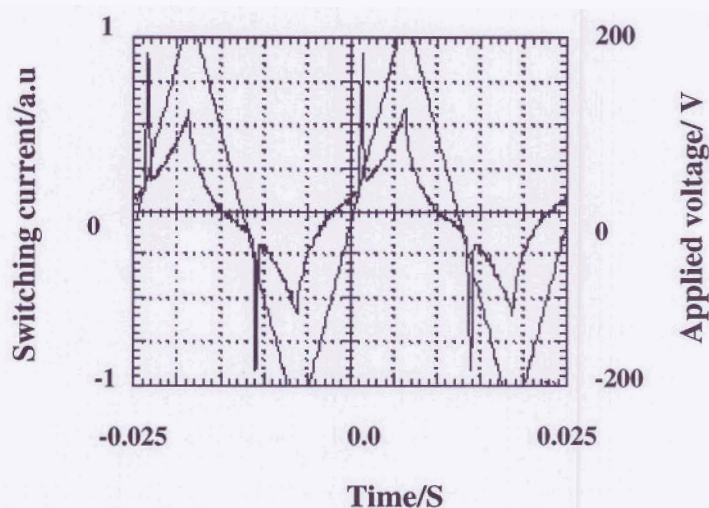


Fig. 2.35. Switching current response obtained in the mesophase of compound 2.H.5 by applying a triangular voltage ($\pm 220 \text{ V}$, 40 Hz) at 160°C . Sample thickness, $11.0 \mu\text{m}$; spontaneous polarization $\approx 290 \text{ nC cm}^{-2}$.

exists. In other words, this is an alternative method for confirming ferroelectric switching behaviour. The modified triangular-wave obtained for the mesophase of compound **2.H.5** is shown in figure 2.36 confirming the ferroelectric ground state. The textural features obtained for this mesophase are not comparable to any of the known smectic ferroelectric phases which are reported in the literature [41, 90, 91, 92] and also these are achiral molecules exhibiting ferroelectricity. Hence we have designated this mesophase as B_{X1} (SmC_sP_F) to differentiate it from other known smectic ferroelectric phases. Recently, Dantlgraber *et al.* [93] reported ferroelectric smectic liquid crystals formed by achiral polyphilic bent-core molecules. The mesomorphic behaviour described by them appears to be the same as those of the B_{X1} phase.

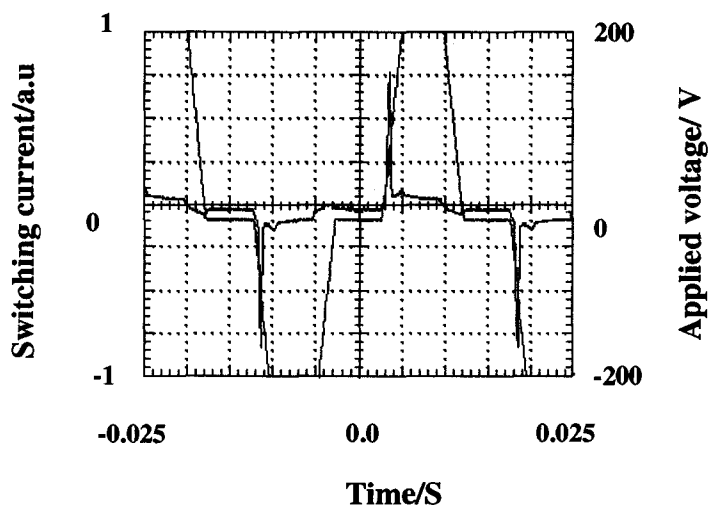


Fig.2.36. Switching current response obtained in the mesophase of compound **2.H.5** by applying a modified triangular voltage (± 220 V, 33 Hz) at 160°C . Sample thickness, $11\ \mu\text{m}$; spontaneous polarization $\approx 290\ \text{nC cm}^{-2}$.

Interestingly, the mesomorphic properties of higher homologues (compounds **2.H.7**, **2.H.8**, **2.H.9** and **2.H.10**) are completely different. For example, compound **2.H.7** shows the following features. On cooling a thin film of the sample from the isotropic liquid and observing under a polarizing microscope, very long colourful banana leaf-like patterns as well as spherulitic domains could be seen to grow suggesting a two-dimensional ordering of the molecules in the mesophase. In a homogeneously aligned cell, the compound shows uniformly aligned very long banana leaf-like textures as shown in figure 2.37. The clearing enthalpy values obtained for this mesophase are of the order of $22\text{--}23\ \text{kJ mol}^{-1}$.

The X-ray pattern of a non-oriented sample shows many sharp reflections in the small angle region as shown in table 2.11. Compound **2.H.7** shows the following interesting XRD pattern. Four sharp reflections obtained in the small region at $d_1=44.1\ \text{\AA}$, $d_2=25.7\ \text{\AA}$, $d_3=22\ \text{\AA}$ and

$d_4=14.7$ Å. These reflections are in the ratio of 1: $1/\sqrt{3}$:1/2 :1/3 and is indicative of a hexagonal columnar phase. Hence, these reflections can be indexed as (01), (11), (02) and (03) respectively, with a lattice parameter value, $a=50.9$ Å. This mesophase has been designated as Col_{hF}. The X-ray angular intensity profile obtained in the Col_{hF} mesophase of compound **2.H.7** is shown in figure 2.38. The XRD pattern obtained for compound **2.H.8** cannot be indexed for a hexagonal lattice but can be fit into a rectangular lattice. Hence this mesophase has been designated as Col_{rF}. The small angle reflections obtained for compounds **2.H.9** and **2.H.10** cannot be indexed for either a hexagonal or a rectangular lattice but can be indexed for an oblique lattice as shown in table 2.11. A wide-angle diffuse peak at about 4.8 Å indicates a fluid-like ordering of the molecules for all these mesophases. However, further studies have to be carried out to confirm the exact structure of these mesophases.

By the application of a triangular-wave electric field (± 250 V at 30 Hz) for compound **2.H.7**, the mesophase shows a single polarization current peak for each half cycle suggesting a ferroelectric type switching for the mesophase. The single polarization current peak obtained, exists even at a frequency of 0.1 Hz confirming the ferroelectric ground state for the mesophase. This experiment further confirms that even at high electric fields (± 25 V μm^{-1}) as well as at a low frequency (0.1Hz) the mesophase is ferroelectric only. In order to establish the existing ferroelectric ground state, modified triangular-wave experiments were carried out and the resultant ferroelectric current response obtained in Col_{hF} mesophase is shown in figure 2.39. Similar ferroelectric switching behaviour could be observed for the remaining Col_{rF} and Col_{obF} mesophases of compounds **2.H.8**, **2.H.9** and **2.H.10**. Typical photomicrographs obtained in the B_{X1} as well as in the Col_{hF} ferroelectric phases under a triangular-wave electric field are shown in figure 2. 40.

A plot of transition temperatures as a function of n-alkoxy chain length for this series is shown in figure 2.41. As usual, the B₁-I transition points show a downward trend and the B_{X1}-I transition points lie on a smooth curve. Interestingly, a new phase sequence such as, different columnar phases which are separated by a smectic phase on ascending the homologous series could be seen.

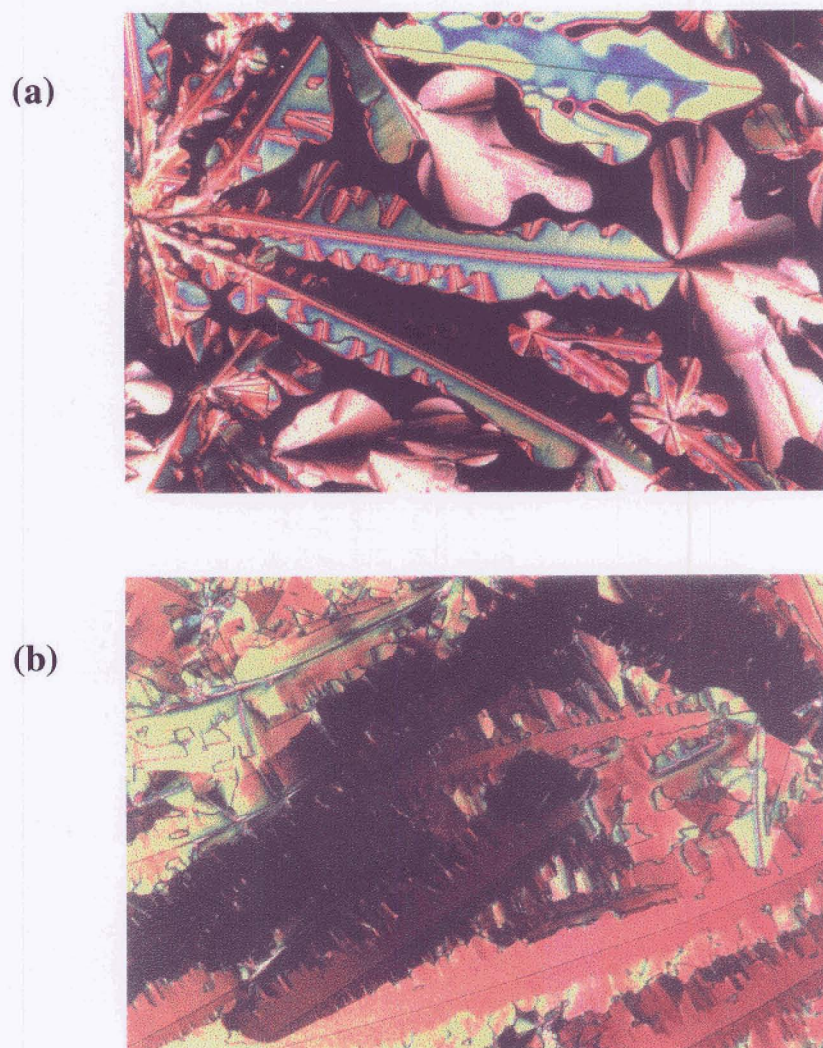


Fig. 2.37. The optical photomicrographs of $\text{Col}_{\text{hF}} (\text{B}_{\text{X}2})$ phase (a) long banana leaf-like texture and (b) uniform leaf-like texture obtained on slow cooling in a homogeneously aligned cell of compound 2.H.7.

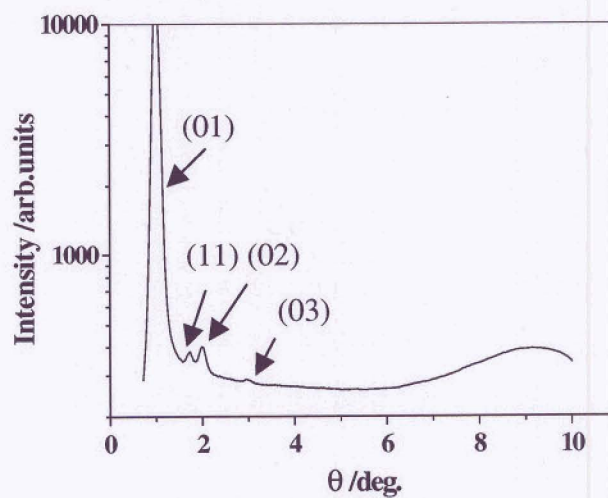


Fig. 2.38. X-Ray angular intensity profile obtained in the $\text{Col}_{\text{hF}} (\text{B}_{\text{X}2})$ mesophase of compound 2.H.7.

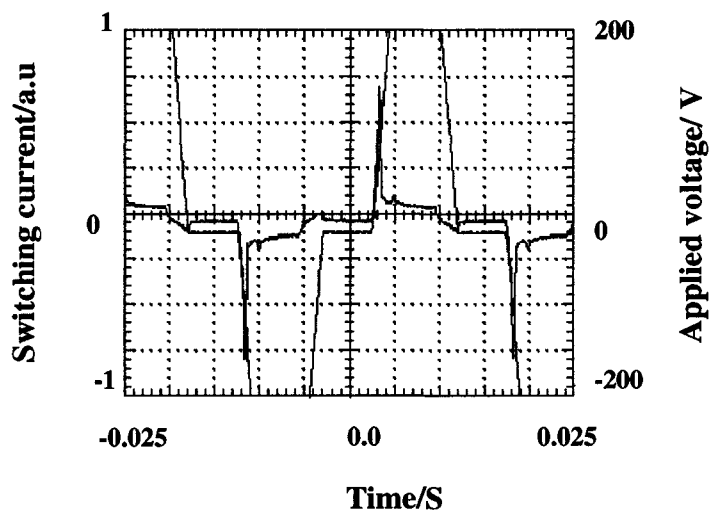


Fig. 2.39. Switching current response obtained in the mesophase of compound 2.H.7 by applying a modified triangular voltage (± 250 V, 33 Hz) at 160°C . Sample thickness, $12.8\ \mu\text{m}$; spontaneous polarization $\approx 400\ \text{nC cm}^{-2}$.

Table. 2.11. The d-spacings ($\text{\AA}$) obtained in the mesophases of compounds of series 2.VIII. The XRD measurements have been carried out on mesophases obtained on cooling.

Compound	d-spacings / $\text{\AA}$	Phase type
2.H.3	34.9 $\text{\AA}$ (11), 21.3 $\text{\AA}$ (02), 17.4 $\text{\AA}$ (22), 13.9 $\text{\AA}$ (13) $a=60.9\ \text{\AA}$ and $b=42.6\ \text{\AA}$	B_1 or Col_r
2.H.5	40.5 $\text{\AA}$ (01), 20.3 $\text{\AA}$ (02), 13.6 $\text{\AA}$ (03)	B_{X1} or SmC_sP_F
2.H.7	44.1 $\text{\AA}$ (01), 25.7 $\text{\AA}$ (11), 22.0 $\text{\AA}$ (02), 14.7 $\text{\AA}$ (03) $a=50.9\ \text{\AA}$	Col_{hF} (B_{X2})
2.H.8	45.5 $\text{\AA}$ (11), 37.6 $\text{\AA}$ (02), 26.6 $\text{\AA}$ (21), 22.8 $\text{\AA}$ (13 or 22), 17.7 $\text{\AA}$ (14); $a=57.1\ \text{\AA}$ and $b=75.2\ \text{\AA}$; Calcd: 45.5 $\text{\AA}$ (11), 37.6 $\text{\AA}$ (02), 26.7 $\text{\AA}$ (21), 23.0 $\text{\AA}$ (13), 22.8 (14), 17.9 (14).	Col_{rF} (B_{X2})
2.H.9	46.5 $\text{\AA}$ (10), 35.1 $\text{\AA}$ (01), 29.4 $\text{\AA}$ (11), 26.9 $\text{\AA}$ (11), 23.2 $\text{\AA}$ (20), 18.6 $\text{\AA}$ (21), 15.7 $\text{\AA}$ (12 or 30); $a=46.7\text{\AA}$, $b=35.3\text{\AA}$ and $\beta=84.6^\circ$; Calcd: 26.8 $\text{\AA}$ (11), 23.3 $\text{\AA}$ (20), 18.6 $\text{\AA}$ (21), 15.9 $\text{\AA}$ (12) or 15.5 $\text{\AA}$ (30)	Col_{obF} (B_{X2})
2.H.10	48.7 $\text{\AA}$ (10), 31.4 $\text{\AA}$ (01), 27.0 $\text{\AA}$ (11), 24.3 (20), 19.8 (21) $a=48.8\ \text{\AA}$, $b=31.4\ \text{\AA}$ and $\beta=87.2^\circ$; Calcd: 24.4 (20), 19.8 (21)	Col_{obF} (B_{X2})

This represents the first example of different mesophase structures ($\text{SmC}_\text{sP}_\text{F}$, Col_hF , Col_rF and Col_obF) obtained on ascending the homologous series and all of which exhibit ferroelectric switching properties. This is probably due to the fact that a fluorine substitution at *ortho* position increases the entropy of the terminal chains. Hence, it destabilizes the antiferroelectric phase due to the weak inter-layer interactions.

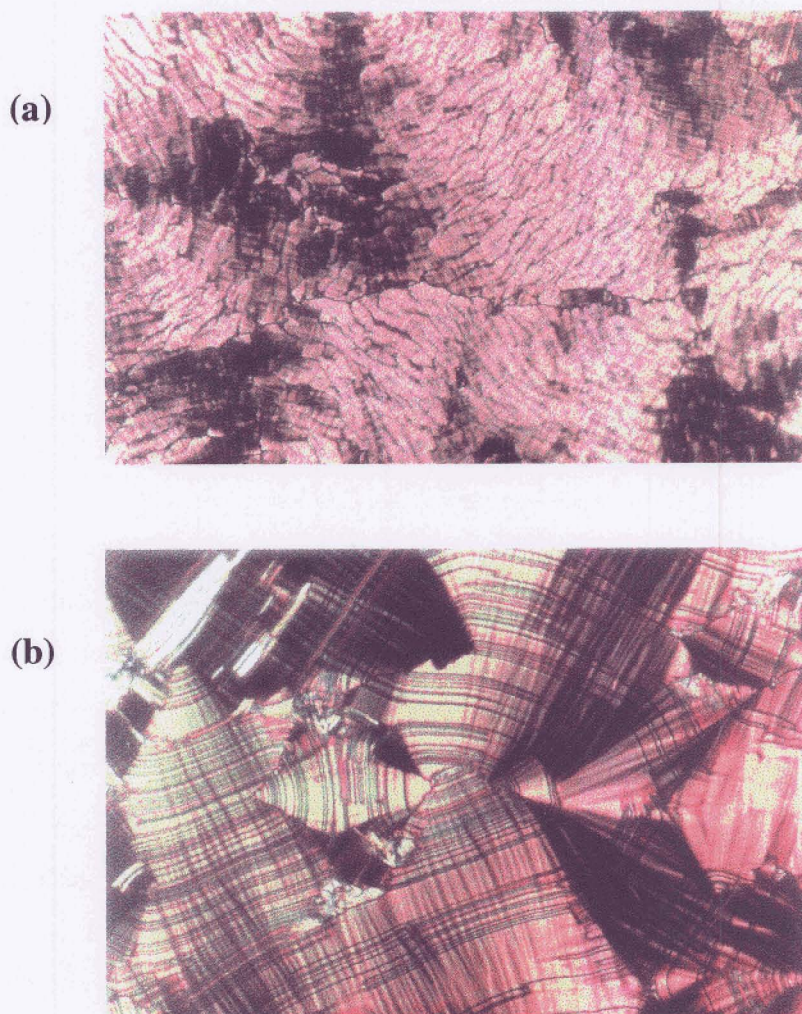


Fig. 2.40. Textural photomicrographs obtained in (a) $\text{SmC}_\text{sP}_\text{F}$ (B_{x1}) phase of compound 2.H.5 (b) Col_hF (B_{x2}) phase of compound 2.H.7 under a triangular-wave electric field (above the threshold voltage).

In general, the mesophases appear dark under a polarizing microscope and may be ferro- and/or antiferro-electric depending on the polarization directions in adjacent layers. The origin for the chiral domains of opposite handedness is shown in figure 2.31. However, the exact structure of these chiral domains is still a complex problem. It has not been possible to obtain a monodomain sample of these mesophases to confirm the exact structure of these chiral

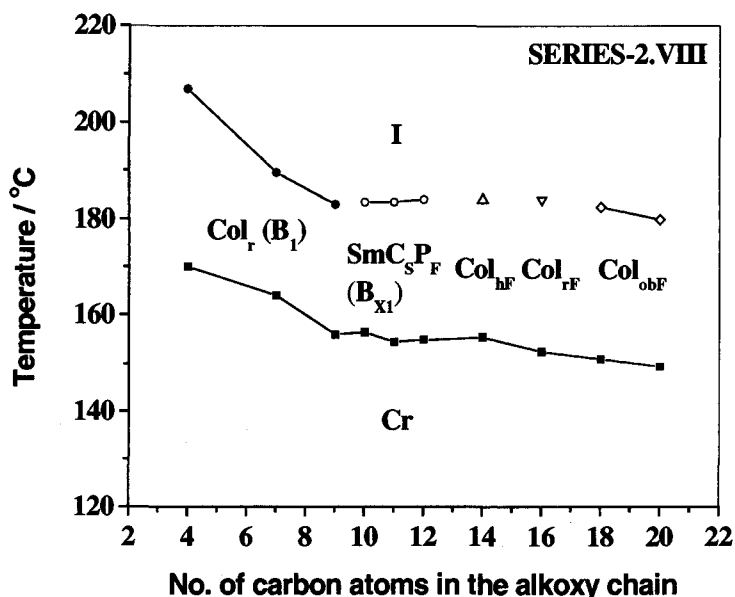


Fig. 2.41. A plot of transition temperatures as a function of n-alkoxy chain length obtained for compounds of series 2.VIII.

domains. As described by Dantlgraber *et al.* [93], the optical biaxiality expected in BC molecules is due to the polar order and a tilt with respect to the layer normal. In ferroelectric liquid crystals, the layer polarization can be compensated by the formation of a helix, which can be generated perpendicular to the layer planes (SmC*-like) where by the pitch of this helix is different from the wavelength of the visible light. The other possibility is the formation of helix parallel to the layer planes (TGB-like). Since the molecules are tilted within the smectic layers, the phase structure may be similar to the TGB_C or TGB_C* phases. In addition, the helical twist can occur on either side (unlike in conventional TGB-phases) leading to the domains of opposite chirality. In both the cases, the helical superstructures are formed in which the polar axis of BC molecules align parallel in successive layers which can lead to optical uniaxiality of the mesophases.

Comparison between the homologous series of 2.I, 2.II and 2.III (terminal n-alkyl chains):

The influence of fluorine can be seen as it reduces both the melting as well as clearing temperatures of compounds of series 2.II and 2.III. The reduction in melting points varies from about 20-50°C and for the clearing temperatures it is about 10-30°C. Though the size of fluorine (1.47 Å) is comparable to that of hydrogen (1.2 Å), its influence is significant. For

example, the thermal range of the mesophase increases as a result of fluorine substitution. In series **2.I**, for compound **2.A.9**, 6.5° thermal range of the B₂ phase was observed while in the case of fluorine substituted analogues (series **2.II** and **2.III**) it is about three times this value.

Compounds of series **2.I** show only B₁ and B₂ mesophases while those of series **2.II** and **2.III**, exhibit a B₁, B₂ and a nematic phase. In the case of compound **2.A.1**, no mesophase was observed while the corresponding analogues of series **2.II** and **2.III** show a columnar B₁ and nematic phases respectively. This is probably due to a reduction in the melting points and electronic effects due to the presence of fluorine substituent.

A comparison of series **2.II** and **2.III**, shows that the reduction in melting as well as clearing temperatures are higher in the latter. The nematic phase is more stabilized if a fluorine is present at *meta* position (**2.C.2**, up to n=5) when compared to the *ortho* analogue (**2.B.5**, n=5). For compound **2.B.4** of series **2.II**, a columnar B₁ phase is seen while the corresponding analogue in series **2.I** and **2.III**, it is absent. Compound **2.A.6** of series **2.I** and **2.B.9** of **2.II** show a B₂ phase where as in series **2.III**, compound **2.C.6** (same chain length) shows a B₁ phase. These observations indicate that orientation directions of the dipoles due to the presence of fluorine with respect to the polar axis, determines the mesophase type as well as stability as also pointed out by Dantlgraber *et al.* [94].

Comparison between the homologous series of 2.IV, 2.V and 2.VI (terminal n-alkoxy chains):

As usual, the reduction in melting as well as clearing temperatures are seen. The introduction of fluorine in the middle phenyl ring shows rich polymesomorphism when compared to the unsubstituted parent compounds. For example, compound **2.D.1** of series **2.IV** shows a nematic and a columnar B₁ phase while the corresponding compound in series **2.V** shows a B₆ phase in addition to nematic and B₁ phases. The corresponding homologue in series **2.VI** (**2.F.3**), shows two different SmA phases and a columnar phase along with a nematic and a B₁ phase. The fluorine substitution in the middle phenyl ring has more tendency to form calamitic phases in addition to banana phases especially for shorter chains. Also compound **2.E.9** of series **2.V** shows a B₂ phase while the corresponding analogue of series **2.VI** shows a columnar B₁ phase. From this, one can infer that fluorine in the *meta* position of the middle phenyl ring stabilizes the columnar phase when compared to smectic phases. Fluorine at *ortho* position induces a B₆ phase (compound **2.E.3**) while the fluorine at *meta* position induces an

additional SmA and columnar phases when compared to the parent compounds. It can be seen that a fluorine substitution at *ortho* position considerably reduces the melting points (about 20°) without affecting the clearing temperatures. The most interesting point is that a fluorine substitution at *ortho* position stabilizes the ground state chiral structure of the B₂ mesophase which is present in the parent system for the higher homologues. A fluorine substitution at *meta* position stabilizes the ground state racemic structure. It is evident from these observations that the position of lateral dipole such as a fluorine substituent can change the tilt sense of BC molecules such that the phase could be either chiral or racemic.

Comparison between n-alkyl (2.I, 2.II and 2.III) and n-alkoxy (2.IV, 2.V and 2.VI) terminal chains:

As seen in the literature as well as in the presently investigated homologous series of compounds, terminal n-alkoxy chains are definitely better than n-alkyl chains in stabilizing the mesophases. For example, compound 2.A.1 of series 2.I is not liquid crystalline while the corresponding n-alkoxy compound shows nematic and columnar B₁ phases. An interesting point to note is that the melting points are reduced by about 30° in n-alkoxy series 2.IV when compared to n-alkyl series 2.I while the clearing temperatures are about the same. However, when fluorine is substituted at *ortho* position in the middle phenyl ring, the n-alkoxy derivatives have lower melting temperatures as compared to the corresponding n-alkyl derivatives and the clearing temperatures are about the same. Similarly when a fluorine is substituted at *meta* position of the middle phenyl ring, the n-alkyl terminal chain compounds have lower melting as well as clearing temperatures when compared to the corresponding n-alkoxy substituted compounds.

Influence of fluorine substitution in the middle- and the outer-phenyl rings:

As described earlier, the antiferroelectric switching behaviour of the mesophases is retained for the higher homologues when fluorine is substituted at *ortho* position to the carboxylate group either in the middle phenyl ring or on the outer phenyl ring of the arms of these BC molecules. For example, the chiral smectic phase (B₂^{*}) obtained in the parent compounds, is retained even after introducing a fluorine at *ortho* position (compound 2.E.11). The phase sequence for the higher homologues of series 2.IV, 2.V and 2.VII are shown in tables 2.4, 2.5 and 2.7 respectively. Some additional phases are induced for the lower homologues when a fluorine is present in the middle phenyl ring. However, a fluorine at *meta* position with

respect to the carboxylate group of middle- as well as outer-phenyl ring has a big influence as shown in tables 2.6 and 2.8. Only racemic ground state of a B_2 phase is obtained if a fluorine is substituted at *meta* position of the middle phenyl ring in contrast to the parent compounds.

However, when fluorine is substituted at *ortho* position with respect to the n-alkoxy chain, completely different mesophase switching characteristics are observed. As described for compounds of series 2.VIII, the middle homologues (compounds 2.H.4, 2.H.5 and 2.H.6) show a new lamellar ferroelectric phase (B_{X1} or SmC_5P_F) while the parent compounds show an antiferroelectric chiral B_2 phase. The higher homologues (compounds 2.H.7, 2.H.8, 2.H.9 and 2.H.10) show two-dimensional new ferroelectric phases namely, Col_{hF} , Col_{rF} and Col_{obF} on ascending the homologous series whereas the parent compounds show only an antiferroelectric chiral B_2 phase. This clearly reveals that fluorine substitution at this position seems to be very effective in generating switchable mesophases, particularly the ferroelectric phases. In addition, fluorine at this position increases melting as well as clearing temperatures when compared to either parent compounds or any other fluorine substituted compounds.

Experimental:

General methods of investigation

In general, the intermediates and the target compounds were purified by column chromatography on silica gel, (ACME make, 60-120 mesh) using suitable solvents or mixtures of solvents for elution. Those, which are liquids were further purified using distillation method either under water suction or under high vacuum. All the compounds were crystallized using appropriate solvents or mixtures of solvents to constant melting points. Merck Kieselgel 60F₂₅₄ precoated thin layer chromatographic plates (manufactured by Merck, Germany) were used to check the purity of all the compounds by exposing the plates to a UV lamp at 254nm. The normal phase high performance liquid chromatography on porasil column, (3.9mm x 300mm, Waters Associates Inc.) was used to determine the purity of all the target compounds using 1% ethylacetate in dichloromethane as an eluent. The yield obtained for all the intermediate compounds was in the range of 70-90% while for the final compounds it was about 60-80%. ¹H NMR spectra were recorded to confirm the chemical structure of all the compounds and ¹³C NMR spectra were also recorded for the target compounds on a Bruker AMX 400 spectrometer using 1% tetramethylsilane (TMS) in deuteriochloroform or deuterioacetone as an internal standard. The chemical shift values obtained are given in δ (ppm) with respect to TMS. Infrared absorption spectra were recorded on a Shimadzu FT IR-8400 spectrophotometer using nujol mull (unless otherwise mentioned). The wavenumber values are given in cm⁻¹. The elemental analysis was carried out for both intermediates and the target compounds on a Carlo-Erba 1106 analyzer except for the fluoro substituted compounds.

The mesophase behaviour of all the compounds was examined under a Leitz Laborlux 12 POL/Olympus BX50 polarized light microscope attached with a FP82HT heating stage and a FP90 central processor by sandwiching the sample between a glass slide and a coverslip. The transition temperatures and the associated enthalpies were obtained from thermograms recorded on a Perkin-Elmer, Model Pyris 1D differential scanning calorimeter. The calorimeter was calibrated using pure indium as a standard. The temperatures are given in °C and the enthalpy values are calculated and reported as kJ mol⁻¹. The cooling and heating rates were 5°C min⁻¹. The electro-optical switching characteristics were examined under a polarizing microscope using a simple experimental set up where the polyimide coated ITO

cells with samples were cooled slowly from the isotropic liquid by the application of a dc field using a Regulated Dual dc Power Supply (LD 6401).

X-Ray diffraction measurements

X-Ray diffraction measurements on the mesophases exhibited by BC compounds provide very useful information regarding the structure of the mesophase. This method has been used extensively in the present investigations.

The X-rays were produced (4kW) by a rotating anode generator (Rigaku, Ultrax 18). Graphite crystal has been used to obtain monochromatic X-rays of wavelength 1.54 Å which is the characteristic wavelength of Cu-K α radiation. For collimation and to avoid the parasitic scattering, double-slit arrangement has been used. This will produce X-rays of 0.5 × 0.5 mm cross sectional area to strike the sample. The samples were taken in 0.5-1.0 mm diameter Lindemann capillaries and X-ray diffraction measurements were carried out on cooling the sample from isotropic liquid to the mesophase. The computer controlled heater could be maintained to an accuracy of about ±1°C. The resultant diffraction patterns were recorded using a 2D image plate detector (Marresearch) which is also controlled by a computer as shown in figure 2.1a.

The d-spacings were calculated using the well known Bragg's law $n\lambda = 2d \sin\theta$.

Where, $n = 1$ (for first order reflection)

$\lambda = 1.54 \text{ Å}$ (for Cu-K α radiation)

d is the spacing obtained from the mesophase

θ is Bragg angle, which can be calculated as follows

$$\theta = \frac{1}{2} \times \tan^{-1} (R/D)$$

R = radius of the diffraction pattern

D = distance between the sample and detector which can be measured using sodium chloride crystals as a standard.

$$\text{spacing, } d = 1.54/2 \times \sin\theta$$

Hence,

The tilt angle of molecules in the mesophase can be calculated as follows.

Tilt angle $\theta = \cos^{-1}(d/L)$

Where, d is the spacing obtained from XRD experiment and
 L is the measured molecular length

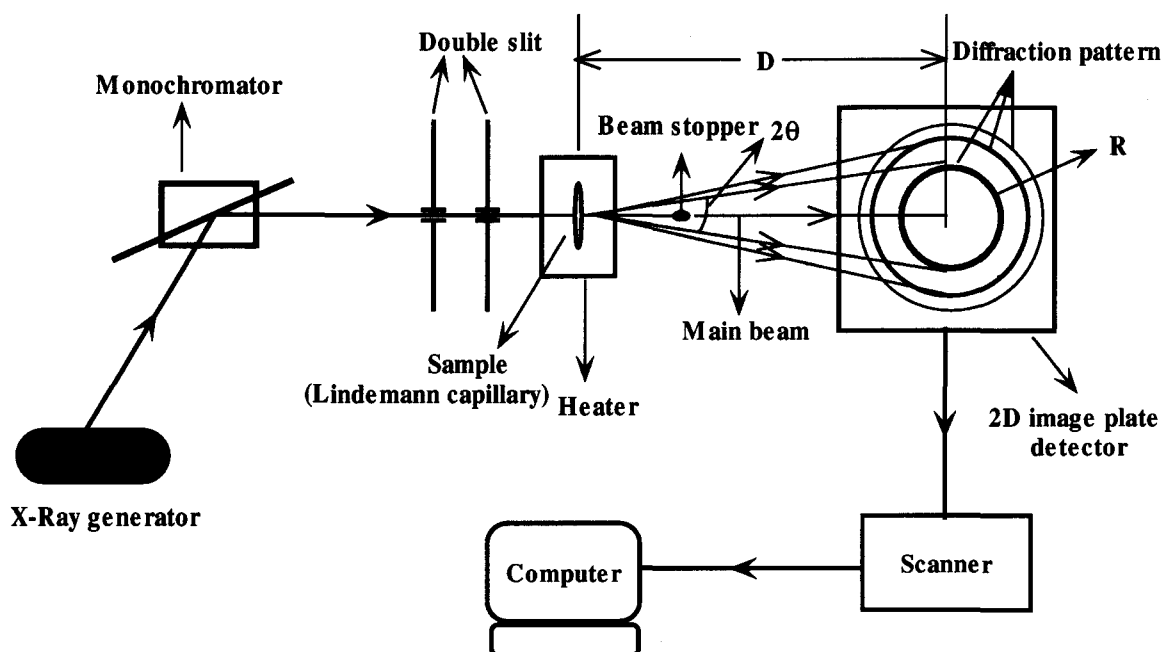


Fig. 2.1a. A block diagram of X-ray set-up used to obtain the diffraction pattern of different mesophases.

The polarization measurements (P_s) - Triangular-wave method

In order to study the electro-optical response, particularly the ferro- and antiferro-electric liquid crystalline behaviour and to measure the spontaneous polarization of the mesophase, triangular-wave method was employed.

The sample was taken between two indium tin oxide (ITO) coated conducting cells, which was constructed for homogeneous alignment (planar alignment) and unidirectionally rubbed. The cell thickness was adjusted suitably using mylar spacers and the sample was filled in the isotropic state avoiding air bubbles. The resistance of the cell was measured after filling the sample by checking the drop in voltage. The polarization measurements were always carried out on slow cooling of the isotropic liquid to the mesophase which resulted in good alignment. The triangular waves were produced using a waveform generator (WAVETEK, MODEL 39) which was amplified using an amplifier (TREK MODEL 601B-3). As shown in figure 2.1b, the amplifier output was divided into two channels which are represented as CH1 and CH2. The waveform CH1 is directly connected to an oscilloscope (Tektronix TDS 220) as a reference. The CH2 is the resultant waveform and is the output signal from the sample.

To measure the current from the applied voltage, a resistor ($10\text{ k}\Omega$ or $1\text{ k}\Omega$) was used across the series. The resultant trace obtained on the oscilloscope screen is a plot of switching current (mA) versus time (mS).

$$\text{Polarization} = \text{dipole moment} / \text{unit volume}$$

The spontaneous polarization value was calculated by integrating the area under the peaks obtained in the experiment. The polarization value can be calculated as follows.

$$\text{Polarization} = \text{current (i)} \times \text{time (t)} / \text{cell area}$$

Where, i = voltage (V in volts)/ resistance (R in ohms)

t = response time in milliseconds.

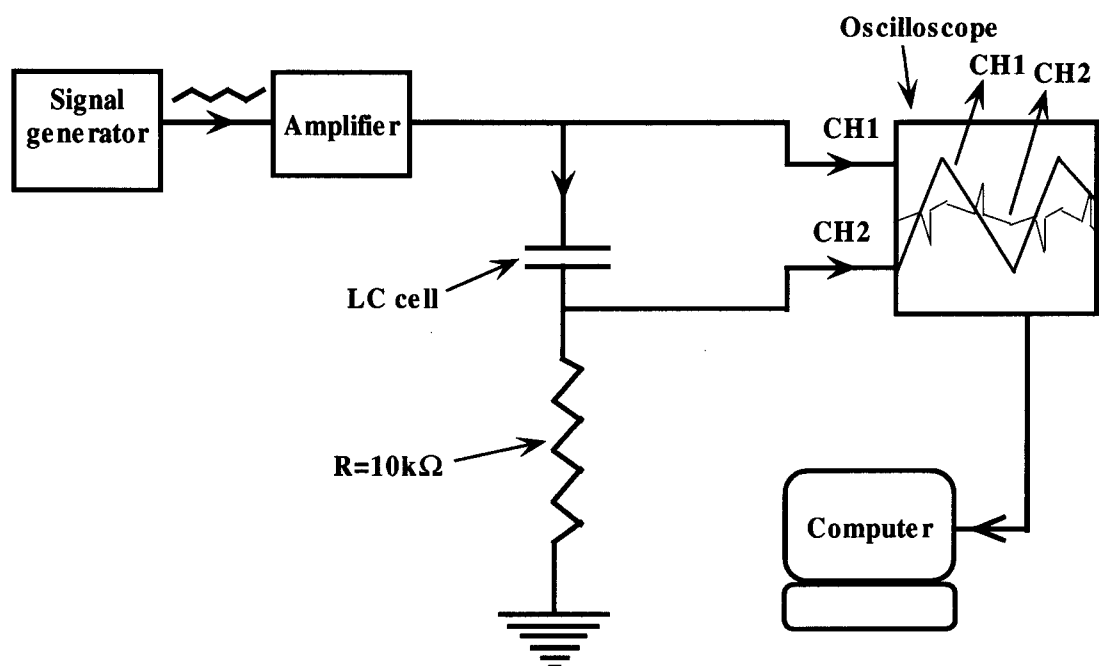


Fig. 2.1b. A block diagram of a simple circuit used to measure the spontaneous polarization.

4-Bromo-2-fluoroanisole, (2.1)

This was prepared using a procedure described by Kelly [81]. Thus, a solution of bromine (41.3g, 0.26 mol) in dry dichloromethane (50 ml) was added dropwise to a solution of 2-fluoroanisole (32.5g, 0.26 mol) in dry dichloromethane (100 ml) over a period of 2 hours at room temperature. The red colour slowly disappears and simultaneously liberation of HBr was observed. The resultant reaction mixture was stirred overnight, poured into ice-cold water

and extracted with dichloromethane (3× 50 ml). The organic solution was then washed with 10 % sodium bicarbonate solution (2 × 50 ml), water (3 × 100 ml) and dried (sodium sulphate). The liquid so obtained after the removal of solvent was distilled under reduced pressure to yield 4-bromo-2-fluoroanisole. Yield, 49 g (93%); b.p. $\approx$ 55°C at 1.2 mm of Hg (Reported [81] b.p. 98°C at 20 mm).

4-Bromo-3-fluoroanisole, (2.2)

This was prepared following a procedure as described for compound **2.1**, using 3-fluoroanisole as the starting material.

Yield, 82%; b.p. $\approx$ 65°C at 1.5 mm of Hg (Reported [81] b.p. 214-216 at atm. pressure).

4-Methoxy-2-fluorobenzonitrile, (2.3)

This was prepared using a procedure described by Kelly [81]. Thus, a solution of 4-bromo-3-fluoroanisole (49 g, 0.24 mol), anhydrous cuprous cyanide (32 g, 0.36 mol) and dry N, N-dimethylformamide (250 ml) was refluxed for 15 hours under anhydrous conditions. The cooled reaction mixture was added to a solution of anhydrous ferric chloride (35 g) and conc. hydrochloric acid (HCl) (10 ml) in water (400 ml) and the solution was heated at 60°C for one hour. The resultant reaction mixture was extracted using solvent ether (5 × 200 ml) and the combined organic solution was washed with 5N HCl (2 × 100 ml), ice cold aqueous 5% sodium hydroxide solution (2 × 100 ml) and finally with water (5 × 100 ml) and dried over anhydrous sodium sulphate. The solvent was removed, the solid material so obtained was passed through a column of silica gel using a mixture of chloroform and petroleum ether (b.p. 60-80°C) as an eluent. Removal of solvent afforded a solid material which was crystallized from a mixture of benzene and petroleum-ether (b.p. 60-80°C). Yield, 25 g (69%); m.p. 60-61°C (Reported [81] m.p. 59-60°C).

4-Methoxy-3-fluorobenzonitrile, (2.4)

This was prepared following a procedure as described for compound **2.3**, using 4-bromo-2-fluoroanisole as the starting material.

Yield, 63%; m.p. 98-99°C (Reported [81] m.p. 98-99°C).

4-Hydroxy-2-fluorobenzonitrile, (2.5)

A homogeneously mixed 4-methoxy-2-fluorobenzonitrile (25 g, 0.17 mol), anhydrous aluminium chloride (44 g, 0.33 mol) and analar sodium chloride (9.7 g, 0.17 mol) was heated to 195°C for 1 hour in a sublimation jacket. After confirming the completion of the reaction

by TLC, the molten reaction mixture was carefully added to ice cold HCl. This was extracted with ether (3×100 ml), the combined organic solution was washed with water (3×100 ml) and dried over anhydrous sodium sulphate. The solid so obtained after the removal of solvent was purified by column chromatography on silica gel using 5% ethyl acetate in chloroform as an eluent. Removal of solvent gave a product which was crystallized from toluene. Yield, 18.8 g (83%); m.p. 119-120°C (Reported [81] m.p. 117-118°C).

4-Hydroxy-2-fluorobenzoic acid, (2.6)

A solution of 4-hydroxy-2-fluorobenzonitrile (17 g, 0.12 mol), sodium hydroxide (28 g, 0.7 mol) and water (250 ml) was refluxed for 60 hours. The reaction mixture was then cooled to room temperature, poured into ice-cold HCl. The precipitate obtained was filtered off, washed with water until the washings were free from acid and dried. This was crystallized using a minimum amount of water. Yield, 15.1g (78%); m.p. 202-204°C (Reported [82] m.p. 204-205.5°C).

4-Methoxy-3-fluorobenzoic acid, (2.7)

A solution of 4-methoxy-3-fluorobenzonitrile (25 g, 0.16 mol), concentrated H_2SO_4 (25 ml), water (25 ml) and glacial acetic acid (250 ml) was refluxed for 48 hours. The cooled reaction mixture was poured into water. The precipitate obtained was filtered off, washed thoroughly with water and dried. This was crystallized from ethanol. Yield, 21g (75%); m.p. 209-211°C (Reported [85] m.p. 210-211.5°C).

4-Hydroxy-3-fluorobenzoic acid, (2.8)

A solution of 4-methoxy-3-fluorobenzonitrile (20 g), 49% hydrobromic acid (200 ml) and acetic acid (200 ml) was refluxed for 10 hours. The resultant solution was poured into ice-cold water. This was extracted with ether (3×100 ml) and the organic solution was washed several times with water. Removal of solvent gave a solid residue which was crystallized using a minimum amount of water. Yield, 15g (82%); m.p. 161-162°C (Reported [82] m.p. 159-160.5°C).

Ethyl-4-hydroxy-2-fluorobenzoate, (2.9)

A mixture of 4-hydroxy-2-fluorobenzoic acid (15 g), ethanol (200 ml) and a catalytic amount of con. H_2SO_4 was refluxed for about 40 hours. Excess ethanol was distilled off and the reaction mixture poured into ice-water. The resultant solution was extracted using ether (3×100 ml), the organic solution was washed with ice-cold aqueous 5% NaHCO_3 solution (2×50

ml) and finally several times with water and dried over sodium sulphate. The residue so obtained after the removal of solvent was purified by column chromatography using chloroform as an eluent. The product obtained after the removal of solvent was crystallized from benzene. Yield, 14.2 g (87%); m.p. 130-131°C.

Ethyl-4-hydroxy-3-fluorobenzoate, (2.10)

This was prepared following a procedure described above for compound **2.9**, using 4-hydroxy-3-fluorobenzoic acid as the starting material. Yield, 85%; m.p. 80-81°C.

Ethyl-4-benzyloxy-2-fluorobenzoate, (2.11)

A mixture of ethyl-4-hydroxy-2-fluorobenzoate (10 g, 54.3 mmol), benzyl chloride (8.2 g, 65.2 mmol), anhydrous K₂CO₃ (22.5 g, 163 mmol) and butan-2-one (150 ml) was refluxed for 18 hours. Excess butan-2-one was distilled off and the reaction mixture poured into ice-cold HCl. The resultant solution was extracted using solvent ether (3 × 100 ml). The combined organic solution was washed with ice-cold aqueous 5% sodium hydroxide solution (2 × 50 ml), water (3 × 100 ml) and dried over anhydrous sodium sulphate. Removal of solvent gave a liquid which was purified by column chromatography on silica gel using a mixture of chloroform and petroleum ether (b.p. 60-80°C) as an eluent. The liquid so obtained after the removal of solvent was distilled under reduced pressure. Yield, 13.2 g (90%); b.p. ≈160°C at 0.7 mm of Hg.

Ethyl-4-benzyloxy-3-fluorobenzoate, (2.12)

This was prepared following a procedure described above for compound **2.11**, using ethyl-4-hydroxy-3-fluorobenzoate as the starting material. Yield, 88%; m.p. 64-65°C.

4-Benzyloxy-2-fluorobenzoic acid, (2.13)

A mixture of ethyl-4-benzyloxy-2-fluorobenzoate (12 g), 10% alcoholic KOH (10 g of KOH dissolved in 10 ml of water and 90 ml of ethanol added to that) was refluxed for 8 hours. Excess ethanol was distilled off and the cooled reaction mixture was poured into ice-cold HCl. The resultant precipitate was filtered off, washed thoroughly with water until the washings were neutral to litmus paper. The solid material so obtained was crystallized from toluene. Yield, 9.5 g (88%); m.p. 166-167°C.

4-Benzyloxy-3-fluorobenzoic acid, (2.14)

This was prepared following a procedure described above for compound **2.13**, using ethyl-4-benzyloxy-3-fluorobenzoate as the starting material. Yield 86%; m.p. 189-190°C.

4-n-Hexadecyloxy-2-fluorobenzonitrile, (2.15)

A mixture of 4-hydroxy-2-fluorobenzonitrile (3.4 g, 24.8 mmol), 1-bromohexadecane (8.2 g, 27.3 mmol), anhydrous K_2CO_3 (10.3 g, 75 mmol) and butan-2-one (100 ml) was refluxed for 24 hours. Excess solvent was distilled off and the cooled reaction mixture was poured into ice-cold water. The resultant solution was extracted using solvent ether (3×50 ml) and the organic solution was washed with cold aqueous 5% sodium hydroxide solution and dried over anhydrous sodium sulphate. The solid obtained after the removal of solvent was purified by column chromatography on silica gel using a mixture of chloroform and petroleum-ether (b.p. 60-80°C) as an eluent. Removal of solvent from the eluate gave a white solid material which was crystallized using petroleum-ether (b.p. 60-80°C). Yield, 7.5 g (83%); m.p. 60-61°C.

4-n-Hexadecyloxy-2-fluorobenzoic acid, (2.16)

A solution of 4-n-hexadecyloxy-2-fluorobenzonitrile (7 g), conc. sulphuric acid (7 ml), water (7 ml) and glacial acetic acid (70 ml) was refluxed for 18 hours. The resultant reaction mixture was poured into ice-water. The solid material separated was filtered off, washed

The physical data of the cognate preparations of other 4-n-alkoxy-2-fluorobenzoic acids are given in table 2.A.

Table. 2.A

No.	n	Observed m.p. (°C)	Reported m.p. (°C)	Reference
1	3	123.0	-	-
2	4	109.0	107.0	[82]
3	5	106.0	104.0-105.0	[82]
4	6	109.0	108.0	[82]
5	7	94.0	-	-
6	8	94.5	-	-
7	9	87.5	-	-
8	10	94.0	-	-
9	11	90.0	-	-
10	12	98.0	-	-
11	14	96.0	-	-
12	18	100.0	99.5	[87]

thoroughly with water until the washings is neutral to litmus and dried. This was crystallized from ethanol. Yield, 5.8 g (79 %); m.p. 99°C (Reported [87] m.p. 99 °C).

Methyl-4-hydroxy-3-fluorobenzoate, (2.17)

This was prepared following a procedure similar to the one described for compound **2.9** using 4-hydroxy-3-fluorobenzoic acid as the starting material. m.p. 92-93°C.

Methyl-4-n-octadecyloxy-3-fluorobenzoate, (2.18)

This was prepared following a procedure described for compound **2.15** using methyl-4-hydroxy-3-fluorobenzoate as the starting material.

The low melting solid product obtained was directly used up in the next step.

4-n-Octadecyloxy-3-fluorobenzoic acid, (2.19)

This was prepared following a procedure described for compound **2.13** using compound **2.18**. Yield, 89%; m.p. 114-115°C (Reported [85] m.p. 114°C).

The physical data of the cognate preparations of other 4-n-alkoxy-3-fluorobenzoic acids are given in table **2.B**.

Table. 2.B

No.	n	Observed m.p. (°C)	Reported m.p. (°C)	Reference
1	4	143.0	143.5	[85]
2	5	138.0	137.5	[85]
3	6	130.0	129.5	[85]
4	7	124.0	124.0	[85]
5	8	118.0	117.0	[85]
6	9	112.5	112.0	[85]
7	10	109.0	108.0	[85]
8	11	113.5	-	-
9	12	109.0	108.5	[85]
10	14	113.0	-	-
11	16	114.5	94.0	[85]
12	20	116.5	-	-

2,7-Naphthylene bis (4-benzyloxybenzoate), (2.20)

A mixture of 2,7-dihydroxynaphthalene (1.6g, 10 mmol), 4-benzyloxybenzoic acid (4.56g, 20 mmol), 4-(N, N-dimethylamino)pyridine (DMAP) (0.4g, 2 mmol) and dry chloroform (25ml) was stirred for 10 minutes. To this mixture, N, N'-dicyclohexylcarbodiimide (DCC) (4.12 g, 22 mmol) was added and the stirring continued for 10 hours at room temperature. The precipitated N, N' -dicyclohexylurea was filtered off and washed with excess of chloroform (100 ml). The combined organic solution was washed with 5% aqueous acetic acid (2 × 50ml), cold 5% aqueous sodium hydroxide (2 × 50 ml) and finally washed with water (3 × 50 ml) and dried over anhydrous sodium sulphate. The solvent was removed and the solid material so obtained was purified by column chromatography on silica gel using 1% ethyl acetate in chloroform as an eluent. Removal of solvent from the eluate afforded a white solid. This was crystallized from a mixture of chloroform and acetonitrile. Yield, 4.8 g (81%); m.p. 217.5–218.5°C; $\nu_{\max}$: 2920, 2860, 1730, 1605, 1580, 1500, 1460, 1280, 1120 cm^{-1} ; δ_{H} : 8.21-8.19(d, 4H, ^3J 8.84Hz, Ar-H), 7.92-7.90(d, 2H, ^3J 8.0 Hz, Ar-H), 7.655-7.650(d, 2H, ^4J 11.96Hz, Ar-H), 7.46-7.33(m, 12H, Ar-H), 7.09-7.07(d, 4H, ^3J 8.84Hz, Ar-H). 5.18 (s, 4H, 2 × ArCH₂O-). Elemental analysis: C₃₈H₂₈O₆ requires, C, 78.60; H, 4.86%; found, C, 78.52; H, 4.59%.

2,7-Naphthylene bis(4-hydroxybenzoate), (2.21)

2,7-Naphthylene bis (4-benzyloxybenzoate) (4.5 g, 11.25 mmol) was dissolved in 1,4-dioxane (50 ml) and 5% Pd-C catalyst (1.2 g) was added to it. The mixture was stirred at 50°C in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. The resultant mixture was filtered in hot condition and the solvent removed under reduced pressure. The solid material so obtained was passed through a column of silica gel and eluted using a mixture of 5% acetone in chloroform. Removal of solvent from the eluate gave a white material, which was crystallized using a mixture of 1,4-dioxane and petroleum-ether (b.p. 60–80°C). Yield, 3.0 g (89%); m.p. > 250°C (d); $\nu_{\max}$: 3330, 1720, 1605, 1280, 1120 cm^{-1} ; δ_{H} : 9.73 (s, 2H, 2 × Ar–OH, exchangeable with D₂O), 8.26-8.17(m, 6H, Ar-H), 7.94-7.93(d, 2H, ^4J 2.2Hz, Ar-H), 7.59-7.56(m, 2H, Ar-H), 7.18-7.14 (m, 4H, Ar-H). Elemental analysis: C₂₄H₁₆O₆ requires, C, 72.06; H, 4.03%; found, C, 72.43; H, 3.97%.

2,7-Naphthylene bis(2-fluoro-4-benzyloxybenzoate), (2.22)

This was synthesized following a procedure described for preparation of compound **2.20**, using 2-fluoro-4-benzyloxybenzoic acid instead of 4-benzyloxybenzoic acid. Yield, 78%; m.p. 181.5-182°C; $\nu_{\max}$: 2915, 2850, 1735, 1718, 1620, 1515, 1460, 1340, 1260, 1123 cm^{-1} ;

δ_{H} : 8.13-8.08(m, 2H, Ar-H), 7.92-7.9(d, 2H, $^3\text{J}8.88$ Hz, Ar-H), 7.67-7.66(d, 2H, $^4\text{J}1.96$ Hz, Ar-H), 7.47-7.34(m, 12H, Ar-H), 6.89-6.86(dd, 2H, $^3\text{J}8.8$ Hz, $^4\text{J}2.36$ Hz, Ar-H), 6.82-6.78(dd, 2H, $^3\text{J}12.54$ Hz, $^4\text{J}2.35$ Hz, Ar-H), 5.15 (s, 4H, $2 \times \text{ArCH}_2\text{O}-$).

2,7-Naphthylene bis(2-fluoro-4-hydroxybenzoate), (2.23)

This was synthesized following a procedure described for preparation of compound **2.21**, using 2,7-naphthylene bis(2-fluoro-4-benzyloxybenzoate) as the starting material. Yield, 90%; m.p. $>250^\circ\text{C}$ (d); ν_{max} : 3330, 2905, 2840, 1712, 1700, 1615, 1595, 1450, 1260, 1123cm^{-1} ; δ_{H} : 10.0(s, 2H, $2 \times \text{Ar-OH}$, exchangeable with D_2O), 8.21-8.17(m, 4H, Ar-H), 7.948-7.943(d, 2H, $^4\text{J}2.2$ Hz, Ar-H), 7.6-7.57(dd, 2H, $^3\text{J}8.9$ Hz, $^4\text{J}2.28$ Hz, Ar-H), 7.01-6.98(dd, 2H, $^3\text{J}8.72$ Hz, $^4\text{J}2.32$ Hz, Ar-H), 6.91-6.87(dd, 2H, $^3\text{J}10.52$ Hz, $^4\text{J}2.35$ Hz, Ar-H).

2,7-Naphthylene bis(3-fluoro-4-benzyloxybenzoate), (2.24)

This was synthesized following a procedure described for preparation of compound **2.20**, using 3-fluoro-4-benzyloxybenzoic acid instead of 4-benzyloxybenzoic acid. Yield, 80%; m.p. $177.5-178^\circ\text{C}$; ν_{max} : 2900, 2840, 1720, 1610, 1510, 1435, 1450, 1380, 1290, 1190cm^{-1} ; δ_{H} : 7.99-7.87(m, 6H, Ar-H), 7.65-7.64(d, 2H, $^4\text{J}1.06$ Hz, Ar-H), 7.5-7.32(m, 12H, Ar-H), 7.15-7.08(m, 2H, Ar-H), 5.15 (s, 4H, $2 \times \text{ArCH}_2\text{O}-$).

2,7-Naphthylene bis(3-fluoro-4-hydroxybenzoate), (2.25)

This was prepared following a procedure described for preparation of compound **2.21**. Yield, 88%; m.p. $232-233^\circ\text{C}$; ν_{max} : 3354, 2923, 2854, 1706, 1622, 1600, 1458, 1275, 1199cm^{-1} ; δ_{H} : 9.9(s, 2H, $2 \times \text{Ar-OH}$, exchangeable with D_2O), 8.21-8.19(d, 2H, $^3\text{J}8.96$ Hz, Ar-H), 8.08-8.04(m, 4H, Ar-H), 7.967-7.961(d, 2H, $^4\text{J}2.24$ Hz, Ar-H), 7.62-7.59(dd, 2H, $^3\text{J}7.8$ Hz, $^4\text{J}2.24$ Hz, Ar-H), 7.36-7.31(m, 2H, Ar-H).

2,7-Naphthylene bis[4-(4-*n*-butylbenzoyloxy) benzoate], (2.A.1)

A mixture of 2,7-naphthylene bis (4-hydroxybenzoate) (200mg, 0.5 mmol), 4-*n*-butylbenzoic acid (178 mg, 1mmol), DMAP (13mg, 0.1 mmol) and dry chloroform(5 ml) was stirred for 10 minutes. To this mixture, DCC (450 mg, 1.1 mmol) was added and the stirring was continued for 10 hours at room temperature. The precipitated N, N'-dicyclohexylurea was filtered off and washed with an excess of chloroform (25 ml). Removal of solvent afforded a solid material, which was purified by column chromatography on silica gel using chloroform as an eluent. The white material so obtained after removal of solvent from the eluate was crystallized using a mixture of chloroform and acetonitrile. Yield, 280 mg (78%); m.p.

206.5°C; $\nu_{\max}$: 2924, 2854, 1740, 1718, 1603, 1458, 1269, 1059 cm^{-1} ; δ_{H} : 8.35-8.33(d, 4H, $^3\text{J}_{8.72}$ Hz, Ar-H), 8.14-8.12(d, 4H, $^3\text{J}_{8.2}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3\text{J}_{8.88}$ Hz, Ar-H), 7.709-7.704(d, 2H, $^4\text{J}_{2.08}$ Hz, Ar-H), 7.46-7.33(m, 10H, Ar-H), 2.74-2.70(t, 4H, $^3\text{J}_{7.6}$ Hz, 2 $\times$ Ar-CH₂-), 1.7-1.61(quin, 4H, $^3\text{J}_{7.6}$ Hz, 2 $\times$ Ar-CH₂-CH₂-CH₂-), 1.4-1.33(m, 4H, 2 $\times$ -CH₂-CH₂-CH₃), 0.97-0.90(t, 6H, $^3\text{J}_{7.2}$ Hz, 2 $\times$ -CH₂-CH₃). Elemental analysis: C₄₆H₄₀O₈ requires, C, 76.65; H, 5.59%; found, C, 76.72; H, 5.57%.

2,7-Naphthylene bis[4-(4-n-pentylbenzoyloxy) benzoate], (2.A.2)

This and other homologues were synthesized following a procedure described for the preparation of compound 2.A.1.

Yield, 76%; m.p. 191°C; $\nu_{\max}$: 2924, 2855, 1739, 1602, 1458, 1375, 1265, 1060 cm^{-1} ; δ_{H} : 8.35-8.33(d, 4H, $^3\text{J}_{8.7}$ Hz, Ar-H), 8.15-8.13(d, 4H, $^3\text{J}_{8.3}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3\text{J}_{8.86}$ Hz, Ar-H), 7.708-7.703(d, 2H, $^4\text{J}_{2.0}$ Hz, Ar-H), 7.47-7.35(m, 10H, Ar-H), 2.73-2.7(t, 4H, $^3\text{J}_{7.52}$ Hz, 2 $\times$ Ar-CH₂-), 1.71-1.62(quin, 4H, $^3\text{J}_{7.68}$ Hz, 2 $\times$ Ar-CH₂-CH₂-CH₂-), 1.39-1.34(m, 8H, 4 $\times$ -CH₂-), 0.96-0.89(t, 6H, $^3\text{J}_{6.84}$ Hz, 2 $\times$ -CH₂-CH₃); δ_{C} : 165.5, 165.3, 156.2, 150.6, 150.1, 135.2, 132.7, 131.1, 130.5, 130.2, 129.5, 127.7, 127.2, 122.8, 121.9, 119.3, 36.7, 32.1, 31.5, 23.2, 14.7. Elemental analysis: C₄₈H₄₄O₈ requires, C, 76.98; H, 5.92%; found, C, 76.68; H, 5.88%.

2,7-Naphthylene bis[4-(4-n-hexylbenzoyloxy) benzoate], (2.A.3)

Yield, 75%; m.p. 175°C; $\nu_{\max}$: 2924, 2855, 1740, 1726, 1603, 1508, 1458, 1375, 1265, 1061 cm^{-1} ; δ_{H} : 8.35-8.33(d, 4H, $^3\text{J}_{8.7}$ Hz, Ar-H), 8.14-8.12(d, 4H, $^3\text{J}_{8.3}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3\text{J}_{8.86}$ Hz, Ar-H), 7.709-7.703(d, 2H, $^4\text{J}_{2.2}$ Hz, Ar-H), 7.41-7.33(m, 10H, Ar-H), 2.73-2.69(t, 4H, $^3\text{J}_{7.48}$ Hz, 2 $\times$ Ar-CH₂-), 1.68-1.63(quin, 4H, $^3\text{J}_{7.56}$ Hz, 2 $\times$ Ar-CH₂-CH₂-CH₂-), 1.39-1.22(m, 12H, 6 $\times$ -CH₂-), 0.91-0.88(t, 6H, $^3\text{J}_{6.82}$ Hz, 2 $\times$ -CH₂-CH₃); δ_{C} : 165.4, 165.2, 156.1, 150.6, 150.0, 135.1, 132.6, 131.0, 130.4, 130.1, 129.5, 127.7, 127.2, 122.8, 121.9, 119.3, 36.8, 32.4, 31.8, 29.6, 23.3, 14.7. Elemental analysis: C₅₀H₄₈O₈ requires, C, 77.23; H, 6.23%; found, C, 77.29; H, 6.2%.

2,7-Naphthylene bis[4-(4-n-heptylbenzoyloxy) benzoate], (2.A.4)

Yield, 77%; m.p. 172°C; $\nu_{\max}$: 2923, 2855, 1740, 1726, 1603, 1508, 1458, 1375, 1265, 1059 cm^{-1} ; δ_{H} : 8.35-8.33(d, 4H, $^3\text{J}_{8.72}$ Hz, Ar-H), 8.15-8.13(d, 4H, $^3\text{J}_{8.2}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3\text{J}_{8.84}$ Hz, Ar-H), 7.709-7.704(d, 2H, $^4\text{J}_{2.0}$ Hz, Ar-H), 7.41-7.33(m, 10H, Ar-H), 2.73-2.69(t, 4H, $^3\text{J}_{7.44}$ Hz, 2 $\times$ Ar-CH₂-), 1.68-1.66(quin, 4H, $^3\text{J}_{7.0}$ Hz, 2 $\times$ Ar-CH₂-CH₂-CH₂-),

1.34-1.29(m, 16H, 8 × -CH₂-), 0.91-0.87(t, 6H, ³J6.76 Hz, 2 × -CH₂- CH₃); δ_C: 165.5, 165.3, 156.2, 150.6, 150.1, 135.1, 132.6, 131.1, 130.2, 130.1, 129.5, 127.7, 127.2, 122.8, 121.9, 119.3, 36.8, 32.5, 31.8, 29.9, 29.8, 23.3, 14.7. Elemental analysis: C₅₂H₅₂O₈ requires, C, 77.59; H, 6.51%; found, C, 77.34, H 6.5%.

2,7-Naphthylene bis[4-(4-n-octylbenzoyloxy) benzoate], (2.A.5)

Yield, 79%; m.p. 168.5°C; ν_{max}: 2922, 2852, 1740, 1726, 1603, 1508, 1456, 1375, 1265, 1061 cm⁻¹; δ_H: 8.35-8.33(d, 4H, ³J8.72 Hz, Ar-H), 8.15-8.13(d, 4H, ³J8.2 Hz, Ar-H), 7.96-7.94(d, 2H, ³J8.88 Hz, Ar-H), 7.709-7.704(d, 2H, ⁴J2.04 Hz, Ar-H), 7.41-7.33(m, 10H, Ar-H), 2.73-2.71(t, 4H, ³J7.52 Hz, 2 × Ar-CH₂-), 1.68-1.63(quin, 4H, ³J6.84 Hz, 2 × Ar-CH₂-CH₂-CH₂-), 1.33-1.28(m, 20H, 10 × -CH₂-), 0.90-0.87(t, 6H, ³J6.64 Hz, 2 × -CH₂- CH₃); δ_C: 165.6, 165.3, 156.1, 150.6, 150.0, 135.1, 132.6, 131.1, 130.2, 130.1, 129.5, 127.7, 127.2, 122.8, 121.9, 119.3, 36.8, 32.5, 31.8, 30.1, 29.9, 29.8, 23.3, 14.7. Elemental analysis: C₅₄H₅₆O₈ requires, C, 77.86; H, 6.77%; found, C, 77.49; H, 6.8%.

2,7-Naphthylene bis[4-(4-n-nonylbenzoyloxy) benzoate], (2.A.6)

Yield, 80%; m.p. 167.5°C; ν_{max}: 2924, 2852, 1740, 1724, 1603, 1508, 1458, 1375, 1265, 1061 cm⁻¹; δ_H: 8.35-8.32(d, 4H, ³J8.64 Hz, Ar-H), 8.15-8.12(d, 4H, ³J8.16 Hz, Ar-H), 7.96-7.95(d, 2H, ³J8.92 Hz, Ar-H), 7.709-7.704(d, 2H, ⁴J2.04 Hz, Ar-H), 7.41-7.33(m, 10H, Ar-H), 2.73-2.69(t, 4H, ³J7.64 Hz, 2 × Ar-CH₂-), 1.66-1.63(quin, 4H, ³J7.24 Hz, 2 × Ar-CH₂-CH₂-CH₂-), 1.33-1.27(m, 24H, 12 × -CH₂-), 0.90-0.85(t, 6H, ³J7.0 Hz, 2 × -CH₂- CH₃); δ_C: 165.4, 165.2, 156.1, 150.6, 150.0, 135.1, 132.6, 131.1, 130.4, 130.1, 129.5, 127.7, 127.2, 122.8, 121.9, 119.3, 36.8, 32.6, 31.8, 30.2, 30.1, 29.9, 29.8, 23.3, 14.7. Elemental analysis: C₅₆H₆₀O₈ requires, C, 78.12; H, 7.02%; found, C, 77.68; H, 7.05%.

2,7-Naphthylene bis[4-(4-n-decylbenzoyloxy) benzoate], (2.A.7)

Yield, 83%; m.p. 164.5°C; ν_{max}: 2922, 2852, 1740, 1726, 1605, 1508, 1458, 1375, 1265, 1061 cm⁻¹; δ_H: 8.35-8.33(d, 4H, ³J8.8 Hz, Ar-H), 8.14-8.12(d, 4H, ³J8.24 Hz, Ar-H), 7.96-7.94(d, 2H, ³J8.88 Hz, Ar-H), 7.708-7.703(d, 2H, ⁴J2.0 Hz, Ar-H), 7.41-7.33(m, 10H, Ar-H), 2.74-2.68(t, 4H, ³J7.68 Hz, 2 × Ar-CH₂-), 1.65-1.62(quin, 4H, ³J7.25 Hz, 2 × Ar-CH₂-CH₂-CH₂-), 1.32-1.28(m, 28H, 14 × -CH₂-), 0.91-0.86(t, 6H, ³J7.1 Hz, 2 × -CH₂- CH₃); δ_C: 165.4, 165.2, 156.1, 150.6, 150.0, 135.1, 132.6, 131.1, 130.4, 130.1, 129.5, 127.7, 127.2, 122.8, 121.9, 119.3, 36.8, 32.6, 31.8, 30.3, 30.1, 30.0, 29.9, 29.8, 23.4, 14.8. Elemental analysis: C₅₈H₆₄O₈ requires, C, 78.35; H, 7.25%; found, C, 78.21; H, 7.25%.

2,7-Naphthylene bis[4-(4-n-undecylbenzoyloxy) benzoate], (2.A.8)

Yield, 81%; m.p. 164.5°C; $\nu_{\max}$: 2924, 2853, 1740, 1724, 1603, 1508, 1458, 1375, 1265, 1061 cm^{-1} ; δ_{H} : 8.35-8.33(d, 4H, ^3J 8.36 Hz, Ar-H), 8.15-8.13(d, 4H, ^3J 7.92 Hz, Ar-H), 7.96-7.94(d, 2H, ^3J 8.84 Hz, Ar-H), 7.708-7.703(d, 2H, ^4J 2.0 Hz, Ar-H), 7.41-7.33(m, 10H, Ar-H), 2.73-2.69(t, 4H, ^3J 7.6 Hz, $2 \times \text{Ar-CH}_2$ -), 1.66-1.64(quin, 4H, ^3J 7.24 Hz, $2 \times \text{Ar-CH}_2$ -CH₂-CH₂-), 1.33-1.27(m, 32H, $16 \times$ -CH₂-), 0.90-0.86(t, 6H, ^3J 6.88 Hz, $2 \times$ -CH₂-CH₃); δ_{C} : 165.3, 165.2, 156.2, 150.6, 150.1, 135.2, 132.6, 131.1, 130.4, 130.1, 129.5, 127.7, 127.2, 122.8, 121.9, 119.3, 118.6, 36.8, 32.6, 31.8, 30.3, 30.2, 30.1, 30.0, 29.9, 23.4, 14.8. Elemental analysis: C₆₀H₆₈O₈ requires, C, 78.57; H, 7.47%; found, C, 78.57; H, 7.52%.

2,7-Naphthylene bis[4-(4-n-dodecylbenzoyloxy) benzoate], (2.A.9)

Yield, 82%; m.p. 162.5°C; $\nu_{\max}$: 2924, 2853, 1740, 1724, 1603, 1508, 1458, 1377, 1267, 1061 cm^{-1} ; δ_{H} : 8.35-8.33(d, 4H, ^3J 8.36 Hz, Ar-H), 8.15-8.13(d, 4H, ^3J 7.92 Hz, Ar-H), 7.97-7.94(d, 2H, ^3J 8.84 Hz, Ar-H), 7.708-7.704(d, 2H, ^4J 2.02 Hz, Ar-H), 7.41-7.33(m, 10H, Ar-H), 2.73-2.69(t, 4H, ^3J 7.6 Hz, $2 \times \text{Ar-CH}_2$ -), 1.67-1.65(quin, 4H, ^3J 7.24 Hz, $2 \times \text{Ar-CH}_2$ -CH₂-CH₂-), 1.33-1.27(m, 36H, $18 \times$ -CH₂-), 0.90-0.87(t, 6H, ^3J 6.88 Hz, $2 \times$ -CH₂-CH₃); δ_{C} : 165.3, 165.2, 156.2, 150.6, 150.1, 135.2, 132.6, 131.1, 130.4, 130.1, 129.5, 127.7, 127.2, 122.8, 121.9, 119.3, 118.6, 36.8, 32.6, 31.8, 30.3, 30.2, 30.1, 30.0, 29.9, 23.4, 14.8. Elemental analysis: C₆₂H₇₂O₈ requires, C, 78.78; H, 7.67%; found, C, 79.06; H, 7.79%.

2,7-Naphthylene bis[4-(4-n-tetradecylbenzoyloxy) benzoate], (2.A.10)

Yield, 81%; m.p. 159.0°C; $\nu_{\max}$: 2922, 2853, 1740, 1724, 1603, 1508, 1458, 1375, 1265, 1061 cm^{-1} ; δ_{H} : 8.35-8.33(m, 4H, Ar-H), 8.14-8.12(d, 4H, ^3J 8.24 Hz, Ar-H), 7.96-7.94(d, 2H, ^3J 8.96 Hz, Ar-H), 7.709-7.704(d, 2H, ^4J 2.16 Hz, Ar-H), 7.41-7.33(m, 10H, Ar-H), 2.73-2.69(t, 4H, ^3J 7.52 Hz, $2 \times \text{Ar-CH}_2$ -), 1.68-1.64(quin, 4H, ^3J 7.16 Hz, $2 \times \text{Ar-CH}_2$ -CH₂-CH₂-), 1.33-1.26(m, 44H, $22 \times$ -CH₂-), 0.90-0.86(t, 6H, ^3J 6.64 Hz, $2 \times$ -CH₂-CH₃); δ_{C} : 164.7, 164.6, 155.4, 149.9, 149.3, 135.0, 132.0, 130.4, 129.5, 128.8, 128.5, 127.0, 126.5, 122.2, 121.3, 118.7, 36.2, 32.0, 31.8, 30.3, 30.2, 30.1, 30.0, 29.9, 23.4, 22.7, 14.2. Elemental analysis: C₆₆H₈₀O₈ requires, C, 79.16; H, 8.05%; found, C, 79.04; H, 8.13%.

2,7-Naphthylene bis[4-(4-n-hexadecylbenzoyloxy) benzoate], (2.A.11)

Yield, 78%; m.p. 152.0°C; $\nu_{\max}$: 2922, 2852, 1740, 1724, 1603, 1508, 1458, 1375, 1267, 1061 cm^{-1} ; δ_{H} : 8.35-8.32(m, 4H, Ar-H), 8.14-8.12(d, 4H, ^3J 8.28 Hz, Ar-H), 7.96-7.94(d, 2H, ^3J 8.96 Hz, Ar-H), 7.709-7.704(d, 2H, ^4J 2.16 Hz, Ar-H), 7.41-7.33(m, 10H, Ar-H), 2.73-

2.69(t, 4H, $^3J_{7.52}$ Hz, $2 \times \text{Ar-CH}_2-$), 1.68-1.64(quin, 4H, $^3J_{7.0}$ Hz, $2 \times \text{Ar-CH}_2-\underline{\text{CH}_2}-\text{CH}_2-$), 1.33-1.26(m, 52H, $26 \times -\text{CH}_2-$), 0.90-0.86(t, 6H, $^3J_{6.64}$ Hz, $2 \times -\text{CH}_2-\underline{\text{CH}_3}$); δ_{C} : 164.7, 164.6, 155.5, 149.9, 149.4, 135.1, 132.0, 130.4, 129.7, 129.5, 128.8, 128.4, 127.0, 126.5, 122.2, 121.3, 118.7, 36.2, 32.0, 31.2, 30.3, 30.0, 29.7, 29.6, 29.5, 29.4, 29.3, 22.7, 14.2. Elemental analysis: $\text{C}_{70}\text{H}_{88}\text{O}_8$ requires, C, 79.5; H, 8.39%; found, C, 79.53, H, 8.48%.

2,7-Naphthylene bis[4-(4-n-octadecylbenzoyloxy) benzoate], (2.A.12)

Yield, 79%; m.p. 149.0°C; ν_{max} : 2922, 2852, 1740, 1732, 1604, 1508, 1458, 1375, 1261, 1055 cm^{-1} ; δ_{H} : 8.33-8.32(m, 4H, Ar-H), 8.14-8.12(d, 4H, $^3J_{8.2}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3J_{8.92}$ Hz, Ar-H), 7.709-7.703(d, 2H, $^4J_{2.08}$ Hz, Ar-H), 7.41-7.33(m, 10H, Ar-H), 2.73-2.69(t, 4H, $^3J_{7.52}$ Hz, $2 \times \text{Ar-CH}_2-$), 1.68-1.62(quin, 4H, $^3J_{7.6}$ Hz, $2 \times \text{Ar-CH}_2-\underline{\text{CH}_2}-\text{CH}_2-$), 1.33-1.22(m, 60H, $30 \times -\text{CH}_2-$), 0.89-0.86(t, 6H, $^3J_{6.52}$ Hz, $2 \times -\text{CH}_2-\underline{\text{CH}_3}$); δ_{C} : 164.7, 164.6, 155.5, 149.9, 149.4, 134.5, 132.0, 130.4, 129.5, 128.8, 128.4, 127.0, 126.5, 122.2, 121.3, 118.7, 36.2, 32.0, 31.2, 30.3, 30.0, 29.7, 29.5, 29.4, 29.3, 29.2, 22.7, 14.2. Elemental analysis: $\text{C}_{74}\text{H}_{96}\text{O}_8$ requires, C, 79.82; H, 8.69%; found, C, 79.59; H, 8.9%.

2,7-Naphthylene bis[4-(4-methylbenzoyloxy) 2-fluorobenzoate], (2.B.1)

Yield, 72%; m.p. 217.5°C; ν_{max} : 2924, 2854, 1743, 1735, 1610, 1508, 1458, 1234, 1117 cm^{-1} ; δ_{H} : 8.27-8.22(m, 2H, Ar-H), 8.10-8.08(d, 4H, $^3J_{8.0}$ Hz, Ar-H), 7.96-7.93(d, 2H, $^3J_{8.8}$ Hz, Ar-H), 7.728-7.722(d, 2H, $^4J_{2.08}$ Hz, Ar-H), 7.41-7.38(dd, 2H, $^3J_{8.6}$ Hz, $^4J_{2.0}$ Hz, Ar-H), 7.35-7.33(d, 4H, $^3J_{8.0}$ Hz, Ar-H), 7.23-7.20(m, 4H, Ar-H), 2.47(s, 6H, $2 \times \text{Ar-CH}_3$); δ_{C} : 164.1, 162.1, 161.5, 156.0, 150.0, 149.2, 134.3, 133.4, 130.4, 129.7, 129.4, 128.8, 125.8, 121.2, 118.6, 117.8, 111.4, 111.2, 21.7.

2,7-Naphthylene bis[4-(4-ethylbenzoyloxy) 2-fluorobenzoate], (2.B.2)

Yield, 70%; m.p. 188.5°C; ν_{max} : 2924, 2854, 1742, 1610, 1508, 1458, 1234, 1117 cm^{-1} ; δ_{H} : 8.27-8.22(m, 2H, Ar-H), 8.13-8.11(d, 4H, $^3J_{8.4}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3J_{9.2}$ Hz, Ar-H), 7.729-7.723(d, 2H, $^4J_{2.06}$ Hz, Ar-H), 7.41-7.36(m, 6H, Ar-H), 7.23-7.2(m, 4H, Ar-H), 2.8-2.74(q, 4H, $^3J_{7.6}$ Hz, $2 \times \text{Ar-CH}_2-\underline{\text{CH}_3}$), 1.32-1.28(t, 6H, $^3J_{7.6}$ Hz, $2 \times \text{Ar-CH}_2-\underline{\text{CH}_3}$); δ_{C} : 164.1, 162.1, 161.5, 156.0, 150.0, 149.2, 134.3, 133.4, 130.5, 129.7, 129.4, 128.3, 125.8, 121.2, 118.6, 117.8, 111.4, 111.2, 29.0, 15.1.

2,7-Naphthylene bis[4-(4-n-propylbenzoyloxy) 2-fluorobenzoate], (2.B.3)

Yield, 71%; m.p. 171.0°C; ν_{max} : 2926, 2856, 1740, 1724, 1608, 1508, 1456, 1234, 1116 cm^{-1} ; δ_{H} : 8.26-8.22(m, 2H, Ar-H), 8.13-8.10(d, 4H, $^3J_{8.4}$ Hz, Ar-H), 7.95-7.93(d, 2H, $^3J_{8.8}$ Hz, Ar-

H), 7.729-7.723(d, 2H, $^4J_{2.0}$ Hz, Ar-H), 7.41-7.38(dd, 2H, $^3J_{8.8}$ Hz, $^4J_{2.0}$ Hz, Ar-H), 7.35-7.33(d, 4H, $^3J_{8.0}$ Hz, Ar-H), 7.22-7.2(m, 4H, Ar-H), 2.72-2.68(t, 4H, $^3J_{8.0}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-}$), 1.75-1.66(m, 4H, $^3J_{7.6}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-CH}_3$), 0.99-0.96(t, 6H, $^3J_{7.6}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-CH}_3$); δ_C : 164.1, 162.1, 161.5, 156.1, 149.8, 149.0, 134.3, 133.5, 130.4, 129.7, 129.4, 128.9, 126.1, 121.1, 118.6, 117.9, 111.5, 111.2, 38.1, 24.1, 13.7.

2,7-Naphthylene bis[4-(4-n-butylbenzoyloxy) 2-fluorobenzoate], (2.B.4)

Yield, 73%; m.p. 160.0°C; $\nu_{\max}$: 2924, 2856, 1742, 1724, 1610, 1508, 1458, 1234, 1114 cm^{-1} ; δ_H : 8.26-8.22(m, 2H, Ar-H), 8.13-8.10(d, 4H, $^3J_{8.4}$ Hz, Ar-H), 7.95-7.93(d, 2H, $^3J_{8.8}$ Hz, Ar-H), 7.727-7.721(d, 2H, $^4J_{2.4}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3J_{8.8}$ Hz, $^4J_{2.0}$ Hz, Ar-H), 7.36-7.33(d, 4H, $^3J_{8.4}$ Hz, Ar-H), 7.23-7.19(m, 4H, Ar-H), 2.74-2.7(t, 4H, $^3J_{7.6}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-}$), 1.69-1.61(quin, 4H, $^3J_{7.6}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.43-1.34(m, 4H, $2 \times \text{-CH}_2\text{-CH}_2\text{-CH}_3$), 0.97-0.94(t, 6H, $^3J_{7.2}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$); δ_C : 164.1, 162.1, 161.5, 156.1, 150.0, 149.0, 134.3, 133.5, 130.4, 129.7, 129.4, 128.8, 126.1, 121.1, 118.6, 117.8, 115.4, 111.5, 111.2, 35.8, 33.2, 22.3, 13.8.

2,7-Naphthylene bis[4-(4-n-pentylbenzoyloxy) 2-fluorobenzoate], (2.B.5)

Yield, 70%; m.p. 143.0°C; $\nu_{\max}$: 2924, 2855, 1745, 1730, 1610, 1508, 1458, 1234, 1114 cm^{-1} ; δ_H : 8.26-8.22(m, 2H, Ar-H), 8.13-8.10(d, 4H, $^3J_{8.28}$ Hz, Ar-H), 7.96-7.93(d, 2H, $^3J_{8.92}$ Hz, Ar-H), 7.728-7.723(d, 2H, $^4J_{2.2}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3J_{8.86}$ Hz, $^4J_{2.2}$ Hz, Ar-H), 7.36-7.33(d, 4H, $^3J_{8.24}$ Hz, Ar-H), 7.23-7.19(m, 4H, Ar-H), 2.73-2.71(t, 4H, $^3J_{7.52}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-}$), 1.71-1.63(quin, 4H, $^3J_{7.56}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.36-1.32(m, 8H, $4 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 0.93-0.89(t, 6H, $^3J_{7.04}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$); δ_C : 164.2, 162.2, 161.5, 156.1, 150.2, 149.0, 134.4, 133.6, 130.5, 129.8, 129.5, 128.9, 126.1, 121.2, 118.7, 117.9, 115.4, 111.6, 111.3, 36.1, 31.5, 30.8, 22.5, 14.0.

2,7-Naphthylene bis[4-(4-n-hexylbenzoyloxy) 2-fluorobenzoate], (2.B.6)

Yield, 72%; m.p. 150.0°C; $\nu_{\max}$: 2924, 2856, 1740, 1612, 1508, 1458, 1234, 1118 cm^{-1} ; δ_H : 8.26-8.22(m, 2H, Ar-H), 8.12-8.10(d, 4H, $^3J_{8.28}$ Hz, Ar-H), 7.96-7.93(d, 2H, $^3J_{8.96}$ Hz, Ar-H), 7.728-7.723(d, 2H, $^4J_{2.2}$ Hz, Ar-H), 7.41-7.37(dd, 2H, $^3J_{8.86}$ Hz, $^4J_{2.2}$ Hz, Ar-H), 7.35-7.33(d, 4H, $^3J_{8.28}$ Hz, Ar-H), 7.23-7.19(m, 4H, Ar-H), 2.73-2.71(t, 4H, $^3J_{7.56}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-}$), 1.70-1.63(quin, 4H, $^3J_{7.72}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.38-1.33(m, 12H, $6 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 0.91-0.88(t, 6H, $^3J_{7.04}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$); δ_C : 164.2, 162.2, 161.5, 156.1,

150.2, 149.1, 134.4, 133.5, 130.5, 129.8, 129.5, 128.9, 126.1, 121.2, 118.7, 117.9, 115.4, 111.5, 111.3, 36.2, 31.7, 31.0, 28.9, 22.5, 14.1.

2,7-Naphthylene bis[4-(4-n-heptylbenzoyloxy) 2-fluorobenzoate], (2.B.7)

Yield, 68%; m.p. 148.0°C; $\nu_{\max}$: 2924, 2855, 1747, 1730, 1610, 1508, 1458, 1232, 1117 cm^{-1} ; δ_{H} : 8.26-8.22(m, 2H, Ar-H), 8.12-8.10(d, 4H, $^3\text{J}_{8.12}$ Hz, Ar-H), 7.95-7.93(d, 2H, $^3\text{J}_{8.88}$ Hz, Ar-H), 7.728-7.723(d, 2H, $^4\text{J}_{1.84}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3\text{J}_{8.84}$ Hz, $^4\text{J}_{2.08}$ Hz, Ar-H), 7.35-7.33(d, 4H, $^3\text{J}_{8.12}$ Hz, Ar-H), 7.22-7.20(m, 4H, Ar-H), 2.73-2.71(t, 4H, $^3\text{J}_{7.48}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-}$), 1.68-1.66(quin, 4H, $^3\text{J}_{7.70}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.34-1.29(m, 16H, $8 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 0.91-0.87(t, 6H, $^3\text{J}_{7.04}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$); δ_{C} : 164.2, 162.2, 161.5, 156.1, 150.2, 149.1, 134.4, 133.5, 130.5, 129.8, 129.5, 128.9, 126.1, 121.2, 118.7, 117.9, 115.4, 111.5, 111.3, 36.2, 31.8, 31.1, 29.2, 29.1, 22.6, 14.1.

2,7-Naphthylene bis[4-(4-n-octylbenzoyloxy) 2-fluorobenzoate], (2.B.8)

Yield, 70%; m.p. 154.0°C; $\nu_{\max}$: 2924, 2852, 1737, 1700, 1612, 1508, 1425, 1234, 1117 cm^{-1} ; δ_{H} : 8.26-8.22(m, 2H, Ar-H), 8.13-8.10(d, 4H, $^3\text{J}_{8.28}$ Hz, Ar-H), 7.95-7.93(d, 2H, $^3\text{J}_{8.92}$ Hz, Ar-H), 7.729-7.724(d, 2H, $^4\text{J}_{2.16}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3\text{J}_{8.86}$ Hz, $^4\text{J}_{2.2}$ Hz, Ar-H), 7.35-7.33(d, 4H, $^3\text{J}_{8.28}$ Hz, Ar-H), 7.23-7.19(m, 4H, Ar-H), 2.73-2.71(t, 4H, $^3\text{J}_{7.48}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-}$), 1.68-1.63(quin, 4H, $^3\text{J}_{7.70}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.33-1.28(m, 20H, $10 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 0.91-0.87(t, 6H, $^3\text{J}_{7.08}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$); δ_{C} : 164.2, 162.2, 161.6, 156.2, 150.2, 149.0, 134.4, 133.6, 130.5, 129.8, 129.5, 128.9, 126.1, 121.2, 118.7, 118.0, 111.6, 111.3, 36.2, 31.9, 31.1, 29.5, 29.3, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-nonylbenzoyloxy) 2-fluorobenzoate], (2.B.9)

Yield, 71%; m.p. 153.0°C; $\nu_{\max}$: 2924, 2855, 1747, 1728, 1608, 1508, 1458, 1232, 1117 cm^{-1} ; δ_{H} : 8.26-8.22(m, 2H, Ar-H), 8.12-8.10(d, 4H, $^3\text{J}_{8.2}$ Hz, Ar-H), 7.95-7.93(d, 2H, $^3\text{J}_{8.92}$ Hz, Ar-H), 7.728-7.723(d, 2H, $^4\text{J}_{2.12}$ Hz, Ar-H), 7.41-7.38(dd, 2H, $^3\text{J}_{8.82}$ Hz, $^4\text{J}_{2.2}$ Hz, Ar-H), 7.35-7.33(d, 4H, $^3\text{J}_{8.2}$ Hz, Ar-H), 7.23-7.19(m, 4H, Ar-H), 2.73-2.69(t, 4H, $^3\text{J}_{7.56}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-}$), 1.68-1.61(quin, 4H, $^3\text{J}_{7.48}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.33-1.27(m, 24H, $12 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 0.90-0.87(t, 6H, $^3\text{J}_{7.04}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$); δ_{C} : 164.2, 162.2, 161.6, 156.2, 150.2, 149.0, 134.4, 133.6, 130.5, 129.8, 129.5, 128.9, 126.1, 121.2, 118.7, 118.0, 111.6, 111.3, 36.2, 31.9, 31.1, 29.5, 29.5, 29.3, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-decylbenzoyloxy) 2-fluorobenzoate], (2.B.10)

Yield, 72%; m.p. 150.0°C; $\nu_{\max}$: 2922, 2852, 1747, 1730, 1608, 1508, 1458, 1280, 1117 cm^{-1} ; δ_{H} : 8.26-8.22(m, 2H, Ar-H), 8.12-8.10(d, 4H, $^3\text{J}_{8.24}$ Hz, Ar-H), 7.95-7.93(d, 2H, $^3\text{J}_{8.92}$ Hz, Ar-H), 7.728-7.723(d, 2H, $^4\text{J}_{2.12}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3\text{J}_{8.46}$ Hz, $^4\text{J}_{2.2}$ Hz, Ar-H), 7.35-7.33(d, 4H, $^3\text{J}_{8.24}$ Hz, Ar-H), 7.23-7.19(m, 4H, Ar-H), 2.73-2.69(t, 4H, $^3\text{J}_{7.52}$ Hz, 2 $\times$ Ar-CH₂-CH₂-), 1.68-1.62(quin, 4H, $^3\text{J}_{7.64}$ Hz, 2 $\times$ Ar-CH₂-CH₂-CH₂-), 1.33-1.27(m, 28H, 14 $\times$ -CH₂-CH₂-CH₂-), 0.90-0.87(t, 6H, $^3\text{J}_{7.0}$ Hz, 2 $\times$ -CH₂-CH₃); δ_{C} : 164.2, 162.2, 161.6, 156.2, 150.2, 149.0, 134.4, 133.6, 130.5, 129.8, 129.5, 128.9, 126.1, 121.2, 118.7, 118.0, 111.6, 111.3, 36.2, 31.9, 31.1, 29.6, 29.5, 29.3, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-undecylbenzoyloxy) 2-fluorobenzoate], (2.B.11)

Yield, 69%; m.p. 135.5°C; $\nu_{\max}$: 2924, 2854, 1747, 1728, 1608, 1508, 1458, 1280, 1117 cm^{-1} ; δ_{H} : 8.26-8.22(m, 2H, Ar-H), 8.12-8.10(d, 4H, $^3\text{J}_{8.32}$ Hz, Ar-H), 7.96-7.93(d, 2H, $^3\text{J}_{9.0}$ Hz, Ar-H), 7.728-7.723(d, 2H, $^4\text{J}_{2.16}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3\text{J}_{8.88}$ Hz, $^4\text{J}_{2.24}$ Hz, Ar-H), 7.35-7.33(d, 4H, $^3\text{J}_{8.36}$ Hz, Ar-H), 7.23-7.19(m, 4H, Ar-H), 2.73-2.69(t, 4H, $^3\text{J}_{7.56}$ Hz, 2 $\times$ Ar-CH₂-CH₂-), 1.66-1.64(quin, 4H, $^3\text{J}_{7.6}$ Hz, 2 $\times$ Ar-CH₂-CH₂-CH₂-), 1.32-1.27(m, 32H, 16 $\times$ -CH₂-CH₂-CH₂-), 0.90-0.87(t, 6H, $^3\text{J}_{7.04}$ Hz, 2 $\times$ -CH₂-CH₃); δ_{C} : 164.2, 162.2, 161.6, 156.2, 150.2, 149.0, 134.4, 133.6, 130.5, 129.8, 129.5, 128.9, 126.1, 121.2, 118.6, 117.9, 111.5, 111.3, 36.1, 31.9, 31.1, 29.6, 29.4, 29.2, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-dodecylbenzoyloxy) 2-fluorobenzoate], (2.B.12)

Yield, 68%; m.p. 133.5°C; $\nu_{\max}$: 2924, 2854, 1747, 1728, 1608, 1508, 1458, 1280, 1117 cm^{-1} ; δ_{H} : 8.26-8.22(m, 2H, Ar-H), 8.12-8.10(d, 4H, $^3\text{J}_{8.28}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3\text{J}_{8.96}$ Hz, Ar-H), 7.729-7.723(d, 2H, $^4\text{J}_{2.4}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3\text{J}_{8.86}$ Hz, $^4\text{J}_{2.2}$ Hz, Ar-H), 7.35-7.33(d, 4H, $^3\text{J}_{8.28}$ Hz, Ar-H), 7.23-7.19(m, 4H, Ar-H), 2.73-2.69(t, 4H, $^3\text{J}_{7.52}$ Hz, 2 $\times$ Ar-CH₂-CH₂-), 1.68-1.64(quin, 4H, $^3\text{J}_{7.64}$ Hz, 2 $\times$ Ar-CH₂-CH₂-CH₂-), 1.33-1.27(m, 36H, 18 $\times$ -CH₂-CH₂-CH₂-), 0.90-0.87(t, 6H, $^3\text{J}_{7.04}$ Hz, 2 $\times$ -CH₂-CH₃); δ_{C} : 164.2, 162.2, 161.6, 156.2, 150.2, 149.0, 134.4, 133.5, 130.4, 129.7, 129.4, 128.9, 126.0, 121.2, 118.6, 117.9, 111.5, 111.3, 36.1, 31.9, 31.1, 29.6, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-tetradecylbenzoyloxy) 2-fluorobenzoate], (2.B.13)

Yield, 69%; m.p. 130.0°C; $\nu_{\max}$: 2922, 2852, 1747, 1728, 1608, 1508, 1458, 1280, 1116 cm^{-1} ; δ_{H} : 8.27-8.22(m, 2H, Ar-H), 8.12-8.10(d, 4H, $^3\text{J}_{8.16}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3\text{J}_{8.84}$ Hz, Ar-H), 7.729-7.724(d, 2H, $^4\text{J}_{2.3}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3\text{J}_{8.8}$ Hz, $^4\text{J}_{2.2}$ Hz, Ar-H),

7.35-7.33(d, 4H, $^3J_{8.12}$ Hz, Ar-H), 7.22-7.19(m, 4H, Ar-H), 2.73-2.69(t, 4H, $^3J_{7.44}$ Hz, $2 \times$ Ar-CH₂-CH₂-), 1.66-1.60(m, 4H, $2 \times$ Ar-CH₂-CH₂-CH₂-), 1.32-1.26(m, 44H, $22 \times$ -CH₂-CH₂-CH₂-), 0.90-0.86(t, 6H, $^3J_{6.48}$ Hz, $2 \times$ -CH₂-CH₃); δ_C : 164.2, 162.2, 161.6, 156.2, 150.2, 149.0, 134.4, 133.5, 130.4, 129.7, 129.5, 128.9, 126.0, 121.2, 118.6, 117.9, 111.5, 111.3, 36.1, 31.9, 31.1, 29.7, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-hexadecylbenzoyloxy) 2-fluorobenzoate], (2.B.14)

Yield, 70%; m.p. 125.0°C; $\nu_{\max}$: 2920, 2852, 1747, 1728, 1610, 1508, 1458, 1280, 1117 cm⁻¹; δ_H : 8.27-8.22(m, 2H, Ar-H), 8.13-8.11(d, 4H, $^3J_{8.12}$ Hz, Ar-H), 7.96-7.93(d, 2H, $^3J_{8.92}$ Hz, Ar-H), 7.726-7.722(d, 2H, $^4J_{1.84}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3J_{8.66}$ Hz, $^4J_{2.04}$ Hz, Ar-H), 7.35-7.33(d, 4H, $^3J_{8.16}$ Hz, Ar-H), 7.22-7.19(m, 4H, Ar-H), 2.73-2.69(t, 4H, $^3J_{7.4}$ Hz, $2 \times$ Ar-CH₂-CH₂-), 1.66-1.60(m, 4H, $2 \times$ Ar-CH₂-CH₂-CH₂-), 1.32-1.26(m, 52H, $26 \times$ -CH₂-CH₂-CH₂-), 0.90-0.86(t, 6H, $^3J_{6.52}$ Hz, $2 \times$ -CH₂-CH₃); δ_C : 164.2, 162.2, 161.6, 156.2, 150.2, 149.0, 134.4, 133.5, 130.4, 129.7, 129.5, 128.9, 126.0, 121.2, 118.6, 117.9, 111.5, 111.3, 36.1, 31.9, 31.1, 29.7, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-octadecylbenzoyloxy) 2-fluorobenzoate], (2.B.15)

Yield, 70%; m.p. 114.0°C; $\nu_{\max}$: 2920, 2852, 1730, 1616, 1510, 1465, 1280, 1111 cm⁻¹; δ_H : 8.25-8.22(m, 2H, Ar-H), 8.13-8.11(d, 4H, $^3J_{8.08}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3J_{8.92}$ Hz, Ar-H), 7.726-7.722(d, 2H, $^4J_{1.84}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3J_{8.68}$ Hz, $^4J_{1.88}$ Hz, Ar-H), 7.35-7.33(d, 4H, $^3J_{8.08}$ Hz, Ar-H), 7.22-7.19(m, 4H, Ar-H), 2.73-2.69(t, 4H, $^3J_{7.56}$ Hz, $2 \times$ Ar-CH₂-CH₂-), 1.66-1.60(m, 4H, $2 \times$ Ar-CH₂-CH₂-CH₂-), 1.32-1.2(m, 60H, $30 \times$ -CH₂-CH₂-CH₂-), 0.89-0.86(t, 6H, $^3J_{6.4}$ Hz, $2 \times$ -CH₂-CH₃); δ_C : 164.2, 162.2, 161.6, 156.2, 150.2, 149.0, 134.4, 133.5, 130.4, 129.7, 129.5, 128.8, 126.0, 121.2, 118.6, 117.9, 115.4, 111.5, 111.2, 36.1, 31.9, 31.1, 29.7, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-butylbenzoyloxy) 3-fluorobenzoate], (2.C.1)

Yield, 66%; m.p. 185.5°C; $\nu_{\max}$: 2924, 2854, 1749, 1742, 1608, 1508, 1460, 1292, 1117 cm⁻¹; δ_H : 8.15-8.08(m, 8H, Ar-H), 7.97-7.95(d, 2H, $^3J_{8.8}$ Hz, Ar-H), 7.709-7.704(d, 2H, $^4J_{2.0}$ Hz, Ar-H), 7.47-7.44(m, 2H, Ar-H), 7.4-7.34(m, 6H, Ar-H), 2.74-2.7(t, 4H, $^3J_{7.6}$ Hz, $2 \times$ Ar-CH₂-CH₂-), 1.69-1.63(quin, 4H, $^3J_{7.2}$ Hz, $2 \times$ Ar-CH₂-CH₂-CH₂-), 1.43-1.34(m, 4H, $2 \times$ -CH₂-CH₂-CH₃), 0.97-0.93(t, 6H, $^3J_{7.2}$ Hz, $2 \times$ -CH₂-CH₃); δ_C : 163.6, 163.1, 155.3, 152.9, 150.1, 149.1, 143.2, 134.3, 130.5, 129.7, 129.5, 128.8, 128.4, 126.8, 125.6, 124.3, 121.1, 118.8, 118.5, 35.8, 33.2, 22.3, 13.8.

2,7-Naphthylene bis[4-(4-n-pentylbenzoyloxy) 3-fluorobenzoate], (2.C.2)

Yield, 65%; m.p. 154.5°C; $\nu_{\max}$: 2924, 2854, 1742, 1720, 1608, 1508, 1460, 1292, 1116 cm^{-1} ; δ_{H} : 8.15-8.09(m, 8H, Ar-H), 7.97-7.95(d, 2H, $^3J_{9.2}$ Hz, Ar-H), 7.71-7.705(d, 2H, $^4J_{2.0}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.34(m, 6H, Ar-H), 2.73-2.7(t, 4H, $^3J_{7.2}$ Hz, $2 \times \text{Ar}-\text{CH}_2-\text{CH}_2-$), 1.7-1.63(quin, 4H, $^3J_{7.6}$ Hz, $2 \times \text{Ar}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 1.36-1.34(m, 8H, $4 \times -\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 0.93-0.89(t, 6H, $^3J_{6.8}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$); δ_{C} : 163.6, 155.4, 152.9, 150.1, 149.1, 143.2, 134.3, 130.6, 129.7, 129.5, 128.8, 128.4, 126.8, 125.6, 124.3, 121.1, 118.8, 118.5, 36.0, 31.4, 30.7, 22.4, 13.9.

2,7-Naphthylene bis[4-(4-n-hexylbenzoyloxy) 3-fluorobenzoate], (2.C.3)

Yield, 65%; m.p. 173.5°C; $\nu_{\max}$: 2924, 2854, 1742, 1610, 1510, 1460, 1298, 1115 cm^{-1} ; δ_{H} : 8.15-8.09(m, 8H, Ar-H), 7.97-7.95(d, 2H, $^3J_{8.88}$ Hz, Ar-H), 7.71-7.706(d, 2H, $^4J_{2.04}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.34(m, 6H, Ar-H), 2.73-2.7(t, 4H, $^3J_{7.52}$ Hz, $2 \times \text{Ar}-\text{CH}_2-\text{CH}_2-$), 1.68-1.62(quin, 4H, $^3J_{7.36}$ Hz, $2 \times \text{Ar}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 1.33-1.25(m, 12H, $6 \times -\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 0.91-0.88(t, 6H, $^3J_{6.84}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$); δ_{C} : 163.7, 155.4, 152.9, 150.2, 149.2, 143.2, 134.4, 130.6, 129.6, 129.5, 128.9, 128.4, 126.8, 125.6, 124.4, 121.1, 118.8, 118.6, 36.1, 31.7, 30.7, 28.9, 22.6, 14.1.

2,7-Naphthylene bis[4-(4-n-heptylbenzoyloxy) 3-fluorobenzoate], (2.C.4)

Yield, 66%; m.p. 161.0°C; $\nu_{\max}$: 2924, 2854, 1747, 1722, 1610, 1510, 1460, 1298, 1117 cm^{-1} ; δ_{H} : 8.19-8.09(m, 8H, Ar-H), 7.97-7.95(d, 2H, $^3J_{8.92}$ Hz, Ar-H), 7.71-7.706(d, 2H, $^4J_{2.0}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.34(m, 6H, Ar-H), 2.73-2.7(t, 4H, $^3J_{7.52}$ Hz, $2 \times \text{Ar}-\text{CH}_2-\text{CH}_2-$), 1.68-1.64(quin, 4H, $^3J_{7.16}$ Hz, $2 \times \text{Ar}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 1.34-1.29(m, 16H, $8 \times -\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 0.90-0.87(t, 6H, $^3J_{6.68}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$); δ_{C} : 163.7, 155.4, 152.9, 150.2, 149.2, 143.2, 134.3, 130.6, 129.6, 129.5, 128.8, 128.4, 126.8, 125.6, 124.3, 121.1, 118.8, 118.6, 36.1, 31.8, 31.0, 29.4, 29.2, 22.6, 14.1.

2,7-Naphthylene bis[4-(4-n-octylbenzoyloxy) 3-fluorobenzoate], (2.C.5)

Yield, 65%; m.p. 137.0°C; $\nu_{\max}$: 2924, 2853, 1759, 1734, 1608, 1508, 1458, 1288, 1116 cm^{-1} ; δ_{H} : 8.16-8.09(m, 8H, Ar-H), 7.97-7.95(d, 2H, $^3J_{8.84}$ Hz, Ar-H), 7.715-7.71(d, 2H, $^4J_{1.96}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.34(m, 6H, Ar-H), 2.73-2.7(t, 4H, $^3J_{7.6}$ Hz, $2 \times \text{Ar}-\text{CH}_2-\text{CH}_2-$), 1.68-1.63(quin, 4H, $^3J_{7.36}$ Hz, $2 \times \text{Ar}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 1.33-1.29(m, 20H, $10 \times -\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 0.91-0.87(t, 6H, $^3J_{6.44}$ Hz, $2 \times -\text{CH}_2-\text{CH}_3$); δ_{C} : 163.7, 155.4, 152.8, 150.2, 149.1,

143.1, 134.3, 130.6, 129.6, 129.5, 128.8, 128.4, 126.8, 125.6, 124.3, 121.1, 118.8, 118.6, 36.1, 31.8, 31.0, 29.4, 29.2, 22.6, 14.1.

2,7-Naphthylene bis[4-(4-n-nonylbenzoyloxy) 3-fluorobenzoate], (2.C.6)

Yield, 65%; m.p. 133.0°C; $\nu_{\max}$: 2924, 2853, 1759, 1732, 1608, 1508, 1458, 1290, 1117 cm^{-1} ; δ_{H} : 8.16-8.09(m, 8H, Ar-H), 7.97-7.95(d, 2H, $^3\text{J}_{9.24}$ Hz, Ar-H), 7.71-7.70(d, 2H, $^4\text{J}_{2.68}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.33(m, 6H, Ar-H), 2.73-2.7(t, 4H, $^3\text{J}_{7.96}$ Hz, $2 \times \text{Ar}-\underline{\text{CH}_2}-\text{CH}_2-$), 1.7-1.66(quin, 4H, $^3\text{J}_{6.96}$ Hz, $2 \times \text{Ar}-\text{CH}_2-\underline{\text{CH}_2}-\text{CH}_2-$), 1.34-1.27(m, 24H, $12 \times -\text{CH}_2-\underline{\text{CH}_2}-\text{CH}_2-$), 0.90-0.86(t, 6H, $^3\text{J}_{6.96}$ Hz, $2 \times -\text{CH}_2-\underline{\text{CH}_3}$); δ_{C} : 163.7, 155.4, 152.8, 150.2, 149.1, 143.1, 134.3, 130.6, 129.6, 129.5, 128.8, 128.4, 126.8, 125.6, 124.4, 121.1, 118.8, 118.6, 36.1, 31.8, 31.1, 29.4, 29.1, 22.6, 14.1.

2,7-Naphthylene bis[4-(4-n-decylbenzoyloxy) 3-fluorobenzoate], (2.C.7)

Yield, 66%; m.p. 128.5°C; $\nu_{\max}$: 2924, 2852, 1759, 1734, 1608, 1508, 1458, 1288, 1122 cm^{-1} ; δ_{H} : 8.16-8.09(m, 8H, Ar-H), 7.97-7.95(d, 2H, $^3\text{J}_{8.96}$ Hz, Ar-H), 7.71-7.70(d, 2H, $^4\text{J}_{2.16}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.34(m, 6H, Ar-H), 2.73-2.7(t, 4H, $^3\text{J}_{7.52}$ Hz, $2 \times \text{Ar}-\underline{\text{CH}_2}-\text{CH}_2-$), 1.68-1.62(quin, 4H, $^3\text{J}_{6.84}$ Hz, $2 \times \text{Ar}-\text{CH}_2-\underline{\text{CH}_2}-\text{CH}_2-$), 1.32-1.27(m, 28H, $14 \times -\text{CH}_2-\underline{\text{CH}_2}-\text{CH}_2-$), 0.90-0.87(t, 6H, $^3\text{J}_{6.64}$ Hz, $2 \times -\text{CH}_2-\underline{\text{CH}_3}$); δ_{C} : 163.6, 155.4, 150.2, 149.2, 143.2, 134.4, 130.6, 129.6, 129.5, 128.8, 126.8, 125.6, 124.4, 121.1, 118.8, 118.6, 36.1, 31.9, 31.1, 29.5, 29.2, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-undecylbenzoyloxy) 3-fluorobenzoate], (2.C.8)

Yield, 68%; m.p. 121.5°C; $\nu_{\max}$: 2924, 2852, 1749, 1734, 1608, 1510, 1466, 1294, 1111 cm^{-1} ; δ_{H} : 8.16-8.09(m, 8H, Ar-H), 7.97-7.95(d, 2H, $^3\text{J}_{8.92}$ Hz, Ar-H), 7.71-7.70(d, 2H, $^4\text{J}_{2.04}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.34(m, 6H, Ar-H), 2.73-2.7(t, 4H, $^3\text{J}_{7.48}$ Hz, $2 \times \text{Ar}-\underline{\text{CH}_2}-\text{CH}_2-$), 1.68-1.64(quin, 4H, $^3\text{J}_{6.72}$ Hz, $2 \times \text{Ar}-\text{CH}_2-\underline{\text{CH}_2}-\text{CH}_2-$), 1.33-1.27(m, 32H, $16 \times -\text{CH}_2-\underline{\text{CH}_2}-\text{CH}_2-$), 0.90-0.87(t, 6H, $^3\text{J}_{6.64}$ Hz, $2 \times -\text{CH}_2-\underline{\text{CH}_3}$); δ_{C} : 163.7, 155.4, 152.9, 150.2, 149.1, 143.1, 134.3, 130.6, 129.7, 129.6, 129.5, 128.8, 128.4, 126.8, 125.6, 124.3, 121.1, 118.8, 118.6, 36.1, 31.9, 31.1, 29.6, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-dodecylbenzoyloxy) 3-fluorobenzoate], (2.C.9)

Yield, 66%; m.p. 119.0°C; $\nu_{\max}$: 2924, 2852, 1747, 1735, 1608, 1510, 1460, 1294, 1117 cm^{-1} ; δ_{H} : 8.15-8.09(m, 8H, Ar-H), 7.97-7.95(d, 2H, $^3\text{J}_{8.96}$ Hz, Ar-H), 7.71-7.70(d, 2H, $^4\text{J}_{2.12}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.34(m, 6H, Ar-H), 2.73-2.7(t, 4H, $^3\text{J}_{7.56}$ Hz, $2 \times \text{Ar}-$

CH₂-CH₂-), 1.67-1.64(quin, 4H, ³J7.6 Hz, 2 × Ar-CH₂-CH₂-CH₂-), 1.33-1.27(m, 36H, 18 × -CH₂-CH₂-CH₂-), 0.90-0.87(t, 6H, ³J6.6 Hz, 2 × -CH₂-CH₃); δ_C: 163.7, 155.4, 152.9, 150.2, 149.1, 143.2, 134.3, 130.6, 129.7, 129.6, 129.5, 128.8, 128.4, 126.8, 125.6, 124.3, 121.1, 118.8, 118.6, 36.1, 31.9, 31.1, 29.6, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-tetradecylbenzoyloxy) 3-fluorobenzoate], (2.C.10)

Yield, 65%; m.p. 116.0°C; ν_{max}: 2920, 2850, 1747, 1732, 1608, 1510, 1460, 1292, 1117 cm⁻¹; δ_H: 8.15-8.01(m, 8H, Ar-H), 7.97-7.95(d, 2H, ³J8.92 Hz, Ar-H), 7.71-7.70(d, 2H, ⁴J1.96 Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.34(m, 6H, Ar-H), 2.73-2.69(t, 4H, ³J7.6 Hz, 2 × Ar-CH₂-CH₂-), 1.66-1.63(quin, 4H, ³J7.36 Hz, 2 × Ar-CH₂-CH₂-CH₂-), 1.33-1.22(m, 44H, 22 × -CH₂-CH₂-CH₂-), 0.9-0.86(t, 6H, ³J6.44 Hz, 2 × -CH₂-CH₃); δ_C: 163.7, 155.4, 152.9, 150.2, 149.1, 143.2, 134.3, 130.6, 129.6, 128.8, 128.4, 126.8, 125.6, 124.3, 121.1, 118.8, 118.6, 36.1, 31.9, 31.1, 29.6, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-hexadecylbenzoyloxy) 3-fluorobenzoate], (2.C.11)

Yield, 62%; m.p. 111.5°C; ν_{max}: 2920, 2852, 1747, 1734, 1608, 1510, 1458, 1294, 1117 cm⁻¹; δ_H: 8.15-8.09(m, 8H, Ar-H), 7.97-7.95(d, 2H, ³J8.92 Hz, Ar-H), 7.71-7.70(d, 2H, ⁴J2.08 Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.34(m, 6H, Ar-H), 2.73-2.69(t, 4H, ³J7.52 Hz, 2 × Ar-CH₂-CH₂-), 1.68-1.64(quin, 4H, ³J7.36 Hz, 2 × Ar-CH₂-CH₂-CH₂-), 1.33-1.21(m, 52H, 26 × -CH₂-CH₂-CH₂-), 0.9-0.86(t, 6H, ³J6.52 Hz, 2 × -CH₂-CH₃); δ_C: 163.7, 155.4, 150.2, 149.1, 143.2, 134.3, 130.6, 129.6, 128.8, 128.4, 126.8, 125.6, 124.3, 121.1, 118.8, 118.6, 36.1, 31.9, 31.1, 29.7, 29.4, 29.3, 29.2, 29.1, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-octadecylbenzoyloxy) 3-fluorobenzoate], (2.C.12)

Yield, 60%; m.p. 111.0°C; ν_{max}: 2916, 2850, 1747, 1732, 1608, 1510, 1458, 1294, 1117 cm⁻¹; δ_H: 8.15-8.09(m, 8H, Ar-H), 7.97-7.95(d, 2H, ³J8.88 Hz, Ar-H), 7.71-7.70(d, 2H, ⁴J2.12 Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.34(m, 6H, Ar-H), 2.73-2.69(t, 4H, ³J7.24 Hz, 2 × Ar-CH₂-CH₂-), 1.67-1.64(quin, 4H, ³J7.38 Hz, 2 × Ar-CH₂-CH₂-CH₂-), 1.33-1.22(m, 60H, 30 × -CH₂-CH₂-CH₂-), 0.9-0.86(t, 6H, ³J6.64 Hz, 2 × -CH₂-CH₃); δ_C: 163.7, 150.2, 149.2, 143.2, 134.4, 130.6, 129.6, 128.9, 128.5, 126.8, 125.6, 124.3, 121.1, 118.8, 118.6, 43.8, 36.2, 31.9, 31.1, 29.7, 29.5, 29.3, 29.2, 29.1, 22.7, 14.1.

2,7-Naphthylene bis[4-(4-n-butyloxybenzoyloxy) benzoate], (2.D.1)

Yield, 67%; m.p. 197.5°C; $\nu_{\max}$: 2924, 2855, 1732, 1603, 1458, 1259, 1057 cm^{-1} ; δ_{H} : 8.34-8.32(d, 4H, ^3J 8.68 Hz, Ar-H), 8.18-8.15(d, 4H, ^3J 8.86 Hz, Ar-H), 7.96-7.94(d, 2H, ^3J 8.86 Hz, Ar-H), 7.709-7.704(d, 2H, ^4J 1.96 Hz, Ar-H), 7.41-7.37(m, 6H, Ar-H), 7.01-6.98(d, 4H, ^3J 8.92 Hz, Ar-H), 4.09-4.05(t, 4H, ^3J 6.48 Hz, $2 \times \text{Ar-OCH}_2-$), 1.86-1.79(quin, 4H, ^3J 6.56 Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-\text{CH}_2-$), 1.6-1.48(m, 4H, $2 \times -\text{CH}_2-\text{CH}_2-\text{CH}_3$), 1.02-0.99(t, 6H, ^3J 7.4 Hz, $2 \times -\text{CH}_2-\text{CH}_3$). Elemental analysis: $\text{C}_{46}\text{H}_{40}\text{O}_{10}$ requires, C, 73.39; H, 5.36%; found, C, 72.99; H, 5.29 %.

2,7-Naphthylene bis[4-(4-n-undecyloxybenzoyloxy) benzoate], (2.D.5)

Yield, 72%; m.p. 135.5°C; $\nu_{\max}$: 2924, 2851, 1732, 1605, 1510, 1464, 1377, 1254, 1078 cm^{-1} ; δ_{H} : 8.34-8.32(d, 4H, ^3J 8.64 Hz, Ar-H), 8.17-8.15(d, 4H, ^3J 8.8 Hz, Ar-H), 7.96-7.94(d, 2H, ^3J 8.92 Hz, Ar-H), 7.709-7.705(d, 2H, ^4J 1.72 Hz, Ar-H), 7.41-7.37(m, 6H, Ar-H), 7.01-6.98(d, 4H, ^3J 8.84 Hz, Ar-H), 4.08-4.05(t, 4H, ^3J 6.48 Hz, $2 \times \text{Ar-OCH}_2-$), 1.87-1.8 (quin, 4H, ^3J 6.68 Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-\text{CH}_2-$), 1.5-1.45(quin, 4H, $2 \times -\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 1.4-1.2(m, 28H, $14 \times -\text{CH}_2-$), 0.91- 0.87(t, 6H, ^3J 6.44 Hz, $2 \times -\text{CH}_2-\text{CH}_3$); Elemental analysis: $\text{C}_{60}\text{H}_{68}\text{O}_{10}$ requires, C, 75.92; H, 7.22%; found, C, 76.03; H, 7.20 %.

2,7-Naphthylene bis[4-(4-n-hexadecyloxybenzoyloxy) benzoate], (2.D.6)

Yield, 70%; m.p. 122.0°C; $\nu_{\max}$: 2920, 2851, 1732, 1605, 1508, 1464, 1377, 1288, 1078 cm^{-1} ; δ_{H} : 8.34-8.32(d, 4H, ^3J 8.72 Hz, Ar-H), 8.17-8.15(d, 4H, ^3J 8.88 Hz, Ar-H), 7.96-7.94(d, 2H, ^3J 8.92 Hz, Ar-H), 7.709-7.704(d, 2H, ^4J 1.84 Hz, Ar-H), 7.41-7.37(m, 6H, Ar-H), 7.01-6.98(d, 4H, ^3J 8.92 Hz, Ar-H), 4.07-4.04(t, 4H, ^3J 6.52 Hz, $2 \times \text{Ar-OCH}_2-$), 1.86-1.8(quin, 4H, ^3J 6.68 Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_2-\text{CH}_2-$), 1.52-1.45(quin, 4H, $2 \times -\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 1.33-1.26(m, 48H, $24 \times -\text{CH}_2-$), 0.90-0.87(t, 6H, ^3J 6.52 Hz, $2 \times -\text{CH}_2-\text{CH}_3$); Elemental analysis: $\text{C}_{70}\text{H}_{88}\text{O}_{10}$ requires, C, 77.17; H, 8.14%; found, C, 76.80, H, 8.06 %.

2,7-Naphthylene bis[4-(4-ethoxybenzoyloxy) 2-fluorobenzoate], (2.E.1)

Yield, 62%; m.p. 168.0°C; $\nu_{\max}$: 2924, 2855, 1740, 1610, 1508, 1458, 1240, 1117 cm^{-1} ; δ_{H} : 8.26-8.22(m, 2H, Ar-H), 8.16-8.14(d, 4H, ^3J 8.92 Hz, Ar-H), 7.96-7.94(d, 2H, ^3J 8.96 Hz, Ar-H), 7.729-7.724(d, 2H, ^4J 2.12 Hz, Ar-H), 7.42-7.39(dd, 2H, ^3J 8.86 Hz, ^4J 2.24 Hz, Ar-H), 7.23-7.19(m, 4H, Ar-H), 7.01-6.99(d, 4H, ^3J 8.92 Hz, Ar-H), 4.17-4.12(q, 4H, ^3J 7.0 Hz, $2 \times \text{Ar-OCH}_2-\text{CH}_3$), 1.5-1.46(t, 6H, ^3J 6.96 Hz, $2 \times \text{Ar-CH}_2-\text{CH}_3$).

2,7-Naphthylene bis[4-(4-n-propyloxybenzoyloxy) 2-fluorobenzoate], (2.E.2)

Yield, 65%; m.p. 162.0°C; $\nu_{\max}$: 2922, 2854, 1738, 1605, 1508, 1458, 1240, 1116 cm^{-1} ; δ_{H} : 8.26-8.22(m, 2H, Ar-H), 8.16-8.14(d, 4H, $^3\text{J}_{8.84}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3\text{J}_{8.88}$ Hz, Ar-H), 7.729-7.724(d, 2H, $^4\text{J}_{2.08}$ Hz, Ar-H), 7.42-7.39(dd, 2H, $^3\text{J}_{8.74}$ Hz, $^4\text{J}_{2.2}$ Hz, Ar-H), 7.22-7.19(m, 4H, Ar-H), 7.01-6.99(d, 4H, $^3\text{J}_{8.88}$ Hz, Ar-H), 4.05-4.02(t, 4H, $^3\text{J}_{6.56}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-), 1.91-1.83(m, 4H, Ar-H), 1.1-1.06(t, 6H, $^3\text{J}_{7.4}$ Hz, 2 $\times$ -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-butyloxybenzoyloxy) 2-fluorobenzoate], (2.E.3)

Yield, 70%; m.p. 142.0°C; $\nu_{\max}$: 2923, 2854, 1736, 1720, 1605, 1508, 1456, 1240, 1117 cm^{-1} ; δ_{H} : 8.26-8.22(m, 2H, Ar-H), 8.17-8.13(d, 4H, $^3\text{J}_{8.92}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3\text{J}_{8.96}$ Hz, Ar-H), 7.729-7.723(d, 2H, $^4\text{J}_{2.16}$ Hz, Ar-H), 7.42-7.39(dd, 2H, $^3\text{J}_{8.86}$ Hz, $^4\text{J}_{2.24}$ Hz, Ar-H), 7.23-7.19(m, 4H, Ar-H), 7.01-6.99(d, 4H, $^3\text{J}_{8.96}$ Hz, Ar-H), 4.09-4.06(t, 4H, $^3\text{J}_{6.48}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-), 1.86-1.79(quin, 4H, $^3\text{J}_{6.6}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-CH₂-), 1.56-1.48(m, 4H, 2 $\times$ -CH₂-CH₂-CH₃), 1.02-0.99(t, 6H, $^3\text{J}_{7.36}$ Hz, 2 $\times$ -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-pentyloxybenzoyloxy) 2-fluorobenzoate], (2.E.4)

Yield, 72%; m.p. 154.0°C; $\nu_{\max}$: 2924, 2854, 1738, 1720, 1608, 1508, 1456, 1238, 1116 cm^{-1} ; δ_{H} : 8.19-8.12(m, 2H, Ar-H), 8.09-8.07(d, 4H, $^3\text{J}_{8.8}$ Hz, Ar-H), 7.89-7.86(d, 2H, $^3\text{J}_{8.88}$ Hz, Ar-H), 7.729-7.723(d, 2H, $^4\text{J}_{2.16}$ Hz, Ar-H), 7.34-7.32(dd, 2H, $^3\text{J}_{8.86}$ Hz, $^4\text{J}_{2.24}$ Hz, Ar-H), 7.23-7.13(m, 4H, Ar-H), 6.94-6.92(d, 4H, $^3\text{J}_{8.84}$ Hz, Ar-H), 4.0-3.98(t, 4H, $^3\text{J}_{6.56}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-), 1.80-1.74(quin, 4H, $^3\text{J}_{6.76}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-CH₂-), 1.47-1.31(m, 8H, 4 $\times$ -CH₂-CH₂-CH₂-), 0.9-0.87(t, 6H, $^3\text{J}_{7.04}$ Hz, 2 $\times$ -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-hexyloxybenzoyloxy) 2-fluorobenzoate], (2.E.5)

Yield, 75%; m.p. 120.5°C; $\nu_{\max}$: 2920, 2854, 1740, 1724, 1608, 1510, 1456, 1238, 1117 cm^{-1} ; δ_{H} : 8.26-8.22(m, 2H, Ar-H), 8.16-8.14(d, 4H, $^3\text{J}_{8.76}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3\text{J}_{8.84}$ Hz, Ar-H), 7.729-7.724(d, 2H, $^4\text{J}_{2.04}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3\text{J}_{8.8}$ Hz, $^4\text{J}_{2.12}$ Hz, Ar-H), 7.22-7.19(m, 4H, Ar-H), 7.01-6.98(d, 4H, $^3\text{J}_{8.8}$ Hz, Ar-H), 4.08-4.05(t, 4H, $^3\text{J}_{6.56}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-), 1.87-1.8(quin, 4H, $^3\text{J}_{6.72}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-CH₂-), 1.55-1.35(m, 12H, 6 $\times$ -CH₂-CH₂-CH₂-), 0.94-0.91(t, 6H, $^3\text{J}_{7.0}$ Hz, 2 $\times$ -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-heptyloxybenzoyloxy) 2-fluorobenzoate], (2.E.6)

Yield, 71%; m.p. 127.0°C; $\nu_{\max}$: 2924, 2854, 1742, 1725, 1610, 1514, 1456, 1238, 1117 cm^{-1} ; δ_{H} : 8.26-8.22(m, 2H, Ar-H), 8.16-8.14(d, 4H, $^3\text{J}_{8.92}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3\text{J}_{8.92}$ Hz,

Ar-H), 7.729-7.723(d, 2H, $^4J_{2.16}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3J_{8.86}$ Hz, $^4J_{2.2}$ Hz, Ar-H), 7.23-7.19(m, 4H, Ar-H), 7.01-6.98(d, 4H, $^3J_{8.96}$ Hz, Ar-H), 4.07-4.05(t, 4H, $^3J_{6.52}$ Hz, $2 \times$ Ar-OCH₂-CH₂-), 1.87-1.8(quin, 4H, $^3J_{6.72}$ Hz, $2 \times$ Ar-OCH₂-CH₂-CH₂-), 1.55-1.30(m, 16H, $8 \times$ -CH₂-CH₂-CH₂-), 0.93-0.87(t, 6H, $^3J_{7.0}$ Hz, $2 \times$ -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-octyloxybenzoyloxy) 2-fluorobenzoate], (2.E.7)

Yield, 73%; m.p. 112.5°C; $\nu_{\max}$: 2925, 2850, 1738, 1720, 1610, 1514, 1458, 1238, 1118 cm⁻¹; δ_{H} : 8.26-8.18(m, 2H, Ar-H), 8.16-8.14(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 7.96-7.93(d, 2H, $^3J_{9.0}$ Hz, Ar-H), 7.728-7.723(d, 2H, $^4J_{1.96}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3J_{8.86}$ Hz, $^4J_{2.12}$ Hz, Ar-H), 7.22-7.19(m, 4H, Ar-H), 7.01-6.99(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3J_{6.52}$ Hz, $2 \times$ Ar-OCH₂-CH₂-), 1.87-1.8(quin, 4H, $^3J_{6.68}$ Hz, $2 \times$ Ar-OCH₂-CH₂-CH₂-), 1.55-1.30(m, 20H, $10 \times$ -CH₂-CH₂-CH₂-), 0.92-0.88(t, 6H, $^3J_{6.92}$ Hz, $2 \times$ -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-nonyloxybenzoyloxy) 2-fluorobenzoate], (2.E.8)

Yield, 67%; m.p. 124.0°C; $\nu_{\max}$: 2925, 2850, 1738, 1715, 1606, 1516, 1460, 1236, 1118 cm⁻¹; δ_{H} : 8.26-8.22(m, 2H, Ar-H), 8.16-8.14(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 7.96-7.94(d, 2H, $^3J_{8.92}$ Hz, Ar-H), 7.728-7.724(d, 2H, $^4J_{2.16}$ Hz, Ar-H), 7.41-7.39(dd, 2H, $^3J_{8.86}$ Hz, $^4J_{2.16}$ Hz, Ar-H), 7.23-7.19(m, 4H, Ar-H), 7.01-6.99(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.08-4.04(t, 4H, $^3J_{6.56}$ Hz, $2 \times$ Ar-OCH₂-CH₂-), 1.87-1.8(quin, 4H, $^3J_{6.68}$ Hz, $2 \times$ Ar-OCH₂-CH₂-CH₂-), 1.54-1.30(m, 24H, $12 \times$ -CH₂-CH₂-CH₂-), 0.91-0.88(t, 6H, $^3J_{7.0}$ Hz, $2 \times$ -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-decyloxybenzoyloxy) 2-fluorobenzoate], (2.E.9)

Yield, 67%; m.p. 108.5°C; $\nu_{\max}$: 2924, 2850, 1740, 1605, 1516, 1460, 1236, 1120 cm⁻¹; δ_{H} : 8.19-8.15(m, 2H, Ar-H), 8.09-8.06(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 7.89-7.86(d, 2H, $^3J_{8.88}$ Hz, Ar-H), 7.728-7.724(d, 2H, $^4J_{2.16}$ Hz, Ar-H), 7.34-7.32(dd, 2H, $^3J_{8.84}$ Hz, $^4J_{2.16}$ Hz, Ar-H), 7.19-7.12(m, 4H, Ar-H), 6.94-6.91(d, 4H, $^3J_{8.92}$ Hz, Ar-H), 4.01-3.97(t, 4H, $^3J_{6.52}$ Hz, $2 \times$ Ar-OCH₂-CH₂-), 1.8-1.73(quin, 4H, $^3J_{6.84}$ Hz, $2 \times$ Ar-OCH₂-CH₂-CH₂-), 1.46-1.21(m, 28H, $14 \times$ -CH₂-CH₂-CH₂-), 0.84-0.80(t, 6H, $^3J_{7.0}$ Hz, $2 \times$ -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-undecyloxybenzoyloxy) 2-fluorobenzoate], (2.E.10)

Yield, 68%; m.p. 112.5°C; $\nu_{\max}$: 2924, 2850, 1740, 1715, 1604, 1518, 1460, 1236, 1120 cm⁻¹; δ_{H} : 8.19-8.15(m, 2H, Ar-H), 8.09-8.06(d, 4H, $^3J_{8.88}$ Hz, Ar-H), 7.89-7.87(d, 2H, $^3J_{8.92}$ Hz, Ar-H), 7.656-7.65(d, 2H, $^4J_{2.16}$ Hz, Ar-H), 7.34-7.31(dd, 2H, $^3J_{8.7}$ Hz, $^4J_{2.2}$ Hz, Ar-H), 7.19-7.12(m, 4H, Ar-H), 6.94-6.91(d, 4H, $^3J_{8.96}$ Hz, Ar-H), 4.0-3.97(t, 4H, $^3J_{6.52}$ Hz, $2 \times$

Ar-OCH₂-CH₂-), 1.8-1.73(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.47-1.21(m, 32H, 16 × -CH₂-CH₂-CH₂-), 0.83-0.80(t, 6H, ³J7.2 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-dodecyloxybenzoyloxy) 2-fluorobenzoate], (2.E.11)

Yield, 66%; m.p. 107.0°C; ν_{max}: 2924, 2850, 1740, 1725, 1608, 1518, 1468, 1236, 1120 cm⁻¹; δ_H: 8.19-8.15(m, 2H, Ar-H), 8.09-8.06(d, 4H, ³J8.89 Hz, Ar-H), 7.89-7.87(d, 2H, ³J8.92 Hz, Ar-H), 7.656-7.65(d, 2H, ⁴J2.12 Hz, Ar-H), 7.34-7.31(dd, 2H, ³J8.6 Hz, ⁴J2.2 Hz, Ar-H), 7.19-7.13(m, 4H, Ar-H), 6.94-6.91(d, 4H, ³J8.90 Hz, Ar-H), 4.0-3.96(t, 4H, ³J6.5 Hz, 2 × Ar-OCH₂-CH₂-), 1.8-1.73(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.47-1.22(m, 36H, 18 × -CH₂-CH₂-CH₂-), 0.83-0.80(t, 6H, ³J7.24 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-tetradecyloxybenzoyloxy) 2-fluorobenzoate], (2.E.12)

Yield, 65%; m.p. 98.5°C; ν_{max}: 2924, 2850, 1742, 1724, 1608, 1518, 1468, 1238, 1118 cm⁻¹; δ_H: 8.19-8.15(m, 2H, Ar-H), 8.09-8.06(d, 4H, ³J8.84 Hz, Ar-H), 7.89-7.87(d, 2H, ³J8.96 Hz, Ar-H), 7.656-7.65(d, 2H, ⁴J2.0 Hz, Ar-H), 7.34-7.31(dd, 2H, ³J8.84 Hz, ⁴J2.2 Hz, Ar-H), 7.19-7.12(m, 4H, Ar-H), 6.94-6.91(d, 4H, ³J8.92 Hz, Ar-H), 4.0-3.97(t, 4H, ³J6.48 Hz, 2 × Ar-OCH₂-CH₂-), 1.8-1.73(quin, 4H, ³J6.76 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.53-1.2(m, 44H, 22 × -CH₂-CH₂-CH₂-), 0.83-0.79(t, 6H, ³J7.04 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-hexadecyloxybenzoyloxy) 2-fluorobenzoate], (2.E.13)

Yield, 62%; m.p. 104.0°C; ν_{max}: 2922, 2850, 1742, 1720, 1608, 1518, 1468, 1240, 1117 cm⁻¹; δ_H: 8.19-8.15(m, 2H, Ar-H), 8.09-8.06(d, 4H, ³J8.92 Hz, Ar-H), 7.89-7.87(d, 2H, ³J8.96 Hz, Ar-H), 7.656-7.65(d, 2H, ⁴J2.2 Hz, Ar-H), 7.34-7.31(dd, 2H, ³J8.84 Hz, ⁴J2.2 Hz, Ar-H), 7.19-7.12(m, 4H, Ar-H), 6.93-6.91(d, 4H, ³J8.96 Hz, Ar-H), 4.0-3.97(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-CH₂-), 1.78-1.72(quin, 4H, ³J6.72 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.46-1.19(m, 52H, 26 × -CH₂-CH₂-CH₂-), 0.83-0.79(t, 6H, ³J7.0 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-octadecyloxybenzoyloxy) 2-fluorobenzoate], (2.E.14)

Yield, 64%; m.p. 103.5°C; ν_{max}: 2920, 2850, 1738, 1718, 1608, 1518, 1468, 1235, 1117 cm⁻¹; δ_H: 8.19-8.15(m, 2H, Ar-H), 8.09-8.06(d, 4H, ³J8.88 Hz, Ar-H), 7.89-7.87(d, 2H, ³J8.96 Hz, Ar-H), 7.656-7.65(d, 2H, ⁴J2.16 Hz, Ar-H), 7.34-7.31(dd, 2H, ³J8.88 Hz, ⁴J2.2 Hz, Ar-H), 7.19-7.12(m, 4H, Ar-H), 6.94-6.91(d, 4H, ³J8.96 Hz, Ar-H), 4.0-3.97(t, 4H, ³J6.52 Hz, 2 × Ar-OCH₂-CH₂-), 1.78-1.74(quin, 4H, ³J7.0 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.41-1.15(m, 60H, 30 × -CH₂-CH₂-CH₂-), 0.83-0.79(t, 6H, ³J7.04 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-ethoxybenzoyloxy) 3-fluorobenzoate], (2.F.1)

Yield, 62%; m.p. 194.0°C; $\nu_{\max}$: 2924, 2850, 1740, 1606, 1510, 1455, 1245, 1115 cm^{-1} ; δ_{H} : 8.23-8.17(d, 4H, $^3\text{J}_{8.88}$ Hz, Ar-H), 8.12-8.01(m, 4H, Ar-H), 7.97-7.95(d, 2H, $^3\text{J}_{8.92}$ Hz, Ar-H), 7.71-7.70(d, 2H, $^4\text{J}_{2.08}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.37(dd, 2H, $^3\text{J}_{8.88}$ Hz, $^4\text{J}_{2.2}$ Hz, Ar-H), 7.01-6.99(d, 4H, $^3\text{J}_{8.92}$ Hz, Ar-H), 4.17-4.12(q, 4H, $^3\text{J}_{7.0}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_3$), 1.49-1.46(t, 6H, $^3\text{J}_{6.96}$ Hz, $2 \times \text{Ar-CH}_2\text{-CH}_3$).

2,7-Naphthylene bis[4-(4-n-propyloxybenzoyloxy) 3-fluorobenzoate], (2.F.2)

Yield, 63%; m.p. 208.0°C; $\nu_{\max}$: 2924, 2850, 1742, 1606, 1510, 1455, 1245, 1116 cm^{-1} ; δ_{H} : 8.18-8.16(d, 4H, $^3\text{J}_{8.88}$ Hz, Ar-H), 8.12-8.08(m, 4H, Ar-H), 7.97-7.95(d, 2H, $^3\text{J}_{8.96}$ Hz, Ar-H), 7.709-7.704(d, 2H, $^4\text{J}_{2.2}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.37(dd, 2H, $^3\text{J}_{8.86}$ Hz, $^4\text{J}_{2.24}$ Hz, Ar-H), 7.01-6.99(d, 4H, $^3\text{J}_{8.92}$ Hz, Ar-H), 4.05-4.01(t, 4H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.91-1.82(m, 4H, Ar-H), 1.09-1.06(t, 6H, $^3\text{J}_{7.4}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

2,7-Naphthylene bis[4-(4-n-butyloxybenzoyloxy) 3-fluorobenzoate], (2.F.3)

Yield, 64%; m.p. 170.0°C; $\nu_{\max}$: 2924, 2854, 1738, 1608, 1510, 1455, 1250, 1112 cm^{-1} ; δ_{H} : 8.19-8.17(d, 4H, $^3\text{J}_{7.24}$ Hz, Ar-H), 8.12-8.08(m, 4H, Ar-H), 7.97-7.95(d, 2H, $^3\text{J}_{8.96}$ Hz, Ar-H), 7.708-7.704(d, 2H, $^4\text{J}_{2.0}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.39-7.37(dd, 2H, $^3\text{J}_{8.84}$ Hz, $^4\text{J}_{2.12}$ Hz, Ar-H), 7.01-6.99(d, 4H, $^3\text{J}_{8.84}$ Hz, Ar-H), 4.09-4.06(t, 4H, $^3\text{J}_{6.44}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.80-1.79(quin, 4H, $^3\text{J}_{6.88}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.54-1.48(m, 4H, $2 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.0-0.98(t, 6H, $^3\text{J}_{7.04}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

2,7-Naphthylene bis[4-(4-n-pentyloxybenzoyloxy) 3-fluorobenzoate], (2.F.4)

Yield, 65%; m.p. 182.0°C; $\nu_{\max}$: 2924, 2853, 1736, 1605, 1510, 1455, 1250, 1108 cm^{-1} ; δ_{H} : 8.19-8.17(d, 4H, $^3\text{J}_{8.84}$ Hz, Ar-H), 8.13-8.08(m, 4H, Ar-H), 7.97-7.95(d, 2H, $^3\text{J}_{8.92}$ Hz, Ar-H), 7.71-7.70(d, 2H, $^4\text{J}_{2.08}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.37(dd, 2H, $^3\text{J}_{8.86}$ Hz, $^4\text{J}_{2.2}$ Hz, Ar-H), 7.01-6.99(d, 4H, $^3\text{J}_{8.92}$ Hz, Ar-H), 4.08-4.05(t, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.88-1.81(quin, 4H, $^3\text{J}_{6.84}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.54-1.37(m, 8H, $4 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 0.97-0.94(t, 6H, $^3\text{J}_{7.12}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

2,7-Naphthylene bis[4-(4-n-hexyloxybenzoyloxy) 3-fluorobenzoate], (2.F.5)

Yield, 61%; m.p. 156.0°C; $\nu_{\max}$: 2924, 2852, 1738, 1608, 1510, 1455, 1250, 1108 cm^{-1} ; δ_{H} : 8.19-8.17(d, 4H, $^3\text{J}_{8.88}$ Hz, Ar-H), 8.13-8.09(m, 4H, Ar-H), 7.97-7.95(d, 2H, $^3\text{J}_{8.92}$ Hz, Ar-H), 7.71-7.70(d, 2H, $^4\text{J}_{2.2}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.37(dd, 2H, $^3\text{J}_{8.86}$ Hz,

⁴J2.12 Hz, Ar-H), 7.01-6.99(d, 4H, ³J8.92 Hz, Ar-H), 4.08-4.05(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-CH₂-), 1.87-1.80(quin, 4H, ³J6.72 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.53-1.34(m, 12H, 6 × -CH₂-CH₂-CH₂-), 0.94-0.91(t, 6H, ³J6.96 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-heptyloxybenzoyloxy) 3-fluorobenzoate], (2.F.6)

Yield, 60%; m.p. 154.0°C; $\nu_{\max}$: 2918, 2848, 1740, 1608, 1510, 1450, 1250, 1108 cm⁻¹; δ_{H} : 8.18-8.16(d, 4H, ³J8.88 Hz, Ar-H), 8.12-8.08(m, 4H, Ar-H), 7.97-7.95(d, 2H, ³J8.92 Hz, Ar-H), 7.709-7.704(d, 2H, ⁴J2.08 Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.37(dd, 2H, ³J8.84 Hz, ⁴J2.2 Hz, Ar-H), 7.01-6.99(d, 4H, ³J8.92 Hz, Ar-H), 4.08-4.04(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-CH₂-), 1.87-1.80(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.54-1.32(m, 16H, 8 × -CH₂-CH₂-CH₂-), 0.92-0.89(t, 6H, ³J6.72 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-octyloxybenzoyloxy) 3-fluorobenzoate], (2.F.7)

Yield, 63%; m.p. 147.5°C; $\nu_{\max}$: 2922, 2848, 1736, 1610, 1515, 1430, 1290, 1116 cm⁻¹; δ_{H} : 8.18-8.16(d, 4H, ³J8.84 Hz, Ar-H), 8.12-8.08(m, 4H, Ar-H), 7.97-7.95(d, 2H, ³J8.92 Hz, Ar-H), 7.709-7.703(d, 2H, ⁴J2.12 Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.37(dd, 2H, ³J8.86 Hz, ⁴J2.2 Hz, Ar-H), 7.01-6.99(d, 4H, ³J8.88 Hz, Ar-H), 4.08-4.04(t, 4H, ³J6.52 Hz, 2 × Ar-OCH₂-CH₂-), 1.87-1.80(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.54-1.30(m, 20H, 10 × -CH₂-CH₂-CH₂-), 0.91-0.88(t, 6H, ³J6.64 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-nonyloxybenzoyloxy) 3-fluorobenzoate], (2.F.8)

Yield, 65%; m.p. 136.0°C; $\nu_{\max}$: 2922, 2848, 1738, 1610, 1510, 1430, 1290, 1116 cm⁻¹; δ_{H} : 8.19-8.16(d, 4H, ³J8.88 Hz, Ar-H), 8.13-8.09(m, 4H, Ar-H), 7.97-7.95(d, 2H, ³J8.92 Hz, Ar-H), 7.71-7.708(d, 2H, ⁴J2.16 Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.37(dd, 2H, ³J8.88 Hz, ⁴J2.2 Hz, Ar-H), 7.01-6.99(d, 4H, ³J8.92 Hz, Ar-H), 4.08-4.04(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-CH₂-), 1.87-1.80(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.54-1.30(m, 24H, 12 × -CH₂-CH₂-CH₂-), 0.91-0.88(t, 6H, ³J6.64 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-decyloxybenzoyloxy) 3-fluorobenzoate], (2.F.9)

Yield, 61%; m.p. 136.0°C; $\nu_{\max}$: 2922, 2848, 1740, 1610, 1510, 1430, 1290, 1118 cm⁻¹; δ_{H} : 8.18-8.16(d, 4H, ³J8.56 Hz, Ar-H), 8.13-8.09(m, 4H, Ar-H), 7.97-7.95(d, 2H, ³J8.88 Hz, Ar-H), 7.71-7.708(d, 2H, ⁴J2.10 Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.37(dd, 2H, ³J8.74 Hz, ⁴J1.8 Hz, Ar-H), 7.01-6.99(d, 4H, ³J8.6 Hz, Ar-H), 4.08-4.04(t, 4H, ³J6.52 Hz, 2 × Ar-OCH₂-

CH₂-), 1.87-1.80(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.53-1.28(m, 28H, 14 × -CH₂-CH₂-CH₂-), 0.90-0.87(t, 6H, ³J6.16 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-undecyloxybenzoyloxy) 3-fluorobenzoate], (2.F.10)

Yield, 62%; m.p. 134.0°C; ν_{max}: 2920, 2848, 1740, 1608, 1510, 1430, 1290, 1118 cm⁻¹; δ_H: 8.18-8.16(d, 4H, ³J8.84 Hz, Ar-H), 8.13-8.08(m, 4H, Ar-H), 7.97-7.95(d, 2H, ³J8.92 Hz, Ar-H), 7.709-7.704(d, 2H, ⁴J2.12 Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.37(dd, 2H, ³J8.84 Hz, ⁴J2.2 Hz, Ar-H), 7.01-6.99(d, 4H, ³J8.92 Hz, Ar-H), 4.08-4.04(t, 4H, ³J6.56 Hz, 2 × Ar-OCH₂-CH₂-), 1.87-1.79(quin, 4H, ³J6.64 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.53-1.28(m, 32H, 16 × -CH₂-CH₂-CH₂-), 0.90-0.87(t, 6H, ³J6.56 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-dodecyloxybenzoyloxy) 3-fluorobenzoate], (2.F.11)

Yield, 65%; m.p. 130.5°C; ν_{max}: 2920, 2848, 1745, 1730, 1610, 1510, 1440, 1290, 1118 cm⁻¹; δ_H: 8.11-8.09(d, 4H, ³J8.92 Hz, Ar-H), 8.06-8.01(m, 4H, Ar-H), 7.9-7.88(d, 2H, ³J8.92 Hz, Ar-H), 7.64-7.63(d, 2H, ⁴J2.16 Hz, Ar-H), 7.41-7.37(m, 2H, Ar-H), 7.33-7.3(dd, 2H, ³J8.86 Hz, ⁴J2.2 Hz, Ar-H), 6.94-6.92(d, 4H, ³J8.92 Hz, Ar-H), 4.0-3.97(t, 4H, ³J6.52 Hz, 2 × Ar-OCH₂-CH₂-), 1.79-1.73(quin, 4H, ³J6.68 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.43-1.20(m, 36H, 18 × -CH₂-CH₂-CH₂-), 0.83-0.8(t, 6H, ³J6.68 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-tetradecyloxybenzoyloxy) 3-fluorobenzoate], (2.F.12)

Yield, 64%; m.p. 127.0°C; ν_{max}: 2920, 2848, 1745, 1728, 1610, 1512, 1440, 1290, 1120 cm⁻¹; δ_H: 8.18-8.16(d, 4H, ³J8.84 Hz, Ar-H), 8.12-8.08(m, 4H, Ar-H), 7.97-7.95(d, 2H, ³J8.96 Hz, Ar-H), 7.709-7.704(d, 2H, ⁴J2.08 Hz, Ar-H), 7.47-7.44(m, 2H, Ar-H), 7.4-7.37(dd, 2H, ³J8.82 Hz, ⁴J2.2 Hz, Ar-H), 7.01-6.99(d, 4H, ³J8.92 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.52 Hz, 2 × Ar-OCH₂-CH₂-), 1.87-1.8(quin, 4H, ³J6.76 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.52-1.27(m, 44H, 22 × -CH₂-CH₂-CH₂-), 0.9-0.87(t, 6H, ³J6.48 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-hexadecyloxybenzoyloxy) 3-fluorobenzoate], (2.F.13)

Yield, 65%; m.p. 124.0°C; ν_{max}: 2924, 2848, 1742, 1728, 1610, 1512, 1440, 1290, 1120 cm⁻¹; δ_H: 8.18-8.16(d, 4H, ³J8.8 Hz, Ar-H), 8.13-8.09(m, 4H, Ar-H), 7.97-7.95(d, 2H, ³J8.92 Hz, Ar-H), 7.709-7.704(d, 2H, ⁴J2.04 Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.37(dd, 2H, ³J8.82 Hz, ⁴J1.92 Hz, Ar-H), 7.01-6.98(d, 4H, ³J8.8 Hz, Ar-H), 4.07-4.04(t, 4H, ³J6.52 Hz, 2 × Ar-OCH₂-CH₂-), 1.87-1.81(quin, 4H, ³J6.52 Hz, 2 × Ar-OCH₂-CH₂-CH₂-), 1.48-1.22(m, 52H, 26 × -CH₂-CH₂-CH₂-), 0.9-0.86(t, 6H, ³J6.48 Hz, 2 × -CH₂-CH₃).

2,7-Naphthylene bis[4-(4-n-octadecyloxybenzoyloxy) 3-fluorobenzoate], (2.F.14)

Yield, 63%; m.p. 123.5°C; $\nu_{\max}$: 2924, 2850, 1742, 1610, 1512, 1440, 1290, 1117 cm^{-1} ; δ_{H} : 8.18-8.16(d, 4H, $^3\text{J}_{8.84}$ Hz, Ar-H), 8.13-8.08(m, 4H, Ar-H), 7.97-7.95(d, 2H, $^3\text{J}_{8.96}$ Hz, Ar-H), 7.709-7.704(d, 2H, $^4\text{J}_{2.0}$ Hz, Ar-H), 7.48-7.44(m, 2H, Ar-H), 7.4-7.37(dd, 2H, $^3\text{J}_{8.84}$ Hz, $^4\text{J}_{1.92}$ Hz, Ar-H), 7.01-6.99(d, 4H, $^3\text{J}_{8.84}$ Hz, Ar-H), 4.07-4.04(t, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.87-1.81(quin, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.48-1.26(m, 60H, $30 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 0.89-0.86(t, 6H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

2,7-Naphthylene bis[4-(2-fluoro-4-n-butyloxybenzoyloxy)benzoate], (2.G.1)

Yield, 65%; m.p. 182.0°C; $\nu_{\max}$: 2924, 2854, 1736, 1618, 1510, 1460, 1265, 1132 cm^{-1} ; δ_{H} : 8.34-8.32(d, 4H, $^3\text{J}_{8.64}$ Hz, Ar-H), 8.08-8.04(t, 2H, $^3\text{J}_{8.64}$ Hz, Ar-H), 7.95-7.93(d, 2H, $^3\text{J}_{8.88}$ Hz, Ar-H), 7.709-7.704(d, 2H, $^4\text{J}_{1.8}$ Hz, Ar-H), 7.42-7.37(m, 6H, Ar-H), 6.81-6.78(dd, 2H, $^3\text{J}_{8.84}$ Hz, $^4\text{J}_{2.08}$ Hz, Ar-H), 6.73-6.69(dd, 2H, $^3\text{J}_{12.72}$ Hz, $^4\text{J}_{2.16}$ Hz, Ar-H), 4.07-4.03(t, 4H, $^3\text{J}_{6.44}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.85-1.78(quin, 4H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.54-1.47(m, 4H, $2 \times \text{-CH}_2\text{-CH}_2\text{-CH}_3$), 1.0-0.99(t, 6H, $^3\text{J}_{7.36}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

2,7-Naphthylene bis[4-(2-fluoro-4-n-heptyloxybenzoyloxy)benzoate], (2.G.2)

Yield, 68%; m.p. 136.5°C; $\nu_{\max}$: 2924, 2854, 1740, 1728, 1620, 1510, 1455, 1271, 1132 cm^{-1} ; δ_{H} : 8.34-8.32(d, 4H, $^3\text{J}_{8.64}$ Hz, Ar-H), 8.08-8.04(t, 2H, $^3\text{J}_{8.6}$ Hz, Ar-H), 7.95-7.93(d, 2H, $^3\text{J}_{8.88}$ Hz, Ar-H), 7.709-7.704(d, 2H, $^4\text{J}_{1.9}$ Hz, Ar-H), 7.42-7.37(m, 6H, Ar-H), 6.81-6.78(dd, 2H, $^3\text{J}_{8.86}$ Hz, $^4\text{J}_{2.16}$ Hz, Ar-H), 6.73-6.69(dd, 2H, $^3\text{J}_{12.68}$ Hz, $^4\text{J}_{2.16}$ Hz, Ar-H), 4.06-4.02(t, 4H, $^3\text{J}_{6.48}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.86-1.79(quin, 4H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.49-1.44(quin, 4H, $^3\text{J}_{7.24}$ Hz, $2 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.4-1.33(m, 12H, $6 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 0.93-0.89(t, 6H, $^3\text{J}_{6.64}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

2,7-Naphthylene bis[4-(2-fluoro-4-n-undecyloxybenzoyloxy)benzoate], (2.G.3)

Yield, 66%; m.p. 112.5°C; $\nu_{\max}$: 2924, 2852, 1749, 1728, 1618, 1603, 1510, 1460, 1263, 1134 cm^{-1} ; δ_{H} : 8.34-8.32(d, 4H, $^3\text{J}_{8.68}$ Hz, Ar-H), 8.08-8.04(t, 2H, $^3\text{J}_{8.64}$ Hz, Ar-H), 7.95-7.93(d, 2H, $^3\text{J}_{8.92}$ Hz, Ar-H), 7.709-7.705(d, 2H, $^4\text{J}_{1.76}$ Hz, Ar-H), 7.42-7.37(m, 6H, Ar-H), 6.80-6.78(dd, 2H, $^3\text{J}_{8.84}$ Hz, $^4\text{J}_{2.08}$ Hz, Ar-H), 6.73-6.69(dd, 2H, $^3\text{J}_{12.68}$ Hz, $^4\text{J}_{2.12}$ Hz, Ar-H), 4.06-4.02(t, 4H, $^3\text{J}_{6.48}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.86-1.79(quin, 4H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.49-1.44(quin, 4H, $^3\text{J}_{6.84}$ Hz, $2 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.4-1.25(m, 28H, $14 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 0.91-0.87(t, 6H, $^3\text{J}_{6.4}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

2,7-Naphthylene bis[4-(2-fluoro-4-n-tetradecyloxybenzoyloxy)benzoate], (2.G.4)

Yield, 69%; m.p. 115.5°C; $\nu_{\max}$: 2922, 2852, 1740, 1742, 1618, 1603, 1508, 1458, 1275, 1132 cm^{-1} ; δ_{H} : 8.34-8.32(d, 4H, $^3\text{J}_{8.72}$ Hz, Ar-H), 8.08-8.04(t, 2H, $^3\text{J}_{8.64}$ Hz, Ar-H), 7.95-7.93(d, 2H, $^3\text{J}_{8.92}$ Hz, Ar-H), 7.709-7.705(d, 2H, $^4\text{J}_{2.0}$ Hz, Ar-H), 7.42-7.37(m, 6H, Ar-H), 6.80-6.78(dd, 2H, $^3\text{J}_{8.86}$ Hz, $^4\text{J}_{2.16}$ Hz, Ar-H), 6.73-6.69(dd, 2H, $^3\text{J}_{12.7}$ Hz, $^4\text{J}_{2.24}$ Hz, Ar-H), 4.06-4.02(t, 4H, $^3\text{J}_{6.48}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.86-1.79(quin, 4H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.47-1.44(quin, 4H, $^3\text{J}_{7.64}$ Hz, $2 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.38-1.25(m, 40H, $20 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 0.90-0.87(t, 6H, $^3\text{J}_{6.56}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

2,7-Naphthylene bis[4-(2-fluoro-4-n-octadecyloxybenzoyloxy)benzoate], (2.G.5)

Yield, 70%; m.p. 113.0°C; $\nu_{\max}$: 2914, 2852, 1740, 1732, 1628, 1508, 1458, 1286, 1133 cm^{-1} ; δ_{H} : 8.34-8.32(d, 4H, $^3\text{J}_{8.48}$ Hz, Ar-H), 8.08-8.04(t, 2H, $^3\text{J}_{8.64}$ Hz, Ar-H), 7.95-7.93(d, 2H, $^3\text{J}_{8.92}$ Hz, Ar-H), 7.71-7.705(d, 2H, $^4\text{J}_{1.84}$ Hz, Ar-H), 7.42-7.37(m, 6H, Ar-H), 6.80-6.78(dd, 2H, $^3\text{J}_{8.86}$ Hz, $^4\text{J}_{2.08}$ Hz, Ar-H), 6.73-6.69(dd, 2H, $^3\text{J}_{12.7}$ Hz, $^4\text{J}_{2.16}$ Hz, Ar-H), 4.06-4.02(t, 4H, $^3\text{J}_{6.48}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.84-1.80(quin, 4H, $^3\text{J}_{6.92}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.47-1.44(quin, 4H, $^3\text{J}_{7.6}$ Hz, $2 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.38-1.25(m, 56H, $28 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 0.90-0.87(t, 6H, $^3\text{J}_{6.48}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

2,7-Naphthylene bis[4-(3-fluoro-4-n-butyloxybenzoyloxy)benzoate], (2.H.1)

Yield, 67%; m.p. 170.0°C; $\nu_{\max}$: 2924, 2854, 1736, 1601, 1462, 1267, 1132 cm^{-1} ; δ_{H} : 8.34-8.32(d, 4H, $^3\text{J}_{8.72}$ Hz, Ar-H), 7.99-7.9(m, 6H, Ar-H), 7.709-7.704(d, 2H, $^4\text{J}_{2.04}$ Hz, Ar-H), 7.40-7.37(m, 6H, Ar-H), 7.08-7.03(t, 2H, $^3\text{J}_{8.24}$ Hz, Ar-H), 4.17-4.13(t, 4H, $^3\text{J}_{6.48}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.9-1.83 (quin, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.59-1.50(m, 4H, $2 \times \text{-CH}_2\text{-CH}_2\text{-CH}_3$), 1.03-0.99(t, 6H, $^3\text{J}_{7.36}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

2,7-Naphthylene bis[4-(3-fluoro-4-n-heptyloxybenzoyloxy)benzoate], (2.H.2)

Yield, 69%; m.p. 164.0°C; $\nu_{\max}$: 2926, 2854, 1736, 1728, 1618, 1460, 1283, 1136 cm^{-1} ; δ_{H} : 8.34-8.32(d, 4H, $^3\text{J}_{8.64}$ Hz, Ar-H), 7.99-7.9(m, 6H, Ar-H), 7.709-7.704(d, 2H, $^4\text{J}_{1.84}$ Hz, Ar-H), 7.41-7.37(m, 6H, Ar-H), 7.07-7.03(t, 2H, $^3\text{J}_{8.28}$ Hz, Ar-H), 4.16-4.12(t, 4H, $^3\text{J}_{6.52}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-}$), 1.91-1.84(quin, 4H, $^3\text{J}_{6.6}$ Hz, $2 \times \text{Ar-OCH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.50-1.47(quin, 4H, $^3\text{J}_{7.92}$ Hz, $2 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 1.41-1.33(m, 12H, $6 \times \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$), 0.93-0.89(t, 6H, $^3\text{J}_{6.64}$ Hz, $2 \times \text{-CH}_2\text{-CH}_3$).

2,7-Naphthylene bis[4-(3-fluoro-4-n-nonyloxybenzoyloxy)benzoate], (2.H.3)

Yield, 66%; m.p. 156.0°C; $\nu_{\max}$: 2924, 2852, 1736, 1726, 1618, 1460, 1283, 1140 cm^{-1} ; δ_{H} : 8.34-8.32(d, 4H, $^3J_{8.64}$ Hz, Ar-H), 7.99-7.9(m, 6H, Ar-H), 7.709-7.705(d, 2H, $^4J_{1.56}$ Hz, Ar-H), 7.41-7.37(m, 6H, Ar-H), 7.07-7.03(t, 2H, $^3J_{8.28}$ Hz, Ar-H), 4.16-4.12(t, 4H, $^3J_{6.52}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-), 1.91-1.84(quin, 4H, $^3J_{6.68}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-CH₂-), 1.52-1.47(quin, 4H, $^3J_{7.2}$ Hz, 2 $\times$ -CH₂-CH₂-CH₂-), 1.38-1.3(m, 20H, 10 $\times$ -CH₂-CH₂-CH₂-), 0.91-0.88(t, 6H, $^3J_{6.24}$ Hz, 2 $\times$ -CH₂-CH₃).

2,7-Naphthylene bis[4-(3-fluoro-4-n-decyloxybenzoyloxy)benzoate], (2.H.4)

Yield, 68%; m.p. 156.5°C; $\nu_{\max}$: 2924, 2853, 1736, 1728, 1618, 1458, 1283, 1140 cm^{-1} ; δ_{H} : 8.34-8.32(d, 4H, $^3J_{8.68}$ Hz, Ar-H), 7.99-7.9(m, 6H, Ar-H), 7.71-7.705(d, 2H, $^4J_{1.88}$ Hz, Ar-H), 7.41-7.37(m, 6H, Ar-H), 7.07-7.03(t, 2H, $^3J_{8.28}$ Hz, Ar-H), 4.16-4.12(t, 4H, $^3J_{6.56}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-), 1.91-1.84(quin, 4H, $^3J_{6.64}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-CH₂-), 1.50-1.46(quin, 4H, $^3J_{7.12}$ Hz, 2 $\times$ -CH₂-CH₂-CH₂-), 1.38-1.29(m, 24H, 12 $\times$ -CH₂-CH₂-CH₂-), 0.91-0.87(t, 6H, $^3J_{6.44}$ Hz, 2 $\times$ -CH₂-CH₃).

2,7-Naphthylene bis[4-(3-fluoro-4-n-undecyloxybenzoyloxy)benzoate], (2.H.5)

Yield, 69%; m.p. 154.5°C; $\nu_{\max}$: 2916, 2851, 1736, 1728, 1618, 1458, 1283, 1142 cm^{-1} ; δ_{H} : 8.35-8.32(d, 4H, $^3J_{8.64}$ Hz, Ar-H), 7.99-7.9(m, 6H, Ar-H), 7.709-7.705(d, 2H, $^4J_{1.8}$ Hz, Ar-H), 7.41-7.38(m, 6H, Ar-H), 7.07-7.03(t, 2H, $^3J_{8.24}$ Hz, Ar-H), 4.15-4.12(t, 4H, $^3J_{6.52}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-), 1.91-1.84(quin, 4H, $^3J_{6.64}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-CH₂-), 1.52-1.46(quin, 4H, $^3J_{7.2}$ Hz, 2 $\times$ -CH₂-CH₂-CH₂-), 1.38-1.28(m, 28H, 14 $\times$ -CH₂-CH₂-CH₂-), 0.91-0.87(t, 6H, $^3J_{6.4}$ Hz, 2 $\times$ -CH₂-CH₃).

2,7-Naphthylene bis[4-(3-fluoro-4-n-dodecyloxybenzoyloxy)benzoate], (2.H.6)

Yield, 72%; m.p. 155.0°C; $\nu_{\max}$: 2916, 2849, 1736, 1728, 1608, 1458, 1283, 1142 cm^{-1} ; δ_{H} : 8.35-8.32(d, 4H, $^3J_{8.72}$ Hz, Ar-H), 7.99-7.9 (m, 6H, Ar-H), 7.71-7.705(d, 2H, $^4J_{1.92}$ Hz, Ar-H), 7.41-7.37(m, 6H, Ar-H), 7.07-7.03(t, 2H, $^3J_{8.28}$ Hz, Ar-H), 4.15-4.12(t, 4H, $^3J_{6.52}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-), 1.91-1.84(quin, 4H, $^3J_{6.6}$ Hz, 2 $\times$ Ar-OCH₂-CH₂-CH₂-), 1.52-1.46(quin, 4H, $^3J_{7.32}$ Hz, 2 $\times$ -CH₂-CH₂-CH₂-), 1.38-1.28(m, 32H, 16 $\times$ -CH₂-CH₂-CH₂-), 0.91-0.87(t, 6H, $^3J_{6.52}$ Hz, 2 $\times$ -CH₂-CH₃).