Chapter 3

Synthesis and mesomorphic properties of

(i) **5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-alkylbiphenyl-4′-carbonyloxy)-benzoates]**

(ii) **5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-alkylbiphenyl-4′-carbonyloxy)-2-fluorobenzoates]**

(iii) **5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-alkylbiphenyl-4′-carbonyloxy)-3-fluorobenzoates]**

Introduction

The mesomorphic behaviour of compounds composed of bent-core (BC) molecules is very sensitive to small changes in the molecular structure. In this regard, lateral substituents on the core strongly influence the mesomorphic properties either by changing the packing of the molecules or by influencing the polar properties of the molecules. Thus, introduction of a lateral substituent in such a system can stabilize, destabilize or induce a mesophase. The effect of a lateral substituent on the mesomorphic behaviour is mainly governed by the nature, position and number of the substituents.

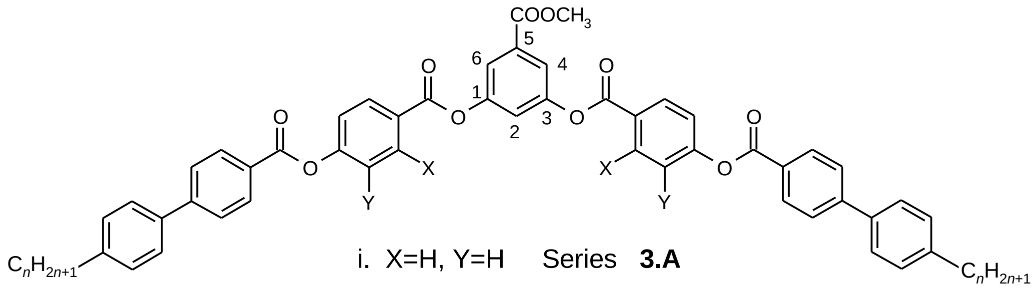
In bent-core molecules, lateral substituents can be introduced on any phenyl ring of the core. There are numerous studies on the influence of lateral substituents at different positions on the central phenyl ring as well as on other phenyl rings [1-10]. Weissflog *et al*. [2] investigated a number of compounds containing substituents like nitro, methyl, chloro, cyano and fluoro at different positions on the core. A methyl substituent at the obtuse angle induced a B_5 and a nitro substituent at the same position induced a B_7 phase, while the analogous unsubstituted compounds exhibit B_2 phase. New phase sequences such as B_2-SmA, B_2-N, B_2-SmA-SmC were obtained in compounds derived from 4-chloro- and 4-cyano-resorcinol which contain fluoro substituents *ortho* to the terminal *n*-alkoxy chains. Similarly, in derivatives of 4,6-dichlororesorcinol, calamitic phases were obtained along with banana phases. In a derivative of 5-fluororesorcinol, which is substituted by fluoro groups *ortho* to the terminal *n*-alkoxy chains, a tetramorphism was observed.

Sadashiva *et al*. [3,4] carried out systematic investigations of the effect of lateral substituents in the middle phenyl ring of the wings of the BC molecules. The electron withdrawing substituent such as fluoro, chloro and electron donating substituents such as methyl, ethyl, methoxy were examined. The chloro and methyl groups, which have approximately the same Van der Waal’s radius, show different mesophase behaviour. These studies indicate that unlike in calamitic liquid crystals, dipolar effects are more prominent than steric effects in determining the mesophase behaviour in BC compounds.

The effect of lateral substituents on the outer phenyl rings of the banana-shaped compounds has also been reported by several groups [5-9]. Recently, Dunemann *et al*. reported [10] several BC compounds which are resorcinol derivatives and contain chloro, bromo and methyl substituents on the outer phenyl rings *ortho* to the terminal chains and fluoro, chloro, cyano, nitro and methyl groups in different positions of the central ring.

However, the effect of a substituent at position 5 of the central phenyl ring is less studied. There are only a few examples reported so far, which are five-ring BC compounds derived from methyl 3,5-dihydroxybenzoate [12], 5-methylresorcinol [13], 5-fluororesorcinol [2,14,15], and 5-vinylresorcinol [16]. Until now, there is only one report [17] of seven-ring BC mesogens containing a substituent at the apex of the central phenyl ring. These are symmetrical ester compounds derived from 5-cyanoresorcinol that exhibit interesting mesomorphic properties.

In this chapter, the synthesis and mesomorphic properties of three new series of seven-ring BC compounds with a bulky methoxy carbonyl group at position 5 of the central phenyl ring are described. The compounds are symmetrical about the central phenyl ring and have the general molecular structure shown below (structure **3.1**).



i. X=H, Y=H Series **3.A**

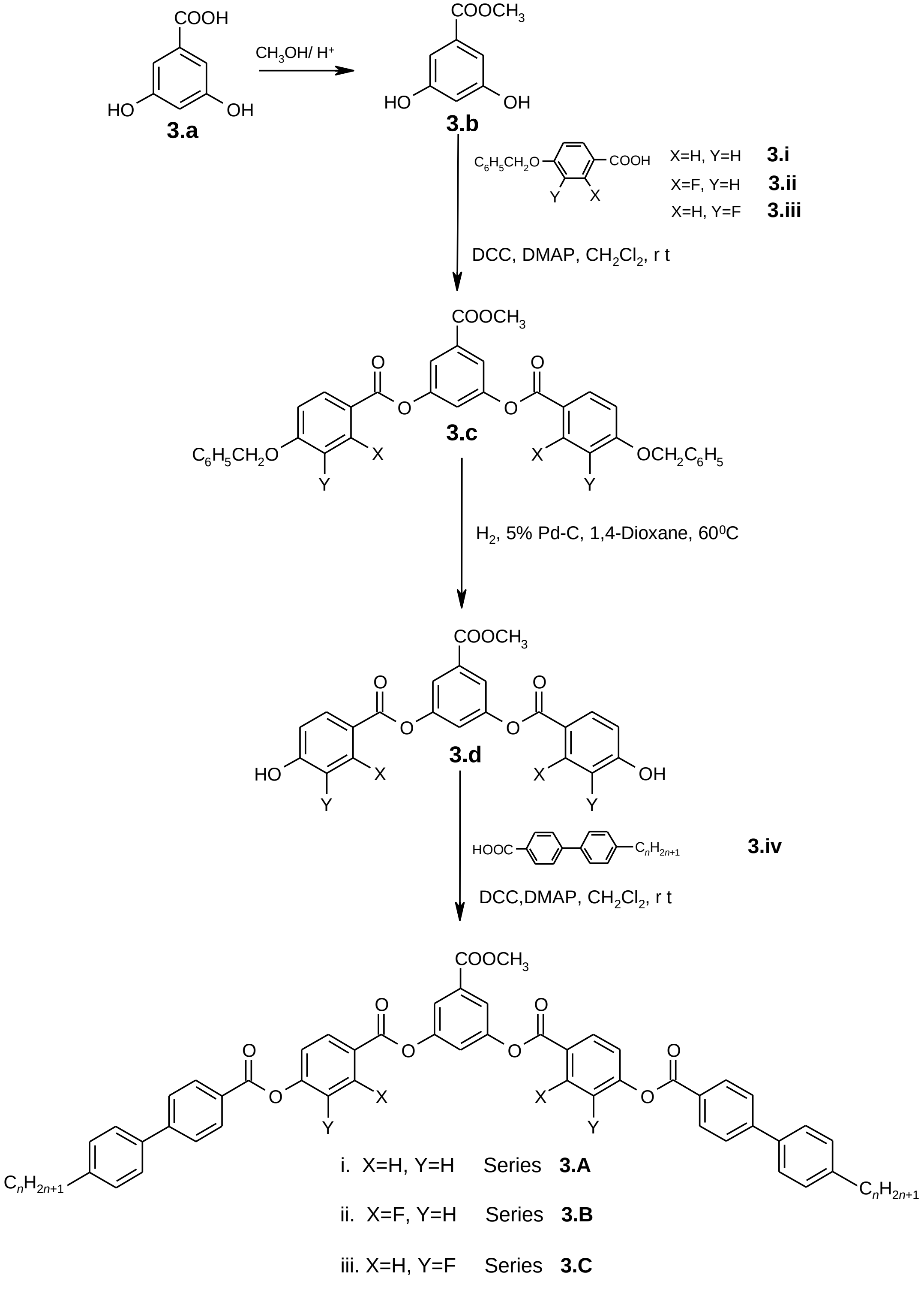
ii. X=F, Y=H Series **3.B**

iii. X=H, Y=F Series **3.C**

Structure 3.1

Synthesis

The seven-ring bent-core compounds were prepared using sequential esterification and hydrogenolysis procedures as shown in scheme **3.1**. *N*, *N′*-Dicyclohexylcarbodiimide (DCC) was used as a coupling reagent and 4-(*N*, *N*-dimethylamino)pyridine (DMAP) as catalyst in the esterification reaction. Hydrogenolysis was performed using 5% Pd-C catalyst in an atmosphere of



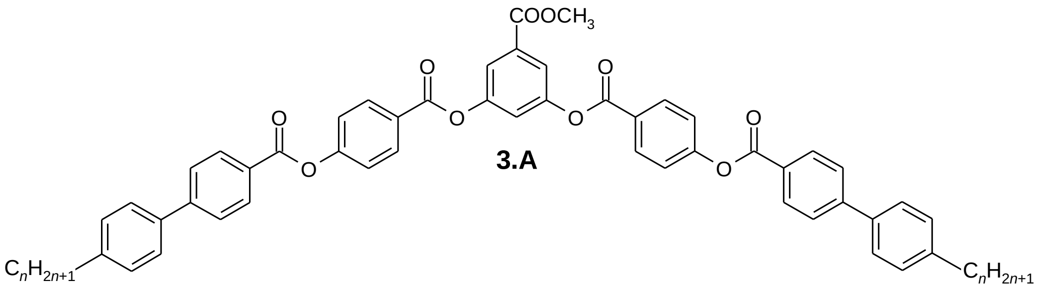
Scheme 3.1: Synthetic route followed to obtain the bent-core compounds.

hydrogen at 60˚C. Methyl 3,5-dihydroxybenzoate was prepared by the esterification of 3,5-dihydroxybenzoic acid with methanol using concentrated sulphuric acid as a catalyst. 2-Fluoro-4-benzyloxybenzoic acid and 3-Fluoro-4-benzyloxybenzoic acid were prepared following procedures described in the literature [18-20]. 4-*n*-Alkylbiphenyl-4-carboxylic acids were prepared as described in the literature [21]. The target compounds were purified by chromatography on silica gel followed by crystallization using suitable analytical grade solvents.

Results and discussion

The transition temperatures and the associated enthalpy values obtained for the compounds of series **3.A** are summarized in table **3.1**. Compounds of this series do not contain any lateral substituent in the arms of the bent-core. The compounds **3.A.1** and **3.A.2** are enantiotropic mesomorphic and exhibit similar textures. The mesophase grows from the isotropic state in the form batonnets, which coalesce to form a focal-conic texture. A typical photomicrograph of batonnets developing from the isotropic state obtained for compound **3.A.1** is shown in figure **3.1a**. These textural features indicate a SmA phase. However, a homeotropic alignment of the sample could not be obtained and further a schlieren texture was observed on shearing the sample (figure **3.1b**). These observations rule out the possibility of a SmA phase and suggest a B_6 (SmC_{int}) phase [1, 3, 4, 6, 22-24], which was confirmed through XRD measurements (described later). It is interesting to point out here that the B_6 phase has a large thermal range, for example 28˚C for compound **3.A.1**. Homologues **3.A.3-6** exhibit a monotropic mesophase and show a variety of textures. When a sample of compound **3.A.3** was cooled slowly from the isotropic state, dendritic patterns develop which coalesce into a mosaic-like texture. Such textures are typical for a B_1 phase [1, 3-6, 8, 9, 11, 22-27] and a dendritic growth pattern obtained for compound **3.A.3** is shown in figure **3.1c**. Similar texture was observed for compound **3.A.4** also. However, the mesophase of compounds **3.A.5** and **3.A.6** nucleates from isotropic state forming different patterns as shown in figure **3.1d**, **3.1e** and **3.1f** respectively. The mesophase of all these compounds has been characterized as Col_rP_{AF}, on the basis of XRD studies and electro-optical investigations (described later).

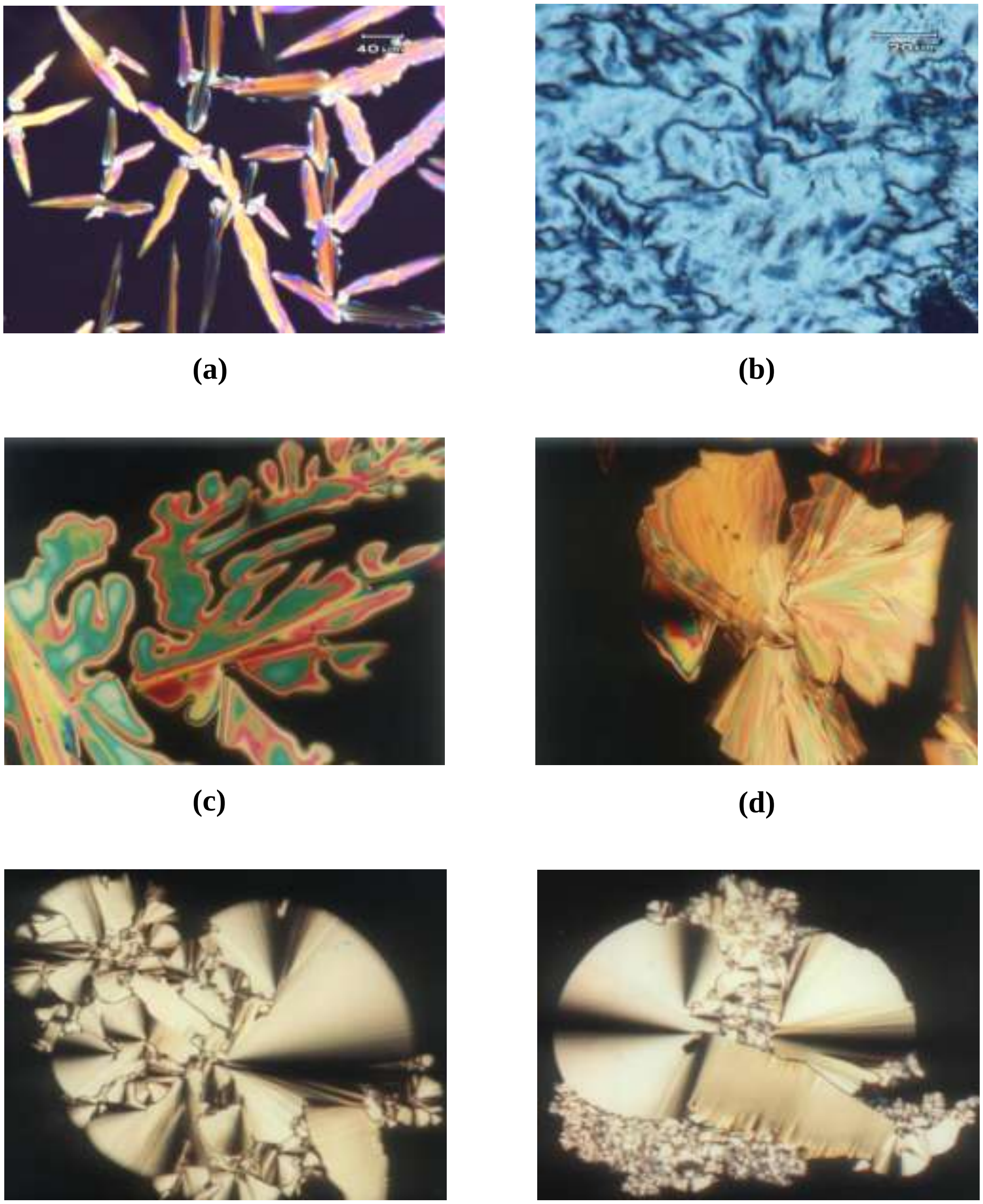
Table 3.1: Transition temperatures (˚C) and the associated enthalpy values (kJ mol^{-1}, in italics) for the compounds of series 3.A.



3.A

Compound	*n*	Cr		B_{2x}		Col_rP_{AF}		B_6		I
3.A.1	7	.	147.5* *105.5*	-		-		.	175.5 *16.5*	.
3.A.2	8	.	154.5* *100.0*	-		-		.	162.5 *16.5*	.
3.A.3	9	.	157.5 *57.0*	-		(.	153.0) *17.0*	-		.
3.A.4	10	.	156.5 *56.0*	-		(.	145.0) *16.5*	-		.
3.A.5	11	.	154.5 *59.0*	-		(.	141.0) *17.0*	-		.
3.A.6	12	.	153.5 *59.5*	-		(.	137.5) *18.0*	-		.
3.A.7	14	.	150.0 *59.5*	(.	141.0) *18.5*	-		-		.
3.A.8	16	.	145.0 *40.0*	.	146.0 *18.5*	-		-		.
3.A.9	18	.	143.0* *41.0*	.	146.5 *19.0*	-		-		.

Abbreviations: Cr-Crystalline phase; B_{2x}-Variant of a B_2 phase; Col_rP_{AF}- Polar columnar phase with a rectangular lattice and exhibiting antiferroelectric properties; B_6-Intercalated smectic C phase; I-Isotropic phase; **.** Phase exists; - Phase does not exist. * Compound has crystal-crystal transition and enthalpy denoted is the sum of all such transitions.



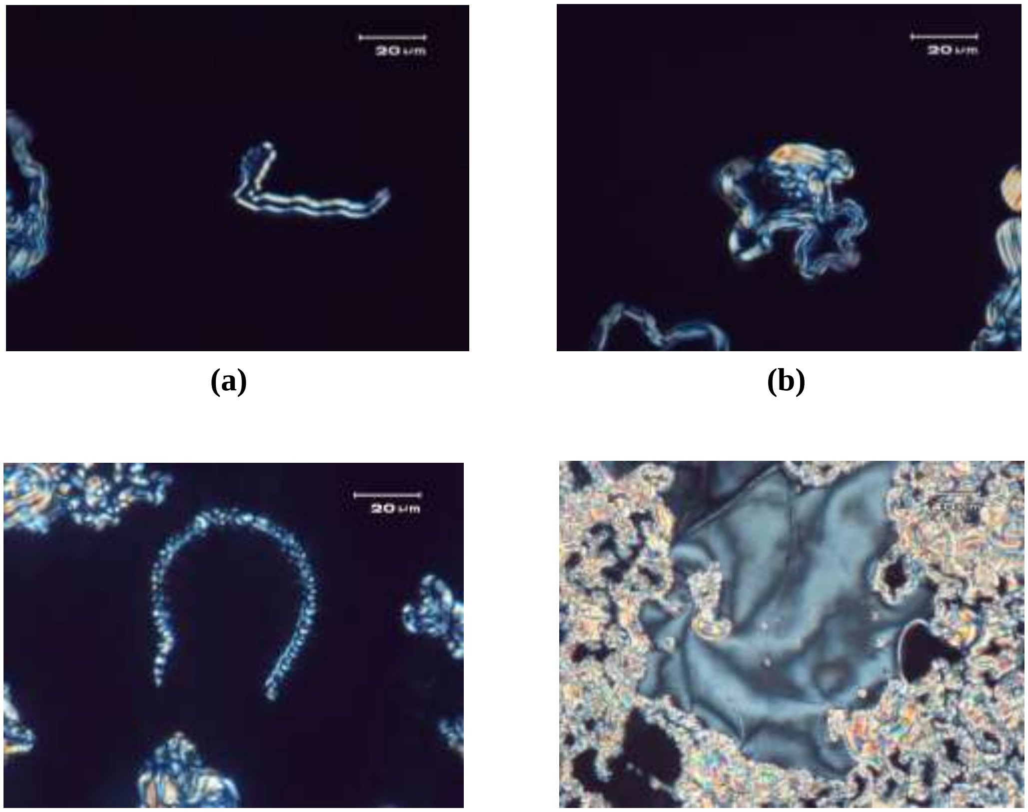
(a) (b)

(c) (d)

(e) (f)

Figure 3.1: (a) A photomicrograph of batonnets growing from isotropic phase of compound 3.A.1, T=175˚C; (b) a schlieren texture obtained on shearing the focal-conic texture of compound 3.A.1, T=160˚C; (c) a dendritic pattern obtained for the mesophase of compound 3.A.3, T=152.5˚C; (d) an optical texture obtained for the mesophase of compound 3.A.5, T=140.5˚C; (e) and (f) photomicrographs of the textures obtained for the mesophase of compound 3.A.6 at two different regions of the same sample, T=137˚C.

The mesophase of homologues **3.A.7-9** display similar optical textures. Compound **3.A.7** exhibits a monotropic phase while the mesophase exhibited by compounds **3.A.8** and **3.A.9** is enantiotropic. The mesophase develops from the isotropic state in the form of filaments, which immediately collapses to form an undefined birefringent texture as shown in figure **3.2a** and **b** as well as a helical pattern (figure **3.2c**). However, a schlieren texture was also observed for the mesophase of these compounds, which is shown in figure **3.2d**. These textural features are reminiscent of those observed for the B_{2x} phase of BC compounds derived from 5-cyano- [17] and



(a) **(b)**

(c) **(d)**

Figure 3.2: Photomicrographs of the textures obtained for the mesophase of compound 3.A.7. (a) A filament growing from the isotropic liquid, T=140.8˚C; (b) undefined texture obtained on collapse of the filament shown in (a), T=140.8˚C; (c) a helical pattern, T=140.8˚C; (d) a fringe pattern and a schlieren texture, T=138˚C.

5-chloro-resorcinol [Chapter 2]. The mesophase exhibited by compounds **3.A.7-9** has also been identified as B_{2x} on the basis of XRD and electro-optical studies.

A plot of temperature as a function of number of carbon atoms in the terminal chain for this series of compounds is shown in figure **3.3**. A smooth curve relationship is obtained for the like clearing points, which is quite typical for such transitions.

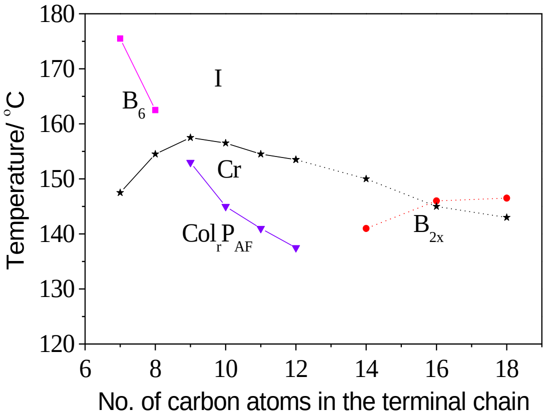
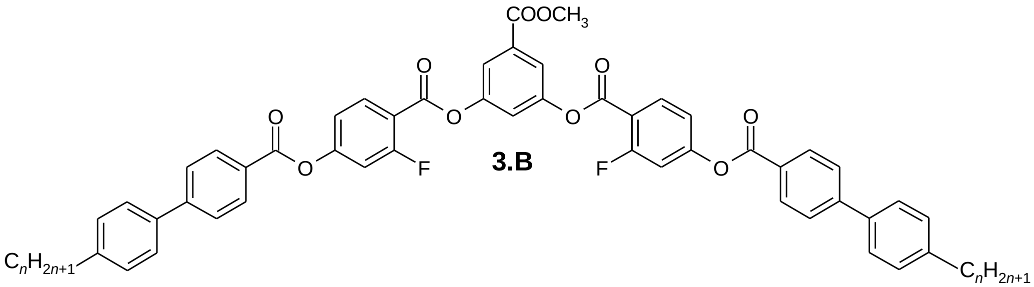


Figure 3.3: A plot of transition temperature as a function of the number of carbon atoms in the terminal chain for compounds of series 3.A.

The compounds of series **3.B** contain a fluoro substituent *ortho* to the ester carbonyl group connected to the central phenyl ring. The transition temperatures and the enthalpy values obtained for the compounds of this series are collected in table **3.2**. As can be seen from the table all the mesophases observed in the non-substituted parent compounds are retained. However, the melting points (except compound **3.B.1**) and the clearing temperatures are reduced and the effect is more pronounced in the melting points than the clearing temperatures. For example, there is a decrease of 32˚C in the melting point and 1.5˚C in the clearing temperature for compound **3.B.9** (*n*=16), compared to the corresponding parent compound **3.A.8**. Compounds **3.B.1** and **3.B.2** exhibit a B_6 phase. Compound **3.B.3** with a chain length *n*=8 exhibits a enantiotropic Col_rP_{AF} phase, while the analogous parent compound with *n*=8 exhibits a B_6 phase. A Col_rP_{AF} phase was observed for a compound with chain length *n*=9 in series **3.A** which is monotropic. On increasing the chain length, the temperature range of the Col_rP_{AF} phase decreases for homologues **3.B.4**, **3.B.5** and the phase becomes monotropic for compound **3.B.6**. The textural features obtained for these compounds are similar to those exhibited by the parent compounds of series **3.A**. The photomicrographs of the textures obtained for compound **3.B.6** is shown in figure **3.4**.

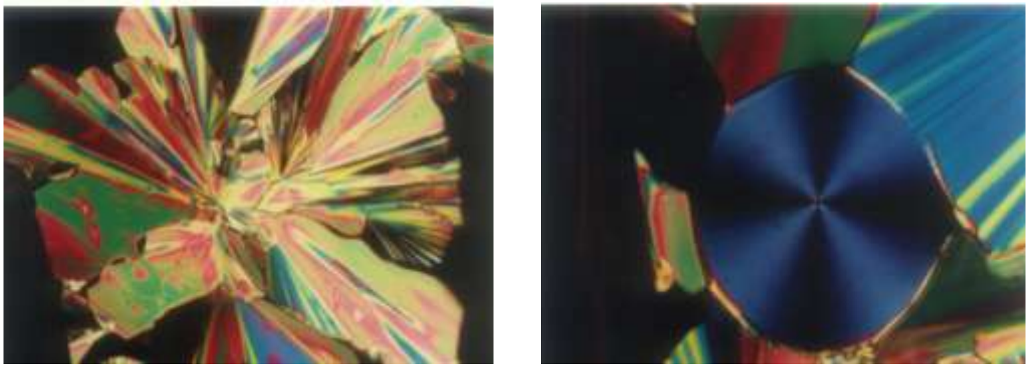
Table 3.2: Transition temperatures (˚C) and the associated enthalpy values (kJ mol^{-1}, in italics) for the compounds of series 3.B.



3.B

Compound	*n*	Cr		B_{2x}		Col_rP_{AF}		B_6		I
3.B.1	6	.	150.0^{*} *50.0*	-		-		.	165.0 *15.0*	.
3.B.2	7	.	127.5^{*} *34.0*	-		-		.	157.0 *16.5*	.
3.B.3	8	.	126.5^{*} *44.0*	-		.	149.0 *18.0*	-		.
3.B.4	9	.	139.0 *30.0*	-		.	144.0 *18.5*	-		.
3.B.5	10	.	137.5 *27.5*	-		.	139.5 *17.0*	-		.
3.B.6	11	.	139.5 *53.5*	-		(.	135.5) *19.0*	-		.
3.B.7	12	.	139.5^{*} *75.5*	(.	135.4)	(.	135.6)$^{\spadesuit}$ *19.0*	-		.
3.B.8	14	.	132.5^{*} *42.0*	.	141.0 *21.0*	-		-		.
3.B.9	16	.	113.0^{*} *36.0*	.	144.5 *20.5*	-		-		.
3.B.10	18	.	122.5^{*} *76.0*	.	145.0 *21.5*	-		-		.

Abbreviations: See table **3.1**; $^{\spadesuit}$ Compound exhibits a transition from Col_rP_{AF} to B_{2x} phase upon cooling the isotropic phase and enthalpy denoted is the sum of both the transitions.



(a) **(b)**

Figure 3.4: Optical photomicrographs of the textures obtained for the Col_rP_{AF} phase of compound 3.B.6. (a) T=135˚C; (b) T=130˚C.

Interestingly, when a sample of compound **3.B.7** is cooled slowly from the isotropic state and observed under a microscope, two types of textures grow simultaneously as shown in figure **3.5a** and **b**. One is reminiscent of that exhibited by Col_rP_{AF} phase of lower homologues and other is typical of the texture shown by the B_{2x} phase exhibited by the higher homologues. This

(a) **(b)**

Figure 3.5: Optical photomicrographs showing the simultaneous appearance of Col_rP_{AF} and B_{2x} phases, on slow cooling of the isotropic liquid of compound 3.B.7; (a) T=135.4˚C, (b) T=135˚C.

textural feature remains the same till crystallization and on heating the fingerprint texture disappears first followed by focal-conic circular domain. In a DSC thermogram obtained for this compound, a splitting in the clearing transition peak could be clearly observed, suggesting a very narrow width between the two phases. A DSC thermogram obtained for compound **3.B.7** is shown in figure **3.6**. These observations suggest a probable coexistence of Col$_r$P$_{AF}$ and B$_{2x}$ phases, which is further supported by the electro-optical investigations (described later).

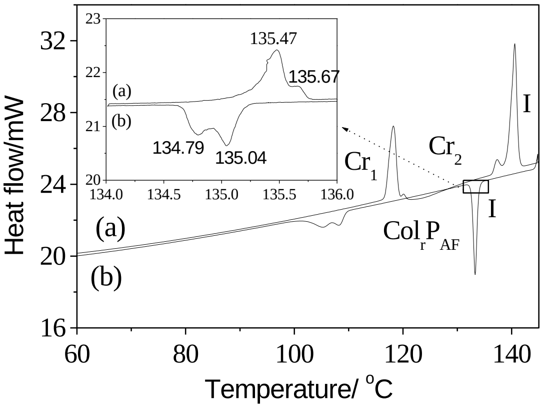


Figure 3.6: A DSC thermogram obtained for compound 3.B.7. (a) Heating cycle, (b) cooling cycle; scanning rate 5°C min^{-1} (first scan). Inset shows the monotropic Col$_r$P$_{AF}$ to B$_{2x}$ transition; scanning rate 0.1°C min^{-1}.

It is appropriate to point here that, there are only a few examples known so far in which a transition from a columnar B$_1$ phase with a centered rectangular lattice (Col$_r$) to a lamellar antiferroelectric B$_2$ phase [26-29] occurs. The B$_1$ phase reported in these examples is non-switchable except in one case [28] where an optical response was observed, but no polarization peak could be obtained. Importantly, compound, **3.B.7** represents the first example where a transition from a switchable columnar phase to a switchable lamellar phase occurs. The occurrence of such a transition in the present series is due to the close proximity of the clearing temperatures of the Col$_r$P$_{AF}$ and B$_{2x}$ phases exhibited by successive homologues **3.B.6** and **3.B.7** and this has been pointed out for a non-switchable B$_1$ phase to a switchable B$_2$ phase earlier [29].

The mesophase exhibited by compounds **3.B.8-10** is identified as a B_{2x} phase. A plot of transition temperature *versus* the number of carbon atoms in the terminal chain for this series of compounds is shown in figure **3.7**. It can be seen that the clearing points follow a smooth curve and the slope of the curves are similar to those observed in series **3.A**.

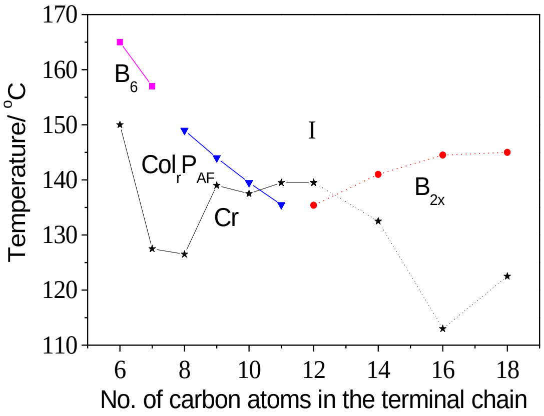
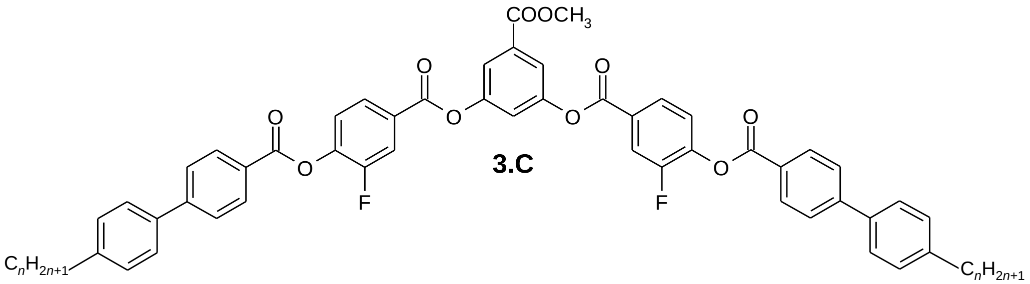


Figure 3.7: A plot of transition temperature as a function of the number of carbon atoms in the terminal chain for compounds of series 3.B.

The transition temperatures and the associated enthalpy values obtained for the compounds of series **3.C** are given in table **3.3**. The compounds of series **3.C** contain a fluoro substituent *meta* to the ester carbonyl group connected to the central phenyl ring. All the homologues of this series exhibit a enantiotropic mesophase. In general, the melting and clearing temperatures are suppressed drastically and a wider temperature range for the mesophases is observed as compared to the unsubstituted parent compounds **3.A** as well as *ortho* fluoro substituted compounds of series **3.B**. For example, a thermal range of 52.5˚C was observed for compound **3.C.8**, while the analogous parent compound **3.A.9** and *ortho* fluoro substituted compound **3.B.10** have thermal range of 3.5°C and 22.5˚C respectively. In addition, the B_{2x} phase appears in this series for a compound (**3.C.7**) with a chain length, *n*=16 which occurs for shorter chain lengths in the other two series (**3.A** and **3.B**) of compounds. The occurrence of Col_rP_{AF} phase is extended to a homologue (compound **3.C.6**) with a longer chain length, *n*=14. A plot of transition temperature against the number of carbon atoms in the terminal chain for the compounds of series **3.C** is shown in figure **3.8**. Again, it can be seen that the clearing transition points involving Col$_r$P$_{AF}$ and B_{2x} phases lie on smooth curves.

Table 3.3: Transition temperatures (˚C) and the associated enthalpy values (kJ mol^{-1}, in italics) for the compounds of series 3.C.



3.C

Compound	*n*	Cr		B_{2x}		Col$_r$P$_{AF}$		B_6		I
3.C.1	8	.	136.5 *53.5*	-		-		.	152.5 *16.5*	.
3.C.2	9	.	137.5 *55.0*	-		.	145.5 *17.5*	-		.
3.C.3	10	.	110.5 *20.5*	-		.	137.0 *17.5*	-		.
3.C.4	11	.	93.0 *18.5*	-		.	132.5 *17.5*	-		.
3.C.5	12	.	96.5 *20.0*	-		.	127.0 *16.5*	-		.
3.C.6	14	.	82.5* *24.5*	-		.	122.0 *16.5*	-		.
3.C.7	16	.	73.5* *12.5*	.	123.0 *15.5*	-		-		.
3.C.8	18	.	72.5* *35.0*	.	125.0 *14.5*	-		-		.

Abbreviations: See table **3.1**

In order to examine the mesophase structure, XRD measurements were carried out on unoriented samples of various compounds representing all the three homologous series. The XRD data obtained for the mesophase of compounds investigated is presented in table **3.4**.

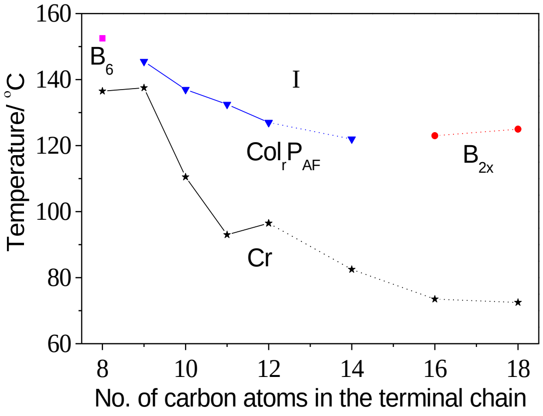


Figure 3.8: A plot of transition temperature as a function of the number of carbon atoms in the terminal chain for the compounds of series 3.C.

The XRD pattern of compound **3.A.1** at 160˚C showed a single reflection in the small angle region with spacing (*d*) of 23.5Å. This layer spacing is smaller than half the calculated molecular length (*l*=52.7Å). The molecular length was calculated considering a most extended form with all *trans* conformation of the *n*-alkyl chains and an opening angle of 120˚. This clearly indicates an intercalation as well as tilting of the molecules in the mesophase. On the basis of microscopic observations and the obtained XRD data, this mesophase is identified as B_6 phase [1, 22].

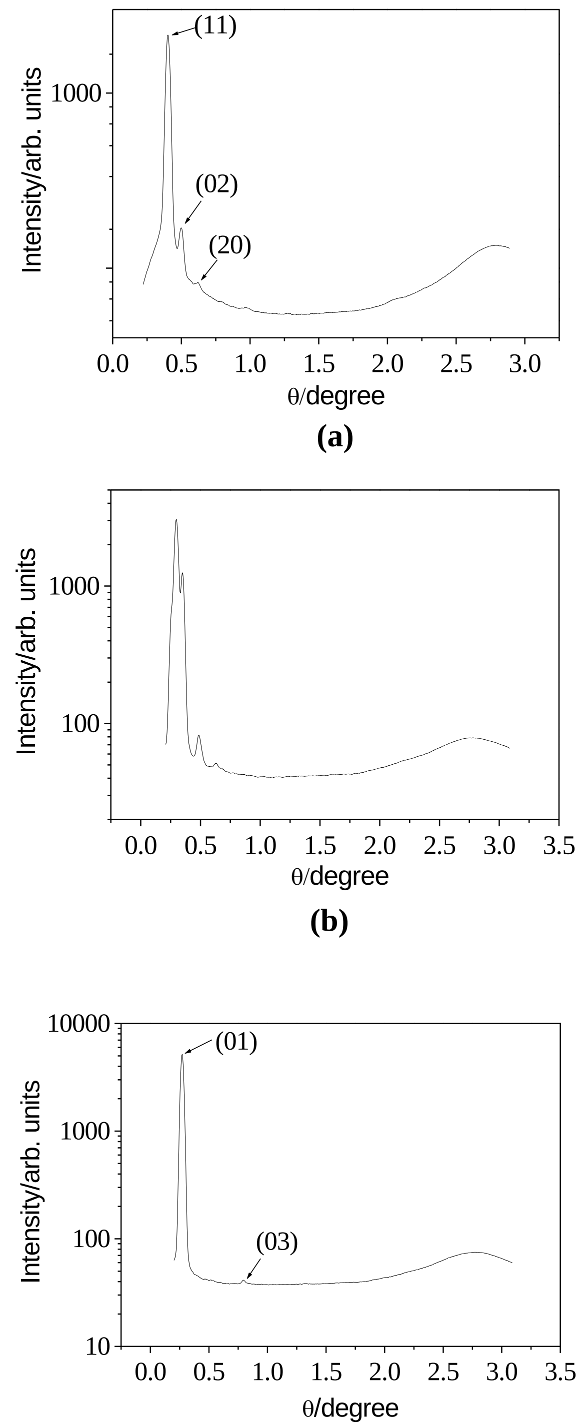
The XRD pattern of compound **3.A.4** at 135˚C showed four reflections in the small angle region with spacing corresponding to 31.2Å, 25.1Å, 20.2Å and 12.9Å. These reflections can be indexed as (11), (02), (20) and (31) respectively, for a centered rectangular lattice with parameters *a*=39.7Å and *b*=50.2Å. This mesophase shows antiferroelectric behaviour under a triangular-wave field. Hence, the mesophase is designated as Col_rP_{AF}. The X-ray angular intensity profile obtained for the mesophase of compound **3.A.4** at 135˚C is shown in figure **3.9a**. Similar XRD patterns obtained for the mesophase of compounds belonging to three series **3.A**, **3.B** and **3.C** have also been characterized as Col_rP_{AF} phase. However, the XRD pattern obtained for the mesophase of compound **3.B.7** is slightly different from that obtained for compound **3.A.4**. The X-ray diffractogram obtained for compound **3.B.7** at 125˚C is shown in figure **3.9b**. A monodomain sample would have given more information about the phase structure, and this could not be obtained for compound **3.B.7**. The XRD pattern of the mesophase of compound **3.B.7**, which is different from that of the Col_rP_{AF} phase exhibited by other homologues of the series, gives an indication that, the difference might be due to the co-existence of Col_rP_{AF} and B_{2x} phases.

The mesophase of compound **3.A.8** showed two reflections in the small angle region. These reflections with spacing of 46.5Å and 15.6Å are in the ratio 1:1/3 indicating a lamellar ordering in the mesophase. The first order layer spacing is smaller than the calculated molecular length suggesting a tilt of the molecules in the smectic layers. Similar XRD patterns were obtained for the B_{2x} mesophase of other compounds and the X-ray diffractogram obtained for compound **3.A.8** at 130˚C is shown in figure **3.9c**.

In all the cases, a diffuse reflection was obtained in the wide-angle region at a distance of 4.2Å. This corresponds to an average molecular distance and suggests a liquid-like in-plane order.

Table 3.4: The spacings (Å) obtained for different mesophases and the corresponding Miller indices (shown in brackets) for representative compounds belonging to series 3.A, 3.B and 3.C.

Compound	*n*	*d*-spacings/Å	Lattice parameters/Å		Phase type
			a	*b*	
3.A.1	7	23.5 (01)	-	-	B_6
3.A.2	8	26.4 (01)	-	-	B_6
3.A.4	10	31.2 (11), 25.1 (02), 20.2 (20), 12.9 (31)	39.7	50.2	Col_rP_{AF}
3.A.6	12	37.84 (11), 30.1 (02), 24.1 (20)	48.6	60.2	Col_rP_{AF}
3.A.8	16	46.5 (01), 15.6 (03)	-	-	B_{2x}
3.B.2	7	23.8 (01)	-	-	B_6
3.B.3	8	26.0 (11), 24.4 (02)	30.8	48.8	Col_rP_{AF}
3.B.6	11	38.7 (11), 30.1 (02), 25.9 (20), 18.9 (13)	50.6	60.2	Col_rP_{AF}
3.B.9	16	45.5 (01), 22.7 (02)	-	-	B_{2x}
3.C.1	8	26.0 (01)	-	-	B_6
3.C.3	10	30.1 (11), 25.8 (02), 18.9 (20)	37.1	51.6	Col_rP_{AF}
3.C.5	12	36.2 (11), 27.0 (02), 24.6 (20), 15.7(31)	48.8	54.0	Col_rP_{AF}
3.C.7	16	46.8 (01), 15.5 (03)	-	-	B_{2x}



(a)

(b)

(c)

Figure 3.9: X-Ray angular intensity profile obtained for the mesophase of compounds (a) 3.A.4, T= 135˚C; (b) 3.B.7, T= 125˚C; (c) 3.A.8, T= 130˚C.

Electric field experiments were carried out on the mesophases of different compounds belonging to all the three series. ITO coated polyimide cells (EHC, Japan) with a thickness of 8 μm were used for these experiments. The mesophase of compounds **3.A.1** and **3.A.2** does not respond to an applied electric field. This is in consistent with the behaviour reported for the B_6 phase. The mesophase of compounds **3.A.3-6** show antiferroelectric behaviour under a triangular-wave field. The electro-optical behaviour exhibited by the mesophase of compounds **3.A.7-9** is similar and was also found to show antiferroelectric characteristics.

The switching behaviour of the compounds of series **3.B** is discussed in detail. As mentioned earlier no electro-optical switching was observed in the B_6 phase of compounds **3.B.1** and **3.B.2**. The mesophase of compounds **3.B.3-7** show antiferroelectric behaviour under a triangular-wave. For example, when a sample of compound **3.B.6** was cooled under a triangular-wave electric field, two well-separated peaks per half period of the applied voltage were observed indicating an antiferroelectric behaviour. The current response trace obtained under a field of $350V_{PP}$ and a frequency of 10 Hz in the mesophase of compound **3.B.6** is shown in figure **3.10**. The calculated polarization value is about 500 nC cm^{-2}. The photomicrographs obtained under the field and on removal of the field are shown in figure **3.11a** and **b** respectively. A smooth fan-shaped texture was obtained under the field and on turning off the field a colour change and lines running along the fans were observed. Switching behaviour of this mesophase under a dc electric field is similar to the optical observations made using a triangular-wave field.

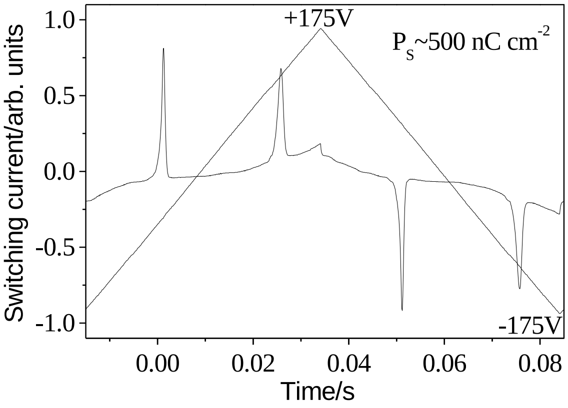


Figure 3.10: Current response trace obtained for the mesophase of compound 3.B.6; $350V_{PP}$, 10 Hz, T=125°C.

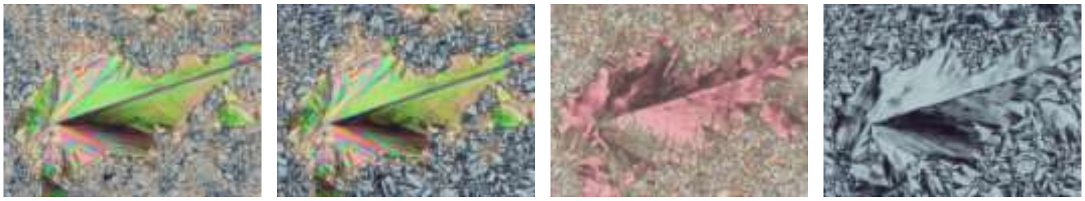
(a) **(b)**

Figure 3.11: Textures of compound 3.B.6 obtained under triangular-wave field, T=135°C. (a) 350V$_{PP}$, 10 Hz; (b) 0V.

The optical observation of the switching behaviour in compound **3.B.6** indicates that the relaxation of the molecules from the switched state to the ground state takes place *via* a collective rotation around a cone. This is contrary to the observation that, in orthogonal Col$_r$P$_{AF}$ phase, switching takes place by rotation of the molecules around their long axes [30]. This is because, the rotation around a cone is restricted due to the boundaries between the ribbons. However, the switching process observed in the mesophase of compound **3.B.6** is unusual and the mechanism is not clear.

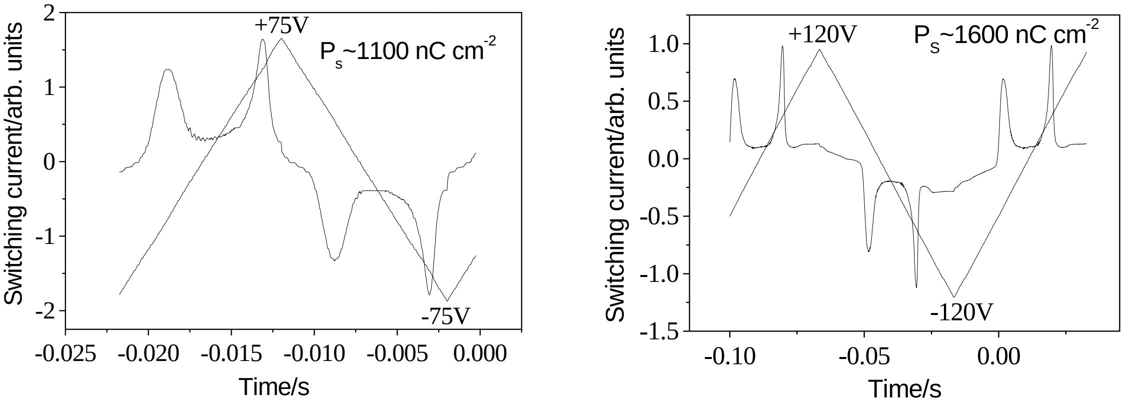
It is interesting to point out here that, the switching around a cone was observed only for the mesophase of compounds **3.A.6** and **3.B.6**. In the Col$_r$P$_{AF}$ phase of the remaining compounds, a switching along the long molecular axis was observed.

Further, an interesting switching behaviour was observed in compound **3.B.7**. On slow cooling a sample of compound **3.B.7** from the isotropic phase, a banana-leaf like texture and a finger print texture develop simultaneously. On application of a triangular-wave electric field, at a threshold of 13 Vμm^{-1}, two well separated peaks per half period of the applied voltage start growing. Simultaneously, optical textures were observed under a polarizing microscope. A change in the finger print region (becomes more birefringent) could be clearly seen, while the fan-shaped texture remained intact (figure **3.12a**). On turning off the field, the birefringence in the finger print region decreases (figure **3.12b**). On increasing the voltage further, beyond 28 Vμm^{-1}, the peaks rise sharply and a change in the fan-shaped texture could be observed (figure **3.12c**). On turning off the field a uniform low birefringent texture was obtained (figure **3.12d**). These observations indicate a probable coexistence of Col_rP_{AF} and B_{2x} phases. If such a structure is considered, the first threshold voltage corresponds to the switching of the B_{2x} phase and the second threshold corresponds to the switching of the polar columnar phase. There is also a possibility that, the switching of the fan-shaped texture at higher voltages might correspond to an irreversible field induced transition from Col_r to a $SmCP_A$ phase [28, 31]. The current response traces obtained under these conditions are shown in figure **3.13a** and **b** respectively. The polarization value



(a) **(b)** **(c)** **(d)**

Figure 3.12: Optical photomicrographs of textures of compound 3.B.7 obtained under triangular-wave field, T=128°C. (a) $150V_{PP}$, 50 Hz; (b) 0V (on turning off from $150V_{PP}$); (c) $240V_{pp}$, 10 Hz; (d) 0V (on turning off from $240V_{PP}$).



(a) **(b)**

Figure 3.13: Current response traces obtained for compound 3.B.7, T=128°C. (a) $150V_{PP}$, 50 Hz; (b) $240V_{PP}$, 10 Hz.

obtained by integrating the area under the curves increase from 1100 nC cm^{-2} to 1600 nC cm^{-2} on increasing the voltage.

The mesophase of compounds **3.B.8-10** also exhibits antiferroelectric switching behaviour under a triangular-wave field. A current response trace obtained for the mesophase of compound **3.B.9** at a voltage of 300V$_{PP}$ and a frequency of 10 Hz is shown in figure **3.14**. A high polarization value of 1130 nC cm^{-2} was calculated from the current response trace.

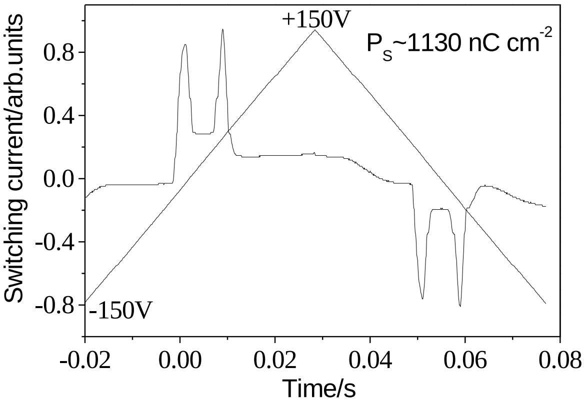
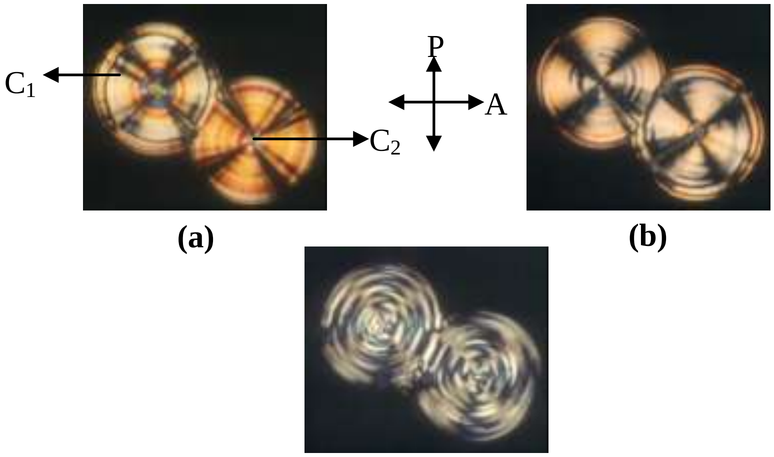


Figure 3.14: Current response trace obtained for the mesophase of compound 3.B.9 at 135˚C, 300V$_{PP}$, 10 Hz.

When a sample of compound **3.B.9** was cooled slowly under a dc electric field of 4Vμm^{-1}, the mesophase grows in the form of circular domains in which extinction cross are tilted with respect to the crossed polarizers. As shown in figure **3.15a**, the extinction cross in domain C_1 is tilted in a clock-wise direction while in domain C_2, it is tilted in a counter clock-wise direction. On reversing the polarity of the field, the extinction crosses in the domains C_1 and C_2 tilt in opposite directions (figure **3.15b**). On turning off the field, the brushes relax along the direction of crossed polarizers (figure **3.15c**). These observations indicate a synclinic ferroelectric structure (SmC$_s$P$_F$) under the field, which relaxes to anticlinic antiferroelectric structure (SmC$_a$P$_A$) on removal of the field thus suggesting a chiral antiferroelectric ground state structure for the mesophase.



(a) (b)

(c)

Figure 3.15: Optical textures of the mesophase of compound 3.B.9 under a dc electric field, T=144˚C. (a) +4 Vμm^{-1}; (b) -4 Vμm^{-1}; (c) 0V.

The compound **3.C.1,** which exhibits a B_6 phase, does not show any electro-optical response. The rectangular columnar mesophase of compounds **3.C.2-6** and the tilted lamellar phase of compounds **3.C.7** and **3.C.8** show antiferroelectric behaviour.

A comparison of the mesomorphic behaviour of the compounds of series **3.B** and **3.C** with the analogous compounds derived from 5-chlororesorcinol (series **2.A** and **2.B**, described in chapter **1**) indicates the profound influence of the polar nature of the substituent on the mesomorphic behaviour of BC compounds. It can be seen that replacement of a chloro group by a methoxy carbonyl group results in a antiferroelectrically switchable columnar phase. Further, both melting points and clearing transition temperatures are lowered substantially. For example, in compound **3.C.8** (*n*=18), the melting point is reduced by 62.5˚C and clearing temperature is reduced by 29˚C compared to the analogous compound derived from 5-chlororesorcinol (**2.B.11**, Cr 135˚C B_{2x} 154˚C I).

Conclusions

Three new homologous series of compounds derived from methyl 3,5-dihydroxybenzoate are synthesized and their mesomorphic properties investigated. Three types of mesophases are observed. In general, the lower homologues show a B_6 mesophase, middle homologues exhibit a Col_rP_{AF} phase and the higher homologues exhibit a B_{2x} phase. Interestingly in one of the homologues (**3.B.7**) of series **3.B**, a transition from $\mathrm{Col_rP_{AF}}$ to a $\mathrm{B_{2x}}$ phase occurs, which is the first observation of such a transition. The compounds with a fluoro substituent *meta* to the ester carbonyl group connecting the central phenyl ring show $\mathrm{Col_rP_{AF}}$ phase even for fairly long terminal chains (*n*=14). The dc field experiments indicate a homochiral antiferroelectric ground state structure for the $\mathrm{B_{2x}}$ phase.

Synthesis

Methyl 3, 5-dihydroxybenzoate, 3.b

To a solution of 3, 5-dihydroxybenzoic acid, **3.a** (25 gm) in methanol (250 ml), a catalytic amount of conc. H_2SO_4 was added and the resulting mixture was refluxed for about 24 hours. Excess of methanol was distilled off, the reaction mixture was cooled and poured into ice-cold water. The resulting solution was extracted using ether (4×100 ml), and the ethereal solution was washed with 5% $NaHCO_3$ solution (2×100 ml), then with brine solution several times and dried over anhydrous sodium sulphate. The solvent was evaporated and the residue obtained was passed through a column of silica gel and eluted using a mixture of chloroform and ethyl acetate (3:1). The product obtained after removal of the solvent was crystallized using water. Yield: 22g (81 %), m. p. 166-167.5˚C. ν_{max}: 3381, 3249, 3089, 2923, 2854, 2630, 2505, 1703, 1697, 1693, 1687, 1681, 1633, 1487, 1444, 1346, 1309, 1263, 1176, 1103, 1016 cm^{-1}; δ_H (CD_3COCD_3): 8.8 (s, 2H, 2×Ar-OH exchangeable with D_2O), 6.97 (d, ^4J 2.08 Hz, 2H, Ar-H), 6.56 (t, 1H, Ar-H), 3.8 (s, 3H, Ar-$COOCH_3$); $C_8H_8O_4$ requires C 57.15, H 4.79; found C 56.82, H 4.56 %.

5-Methoxycarbonyl-1, 3-phenylene bis (4-benzyloxybenzoate), 3.c (X=H, Y=H)

A mixture of methyl 3,5-dihydroxybenzoate, **3.b** (1g, 5.9 mmol), 4-benzyloxybenzoic acid, **3.i** (2.71g, 11.8 mmol) and a catalytic amount of DMAP was stirred for 15 minutes at room temperature. To this stirred mixture, DCC (2.7g, 13 mmol) was added and stirring continued for a further 8 hours. The precipitated urea was filtered off and washed with excess of chloroform. The solvent from the filtrate was evaporated and the residue obtained was passed through a column of silica gel and eluted with chloroform. The material obtained on removal of solvent from the eluate was crystallized using a mixture of chloroform and hexane. Yield: 3g (85%), m. p. 126-127˚C. ν_{max}: 2923, 2852, 1737, 1735, 1732, 1714, 1606, 1456, 1251, 1168, 1132, 1074 cm^{-1}; δ_H: 8.12 (d, ^3J 8.64 Hz, 4H, Ar-H), 7.78 (d, 2H, Ar-H), 7.43-7.33 (m, 11H, Ar-H), 7.03 (d, ^4J 8.68 Hz, 4H, Ar-H), 5.14 (s, 4H, 2× -OCH_2-Ar), 3.92 (s, 3H, Ar-$COOCH_3$); $C_{36}H_{28}O_8$ requires C 73.46, H 4.78; found C 73.12, H 4.63 %.

5-Methoxycarbonyl-1, 3-phenylene bis (4-hydroxybenzoate), 3.d (X=H, Y=H)

Compound **3.c**, X=H, Y=H (3g, 5.1 mmol) was dissolved in 1,4-dioxane (50 ml) and to this solution 5% Pd-C catalyst (0.6g) was added. The mixture was stirred in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. The solution was filtered hot and the solvent from the filtrate was evaporated. The residue obtained was crystallized using a mixture of acetone and chloroform. Yield: 1.8g (90%), m. p. 199-200˚C. ν_{max}: 3328, 2923, 2852, 1745, 1737, 1714, 1591, 1608, 1514, 1452, 1377, 1267, 1238, 1172, 1136 cm^{-1}; δ_H (DMSO-d_6): 10.58 (s, 2H, 2×Ar-OH, D_2O exchangeable), 8.00 (d, ^3J 8.52 Hz, 4H, Ar-H), 7.73(d, ^4J 1.8 Hz, 2H, Ar-H), 7.59 (t, 1H, Ar-H), 6.92 (d, ^3J 8.64 Hz, 4H, Ar-H), 3.32(s, 3H, Ar-$COOCH_3$); $C_{22}H_{16}O_8$ requires C 64.70, H 3.95; found C 64.5, H 4.0 %.

5-Methoxycarbonyl-1, 3-phenylene bis (2-fluoro-4-benzyloxybenzoate), **3.c (X=F, Y=H)**

This was prepared following a procedure described for compound **3.c**, (X=H, Y=H) using 2-fluoro-4-benzyloxybenzoic acid, **3.ii**. Yield 80%, m. p. 110-111.5˚C. ν_{max}: 2923, 2852, 1745, 1743, 1714, 1618, 1589, 1504, 1461, 1377, 1244 cm^{-1}; δ_H: 8.07-8.03 (dd, ^3J 8.6 Hz, 2H, Ar-H), 7.82 (d, ^4J 2.12 Hz, 2H, Ar-H), 7.43-7.39 (m, 11H, Ar-H), 6.88-6.85 (dd, ^3J 8.84 Hz, ^4J 2.2 Hz, 2H, Ar-H), 6.80-6.76 (dd, ^3J 12.4 Hz, ^4J 2.2 Hz, 2H, Ar-H), 5.14 (s, 4H, 2×-OCH_2-Ar), 3.92 (s, Ar-$COOCH_3$); $C_{36}H_{26}F_2O_8$ requires C 69.23, H 4.19; found C 69.0, H 3.89 %.

5-Methoxycarbonyl-1, 3-phenylene bis (2-fluoro-4-hydroxybenzoate), 3.d (X=F, Y=H)

This was synthesized following a procedure described for compound **3.d**, (X=H, Y=H) using 5-methoxycarbonyl-1, 3-phenylene bis (2-fluoro-4-benzyloxybenzoate), **3.c**, (X=F, Y=H) as starting material. Yield 92%, m. p. 240-241˚C. ν_{max}: 3359, 3298, 3132, 2922, 2852, 2723, 1743 1733, 1705, 1622, 1591, 1508, 1463, 1377, 1319, 1251, 1209, 1137 cm^{-1}; δ_H (DMSO-d_6): 11.07 (s, 2H, 2×Ar-OH, D_2O exchangeable), 7.80-7.95 (dd, ^3J 8.8 Hz, 2H, Ar-H), 7.75 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.60 (t, ^4J 2.0 Hz, 1H, Ar-H), 6.79-6.76 (dd, ^3J 8.7 Hz, ^4J 1.96 Hz, 2H, Ar-H), 6.74-6.70 (dd, ^3J 13.04 Hz, ^4J 1.80 Hz, 2H, Ar-H), 3.87 (s, Ar-$COOCH_3$); $C_{22}H_{14}F_2O_8$ requires C 59.47, H 3.17; found C 58.99, H 2.92 %.

5-Methoxycarbonyl-1, 3-phenylene bis (3-fluoro-4-benzyloxybenzoate), **3.c (X=H, Y=F)**

This was prepared following a procedure described for compound **3.c**, (X=H, Y=H) using 3-fluoro-4-benzyloxybenzoic acid, **3.iii**. Yield 82%, m. p. 112-113˚C. ν_{max}: 2923, 2854, 1732, 1691, 1616, 1593, 1521, 1456, 1431, 1280 cm^{-1}; δ_H: 7.94-7.89 (m, 4H, Ar-H), 7.81 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.75-7.34 (m, 11H, Ar-H), 7.11-7.07 (dd, ^{3}J 8.30 Hz, 2H, Ar-H), 5.25 (s, 4H, 2× -OCH$_2$-Ar), 3.95 (s, 3H, Ar-COOCH$_3$); $C_{36}H_{26}F_2O_8$ requires C 69.23, H 4.19; found C 68.8, H 4.29 %.

5-Methoxycarbonyl-1, 3-phenylene bis (3-fluoro-4-hydroxybenzoate), 3.d (X=H, Y=F)

This was synthesized following a procedure described for compound **3.d**, (X=H, Y=H) using 5-methoxycarbonyl-1, 3-phenylene bis (3-fluoro-4-benzyloxybenzoate), **3.c**, (X=H, Y=F) as starting material. Yield 90%, m. p. 228-230°C. ν_{max}: 3354, 3298, 2923, 2852, 2723, 1735, 1733, 1718, 1712, 1618, 1596, 1523, 1460, 1377, 1311, 1292, 1276, 1207, 1184, 1141, 1112 cm^{-1}; δ_H (DMSO-d$_6$): 11.14 (s, 2H, 2×Ar-OH, D$_2$O exchangeable), 7.88-7.83 (m, 4H, Ar-H), 7.75 (d, ^{4}J 2.04 Hz, 2H, Ar-H), 7.63 (t, ^{4}J 2.04 Hz, 1H, Ar-H), 7.15-7.11 (dd, ^{3}J 8.52 Hz, 2H, Ar-H), 3.87 (s, Ar-COOCH$_3$); $C_{22}H_{14}F_2O_8$ requires C 59.47, H 3.17; found C 59.94, H 3.26 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-heptylbiphenyl-4′-carbonyloxy)benzoate], 3.A.1

A mixture of 5-methoxycarbonyl-1, 3-phenylene bis (4-benzyloxybenzoate), **3.c**, (X=H, Y=H) (0.2g, 0.34 mmol), 4-*n*-heptylbiphenyl 4-carboxylic acid (0.20g, 0.68 mmol) and a catalytic amount of DMAP was stirred for 15 minutes at room temperature. To this stirred mixture, DCC (0.15g 0.75 mmol)) was added and stirring continued for a further 2 hours. The precipitated urea was filtered off and washed thoroughly with chloroform. The filtrate was concentrated and the residue obtained was purified by column chromatography on silica gel using 1% ethyl acetate in chloroform as eluent. The material obtained on removal of the solvent was further purified by repeated crystallization using a mixture of chloroform and acetonitrile. Yield 0.32g (82%), m. p. 147.5°C. ν_{max}: 2923, 2852, 1739, 1735, 1728, 1602, 1463, 1377, 1255, 1236, 1193, 1130, 1056, 1014 cm^{-1}; δ_H: 8.30 (d, ^{3}J 8.76 Hz, 4H, Ar-H), 8.27 (d, ^{3}J 8.40 Hz, 4H, Ar-H), 7.87 (d, ^{4}J 2.12 Hz, 2H, Ar-H), 7.75 (d, ^{3}J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^{3}J 8.12 Hz, 4H, Ar-H), 7.46 (t, 1H, Ar-H), 7.43 (d, ^{3}J 8.72 Hz, 4H, Ar-H), 7.30 (d, ^{3}J 8.10 Hz, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, ^{3}J 7.7 Hz, 4H, 2× Ar-CH$_2$-), 1.67-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.44-1.29 (m, 16H, 2×(-CH$_2$-)$_4$), 0.89 (t, ^{3}J 6.80 Hz, 6H, 2×-CH$_3$); $C_{62}H_{60}O_{10}$ requires C 77.16, H 6.26; found C 77.39, H 6.26 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-octylbiphenyl-4′-carbonyloxy)benzoate], 3.A.2

This compound and the remaining homologues were prepared following a procedure similar to the one described for compound **3.A.1**. Yield 78%, m. p. 154.5˚C. ν_{max}: 2923, 2854, 1747, 1739, 1733, 1458, 1259, 1236, 1163, 1056, 1014 cm^{-1}; δ_H: 8.30 (d, ^3J 8.76 Hz, 4H, Ar-H), 8.27 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.87 (d, ^4J 2.12 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.12 Hz, 4H, Ar-H), 7.46 (t, 1H, Ar-H), 7.43 (d, ^3J 8.72 Hz, 4H, Ar-H), 7.30 (d, ^3J 8.10 Hz, 4H, Ar-H), 3.95 (s, 3H, Ar-$COOCH_3$), 2.67 (t, ^3J 7.7 Hz, 4H, 2× Ar-CH_2-), 1.67-1.62 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.47-1.19 (m, 20H, 2×(-CH_2-$)_5$), 0.89 (t, ^3J 6.80 Hz, 6H, 2×-CH_3); $C_{64}H_{64}O_{10}$ requires C 77.40, H 6.48; found C 77.84, H 6.46 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-nonylbiphenyl-4′-carbonyloxy)benzoate], 3.A.3

Yield 86%, m. p. 157.5˚C. ν_{max}: 2922, 2852, 1732, 1730, 1602, 1458, 1257 1064 cm^{-1}; δ_H: 8.30 (d, ^3J 8.76 Hz, 4H, Ar-H), 8.27 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.87 (d, ^4J 2.12 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.12 Hz, 4H, Ar-H), 7.46 (t, 1H, Ar-H), 7.43 (d, ^3J 8.72 Hz, 4H, Ar-H), 7.30 (d, ^3J 8.10 Hz, 4H, Ar-H), 3.95 (s, 3H, Ar-$COOCH_3$), 2.67 (t, ^3J 7.7Hz, 4H, 2× Ar-CH_2-), 1.67-1.62 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.34-1.16 (m, 24H, 2×(-CH_2-$)_6$), 0.88 (t, ^3J 6.80 Hz, 6H, 2×-CH_3); $C_{66}H_{68}O_{10}$ requires C 77.63, H 6.70; found C 77.66, H 6.73 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-decylbiphenyl-4′-carbonyloxy)benzoate], 3.A.4

Yield 81%, m. p. 156.5˚C. ν_{max}: 2923, 2852, 1732, 1730, 1728, 1602, 1506, 1458, 1261, 1064 cm^{-1}; δ_H: 8.30 (d, ^3J 8.76 Hz, 4H, Ar-H), 8.27 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.87 (d, ^4J 2.12 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.12 Hz, 4H, Ar-H), 7.46 (t, 1H, Ar-H), 7.43 (d, ^3J 8.72 Hz, 4H, Ar-H), 7.30 (d, ^3J 8.10 Hz, 4H, Ar-H), 3.95 (s, 3H, Ar-$COOCH_3$), 2.67 (t, ^3J 7.7 Hz, 4H, 2× Ar-CH_2-), 1.67-1.62 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.34-1.12 (m, 28H, 2×(-CH_2-$)_7$), 0.88 (t, ^3J 6.80 Hz, 6H, 2×-CH_3); $C_{68}H_{72}O_{10}$ requires C 77.84, H 6.91; found C 77.96, H 6.96 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-undecylbiphenyl-4′-carbonyloxy)benzoate], 3.A.5

Yield 75%, m. p. 154.5˚C. ν_{max}: 2923, 2852, 1733, 1728, 1458, 1261, 1066, 1018 cm^{-1}; δ_H: 8.30 (d, ^3J 8.76 Hz, 4H, Ar-H), 8.27 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.87 (d, ^4J 2.12 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.12 Hz, 4H, Ar- H), 7.46 (t, 1H, Ar-H), 7.43 (d, ^3J 8.72 Hz, 4H, Ar-H), 7.30 (d, ^3J 8.10 Hz, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, ^3J 7.7 Hz, 4H, 2× Ar-CH$_2$-), 1.67-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.48-1.26 (m, 32H, 2×(-CH$_2$-)$_8$), 0.88 (t, ^3J 6.80 Hz, 6H, 2×-CH$_3$); $C_{70}H_{76}O_{10}$ requires C 78.04, H 7.10; found C 78.02, H 7.11 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-dodecylbiphenyl-4′-carbonyloxy)benzoate], 3.A.6

Yield 78%, m. p. 153.5˚C. ν_{max}: 2922, 2850, 1732, 1730, 1602, 1506, 1259, 1064, 1016 cm^{-1}; δ_H: 8.30 (d, ^3J 8.76 Hz, 4H, Ar-H), 8.27 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.87 (d, ^4J 2.12 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.12 Hz, 4H, Ar-H), 7.46 (t, 1H, Ar-H), 7.43 (d, ^3J 8.72 Hz, 4H, Ar-H), 7.30 (d, ^3J 8.10 Hz, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, ^3J 7.7 Hz, 4H, 2× Ar-CH$_2$-), 1.68-1.64 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2\text{-}}$), 1.34-1.27 (m, 36H, 2×(-CH$_2$-)$_9$), 0.88 (t, ^3J 6.80 Hz, 6H, 2×-CH$_3$); $C_{72}H_{80}O_{10}$ requires C 78.16, H 7.24; found C 77.89, H 7.39 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-tetradecylbiphenyl-4′-carbonyloxy)benzoate], 3.A.7

Yield 74%, m. p. 151.0˚C. ν_{max}: 2922, 2850, 1732, 1730, 1602, 1506, 1259, 1203, 1164, 1134, 1064, 1016, 1004 cm^{-1}; δ_H: 8.30 (d, ^3J 8.76 Hz, 4H, Ar-H), 8.27 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.87 (d, ^4J 2.12 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.12 Hz, 4H, Ar-H), 7.46 (t, 1H, Ar-H), 7.43 (d, ^3J 8.72 Hz, 4H, Ar-H), 7.30 (d, ^3J 8.10 Hz, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, ^3J 7.7 Hz, 4H, 2× Ar-CH$_2$-), 1.68-1.64 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.34-1.27 (m, 44H, 2×(-CH$_2$-)$_{11}$), 0.88 (t, ^3J 6.80 Hz, 6H, 2×-CH$_3$); $C_{76}H_{88}O_{10}$ requires C 78.52, H 7.58; found C 78.31, H 7.67 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-hexadecylbiphenyl-4′-carbonyloxy)benzoate], 3.A.8

Yield 82%, m. p. 145.0˚C. ν_{max}: 2920, 2850, 1733, 1730, 1728, 1602, 1506, 1259, 1203, 1164, 1134, 1064, 1016, 1004 cm^{-1}; δ_H: 8.30 (d, ^3J 8.76 Hz, 4H, Ar-H), 8.27 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.87 (d, ^4J 2.12 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.12 Hz, 4H, Ar-H), 7.46 (t, 1H, Ar-H), 7.43 (d, ^3J 8.72 Hz, 4H, Ar-H), 7.30 (d, ^3J 8.10 Hz, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, ^3J 7.7 Hz, 4H, 2× Ar-CH$_2$-), 1.68-1.64 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.45-1.28 (m, 52H, 2×(-CH$_2$-)$_{13}$), 0.88 (t, ^3J 6.80 Hz, 6H, 2×-CH$_3$); $C_{80}H_{96}O_{10}$ requires C 78.85, H 7.88; found C 79.18, H 8.02 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-octadecylbiphenyl-4′-carbonyloxy)benzoate], 3.A.9

Yield 84%, m. p. 143.0˚C. ν_{max}: 2920, 2850, 1737, 1730, 1602, 1506, 1259, 1203, 1064, 1016, 1004 cm^{-1}; δ_H: 8.30 (d, ^3J 8.76 Hz, 4H, Ar-H), 8.27 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.87 (d, ^4J 2.12 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.12 Hz, 4H, Ar-H), 7.46 (t, 1H, Ar-H), 7.43 (d, ^3J 8.72 Hz, 4H, Ar-H), 7.30 (d, ^3J 8.10 Hz, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, ^3J 7.7Hz, 4H, 2× Ar-CH$_2$-), 1.68-1.64 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.34-1.25 (m, 60H, 2×(-CH$_2$-)$_{15}$), 0.88 (t, ^3J 6.80 Hz, 6H, 2×-CH$_3$); $C_{84}H_{104}O_{10}$ requires C 79.14, H 8.17; found C 79.49, H 8.32 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-hexylbiphenyl-4′-carbonyloxy)-2-fluoro-benzoate], 3.B.1

Yield 88%, m. p. 150.0˚C. ν_{max}: 2923, 2854, 1733, 1732, 1604, 1460, 1377, 1236, 1056 cm^{-1}; δ_H: 8.25 (d, ^3J 8.48 Hz, 4H, Ar-H), 8.23-8.19 (m, 2H, Ar-H), 7.89 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.47 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.26-7.22 (m, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, ^3J 7.6 Hz, 4H, 2× Ar-CH$_2$-), 1.67-1.60 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.46-1.34 (m, 12H, 2×(-CH$_2$-)$_3$), 0.88 (t, 6H, 2×-CH$_3$); $C_{60}H_{54}F_2O_{10}$ requires C 74.06, H 5.58; found C 74.16, H 5.56 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-heptylbiphenyl-4′-carbonyloxy)-2-fluoro-benzoate], 3.B.2

Yield 83%, m. p. 127.5˚C. ν_{max}: 2923, 2852, 1743, 1733, 1732, 1739, 1604, 1458, 1247, 1134, 1055 cm^{-1}; δ_H: 8.25 (d, ^3J 8.48 Hz, 4H, Ar-H), 8.23-8.19 (m, 2H, Ar-H), 7.89 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.47 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.26-7.22 (m, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, ^3J 7.6 Hz, 4H, 2× Ar-CH$_2$-), 1.67-1.60 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.46-1.18 (m, 16H, 2×(-CH$_2$-)$_4$), 0.89 (t, 6H, 2×-CH$_3$); $C_{62}H_{58}F_2O_{10}$ requires C 74.38, H 5.85; found C 73.95, H 6.04 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-octylbiphenyl-4′-carbonyloxy)-2-fluoro-benzoate], 3.B.3

Yield 78%, m. p. 126.5˚C. ν_{max}: 2923, 2852, 1743, 1733, 1732, 1739, 1604, 1458, 1247, 1134, 1055 cm^{-1}; δ_H: 8.25 (d, ^3J 8.48 Hz, 4H, Ar-H), 8.23-8.19 (m, 2H, Ar-H), 7.89 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.47 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.26-7.22 (m, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, ^3J 7.6 Hz, 4H, 2× Ar-CH$_2$-), 1.67-1.60 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.34-1.28 (m, 20H, 2×(-CH$_2$-)$_5$), 0.89 (t, 6H, 2×-CH$_3$); $C_{64}H_{62}F_2O_{10}$ requires C 74.69, H 6.07; found C 74.21, H 5.80 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-nonylbiphenyl-4′-carbonyloxy)-2-fluoro-benzoate], 3.B.4

Yield 75%, m. p. 139.0˚C. ν_{max}: 2923, 2852, 1733, 1730, 1606, 1465, 1278, 1249 cm^{-1}; δ_H: 8.25 (d, ^3J 8.48 Hz, 4H, Ar-H), 8.23-8.19 (m, 2H, Ar-H), 7.89 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.47 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.26-7.22 (m, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, ^3J 7.6 Hz, 4H, 2× Ar-CH$_2$-), 1.67-1.60 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.46-1.28 (m, 24H, 2×(-CH$_2$-)$_6$), 0.89 (t, 6H, 2× -CH$_3$); $C_{66}H_{66}F_2O_{10}$ requires C 74.98, H 6.28; found C 74.79, H 6.45 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-decylbiphenyl-4′-carbonyloxy)-2-fluoro-benzoate], 3.B.5

Yield 78%, m. p. 137.5˚C. ν_{max}: 2923, 2852, 1739, 1732, 1726, 1606, 1461, 1377, 1274, 1238, 1124, 1053 cm^{-1}; δ_H: 8.25 (d, ^3J 8.48 Hz, 4H, Ar-H), 8.23-8.19 (m, 2H, Ar-H), 7.89 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.47 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.26-7.22 (m, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, ^3J 7.6 Hz, 4H, 2× Ar-CH$_2$-), 1.67-1.60 (quin, 4H, 2×Ar-CH$_2$-$\underline{\mathrm{CH}_2}$-), 1.45-1.27 (m, 28H, 2× (-CH$_2$-)$_7$), 0.89 (t, 6H, 2×-CH$_3$); $C_{68}H_{70}F_2O_{10}$ requires C 75.26, H 6.49; found C 75.49, H 6.60 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-undecylbiphenyl-4′-carbonyloxy)-2-fluoro-benzoate], 3.B.6

Yield 76%, m. p. 139.5˚C. ν_{max}: 2922, 2850, 1735, 1730, 1606, 1589, 1496, 1431, 1276, 1247, 1134, 1055 cm^{-1}; δ_H: 8.25 (d, ^3J 8.48 Hz, 4H, Ar-H), 8.23-8.19 (m, 2H, Ar-H), 7.89 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.47 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.26-7.22 (m, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, ^3J 7.6Hz, 4H, 2× Ar-CH$_2$-), 1.67-1.60 (quin, 4H, 2×Ar-CH$_2$-$\underline{\mathrm{CH}_2}$-), 1.45-1.27 (m, 32H, 2× (-CH$_2$-)$_8$), 0.89 (t, 6H, 2×-CH$_3$); $C_{70}H_{74}F_2O_{10}$ requires C 75.52, H 6.69; found C 75.67, H 6.60 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-dodecylbiphenyl-4′-carbonyloxy)-2-fluoro-benzoate], 3.B.7

Yield 82%, m. p. 139.5˚C. ν_{max}: 2923, 2850, 1735, 1732, 1606, 1589, 1433, 1276, 1247, 1130 cm^{-1}; δ_H: 8.25 (d, ^3J 8.48 Hz, 4H, Ar-H), 8.23-8.19 (m, 2H, Ar-H), 7.89 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.47 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.26-7.21 (m, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, 4H, ^3J 7.6 Hz, 2× Ar-CH$_2$-), 1.67-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{\mathrm{CH}_2\text{-}}$), 1.34-1.27 (m, 36H, 2×(-CH$_2$-)$_9$), 0.88 (t, 6H, 2×-CH$_3$); $C_{72}H_{78}F_2O_{10}$ requires C 75.78, H 6.88; found C 75.5, H 7.15 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-tetradecylbiphenyl-4′-carbonyloxy)-2-fluoro-benzoate], 3.B.8

Yield 80%, m. p. 132.5˚C. ν_{max}: 2923, 2852, 1733, 1606, 1591, 1458, 1375, 1247, 1236, 1045 cm^{-1}; δ_H: 8.25 (d, ^3J 8.48 Hz, 4H, Ar-H), 8.23-8.19 (m, 2H, Ar-H), 7.89 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.47 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.26-7.21 (m, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, 4H, ^3J 7.6 Hz, 2× Ar-CH$_2$-), 1.67-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{\text{CH}_2\text{-}}$), 1.34-1.27 (m, 44H, 2×(-CH$_2$-)$_{11}$), 0.88 (t, 6H, 2×-CH$_3$); $C_{76}H_{86}F_2O_{10}$ requires C 76.23, H 7.23; found C 75.87, H 7.07 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-hexadecylbiphenyl-4′-carbonyloxy)-2-fluoro-benzoate], 3.B.9

Yield 72%, m. p. 113.0˚C. ν_{max}: 2922, 2850, 1749, 1739, 1732, 1458, 1272, 1247, 1055 cm^{-1}; δ_H: 8.25 (d, ^3J 8.48 Hz, 4H, Ar-H), 8.23-8.19 (m, 2H, Ar-H), 7.89 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.47 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.26-7.21 (m, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, 4H, ^3J 7.6 Hz, 2× Ar-CH$_2$-), 1.67-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{\text{CH}_2\text{-}}$), 1.34-1.27 (m, 52H, 2×(-CH$_2$-)$_{13}$), 0.88 (t, 6H, 2×-CH$_3$); $C_{80}H_{94}F_2O_{10}$ requires C 76.65, H 7.55; found C 76.45, H 7.46 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-octadecylbiphenyl-4′-carbonyloxy)-2-fluoro-benzoate], 3.B.10

Yield 76%, m. p. 122.5˚C. ν_{max}: 2922, 2850, 1732, 1730, 1604, 1465, 1276, 1253, 1168, 1151, 1128 cm^{-1}; δ_H: 8.25 (d, ^3J 8.48 Hz, 4H, Ar-H), 8.23-8.19 (m, 2H, Ar-H), 7.89 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.75 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.47 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.26-7.21 (m, 4H, Ar-H), 3.95 (s, 3H, Ar-COOCH$_3$), 2.67 (t, 4H, ^3J 7.6 Hz, 2× Ar-CH$_2$-), 1.67-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{\text{CH}_2}$-), 1.45-1.26 (m, 60H, 2×(-CH$_2$-)$_{15}$), 0.88 (t, 6H, 2×-CH$_3$); $C_{84}H_{102}F_2O_{10}$ requires C 77.03, H 7.81; found C 76.86, H 7.65 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-octylbiphenyl-4′-carbonyloxy)-3-fluoro-benzoate], 3.C.1

Yield 89%, m. p. 136.5˚C. ν_{max}: 2923, 2854, 1751, 1743, 1732, 1730, 1604, 1596, 1508, 1461, 1290, 1255, 1172 cm^{-1}; δ_H: 8.28 (d, ^3J 8.40 Hz, 4H, Ar-H), 8.10-8.05 (m, 4H, Ar- H), 7.88 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.76 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.10 Hz, 4H, Ar-H), 7.51-7.47 (m, 2H, Ar-H), 7.45 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31(d, ^3J 8.10 Hz, 4H, Ar-H), 3.96 (s, 3H, Ar-COOCH$_3$), 2.67 (t, 4H, ^3J 7.7 Hz, 2× Ar-CH$_2$-), 1.68-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.47-1.17 (m, 20H, 2×(-CH$_2$-)$_5$), 0.88 (t, ^3J 6.7 Hz, 6H, 2×-CH$_3$); $C_{64}H_{62}F_2O_{10}$ requires C 74.69, H 6.06; found C 74.52, H 6.32 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-nonylbiphenyl-4′-carbonyloxy)-3-fluoro-benzoate], 3.C.2

Yield 83%, m. p. 137.5˚C. ν_{max}: 2923, 2854, 1745, 1732, 1606, 1508, 1456, 1290, 1257, 1172, 1110 cm^{-1}; δ_H: 8.28 (d, ^3J 8.40 Hz, 4H, Ar-H), 8.10-8.05 (m, 4H, Ar-H), 7.88 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.76 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.10 Hz, 4H, Ar-H), 7.51-7.47 (m, 2H, Ar-H), 7.45 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.10 Hz, 4H, Ar-H), 3.96 (s, 3H, Ar-COOCH$_3$), 2.67 (t, 4H, ^3J 7.7 Hz, 2× Ar-CH$_2$-), 1.68-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.47-1.17 (m, 24H, 2×(-CH$_2$-)$_6$), 0.88 (t, ^3J 6.7 Hz, 6H, 2×-CH$_3$); $C_{66}H_{66}F_2O_{10}$ requires C 74.98, H 6.29; found C 74.54, H 6.26 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-decylbiphenyl-4′-carbonyloxy)-3-fluoro-benzoate], 3.C.3

Yield 87%, m. p. 110.5˚C. ν_{max}: 2923, 2854, 1745, 1606, 1508, 1463, 1286, 1259, 1174, 1112 cm^{-1}; δ_H: 8.28 (d, ^3J 8.40 Hz, 4H, Ar-H), 8.10-8.05 (m, 4H, Ar-H), 7.88 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.76 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.10 Hz, 4H, Ar-H), 7.51-7.47 (m, 2H, Ar-H), 7.45 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31(d, ^3J 8.10 Hz, 4H, Ar-H), 3.96 (s, 3H, Ar-COOCH$_3$), 2.67 (t, 4H, ^3J 7.7 Hz, 2× Ar-CH$_2$-), 1.68-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2\text{-}}$), 1.47-1.17 (m, 28H, 2×(-CH$_2$-)$_7$), 0.88 (t, ^3J 6.7 Hz, 6H, 2×-CH$_3$); $C_{68}H_{70}F_2O_{10}$ requires C 75.26, H 6.49; found C 74.85, H 6.25 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-undecylbiphenyl-4′-carbonyloxy)-3-fluorobenzoate], 3.C.4

Yield 78%, m. p. 93.0˚C. ν_{max}: 2923, 2852, 1743, 1735, 1728, 1595, 1606, 1508, 1458, 1290, 1259, 1176, 1058 cm^{-1}; δ_H: 8.28 (d, ^3J 8.40 Hz, 4H, Ar-H), 8.10-8.05 (m, 4H, Ar-H), 7.88 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.76 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.10 Hz, 4H, Ar-H), 7.51-7.47 (m, 2H, Ar-H), 7.45 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31(d, ^3J 8.10 Hz, 4H, Ar-H), 3.96 (s, 3H, Ar-COOCH$_3$), 2.67(t, 4H, ^3J 7.7 Hz, 2× Ar-CH$_2$-), 1.68-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.48-1.27 (m, 32H, 2×(-CH$_2$-)$_8$), 0.88 (t, ^3J 6.7 Hz, 6H, 2×-CH$_3$); $C_{70}H_{74}F_2O_{10}$ requires C 75.52, H 6.69; found C 75.11, H 6.73 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-dodecylbiphenyl-4′-carbonyloxy)-3-fluorobenzoate], 3.C.5

Yield 83%, m. p. 96.5˚C. ν_{max}: 2922, 2852, 1745, 1743, 1735, 1606, 1508, 1463, 1431, 1377, 1288, 1176, 1132, 1058, 1016, 1004 cm^{-1}; δ_H: 8.28 (d, ^3J 8.40 Hz, 4H, Ar-H), 8.10-8.05 (m, 4H, Ar-H), 7.88 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.76 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.10 Hz, 4H, Ar-H), 7.51-7.47 (m, 2H, Ar-H), 7.45 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.10 Hz, 4H, Ar-H), 3.96 (s, 3H, Ar-COOCH$_3$), 2.67 (t, 4H, ^3J 7.7 Hz, 2× Ar-CH$_2$-), 1.68-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.34-1.27 (m, 36H, 2×(-CH$_2$-)$_9$), 0.88 (t, ^3J 6.7 Hz, 6H, 2×-CH$_3$); $C_{72}H_{78}F_2O_{10}$ requires C 75.78, H 6.88; found C 75.45, H 6.66 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-tetradecylbiphenyl-4′-carbonyloxy)-3-fluorobenzoate], 3.C.6

Yield 85%, m. p. 82.5˚C. ν_{max}: 2922, 2852, 1745, 1743, 1735, 1606, 1508, 1463, 1431, 1377, 1288, 1176, 1132, 1058, 1016, 1004 cm^{-1}; δ_H: 8.28 (d, ^3J 8.40 Hz, 4H, Ar-H), 8.10-8.05 (m, 4H, Ar-H), 7.88 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.76 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.10 Hz, 4H, Ar-H), 7.51-7.47 (m, 2H, Ar-H), 7.45 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.10 Hz, 4H, Ar-H), 3.96 (s, 3H, Ar-COOCH$_3$), 2.67 (t, 4H, ^3J 7.7 Hz, 2× Ar-CH$_2$-), 1.68-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.34-1.27 (m, 44H, 2×(-CH$_2$-)$_{11}$), 0.88 (t, ^3J 6.7 Hz, 6H, 2×-CH$_3$); $C_{76}H_{86}F_2O_{10}$ requires C 76.23, H 7.23; found C 76.29, H 7.23 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-hexadecylbiphenyl-4′-carbonyloxy)-3-fluorobenzoate], 3.C.7

Yield 87%, m. p. 73.5˚C. ν_{max}: 2920, 2848, 1745, 1730, 1606, 1504, 1467, 1429, 1400, 1176, 1257, 1211, 1112, 1058, 1016, 1004 cm^{-1}; δ_H: 8.28 (d, ^3J 8.40 Hz, 4H, Ar-H), 8.10-8.05 (m, 4H, Ar-H), 7.88 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.76 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.10 Hz, 4H, Ar-H), 7.51-7.47 (m, 2H, Ar-H), 7.45 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31(d, ^3J 8.10 Hz, 4H, Ar-H), 3.96 (s, 3H, Ar-COOCH$_3$), 2.67 (t, 4H, ^3J 7.7 Hz, 2× Ar-CH$_2$-), 1.68-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.34-1.26 (m, 52H, 2×(-CH$_2$-)$_{13}$), 0.88 (t, ^3J 6.7 Hz, 6H, 2×-CH$_3$); $C_{80}H_{94}F_2O_{10}$ requires C 76.65, H 7.55; found C 76.95 H 7.42 %.

5-Methoxycarbonyl-1, 3-phenylene bis [4-(4-*n*-octadecylbiphenyl-4′-carbonyloxy)-3-fluorobenzoate], 3.C.8

Yield 80%, m. p. 72.5˚C. ν_{max}: 2920, 2848, 1745, 1730, 1606, 1504, 1467, 1429, 1400, 1176, 1257, 1211, 1112, 1058, 1016, 1004 cm^{-1}; δ_H: 8.28 (d, ^3J 8.40 Hz, 4H, Ar-H), 8.10-8.05 (m, 4H, Ar-H), 7.88 (d, ^4J 2.16 Hz, 2H, Ar-H), 7.76 (d, ^3J 8.40 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.10 Hz, 4H, Ar-H), 7.51-7.47 (m, 2H, Ar-H), 7.45 (t, ^4J 2.2 Hz, 1H, Ar-H), 7.31 (d, ^3J 8.10 Hz, 4H, Ar-H), 3.96 (s, 3H, Ar-COOCH$_3$), 2.67 (t, 4H, ^3J 7.7 Hz, 2× Ar-CH$_2$-), 1.68-1.62 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.34-1.26 (m, 60H, 2×(-CH$_2$-)$_{15}$), 0.88 (t, ^3J 6.7 Hz, 6H, 2×-CH$_3$); $C_{84}H_{102}F_2O_{10}$ requires C 77.03, H 7.84; found C 77.38, H 7.52 %.

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