Chapter 4

Synthesis and mesomorphic properties of

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

Series- 4.1

(ii) **4-Chlorophenyl-4-[3-{4-(4-*n*-alkoxybenzoyloxy)benzoyloxy}benzoyloxy] benzoates]**

Series- 4.11

(iii) **4-Chlorophenyl-4-[3-{4-(3-fluoro-4-*n*-octadecyloxybenzoyloxy)benzoyloxy} benzoyloxy]benzoate]**

Compound- 4.C.1

(iv) **4-Chlorophenyl-4-[3-{4-(4-*n*-decylbiphenylcarbonyloxy)benzoyloxy} benzoyloxy]benzoate]**

Compound- 4.D.1

(v) **4-Trifluoromethylphenyl-4-[3-{4-(4-*n*-alkoxybenzoyloxy)benzoyloxy} benzoyloxy]benzoates]**

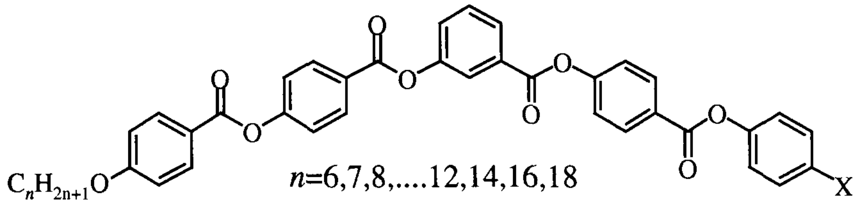
Series- 4.111

Introduction

Pattern formation in liquid crystals is a subject of considerable importance. The occurrence of filamentary growth patterns at the isotropic to the smectic A phase transition in calamitic liquid crystals is not new and has been seen in a number of different mixtures as well as in pure mesogenic materials [79]. One of the pure compounds which was examined in detail by Palffy-Muhoray ***et*** *al.* [80] is 4′-decyloxyphenyl-4-(4-cyano-4-oxybiphenyl) butanoate which showed filaments when the isotropic phase was cooled slowly to the smectic A phase. The growth of such long cylindrical structures in smectic A liquid crystal has been attributed to the negative interfacial tension anisotropy [79, 80]. Such filamentary growth patterns have also been observed in smectic C liquid crystal exhibited by some binary mixtures [81].

Since the discovery [15] of electro-optical switching in an achiral compound composed of banana-shaped molecules, several hundred compounds with bent molecular structure and exhibiting mesophases have been reported [15, 20, 28, 29, 32, 41, 53, 73] and most of these are symmetrical systems about the central phenyl ring. However, unsymmetrical bent-core mesogens are also known, but are very few in number, [28, 47, 75-77]. Normally, banana-shaped mesogens contain two terminal chains and systems containing only one chain and some other substituent at the second terminal position have not been explored thoroughly. Terminally cyano substituted derivatives have been reported [75-77] to exhibit uniaxial as well as polar biaxial smectic A phases. A cyano group has a large dipole moment and hence it was envisaged to explore the mesomorphic properties of bent-core compounds with terminal groups having smaller dipole moment.

In this chapter, the synthesis and mesomorphic behaviour of several unsymmetrical bent-core compounds containing only one terminal chain has been described. The compounds investigated here are derived from 3-hydroxybenzoic acid. The unsymmetrically substituted bent-core compounds studied here contain a fluoro, a chloro, or a trifluoromethyl group at the other terminal position. The terminally chloro substituted compounds show filamentary growth patterns at the isotropic phase to the mesophase transition. All the unsymmetrical bent-core compounds described here are esters having the general molecular structure 4.



n=6,7,8,....12,14,16,18

X= F, Series- **4.1**

X= Cl, Series- **4.11**

X= CF,, Series- **4.III**

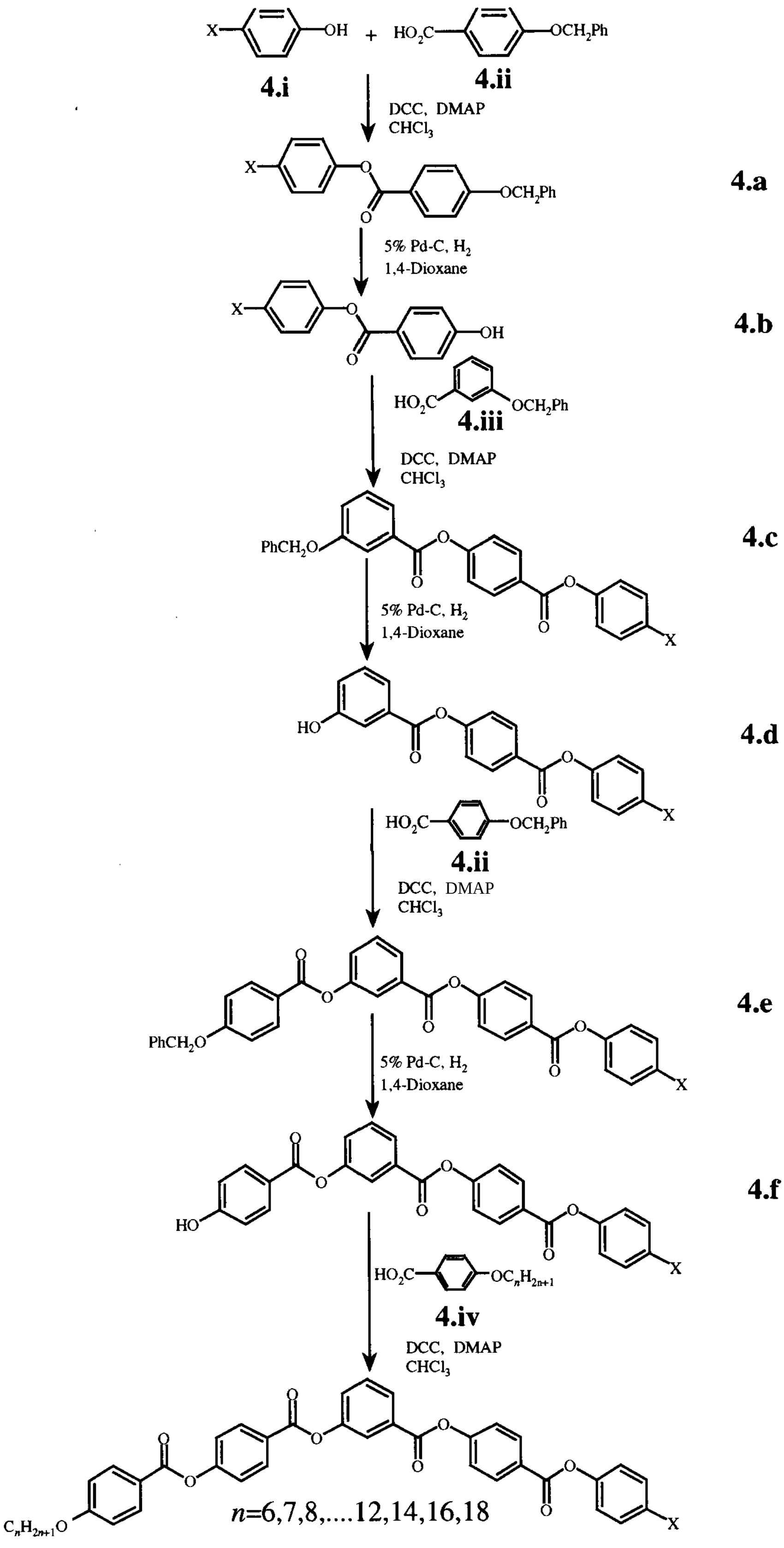
Structure 4

Synthesis

The synthetic route employed to prepare the unsymmetrical bent-core compounds, which belong to three series viz, **4.I-4.III** is shown in scheme **4.1.** The preparation of 4-benzyloxybenzoic acid has already been described in Chapter 2 and 3-benzyloxybenzoic acid was prepared following a similar procedure using 3-hydroxybenzoic acid as starting material. 4-Fluorophenol, 4-chlorophenol, and 4-trifluoromethylphenol were commercial compounds and used without further purification.

Results and discussion

The transition temperatures and the associated enthalpy values for three compounds containing a terminal fluoro substituent are summarized in table **4.1.** Since compounds **4.A.1** and **4.A.2** with n-tetradecyloxy- and n-hexadecyloxy- terminal chains respectively were monotropic mesomorphic, the lower homologues were not prepared. However, compound **4.A.3** is enantiotropic with a thermal range of 5°C for the mesophase. When a thin film of the isotropic phase of this compound was cooled and observed under a polarizing microscope, focal-conic texture normally seen for a smectic phase was obtained. A typical focal-conic texture obtained for compound **4.A.3** is shown in figure **4.1.** However, when the same sample was sandwiched between two glass slides which were treated for a homeotropic alignment of the sample, a schlieren texture was obtained, thus eliminating the possibility of the mesophase being a smectic A phase. Interestingly, the schlieren texture shows defects of strength ±1/2, ±1, ±3/2 etc.



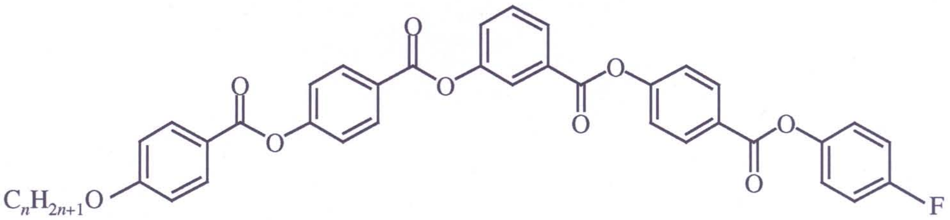
X= F,	Series- 4.I
X= Cl,	Series- 4.II
X= CF_3	Series- 4.III

Structure 4

Scheme 4.1: Synthetic route used to prepare the unsymmetrical bent-core compounds.

The two-brush defect is a characteristic feature of an antiferroelectric ordering in the smectic phase [78]. An optical photomicrograph showing these defects is shown in figure **4.2.** The two-brush defects are dispirations, which are defect patterns in the in-plane director and screw dislocations [78, 82].

Table 4.1. Transition temperatures (°C) and the associated enthalpies (kJ mol^{-1}) for compounds of series 4.I



Compound	n	Cr		SmCP$_A$		I
4.A.1	14	.	125.5^a *87.6*	(.	122.0) *12.6*	.
4.A.2	16	.	125.0^a *99.6*	(.	124.5) *13.1*	.
4.A.3	18	.	122.0^a *89.8*	.	127.0 *13.3*	.

Key: Cr: crystalline phase; SmCP$_A$: polar antiferroelectric smectic C phase; I: isotropic phase; ( ): indicates monotropic mesophase; a: compound has crystal-crystal transition; enthalpy denoted is the sum of all previous transitions.

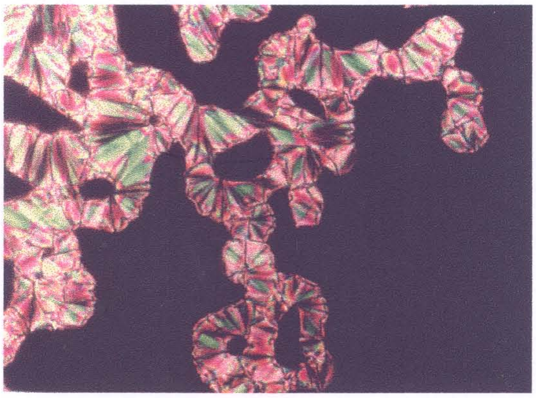


Figure 4.1: An optical photomicrograph of SmCP$_A$ phase growing from isotropic phase of compound 4.A.3.

Figure 4.2: An optical photomicrograph of the schlieren texture of $SmCP_A$ phase exhibited by compound 4.A.3.

The XRD studies on non-oriented samples were carried out to confirm the mesophase structure. Compound **4.A.3** gave two reflections in the small angle region, which are in the ratio of **1:1/2,** clearly indicating a lamellar ordering for the mesophase. The first order layer reflection is less than the full molecular length, which was measured by assuming the methylene units of n-alkoxy chain in a fully extended all trans conformation. The wide-angle diffuse peak at 4.6Å confirms the fluidity of the sample. The obtained d values for compound **4.A.3** are given **in** table **4.5.**

To examine the effect of an electric field on this mesophase, the standard **triangular**-wave method was employed. Compound **4.A.3** was taken **in** a cell treated for homogeneous alignment of the sample and having a thickness of **15.4µm.** The sample was cooled from the isotropic phase under a triangular-wave electric field. At a threshold of **$250V_{pp}$** at **430Hz,** two polarization current peaks were obtained indicating an **antiferroelectric** ground state for the mesophase. A switching current response obtained for compound **4.A.3** is shown in figure **4.3.** Interestingly when the mesophase was observed under a polarizing microscope the orientation of the brushes of the circular domains were unaltered both with and without the triangular-wave electric field.

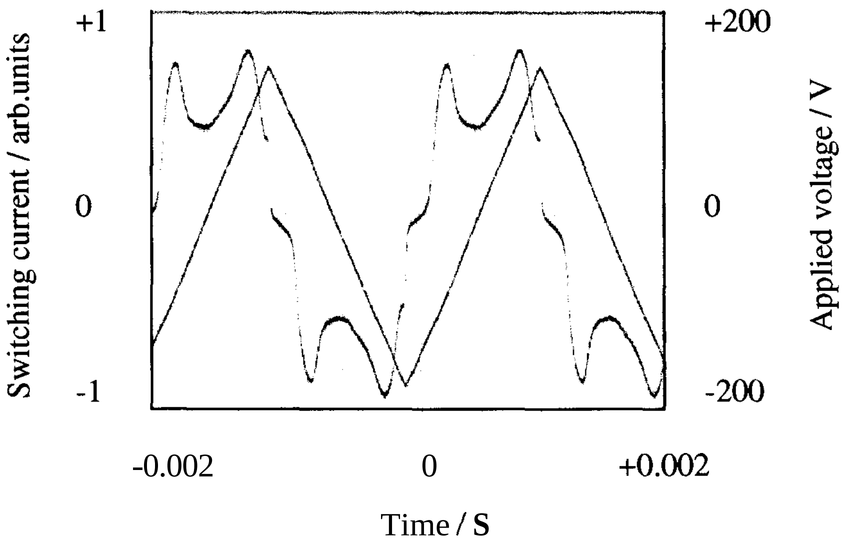


Figure 4.3: The switching current response trace obtained for the mesophase of compound 4.A.3 by applying a triangular-wave electric field (320 V_{pp}) at 450Hz; cell thickness 15.4μm; saturated polarization ≈ 115 nC cm^{-2}.

The transition temperatures and the associated enthalpy values obtained for compounds of series **4.11**, which contain a chloro terminal substituent are summarized in table **4.2.** Compound **4.B.1** is non-mesomorphic, compounds **4.B.2** and **4.B.3** are monotropic mesomorphic and the remaining are enantiotropic and all these compounds show the same type of mesophase. As a result of chloro substitution, a marginal increase in the melting points and large increase in the clearing points have been obtained (compare compounds **4.A.1-4.A.3** with compounds **4.B.7-4.B.9).**

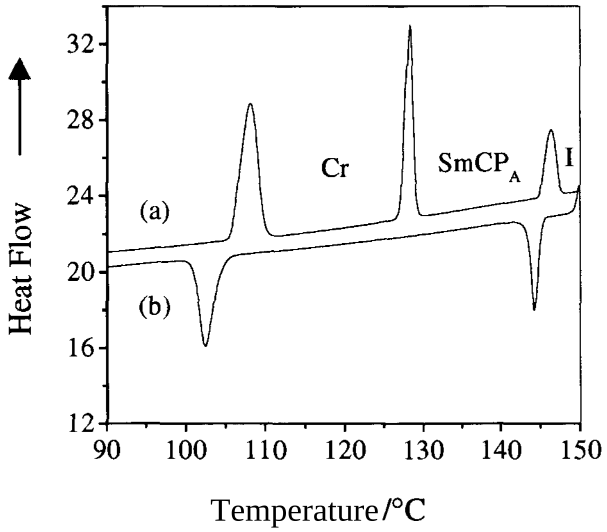
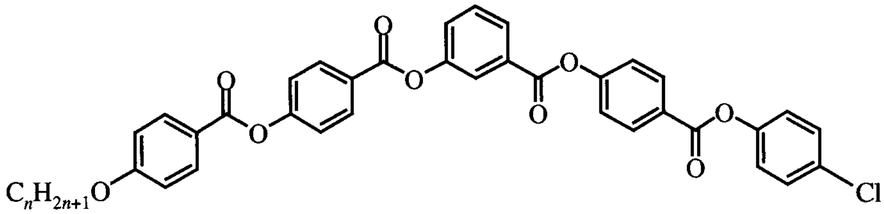


Figure 4.4: A DSC **thermogram obtained for compound 4.B.8; (a) heating cycle; (b) cooling cycle; rate 5°C min^{-1}.**

The melting enthalpy is fairly high and is in the range of 60-90 kJ mol^{-1}, while the clearing enthalpy value obtained is similar to those obtained for smectic phases of bent-core compounds and is in the range of 12-15 kJ mol^{-1}. A DSC thermogram obtained for compound **4.B.8** is shown in figure **4.4.**

Table 4.2: Transition temperatures (°C) and the associated enthalpies (kJ mol^{-1}) for compounds of series 4.11



Compound	n	Cr		SmCP$_A$		I
4.B.1	6	•	147.0^{a} *59.9*	-		•
4.B.2	8	•	139.0^{a} *62.1*	(•	132.0) *12.2*	•
4.B.3	9	•	137.0^{a} *74.1*	(•	135.0) *12.9*	•
4.B.4	10	•	133.0^{a} *58.0*	•	138.0 *13.5*	•
4.B.5	11	•	129.0^{a} *67.4*	•	140.0 *14.3*	•
4.B.6	12	•	128.5^{a} *65.8*	•	141.5 *14.6*	•
4.B.7	14	•	130.0^{a} *70.3*	•	144.5 *15.0*	•
4.B.8	16	•	127.0^{a} *82.2*	•	145.0 *15.4*	•
4.B.9	18	•	126.0^{a} *88.4*	•	146.0 *15.3*	•

An interesting feature of the mesophase of these compounds is the way they grow from the isotropic phase. For example, when a thin a film of a sample of compound **4.B.8** was cooled very slowly from the isotropic phase, filaments start to develop and grow in size. Sometimes the fully developed filaments curl up to form a texture, which looks, like a bird's nest. The growth of these filaments at different intervals of time is shown as photomicrographs in figure **4.5 (a-e).**

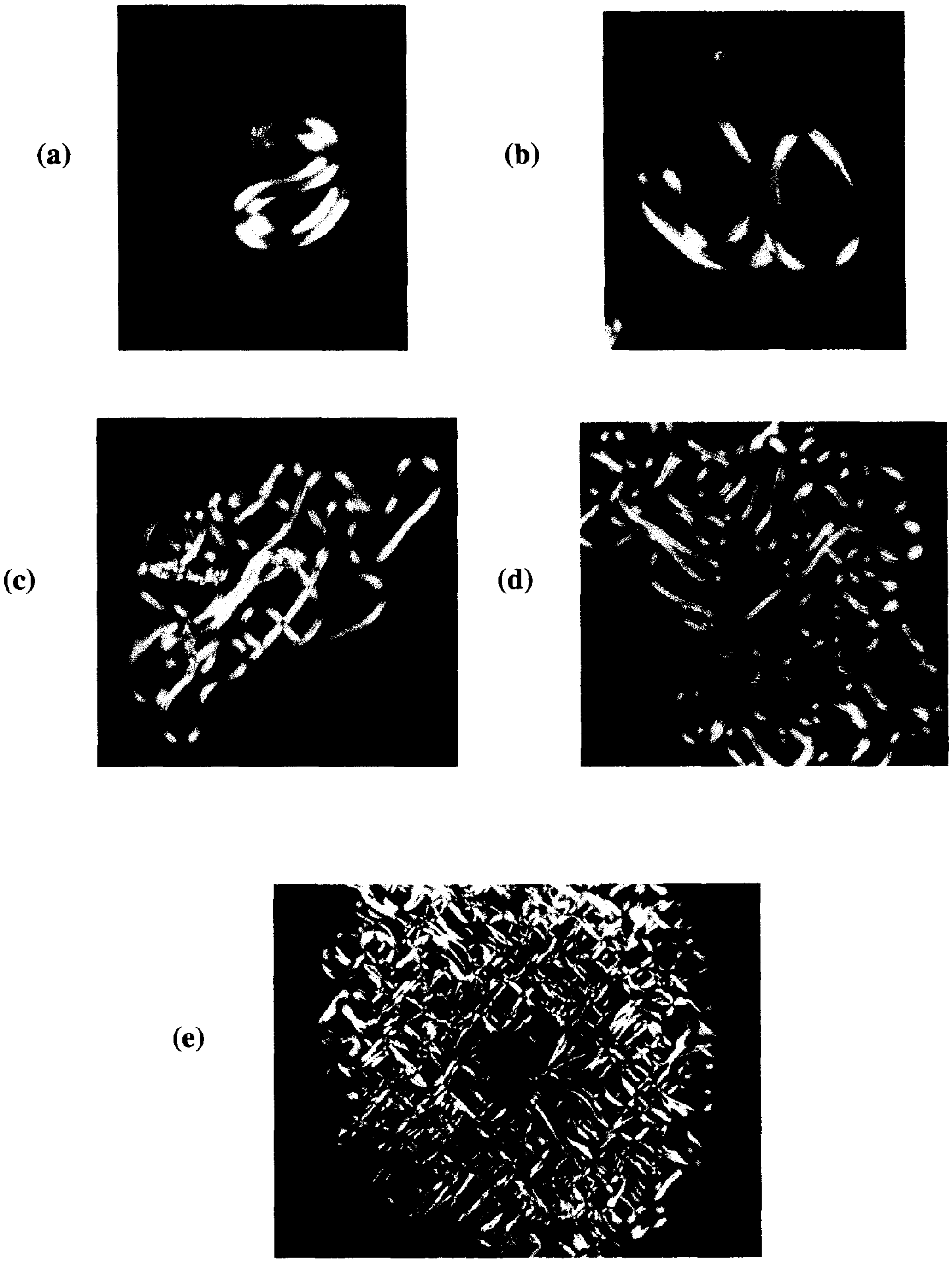


Figure 4.5 (a-e): Stepwise growth of filamentary textures on cooling the isotropic phase of compound 4.B.8.

These filaments are unstable and collapse to form a focal-conic texture. The stability of the filaments appears to increase with increase in the length of the *n*-alkoxy chain. Photomicrographs of the partial collapse of the filaments exhibited by compound **4.B.8** are shown in figure **4.6 (a)** and **(b).**

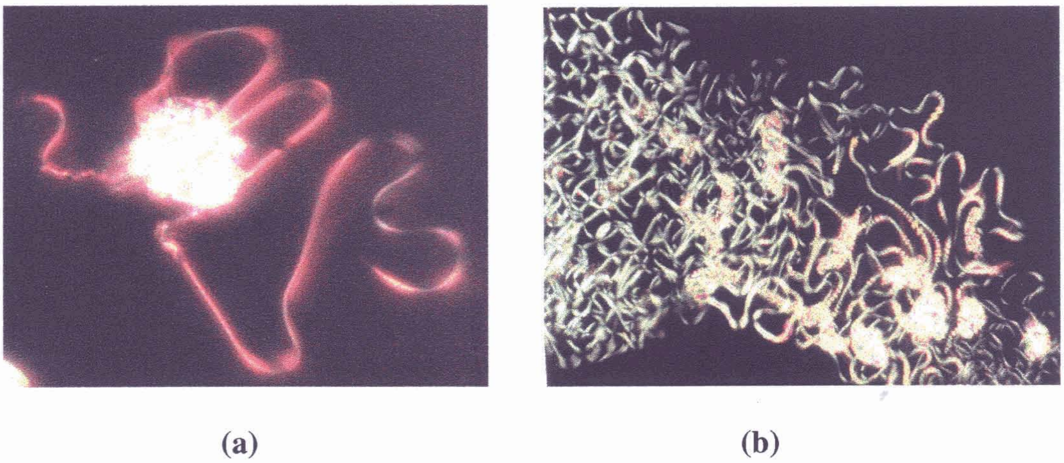

(a) (b)

Figure 4.6(a) and (b): Optical photomicrographs showing the collapse of the filaments exhibited by compound 4.B.8.

Depending on the rate of cooling and type of cell used, fan-shaped texture with irregularly spaced concentric arcs or schlieren texture with multiple defects were obtained. A typical fan-shaped texture obtained for compound **4.B.8** is shown in figure **4.7** and the schlieren textures are shown in figure **4.8 (a)** and **(b).** As we shall see later, the mesophase exhibited by all these compounds were characterized as a polar smectic C ($SmCP_A$) phase with antiferroelectric properties.

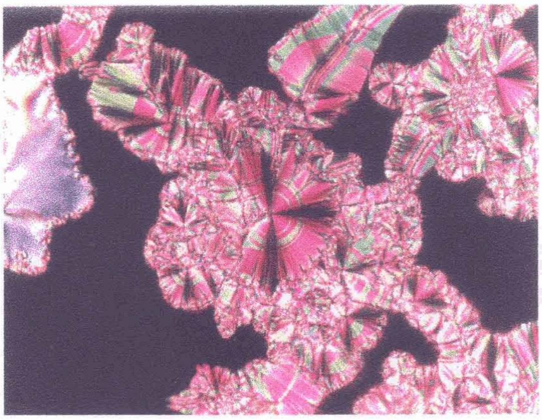


Figure 4.7: An optical photomicrograph of the fan-shaped texture obtained for compound 4.B.8.

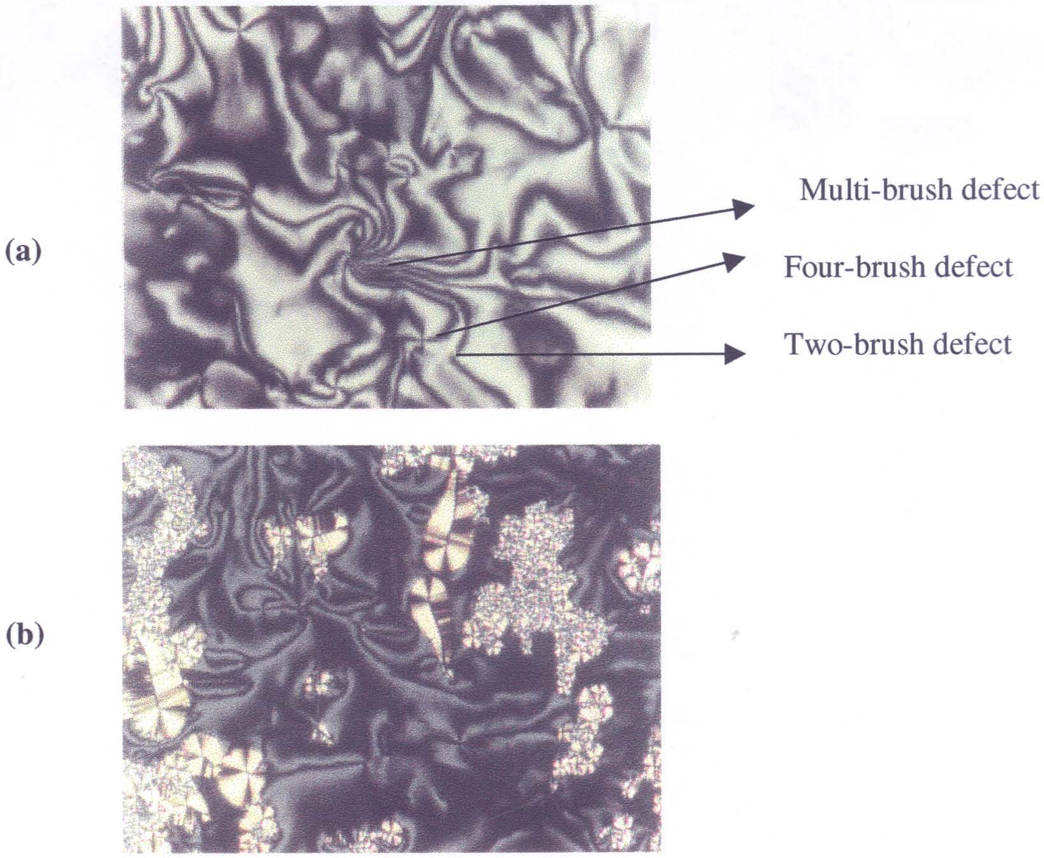


Figure 4.8 (a) and (b): Optical photomicrographs of schlieren texture obtained in a homeotropically aligned cell of a sample of compound 4.B.8.

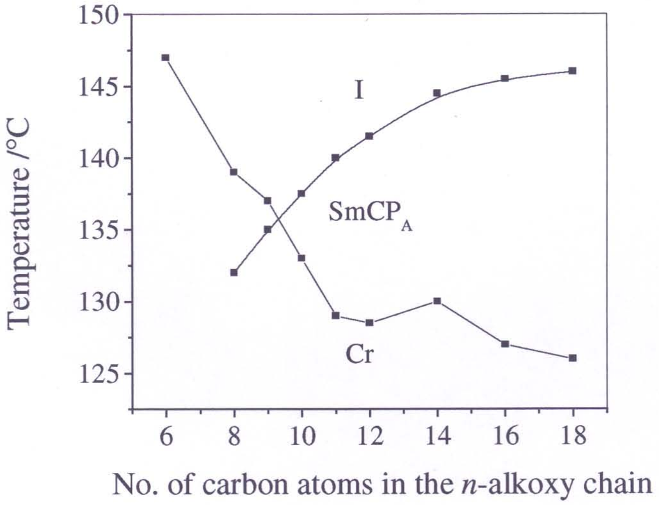
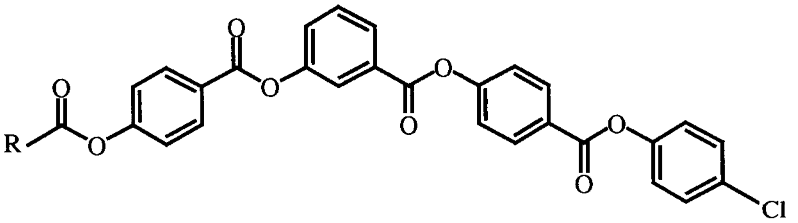


Figure 4.9: A Plot of transition temperatures as a function of the number of carbon atoms in the *n*-alkoxy chain for the compounds of series 4.II.

A plot of the transition temperatures as a function of the n-alkoxy chain length for the compounds of series 4.11 is shown in figure 4.9. It can be seen that the clearing temperature rises initially and then almost levels off on increasing the chain length.

By introducing a fluorine substituent *ortho* to the terminal n-octadecyloxy chain of compound 4.B.9, compound 4.C.1 was obtained which showed the $SmCP_A$ phase with a 23°C thermal range. However, when the terminal n-octadecyloxyphenyl group was replaced by 4-*n*-decylbiphenyl moiety (compound **4.D.1**), the melting point increased by 26°C while the clearing temperature went up by 51°C, and the same mesophase was retained with a wider thermal range. The transition temperatures and the associated enthalpies for these two compounds are shown in table 4.3.

Table 4.3: Transition temperatures (°C) and the associated enthalpies (kJ mol^{-1}) for compounds of



R	Compound	Cr		$SmCP_A$		I
3-Fluoro-4-*n*-octadecyloxyphenyl	**4.C.1**	•	125.0^a *70.3*	•	148.0 *15.8*	•
4-*n*-Decylbiphenyl	**4.D.1**	•	152.0^a *91.0*	•	197.0 *15.0*	•

The mesophase structure was confirmed by carrying out XRD studies on non-oriented samples. A sample of an appropriate compound was heated to the isotropic phase and after drawing this liquid into a Lindemann capillary, the ends were sealed. The d-value of reflections obtained in the small angle region clearly indicates lamellar ordering for the mesophase. The first order layer reflection was less than the full molecular length in each case, which was measured by assuming the methylene units of the n-alkoxy chain in a fully extended all trans conformation. The calculated tilt angle was of the order of 25-30". The higher order reflections (up to 4 reflections) clearly indicate the formation of a well-defined layer structure for the mesophase. The wide-angle diffuse peak at 4.6 Å observed in all the compounds is indicative of the absence of in-plane periodicity. The layer spacing remained constant throughout the mesophase range of the compounds. The layer spacings obtained for different compounds are given in table **4.5.** The X-ray angular intensity profile obtained for compound **4.B.8** showing four orders of smectic reflections is shown in figure **4.10.** Thus, from XRD studies, the mesophase under investigation can be concluded as a tilted smectic phase.

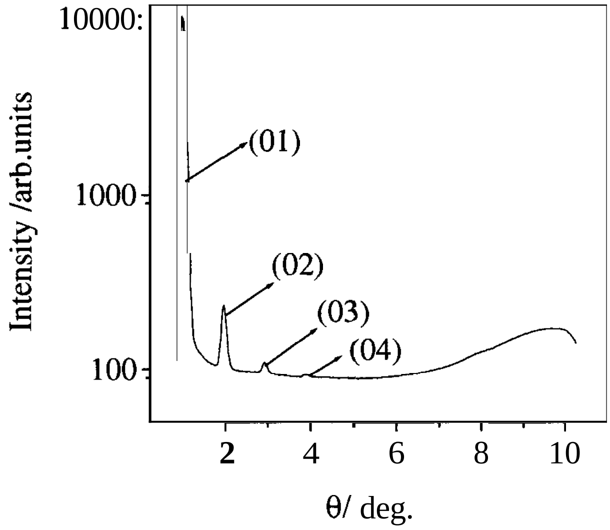


Figure 4.10: An X-ray angular intensity profile obtained for the SmCP$_A$ phase of compound 4.B.8.

The electro-optical switching behaviour of the mesophase of the compounds was carried out by the standard triangular-wave method. Compound **4.B.8,** was taken in a ITO coated cell of uniform thickness of 9.6μm, the inner surfaces of which were treated for homogeneous alignment of the sample. The sample was cooled slowly from the isotropic phase under a triangular-wave electric field. At a threshold of 110V$_{pp}$ and frequency of 200 Hz, two polarization current peaks per half cycle was observed indicating an antiferroelectric ground state for the mesophase. The switching current response obtained for this compound is shown in figure **4.11.** The saturated polarization value obtained by integrating the area under the two current peaks is about 125 nC cm^{-2}. The dark brushes of circular domains of the mesophase orient parallel to the polarizer or analyzer when they are crossed, under an external electric field. However, on switching off the electric field there was no change in the orientation of the brushes. Nevertheless the irregular stripes on the domains were observed on switching off the electric field and also one could see a colour change of the circular domains. However, the two polarization current peaks per half cycle clearly indicate the antiferroelectric nature of the mesophase. The optical features obtained for the mesophase of compound **4.B.8** under a triangular-wave electric field and without field are shown in figure **4.12 (a)** and **(b)** respectively. Thus, from XRD data and electro-optical studies, it can concluded that the mesophase is a polar smectic C phase with antiferroelectric characteristics viz. $SmCP_A$ phase.

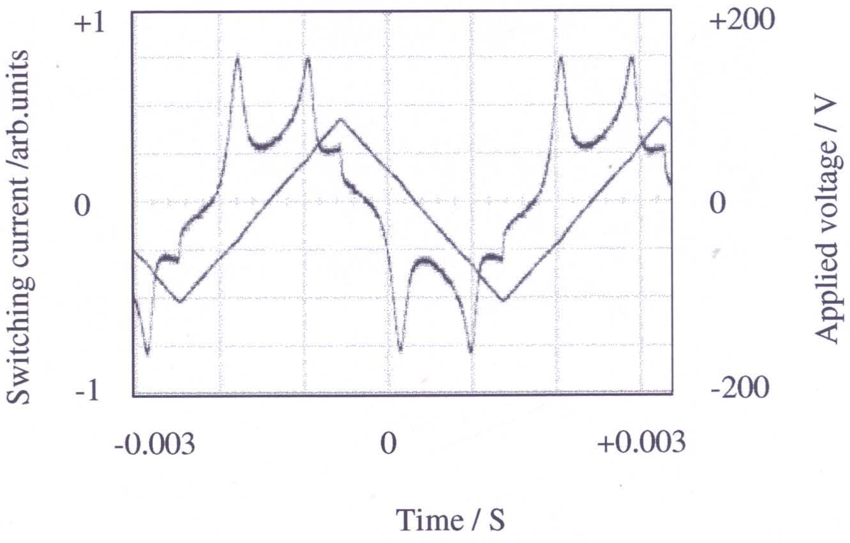
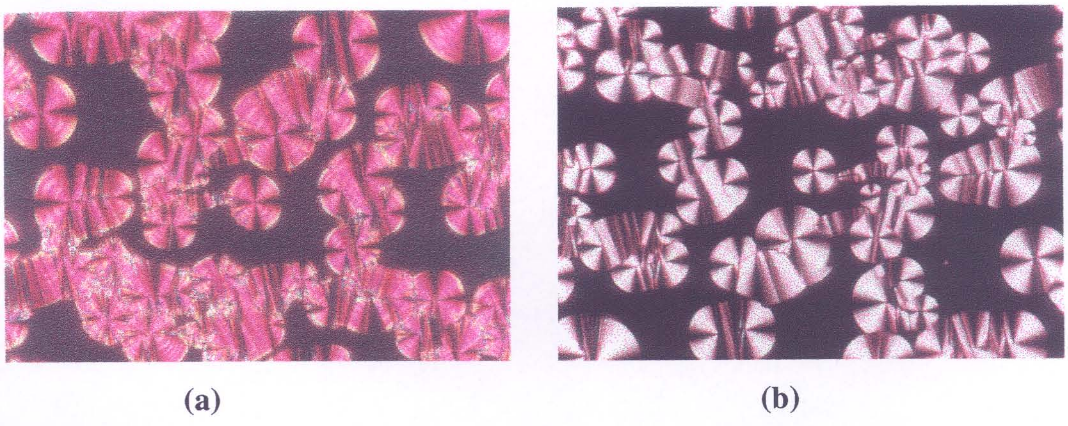


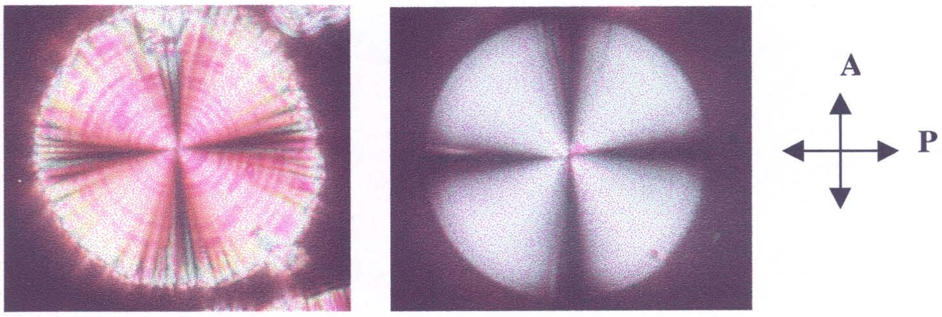
Figure 4.11: The switching current response trace obtained for the mesophase of compound 4.B.8 by applying a triangular-wave electric field (190 V_{pp}) at 250Hz; cell thickness 9.6μm; saturated polarization ≈ 125 nC cm^{-2}.



(a) **(b)**

Figure 4.12: Optical photomicrographs (a) without triangular-wave electric field, (b) with triangular-wave electric field; temperature 143.0°C; compound 4.B.8.

The optical features observed are the same even under a dc electric field. For example, compound **4.C.1** was taken in a cell of 9.3μm, treated for homogeneous alignment of a sample. On applying a voltage of $4V\mu m^{-1}$, smooth circular domains with brushes parallel to optic axes were obtained. However, on switching off the field, no change in the orientation of the brushes could be seen, but irregular concentric stripes appeared on the domains. One could also see a sharp change in the colour of the domains. These optical features are exemplified in figure **4.13 (a)** and **(b)**.

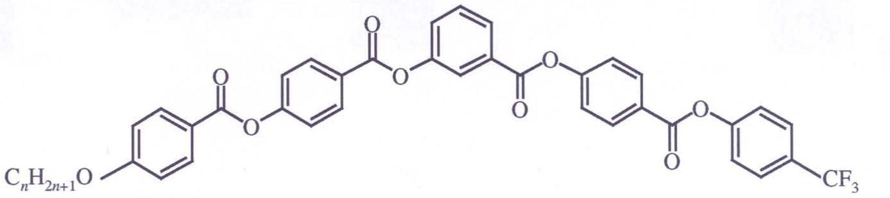


(a) **(b)**

Figure 4.13: Optical photomicrographs (a) without dc electric field, (b) with dc electric field, $4V\mu m^{-1}$; temperature 143.0°C; compound 4.C.1.

Four compounds having a terminal trifluoromethyl group were synthesized and their mesomorphic behaviour observed are as follows. The dipole moment of this group is almost half that of the cyano group. The transition temperatures and the associated enthalpy values for these four compounds **4.E.1-4.E.4** are summarized in table **4.4**. Although the melting points are higher as compared to the analogous chloro substituted compounds, all are enantiotropic mesomorphic with a thermal range for the mesophase slightly shorter. The filamentary textures were seen in these compounds also, but they were extremely short lived. The mesophase of these compounds do exhibit schlieren texture with both two- and four-brush strength defects but predominantly a focal-conic texture with concentric arcs was obtained. Also, no homeotropic region could be observed. A typical photomicrograph of a fan-shaped texture with unequally spaced concentric arcs obtained for compound **4.E.4** is shown in figure **4.14**.

Table 4.4: Transition temperatures (°C) and the associated enthalpies (kJ $\mathrm{mol^{-1}}$) for compounds of series 4.III



Compound	*n*	Cr		$\mathrm{SmCP_A}$		I
4.E.1	12	.	150.5 *34.4*	.	158.0 *16.4*	.
4.E.2	14	.	146.5 *35.3*	.	159.0 *17.1*	.
4.E.3	16	.	144.0 *33.7*	.	160.0 *17.4*	.
4.E.4	18	.	141.0 *32.2*	.	159.0 *17.5*	.

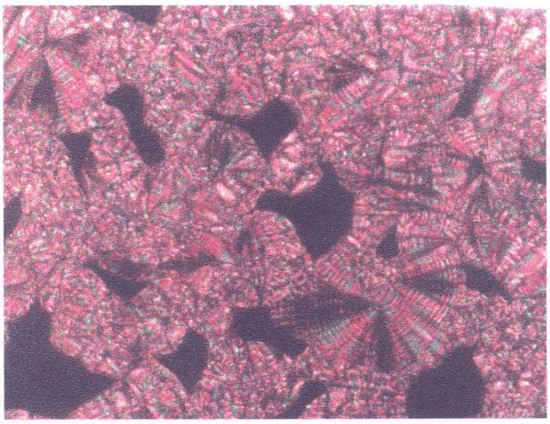


Figure 4.14: An optical photomicrograph of $\mathrm{SmCP_A}$ phase growing from the isotropic liquid of compound 4.E.4.

In order to establish the nature of the mesophase, XRD and electro-optical studies were carried out on the mesophase of compound **4.E.4**. The XRD studies reveal that the mesophase is a tilted smectic phase. The obtained d-spacings for compound **4.E.4**. is given in table **4.5.** The electro-optical studies were carried out on representative compounds of series **4.III** (compound **4.E.4)** and a typical switching current response trace obtained is shown in figure **4.15.** Based on these experimental observations the mesophase has been labeled as $SmCP_A$.

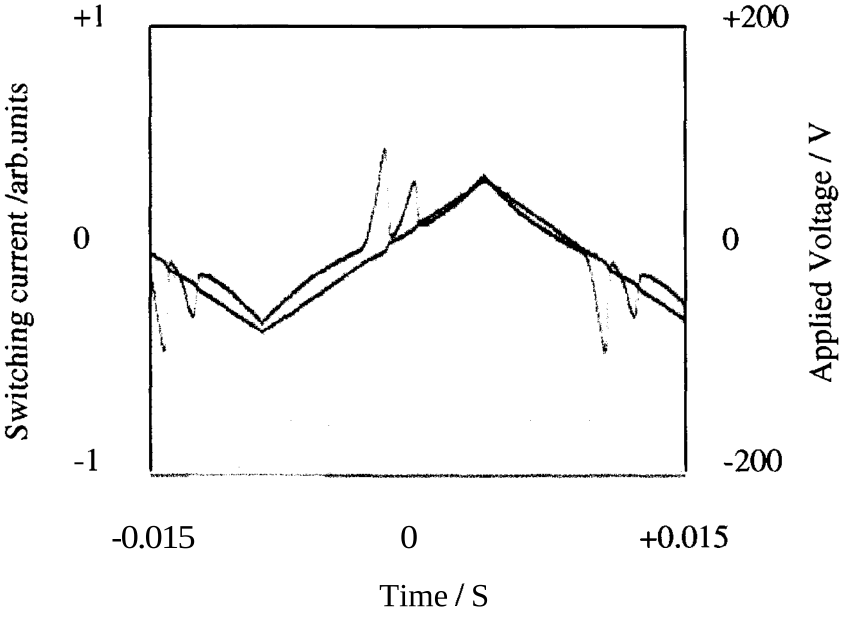


Figure 4.15: The switching current response trace obtained for the mesophase of compound 4.E.4 by applying a triangular-wave electric field (130 V_{pp}) at 40Hz; cell thickness 14.2μm; saturated polarization ≈ 190 nC cm^{-2}.

The layer spacings obtained from XRD studies and the measured molecular length for various compounds studied are given in table **4.5.**

In this unsymmetrically substituted compounds the terminal electronegative substituent interacts with the electropositive methyl group of the n-alkoxy chain in adjacent layers thus stabilizing the smectic phase with antiferroelectric ordering of the molecules.

As in the case of smectic A and smectic C phases of calamitic liquid crystals, the filamentary growth patterns of the $SmCP_A$ phase can also be attributed to the negative interfacial tension anisotropy.

Table 4.5: Layer spacings (d) from XRD studies and the corresponding molecular length (L) of compounds by assuming the n-alkoxy chain to be in a fully extended all trans conformation

Compound	Layer spacings d (Å)	Measured molecular length L (Å)
4.A.3	45.1 (01), 14.9 (03)	53.5
4.B.4	38.7 (01), 19.3 (02)	43.8
4.B.6	41.8 (01), 20.9 (02)	46.4
4.B.7	44.4 (01), 22.2 (02)	48.3
4.B.8	45.2 (01), 22.6 (02) 15.1 (03), 11.3 (04)	51.7
4.E.4	45.7 (01), 22.7 (02)	49.0

Summary

Several bent-core compounds unsymmetrically substituted about the central phenyl ring belonging to three different series are described. These contain fluoro, chloro, or trifluoromethyl group as one of the terminal substituents, while at the other end an n-alkoxy chain is attached. The mesophase exhibited by these compounds were characterized as a polar smectic C phase with antiferroelectric properties. The terminally chloro substituted compounds showed filamentary growth pattern at the isotropic phase to the $SmCP_A$ phase transition which is rather unusual. This represents the first homologous series of bent-core compounds exhibiting such filamentary growth pattern at the isotropic-$SmCP_A$ phase transition.

Experimental

The synthesis of 4-benzyloxybenzoic acid, **4.ii** was already described in Chapter **2.** 3- Benzyloxybenzoic acid, **4.iii** was prepared using a procedure similar to that as described in Chapter **2** for 4-benzyloxybenzoicacid, but using 3-hydroxybenzoic acid as starting material. 4-n-alkoxybenzoic acids, **4.iv** [63], 3-Fluoro-4-n-octadecyloxybenzoic acid, [63] and 4-n-dodecylbiphenyl-4-carboxylic acid [70] were prepared according to procedures described in the literature. 4-Fluorophenol, 4-chlorophenol and 4-trifluoromethylphenol are commercial compounds and were used without further purification.

4-Fluorophenyl-4-benzyloxybenzoate,4.a (X=F)

A mixture of 4-fluorophenol, **4.i** (X=F) (4.03g, 36mmol), 4-benzyloxybenzoic acid, **4.ii** (8.2g, 31mmol), catalytic amount of 4-(N, N-dimethylamino) pyridine (DMAP), dry chloroform (50ml) was stirred for ten minutes. To this mixture N, N'-dicyclohexylcarbodiimide (DCC, 8.2g, 39.6mmol) was added and the contents were stirred for ten hours at room temperature. The precipitated N, N'-dicyclohexylurea was filtered off. The filtrate was diluted with chloroform and washed successively with 5% acetic acid (2 x 25ml), 5% ice-cold sodium hydroxide solution (2 x 25ml), water (3 x 50ml) and dried over anhydrous sodium sulphate. Removal of solvent gave a residue, which was chromatographed on silica gel using chloroform as eluent. Removal of solvent from the eluate afforded a white material, which was crystallized from a mixture of chloroform and acetonitrile. Yield, 8.2g (78%); m.p. 167-168°C; ν_{max} (nujol): 2924, 2855, 1726, 1605, 1508, 1278, 1254 cm^{-1}; δ_H: 8.15-8.12 (dd, 2H, ^3J8.92Hz, ^4J2.0Hz, Ar-H), 7.46-7.34 (m, 4H, Ar-H), 7.18-7.13 (m, 3H, Ar-H), 7.12-7.10 (d, 2H, ^3J8.92Hz, Ar-H), 7.08-7.05 (dd, 2H, ^3J11.0Hz, ^4J2.08Hz, Ar-H), 5.16 (s, 2H, -O-CH$_2$-Ar).

4-Fluorophenyl-4-hydroxybenzoate, 4.b (X=F)

4-Fluorophenyl-4-benzyloxybenzoate 4.a (X=F), (8.0g, 24.8mmol) was dissolved in 1, 4-dioxane (100ml) and 5% Pd-C catalyst (2g) was added to it. The mixture was stirred at 50°C in an atmosphere of hydrogen, till the required quantity of hydrogen was absorbed. The mixture was then filtered and the solvent removed under reduced pressure. The residue obtained was crystallized from a mixture of 1, 4-dioxane and petroleum-ether (b.p. 60-80°C). Yield, 4.3g (75%); m.p. 173-174°C; ν_{max} (nujol): 3309, 3074, 2922, 2855, 1697, 1585, 1514, 1275 cm^{-1}; δ_H(CD_3COCD_3): 9.6 (s, 1H, Ar-OH, exchangeable with D_2O), 8.05-8.03 (d, 2H, ^{3}J8.72Hz, Ar-H), 7.31-7.19 (m, 4H, Ar-H), 7.01-6.99 (d, 2H, ^{3}J8.72Hz, Ar-H).

4-Fluorophenyl-4-(3-benzyloxybenzoyloxy)benzoate, 4.c (X=F)

This was synthesized following a procedure described for the preparation of compound **4.a** (X=F). Quantities: compound **4.b** (X=F), (4.0g, 17.2mmol), 3-benzyloxybenzoic acid, **4.iii** (3.92g, 17.2mmol), DCC (3.89g, 18.9mmol), DMAP (cat. amount) and dry chloroform (30ml). Yield, 6.2g (81%); m.p. 140-141°C; ν_{max} (nujol): 2924, 2855, 1735, 1732, 1605, 1586, 1263, 1069 cm^{-1}; δ_H: 8.29-8.27 (dd, 2H, ^{3}J8.8Hz, ^{4}J2.0Hz, Ar-H), 7.85-7.81 (m, 2H, Ar-H), 7.48-7.33 (m, 7H, Ar-H), 7.30-7.27 (m, 2H, Ar-H), 7.21-7.10 (m, 4H, Ar-H), 5.16 (s, 2H, -O-CH_2-Ar).

4-Fluorophenyl-4-(3-hydroxybenzoyloxy)benzoate, 4.d (X=F)

This was synthesized following a procedure described for the preparation of compound **4.b** (X=F). Quantities: compound **4.c** (X=F), (6.0g, 17mmol), 1, 4-dioxane (100ml) and 5% Pd-C (1.3g). Yield, 3.8g (79%); m.p. 182.5-183.5°C; ν_{max} (nujol): 3445, 2924, 2855, 1720, 1607, 1505, 1458, 1270 cm^{-1}; δ_H(CD_3COCD_3): 9.25 (s, 1H, Ar-OH, exchangeable with D_2O), 8.43-8.41 (d, 2H, ^{3}J8.6Hz, Ar-H), 7.82-7.80 (d, 1H, ^{3}J7.64Hz, Ar-H), 7.66 (s, 1H, Ar-H), 7.41-7.37 (m, 3H, Ar-H), 7.21-7.10 (m, 5H, Ar-H).

4-Fluorophenyl-4-[3-(4-benzyloxybenzoyloxy)benzoyloxy]benzoate, 4.e (X=F)

This was synthesized following a procedure described for the preparation of compound **4.a** (X=F). Quantities: compound **4.d** (X=F), (3.8g, 10.8mmol), 4-benzyloxybenzoic acid, **4.ii** (2.46g, 10.8mmol), DCC (2.45g, 11.7mmol), DMAP (cat. amount) and dry chloroform (30ml). Yield, 4.3g (72%); m.p. 171.5-172.5°C; ν_{max} (nujol): 2924, 2855, 1744, 1730, 1603, 1504, 1250, 1060 cm^{-1}; δ_H: 8.29-8.27 (dd, 2H, ^{3}J8.8Hz, ^{4}J2.0Hz, Ar-H), 8.19-8.17 (dd, 2H, ^{3}J8.96Hz, ^{4}J2.0Hz, Ar-H), 8.16-8.06 (m, 2H, Ar-H), 7.63-7.59 (t, 1H, ^{3}J8.04Hz, Ar-H), 7.54-7.51 (m, 1H, Ar-H), 7.47-7.35 (m, 7H, Ar-H), 7.21-7.07 (m, 6H, Ar-H), 5.18 (s, 2H, -O-CH_2-Ar).

4-Fluorophenyl-4-[3-(4-hydroxybenzoyloxy)benzoyloxy]benzoate, 4.f (X=F)

This was synthesized following a procedure described for the preparation of compound 4.b (X=F). Quantities: compound 4.e (X=F), (4.0g, 7.1mmol), 1, 4-dioxane (50ml) and 5% Pd-C (0.8g). Yield, 2.7g (80%); m.p. 185-186°C; v, (nujol): 3345, 3275, 1732, 1696,1597,1508,1236,1092 cm^{-1}; δ_H (CD_3COCD_3): 9.68 (s, 1H, Ar-OH, exchangeable with D_2O), 8.31-8.29 (d, 2H, ^3J8.72Hz, Ar-H), 8.16-8.08 (m, 4H, Ar-H), 7.75-7.71 (t, 1H, ^3J8.0Hz, Ar-H) 7.68-7.64 (m, 1H, Ar-H), 7.59-7.57 (d, 2H, ^3J8.76Hz, Ar-H), (7.39-7.21 (m, 4H, Ar-H), 7.03-7.01 (d, 2H, ^3J8.76Hz, Ar-H).

4-Chlorophenyl-4-benzyloxybenzoate, 4.a (X=Cl)

This was synthesized following a procedure described for the preparation of compound 4.a (X=F). Quantities: 4-chlorophenol4.i (X=Cl), (4.0g, 31mmol), 4-benzyloxy-benzoic acid, **4.ii** (7.0g, 31mmol), DCC (7.02g, 34mmol), DMAP (cat. amount), dry chloroform (50ml). Yield, 8.2g (78%); m.p. 171-171.5°C; ν_{max} (nujol): 2924, 2855, 1726, 1602, 1280, 1062 cm^{-1}; δ_H: 8.29-8.27 (dd, 2H, ^3J8.76Hz, ^4J2.1Hz, Ar-H), 7.84-7.81 (m, 2H, Ar-H), 7.48-7.27 (m, 7H, Ar-H), 7.19-7.17 (dd, 2H, ^3J8.76Hz, ^4J2.1Hz, Ar-H), 5.2 (s, 2H, -O-CH_2-Ar). Elemental analysis; $C_{20}H_{15}O_3Cl$ requires C, 70.91; H, 4.46%; found C, 71.36; H, 4.55%.

4-Chlorophenyl-4-hydroxybenzoate, 4.b (X=Cl)

This was synthesized following a procedure described for the preparation of compound 4.b (X=F). Quantities: compound 4.a (X=Cl), (8.0g, 23.6mmol), 1, 4-dioxane (100ml) and 5% Pd-C (1.7g). Yield, 4.5g (76.5%); m.p. 196-197°C; ν_{max} (nujol): 3352, 2924, 2854, 1703, 1608, 1273, 690 cm^{-1}; δ_H (CD_3COCD_3): 9.8 (s, 1H, Ar-OH, exchangeable with D_2O), 8.19-8.16 (d, 2H, ^3J8.8Hz, Ar-H), 7.62-7.60 (d, 2H, ^3J8.8Hz, Ar-H), 7.42-7.40 (d, 2H, ^3J8.8Hz, Ar-H), 7.14-7.12 (d, 2H, ^3J8.8Hz, Ar-H). Elemental analysis: $C_{13}H_9O_3Cl$ requires C, 62.79; H, 3.65%; found C, 63.11; H, 3.89%.

4-Chlorophenyl-4-(3-benzyloxybenzoyloxy), 4.c (X=Cl)

This was synthesized following a procedure described for the preparation of compound 4.a (X=F). Quantities: compound 4.b (X=Cl), (4.3g, 17.3mmol), 3-benzyloxy-benzoic acid, **4.iii** (3.95g, 17.3mmol), DCC (3.93g, 19.1mmol), DMAP (cat. amount) and dry chloroform (30ml). Yield, 5.8g (73%); m.p. 137.5-138°C; ν_{max} (nujol): 2924, 2854, 1730, 1589, 1275, 1062 cm^{-1}; δ_H: 8.15-8.13 (dd, 2H, ^{3}J8.96Hz, ^{4}J2.0Hz, Ar-H), 7.46-7.36 (m, 11H, Ar-H), 7.16-7.14 (dd, 2H, ^{3}J8.88Hz, ^{4}J2.2Hz, Ar-H), 7.07-7.05 (dd, 2H, ^{3}J8.92Hz, ^{4}J2.0Hz, Ar-H), 5.20 (s, 2H, -O-CH$_2$-Ar). Elemental analysis: $C_{27}H_{19}O_5Cl$ requires C, 70.67; H, 4.17%; found C, 70.25; H, 4.07%.

4-Chlorophenyl-4-(3-hydroxybenzoyloxy)bemoate,4.d (X=Cl)

This was prepared following a procedure described for the synthesis of compound **4.b** (X=F). Quantities: compound **4.c** (X=Cl), (5.5g, 12mmol), 1, 4-dioxane (50ml) and 5% Pd-C (1.3g). Yield, 3.5g (79%); m.p. 163-164°C; ν_{max} (nujol): 3349, 2924, 2855, 1720, 1605, 1456, 1196, 1062,752 cm^{-1}; δ_H (CD_3COCD_3): 9.25 (s, 1H, Ar-OH, exchangeable with D_2O), 8.43-8.41 (dd, 2H, ^{3}J8.88Hz, ^{4}J2.1Hz, Ar-H), 7.84-7.77 (m, 2H, Ar-H), 7.7-7.63 (m, 4H, Ar-H), 7.59-7.57 (t, 1H, ^{3}J8.0Hz, Ar-H), 7.45-7.43 (dd, 2H, ^{3}J8.88Hz, ^{4}J2.1Hz, Ar-H), 7.36-7.33 (m, 1H, Ar-H,). Elemental analysis: $C_{20}H_{13}O_5Cl$ requires C, 65.14; H, 3.55%; found C, 64.98; H, 3.55%.

4-Chlorophenyl-4-[3-(4-benzyloxybenzoyloxy)benzoyloxy]benzoate, 4.e (X=Cl)

This was synthesized following a procedure described for the preparation of compound **4.a** (X=F). Quantities: compound **4.d** (X=Cl), (3.5g, 9.5mmol), 4- benzyloxy-benzoic acid, **4.ii** (2.17g, 9.5mmol), DCC (2.16g, 10.5 mmol), DMAP (cat.amount), dry chloroform (20ml). Yield, 4.0g (72%); m.p. 178.5-179.5°C; ν_{max} (nujol): 2924, 2855, 1732, 1603, 1458, 1252, 1065 cm^{-1}; δ_H: 8.29-8.27 (d, 2H, ^{3}J8.72Hz, Ar-H), 8.19-8.17 (d, 2H, ^{3}J8.88Hz, Ar-H), 8.13-8.06 (m, 2H, Ar-H), 7.62-7.58 (t, 1H, ^{3}J8.0Hz, Ar-H), 7.54-7.52 (m, 1H, Ar-H), 7.46-7.35 (m, 9H, Ar-H), 7.19-7.16 (d, 2H, ^{3}J8.8Hz, Ar-H), 7.09-7.07(d, 2H, ^{3}J8.88Hz, Ar-H), 5.18 (s, 2H, -O-CH$_2$-Ar). Elemental analysis: $C_{34}H_{23}O_7Cl$ requires C, 70.53; H, 4.0%; found C, 70.45; H, 4.09%.

4-Chlorophenyl-4-[3-(4-hydroxybenzoyloxy)benzoyloxy]benzoate, 4.f (X=Cl)

This was prepared following a procedure described for the synthesis of compound **4.b** (X=F). Quantities: compound **4.e** (X=Cl), (3.5g, 6.1mmol), 1, 4-dioxane (35ml), 5% Pd-C (0.8g). Yield, 2.2g (75%); m.p. 174.5-175.5°C; ν_{max} (nujol): 3456, 3369, 2924, 2855, 1740, 1715,1609,1269,1063 cm^{-1}; δ_H (CD_3COCD_3): 9.59 (s, 1H, Ar-OH, exchangeable with D_2O), 8.44-8.42 (dd, 2H, ^{3}J8.72Hz, ^{4}J2.0Hz, Ar-H), 8.29-8.21 (m, 4H, Ar-H), 7.88-7.84 (t, 1H, ^{3}J8.0Hz, Ar-H) 7.82-7.79 (m, 1H, Ar-H), 7.73-7.71 (dd, 2H, ^{3}J8.76Hz, ^{4}J2.0Hz, Ar-H), 7.66-

7.64 (dd, 2H, ^3J8.88Hz, ^4J2.1Hz, Ar-H), 7.53-7.51 (dd, 2H, ^3J8.88Hz, ^4J2.1Hz, Ar-H), 7.17-7.15 (dd, 2H, ^3J8.88Hz, ^4J2.0Hz, Ar-H). Elemental analysis: $C_{27}H_{17}O_7Cl$ requires C, 66.33; H, 3.51%; found C, 66.77; H, 3.67%.

4-Trifluoromethylphenyl-4-benzyloxybenzoate, 4.a ($X=CF_3$)

This was synthesized following a procedure described for the preparation of compound **4.a** (X=F). Quantities: 4-trifluoromethylphenol 4.i ($X=CF_3$), (2.5g, 15.4mmol), 4-benzyloxybenzoic acid, **4.ii** (3.5g, 15.4mmol), DCC (3.5g, 16.9mmol), DMAP (cat. amount), dry chloroform (30ml). Yield, 5.1g (89%); m.p. 186-187°C; ν_{max} (nujol): 2924, 2855, 1728, 1603, 1456, 1330, 1164, 1059 cm^{-1}; δ_H: 8.17-8.14 (dd, 2H, ^3J8.92Hz, ^4J2.0Hz, Ar-H), 7.71-7.68 (d, 2H, ^3J8.52Hz, Ar-H), 7.47-7.32 (m, 7H, Ar-H), 7.09-7.06 (dd, 2H, ^3J8.92Hz, ^4J2.0Hz, Ar-H), 5.17 (s, 2H, $-O-CH_2-Ar$).

4-Trifluoromethylphenyl-4-hydroxybenzoate, 4.b ($X=CF_3$)

This was synthesized following a procedure described for the preparation of compound **4.b** (X=F). Quantities: compound **4.a** ($X=CF_3$), (5.0g, 13mmol), 1, 4-dioxane (75ml), 5% Pd-C (1.1g). Yield, 3.45g (90%); m.p. 165-166°C; ν_{max} (nujol): 3916, 2924, 2855, 1709, 1605, 1589, 1321, 1281, 1163 cm^{-1}; δ_H (CD_3COCD_3): 9.6 (s, 1H, Ar-OH, exchangeable with D_2O), 8.22-8.19 (dd, 2H, ^3J8.72Hz, ^4J2.0Hz, Ar-H), 7.98-7.96 (d, 2H, ^3J8.56Hz, Ar-H), 7.68-7.66 (d, 2H, ^3J8.56Hz, Ar-H), 7.19-7.16 (dd, 2H, ^3J8.72Hz, ^4J2.0Hz, Ar-H).

4-Trifluoromethylphenyl-4-(3-benzyloxybenzoyloxy)benzoate, 4.c ($X=CF_3$)

This was synthesized following a procedure described for the preparation of compound **4.a** (X=F). Quantities: compound **4.b** ($X=CF_3$), (3.3g, 11.7mmol), 3-benzyloxy-benzoic acid, **4.iii** (2.67g, 11.7mmol), DCC (2.65g, 13mmol), DMAP (cat. amount) and dry chloroform (30ml). Yield, 5.3g (90%); m.p. 165.5-166.5°C; ν_{max} (nujol): 2924, 2855, 1740, 1732, 1600, 1275, 1161, 1059 cm^{-1}; δ_H: 8.31-8.28 (dd, 2H, ^3J8.84Hz, ^4J2.04Hz, Ar-H), 7.85-7.81 (m, 2H, Ar-H), 7.73-7.71 (d, 2H, ^3J8.52Hz, Ar-H), 7.48-7.36 (m, 10H, Ar-H), 7.30-7.27 (m, 1H, Ar-H), 5.16 (s, 2H, $-O-CH_2-Ar$).

4-Trifluoromethylphenyl-4-(3-hydroxybenzoyloxy)benzoate, 4.d ($X=CF_3$)

This was synthesized following a procedure described for the preparation of compound **4.b** (X=F). Quantities: compound **4c** ($X=CF_3$), (5.0g, 10.1mmol), 1, 4-dioxane (85ml), 5% Pd-C (1.2g). Yield, 4.1g (91%); m.p. 165-166°C; ν_{max} (nujol): 3464, 3298, 2924, 2855,1728,1717,1603,1589,1456,1292,1061 cm^{-1}; δ_H (CD_3COCD_3): 9.04 (s, 1H, Ar-OH, exchangeable with D_2O), 8.46-8.44 (dd, 2H, ^3J8.64Hz, ^4J1.8Hz, Ar-H), 8.02-8.0 (d, 2H, ^3J8.64Hz, Ar-H), 7.85-7.83 (d, 2H, ^3J7.68Hz, Ar-H), 7.80-7.79 (t, 1H, ^4J2.2Hz, Ar-H), 7.75-7.73 (d, 2H, ^3J8.64Hz, Ar-H), 7.70-7.68 (dd, 2H, ^3J8.64Hz, ^4J1.8Hz, Ar-H), 7.37-7.34 (m, 1H, Ar-H).

4-Trifluoromethylphenyl-4-[3-(4-benzyloxybenzoyloxy)benzoyloxy]benzoate, 4e ($X=CF_3$)

This was synthesized following a procedure described for the preparation of compound **4.a** (X=F). Quantities: compound **4d** ($X=CF_3$), (2.5g, 6.2mmol), 4-benzyloxy-benzoic acid, **4.ii** (1.42g, 6.2mmol), DCC (1.40g, 6.8mmol), DMAP (cat. amount) and dry chloroform (25ml). Yield, 3.0g (80%); m.p. 180.5-181.5°C; ν_{max} (nujol): 2924, 2855, 1734, 1605, 1458, 1256, 1076 cm^{-1}; δ_H: 8.31-8.28 (d, 2H, ^3J8.88Hz, Ar-H), 8.19-8.17 (d, 2H, ^3J9.0Hz, Ar-H), 8.17-8.06 (m, 2H, Ar-H), 7.73-7.71 (d, 2H, ^3J8.52Hz, Ar-H), 7.63-7.59 (t, 1H, ^3J8.0Hz, Ar-H), 7.54-7.51 (m, 1H, Ar-H), 7.47-7.35(m, 9H, Ar-H), 7.09-7.07 (d, 2H, ^3J9.0Hz, Ar-H), 5.18 (s, 2H, $-O-CH_2-Ar$).

4-Trifluoromethylphenyl-4- [3-(4-hydroxybenzoyloxy)benzoyloxy]benzoate, 4f ($X=CF_3$)

This was synthesized following a procedure described for the preparation of compound **4.b** (X=F). Quantities: compound **4e** ($X=CF_3$), (3.0g, 4.9mmol), 1, 4-dioxane (45ml), 5% Pd-C (0.7g). Yield, 2.1g (84%); m.p. 215-216°C; ν_{max} (nujol): 3406, 2924, 2855, 1740, 1705, 1593, 1281, 1163, 1057 cm^{-1}; δ_H (CD_3COCD_3): 9.57 (s, 1H, Ar-OH, exchangeable with D_2O), 8.47-8.45 (dd, 2H, ^3J8.84Hz, ^4J2.04Hz, Ar-H), 8.29-8.22 (m, 4H, Ar-H), 8.02-8.0 (d, 2H, ^3J8.52Hz, Ar-H), 7.89-7.85 (t, 1H, ^3J7.96Hz, Ar-H), 7.82-7.79 (m, 1H, Ar-H), 7.75-7.73 (dd, 4H, ^3J8.8Hz, ^4J1.92Hz, Ar-H), 7.18-7.16 (dd, 2H, ^3J8.84Hz, ^4J2.0Hz, Ar-H).

4-Fluorophenyl-4-[3-{4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 4.A.1

This was synthesized following a procedure described for the preparation of compound **4.a** (X=F). Quantities: compound **4.f** (X=F), (0.2g, 0.4mmol), 4-n-tetradecyloxy-benzoic acid, **4.iv** (*n*=14) (0.14g, 0.4mmol), DCC (0.098g, 0.46mmol), DMAP (cat. amount), dry chloroform (10 ml). Yield, 0.26g (78%); m.p. 125.5°C; ν_{max}: 3074, 2920, 2851, 1732, 1605, 1510, 1163, 1074 cm^{-1}; δ_H: 8.32-8.28 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.65-7.61 (t, 1H, ^3J8.04Hz, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.41-7.39 (d, 4H, ^3J8.68Hz, Ar-H), 7.21-7.10 (m, 4H, Ar-H), 7.0-6.98 (d, 2H, ^3J8.92Hz, Ar-H), 4.07-4.04 (t, 2H, ^3J6.52Hz, Ar-O-CH_2-), 1.86-1.79 (quin, 2H, ^3J7.0Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.52-1.26 (m, 22H, 11 x -CH_2-), 0.90-0.86 (t, 3H, ^3J6.64Hz, -CH_3).

4-Fluorophenyl-4-[3-{4-(4-*n*-hexadecyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 4.A.2

Yield, 75%; m.p. 125.0°C; ν_{max}: 3074, 2920, 2851, 1736, 1605, 1512,1163,1076 cm^{-1}; δ_H: 8.32-8.28 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.65-7.61 (t, 1H, ^3J7.96Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.39 (d, 4H, ^3J8.64Hz, Ar-H), 7.21-7.10 (m, 4H, Ar-H), 7.0-6.98 (d, 2H, ^3J8.88Hz, Ar-H), 4.07-4.04 (t, 2H, ^3J6.52Hz, Ar-O-CH_2-), 1.86-1.79 (quin, 2H, ^3J7.04Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.52-1.26 (m, 26H, 13 x -CH_2-), 0.90-0.86 (t, 3H, ^3J6.56Hz, -CH_3).

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

Yield, 77%; m.p. 122.0°C; ν_{max}: 3072, 2914, 2849, 1738, 1732, 1605, 1512, 1163, 1076 cm^{-1}; δ_H: 8.32-8.27 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.65-7.61 (t, 1H, ^3J8.04 Hz, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.41-7.39 (d, 4H, ^3J8.6Hz, Ar-H), 7.21-7.10 (m, 4H, Ar-H), 7.0-6.98 (d, 2H, ^3J8.96Hz, Ar-H), 4.07-4.04 (t, 2H, ^3J6.56Hz, Ar-O-CH_2-), 1.86-1.79 (quin, 2H, ^3J7.04Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.52-1.26 (m, 30H, 15 ×-CH_2-), 0.89-0.86 (t, 3H, ^3J6.68Hz, -CH_3).

4-Chlorophenyl-4-[3-{4-(4-*n*-hexyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate,

4.B.1

Yield, 68%; m.p. 147.0°C; ν_{max}: 3072, 2924, 2858, 1736, 1731, 1609, 1512, 1165, 1063 cm^{-1}; δ_H: 8.31-8.27 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.64-7.60 (t, 1H, ^{3}J8.08 Hz, Ar-H), 7.57-7.55 (m, 1H, Ar-H), 7.42-7.39 (m, 6H, Ar-H), 7.19-7.17 (dd, 2H, ^{3}J8.8Hz, ^{4}J1.96Hz, Ar-H), 7.0-6.98 (d, 2H, ^{3}J8.88Hz, Ar-H), 4.07-4.04 (t, 2H, ^{3}J6.56Hz, Ar-O-CH_2-), 1.86-1.79 (quin, 2H, ^{3}J6.72Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.49-1.36 (m, 6H, 3 x -CH_2-), 0.93-0.90 (t, 3H, ^{3}J6.72Hz, -CH_3). Elemental analysis: $C_{40}H_{33}O_9Cl$ requires C, 69.31; H, 4.80%; found C, 69.27; H, 4.93%.

4-Chlorophenyl-4-[3-{4-(4-*n*-octyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate,

4.B.2

Yield, 65%; m.p. 139.0°C; ν_{max}: 3067, 2920, 2856, 1749, 1736, 1730, 1607, 1161, 1057 cm^{-1}; δ_H: 8.31-8.27 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.65-7.61 (t, 1H, ^{3}J8.08 Hz, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.42-7.39 (m, 6H, Ar-H), 7.19-7.17 (dd, 2H, ^{3}J8.84Hz, ^{4}J2.2Hz, Ar-H), 7.0-6.98 (d, 2H, ^{3}J8.92Hz, Ar-H), 4.07-4.04 (t, 2H, ^{3}J6.56Hz, Ar-O-CH_2-), 1.86-1.79 (quin, 2H, ^{3}J7.04Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.49-1.30(m, 10H, 5 x -CH_2-), 0.91-0.88 (t, 3H, ^{3}J6.72Hz, -CH_3). Elemental analysis: $C_{42}H_{37}O_9Cl$ requires C, 69.95; H, 5.17%; found C, 70.38; H, 5.24%.

4-Chlorophenyl-4-[3-{4-(4-*n*-nonyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate,

4.B.3

Yield, 60%; m.p. 137.0°C; ν_{max}: 3072, 2918, 2853, 1736, 1730, 1607, 1258, 1161, 1070 cm^{-1}; δ_H: 8.31-8.27 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.65-7.61 (t, 1H, ^{3}J8.08 Hz, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.42-7.39 (m, 6H, Ar-H), 7.19-7.17 (dd, 2H, ^{3}J8.84Hz, ^{4}J2.2Hz, Ar-H), 7.0-6.98 (d, 2H, ^{3}J8.96Hz, Ar-H), 4.07-4.04 (t, 2H, ^{3}J6.56Hz, Ar-O-CH_2-), 1.86-1.79 (quin, 2H, ^{3}J7.04Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.50-1.30 (m, 12H, 6 x -CH_2-), 0.91-0.87 (t, 3H, ^{3}J6.72Hz, -CH_3). Elemental analysis: $C_{43}H_{39}O_9Cl$ requires C, 70.25; H, 5.35%; found C, 70.38; H, 5.38%.

4-Chlorophenyl-4-[3-{4-(4-*n*-decyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate,

4.B.4

Yield, 71%; m.p. 133.0°C; ν_{max}: 3072, 2916, 2851, 1736, 1734, 1730, 1607, 1278, 1161, 1070 cm^{-1}; δ_H: 8.31-8.27 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.65-7.61 (t, 1H, ^{3}J8.12Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.42-7.39 (m, 6H, Ar-H), 7.19-7.17 (dd, 2H, ^{3}J8.84Hz, ^{4}J2.2Hz, Ar-H), 7.0-6.98 (d, 2H, ^{3}J8.84Hz, Ar-H), 4.07-4.04 (t, 2H, ^{3}J6.56Hz, Ar-O-CH_2-), 1.85-1.79 (quin, 2H, ^{3}J7.08Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.50-1.28 (m, 14H, 7 x -CH_2-), 0.91-0.87 (t, 3H, ^{3}J6.76Hz, -CH_3). Elemental analysis: $C_{44}H_{41}O_9Cl$ requires C, 70.53; H, 5.52%; found C, 70.36; H, 5.59%.

4-Chlorophenyl-4-[3-{4-(4-*n*-undecyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate,

4.B.5

Yield, 66%; m.p. 129.0°C; ν_{max}: 3076, 2916, 2851, 1738, 1734, 1728, 1605, 1278, 1161, 1072 cm^{-1}; δ_H: 8.31-8.27 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.65-7.61 (t, 1H, ^{3}J8.0Hz, Ar-H), 7.57-7.55 (m, 1H, Ar-H), 7.41-7.39 (m, 6H, Ar-H), 7.19-7.17 (dd, 2H, ^{3}J8.8Hz, ^{4}J1.92Hz, Ar-H), 7.0-6.98 (d, 2H, ^{3}J8.84Hz, Ar-H), 4.07-4.04 (t, 2H, ^{3}J6.56Hz, Ar-O-CH_2-), 1.85-1.79 (quin, 2H, ^{3}J7.0Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.49-1.28 (m, 16H, 8 x -CH_2-), 0.90-0.87 (t, 3H, ^{3}J6.76Hz, -CH_3). Elemental analysis: $C_{45}H_{43}O_9Cl$ requires C, 70.81; H, 5.68%; found C, 70.55; H, 5.57%.

4-Chlorophenyl-4-[3-{4-(4-*n*-dodecyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate,

4.B.6

Yield, 69%; m.p. 128.5°C; ν_{max}: 3063, 2916, 2851, 1736, 1734, 1730, 1609, 1278, 1161, 1072 cm^{-1}; δ_H: 8.31-8.27 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.64-7.61 (t, 1H, ^{3}J7.92Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.39 (m, 6H, Ar-H), 7.19-7.17 (dd, 2H, ^{3}J8.72Hz, ^{4}J1.92Hz, Ar-H), 7.0-6.98 (d, 2H, ^{3}J8.76Hz, Ar-H), 4.07-4.04 (t, 2H, ^{3}J6.6Hz, Ar-O-CH_2-), 1.85-1.79 (quin, 2H, ^{3}J7.0Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.48-1.27 (m, 18H, 9 x -CH_2-), 0.90-0.87 (t, 3H, ^{3}J6.64Hz, -CH_3). Elemental analysis: $C_{46}H_{45}O_9Cl$ requires C, 71.08; H, 5.84%; found C, 70.98; H, 5.90%.

4-Chlorophenyl-4-[3-{4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 4.B.7

Yield, 70%; m.p. 130.0°C; ν_{max}: 3063, 2916, 2849, 1736, 1732, 1728, 1607, 1279, 1161, 1072 cm^{-1}; δ_H: 8.31-8.27 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.64-7.60 (t, 1H, ^{3}J8.04Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.39 (m, 6H, Ar-H), 7.19-7.17 (dd, 2H, ^{3}J8.88Hz, ^{4}J2.2Hz, Ar-H), 7.0-6.98 (d, 2H, ^{3}J8.92Hz, Ar-H), 4.07-4.04 (t, 2H, ^{3}J6.56Hz, Ar-O-CH$_2$-), 1.87-1.80 (quin, 2H, ^{3}J7.08Hz, Ar-O-CH$_2$-$\underline{CH_2}$-), 1.48-1.27 (m, 22H, 11 x -CH$_2$-), 0.90-0.87 (t, 3H, ^{3}J6.68Hz, -CH$_3$). Elemental analysis: $C_{48}H_{49}O_9Cl$ requires C, 71.59; H, 6.13%; found C, 71.65; H, 6.22%.

4-Chlorophenyl-4-[3-{4-(4-*n*-hexadecyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 4.B.8

Yield, 63%; m.p. 127.0°C; ν_{max}: 3076, 2916, 2849, 1736, 1732, 1728, 1609, 1279, 1074 cm^{-1}; δ_H: 8.31-8.27 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.64-7.60 (t, 1H, ^{3}J8.0Hz, Ar-H), 7.57-7.55 (m, 1H, Ar-H), 7.42-7.39 (m, 6H, Ar-H), 7.19-7.17 (dd, 2H, ^{3}J8.68Hz, ^{4}J2.1Hz, Ar-H), 7.0-6.98 (d, 2H, ^{3}J8.8Hz, Ar-H), 4.07-4.04 (t, 2H, ^{3}J6.52Hz, Ar-O-CH$_2$-), 1.86-1.79 (quin, 2H, ^{3}J6.68Hz, Ar-O-CH$_2$-$\underline{CH_2}$-), 1.48-1.22 (m, 26H, 13 x -CH$_2$-), 0.89-0.86 (t, 3H, ^{3}J6.72Hz, -CH$_3$). Elemental analysis: $C_{50}H_{53}O_9Cl$ requires C, 72.06; H, 6.41%; found C, 71.89; H, 6.46%.

4-Chlorophenyl-4-[3-{4-(4-*n*-octadecyloxybenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 4.B.9

Yield, 67%; m.p. 126.0°C; ν_{max}: 3076, 2914, 2849, 1735, 1732, 1728, 1605, 1283, 1074 cm^{-1}; δ_H: 8.31-8.27 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.64-7.60 (t, 1H, ^{3}J8.04Hz, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.42-7.39 (m, 6H, Ar-H), 7.19-7.17 (dd, 2H, ^{3}J8.72Hz, ^{4}J2.08Hz, Ar-H), 7.0-6.98 (d, 2H, ^{3}J8.84Hz, Ar-H), 4.07-4.04 (t, 2H, ^{3}J6.56Hz, Ar-O-CH$_2$-), 1.86-1.79 (quin, 2H, ^{3}J7.0Hz, Ar-O-CH$_2$-$\underline{CH_2}$-), 1.48-1.21 (m, 30H, 15 x -CH$_2$-), 0.90-0.86 (t, 3H, ^{3}J6.72Hz, -CH$_3$). Elemental analysis: $C_{52}H_{57}O_9Cl$ requires C, 72.50; H, 6.67%; found C, 72.92; H, 6.78%.

4-Chlorophenyl-4-[3-{4-(3-fluoro-4-*n*-octadecyloxybenzoyloxy)benzoyloxy}benzoyloxy] benzoate, 4.C.1

Yield, 61%; m.p. 125.0°C; ν_{max}: 3063, 2914, 2849, 1737, 1732, 1728, 1607, 1281, 1074 cm^{-1}; δ_H: 8.32-8.27 (m, 4H, Ar-H), 8.16-7.9 (m, 4H, Ar-H), 7.65-7.60 (t, 1H, ^3J7.96Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.41-7.39 (m, 5H, Ar-H), 7.19-7.17 (d, 2H, ^3J8.64Hz, Ar-H), 7.0-6.98 (m, 2H, Ar-H), 4.15-4.12 (t, 2H, ^3J6.48Hz, Ar-O-CH_2-), 1.90-1.85 (quin, 2H, ^3J7.0Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.52-1.26 (m, 30H, 15 x -CH_2-), 0.90-0.86 (t, 3H, ^3J6.76Hz, -CH_3).

4-Chlorophenyl-4-[3-{4-(4-*n*-decylbiphenylcarbonyloxy)benzoyloxy}benzoyloxy] benzoate, 4.D.1

Yield, 69%; m.p. 152.0°C; ν; 3067, 2914, 2849, 1734, 1730, 1728, 1603, 1269, 1074 cm^{-1}; δ_H: 8.34-8.26 (m, 6H, Ar-H), 8.16-8.10 (m, 2H, Ar-H), 7.76-7.74 (d, 2H, ^3J8.4Hz, Ar-H), 7.65-7.56 (m, 4H, Ar-H), 7.45-7.39 (m, 6H, Ar-H), 7.32-7.30 (d, 2H, ^3J8.04Hz, Ar-H), 7.19-7.17 (d, 2H, ^3J8.76Hz, Ar-H), 2.69-2.66 (t, 2H, ^3J7.68Hz, Ar-CH_2-), 1.70-1.64 (quin, 2H, ^3J7.16Hz, Ar-CH_2-$C\underline{H}_2$-), 1.53-1.28 (m, 14H, 7 x -CH_2-), 0.90-0.86 (t, 3H, ^3J6.48Hz, -CH_3).

4-Trifluoromethylphenyl-4-[3-{4-(4-*n*-dodecyloxybenzoyloxy)benzoyloxy}benzoyloxy] benzoate, 4.E.1

Yield, 77%; m.p. 150.5°C; ν_{max}: 3080, 2920, 2855, 1744, 1736, 1733, 1609, 1263, 1163, 1059 cm^{-1}; δ_H: 8.32-8.29 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.73-7.71 (d, 2H, ^3J8.72Hz, Ar-H), 7.65-7.61 (t, 1H, ^3J8.04Hz, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.42-7.36 (m, 6H, Ar-H), 7.0-6.98 (d, 2H, ^3J8.92Hz, Ar-H), 4.07-4.04 (t, 2H, ^3J6.56Hz, Ar-O-CH_2-), 1.86-1.79 (quin, 2H, ^3J7.0Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.49-1.27 (m, 18H, 9 x -CH_2-), 0.90-0.87 (t, 3H, ^3J6.64Hz, -CH_3).

4-Trifluoromethylphenyl-4-[3-{4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy}benzoyloxy] benzoate, 4.E.2

Yield, 79%; m.p. 146.5°C; ν_{max}: 3080, 2916, 2851, 1744, 1734, 1609, 1261, 1163, 1061 cm^{-1}; δ_H: 8.32-8.29 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.73-7.71 (d, 2H, ^3J8.64Hz, Ar-H), 7.65-7.61 (t, 1H, ^3J8.0Hz, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.42-7.36 (m, 6H, Ar-H), 7.0-6.98 (d, 2H, ^3J8.88Hz, Ar-H), 4.07-4.04 (t, 2H, ^3J6.52Hz, Ar-O-CH_2-), 1.86-

1.79 (quin, 2H, ^3J7.04Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.50-1.26 (m, 22H, 11 × -CH$_2$-), 0.90-0.87 (t, 3H, ^3J6.6Hz, -CH$_3$).

4-Trifluoromethylphenyl-4-[3-{4-(4-*n*-hexadecyloxybenzoyloxy)benzoyloxy}benzoyloxy] benzoate, 4.E.3

Yield, 73%; m.p. 144.0°C; ν_{max}: 3080, 2916, 2851, 1746, 1732, 1611, 1261, 1163, 1061 cm^{-1}; δ_H: 8.32-8.29 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.73-7.71 (d, 2H, ^3J8.6Hz, Ar-H), 7.65-7.61 (t, 1H, ^3J7.92Hz, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.42-7.36 (m, 6H, Ar-H), 7.0-6.98 (d, 2H, ^3J8.8Hz, Ar-H), 4.07-4.04 (t, 2H, ^3J6.52Hz, Ar-O-CH$_2$-), 1.86-1.79 (quin, 2H, ^3J7.0Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.50-1.26 (m, 26H, 13 ×-CH$_2$-), 0.89-0.86 (t, 3H, ^3J6.52Hz, -CH$_3$).

4-Trifluoromethylphenyl-4-[3-(4-(4-*n*octadecyloxybenzoyloxy)benzoyloxy}benzoyloxy] benzoate, 4.E.4

Yield, 73%; m.p. 141.0°C; ν_{max}: 3080, 2916, 2851, 1744, 1736, 1732, 1607, 1261, 1163, 1061 cm^{-1}; δ_H: 8.32-8.29 (m, 4H, Ar-H), 8.17-8.09 (m, 4H, Ar-H), 7.73-7.71 (d, 2H, ^3J8.52Hz, Ar-H), 7.65-7.61 (t, 1H, ^3J8.04Hz, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.42-7.36 (m, 6H, Ar-H), 7.0-6.98 (d, 2H, ^3J8.96Hz, Ar-H), 4.07-4.04 (t, 2H, ^3J6.56Hz, Ar-O-CH$_2$-), 1.86-1.79 (quin, 2H, ^3J7.0Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.50-1.26 (m, 30H, 15 x -CH$_2$-), 0.89-0.86 (t, 3H, ^3J6.68Hz, -CH$_3$).