

## Chapter 6

### Synthesis and mesomorphic properties of

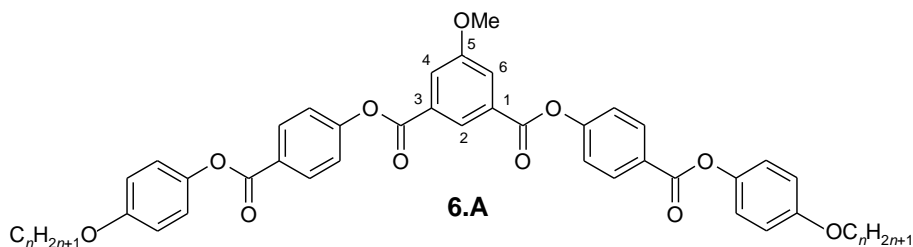
- (i) **5-Methoxy bis [4-(*n*-alkoxyphenyloxycarbonyl)phenyl]isophthalates,  
(compounds 6.A.1-6.A.8)**
- (ii) **5-Methoxy bis [4-(*n*-octadecyloxyphenyloxycarbonyl)-3-fluorophenyl]isophthalate,  
(compound 6.A.9)**
- (iii) **5-Methoxy bis [4-(*n*-octadecyloxyphenyloxycarbonyl)-2-fluorophenyl]isophthalate,  
(compound 6.A.10)**
- (iv) **5-Methoxy bis [4-(*n*-alkyloxycarbonylphenyloxycarbonyl)phenyl]isophthalates,  
(compounds 6.B.1-6.B.3)**
- (v) **5-Methoxy bis [4-(*n*-alkylcarbonyloxyphenyloxycarbonyl)phenyl]isophthalates,  
(compounds 6.C.1-6.C.5)**

## Introduction

It is well known that the mesomorphic properties of compounds exhibiting calamitic phases can be modified by using suitable lateral substituents. The influence of lateral substituents on the mesomorphic behaviour of bent-core compounds have been investigated quite extensively [1-9]. The results from these studies indicate that dipolar effects are dominant than steric factors, which is quite contrary to those observed in calamitic liquid crystals [3]. The results obtained on the investigations carried out so far on a number of bent-core compounds indicate that the nature, size and position of the substituent has a strong bearing on the type of mesophase formed. For example, in a five-ring system with a central phenyl unit, a cyano substituent in position 2 [10] gives rise to a B<sub>7</sub> mesophase, while the same substituent at position 5 [2] does not favour the formation of any mesophase. Interestingly, a 4-cyano substituent gives rise to the formation of both B and calamitic mesophases [11]. It has also been shown from a number of studies on five-ring BC compounds that groups like cyano, methyl or methoxy at the apex position (position 5) prevent the formation of any mesophase [2]. However, there are a couple of examples of a five-ring BC compound containing a substituent at position 5 of the central phenyl ring and exhibiting a switchable phase. They are derived from methyl 3,5-dihydroxybenzoate [12], 5-fluororesorcinol [13], 5-methylresorcinol [14] and 5-vinylresorcinol [15].

Nguyen *et al.* [16] have reported several five-ring bent-core compounds derived from isophthalic acid and containing lateral substituents at position 2 and 6 (positions shown in structure **6.1**) of the central ring and exhibiting interesting mesophases. However, so far there is no report of a five-ring bent-core compound derived from 5-substituted isophthalic acid and exhibiting a mesophase.

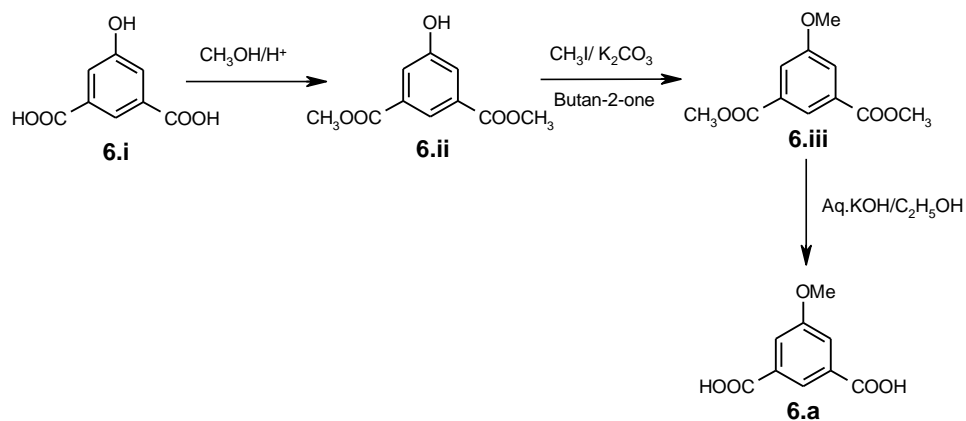
In this chapter, the first observation of an electro-optically switchable phase in five-ring BC compounds containing a bulky substituent at position 5 is described. These are derived from 5-methoxyisophthalic acid and have the general structure **6.1**.



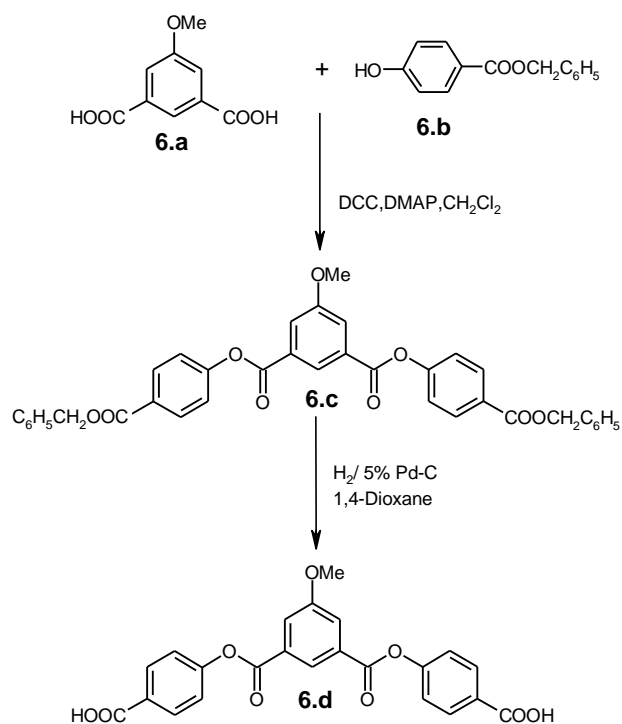
**Structure 6.1**

## Synthesis

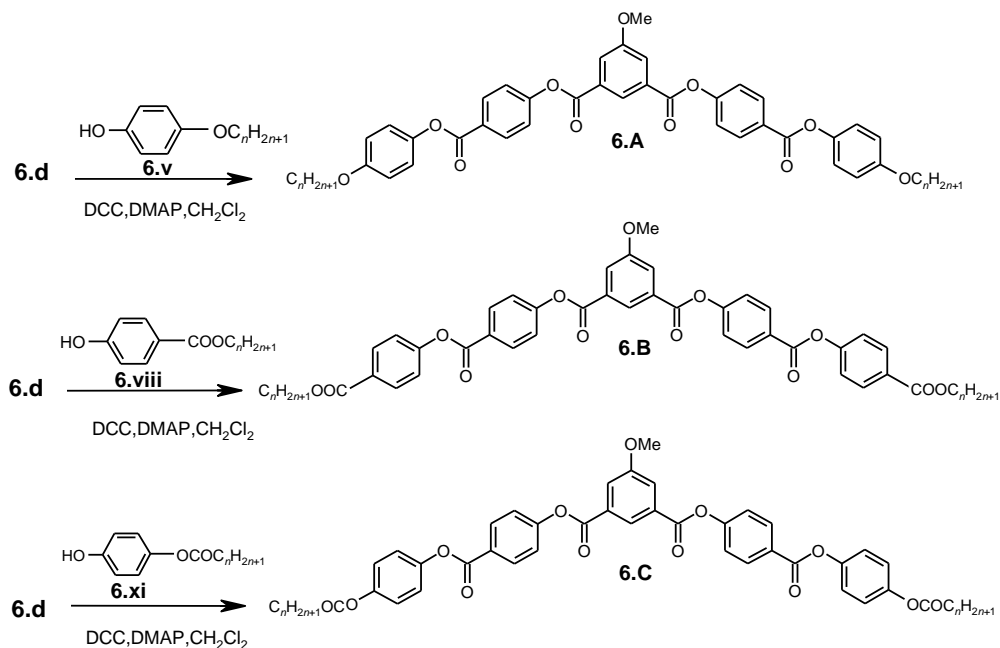
5-Methoxyisophthalic acid was prepared from commercially available 5-hydroxyisophthalic acid, **6.i**, as shown in scheme **6.1**. 5-Methoxyisophthalic acid, **6.a** was esterified with benzyl 4-hydroxybenzoate, **6.b** using *N, N'*-dicyclohexylcarbodiimide (DCC) and a catalytic amount of 4-(*N, N*-dimethylamino)pyridine (DMAP) to obtain compound **6.c**. The benzyl group in compound **6.c** was cleaved using H<sub>2</sub> and 5% Pd-C catalyst to get the bis carboxylic acid **6.d** as shown in scheme **6.2**. The symmetrical five-ring bent-core compounds, **6.A**, **6.B** and **6.C** were prepared by condensing the bis carboxylic acid with two equivalents of appropriate 4-*n*-alkoxyphenols, *n*-alkyl 4-hydroxybenzoates and 4-hydroxyphenyl *n*-alkanoates respectively following the pathway shown in scheme **6.3**. Similarly, compounds **6.A.9** and **6.A.10** were prepared by condensing 4-*n*-octadecyloxyphenyl 3-fluoro-4-hydroxybenzoate and 4-*n*-octadecyloxyphenyl 2-fluoro-4-hydroxybenzoate with 5-methoxyisophthalic acid as depicted in scheme **6.4**. 4-*n*-Alkoxyphenols were prepared by monoalkylation of quinol with appropriate *n*-alkyl bromides in presence of anhydrous potassium carbonate. *n*-Alkyl 4-hydroxybenzoates and 4-hydroxyphenyl *n*-alkanoates were prepared from commercially available 4-benzyloxybenzoic acid and 4-(benzyloxy)phenol following the pathway shown in scheme **6.5**. 4-*n*-Octadecyloxyphenyl 3-fluoro-4-hydroxybenzoate and 4-*n*-octadecyloxyphenyl 2-fluoro-4-hydroxybenzoate were prepared following the synthetic route shown in scheme **6.6**. All the compounds were purified by column chromatography on silica gel and repeated crystallization using analytical grade solvents.



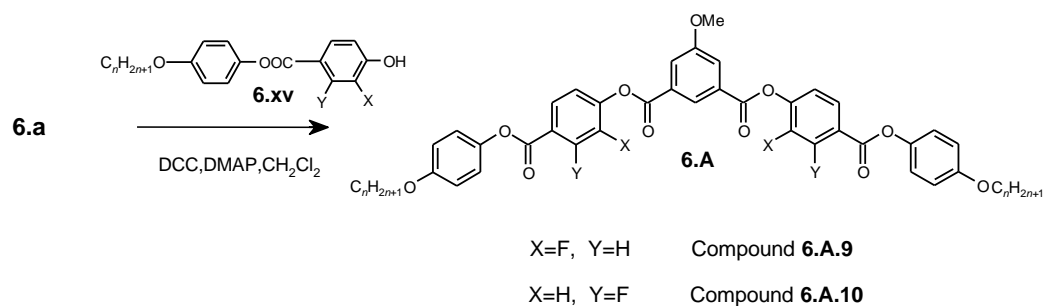
**Scheme 6.1: Synthetic pathway employed for the preparation of 5-methoxyisophthalic acid (6.a).**



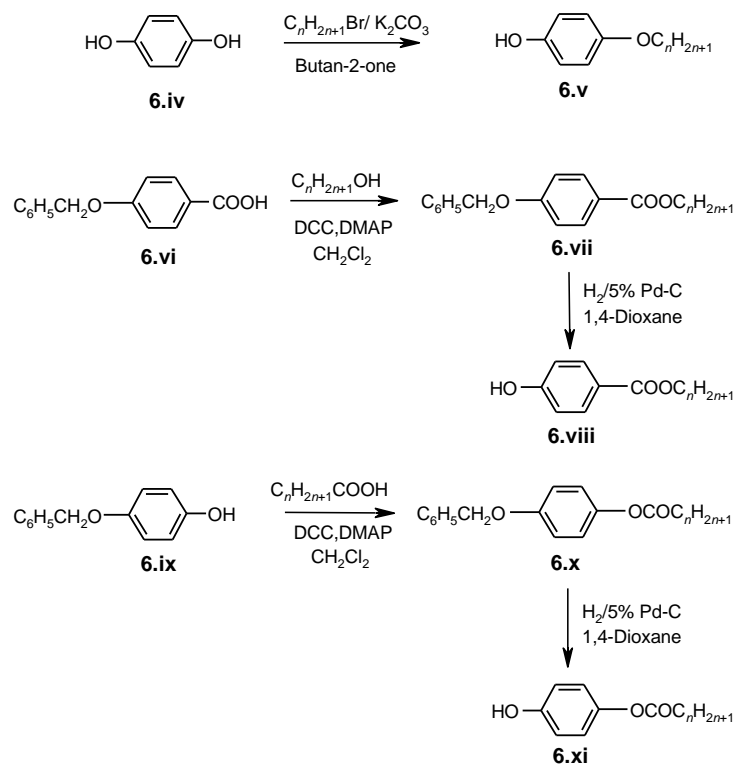
**Scheme 6.2: Synthetic pathway used for the preparation of compound 6.d.**



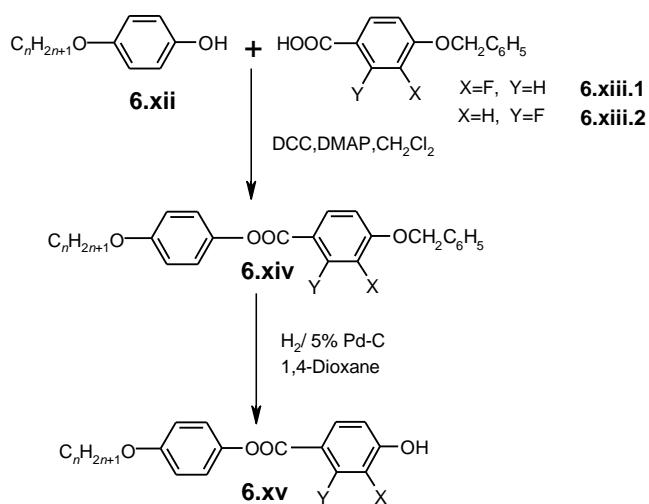
**Scheme 6.3: Synthetic route employed for the preparation of bent-core compounds 6.A, 6.B and 6.C.**



**Scheme 6.4: Synthetic pathway employed for the preparation of bent-core compounds 6.A.9 and 6.A.10.**



**Scheme 6.5:** Synthetic route followed to prepare 4-*n*-alkoxyphenols (**6.v**), *n*-alkyl 4-hydroxybenzoates (**6.viii**) and 4-hydroxyphenyl *n*-alkanoates (**6.xi**).

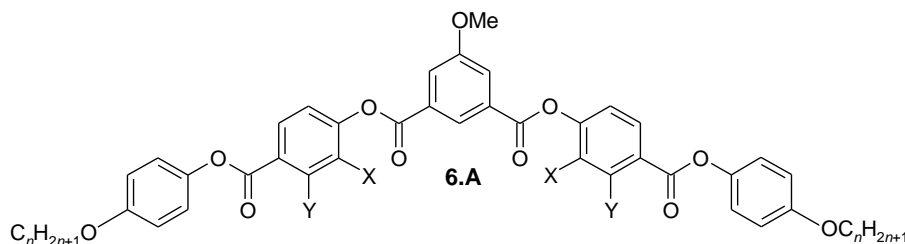


**Scheme 6.6:** Synthetic pathway followed to prepare compounds **6.xv**.

## Results and discussion

Symmetrical five-ring bent-core compounds having the general structure **6.A** with a bulky methoxy substituent at position 5 were investigated for mesomorphic properties. The transition temperatures together with the associated enthalpy values obtained for these compounds are summarized in table **6.1**.

**Table 6.1: Transition temperatures (°C) and the associated enthalpy values (kJ mol<sup>-1</sup>, in italics) for the compounds of series 6.A.**



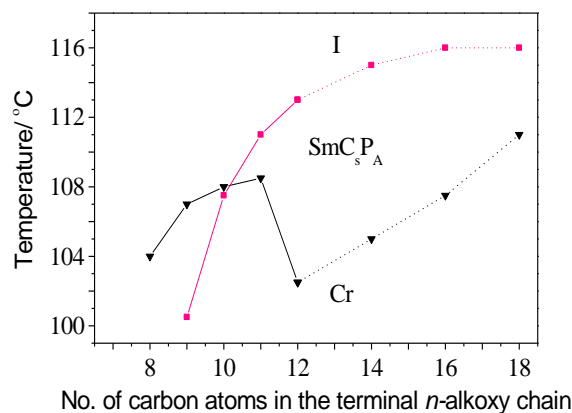
Compound	<i>n</i>	X	Y	Cr	SmC <sub>s</sub> P <sub>A</sub>	I		
<b>6.A.1</b>	8	H	H	·	104.0 <i>52.0</i>	-	·	
<b>6.A.2</b>	9	H	H	·	107.0 <i>60.5</i>	(. 100.5)	·	
<b>6.A.3</b>	10	H	H	·	108.0 <i>51.5</i>	(. 107.0)	·	
<b>6.A.4</b>	11	H	H	·	108.5 <i>65.5</i>	·	111.0 <i>16.0</i>	·
<b>6.A.5</b>	12	H	H	·	102.5 <i>49.5</i>	·	113.5 <i>15.5</i>	·
<b>6.A.6</b>	14	H	H	·	105.0 <i>63.0</i>	·	115.0 <i>16.5</i>	·
<b>6.A.7</b>	16	H	H	·	107.5 <i>67.5</i>	·	116.0 <i>16.0</i>	·
<b>6.A.8</b>	18	H	H	·	111.0 <i>77.5</i>	·	116.0 <i>16.0</i>	·
<b>6.A.9</b>	18	F	H	·	116.0 <i>154.5</i>	(. 103.0) <sup>‡</sup>	·	
<b>6.A.10</b>	18	H	F	·	117.0 <i>103.5</i>	(. 100.7) <sup>‡</sup>	·	

Abbreviations for tables **6.1,6.2** and **6.3**: Cr-Crystalline phase; SmC<sub>s</sub>P<sub>A</sub>-Polar smectic C phase, s and A refers to synclinc and antiferroelectric; SmA-Uniaxial smectic A phase; I-Isotropic phase; · Phase exists; - Phase does not exist; <sup>‡</sup> Enthalpy could not be measured from DSC as the sample crystallizes immediately; () Monotropic transition.

Compound **6.A.1** is non-mesomorphic, while the remaining showed a mesophase. When a sample of compound **6.A.6** was cooled slowly from the isotropic phase, schlieren and focal-conic textures developed which is typical for a SmCP phase. This phase has been identified as SmC<sub>s</sub>P<sub>A</sub> based on XRD studies and electro-optical investigations (described later). A photomicrograph of the texture exhibited by the mesophase of compound **6.A.6** is shown in figure **6.1**. Infact, all the remaining homologues (**6.A.2-8**) exhibit similar pattern suggesting that the mesophase is of the same type. A plot of the transition temperature as a function of the number of carbon atoms in the terminal *n*-alkoxy chain for these compounds is shown in figure **6.2**. It can be seen that the



**Figure 6.1: Photomicrograph of the texture obtained for the mesophase of compound 6.A.6, T=110°C.**



**Figure 6.2: A plot of transition temperature as a function of the number of carbon atoms in the terminal chain for the compounds 6.A.1-6.A.8.**

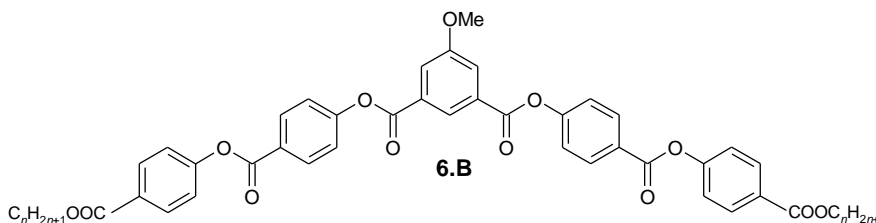


clearing temperature curve is smooth and rises initially and levels off on ascending the homologous series. This is quite typical for the SmCP phase in general and has been observed in a number of different homologous series of compounds [3, 5].

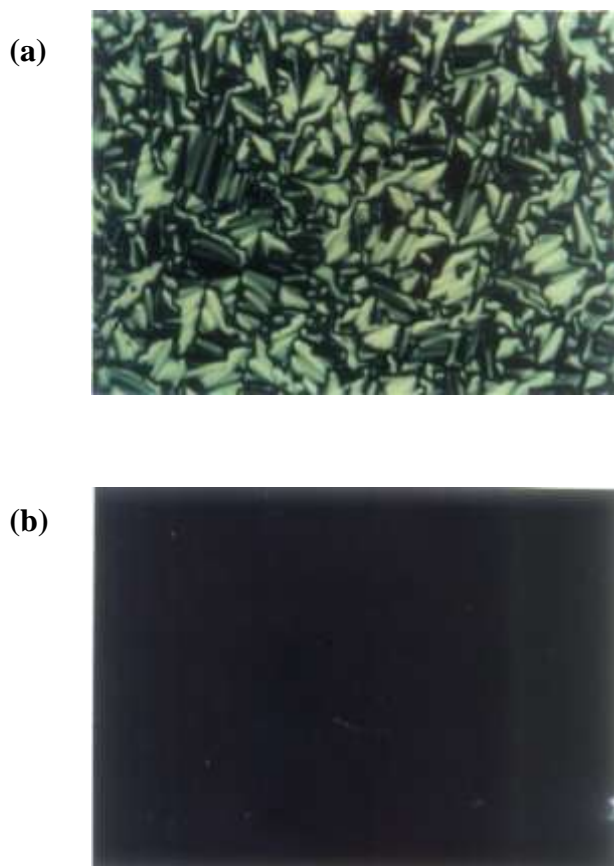
The mesophase of compound **6.A.8** is enantiotropic with a thermal range of 5°C. When a lateral fluoro substituent is introduced on the middle phenyl ring of the arms of compound **6.A.8** either at *meta* or *ortho* position with respect to the carbonyl group (compounds **6.A.9** and **6.A.10** respectively), the mesophase gets destabilized and becomes metastable. This is in complete contrast to what has been observed in five-ring compounds derived from resorcinol [5]. This once again emphasizes the fact that in bent-core compounds, the dipolar effects are dominant than steric factors [3].

Interestingly, when the terminal *n*-alkoxy chains are replaced by *n*-alkyl carboxylate groups, the occurrence of the mesophase is suppressed and only a metastable SmA phase is obtained. The transition temperatures and the associated enthalpy values of these compounds (**6.B**) are summarized in table **6.2**. The nature of this phase was confirmed by observing the texture of a sample of compound **6.B.2** in separate cells treated for homogeneous and homeotropic alignment of the molecules as shown in figure **6.3a** and **b** respectively.

**Table 6.2: Transition temperatures (°C) and the associated enthalpy values (kJ mol<sup>-1</sup>, in italics) for the compounds of series 6.B.**



Compound	<i>n</i>	Cr	SmA	I
<b>6.B.1</b>	10	.	87.5 <i>56.0</i>	- .
<b>6.B.2</b>	14	.	100.5 <i>155.5</i>	(. <i>68.5</i> ) <i>7.0</i>
<b>6.B.3</b>	18	.	92.5 <i>111.0</i>	(. <i>78.0</i> ) <i>5.5</i>



**Figure 6.3: Photomicrographs of the SmA phase of compound 6.B.2, T=67.3°C**

**a) Homogeneously aligned sample; b) homeotropically aligned sample.**

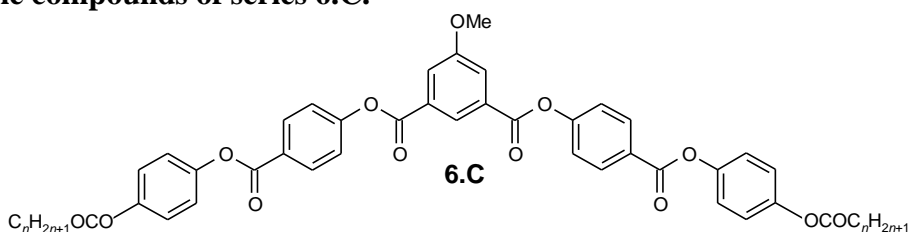
Electro-optical studies and XRD measurements could not be carried out for the mesophase of these compounds, since they are highly metastable.

The occurrence of a calamitic phase can be attributed to an increase ( $>140^\circ$ ) in the bend angle between the two arms of the bent-core molecule. However, a possible explanation in the present case could be that the rotational freedom of the molecules along their long axis is facilitated by the flexible terminal *n*-alkyl carboxylate groups which in turn will inhibit a steric packing along the bend direction resulting in a calamitic phase. It is interesting to point out here that in a bent-core system containing terminal perfluorinated chains with a bend angle of  $125^\circ$ , a SmA phase has been observed [12]. In addition, it has been reported [16] that in the case of a Schiff's base ester with terminal *n*-tetradecyloxy chain and derived from isophthalic acid, the

formation of mesophase is prevented. However, switchable phases are obtained, when the terminal *n*-alkoxy chain is replaced by a *n*-alkyl carboxylate group.

The analogous five-ring bent-core compounds with terminal *n*-alkanoate groups were also synthesized. The transition temperatures and the associated enthalpy values obtained for this series of compounds are summarized in table 6.3. As can be seen from the table, the melting points and the clearing transition temperatures are enhanced compared to the analogous *n*-alkoxy terminated compounds. A dimorphism for compounds 6.C.1-4 and a polymorphism for compound 6.C.5 is observed. Compounds 6.C.1 and 6.C.2 exhibit two monotropic mesophases. As the chain length is increased, for compound 6.C.3, higher temperature phase becomes enantiotropic, and on further increasing the chain length, for compound 6.C.4, both the mesophases become enantiotropic. Interestingly, compound 6.C.5 exhibits two additional mesophases, one at a higher temperature and another at a lower temperature with respect to the two mesophases exhibited by lower homologues. Among these four phase transitions, three of them are enantiotropic and the

**Table 6.3: Transition temperatures (°C) and the associated enthalpy values (kJ mol<sup>-1</sup>, in italics) for the compounds of series 6.C.**

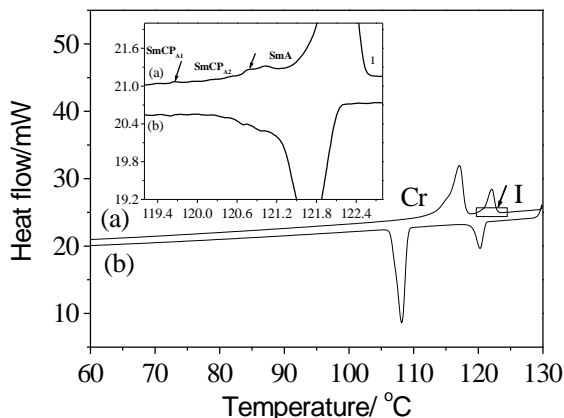


Compound	<i>n</i>	Cr	SmCP <sub>A1</sub>	SmCP <sub>A2</sub>	SmA	I
<b>6.C.1</b>	10	. 110.5 <i>49.0</i>	(. 105.0) <sup>†</sup>	(. 107.0) <i>14.0</i>	-	.
<b>6.C.2</b>	11	. 114.5 <i>50.5</i>	(. 108.0) <sup>‡</sup>	(. 112.0) <i>15.5</i>	-	.
<b>6.C.3</b>	13	. 114.0 <i>43.0</i>	(. 113.0) <i>0.02</i>	. 118.5 <i>15.5</i>	-	.
<b>6.C.4</b>	15	. 114.5 <i>38.0</i>	. 115.5 <i>0.003</i>	. 119.0 <i>14.5</i>	-	.
<b>6.C.5<sup>#</sup></b>	17	. 117.0 <i>50.5</i>	. 119.6 <i>0.02</i>	. 121.0 <i>0.04</i>	. 122.0 <i>10.5</i>	.

<sup>†</sup>The phase transition was observed under a microscope; # Compound exhibits a monotropic transition to a switchable phase at 112.5°C, and the XRD studies could not be carried out as the sample crystallizes rapidly.

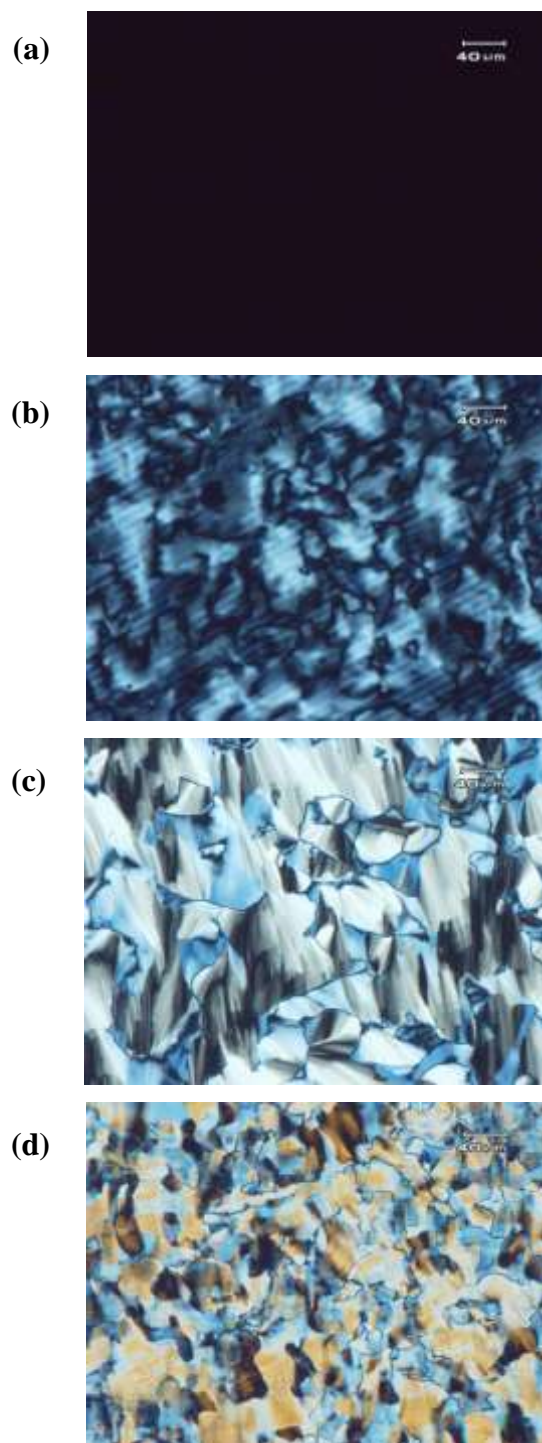
transitions could be detected by calorimetry, although the enthalpy accompanying the phase transitions is relatively small. The lowest temperature phase is monotropic and is observed only under a polarizing microscope. A DSC thermogram obtained for compound **6.C.5** is shown in figure **6.4**.

The homologues **6.C.1-4** exhibit similar optical textures. Both schlieren and focal-conic textures could be observed for the mesophase when viewed between untreated glass slides and the textural changes are minimal at the phase transitions. However, clear textural changes could be observed in a glass slide treated for homeotropic alignment and the same obtained for a sample of compound **6.C.5** is shown in figure **6.5**. On slow cooling from the isotropic phase in a cell treated for homeotropic alignment, optical extinction (figure **6.5a**) was observed in the higher temperature phase. On the contrary, a focal-conic texture was observed for this mesophase when the cell was treated for homogeneous alignment. XRD studies could not be carried out on the mesophase and no electro-optical switching was observed in the mesophase. On the basis of textural features, the



**Figure 6.4: A DSC thermogram obtained for compound 6.C.5; (a) heating cycle, (b) cooling cycle; scan rate 5 °C min<sup>-1</sup>. The inset shows an enlarged view of the phase transitions; scan rate 0.5 °C min<sup>-1</sup>.**

mesophase has been identified as SmA. On cooling to 120.5 °C, a schlieren texture (**6.5b**) develops over the dark region indicating a tilted arrangement of the molecules. On cooling to 118.9 °C, a change in the schlieren texture could be observed and birefringence of the texture also increases (figure **6.5c**). The lower homologues also exhibit similar textural changes (figure **6.5b** and **c**) at the phase transition. These two phases have been found to be lamellar from



**Figure 6.5: Optical textures obtained for a sample of compound 6.C.5 in a cell treated for homeotropic alignment. (a)  $T=121.3^{\circ}\text{C}$ ; (b)  $T=120.5^{\circ}\text{C}$ ; (c)  $T=118.9^{\circ}\text{C}$ ; (d)  $T=110^{\circ}\text{C}$ .**

XRD studies and antiferroelectric behaviour was observed in switching experiments (described later). On the basis of these results, the lower temperature mesophase is designated as SmCP<sub>A1</sub> and higher temperature mesophase is designated as SmCP<sub>A2</sub>. On further cooling, at 110°C a textural change was observed indicating a phase transition (figure 6.5d). XRD measurements could not be carried out on this mesophase as the sample crystallizes rapidly. However, electro-optical investigations could be carried out which indicated an antiferroelectric behaviour for the mesophase.

The behaviour of all the three different types of BC compounds investigated here suggests that it is difficult to relate the chemical structure to the type of mesophase exhibited by them.

In order to examine the mesophase structure of the compounds, XRD measurements were carried out on powder samples. Each sample was taken in a sealed Lindemann capillary (diameter 0.7mm) and cooled slowly from the isotropic phase to the mesophase. An unoriented sample of compound 6.A.4 showed two reflections in the small angle region with spacing (*d*) of 45.8Å and 22.9Å which are in the ratio 1:1/2, indicating a lamellar ordering of the molecules in the mesophase. Similarly compound 6.A.6 showed two reflections in the small angle region with the *d*-spacing 50.6Å and 25.3Å, which again indicated a lamellar ordering. The first order layer spacing was found to be smaller than the measured molecular length (*l*) assuming an all *trans* conformation of the terminal *n*-alkoxy chains (for example *l* ~ 63.0Å for compound 6.A.6). This suggests tilting of the molecules in the mesophase with a tilt angle of about 36.5°.

XRD patterns obtained for the mesophase of compounds 6.C.3 and 6.C.4 also showed equally spaced reflections in the small angle region at 115°C and 117°C respectively, indicating a layered arrangement of the molecules in the mesophase. The *d*-spacing obtained was found to be temperature independent. Compound 6.C.5 showed only one reflection in the small angle region at 119°C and the layer spacing was the same at 114°C, indicating that the mesophases are lamellar. The measured layer spacing (*d* in Å) along with the corresponding Miller indices obtained for all these compounds are shown in table 6.4.

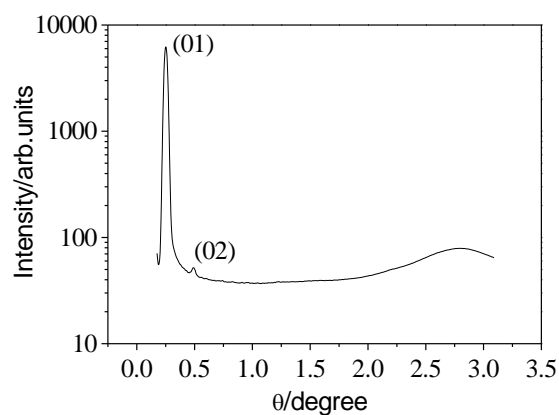
In all the cases a diffuse reflection was observed in the wide-angle region at about 4.4Å indicating the fluidity of the phase. XRD results coupled with electro-optical studies (described below) suggest that the phase exhibited by compounds of series 6.A and 6.C is SmCP<sub>A</sub> (except the highest temperature phase of compound 6.C.5, which is SmA). An X-ray diffractogram obtained

for the mesophase of compound **6.A.6** is shown in figure **6.6** and is typical for the other homologues as well.

**Table 3: X-Ray diffraction data obtained for the mesophase of compounds of series 6.A and 6.C.**

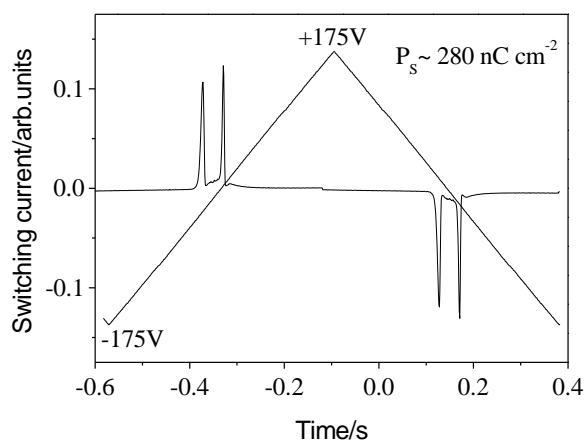
Compound	<i>d</i> -spacing/Å	Temperature/°C
<b>6.A.4</b>	45.8 (01), 22.9 (02)	103
<b>6.A.6</b>	50.6 (01), 25.3 (02)	108
<b>6.C.3*</b>	53.5 (01), 26.7 (02)	115
<b>6.C.4*</b>	57.4 (01), 28.8 (02)	117
<b>6.C.5*</b>	54.3 (01)	119

\* The layer spacing is temperature independent



**Figure 6.6: X-Ray angular intensity profile obtained for the mesophase of compound 6.A.6, T=108°C.**

The electro-optical switching behaviour of the mesophase exhibited by the above compounds was studied using ITO coated cells treated with polyimide, which aids homogeneous alignment of the molecules. The switching polarization measurements were carried out by employing a triangular-wave and modified triangular-wave electric field methods. For example, a sample of compound **6.A.6** in its isotropic state was filled in to a cell of thickness  $8\ \mu\text{m}$  through capillary action. The sample was cooled slowly from the isotropic phase to the mesophase and a triangular-wave voltage at a frequency of  $100\text{Hz}$  was applied and increased gradually. Two current peaks per half period of the applied voltage were observed at a threshold of  $8.5\text{V}\mu\text{m}^{-1}$ , indicating an antiferroelectric ground state for the mesophase. The current response trace obtained for compound **6.A.6** at  $110^\circ\text{C}$  is shown in figure **6.7**. The switching polarization value obtained from the current response trace was  $280\ \text{nC cm}^{-2}$ .

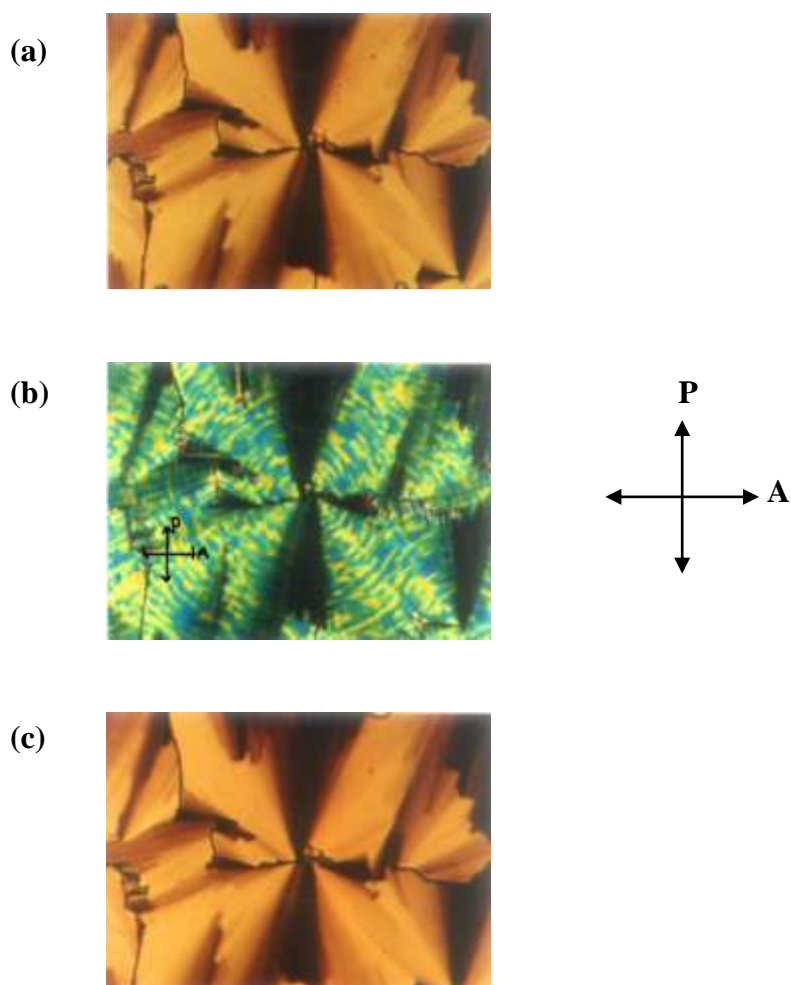


**Figure 6.7: Switching current response trace obtained for the mesophase of compound 6.A.6 by applying a triangular voltage; Cell gap= $8\ \mu\text{m}$ ;  $T=110^\circ\text{C}$ ;  $1\ \text{Hz}$ ;  $350\text{V}_{\text{pp}}$ .**

Experiments were also carried out on the same sample using a dc field. On slow cooling the isotropic liquid under a dc voltage of  $5\ \text{V}\mu\text{m}^{-1}$  aligned domains were obtained in which extinction brushes were oriented parallel to the crossed polarizers. The orientation of the brushes was same either on reversing the sign of the applied voltage or on switching off the field. However, a colour change and stripes could be observed on the smooth domains on terminating the field. This indicates that the molecular organization in the ground state is possibly synclinic in



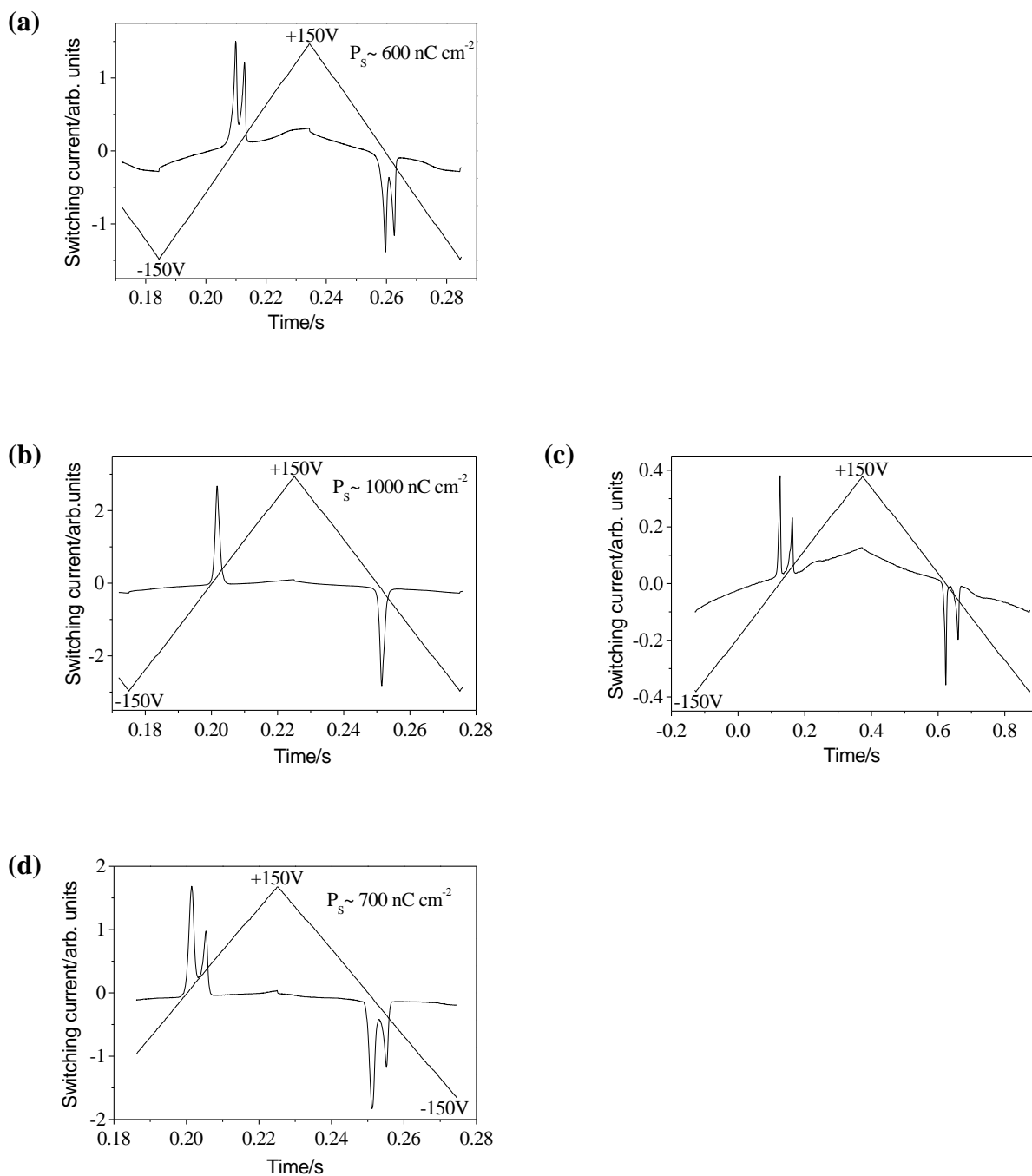
adjacent layers and there is a change in the clinicity after a few layers. This alternation of clinicity after a few layers is repeated so that there exists a number of domains with opposite clinicity [17] containing anticlinic-ferroelectric correlations at the interlayer boundaries [18,19]. A schematic representation of a possible molecular organization in such racemic domains is given in chapter 2. (figure 2.11). The stripes observed are indicative of the domain walls where the tilt direction changes. Photomicrographs illustrating the switching behaviour of the mesophase under a dc field of  $+5 \text{ V}\mu\text{m}^{-1}$ ,  $0 \text{ V}$  and  $-5 \text{ V}\mu\text{m}^{-1}$  are shown in figure 6.8a, b and c respectively.



**Figure 6.8: Photomicrographs of SmCP<sub>A</sub> phase of compound 6.A.6 obtained under a dc field of a)  $+5.0 \text{ V}\mu\text{m}^{-1}$  ; b)  $0 \text{ V}\mu\text{m}^{-1}$ ; c)  $-5.0 \text{ V}\mu\text{m}^{-1}$ .**

Electro-optical investigations were carried out on the mesophases exhibited by compounds of series **6.C**. For example, a sample of compound **6.C.5** in a polyimide coated ITO cell of thickness 12.9  $\mu\text{m}$  was cooled from the isotropic phase and triangular-wave electric field of 300  $V_{\text{PP}}$  at a frequency of 10 Hz was applied. Voltage and frequency were maintained constant until the sample crystallizes. No switching was observed in the SmA phase. However, on cooling, at 120.5°C two current peaks start developing, indicating an antiferroelectric behaviour. Simultaneously textural changes were also observed under the polarizing microscope. The polarization value calculated from current response trace is about 600  $\text{nC cm}^{-2}$ . On decreasing the temperature, at 118.5°C, the amplitude of one of the two current peaks start decreasing while that of the other increases accompanied by a textural change. On maintaining the temperature for a while, the smaller peak disappears completely. Thus a single peak per half period of the applied voltage could be seen. The polarization value increases from 600 to 1000  $\text{nC cm}^{-2}$ . The single peak however, separates into two on decreasing the frequency to 1 Hz confirming the antiferroelectric behaviour. On further cooling from 118.5°C, under a voltage of 300 $V_{\text{PP}}$  and a frequency of 10 Hz, the single peak observed changes into two peaks at 111°C accompanied by a corresponding textural change. The current response traces obtained at 119°C, 115°C and 110°C under a triangular voltage of 300  $V_{\text{PP}}$  and 10 Hz are shown in figures **6.9a, b** and **d** respectively. The current response trace obtained at 115°C, 300  $V_{\text{PP}}$  and 1 Hz is shown in figure **6.9c**. The corresponding textural changes under the field and on switching off the field are shown in figures **6.10a, b, c** and **d, e, f** respectively. It is interesting to note that the optical observation made under a dc field is similar to that observed using a triangular-wave field.

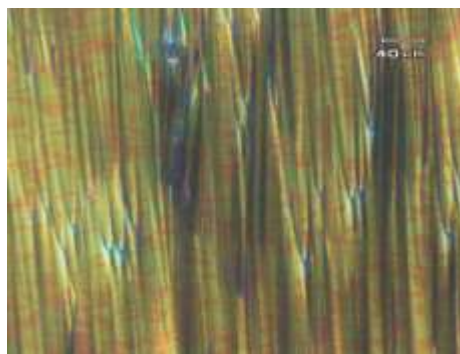
On the basis of calorimetric data, textural observations, XRD and electro-optical studies, the sequence of phases exhibited by compound **6.C.5** is identified as  $\text{Cr} \rightarrow \text{SmCP}_{\text{A1}} \rightarrow \text{SmCP}_{\text{A2}} \rightarrow \text{SmA} \rightarrow \text{I}$ . Although the monotropic phase exhibited by compound **6.C.5** shows antiferroelectric behaviour, XRD studies could not be carried out. The mesophases exhibited by homologues **6.C.1-4** show a behaviour as similar to those of  $\text{SmCP}_{\text{A1}}$  and  $\text{SmCP}_{\text{A2}}$  phases, and hence designated as the same.



**Figure 6.9: Current response traces obtained for the mesophases exhibited by compound 6.C.5 in a ITO coated polyimide cell of thickness 12.9  $\mu\text{m}$ . (a) 119°C, 300V<sub>PP</sub>, 10 Hz; (b) 115°C, 300V<sub>PP</sub>, 10 Hz; (c) 115°C, 300V<sub>PP</sub>, 1 Hz; (d) 110°C, 300V<sub>PP</sub>, 10 Hz.**



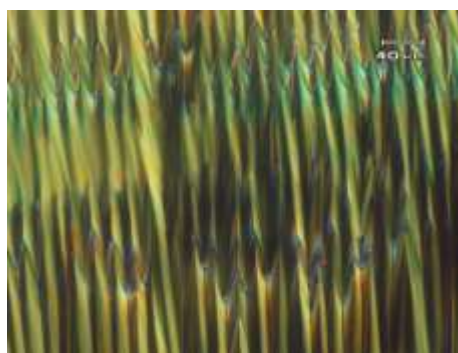
(a)



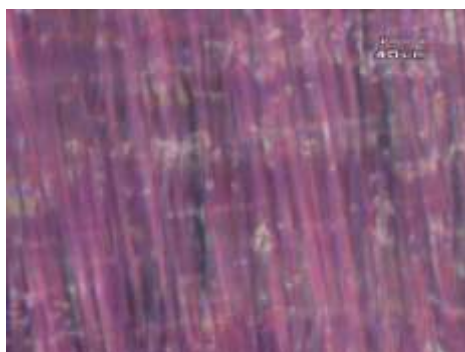
(b)



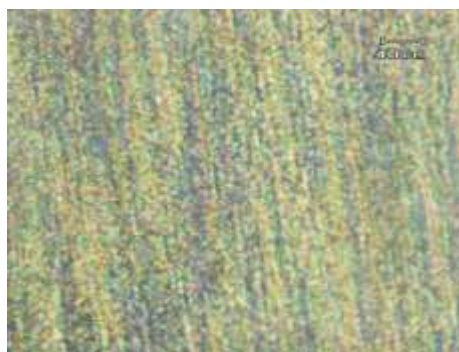
(c)



(d)



(e)



(f)

**Figure 6.10: Optical textures obtained for the mesophases exhibited by compound 6.C.5 in a ITO coated polyimide cell of thickness 12.9  $\mu\text{m}$ . (a), (c) and (e): Under a triangular-wave voltage of 300  $V_{PP}$  and a frequency of 10 Hz at 119°C, 115°C and 110°C respectively. (b), (d) and (f): On switching off the field at 119°C, 115°C and 110°C respectively.**

## Conclusions

Three series of five-ring bent-core compounds derived from 5-methoxyisophthalic acid have been synthesized and investigated for their mesomorphic properties. All these compounds have similar molecular structure but differ in the way the terminal linking groups are attached. Compounds with terminal *n*-alkoxy chains show a polar smectic C phase with antiferroelectric properties, whereas compounds with terminal *n*-alkyl carboxylate groups exhibit a metastable SmA phase. Compounds containing terminal *n*-alkanoate groups also exhibit SmCP<sub>A</sub> phases. Interestingly, a polymorphism was observed for a homologue of this series with *n*=17. The investigations carried out here emphasize the profound influence of the nature of the terminal-linking group on the mesophase behaviour of bent-core compounds. It should be also mentioned that the studies on compounds derived from isophthalic acid are very limited, although they exhibit interesting phases and phase sequences. The present series of compounds represent the first series of five-ring BC compounds containing a bulky substituent at position 5, which also exhibit an electro-optically switchable mesophase.

## Synthesis

5-Hydroxyisophthalic acid, benzyl 4-hydroxybenzoate, quinol and 4-benzyloxyphenol were obtained commercially and used without further purification. 4-*n*-Alkoxyphenols were prepared by monoalkylation of quinol with appropriate *n*-alkyl bromides in presence of anhydrous potassium carbonate. 4-Benzyloxybenzoic acid was prepared by a etherification reaction between benzyl chloride and methyl 4-hydroxybenzoate, followed by saponification and acidification. 2-Fluoro-4-benzyloxybenzoic acid and 3-fluoro-4-benzyloxybenzoic acid were prepared following procedures described in the literature [20-22].

### Dimethyl 5-hydroxyisophthalate, 6.ii

To a solution of 5-hydroxyisophthalic acid, **6.i** (25 g) in methanol (300 ml), a catalytic amount of conc. H<sub>2</sub>SO<sub>4</sub> was added and the resulting mixture was refluxed for about 24 hours. Excess of methanol was distilled off, the reaction mixture was cooled and poured into ice-cold water. This mixture was extracted using ether (4×100 ml), the combined ethereal solution was washed with 5% NaHCO<sub>3</sub> solution (2×100 ml) and then with brine solution several times and dried over anhydrous sodium sulphate. The solvent was evaporated and the residue obtained was passed through a column of silica gel and eluted using a mixture of 20% methanol in chloroform. The product obtained after removal of the solvent was crystallized using chloroform. Yield: 25g (86 %), m. p. 161-163°C.

### Dimethyl 5-Methoxyisophthalate, 6.iii

A mixture of dimethyl 5-hydroxyisophthalate, **6.ii** (20g 0.095 mol), methyl iodide (6.5ml, 0.10 mol) and anhydrous potassium carbonate (39.5g, 0.29 mol) in butan-2-one (250 ml) was refluxed for 24 hours. Excess solvent was distilled off, the reaction mixture was cooled and poured into ice-cold water. This mixture was extracted using chloroform (3×100 ml). The organic solution was washed with aqueous 5% NaOH solution (2 × 100 ml) followed by excess of water and dried over anhydrous sodium sulphate. The solvent was removed and the residue obtained was passed through a column of silica gel and eluted using chloroform. The product thus obtained on removal of the solvent was crystallized using methanol. Yield 20g (93%), m. p. 111-112°C.  $\nu_{\max}$ : 2923, 2852, 1737, 1732, 1728, 1593, 1463, 1446, 1433, 1226, 1244 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.25 (t, <sup>4</sup>*J* 1.32 Hz, 1H, Ar-

H), 7.73 (d,  $^4J$  1.32 Hz, 2H, Ar-H), 3.93 (s, 3H, Ar-OCH<sub>3</sub>), 3.89 (s, 6H, 2×Ar-COOCH<sub>3</sub>); C<sub>11</sub>H<sub>12</sub>O<sub>5</sub> requires C 58.93, H 5.38; found C 58.73, H 5.27 %.

#### **5-Methoxyisophthalic acid, 6.a**

To a solution of dimethyl 5-methoxyisophthalate, **6.iii** (20g, 0.09 mol) in ethanol (250 ml), potassium hydroxide (25g, 0.44 mol) and water (25 ml) was refluxed overnight. The excess of ethanol was distilled off, reaction mixture was cooled and poured into ice-cold water. The resulting solution was acidified with conc. HCl and heated on a water-bath for an hour and cooled. The white precipitate thus obtained was filtered off, washed several times with ice-cold water until the washings were neutral to litmus and dried. The material so obtained was crystallized using water. Yield 15g (85%), m. p. 272-274.5°C.  $\nu_{\max}$ : 2922, 2852, 2650, 2567, 2189, 1703, 1697, 1693, 1681, 1596, 1461 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (DMSO-d<sub>6</sub>): 8.34 (t,  $^4J$  1.32 Hz, 1H, Ar-H), 7.79 (d,  $^4J$  1.32 Hz, 2H, Ar-H), 3.95 (s, 3H, Ar-OCH<sub>3</sub>); C<sub>9</sub>H<sub>8</sub>O<sub>5</sub> requires C 55.10, H 4.10; found C 55.33, H 3.98 %.

#### **5-Methoxy bis (1-benzyloxycarbonylphenyl)isophthalate, 6.c**

5-Methoxyisophthalic acid, **6.a** (3g, 15.3 mmol) and benzyl 4-hydroxybenzoate, **6.b** (7g, 30.6 mmol) in dry dichloromethane (50 ml) with a catalytic amount of DMAP was stirred for 10 minutes. To this mixture, DCC (6.9g, 34 mmol) was added and stirring continued for 24 hours at room temperature. The precipitated *N, N'*-dicyclohexylurea was filtered off and washed with an excess of chloroform. Evaporation of the solvent from the filtrate gave a white product, which was passed through a column of silica gel using chloroform as an eluant. The required material thus obtained was further purified by repeated crystallization using ethanol. Yield 9g (95%), m. p. 117.5-119°C.  $\nu_{\max}$ : 2923, 2854, 1749, 1724, 1604, 1460 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.59 (t, 1H, Ar-H), 8.17 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.96 (d,  $^4J$  1.24 Hz, 2H, Ar-H), 7.46-7.35 (m, 10H, Ar-H), 7.32 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 5.38 (s, 4H, 2×-COO-CH<sub>2</sub>-Ar), 3.96 (s, 3H, Ar-O-CH<sub>3</sub>); C<sub>37</sub>H<sub>28</sub>O<sub>9</sub> requires C 72.09, H 4.64; found C 71.61, H 4.66 %.

#### **4-({3-[(4-carboxyphenoxy)carbonyl]-5-methoxybenzoyl}oxy)benzoic acid, 6.d**

To compound **6.c** (5g, 8.1mmol) in 1,4-dioxane (40ml), 5% Pd-C catalyst (1g) was added. The mixture was stirred in an atmosphere of hydrogen at 60°C until the absorption of hydrogen ceased.

The solution was filtered hot and the filtrate allowed to cool slowly. The crystallized product was filtered and dried. Yield 3g (85%), m. p. 261-269°C.  $\nu_{\max}$ : 3078, 2923, 2852, 2673, 2551, 1741, 1749, 1693, 1697, 1685, 1602, 1456  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (DMSO- $d_6$ ): 13.08 (s, 2H, 2 $\times$ Ar-COOH), 8.42 (t, 1H, Ar-H), 8.07 (d,  $^3J$  8.64 Hz, 4H, Ar-H), 7.97 (d,  $^4J$  1.24Hz, 2H, Ar-H), 7.49 (d,  $^3J$  8.64 Hz, 4H, Ar-H), 3.99 (s, 3H, Ar-OCH<sub>3</sub>). C<sub>23</sub>H<sub>16</sub>O<sub>9</sub> requires C 63.31, H 3.69; found C 63.12, H 3.88 %.

#### ***n*-Decyl 4-benzyloxybenzoate, 6.vii.1**

A mixture of 4-benzyloxybenzoic acid, **6.vi** (2g, 8.8 mmol), *n*-decanol (1.4g, 8.8 mmol) and a catalytic amount of DMAP in dry dichloromethane (30 ml) was stirred for 15 minutes. To this, DCC (2g, 9.6 mmol) was added and stirred for a further 2 hours. The precipitated *N, N'*-dicyclohexylurea was filtered off and washed with excess of chloroform. Removal of solvent from the filtrate provided a residue, which was chromatographed on silica gel using chloroform as eluant. The solvent was removed from the eluate, to obtain a white material, which was crystallized using ethanol. Yield 2.5g (77%), m. p. 35-36°C.  $\nu_{\max}$ : 2922, 2852, 1720, 1718, 1710, 1606, 1510, 1465, 1272, 1166  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 7.99 (d,  $^3J$  8.8 Hz, 2H, Ar-H), 7.44-7.34 (m, 5H, Ar-H), 6.99 (d,  $^3J$  8.8 Hz, 2H, Ar-H), 5.12 (s, 2H, -OCH<sub>2</sub>-Ar), 4.28 (t,  $^3J$  6.64 Hz, 2H, Ar-COO-CH<sub>2</sub>-), 1.76-1.70 (m, 2H, Ar-COO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.25 (m, 14H, (-CH<sub>2</sub>)<sub>7</sub>), 0.87 (t,  $^3J$  6.64 Hz, 3H, -CH<sub>3</sub>); C<sub>24</sub>H<sub>32</sub>O<sub>3</sub> requires C 78.26, H 8.6; found C 78.5, H 9.0 %.

#### ***n*-Decyl 4-hydroxybenzoate, 6.viii.1**

Compound, **6.vii.1** (2.5g) was dissolved in 1,4-dioxane (50 ml) and to this solution 5% Pd-C catalyst (0.5g) was added. The mixture was stirred in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. The solution was filtered hot and the solvent from the filtrate was evaporated. The residue obtained was crystallized using *n*-hexane. Yield 1.6g (85%), m. p. 41-42°C.  $\nu_{\max}$ : 3388, 2918, 2852, 1689, 1604, 1587, 1510, 1469, 1280, 1218, 1164, 1124  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 7.96 (d,  $^3J$  8.7 Hz, 2H, Ar-H), 6.85 (d,  $^3J$  8.6 Hz, 2H, Ar-H), 4.27 (t,  $^3J$  6.64 Hz, 2H, Ar-COO-CH<sub>2</sub>-), 1.76-1.73 (m, 2H, Ar-COO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.25 (m, 14H, (-CH<sub>2</sub>)<sub>7</sub>), 0.88 (t,  $^3J$  6.64 Hz, 3H, -CH<sub>3</sub>); C<sub>17</sub>H<sub>26</sub>O<sub>3</sub> requires C 73.38, H 9.3; found C 73.47, H 9.5 %.



#### ***n*-Tetradecyl 4-benzyloxybenzoate, 6.vii.2**

Yield 79%, m. p. 53-54°C.  $\nu_{\max}$ : 2952, 2920, 2850, 1722, 1720, 1716, 1608, 1469, 1454, 1284, 1251  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 7.96 (d,  $^3J$  8.68 Hz, 2H, Ar-H), 7.44-7.34 (m, 5H, Ar-H), 6.95 (d,  $^3J$  8.68 Hz, 2H, Ar-H), 5.12 (s, 2H, -OCH<sub>2</sub>-Ar), 4.26 (t,  $^3J$  6.64 Hz, 2H, Ar-COO-CH<sub>2</sub>-), 1.76-1.71 (m, 2H, Ar-COO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.25 (m, 22H, (-CH<sub>2</sub>)<sub>11</sub>), 0.88 (t,  $^3J$  6.64 Hz, 3H, -CH<sub>3</sub>); C<sub>28</sub>H<sub>40</sub>O<sub>3</sub> requires C 79.2, H 9.49; found C 78.79, H 9.8 %.

#### ***n*-Tetradecyl 4-hydroxybenzoate, 6.viii.2**

Yield 87%, m. p. 63-64.5°C.  $\nu_{\max}$ : 3388, 2920, 2852, 1681, 1679, 1604, 1512, 1465, 1282, 1209, 1161  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 7.98 (d,  $^3J$  8.67 Hz, 2H, Ar-H), 6.84 (d,  $^3J$  8.67 Hz, 2H, Ar-H), 4.26 (t,  $^3J$  6.64 Hz, 2H, Ar-COO-CH<sub>2</sub>-), 1.76-1.72 (m, 2H, Ar-COO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.43-1.24 (m, 22H, (-CH<sub>2</sub>)<sub>11</sub>), 0.89 (t,  $^3J$  6.64 Hz, 3H, -CH<sub>3</sub>); C<sub>21</sub>H<sub>34</sub>O<sub>3</sub> requires C 75.4, H 10.25; found C 75.27, H 10.4 %.

#### ***n*-Octadecyl 4-benzyloxybenzoate, 6.vii.3**

Yield 80%, m. p. 64-65°C.  $\nu_{\max}$ : 2952, 2918, 2850, 1724, 1722, 1716, 1608, 1471, 1454, 1382, 1251, 1128  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 7.98 (d,  $^3J$  8.66 Hz, 2H, Ar-H), 7.42-7.35 (m, 5H, Ar-H), 6.96 (d,  $^3J$  8.65 Hz, 2H, Ar-H), 5.12 (s, 2H, -OCH<sub>2</sub>-Ar), 4.26 (t,  $^3J$  6.64 Hz, 2H, Ar-COO-CH<sub>2</sub>-), 1.77-1.73 (m, 2H, Ar-COO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.43-1.24 (m, 30H, (-CH<sub>2</sub>)<sub>15</sub>), 0.88 (t,  $^3J$  6.64 Hz, 3H, -CH<sub>3</sub>); C<sub>32</sub>H<sub>48</sub>O<sub>3</sub> requires C 79.95, H 10.0; found C 79.6, H 9.8 %.

#### ***n*-Octadecyl 4-hydroxybenzoate, 6.viii.3**

Yield 85%, m. p. 74-75.5°C.  $\nu_{\max}$ : 3396, 2918, 2850, 1687, 1602, 1587, 1278, 1164  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 7.97 (d,  $^3J$  8.77 Hz, 2H, Ar-H), 6.86 (d,  $^3J$  8.7 Hz, 2H, Ar-H), 4.25 (t,  $^3J$  6.64 Hz, 2H, Ar-COO-CH<sub>2</sub>-), 1.75-1.71 (m, 2H, Ar-COO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.24 (m, 30H, (-CH<sub>2</sub>)<sub>15</sub>), 0.88 (t,  $^3J$  6.64 Hz, 3H, -CH<sub>3</sub>); C<sub>25</sub>H<sub>42</sub>O<sub>3</sub> requires C 76.9, H 10.7; found C 77.0, H 10.59 %.

#### **4-Benzyloxyphenyl *n*-decanoate, 6.x.1**

4-Benzyloxyphenol, **6.ix** (2g, 10 mmol), *n*-decanoic acid (1.86g, 10 mmol) and a catalytic amount of DMAP in dichloromethane (50 ml) was stirred for 15 minutes at room temperature. To this stirred mixture, DCC (2.26g, 11 mmol) was added and stirring continued for a further 2 hours. The precipitated *N, N'*-dicyclohexylurea was filtered off and washed thoroughly with chloroform. The

filtrate was concentrated to obtain a material, which was passed through a column of silica gel using chloroform as an eluant. The product obtained from the column was further purified by crystallization using *n*-hexane. Yield 3g (82%); m. p. 74-75°C;  $\nu_{\max}$ : 2922, 2850, 1720, 1718, 1606, 1465, 1377, 1272, 1251, 1166, 1022  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 7.43- 7.28 (m, 7H, Ar-H), 6.97 (d,  $^3J$  8.40 Hz, 2H, Ar-H), 5.04 (s, 2H, -OCH<sub>2</sub>-Ar), 2.52 (t,  $^3J$  7.52 Hz, 2H, Ar-OCO-CH<sub>2</sub>-), 1.77-1.69 (quin,  $^3J$  7.32 Hz, 2H, Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.03 (m, 14H, (-CH<sub>2</sub>)<sub>7</sub>), 0.97 (t,  $^3J$  6.44 Hz, 3H, -CH<sub>3</sub>); C<sub>24</sub>H<sub>32</sub>O<sub>3</sub> requires C 78.91, H 8.46; found C 78.46, H 8.92 %.

#### 4-Hydroxyphenyl *n*-decanoate, 6.xi.1

Compound **6.x.1**, (3.0g) in 1,4-dioxane (30 ml) and 5% Pd-C (0.6g) were stirred in an atmosphere of hydrogen at 60°C until the reaction was complete which was monitored by thin layer chromatography using Merck 60 silica gel plates. The reaction mixture was filtered hot and the solvent was evaporated to obtain the product, which was crystallized using a mixture of *n*-hexane and 1,4-dioxane. Yield 2g (88%); m. p. 77-78°C;  $\nu_{\max}$ : 3388, 3192, 3126, 3072, 2920, 2850, 1751, 1747, 1745, 1465, 1377, 1207  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 6.92 (d,  $^3J$  8.92 Hz, 2H, Ar-H), 6.79 (d,  $^3J$  8.92 Hz, 2H, Ar-H), 4.86 (s, 1H, Ar-OH, D<sub>2</sub>O exchangeable), 2.52 (t,  $^3J$  7.48 Hz, 2H, Ar-OCO-CH<sub>2</sub>-), 1.77-1.69 (quin,  $^3J$  7.28 Hz, 2H, Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.25 (m, 14H, (-CH<sub>2</sub>)<sub>7</sub>), 0.97 (t,  $^3J$  6.56 Hz, 3H, -CH<sub>3</sub>); C<sub>17</sub>H<sub>26</sub>O<sub>3</sub> requires C 73.35, H 9.40; found C 73.58, H 9.48 %.

#### 4-Benzyloxyphenyl *n*-undecanoate, 6.x.2

Yield 85%, m. p. 75-76°C.  $\nu_{\max}$ : 2922, 2850, 1757, 1745, 1733, 1506, 1458, 1377, 1205, 1151, 1022  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 7.43- 7.28 (m, 7H, Ar-H), 6.97 (d,  $^3J$  8.40 Hz, 2H, Ar-H), 5.04 (s, 2H, -OCH<sub>2</sub>-Ar), 2.52 (t,  $^3J$  7.52 Hz, 2H, Ar-OCO-CH<sub>2</sub>-), 1.77-1.69 (quin,  $^3J$  7.32 Hz, 2H, Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.03 (m, 16H, (-CH<sub>2</sub>)<sub>8</sub>), 0.97 (t,  $^3J$  6.44 Hz, 3H, -CH<sub>3</sub>); C<sub>25</sub>H<sub>34</sub>O<sub>3</sub> requires C 79.15, H 8.67; found C 78.87, H 9.05 %.

#### 4-Hydroxyphenyl *n*-undecanoate, 6.xi.2

Yield 87%, m. p. 80-81°C.  $\nu_{\max}$ : 3386, 3192, 3126, 3072, 2920, 2850, 1751, 1747, 1745, 1465, 1377, 1207  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 6.92 (d,  $^3J$  8.92 Hz, 2H, Ar-H), 6.79 (d,  $^3J$  8.92 Hz, 2H, Ar-H), 4.86 (s, 1H, Ar-OH, D<sub>2</sub>O exchangeable), 2.52 (t,  $^3J$  7.48 Hz, 2H, Ar-OCO-CH<sub>2</sub>-), 1.77-1.69 (quin,  $^3J$  7.28 Hz,

2H, Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.25 (m, 16H, (-CH<sub>2</sub>-)<sub>8</sub>), 0.97 (t, <sup>3</sup>J 6.56 Hz, 3H, -CH<sub>3</sub>); C<sub>18</sub>H<sub>28</sub>O<sub>3</sub> requires C 73.94, H 9.64; found C 74.24, H 10.0 %.

#### 4-Benzoyloxyphenyl *n*-tridecanoate, 6.x.3

Yield 81%, m. p. 79-80°C.  $\nu_{\max}$ : 2922, 2850, 1757, 1745, 1737, 1506, 1463, 1377, 1207, 1153, 1022 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 7.43- 7.28 (m, 7H, Ar-H), 6.97 (d, <sup>3</sup>J 8.40 Hz, 2H, Ar-H), 5.04 (s, 2H, -OCH<sub>2</sub>-Ar), 2.52 (t, <sup>3</sup>J 7.52 Hz, 2H, Ar-OCO-CH<sub>2</sub>-), 1.77-1.69 (quin, <sup>3</sup>J 7.32 Hz, 2H, Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.03 (m, 20H, (-CH<sub>2</sub>-)<sub>10</sub>), 0.97 (t, <sup>3</sup>J 6.44 Hz, 3H, -CH<sub>3</sub>); C<sub>27</sub>H<sub>38</sub>O<sub>3</sub> requires C 79.58, H 9.06; found C 78.89, H 9.68 %.

#### 4-Hydroxyphenyl *n*-tridecanoate, 6.xi.3

Yield 88%, m. p. 88-89°C.  $\nu_{\max}$ : 3385, 3192, 3126, 3072, 2920, 2850, 1751, 1747, 1745, 1465, 1377, 1207 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 6.92 (d, <sup>3</sup>J 8.92 Hz, 2H, Ar-H), 6.79 (d, <sup>3</sup>J 8.92 Hz, 2H, Ar-H), 4.86 (s, 1H, Ar-OH, D<sub>2</sub>O exchangeable), 2.52 (t, <sup>3</sup>J 7.48 Hz, 2H, Ar-OCO-CH<sub>2</sub>-), 1.77-1.69 (quin, <sup>3</sup>J 7.28 Hz, 2H, Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.25 (m, 20H, (-CH<sub>2</sub>-)<sub>10</sub>), 0.97 (t, <sup>3</sup>J 6.56 Hz, 3H, -CH<sub>3</sub>); C<sub>20</sub>H<sub>32</sub>O<sub>3</sub> requires C 74.97, H 10.05; found C 75.06, H 10.22 %.

#### 4-Benzoyloxyphenyl *n*-pentadecanoate, 6.x.4

Yield 78%, m. p. 84-85°C.  $\nu_{\max}$ : 2920, 2850, 1751, 1747, 1745, 1506, 1463, 1377, 1207, 1154, 1095 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 7.43- 7.28 (m, 7H, Ar-H), 6.97 (d, <sup>3</sup>J 8.40 Hz, 2H, Ar-H), 5.04 (s, 2H, -OCH<sub>2</sub>-Ar), 2.52 (t, <sup>3</sup>J 7.52 Hz, 2H, Ar-OCO-CH<sub>2</sub>-), 1.77-1.69 (quin, <sup>3</sup>J 7.32 Hz, 2H, Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.03 (m, 24H, (-CH<sub>2</sub>-)<sub>12</sub>), 0.97 (t, <sup>3</sup>J 6.44 Hz, 3H, -CH<sub>3</sub>); C<sub>29</sub>H<sub>42</sub>O<sub>3</sub> requires C 79.41, H 9.64; found C 79.69, H 9.69 %.

#### 4-Hydroxyphenyl *n*-pentadecanoate, 6.xi.4

Yield 85%, m. p. 89-89.5°C.  $\nu_{\max}$ : 3387, 3195, 3070, 2920, 2850, 1751, 1747, 1745, 1716, 1463, 1377, 1205 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 6.92 (d, <sup>3</sup>J 8.92 Hz, 2H, Ar-H), 6.79 (d, <sup>3</sup>J 8.92 Hz, 2H, Ar-H), 4.86 (s, 1H, Ar-OH, D<sub>2</sub>O exchangeable), 2.52 (t, <sup>3</sup>J 7.48 Hz, 2H, Ar-OCO-CH<sub>2</sub>-), 1.77-1.69 (quin, <sup>3</sup>J 7.28 Hz, 2H, Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.25 (m, 24H, (-CH<sub>2</sub>-)<sub>12</sub>), 0.97 (t, <sup>3</sup>J 6.56 Hz, 3H, -CH<sub>3</sub>); C<sub>22</sub>H<sub>36</sub>O<sub>3</sub> requires C 75.82, H 10.40; found C 75.45, H 10.50 %.

#### 4-Benzoyloxyphenyl *n*-heptadecanoate, 6.x.5

Yield 80%, m. p. 86-87°C.  $\nu_{\max}$ : 2920, 2850, 1745, 1508, 1463, 1377, 1207, 1196, 1153, 1022  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 7.43- 7.28 (m, 7H, Ar-H), 6.97 (d,  $^3J$  8.40 Hz, 2H, Ar-H), 5.04 (s, 2H, -OCH<sub>2</sub>-Ar), 2.52 (t,  $^3J$  7.52 Hz, 2H, Ar-OCO-CH<sub>2</sub>-), 1.77-1.69 (quin,  $^3J$  7.32 Hz, 2H, Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.03 (m, 28H, (-CH<sub>2</sub>)<sub>14</sub>), 0.97 (t,  $^3J$  6.44 Hz, 3H, -CH<sub>3</sub>); C<sub>31</sub>H<sub>46</sub>O<sub>3</sub> requires C 79.73, H 9.93; found C 80.17, H 10.15 %.

#### 4-Hydroxyphenyl *n*-heptadecanoate, 6.xi.5

Yield 85%, m. p. 93-94°C.  $\nu_{\max}$ : 3387, 3184, 3120, 3070, 2920, 2850, 1747, 1716, 1463, 1377, 1205  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 6.92 (d,  $^3J$  8.92 Hz, 2H, Ar-H), 6.79 (d,  $^3J$  8.92 Hz, 2H, Ar-H), 4.86 (s, 1H, Ar-OH, D<sub>2</sub>O exchangeable), 2.52 (t,  $^3J$  7.48 Hz, 2H, Ar-OCO-CH<sub>2</sub>-), 1.77-1.69 (quin,  $^3J$  7.28 Hz, 2H, Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.25 (m, 28H, (-CH<sub>2</sub>)<sub>14</sub>), 0.97 (t,  $^3J$  6.56 Hz, 3H, -CH<sub>3</sub>); C<sub>24</sub>H<sub>40</sub>O<sub>3</sub> requires C 76.55, H 10.69; found C 76.3, H 10.99 %.

#### 4-*n*-Octadecyloxyphenyl 3-fluoro-4-benzyloxybenzoate, 6.xiv.1, X=F, Y=H

A mixture of 4-*n*-octadecyloxyphenol, **6.xii** (1.5g, 4 mmol), 3-fluoro-4-benzyloxybenzoic acid, **6.xiii.1**, (X=F, Y=H), (1g, 4 mmol), and a catalytic amount of DMAP in dry dichloromethane (25 ml) was stirred for 10 minutes. To this mixture, DCC (1g, 4.4 mmol) was added and stirred for about 4 hours at room temperature. The precipitated *N, N'*-dicyclohexylurea was filtered off and washed with an excess of dichloromethane. The residue obtained on removal of solvent was chromatographed on silica gel using chloroform as an eluant. The material obtained on removal of solvent was further purified by crystallization using *n*-hexane. Yield 2.2g (90%), m. p. 108-109°C.  $\nu_{\max}$ : 2918, 2850, 1737, 1728, 1726, 1512, 1463, 1436, 1207  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 7.93-7.89 (m, 2H, Ar-H), 7.47-7.35 (m, 6H, Ar-H), 7.08 (d,  $^3J$  8.96 Hz, 2H, Ar-H), 6.91 (d,  $^3J$  8.96 Hz, 2H, Ar-H), 5.24 (s, 2H, -OCH<sub>2</sub>-Ar), 3.95 (t,  $^3J$  6.52 Hz, 2H, Ar-OCH<sub>2</sub>-), 1.82-1.75 (quin, 2H, Ar-OCH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 30H, (-CH<sub>2</sub>)<sub>15</sub>), 0.87 (t,  $^3J$  6.52 Hz, 3H, -CH<sub>3</sub>); C<sub>38</sub>H<sub>51</sub>FO<sub>4</sub> requires C 77.26, H 8.69; found C 76.8, H 9.05 %.

#### 4-*n*-Octadecyloxyphenyl 3-fluoro-4-hydroxybenzoate, 6.xv.1, X=F, Y=H

Compound **6.xiv.1** (2g) was dissolved in 1,4-dioxane (30 ml) and 5% Pd-C catalyst (0.4g) was added to it. The mixture was stirred at 60°C in an atmosphere of hydrogen till the required

quantity of hydrogen was absorbed. The resulting mixture was filtered hot and the solvent removed under reduced pressure. The material so obtained was crystallized using *n*-hexane. Yield 1.5g (88%), m. p. 111-112°C.  $\nu_{\max}$ : 3382, 2920, 2850, 1735, 1728, 1614, 1585, 1461, 1290  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 7.88-7.84 (m, 2H, Ar-H), 7.47-7.35 (m, 1H, Ar-H), 7.10 (d,  $^3J$  8.96 Hz, 2H, Ar-H), 6.93 (d,  $^3J$  8.96 Hz, 2H, Ar-H), 3.99 (t,  $^3J$  6.52 Hz, 2H, Ar-OCH<sub>2</sub>-), 1.83-1.77 (quin, 2H, Ar-OCH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.28 (m, 30H, (-CH<sub>2</sub>)<sub>15</sub>), 0.88 (t,  $^3J$  6.52 Hz, 3H, -CH<sub>3</sub>); C<sub>31</sub>H<sub>45</sub>FO<sub>4</sub> requires C 74.37, H 9.05; found C 74.0, H 9.29 %.

#### **4-*n*-Octadecyloxyphenyl 2-fluoro-4-benzyloxybenzoate, 6.xiv.2, X=H, Y=F**

This compound was prepared following a procedure described for the synthesis of compound **6.xiv.1** using 2-fluoro-4-benzyloxybenzoic acid, **6.xiii.2**. Yield 85%, m. p. 111-113°C.  $\nu_{\max}$ : 2920, 2850, 1718, 1685, 1458, 1377  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.06-8.02 (dd,  $^3J$  8.6 Hz, 1H, Ar-H), 7.42-7.36 (m, 5H, Ar-H), 7.10 (d,  $^3J$  8.96 Hz, 2H, Ar-H), 6.90 (d,  $^3J$  8.6 Hz, 2H, Ar-H), 6.86-6.83 (dd,  $^3J$  8.84 Hz,  $^4J$  2.24 Hz, 1H, Ar-H), 6.79-6.75 (dd,  $^3J$  12.48 Hz,  $^4J$  2.28 Hz, 1H, Ar-H), 5.13 (s, 2H, -OCH<sub>2</sub>-Ar), 3.94 (t,  $^3J$  6.8 Hz, 2H, Ar-OCH<sub>2</sub>-), 1.81-1.74 (quin, 2H, Ar-OCH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 30H, (-CH<sub>2</sub>)<sub>15</sub>), 0.87 (t,  $^3J$  6.4 Hz, 3H, -CH<sub>3</sub>); C<sub>38</sub>H<sub>51</sub>FO<sub>4</sub> requires C 77.26, H 8.69; found C 76.92, H 8.89 %.

#### **4-*n*-Octadecyloxyphenyl 2-fluoro-4-hydroxybenzoate, 6.xv.2, X=H, Y=F**

This compound was prepared following a procedure described for the synthesis of compound **6.xv.1** using **6.xiv.2** as starting material. Yield 86%, m. p. 142-143°C.  $\nu_{\max}$ : 3382, 2920, 2850, 1730, 1728, 1718, 1714, 1614, 1585, 1508, 1461, 1290  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.03-8.0 (dd,  $^3J$  8.6 Hz, 1H, Ar-H), 7.12 (d,  $^3J$  8.96 Hz, 2H, Ar-H), 6.96 (d,  $^3J$  8.6 Hz, 2H, Ar-H), 6.84-6.79 (dd,  $^3J$  8.84 Hz,  $^4J$  2.24 Hz, 1H, Ar-H), 6.74-6.69 (dd,  $^3J$  12.48 Hz,  $^4J$  2.28 Hz, 1H, Ar-H), 4.0 (t,  $^3J$  6.8 Hz, 2H, Ar-OCH<sub>2</sub>-), 1.84-1.76 (quin, 2H, Ar-OCH<sub>2</sub>-CH<sub>2</sub>-), 1.51-1.32 (m, 30H, (-CH<sub>2</sub>)<sub>15</sub>), 0.89 (t,  $^3J$  6.4 Hz, 3H, -CH<sub>3</sub>); C<sub>31</sub>H<sub>45</sub>FO<sub>4</sub> requires C 74.37, H 9.05; found C 74.1, H 9.45 %.

#### **5-Methoxy bis [4-(*n*-octyloxyphenyloxycarbonyl)phenylisophthalate], 6.A.1**

This compound was prepared following a procedure similar to that described for compound **6.c**. Quantities: Compound **6.d** (0.2g, 0.45 mmol), 4-*n*-octyloxyphenol, **6.ii** (0.2g, 0.91 mmol), DCC (0.2g, 0.99 mmol), DMAP (cat.amount) and dry dichloromethane (10 ml). Yield 0.3g (78%), m. p.

104°C.  $\nu_{\max}$ : 2923, 2845, 1739, 1732, 1596, 1508, 1458  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.64 (t, 1H, Ar-H), 8.30 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.99 (d,  $^4J$  1.2 Hz, 2H, Ar-H), 7.40 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.12 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 6.93 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 3.98 (s, 3H, Ar-OCH<sub>3</sub>), 3.96 (t,  $^3J$  6.48 Hz, 4H, 2×Ar-OCH<sub>2</sub>-), 1.8-1.75 (quin,  $^3J$  6.64 Hz, 4H, 2×Ar-OCH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.26 (m, 20H, 2 × (-CH<sub>2</sub>)<sub>5</sub>), 0.88 (t,  $^3J$  6.44 Hz, 6H, 2×-CH<sub>3</sub>); C<sub>51</sub>H<sub>56</sub>O<sub>11</sub> requires C 72.41, H 6.66; found C 72.24, H 6.65 %.

### **5-Methoxy bis [4-(*n*-nonyloxyphenyloxycarbonyl)phenylisophthalate], 6.A.2**

Yield 80%, m. p. 107°C.  $\nu_{\max}$ : 2923, 2845, 1738, 1730, 1598, 1508, 1458  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.64 (t, 1H, Ar-H), 8.30 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.99 (d,  $^4J$  1.2 Hz, 2H, Ar-H), 7.40 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.12 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 6.93 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 3.98 (s, 3H, Ar-OCH<sub>3</sub>), 3.96 (t,  $^3J$  6.48 Hz, 4H, 2×Ar-OCH<sub>2</sub>-), 1.8-1.75 (quin,  $^3J$  6.64 Hz, 4H, 2×Ar-OCH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.26 (m, 24H, 2 × (-CH<sub>2</sub>)<sub>6</sub>), 0.88 (t,  $^3J$  6.44 Hz, 6H, 2×-CH<sub>3</sub>); C<sub>53</sub>H<sub>60</sub>O<sub>11</sub> requires C 72.91, H 6.95; found C 73.07, H 7.14 %.

### **5-Methoxy bis [4-(*n*-decyloxyphenyloxycarbonyl)phenylisophthalate], 6.A.3**

Yield 75%, m. p. 108°C.  $\nu_{\max}$ : 2922, 2852, 1737, 1728, 1600, 1508, 1465  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.64 (t, 1H, Ar-H), 8.30 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.99 (d,  $^4J$  1.2 Hz, 2H, Ar-H), 7.40 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.12 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 6.93 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 3.98 (s, 3H, Ar-OCH<sub>3</sub>), 3.96 (t,  $^3J$  6.48 Hz, 4H, 2×Ar-OCH<sub>2</sub>-), 1.8-1.75 (quin,  $^3J$  6.64 Hz, 4H, 2×Ar-OCH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.26 (m, 28H, 2 × (-CH<sub>2</sub>)<sub>7</sub>), 0.88 (t,  $^3J$  6.44 Hz, 6H, 2×-CH<sub>3</sub>); C<sub>55</sub>H<sub>64</sub>O<sub>11</sub> requires C 73.31, H 7.16; found C 72.98, H 7.20 %.

### **5-Methoxy bis [4-(*n*-undecyloxyphenyloxycarbonyl)phenylisophthalate], 6.A.4**

Yield 80%, m. p. 108.5°C.  $\nu_{\max}$ : 2920, 2852, 2665, 1737, 1728, 1600, 1465  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.64 (t, 1H, Ar-H), 8.30 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.99 (d,  $^4J$  1.2 Hz, 2H, Ar-H), 7.40 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.12 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 6.93 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 3.98 (s, 3H, Ar-OCH<sub>3</sub>), 3.96 (t,  $^3J$  6.48 Hz, 4H, 2×Ar-OCH<sub>2</sub>-), 1.8-1.75 (quin,  $^3J$  6.64 Hz, 4H, 2×Ar-OCH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.26 (m, 32H, 2 × (-CH<sub>2</sub>)<sub>8</sub>), 0.88 (t,  $^3J$  6.44 Hz, 6H, 2×-CH<sub>3</sub>); C<sub>57</sub>H<sub>68</sub>O<sub>11</sub> requires C 73.68, H 7.37; found C 73.91, H 7.26 %.

**5-Methoxy bis [4-(*n*-dodecyloxyphenyloxycarbonyl)phenylisophthalate], 6.A.5**

Yield 76%, m. p. 102.5°C.  $\nu_{\max}$ : 2920, 2852, 2665, 1735, 1728, 1508, 1465  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.64 (t, 1H, Ar-H), 8.30 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.99 (d,  $^4J$  1.2 Hz, 2H, Ar-H), 7.40 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.12 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 6.93 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 3.98 (s, 3H, Ar-OCH<sub>3</sub>), 3.96 (t,  $^3J$  6.48 Hz, 4H, 2×Ar-OCH<sub>2</sub>-), 1.8-1.75 (quin,  $^3J$  6.64 Hz, 4H, 2×Ar-OCH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.26 (m, 36H, 2 × (-CH<sub>2</sub>)<sub>9</sub>), 0.88 (t,  $^3J$  6.44 Hz, 6H, 2×-CH<sub>3</sub>); C<sub>59</sub>H<sub>72</sub>O<sub>11</sub> requires C 74.03, H 7.58; found C 73.81, H 7.69 %.

**5-Methoxy bis [4-(*n*-tetradecyloxyphenyloxycarbonyl)phenylisophthalate], 6.A.6**

Yield 82%, m. p. 105°C.  $\nu_{\max}$ : 2920, 2852, 2665, 1737, 1735, 1728, 1600, 1508, 1465  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.64 (t, 1H, Ar-H), 8.30 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.99 (d,  $^4J$  1.2 Hz, 2H, Ar-H), 7.40 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.12 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 6.93 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 3.98 (s, 3H, Ar-OCH<sub>3</sub>), 3.96 (t,  $^3J$  6.48 Hz, 4H, 2×Ar-OCH<sub>2</sub>-), 1.8-1.75 (quin,  $^3J$  6.64 Hz, 4H, 2×Ar-OCH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.26 (m, 44H, 2 × (-CH<sub>2</sub>)<sub>11</sub>), 0.88 (t,  $^3J$  6.44 Hz, 6H, 2×-CH<sub>3</sub>); C<sub>63</sub>H<sub>80</sub>O<sub>11</sub> requires C 74.68, H 7.95; found C 74.91, H 7.99 %.

**5-Methoxy bis [4-(*n*-hexadecyloxyphenyloxycarbonyl)phenylisophthalate], 6.A.7**

Yield 81%, m. p. 107.5°C.  $\nu_{\max}$ : 2920, 2852, 1737, 1735, 1728, 1600, 1508, 1463  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.64 (t, 1H, Ar-H), 8.30 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.99 (d,  $^4J$  1.2 Hz, 2H, Ar-H), 7.40 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.12 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 6.93 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 3.98 (s, 3H, Ar-OCH<sub>3</sub>), 3.96 (t,  $^3J$  6.48 Hz, 4H, 2×Ar-OCH<sub>2</sub>-), 1.8-1.75 (quin,  $^3J$  6.64 Hz, 4H, 2×Ar-OCH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.26 (m, 52H, 2 × (-CH<sub>2</sub>)<sub>13</sub>), 0.88 (t,  $^3J$  6.44 Hz, 6H, 2×-CH<sub>3</sub>); C<sub>67</sub>H<sub>88</sub>O<sub>11</sub> requires C 75.25, H 8.28; found C 74.93, H 8.61 %.

**5-Methoxy bis [4-(*n*-octadecyloxyphenyloxycarbonyl)phenylisophthalate], 6.A.8**

Yield 79%, m. p. 111°C.  $\nu_{\max}$ : 2920, 2852, 2723, 1737, 1735, 1728, 1600, 1508, 1463  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.64 (t, 1H, Ar-H), 8.30 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.99 (d,  $^4J$  1.2 Hz, 2H, Ar-H), 7.40 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.12 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 6.93 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 3.98 (s, 3H, Ar-OCH<sub>3</sub>), 3.96 (t,  $^3J$  6.48 Hz, 4H, 2×Ar-OCH<sub>2</sub>-), 1.8-1.75 (quin,  $^3J$  6.64 Hz, 4H, 2×Ar-OCH<sub>2</sub>-CH<sub>2</sub>-),

1.46-1.26 (m, 60H,  $2 \times (-\text{CH}_2-)_{15}$ ), 0.88 (t,  $^3J$  6.44 Hz, 6H,  $2 \times -\text{CH}_3$ );  $\text{C}_{71}\text{H}_{96}\text{O}_{11}$  requires C 75.77, H 8.58; found C 75.47, H 8.71 %.

#### **5-Methoxy bis [4-(*n*-octadecyloxyphenyloxycarbonyl)-3-fluorophenylisophthalate], 6.A.9**

This compound was prepared following a procedure similar to the one described for compound **6.A.1**. Quantities: 5-Methoxyisophthalic acid, **6.a** (0.059g, 0.3 mmol), compound **6.xii.1** (0.3g, 0.6 mmol), DCC (0.14g, 0.66 mmol), DMAP (cat.amount) and dry dichloromethane (20 ml). Yield 0.28g (80%), m. p. 116°C.  $\nu_{\text{max}}$ : 2916, 2852, 1753, 1739, 1735, 1595, 1510, 1473, 1429, 1344, 1195, 1045  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.66 (t,  $^4J$  1.32 Hz, 1H, Ar-H), 8.09-8.05 (m, 4H, Ar-H), 8.01 (d,  $^4J$  1.36 Hz, 2H, Ar-H), 7.46-7.42 (m, 2H, Ar-H), 7.12 (d,  $^3J$  9.0 Hz, 4H, Ar-H), 6.93 (d,  $^3J$  9.0 Hz, 4H, Ar-H), 3.98 (s, 3H, Ar-OCH<sub>3</sub>), 3.96 (t,  $^3J$  6.68 Hz, 4H,  $2 \times \text{Ar-OCH}_2-$ ), 1.82-1.75 (quin,  $^3J$  6.68 Hz, 4H,  $2 \times \text{Ar-OCH}_2-\underline{\text{CH}_2-}$ ), 1.46-1.26 (m, 60H,  $2 \times (-\text{CH}_2-)_{15}$ ), 0.88 (t,  $^3J$  6.52 Hz, 6H,  $2 \times -\text{CH}_3$ );  $\text{C}_{71}\text{H}_{94}\text{F}_2\text{O}_{13}$  requires C 73.45, H 8.15; found C 73.42, H 8.16 %.

#### **5-Methoxy bis [4-(*n*-octadecyloxyphenyloxycarbonyl)-2-fluorophenylisophthalate], 6.A.10**

This was synthesized following a procedure described for compound **6.A.9** using compound **6.xii.2**. Yield 78%, m. p. 117.0°C.  $\nu_{\text{max}}$ : 2922, 2850, 1749, 1739, 1732, 1608, 1606, 1467, 1272, 1056  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.58 (t,  $^4J$  1.32 Hz, 1H, Ar-H), 8.23-8.19 (m, 2H, Ar-H), 7.98 (d,  $^4J$  1.32 Hz, 2H, Ar-H), 7.23-7.19 (m, 4H, Ar-H), 7.14 (d,  $^3J$  9.0 Hz, 4H, Ar-H), 6.93 (d,  $^3J$  9.0 Hz, 4H, Ar-H), 3.98 (s, 3H, Ar-OCH<sub>3</sub>), 3.96 (t,  $^3J$  6.6 Hz, 4H,  $2 \times \text{Ar-OCH}_2-$ ), 1.82-1.75 (quin,  $^3J$  6.64 Hz, 4H,  $2 \times \text{Ar-OCH}_2-\underline{\text{CH}_2-}$ ), 1.46-1.26 (m, 60H,  $2 \times (-\text{CH}_2-)_{15}$ ), 0.88 (t,  $^3J$  6.52 Hz, 6H,  $2 \times -\text{CH}_3$ );  $\text{C}_{71}\text{H}_{94}\text{F}_2\text{O}_{13}$  requires C 73.45, H 8.15; found C 73.46, H 8.17 %.

#### **5-Methoxy bis [4-(*n*-decyloxyphenyloxycarbonyl)phenylisophthalate], 6.B.1**

This compound was prepared following a procedure similar to that used for compound **6.A.1**. Quantities: Compound **6.d** (0.2g, 0.45 mmol), *n*-decyl 4-hydroxybenzoate, **6.viii.1** (0.25g, 0.91 mmol), DCC (0.2g, 0.99 mmol), DMAP (cat.amount) and dry dichloromethane (10 ml). Yield 0.35g (81%), m. p. 87.5°C.  $\nu_{\text{max}}$ : 2923, 2852, 1739, 1733, 1716, 1714, 1600, 1458, 1269, 1191  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.64 (t, 1H, Ar-H), 8.32 (d,  $^3J$  8.48 Hz, 4H, Ar-H), 8.14 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 8.00 (d,  $^3J$  1.32 Hz, 2H, Ar-H), 7.43 (d,  $^3J$  8.70 Hz, 4H, Ar-H), 7.32 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 4.33 (t,



$^3J$  6.6 Hz, 4H, 2×Ar-COO-CH<sub>2</sub>-), 3.99 (s, 3H, Ar-OCH<sub>3</sub>), 1.81-1.74 (quin,  $^3J$  6.64 Hz, 4H, 2×Ar-COO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 28H, 2 × (-CH<sub>2</sub>-)<sub>7</sub>), 0.88 (t,  $^3J$  6.52 Hz, 6H, 2×-CH<sub>3</sub>); C<sub>57</sub>H<sub>64</sub>O<sub>13</sub> requires C 71.58, H 6.73; found C 71.37, H 6.98 %.

#### **5-Methoxy bis [4-(*n*-tetradecyloxycarbonylphenyloxycarbonyl)phenylisophthalate], 6.B.2**

Yield 79%, m. p. 102°C.  $\nu_{\max}$ : 2920, 2852, 1735, 1724, 1722, 1600, 1458, 1286 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.64 (t, 1H, Ar-H), 8.32 (d,  $^3J$  8.48 Hz, 4H, Ar-H), 8.14 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 8.00 (d,  $^4J$  1.32 Hz, 2H, Ar-H), 7.43 (d,  $^3J$  8.70 Hz, 4H, Ar-H), 7.32 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 4.33 (t,  $^3J$  6.6 Hz, 4H, 2×Ar-COO-CH<sub>2</sub>-), 3.99 (s, 3H, Ar-OCH<sub>3</sub>), 1.81-1.74 (quin,  $^3J$  6.64 Hz, 4H, 2×Ar-COO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 44H, 2 × (-CH<sub>2</sub>-)<sub>11</sub>), 0.88 (t,  $^3J$  6.52 Hz, 6H, 2×-CH<sub>3</sub>); C<sub>65</sub>H<sub>80</sub>O<sub>13</sub> requires C 73.01, H 7.53; found C 73.47, H 7.68 %.

#### **5-Methoxy bis [4-(*n*-octadecyloxycarbonylphenyloxycarbonyl)phenylisophthalate], 6.B.3**

Yield 82%, m. p. 94.5°C.  $\nu_{\max}$ : 2920, 2850, 1739, 1724, 1720, 1600, 1456, 1286 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.64 (t, 1H, Ar-H), 8.32 (d,  $^3J$  8.48 Hz, 4H, Ar-H), 8.14 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 8.00 (d,  $^4J$  1.32 Hz, 2H, Ar-H), 7.43 (d,  $^3J$  8.70 Hz, 4H, Ar-H), 7.32 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 4.33 (t,  $^3J$  6.6 Hz, 4H, 2×Ar-COO-CH<sub>2</sub>-), 3.99 (s, 3H, Ar-OCH<sub>3</sub>), 1.81-1.74 (quin,  $^3J$  6.64 Hz, 4H, 2×Ar-COO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 60H, 2 × (-CH<sub>2</sub>-)<sub>15</sub>), 0.88 (t,  $^3J$  6.52 Hz, 6H, 2×-CH<sub>3</sub>); C<sub>73</sub>H<sub>96</sub>O<sub>13</sub> requires C 74.21, H 8.19; found C 74.5, H 8.34 %.

#### **5-Methoxy bis [4-(*n*-decylcarbonyloxyphenyloxycarbonyl)phenylisophthalate], 6.C.1**

This compound was synthesized following a procedure similar to that described for compound **6.A.1**. Quantities: Compound **6.d** (0.2g, 0.45 mmol), 4-hydroxyphenyl *n*-decanoate, **6.xi.1** (0.25g, 0.91 mmol), DCC (0.2g, 0.99 mmol), DMAP (cat.amount) and dry dichloromethane (10 ml). Yield 0.36g (83%), m. p. 110.5°C.  $\nu_{\max}$ : 2922, 2852, 1756, 1742, 1728, 1726, 1602, 1465, 1190 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.64 (t,  $^4J$  1.30 Hz, 1H, Ar-H), 8.30 (d,  $^3J$  8.72 Hz, 4H, Ar-H), 8.00 (d,  $^4J$  1.36 Hz, 2H, Ar-H), 7.41 (d,  $^3J$  8.72 Hz, 4H, Ar-H), 7.24 (d,  $^3J$  8.92 Hz, 4H, Ar-H), 7.15 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 3.99 (s, 3H, Ar-OCH<sub>3</sub>), 2.56 (t,  $^3J$  7.44 Hz, 4H, 2×Ar-OCO-CH<sub>2</sub>-), 1.79-1.72 (quin, 4H, 2×Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.28 (m, 28H, 2 × (-CH<sub>2</sub>-)<sub>7</sub>), 0.88 (t,  $^3J$  6.44Hz, 6H, 2×-CH<sub>3</sub>); C<sub>57</sub>H<sub>64</sub>O<sub>13</sub> requires C 71.53, H 6.73; found C 71.62, H 6.76 %.

**5-Methoxy bis [4-(*n*-undecylcarbonyloxyphenyloxycarbonyl)phenylisophthalate], 6.C.2**

Yield 80%, m. p. 114.5°C.  $\nu_{\max}$ : 2922, 2852, 1757, 1741, 1728, 1726, 1602, 1506, 1465, 1190  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.64 (t,  $^4J$  1.30 Hz, 1H, Ar-H), 8.30 (d,  $^3J$  8.72 Hz, 4H, Ar-H), 8.00 (d,  $^4J$  1.36 Hz, 2H, Ar-H), 7.41 (d,  $^3J$  8.72 Hz, 4H, Ar-H), 7.24 (d,  $^3J$  8.92 Hz, 4H, Ar-H), 7.15 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 3.99 (s, 3H, Ar-OCH<sub>3</sub>), 2.56 (t,  $^3J$  7.44 Hz, 4H, 2×Ar-OCO-CH<sub>2</sub>-), 1.79-1.72 (quin, 4H, 2×Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.27 (m, 32H, 2 × (-CH<sub>2</sub>)<sub>8</sub>), 0.88 (t,  $^3J$  6.44Hz, 6H, 2×-CH<sub>3</sub>); C<sub>59</sub>H<sub>68</sub>O<sub>13</sub> requires C 71.93, H 6.95; found C 71.78, H 6.98 %.

**5-Methoxy bis [4-(*n*-tridecylcarbonyloxyphenyloxycarbonyl)phenylisophthalate], 6.C.3**

Yield 79%, m. p. 114.0°C.  $\nu_{\max}$ : 2922, 2850, 1757, 1741, 1739, 1728, 1726, 1506, 1465, 1377, 1284, 1190  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.64 (t,  $^4J$  1.30 Hz, 1H, Ar-H), 8.30 (d,  $^3J$  8.72 Hz, 4H, Ar-H), 8.00 (d,  $^4J$  1.36 Hz, 2H, Ar-H), 7.41 (d,  $^3J$  8.72 Hz, 4H, Ar-H), 7.24 (d,  $^3J$  8.92 Hz, 4H, Ar-H), 7.15 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 3.99 (s, 3H, Ar-OCH<sub>3</sub>), 2.56 (t,  $^3J$  7.44 Hz, 4H, 2×Ar-OCO-CH<sub>2</sub>-), 1.79-1.72 (quin, 4H, 2×Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.12 (m, 40H, 2 × (-CH<sub>2</sub>)<sub>10</sub>), 0.88 (t,  $^3J$  6.44Hz, 6H, 2×-CH<sub>3</sub>); C<sub>63</sub>H<sub>76</sub>O<sub>13</sub> requires C 72.68, H 7.35; found C 72.59, H 7.45 %.

**5-Methoxy-bis [4-(*n*-pentadecylcarbonyloxyphenyloxycarbonyl)phenylisophthalate], 6.C.4**

Yield 82%, m. p. 114.5°C.  $\nu_{\max}$ : 2922, 2850, 1741, 1739, 1728, 1726, 1604, 1506, 1465, 1238, 1190  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.64 (t,  $^4J$  1.30 Hz, 1H, Ar-H), 8.30 (d,  $^3J$  8.72 Hz, 4H, Ar-H), 8.00 (d,  $^4J$  1.36 Hz, 2H, Ar-H), 7.41 (d,  $^3J$  8.72 Hz, 4H, Ar-H), 7.24 (d,  $^3J$  8.92 Hz, 4H, Ar-H), 7.15 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 3.99 (s, 3H, Ar-OCH<sub>3</sub>), 2.56 (t,  $^3J$  7.44 Hz, 4H, 2×Ar-OCO-CH<sub>2</sub>-), 1.79-1.72 (quin, 4H, 2×Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.26 (m, 48H, 2 × (-CH<sub>2</sub>)<sub>12</sub>), 0.88 (t,  $^3J$  6.44Hz, 6H, 2×-CH<sub>3</sub>); C<sub>67</sub>H<sub>84</sub>O<sub>13</sub> requires C 73.36, H 7.71; found C 73.56, H 7.84 %.

**5-Methoxy bis [4-(*n*-heptadecylcarbonyloxyphenyloxycarbonyl)phenylisophthalate], 6.C.5**

Yield 81%, m. p. 117°C.  $\nu_{\max}$ : 2922, 2852, 1741, 1737, 1730, 1701, 1458, 1377  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.64 (t,  $^4J$  1.30 Hz, 1H, Ar-H), 8.30 (d,  $^3J$  8.72 Hz, 4H, Ar-H), 8.00 (d,  $^4J$  1.36 Hz, 2H, Ar-H), 7.41 (d,  $^3J$  8.72 Hz, 4H, Ar-H), 7.24 (d,  $^3J$  8.92 Hz, 4H, Ar-H), 7.15 (d,  $^3J$  8.96 Hz, 4H, Ar-H), 3.99 (s, 3H, Ar-OCH<sub>3</sub>), 2.57 (t,  $^3J$  7.44 Hz, 4H, 2×Ar-OCO-CH<sub>2</sub>-), 1.79-1.72 (quin, 4H, 2×Ar-OCO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.11 (m, 56H, 2 × (-CH<sub>2</sub>)<sub>14</sub>), 0.88 (t,  $^3J$  6.44 Hz, 6H, 2×-CH<sub>3</sub>); C<sub>71</sub>H<sub>92</sub>O<sub>13</sub> requires

C 73.93, H 8.03; found C 74.28, H 7.98 %.

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