

## Chapter 2

Synthesis and mesomorphic properties of

- (i) **1, 3-Phenylene bis[4-(4-*n*-alkylbiphenyl-4-carbonyloxy)benzoates]**  
Series- 2.I
- (ii) **1, 3-Phenylene bis[4-(4-*n*-alkylbiphenyl-4-carbonyloxy)-2-fluorobenzoates]**  
Series- 2.II
- (iii) **1, 3-Phenylene bis[4-(4-*n*-alkylbiphenyl-4-carbonyloxy)-2-methylbenzoates]**  
Series- 2.III
- (iv) **1, 3-Phenylene bis[4-(4-*n*-alkylbiphenyl-4-carbonyloxy)-2-ethylbenzoates]**  
Series- 2.IV
- (v) **1, 3-Phenylene bis[4-(4-*n*-alkylbiphenyl-4-carbonyloxy)-3-fluorobenzoates]**  
Series- 2.V
- (vi) **1, 3-Phenylene bis[4-(4-*n*-alkylbiphenyl-4-carbonyloxy)-3-methoxybenzoates]**  
Series- 2.VI

## Introduction

The discovery of ferroelectricity by Niori *et al.* [15] in achiral banana-shaped compounds opened up a new sub-field of liquid crystals namely banana liquid crystals. This discovery led to an intense activity of synthesizing new achiral bent-core materials and studying their mesophase behaviour. The interesting concept of layer chirality by achiral molecules has been explained by Link *et al.* [18] and Heppke and Moro [19]. Link *et al.* [18] have carried out intricate experiments on the mesophase exhibited by achiral bent-core compounds and explained beautifully the chirality in the smectic banana (B) phase. Because of rotational hindrance over the long molecular axis, these molecules are packed in layers along the bend direction leading to a polar order. These molecules are tilted and arranged in layers, thus breaking the symmetry from  $C_{2v}$  to  $C_2$ . The mirror image of the co-ordinate system defined by the polar, tilt and layer planes is non-superimposable, thus leading to a layer chirality, which in turn leads to chiral mesophases.

Since 1996, hundreds of bent-core compounds have been reported in the literature. The bend angle between the two hydroxyl groups of resorcinol is  $120^\circ$  and hence is an obvious choice for the chemists to synthesize compounds derived from it with different chemical architecture. Many of the compounds are symmetrical about the central phenyl ring and are usually terminated with two (n-alkyl/ n-alkoxy) chains. The bridging groups used are -CH=N-, -COO-, -N=N-, -CH=CH-, -C $\equiv$ C- etc. [28]. A review of the literature indicates that normally five phenyl rings are required for generating B phases and most of the compounds reported are five-ring Schiff's bases [15, 20, 28, 47]. Seven-ring compounds exhibiting B phases are also known but are very few in number [29, 56, 57].

## Effect of lateral substituents

The influence of lateral substituents is an important factor in the study of the properties of liquid crystals. Primarily, lateral substituents are used to reduce the melting and clearing temperatures. Apart from these, lateral substituents may be used to effectively modify the physical parameters of liquid crystals. The position, size and polarity of the substituents play an important role in stabilizing / destabilizing / inducing mesophases. In bent-core compounds one can have substituents on the

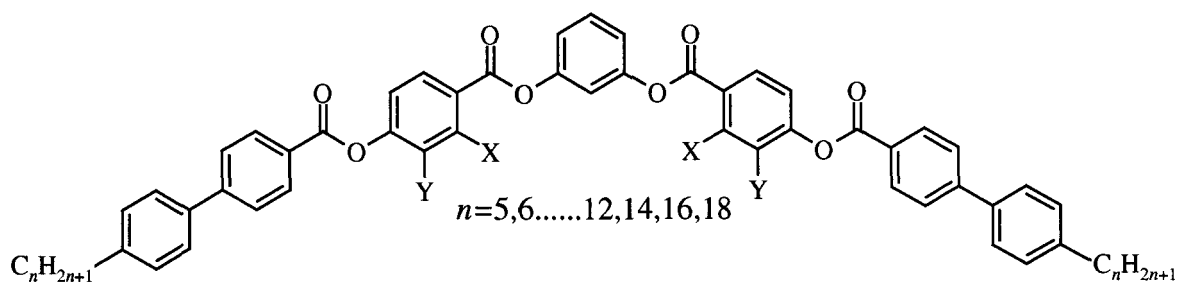
1) central phenyl ring, 2) middle phenyl rings of the arms, 3) outer phenyl rings.

A majority of the compounds reported so far have substituents either on the central phenyl ring or outer phenyl ring. The number of compounds which have a lateral substituent in the arms of the bent-core molecules, are very few [29, 57]. More over the thermal range of the mesophases exhibited by five-ring esters is rather small and therefore, it was decided to investigate the influence of different lateral substituents on the mesomorphic properties of seven-ring compounds.

In this chapter, the synthesis and characterization of the mesophases exhibited by several compounds derived from resorcinol and containing seven-rings in the core are discussed. The effects of different lateral substituents in the middle phenyl ring of the wings of the bent-core molecules on the mesophases are examined. This kind of study enables one to understand the relationships between molecular structure and mesomorphic behaviour in bent-core compounds. In this study, the unsubstituted or the parent compounds are required for comparison. These seven-ring unsubstituted compounds were chosen because they have large mesophase range ( $-100^{\circ}\text{C}$ ), which allows one to examine the effect of lateral substituents of various dimensions. For this purpose two sets of substituents were chosen.

- 1) Electron withdrawing substituents such as fluorine.
- 2) Electron donating substituents such as methyl, ethyl or a methoxy group.

The influence of the substituent in the two available positions (X and Y) of the middle phenyl ring of the arms of the bent-core compounds have been studied. The compounds investigated have the general molecular structure 2.1 shown below.



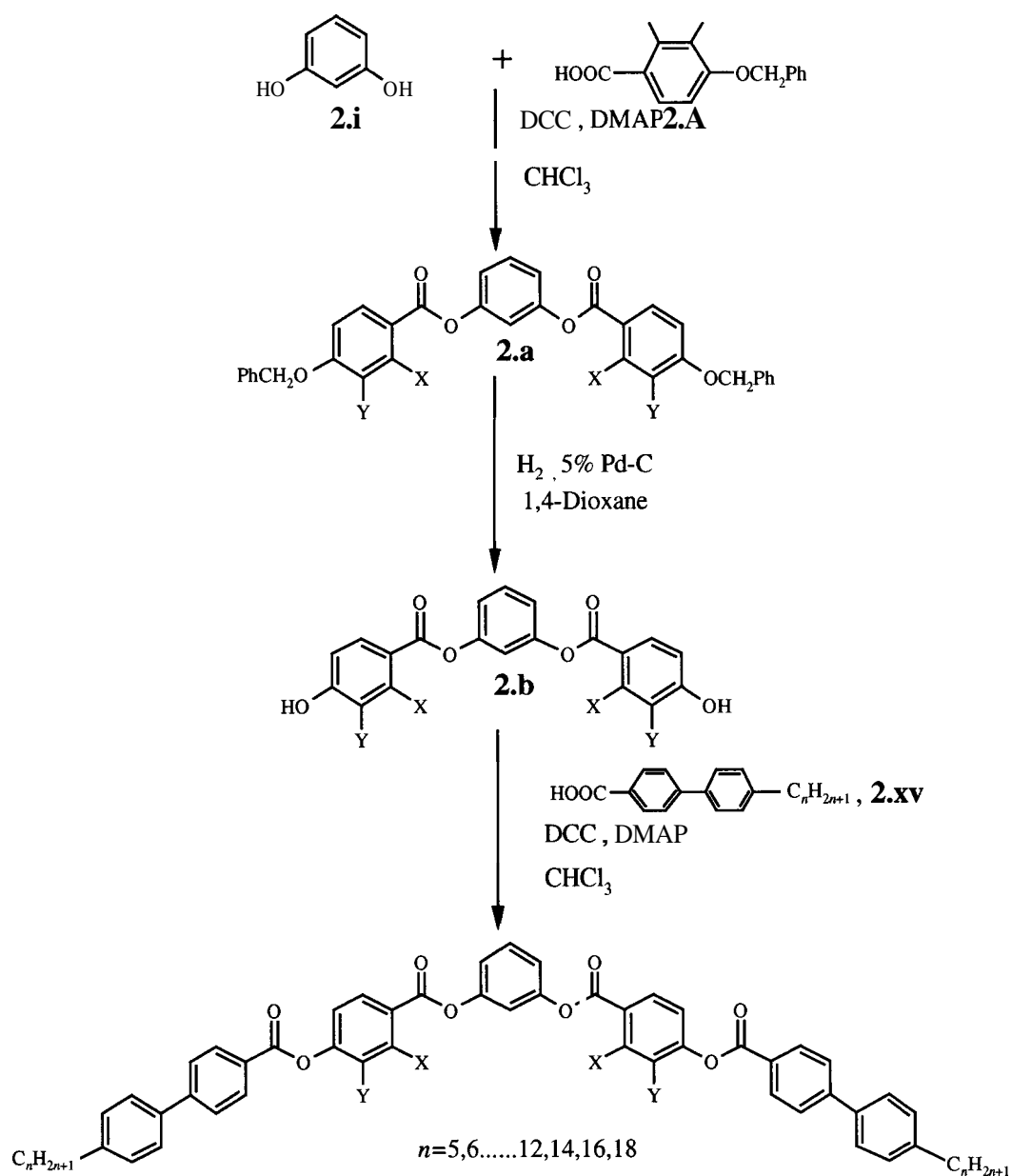
**Structure 2.I**

X= H,	Y= H	Series- 2.1
X= F,	Y= H	Series- 2.11
X= CH <sub>3</sub> ,	Y= H	Series- 2.111
X= C <sub>2</sub> H <sub>5</sub> ,	Y= H	Series- <b>2.IV</b>
X= H,	Y= F	Series- 2.V
X= H,	Y=OCH <sub>3</sub>	Series- <b>2.VI</b>

## Synthesis

The banana-shaped compounds belonging to the six different series (series 2.1 to **2.VI**) were synthesized following a pathway shown in scheme 2.1. Analytical grade resorcinol was obtained commercially and used without further purification. 4-Benzyloxybenzoic acid (**2.A.i**), 2-fluoro-4-benzyloxybenzoic acid (**2.A.ii**) and 3-fluoro-4-benzyloxybenzoic acid (**2.A.iii**) were prepared following procedures described in the literature [59-61].

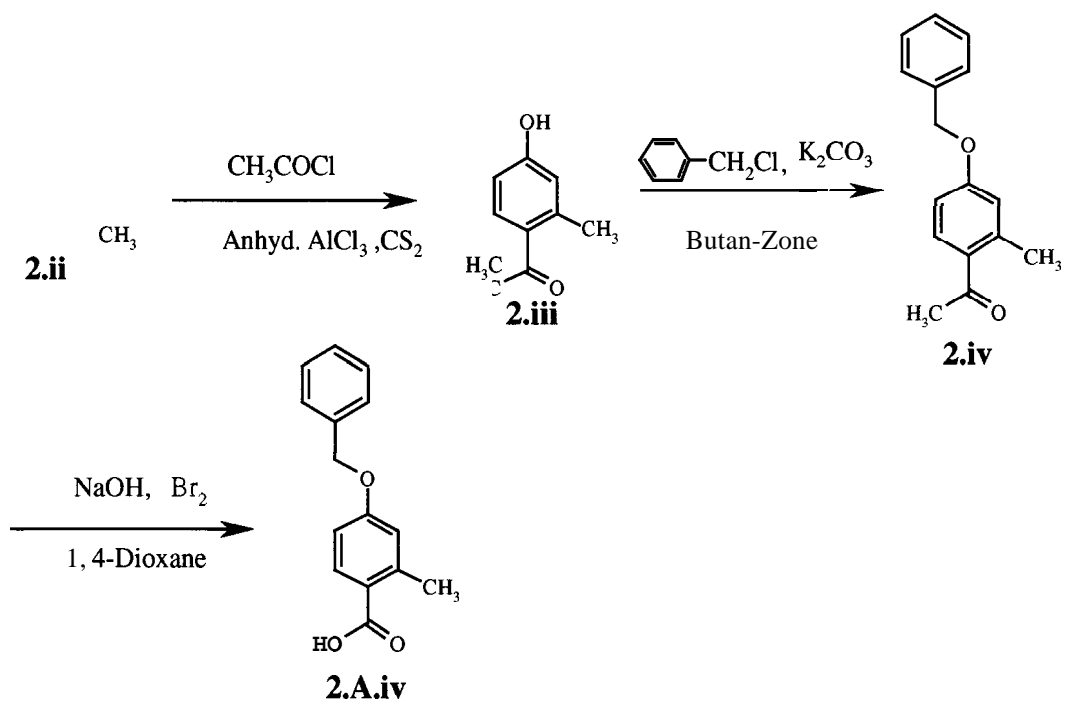
2-Methyl-4-benzyloxybenzoic acid (**2.A.iv**) and 2-ethyl-4-benzyloxybenzoic acid (**2.A.v**) were prepared according to procedure described in the literature [69]. 3-Methoxy-4-benzyloxybenzoic acid (**2.A.vi**) was prepared following a similar procedure that described for 4-benzyloxybenzoic acid [59]. The synthetic pathway used for the preparation of 2-methyl-4-benzyloxybenzoic acid, 2-ethyl-4-benzyloxybenzoic acid and 3-methoxy-4-benzyloxybenzoic acid are shown in schemes 2.2, 2.3 and 2.4 respectively. 4-*n*-Alkylbiphenyl-4-carboxylic acid, (**2.x.v**) was synthesized according to a procedure described previously [70], and the synthetic route is shown in scheme 2.5. The melting points obtained for cognate preparations along with the reported values are summarized in table 2.10. Resorcinol was condensed with an appropriate 4-benzyloxybenzoic acid in the presence of a dehydrating agent (DCC) and catalyst (DMAP) in dry chloroform. The resultant dibenzyloxy ester was purified and subjected to hydrogenolysis in the presence of 5% Pd-C in 1, 4-dioxane. The bisphenol thus obtained was purified and esterified with a 4-*n*-alkylbiphenyl-4-carboxylic acid to obtain the target materials.



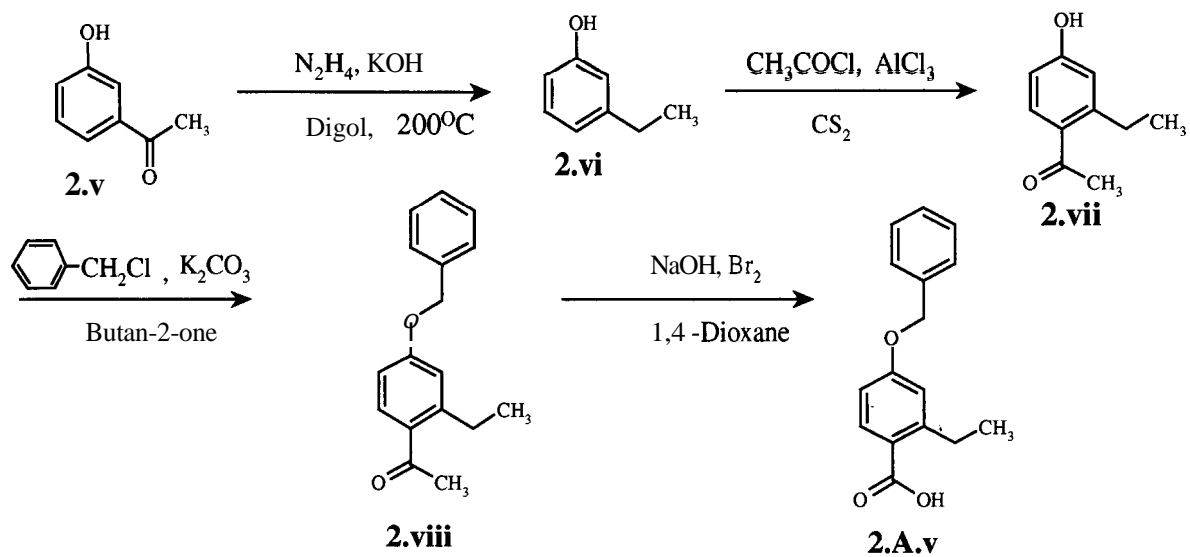
**Structure 2.1**

<b>2.A</b>	X= H,	Y= H	4-Benzyloxybenzoic acid,	<b>2.A.i</b>
	X= F,	Y= H	<b>2-Fluoro-4-benzyloxybenzoic acid,</b>	<b>2.A.ii</b>
	X= CH <sub>3</sub> ,	Y= H	2-Methyl-4-benzyloxybenzoic acid,	<b>2.A.iii</b>
	X= C <sub>2</sub> H <sub>5</sub> ,	Y= H	<b>2-Ethyl-4-benzyloxybenzoic acid,</b>	<b>2.A.iv</b>
	X= H,	Y= F	3-Fluoro-4-benzyloxybenzoic acid,	<b>2.A.v</b>
	X= H,	Y=OCH <sub>3</sub>	3-Methoxy-4-benzyloxybenzoic acid,	<b>2.A.vi</b>

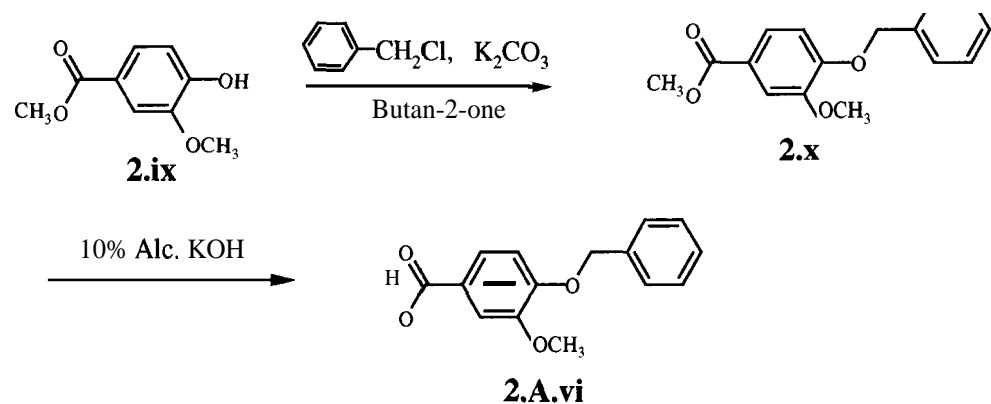
**Scheme 2.1: Synthetic pathway used to obtain the bent-core compounds of series 2.1- 2.VI.**



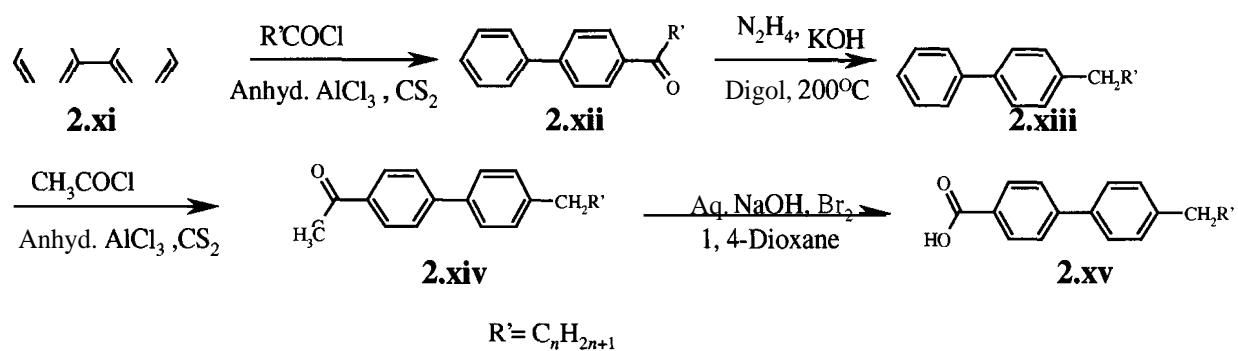
**Scheme 2.2: Synthetic route employed for the preparation of 2-methyl-4-benzyloxybenzoic acid.**



**Scheme 2.3: Synthetic route employed for the preparation of 2-ethyl-4-benzyloxybenzoic acid.**



**Scheme 2.4: Synthetic route employed for the preparation of 3-methoxy-4-benzyloxybenzoic acid.**



**Scheme 2.5: Synthetic route employed for the preparation of 4-n-alkylbiphenyl-4-carboxylic acid.**

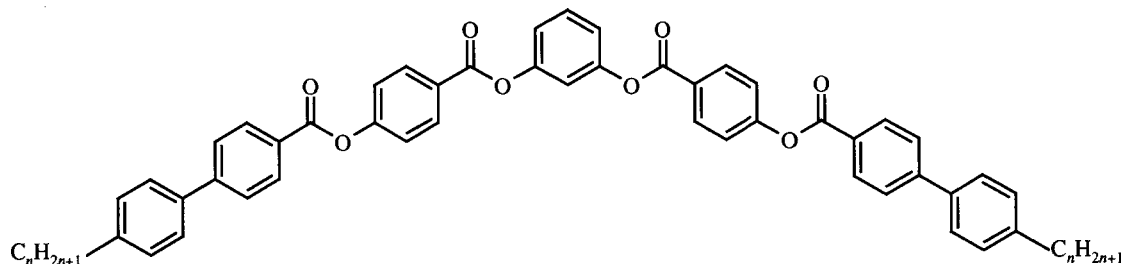
## Results and discussion

The phase transition temperatures and the associated enthalpies for the six series of compounds viz. **2.I-2.VI** are summarized in tables **2.1-2.6** respectively. The mesophases exhibited by all the compounds could be easily identified from their characteristic optical textures. Three different types of mesophases were observed in all the six series of compounds. The phases **B<sub>6</sub>-B<sub>1</sub>-B<sub>2</sub>** were observed on increasing the terminal n-alkyl chain length.

In order to assess the effect of lateral substituents on the mesophases of these banana-shaped compounds, it would be useful, initially, to look at the trend in the mesomorphic behaviour of the unsubstituted parent compounds, particularly along a homologous series. The transition temperatures and the associated enthalpies for the unsubstituted parent compounds are summarized in table **2.1**. As can be seen, only one compound **2.A.1** is dimesomorphic. On cooling the isotropic liquid of this compound, batonnets appear and coalesce into a characteristic fan-shaped texture and this mesophase has a thermal range of 11°C. Sometimes, a schlieren texture was also observed. No homeotropic region could be observed, which excludes the possibility of this mesophase being a smectic **A** phase. Based on this observation (as well as XRD studies) the mesophase has been identified as a **B<sub>6</sub>** phase. On cooling the sample to 245°C, a marginal change in the texture could be observed and the associated enthalpy value for the transition was 0.4 kJ mol<sup>-1</sup>. If the **B<sub>6</sub>** phase has schlieren texture, then at the transition it will transform to a mosaic texture. The texture is characteristic of a columnar **B<sub>1</sub>** phase and has been assigned as such. Also, such a transition has already been reported in the literature [29]. Compounds **2.A.2** to **2.A.6** are monomesomorphic. On cooling from the isotropic phase the mesophase exhibited either a mosaic or colourful spherulitic texture. The enthalpy value for the mesophase to isotropic phase was about 24 kJ mol<sup>-1</sup>. These textural features and enthalpy values indicated that the mesophase is indeed **B<sub>1</sub>**. A typical photomicrograph of the spherulitic pattern obtained for the **B<sub>1</sub>** mesophase of compound **2.A.5** is shown in figure **2.1**. To confirm the structure of this mesophase XRD studies were carried out. For example, the diffraction pattern of compound **2.A.5** showed two reflections in the small angle region at  $d_1=32.7\text{Å}$  and  $d_2=24.8\text{Å}$  which can be indexed to (11) and (02) reflections respectively with lattice parameters  $a=43.5\text{Å}$  and  $b=49.6\text{Å}$ . This is similar to patterns observed for the **B<sub>1</sub>** phase of standard compounds [28]. The X-ray angular intensity profile obtained for compound **2.A.5** is shown in figure **2.2**. Thus, this mesophase has been identified as a **B<sub>1</sub>** mesophase.



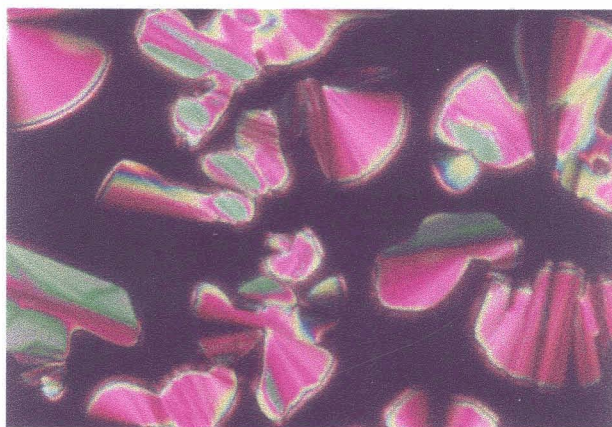
**Table 2.1: Transition temperatures (°C) and the associated enthalpies (kJ mol<sup>-1</sup>) for compounds of series 2.1**



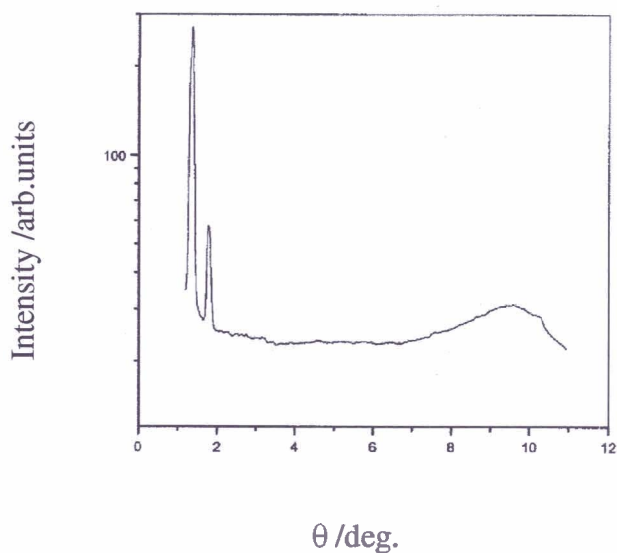
Compound	n	Cr	B <sub>2</sub>	B <sub>1</sub>	B <sub>6</sub>	I	
<b>2.A.1</b>	5	.	175.0	-	.	246.0	.
			36.2			0.4	257.0
<b>2.A.2</b>	6	.	165.0	-	.	240.0	-
			39.6			23.6	
<b>2.A.3</b>	7	.	163.5 <sup>a</sup>	-	.	235.0	-
			50.7			23.5	
<b>2.A.4</b>	8	.	153.5	-	.	226.0	-
			36.1			23.8	
<b>2.A.5</b>	9	.	141.0	-	.	219.0	-
			51.0			24.2	
<b>2.A.6</b>	10	.	159.0	-	.	211.0	-
			42.9			23.8	
<b>2.A.7</b>	11	.	151.0 <sup>a</sup>	.	209.0	-	-
			61.4		25.5		
<b>2.A.8</b>	12	.	121.0 <sup>a</sup>	.	209.0	-	-
			53.1		27.0		
<b>2.A.9</b>	14	.	118.0	.	208.5	-	-
			45.1		27.7		
<b>2.A.10</b>	16	.	117.5	.	206.5	-	-
			43.8		28.7		
<b>2.A.11</b>	18	.	117.0	.	204.0	-	-
			48.1		28.5		

Key: Cr:crystalline phase; B<sub>1</sub>: two-dimensional rectangular banana phase; B<sub>2</sub>: lamellar antiferroelectric banana phase; B<sub>6</sub>: intercalated smectic banana phase; I: isotropic phase; a: has crystal-crystal transition and enthalpy denoted is the sum of all transitions. (Nomenclature as adopted at the International Workshop on Banana-Shaped Liquid Crystals: "Chirality by Achiral Molecules" held in Berlin, December 1997).

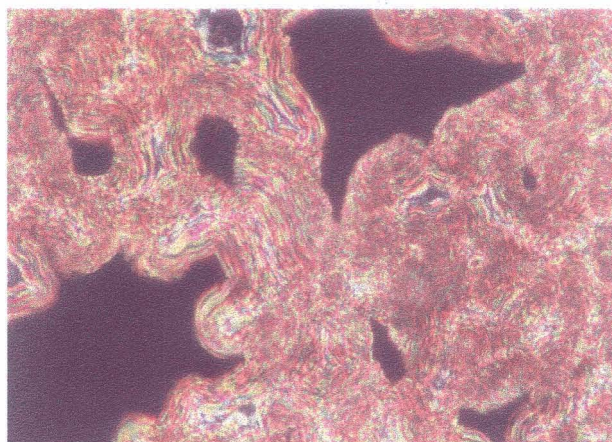
On increasing the terminal **alkyl** chain length (compounds **2.A.7** and **2.A.8**), the mesophase **behaviour** changed. For example, on cooling the isotropic phase of compound **2.A.8**, fingerprint or fringe pattern was observed. This is a characteristic feature of a  $B_2$  phase. A typical photomicrograph of a fringe pattern obtained for compound **2.A.8** is shown in figure **2.3**. XRD studies on compound **2.A.8** gave four orders of reflection in the small angle region which were in the ratio of  $1:1/2:1/3:1/4$  indicating that the mesophase was smectic. The X-ray **diffractogram** showing smectic reflections for compound **2.A.8** is shown in figure **2.4**.



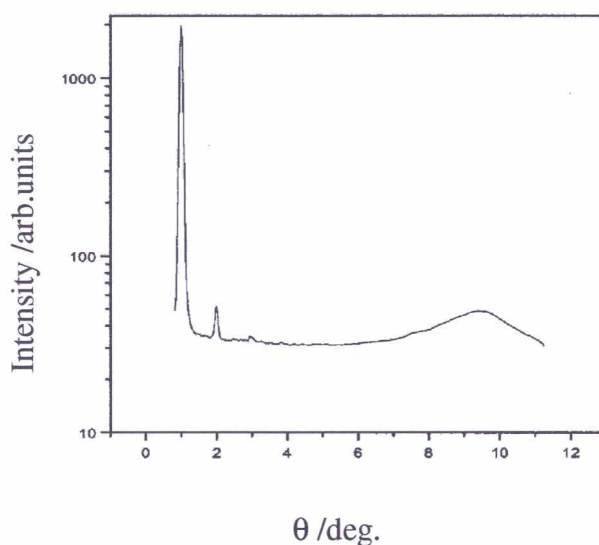
**Figure 2.1:** An optical photomicrograph of spherulitic pattern obtained for  $B_1$  phase of compound **2.A.5**.



**Figure 2.2:** The X-ray angular intensity profile obtained for  $B_1$  phase of compound **2.A.5**.



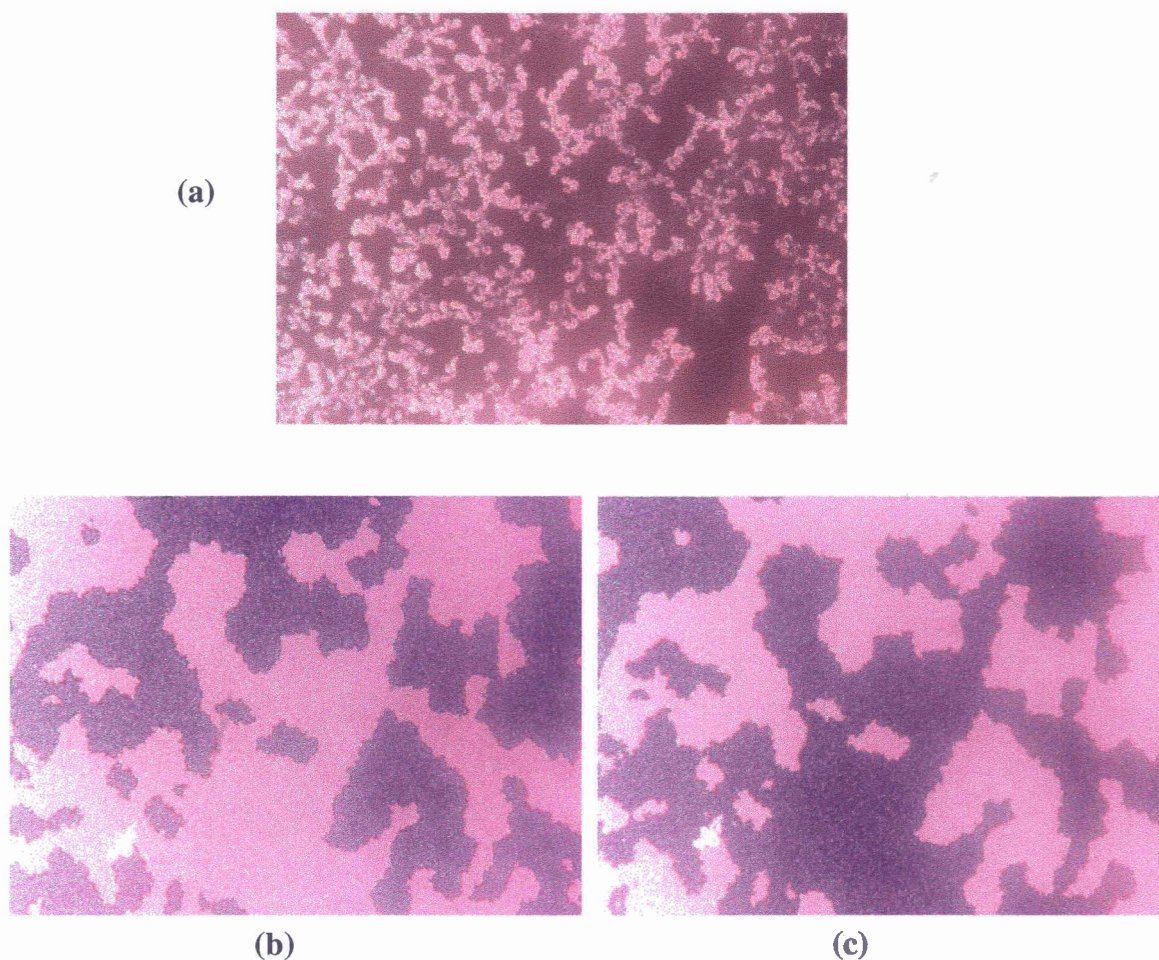
**Figure 2.3:** An optical photomicrograph of fringe pattern obtained for  $B_2$  phase of compound 2.A.8.



**Figure 2.4:** The X-ray angular intensity profile obtained for  $B_2$  phase of compound 2.A.8.

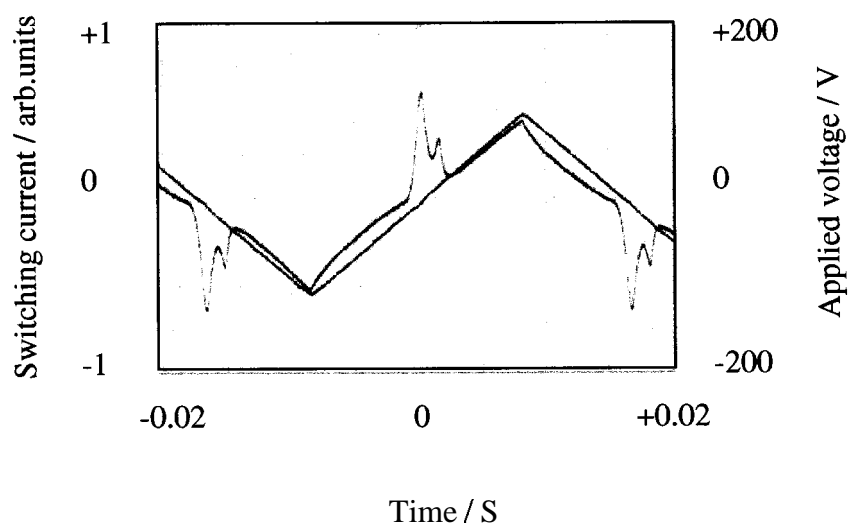
In order to examine the electro-optical **behaviour** of this mesophase, a triangular-wave electric field experiment was carried out on the mesophase of compound **2.A.8**. The two polarization current peaks per half cycle indicated that the mesophase has an **antiferroelectric** ground state. However, on increasing the **alkyl** chain length further, the mesophase appeared in a

different form (compounds 2.A.9 to **2.A.11**) under a polarizing microscope. On slow cooling of the isotropic phase of compound 2.A.9, small-fractal domains appeared which coalesced to give a grainy texture. A typical texture observed is shown in figure 25 (a). When the polarizer and analyzer of the microscope were crossed one could see the dark texture. However, when the analyzer was rotated by  $5^\circ$ , one could see some domains appearing bright (figure 25 (b)) and by rotating the analyzer in the opposite direction by the same degree from the original position, these domains became darker (figure 25 (c)).



**Figure 25: Optical textures of  $B_2$  phase of compound 2A.9 with polarizers making an angle of  $5^\circ$ ; (a) the fractal growth of mesophase from the isotropic phase; (b) chiral domains of the  $B_2$  mesophase; (c) the same region obtained after rotating the analyzer in counter clock-wise direction.**

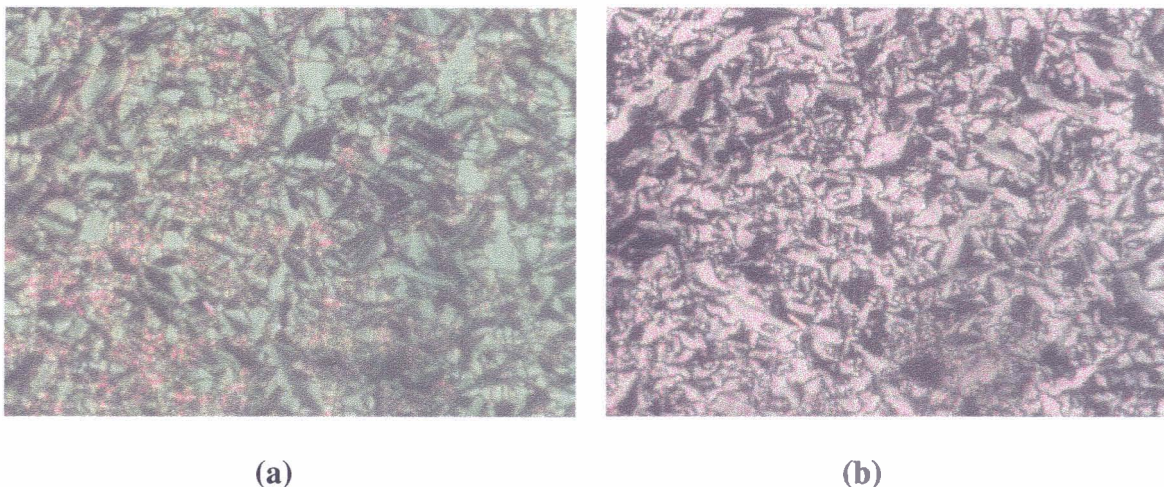
This clearly indicates that there are two domains in the same sample having opposite handedness. This  $5^\circ$  is the optical rotation of the mesophase. The mesophase is highly viscous and difficult to displace the cover slip. The X-ray data of the mesophase of these compounds suggests a lamellar order. (The  $d$  value for compound **2.A.9** is given in table **2.7**). The electro-optical studies of compound **2.A.9** can be summarized as follows. When a sample of compound **2.A.9** was cooled from the isotropic phase in a cell treated for homogeneous alignment of the sample and a thickness  $8.7\mu\text{m}$ , chiral domains of opposite handedness of low birefringence were observed. However, when the compound was cooled slowly from the isotropic phase under a triangular-wave electric field, at  $200V_{pp}$  two polarization current peaks were observed per half cycle indicating an antiferroelectric ground state. The current response trace obtained for compound **2.A.9** is shown in figure **2.6**. When the sample was observed under a polarizing microscope highly birefringent texture was observed which is due to a synclinic molecular arrangement caused by the influence of external electric field ( $\text{SmC}_s\text{P}_F$ ).



**Figure 2.6: Switching current response obtained for the mesophase of compound 2.A.9 by applying a triangular voltage ( $200V_{pp}$ ,  $30\text{Hz}$ ), sample thickness  $8.7\mu\text{m}$ ;  $180^\circ\text{C}$ ; saturated polarization  $\approx 321\text{ nC cm}^{-2}$ .**

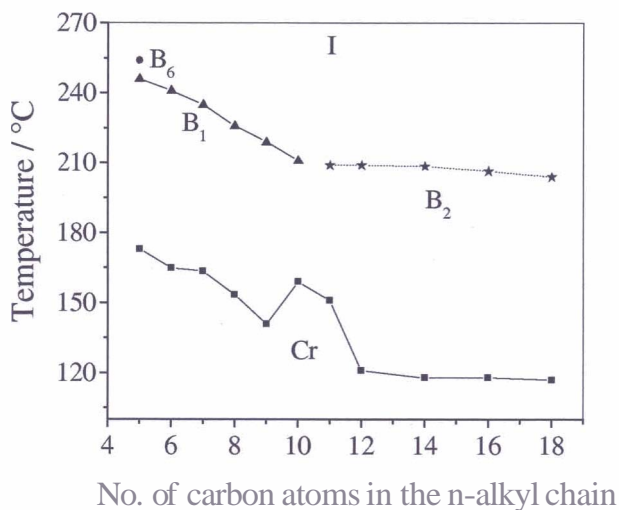


However, when the field was turned off the texture became less birefringent which is due to the **antclinic** nature of the bent-core molecules in the ground state ( $\text{SmC}_A\text{P}_A$ ). Thus, the ground state texture of the compound is homogeneously **chiral** ( $\text{SmC}_A\text{P}_A$ ). The optical photomicrographs obtained under a triangular-wave electric field and without the field are shown in figure 2.7.



**Figure 2.7: Optical photomicrographs obtained for the mesophase of compound 2.A.9 (a) under a triangular-wave electric field;(b) without the applied field.**

A plot of the transition temperatures as a function of the length of the terminal **alkyl** chain for this series of compounds is shown in figure 2.8.



**Figure 2.8: A Plot of transition temperatures Vs the number of carbon atoms in the *n*-alkyl chain for the compounds of series 2.1.**

One can see that the  $B_1$  to isotropic phase temperatures fall on a smooth curve, on ascending the series. The  $B_2$  to isotropic phase transition points also fall on a smooth curve. It can be seen from the graph that the clearing temperatures of the three compounds with domains of opposite chirality also follow this curve. This indicates that although the texture is different from that normally seen for the  $B_2$  phase, the mesophase of these three compounds can be classified as  $B_2$  (supported by XRD and electro-optical studies). Similar textures have been observed previously by Heppke *et al.* [46] and Thisayukta *et al.* [55]. While the sulphur containing compounds [46] show switching behaviour, those substituted by a central naphthylene unit are smectic and switching characteristics have not been reported [55].

As pointed by Tschierske and Dantlgraber [22] these domains of opposite handedness can be explained by

- 1) Helical arrangement of the molecules with the helical axis perpendicular to the substrate surfaces. In this structure, the pitch of the helix exceeds the wavelength of the visible light and the helical twist changes in different domains.
- 2) The helical axis can be either perpendicular to the layer plane ( $Sm\ C^*$  like) or parallel to the layer planes (TGB-like).

In both these cases the mesophase is optically uniaxial. However, on rotating the polarizer or analyzer by  $5^\circ$  one can observe the less intense textures. Recently, there have been two reports, which explain the occurrence of chiral domains of opposite handedness for a  $B_2$  mesophase in different systems [67, 68].

Ortega *et al.* [67] have reported the segregation of chiral domains with opposite gyrations for the  $B_2$  phase and explained the isotropic optical texture when the polarizer and the analyzer were crossed. The optical textures were interpreted in terms of  $SmC_A P_A$  structure in small domains with random orientations. The schematic representation of the small domains responsible for the optical isotropic texture (figure 2.9 (a)) and the helicoidal arrangement of the bent-core molecules in  $SmC_A P_A$  phase have been proposed and are shown in figure 2.9 (b).



After Ortega *et al.* [67]

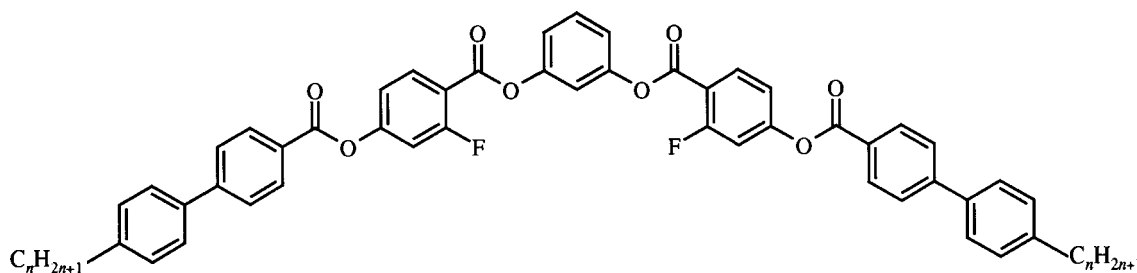
**Figure 2.9: (a) Schematic representation of small domains that are present in a SmC<sub>A</sub>P<sub>A</sub> structure. (b) helicoidal arrangement described by the molecular wings of bent-core molecules in the homochiral antiferroelectric configuration.**

The transition temperatures together with the associated enthalpies for the compounds of series 2.11 (X = F, Y = H) are collected in table 2.2. The effect of the fluoro substituent, which is *ortho* to the carbonyl group of the middle phenyl ring, on the mesophases is rather interesting. All the three mesophases observed in the parent compounds are retained. The melting and clearing temperatures are reduced in every case. While the temperature range of the **B**<sub>6</sub> phase has been reduced from 11°C to 2°C (compounds 2.A.1 and **2.B.1**), those for the **B**<sub>1</sub> and **B**<sub>2</sub> phases are increased. Compounds 2.B.2-2.B.5 show similar kind of optical features (mosaic texture) when cooled from the isotropic phase. This is a typical feature of the **B**<sub>1</sub> phase. The XRD studies on the representative compound (2.B.4) confirms the two-dimensional lattice of the **B**<sub>1</sub> phase and the d-spacings obtained are given in table 2.7. Compound 2.A.6 exhibits a **B**<sub>1</sub> phase while the corresponding fluoro substituted compound 2.B.6 shows a **B**<sub>2</sub> phase with a thermal range of 80°C. Compounds 2.B.6-2.B.8 show fingerprint / fringe texture on cooling from the isotropic phase which is a characteristic feature of the **B**<sub>2</sub> phase. As observed in series 2.1, compounds 2.B.9- 2.B.12 exhibit a grainy texture with domains of opposite handedness as described earlier. The XRD studies on compound 2.B.9 reveal a smectic ordering of the mesophase and the d-spacings obtained are given in table 2.7. As explained earlier, the mesophase of these three compounds has been designated as a **B**<sub>2</sub> phase.

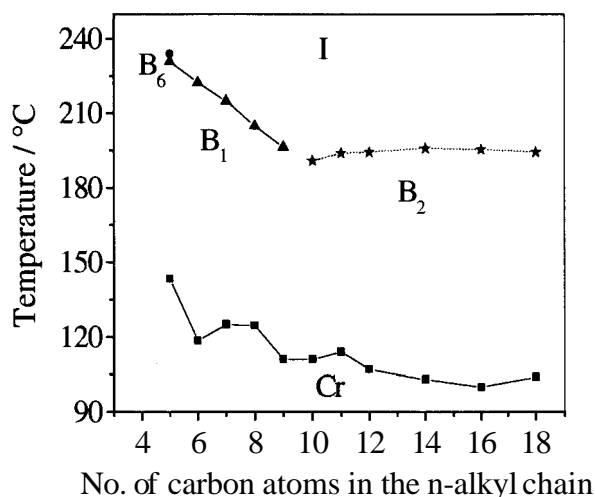


A plot of the transition temperatures against the number of carbon atoms in the alkyl chain for the compounds of series **2.11** is shown in figure **2.10**. Here also one can see the clearing transition points falling on two curves, one for the **B<sub>1</sub>** phase and the other for the **B<sub>2</sub>** phase. The slopes of the two curves are very similar to those observed for homologues of series **2.1**.

**Table 2.2: Transition temperatures (°C) and the associated enthalpies (kJ mol<sup>-1</sup>) for compounds of series 2.11**



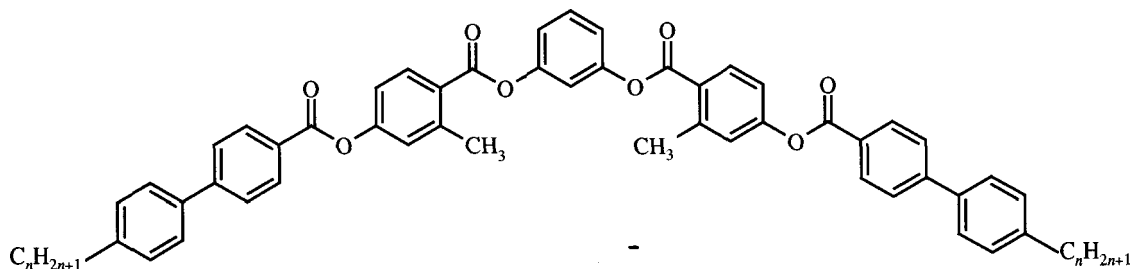
Compound	n	Cr	B <sub>2</sub>	B <sub>1</sub>	B <sub>6</sub>	I
<b>2.B.1</b>	5	. 143.5 29.6	-	. 232.0 0.02	. 234.0 16.9	.
<b>2.B.2</b>	6	. 134.0 37.6	-	. 222.5 21.6	-	.
<b>2.B.3</b>	7	. 125.0 29.7	-	. 215.0 22.5	-	.
<b>2.B.4</b>	8	. 124.5 29.8	-	. 205.0 22.6	-	.
<b>2.B.5</b>	9	. 110.0 28.2	-	. 196.5 21.5	-	.
<b>2.B.6</b>	<b>10</b>	. 111.0 29.2	. 191.0 22.9	-	-	. [29]
<b>2.B.7</b>	11	. 114.0 31.8	. 194.0 23.0	-	-	. [29]
<b>2.B.8</b>	12	. 107.0 50.4	. 194.5 22.5	-	-	. [29]
<b>2.B.9</b>	14	. 103.0 72.6	. 196.0 27.7	-	-	.
<b>2.B.10</b>	16	. 100.0 85.1	. 195.5 29.0	-	-	.
<b>2.B.11</b>	18	. 104.0 74.0	. 194.5 29.9	-	-	.



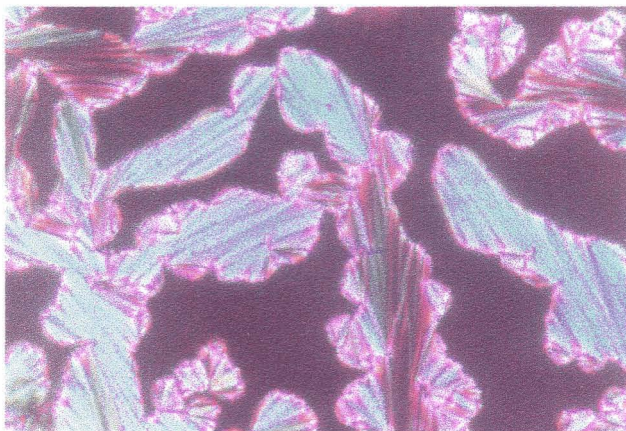
**Figure 2.10: A Plot of transition temperatures Vs the number of carbon atoms in the n-alkyl chain for the compounds of series 2.11.**

In table 2.3, the transition temperatures and the associated enthalpies for the compounds of series **2.III** are summarized. The effect of the lateral methyl group, which is *ortho* to the carbonyl group, can be seen here. There is a general reduction in the melting and clearing points as compared to the unsubstituted compounds. In addition, one can see that the **B<sub>1</sub>** phase of compounds 2.A.2 and 2.A.3 is suppressed and the **B<sub>6</sub>** phase is induced in compounds 2.C.2 and 2.C.3. All the three compounds (2.C.1-2.C.3) are dimesomorphic. On slow cooling the isotropic liquid of compound 2.C.3, batonnets start to appear and eventually coalesce to a focal-conic texture. No homeotropic region was observed. This is a characteristic feature of a **B<sub>6</sub>** mesophase. On cooling this **B<sub>6</sub>** mesophase to 174°C, a transition took place to a **B<sub>1</sub>** mesophase. No major change was observed in the focal-conic texture. However, the transition can be clearly seen on a DSC thermogram. Typical textures growing from the isotropic liquid and the completely formed focal-conic texture exhibited by compound 2.C.3 are shown in figures 2.11 and 2.12 respectively. These two mesophases have also been investigated by XRD studies. The X-ray diffraction pattern of compound 2.C.3 at 180°C showed a diffuse peak in the wide angle region with a spacing of about 4.8Å which is indicative of a liquid-like in-plane order. In the small angle region, two peaks were observed which are in the ratio 1:2, indicating a lamellar ordering and can be indexed to (01), (02) reflections.

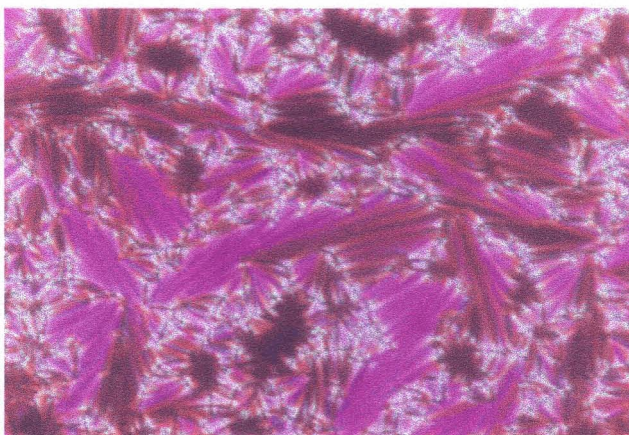
**Table 2.3: Transition temperatures (°C) and the associated enthalpies (kJ mol<sup>-1</sup>) for compounds of series 2.III**



Compound	<i>n</i>	Cr	B <sub>2</sub>	B <sub>1</sub>	B <sub>6</sub>	I	
<b>2.C.1</b>	5	.	143.0 <sup>a</sup>	-	(. 127.0)	. 201.0	.
			52.3		0.02	13.4	
<b>2.C.2</b>	6	.	143.5 <sup>a</sup>	-	. 155.0	. 190.0	.
			43.3		0.11	14.5	
<b>2.C.3</b>	7	.	118.5	-	. 175.0	. 182.0	.
			30.9		0.12	15.6	
<b>2.C.4</b>	8	.	104.0	-	. 172.0	-	.
			28.0		18.6		
<b>2.C.5</b>	9	.	101.0	-	. 167.5	-	.
			24.8		19.9		
<b>2.C.6</b>	10	.	119.5 <sup>a</sup>	-	. 162.0	-	.
			39.6		19.9		
<b>2.C.7</b>	11	.	112.5	-	. 157.0	-	.
			40.5		21.6		
<b>2.C.8</b>	12	.	115.0 <sup>a</sup>	. 154.5	-	-	.
			61.9	23.1			
<b>2.C.9</b>	14	.	103.0	. 156.5	-	-	.
			28.6	24.2			
<b>2.C.10</b>	16	.	103.5 <sup>a</sup>	. 156.0	-	-	.
			74.1	25.0			
<b>2.C.11</b>	18	.	103.0	. 155.0	-	-	.
			84.8	24.2			



**Figure 2.11:** An optical photomicrograph showing the B<sub>6</sub> mesophase growing from the isotropic phase of compound 2.C.3.



**Figure 2.12:** An optical photomicrograph of the focal-conic texture of B<sub>6</sub> mesophase obtained for compound 2.C.3.

The  $d$  value corresponding to the first reflection in the small angle region was  $22.9\text{\AA}$ , which is about half the molecular length. The molecular length was measured by assuming the  $n$ -alkyl chain to be in the most extended all trans conformation. This suggests an intercalated structure for the mesophase as also reported by Shen *et al.* [27] and Pelzl *et al.* [28]. A typical X-ray angular intensity profile obtained for the mesophase of compound **2.C.3** at  $180^\circ\text{C}$  is shown in figure 2.13. This mesophase with a focal-conic texture has been identified as a  $B_6$  phase. On further cooling to  $165^\circ\text{C}$ , an additional reflection in the small angle region at  $d= 24.8\text{\AA}$ , appeared and can be indexed to (11) reflection of a two-dimensional rectangular lattice. The XRD patterns obtained in both  $B_6$  and  $B_1$  phases are shown in figure 2.14 (a) and (b) respectively.

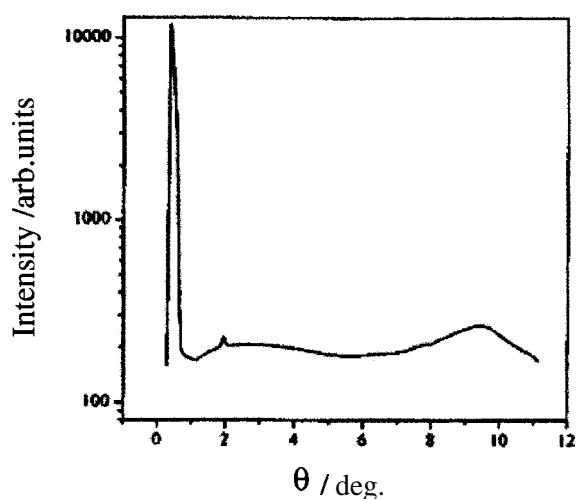


Figure 2.13: The X-ray angular intensity profile of an unoriented sample of compound **2.C.3** at  $180^\circ\text{C}$ .

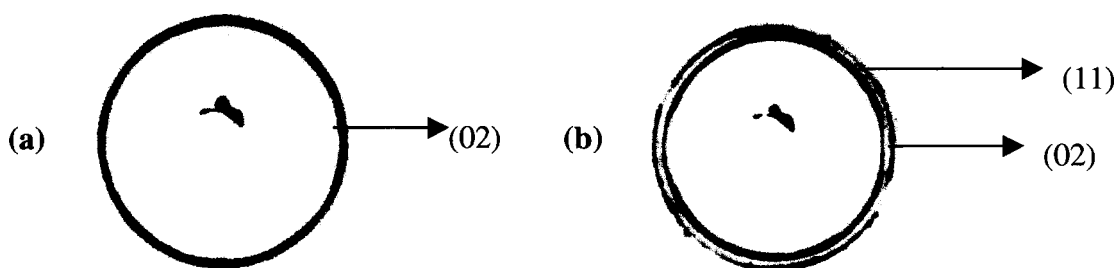
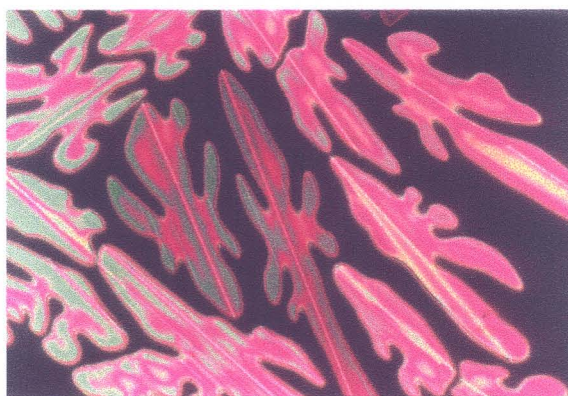


Figure 2.14: An X-ray diffraction pattern of (a)  $B_6$  phase at  $180^\circ\text{C}$  and (b)  $B_1$  phase at  $150^\circ\text{C}$  of compound **2.C.3**.

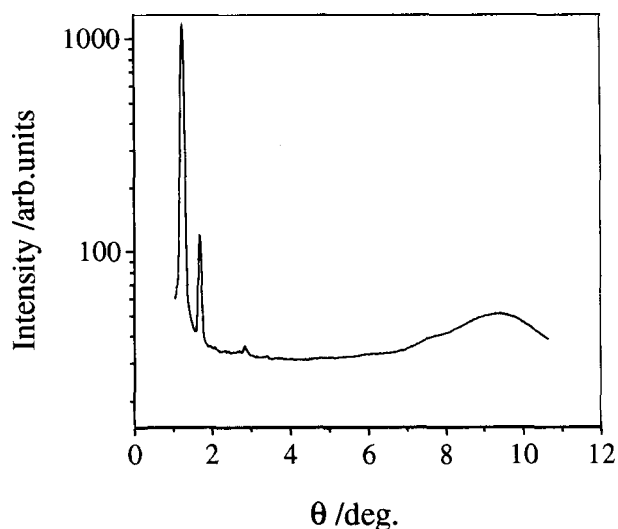
The compounds **2.C.4-2.C.7** show similar type of mesophase on slow cooling from the isotropic phase. Normally, a mosaic texture was observed on cooling. A typical texture growing from the isotropic phase of compound **2.C.7** is shown in figure **2.15**.



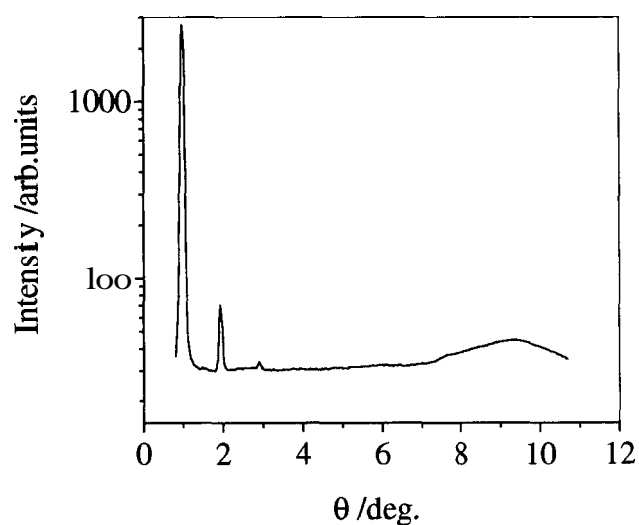
**Figure 2.15:** A photomicrograph of the mosaic texture growing from the isotropic phase of compound **2.C.7**.

In order to examine the structure of the mesophase, XRD studies were carried out on non-oriented samples. The XRD pattern of an unoriented sample of compound **2.C.7** showed three reflections in the small angle region with  $d_1 = 35.5\text{\AA}$ ,  $d_2 = 26.1\text{\AA}$  and  $d_3 = 15.8\text{\AA}$  which can be indexed as (11), (02) and (31) reflections of a two-dimensional rectangular lattice. The lattice parameters are  $a = 48.6\text{\AA}$  and  $b = 52.2\text{\AA}$ . From the mosaic texture and the XRD data, this phase has been identified as a  $B_1$  mesophase. The X-ray angular intensity profile obtained for the mesophase of this compound is shown in figure **2.16**.

The compounds **2.C.8-2.C.11** are monomesomorphic and show fingerprint or fringe texture on cooling the isotropic phase. This is one of the characteristic textural features of the smectic antiferroelectric  $B_2$  phase. To confirm the smectic ordering in the mesophase, XRD studies were carried out. The diffraction pattern obtained for compound **2.C.8** at  $140^\circ\text{C}$  showed three reflections in the small angle region with  $d$  values of  $45.5\text{\AA}$ ,  $22.8\text{\AA}$  and  $15.2\text{\AA}$ . These are in the ratio  $1:1/2:1/3$  which is typical for a lamellar ordering. The tilt of the molecules has been estimated to be about  $46^\circ$ . The diffuse wide-angle reflection at about  $4.6\text{\AA}$  is due to the mobility of the alkyl chains. An X-ray angular intensity profile obtained for the mesophase of compound **2.C.8** at  $140^\circ\text{C}$  is given in figure **2.17**.

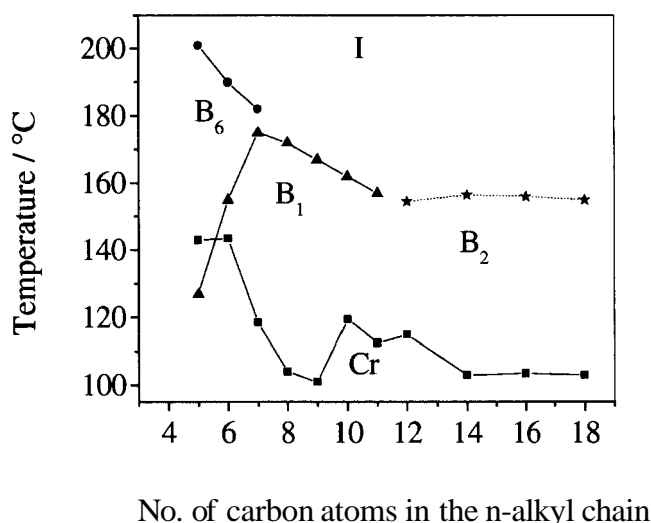


**Figure 2.16: The X-ray angular intensity profile obtained for an unoriented sample of compound 2.C.7 at 150°C.**



**Figure 2.17: The X-ray angular intensity profile obtained for an unoriented sample of compound 2.C.8 at 140°C.**

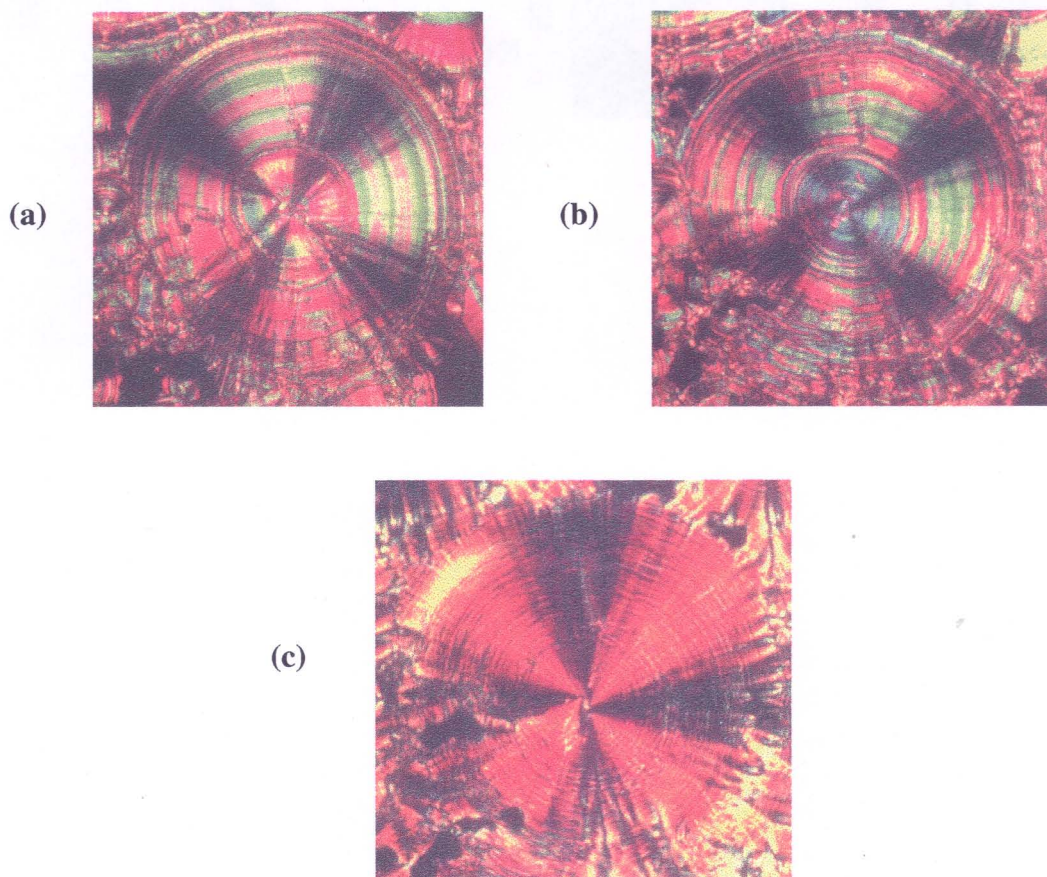
A plot of the melting and clearing temperatures against the number of carbon atoms in the n-alkyl chain for compounds of this series is shown in figure 2.18. Again, it can be seen that the clearing transition points involving the two phases  $B_6$  and  $B_2$  lie on smooth curves. However, for the  $B_1$  mesophase, there is an initial steep rise followed by a smooth descent for this transition.



**Figure 2.18: A Plot of transition temperatures Vs the number of carbon atoms in the n-alkyl chain for the compounds of series 2.III.**

An experiment to study the effect of a dc electric field on the mesophase of compound **2.C.8** was performed to evaluate the ground state structure. For carrying out this study, a sample of compound **2.C.8** was taken in a cell of  $11\mu\text{m}$  thickness, constructed with conducting glass plates, which were coated with polyimide and rubbed for homogeneous alignment. The sample was filled in the isotropic phase, cooled slowly, and viewed between crossed polarizers under a microscope. On applying a field of  $30\text{V}$ , colourful spherulites began to appear which stabilized around  $35\text{V}$ . The orientation of the brushes changed on reversing the polarity of the applied field. On switching off the field, the dark brushes reorient along the direction of the crossed polarizers. The orientation of the brushes with and without an electric field confirms the anticlinic antiferroelectric ground state of the  $B_2$  mesophase ( $\text{SmC}_A\text{P}_A$ ). The changes in the rotation of the brushes due to the applied field for compound **2.C.8** at  $150^\circ\text{C}$  are shown in figures **2.19 (a), (b)** and without the field **(c)**. This type of behaviour is typical for the  $B_2$  phase.

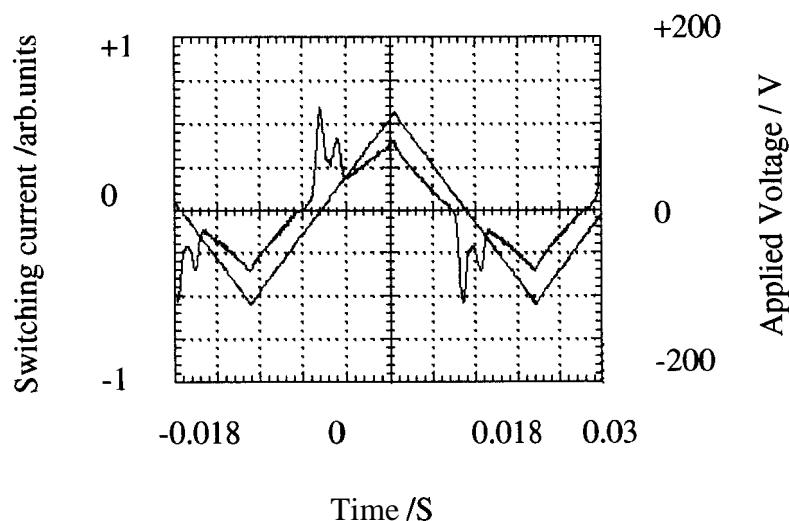




**Figure 2.19: Photomicrographs showing the effect of dc electric field on the mesophase of compound 2.C.8 at 150°C; a)  $E = +35$  V b)  $E = -35$  V c)  $E = 0$  V; cell thickness 11 $\mu$ m The rotation of the brushes illustrates that the ground state of the mesophase is SmC<sub>A</sub>P<sub>A</sub>.**

To examine the switching behaviour of this phase, and to measure the polarization value, the triangular-wave electric field experiments were carried out. For this purpose, a cell of 11 $\mu$ m thickness was constructed for homogeneous alignment, and a sample of compound 2.C.8 was filled in the isotropic phase and cooled slowly. As the transition to the mesophase took place, the applied field was increased gradually to get a good alignment. By applying a sufficiently high (220 V<sub>PP</sub> at 15Hz) triangular voltage, two polarization current peaks per half cycle could be seen on the oscilloscope screen. A typical switching current response obtained for the mesophase of this compound is shown in figure 2.20. The apparent saturated polarization  $P_S$  was calculated

from the area under the current peaks, and was about  $350 \text{ nC cm}^{-2}$ . This clearly indicates that the mesophase under investigation is antiferroelectric in nature. Therefore, it can be concluded from these studies that the mesophase is indeed  $B_2$ .

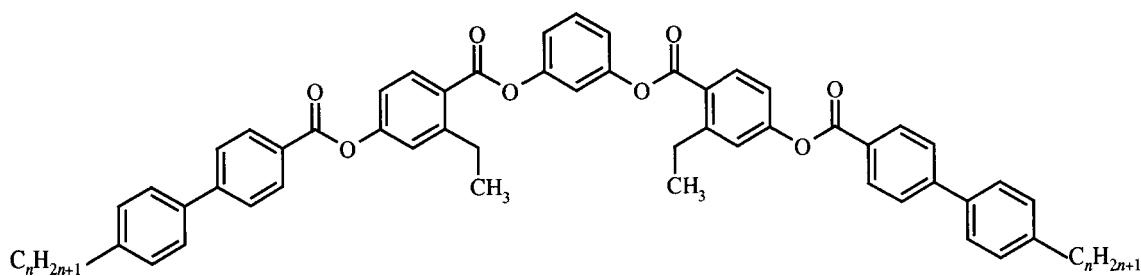


**Figure 2.20: Switching current response obtained for the mesophase of compound 2.C.8 by applying a triangular voltage ( $220V_{pp}$ , 15Hz); cell thickness  $11\mu\text{m}$ ;  $150^\circ\text{C}$ ; saturated polarization  $\approx 350 \text{ nC cm}^{-2}$ .**

In order to see the effect of a slightly larger lateral substituent, an ethyl group was introduced in place of the methyl group (series **2.IV**). The transition temperatures and the corresponding enthalpy values of these compounds **2.D.1** to **2.D.11** are collected in table **2.4**. As before, there was a reduction in the melting points while the clearing temperatures were suppressed drastically. More interestingly, the existence of the  $B_6$  phase was enhanced while those of the  $B_1$  and  $B_2$  phases were suppressed. For, example, compound **2.A.1** has a thermal range of  $11^\circ\text{C}$  for the  $B_6$  phase and compounds **2.A.1** to **2.A.6** show a fairly wide thermal range for the  $B_1$  phase ( $> 52^\circ\text{C}$ ). In contrast, the analogous ethyl substituted compounds **2.D.1** to **2.D.5** show a  $B_6$  phase while the  $B_1$  phase was completely eliminated for these compounds. The structure of the  $B_6$  mesophase was confirmed from XRD studies and the d-value obtained for compounds **2.D.3** and **2.D.5** are given in table **2.7**. Similarly compounds **2.A.7** to **2.A.11** show wide thermal ranges ( $58^\circ\text{C}$  to  $90^\circ\text{C}$ ) for the  $B_2$  phase while the analogous ethyl substituted compounds **2.D.7** and **2.D.8** show a metastable  $B_1$  phase and compounds **2.D.9** to **2.D.11** exhibit

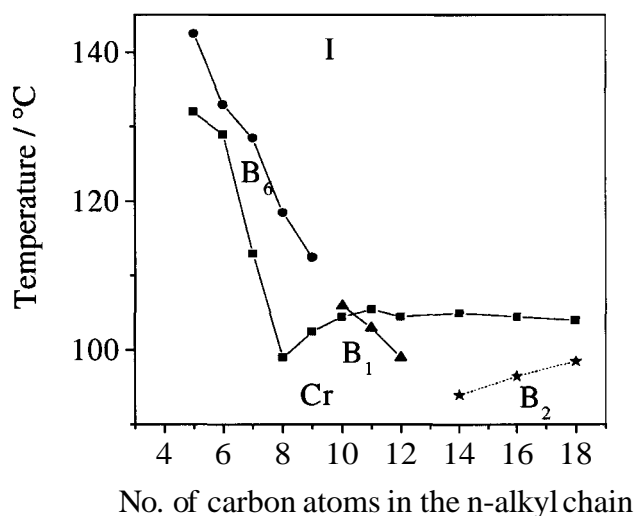
a metastable  $B_2$  phase. The structure of  $B_1$  and  $B_2$  phases of this series of compounds were also confirmed by XRD studies and the d-values obtained for compounds **2.D.6** and **2.D.11** are given in table 2.7.

**Table 2.4: Transition temperatures ( $^{\circ}\text{C}$ ) and the associated enthalpies ( $\text{kJ mol}^{-1}$ ) for compounds of series 2.IV**



Compound	n	Cr	$B_2$	$B_1$	$B_6$	I
<b>2.D.1</b>	5	. 132.0	-	-	. 142.5	.
		40.6			10.0	
<b>2.D.2</b>	6	. 129.0	-	-	. 133.0	.
		32.6			10.2	
<b>2.D.3</b>	7	. 113.0	-	-	. 128.5	.
		30.1			11.4	
<b>2.D.4</b>	8	. 99.0 <sup>a</sup>	-	-	. 118.5	.
		27.6			11.3	
<b>2.D.5</b>	9	. 102.5	-	-	. 112.5	.
		36.7			12.3	
<b>2.D.6</b>	10	. 104.5	-	. 106.0	-	.
		36.0		12.8		
<b>2.D.7</b>	11	. 105.5 <sup>a</sup>	-	(. 103.0)	-	.
		56.5		13.9		
<b>2.D.8</b>	12	. 104.5	-	(. 99.0)	-	.
		56.1		15.4		
<b>2.D.9</b>	14	. 105.0	(. 94.0)	-	-	.
		58.5	18.9			
<b>2.D.10</b>	16	. 104.5	(. 96.5)	-	-	.
		58.3	15.1			
<b>2.D.11</b>	18	. 104.0	(. 98.5)	-	-	.
		67.5	21.3			

The ethyl group destabilizes the  $B_1$  and  $B_2$  phases while stabilizing the  $B_6$  phase upto  $n$ -nonyl chain. A plot of the transition temperatures as a function of the terminal alkyl chain length for this series is shown in figure 2.21. The slope for the  $B_6$  to isotropic transition points curve is quite steep. Three homologues each of this series show the  $B_1$  and  $B_2$  phases and the clearing temperatures for these phases lie on curves, which are typical for such transitions.

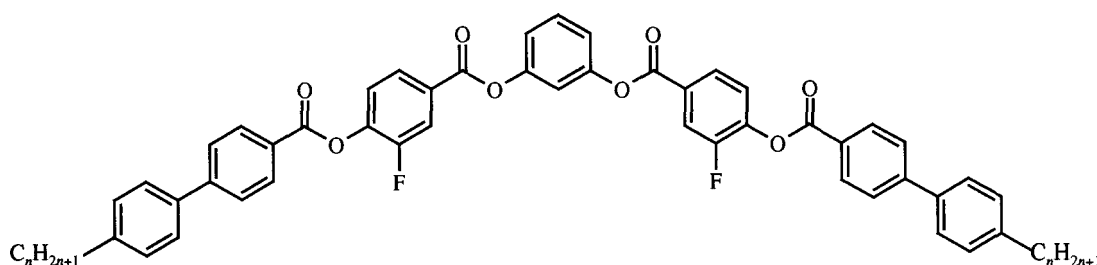


**Figure 2.21: A Plot of transition temperatures Vs the number of carbon atoms in the  $n$ -alkyl chain for the compounds of series 2.IV.**

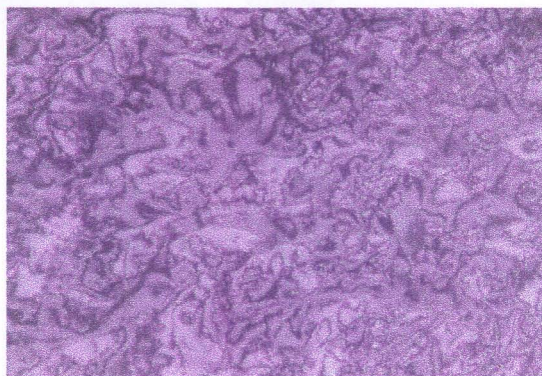
The transition temperatures and the associated enthalpies for compounds of series 2.V are summarized in table 2.5. In this series, the fluoro substituent is in the *meta* position with respect to the carbonyl group of the middle phenyl ring. It is interesting to note that as in the previous series of compounds there is a suppression of the clearing temperatures but in contrast the melting points increase for four homologues (compounds 2.E.8 to 2.E.11). While the existence of the  $B_6$  phase is unaffected, the smectic  $B_2$  phase is eliminated in two of the compounds (2.E.7 and 2.E.8) as compared to the parent analogues and the appearance of  $B_1$  phase is enhanced as eight of the eleven homologues show this phase. Compounds 2.E.2 to 2.E.8 show mosaic texture when cooled from the isotropic phase which is common for  $B_1$  phase. The structure of  $B_1$  phase was confirmed by studying compound 2.E.5 as a representative example and the  $d$ -values obtained are given in table 2.7.

Compounds **2.E.9-2.E.11** show similar optical features. On cooling a sample of a compound exhibiting a  $B_2$  mesophase, sometimes a schlieren texture could be observed. A typical photomicrograph of a schlieren texture obtained for compound **2.E.9** is shown in figure **2.22**. The smectic ordering of  $B_2$  phase was confirmed from XRD studies and the data obtained are given in table **2.7**.

**Table 2.5: Transition temperatures ( $^{\circ}C$ ) and the associated enthalpies ( $kJ\ mol^{-1}$ ) for compounds of series 2.V**

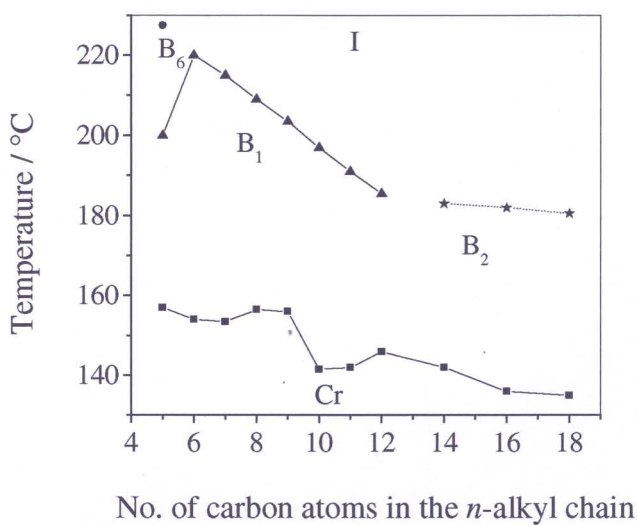


Compound	n	Cr	$B_2$	$B_1$	$B_6$	I
<b>2.E.1</b>	5	. 157.0 32.6	-	. 200.0 0.4	. 227.5 15.0	.
<b>2.E.2</b>	6	. 154.0 23.3	-	. 220.0 19.6	-	.
<b>2.E.3</b>	7	. 153.5 21.1	-	. 215.0 20.9	-	.
<b>2.E.4</b>	8	. 156.5 56.7	-	. 209.0 22.1	-	.
<b>2.E.5</b>	9	. 156.0 57.5	-	. 203.5 22.2	-	.
<b>2.E.6</b>	10	. 141.5 28.0	-	. 197.0 22.7	-	.
<b>2.E.7</b>	11	. 142.0 35.9	-	. 191.0 22.1	-	.
<b>2.E.8</b>	12	. 146.0 40.0	-	. 185.5 22.1	-	.
<b>2.E.9</b>	14	. 142.0 47.4	. 183.0 23.8	-	-	.
<b>2.E.10</b>	16	. 136.0 <sup>a</sup> 49.2	. 182.0 21.3	-	-	.
<b>2.E.11</b>	18	. 135.0 57.4	. 180.5 24.2	-	-	.



**Figure 2.22:** An optical photomicrograph of schlieren texture of B<sub>2</sub> mesophase obtained for compound 2.E.9.

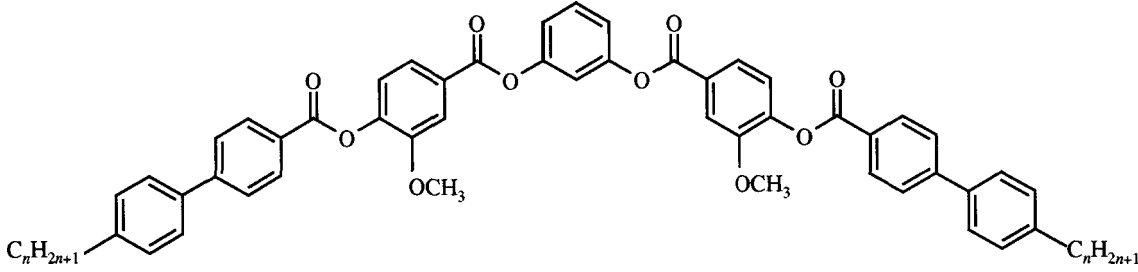
A plot of the transition temperatures as a function of the *n*-alkyl chain length for the compounds of series 2.V is shown in figure 2.23. As usual, the curves for the clearing temperatures of B<sub>1</sub> and B<sub>2</sub> phases show trends seen previously.



**Figure 2.23:** A Plot of transition temperatures Vs the number of carbon atoms in the *n*-alkyl chain for the compounds of series 2.V.

Three compounds with bulky methoxy group as a lateral substituent were also prepared (table 2.6). The enantiotropic mesophase present in the parent compounds (series 2.1) were replaced by monotropic behaviour but without affecting the type of mesophase. Since the mesophases for the homologues examined were monotropic, the other homologues were not prepared.

**Table 2.6: Transition temperatures (°C) and the associated enthalpies (kJ mol<sup>-1</sup>) for compounds of series 2.VI**



Compound	n	Cr	B <sub>2</sub>	B <sub>1</sub>	I
<b>2.F.1</b>	10	. 124.0 46.3	-	(. 119.5)	15.0
<b>2.F.2</b>	11	. 124.0 52.0	(. 123.5)	-	
<b>2.F.3</b>	12	. 130.5 62.1	(. 127.5)	-	

The mesophase types in all the series of compounds were confirmed by characteristic textural observation under a polarizing microscope, XRD studies for different mesophases of representative compounds and electro-optical switching characteristics. The d values obtained from XRD studies are summarized in table 2.7.

**Table 2.7: The d spacings obtained from XRD studies for the mesophases of various compounds with the corresponding Miller indices**

Compound	d-spacing Å Miller indices	Lattice parameter		Mesophase	Temp / °C
		a	b		
<b>2.A.5</b>	32.2(11), 24.8 (02)	43.4	48.7	B <sub>1</sub>	155°
<b>2.A.8</b>	44.1(01), 22.0 (02)			B <sub>2</sub>	150°
<b>2.A.9</b>	46.1(01), 23.1 (02)			B <sub>2</sub>	160°
<b>2.B.4</b>	28.3(11), 23.4 (02)	35.5	46.8	B <sub>1</sub>	185°
<b>2.B.9</b>	44.4(01), 22.2 (02), 14.8 (03), 11.1 (04)			B <sub>2</sub>	188°
<b>2.C.3</b>	22.9 (01), 11.4 (02)			B <sub>6</sub>	180°
	22.9 (02), 24.8 (11), 11.4 (04)	29.5	45.8	B <sub>1</sub>	145°
<b>2.C.7</b>	35.5 (11), 26.1 (02), 15.8 (31)	48.6	52.2	B <sub>1</sub>	150°
<b>2.C.8</b>	45.5 (01), 22.8 (02) 15.2 (03)			B <sub>2</sub>	140°
<b>2.C.11</b>	50.2(01)			B <sub>2</sub>	150°
<b>2.D.3</b>	23.7(02)			B <sub>6</sub>	120°
<b>2.D.5</b>	24.9 (02)			B <sub>6</sub>	110°
<b>2.D.6</b>	29.2 (11), 25.3 (02)	35.8	50.6	B <sub>1</sub>	105°
<b>2.D.11</b>	48.7 (01), 24.4 (02), 16.2 (03)			B <sub>2</sub>	97°
<b>2.E.5</b>	32.6 (11), 24.9 (02)	43.1	49.8	B <sub>1</sub>	180°
<b>2.E.10</b>	47.3 (01), 15.9 (03)			B <sub>2</sub>	175°



### A comparison of the effect of lateral substituents

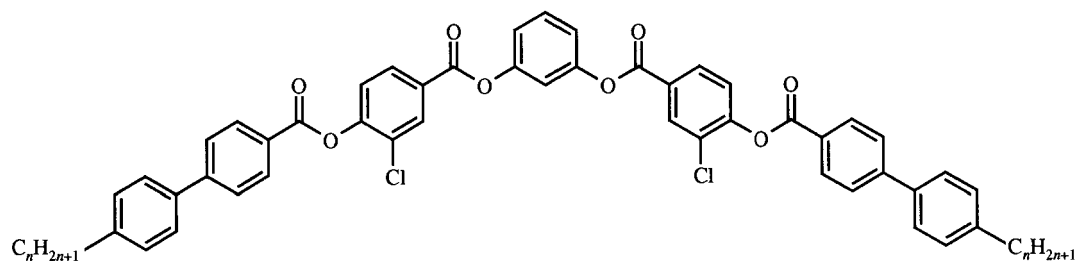
The effect of *ortho* and *meta* fluorine substituents on the mesomorphic properties of these compounds (series **2.11** and **2.V**) may be summarized as follows. All the compounds of series **2.V** have higher melting points while the clearing temperatures are lowered generally except for compounds **2.E.3**, **2.E.4** and **2.E.5**. However, the existence of the lamellar **B<sub>2</sub>** phase seems to be favoured in the *ortho* substituted derivatives.

For comparison, the transition temperatures and the associated enthalpy values of compounds with a chloro and methyl substituent in *meta* position, which are reported in the literature [29] are summarized in tables **2.8** and **2.9** respectively.

It is interesting to compare the effect of fluoro and chloro substituents in *meta* position (series **2.V** and series **1**). The *meta* fluoro substituted compounds and the corresponding chloro analogues behave similarly along the series though there is a drastic reduction in clearing temperatures in the latter case because of its larger dimension. Also, it is interesting to note that the electron withdrawing groups such as fluoro and chloro, whose dipole vectors are in the bend direction, favor the formation of columnar **B<sub>1</sub>** mesophase over a smectic phase. A Similar trend has been observed in different system studied by Dantlgraber *et al.* [72].

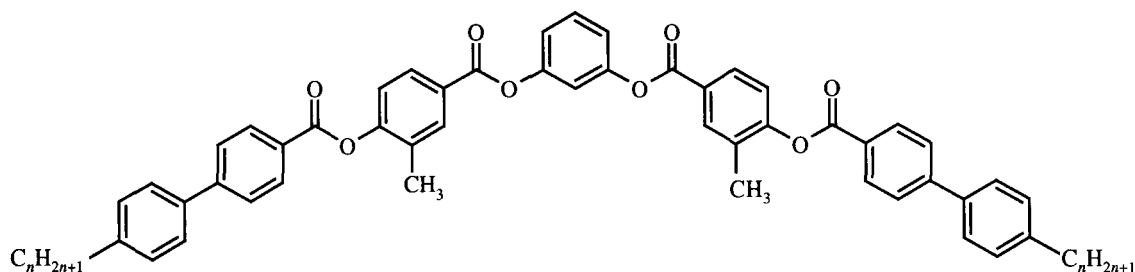
A comparison between compounds of series **2.111** and series **2** which have a methyl substituent in *ortho* and *meta* positions respectively can be summarized as follows. The former derivatives (series **2.111**) exhibit the **B<sub>6</sub>**, **B<sub>1</sub>** and **B<sub>2</sub>** mesophases over an extended range of temperature since the melting points are suppressed while the clearing temperatures are higher. Thus, the compounds of series **2.111** have a large thermal range for the mesophases. It is very clear from these examples that the substituent at *meta* position affect the mesophases drastically when compared to the *ortho* substituted analogues.

**Table 2.8: Transition temperatures (°C) and the associated enthalpies (kJ mol<sup>-1</sup>) for compounds of series 1 [29]**



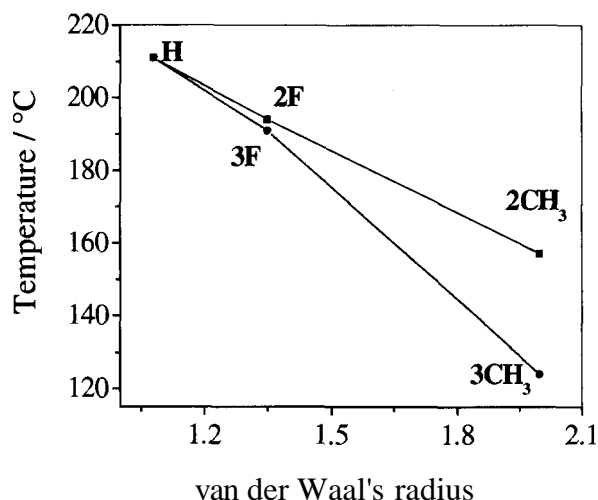
Compound	n	Cr	B <sub>1</sub>	B <sub>6</sub>	I
<b>1</b>	5	. 164.5	. 168.0	. 178.5	.
		54.8	0.6	12.5	.
<b>2</b>	6	. 163.0	. 173.0	-	.
		23.3	15.5		
<b>3</b>	7	. 125.0	. 171.0	-	.
		50.2	17.0		
<b>4</b>	8	. 131.5	. 165.5	-	.
		35.0	16.7		
<b>5</b>	9	. 133.5	. 163.5	-	.
		46.7	17.2		
<b>6</b>	10	. 132.0	. 156.5	-	.
		20.2	16.1		
<b>7</b>	11	. 128.0	. 153.0	-	.
		15.9	15.4		
<b>8</b>	12	. 131.0	. 148.0	-	.
		15.2	14.3		

**Table 2.9: Transition temperatures ( $^{\circ}\text{C}$ ) and the associated enthalpies ( $\text{kJ mol}^{-1}$ ) for compounds of series 2 [29]**



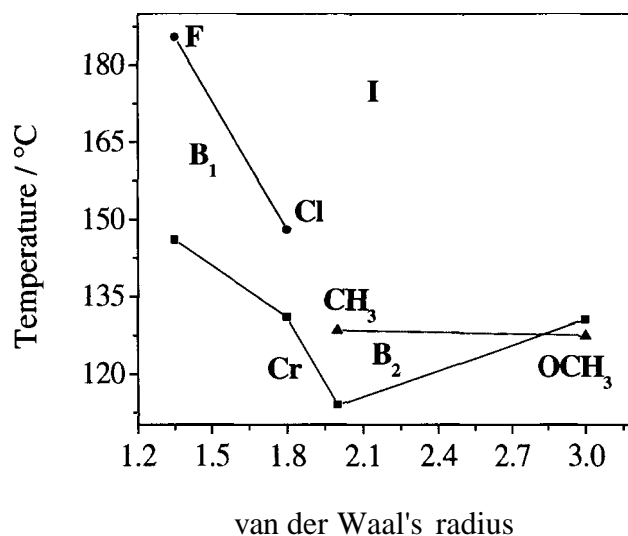
Compound	n	Cr	B <sub>2</sub>	B <sub>1</sub>	B <sub>6</sub>	I
<b>9</b>	5	. 161.5 43.7	-	-	166.5	.
<b>10</b>	6	. 159.0 71.1	-	-	(. 154.5)	.
<b>11</b>	7	. 146.0 46.2	-	-	147.5	.
<b>12</b>	8	. 139.5 54.6	-	(. 138.5)	-	
<b>13</b>	9	. 142.0 69.6	-	(. 134.0)	-	
<b>14</b>	10	. 139.0 68.2	-	(. 127.5)	-	
<b>15</b>	11	. 138.5 74.4	(. 124.0)	-		
<b>16</b>	12	. 114.0 56.4	. 128.5	-		
<b>18</b>	18	. 119.0 51.9	. 130.0	-		
			13.4			

A comparative plot of clearing temperatures with van der Waal's radii of substituents in *ortho* and *meta* positions is shown in figure 2.24 for the n-dodecyloxy homologue. It can be seen clearly that compounds with substitution at *ortho* position (2F, 2CH<sub>3</sub>) have higher clearing temperatures than substituents at *meta* position (3F, 3CH<sub>3</sub>) in this seven-ring ester bent-core compounds. Due to this reason, the *ortho* substituted derivatives have larger thermal range for the mesophase/s.



**Figure 2.24:** A comparative plot of clearing temperatures as a function of the size of the lateral substituent in *ortho* and *meta* positions w.r.t. carboxylate group of the middle phenyl ring of the wings of the seven-ring ester compounds.

It is also interesting to note that in this type of banana-shaped compounds electron donating as well as electron withdrawing substituents in *meta* position, affect the layered mesophase to a great extent. Also, it is pleasantly surprising to note that chloro and methyl groups having approximately the same van der Waal's radius behave differently along a homologous series. This comparison is shown for the n-dodecyloxy homologue in figure 2.25. The *meta* chloro substituted compounds exhibit the columnar rectangular ( $B_1$ ) phase while the corresponding homologue with a methyl substituent shows a layered antiferroelectric phase ( $B_2$ ). Thus we can conclude that "**dipolar effects**" are significant over "**steric effects**" in this type of bent-core mesogens unlike in calamitic liquid crystals.



**Figure 2.25:** A comparative plot of clearing temperatures as a function of the size of the lateral substituent in *meta* position w.r.t. carboxylate group of the middle phenyl ring of the wings of the seven-ring ester compounds.

### Summary:

A systematic study of the mesomorphic properties of sixtysix compounds belonging to six different homologous series were investigated. The effect of different lateral substituents such as fluoro, methyl, ethyl and methoxy groups were studied. Bulkier substituents such as ethyl and methoxy groups destabilize the  $B_1$  and  $B_2$  phases.

In general, substitution at *meta* position w.r.t. the carbonyl group of the middle phenyl ring of the arms of bent-core compounds will reduce the thermal range of the mesophase when compared to those substituted at *ortho* position in these seven-ring materials.

The substituents such as chloro and methyl groups, which have approximately the same van der Waal's radius, show different mesophase behaviour. Thus, unlike in calamitic liquid crystals dipolar factors are more significant than steric factors in these bent-core compounds.

## Experimental

### General

In general, all the compounds were purified by column chromatography on silica gel (60-120 mesh), and crystallized from analytical grade solvents. The liquid samples were purified by distillation under reduced pressure. The purity of the sample was checked by thin layer chromatography (TLC), (Merck Kieselgel 60F<sub>254</sub>). The chemical structures of the compounds were determined by spectroscopic techniques. Infrared spectra were recorded on a Shimadzu FTIR-8400 spectrophotometer, using nujol mull for intermediate compounds and KBr disk for target compounds. <sup>1</sup>H NMR spectra were recorded on a Bruker AMX 400 spectrometer, using tetramethylsilane (TMS) as an internal standard and deuteriochloroform as solvent unless otherwise specified. The chemical shift values ( $\delta$ ) are in parts per million (ppm) with respect to TMS. The elemental analyses were carried out for all the intermediate and final compounds except fluoro substituted compounds using a Carlo-Erba 1106 elemental analyzer.

The optical textures and thermal behaviour were examined under a Leitz Laborlux 12 POL /Olympus BX50 polarizing microscope equipped with a Mettler FP52 heating stage and a FP5 controller. The samples were sandwiched between an untreated glass plate and a coverslip. The transition temperatures and the associated enthalpies were determined on a Perkin-Elmer, Model Pyris 1D Differential Scanning Calorimeter (DSC), which was calibrated using indium as a standard. X-ray diffraction (XRD) measurements were carried out on non-oriented samples using Cu-K $\alpha$  radiation from a Rigaku Ultrax 18 rotating anode generator with a graphite crystal monochromator. The samples were taken in Lindemann capillaries (0.7mm), and the temperature of the heater was controlled to  $\pm 0.1^\circ\text{C}$ . The diffraction patterns were collected on a two-dimensional image plate detector (Marresearch). The Polarization measurements were carried out using standard triangular-wave method on home made polyimide coated ITO cells. The thickness of the cells was adjusted using Mylar spacers and the thickness was measured using interferometric techniques. The electro-optical experiments were performed by applying dc fields using a regulated dual DC power supply (LD 6401) on polyimide coated ITO cells and simultaneously observing the samples under a polarizing microscope.

## Synthesis

### 4-Benzyloxybenzoic acid, 2.A.i

This was synthesized following a procedure described in the literature [59].  
m. p. 191-191.5°C (reported 188°C).

### 2-Fluoro-4-benzyloxybenzoic acid, 2.A.ii

This was synthesized following a procedure described in the literature [59-61].  
m.p. 167-168°C.

### 2-Methyl-4-hydroxyacetophenone, 2.iii

This was prepared by following a procedure described in the literature [69]. A mixture of m-cresol, **2.ii** (53.5g, 0.495mol), carbon disulphide, (275ml), anhydrous aluminium chloride, (146.8g, 1.1mol) was taken in a three-necked flask, fitted with a mechanical stirrer, a reflux condenser and a pressure equalizing separatory funnel. The mixture was stirred in ice-cold condition. To this was added acetyl chloride (38.9g, 0.495 mol) over a period of one hour. The stirring was continued for four hours and left overnight. The reaction mixture was refluxed for two hours and the solvent was distilled off. The dark brown reaction mixture was cooled and decomposed with ice-cold hydrochloric acid. The mixture was extracted with ether (3 × 300 ml), washed with 10% hydrochloric acid (2 x 50 ml) and water (3 x 100 ml) and dried over anhydrous sodium sulphate. The removal of the solvent gave a dark brown compound, which was recrystallized from toluene. Yield, 50g (67%); m.p. 128-129°C (reported 128°C).

### 2-Methyl-4-benzyloxyacetophenone, 2.iv

A mixture of 2-methyl-4-hydroxyacetophenone, **2.iii** (15.0g, 0.1mol), benzyl chloride (13.9g, 0.1mol), anhydrous potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, 41.4g, 0.3mol) and butan-2-one (200 ml) was refluxed for about eighteen hours. Solvent butan-2-one was distilled off and the reaction mixture was poured into ice-cold water and extracted with ether (3 x 300 ml), the combined ethereal extracts was washed with 5% ice-cold sodium hydroxide solution (2 x 50 ml), water (3 x 100 ml) and dried over anhydrous sodium sulphate. The removal of solvent gave a low melting solid, which was purified by column chromatography on silica gel using a mixture of chloroform and petroleum ether (b.p. 60-80°C) as an eluent. The low melting compound obtained after

removal of solvent was recrystallized from petroleum ether (b.p. 60-80°C). Yield, 21g (87.5%); m.p. 51-52°C.

### 2-Methyl-4-benzyloxybenzoic acid, **2.A.iii**

A solution of sodium hypobromite was prepared at 0°C, by dissolving bromine (106.9g, 0.67mol), in sodium hydroxide (53.5g, 1.34mol), and water (400ml). This solution was added to a vigorously stirred 2-methyl-4-hydroxyacetophenone, **2.iv** (40.0g, 0.167mol), in 1, 4-dioxane (400ml). Stirring was continued and the temperature was raised to 70°C and held for one hour to ensure completion of the reaction. Aqueous sodium metabisulphite was added to neutralize the excess bromine in the reaction mixture. The reaction mixture was then diluted with water and distilled to remove 1, 4-dioxane and water. This concentrated solution was cooled and poured into ice-cold water and hydrochloric acid. The white product thus precipitated was filtered off, washed thoroughly with water and dried. The compound was recrystallized from ethanol. Yield, 32g (80%); m.p. 130-131°C.

### 3-Ethylphenol, **2.vi**

This was prepared by following a procedure described in the literature [71]. A mixture of 3-hydroxyacetophenone, **2.v** (36.5g, 0.268mol), diethylene glycol (300ml), 90% hydrazine hydrate (30 ml) and potassium hydroxide (40g) were placed in a round bottom flask fitted with a reflux condenser and refluxed for one hour. The temperature was slowly raised to 190°C while distilling off the solvent and it was refluxed for four hours. The reaction mixture was cooled and poured into ice-cold water and hydrochloric acid and extracted with ether (3 x 300 ml), the combined ethereal solution was washed with water (3 x 300 ml) and dried over anhydrous sodium sulphate. The liquid, which was obtained after removal of solvent was distilled under reduced pressure. Yield, 26.0g (80%); b.p. 65-67°C at 1mm of Hg.

### 2-Ethyl-4-hydroxyacetophenone, **2.vii**

This was synthesized following a procedure described for preparation of compound **2.iii**, using 3-ethylphenol, **2.vi** instead of m-cresol, **2.ii**. Yield, 65%, m.p. 107-108°C.



### **2-Ethyl-4-benzyloxyacetophenone, 2.viii**

This was synthesized following a procedure described for the preparation of compound **2.iv**, using 2-ethyl-4-hydroxyacetophenone, **2.vii** instead of 2-methyl-4-hydroxyacetophenone, **2.iii**. The resultant compound was a liquid, which was purified by column chromatography on silica gel using chloroform and petroleum ether (b.p. 60-80°C) as eluent. Yield, 86%.

### **2-Ethyl-4-benzyloxybenzoic acid, 2.A.iv**

This was synthesized following a procedure described for the preparation of compound **2.A.iii**, using 2-ethyl-4-benzyloxyacetophenone, **2.viii** instead of 2-methyl-4-benzyloxyacetophenone, **2.iv**. Yield, 78%; m.p. 135-136°C.

### **3-Fluoro-4-benzyloxybenzoic acid, 2.A.v**

This was synthesized following a procedure described in the literature [59-61].  
m.p. 187-188°C.

### **Methyl-3-methoxy-4-benzyloxybenzoate, 2x**

This was synthesized by the benzylation of commercial methyl vanillate, **2.ix** using benzyl chloride in the presence of anhydrous potassium carbonate. Yield, 90%; m.p. 86-86.5°C.

### **3-Methoxy-4-benzyloxybenzoic acid, 2.A.vi**

Methyl-3-methoxy-4-benzyloxybenzoate, 2x (10g, 0.036mol) and alcoholic 10% potassium hydroxide solution was **refluxed** for about five hours. Excess ethanol was distilled off and the reaction mixture was poured into a mixture of ice-cold water and hydrochloric acid. The precipitated solid was separated by filtration and washed with water several times until it was free from acid and dried. This compound was crystallized from ethanol. Yield, 8.3g (88%); m.p. 173.5-174.5°C.

#### 4-*n*-Alkylbiphenyl-4-carboxylic acids, 2.xv

These were synthesized following a procedure described in the literature [70]. The melting points obtained are tabulated in table 2.10 along with the reported values.

**Table 2.10: The melting points of 4-*n*-alkylbiphenyl-4-carboxylic acid**

No.	n	Observed m.p. °C	Reported m.p. °C [84]
1	5	176	176
2	6	169	165
3	7	160	156
4	8	149	147
5	9	140	135
6	10	132	130
7	11	128	-
8	12	120	-
9	14	109	110
10	16	105.5	103
11	18	102	-

#### 1, 3-Phenylene bis(4-benzyloxybenzoate), 2.a (X=H, Y=H)

A mixture of resorcinol, 2.i (2.27g, 20mmol), 4-benzyloxybenzoic acid, 2.A.i (9.12g, 40mmol) and 4-(N, N-dimethylamino) pyridine (DMAP) (0.5g, 4mmol) in dry chloroform (50ml) was stirred for ten minutes. To this mixture was added N, N'-dicyclohexylcarbodiimide (DCC) (9.05g, 44mmol) and stirred for ten hours at room temperature. The N, N'-dicyclohexylurea formed was filtered off and washed with chloroform (15ml). The combined filtrate was washed with 5% aqueous acetic acid solution (2 x 50 ml), 5% aqueous sodium hydroxide solution (2 x 50ml) and water (3 x 50ml) and dried over anhydrous sodium sulphate. The solvent was removed from the solution, which yielded a white residue. This was chromatographed on silica gel using chloroform as an eluent and the white material thus obtained after evaporating

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

### **1, 3-Phenylene bis(4-hydroxybenzoate), 2.b (X=H, Y=H)**

A mixture of 1, 3-phenylene bis(4-benzyloxybenzoate), 2.a (X=H, Y=H) (8.5g, 0.015mol), 5% Pd-C catalyst (2.0g) and 1, 4-dioxane (150ml) was stirred at 50°C in an atmosphere of hydrogen until the calculated quantity of hydrogen was absorbed. The reaction mixture was filtered and removal of solvent from the filtrate gave a residue, which was crystallized from a mixture of 1, 4-dioxane and petroleum ether (b.p. 60-80°C). Yield, 92%; m.p. 237-238°C;  $\nu_{\max}$  (nujol): 3350, 2924, 2850, 1705, 1598, 1460, 1245, 1128  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CD}_3\text{COCD}_3$ ): 9.7 (s, 2H,  $2 \times \text{Ar}-\text{OH}$ , exchangeable with  $\text{D}_2\text{O}$ ), 8.08-8.05 (d, 4H,  $^3\text{J}8.84\text{Hz}$ , Ar-H), 7.56-7.52 (t, 1H,  $^3\text{J}8.32\text{Hz}$ , Ar-H), 7.22-7.2 (m, 3H, Ar-H), 7.02-6.99 (d, 4H,  $^3\text{J}8.84\text{Hz}$ , Ar-H). Elemental analysis:  $\text{C}_{20}\text{H}_{14}\text{O}_6$  requires C, 68.57; H, 4.03%; found C, 69.01; H, 3.64%.

### **1, 3-Phenylene bis(2-fluoro-4-benzyloxybenzoate), 2.a (X=F, Y=H)**

This was synthesized following a procedure described for the preparation of compound 2.a (X=H, Y=H), using 2-fluoro-4-benzyloxybenzoic acid, **2.A.ii** instead of 4-benzyloxybenzoic acid, 2.A.i. Yield, 79.5%; m.p. 161-162°C;  $\nu_{\max}$  (nujol): 2924, 2854, 1726, 1620, 1599, 1454, 1254, 1130  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.07-8.03 (t, 2H,  $^3\text{J}8.6\text{Hz}$ , Ar-H), 7.47-7.36 (m, 11H, Ar-H), 7.17-7.13 (m, 3H, Ar-H), 6.87-6.84 (dd, 2H,  $^3\text{J}8.86\text{Hz}$ ,  $^4\text{J}2.36\text{Hz}$ , Ar-H), 6.79-6.76 (dd, 2H,  $^3\text{J}12.60\text{Hz}$ ,  $^4\text{J}2.32\text{Hz}$ , Ar-H), 5.14 (s, 4H,  $2 \times -\text{O}-\text{CH}_2-\text{Ar}$ ).

### **1, 3-Phenylene bis(2-fluoro-4-hydroxybenzoate), 2.b (X=F, Y=H)**

This was synthesized following a procedure described for the preparation of compound 2.b (X=H, Y=H), using 1, 3-phenylene bis(2-fluoro-4-benzyloxybenzoate), 2.a (X=F, Y=H) as starting material. Yield, 88%; m.p. 270-271°C;  $\nu_{\max}$  (nujol): 3340, 2924, 2855, 1713, 1614, 1599, 1452, 1255, 1126  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CD}_3\text{COCD}_3$ ): 9.97 (s, 2H,  $2 \times \text{Ar}-\text{OH}$ , exchangeable with  $\text{D}_2\text{O}$ ),

8.17-8.13 (t, 2H,  $^3J_{8.68\text{Hz}}$ , Ar-H), 7.69-7.65 (t, 1H,  $^3J_{8.32\text{Hz}}$ , Ar-H), 7.37-7.33 (m, 3H, Ar-H), 6.99-6.96 (dd, 2H,  $^3J_{8.74\text{Hz}}$ ,  $^4J_{2.28\text{Hz}}$ , Ar-H), 6.89-6.85 (dd, 2H,  $^3J_{12.82\text{Hz}}$ ,  $^4J_{2.32\text{Hz}}$ , Ar-H).

### **1, 3-Phenylene bis(2-methyl-4-benzyloxybenzoate), 2.a (X=CH<sub>3</sub>, Y=H)**

This was synthesized following a procedure described for the preparation of compound **2.a** (X=H, Y=H), using 2-methyl-4-benzyloxybenzoic acid, **2.A.iii** instead of 4-benzyloxybenzoic acid, **2.A.i**. Yield, 78%; m.p. 128-129°C;  $\nu_{\text{max}}$  (nujol): 2924, 2855, 1720, 1605, 1225, 1120  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.19-8.16 (d, 2H,  $^3J_{9.64\text{Hz}}$ , Ar-H), 7.48-7.33 (m, 12H, Ar-H), 7.13-7.11 (d, 2H,  $^3J_{7.32\text{Hz}}$ , Ar-H), 6.90-6.88 (d, 4H,  $^3J_{7.12\text{Hz}}$ , Ar-H), 5.14 (s, 4H, 2 x -O-CH<sub>2</sub>-Ar), 2.66 (s, 6H, 2 x Ar-CH<sub>3</sub>). Elemental analysis: C<sub>36</sub>H<sub>30</sub>O<sub>6</sub> requires C, 77.40; H, 5.41%; found C, 76.98; H, 5.34%.

### **1, 3-Phenylene bis(2-methyl-4-hydroxybenzoate), 2.b (X=CH<sub>3</sub>, Y=H)**

This was synthesized following a procedure described for the preparation of compound **2.b** (X=H, Y=H), using 1, 3-phenylene bis(2-methyl-4-benzyloxybenzoate), **2.a** (X=CH<sub>3</sub>, Y=H) as starting material. Yield, 85%; m.p. > 255°C (dec);  $\nu_{\text{max}}$  (nujol): 3380, 2920, 2858, 1700, 1605, 1220 and 1120  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (CD<sub>3</sub>COCD<sub>3</sub>): 9.8 (s, 2H, 2 x Ar-OH, exchangeable with D<sub>2</sub>O), 8.07-8.0 (m, 4H, Ar-H), 7.66-7.64 (t, 1H,  $^3J_{8.4\text{Hz}}$ , Ar-H), 7.33-7.3 (m, 3H, Ar-H), 7.14-7.11 (d, 2H,  $^3J_{8.4\text{Hz}}$ , Ar-H), 2.40 (s, 6H, 2 x Ar-CH<sub>3</sub>). Elemental analysis: C<sub>22</sub>H<sub>18</sub>O<sub>6</sub> requires C, 69.84; H, 4.79%; found C, 69.38; H, 4.71%.

### **1, 3-Phenylene bis(2-ethyl-4-benzyloxybenzoate), 2.a (X=C<sub>2</sub>H<sub>5</sub>, Y=H)**

This was synthesized following a procedure described for the preparation of compound **2.a** (X=H, Y=H), using 2-ethyl-4-benzyloxybenzoic acid, **2.A.iv** instead of 4-benzyloxybenzoic acid, **2.A.i**. Yield, 83%; m.p. 88-89°C  $\nu_{\text{max}}$  (nujol): 3068, 2924, 2855, 1736, 1732, 1605, 1226, 1124, 1022  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.17-8.15 (d, 2H,  $^3J_{8.72\text{Hz}}$ , Ar-H), 7.48-7.33 (m, 12H, Ar-H), 7.13-7.11 (dd, 2H,  $^3J_{7.24\text{Hz}}$ ,  $^4J_{2.12\text{Hz}}$ , Ar-H), 6.93-6.87 (m, 4H, Ar-H), 5.14 (s, 4H, 2 x -O-CH<sub>2</sub>-Ar), 3.08-3.03 (q, 4H,  $^3J_{7.44\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 1.28-1.24 (t, 6H,  $^3J_{7.44\text{Hz}}$ , 2 x -CH<sub>2</sub>-CH<sub>3</sub>). Elemental analysis: C<sub>38</sub>H<sub>34</sub>O<sub>6</sub> requires C, 77.80; H, 5.84%; found C, 77.48; H, 6.0%.

### **1, 3-Phenylene bis(2-ethyl-4-hydroxybenzoate), 2.b (X=C<sub>2</sub>H<sub>5</sub>, Y=H)**

This was synthesized following a procedure described for the preparation of compound **2.b** (X=H, Y=H), using 1, 3-phenylene bis(2-ethyl-4-benzyloxybenzoate), **2.a** (X=C<sub>2</sub>H<sub>5</sub>, Y=H) as starting material. Yield, 78%; m.p. 198-199 °C  $\nu_{\max}$  (nujol): 3408, 3032, 2924, 2855, 1713, 1707, 1601, 1303, 1047 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (CD<sub>3</sub>COCD<sub>3</sub>): 9.6 (s, 2H, 2 x Ar-OH, exchangeable with D<sub>2</sub>O) 8.24-8.22 (d, 2H, <sup>3</sup>J 8.48Hz Ar-H), 7.68-7.64 (t, 1H, <sup>3</sup>J 8.2Hz, Ar-H), 7.36-7.31 (m, 3H, Ar-H), 6.99-6.95 (m, 4H, Ar-H), 3.17-3.12 (q, 4H, <sup>3</sup>J 7.4Hz, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 1.37-1.33 (t, 6H, <sup>3</sup>J 7.44Hz, 2 x -CH<sub>2</sub>-CH<sub>3</sub>). Elemental analysis: C<sub>24</sub>H<sub>22</sub>O<sub>6</sub> requires C, 70.93, H, 5.46%; found C, 70.75; H, 5.39%.

### **1, 3-Phenylene bis(3-fluoro-4-benzyloxybenzoate), 2.a (X=H, Y=F)**

This was synthesized following a procedure described for the preparation of compound **2.a** (X=H, Y=H), using 3-fluoro-4-benzyloxybenzoic acid, **2.A.v** instead of 4-benzyloxybenzoic acid, **2.A.i**. Yield, 78%; m.p. 142-143 °C;  $\nu_{\max}$  (nujol): 2920, 2854, 1732, 1605, 1456, 1270, 1118 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 7.94-7.9 (m, 4H, Ar-H), 7.47-7.34 (m, 10H, Ar-H), 7.15-7.07 (m, 6H, Ar-H), 5.24 (s, 4H, 2 x -O-CH<sub>2</sub>-Ar).

### **1, 3-Phenylene bis(3-fluoro-4-hydroxybenzoate), 2.b (X=H, Y=F)**

This was prepared following a procedure described for compound **2.b** (X=H, Y=H), using 1, 3-phenylene bis(3-fluoro-4-benzyloxybenzoate) **2.a** (X=H, Y=F), as starting material. Yield, 89%; m.p. 198-199 °C;  $\nu_{\max}$  (nujol): 3355, 2924, 2850, 1705, 1598, 1460, 1240, 1128 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (CD<sub>3</sub>COCD<sub>3</sub>): 9.89 (s, 2H, 2 x Ar-OH, exchangeable with D<sub>2</sub>O), 7.91-7.87 (m, 4H, Ar-H), 7.56-7.52 (t, 1H, <sup>3</sup>J 8.3Hz, Ar-H), 7.26-7.19 (m, 5H, Ar-H).

### **1, 3-Phenylene bis(3-methoxy-4-benzyloxybenzoate), 2.a (X=H, Y=OCH<sub>3</sub>)**

This was synthesized following a procedure described for the preparation of compound **2.a** (X=H, Y=H), using 3-methoxy-4-benzyloxybenzoic acid, **2.A.vi** instead of 4-benzyloxybenzoic acid **2.A.i**. Yield, 78%; m.p. 153-154 °C;  $\nu_{\max}$  (nujol): 2924, 2855, 1730, 1596, 1463, 1211, 1022 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 7.80-7.77 (dd, 2H, <sup>3</sup>J 8.44Hz, <sup>4</sup>J 1.88Hz, Ar-H), 7.690-7.686 (d, 2H, <sup>4</sup>J 1.76Hz, Ar-H), 7.49-7.31 (m, 11H, Ar-H), 7.14-7.12 (m, 3H, Ar-H), 6.98-6.96 (d, 2H,

$^3\text{J}8.52\text{Hz}$ , Ar-H), 5.26 (s, 4H,  $2 \times -\text{O}-\text{CH}_2-\text{Ar}$ ), 3.97 (s, 6H,  $2 \times \text{Ar}-\text{OCH}_3$ ). Elemental analysis:  $\text{C}_{36}\text{H}_{30}\text{O}_8$  requires C, 73.21; H, 5.12%; found C, 73.58; H, 5.35%.

### **1, 3-Phenylene bis(3-methoxy-4-hydroxybenzoate), 2.b (X=H, Y=OCH<sub>3</sub>)**

This was synthesized following a procedure described for the preparation of compound 2.b (X=H, Y=H), using 1, 3-phenylene bis(3-methoxy-4-benzyloxybenzoate) 2.a (X=H, Y=OCH<sub>3</sub>), as starting material. Yield, 85%; m.p 167-168°C;  $\nu_{\text{max}}$  (nujol): 3391, 3263, 2924, 2855, 1713, 1693, 1587, 1288, 1037  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CD}_3\text{COCD}_3$ ): 8.79 (s, 2H,  $2 \times \text{Ar}-\text{OH}$ , exchangeable with  $\text{D}_2\text{O}$ ), 7.76-7.74 (dd, 2H,  $^3\text{J}8.28\text{Hz}$ ,  $^4\text{J}1.96\text{Hz}$ , Ar-H), 7.707-7.702 (d, 2H,  $^4\text{J}1.92\text{Hz}$ , Ar-H), 7.56-7.52 (t, 1H,  $^3\text{J}8.36\text{Hz}$ , Ar-H), 7.23-7.20 (m, 3H, Ar-H), 7.00- 6.98 (d, 2H,  $^3\text{J}8.32\text{Hz}$ , Ar-H), 3.94 (s, 6H,  $2 \times \text{Ar}-\text{OCH}_3$ ). Elemental analysis:  $\text{C}_{22}\text{H}_{18}\text{O}_8$  requires C, 64.39; H, 4.42%; found C, 63.95; H, 4.50%.

### **1, 3-Phenylene bis[4-(4-*n*-pentylbiphenyl-4-carbonyloxy)benzoate], 2.A.1**

A mixture of 1, 3-phenylene bis[4-hydroxybenzoate] 2.b (X=H, Y=H), (0.150g, 0.43mmol), 4-*n*-pentylbiphenyl-4-carboxylic acid **2.xv** ( $n=5$ ), (0.23g, 0.86mmol), cat.amount of 4-(N, N-dimethylamino) pyridine and dry chloroform (50ml) was stirred for ten min. To this mixture was added N, N'-dicyclohexylcarbodiimide (0.194g, 0.95mol) and stirred for ten hours at room temperature. The N, N'-dicyclohexylurea formed was filtered off and washed with chloroform (15ml). The combined filtrate was washed with 5% aqueous acetic acid solution (2 x 15ml), 5% aqueous sodium hydroxide solution (2 x 15ml) and water (3 x 25ml) and dried over anhydrous sodium sulphate. The solvent was distilled off to give a white residue, which was chromatographed on silica gel using chloroform as an eluent. The white material obtained after evaporating the solvent was crystallized using a mixture of chloroform and acetonitrile.

Yield, 0.28g (75%); m.p. 175.0°C;  $\nu_{\text{max}}$ : 3076, 2954, 2928, 2855, 1740, 1738, 1603, 1259  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.32-8.30 (d, 4H,  $^3\text{J}8.72\text{Hz}$ , Ar-H), 8.28-8.26 (d, 4H,  $^3\text{J}8.36\text{Hz}$ , Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}8.36\text{Hz}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}8.12\text{Hz}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}8.28\text{Hz}$ , Ar-H), 7.43-7.41 (d, 4H,  $^3\text{J}8.72\text{Hz}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}8.12\text{Hz}$ , Ar-H), 7.23-7.19 (m, 3H, Ar-H), 2.70-2.66 (t, 4H,  $^3\text{J}7.56\text{Hz}$ ,  $2 \times \text{Ar}-\text{CH}_2-$ ), 1.71-1.64 (quin, 4H,  $^3\text{J}7.6\text{Hz}$ ,  $2 \times \text{Ar}-\text{CH}_2-\text{CH}_2-$ ), 1.38-1.34 (m, 8H,  $4 \times -\text{CH}_2-$ ), 0.94-0.90 (t, 6H,  $^3\text{J}6.72\text{Hz}$ ,  $2 \times -\text{CH}_3$ ). Elemental analysis:  $\text{C}_{56}\text{H}_{50}\text{O}_8$  requires C, 79.04; H, 5.92%; found C, 78.81; H, 5.79%.

### **1, 3-Phenylene bis[4-(4-*n*-hexylbiphenyl-4-carboxyloxy)benzoate], 2.A.2**

Yield, 73%; m.p. 165.0°C;  $\nu_{\max}$ : 3069, 2957, 2926, 2855, 1742, 1738, 1736, 1603, 1257  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.32-8.30 (d, 4H,  $^3\text{J}_{8.72\text{Hz}}$ , Ar-H), 8.28-8.26 (d, 4H,  $^3\text{J}_{8.44\text{Hz}}$ , Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.44\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{8.16\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.28\text{Hz}}$ , Ar-H), 7.43-7.41 (d, 4H,  $^3\text{J}_{8.72\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{8.16\text{Hz}}$ , Ar-H), 7.24-7.19 (m, 3H, Ar-H), 2.70-2.66 (t, 4H,  $^3\text{J}_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.71-1.63 (quin, 4H,  $^3\text{J}_{7.6\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.38-1.34 (m, 12H, 6 x -CH<sub>2</sub>-), 0.93-0.89 (t, 6H,  $^3\text{J}_{6.88\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>58</sub>H<sub>54</sub>O<sub>8</sub> requires C, 79.25; H, 6.19%; found C, 79.50; H, 6.16%.

### **1, 3-Phenylene bis[4-(4-*n*-heptylbiphenyl-4-carboxyloxy)benzoate], 2.A.3**

Yield, 74%; m.p. 163.5°C;  $\nu_{\max}$ : 3071, 2962, 2924, 2853, 1738, 1736, 1732, 1603, 1256  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.32-8.30 (d, 4H,  $^3\text{J}_{8.76\text{Hz}}$ , Ar-H), 8.28-8.26 (d, 4H,  $^3\text{J}_{8.48\text{Hz}}$ , Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.48\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{8.16\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.32\text{Hz}}$ , Ar-H), 7.43-7.41 (d, 4H,  $^3\text{J}_{8.76\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{8.16\text{Hz}}$ , Ar-H), 7.24-7.19 (m, 3H, Ar-H), 2.70-2.66 (t, 4H,  $^3\text{J}_{7.52\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.71-1.63 (quin, 4H,  $^3\text{J}_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.38-1.34 (m, 16H, 8 x -CH<sub>2</sub>-), 0.92-0.88 (t, 6H,  $^3\text{J}_{6.72\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>60</sub>H<sub>58</sub>O<sub>8</sub> requires C, 79.45; H, 6.44%; found C, 79.21; H, 6.38%.

### **1, 3-Phenylene bis[4-(4-*n*-octylbiphenyl-4-carboxyloxy)benzoate], 2.A.4**

Yield, 70%; m.p. 153.5°C;  $\nu_{\max}$ : 3069, 2957, 2924, 2853, 1742, 1738, 1736, 1734, 1603, 1256  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.32-8.30 (d, 4H,  $^3\text{J}_{8.72\text{Hz}}$ , Ar-H), 8.28-8.26 (d, 4H,  $^3\text{J}_{8.44\text{Hz}}$ , Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.44\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{8.16\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.36\text{Hz}}$ , Ar-H), 7.43-7.41 (d, 4H,  $^3\text{J}_{8.72\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{8.12\text{Hz}}$ , Ar-H), 7.23-7.19 (m, 3H, Ar-H), 2.69-2.66 (t, 4H,  $^3\text{J}_{7.52\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H,  $^3\text{J}_{7.64\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.35-1.29 (m, 20H, 10 x -CH<sub>2</sub>-), 0.91-0.87 (t, 6H,  $^3\text{J}_{6.64\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>62</sub>H<sub>62</sub>O<sub>8</sub> requires C, 79.63; H, 6.68%; found C, 79.84; H, 6.81%.

### **1, 3-Phenylene bis[4-(4-*n*-nonylbiphenyl-4-carboxyloxy)benzoate], 2.A.5**

Yield, 76%; m.p. 141.0°C;  $\nu_{\max}$ : 3072, 2957, 2922, 2853, 1742, 1740, 1736, 1603, 1256  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.32-8.30 (d, 4H,  $^3\text{J}_{8.72\text{Hz}}$ , Ar-H), 8.28-8.26 (d, 4H,  $^3\text{J}_{8.48\text{Hz}}$ , Ar-H), 7.76-7.74 (d,

4H,  $^3J_{8.48\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{8.16\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{8.36\text{Hz}}$ , Ar-H), 7.43-7.41 (d, 4H,  $^3J_{8.72\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{8.16\text{Hz}}$ , Ar-H), 7.23-7.19 (m, 3H, Ar-H), 2.69-2.66 (t, 4H,  $^3J_{7.52\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.69-1.63 (quin, 4H,  $^3J_{7.6\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.35-1.29 (m, 24H, 12 x -CH<sub>2</sub>-), 0.91-0.87 (t, 6H,  $^3J_{6.64\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>64</sub>H<sub>66</sub>O<sub>8</sub> requires C, 79.81; H, 6.91%; found C, 79.90; H, 6.99%.

### **1, 3-Phenylene bis[4-(4-*n*-decylbiphenyl-4-carboxyloxy)benzoate], 2.A.6**

Yield, 72%; m.p. 159.0°C;  $\nu_{\text{max}}$ : 3065, 2957, 2922, 2851, 1742, 1736, 1734, 1603, 1256 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.32-8.30 (d, 4H,  $^3J_{8.72\text{Hz}}$ , Ar-H), 8.28-8.26 (d, 4H,  $^3J_{8.44\text{Hz}}$ , Ar-H), 7.76-7.74 (d, 4H,  $^3J_{8.44\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{8.28\text{Hz}}$ , Ar-H), 7.43-7.41 (d, 4H,  $^3J_{8.72\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.23-7.19 (m, 3H, Ar-H), 2.70-2.66 (t, 4H,  $^3J_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.69-1.63 (quin, 4H,  $^3J_{7.44\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.35-1.28 (m, 28H, 14 x -CH<sub>2</sub>-), 0.91-0.87 (t, 6H,  $^3J_{6.48\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>66</sub>H<sub>70</sub>O<sub>8</sub> requires C, 79.97; H, 7.12%; found C, 79.65; H, 7.14%.

### **1, 3-Phenylene bis[4-(4-*n*-undecylbiphenyl-4-carboxyloxy)benzoate], 2.A.7**

Yield, 68%; m.p. 151.0°C;  $\nu_{\text{max}}$ : 3072, 2954, 2922, 2851, 1740, 1738, 1732, 1603, 1256 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.32-8.30 (d, 4H,  $^3J_{8.72\text{Hz}}$ , Ar-H), 8.28-8.26 (d, 4H,  $^3J_{8.4\text{Hz}}$ , Ar-H), 7.76-7.74 (d, 4H,  $^3J_{8.4\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{8.28\text{Hz}}$ , Ar-H), 7.43-7.41 (d, 4H,  $^3J_{8.72\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.23-7.19 (m, 3H, Ar-H), 2.69-2.66 (t, 4H,  $^3J_{7.6\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H,  $^3J_{7.44\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.35-1.27 (m, 32H, 16 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H,  $^3J_{6.6\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>68</sub>H<sub>74</sub>O<sub>8</sub> requires C, 80.13; H, 7.32%; found C, 79.93; H, 7.40%.

### **1, 3-Phenylene bis[4-(4-*n*-tetradecylbiphenyl-4-carboxyloxy)benzoate], 2.A.9**

Yield, 76%; m.p. 118.0°C;  $\nu_{\text{max}}$ : 3080, 2953, 2916, 2849, 1732, 1730, 1728, 1603, 1288 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.32-8.30 (d, 4H,  $^3J_{8.72\text{Hz}}$ , Ar-H), 8.28-8.26 (d, 4H,  $^3J_{8.44\text{Hz}}$ , Ar-H), 7.76-7.74 (d, 4H,  $^3J_{8.44\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{8.28\text{Hz}}$ , Ar-H), 7.43-7.41 (d, 4H,  $^3J_{8.72\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.23-7.19 (m, 3H, Ar-H), 2.70-2.66 (t, 4H,  $^3J_{7.48\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.69-1.65 (quin, 4H,  $^3J_{7.52\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.35-



1.27 (m, 44H, 22 × -CH<sub>2</sub>-), 0.90-0.87 (t, 6H, <sup>3</sup>J6.6Hz, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>74</sub>H<sub>86</sub>O<sub>8</sub> requires C, 80.55; H, 7.86%; found C, 80.8 ; H, 7.86%.

### **1, 3-Phenylene bis[4-(4-*n*-hexadecylbiphenyl-4-carbonyloxy)benzoate], 2.A.10**

Yield, 77%; m.p. 117.5°C;  $\nu_{\max}$ : 3080, 2953, 2916, 2849, 1732, 1730, 1728, 1600, 1288 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.32-8.30 (d, 4H, <sup>3</sup>J8.72Hz, Ar-H), 8.28-8.26 (d, 4H, <sup>3</sup>J8.44Hz, Ar-H), 7.76-7.74 (d, 4H, <sup>3</sup>J8.44Hz, Ar-H), 7.60-7.58 (d, 4H, <sup>3</sup>J8.12Hz, Ar-H), 7.53-7.49 (t, 1H, <sup>3</sup>J8.28Hz, Ar-H), 7.43-7.41 (d, 4H, <sup>3</sup>J8.72Hz, Ar-H), 7.32-7.30 (d, 4H, <sup>3</sup>J8.12Hz, Ar-H), 7.23-7.19 (m, 3H, Ar-H), 2.70-2.66 (t, 4H, <sup>3</sup>J7.52Hz, 2 x Ar-CH<sub>2</sub>-), 1.69-1.65 (quin, 4H, <sup>3</sup>J7.52Hz, 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.35-1.27 (m, 52H, 26 × -CH<sub>2</sub>-), 0.90-0.87 (t, 6H, <sup>3</sup>J6.6Hz, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>78</sub>H<sub>94</sub>O<sub>8</sub> requires C, 80.79; H, 8.17%; found C, 80.97; H, 8.18%.

### **1, 3-Phenylene bis[4-(4-*n*-octadecylbiphenyl-4-carbonyloxy) benzoate], 2.A.11**

Yield, 73%; m.p. 117.0°C;  $\nu_{\max}$ : 3080, 2955, 2916, 2849, 1732, 1730, 1728, 1600, 1288 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.32-8.29 (d, 4H, <sup>3</sup>J8.68Hz, Ar-H), 8.28-8.26 (d, 4H, <sup>3</sup>J8.36Hz, Ar-H), 7.76-7.74 (d, 4H, <sup>3</sup>J8.36Hz, Ar-H), 7.60-7.58 (d, 4H, <sup>3</sup>J8.12Hz, Ar-H), 7.53-7.49 (t, 1H, <sup>3</sup>J8.2Hz, Ar-H), 7.43-7.41 (d, 4H, <sup>3</sup>J8.68Hz, Ar-H), 7.32-7.30 (d, 4H, <sup>3</sup>J8.12Hz, Ar-H), 7.21-7.19 (m, 3H, Ar-H), 2.69-2.65 (t, 4H, <sup>3</sup>J7.6Hz, 2 × Ar-CH<sub>2</sub>-), 1.66-1.64 (quin, 4H, <sup>3</sup>J7.48Hz, 2 × Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.26 (m, 60H, 30 x -CH<sub>2</sub>-), 0.90-0.86 (t, 6H, <sup>3</sup>J6.6Hz, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>82</sub>H<sub>102</sub>O<sub>8</sub> requires C, 81.01; H, 8.46%; found C, 80.90; H, 8.45%.

### **1, 3-Phenylene bis[4-(4-*n*-pentylbiphenyl-4-carbonyloxy)-2-fluorobenzoate], 2.B.1**

Yield, 65%; m.p. 143.5°C;  $\nu_{\max}$ : 3101, 3026, 2953, 2855, 1742, 1734, 1732, 1730, 1605, 1242, 1136, 1051, 766 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.26-8.19 (m, 6H, Ar-H), 7.76-7.74 (d, 4H, <sup>3</sup>J8.28Hz, Ar-H), 7.60-7.58 (d, 4H, <sup>3</sup>J8.08Hz, Ar-H), 7.53-7.49 (t, 1H, <sup>3</sup>J8.28Hz, Ar-H), 7.32-7.30 (d, 4H, <sup>3</sup>J8.08Hz, Ar-H), 7.25-7.21 (m, 7H, Ar-H), 2.70-2.66 (t, 4H, <sup>3</sup>J7.48Hz, 2 × Ar-CH<sub>2</sub>-), 1.69-1.58 (quin, 4H, <sup>3</sup>J7.6Hz, 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.40-1.32 (m, 8H, 4 x -CH<sub>2</sub>-), 0.92-0.88 (t, 6H, <sup>3</sup>J6.8Hz, 2 × -CH<sub>3</sub>).

### **1, 3-Phenylene bis[4-(4-*n*-hexylbiphenyl-4-carbonyloxy)-2-fluorobenzoate], 2.B.2**

Yield, 68%; m.p. 134.0°C;  $\nu_{\max}$ : 3103, 3026, 2957, 2855, 1753, 1751, 1736, 1732, 1605, 1242, 1132, 1049, 764  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.26-8.19 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.32\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{8.12\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.28\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{8.12\text{Hz}}$ , Ar-H), 7.25-7.21 (m, 7H, Ar-H), 2.70-2.66 (t, 4H,  $^3\text{J}_{7.6\text{Hz}}$ , 2  $\times$  Ar-CH<sub>2</sub>-), 1.70-1.62 (quin, 4H,  $^3\text{J}_{7.64\text{Hz}}$ , 2  $\times$  Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.38-1.32 (m, 12H, 6  $\times$  -CH<sub>2</sub>-), 0.93-0.90 (t, 6H,  $^3\text{J}_{6.72\text{Hz}}$ , 2  $\times$  -CH<sub>3</sub>).

### **1, 3-Phenylene bis[4-(4-*n*-heptylbiphenyl-4-carbonyloxy)-2-fluorobenzoate], 2.B.3**

Yield, 72%; m.p. 125.0°C;  $\nu_{\max}$ : 3103, 2923, 2852, 1746, 1736, 1732, 1605, 1238, 1128, 1049, 764  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.26-8.19 (m, 6H, Ar-H), 7.77-7.75 (d, 4H,  $^3\text{J}_{8.36\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{8.08\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.2\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{8.08\text{Hz}}$ , Ar-H), 7.25-7.21 (m, 7H, Ar-H), 2.69-2.66 (t, 4H,  $^3\text{J}_{7.6\text{Hz}}$ , 2  $\times$  Ar-CH<sub>2</sub>-), 1.70-1.62 (quin, 4H,  $^3\text{J}_{7.8\text{Hz}}$ , 2  $\times$  Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.40-1.30 (m, 16H, 8  $\times$  -CH<sub>2</sub>-), 0.91-0.88 (t, 6H,  $^3\text{J}_{6.62\text{Hz}}$ , 2  $\times$  -CH<sub>3</sub>).

### **1, 3-Phenylene bis[4-(4-*n*-octylbiphenyl-4-carbonyloxy)-2-fluorobenzoate], 2.B.4**

Yield, 63%; m.p. 124.5°C;  $\nu_{\max}$ : 3103, 2924, 2856, 1746, 1732, 1605, 1236, 1126, 1049, 764  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.26-8.19 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.6\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{8.24\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.2\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{8.24\text{Hz}}$ , Ar-H), 7.25-7.21 (m, 7H, Ar-H), 2.69-2.65 (t, 4H,  $^3\text{J}_{7.56\text{Hz}}$ , 2  $\times$  Ar-CH<sub>2</sub>-), 1.68-1.62 (quin, 4H,  $^3\text{J}_{7.64\text{Hz}}$ , 2  $\times$  Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.39-1.28 (m, 20H, 10  $\times$  -CH<sub>2</sub>-), 0.90-0.87 (t, 6H,  $^3\text{J}_{6.68\text{Hz}}$ , 2  $\times$  -CH<sub>3</sub>).

### **1, 3-Phenylene bis[4-(4-*n*-nonylbiphenyl-4-carbonyloxy)-2-fluorobenzoate], 2.B.5**

Yield, 69%; m.p. 110.0°C;  $\nu_{\max}$ : 3105, 2924, 2856, 1748, 1735, 1605, 1238, 1124, 1049, 764  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.26-8.19 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.56\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{8.24\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.32\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{8.24\text{Hz}}$ , Ar-H), 7.25-7.21 (m, 7H, Ar-H), 2.69-2.65 (t, 4H,  $^3\text{J}_{7.44\text{Hz}}$ , 2  $\times$  Ar-CH<sub>2</sub>-), 1.68-1.62 (quin, 4H,  $^3\text{J}_{7.6\text{Hz}}$ , 2  $\times$  Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.39-1.28 (m, 24H, 12  $\times$  -CH<sub>2</sub>-), 0.90-0.87 (t, 6H,  $^3\text{J}_{6.72\text{Hz}}$ , 2  $\times$  -CH<sub>3</sub>).

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

Yield, 71%; m.p. 103.0°C;  $\nu_{\max}$ : 3103, 2916, 2849, 1744, 1734, 1728, 1603, 1256, 1139, 756  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.26-8.19 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.56\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{8.04\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.32\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{8.04\text{Hz}}$ , Ar-H), 7.25-7.21 (m, 7H, Ar-H), 2.69-2.65 (t, 4H,  $^3\text{J}_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.69-1.62 (quin, 4H,  $^3\text{J}_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.39-1.26 (m, 44H, 22 x -CH<sub>2</sub>-), 0.90-0.86 (t, 6H,  $^3\text{J}_{6.66\text{Hz}}$ , 2 x -CH<sub>3</sub>).

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

Yield, 65%; m.p. 100.0°C;  $\nu_{\max}$ : 3124, 2849, 1744, 1740, 1734, 1608, 1254, 1059, 758  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.26-8.19 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.28\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{8.12\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.32\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{8.12\text{Hz}}$ , Ar-H), 7.25-7.21 (m, 7H, Ar-H), 2.69-2.65 (t, 4H,  $^3\text{J}_{7.6\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.69-1.62 (quin, 4H,  $^3\text{J}_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.39-1.26 (m, 52H, 26 x -CH<sub>2</sub>-), 0.89-0.86 (t, 6H,  $^3\text{J}_{6.68\text{Hz}}$ , 2 x -CH<sub>3</sub>).

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

Yield, 68%; m.p. 104.0°C;  $\nu_{\max}$ : 3101, 2918, 2849, 1736, 1732, 1607, 1258, 1140, 760  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.26-8.19 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.28\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{8.04\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.32\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{8.12\text{Hz}}$ , Ar-H), 7.25-7.21 (m, 7H, Ar-H), 2.69-2.65 (t, 4H,  $^3\text{J}_{7.76\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.69-1.62 (quin, 4H,  $^3\text{J}_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.39-1.26 (m, 60H, 30 x -CH<sub>2</sub>-), 0.90-0.86 (t, 6H,  $^3\text{J}_{6.68\text{Hz}}$ , 2 x -CH<sub>3</sub>).

**1, 3-Phenylene bis[4-(4-*n*-pentylbiphenyl-4-carboxyloxy)-2-methylbenzoate], 2.C.1**

Yield, 75%; m.p. 143.0°C;  $\nu_{\max}$ : 3081, 2957, 2930, 2855, 1738, 1734, 1730, 1605, 1275, 1225, 1130, 1042, 768  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.30-8.25 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.36\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{8.04\text{Hz}}$ , Ar-H), 7.52-7.49 (t, 1H,  $^3\text{J}_{7.84\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{8.04\text{Hz}}$ , Ar-H), 7.25-7.17 (m, 7H, Ar-H), 2.74 (s, 6H, 2 x Ar-CH<sub>3</sub>), 2.70-2.66 (t, 4H,  $^3\text{J}_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H,  $^3\text{J}_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.40-1.34 (m, 8H, 4 x -CH<sub>2</sub>-), 0.94-0.91 (t, 6H,  $^3\text{J}_{6.72\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>58</sub>H<sub>54</sub>O<sub>8</sub> requires C, 79.25; H, 6.19%; found C, 79.53; H, 6.27%.

### **1, 3-Phenylene bis[4-(4-*n*-hexylbiphenyl-4-carboxyloxy)-2-methylbenzoate], 2.C.2**

Yield, 70%; m.p. 143.5°C;  $\nu_{\max}$ : 3089, 2957, 2926, 2853, 1738, 1736, 1732, 1605, 1280, 1225, 1130, 1042, 764  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.30-8.25 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.28\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{8.04\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.04\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{8.04\text{Hz}}$ , Ar-H), 7.25-7.17 (m, 7H, Ar-H), 2.73 (s, 6H, 2 x Ar-CH<sub>3</sub>), 2.70-2.66 (t, 4H,  $^3\text{J}_{7.44\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H,  $^3\text{J}_{7.6\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.29 (m, 12H, 6x -CH<sub>2</sub>-), 0.92-0.89 (t, 6H,  $^3\text{J}_{6.76\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>60</sub>H<sub>58</sub>O<sub>8</sub> requires C, 79.45; H, 6.44%; found C, 79.68; H, 6.52%.

### **1, 3-Phenylene bis[4-(4-*n*-heptylbiphenyl-4-carboxyloxy)-2-methylbenzoate], 2.C.3**

Yield, 72%; m.p. 118.5°C;  $\nu_{\max}$ : 3063, 2957, 2926, 2853, 1734, 1732, 1605, 1279, 1238, 1134, 1045, 764  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.30-8.25 (m, 6H, Ar-H), 7.75-7.73 (d, 4H,  $^3\text{J}_{8.28\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{8.0\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.04\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{8.0\text{Hz}}$ , Ar-H), 7.25-7.17 (m, 7H, Ar-H), 2.73 (s, 6H, 2 x Ar-CH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3\text{J}_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.67-1.63 (quin, 4H,  $^3\text{J}_{7.68\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.30 (m, 16H, 8 x -CH<sub>2</sub>-), 0.91-0.88 (t, 6H,  $^3\text{J}_{6.56\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>62</sub>H<sub>62</sub>O<sub>8</sub> requires C, 79.63; H, 6.68%; found C, 79.26; H, 6.78%.

### **1, 3-Phenylene bis[4-(4-*n*-octylbiphenyl-4-carboxyloxy)-2-methylbenzoate], 2.C.4**

Yield, 70%; m.p. 104.0°C;  $\nu_{\max}$ : 3071, 1736, 1734, 1730, 1604, 1267, 1224, 1130, 1043, 766  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.30-8.25 (m, 6H, Ar-H), 7.75-7.73 (d, 4H,  $^3\text{J}_{8.24\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{7.96\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.04\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{7.96\text{Hz}}$ , Ar-H), 7.25-7.17 (m, 7H, Ar-H), 2.73 (s, 6H, 2 x Ar-CH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3\text{J}_{7.48\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.67-1.63 (quin, 4H,  $^3\text{J}_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.29 (m, 20H, 10 x -CH<sub>2</sub>-), 0.91-0.87 (t, 6H,  $^3\text{J}_{6.66\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>64</sub>H<sub>66</sub>O<sub>8</sub> requires C, 79.81; H, 6.91%; found C, 79.82; H, 6.95%.

### **1, 3-Phenylene bis[4-(4-*n*-nonylbiphenyl-4-carboxyloxy)-2-methylbenzoate], 2.C.5**

Yield, 76%; m.p. 101.0°C;  $\nu_{\max}$ : 3074, 2956, 2922, 2851, 1736, 1732, 1605, 1267, 1227, 1132, 1045, 764  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.30-8.25 (m, 6H, Ar-H), 7.75-7.73 (d, 4H,  $^3\text{J}_{8.36\text{Hz}}$ , Ar-H), 7.60-7.58

(d, 4H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.25-7.17 (m, 7H, Ar-H), 2.74 (s, 6H, 2 x Ar-CH<sub>3</sub>), 2.69-2.66 (t, 4H,  $^3J_{7.72\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.67-1.63 (quin, 4H,  $^3J_{7.72\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.41-1.28 (m, 24H, 12 x -CH<sub>2</sub>-), 0.91-0.87 (t, 6H,  $^3J_{6.6\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>66</sub>H<sub>70</sub>O<sub>8</sub> requires C, 79.97; H, 7.12%; found C, 80.32; H, 7.28%.

### **1, 3-Phenylene bis[4-(4-*n*-decylbiphenyl-4-carboxyloxy)-2-methylbenzoate], 2.C.6**

Yield, 72%; m.p. 119.5°C;  $\nu_{\text{max}}$ : 3058, 2957, 2922, 2851, 1736, 1734, 1730, 1605, 1267, 1227, 1130, 1043, 766 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.30-8.25 (m, 6H, Ar-H), 7.75-7.73 (d, 4H,  $^3J_{8.32\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.25-7.17 (m, 7H, Ar-H), 2.73 (s, 6H, 2 x Ar-CH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3J_{7.64\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.67-1.63 (quin, 4H,  $^3J_{7.92\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.41-1.27 (m, 28H, 14 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H,  $^3J_{6.52\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>68</sub>H<sub>74</sub>O<sub>8</sub> requires C, 80.13; H, 7.32%; found C, 80.22; H, 7.5%.

### **1, 3-Phenylene bis[4-(4-*n*-undecylbiphenyl-4-carboxyloxy)-2-methylbenzoate], 2.C.7**

Yield, 78%; m.p. 112.5°C;  $\nu_{\text{max}}$ : 3076, 2954, 2924, 2851, 1744, 1732, 1720, 1605, 1268, 1225, 1128, 1043, 766 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.30-8.25 (m, 6H, Ar-H), 7.75-7.73 (d, 4H,  $^3J_{8.36\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{8.06\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.25-7.17 (m, 7H, Ar-H), 2.74 (s, 6H, 2 x Ar-CH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3J_{7.52\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H,  $^3J_{7.44\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.28 (m, 32H, 16 x -CH<sub>2</sub>-), 0.91-0.87 (t, 6H,  $^3J_{6.56\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>70</sub>H<sub>78</sub>O<sub>8</sub> requires C, 80.27; H, 7.51%; found C, 80.57; H, 7.6%.

### **1, 3-Phenylene bis[4-(4-*n*-dodecylbiphenyl-4-carboxyloxy)-2-methylbenzoate], 2.C.8**

Yield, 76%; m.p. 115.0°C;  $\nu_{\text{max}}$ : 3076, 2953, 2922, 2851, 1732, 1722, 1605, 1261, 1227, 1128, 1045, 768 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.30-8.24 (m, 6H, Ar-H), 7.75-7.73 (d, 4H,  $^3J_{8.32\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{7.98\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.25-7.17 (m, 7H, Ar-H), 2.73 (s, 6H, 2 x Ar-CH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3J_{7.7\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.67-1.63 (quin, 4H,  $^3J_{7.08\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.41-1.27 (m, 36H, 14 x -CH<sub>2</sub>-), 0.90-0.87 (t,

6H,  $^3J_{6.52\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>72</sub>H<sub>82</sub>O<sub>8</sub> requires C, 80.41; H, 7.69%; found C, 80.25; H, 7.91%.

### **1, 3-Phenylene bis[4-(4-*n*-tetradecylbiphenyl-4-carboxyloxy)-2-methylbenzoate], 2.C.9**

Yield, 71%; m.p. 103.0°C;  $\nu_{\text{max}}$ : 3072, 2955, 2920, 2849, 1740, 1734, 1732, 1605, 1267, 1225, 1128, 1045, 768 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.30-8.24 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3J_{8.32\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{7.98\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.25-7.17 (m, 7H, Ar-H), 2.73 (s, 6H, 2 x Ar-CH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3J_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.67-1.63 (quin, 4H,  $^3J_{7.64\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.41-1.27 (m, 44H, 22 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H,  $^3J_{6.56\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>76</sub>H<sub>90</sub>O<sub>8</sub> requires C, 80.67; H, 8.02%; found C, 80.95; H, 7.96%.

### **1, 3-Phenylene bis[4-(4-*n*-hexadecylbiphenyl-4-carboxyloxy)-2-methylbenzoate], 2.C.10**

Yield, 74%; m.p. 103.5°C;  $\nu_{\text{max}}$ : 3060, 2920, 2849, 1736, 1734, 1732, 1607, 1271, 1229, 1138, 1037, 760 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.30-8.24 (m, 6H, Ar-H), 7.75-7.73 (d, 4H,  $^3J_{8.32\text{Hz}}$ , Ar-H), 7.59-7.57 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{7.98\text{Hz}}$ , Ar-H), 7.31-7.29 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.25-7.17 (m, 7H, Ar-H), 2.73 (s, 6H, 2 x Ar-CH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3J_{7.68\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.67-1.63 (quin, 4H,  $^3J_{7.44\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.41-1.27 (m, 52H, 26 x -CH<sub>2</sub>-), 0.90-0.86 (t, 6H,  $^3J_{6.52\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>80</sub>H<sub>98</sub>O<sub>8</sub> requires C, 80.91; H, 8.32%; found C, 80.58; H, 8.16%.

### **1, 3-Phenylene bis[4-(4-*n*-octadecylbiphenyl-4-carboxyloxy)-2-methylbenzoate], 2.C.11**

Yield, 73%; m.p. 103.0°C;  $\nu_{\text{max}}$ : 3072, 2920, 2849, 1734, 1732, 1720, 1607, 1271, 1229, 1138, 1047, 762 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.30-8.24 (m, 6H, Ar-H), 7.75-7.73 (d, 4H,  $^3J_{8.36\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{7.96\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.25-7.17 (m, 7H, Ar-H), 2.73 (s, 6H, 2 x Ar-CH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3J_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.67-1.63 (quin, 4H,  $^3J_{7.44\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.41-1.26 (m, 60H, 30 x -CH<sub>2</sub>-), 0.90-0.86 (t, 6H,  $^3J_{6.6\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>84</sub>H<sub>106</sub>O<sub>8</sub> requires C, 81.12; H, 8.59%; found C, 81.32; H, 8.8%.

### **1, 3-Phenylene bis[4-(4-*n*-pentylbiphenyl-4-carbonyloxy)-2-ethylbenzoate], 2.D.1**

Yield, 69%; m.p. 132.0°C;  $\nu_{\max}$ : 3084, 2957, 2926, 2855, 1740, 1734, 1732, 1605, 1269, 1225, 1128, 1037, 766  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.28-8.25 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.12\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{7.8\text{ Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{7.98\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{7.88\text{Hz}}$ , Ar-H), 7.24-7.18 (m, 7H, Ar-H), 3.16-3.11 (q, 4H,  $^3\text{J}_{7.44\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 2.70-2.66 (t, 4H,  $^3\text{J}_{7.64\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.64 (quin, 4H,  $^3\text{J}_{7.44\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.38-1.30 (m, 14H, 4 x -CH<sub>2</sub>- 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 0.92-0.88 (t, 6H,  $^3\text{J}_{6.64\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>60</sub>H<sub>58</sub>O<sub>8</sub> requires C, 79.45; H, 6.44%; found C, 79.12; H, 6.2%.

### **1, 3-Phenylene bis[4-(4-*n*-hexylbiphenyl-4-carbonyloxy)-2-ethylbenzoate], 2.D.2**

Yield, 71%; m.p. 129.0°C;  $\nu_{\max}$ : 3079, 2957, 2930, 2857, 1748, 1735, 1733, 1604, 1267, 1225, 1128, 1078, 766  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.28-8.25 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.12\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{7.88\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{7.8\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{7.88\text{Hz}}$ , Ar-H), 7.24-7.18 (m, 7H, Ar-H), 3.16-3.11 (q, 4H,  $^3\text{J}_{7.44\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 2.70-2.66 (t, 4H,  $^3\text{J}_{7.6\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.64 (quin, 4H,  $^3\text{J}_{7.44\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.38-1.30 (m, 18H, 6 x -CH<sub>2</sub>-, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 0.92-0.88 (t, 6H,  $^3\text{J}_{6.64\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>62</sub>H<sub>62</sub>O<sub>8</sub> requires C, 79.63; H, 6.68%; found C, 79.75; H, 6.52%.

### **1, 3-Phenylene bis[4-(4-*n*-heptylbiphenyl-4-carbonyloxy)-2-ethylbenzoate], 2.D.3**

Yield, 70%; m.p. 113.0°C;  $\nu_{\max}$ : 3080, 2959, 2926, 2853, 1740, 1732, 1730, 1605, 1269, 1225, 1078, 1038, 766  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.28-8.25 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.08\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}_{7.72\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}_{8.04\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}_{7.72\text{Hz}}$ , Ar-H), 7.24-7.18 (m, 7H, Ar-H), 3.16-3.11 (q, 4H,  $^3\text{J}_{7.4\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 2.70-2.66 (t, 4H,  $^3\text{J}_{7.68\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.64 (quin, 4H,  $^3\text{J}_{7.48\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.38-1.30 (m, 22H, 8 x -CH<sub>2</sub>-, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 0.92-0.88 (t, 6H,  $^3\text{J}_{6.68\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>64</sub>H<sub>66</sub>O<sub>8</sub> requires C, 79.81; H, 6.91%; found C, 79.46; H, 6.92%.

### **1, 3-Phenylene bis[4-(4-*n*-octylbiphenyl-4-carbonyloxy)-2-ethylbenzoate], 2.D.4**

Yield, 76%; m.p. 99.0°C;  $\nu_{\max}$ : 3078, 2957, 2924, 2853, 1740, 1734, 1732, 1605, 1265, 1226, 1128, 1037, 1038, 766  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.28-8.25 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}_{8.12\text{Hz}}$ , Ar-

H), 7.60-7.58 (d, 4H,  $^3J_{7.84\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{7.84\text{Hz}}$ , Ar-H), 7.24-7.18 (m, 7H, Ar-H), 3.16-3.11 (q, 4H,  $^3J_{7.4\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3J_{7.56\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.64 (quin, 4H,  $^3J_{7.48\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.38-1.30 (m, 26H, 10 x -CH<sub>2</sub>-, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 0.91-0.87 (t, 6H,  $^3J_{6.6\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>66</sub>H<sub>70</sub>O<sub>8</sub> requires C, 79.97; H, 7.12%; found C, 79.71; H, 7.21%.

### **1, 3-Phenylene bis 4-(4-*n*-nonylbiphenyl-4-carboxyloxy)-2-ethylbenzoate], 2.D.5**

Yield, 74%; m.p. 102.5°C;  $\nu_{\text{max}}$ : 3075, 2959, 2922, 2851, 1740, 1734, 1716, 1605, 1265, 1234, 1134, 1042, 768 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.28-8.25 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3J_{8.32\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{7.92\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{7.96\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{7.92\text{Hz}}$ , Ar-H), 7.24-7.18 (m, 7H, Ar-H), 3.16-3.11 (q, 4H,  $^3J_{7.4\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3J_{7.6\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.64 (quin, 4H,  $^3J_{7.48\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.36-1.28 (m, 30H, 12 x -CH<sub>2</sub>-, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 0.91-0.87 (t, 6H,  $^3J_{6.6\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>68</sub>H<sub>74</sub>O<sub>8</sub> requires C, 80.13; H, 7.32%; found C, 79.82; H, 7.59%.

### **1, 3-Phenylene bis[4-(4-*n*-decylbiphenyl-4-carboxyloxy)-2-ethylbenzoate], 2.D.6**

Yield, 78%; m.p. 104.5°C;  $\nu_{\text{max}}$ : 3072, 2961, 2922, 2851, 1742, 1744, 1715, 1605, 1267, 1234, 1134, 1042, 768 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.28-8.25 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3J_{8.2\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{7.88\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{8.0\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{7.88\text{Hz}}$ , Ar-H), 7.24-7.18 (m, 7H, Ar-H), 3.16-3.11 (q, 4H,  $^3J_{7.44\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3J_{7.64\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.64 (quin, 4H,  $^3J_{7.28\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.28 (m, 34H, 14 x -CH<sub>2</sub>-, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 0.90-0.87 (t, 6H,  $^3J_{6.58\text{Hz}}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>70</sub>H<sub>78</sub>O<sub>8</sub> requires C, 80.27; H, 7.51%; found, C, 80.01; H, 7.62%.

### **1, 3-Phenylene bis [4-(4-*n*-undecylbiphenyl-4-carboxyloxy)2-ethylbenzoate], 2.D.7**

Yield, 79%; m.p. 105.5°C;  $\nu_{\text{max}}$ : 3072, 2959, 2922, 2851, 1742, 1734, 1715, 1605, 1267, 1234, 1134, 1042, 768 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.28-8.25 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3J_{8.08\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{7.84\text{Hz}}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3J_{7.96\text{Hz}}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3J_{7.84\text{Hz}}$ , Ar-H), 7.24-7.18 (m, 7H, Ar-H), 3.16-3.11 (q, 4H,  $^3J_{7.4\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3J_{7.6\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.64 (quin, 4H,  $^3J_{7.04\text{Hz}}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.28



(m, 38H, 16 x -CH<sub>2</sub>-, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 0.90-0.87 (t, 6H, <sup>3</sup>J6.72Hz, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>72</sub>H<sub>82</sub>O<sub>8</sub> requires C, 80.41; H, 7.69%; found C, 80.10; H, 7.59%.

### **1, 3-Phenylene bis[4-(4-*n*-dodecylbiphenyl-4-carbonyloxy)-2-ethylbenzoate], 2.D.8**

Yield, 72%; m.p. 104.5°C;  $\nu_{\max}$ : 3072, 2961, 2922, 2851, 1742, 1734, 1717, 1605, 1267, 1234, 1134, 1042, 768 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.28-8.25 (m, 6H, Ar-H), 7.76-7.74 (d, 4H, <sup>3</sup>J8.2Hz, Ar-H), 7.60-7.58 (d, 4H, <sup>3</sup>J7.88Hz, Ar-H), 7.53-7.49 (t, 1H, <sup>3</sup>J7.92Hz, Ar-H), 7.32-7.30 (d, 4H, <sup>3</sup>J7.88Hz, Ar-H), 7.24-7.18 (m, 7H, Ar-H), 3.16-3.11 (q, 4H, <sup>3</sup>J7.4Hz, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 2.69-2.65 (t, 4H, <sup>3</sup>J7.56Hz, 2 x Ar-CH<sub>2</sub>-), 1.68-1.64 (quin, 4H, <sup>3</sup>J7.28Hz, 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.27 (m, 42H, 18 x -CH<sub>2</sub>-, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 0.90-0.87 (t, 6H, <sup>3</sup>J6.58Hz, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>74</sub>H<sub>86</sub>O<sub>8</sub> requires C, 80.55; H, 7.86%; found C, 80.62; H, 8.04%.

### **1, 3-Phenylene bis[4-(4-*n*-tetradecylbiphenyl-4-carbonyloxy)-2-ethylbenzoate], 2.D.9**

Yield, 70%; m.p. 105.0°C;  $\nu_{\max}$ : 3072, 2957, 2920, 2851, 1742, 1730, 1715, 1605, 1267, 1234, 1042, 768 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.28-8.25 (m, 6H, Ar-H), 7.76-7.74 (d, 4H, <sup>3</sup>J8.36Hz, Ar-H), 7.60-7.58 (d, 4H, <sup>3</sup>J8.08Hz, Ar-H), 7.53-7.49 (t, 1H, <sup>3</sup>J8.04Hz, Ar-H), 7.32-7.30 (d, 4H, <sup>3</sup>J8.08Hz, Ar-H), 7.24-7.18 (m, 7H, Ar-H), 3.16-3.11 (q, 4H, <sup>3</sup>J7.48Hz, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 2.69-2.65 (t, 4H, <sup>3</sup>J7.48, 2 x Ar-CH<sub>2</sub>-), 1.68-1.64 (quin, 4H, <sup>3</sup>J7.56Hz, 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.27 (m, 50H, 22 x -CH<sub>2</sub>-, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 0.90-0.87 (t, 6H, <sup>3</sup>J6.64Hz, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>78</sub>H<sub>94</sub>O<sub>8</sub> requires C, 80.79; H, 8.17%; found C, 80.33; H, 8.40%.

### **1, 3-Phenylene bis[4-(4-*n*-hexadecylbiphenyl-4-carbonyloxy)-2-ethylbenzoate], 2.D.10**

Yield, 76%; m.p. 104.5°C;  $\nu_{\max}$ : 3071, 2957, 2920, 2849, 1736, 1730, 1716, 1605, 1267, 1234, 1134, 768 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.28-8.25 (m, 6H, Ar-H), 7.76-7.74 (d, 4H, <sup>3</sup>J8.36Hz, Ar-H), 7.60-7.58 (d, 4H, <sup>3</sup>J8.12Hz, Ar-H), 7.53-7.49 (t, 1H, <sup>3</sup>J8.08Hz, Ar-H), 7.32-7.30 (d, 4H, <sup>3</sup>J8.12Hz, Ar-H), 7.24-7.18 (m, 7H, Ar-H), 3.16-3.11 (q, 4H, <sup>3</sup>J7.44Hz, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 2.69-2.65 (t, 4H, <sup>3</sup>J7.52, 2 x Ar-CH<sub>2</sub>-), 1.68-1.64 (quin, 4H, <sup>3</sup>J7.56Hz, 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.27 (m, 58H, 26 x -CH<sub>2</sub>-, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 0.90-0.87 (t, 6H, <sup>3</sup>J6.52Hz, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>82</sub>H<sub>102</sub>O<sub>8</sub> requires C, 81.02; H, 8.46%; found C, 80.74; H, 8.85%.

### **1, 3-Phenylene bis[4-(4-*n*-octadecylbiphenyl-4-carbonyloxy)-2-ethylbenzoate], 2.D.11**

Yield, 68%; m.p. 104.0°C;  $\nu_{\max}$ : 3072, 2957, 2920, 2849, 1740, 1734, 1730, 1717, 1605, 1267, 1234, 1134, 1042, 766  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.28-8.25 (m, 6H, Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}8.08\text{Hz}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}7.76\text{Hz}$ , Ar-H), 7.53-7.49 (t, 1H,  $^3\text{J}7.84\text{Hz}$ , Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}7.8\text{Hz}$ , Ar-H), 7.24-7.18 (m, 7H, Ar-H), 3.16-3.11 (q, 4H,  $^3\text{J}7.56\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3\text{J}7.68\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.64 (quin, 4H,  $^3\text{J}7.56\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.26 (m, 66H, 30 x -CH<sub>2</sub>-, 2 x Ar-CH<sub>2</sub>-CH<sub>3</sub>), 0.90-0.87 (t, 6H,  $^3\text{J}6.84\text{Hz}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>86</sub>H<sub>110</sub>O<sub>8</sub> requires C, 81.22; H, 8.72%; found C, 81.60; H, 8.84%.

### **1, 3-Phenylene bis[4-(4-*n*-pentylbiphenyl-4-carbonyloxy)-3-fluorobenzoate], 2.E.1**

Yield, 63%; m.p. 157.0°C;  $\nu_{\max}$ : 3074, 2957, 2922, 2854, 1749, 1739, 1604, 1508, 1298, 1178, 1057, 758  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H,  $^3\text{J}8.32\text{Hz}$ , Ar-H), 8.10-8.06 (m, 4H, Ar-H), 7.77-7.74 (d, 4H,  $^3\text{J}8.32\text{Hz}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}8.12\text{Hz}$ , Ar-H), 7.55-7.45 (m, 3H, Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}8.12\text{Hz}$ , Ar-H), 7.22-7.19 (m, 3H, Ar-H), 2.70-2.66 (t, 4H,  $^3\text{J}7.6\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-), 1.69-1.65 (quin, 4H,  $^3\text{J}7.72\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.38-1.34 (m, 8H, 4 x -CH<sub>2</sub>-), 0.94-0.90 (t, 6H,  $^3\text{J}6.76\text{Hz}$ , 2 x -CH<sub>3</sub>).

### **1, 3-Phenylene bis[4-(4-*n*-hexylbiphenyl-4-carbonyloxy)-3-fluorobenzoate], 2.E.2**

Yield, 65%; m.p. 154.0°C;  $\nu_{\max}$ : 3074, 2957, 2922, 2854, 1748, 1740, 1604, 1508, 1298, 1178, 1057, 760  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H,  $^3\text{J}8.2\text{Hz}$ , Ar-H), 8.10-8.05 (m, 4H, Ar-H), 7.78-7.75 (d, 4H,  $^3\text{J}8.24\text{Hz}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}8.08\text{Hz}$ , Ar-H), 7.54-7.45 (m, 3H, Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}8.08\text{Hz}$ , Ar-H), 7.22-7.19 (m, 3H, Ar-H), 2.69-2.65 (t, 4H,  $^3\text{J}7.6\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-), 1.69-1.65 (quin, 4H,  $^3\text{J}7.6\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.38-1.34 (m, 12H, 6 x -CH<sub>2</sub>-), 0.92-0.88 (t, 6H,  $^3\text{J}6.64\text{Hz}$ , 2 x -CH<sub>3</sub>).

### **1, 3-Phenylene bis[4-(4-*n*-heptylbiphenyl-4-carbonyloxy)-3-fluorobenzoate], 2.E.3**

Yield, 70%; m.p. 153.5°C;  $\nu_{\max}$ : 3074, 2961, 2924, 2855, 1742, 1740, 1603, 1292, 1173, 1057, 764  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H,  $^3\text{J}8.36\text{Hz}$ , Ar-H), 8.10-8.05 (m, 4H, Ar-H), 7.77-7.74 (d, 4H,  $^3\text{J}8.36\text{Hz}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}8.12\text{Hz}$ , Ar-H), 7.54-7.45 (m, 3H, Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}8.12\text{Hz}$ , Ar-H), 7.22-7.19 (m, 3H, Ar-H), 2.69-2.65 (t, 4H,  $^3\text{J}7.52\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-

1.63 (quin, 4H,  $^3J_{7.68\text{Hz}}$ , 2 × Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.36-1.30 (m, 16H, 8 x -CH<sub>2</sub>-), 0.91-0.87 (t, 6H,  $^3J_{6.68\text{Hz}}$ , 2 × -CH<sub>3</sub>).

**1, 3-Phenylene bis[4-(4-*n*-octylbiphenyl-4-carbonyloxy)-3-fluorobenzoate], 2.E.4**

Yield, 68%; m.p. 156.5°C;  $\nu_{\text{max}}$ : 3072, 2957, 2924, 2855, 1742, 1740, 1601, 1292, 1173, 1055, 764 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H,  $^3J_{8.28\text{Hz}}$ , Ar-H), 8.10-8.06 (m, 4H, Ar-H), 7.77-7.74 (d, 4H,  $^3J_{8.28\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.55-7.45 (m, 3H, Ar-H), 7.32-7.30 (d, 4H,  $^3J_{8.04\text{Hz}}$ , Ar-H), 7.22-7.19 (m, 3H, Ar-H), 2.69-2.65 (t, 4H,  $^3J_{7.52\text{Hz}}$ , 2 × Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H,  $^3J_{7.52\text{Hz}}$ , 2 × Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.28 (m, 20H, 10 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H,  $^3J_{6.68\text{Hz}}$ , 2 × -CH<sub>3</sub>).

**1, 3-Phenylene bis[4-(4-*n*-nonylbiphenyl-4-carbonyloxy)-3-fluorobenzoate], 2.E.5**

Yield, 71%; m.p. 156.0°C;  $\nu_{\text{max}}$ : 3022, 2926, 2855, 1744, 1742, 1603, 1292, 1258, 1173, 1055, 764 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H,  $^3J_{8.32\text{Hz}}$ , Ar-H), 8.10-8.06 (m, 4H, Ar-H), 7.77-7.75 (d, 4H,  $^3J_{8.32\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.55-7.45 (m, 3H, Ar-H), 7.32-7.30 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.22-7.19 (m, 3H, Ar-H), 2.69-2.65 (t, 4H,  $^3J_{7.64\text{Hz}}$ , 2 × Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H,  $^3J_{7.92\text{Hz}}$ , 2 × Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.28 (m, 24H, 12 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H,  $^3J_{6.6\text{Hz}}$ , 2 × -CH<sub>3</sub>).

**1,3-Phenylene bis[4-(4-*n*-decylbiphenyl-4-carbonyloxy)-3-fluorobenzoate], 2.E.6**

Yield, 74%; m.p. 141.5°C;  $\nu_{\text{max}}$ : 3072, 2955, 2920, 2849, 1740, 1736, 1605, 1294, 1267, 1180, 762 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H,  $^3J_{8.44\text{Hz}}$ , Ar-H), 8.10-8.06 (m, 4H, Ar-H), 7.77-7.75 (d, 4H,  $^3J_{8.44\text{Hz}}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.55-7.45 (m, 3H, Ar-H), 7.32-7.30 (d, 4H,  $^3J_{8.12\text{Hz}}$ , Ar-H), 7.23-7.20 (m, 3H, Ar-H), 2.69-2.65 (t, 4H,  $^3J_{7.64\text{Hz}}$ , 2 × Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H,  $^3J_{7.64\text{Hz}}$ , 2 × Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.27 (m, 28H, 14 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H,  $^3J_{6.64\text{Hz}}$ , 2 × -CH<sub>3</sub>).

**1, 3-Phenylene bis[4-(4-*n*-undecylbiphenyl-4-carbonyloxy)-3-fluorobenzoate], 2.E.7**

Yield, 75%; m.p. 142.0°C;  $\nu_{\text{max}}$ : 3072, 2955, 2920, 2849, 1738, 1736, 1605, 1292, 1180, 761 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H,  $^3J_{8.32\text{Hz}}$ , Ar-H), 8.10-8.06 (m, 4H, Ar-H), 7.77-7.75 (d, 4H,

<sup>3</sup>J8.32Hz, Ar-H), 7.60-7.58 (d, 4H, <sup>3</sup>J8.12Hz, Ar-H), 7.55-7.45 (m, 3H, Ar-H), 7.32-7.30 (d, 4H, <sup>3</sup>J8.12Hz, Ar-H), 7.22-7.19 (m, 3H, Ar-H), 2.69-2.65 (t, 4H, <sup>3</sup>J7.48Hz, 2 × Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H, <sup>3</sup>J7.48Hz, 2 × Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.27 (m, 32H, 16 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H, <sup>3</sup>J6.48Hz, 2 × -CH<sub>3</sub>).

### **1, 3-Phenylene bis[4-(4-*n*-dodecylbiphenyl-4-carbonyloxy)-3-fluorobenzoate], 2.E.8**

Yield, 69%; m.p. 146.0°C;  $\nu_{\max}$ : 3072, 2955, 2918, 2849, 1738, 1732, 1605, 1292, 1180, 767 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H, <sup>3</sup>J8.36Hz, Ar-H), 8.10-8.06 (m, 4H, Ar-H), 7.77-7.75 (d, 4H, <sup>3</sup>J8.36Hz, Ar-H), 7.60-7.58 (d, 4H, <sup>3</sup>J8.12Hz, Ar-H), 7.53-7.45 (m, 3H, Ar-H), 7.32-7.30 (d, 4H, <sup>3</sup>J8.12Hz, Ar-H), 7.22-7.19 (m, 3H, Ar-H), 2.69-2.65 (t, 4H, <sup>3</sup>J7.64Hz, 2 × Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H, <sup>3</sup>J7.92Hz, 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.27 (m, 36H, 18 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H, <sup>3</sup>J6.52Hz, 2 × -CH<sub>3</sub>).

### **1, 3-Phenylene bis[4-(4-*n*-tetradecylbiphenyl-4-carbonyloxy)-3-fluorobenzoate], 2.E.9**

Yield, 72 %; m.p. 142.0°C;  $\nu_{\max}$ : 3072, 2955, 2918, 2849, 1741, 1736, 1605, 1292, 1181, 768 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H, <sup>3</sup>J8.44Hz, Ar-H), 8.10-8.06 (m, 4H, Ar-H), 7.77-7.75 (d, 4H, <sup>3</sup>J8.44Hz, Ar-H), 7.60-7.58 (d, 4H, <sup>3</sup>J8.16Hz, Ar-H), 7.52-7.45 (m, 3H, Ar-H), 7.32-7.30 (d, 4H, <sup>3</sup>J8.16Hz, Ar-H), 7.22-7.20 (m, 3H, Ar-H), 2.69-2.65 (t, 4H, <sup>3</sup>J7.64Hz, 2 × Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H, <sup>3</sup>J7.52Hz, 2 × Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.26 (m, 44H, 22 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H, <sup>3</sup>J6.6Hz, 2 × -CH<sub>3</sub>).

### **1, 3-Phenylene bis[4-(4-*n*-hexadecylbiphenyl-4-carbonyloxy)-3-fluorobenzoate], 2.E.10**

Yield, 78%; m.p. 136.0°C;  $\nu_{\max}$ : 3072, 2955, 2918, 2849, 1740, 1738, 1736, 1607, 1292, 1180, 767 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H, <sup>3</sup>J8.32Hz, Ar-H), 8.09-8.06 (m, 4H, Ar-H), 7.77-7.75 (d, 4H, <sup>3</sup>J8.32Hz, Ar-H), 7.60-7.58 (d, 4H, <sup>3</sup>J8.12Hz, Ar-H), 7.53-7.45 (m, 3H, Ar-H), 7.32-7.30 (d, 4H, <sup>3</sup>J8.12Hz, Ar-H), 7.22-7.20 (m, 3H, Ar-H), 2.69-2.65 (t, 4H, <sup>3</sup>J7.48Hz, 2 × Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H, <sup>3</sup>J7.6Hz, 2 × Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.26 (m, 52H, 26 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H, <sup>3</sup>J6.68Hz, 2 × -CH<sub>3</sub>).

**1, 3-Phenylene bis[4-(4-*n*-octadecylbiphenyl-4-carboxyloxy)-3-fluorobenzoate], 2.E.11**

Yield, 80%; m.p. 135.0°C;  $\nu_{\max}$ : 3072,2955, 2918,2849, 1740, 1738, 1605, 1292, 1180, 768  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H,  $^3\text{J}8.56\text{Hz}$ , Ar-H), 8.09-8.06 (m, 4H, Ar-H), 7.77-7.75 (d, 4H,  $^3\text{J}8.56\text{Hz}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}8.24\text{Hz}$ , Ar-H), 7.53-7.45 (m, 3H, Ar-H), 7.32-7.30 (d, 4H,  $^3\text{J}8.24\text{Hz}$ , Ar-H), 7.22-7.20 (m, 3H, Ar-H), 2.69-2.65 (t, 4H,  $^3\text{J}7.62\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H,  $^3\text{J}7.6\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.26 (m, 60H, 30 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H,  $^3\text{J}6.66\text{Hz}$ , 2 x -CH<sub>3</sub>).

**1, 3-Phenylene bis[4-(4-*n*-decylbiphenyl-4-carboxyloxy)-3-methoxybenzoate], 2.F.1**

Yield, 65%; m.p. 124.0°C;  $\nu_{\max}$ : 3050,2957, 2924,2853, 1744, 1736, 1605, 1285, 1169, 1061  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H,  $^3\text{J}8.36\text{Hz}$ , Ar-H), 7.93-7.91 (dd, 2H,  $^3\text{J}8.24\text{Hz}$ ,  $^4\text{J}11.72\text{Hz}$ , Ar-H), 7.85-7.84 (d, 2H,  $^4\text{J}11.56\text{Hz}$ , Ar-H), 7.76-7.74 (d, 4H,  $^3\text{J}8.36\text{Hz}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}8.08\text{Hz}$ , Ar-H), 7.54-7.50 (m, 1H, Ar-H), 7.35-7.30 (m, 6H, Ar-H), 7.22-7.19 (m, 3H, Ar-H), 3.93 (s, 6H, 2 x Ar-OCH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3\text{J}7.6\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H,  $^3\text{J}7.6\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.35-1.27 (m, 28H, 14 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H,  $^3\text{J}6.56\text{Hz}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>68</sub>H<sub>74</sub>O<sub>10</sub> requires C, 77.69; H, 7.09%; found C, 78.10; H, 6.86%.

**1, 3-Phenylene bis[4-(4-*n*-undecylbiphenyl-4-carboxyloxy)-3-methoxybenzoate], 2.F.2**

Yield, 70%; m.p. 124.0°C;  $\nu_{\max}$ : 3028,2954,2924,2852, 1738, 1736, 1605, 1285, 1169, 1061  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H,  $^3\text{J}8.32\text{Hz}$ , Ar-H), 7.93-7.91 (dd, 2H,  $^3\text{J}8.24\text{Hz}$ ,  $^4\text{J}11.64\text{Hz}$ , Ar-H), 7.85-7.84 (d, 2H,  $^4\text{J}11.52\text{Hz}$ , Ar-H), 7.75-7.73 (d, 4H,  $^3\text{J}8.32\text{Hz}$ , Ar-H), 7.60-7.58 (d, 4H,  $^3\text{J}8.04\text{Hz}$ , Ar-H), 7.54-7.50 (m, 1H, Ar-H), 7.34-7.30 (m, 6H, Ar-H), 7.21-7.19 (m, 3H, Ar-H), 3.93 (s, 6H, 2 x Ar-OCH<sub>3</sub>), 2.69-2.65 (t, 4H,  $^3\text{J}7.56\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H,  $^3\text{J}7.44\text{Hz}$ , 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.35-1.27 (m, 32H, 16 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H,  $^3\text{J}6.6\text{Hz}$ , 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>70</sub>H<sub>78</sub>O<sub>10</sub> requires C, 77.89; H, 7.28 %; found C, 77.48; H, 7.18%.

**1, 3-Phenylene bis[4-(4-*n*-dodecylbiphenyl-4-carboxyloxy)-3-methoxybenzoate], 2.F.3**

Yield, 68%; m.p. 130.5°C;  $\nu_{\max}$ : 3080,2953,2922,2851,1740, 1734, 1726, 1605, 1285, 1169, 1061  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 4H,  $^3\text{J}8.4\text{Hz}$ , Ar-H), 7.93-7.91 (dd, 2H,  $^3\text{J}8.28\text{Hz}$ ,  $^4\text{J}11.8\text{Hz}$ , Ar-H), 7.85-7.84 (d, 2H,  $^4\text{J}11.8\text{Hz}$ , Ar-H), 7.75-7.73 (d, 4H,  $^3\text{J}8.44\text{Hz}$ , Ar-H), 7.60-7.58 (d, 4H,

<sup>3</sup>J8.12Hz, Ar-H), 7.54-7.50 (m, 1H, Ar-H), 7.34-7.30 (m, 6H, Ar-H), 7.21-7.19 (m, 3H, Ar-H), 3.93 (s, 6H, 2 x Ar-OCH<sub>3</sub>), 2.69-2.65 (t, 4H, <sup>3</sup>J7.6Hz, 2 x Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 4H, <sup>3</sup>J7.56Hz, 2 x Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.35-1.27 (m, 36H, 18 x -CH<sub>2</sub>-), 0.90-0.87 (t, 6H, <sup>3</sup>J6.56Hz, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>72</sub>H<sub>82</sub>O<sub>10</sub> requires C, 78.09; H, 7.46 %; found C, 78.15; H, 7.45%.