

Chapter 8

Synthesis and mesomorphic properties of

- (i) **4-*n*-Alkoxyphenyl-4-[3-{4-(4-*n*-alkoxybenzoyloxy)benzoyloxy}benzoyloxy] benzoates**

Series- 8.1

- (ii) **4-*n*-Alkoxyphenyl-4-[3-{4-(2-fluoro-4-*n*-alkoxybenzoyloxy)benzoyloxy} benzoyloxy]benzoates**

Series- 8.11

- (iii) **4-*n*-Alkoxyphenyl-4-[3-{4-(3-fluoro-4-*n*-alkoxybenzoyloxy)benzoyloxy} benzoyloxy]benzoates**

Series- 8.III

- (iv) **4-*n*-Alkoxyphenyl-4-[3-{4-(4-*n*-dodecyloxybiphenyl-4-carbonyloxy) benzoyloxy}benzoyloxy]benzoates**

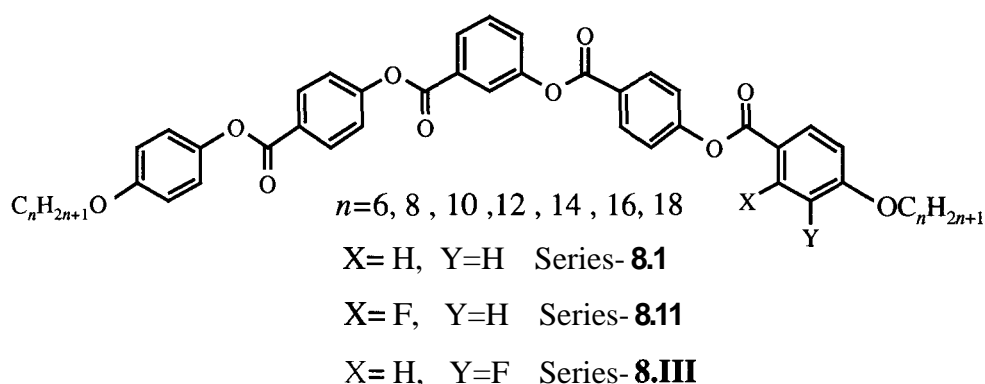
Series- 8.IV

Introduction

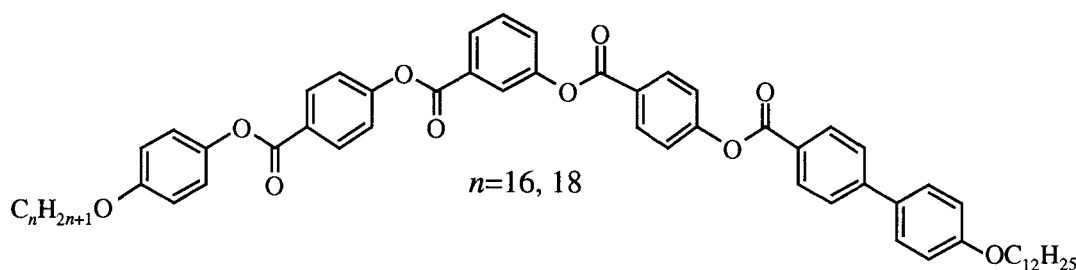
A majority of bent-core compounds reported in the literature have a 1, 3-phenylene central unit. The first unsymmetrical compound derived from 3-carboxybenzaldehyde and exhibiting a mesophase was reported by Bedel *et al.* [74]. These are Schiff's base esters. The compounds obtained from 3-hydroxybenzoic acid containing an n-alkoxy chain in one of the terminal positions and a cyano group at the other terminal position have led to the first observation of a biaxial smectic A phase in single component systems [75-77].

The influence of fluorine as a lateral substituent on the mesomorphic properties has been studied in a number of different systems. The position of a fluorine substituent is very important for obtaining the mesophases with modified properties [23, 31, 51, 53, 58, 73]. A majority of the compounds have symmetrical fluorine substitution on both arms of the bent-core molecules and are derived from resorcinol [23, 51, 53, 73]. Compounds derived from benzene 1, 3-dialdehyde containing fluorine substituent on both the arms have also been reported [30, 31].

In this chapter, the synthesis and mesomorphic properties of compounds derived from 3-hydroxybenzoic acid are described. Two homologous series of compounds have fluorine substituent on only one of the arms of the bent-core molecules. The general structures of the unsymmetrical compounds investigated are shown as structures **8.1** and **8.11**.



Structure 8.1



Structure 8.11

Synthesis

The synthetic pathways used to prepare these unsymmetrical compounds are shown in schemes **8.1** and **8.2**. 4-*n*-Alkoxyphenols were prepared by monoalkylation of quinol with appropriate *n*-alkylbromides in the presence of anhydrous potassium carbonate. 4-Benzyloxybenzoic acid, 3-benzyloxybenzoic acid [59], 2-fluoro-4-*n*-alkoxybenzoic acids and 3-fluoro-4-*n*-alkoxybenzoic acids [61, 63] were synthesized according to procedures described in the literature. 4-*n*-Dodecyloxybiphenyl-4-carboxylic acid was prepared following a procedure described in the literature [110].

Results and discussion

The transition temperatures and the associated enthalpies for the unsymmetrical compounds of series **8.I** are summarized in table **8.1**. These are unsubstituted compounds. Three different types of mesophases were observed for the homologues of this series. When a sample of compound **8.A.1** was cooled from the isotropic phase, mosaic texture was observed which is a typical feature of a two-dimensional columnar B₁ phase. A photomicrograph obtained for the mesophase of compound **8.A.1** is shown in figure **8.1**.

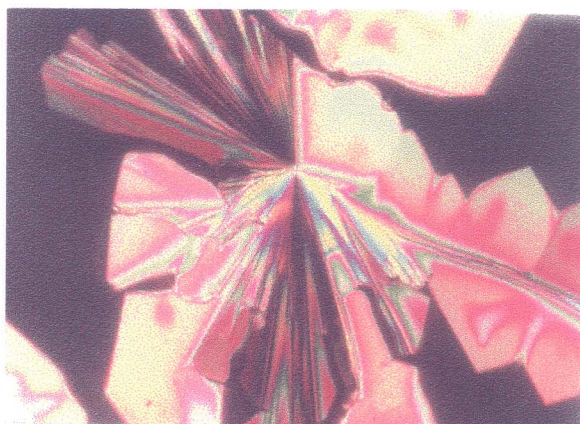
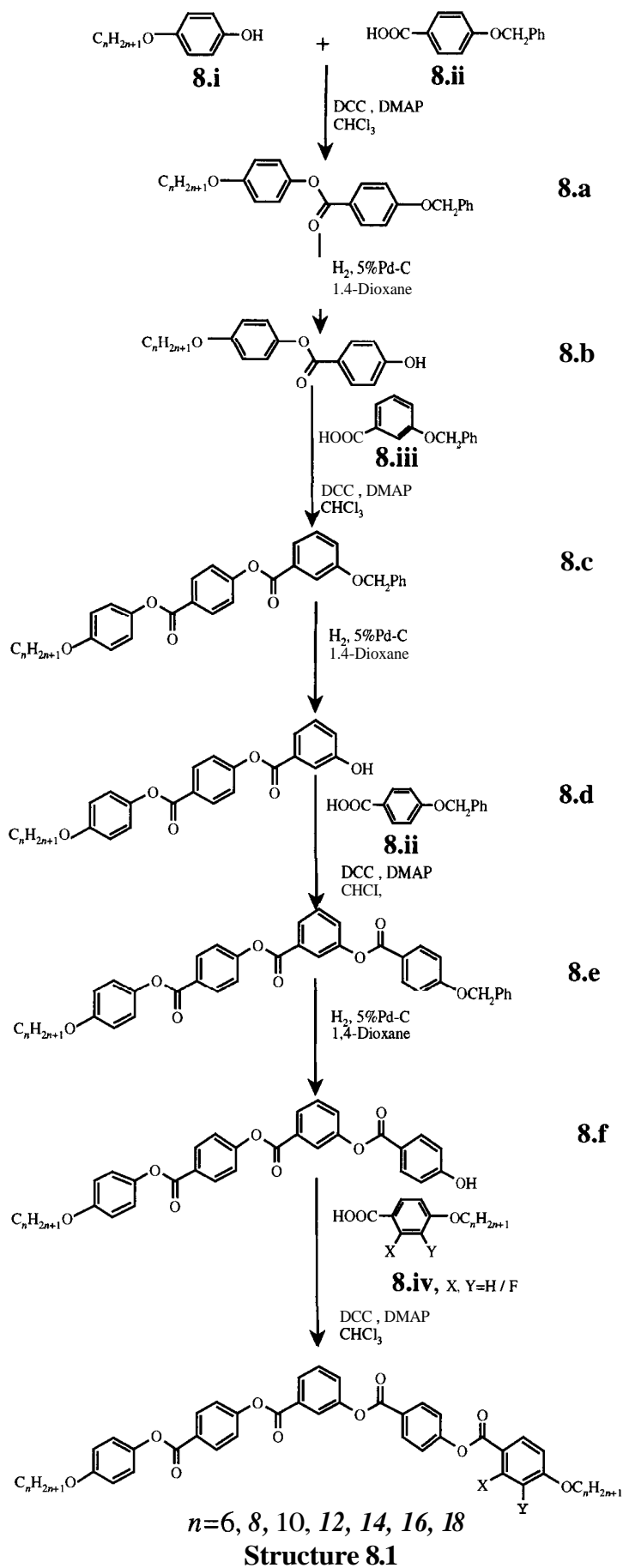
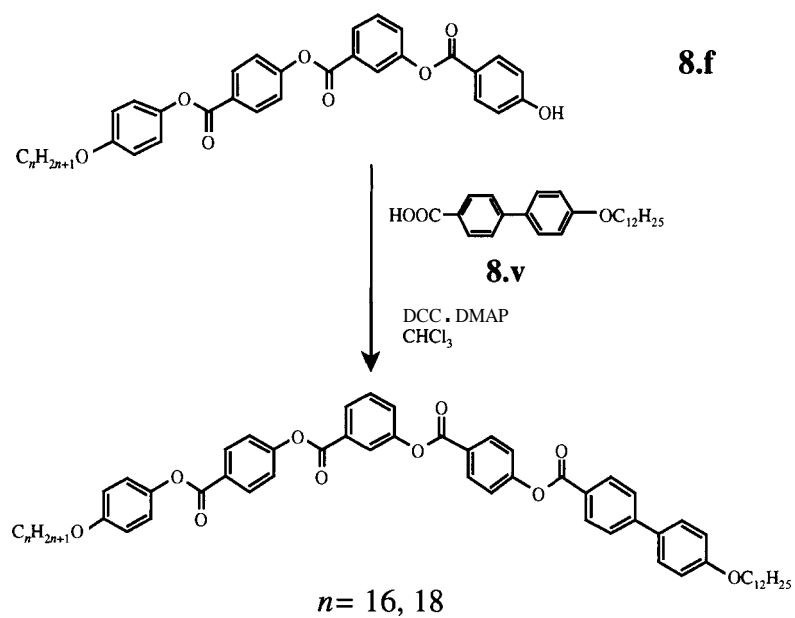


Figure 8.1: An optical photomicrograph obtained for the B₁ phase of compound **8.A.1** on cooling the isotropic phase.



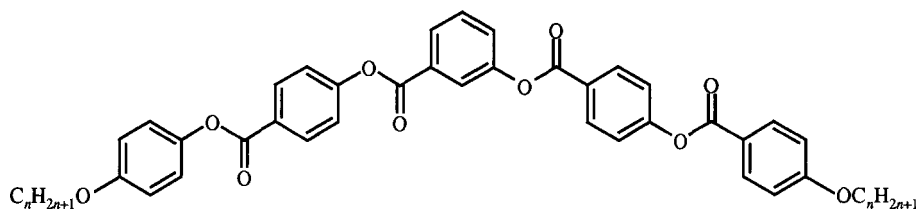
Scheme 8.1: Synthetic pathway used to prepare the bent-core compounds of series 8.I-8.III.



Structure 8.11

Scheme 8.2: Synthetic pathway used to prepare the bent-core compounds of series 8.IV.

Table 8.1: Transition temperatures ($^{\circ}\text{C}$) and the associated enthalpies (kJ mol^{-1}) for the unsymmetrical compounds of series 8.1



| Compound | n | Cr | SmCP _F | B _X | B _Y | B ₁ | I |
|--------------|-----|----------------------|-------------------|----------------|----------------|----------------|---|
| 8.A.1 | 6 | . 142.0 ^a | - | - | - | (. 134.0) | . |
| | | 88.7 | | | | 15.5 | |
| 8.A.2 | 8 | . 124.0 | - | . 136.0 | - | - | . |
| | | 39.2 | | 18.0 | | | |
| 8.A.3 | 10 | . 102.0 | - | - | . 137.0 | - | . |
| | | 42.2 | | | 19.7 | | |
| 8.A.4 | 12 | . 107.0 | - | - | . 138.0 | - | . |
| | | 49.7 | | | 20.8 | | |
| 8.A.5 | 14 | . 111.0 ^a | . 138.5 | - | - | - | . |
| | | 96.6 | 20.6 | | | | |
| 8.A.6 | 16 | . 114.0 ^a | . 138.0 | - | - | - | . |
| | | 104.2 | 20.7 | | | | |
| 8.A.7 | 18 | . 115.5 ^a | . 137.5 | - | - | - | . |
| | | 111.6 | 20.7 | | | | |

Key: Cr: crystalline phase; SmCP_F: smectic ferroelectric mesophase; SmCP_A: smectic antiferroelectric mesophase; B: unknown B phase, B_Y: unknown B phase; B₁: two-dimensional rectangular columnar phase; I: isotropic phase; a: compound has crystal-crystal transition and enthalpy denoted is the sum of all such transitions.

To confirm the mesophase structure, XRD studies were carried out. For compound 8.A.1, three reflections at $d_1=31.2$, $d_2=19.8$, $d_3=12.6$ Å were obtained in the small angle region which could be indexed to (11), (02) and (13) planes of a rectangular lattice with lattice parameters, $a=50.7$ and $b=39.6$. The X-ray angular intensity profile obtained for the mesophase of compound 8.A.1 is shown in figure 8.2.

On increasing the terminal chain length by two methylene units symmetrically compound 8.A.2 was obtained. On cooling the isotropic phase of this compound a leaves-like texture was observed. An optical photomicrograph obtained for the mesophase of compound 8.A.2 is shown in figure 8.3. To confirm the mesophase structure, XRD studies were carried out. Many reflections in the small angle region at $d_1=59.2$, $d_2=38.7$, $d_3=30.9$, $d_4=27.8$,

$d_5=21.0$ and $d_6=13.7\text{\AA}$ were seen. However, a monodomain sample could not be obtained and hence it was not possible to index these reflections. The diffuse peak in the wide-angle region confirmed the fluidity of the mesophase. The X-ray angular intensity profile obtained for the mesophase of compound **8.A.2** is shown in figure **8.4**. Although the textural feature of a B_1 mesophase was observed, the many reflections obtained in the XRD pattern point towards a variant of the B_1 mesophase. A perfectly oriented monodomain sample is necessary to unambiguously index the reflections and such a sample could not be obtained. Hence, this mesophase has been designated as a B_X phase.

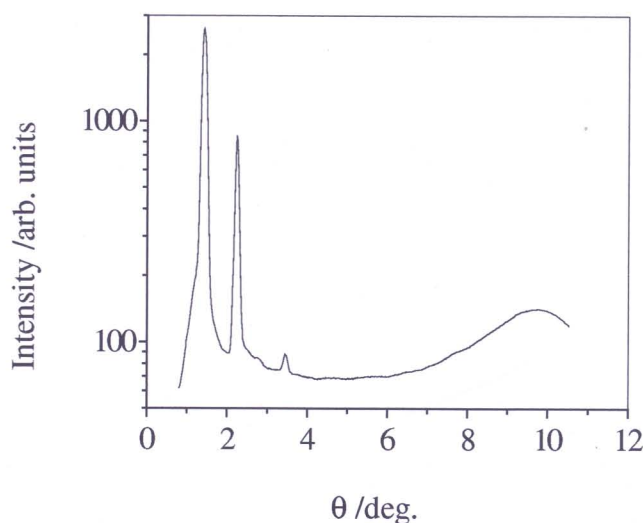


Figure 8.2: The X-ray angular intensity profile obtained for the mesophase of compound **8.A.1**.

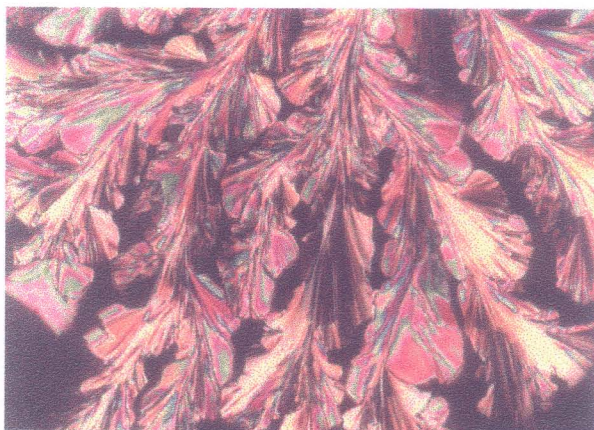


Figure 8.3: An optical photomicrograph obtained for the B_X phase of compound **8.A.2** on cooling the isotropic phase.

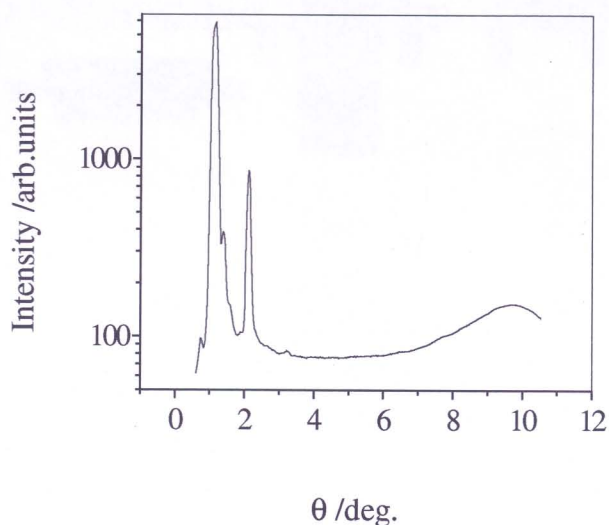


Figure 8.4: The X-ray angular intensity profile obtained for the mesophase of compound 8.A.2.

The compound with *n*-decyloxy terminal chains, **8.A.3** shows a different type of spherulitic pattern on cooling the isotropic phase. An optical texture obtained on cooling the isotropic phase of compound **8.A.3** is shown in figure 8.5.

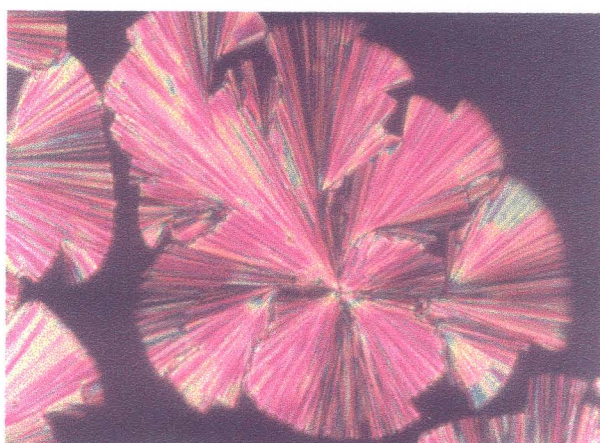


Figure 8.5: An optical photomicrograph obtained for mesophase of compound 8.A.3 on cooling the isotropic phase.

Compound **8.A.4** showed different optical textures on cooling the isotropic phase and the optical photomicrographs are shown in figure 8.6.

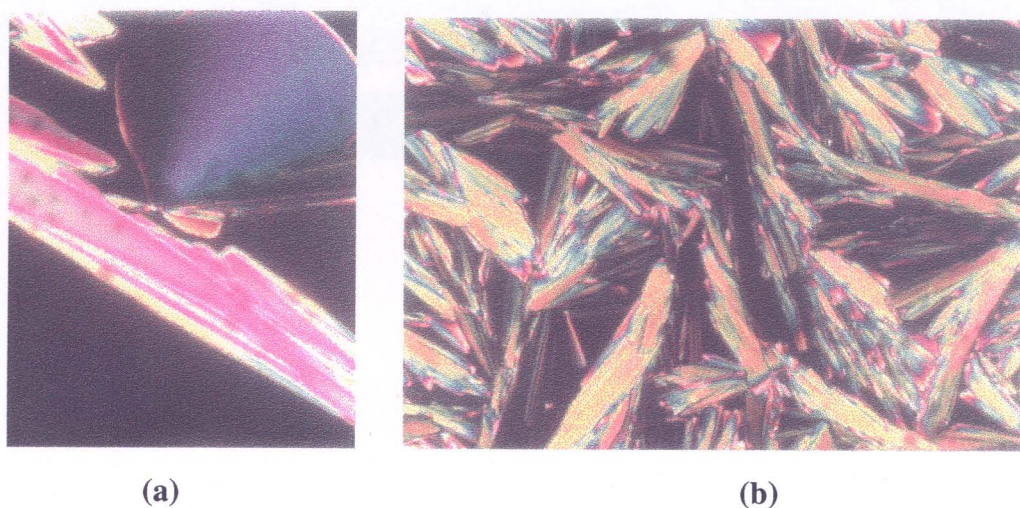


Figure 8.6: Photomicrographs obtained for the mesophase of compound 8.A.4;
(a) cooling from the isotropic phase; (b) completely formed texture in some other region.

To confirm the mesophase structure of these two compounds, XRD studies were carried out. Four reflections in the small angle region at $d_1=65.9$, $d_2=42.4$, $d_3=31.2$ and $d_4=21.6$, were obtained for compound **8.A.3**. Similar XRD pattern was observed for compound **8.A.4** also. Therefore, the mesophases of compounds **8.A.3** and **8.A.4** are the same and assigned the symbol B_Y . The X-ray angular intensity profile obtained for the mesophase of compound **8.A.3** is shown in figure **8.7**.

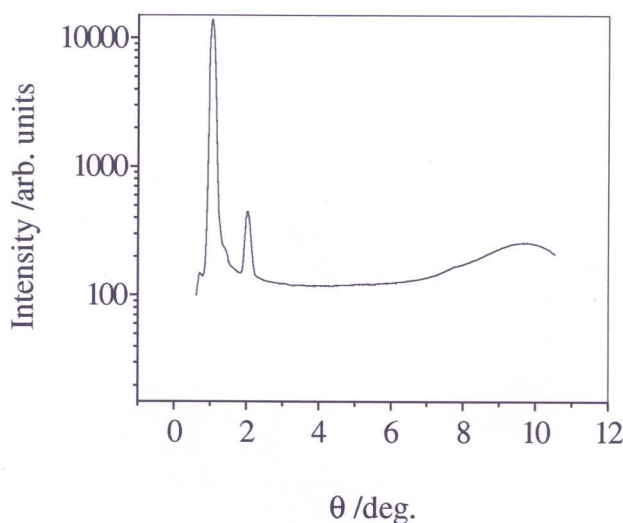


Figure 8.7: The X-ray angular intensity profile obtained for the mesophase of compound 8.A.3.

However, the mesophase of compound **8.A.4** could be partially oriented. The XRD pattern obtained for this compound clearly ruled out the possibility of this mesophase being a simple smectic. But, one can clearly see three reflections, which are due to smectic ordering of the molecules. The partially oriented XRD pattern obtained for the mesophase of compound **8.A.4** is shown in figure **8.8**.

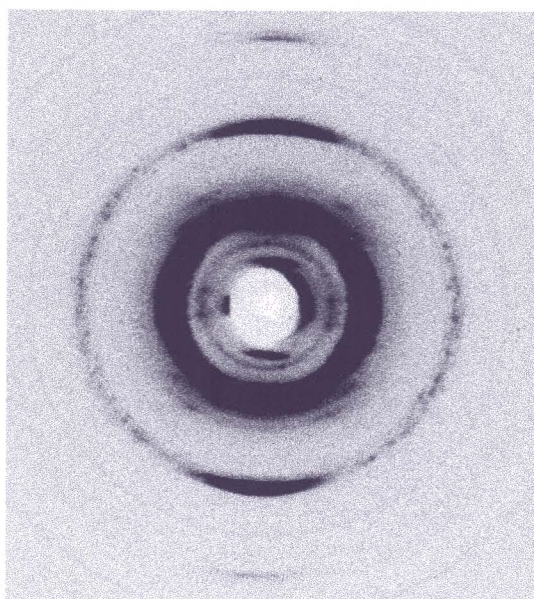
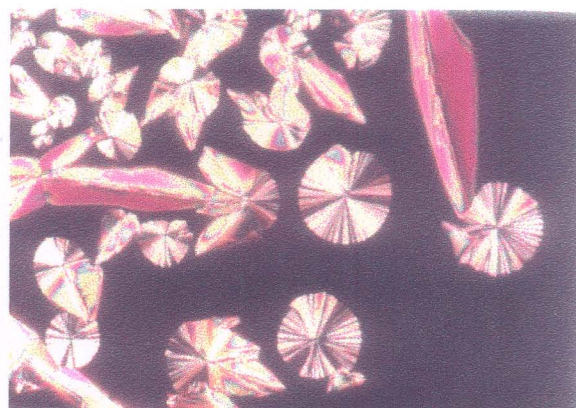


Figure 8.8: A partially oriented XRD pattern obtained for the mesophase of compound **8.A.4**.

On increasing the terminal alkyl chain length further, compounds (**8.A.5-8.A.7**) were obtained and these show similar optical textures. The textures obtained for the mesophases of compounds **8.A.5** and **8.A.7** are shown in figure **8.9 (a)** and **(b)** respectively.



(a)



(b)

Figure 8.9: Optical photomicrographs of the mesophases appearing on cooling the isotropic phase; **(a)** compound **8.A.5**; **(b)** compound **8.A.7**.

In order to examine the mesophase structures, XRD studies were carried out. The reflections obtained in the small angle region for all the three compounds (compound **8.A.5-8.A.7**) were in the ratio of 1:1/2:1/3 indicating smectic ordering of the molecules in the mesophase. The X-ray angular intensity profile obtained for the mesophase of compound **8.A.6** is shown in figure 8.10. The d-spacings obtained from XRD studies for all the compounds (**8.A.1-8.A.7**) are given in table 8.5.

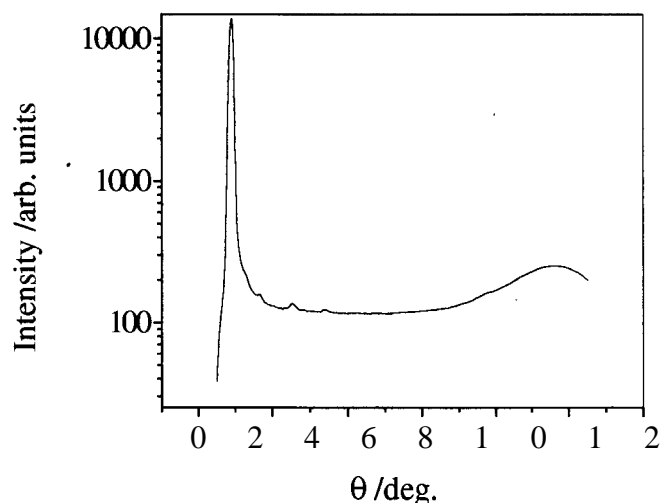


Figure 8.10: The X-ray angular intensity profile obtained for the mesophase of compound 8.A.6.

To examine the effect of electric field on the mesophases of compounds of series 8.1, triangular-wave method was employed. The electric field experiments were carried out on the mesophase of compounds **8.A.2-8.A.7**. No electric field response was obtained for compounds **8.A.2-8.A.4** atleast upto $\pm 15\text{V}\mu\text{m}^{-1}$. However, compounds **8.A.5-8.A.7** showed a response to an applied electric field.

Compound **8.A.5** was taken in a ITO coated cell treated for homogeneous alignment of the sample of thickness $10.3\mu\text{m}$. The sample was cooled very slowly from the isotropic phase. On applying a triangular-wave electric field of 480V_{pp} at 40Hz , one polarization current peak per half cycle was obtained indicating a ferroelectric ground state for the mesophase. No splitting of the peaks were observed even at low frequencies. A switching current response trace obtained for the mesophase of compound **8.A.5** is shown in figure **8.11(a)**. To confirm the ferroelectric behaviour of the mesophase, modified triangular-wave method was employed. Since there is a time delay between $-V$ and $+V$, there will be ample time for the molecules to relax into the antiferroelectric ground state.

On applying a voltage of $420V_{pp}$ at 33Hz, one polarization current peak per half cycle was obtained in the modified triangular-wave, which substantiated a ferroelectric ground state for the mesophase. A switching current response trace obtained for the mesophase of compound **8.A.5** is shown in figure 8.11 (b).

Similar behavior was observed for compounds 8.A.6 and 8.A.7 also. Switching current response traces obtained for the mesophase of compound 8.A.6 with a triangular-wave and a modified triangular-wave are given in figure 8.12 (a) and (b) respectively.

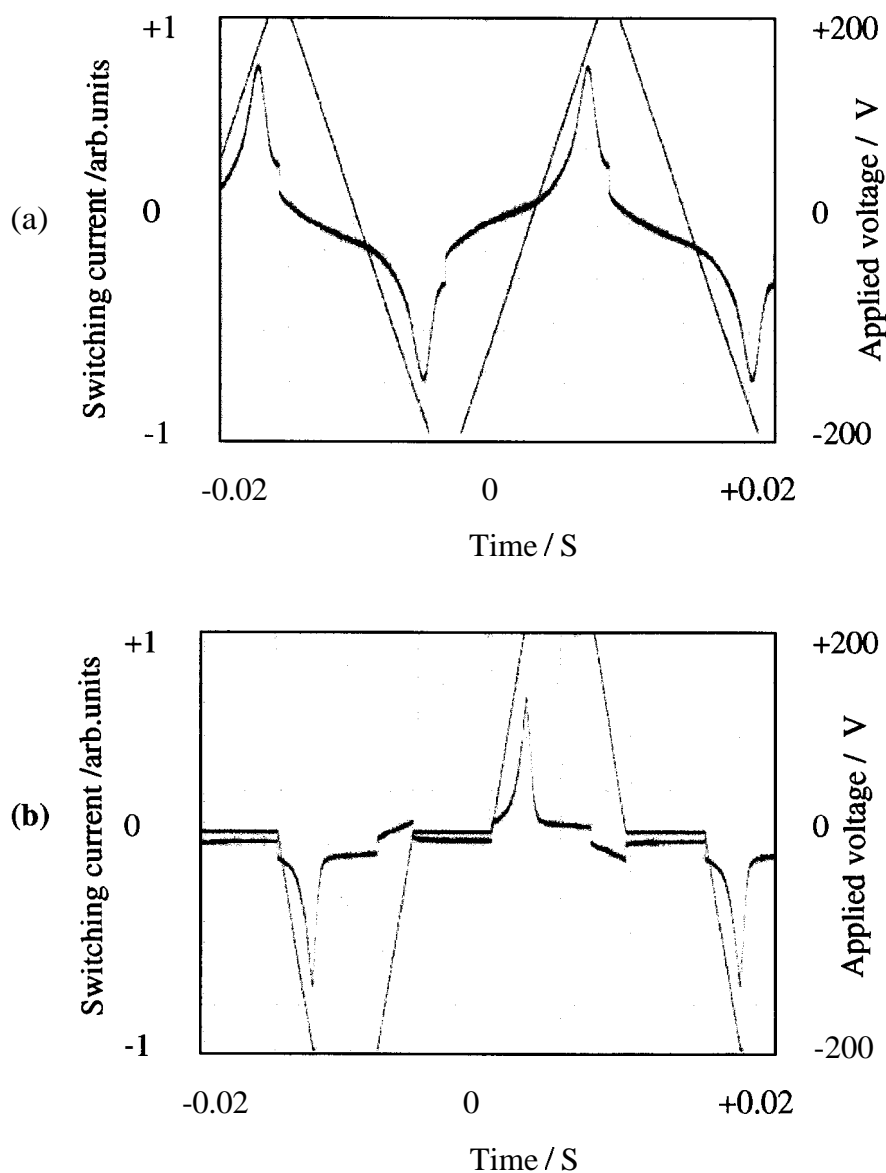


Figure 8.11: Switching current response trace obtained for the mesophase of compound **8.A.5** by applying (a) a triangular-wave electric field ($480V_{pp}$, $40Hz$); (b) a modified triangular-wave electric field ($420V_{pp}$, $33Hz$); cell thickness $10.3\mu m$; the saturated polarization value $\approx 225 nC cm^{-2}$.

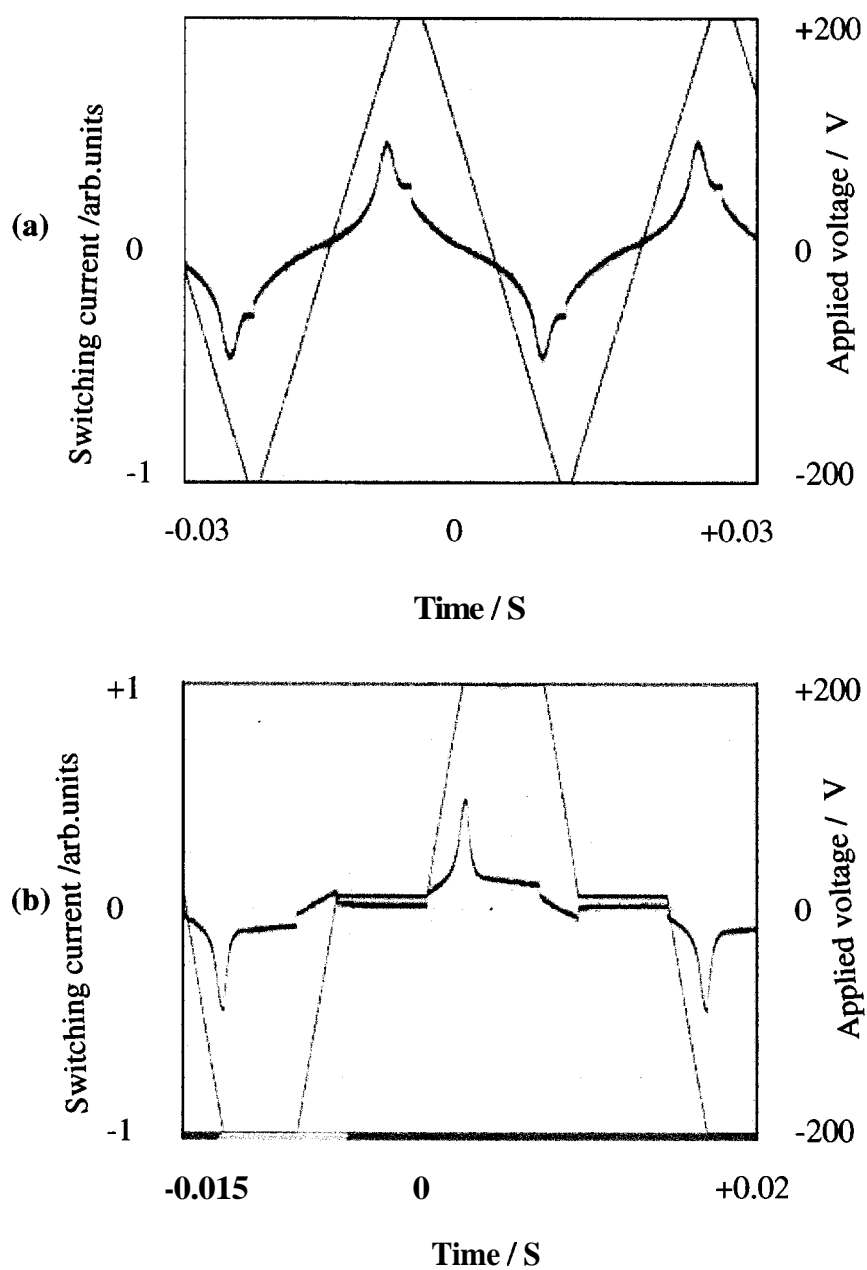
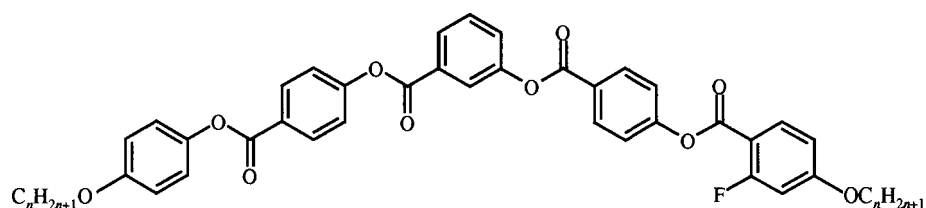


Figure 8.12: Switching current response trace obtained for the mesophase of compound 8.A.6 by applying (a) a triangular-wave electric field ($458V_{pp}$, 30Hz,); (b) a modified triangular-wave electric field ($440V_{pp}$, 33Hz,); cell thickness $10.3\mu\text{m}$; the saturated polarization value $\approx 210 \text{ nC cm}^{-2}$.

The transition temperatures and the associated enthalpies for the unsymmetrical compounds of series **8.11** are summarized in table **8.2**. These compounds were substituted with fluorine on only one of the arms of the bent-core molecules. The fluorine substituent is in *meta* position w.r.t the n-alkoxy chain. Three different types of mesophases were observed for the homologues of this series. The mesomorphic behaviour was similar to those of unsubstituted compounds except for the higher homologues. When a sample of compound **8.B.1** was cooled from the isotropic phase, a mosaic texture similar to that obtained for a B₁ phase was observed. A typical photomicrograph obtained for the mesophase of compound **8.B.1** is shown in figure **8.13**. To confirm the mesophase structure, XRD studies were carried out. Three reflections at $d_1= 28.9$, $d_2= 19.8$ and $d_3= 12.3$ in the small angle region were obtained and these could be indexed to (11), (02) and (13) planes of a rectangular lattice. The X-ray angular intensity profile obtained for the mesophase of compound **8.B.1** is shown in figure **8.14**.

Table 8.2: Transition temperatures (°C) and the associated enthalpies (kJ mol⁻¹) for the unsymmetrical compounds of series 8.11



| Compound | <i>n</i> | Cr | B ₂ | B _X | B _Y | B ₁ | I |
|--------------|----------|----------------------|----------------|----------------|----------------|----------------|---|
| 8.B.1 | 6 | . 131.0 | - | - | - | (. 114.0) | |
| | | 47.8 | | | | 12.0 | |
| 8.B.2 | 8 | . 123.0 | - | (. 118.5) | - | - | |
| | | 54.6 | | 16.0 | | | |
| 8.B.3 | 10 | . 116.0 | - | - | . 120.0 | - | |
| | | 23.6 | | | 17.3 | | |
| 8.B.4 | 12 | . 112.5 ^a | - | - | . 123.5 | - | |
| | | 61.6 | | | 18.5 | | |
| 8.B.5 | 14 | . 112.0 | . 126.0 | - | - | - | |
| | | 80.8 | 19.7 | | | | |
| 8.B.6 | 16 | . 109.0 | . 127.0 | - | - | - | |
| | | 73.4 | 19.5 | | | | |
| 8.B.7 | 18 | . 108.0 | . 128.0 | - | - | - | |
| | | 78.7 | 20.0 | | | | |



Figure 8.13: An optical photomicrograph obtained for the B_1 phase of compound 8.B.1 on cooling the isotropic phase.

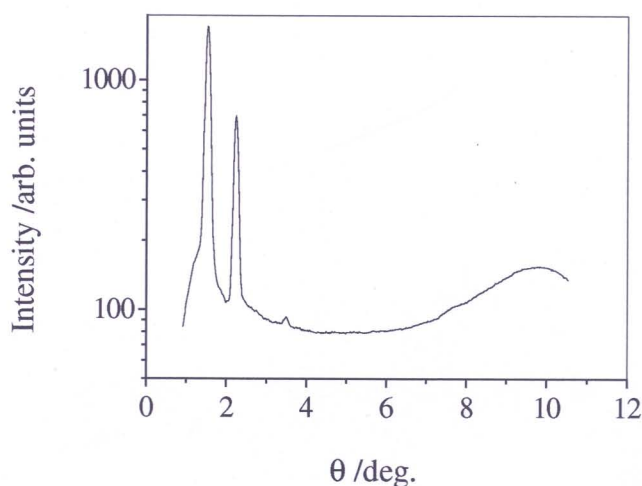


Figure 8.14: The X-ray angular intensity profile obtained for the mesophase of compound 8.B.1.

On increasing the terminal chain length by two methylene units, compound **8.B.2** was obtained. On cooling the isotropic phase of a sample of this compound a texture resembling leaves and a mosaic texture were obtained. An optical photomicrograph of a mosaic texture obtained for this mesophase of compound **8.B.2** is shown in figure **8.15**. To confirm the mesophase structure, XRD studies were carried out. Many reflections in the small angle region at $d_1=40.9$, $d_2=33.2$, $d_3=26.0$, $d_4=20.6$ and $d_5=16.7$ were obtained. However, an oriented XRD pattern could not be obtained and hence it was difficult to index the reflections.

An X-ray angular intensity profile obtained for the mesophase of compound **8.B.2** is shown in figure **8.16**.

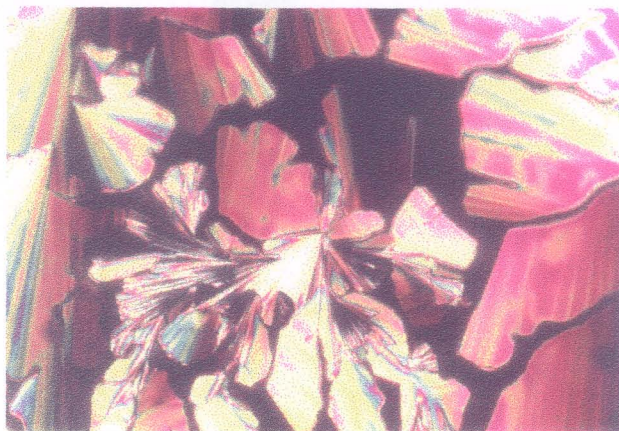


Figure 8.15: An optical photomicrograph obtained for the mesophase of compound **8.B.2** on cooling the isotropic phase.

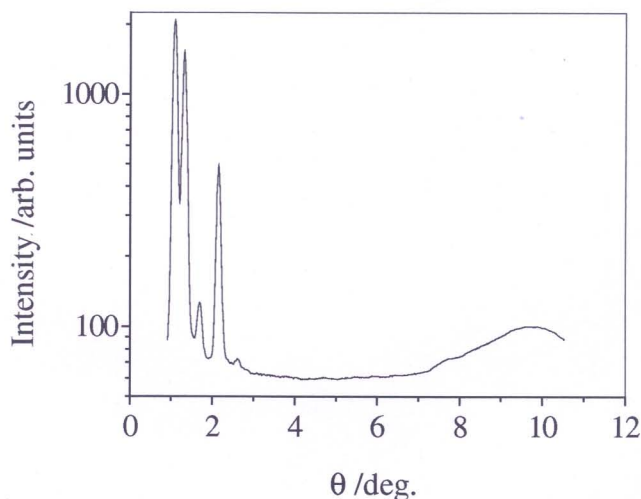


Figure 8.16: The X-ray angular intensity profile obtained for the mesophase of compound **8.B.2**.

Compounds **8.B.3** and **8.B.4** show different optical textures on cooling the respective isotropic phases. Optical textures obtained on cooling the isotropic phase for these compounds are shown in figure **8.17 (a)** and **(b)** respectively. These compounds show similar XRD patterns and are comparable to those seen for the unsubstituted analogues (compounds **8.A.3** and **8.A.4**).

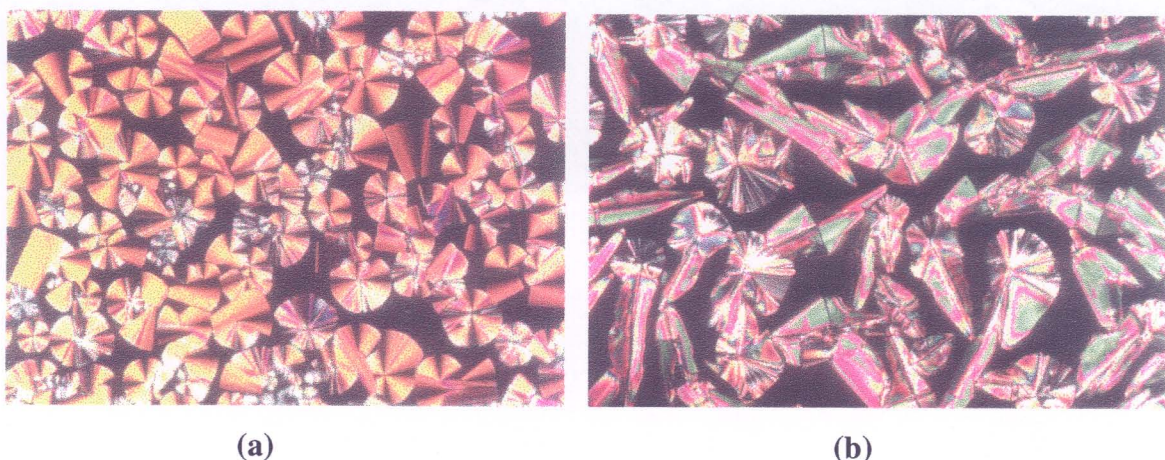


Figure 8.17: Optical photomicrographs obtained for the mesophase of; (a) compound 8.B.3; (b) compound 8.B.4; on cooling the isotropic phase.

The mesophase structure was established from XRD studies and the X-ray angular intensity profile obtained for compound 8.B.3 is shown in figure 8.18. The d-spacings obtained for the mesophases of compounds 8.B.3 and 8.B.4 are given in table 8.5.

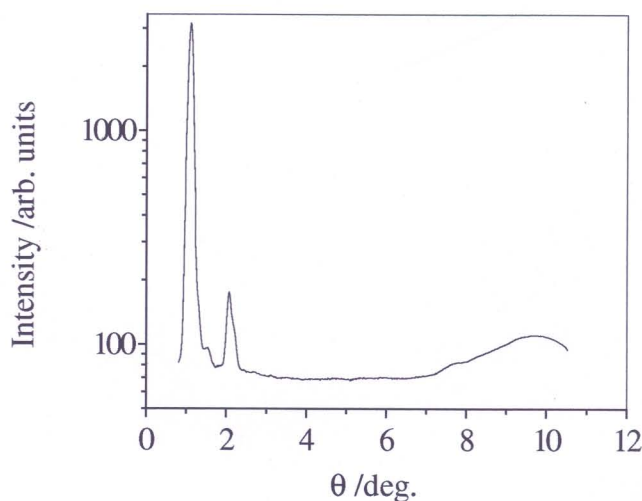


Figure 8.18: The X-ray angular intensity profile obtained for the mesophase of compound 8.B.3.

On increasing the alkyl chain length further, compounds 8.B.5-8.B.7 were obtained which show completely different optical textures. On slow cooling a sample of compound 8.B.5, banana leaf-like textures were observed and an optical photomicrograph exhibiting these features is shown in figure 8.19 (a). Compound 8.B.6 showed a fringe pattern, which is a typical feature of a B₂ phase. An optical photomicrograph obtained for the mesophase of compound 8.B.6 is shown in figure 8.19 (b). The XRD studies on these three homologues

(**8.B.5-8.B.7**) showed smectic reflections in the small angle region. The X-ray angular intensity profile obtained for the mesophase of compound **8.B.5** is shown in figure **8.20**. The d-spacings obtained for all the compounds of the homologous series **8.II** are given in table **8.5**.

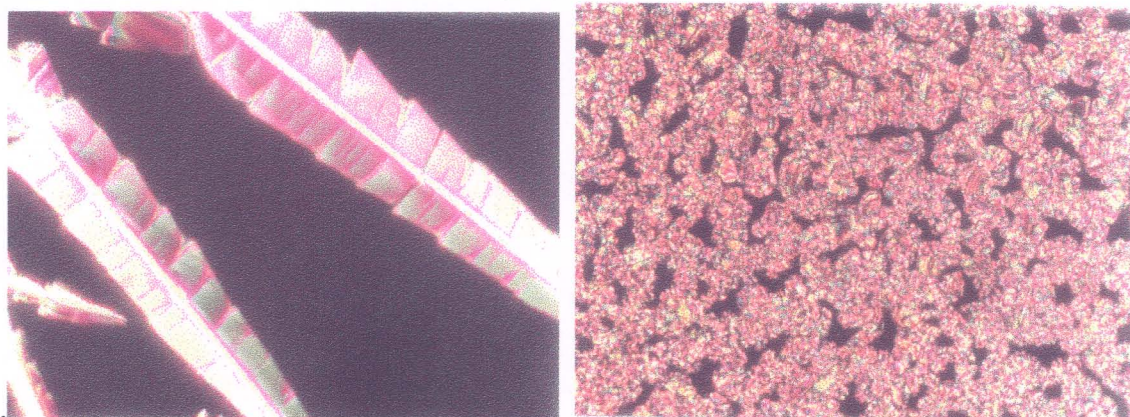


Figure 8.19: (a) An optical photomicrograph showing banana leaf-like texture obtained for the mesophase of compound **8.B.5**; (b) fringe pattern obtained for the mesophase of compound **8.B.6**.

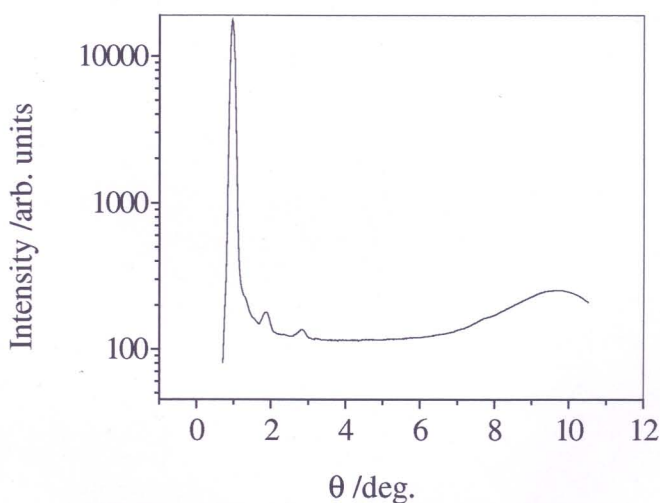


Figure 8.20: The X-ray angular intensity profile obtained for the mesophase of compound **8.B.5**.

Electro-optical studies were carried out for the mesophase of compounds **8.B.2-8.B.7**. No electric field response was observed for compounds **8.B.2-8.B.4** atleast upto $\pm 25 \text{ V}\mu\text{m}^{-1}$. However, compounds **8.B.5-8.B.7** showed a response to an applied electric field.

Compound **8.B.5** was taken in a ITO coated cell treated for homogeneous alignment of the sample of thickness 9.7p.m. The sample was cooled very slowly from the isotropic phase. On applying a triangular-wave electric field of $195V_{pp}$ at 15Hz, two polarization current peaks per half cycle were obtained indicating an antiferroelectric ground state for the mesophase. A typical switching current response trace obtained for the mesophase of compound **8.B.5** is shown in figure **8.21**.

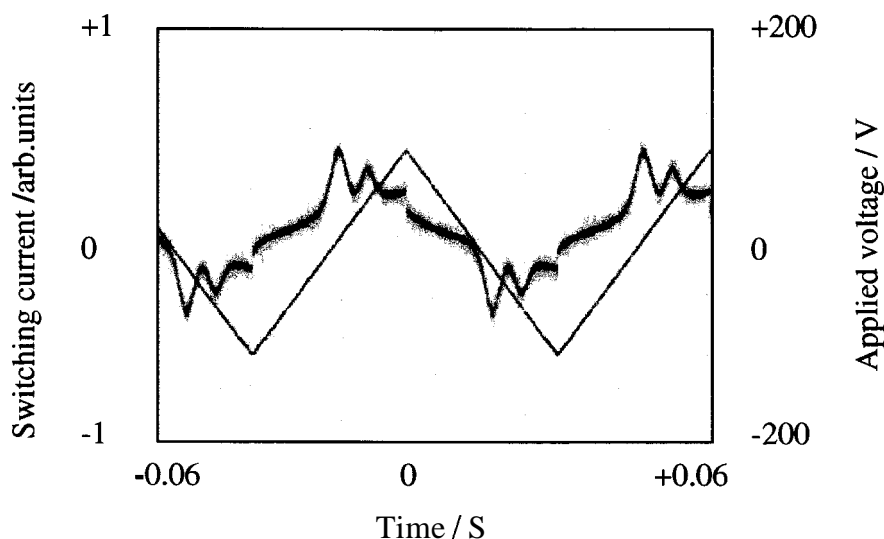


Figure 8.21: Switching current response trace obtained for the mesophase of compound 8.B.5 by applying a triangular-wave electric field ($195V_{pp}$, 15Hz); cell thickness $12.8\mu\text{m}$; the saturated polarization value $\approx 115 \text{ nC cm}^{-2}$.

Similarly, triangular-wave electric field experiments were carried out on the mesophase of compound **8.B.6** also and the behaviour was the same. A typical switching current response obtained is shown in figure **8.22**.

To confirm the tilt sense in the adjacent layers of these antiferroelectric phases, dc field experiments were carried out on the mesophase of compound **8.B.7**. On cooling the isotropic phase under a field of $5.5 \text{ V}\mu\text{m}^{-1}$, circular domains with extinction cross which make an angle w.r.t. the direction of the analyzer were observed. Interestingly by the application of the electric field the extinction brushes of domain **1** rotate in an anticlockwise direction, while those of domain **2** rotate in a clockwise direction w.r.t the crossed polarizers (figure **8.23 (a)**). On reversing the polarity of the applied field the brushes of the two domains rotate in counterclockwise directions (figure **8.23 (b)**). On switching off the electric field the dark extinction cross rotates along the analyzer direction (figure **8.23 (c)**) and is an evidence for the anticlinic antiferroelectric (SmC_AP_A) ordering of the bent-core molecules in adjacent

layers in these circular domains. These two domains are conglomerates (opposite polarity and tilt) and photomicrographs obtained under a dc electric field and without the field are shown in figure 8.23.

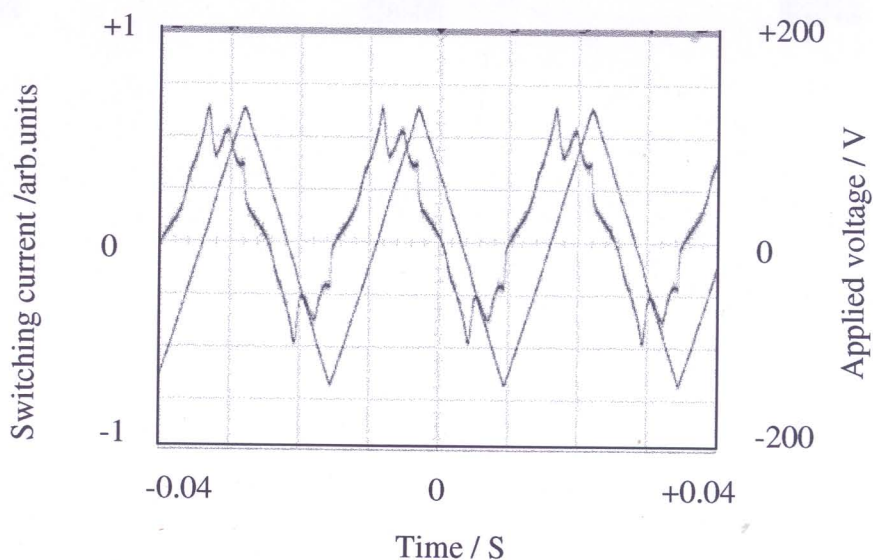


Figure 8.22: Switching current response trace obtained for the mesophase of compound 8.B.6 by applying a triangular-wave electric field ($195V_{pp}$, 15Hz); cell thickness $12.8\mu\text{m}$; the saturated polarization value $\approx 90 \text{ nC cm}^{-2}$.

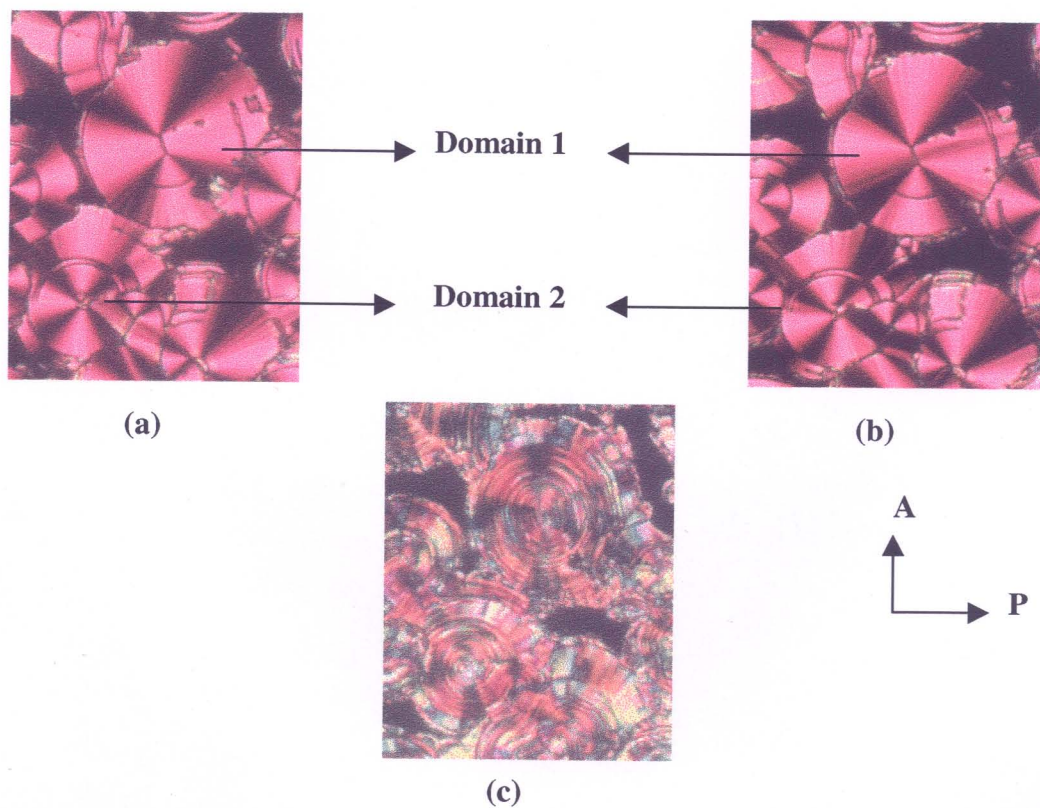
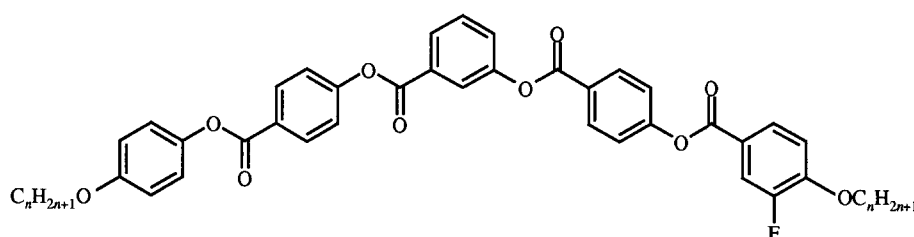


Figure 8.23: The effect of dc electric field on the mesophase of compound 8.B.6; (a) $+5.5 \text{ V}\mu\text{m}^{-1}$; (b) $-5.5 \text{ V}\mu\text{m}^{-1}$; (c) 0V .

The fluorine substituent *ortho* to the n-alkoxy chain in symmetrical systems showed interesting mesophase properties including ferroelectricity [23, 31, 51, 73]. A majority of these compounds are symmetrical and have 1, 3-phenylene central unit. On the other hand, the compounds of series **8.III** are unsymmetrical and have a fluorine substituent on only one of the arms, which is *ortho* to the n-alkoxy chain. The transition temperatures and the associated enthalpies for the unsymmetrical compounds of series **8.III** are summarized in table **8.3**. All the compounds are enantiotropic and are monomesomorphic.

Table 8.3: Transition temperatures ($^{\circ}\text{C}$) and the associated enthalpies (kJ mol^{-1}) for the compounds of series **8.111**



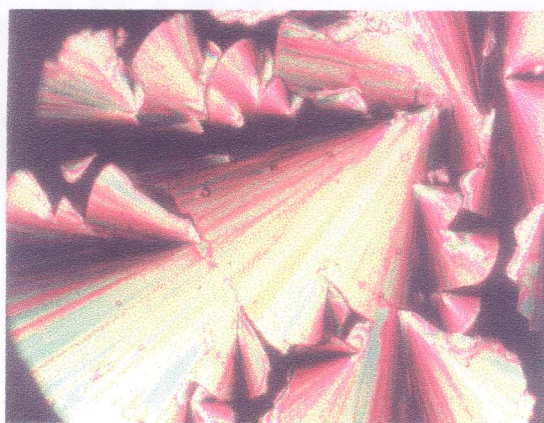
| Compound | n | Cr | Bz | I |
|--------------|----|--------------------|-------|---|
| 8.C.1 | 6 | 127.5 ^a | 145.0 | . |
| | | 56.9 | 17.4 | . |
| 8.C.2 | 8 | 125.0 | 147.5 | . |
| | | 28.1 | 19.6 | . |
| 8.C.3 | 10 | 122.0 ^a | 147.0 | . |
| | | 51.7 | 20.9 | . |
| 8.C.4 | 12 | 119.0 ^a | 147.5 | . |
| | | 55.2 | 21.8 | . |
| 8.C.5 | 14 | 118.0 ^a | 146.5 | . |
| | | 62.4 | 22.3 | . |
| 8.C.6 | 16 | 118.0 ^a | 145.0 | . |
| | | 60.6 | 22.3 | . |
| 8.C.7 | 18 | 118.0 ^a | 143.0 | . |
| | | 64.7 | 23.2 | . |

All the compounds showed textures characteristic of a columnar phase. Various textures obtained for compounds of series **8.III** are shown in figure **8.24**.

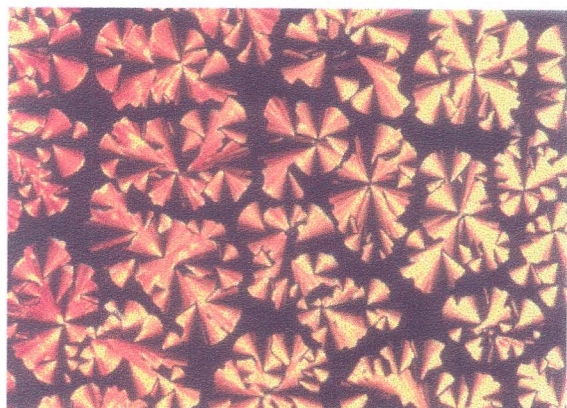
To investigate the mesophase structure, XRD studies were carried out and the d-spacings obtained for all the compounds are given in table **8.5**. The X-ray angular intensity profile obtained for one of the compounds (compound **8.C.5**) is shown in figure **8.25**. No electric field response was observed for compounds of series **8.III** atleast upto $\pm 30\text{V}\mu\text{m}^{-1}$.



(a)



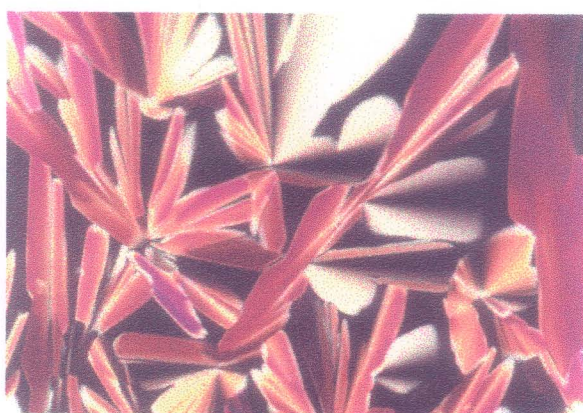
(b)



(c)



(d)



(e)

Figure 8.24: Photomicrographs of the mesophase of (a) compound 8.C.1; (b) compound 8.C.2; (c) compound 8.C.3; (d) compound 8.C.4; (e) compound 8.C.7, obtained on cooling the respective isotropic phases.

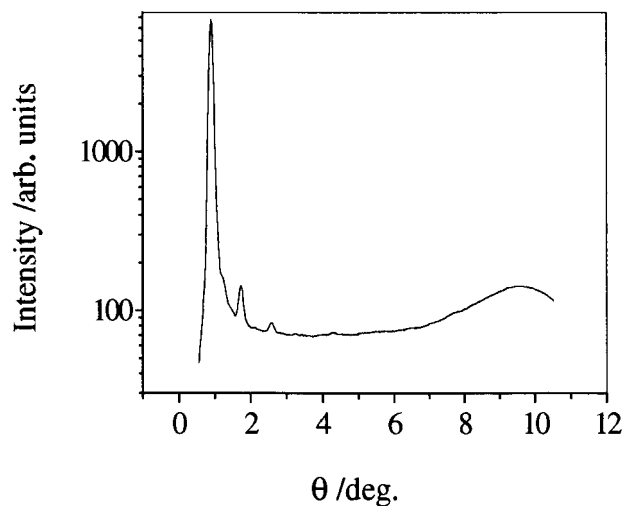


Figure **8.25**: The X-ray angular intensity profile obtained for the mesophase of compound **8.C.5**.

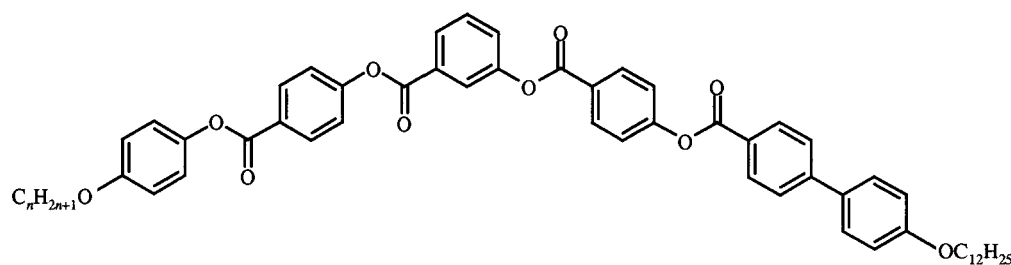
A Comparison of the mesomorphic properties of compounds of series **8.11** and **8.111** shows some interesting results. These two series of compounds are isomeric and differ by the position of the fluorine substituent. The compounds of series **8.III** are enantiotropic and show a large thermal range for the mesophase. The compounds of series **8.11** show four different types of mesophases (**B₁**, **B_X**, **B_Y** and **B₂**) while compounds of series **8.III** show only one type of mesophase (**B_Z**) which are non-layered and non-switchable phases. Thus, the substitution position of fluorine plays an important role in inducing different mesophase properties.

Two additional compounds were synthesized to see the effect of replacing a phenyl ring by a biphenyl moiety in one of the arms. The transition temperatures and the associated enthalpies for these compounds are given in table **8.4**. Three types of mesophases were observed under a polarizing microscope. On cooling a sample of compound **8.D.2** from the isotropic phase in a cell treated for homogeneous alignment of the sample, a planar texture similar to that seen for a smectic **A** phase was obtained. On lowering the temperature to 198.5°C, a change in the texture was observed and on further cooling to 179°C another transition could be seen. Photomicrographs of the three mesophases obtained for a homogeneously aligned sample of compound **8.D.2** are shown in figure **8.26** (a), (b) and (c) respectively. The transitions could also be observed when the sample was taken in a cell treated for homeotropic alignment. On cooling the isotropic phase, both homeotropic texture

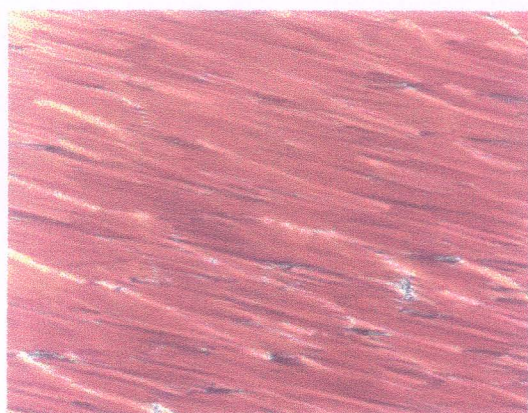
as well as smooth focal-conic texture were observed. On lowering the temperature to 199.0°C, the homeotropic texture was transformed to a schlieren texture and the focal-conic texture became a broken focal-conic texture. This is typical for SmA to SmC phase transition. On further cooling the mesophase to 179°C, the texture was transformed to an undefined texture. Photomicrographs of the textures obtained for the three mesophases of a homeotropically aligned sample of compound **8.D.2** are shown in figure **8.26 (d), (e) and (f)** respectively. However, in the DSC thermogram only two transitions could be seen. Although the transition from SmA to SmC phase could be seen under a polarizing microscope, the same could not be observed on a DSC thermogram.

To confirm the mesophase structure XRD studies were carried out. The reflections obtained in the small angle region in the SmX phase of compounds **8.D.1** and **8.D.2** are in the ratio of 1: 1/2 indicating a smectic ordering of the molecules. The d-spacings obtained for compounds **8.D.1** and **8.D.2** are given in table **8.5**. However, no change in the layer spacings was observed in the smectic C phase. No electro-optical response was detected in the SmX phase atleast upto 15V μm^{-1} .

Table 8.4: Transition temperatures (°C) and the associated enthalpies (kJ mol⁻¹) for the compounds of series 8.IV



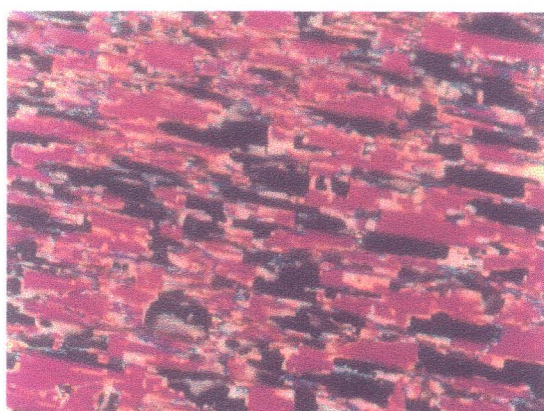
| Compound | n | Cr | SmX | SmC | SmA | I |
|--------------|----|----------------------|---------|---------|---------|---|
| 8.D.1 | 16 | . 141.0 ^a | - 183.0 | . 197.0 | . 200.5 | |
| | | 88.7 | 3.9 | - | 10.4 | |
| 8.D.2 | 18 | . 140.0 ^a | - 180.0 | . 199.0 | . 200.0 | |
| | | 98.2 | 3.1 | | 10.3 | |



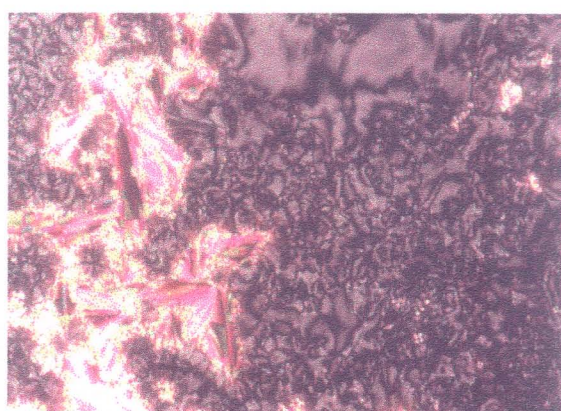
(a)



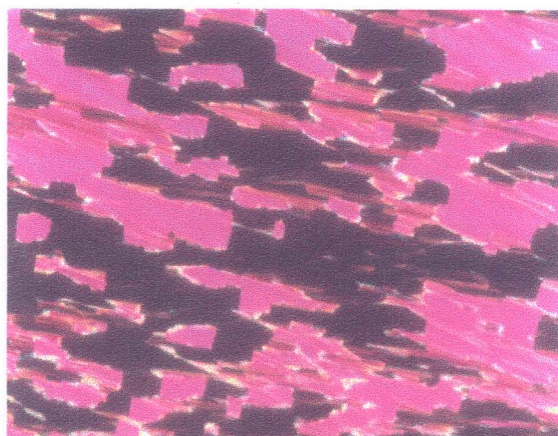
(d)



(b)



(e)



(c)



(f)

Figure 8.26: Optical photomicrographs obtained for the mesophase of compound 8.D.2 in a homogeneously aligned cell; (a) SmA phase; (b) SmC phase; (c) SmX phase; (d) , (e) and (f) show the corresponding mesophase transitions in a homeotropically aligned cell.

Table 8.5: The layer spacings (d) obtained from XRD studies for the mesophases of compounds of series 8.I-8.III and the corresponding molecular length (L) by considering the methylene units of the n-alkoxy chain in fully extended all *trans* conformation

| Compound | d-spacings | | | | | | Measured molecular length, L /Å | Phase type |
|--------------|----------------|----------------|----------------|----------------|----------------|----------------|---------------------------------------|-------------------|
| | d ₁ | d ₂ | d ₃ | d ₄ | d ₅ | d ₆ | | |
| 8.A.1 | 31.2 (11) | 19.8 (02) | 12.6 (13) | - | - | - | 46.6 | B ₁ |
| 8.A.2 | 59.2 | 38.7 | 30.9 | 27.8 | 21.0 | 13.7 | 51.7 | B _X |
| 8.A.3 | 65.9 | 42.4 | 31.2 | 21.6 | - | - | 57.0 | B _Y |
| 8.A.4 | 63.5 | 45.0 | 33.6 | 22.8 | 15.3 | - | 62.5 | B _Y |
| 8.A.5 | 49.1(01) | 24.6 (02) | - | - | - | - | 67.7 | SmCP _F |
| 8.A.6 | 50.8 (01) | 25.8 (02) | 17.1 (03) | 13.0 (04) | - | - | 72.1 | SmCP _F |
| 8.A.7 | 53.4 (01) | 26.6 (02) | 17.9 (03) | 13.4 (04) | - | - | 78.5 | SmCP _F |
| 8.B.1 | 28.9 (11) | 19.8 (02) | 12.3 (13) | - | - | - | 46.6 | B ₁ |
| 8.B.2 | 40.9 | 33.2 | 26.0 | 20.6 | 16.7 | - | 51.7 | B _X |
| 8.B.3 | 40.9 | 28.2 | 20.9 | - | - | - | 57.0 | B _Y |
| 8.B.4 | 68.3 | 43.3 | 33.5 | 21.7 | 14.8 | - | 62.5 | B _Y |
| 8.B.5 | 46.2(01) | 23.1 (02) | 15.4 (03) | - | - | - | 67.7 | B ₂ |
| 8.B.6 | 48.0 (01) | 16.0 (02) | - | - | - | - | 72.1 | B ₂ |
| 8.B.7 | 50.3 (01) | 16.8 (02) | - | - | - | - | 78.5 | B ₂ |
| 8.C.1 | 56.2 | 38.3 | 28.6 | 19.4 | - | - | 46.6 | B _Z |
| 8.C.2 | 55.6 | 41.4 | 30.7 | 20.8 | 13.7 | - | 51.7 | B _Z |
| 8.C.3 | 44.2 | 28.7 | 22.7 | - | - | - | 57.0 | B _Z |
| 8.C.4 | 62.3 | 46.8 | 34.9 | 23.4 | 15.9 | 9.5 | 62.5 | B _Z |
| 8.C.5 | 50.8 | 35.6 | 25.3 | 17.0 | - | - | 67.7 | B _Z |
| 8.C.6 | 52.3 | 35.6 | 27.4 | 18.2 | 13.5 | - | 72.1 | B _Z |
| 8.C.7 | 53.7 | 40.0 | 18.8 | 14.2 | 11.3 | - | 78.5 | B _Z |
| 8.D.1 | 54.8 (01) | 27.2 (02) | - | - | - | - | 70.2 | SmX |
| 8.D.2 | 56.7 (01) | 28.1 (02) | 18.9 (03) | - | - | - | 72.2 | SmX |

Summary

Twentythree compounds belonging to four different homologous series of compounds were synthesized and investigated for their mesomorphic properties. The optical textures and the XRD patterns of some of the compounds are different from what is reported so far for the bent-core compounds and hence these phases are designated as B_X , B_Y and B_Z . Since monodomain samples could not be obtained, the structures of these could not be deduced. Very interestingly, compounds **8.B.5-8.B.7** which have a fluorine substituent *meta* to the terminal n-alkoxy chain show conglomerates which is rather unusual. The mesophase behaviour of the compounds, which have fluorine substituent *ortho* to the n-alkoxy chain, is different from those which have a fluorine substituent in the *meta* position. This indicates that, the position of fluorine substituent has a strong influence on the mesomorphic behaviour in these bent-core compounds.

Experimental:

4-n-Alkoxyphenols, (**8.i**) were prepared by monoalkylation of quinol with appropriate n-alkylbromides in the presence of anhydrous potassium carbonate. 4-Benzyloxybenzoic acid, (**8.ii**) and 3-benzyloxybenzoic acid, (**8.iii**) were prepared according to a procedure described earlier [59]. 4-n-Alkoxybenzoic acids [63], 2-fluoro-4-n-alkoxybenzoic acids and 3-fluoro-4-n-alkoxybenzoic acids, (**8.iv**) [61-63] and 4-n-dodecyloxy-4-carboxylic acid, (**8.v**) [110] were prepared following procedures described in the literature.

4-n-Hexyloxyphenyl-4-benzyloxybenzoate, **8.a** (*n*=6)

A mixture of 4-n-hexyloxyphenol, **8.i** (*n*=6) (3.88g, 20.0mmol), 4-benzyloxybenzoic acid, **8.ii** (4.56g, 20.0mmol), catalytic amount of 4 (N, N-dimethylamino) pyridine (DMAP) and dry chloroform (50ml) were stirred for ten min. To this N, N'-dicyclohexylcarbodiimide (DCC, 2.04g, 22.0mmol) was added and stirred overnight at room temperature. The precipitated N, N'-dicyclohexylurea was filtered off and washed with chloroform (50ml). The filtrate was washed successively with 5% acetic acid (2 x 30ml), 5% ice-cold sodium hydroxide solution (2 x 30ml) and water (3 x 50ml); it was then dried over anhydrous sodium sulphate. Removal of solvent gave a product, which was chromatographed on silica gel using chloroform as eluent. Removal of solvent from the eluate afforded a white product, which was recrystallized from a mixture of chloroform and acetonitrile. Yield, 7.0g (87%); m.p. 127-128°C; ν_{\max} (nujol): 3064, 2926, 2855, 1726, 1724, 1685, 1605, 1510, 1280, 1078 cm^{-1} ; δ_{H} : 8.16-8.14 (d, 2H, $^3\text{J}_{8.76\text{Hz}}$, Ar-H), 7.46-7.35 (m, 5H, Ar-H), 7.11-7.09 (d, 2H, $^3\text{J}_{8.92\text{Hz}}$, Ar-H), 7.06-7.04 (d, 2H, $^3\text{J}_{8.76\text{Hz}}$, Ar-H), 6.93-6.91 (d, 2H, $^3\text{J}_{8.96\text{Hz}}$, Ar-H), 5.16 (s, 2H, -O-CH₂-Ar), 3.97-3.94 (t, 2H, $^3\text{J}_{6.56\text{Hz}}$, Ar-O-CH₂-), 1.82-1.75 (quin, 2H, $^3\text{J}_{7.0\text{Hz}}$, Ar-O-CH₂-CH₂-), 1.49-1.35 (m, 6H, 3 x -CH₂-), 0.94-0.91 (t, 3H, $^3\text{J}_{6.8\text{Hz}}$, -CH₃). Elemental analysis: C₂₆H₂₈O₄ requires C, 77.20; H, 6.98%; found C, 77.63; H, 6.83%.

4-n-Hexyloxyphenyl-4-hydroxybenzoate, **8.b** (*n*=6)

Compound **8.a** (*n*=6), (6.8g, 16.8mmol) was dissolved in 1, 4-dioxane (100 ml), and 5% Pd-C catalyst (1.2g) was added and stirred at 50°C in a hydrogen atmosphere until the required quantity of hydrogen was absorbed. The solution was filtered and removal of solvent gave a white product, which was recrystallized, from a mixture of 1, 4-dioxane and petroleum-ether (b.p. 80-100°C). Yield, 4.7g (89%); m.p. 159.5-160.5°C; ν_{\max} (nujol): 3393, 2926, 2855, 1703, 1609, 1514 cm^{-1} ; δ_{H} (CD₃COCD₃): 9.26 (s, 1H, Ar-OH, exchangeable with

D₂O), 8.05-8.03 (d, 2H, ³J8.68Hz, Ar-H), 7.15-7.12 (d, 2H, ³J9.04Hz, Ar-H), 7.00-6.96 (m, 4H, Ar-H), 4.03-4.0 (t, 2H, ³J6.48Hz, Ar-O-CH₂-), 1.82-1.75 (quin, 2H, ³J6.96Hz, Ar-O-CH₂-CH₂-), 1.50-1.35 (m, 6H, 3 × -CH₂-), 0.93-0.89 (t, 3H, ³J7.0Hz, -CH₃). Elemental analysis: C₁₉H₂₂O₄ requires C, 72.59; H, 7.05%; found C, 72.19; H, 6.91%.

4-*n*-Hexyloxyphenyl-4-(3-benzyloxybenzoyloxy)benzoate, 8.c (n=6)

This was synthesized following a procedure described for the preparation of compound **8.a** (n=6). Quantities: compound **8.b** (n=6), (4.6g, 14mmol), 3-benzyloxybenzoic acid, **8.iii** (3.34g, 14mmol), cat.amount of DMAP, DCC (3.17g, 15.4mmol), dry CHCl₃ (40ml). Yield, 6.0g (78%); m.p. 100-101°C; ν_{max} (nujol): 2924, 2855, 1728, 1604, 1508, 1292, 1074 cm⁻¹; δ_H: 8.29-8.27 (d, 2H, ³J8.76Hz, Ar-H), 7.85-7.83 (m, 2H, Ar-H), 7.48-7.26 (m, 9H, Ar-H), 7.14-7.11 (d, 2H, ³J9.0Hz, Ar-H), 6.95-6.93 (d, 2H, ³J9.04Hz, Ar-H), 5.16 (s, 2H, -O-CH₂-Ar), 3.99-3.96 (t, 2H, ³J6.56Hz, Ar-O-CH₂-), 1.83-1.76 (quin, 2H, ³J7.04Hz, Ar-O-CH₂-CH₂-), 1.49-1.35 (m, 6H, 3 x -CH₂-), 0.94-0.90 (t, 3H, ³J6.8Hz, -CH₃). Elemental analysis: C₃₃H₃₂O₆ requires C, 75.55; H, 6.15%; found C, 75.12; H, 6.02%.

4-*n*-Hexyloxyphenyl-4-(3-hydroxybenzoyloxy)benzoate, 8.d (n=6)

This was synthesized following a procedure described for the preparation of compound **8.b** (n=6). Quantities: compound **8.c** (n=6), (5.7g, 10.9mmol), 5% Pd-C catalyst (1.0g), 1, 4-dioxane (75ml). Yield, 3.8g (81%); m.p. 175.5-176.0°C; ν_{max} (nujol): 3445, 2924, 2855, 1728, 1720, 1607, 1506 cm⁻¹; δ_H (CD₃COCD₃): 9.0 (s, 1H, Ar-OH, exchangeable with D₂O), 8.29-8.27 (d, 2H, ³J8.72Hz, Ar-H), 7.71-7.66 (m, 2H, Ar-H), 7.53-7.51 (d, 2H, ³J8.72Hz, Ar-H), 7.46-7.42 (t, 1H, ³J7.92Hz, Ar-H), 7.23-7.21 (m, 3H, Ar-H), 7.02-7.00 (d, 2H, ³J9.0Hz, Ar-H), 4.04-4.02 (t, 2H, ³J6.48Hz, Ar-O-CH₂-), 1.83-1.76 (quin, 2H, ³J7.04Hz, Ar-O-CH₂-CH₂-), 1.50-1.35 (m, 6H, 3 x -CH₂-), 0.93-0.90 (t, 3H, ³J6.96Hz, -CH₃). Elemental analysis: C₂₆H₂₆O₆ requires C, 71.87; H, 6.03%; found C, 71.45; H, 5.98%.

4-*n*-Hexyloxyphenyl-4-[3-(4-benzyloxybenzoyloxy)benzoyloxy]benzoate, 8.e (n=6)

This was synthesized following a procedure described for the preparation of compound **8.a** (n=6). Quantities: compound **8.d** (n=6), (2.25g, 5.18mmol), 4-benzyloxybenzoic acid, **8.ii** (1.18g, 5.18mmol), cat.amount of DMAP, DCC (1.18g, 5.7mmol), dry CHCl₃ (35ml). Yield, 2.6g (78%); m.p. 128.0-128.5°C; ν_{max} (nujol): 2924, 2855, 1746, 1720, 1605, 1508, 1250, 1074 cm⁻¹; δ_H: 8.29-8.27 (d, 2H, ³J8.6Hz, Ar-H), 8.19-8.17 (d, 2H,

³J8.76Hz, Ar-H), 8.14-8.12 (d, 1H, ³J7.64Hz, Ar-H), 8.06 (s, 1H, Ar-H), 7.62-7.58 (t, 1H, ³J7.92Hz, Ar-H), 7.54-7.52 (m, 1H, Ar-H), 7.47-7.37 (m, 7H, Ar-H), 7.14-7.12 (d, 2H, ³J8.92Hz, Ar-H), 7.10-7.08 (d, 2H, ³J8.8Hz, Ar-H), 6.95-6.92 (d, 2H, ³J8.96Hz, Ar-H), 5.18 (s, 2H, -O-CH₂-Ar), 3.99-3.96 (t, 2H, ³J 6.52Hz, Ar-O-CH₂-), 1.83-1.76 (quin, 2H, ³J6.96Hz, Ar-O-CH₂-CH₂-), 1.48-1.30 (m, 6H, 3 × -CH₂-), 0.94-0.91 (t, 3H, ³J6.8Hz, -CH₃). Elemental analysis: C₄₀H₃₆O₈ requires C, 74.52; H, 5.63%; found C, 74.13; H, 5.56%.

4-*n*-Hexyloxyphenyl-4-[3-(4-hydroxybenzoyloxy)benzoyloxy]benzoate, 8.f (*n*=6)

This was synthesized following a procedure described for the preparation of compound 8.b (*n*=8). Quantities: compound 8.e (*n*=6), (2.5g, 3.88mmol), 5% Pd-C catalyst (0.5g), 1, 4-dioxane (40ml). Yield, 1.7g (79%); m.p. 174.0-175.0°C; ν_{\max} (nujol): 3356, 3277, 2924, 2855, 1732, 1696, 1510 cm⁻¹; δ_{H} (CD₃COCD₃): 9.39 (s, 1H, Ar-OH, exchangeable with D₂O), 8.30-8.28 (d, 2H, ³J8.96Hz, Ar-H), 8.15-8.09 (m, 4H, Ar-H), 7.75-7.71 (t, 1H, ³J8.04Hz, Ar-H), 7.68-7.66 (m, 1H, Ar-H), 7.59-7.56 (d, 2H, ³J8.78Hz, Ar-H), 7.23-7.21 (d, 2H, ³J9.04Hz, Ar-H), 7.04-7.02 (m, 4H, Ar-H), 4.04-4.01 (t, 2H, ³J6.56Hz, Ar-O-CH₂-), 1.83-1.76 (quin, 2H, ³J7.04Hz, Ar-O-CH₂-CH₂-), 1.50-1.32 (m, 6H, 3 x -CH₂-), 0.93-0.90 (t, 3H, ³J6.88Hz, -CH₃). Elemental analysis: C₃₃H₃₀O₈ requires C, 71.47; H, 5.45%; found C, 71.20; H, 5.45%.

The physical constants for cognate preparations have already been given in Chapter 5.

4-*n*-Hexyloxyphenyl-4-[3-{4-(4-*n*-hexyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 8.A.1

This was synthesized following a procedure described for the preparation of compound 8.a (*n*=6). Quantities: compound 8.f, (*n*=6), (0.20g, 0.36mmol), 4-*n*-hexyloxybenzoic acid 8.v X=Y=H, (0.080 0.36mmol), cat.amount of DMAP, DCC (0.082g, 0.4mmol), dry CHCl₃ (10ml). Yield, 75%; m.p. 142.0°C; ν_{\max} : 3072, 2922, 2857, 1736, 1730, 1612, 1508, 1259, 1161, 1069 cm⁻¹; δ_{H} : 8.31-8.27 (m, 4H, Ar-H), 8.17-8.14 (m, 3H, Ar-H), 8.094-8.085 (t, 1H, ⁴J 1.92Hz, Ar-H), 7.64-7.60 (t, 1H, ³J 7.88Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.13-7.11 (d, 2H, ³J8.96Hz, Ar-H), 7.0-6.98 (d, 2H, ³J8.88Hz, Ar-H), 6.95-6.92 (d, 2H, ³J9.0Hz, Ar-H), 4.08-4.05 (t, 2H, ³J6.52Hz, Ar-O-CH₂-), 3.98-3.95 (t, 2H, ³J6.52Hz, Ar-O-CH₂-), 1.87-1.76 (m, 4H, 2 x Ar-O-CH₂-CH₂-), 1.51-1.26 (m, 12H, 6 x -

CH₂-), 0.94-0.91 (m, 6H, 2 × -CH₃). Elemental analysis: C₄₆H₄₆O₁₀ requires C, 72.81; H, 6.11%; found C, 72.83; H, 6.18%.

4-*n*-Octyloxyphenyl-4-[3-{4-(4-*n*-octyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 8.A.2

Yield, 73%; m.p. 124.0°C; ν_{\max} : 3069, 2928, 2855, 1736, 1728, 1605, 1510, 1259, 1161, 1078 cm⁻¹; δ_{H} : 8.31-8.27 (m, 4H, Ar-H), 8.17-8.14 (m, 3H, Ar-H), 8.096-8.086 (t, 1H, ⁴J1.92Hz, Ar-H), 7.64-7.60 (t, 1H, ³J 8.0Hz, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.13-7.11 (dd, 2H, ³J8.96Hz, ⁴J2.2Hz, Ar-H), 7.0-6.98 (dd, 2H, ³J8.88Hz, ⁴J1.84Hz, Ar-H), 6.95-6.92 (dd, 2H, ³J9.04Hz, ⁴J2.2Hz, Ar-H), 4.08-4.05 (t, 2H, ³J6.56Hz, Ar-O-CH₂-), 3.98-3.95 (t, 2H, ³J6.56Hz, Ar-O-CH₂-), 1.87-1.76(m, 4H, 2 × Ar-O-CH₂-CH₂-), 1.51-1.26 (m, 20H, 10 × -CH₂-) 0.91-0.88 (m, 6H, 2 × -CH₃). Elemental analysis: C₅₀H₅₄O₁₀ requires C, 73.69; H, 6.68%; found C, 73.37; H, 6.53%.

4-*n*-Decyloxyphenyl-4-[3-{4-(4-*n*-decyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 8.A.3

Yield, 71%; m.p. 102.0°C; ν_{\max} : 3069, 2928, 2855, 1736, 1728, 1605, 1510, 1259, 1161, 1078 cm⁻¹; δ_{H} : 8.31-8.27 (m, 4H, Ar-H), 8.17-8.14 (m, 3H, Ar-H), 8.095-8.086 (t, 1H, ⁴J1.96Hz, Ar-H), 7.64-7.60 (t, 1H, ³J 8.04Hz, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.13-7.11 (dd, 2H, ³J9.0Hz, ⁴J2.16Hz, Ar-H), 7.0-6.98 (dd, 2H, ³J8.92Hz, ⁴J1.88Hz, Ar-H), 6.95-6.92 (dd, 2H, ³J9.04Hz, ⁴J2.16Hz, Ar-H), 4.08-4.05 (t, 2H, ³J6.52Hz, Ar-O-CH₂-), 3.98-3.95 (t, 2H, ³J6.56Hz, Ar-O-CH₂-), 1.87-1.76(m, 4H, 2 × Ar-O-CH₂-CH₂-), 1.51-1.26 (m, 28H, 14 × -CH₂-), 0.91-0.87 (m, 6H, 2 × -CH₃). Elemental analysis: C₅₄H₆₂O₁₀ requires C, 74.46; H, 7.17%; found C, 74.79; H, 7.20%.

4-*n*-Dodecyloxyphenyl-4-[3-{4-(4-*n*-dodecyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 8.A.4

Yield, 75%; m.p. 107.0°C; ν_{\max} : 3069, 2920, 2851, 1736, 1728, 1605, 1510, 1259, 1161, 1078 cm⁻¹; δ_{H} : 8.31-8.27 (m, 4H, Ar-H), 8.17-8.15 (m, 3H, Ar-H), 8.095-8.086 (t, 1H, ⁴J 1.92Hz, Ar-H), 7.64-7.60 (t, 1H, ³J 8.0Hz, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.14-7.12 (dd, 2H, ³J8.96Hz, ⁴J2.12Hz, Ar-H), 7.0-6.98 (dd, 2H, ³J8.84Hz, ⁴J1.88Hz, Ar-H), 6.95-6.92 (dd, 2H, ³J8.96Hz, ⁴J2.08Hz, Ar-H), 4.08-4.05 (t, 2H, ³J6.52Hz, Ar-O-CH₂-), 3.98-3.95 (t, 2H, ³J6.52Hz, Ar-O-CH₂-), 1.87-1.76(m, 4H, 2 × Ar-O-CH₂-CH₂-),

1.52-1.28 (m, 36H, 18 x -CH₂-), 0.91-0.87 (m, 6H, 2 x -CH₃). Elemental analysis: C₅₈H₇₀O₁₀ requires C, 75.13; H, 7.61%; found C, 75.29; H, 7.35%.

4-*n*-Tetradecyloxyphenyl-4-[3-{4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy}benzoyloxy] benzoate, 8.A.5

Yield, 71%; m.p. 111.0°C; ν_{\max} : 3082, 2916, 2849, 1748, 1740, 1605, 1512, 1259, 1161, 1076 cm⁻¹; δ_{H} : 8.32-8.27 (m, 4H, Ar-H), 8.17-8.14 (m, 3H, Ar-H), 8.092-8.083 (t, 1H, ⁴J2.0Hz, Ar-H), 7.64-7.60 (t, 1H, ³J 8.0Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.13-7.11 (dd, 2H, ³J9.04Hz, ⁴J2.2Hz, Ar-H), 7.0-6.98 (dd, 2H, ³J8.96Hz, ⁴J1.96Hz, Ar-H), 6.95-6.92 (dd, 2H, ³J9.08Hz, ⁴J2.24Hz, Ar-H), 4.08-4.05 (t, 2H, ³J6.56Hz, Ar-O-CH₂-), 3.98-3.95 (t, 2H, ³J6.56Hz, Ar-O-CH₂-), 1.86-1.75(m, 4H, 2 x Ar-O-CH₂-CH₂-), 1.49-1.26 (m, 44H, 22 x -CH₂-), 0.90-0.87 (m, 6H, 2 x -CH₃). Elemental analysis: C₆₂H₇₈O₁₀ requires C, 75.73; H, 8.0%; found C, 75.30; H, 7.93%.

4-*n*-Hexadecyloxyphenyl-4-[3-{4-(4-*n*-hexadecyloxybenzoyloxy)benzoyloxy}benzoyloxy] benzoate, 8.A.6

Yield, 76 %; m.p. 114.0°C; ν_{\max} : 3082, 2916, 2849, 1747, 1740, 1605, 1512, 1259, 1163, 1074 cm⁻¹; δ_{H} : 8.32-8.27 (m, 4H, Ar-H), 8.17-8.14 (m, 3H, Ar-H), 8.092-8.083 (t, 1H, ⁴J1.88Hz, Ar-H), 7.65-7.61 (t, 1H, ³J 8.0Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.13-7.11 (dd, 2H, ³J9.04Hz, ⁴J2.2Hz, Ar-H), 7.0-6.98 (dd, 2H, ³J8.96Hz, ⁴J1.92Hz, Ar-H), 6.94-6.92 (dd, 2H, ³J9.08Hz, ⁴J2.2Hz, Ar-H), 4.08-4.05 (t, 2H, ³J6.56Hz, Ar-O-CH₂-), 3.98-3.95 (t, 2H, ³J6.56Hz, Ar-O-CH₂-), 1.86-1.75(m, 4H, 2 x Ar-O-CH₂-CH₂-), 1.49-1.26 (m, 52H, 26 x -CH₂-), 0.89-0.85 (m, 6H, 2 x -CH₃). Elemental analysis: C₆₆H₈₆O₁₀ requires C, 76.27; H, 8.34%; found C, 76.11; H, 8.38%.

4-*n*-Octadecyloxyphenyl-4-[3-{4-(4-*n*-octadecyloxybenzoyloxy)benzoyloxy}benzoyloxy] benzoate, 8.A.7

Yield, 74%; m.p. 115.5°C; ν_{\max} : 3082, 2916, 2849, 1747, 1740, 1605, 1510, 1258, 1163, 1076 cm⁻¹; δ_{H} : 8.32-8.27 (m, 4H, Ar-H), 8.17-8.14 (m, 3H, Ar-H), 8.092-8.083 (t, 1H, ⁴J1.88Hz, Ar-H), 7.65-7.61 (t, 1H, ³J 8.0Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.13-7.11 (dd, 2H, ³J8.96Hz, ⁴J2.0Hz, Ar-H), 7.0-6.98 (dd, 2H, ³J8.8Hz, ⁴J1.92Hz, Ar-H), 6.94-6.92 (dd, 2H, ³J8.96Hz, ⁴J2.12Hz, Ar-H), 4.08-4.05 (t, 2H, ³J6.52Hz, Ar-O-CH₂-), 3.98-3.95 (t, 2H, ³J6.52Hz, Ar-O-CH₂-), 1.86-1.75(m, 4H, 2 x Ar-O-CH₂-CH₂-),

1.49-1.26 (m, 60H, 30 × -CH₂-), 0.89-0.85 (m, 6H, 2 × -CH₃). Elemental analysis: C₇₀H₉₄O₁₀ requires C, 76.75; H, 8.65%; found C, 76.56; H, 8.68%.

4-*n*-Hexyloxyphenyl-4-[3-{4-(2-fluoro-4-*n*-hexyloxybenzoyloxy)benzoyloxy}benzoyloxy] benzoate, 8.B.1

Yield, 73%; m.p. 131.0°C; ν_{\max} : 3080, 2934, 2860, 1738, 1622, 1508, 1252, 1163, 1069 cm⁻¹; δ_{H} : 8.31-8.27 (m, 4H, Ar-H), 8.16-8.04 (m, 3H, Ar-H), 7.64-7.60 (t, 1H, ³J 8.0Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.42-7.37 (m, 4H, Ar-H), 7.13-7.11 (d, 2H, ³J8.96Hz, Ar-H), 6.95-6.92 (d, 2H, ³J9.04Hz, Ar-H), 6.81-6.78 (dd, 1H, ³J8.84Hz, ⁴J2.24Hz, Ar-H), 6.73-6.69 (dd, 1H, ³J12.76Hz, ⁴J2.28Hz, Ar-H), 4.06-4.02 (t, 2H, ³J6.52Hz, Ar-O-CH₂-), 3.98-3.95 (t, 2H, ³J6.56Hz, Ar-O-CH₂-), 1.86-1.76 (m, 4H, 2 × Ar-O-CH₂-CH₂-), 1.52-1.26 (m, 12H, 6 × -CH₂-), 0.94-0.90 (m, 6H, 2 × -CH₃).

4-*n*-Octyloxyphenyl-4-[3-{4-(2-fluoro-4-*n*-octyloxybenzoyloxy)benzoyloxy}benzoyloxy] benzoate, 8.B.2

Yield, 70%; m.p. 123.0°C; ν_{\max} : 3080, 2922, 2855, 1740, 1730, 1622, 1508, 1280, 1165, 1074 cm⁻¹; δ_{H} : 8.31-8.27 (m, 4H, Ar-H), 8.16-8.04 (m, 3H, Ar-H), 7.64-7.60 (t, 1H, ³J 8.0Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.42-7.37 (m, 4H, Ar-H), 7.13-7.11 (d, 2H, ³J8.96Hz, Ar-H), 6.94-6.92 (d, 2H, ³J9.0Hz, Ar-H), 6.81-6.78 (dd, 1H, ³J8.88Hz, ⁴J2.16Hz, Ar-H), 6.73-6.69 (dd, 1H, ³J12.72Hz, ⁴J2.2Hz, Ar-H), 4.06-4.02 (t, 2H, ³J6.52Hz, Ar-O-CH₂-), 3.98-3.95 (t, 2H, ³J6.52Hz, Ar-O-CH₂-), 1.86-1.76 (m, 4H, 2 × Ar-O-CH₂-CH₂-), 1.47-1.26 (m, 20H, 10 × -CH₂-), 0.90-0.88 (m, 6H, 2 × -CH₃).

4-*n*-Decyloxyphenyl-4-[3-{4-(2-fluoro-4-*n*-decyloxybenzoyloxy)benzoyloxy}benzoyloxy] benzoate, 8.B.3

Yield, 71%; m.p. 116.0°C; ν_{\max} : 3074, 2920, 2853, 1740, 1730, 1622, 1508, 1280, 1165, 1074 cm⁻¹; δ_{H} : 8.31-8.27 (m, 4H, Ar-H), 8.16-8.04 (m, 3H, Ar-H), 7.64-7.60 (t, 1H, ³J 8.0Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.42-7.37 (m, 4H, Ar-H), 7.13-7.11 (d, 2H, ³J9.0Hz, Ar-H), 6.94-6.92 (d, 2H, ³J9.04Hz, Ar-H), 6.81-6.78 (dd, 1H, ³J8.88Hz, ⁴J2.24Hz, Ar-H), 6.73-6.69 (dd, 1H, ³J12.72Hz, ⁴J2.28Hz, Ar-H), 4.06-4.02 (t, 2H, ³J6.52Hz, Ar-O-CH₂-), 3.98-3.95 (t, 2H, ³J6.56Hz, Ar-O-CH₂-), 1.86-1.75 (m, 4H, 2 × Ar-O-CH₂-CH₂-), 1.47-1.26 (m, 28H, 14 × -CH₂-), 0.90-0.87 (m, 6H, 2 × -CH₃).

4-n-Dodecyloxyphenyl-4-[3-(4-(2-fluoro-4-n-dodecyloxybenzoyloxy)benzoyloxy)benzoyloxy] benzoate, 8.B.4

Yield, 69%; m.p. 112.5°C; ν_{\max} : 3072, 2916, 2853, 1740, 1732, 1624, 1510, 1281, 1165, 1074 cm^{-1} ; δ_{H} : 8.31-8.28 (m, 4H, Ar-H), 8.16-8.04 (m, 3H, Ar-H), 7.64-7.60 (t, 1H, ^3J 8.0Hz, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.42-7.37 (m, 4H, Ar-H), 7.14-7.11 (d, 2H, ^3J 8.96Hz, Ar-H), 6.94-6.92 (d, 2H, ^3J 8.96Hz, Ar-H), 6.81-6.78 (dd, 1H, ^3J 8.88Hz, ^4J 2.08Hz, Ar-H), 6.73-6.69 (dd, 1H, ^3J 12.68Hz, ^4J 2.12Hz, Ar-H), 4.06-4.02 (t, 2H, ^3J 6.52Hz, Ar-O-CH₂-), 3.98-3.95 (t, 2H, ^3J 6.52Hz, Ar-O-CH₂-), 1.86-1.75 (m, 4H, 2 x Ar-O-CH₂-CH₂-), 1.47-1.27 (m, 36H, 18 x -CH₂-), 0.90-0.87 (m, 6H, 2 x -CH₃).

4-n-Tetradecyloxyphenyl-4-[3-(4-(2-fluoro-4-ntetradecyloxybenzoyloxy)benzoyloxy)benzoyloxy] benzoate, 8.B.5

Yield, 71%; m.p. 112.0°C; ν_{\max} : 3074, 2916, 2851, 1740, 1730, 1719, 1624, 1508, 1280, 1165, 1074 cm^{-1} ; δ_{H} : 8.31-8.27 (m, 4H, Ar-H), 8.16-8.04 (m, 3H, Ar-H), 7.64-7.60 (t, 1H, ^3J 7.96Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.42-7.37 (m, 4H, Ar-H), 7.13-7.11 (d, 2H, ^3J 8.84Hz, Ar-H), 6.94-6.92 (d, 2H, ^3J 8.88Hz, Ar-H), 6.81-6.78 (dd, 1H, ^3J 8.88Hz, ^4J 2.24Hz, Ar-H), 6.73-6.69 (dd, 1H, ^3J 12.68Hz, ^4J 2.2Hz, Ar-H), 4.06-4.02 (t, 2H, ^3J 6.48Hz, Ar-O-CH₂-), 3.98-3.95 (t, 2H, ^3J 6.48Hz, Ar-O-CH₂-), 1.84-1.75 (m, 4H, 2 x Ar-O-CH₂-CH₂-), 1.46-1.26 (m, 44H, 22 x -CH₂-), 0.90-0.87 (m, 6H, 2 x -CH₃).

4-n-Hexadecyloxyphenyl-4-[3-(4-(2-fluoro-4-n-hexadecyloxybenzoyloxy)benzoyloxy)benzoyloxy] benzoate, 8.B.6

Yield, 68%; m.p. 109.0°C; ν_{\max} : 3072, 2916, 2851, 1740, 1734, 1730, 1624, 1510, 1281, 1167, 1074 cm^{-1} ; δ_{H} : 8.31-8.27 (m, 4H, Ar-H), 8.16-8.04 (m, 3H, Ar-H), 7.64-7.60 (t, 1H, ^3J 8.0Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.42-7.37 (m, 4H, Ar-H), 7.13-7.11 (d, 2H, ^3J 8.96Hz, Ar-H), 6.94-6.92 (d, 2H, ^3J 9.0Hz, Ar-H), 6.81-6.78 (dd, 1H, ^3J 8.96Hz, ^4J 2.24Hz, Ar-H), 6.73-6.69 (dd, 1H, ^3J 12.72Hz, ^4J 2.24Hz, Ar-H), 4.06-4.02 (t, 2H, ^3J 6.48Hz, Ar-O-CH₂-), 3.98-3.95 (t, 2H, ^3J 6.52Hz, Ar-O-CH₂-), 1.84-1.75 (m, 4H, 2 x Ar-O-CH₂-CH₂-), 1.46-1.26 (m, 52H, 26 x -CH₂-), 0.90-0.87 (m, 6H, 2 x -CH₃).

4-*n*-Octadecyloxyphenyl-4-[3-{4-(2-fluoro-4-*n*-octadecyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 8.B.7

Yield, 70%; m.p. 108.0°C; ν_{\max} : 3072, 2916, 2851, 1740, 1738, 1730, 1624, 1510, 1277, 1167, 1074 cm^{-1} ; δ_{H} : 8.31-8.27 (m, 4H, Ar-H), 8.16-8.04 (m, 3H, Ar-H), 7.64-7.60 (t, 1H, $^3\text{J}8.0\text{Hz}$, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.42-7.37 (m, 4H, Ar-H), 7.13-7.11 (d, 2H, $^3\text{J}9.0\text{Hz}$, Ar-H), 6.94-6.92 (d, 2H, $^3\text{J}9.04\text{Hz}$, Ar-H), 6.81-6.78 (dd, 1H, $^3\text{J}8.96\text{Hz}$, $^4\text{J}2.24\text{Hz}$, Ar-H), 6.73-6.69 (dd, 1H, $^3\text{J}12.76\text{Hz}$, $^4\text{J}2.24\text{Hz}$, Ar-H), 4.06-4.02 (t, 2H, $^3\text{J}6.48\text{Hz}$, Ar-O-CH₂-), 3.98-3.95 (t, 2H, $^3\text{J}6.56\text{Hz}$, Ar-O-CH₂-), 1.84-1.75 (m, 4H, 2 x Ar-O-CH₂-CH₂-), 1.46-1.26 (m, 60H, 30 x -CH₂-), 0.90-0.86 (m, 6H, 2 x -CH₃).

4-*n*-Hexyloxyphenyl-4-[3-{4-(3-fluoro-4-*n*-hexyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 8.C.1

Yield, 67%; m.p. 127.5°C; ν_{\max} : 3078, 2930, 2855, 1738, 1616, 1510, 1252, 1163, 1080 cm^{-1} ; δ_{H} : 8.32-8.27 (m, 4H, Ar-H), 8.16-7.97 (m, 3H, Ar-H), 7.92-7.90 (dd, 1H, $^3\text{J}11.4\text{Hz}$, $^4\text{J}2.0\text{Hz}$, Ar-H), 7.64-7.60 (t, 1H, $^3\text{J}7.96\text{Hz}$, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.13-7.11 (d, 2H, $^3\text{J}8.96\text{Hz}$, Ar-H), 7.07-7.03 (t, 1H, $^3\text{J}8.32\text{Hz}$, Ar-H), 6.95-6.92 (d, 2H, $^3\text{J}9.0\text{Hz}$, Ar-H), 4.15-4.12 (t, 2H, $^3\text{J}6.56\text{Hz}$, Ar-O-CH₂-), 3.98-3.95 (t, 2H, $^3\text{J}6.52\text{Hz}$, Ar-O-CH₂-), 1.91-1.84 (quin, 2H, $^3\text{J}7.12\text{Hz}$, Ar-O-CH₂-CH₂-), 1.83-1.76 (quin, 2H, $^3\text{J}7.04\text{Hz}$, Ar-O-CH₂-CH₂-), 1.51-1.26 (m, 12H, 6 x -CH₂-), 0.95-0.91 (m, 6H, 2 x -CH₃).

4-*n*-Octyloxyphenyl-4-[3-{4-(3-fluoro-4-*n*-octyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 8.C.2

Yield, 71%; m.p. 125.0°C; ν_{\max} : 3078, 2930, 2855, 1736, 1616, 1512, 1252, 1163, 1080 cm^{-1} ; δ_{H} : 8.32-8.27 (m, 4H, Ar-H), 8.16-7.97 (m, 3H, Ar-H), 7.92-7.90 (dd, 1H, $^3\text{J}11.4\text{Hz}$, $^4\text{J}1.92\text{Hz}$, Ar-H), 7.64-7.60 (t, 1H, $^3\text{J}7.96\text{Hz}$, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.13-7.11 (d, 2H, $^3\text{J}8.96\text{Hz}$, Ar-H), 7.07-7.03 (t, 1H, $^3\text{J}8.32\text{Hz}$, Ar-H), 6.94-6.92 (d, 2H, $^3\text{J}8.96\text{Hz}$, Ar-H), 4.15-4.12 (t, 2H, $^3\text{J}6.56\text{Hz}$, Ar-O-CH₂-), 3.98-3.95 (t, 2H, $^3\text{J}6.52\text{Hz}$, Ar-O-CH₂-), 1.91-1.84 (quin, 2H, $^3\text{J}7.04\text{Hz}$, Ar-O-CH₂-CH₂-), 1.83-1.76 (quin, 2H, $^3\text{J}6.96\text{Hz}$, Ar-O-CH₂-CH₂-), 1.51-1.26 (m, 20H, 10 x -CH₂-), 0.91-0.87 (m, 6H, 2 x -CH₃).

4-*n*-Decyloxyphenyl-4-[3-{4-(3-fluoro-4-*n*-decyloxybenzoyloxy)benzoyloxy}benzoyloxy] benzoate, 8.C.3

Yield, 68%; m.p. 122.0°C; ν_{\max} : 3078, 2918, 2851, 1738, 1730, 1616, 1605, 1510, 1285, 1163, 1082 cm^{-1} ; δ_{H} : 8.32-8.27 (m, 4H, Ar-H), 8.16-7.96 (m, 3H, Ar-H), 7.93-7.89 (dd, 1H, $^3\text{J}_{11.4\text{Hz}}$, $^4\text{J}_{2.0\text{Hz}}$, Ar-H), 7.64-7.60 (t, 1H, $^3\text{J}_{7.96\text{Hz}}$, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.13-7.11 (d, 2H, $^3\text{J}_{8.96\text{Hz}}$, Ar-H), 7.07-7.03 (t, 1H, $^3\text{J}_{8.28\text{Hz}}$, Ar-H), 6.94-6.92 (d, 2H, $^3\text{J}_{9.0\text{Hz}}$, Ar-H), 4.15-4.12 (t, 2H, $^3\text{J}_{6.56\text{Hz}}$, Ar-O-CH₂-), 3.98-3.95 (t, 2H, $^3\text{J}_{6.56\text{Hz}}$, Ar-O-CH₂-), 1.91-1.84 (quin, 2H, $^3\text{J}_{7.0\text{Hz}}$, Ar-O-CH₂-CH₂-), 1.82-1.75 (quin, 2H, $^3\text{J}_{6.96\text{Hz}}$, Ar-O-CH₂-CH₂-), 1.50-1.26 (m, 28H, 14 x -CH₂-), 0.91-0.87 (m, 6H, 2 x -CH₃).

4-*n*-Dodecyloxyphenyl-4[3-{4-(3-fluoro-4-*n*-dodecyloxybenzoyloxy)benzoyloxy} benzoyloxy] benzoate, 8.C.4

Yield, 72%; m.p. 119.0°C; ν_{\max} : 3067, 2916, 2851, 1738, 1730, 1616, 1604, 1510, 1285, 1163, 1082 cm^{-1} ; δ_{H} : 8.32-8.27 (m, 4H, Ar-H), 8.16-7.96 (m, 3H, Ar-H), 7.93-7.89 (dd, 1H, $^3\text{J}_{11.4\text{Hz}}$, $^4\text{J}_{2.04\text{Hz}}$, Ar-H), 7.64-7.60 (t, 1H, $^3\text{J}_{8.04\text{Hz}}$, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.13-7.10 (d, 2H, $^3\text{J}_{9.0\text{Hz}}$, Ar-H), 7.07-7.03 (t, 1H, $^3\text{J}_{8.28\text{Hz}}$, Ar-H), 6.94-6.92 (d, 2H, $^3\text{J}_{9.04\text{Hz}}$, Ar-H), 4.15-4.12 (t, 2H, $^3\text{J}_{6.6\text{Hz}}$, Ar-O-CH₂-), 3.98-3.95 (t, 2H, $^3\text{J}_{6.56\text{Hz}}$, Ar-O-CH₂-), 1.91-1.84 (quin, 2H, $^3\text{J}_{7.04\text{Hz}}$, Ar-O-CH₂-CH₂-), 1.82-1.75 (quin, 2H, $^3\text{J}_{6.92\text{Hz}}$, Ar-O-CH₂-CH₂-), 1.51-1.26 (m, 36H, 18 x -CH₂-), 0.91-0.87 (m, 6H, 2 x -CH₃).

4-*n*-Tetradecyloxyphenyl-4-[3-{4-(4-*n*-tetradecyloxy-3-fluorobenzoyloxy)benzoyloxy} benzoyloxy] benzoate, 8.C.5

Yield, 71%; m.p. 118.0°C; ν_{\max} : 3067, 2916, 2849, 1738, 1730, 1616, 1604, 1512, 1285, 1163, 1082 cm^{-1} ; δ_{H} : 8.32-8.27 (m, 4H, Ar-H), 8.16-7.96 (m, 3H, Ar-H), 7.93-7.89 (dd, 1H, $^3\text{J}_{11.4\text{Hz}}$, $^4\text{J}_{2.04\text{Hz}}$, Ar-H), 7.64-7.60 (t, 1H, $^3\text{J}_{7.96\text{Hz}}$, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.13-7.10 (d, 2H, $^3\text{J}_{8.96\text{Hz}}$, Ar-H), 7.07-7.03 (t, 1H, $^3\text{J}_{8.32\text{Hz}}$, Ar-H), 6.94-6.92 (d, 2H, $^3\text{J}_{9.04\text{Hz}}$, Ar-H), 4.15-4.12 (t, 2H, $^3\text{J}_{6.56\text{Hz}}$, Ar-O-CH₂-), 3.98-3.95 (t, 2H, $^3\text{J}_{6.52\text{Hz}}$, Ar-O-CH₂-), 1.90-1.84 (quin, 2H, $^3\text{J}_{7.0\text{Hz}}$, Ar-O-CH₂-CH₂-), 1.82-1.75 (quin, 2H, $^3\text{J}_{6.92\text{Hz}}$, Ar-O-CH₂-CH₂-), 1.52-1.26 (m, 44H, 22 x -CH₂-), 0.91-0.87 (m, 6H, 2 x -CH₃).

4-*n*-Hexadecyloxyphenyl-4-[3-{4-(4-*n*-hexadecyloxy-3-fluorobenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 8.C.6

Yield, 72%; m.p. 118.0°C; ν_{\max} : 3069, 2916, 2849, 1738, 1734, 1730, 1616, 1604, 1512, 1285, 1163, 1072 cm^{-1} ; δ_{H} : 8.32-8.27 (m, 4H, Ar-H), 8.16-7.96 (m, 3H, Ar-H), 7.93-7.89 (dd, 1H, $^3\text{J}11.4\text{Hz}$, $^4\text{J}2.04\text{Hz}$, Ar-H), 7.64-7.60 (t, 1H, $^3\text{J}7.96\text{Hz}$, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.13-7.10 (d, 2H, $^3\text{J}9.0\text{Hz}$, Ar-H), 7.07-7.03 (t, 1H, $^3\text{J}8.32\text{Hz}$, Ar-H), 6.94-6.92 (d, 2H, $^3\text{J}9.04\text{Hz}$, Ar-H), 4.15-4.12 (t, 2H, $^3\text{J}6.56\text{Hz}$, Ar-O-CH₂-), 3.98-3.95 (t, 2H, $^3\text{J}6.52\text{Hz}$, Ar-O-CH₂-), 1.90-1.84 (quin, 2H, $^3\text{J}7.08\text{Hz}$, Ar-O-CH₂-CH₂-), 1.82-1.75 (quin, 2H, $^3\text{J}6.96\text{Hz}$, Ar-O-CH₂-CH₂-), 1.52-1.26 (m, 52H, 26 x -CH₂-), 0.91-0.87 (m, 6H, 2 x -CH₃).

4-*n*-Octadecyloxyphenyl-4-[3-{4-(4-*n*-octadecyloxy-3-fluorobenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 8.C.7

Yield, 71%; m.p. 118.0°C; ν_{\max} : 3069, 2916, 2849, 1738, 1730, 1616, 1604, 1508, 1285, 1163, 1072 cm^{-1} ; δ_{H} : 8.32-8.27 (m, 4H, Ar-H), 8.16-7.96 (m, 3H, Ar-H), 7.93-7.89 (dd, 1H, $^3\text{J}11.4\text{Hz}$, $^4\text{J}2.08\text{Hz}$, Ar-H), 7.64-7.60 (t, 1H, $^3\text{J}7.96\text{Hz}$, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.13-7.10 (d, 2H, $^3\text{J}8.92\text{Hz}$, Ar-H), 7.07-7.03 (t, 1H, $^3\text{J}8.28\text{Hz}$, Ar-H), 6.94-6.92 (d, 2H, $^3\text{J}8.96\text{Hz}$, Ar-H), 4.15-4.12 (t, 2H, $^3\text{J}6.52\text{Hz}$, Ar-O-CH₂-), 3.98-3.95 (t, 2H, $^3\text{J}6.48\text{Hz}$, Ar-O-CH₂-), 1.89-1.84 (quin, 2H, $^3\text{J}6.96\text{Hz}$, Ar-O-CH₂-CH₂-), 1.82-1.75 (quin, 2H, $^3\text{J}6.88\text{Hz}$, Ar-O-CH₂-CH₂-), 1.50-1.26 (m, 60H, 30 x -CH₂-), 0.90-0.86 (m, 6H, 2 x -CH₃).

4-*n*-Hexadecyloxyphenyl-4-[3-{4-(4-*n*-dodecyloxybiphenyl-4-carbonyloxy)benzoyloxy}benzoyloxy]benzoate, 8.D.1

Yield, 70%; m.p. 141.0°C; ν_{\max} : 3082, 2916, 2849, 1747, 1740, 1605, 1510, 1282, 1161, 1076 cm^{-1} ; δ_{H} : 8.34-8.32 (dd, 2H, $^3\text{J}8.8\text{Hz}$, $^4\text{J}2.0\text{Hz}$, Ar-H), 8.30-8.28 (dd, 2H, $^3\text{J}8.84\text{Hz}$, $^4\text{J}2.0\text{Hz}$, Ar-H), 8.27-8.24 (d, 2H, $^3\text{J}8.56\text{Hz}$, Ar-H), 8.17-8.09 (m, 2H, Ar-H), 7.73-7.71 (d, 2H, $^3\text{J}8.56\text{Hz}$, Ar-H), 7.64-7.55 (m, 4H, Ar-H), 7.44-7.41 (dd, 2H, $^3\text{J}8.8\text{Hz}$, $^4\text{J}2.0\text{Hz}$, Ar-H), 7.39-7.37 (dd, 2H, $^3\text{J}8.8\text{Hz}$, $^4\text{J}2.0\text{Hz}$, Ar-H), 7.13-7.11 (dd, 2H, $^3\text{J}9.04\text{Hz}$, $^4\text{J}2.24\text{Hz}$, Ar-H), 7.02-7.0 (dd, 2H, $^3\text{J}8.84\text{Hz}$, $^4\text{J}1.92\text{Hz}$, Ar-H), 6.95-6.92 (dd, 2H, $^3\text{J}9.08\text{Hz}$, $^4\text{J}2.24\text{Hz}$, Ar-H), 4.04-4.0 (t, 2H, $^3\text{J}6.56\text{Hz}$, Ar-O-CH₂-), 3.98-3.94 (t, 2H, $^3\text{J}6.52\text{Hz}$, Ar-O-CH₂-), 1.85-1.75 (m, 4H, 2 x Ar-O-CH₂-CH₂-), 1.50-1.26 (m, 44H, 22 x -CH₂-), 0.89-0.86 (m, 6H, 2 x -CH₃). Elemental analysis: C₆₈H₈₂O₁₀ requires C, 77.10; H, 7.80%; found C, 76.67; H, 7.83%.

4-*n*-Octdecyloxyphenyl-4-[3-{4-(4-*n*-dodecyloxybiphenyl-4-carbonyloxy)benzoyloxy} benzoyloxy] benzoate, 8.D.2

Yield, 68%; m.p. 140°C; ν 3082, 2918, 2849, 1748, 1741, 1603, 1512, 1285, 1161, 1076 cm^{-1} ; δ_{H} : 8.34-8.32 (dd, 2H, $^3\text{J}8.76\text{Hz}$, $^4\text{J}2.0\text{Hz}$, Ar-H), 8.30-8.28 (dd, 2H, $^3\text{J}8.84\text{Hz}$, $^4\text{J}2.0\text{Hz}$, Ar-H), 8.27-8.24 (d, 2H, $^3\text{J}8.52\text{Hz}$, Ar-H), 8.17-8.09 (m, 2H, Ar-H), 7.73-7.71 (d, 2H, $^3\text{J} 8.56\text{Hz}$, Ar-H), 7.63-7.54 (m, 4H, Ar-H), 7.44-7.41 (dd, 2H, $^3\text{J}8.76\text{Hz}$, $^4\text{J}2.0\text{Hz}$, Ar-H), 7.39-7.37 (dd, 2H, $^3\text{J}8.76\text{Hz}$, $^4\text{J}2.0\text{Hz}$, Ar-H), 7.13-7.11 (dd, 2H, $^3\text{J}9.04\text{Hz}$, $^4\text{J}2.24\text{Hz}$, Ar-H), 7.02-7.0 (dd, 2H, $^3\text{J}8.84\text{Hz}$, $^4\text{J}1.92\text{Hz}$, Ar-H), 6.95-6.92 (dd, 2H, $^3\text{J}9.04\text{Hz}$, $^4\text{J}2.24\text{Hz}$, Ar-H), 4.04-4.0 (t, 2H, $^3\text{J}6.6\text{Hz}$, Ar-O-CH₂-), 3.98-3.94 (t, 2H, $^3\text{J}6.56\text{Hz}$, Ar-O-CH₂-), 1.84-1.72 (m, 4H, 2 x Ar-O-CH₂-CH₂-), 1.50-1.26 (m, 48H, 24 x -CH₂-), 0.89-0.86 (m, 6H, 2 x -CH₃). Elemental analysis: C₇₀H₈₆O₁₀ requires C, 77.32; H, 7.97%; found C, 77.44; H, 8.09%.

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