Chapter 2

Synthesis and mesomorphic properties of

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

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

Introduction

Banana-shaped mesogens, formed by compounds whose constituent molecules have a bent-core (BC) structure, have been the subject of intense investigations during the past decade. The main reason for interest in such compounds is the polar order and the macroscopic chiral superstructures formed by self-organization of the constituent molecules. Soon after the discovery [1] of electro-optical switching in a mesophase of a BC compound, a clear understanding of the polar order [1] and the supramolecular chirality [2] in such an achiral system was given by Link *et al.* [3] followed by Heppke *et al.* [4]. Because of the intrinsic shape, such bent molecules adopt dense packing in the layers, which restricts the rotational freedom along their long molecular axis. This results in an in-layer polar order despite the molecules being achiral. In addition, the molecules are tilted in such polar layers, which eliminates the reflection symmetry, thus leading to the layer chirality.

Since then, a variety of compounds with a bent molecular structure have been synthesized by various groups and this has yielded a number of new phases and phase sequences. The general symbol B was assigned to the mesophases exhibited by BC compounds to differentiate them from calamitics and mesophases formed by disc-like molecules. However, the letter B signifies the shape of the constituent molecules viz. banana, bow etc. Initially, seven different phases were identified which were called B_1, B_2, B_3,….B_7 [5]. Many aspects concerning these BC compounds including the mesophases exhibited by them, the phase structures and some of the physical properties have been reviewed [6-10].

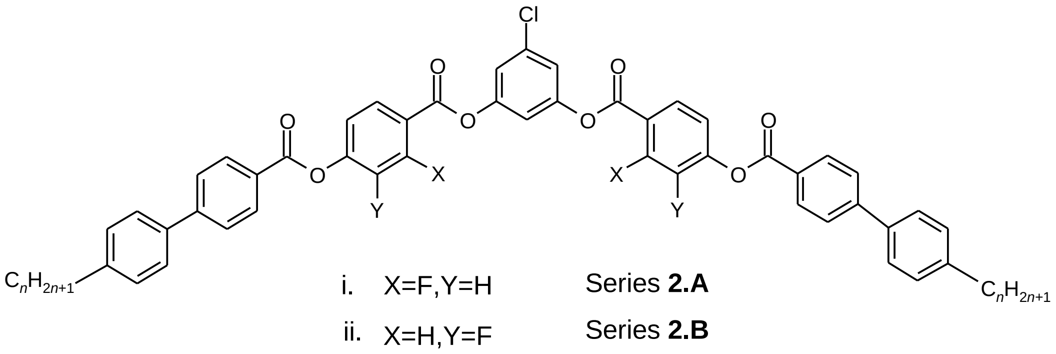
The most widely studied B_2 phase has a tilted layered organization of molecules and can exist in four different types of polar structures [3]. These result from the orientation of polarization and tilt of the molecules in adjacent layers. The polarization can be the same or can be different in the adjacent layers giving rise to “ferro” and “antiferro” electric properties respectively. Further, the tilt direction can be same (syn) or opposite in adjacent layers (anti), which results in 4 different types of polar structures namely SmC_sP_F,, SmC_aP_A-homochiral and SmC_aP_F, SmC_sP_A-racemic.

Among all the mesophases exhibited by BC compounds, the B_7 mesophase [11-13] shows the most beautiful optical textures. One such characteristic texture of this phase is the growth of spiral germs on slow cooling of the isotropic phase. Although there are a large number of BC compounds whose mesophases show the spiral filaments, they differ in their X-ray diffraction (XRD) pattern and electro-optical behaviour. On the basis of available XRD and electro-optical data, broadly two kinds of B_7 mesophases could be distinguished [9]. Mesophases which show medium angle scattering (d=0.7-0.8Å) in the X-ray diffraction (B_7)

[11-18] and those which lack medium angle scattering and show simple layer structure [19-30] with satellites of weak intensity (which indicates undulation) behind the layer reflection (B_7') [30]. It should be pointed out here that, satellites cannot be detected in X-ray diffraction pattern if the undulation wavelength is very long (>100nm). It has been suggested [9] to use the symbol B_7' for these mesophases, which exhibit helical patterns and differ in their XRD patterns shown by the original B_7 phase [12].

Recently the mesomorphic properties of several seven-ring achiral bent-core compounds derived from 5-cyanoresorcinol have been reported [31]. These compounds exhibit B_6, B_1 and B_{2x} phases on ascending the homologous series. Interestingly, the lamellar B_{2x} phase observed in the higher homologues exhibit helical and filamentary textures typical of B_7 phase when observed under a polarizing microscope. It has been suggested that, this B_{2x} phase be classified as a variant of B_7 phase and assigned the symbol B_7' [9]. It is appropriate to mention here that, this is the first report of a seven-ring bent-core mesogen containing a substituent at the apex of the central phenyl ring.

In this chapter, the synthesis and characterization of analogous seven-ring bent-core compounds derived from 5-chlororesorcinol and belonging to two homologous series have been described. The motivation for carrying out this investigation was to examine the effect of replacing the strongly polar cyano substituent, whose vector of the dipole moment is along the arrow axis of the BC molecule, by a chloro group with a weaker dipolar component, but whose contribution is along the same axis. The investigated compounds have the general molecular structure **2.1** shown below.



i. X=F,Y=H Series **2.A**
ii. X=H,Y=F Series **2.B**

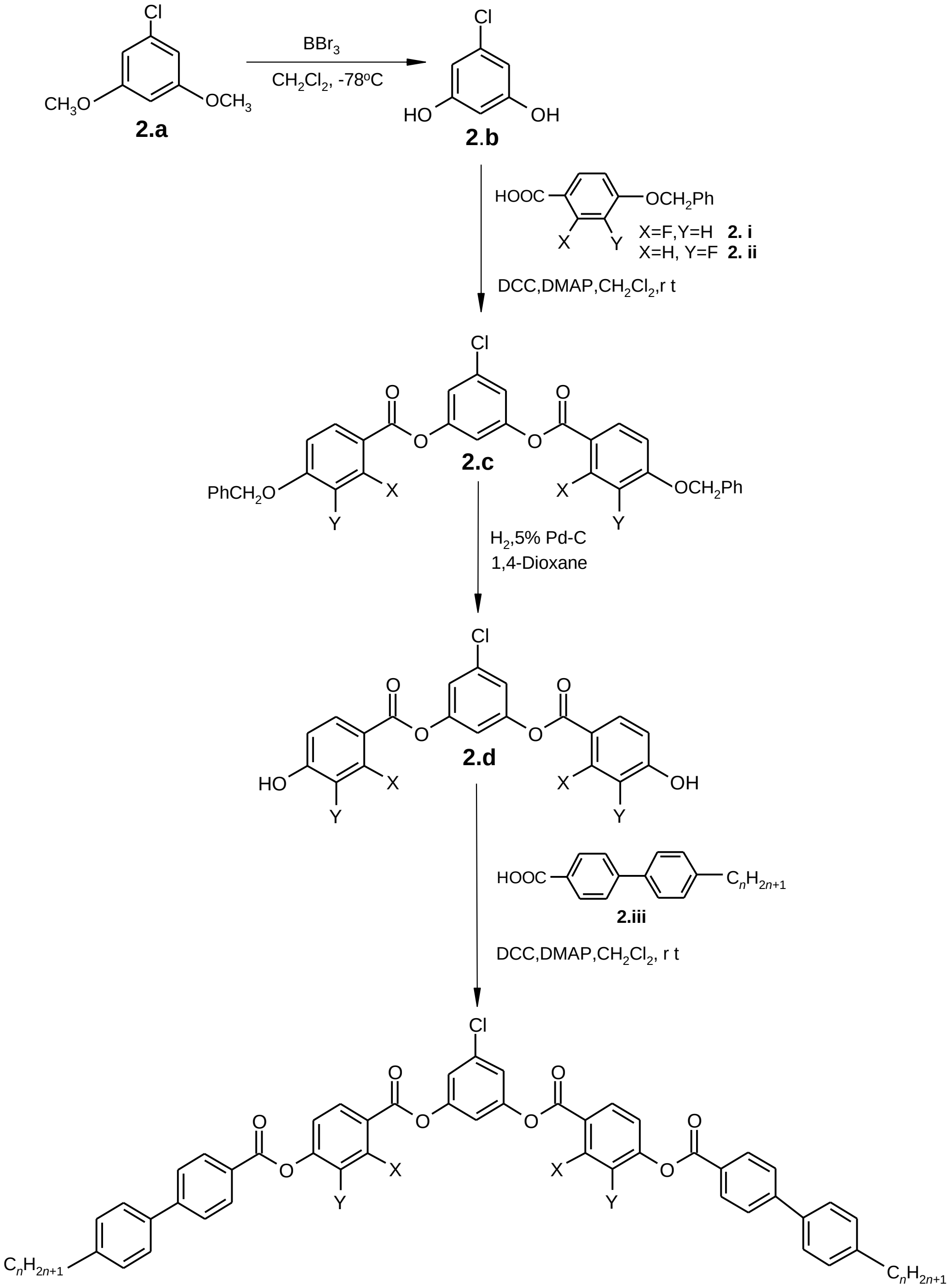
Structure 2.1

Synthesis

The synthesis of the investigated compounds was carried out following a pathway shown in scheme **2.1**. 5-Chlororesorcinol was prepared by demethylation of commercial 1-chloro-3, 5-dimethoxybenzene following a procedure described earlier [31]. 2-Fluoro-4-hydroxybenzoic acid and 3-fluoro-4-hydroxybenzoic acid were synthesized from 3-fluoroanisole and 2-fluoroanisole respectively, following procedures described in the literature [32, 33]. 2-Fluoro-4-benzyloxybenzoic acid and 3-fluoro-4-benzyloxybenzoic acid were prepared following procedures described earlier [34]. 4-*n*-Alkylbiphenyl-4-carboxylic acids were synthesized following a procedure described previously [35]. 5-Chlororesorcinol was esterified with 2-fluoro-4-benzyloxybenzoic acid or 3-fluoro-4-benzyloxybenzoic acid in presence of *N*, *N'*-dicyclohexylcarbodiimide (DCC) and a catalytic amount of 4-(*N*, *N*-dimethylamino)pyridine (DMAP) in dry dichloromethane at room temperature to obtain compound **2.c**. Deprotection of the benzyl group in compound **2.c** was achieved using H_2 and 5% Pd-C catalyst in 1,4-dioxane at 60˚C. The resulting bisphenol **2.d** was esterified with an appropriate 4-*n*-alkylbiphenyl-4-carboxylic acid to obtain the target compounds.

Results and discussion

The transition temperatures and the associated enthalpy values for the compounds of series **2.A** are summarized in table **2.1**. It can be seen in table **2.A**, that compound **2.A.1** is dimorphic. The higher temperature phase exhibits a focal-conic texture, and when viewed between two glass plates treated for homeotropic alignment of the sample, remains birefringent. Hence, the possibility of a SmA phase can be ruled out. The focal-conic texture obtained for this mesophase is shown in figure **2.1a**. Even after shearing the sample, the texture remains birefringent and the shearing results in a schlieren texture and the same is shown in figure **2.1b**. XRD diffraction studies could not be carried out on this mesophase because of the high temperature and no electro-optical switching was observed even at high electric fields. Based on the textural observations, the mesophase has been identified as an intercalated smectic (B_6) phase [6, 36-42]. The enthalpy value of isotropization is 19.9 kJ mol^{-1}, and the thermal range of this mesophase is 18˚C. On cooling the mesophase, a transition takes place at 195˚C with a low enthalpy of 0.34 kJ mol^{-1}, and a small change in the fan-shaped texture occurs. However, there was no significant change in the texture of the mesophase on lowering the temperature further. Interestingly, on shearing the sample one could see a mosaic texture that is normally seen for a classical B_1 phase [6, 36-46] and this is shown in figure **2.1c**.

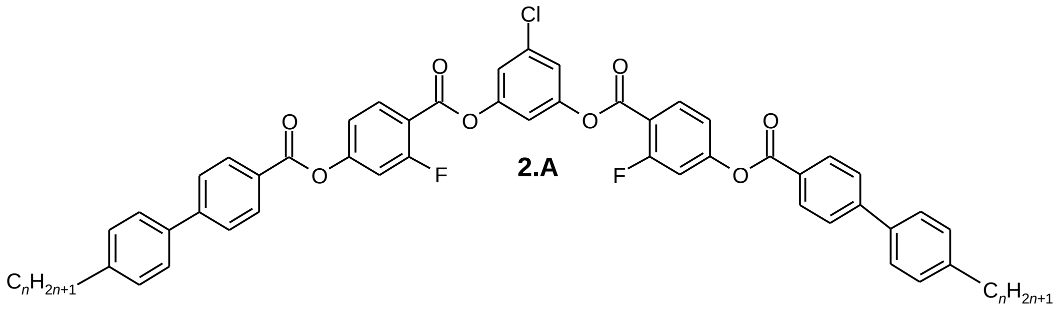


i. X=F,Y=H Series **2. A**

ii. X=H,Y=F Series **2. B**

Scheme 2.1: Synthetic pathway used for the preparation of bent-core compounds 2.A and 2.B.

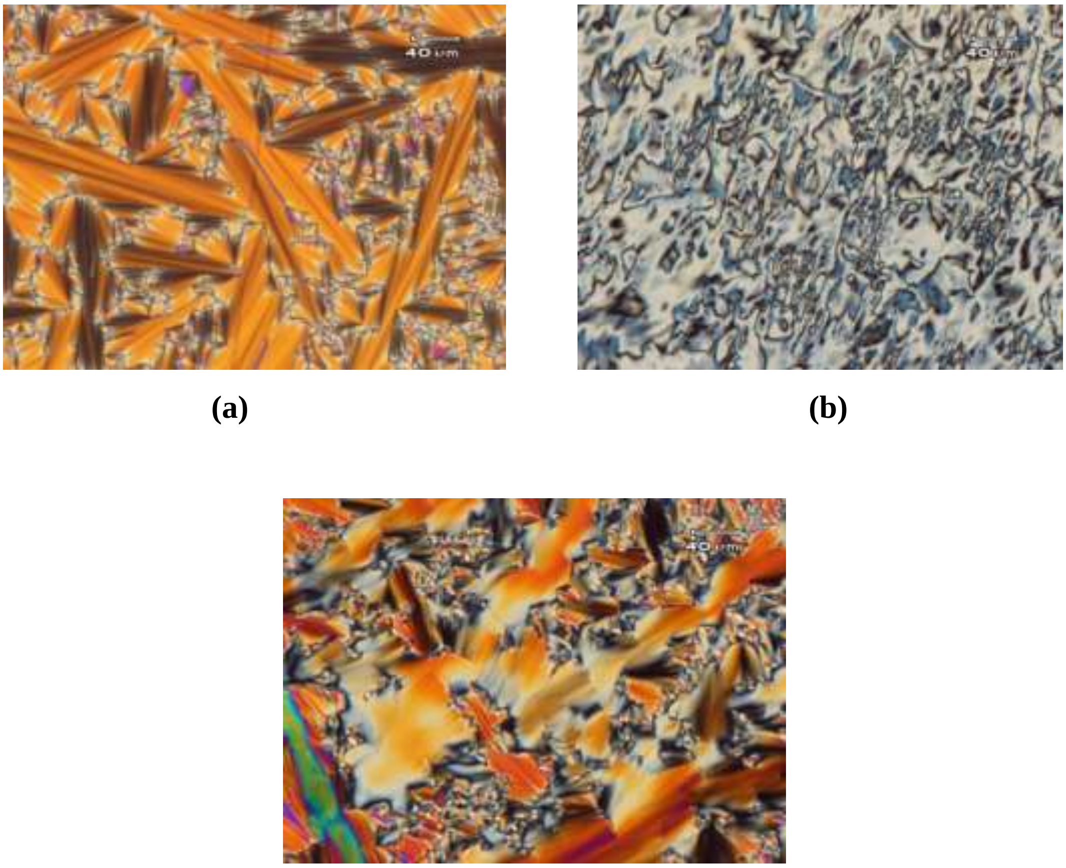
Table 2.1: Transition temperatures (˚C) and the associated enthalpy values (kJ mol^{-1}, in italics) for the compounds of series 2.A.



2.A

Compound	*n*	Cr		B_{2x}		B_1		B_6		I
2.A.1	5	.	182.5	-		.	195.0	.	213.0	.
			46.2				*0.34*		*19.9*	
2.A.2	6	.	188.0	-		.	198.5	-		.
			31.2				*21.7*			
2.A.3	7	.	180.0	-		.	192.0	-		.
			28.3				*23.6*			
2.A.4	8	.	184.0	-		(.	179.5)	-		.
			55.1				*22.8*			
2.A.5	9	.	183.5	-		-		-		.
			55.2							
2.A.6	10	.	180.5	-		-		-		.
			55.1							
2.A.7	11	.	179.0	-		-		-		.
			54.3							
2.A.8	12	.	174.5	-		-		-		.
			63.2							
2.A.9	14	.	170.5	(.	164.0)	-		-		.
			53.8		*23.4*					
2.A.10	16	.	157.5	.	167.0	-		-		.
			21.1		*24.1*					
2.A.11	18	.	157.0	.	167.5	-		-		.
			23.9		*24.0*					

Abbreviations: Cr-Crystalline phase; B_{2x}-Variant of a B_2 phase; B_1-Columnar phase with a rectangular lattice; B_6-Intercalated smectic phase; I-Isotropic phase; **.** Phase exists; - Phase does not exist; () Monotropic transition.



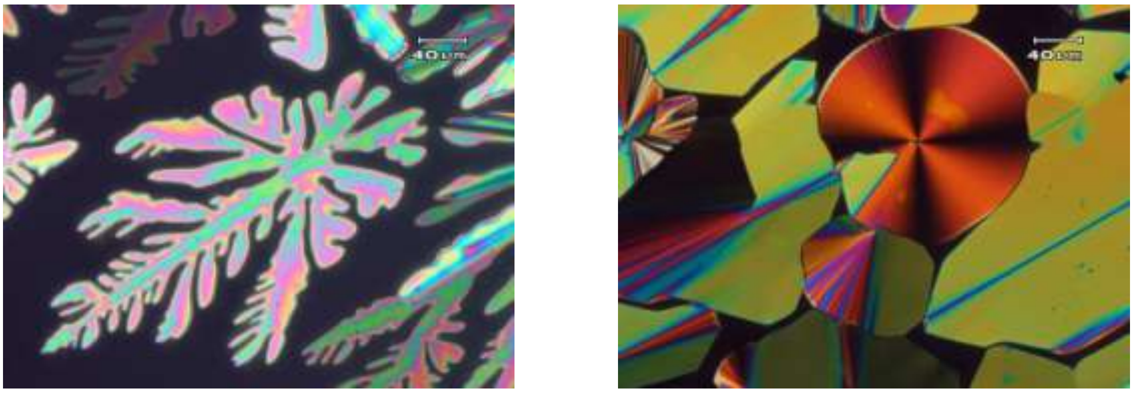
(a)

(b)

(c)

Figure 2.1: (a) Photomicrograph of a focal-conic texture obtained for B_6 phase of compound 2.A.1, T=200˚C; (b) Schlieren texture obtained on shearing the sample shown in (a); (c) Optical texture obtained on shearing the mesophase obtained on cooling from B_6 phase, T=185˚C (same region as in a).

The mesophase of compounds **2.A.2, 2.A.3** and **2.A.4** also exhibit this mosaic texture and except for the mesophase of compound **2.A.4**, which is metastable, the other two are enantiotropic. In addition, the mesophase also exhibits dendritic patterns on slow cooling of the isotropic liquid, which coalesce into a mosaic-like texture. Sometimes spherulitic patterns could also be seen as the mesophase grows from the isotropic state. Photomicrographs of the dendritic growth, mosaics and spherulitic pattern obtained for the mesophase of compound **2.A.3** are shown in figure **2.2a** and **b** respectively. These textural features are reminiscent of a rectangular columnar phase [6, 36-40, 42-46]. In order to determine the structure of this mesophase, XRD studies were carried out. The compound was placed in a 0.7 mm Lindemann capillary and cooled slowly from the isotropic phase into the mesophase and irradiated. The XRD pattern of an unoriented sample of compound **2.A.3** shows two sharp reflections in the small angle region with spacing (*d*) of 24.8Å and 22.2Å. These could be indexed as (11) and (02) reflections of a rectangular lattice with lattice parameters *a*=29.8Å and *b*=44.3Å. A diffuse wide-angle reflection was observed at about 4.6Å, which indicates a liquid-like in-plane order. This mesophase does not respond to an applied electric field. These observations indicate that the mesophase is indeed a B$_1$ phase.



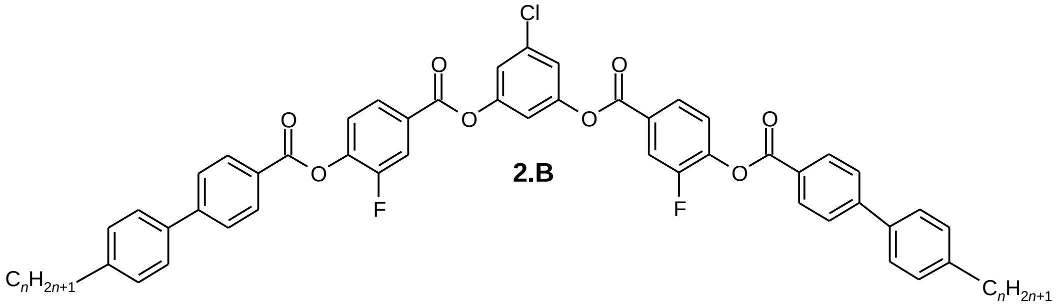
(a) **(b)**

Figure 2.2: Photomicrographs showing the textures obtained for the mesophase of compound 2.A.3. (a) Dendritic growth pattern on slow cooling from the isotropic phase, T=191.5˚C; (b) mosaic and the spherulitic texture, T=189.5˚C.

Surprisingly, compounds **2.A.5-8** did not show any mesophase even on fast cooling of their isotropic phases. However, compounds **2.A.9-11** show a mesophase whose optical textures are all similar. Although compound **2.A.9** shows a metastable phase, the clearing enthalpy values for all three compounds are quite comparable. The optical textures show features reminiscent of those seen for the B$_{2x}$ mesophase exhibited by compounds derived from 5-cyanoresorcinol [31]. Specifically, fingerprint and schlieren textures, patterns showing single-wound helix and filaments were obtained.

The compounds of series **2.B** differ from those of series **2.A** by the position of the fluorine substituent. Unlike the compounds of series **2.A**, all the homologues of series **2.B** are enantiotropic mesomorphic. The transition temperatures and the associated enthalpy values obtained for the compounds of series **2.B** are summarized in table **2.2.**

Table 2.2: Transition temperatures (°C) and the associated enthalpy values (kJ mol^{-1}, in italics) for the compounds of series 2.B.



Compound	*n*	Cr	B_{2x}	B_1	I
2.B.1	5	. 161.0 *31.7*	-	. 209.5 *18.5*	.
2.B.2	6	. 144.5 *32.4*	-	. 199.0 *20.0*	.
2.B.3	7	. 155.0 *56.5*	-	. 193.5 *21.7*	.
2.B.4	8	. 155.0 *56.5*	-	. 186.5 *22.6*	.
2.B.5	9	. 158.5 *59.5*	-	. 181.5 *23.2*	.
2.B.6	10	. 137.5 *21.9*	-	. 173.5 *23.5*	.
2.B.7	11	. 141.0 *22.6*	-	. 167.5 *22.6*	.
2.B.8	12	. 144.5 *23.2*	-	. 160.5 *20.8*	.
2.B.9	14	. 136.5 *23.3*	. 154.5 *20.5*	-	.
2.B.10	16	. 135.5 *23.6*	. 154.5 *20.3*	-	.
2.B.11	18	. 135.0 *20.8*	. 154.0 *20.3*	-	.

Abbreviations: See table **2.A**.

Compounds **2.B.1** to **2.B.8** show the typical mosaic texture seen for the B_1 phase and XRD data clearly show that the mesophase has a rectangular lattice. For example, the XRD pattern of an unoriented sample of compound **2.B.8** showed three reflections in the small angle region with d_1=37.5Å, d_2=26.6Å, and d_3=16.6Å in addition to a diffuse maxima in the wide-angle region. These could be indexed as reflections from (11), (02) and (31) planes, formed by a rectangular lattice with lattice parameters *a*=52.8Å and *b*=53.1Å. The X-ray diffractogram obtained for the mesophase of this compound is shown in figure **2.3**. Again, as mentioned earlier, this phase does not respond to an externally applied electric field. Hence, the mesophase of all these compounds is designated as B_1. It is interesting to note that compound **2.B.1** has a thermal range of 48.5°C for the B_1 phase, which gradually decreases on ascending the series and is only 16°C for compound **2.B.8**. Again, as mentioned earlier, this phase does not respond to an externally applied electric field.

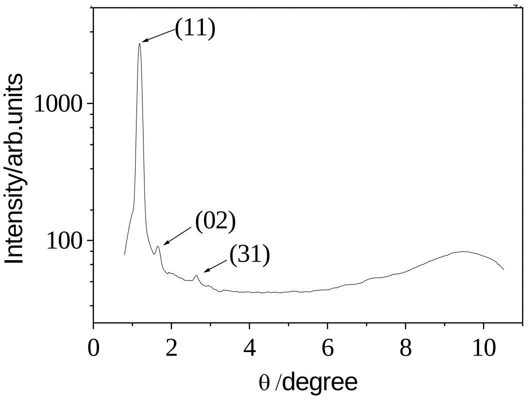


Figure 2.3: X-ray angular intensity profile obtained for the B_1 mesophase of compound 2.B.8, T=150°C.

The remaining three compounds **2.B.9-11** are lamellar as indicated by XRD measurements, and show unusual optical textures. For example, when the isotropic liquid of compound **2.B.11** was cooled slowly, filamentary growth pattern could be seen, and a photomicrograph of a typical filament growing is shown in figure **2.4a**. Predominantly the mesophase exhibited helical pattern, including single, doubly wound helices and filaments and a typical pattern obtained is shown in figure **2.4b**. As the temperature is lowered, the filaments transform to a helical pattern and finally collapse to form an undefined structure (fringe pattern). However, some areas do show schlieren texture and the same is shown in figure **2.4c**. These features are not observed in the classical B_2 phase and, coupled with electro-optical investigations (described later), the mesophase of these three compounds **2.A.9-11** and compounds **2.B.9-11** have been designated as B_{2x} [31].

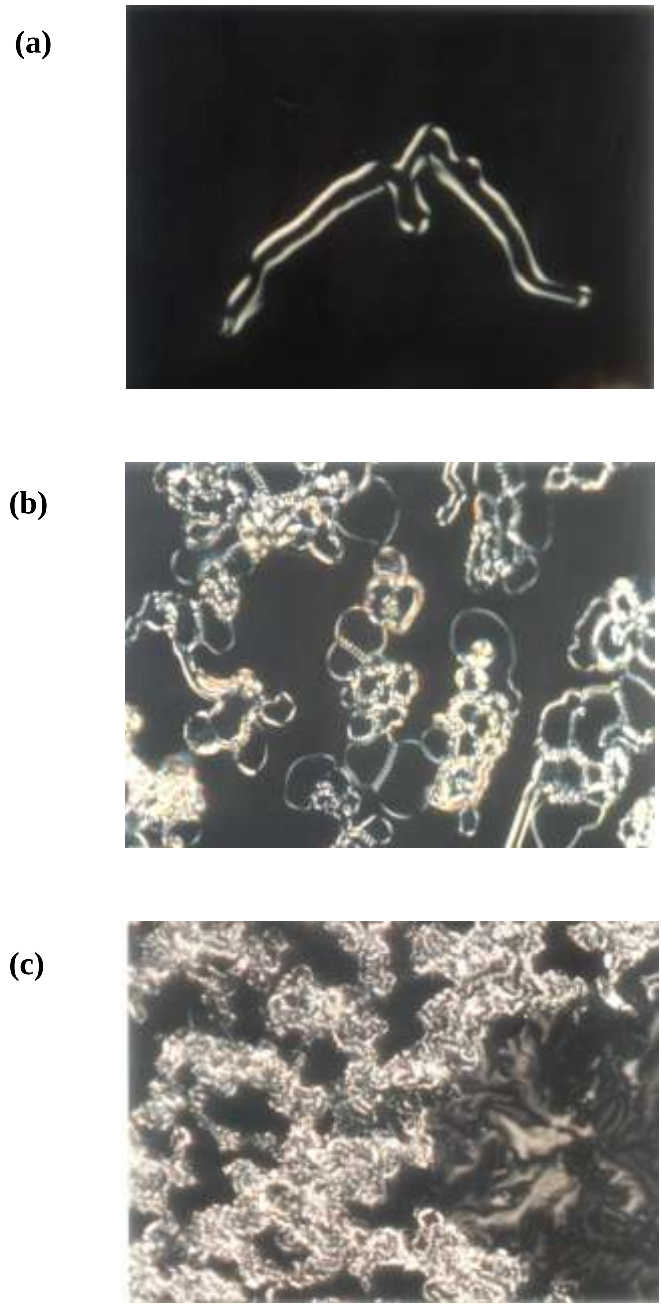


Figure 2.4: Textures obtained for the mesophase of compound 2.B.11. (a) A filament growing on slow cooling of the isotropic phase, T=153.8°C; (b) a texture showing the helical and filamentary pattern in a polyimide coated cell of thickness 6.5 μm, T=153.5°C; (c) an undefined pattern, T=153°C.

The XRD pattern obtained for the mesophase of compound **2.B.11** shows two reflections in the small angle region at d_1=50.8Å, d_2=25.4Å and a diffuse maxima at about 4.6Å in the wide-angle region. These reflections are in the ratio 1:1/2 indicating a lamellar ordering of the molecules in the mesophase. The first order layer spacing is smaller than the measured molecular length (*l*) calculated by assuming the terminal chains to be in an all *trans* conformation and a bend angle of 120˚. This suggests a tilt angle of 53-55˚ (calculated using the relation $\cos\theta = d/l$) for the molecules with respect to the layer normal. The X-ray diffractogram obtained for the mesophase of this compound is shown in figure **2.5**. The XRD data obtained for the unoriented samples of mesophases of eight compounds belonging to series **2.A** and **2.B** are summarized in table **2.3**.

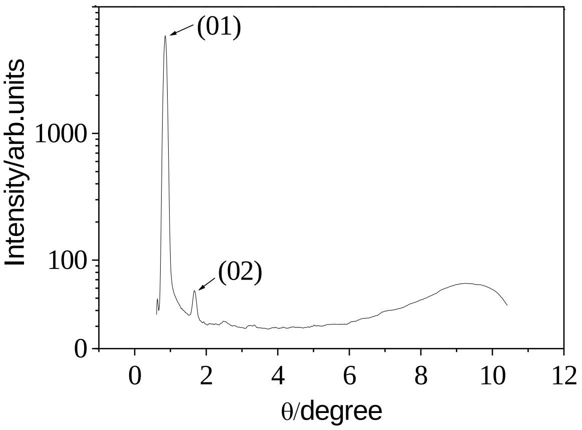


Figure 2.5: X-Ray angular intensity profile obtained for the mesophase of compound 2.B.11, T=145˚C.

A plot of the transition temperature as a function of the length of the terminal *n*-alkyl chain for each of the two homologous series of compounds is shown in figures **2.6** and **2.7** respectively. A comparison of these two plots, clearly reveals that *m*-fluorine substituted compounds (series **2.B**) are better in generating mesophases. Moreover, both the melting and clearing temperatures are lower for these compounds.

Table 2.3: The *d*-spacings (Å) obtained for the mesophases of different compounds belonging to series 2.A and 2.B; the corresponding Miller indices are shown in brackets.

Compound	*d*-spacing/Å(Miller indices)	Lattice parameters/Å		Phase type	T/°C
		a	*b*		
2.A.3	24.8 (11), 22.2 (02)	29.8	44.3	B_1	170
2.A.9	42.8 (01), 21.4 (02)	-	-	B_{2x}	162
2.A.10	44.3 (01), 22.4 (02)	-	-	B_{2x}	162
2.A.11	46.8 (01), 23.4 (02)	-	-	B_{2x}	162
2.B.4	29.8 (11), 24.7 (02)	37.4	49.4	B_1	165
2.B.5	32.7 (11), 25.0 (02)	43.1	50.1	B_1	165
2.B.8	37.5 (11), 26.6 (02), 16.6 (31)	52.8	53.1	B_1	150
2.B.11	50.8 (01), 25.4 (02)	-	-	B_{2x}	145

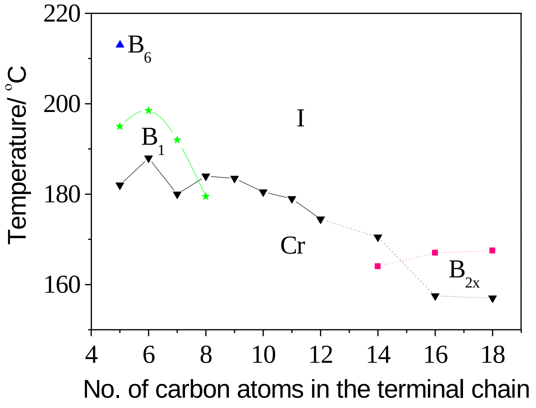


Figure 2.6: A plot of transition temperature *versus* the number of carbon atoms in the *n*-alkyl chain for the compounds of series 2.A.

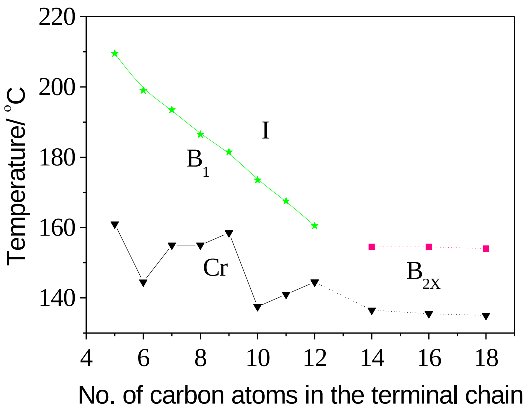


Figure 2.7: A plot of transition temperature *versus* the number of carbon atoms in the *n*-alkyl chain for the compounds of series 2.B.

Electro-optical investigations were carried out on the B_{2x} mesophase exhibited by compounds belonging to both the homologous series. Since the characteristic behaviour was the same, the experimental observations made on compound **2.B.11** are given in detail. For the ac field experiments, a sample of compound **2.B.11** in its isotropic phase was filled into an ITO coated home made cell of uniform thickness of 11.5 μm, which was treated for homogeneous alignment. The sample was cooled slowly from the isotropic phase under a triangular-wave voltage of $40V_{pp}$ and a frequency of 10 Hz, and simultaneously the optical behaviour was observed under a polarizing light microscope. Two polarization current peaks per half cycle were observed at a very low threshold voltage of $60V_{pp}$ and a frequency of 10 Hz, indicating an antiferroelectric ground state for the mesophase. Circular domains were seen under the microscope in which the extinction cross coincides with the direction of the crossed polarizer and analyzer, indicating an anticlinic arrangement of the molecules in the switched ferroelectric state. On switching off the field, the orientation of the cross did not change, but stripes appeared on the domains suggesting relaxation of the molecules to the antiferroelectric ground state. The switching current response obtained in the B_{2x} phase of compound **2.B.11** at 145˚C is shown in figure **2.8** and the corresponding optical photomicrographs obtained with $E=150V_{pp}$ at 10 Hz and E=0V are shown in figure **2.9a** and **b** respectively. The calculated polarization value is about 710 nC cm^{-2}.

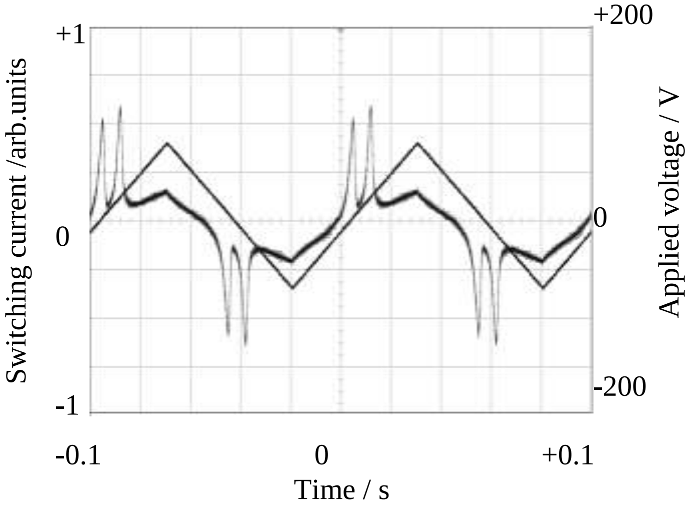
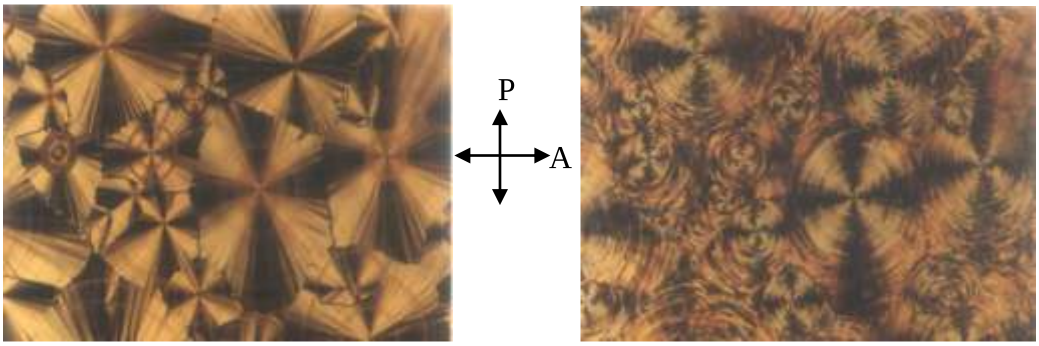


Figure 2.8: Switching current response obtained for the mesophase of compound 2.B.11 by applying a triangular voltage (150V_{pp}, 10 Hz), cell thickness 11.5 μm, T=145°C; polarization $P_S \sim 710$ nC cm^{-2}.



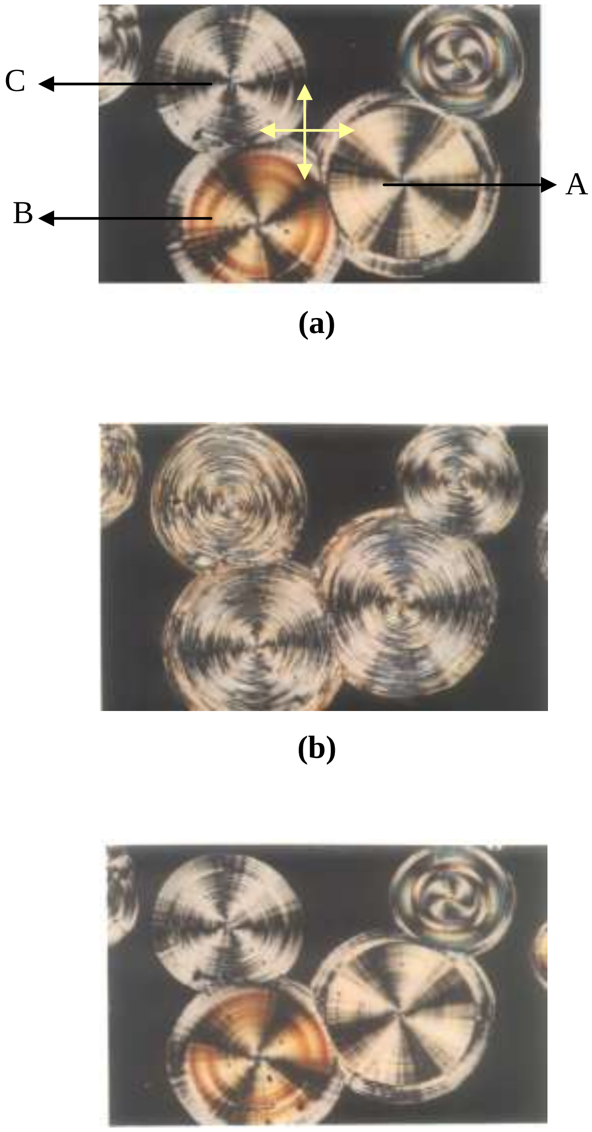
(a)

(b)

Figure 2.9: Optical photomicrographs of the mesophase of compound 2.B.11 obtained by the application of a triangular voltage of (a)150V_{pp}, 10 Hz and (b) 0V, T=145°C.

The mesophase of compound **2.B.11** was also examined under a dc electric field. A cell of thickness 9.9 μm was used for these experiments. On slow cooling of the isotropic phase of this compound under a dc field of 1.5 Vμm^{-1}, various circular domains were obtained. However, the observations were made slightly above this threshold voltage. For example, as shown in figure **2.10** with a field of +2 Vμm^{-1}, two domains **A** and **B** were observed in which the extinction cross rotate in clock-wise and counter clock-wise directions, respectively, with respect to the polarizer and analyzer. On reversing the polarity of the applied field, the extinction which rotated in a clock-wise direction now rotates in an anticlock-wise direction and *vice versa*. On terminating the field, the extinction crosses in these domains orient parallel to the axes of the crossed polarizers. This clearly indicates a synclinic ferroelectric state (SmC$_s$P$_F$) under the field, which relaxes to the anticlinic antiferroelectric (SmC$_a$P$_A$) ground state *via* rotation around the cone and thus represent the two ferroelectric chiral conglomerates [21, 31, 42]. A schematic representation of the arrangement of molecules in adjacent layers under the field and at zero field is shown in figure **2.11**.

In domain **C**, the extinction cross lies parallel to the polarizer and analyzer with the field, and no change of this orientation was observed either on reversing the polarity of the field or on switching off the field. However, low birefringent smooth circular domains obtained with the field, were replaced by highly birefringent stripes appearing on the domains when the field was switched off. These observations are in accord with a layer structure model proposed [3, 47] earlier. According to this model, at zero field, the molecules in adjacent layers have antiferroelectric correlation with a synclinic tilt and a change in the tilt direction takes place after a few layers. In other words there exists a multi-domain structure with change in the clinicity at domain boundaries. The stripes indicate a region where there is a change in the tilt (blue region in the model, figure **2.12**). Under the field clinicity becomes uniform and hence stripes disappear. However, Folcia *et al.* [48] have suggested a reinterpretation of this model for the racemic states (SmC$_s$P$_A$) of the B$_2$ phase in bulk samples. This is because, the field induced SmC$_s$P$_A$ to SmC$_a$P$_F$ transition contradicts the Curie law, as the symmetry of the SmC$_a$P$_F$ phase (C$_{2V}$) is not the intersection between the point group of SmC$_s$P$_A$ (C$_{2h}$) and the point group of the electric filed (C$_{\infty V}$) [48]. Therefore, it was suggested [49] that the Curie law could be satisfied if an additional periodicity in the SmC$_s$P$_A$ structure exists along the layer normal. The equally spaced anticlinic-ferroelectric interlayer boundaries (SmC$_a$P$_F$ correlation at the domain boundaries: light blue region in the model shown in figure **2.12**) meet this requirement. This organization of the molecules changes the symmetry from C$_{2h}$ to C$_{2V}$ and the same is shown as schematic representation in figure **2.12**. These anticlinic-ferroelectric interlayer boundaries are observed as stripes at zero voltage. However, on application of the field, the clinicity becomes uniform and hence the stripes disappear.



(a)

(b)

(c)

Figure 2.10: Photomicrographs obtained for the B_{2x} phase of compound 2.B.11 by the application of dc electric field of (a) + 2 Vμm^{-1}; (b) 0V and (c) –2 Vμm^{-1}.

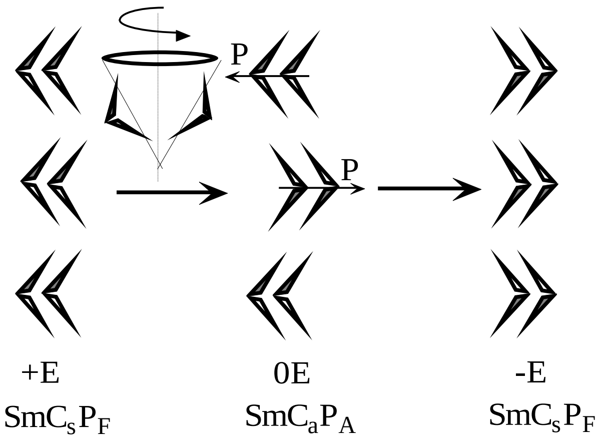


Figure 2.11: Possible molecular organization in domain A (or B) under +E, 0E and -E respectively.

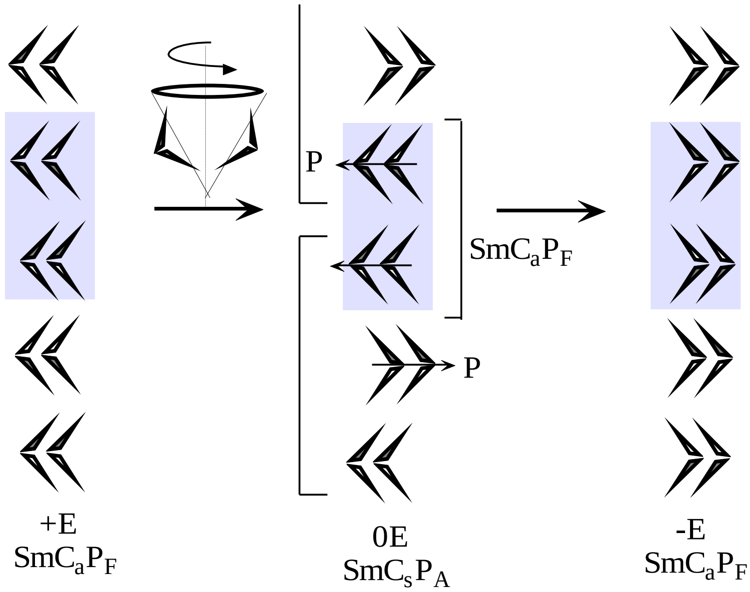
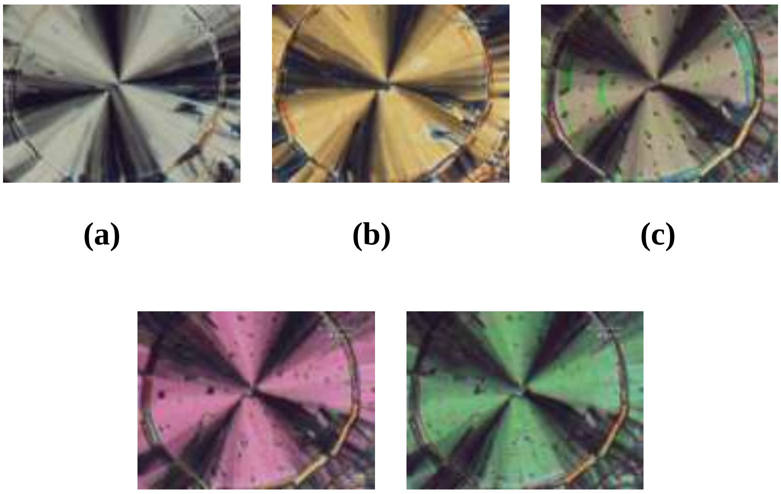


Figure 2.12: Possible molecular organization in domain C under +E, 0E and –E respectively.

Another interesting observation made is the variation of colour as a function of the strength of the applied dc field. For example, on increasing the strength of the field, the colour changes from yellow to green and the extinction brush also rotates linearly with the field and this process is reversible. The different colours of the textures are due to different birefringence values caused by varying molecular orientations as suggested by Ortega *et al*. [50]. These features are shown in figure **2.13**. All the above observations are quite similar to what had been seen for the B_{2x} mesophase exhibited by compounds derived from 5-cyanoresorcinol [31].



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

(d) **(e)**

Figure 2.13: Photomicrographs illustrating the variation of colour and rotation of extinction crosses with the variation of dc field for the mesophase of compound 2.B.11. (a) 1 Vμm^{-1}; (b) 1.5 Vμm^{-1}; (c) 2.0 Vμm^{-1}; (d) 2.5 Vμm^{-1}; (e) 3.0 Vμm^{-1}.

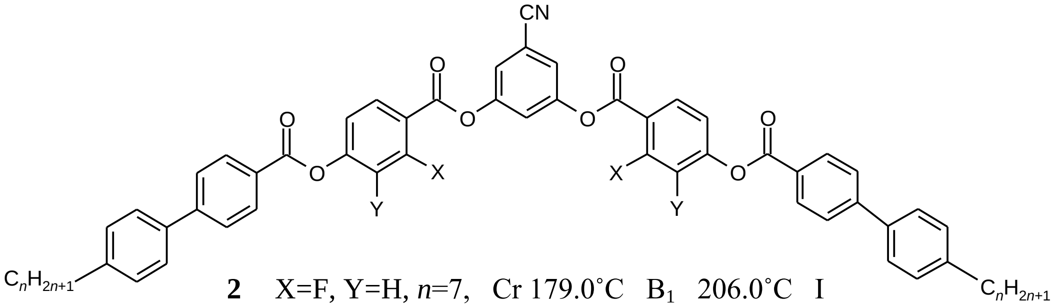
Another interesting feature observed is the growth of the mesophase above the clearing temperature when a sufficiently high dc field is applied. In other words, field-induced mesophase could be obtained. For compound **2.B.11** in a polyimide coated ITO cell of thickness 6.78 μm at 155˚C (isotropic liquid), when a dc field of 43V was applied, the mesophase started to nucleate and covered the whole field of view on enhancing the strength of the applied field (57V). A photomicrograph showing the field induced (57V) growth of the mesophase at 155˚C is shown in figure **2.14**. On increasing the temperature further, the field required to induce the nucleation also increased. This type of observation had already been made [51, 52] and suggests the existence of short-range orientational order of the molecules in the isotropic phase.

Figure 2.14: Photomicrograph showing the field induced mesophase of compound 2.B.11 at a dc electric field of 57V, T=155˚C; cell thickness 6.78 μm.

A comparison of the mesomorphic properties of compounds of series **2.A** with the analogous compounds derived from 5-cyanoresorcinol (series **I** in reference 31) revealed the following points. The replacement of cyano group in series **I** [31] by a chloro group (series **2.A**) resulted in a general reduction in the melting and the clearing temperatures. The reduction in the clearing temperature is larger compared to the melting temperature and hence the thermal range for the mesophase is also reduced. For example, the B_1 phase of compound **2.A.3** (*n*=7) has a thermal range of 12˚C while the corresponding cyano substituted compound (compound **2** shown in structure **2.2**) has a thermal range of 27˚C. In addition, the existence of B_1 phase is suppressed and a B_6 mesophase is induced in a homologue with *n*=5 (**2.A.1**). The B_1 phase becomes monotropic for the homologue with *n*=8 (**2.A.4)** and is completely eliminated for homologue with *n*=9 (**2.A.5**). In contrast, the analogous cyano substituted compounds exhibit enantiotropic B_1 phase. Further, the existence of B_{2x} phase is also suppressed. For example, enantiotropic B_{2x} phase observed for homologues with *n*=11-18 in series **I** derived from 5-cyanoresorcinol [31], is eliminated for homologues with *n*=11, 12

(**2.A.7, 2.A.8**) and is monotropic for *n*=14 (**2.A.9**) in series **2.A** derived from 5-chlororesorcinol.

A similar comparison between the compounds of series **2.B** with the analogous compounds derived from 5-cyanoresorcinol (series **II** in reference 31) indicates a reduction in the melting and clearing points with the effect more pronounced for the clearing temperatures. For example, in compound **2.B.11**, the melting point is reduced by 6.5˚C, while the clearing temperature is reduced by 27˚C resulting in a reduction of temperature range for the mesophase from 39.5˚C (in compound **18** shown in structure **2.2**) to 19˚C. However, the occurrence of the B_1 and B_{2x} mesophases is unaffected.



2 X=F, Y=H, *n*=7, Cr 179.0˚C B_1 206.0˚C I
18 X=H, Y=F, *n*=18, Cr 141.5˚C B_{2x} 181.0˚C I

Structure 2.2 [31]

Conclusions

Synthesis of two new homologous series of seven-ring bent-core esters derived from 5-chlororesorcinol and characterization of the mesophases have been carried out. These represent the first example of BC compounds containing a chloro substituent at position-5 of the central phenyl unit. The lower homologues of both series of compounds exhibit a columnar B_1 phase with a rectangular lattice. Interestingly, the higher homologues show a mixture of three different possible structures, two of which are chiral and the remaining one is racemic. Since the B_{2x} mesophase shows helical pattern similar to that observed in [21], and high resolution XRD could not carried out, it is possible that this mesophase is one among the B_7 class of materials and can be designated by the symbol B_7' [9].

Experimental

General

The intermediate and the target compounds were purified by column chromatography on silica gel (ACME, 60-120 mesh) using appropriate solvents for elution. Schiff's bases were chromatographed on basic alumina. The compounds were further purified by repeated crystallization from suitable analytical grade solvents. Distillation under reduced pressure was carried out to purify the liquid samples. Merck Kieselgel $60F_{254}$ pre-coated thin layer chromatographic plates were used to check the purity of the samples. Silica plates were used for ester compounds while for Schiff's base compounds alumina plates were used. The chemical structure of the compounds was determined using a combination of Infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and elemental analysis techniques. IR (Shimadzu FTIR-8400 spectrophotometer) spectra for intermediate compounds were recorded as nujol mull and as KBr discs for target compounds. ^{1}H and ^{13}C NMR (Bruker AMX 400 spectrometer) spectra were recorded using deuteriochloroform ($CDCl_3$), deuterioacetone (CD_3COCD_3) or deuterated dimethylsulfoxide (DMSO-d_6) as solvents. Tetramethylsilane (TMS) was used as an internal reference. Elemental analysis (Carlo-Erba 1106 analyser) was performed using BBOT [2,5-bis- (5-*tert*.butyl-benzoxazol-2-yl)-thiopen] and sulphanilamide as standards.

The mesomorphic properties were investigated using a combination of polarizing optical microscopy (POM), X-ray diffraction studies (XRD) and electro-optical measurements. Textural observations were made under a polarizing light microscope (Olympus BX50) equipped with a heating stage (Mettler FP82HT) and a central processor (Mettler FP90). The transition temperatures were determined from POM observations as well as from the thermograms obtained on a differential scanning calorimeter (DSC, Perkin-Elmer calorimeter, Model Pyris 1D). Enthalpy values associated with the transitions were also determined from these thermograms. The apparatus was calibrated using pure indium (156.6˚C; $\Delta H=28.56$ J g^{-1}) as a standard and operated at a scanning rate of 5˚C min^{-1} both on heating and cooling cycles.

X-Ray diffraction (XRD) patterns were obtained for unoriented samples and in some cases as oriented samples. In all cases, Cu-K_α ($\lambda=1.54$Å) radiation generated from a 4kW rotating anode X-ray source (Rigaku Ultrax-18) was used. The beam was monochromated using a graphite crystal. The powder samples held in Lindemann capillaries (diameter: 0.7mm, wall thickness: 0.01mm) were cooled slowly from the isotropic state to the mesophase and irradiated. Oriented patterns were obtained by slow cooling of a drop of the sample on a glass plate from the isotropic state. In each case, the sample temperature was controlled to within ± 0.1˚C. The diffraction pattern of the mesophase was recorded on a two-dimensional (Marresearch) image plate.

Polarization measurements were carried out using ITO coated glass cells (with polyimide alignment layers and without any alignment layers) employing the standard triangular-wave method [53]. The glass cells of different thicknesses were either home made or obtained from EHC, Japan. Triangular-wave was generated by a waveform generator (Wavetek, Model 39), connected to an amplifier (Trek Model 601B-3). The current was measured across a 10/1 kΩ resistor and the current response traces were recorded using an oscilloscope (Agilent 54621A). Dielectric measurements were carried out by a Qaudtech 1920 precision LCR meter in the frequency range between 20 Hz and 1 MHz. The dc field experiments were carried out using a regulated dual dc power supply (APLAB, Model LD6401) and simultaneously the optical behaviour was observed under a polarizing microscope.

Synthesis

2-Fluoro-4-benzyloxybenzoic acid, 2.i

This was prepared following a procedure described in the literature [32-34]. m. p. 167-168˚C.

3-Fluoro-4-benzyloxybenzoic acid, 2.ii

This was prepared following a procedure described in the literature [32-34]. m. p. 187-188˚C.

4-*n*-Alkylbiphenyl-4-carboxylic acids, 2.iii

These were prepared following a procedure described in the literature [35].

5-Chlororesorcinol, 2.b

A solution of 5-chloro-1, 3-dimethoxybenzene, **2.a** (5.0g, 28.94 mmol) in dry dichloromethane (50 ml) was cooled to –78˚C. A solution of boron tribromide (29g, 115.8 mmol) in dichloromethane (20 ml) was added to this solution dropwise over a period of 2 hours. The temperature was maintained for 2-3 hours, then allowed slowly to attain room temperature. The reaction mixture was then stirred for about 10 hours at room temperature and heated at reflux for a further 10 hours. Excess of boron tribromide was decomposed carefully by the addition of moist chloroform; the dark reaction mixture obtained on removal of solvent was passed through a column of silica gel using 5% ethyl acetate in chloroform as an eluant. The product isolated was further purified by short-path distillation. Yield 3.5g (83.5%), m. p. 115-116˚C. ν_{max}: 3622, 3261, 2923, 2854, 2692, 2489, 1604, 1469, 1093 cm^{-1}; δ_H: 8.0 (s, 2H, 2×Ar-OH, exchangeable with D_2O), 6.19 (d, ^4J 2.12 Hz, 2H, Ar-H), 6.10 (t, ^4J 2.08 Hz, 1H, Ar-H); $C_6H_5ClO_2$ requires C 49.85, H 3.48; found C 49.55, H 3.40 %.

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

A mixture of 5-chlororesorcinol, **2.b** (1g, 6.9 mmol), 2-fluoro-4-benzyloxybenzoic acid, **2.i** (3.4g, 13.8 mmol), and a catalytic amount of 4-(*N*, *N*-dimethylamino)pyridine (DMAP) in dry dichloromethane (25 ml) was stirred for 10 minutes. To this mixture, *N*, *N*′-dicyclohexylcarbodiimide (DCC) (3.08g, 15.2 mmol) was added and stirred for about 2 hours at room temperature. The precipitated *N*, *N*′-dicyclohexylurea was filtered off and washed with an excess of dichloromethane. The combined organic solution was washed with ice-cold aqueous 5% sodium hydroxide solution (2×50 ml), 5% aqueous acetic acid (2×50 ml) and finally washed with water (3×60 ml) and dried over anhydrous sodium sulphate. The residue obtained on removal of solvent was chromatographed on silica gel using chloroform as an eluant. The material obtained on removal of the solvent was further purified by crystallization using acetonitrile. Yield 3g (75%), m. p. 123-124˚C. ν_{max}: 2923, 2854, 2669, 1743, 1735, 1733, 1730, 1460 cm^{-1}; δ_H: 8.07-8.03 (dd, ^3J 8.64 Hz, 2H, Ar-H), 7.45-7.39 (m, 10H, Ar-H), 7.22 (d, ^4J 2 Hz, 2H, Ar-H), 7.14 (t, ^4J 2 Hz, 1H, Ar-H), 6.90-6.87 (dd, ^3J 8.8 Hz, ^4J 2.3 Hz, 2H, Ar-H), 6.82-6.78 (dd, ^3J 12.6 Hz, ^4J 2.4 Hz, 2H, Ar-H), 5.16 (s, 4H, 2×-OCH_2-Ar); $C_{34}H_{23}ClF_2O_6$ requires C 67.95, H 3.82; found C 67.98, H 3.5 %.

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

Compound **2.c** (3g) was dissolved in 1,4-dioxane (50 ml) and 5% Pd-C catalyst (0.6g) was added to it. The mixture was stirred at 60˚C in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. The resulting mixture was filtered hot and the solvent removed under reduced pressure. The material so obtained was crystallized using a mixture of butan-2-one and petroleum ether (b. p.60-80˚C). Yield 2.0g (87%), m. p. 220-221˚C. ν_{max}: 3371, 2954, 2923, 2854, 1720, 1706, 1616 cm^{-1}; δ_H (DMSO-d_6): 11.09 (s, 2H, 2×Ar-OH, exchangeable with D_2O), 7.96-7.94 (dd, ^3J 8.76 Hz, 2H, Ar-H), 7.44 (d, ^4J 2 Hz, 2H, Ar-H), 7.31 (t, ^4J 2 Hz, 1H, Ar-H), 6.81-6.78 (dd, ^3J 8.72 Hz, ^4J 2.16 Hz, 2H, Ar-H), 6.75-6.72 (dd, ^3J 13.04 Hz, ^4J 2.12 Hz, 2H, Ar-H); $C_{20}H_{11}ClF_2O_6$ requires C 57.09, H 2.61; found C 57.06, H 2.62 %.

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

This was synthesized following a procedure similar to that described for the preparation of compound, **2.c** (X=F, Y=H). Quantities: 5-chlororesorcinol, **2.b** (1g, 6.9 mmol), 3-fluoro-4-benzyloxybenzoic acid, **2.ii** (3.4g, 13.8 mmol), DCC (3.1g, 15.2 mmol), DMAP (cat. amount) and dry dichloromethane (30 ml). Yield 3.5g (83%), m. p. 125-126˚C. ν_{max}: 2923, 2854, 1743, 1735, 1733, 1730, 1460, 1288, 1191, 1132, 1118 cm^{-1}; δ_H: 7.92-7.87 (m, 4H, Ar-H), 7.46-7.36 (m, 10H, Ar-H), 7.17 (d, ^4J 2 Hz, 2H, Ar-H), 7.11-7.07 (m, 3H, Ar-H), 5.16 (s, 4H, 2×-OCH_2-Ar); $C_{34}H_{23}ClF_2O_6$ requires C 67.95, H 3.82; found C 67.66, H 3.48 %.

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

This was prepared following a procedure similar to that described for the preparation of compound, **2.d** (X=F, Y=H). Quantities: compound **2.c**, (X=H, Y=F) (3.3g, 5.5 mmol), 5%

Pd-C (0.75g), 1, 4-dioxane (35 ml). Yield 2.1g (91%), m. p. 208-209˚C. ν_{max}: 3371, 2954, 2923, 2869, 2854, 1720, 1706, 1616, 1593, 1525, 1440, 1375, 1319, 1298, 1282, 1211, 1178, 1132, 1116, 1076 cm^{-1}; $\delta_H(CD_3COCD_3)$: 11.09 (s, 2H, 2×Ar-OH, exchangeable with D_2O),7.92-7.89 (m, 4H, Ar-H), 7.17 (d, ^4J 1.96 Hz, 2H, Ar-H), 7.18-7.14 (m, 3H, Ar-H); $C_{20}H_{11}ClF_2O_6$ requires C 57.09, H 2.61; found C 57.13, H 2.48 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-pentylbiphenyl-4′-carbonyloxy)-2-fluorobenzoate],

2.A.1

A mixture of compound **2.d** (X=F, Y=H) (0.15g, 0.25 mmol), 4-*n*-pentylbiphenyl-4-carboxylic acid, **2.iii** (0.134g, 0.5 mmol) and a catalytic amount of DMAP in dry dichloromethane (8 ml) was stirred for 10 minutes. To this stirred mixture, DCC (0.11g, 0.55 mmol) was added and the stirring continued for about 12 hours. The solvent was removed and the residue purified by column chromatography on silica gel using chloroform as an eluant. The product thus obtained was purified further by repeated crystallization using butan-2-one. Yield 0.2g (72%), m. p. 182.5˚C. ν_{max}: 2956, 2923, 2852, 1745, 1732, 1730, 1616, 1606, 1589, 1587, 1498, 1419, 1276, 1249, 1137, 1058, 1016, 1004 cm^{-1}; δ_H: 8.27 (d, ^3J 8.44 Hz, 4H, Ar-H), 8.24-8.20 (dd, ^3J 8.64 Hz, 2H, Ar-H), 7.78 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.62 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.34 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.29 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.29-7.24 (m, 4H, Ar-H), 7.22 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.70 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.74-1.66 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.41-1.37 (m, 8H, 2×(-CH_2-)$_2$), 0.94 (t, ^3J 6.84 Hz, 6H, 2×-CH_3); $C_{56}H_{47}ClF_2O_8$ requires
C 73.0, H 5.14; found C 72.59, H 5.08 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-hexylbiphenyl-4′-carbonyloxy)-2-fluorobenzoate],

2.A.2

Yield 68%, m. p. 188˚C. ν_{max}: 2927, 2956, 2856, 1755, 1747, 1732, 1604, 1591, 1124 cm^{-1}; δ_H: 8.27 (d, ^3J 8.44 Hz, 4H, Ar-H), 8.24-8.20 (dd, ^3J 8.64 Hz, 2H, Ar-H), 7.78 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.61 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.34 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.29 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.29-7.24 (m, 4H, Ar-H), 7.22 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.70 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.71-1.66 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.41-1.37 (m, 12H, 2×(-CH_2-)$_3$), 0.93 (t, ^3J 6.84 Hz, 6H, 2×-CH_3); δ_C: 164.2, 164.0, 161.2, 156.3, 151.3, 147.0, 143.7, 136.9, 135.0, 133.5, 130.8, 129.0, 127.2, 127.0, 120.1, 118.0, 114.4, 111.5, 111.3, 35.6, 31.5, 31.0, 22.5, 14.0; $C_{58}H_{51}ClF_2O_8$ requires C 73.3, H 5.4; found C 73.03, H 5.44 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-heptylbiphenyl-4′-carbonyloxy)-2-fluorobenzoate], 2.A.3

Yield 69%, m. p. 180˚C. ν_{max}: 2952, 2852, 2923, 1745, 1733, 1730, 1616, 1606, 1577, 1498, 1419, 1278, 1249, 1137, 1058 cm^{-1}; δ_H: 8.27 (d, ^3J 8.44 Hz, 4H, Ar-H), 8.24-8.20 (dd, ^3J 8.64 Hz, 2H, Ar-H), 7.78 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.61 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.34 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.29 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.29-7.24 (m, 4H, Ar-H), 7.22 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.70 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.69-1.67 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.38-1.33 (m, 16H, 2×(-CH_2-)$_4$), 0.92 (t, ^3J 6.84 Hz, 6H, 2×-CH_3); $C_{60}H_{55}ClF_2O_8$ requires C 73.7, H 5.67; found C 73.88, H 5.37 %.

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

Yield 70%, m. p. 184˚C. ν_{max}: 2956, 2927, 2856, 1755, 1747, 1732, 1604, 1591, 1124 cm^{-1}; δ_H: 8.27 (d, ^3J 8.44 Hz, 4H, Ar-H), 8.24-8.20 (dd, ^3J 8.64 Hz, 2H, Ar-H), 7.78 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.61 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.34 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.29 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.29-7.24 (m, 4H, Ar-H), 7.22 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.70 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.69-1.65 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.37-1.31 (m, 20H, 2×(-CH_2-)$_5$), 0.92 (t, ^3J 6.84 Hz, 6H, 2×- CH_3); δ_C: 164, 151.3, 143.7, 137.0, 133.5, 131.0, 129.0, 127.0, 120.0, 118.0, 111.0, 35.7, 32.0, 31.5, 29.5, 29.3, 22.5, 14.1; $C_{62}H_{59}ClF_2O_8$ requires C 74.05, H 5.91; found C 74.48, H 5.57 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-nonylbiphenyl-4′-carbonyloxy)-2-fluorobenzoate], 2.A.5

Yield 75%, m. p. 183.5˚C. ν_{max}: 2954, 2923, 2852, 1747, 1733, 1730, 1616, 1606, 1587, 1498, 1434, 1278, 1249, 1139, 1060 cm^{-1}; δ_H: 8.27 (d, ^3J 8.44 Hz, 4H, Ar-H), 8.24-8.20 (dd, ^3J 8.64 Hz, 2H, Ar-H), 7.78 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.61 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.34 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.29 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.29-7.24 (m, 4H, Ar-H), 7.22 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.70 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.69-1.65 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.37-1.31 (m, 24H, 2×(-CH_2-)$_6$), 0.92 (t, ^3J 6.84 Hz, 6H, 2×- CH_3); $C_{64}H_{63}ClF_2O_8$ requires C 74.37, H 6.14; found C 74.39, H 5.77 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-decylbiphenyl-4′-carbonyloxy)-2-fluorobenzoate], 2.A.6

Yield 78%, m. p. 180.5°C. ν_{max}: 2956, 2927, 2856, 1755, 1747, 1732, 1604, 1591, 1124 cm^{-1}; δ_H: 8.27 (d, ^3J 8.44 Hz, 4H, Ar-H), 8.24-8.20 (dd, ^3J 8.64 Hz, 2H, Ar-H), 7.78 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.61 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.34 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.29 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.29-7.24 (m, 4H, Ar-H), 7.22 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.70 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.69-1.67 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.37-1.30 (m, 28H, 2×(-CH_2-$)_7$), 0.91 (t, ^3J 6.84 Hz, 6H, 2×- CH_3); $C_{66}H_{67}ClF_2O_8$ requires C 74.67, H 6.36; found C 74.45, H 6.15 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-undecylbiphenyl-4′-carbonyloxy)-2-fluorobenzoate], 2.A.7

Yield 74%, m. p. 179°C. ν_{max}: 2954, 2922, 2850, 1747, 1732, 1730, 1728, 1606, 1587, 1433, 1278, 1249, 1141, 1060 cm^{-1}; δ_H: 8.27 (d, ^3J 8.44 Hz, 4H, Ar-H), 8.24-8.20 (dd, ^3J 8.64 Hz, 2H, Ar-H), 7.78 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.61 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.34 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.29 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.29-7.24 (m, 4H, Ar-H), 7.22 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.70 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.69-1.67 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.37-1.30 (m, 32H, 2×(-CH_2-$)_8$), 0.91 (t, ^3J 6.84 Hz, 6H, 2×- CH_3); $C_{68}H_{71}ClF_2O_8$ requires C 74.95, H 6.57; found C 74.88, H 6.37 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-dodecylbiphenyl-4′-carbonyloxy)-2-fluorobenzoate], 2.A.8

Yield 76%, m. p. 174.5°C. ν_{max}: 2922, 2850, 1749, 1747, 1733, 1606, 1506, 1498, 1456, 1436, 1419, 1280, 1249, 1141, 1060 cm^{-1}; δ_H: 8.27 (d, ^3J 8.44 Hz, 4H, Ar-H), 8.24-8.20 (dd, ^3J 8.64 Hz, 2H, Ar-H), 7.78 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.61 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.34 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.29 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.29-7.24 (m, 4H, Ar-H), 7.22 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.70 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.69-1.67 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.37-1.30 (m, 36H, 2×(-CH_2-$)_9$), 0.91 (t, ^3J 6.84 Hz, 6H, 2×- CH_3); $C_{70}H_{75}ClF_2O_8$ requires C 75.22, H 6.76; found C 75.35, H 6.80 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-tetradecylbiphenyl-4′-carbonyloxy)-2-fluorobenzoate], 2.A.9

Yield 71%, m. p. 170.5˚C. ν_{max}: 2954, 2920, 2848, 1745, 1743, 1728, 1616, 1606, 1589, 1498, 1467, 1436, 1421, 1282, 1251, 1141 cm^{-1}; δ_H: 8.27 (d, ^3J 8.44 Hz, 4H, Ar-H), 8.24-8.20 (dd, ^3J 8.64 Hz, 2H, Ar-H), 7.78 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.61 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.34 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.29 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.29-7.24 (m, 4H, Ar-H), 7.22 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.70 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.69-1.67 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.37-1.29 (m, 44H, 2×$(-CH_2-)_{11}$), 0.91 (t, ^3J 6.84 Hz, 6H, 2×- CH_3); $C_{74}H_{83}ClF_2O_8$ requires C 75.7, H 7.13; found C 75.33, H 6.85 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-hexadecylbiphenyl-4′-carbonyloxy)-2-fluorobenzoate], 2.A.10

Yield 74%, m. p. 157.5˚C. ν_{max}: 2954, 2918, 2846, 1759, 1745, 1728, 1595, 1469, 1282, 1253, 1141, 1060 cm^{-1}; δ_H: 8.27 (d, ^3J 8.44 Hz, 4H, Ar-H), 8.24-8.20 (dd, ^3J 8.64 Hz, 2H, Ar-H), 7.78 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.61 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.34 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.29 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.29-7.24 (m, 4H, Ar-H), 7.22 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.70 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.69-1.67 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.37-1.29 (m, 52H, 2×$(-CH_2-)_{13}$), 0.91 (t, ^3J 6.84 Hz, 6H, 2×- CH_3); $C_{78}H_{91}ClF_2O_8$ requires C 76.17, H 7.46; found C 75.96, H 7.09 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-octadecylbiphenyl-4′-carbonyloxy)-2-fluorobenzoate], 2.A.11

Yield 75%, m. p. 157˚C. ν_{max}: 2952, 2918, 2848, 1748, 1732, 1730, 1728, 1595, 1606, 1276, 1251 cm^{-1}; δ_H: 8.27 (d, ^3J 8.44 Hz, 4H, Ar-H), 8.24-8.20 (dd, ^3J 8.64 Hz, 2H, Ar-H), 7.78 (d, ^3J 8.48 Hz, 4H, Ar-H), 7.61 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.34 (d, ^3J 8.16 Hz, 4H, Ar-H), 7.29 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.29-7.24 (m, 4H, Ar-H), 7.22 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.70 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.69-1.67 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.37-1.29 (m, 60H, 2×$(-CH_2-)_{15}$), 0.91 (t, ^3J 6.84 Hz, 6H, 2×- CH_3); $C_{82}H_{99}ClF_2O_8$ requires C 76.58, H 7.76; found C 76.40, H 7.53 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-pentylbiphenyl-4′-carbonyloxy)-3-fluorobenzoate], 2.B.1

Yield 80%, m. p. 161˚C. ν_{max}: 2927, 2956, 2856, 1741, 1739, 1602, 1506, 1427, 1255, 1172, 1055 cm^{-1}; δ_H: 8.27 (d, ^3J 8.36 Hz, 4H, Ar-H), 8.08-8.03 (m, 4H, Ar-H), 7.75 (d, ^3J 8.36 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.31 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.25 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.16 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.67 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.71-1.66 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.37-1.29 (m, 8H, 2×(-CH_2-)$_2$), 0.92 (t, ^3J 6.56 Hz, 6H, 2×-CH_3); δ_C: 163.5, 162.8, 155.5, 152.9, 151.5, 147.0, 143.7, 137.0, 135.3, 131.0, 129.2, 127.9, 127.2, 127.0, 126.5, 124.5, 120.0, 119.0, 118.7, 114.3, 35.7, 31.6, 31.1, 22.6. 14.0; $C_{56}H_{47}ClF_2O_8$ requires C 73.0, H 5.14; found C 73.06, H 4.73 %.

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

Yield 82%, m. p. 144.5˚C. ν_{max}: 2956, 2923, 2854, 1743, 1741, 1598, 1508, 1429, 1398, 1290, 1257, 1172, 1130, 1110, 1055 cm^{-1}; δ_H: 8.27 (d, ^3J 8.36 Hz, 4H, Ar-H), 8.08-8.03 (m, 4H, Ar-H), 7.75 (d, ^3J 8.36 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.31 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.25 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.16 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.67 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.70-1.62 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.37-1.32 (m, 12H, 2×(- CH_2-)$_3$), 0.90 (t, ^3J 6.56 Hz, 6H, 2×-CH_3); $C_{58}H_{51}ClF_2O_8$ requires C 73.3, H 5.4; found C 73.27, H 5.04 %.

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

Yield 79%, m. p. 155˚C. ν_{max}: 2952, 2925, 2854, 1743, 1598, 1508, 1425, 1292, 1172 cm^{-1}; δ_H: 8.27 (d, ^3J 8.36 Hz, 4H, Ar-H), 8.08-8.03 (m, 4H, Ar-H), 7.75 (d, ^3J 8.36 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.31 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.25 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.16 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.67 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.68-1.63 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.36-1.30 (m, 16H, 2×(- CH_2-)$_4$), 0.89 (t, ^3J 6.56 Hz, 6H, 2×-CH_3); $C_{60}H_{55}ClF_2O_8$ requires C 73.7, H 5.67; found C 73.96, H 5.46 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-octylbiphenyl-4′-carbonyloxy)-3-fluorobenzoate],

2.B.4

Yield 75%, m. p. 154.8˚C. ν_{max}: 2956, 2925, 2854, 1745, 1743, 1741, 1596, 1508, 1425, 1290, 1257, 1172, 1110, 1053 cm^{-1}; δ_H: 8.27 (d, ^3J 8.36 Hz, 4H, Ar-H), 8.08-8.03 (m, 4H, Ar-H), 7.75 (d, ^3J 8.36 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.31 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.25 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.16 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.67 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH$_2$-), 1.68-1.63 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.35-1.26 (m, 20H, 2× (- CH$_2$-)$_5$), 0.89 (t, ^3J 6.56 Hz, 6H, 2×-CH$_3$); $C_{62}H_{59}ClF_2O_8$ requires C 74.05, H 5.91; found C 74.18, H 5.62 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-nonylbiphenyl-4′-carbonyloxy)-3-fluorobenzoate],

2.B.5

Yield 80%, m. p. 158.5˚C. ν_{max}: 2925, 2854, 1745, 1743, 1596, 1508, 1425, 1290, 1257, 1172, 1110, 1053 cm^{-1}; δ_H: 8.27 (d, ^3J 8.36 Hz, 4H, Ar-H), 8.08-8.03 (m, 4H, Ar-H), 7.75 (d, ^3J 8.36 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.31 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.25 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.16 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.67 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH$_2$-), 1.68-1.63 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.35-1.04 (m, 24H, 2×(- CH$_2$-)$_6$), 0.88 (t, ^3J 6.56 Hz, 6H, 2×-CH$_3$); $C_{64}H_{63}ClF_2O_8$ requires C 74.37, H 6.14; found C 74.34, H 5.86 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-decylbiphenyl-4′-carbonyloxy)-3-fluorobenzoate],

2.B.6

Yield 76%, m. p. 137.5˚C. ν_{max}: 2956, 2920, 2848, 1745, 1739, 1596, 1429, 1292, 1276, 1176, 1060 cm^{-1}; δ_H: 8.27 (d, ^3J 8.36 Hz, 4H, Ar-H), 8.08-8.03 (m, 4H, Ar-H), 7.75 (d, ^3J 8.36 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.31 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.25 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.16 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.67 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH$_2$-), 1.68-1.63 (quin, 4H, 2×Ar-CH$_2$-$\underline{CH_2}$-), 1.35-1.27 (m, 28H, 2×(-CH$_2$-)$_7$), 0.88 (t, ^3J 6.56 Hz, 6H, 2×-CH$_3$); $C_{66}H_{67}ClF_2O_8$ requires C 74.67, H 6.36; found C 74.60, H 6.13 %.

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

2.B.7

Yield 79%, m. p. 141˚C. ν_{max}: 2954, 2920, 2848, 1745, 1739, 1735, 1610, 1596, 1508, 1429, 1292, 1276, 1176, 1122, 1060 cm^{-1}; δ_H: 8.27 (d, ^3J 8.36 Hz, 4H, Ar-H), 8.08-8.03 (m, 4H, Ar-

H), 7.75 (d, ^3J 8.36 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.31 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.25 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.16 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.67 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.68-1.63 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.34-1.27 (m, 32H, 2×(- CH_2-)$_8$), 0.88 (t, ^3J 6.56 Hz, 6H, 2×-CH_3); $C_{68}H_{71}ClF_2O_8$ requires C 74.95, H 6.57; found C 75.18, H 6.30 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-dodecylbiphenyl-4′-carbonyloxy)-3-fluorobenzoate], 2.B.8

Yield 82%, m. p. 144.5˚C. ν_{max}: 2956, 2918, 1745, 1739, 1735, 1598, 1506, 1431, 1292, 1276, 1176, 1060, 920 cm^{-1}; δ_H: 8.27 (d, ^3J 8.36 Hz, 4H, Ar-H), 8.08-8.03 (m, 4H, Ar-H), 7.75 (d, ^3J 8.36 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.31 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.25 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.16 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.67 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.68-1.63 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.34-1.27 (m, 36H, 2×(- CH_2-)$_9$), 0.88 (t, ^3J 6.56 Hz, 6H, 2×-CH_3); $C_{70}H_{75}ClF_2O_8$ requires C 75.2, H 6.76; found C 75.14, H 6.42 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-tetradecylbiphenyl-4′-carbonyloxy)-3-fluorobenzoate], 2.B.9

Yield 78%, m. p. 136.5˚C. ν_{max}: 2954, 2918, 2848, 1745, 1739, 1735, 1598, 1506, 1469, 1431, 1292, 1276, 1218, 1176, 1136, 1062, 920 cm^{-1}; δ_H: 8.27 (d, ^3J 8.36 Hz, 4H, Ar-H), 8.08-8.03 (m, 4H, Ar-H), 7.75 (d, ^3J 8.36 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.31 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.25 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.16 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.67 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.68-1.63 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.35-1.12 (m, 44H, 2×(- CH_2-)$_{11}$), 0.88 (t, ^3J 6.56 Hz, 6H, 2×-CH_3); δ_C: 163.5, 162.8, 153.0, 151.5, 147.0, 143.7, 137.0, 131.0, 129.2, 127.8, 127.2, 127.0, 126.5, 124.5, 120.2, 119.0, 118.7, 114.3, 35.7, 31.9, 31.5, 29.7, 29.5, 29.4, 22.7, 14.1; $C_{74}H_{83}ClF_2O_8$ requires C 75.7, H 7.13; found C 75.53, H 7.2 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-hexadecylbiphenyl-4′-carbonyloxy)-3-fluorobenzoate], 2.B.10

Yield 81%, m. p. 135.5˚C. ν_{max}: 2956, 2918, 1745, 1739, 1735, 1610, 1598, 1431, 1292, 1276, 1176, 1136, 1124, 1062 cm^{-1}; δ_H: 8.27 (d, ^3J 8.36 Hz, 4H, Ar-H), 8.08-8.03 (m, 4H, Ar-H), 7.75 (d, ^3J 8.36 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.31

(d, ^3J 8.08 Hz, 4H, Ar-H), 7.25 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.16 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.67 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.68-1.63 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.34-1.26 (m, 52H, 2×(- CH_2-)$_{13}$), 0.88 (t, ^3J 6.56 Hz, 6H, 2×-CH_3); $C_{78}H_{91}ClF_2O_8$ requires C 76.17, H 7.46; found C 75.82, H 7.45 %.

5-Chloro-1, 3-phenylene bis [4-(4-*n*-octadecylbiphenyl-4′-carbonyloxy)-3-fluoro-benzoate], 2.B.11

Yield 80%, m. p. 135˚C. ν_{max}: 2954, 2912, 2848, 1745, 1739, 1735, 1598, 1508, 1431, 1292, 1276, 1176, 1136, 1122, 1060 cm^{-1}; δ_H: 8.27 (d, ^3J 8.36 Hz, 4H, Ar-H), 8.08-8.03 (m, 4H, Ar-H), 7.75 (d, ^3J 8.36 Hz, 4H, Ar-H), 7.59 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.31 (d, ^3J 8.08 Hz, 4H, Ar-H), 7.25 (d, ^4J 2.04 Hz, 2H, Ar-H), 7.16 (t, ^4J 2.04 Hz, 1H, Ar-H), 2.67 (t, ^3J 7.7 Hz, 4H, 2×Ar-CH_2-), 1.68-1.63 (quin, 4H, 2×Ar-CH_2-$\underline{CH_2}$-), 1.34-1.26 (m, 60H, 2×(- CH_2-)$_{15}$), 0.88 (t, ^3J 6.56 Hz, 6H, 2×-CH_3); δ_C: 163.6, 162.8, 153.0, 151.5, 147.0, 143.7, 137.0, 131.0, 129.2, 127.8, 127.2, 126.9, 126.5, 124.5, 120.2, 118.9, 118.7, 114.3, 35.7, 32.0, 31.5, 29.7, 29.5, 29.4, 22.7, 14.1; $C_{82}H_{99}ClF_2O_8$ requires C 76.58, H 7.75; found C 76.38, H 7.45 %.

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