Chapter-5

Synthesis and mesomorphic properties of

(i) **4-*n*-Alkoxyphenyl-4-[3-{4-(4-cyanobenzoyloxy)benzoyloxy}benzoyloxy] benzoates**

Series -5.1

(ii) **4-*n*-Akoxyphenyl-4-[3-{4-(4-nitrobenzoyloxy)benzoyloxy}benzoyloxy] benzoates**

Series -5.11

(iii) **4-n-Hexadecyloxyphenyl-4-[3-{4-(4-nitrobenzoyloxy)-2-fluorobenzoyloxy} benzoyloxy]benzoate**

Compound 5.C.1

(iv) **4-*n*-Hexadecyloxyphenyl-4-[3-{4-(4-nitrobenzoyloxy)-3-fluorobenzoyloxy} benzoyloxy]benzoate**

Compound 5.D.1

(v) **1-[(4-*n*-Dodecyloxybenzoyloxy)-4-benzoyloxy)]phenylene-3-[(4-cyanoenzoyloxy) -4-benzoate]**

Compound 5.E.1

(vi) **1-[(4-*n*-Dodecyloxybenzoyloxy)-4-benzoyloxy)]phenylene-3-[(4-nitrobenzoyloxy) -4-benzoate]**

Compound 5.F.1

(vii) **1-[(4-*n*-Dodecyloxylbenzoyloxy)-4-benzoyloxy)]phenylene-3-[(4-cyanobiphenyl-carbonyloxy)-4-benzoate]**

Compound 5.G.1

(viii) **1-[(4-*n*-Dodecyloxylbenzoyloxy)-4-benzoyloxy)]phenylene-3-[(4-cyanobiphenyl-carbonyloxy)-2-fluoro-4-benzoate]**

Compound 5.H.1

(ix) **1-[(4-*n*-Dodecylbenzoyloxy)-4-benzoyloxy)]phenylene-3-[(4-cyanobiphenyl-carbonyloxy)-3-fluoro-4-benzoate]**

Compound 5.I.1

Introduction

Conventional smectic phases such as SmA and SmC are formed by the orthogonal and tilted arrangements of molecules respectively in the layers. SmA phase belongs to point group $D_{\infty h}$ and is uniaxial, whereas SmC phase belongs to point group C_{2h} and is biaxial.

In general, uniaxiality and biaxiality can be pictorially represented as shown in figure **5.1**.

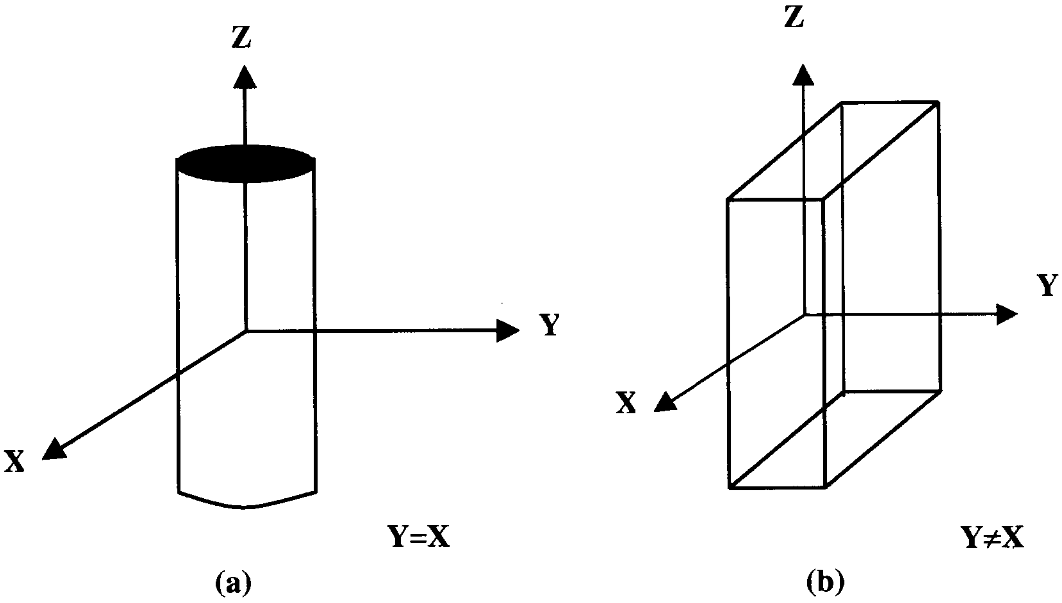


Figure 5.1: Pictorial representation of (a) uniaxial object; (b) biaxial object.

In the case of a uniaxial medium two principal indices of refraction are identical, whereas in the case of a biaxial medium all the three indices of refraction, which are perpendicular to each other, are different.

It was de Gennes [85] who predicted a smectic phase with D_{2h} symmetry and called it a C_{M}, phase where M refers to McMillan [86, 87]. Later Brand *et* al. [88] suggested that C_M phase (biaxial smectic phase) could be realized in systems containing board-like molecules and they predicted distinguishing optical textures based on symmetry arguments. According to them nematic phase has a rotational symmetry with a preferred direction denoted by a director **n.**

In smectic A phase, a layered state, the layer normal is a unit vector p and is indistinguishable from –**p**. In the plane of its layers the director (n) is parallel to layer normal **(p)**.

In conventional smectic C phase the director (n) is at a constant tilt angle to the layer normal (p). The projection of director on layer plane is denoted by vector c. The smectic C phase ground state is invariant unless the two symmetry operations p to –**p** and c to –**c** are performed simultaneously.

In the biaxial smectic (C_M) phase because of the absence of tilt, n is parallel to p. The in-plane preferred direction is characterized by director m and is perpendicular to p. The ground state remains unchanged during a change over from p to –**p** and m to –m. A pictorial representation of molecules in smectic **A,** C and C_M phases are shown in figure 5.2 (a), (b) and (c) respectively.

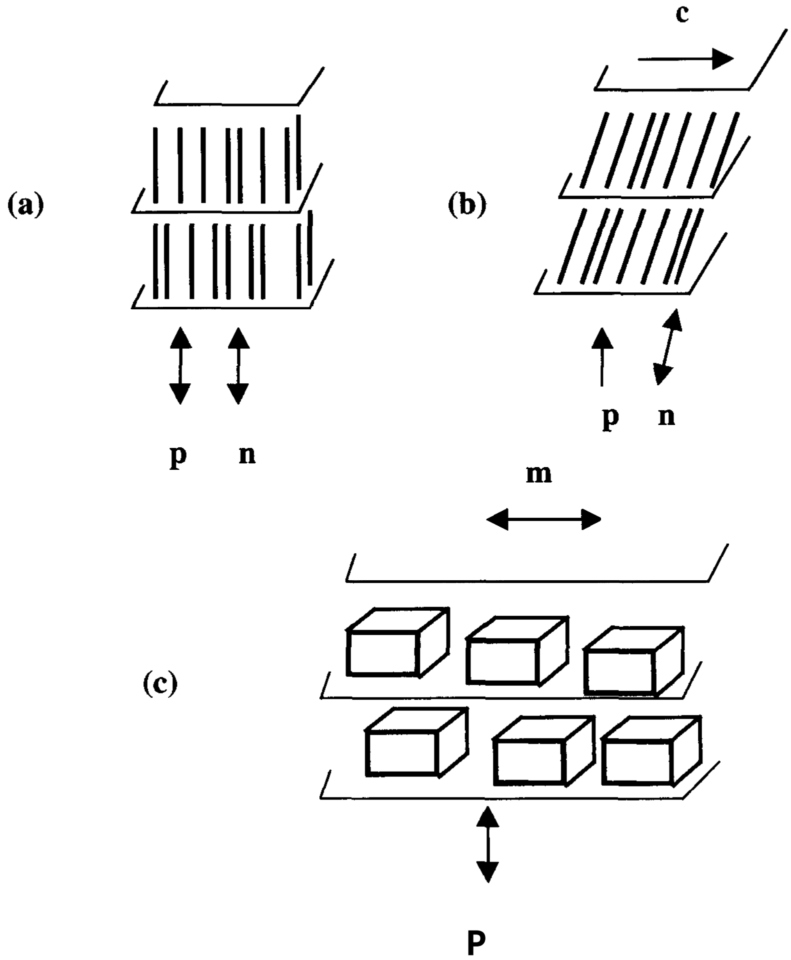


Figure 5.2: Schematic representation of layer normal (p), molecular director (n), projection of molecular director (c), in-plane director (m), for the (a) SmA, (b) **SmC** and (c) $\mathbf{C_M}$ mesophases (after Brand et al. **[88]).**

Defect textures in nematic and smectic phases under a polarizing microscope

The commonly observed textures in nematic and smectic phases are defect textures and /or focal-conic textures and can be explained as follows. In the nematic phase, because of equivalency of **p** and –**p** both ± ½ and ± 1strength defects are observed. Similarly in the case of biaxial smectic phase **p** = -**p** and **m** = -**m** and hence ± ½ and ± 1strength defects are observed.

In the conventional smectic C phase because of unequivalency due to π rotation, ± ½ strength defects are absent and only ± 1 strength defects (equivalency due to 2π rotation) are observed. However, ± ½ strength defects are observed in smectic C phase only when the molecules in the adjacent layers are arranged in an antiferroelectric order and can be explained as arising due to dispirations [78, 82].

Another feature of smectic phases is observation of focal-conic texture. The important property of focal-conics is that they conserve microscopic layer spacing when the layers are curved. Since the curvature energy is less and hence the most probable texture for smectic mesophases. The focal-conic textures of smectic **A** become broken focal-conic at a transition to the smectic C phase. This is to accommodate the mismatch in the layer spacings at the transition. Since **m** = -**m** and no tilt in the biaxial smectic phase, no change in the focal-conic texture will be observed at the transition from uniaxial smectic phase to a biaxial smectic phase.

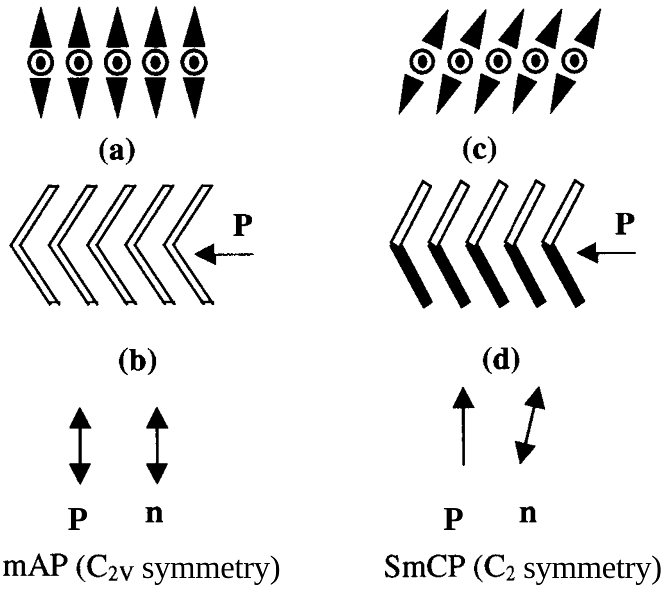


Figure 5.3: Schematic representation of bent-core molecules in (a) biaxial smectic A phase (front view); (b) side view; (c) biaxial smectic C phase (front view); (d) side view.

Compounds composed of banana or bent-core molecules are biaxial in nature due to their intrinsic shape. There are two possibilities for bent-core molecules to arrange themselves in the layers and are shown in figure 5.3.

A brief account of experimental observations of a biaxial smectic A phase.

The first experimental observation of a biaxial smectic A phase was provided by Leube and Finkelmann [89] in a mixture of liquid crystalline side chain polymer and a low molar mass compound. Mixtures with up to 50 mol % of the low molar mass compound show a biaxial nematic phase. On lowering the temperature from biaxial nematic phase, a biaxial smectic A phase was observed. The biaxiality of this smectic phase was confirmed from conoscopic experiments.

The first experimental demonstration of a biaxial smectic A phase in low molar mass compounds was given by Pratibha *et* al. [91] in a mixture of bent-core and a lath-like compound. The bent-core compound showed a smectic antiferroelectric B_2 phase, while the lath-like compound showed a bilayer smectic A (SmA_2) phase. The binary phase diagram involving the above two compaunds reveal a new mesophase (biaxial smectic A_2) at a concentration of 4-13 mol% of the bent-core compound. On lowering the temperature from uniaxial smectic A (SmA_2) phase to a biaxial smectic A (SmA_{2b}) phase, orientational transition of bent-core molecules occurs with the director being orthogonal to the rod-like molecules. The observation of a schlieren texture with both ± ½ and ± lstrength defects with strong fluctuations is a characteristic feature of the biaxial smectic (SmA_{2b}) mesophase.

An unambiguous proof for the existence of a biaxial smectic A phase was provided in a mixture of a metallomesogen and 2, 4, 7-trinitrofluorenone (TNF) [90]. The binary phase diagram explains the observed biaxial smectic phase with 20 mol % of TNF. The face-face interaction between the electron rich metallomesogen and an electron deficient TNF results in a reduction of free rotation of the molecules and hence the observation of biaxial smectic A phase on lowering the temperature from a uniaxial smectic A phase. The schlieren texture of the biaxial smectic A consisted of only ± ½ strength defects and was in agreement with the theoretical prediction of the McMillan phase.

There was also a claim for the observation of a biaxial smectic A phase in an oxadiazole derivative, where the constituent molecules are boomerang in shape [92].

It would not be out of place to mention here that Prehm ***et** al.* [93] have observed a biaxial smectic A phase in some rod-like bolaamphiphiles containing a long semiflourinated chain.

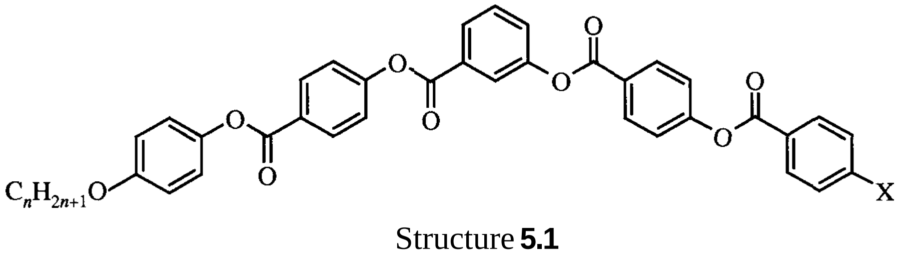
Recently from our laboratory, the synthesis and characterization of the mesophases exhibited by several unsymmetrical compounds composed of strongly polar molecules have been reported [75, 76]. Many of these exhibit the biaxial smectic A phase. Very recently it was shown that the biaxial smectic A phase reported earlier is actually a polar partially bilayer biaxial smectic A (SmA_dP_A) phase [77].

Sufficient experimental proof for a biaxial smectic A phase showing antiferroelectric characteristics has been provided by Eremin ***et** al.* [94] in compounds derived from 4-cyanoresorcinol and containing a fluorine substituent *ortho* to the *n*-alkoxy chain. The mesophase has C_{2V} symmetry and the molecules are arranged in an orthogonal fashion with antiferroelectric ordering of the molecules in adjacent layers.

Schroder ***et** al.* [95] also reported a polar biaxial smectic A phase in a mixture of a bent-core compound and TNF. The obtained mesophase sequence was uniaxial smectic A phase, polar biaxial smectic A phase and a B_2 phase on cooling the isotropic phase.

The design and synthesis of unsymmetrical compounds exhibiting mesophases have not been explored thoroughly, particularly compounds containing only one terminal chain and a small substituent at the other end.

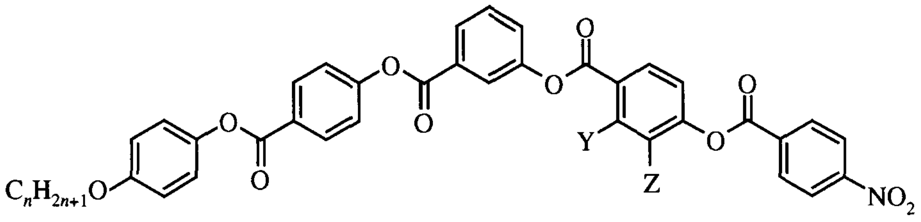
In this chapter, the synthesis and characterization of several unsymmetrical compounds derived from 3-hydroxybenzoic acid as well as 1, 3-dihydroxybenzene are described. These compounds have only one terminal chain while the other end is substituted with a strongly polar cyano or a nitro group. The unsymmetrical compounds described here have the general molecular structures **5.I-5.III** shown below.



Structure **5.1**

X= CN   *n*=8,10,12,14,16,18   Series- **5.1**

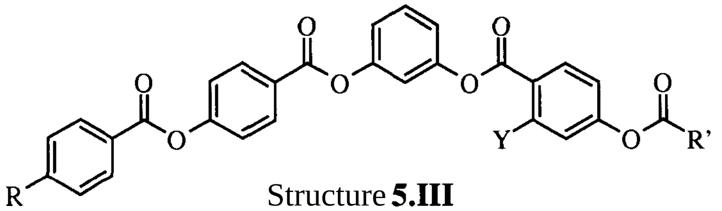
X= NO_2 *n*=8,10,12,14,16,18   Series- **5.11**



Structure 5.11

n=16 Y=F, Z=H compound -5.C.1

n=16 Y=H, Z=F compound -5.D.1



Structure **5.III**

R= n-$C_{12}H_{25}O$ /n-$C_{12}H_{25}$; Y= H / F

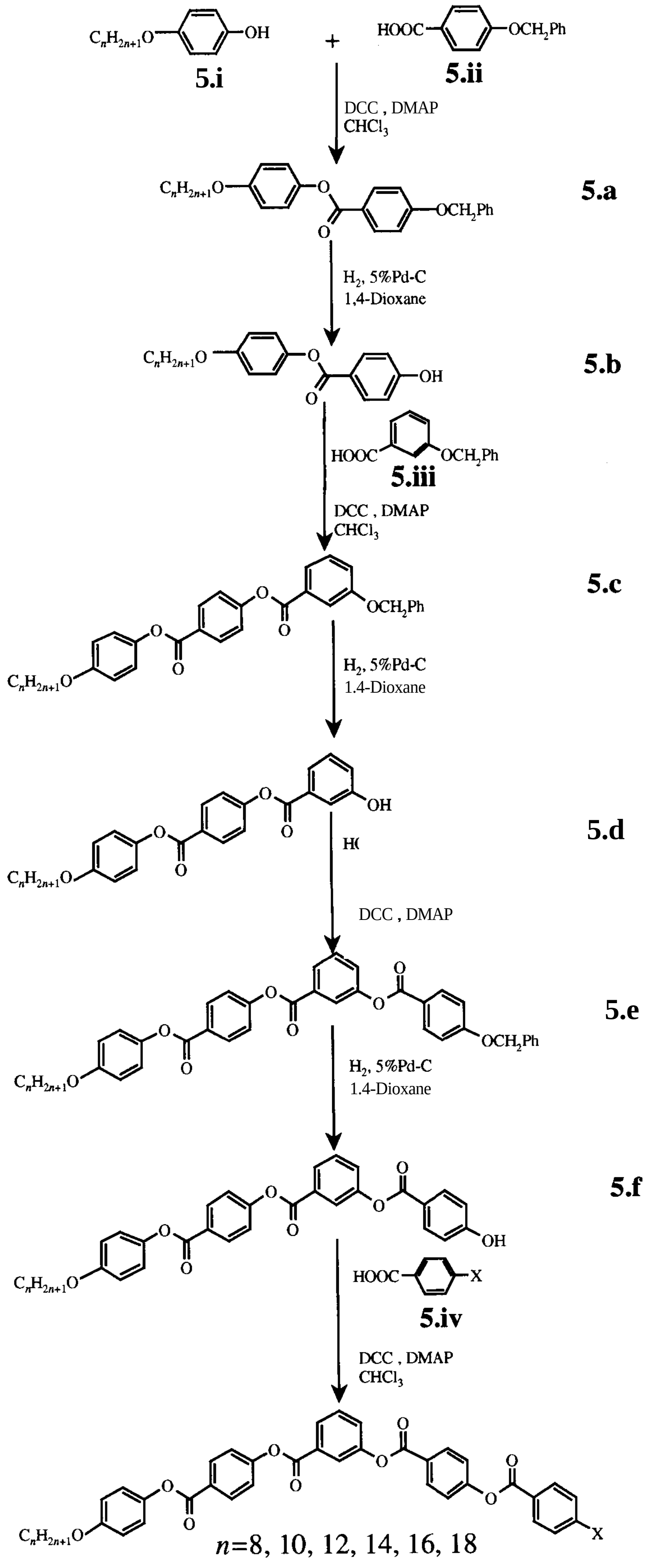
R' = cyanophenyl / **nitrophenyl/** cyanobiphenyl; compounds; **5.E.1-5.I.1**

Synthesis

In general, the target compounds were prepared from either 3-hydroxybenzoic acid or 1, 3-dihydroxybenzene by a series of esterification reactions using DCC and the deprotection reaction using catalytic hydrogenolysis.

Compounds of series 5.1 and 5.11, derived from 3-hydroxybenzoic acid were prepared following the pathway shown in scheme 5.1. Compounds **5.C.1** and 5.D.1 were prepared following a pathway shown in scheme 5.2. However, the unsymmetrical compounds 5.E.1 to **5.I.1** were obtained from resorcinol, following the pathway shown in scheme 5.3.

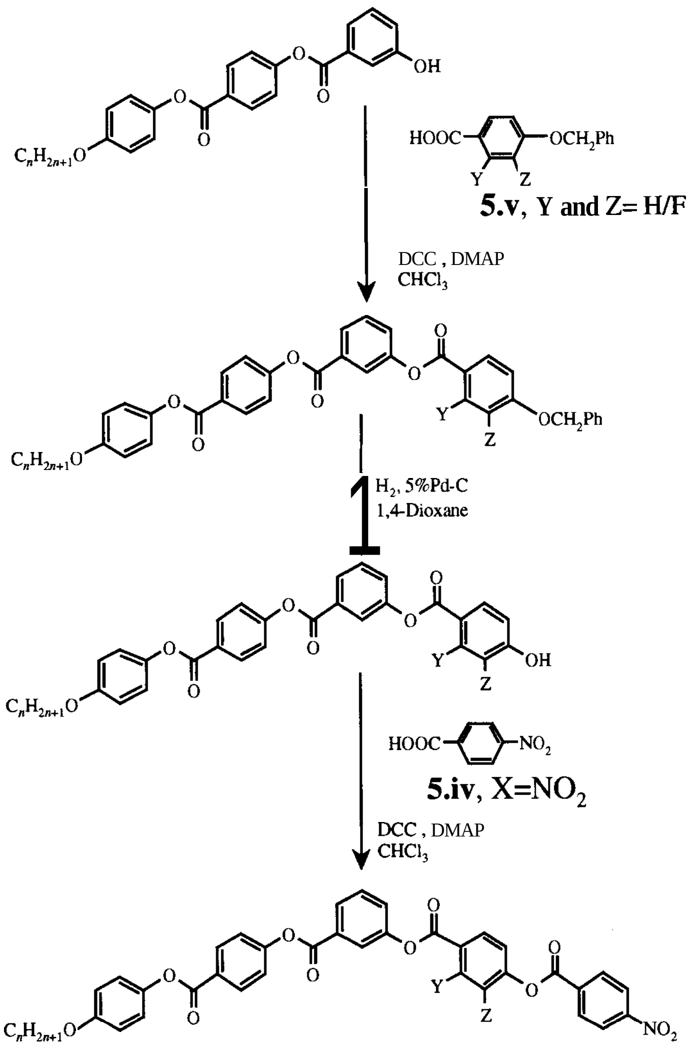
4-n-Alkoxyphenols were prepared by monoalkylation of quinol with appropriate n-alkylbromides in the presence of anhydrous potassium carbonate. 4-Benzyloxybenzoic acid, 3- benzyloxybenzoic acid, **2-fluoro-4-benzyloxybenzoic** acid and 3-fluoro-4-benzyloxy-benzoic acid were synthesized according to procedures described in the literature [59-61]. 3-Benzyloxyphenol was prepared according to a procedure described in the literature [104]. 4-Cyano-, 4-nitro-benzoic acids and benzyl-4-hydroxybenzoate were commercial compounds and used without further purification. 4-Cyanobiphenyl-4-carboxylic acid was prepared according to a procedure described in the literature [97].



$X=NO_2$ or CN

Structure 5.1

Scheme 5.2: Synthetic pathway used to prepare the bent-core compounds of series 5.1 and 5.11.

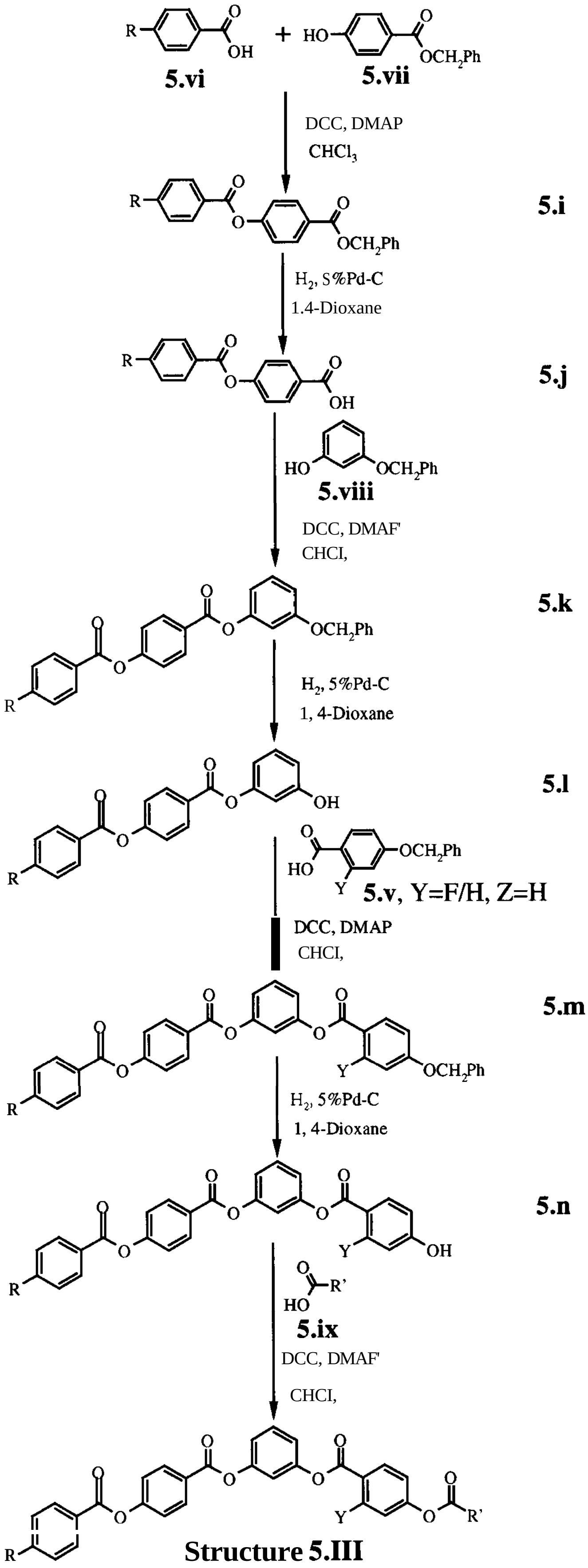


Structure 5.II

n=16 Y=F, Z=H compound- **5.C.1**

n=16 Y=H, Z=F compound- **5.D.1**

Scheme 5.2: Synthetic pathway used to prepare the bent-core compounds 5.C.1 and 5.D.1.



Structure 5.III

R= n-$C_{12}H_{25}O$ / n-$C_{12}H_{25}$; Y= H / F

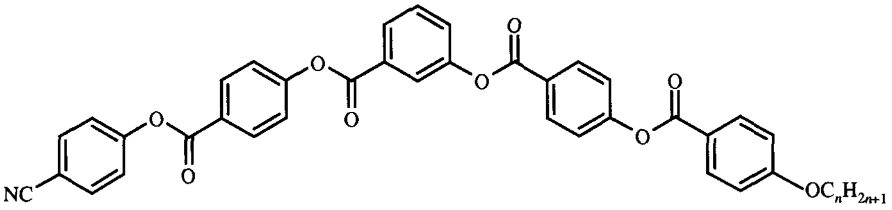
R' = cyanophenyl / nitrophenyl / cyanobiphenyl;compounds; **5.E.1-5.I.1.**

Scheme 5.3: Synthetic pathway used to prepare the bent-core compounds derived from resorcinol (compounds 5.E.1-5.I.1).

Results and discussion

The transition temperatures and the associated enthalpies for the unsymmetrically substituted bent-core compounds derived from 3-hydroxybenzoic acid and containing a cyano terminal group (series 5.1) are summarized in table 5.1. Compounds 5.A.1-5.A.3 are non-mesomorphic, compounds 5.A.4 and 5.A.5 are monotropic mesomorphic and compound 5.A.6 shows an enantiotropic mesophase. All these compounds exhibit the same type of mesophase. When a sample of any of these is cooled slowly from the isotropic phase, both homeotropic regions as well as focal-conic domains could be seen which are typical features of uniaxial smectic A phase. The mesophase structure was confirmed from XRD studies on non-oriented samples. Two reflections in the small angle region indicated that the mesophase was smectic. The wide-angle diffuse peak confirms the fluidity of the mespohase. The d-spacing of first order layer reflection (d= 68.7Å) was more than the measured molecular length (L) by considering the n-alkoxy chain in a fully extended all trans conformation (L=52.4Å) and less than double (2L) and hence the mesophase was assumed to have a partial bilayer structure. The obtained d-spacings for compound **5.A.6** are given in table 5.5.

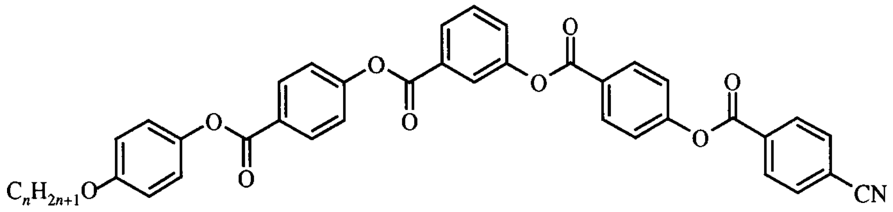
It was reported that a homologous series compounds **1g** [76] show two types of mesophases which were characterized as uniaxial smectic A phase with a partial bilayer structure (SmA_d) and a partial bilayer biaxial smectic A (SmA_{db}) phase. This SmA_{db} phase has now been established as a polar phase with antiferroelectric characteristics [77, 96] and has been designated as SmA_dP_A. The compounds of series 5.1 and **1g** are isomeric in which the position of the terminal cyano and the n-alkoxy chains are interchanged.



1g [76]

A comparison of the mesomorphic properties of these two isomeric series of compounds clearly indicate that reversing the polarity of the ester linkage group has a profound effect of increasing the melting points substantially and destabilizing the occurrence of the biaxial smectic A phase.

Table 5.1: Transition temperatures (°C) and the associated enthalpy values (kJ mol^{-1}) for compounds of series 5.1

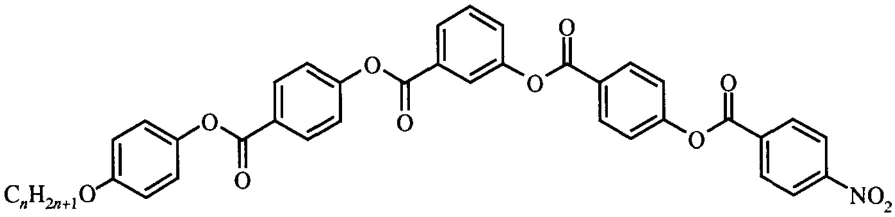


Compound	n	Cr		SmA$_d$		I
5.A.1	8	•	172.0 *66.2*	-		
5.A.2	10	•	158.0 *89.0*	-		
5.A.3	12	•	156.5 *97.2*	-		
5.A. 4	14	•	158.0 *94.3*	(•	154.5) *5.10*	•
5.A.5	16	•	161.5 *78.0*	(•	161.0) *5.56*	•
5.A.6	18	•	161.0 *74.2*		165.0 *5.96*	•

Key: Cr: crystalline phase, SmA$_d$: partial bilayer smectic A phase, SmA$_d$P$_A$: partial bilayer biaxial antiferroelectric smectic A phase, I : isotropic phase, ( ): phase is monotropic.

In the case of compounds of series 5.11, where the terminal cyano group of series 5.1 has been replaced by a nitro group, there is considerable reduction in the melting points. As can be seen in table 5.2, compounds 5.B.1 and 5.B.2 are non-mesomorphic while compound **5.B.3** has a metastable mesophase. Compounds **5.B.4** to 5.B.6 exhibit two mesophases, which were detected both under a polarizing microscope and DSC thermograms. A DSC thermogram obtained for compound 5.B.6 is shown in figure 5.4. Although the clearing enthalpy is quite high that of the mesophase-mesophase transition is rather small and is about 0.1 kJ mol^{-1}.

Table 5.2: Transition temperatures (°C) and the associated enthalpy values (kJ mol^{-1}) for compounds of series 5.11



Compound	*n*	Cr		SmA_dP_A		SmA_d		I
5.B.1	8	•	145.0 *43.0*	-		-		
5.B.2	10	•	143.5 *43.9*	-		-		
5.B.3	12	•	145.0 *47.0*	-		(•	144.0) *3.49*	•
5.B.4	14	•	146.5 *52.9*	(•	145.8) *0.12*		153.0 *4.66*	•
5.B.5	16	•	145.0 *60.0*		149.0 *0.13*		160.5 *5.15*	
5.B.6	18	•	144.0 *65.7*		151.0 *0.10*		166.0 *5.74*	•

When a thin film of a sample of compound **5.B.6** was sandwiched between two untreated glass plates and cooled from the isotropic phase and observed under a polarizing microscope, both homeotropic as well as focal-conic regions could be seen. This mesophase has been identified as a uniaxial smectic A phase with a partial bilayer structure (from XRD studies). On cooling the sample further to a temperature of 150°C, no significant change in the texture was seen. However, when the sample was taken in a cell treated for homogeneous alignment and viewed as above, small change in the focal-conic texture could be seen at the phase transition (150.5°C). The optical photomicrographs of these two mesophases obtained in a cell treated for homogeneous alignment are shown in figure **5.5** **(a)** and **(b)** respectively.

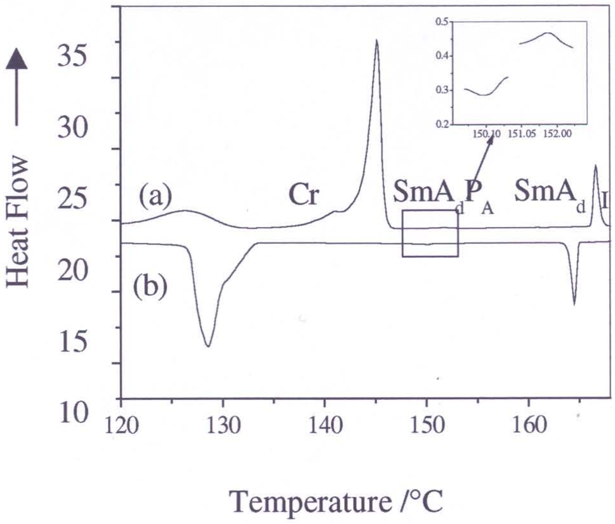


Figure 5.4: A DSC thermogram obtained for compound 5.B.6 showing phase transitions: (a) heating cycle; (b) cooling cycle; rate 5°C $\mathbf{min^{-1}}$; inset shows expanded region of transition from a uniaxial smectic A to a polar biaxial smectic A phase.

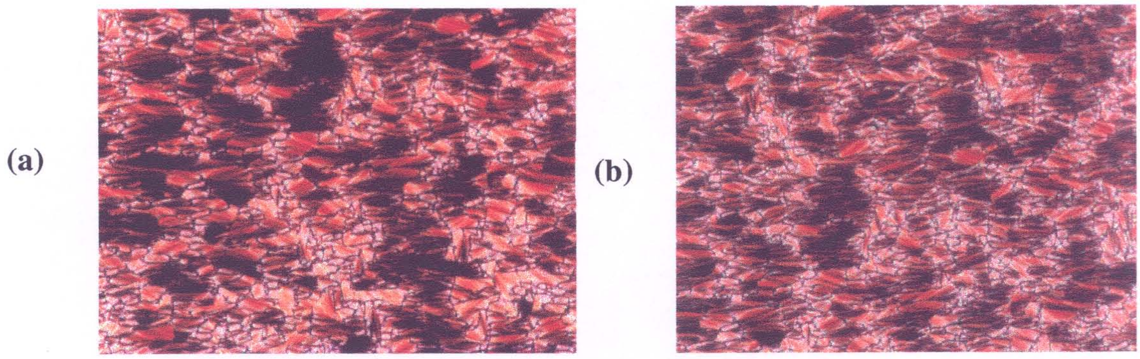

(a)
(b)

Figure 5.5: Optical photomicrographs of (a) uniaxial smectic A phase and (b) biaxial smectic A phase obtained for compound 5.B.6 in a homogeneously aligned cell.

Interestingly, when this compound **5.B.6** was taken in a cell treated for homeotropic alignment and cooled from the isotropic phase, the dark regions of the uniaxial smectic A phase transform to a schlieren texture at the transition to the biaxial smectic A phase. The schlieren texture showed both two- and four-brush strength defects. A photomicrograph of this schlieren texture is shown in figure **5.6**.

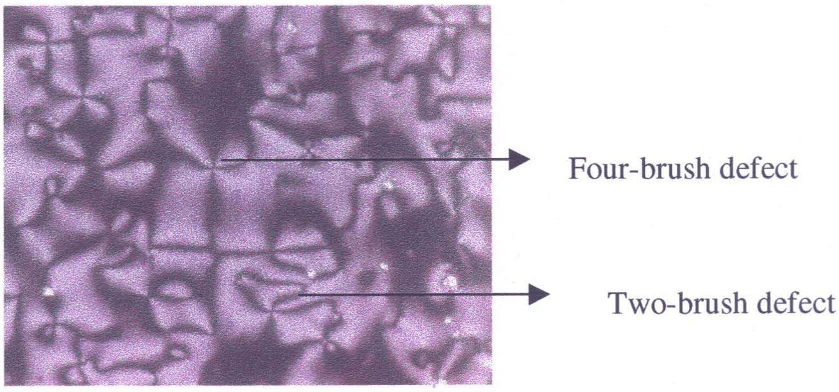


Figure 5.6: Optical photomicrograph of a schlieren texture (showing both two- and four-brush strength defects) of biaxial smectic A phase obtained for compound 5.B.6 in a homeotropically aligned cell.

These optical textures can be attributed to i) an anticlinic smectic C phase or ii) an antiferroelectric smectic phase. Based on XRD studies and electro-optical investigations (described later) it was characterized that the mesophase is a partial bilayer antiferroelectric smectic A (SmA_dP_A) phase.

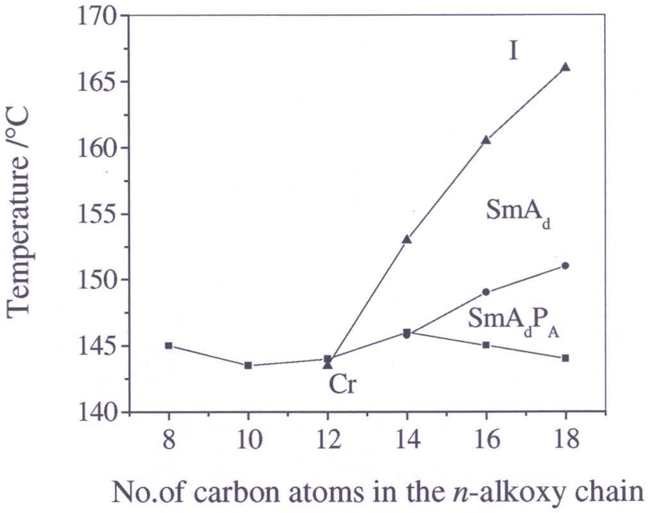


Figure 5.7: A plot of transition temperatures as a function of the *n*-alkoxy chain length for compounds of series 5.II.

A plot of transition temperatures as a function of the n-alkoxy chain length for compounds of series **5.11** is shown in figure **5.7.** As can be seen the clearing transition points rise sharply as compared to the SmA_d to the SmA_dP_A phase transition curve.

To confirm the mesophase structure detailed XRD studies were carried out. Unoriented samples in Lindemann capillaries were used for investigations. For all the compounds investigated two reflections could be seen in the small angle region, which are in the ratio of 1:1/2 suggesting a smectic ordering of the mesophases. The second order reflection is weak suggesting a disordered smectic arrangement of the molecules. In addition, the diffuse scattering in the wide-angle region with a maxima around 4.7Å confirms the fluid-like in-plane order for the mesophases. The layer spacing (d) values obtained for the mesophases of various compounds and the measured molecular length (L) in their most extended form with an all ***trans*** conformation of the terminal n-alkoxy chain are given in table **5.5.** As can be seen in this table, the obtained **d** value for the first order reflection is more than the calculated value of L. Hence the possibility of the lower temperature biaxial phase being a smectic C phase was ruled out. The molecules of these compounds containing a strongly polar terminal substituent organize themselves to be in an antiparallel configuration to compensate for the dipolar interactions. Thus, the antiparallel configuration results in a value for d, which is greater than L but less than 2L. Hence these phases have a partial bilayer structure. It was also found that the layer spacing is independent of the temperature in the two smectic phases. The X-ray angular intensity profile obtained for compound **5.B.6** in the SmA_dP_A phase is shown in figure **5.8.**

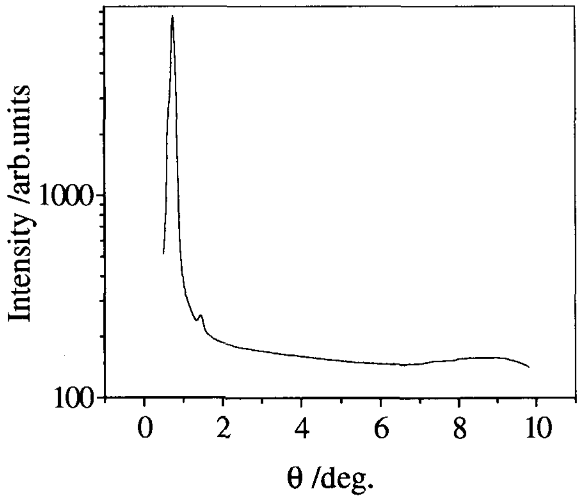
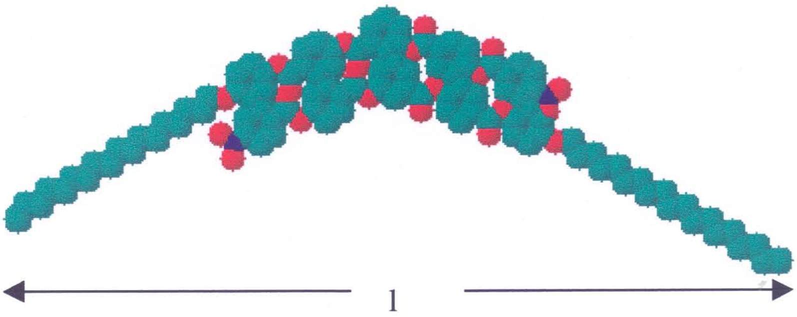


Figure 5.8: An X-ray angular intensity profile obtained for the mesophase of compound 5.B.6 showing smectic characteristics.

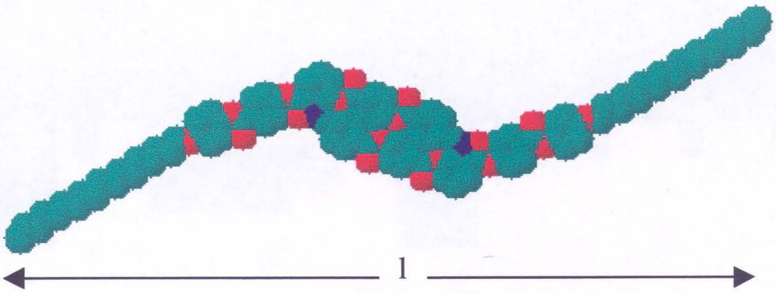
In the case of the nitro substituted compounds, the obtained d value was 59.2 Å and the measured molecular length L is 52.3 Å. The dimeric molecules will then have a configuration as shown in figure **5.9**. In this dimeric system, the molecular length l is 69.8Å, which accounts not only for the experimentally obtained layer spacing but also the lower temperature antiferroelectric biaxial smectic A_d phase. Similar conformations of the *n*-alkoxy chains were considered by Eremin *et al.* [94] and Schroder *et al.* [95] for the systems studied by them.



Compound **5.B.6**: Measured length l= 69.8Å, experimentally obtained d= 59.2Å

Figure 5.9: A space filling model showing the antiparallel arrangement of molecules (dimeric) for compound 5.B.6.

It is interesting to note that the compounds containing a terminal cyano substituent exhibit only one mesophase whereas the analogous nitro substituted compounds show two mesophases. A possible explanation based on XRD studies is as follows. In the case of compound **5.A.6**, the length of the individual molecule L is 52.4Å, while the experimentally obtained value for d is 68.7Å. If one assumes a conformation as shown in figure **5.10** for an antiparallel configuration, then the measured length, l=81Å. Since the chains are fairly long, it is possible to have *gauche* conformations and hence a reduced experimental value. This arrangement of the dimeric molecules also accounts for the occurrence of only the SmA_d phase.



Compound **5.A.6**: Measured length l= 81Å, experimentally obtained d= 68.7Å

Figure 5.10: A space filling model showing the antiparallel arrangement of molecules (dimeric) for compound 5.A.6.

Conoscopy is a useful technique for ascertaining whether a mesophase is uniaxial or biaxial in nature. The conoscopic experiments were carried out on the mesophases exhibited by these compounds. For this experiment, fairly well aligned samples were used and this was achieved as follows. A cell was constructed in which one of the glass plates was coated with ITO for electrical conduction with a gap of 1 mm that was etched out. The other plate was an ordinary glass plate and the inner surfaces of both the plates were treated with octadecyltriethoxysilane, which facilitates a homeotropic alignment of the smectic A liquid crystal. The thickness of the cell was 35μm, which was controlled by using appropriate spacers. A sample of compound **5.B.6** was filled in the above cell and conoscopic observations were made between the crossed polarizers which were set at 45° to the direction of the electric field (190V, 10 kHz). Typical uniaxial pattern was observed in the high temperature smectic A phase. On lowering the temperature to 150.5°C, the isogyres began to split to give the biaxial pattern. On reducing the temperature further the isogyres go out of the field of view. The optical photomicrographs showing the patterns obtained in the uniaxial smectic A (figure **5.11 (a)**) and biaxial smectic A phases for compound **5.B.6** are shown in figure **5.11 (b)** and **(c)** respectively.

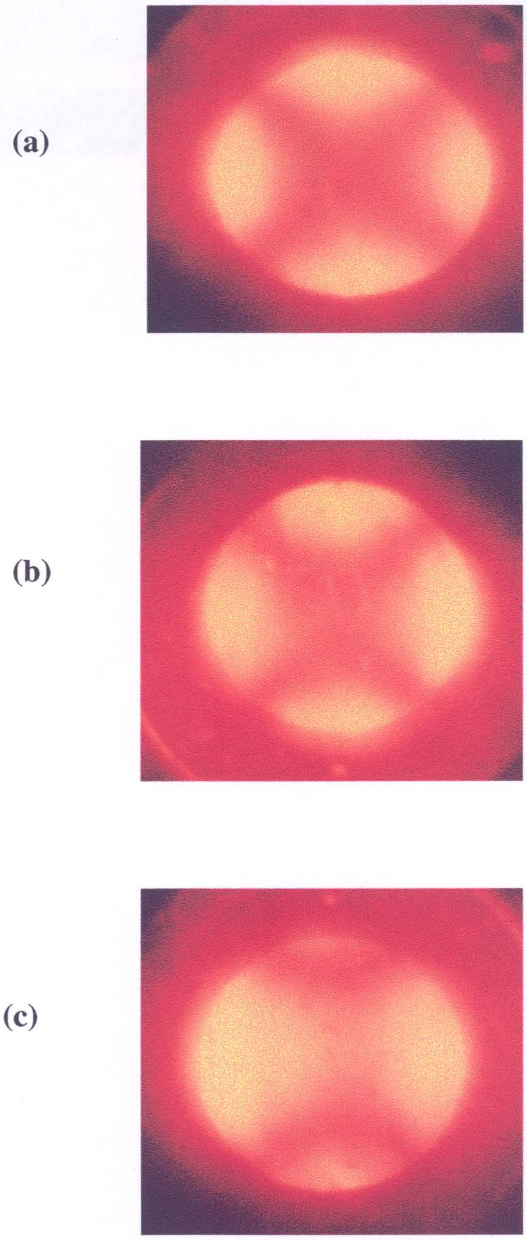
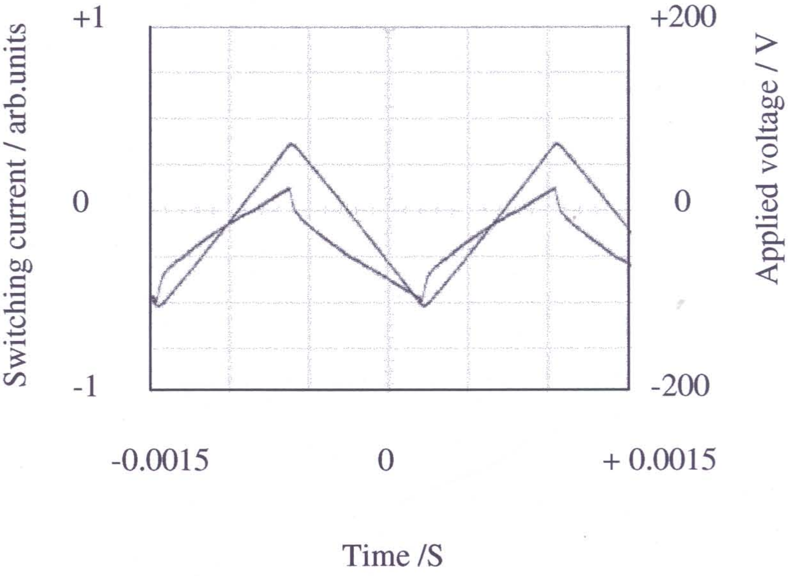


Figure 5.11: Conoscopic patterns obtained for the mesophase of compound 5.B.6, (a) uniaxial smectic A phase at 154°C; (b) and (c) biaxial smectic A phase at 150.5°C and 150.2°C respectively.

In order to examine the electro-optical switching behaviour of the mesophases in these unsymmetrically substituted compounds, triangular-wave electric field experiments were carried out. A sample of compound **5.B.6** in the isotropic phase was filled in a cell of thickness 14μm, which was constructed for aligning the sample homogeneously. When this sample was cooled slowly under a triangular-wave electric field no polarization current peaks were observed even at high voltages in the uniaxial smectic A phase over the entire mesophase range. However, on cooling the sample further to a temperature of 150°C, two polarization current peaks for each half cycle could be obtained at a threshold of 150V_{pp}. This indicates that the lower temperature mesophase has an antiferroelectric ground state structure. The electro-optical current response trace obtained in the SmA_d phase is shown in figure **5.12** **(a)** and the corresponding optical texture obtained is shown in figure **5.12 (b)**.

(a)



(b)

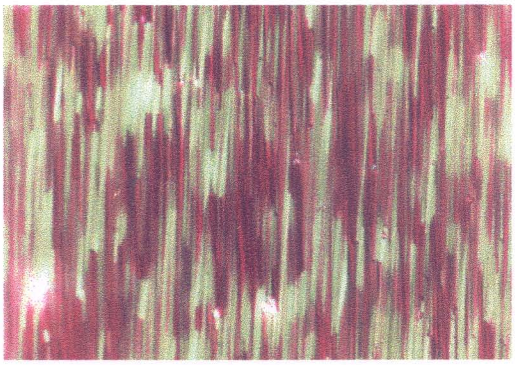


Figure 5.12(a): The switching current response trace obtained for compound 5.B.6 by applying a triangular-wave electric field (192 V_{pp}, frequency 600 Hz) in the uniaxial smectic A phase; cell thickness 14μm. (b) An optical photomicrograph of the mesophase obtained under the above conditions.

The electro-optical current response trace obtained in the SmA_dP_A phase is shown in figure **5.13(a)** and the corresponding optical texture obtained is shown in figure **5.13 (b)**. The saturated polarization value obtained by integrating the area under the curve is about 190 nC cm^{-2}. No optical switching could be observed because of the absence of layer chirality. However, a small change in the form of a smooth focal-conic texture could be observed.

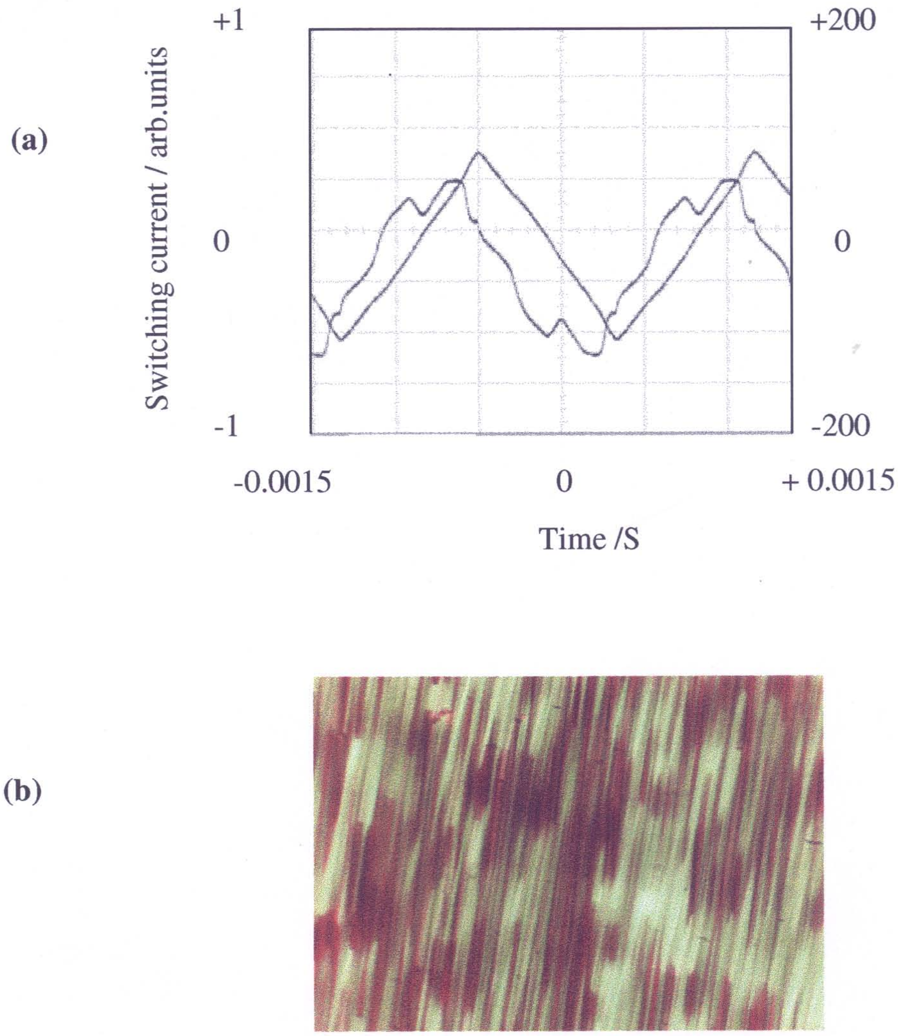
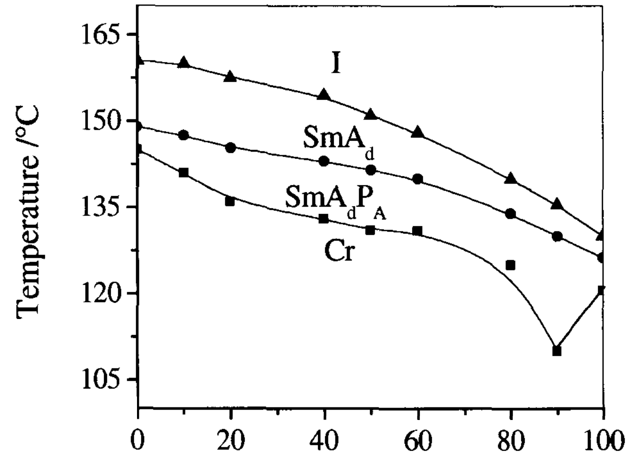


Figure 5.13 (a): The switching current response trace obtained for compound 5.B.6 by applying a triangular-wave electric field (192 V_{pp}, frequency 600 Hz) in the biaxial smectic A phase; cell thickness 14μm; saturated polarization is about 190 nC cm^{-2}.
(b) An optical photomicrograph of the mesophase obtained under the same conditions.

To confirm the identity of the two mesophases observed in these compounds, miscibility studies were carried out between compound **5.B.5** and the well studied compound 4-cyanophenyl-4-{3-[4-(4-*n*-tetradecyloxybenzoyloxy)3-fluorobenzoyloxy]benzoyloxy} benzoate], **li14** [76]. This reference compound has the following sequence of transitions: Cr 120.5°C SmA$_d$P$_A$ 126.2°C SmA$_d$ 130.0°C I. Though this reference compound was reported to be apolar, it has now been established as a polar phase with antiferroelectric characteristics [77]. The binary phase diagram obtained for these two compounds is shown in figure **5.14.** It can be clearly seen from this phase diagram that the two phases of compound **5.B.5** are completely miscible with the mesophases of the standard material over the entire composition range indicating that the two mesophases are the same. In other words, the mesophases exhibited by compound **5.B.5** are SmA$_d$ and SmA$_d$P$_A$ phases as the temperature is lowered from the isotropic phase.

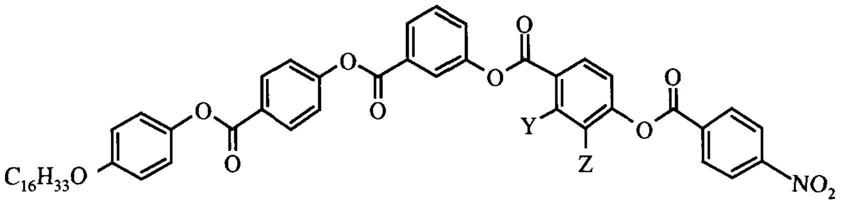


Compound **5.B.5** Wt. % Compound **li14**

Figure 5.14: Binary phase diagram obtained for a mixture of compound 5.B.5 and a reference compound li14 [76].

The introduction of a lateral fluorine substituent on one of the arms containing a strongly polar terminal nitro group has a detrimental effect on the mesophases. For example, the transition temperatures of compounds **5.B.5** (table **5.2**), **5.C.1** and **5.D.1** (table **5.3)** are compared. The parent compound **5.B.5** shows enantiotropic SmA$_d$P$_A$ and SmA$_d$ phases, while in compound **5.C.1,** which has a fluorine substituent *ortho* to the carbonyl group, both the mesophases get eliminated. However, in compound **5.D.1**, though the $\mathrm{SmA_dP_A}$ phase is eliminated, the $\mathrm{SmA_d}$ phase is retained as a monotropic phase. Curiously, inspite of a lateral substituent being introduced, the melting points have been enhanced. This is in contrast to earlier studies [76] where the introduction of a lateral substituent affected the melting points marginally but the mesophases were generally retained.

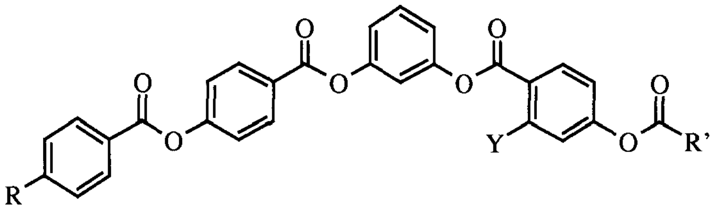
Table 5.3: **Transition temperatures (°C) and the associated enthalpy values (kJ mol^{-1}) for compounds**



Compound	Cr		$\mathrm{SmA_d}$		I
5.C.1,Y=F, Z=H	.	165.0 *62.6*	-		
5.D.1, Y=H, Z=F	.	152.0 *65.2*	(.	149.5) *5.27*	

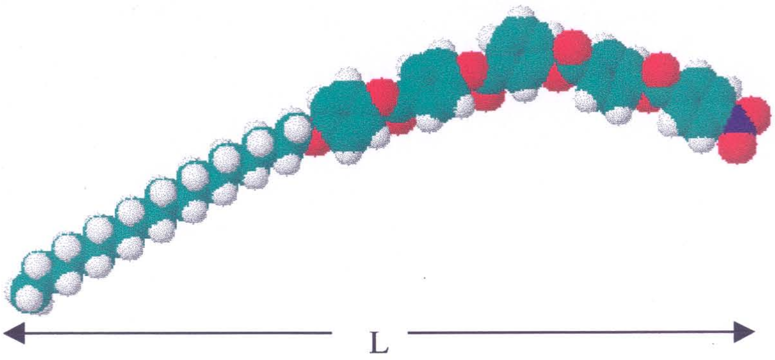
All the compounds exhibiting the polar biaxial smectic A phase studied here so far were derived from 3-hydroxybenzoic acid. In order to explore other possibilities, we have investigated a few compounds derived from resorcinol but substituted unsymmetrically. The transition temperatures and the associated enthalpy values for these are given in table 5.4. Compound 5.E.1 is isomeric with compound 5.A.3 and is non-mesomorphic. Compound 5.B.3 shows a monotropic uniaxial smectic **A** phase, while the corresponding resorcinol derivative (compound 5.F.1) is non-mesomorphic. When a 4-cyanobiphenyl group was introduced in place of the terminal 4-cyanophenyl moiety of compound 5.D.1, the resultant compound 5.G.1 not only became enantiotropic mesomorphic but also exhibited both the $\mathrm{SmA_d}$ and $\mathrm{SmA_dP_A}$ phases. When a fluorine substituent was introduced *ortho* to the carbonyl group (compound **5.H.1**), the melting point went up, the clearing temperature got reduced and the $\mathrm{SmA_dP_A}$ phase became monotropic. Similarly, when the terminal n-dodecyloxy chain was replaced by an n-dodecyl chain, (compound **5.I.1**) the melting and clearing temperatures were marginally affected while the **SmA$_d$P$_A$** phase became highly metastable.

Table 5.4: Transition temperatures (°C) and the associated enthalpy values (kJ mol^{-1}) for compounds



Compound	Cr		SmA$_d$P$_A$		SmA$_d$		I
5.E.1, R=OC$_{12}$H$_{25}$, Y=H R'= 4-cyanophenyl	.	144.0 *40.7*	-		-		
5.F.1, R=OC$_{12}$H$_{25}$, Y=H R'= 4-nitrophenyl	.	150.0 *61.7*	-		-		
5.G.1, R=OC$_{12}$H$_{25}$, Y=H R'= 4-cyanobiphenyl	.	167.0 *71.1*	.	171.5 *0.06*	.	199.5 *3.32*	
5.H.1, R=OC$_{12}$H$_{25}$, Y=F R'= 4-cyanobiphenyl	.	172.0 *65.6*	(.	160.5) *0.04*	.	191.5 *3.35*	
5.I.1, R=C$_{12}$H$_{25}$, Y=F R'= 4-cyanobiphenyl	.	175.0 *60.2*	(.	148.5) *0.07*	.	190.0 *3.11*	

Table 5.5: The d-values obtained from XRD studies of some of the investigated compounds and their molecular length measured by assuming a conformation as shown below wherein the methylene units of *n*-alkoxy chain are in a fully extended all *trans* conformation

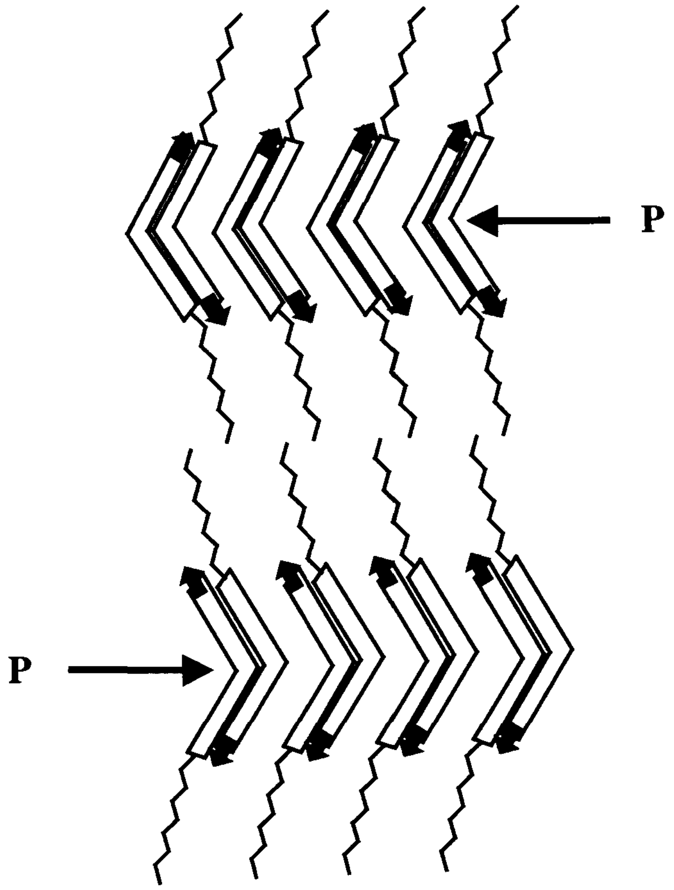


	d values / Å		Molecular length
Compound	d_1	d_2	L /Å
5.A.6	68.7	34.5	52.4
5.B.4	55.6	27.8	47.5
5.B.5	57.6	28.8	50.1
5.B.6	59.2	29.6	52.3
5.G.1	53.2	26.8	48.4

All these experimental observations can be summarized as follows. Because of the achiral layer, the optical textures of the biaxial smectic A phase, under an external electric field does not show any optical switching. The molecular bow plane is orthogonal to the layer plane and the polarization direction is antiparallel in adjacent layers and hence two polarization current peaks are observed in the triangular–wave experiments.

A possible model for the biaxial smectic A phase was proposed for compounds containing a cyano end group and a schematic representation of this is shown in figure **5.15**. This model also holds good for the biaxial smectic phase of nitro substituted compounds (series 5.11). Similar kind of model for orthogonal smectic **A** phase was also proposed by Eremin et *al.*[94].

This model accounts for the optical texture of two- and four-brush strength defects and are dispirartions, which are combination of half strength disclinations caused by defect patterns in the in-plane director and screw dislocations [78, 82].



R.Amaranatha Reddy and B.K.Sadashiva [77].

Figure 5.15: A schematic representation of a polar packing of molecular pairs within the layer with an antiferroelectric ordering between successive layers.

Summary

The mesomorphic behaviour of several unsymmetrical bent-core compounds containing a strongly polar terminal cyano/nitro group was investigated. These compounds were derived from either 3-hydroxybenzoic acid or resorcinol. The mesophase exhibited by these compounds were characterized as partial bilayer uniaxial smectic A (SmA_d) phase or polar partial bilayer biaxial smectic A (SmA_dP_A) phase with antiferroelectric characteristics. In the latter mesophase, the molecules have an orthogonal arrangement and belong to symmetry group C_{2V}. The orientation of the ester linkage group and the number of aromatic rings in the side wings seem to play an important role in inducing particularly, the polar partial bilayer biaxial smectic A phase. In addition, a lateral fluorine substituent on the side arm containing the strongly polar terminal group has a strong influence in destabilizing the occurrence of this SmA_dP_A phase in these materials.

Experimental

4-n-Alkoxyphenols, (5.i) were prepared by monoalkylation of quinol with appropriate n-alkylbromides in the presence of anhydrous potassium carbonate. 3-benzyloxyphenol was prepared following a procedure described in the literature [104]. 4-benzyloxybenzoic acid, (**5.ii**) 3-benzyloxybenzoic acid, (**5.iii**) 2-fluoro-4-benzyloxybenzoic acid (**5.v**, Y=F, Z=H), 3-fluoro-4-benzyloxybenzoic acid (**5.v**, Y=H, Z=F) [59-61] and 4-*n*-alkoxybenzoic acids (**5.vi**) [63] were synthesized according to procedures described in the literature. 4-Cyano-, 4-nitro-benzoic acids (**5.iv**) and benzyl-4-hydroxybenzoate (**5.vii**) were commercial compounds and used without further purification. 4-Cyanobiphenyl-4-carboxylic acid (**5.viii**) was prepared according to a procedure described in the literature [97]. The target compounds were achieved by a series of esterification reactions using DCC and deprotection by hydrogenolysis in the presence of 5% Pd-C catalyst.

4-n-Octyloxyphenyl-4-benzyloxybenzoate, 5.a (*n*=8)

A mixture of 4-n-octyloxyphenol **5.i** (*n*=8), (2.0g, 9.0mmol), 4-benzyloxybenzoic acid, **5.ii** (2.05g, 9.0mmol), catalytic amount of 4 (N, N-dimethylamino) pyridine (DMAP) and dry chloroform (20ml) were stirred for ten min. To this N, N'-dicyclohexylcarbodiimide (DCC, 2.04g, 9.9mmol) was added and stirred overnight at room temperature. The precipitated N, N'-dicyclohexylurea was filtered off. The filtrate was diluted with chloroform (50ml) and washed successively with 5% acetic acid (2 x 25ml), 5% ice-cold sodium hydroxide solution (2 x 25ml) and water (3 x 25ml); it was then dried over anhydrous sodium sulphate. Removal of solvent gave a product, which was chromatographed on silica gel using chloroform as eluent. Removal of solvent from the eluate afforded a white product, which was recrystallized from a mixture of chloroform and acetonitrile. Yield, 3.3g (85%); m.p. 124-125°C; ν_{max} (nujol): 2922, 2855, 1724, 1605, 1510, 1280, 1076 cm^{-1}; δ_H: 8.16-8.14 (d, 2H, ^3J8.8Hz, Ar-H), 7.46-7.35 (m, 5H, Ar-H), 7.11-7.09 (d, 2H, ^3J8.92Hz, Ar-H), 7.06-7.04 (d, 2H, ^3J8.84Hz, Ar-H), 6.93-6.91 (d, 2H, ^3J8.96Hz, Ar-H), 5.16 (s, 2H, -O-CH_2-Ar), 3.97-3.94 (t, 2H, ^3J6.52Hz, Ar-O-CH_2-), 1.82-1.75 (quin, 2H, ^3J7.0Hz, Ar-O-CH_2-$C\underline{\underline{H}}_2$-), 1SO-1.30 (m, 10H, 5 × -CH_2-), 0.91-0.88 (t, 3H, ^3J6.6Hz, -CH_3). Elemental analysis: $C_{28}H_{32}O_4$ requires C, 77.75; H, 7.46%; found C, 77.31; H, 7.30%.

4-n-Octyloxyphenyl-4-hydroxybenzoate,5.b (*n*=8)

Compound 5.a (*n*=8), (3.0g, 6.9mmol) was dissolved in 1, 4-dioxane (50 ml), and 5% Pd-C catalyst (0.6g) was added and stirred at 50°C in an hydrogen atmosphere until the required quantity of hydrogen was absorbed. The solution was filtered and removal of solvent gave a white product, which was recrystallized, from a mixture of 1, 4-dioxane and petroleum-ether (b.p. 80-100°C). Yield, 2.0g (84%); m.p. 158-158.5°C; ν_{max} (nujol): 3379, 3464, 2918, 2851, 1728, 1709, 1609, 1514 cm^{-1}; δ_H (CD_3COCD_3): 9.31(s, 1H, Ar-OH, exchangeable with D_2O), 8.05-8.03 (d, 2H, ^3J8.56Hz, Ar-H), 7.15-7.12 (d, 2H, ^3J9.0Hz, Ar-H), 7.00-6.96 (m, 4H, Ar-H), 4.03-4.0 (t, 2H, ^3J6.48Hz, Ar-O-CH_2-), 1.82-1.75 (quin, 2H, ^3J6.88Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.51-1.35 (m, 10H, 5 x -CH_2-), 0.91-0.89 (t, 3H, ^3J6.6Hz, -CH_3). Elemental analysis: $C_{21}H_{26}O_4$ requires C, 73.66; H, 7.65%; found C, 73.71; H, 7.72%.

4-*n*-Octyloxyphenyl-4-(3-benzyloxybenzoyloxy)benzoate, 5.c (*n*=8)

This was synthesized following a procedure described for the preparation of compound **5.a** (*n*=8). Quantities: compound **5.b** (*n*=8), (1.5g, 4.4mmol), 3-benzyloxybenzoic acid, **5.iii** (1.0g, 4.4mmol), cat.amount of DMAP, DCC (1.0g, 4.84mmol), dry $CHCl_3$ (20ml). Yield, 1.9g (78%); m.p. 100-101°C; ν_{max} (nujol): 2924, 2855, 1732, 1597, 1508, 1292, 1074 cm^{-1}; δ_H: 8.29-8.27 (d, 2H, ^3J8.52Hz, Ar-H), 7.85-7.83 (m, 2H, Ar-H), 7.48-7.26 (m, 9H, Ar-H), 7.14-7.11 (d, 2H, ^3J8.84Hz, Ar-H), 6.95-6.93 (d, 2H, ^3J8.84Hz, Ar-H), 5.16 (s, 2H, -0-CH_2-Ar), 3.98-3.95 (t, 2H, ^3J6.52Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^3J6.96Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.49-1.30 (m, 10H, 5 × -CH_2-), 0.92-0.88 (t, 3H, ^3J.6.48Hz, -CH_3). Elemental analysis: $C_{35}H_{36}O_6$ requires C, 76.06; H, 6.57%; found C, 76.01; H, 6.67%.

4-*n*-Octyloxyphenyl-4-(3-hydroxybenzoyloxy)benzoate, 5.d (*n*=8)

This was synthesized following a procedure described for the preparation of compound **5.b** (*n*=8). Quantities: compound **5.c**, (*n*=8), (1.7g, 3.08 mmol), 5% Pd-C catalyst (0.38g), 1, 4-dioxane (25ml). Yield, 1.1g (79%); m.p. 172-173°C; ν_{max} (nujol): 3445, 2924, 2855, 1720, 1607, 1506 cm^{-1}; δ_H (CD_3COCD_3): 8.93 (s, 1H, Ar-OH, exchangeable with D_2O), 8.29-8.27 (d, 2H, ^3J8.72Hz, Ar-H), 7.71-7.66 (m, 2H, Ar-H), 7.54-7.51 (d, 2H, ^3J8.72Hz, Ar-H), 7.47-7.43 (t, 1H, ^3J7.96Hz, Ar-H), 7.23-7.21 (m, 3H, Ar-H), 7.02-7.00 (d, 2H, ^3J9.0Hz, Ar-H), 4.04-4.02 (t, 2H, ^3J6.48Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^3J6.92Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.50-1.29 (m, 10H, 5 x -CH_2-), 0.89-0.86 (t, 3H, ^3J6.64Hz, -CH_3). Elemental analysis: $C_{28}H_{30}O_6$ requires C, 72.71; H, 6.54%; found C, 72.94; H, 6.64%.

4-*n*-Octyloxyphenyl-4-[3-(4-benzyloxybenzoyloxy)benzoyloxy]benzoate, 5.e (*n*=8)

This was synthesized following a procedure described for the preparation of compound **5.a** (*n*=8). Quantities: compound **5.d** (*n*=8), (1.0g, 2.16mmol), 4-benzyloxybenzoic acid, **5.ii** (0.49g, 2.16mmol), cat.amount of DMAP, DCC (0.49g, 2.38mmol), dry $CHCl_3$ (15ml). Yield, 1.1g (76%); m.p. 127.5-128.5°C; ν_{max} (nujol): 2922, 2855, 1736, 1605, 1512, 1250, 1082 cm^{-1}; δ_H: 8.29-8.27 (d, 2H, ^3J8.48Hz, Ar-H), 8.19-8.17 (d, 2H, ^3J8.64Hz, Ar-H), 8.14-8.12 (d, 1H, ^3J7.68Hz, Ar-H), 8.06 (s, 1H, Ar-H), 7.62-7.58 (t, 1H, ^3J7.92Hz, Ar-H), 7.54-7.52 (m, 1H, Ar-H), 7.46-7.36 (m, 7H, Ar-H), 7.13-7.11 (d, 2H, ^3J8.84Hz, Ar-H), 7.09-7.07 (d, 2H, ^3J8.84Hz, Ar-H), 6.95-6.92 (d, 2H, ^3J8.84Hz, Ar-H), 5.18 (s, 2H, -O-CH$_2$-Ar), 3.98-3.95 (t, 2H, ^3J 6.5Hz, Ar-O-CH$_2$-), 1.83-1.76 (quin, 2H, ^3J7.04Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.48-1.30 (m, 10H, 5 x -CH$_2$-), 0.91-0.88 (t, 3H, ^3J6.64Hz, -CH$_3$). Elemental analysis: $C_{42}H_{40}O_8$ requires C, 74.98; H, 5.99%; found C, 74.63; H, 5.89%.

4-*n*-Octyloxyphenyl-4-[3-(4-hydroxybenzoyloxy)benzoyloxy]benzoate, 5.f (*n*=8)

This was synthesized following a procedure described for the preparation of compound **5.b** (*n*=8). Quantities: compound **5.e** (*n*=8), (1.0g, 1.49mmol), 5% Pd-C catalyst (0.2g), 1, 4-dioxane (20ml). Yield, 0.63g (73%); m.p. 176.5-177.5°C; ν_{max} (nujol): 3285, 2920,2850,1732,1608,1510 cm^{-1}; δ_H (CD_3COCD_3): 9.39 (s, 1H, Ar-OH, exchangeable with D_2O), 8.30-8.28 (d, 2H, ^3J8.8Hz, Ar-H), 8.15-8.09 (m, 4H, Ar-H), 7.75-7.71 (t, 1H, ^3J8.0Hz, Ar-H), 7.68-7.66 (m, 1H, Ar-H), 7.59-7.56 (d, 2H, ^3J8.72Hz, Ar-H), 7.23-7.21 (d, 2H, ^3J9.0Hz, Ar-H), 7.04-7.02 (m, 4H, Ar-H), 4.04-4.01 (t, 2H, ^3J6.48Hz, Ar-O-CH$_2$-), 1.83-1.76 (quin, 2H, ^3J6.96Hz, Ar-O-CH$_2$-C$\underline{H}_2$-,), 1.50-1.32 (m, 10H, 5 x -CH$_2$-), 0.89-0.86 (t, 3H, ^3J6.88Hz, -CH$_3$). Elemental analysis: $C_{35}H_{34}O_8$ requires C, 72.15; H, 5.88%; found C, 72.52; H, 5.85%.

The physical data for cognate preparations are given below

4-n-Decyloxyphenyl-4-benzyloxybenzoate,5.a (*n*=10)

Yield, 84%; m.p. 121.5-122.0°C; ν_{max} (nujol): 2922, 2855, 1728, 1605, 1510, 1280, 1076 cm^{-1}; δ_H: 8.16-8.14 (d, 2H, ^3J8.84Hz, Ar-H), 7.46-7.35 (m, 5H, Ar-H), 7.11-7.09 (d, 2H, ^3J8.88Hz, Ar-H), 7.06-7.04 (d, 2H, ^3J8.84Hz, Ar-H), 6.93-6.91 (d, 2H, ^3J8.92Hz, Ar-H), 5.16 (s, 2H, -O-CH$_2$-Ar), 3.97-3.94 (t, 2H, ^3J6.56Hz, Ar-O-CH$_2$-), 1.82-1.75 (quin, 2H, ^3J7.0Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.50-1.30 (m, 14H, 7 x -CH$_2$-), 0.91-0.88 (t, 3H, ^3J6.56Hz, -CH$_3$). Elemental analysis: $C_{30}H_{36}O_4$ requires C, 78.23; H, 7.88%; found C, 78.02; H, 7.59%.

4-n-Decyloxyphenyl-4-hydroxybenzoate, 5.b **(*n*=10)**

Yield, 82%; m.p. 145-146°C; ν_{max} (nujol): 3398,2922, 2853, 1728, 1709, 1605, 1512 cm^{-1}; δ_H (CD_3COCD_3): 9.34 (s, 1H, Ar-OH, exchangeable with D_2O,), 8.05-8.03 (d, 2H, ^{3}J8.72Hz, Ar-H), 7.15-7.12 (d, 2H, ^{3}J9.0Hz, Ar-H), 7.00-6.96 (m, 4H, Ar-H), 4.03-4.0 (t, 2H, ^{3}J6.48Hz, Ar-O-CH$_2$-), 1.82-1.75 (quin, 2H, ^{3}J6.84Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.52-1.30 (m, 14H, 7 x -CH$_2$-), 0.90-0.89 (t, 3H, ^{3}J6.48Hz, -CH$_3$). Elemental analysis: $C_{23}H_{30}O_4$ requires C, 74.56; H, 8.16%; found C, 74.80; H, 8.25%.

4-*n*-Decyloxyphenyl-4-(3-benzyloxybenzoyloxy)benzoate, 5.c (*n*=10)

Yield, 81%; m.p. 99.5-100.5°C; ν_{max} (nujol): 2924, 2853, 1738, 1605, 1510, 1292, 1074 cm^{-1}; δ_H: 8.29-8.27 (d, 2H, ^{3}J8.56Hz, Ar-H), 7.85-7.83 (m, 2H, Ar-H), 7.48-7.26 (m, 9H, Ar-H), 7.14-7.12 (d, 2H, ^{3}J8.84Hz, Ar-H), 6.95-6.93 (d, 2H, ^{3}J8.84Hz, Ar-H), 5.16 (s, 2H, -O-CH$_2$-Ar), 3.99-3.95 (t, 2H, ^{3}J6.48Hz, Ar-O-CH$_2$-), 1.83-1.76 (quin, 2H, ^{3}J7.0Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.49-1.29 (m, 14H, 7 x -CH$_2$-), 0.92-0.88 (t, 3H, ^{3}J6.56Hz, -CH$_3$). Elemental analysis: $C_{37}H_{40}O_6$ requires C, 76.53; H, 6.94%; found C, 76.86; H, 7.03%.

4-*n*-Decyloxyphenyl-4-(3-hydroxybenzoyloxy)benzoate, 5.d (*n*=10)

Yield, 79%; m.p. 166.5-167.5°C; ν_{max} (nujol): 3443, 2922, 2853, 1720, 1600, 1504 cm^{-1}; δ_H (CD_3COCD_3): 8.90 (s, 1H, Ar-OH, exchangeable with D_2O), 8.29-8.27 (d, 2H, ^{3}J8.68Hz, Ar-H), 7.71-7.66 (m, 2H, Ar-H), 7.54-7.51 (d, 2H, ^{3}J8.72Hz, Ar-H), 7.47-7.43 (t, 1H, ^{3}J7.96Hz, Ar-H), 7.23-7.21 (m, 3H, Ar-H), 7.02-7.00 (d, 2H, ^{3}J9.0Hz, Ar-H), 4.04-4.02 (t, 2H, ^{3}J6.48Hz, Ar-O-CH$_2$-), 1.83-1.76 (quin, 2H, ^{3}J6.92Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.50-1.29 (m, 14H, 7 x -CH$_2$-), 0.90-0.87 (t, 3H, ^{3}J6.56Hz, -CH$_3$). Elemental analysis: $C_{30}H_{34}O_6$ requires C, 73.45; H, 6.99%; found C, 73.50; H, 7.02%.

4-*n*-Decyloxyphenyl-4-[3-(4-benzyloxybenzoyloxy)benzoyloxy]benzoate, 5.e **(*n*=10)**

Yield, 78%; m.p. 116-117°C; ν_{max} (nujol): 2922, 2855, 1736, 1732, 1605, 1512, 1250, 1082 cm^{-1}; δ_H: 8.29-8.27 (d, 2H, ^{3}J8.72Hz, Ar-H), 8.19-8.17 (d, 2H, ^{3}J8.84Hz, Ar-H), 8.14-8.12 (d, 1H, ^{3}J7.72Hz, Ar-H), 8.06 (s, 1H, Ar-H), 7.62-7.58 (t, 1H, ^{3}J8.0Hz, Ar-H), 7.54-7.52 (m, 1H, Ar-H), 7.47-7.36 (m, 7H, Ar-H), 7.13-7.11 (d, 2H, ^{3}J8.96Hz, Ar-H), 7.09-7.07 (d, 2H, ^{3}J8.92Hz, Ar-H), 6.95-6.92 (d, 2H, ^{3}J8.96Hz, Ar-H), 5.18 (s, 2H, -O-CH$_2$-Ar), 3.98-3.95 (t, 2H, ^{3}J 6.52Hz, Ar-O-CH$_2$-), 1.83-1.76 (quin, 2H, ^{3}J7.04Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.48-1.30

(m, 14H, 7 x -CH$_2$-), 0.91-0.88 (t, 3H, ^{3}J6.6Hz, -CH$_3$). Elemental analysis: $C_{44}H_{44}O_8$ requires C, 75.41; H, 6.33%; found C, 75.34; H, 6.45%.

4-*n*-Decyloxyphenyl-4-[3-(4-hydroxybenzoyloxy)benzoyloxy]benzoate, 5.f (*n*=10)

Yield, 73%; m.p. 173-174°C; ν_{max} (nujol): 3459,3285, 2920, 2850, 1732, 1697, 1608, 1510 cm^{-1}; δ_H (CD_3COCD_3): 9.39 (s, 1H, Ar-OH, exchangeable with D_2O), 8.30-8.28 (d, 2H, ^{3}J8.72Hz, Ar-H), 8.15-8.09 (m, 4H, Ar-H), 7.75-7.71 (t, 1H, ^{3}J7.92Hz, Ar-H), 7.68-7.66 (m, 1H, Ar-H), 7.59-7.56 (d, 2H, ^{3}J8.76Hz, Ar-H), 7.23-7.21 (d, 2H, ^{3}J9.04Hz, Ar-H), 7.04-7.02 (m, 4H, Ar-H), 4.04-4.01 (t, 2H, ^{3}J6.48Hz, Ar-0-CHI-), 1.83-1.76 (quin, 2H, ^{3}J6.96Hz, Ar-O-CH$_2$-C$\underline{H}_2$-,), 1.50-1.32 (m, 14H, 7 × -CH$_2$-), 0.89-0.86 (t, 3H, ^{3}J6.6Hz, -CH$_3$). Elemental analysis: $C_{37}H_{38}O_8$ requires C, 72.77; H, 6.27%; found C, 72.30; H, 6.39%.

4-n-Dodecyloxyphenyl-4-benzyloxybenzoate, 5.a (*n*=12)

Yield, 83%; m.p. 119-120°C; ν_{max} (nujol): 2920,2851, 1736, 1603, 1510, 1280, 1076 cm^{-1}; δ_H: 8.16-8.14 (d, 2H, ^{3}J8.8Hz, Ar-H), 7.46-7.35 (m, 5H, Ar-H,), 7.11-7.09 (d, 2H, ^{3}J8.84Hz, Ar-H), 7.06-7.04 (d, 2H, ^{3}J8.8Hz, Ar-H), 6.93-6.91 (d, 2H, ^{3}J8.88Hz, Ar-H), 5.16 (s, 2H, -O-CH$_2$-Ar), 3.97-3.94 (t, 2H, ^{3}J6.48Hz, Ar-0-CHI-), 1.82-1.75 (quin, 2H, ^{3}J7.04Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.50-1.30 (m, 18H, 9 × -CH$_2$-), 0.91-0.88 (t, 3H, ^{3}J6.52Hz, -CH$_3$). Elemental analysis: $C_{32}H_{40}O_4$ requires C, 78.65; H, 8.25%; found C, 78.22; H, 8.09%.

4-n-Dodecyloxyphenyl-4-hydroxybenzoate,5.b (*n*=12)

Yield, 80%; m.p. 137-138°C; ν_{max} (nujol): 3381, 3464, 2920, 2851, 1728, 1709, 1609, 1512 cm^{-1}; δ_H (CD_3COCD_3): 9.31(s, 1H, Ar-OH, exchangeable with D_2O), 8.06-8.04 (d, 2H, ^{3}J8.76Hz, Ar-H), 7.15-7.12 (d, 2H, ^{3}J9.04Hz, Ar-H), 7.00-6.95 (m, 4H, Ar-H), 4.03-4.0 (t, 2H, ^{3}J6.48Hz, Ar-0-CHI-), 1.82-1.75 (quin, 2H, ^{3}J6.92Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.51-1.35 (m, 18H, 9 x -CH$_2$-), 0.91-0.89 (t, 3H, ^{3}J6.64Hz, -CH$_3$). Elemental analysis: $C_{25}H_{34}O_6$ requires C, 75.34; H, 8.60%; found C, 74.96; H, 8.68%.

4-*n*-Dodecyloxyphenyl-4-(3-benzyloxybenzoyloxy)benzoate, 5.c (*n*=12)

Yield, 80%; m.p. 96-97°C; ν_{max} (nujol): 2918, 2851, 1747, 1605, 1463, 1292, 1074 cm^{-1}; δ_H: 8.29-8.27 (d, 2H, ^{3}J8.48Hz, Ar-H), 7.85-7.83 (m, 2H, Ar-H), 7.48-7.26(m, 9H, Ar-H), 7.14-7.12 (d, 2H, ^{3}J8.72Hz, Ar-H), 6.96-6.93 (d, 2H, ^{3}J8.72Hz, Ar-H), 5.16 (s, 2H, -O-CHI-Ar), 3.99-3.95 (t, 2H, ^{3}J6.48Hz, Ar-0-CHI-), 1.83-1.76 (quin, 2H, ^{3}J6.92Hz, Ar-O-CH$_2$-

$C\underline{H}_2$-), 1.49-1.29 (m, 18H, 9 × -CH_2-), 0.92-0.88 (t, 3H, ^{3}J6.48Hz, -CH_3). Elemental analysis: $C_{39}H_{44}O_6$ requires C, 76.95; H, 7.29%; found C, 76.55; H, 7.35%.

4-*n*-Dodecyloxyphenyl-4-(3-hydroxybenzoyloxy)benzoate, 5.d (*n*=12)

Yield, 79%; m.p. 166.5-167.5°C; ν_{max} (nujol): 3441,2918, 2851, 1726, 1597, 1506 cm^{-1}; δ_H (CD_3COCD_3): 8.89 (s, 1H, Ar-OH, exchangeable with D_2O), 8.29-8.27 (d, 2H, ^{3}J8.72Hz, Ar-H), 7.71-7.66 (m, 2H, Ar-H), 7.54-7.51 (d, 2H, ^{3}J8.68Hz, Ar-H), 7.47-7.43 (t, 1H, ^{3}J7.96Hz, Ar-H), 7.23-7.21 (m, 3H, Ar-H), 7.02-7.00 (d, 2H, ^{3}J9.0Hz, Ar-H), 4.04-4.02 (t, 2H, ^{3}J6.48Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^{3}J6.88Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.53-1.30 (m, 18H, 9 x -CH_2-), 0.90-0.87 (t, 3H, ^{3}J6.56Hz, -CH_3). Elemental analysis: $C_{32}H_{38}O_6$ requires C, 74.11; H, 7.39%; found C, 73.80; H, 7.46%.

4-*n*-Dodecyloxyphenyl-4-[3-(4-benzyloxybenzoyloxy)benzoyloxy]benzoate, 5.e (*n*=12)

Yield, 76%; m.p. 116-117°C; ν_{max} (nujol): 2922, 2853, 1736, 1605, 1512, 1250, 1082 cm^{-1}; δ_H: 8.29-8.27 (d, 2H, ^{3}J8.64Hz, Ar-H), 8.19-8.17 (d, 2H, ^{3}J8.84Hz, Ar-H), 8.14-8.12 (d, 1H, ^{3}J7.72Hz, Ar-H), 8.07 (s, 1H, Ar-H), 7.62-7.58 (t, 1H, ^{3}J7.96Hz, Ar-H), 7.54-7.52 (m, 1H, Ar-H), 7.45-7.36 (m, 7H, Ar-H), 7.13-7.11 (d, 2H, ^{3}J8.92Hz, Ar-H), 7.09-7.07 (d, 2H, ^{3}J8.88Hz, Ar-H), 6.95-6.92 (d, 2H, ^{3}J8.96Hz, Ar-H), 5.18 (s, 2H, -O-CH_2-Ar), 3.98-3.95 (t, 2H, ^{3}J 6.48Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^{3}J7.08Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.48-1.30 (m, 18H, 9 × -CH_2-), 0.90-0.87 (t, 3H, ^{3}J6.6Hz, -CH_3). Elemental analysis: $C_{46}H_{48}O_8$ requires C, 75.80; H, 6.64%; found C, 75.53; H, 6.66%.

4-*n*-Dodecyloxyphenyl-4-[3-(4-hydroxybenzoyloxy)benzoyloxy]benzoate, 5.f (*n*=12)

Yield, 78%; m.p. 176-177°C; ν_{max} (nujol): 3277, 3362, 2920, 2853, 1732, 1695, 1608, 1510 cm^{-1}; δ_H (CD_3COCD_3): 9.38 (s, 1H, Ar-OH, exchangeable with D_2O), 8.30-8.28 (d, 2H, ^{3}J8.72Hz, Ar-H), 8.15-8.10 (m, 4H, Ar-H), 7.75-7.71 (t, 1H, ^{3}J7.96Hz, Ar-H), 7.68-7.66 (m, 1H, Ar-H), 7.59-7.56 (d, 2H, ^{3}J8.72Hz, Ar-H), 7.22-7.20 (d, 2H, ^{3}J9.0Hz, Ar-H), 7.04-7.02 (m, 4H, Ar-H), 4.05-4.01 (t, 2H, ^{3}J6.48Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^{3}J6.96Hz, Ar-O-CH_2-$C\underline{H}_2$-,), 1.51-1.26 (m, 18H, 9 x -CH_2-), 0.88-0.86 (t, 3H, ^{3}J6.76Hz, -CH_3). Elemental analysis: $C_{39}H_{42}O_8$ requires C, 73.33; H, 6.63%; found C, 73.56; H, 6.70%.

4-n-Tetradecyloxyphenyl-4-benzyloxybenzoate,5.a (*n*=14)

Yield, 86%; m.p. 117-118°C; ν_{max} (nujol): 2918, 2849, 1740, 1610, 1514, 1252 cm^{-1}; δ_H: 8.16-8.14 (d, 2H, ^3J8.6Hz, Ar-H), 7.46-7.35 (m, 5H, Ar-H), 7.11-7.09 (d, 2H, ^3J8.8Hz, Ar-H), 7.06-7.04 (d, 2H, ^3J8.6Hz, Ar-H), 6.93-6.91 (d, 2H, ^3J8.76Hz, Ar-H), 5.16 (s, 2H, -0-CHı-Ar), 3.97-3.94 (t, 2H, ^3J6.48Hz, Ar-O-CH_2-), 1.82-1.75 (quin, 2H, ^3J7.08Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.50-1.30 (m, 22H, 11 x -CH_2-), 0.90-0.87 (t, 3H, ^3J6.6Hz, -CH_3). Elemental analysis: $C_{34}H_{44}O_4$ requires C, 79.03; H, 8.58%; found C, 79.47; H, 8.9%.

4-n-**Tetradecyloxyphenyl-4-hydroxybenzoate**, 5.b (*n*=14)

Yield, 81%; m.p. 137-138°C; ν_{max} (nujol): 3381, 3464, 2918, 2851, 1728, 1709, 1611, 1514 cm^{-1}; δ_H (CD_3COCD_3): 9.28 (s, 1H, Ar-OH, exchangeable with D_2O), 8.05-8.03 (d, 2H, ^3J8.72Hz, Ar-H), 7.15-7.12 (d, 2H, ^3J9.0Hz, Ar-H), 7.00-6.96 (m, 4H, Ar-H), 4.03-4.0 (t, 2H, ^3J6.48Hz, Ar-O-CH_2-), 1.82-1.75 (quin, 2H, ^3J6.88Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.49-1.29 (m, 22H, 11 x -CH_2-), 0.89-0.86 (t, 3H, ^3J6.52Hz, -CH_3). Elemental analysis: $C_{27}H_{38}O_4$ requires C, 76.02; H, 8.98%; found C, 75.69; H, 8.94%.

4-*n*-Tetradecyloxyphenyl-4-(3-benzyloxybenzoyloxy)benzoate, 5.c (*n*=14)

Yield, 77%; m.p. 96.5-97.5°C; ν_{max} (nujol): 2918, 2851, 1742, 1512, 1463, 1276 cm^{-1}; δ_H: 8.29-8.27 (d, 2H, ^3J8.44Hz, Ar-H), 7.85-7.83 (m, 2H, Ar-H), 7.48-7.26 (m, 9H, Ar-H), 7.14-7.12 (d, 2H, ^3J8.64Hz, Ar-H), 6.96-6.93 (d, 2H, ^3J8.68Hz, Ar-H), 5.16 (s, 2H, -O-CH_2-Ar), 3.99-3.95 (t, 2H, ^3J6.4Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^3J6.88Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.49-1.29 (m, 22H, 11 × -CH_2-), 0.90-0.87 (t, 3H, ^3J6.52Hz, -CH_3). Elemental analysis: $C_{41}H_{48}O_6$ requires C, 77.33; H, 7.60%; found C, 77.32; H, 7.66%.

4-*n*-Tetradecyloxyphenyl-4-(3-hydroxybenzoyloxy)benzoate, 5.d (*n*=14)

Yield, 75%; m.p. 160-160.5°C; ν_{max} (nujol): 3439, 2918, 2851,1726, 1597, 1508 cm^{-1}; δ_H (CD_3COCD_3): 8.95 (s, 1H, Ar-OH, exchangeable with D_2O), 8.29-8.27 (d, 2H, ^3J8.8Hz, Ar-H), 7.71-7.66 (m, 2H, Ar-H), 7.53-7.51 (d, 2H, ^3J8.8Hz, Ar-H), 7.46-7.42 (t, 1H, ^3J7.92Hz, Ar-H), 7.23-7.21 (m, 3H, Ar-H), 7.02-7.00 (d, 2H, ^3J9.04Hz, Ar-H), 4.04-4.02 (t, 2H, ^3J6.48Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^3J6.96Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.50-1.29 (m, 22H, 11 x -CH_2-), 0.89-0.86 (t, 3H, ^3J6.64Hz, -CH_3). Elemental analysis: $C_{34}H_{42}O_6$ requires C, 74.70; H, 7.74%; found C, 74.28; H, 7.64%.

4-*n*-Tetradecyloxyphenyl-4-[3-(4-benzyloxybenzoyloxy)benzoyloxy]benzoate, 5.e (*n*=14)

Yield, 80%; m.p. 119.5-120.5°C; ν_{max} (nujol): 2922, 2851, 1732, 1605, 1512, 1250, 1082 cm^{-1}; δ_H: 8.29-8.27 (d, 2H, ^3J8.64Hz, Ar-H), 8.19-8.17 (d, 2H, ^3J8.8Hz, Ar-H), 8.14-8.12 (d, 1H, ^3J7.64Hz, Ar-H), 8.06 (s, 1H, Ar-H), 7.62-7.58 (t, 1H, ^3J7.92Hz, Ar-H), 7.54-7.52 (m, 1H, Ar-H), 7.46-7.36 (m, 7H, Ar-H), 7.13-7.11 (d, 2H, ^3J8.96Hz, Ar-H), 7.09-7.07 (d, 2H, ^3J8.84Hz, Ar-H), 6.95-6.92 (d, 2H, ^3J8.92Hz, Ar-H), 5.18 (s, 2H, -O-CH_2-Ar), 3.98-3.95 (t, 2H, ^3J 6.52Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^3J6.8Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.47-1.27 (m, 22H, 11 × -CH_2-), 0.90-0.87 (t, 3H, ^3J6.64Hz, -CH_3). Elemental analysis: $C_{48}H_{52}O_8$ requires C, 76.17; H, 6.92%; found C, 76.53; H, 6.99%.

4-*n*-Tetradecyloxyphenyl-4-[3-(4-hydroxybenzoyloxy)benzoyloxy]benzoate, 5.f (*n*=14)

Yield, 74%; m.p. 173.5-174.5°C; ν_{max} (nujol): 3279, 3362, 2920, 2850, 1732, 1695, 1608, 1510 cm^{-1}; δ_H (CD_3COCD_3): 9.39 (s, 1H, Ar-OH, exchangeable with D_2O), 8.30-8.28 (d, 2H, ^3J8.72Hz, Ar-H), 8.15-8.12 (m, 4H, Ar-H), 7.75-7.71 (t, 1H, ^3J7.96Hz, Ar-H), 7.68-7.66 (m, 1H, Ar-H), 7.59-7.56 (d, 2H, ^3J8.72Hz, Ar-H), 7.23-7.21 (d, 2H, ^3J9.0Hz, Ar-H), 7.04-7.02 (m, 4H, Ar-H), 4.05-4.01 (t, 2H, ^3J6.48Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^3J6.88Hz, Ar-O-CH_2-$C\underline{H}_2$-,), 1.51-1.26 (m, 22H, 11 x -CH_2-), 0.88-0.86 (t, 3H, ^3J6.76Hz, -CH_3). Elemental analysis: $C_{41}H_{46}O_8$ requires C, 73.85; H, 6.95%; found C, 73.80; H, 6.98%.

4-n-Hexadecyloxyphenyl-4-benzyloxybenzoate5.a (*n*=16)

Yield, 79%; m.p. 119-119.5°C; ν_{max} (nujol): 2949, 2916, 1740, 1611, 1514, 1252 cm^{-1}; δ_H: 8.15-8.13 (d, 2H, ^3J8.64Hz, Ar-H), 7.46-7.35 (m, 5H, Ar-H), 7.11-7.09 (d, 2H, ^3J8.8Hz, Ar-H), 7.06-7.04 (d, 2H, ^3J8.68Hz, Ar-H), 6.93-6.91 (d, 2H, ^3J8.8Hz, Ar-H), 5.16 (s, 2H, -O-CH_2-Ar), 3.97-3.94 (t, 2H, ^3J6.48Hz, Ar-O-CH_2-), 1.82-1.75 (quin, 2H, ^3J7.0Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.57-1.26 (m, 26H, 13 × -CH_2-), 0.90-0.87 (t, 3H, ^3J6.58Hz, -CH_3). Elemental analysis: $C_{36}H_{48}O_4$ requires C, 79.37; H, 8.88%; found C, 79.73; H, 9.24%.

4-n-Hexadecyloxyphenyl-4-hydroxybenzoate,5.b (*n*=16)

Yield, 82%; m.p. 134-135°C; ν_{max} (nujol): 3381, 2920, 2850, 1728, 1611, 1514 cm^{-1}; δ_H (500MHz, CD_3COCD_3): 9.63 (s, 1H, Ar-OH, exchangeable with D_2O), 8.03-8.01 (d, 2H, ^3J8.56Hz, Ar-H), 7.14-1.12 (d, 2H, ^3J9.12Hz, Ar-H), 7.0-6.95 (m, 4H, Ar-H), 4.01-3.99 (t, 2H, ^3J6.5Hz, Ar-O-CH_2-), 1.80-1.75 (quin, 2H, ^3J7.0Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.51-1.28 (m, 26H, 13 x -CH$_2$-), 0.88-0.86 (t, 3H, ^{3}J6.6Hz, -CH$_3$). Elemental analysis: $C_{29}H_{42}O_4$ requires C, 76.61; H, 9.31%; found C, 77.02; H, 9.75%.

4-*n*-Hexadecyloxyphenyl-4-(3-benzyloxybenzoyloxy)benzoate, 5.c (*n*=16)

Yield, 78%; m.p. 97-98°C; ν_{max} (nujol): 2918, 2849, 1747, 1583, 1512 cm^{-1}; δ_H: 8.29-8.27 (d, 2H, ^{3}J8.56Hz, Ar-H), 7.85-7.83 (m, 2H, Ar-H), 7.48-7.26 (m, 9H, Ar-H), 7.14-7.11 (d, 2H, ^{3}J8.84Hz, Ar-H), 6.95-6.93 (d, 2H, ^{3}J8.84Hz, Ar-H), 5.16 (s, 2H, -O-CH$_2$-Ar), 3.98-3.95 (t, 2H, ^{3}J6.48Hz, Ar-O-CH$_2$-), 1.83-1.76 (quin, 2H, ^{3}J7.0Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.57-1.27 (m, 26H, 13 x -CH$_2$-), 0.90-0.87 (t, 3H, ^{3}J6.4Hz, -CH$_3$). Elemental analysis: $C_{43}H_{52}O_6$ requires C, 77.68; H, 7.88%; found C, 77.90; H, 8.07%.

4-*n*-Hexadecyloxyphenyl-4-(3-hydroxybenzoyloxy)benzoate, 5.d (*n*=16)

Yield, 75%; m.p. 161-161.5°C; ν (nujol): 3439,2918, 2851, 1722, 1604, 1506 cm^{-1}; δ_H (500MHz, CD$_3$COCD$_3$): 8.86 (s, 1H, Ar-OH, exchangeable with D$_2$O), 8.29-8.27 (d, 2H, ^{3}J8.75Hz, Ar-H), 7.71-7.63 (m, 2H, Ar-H), 7.53-7.51 (d, 2H, ^{3}J8.7Hz, Ar-H), 7.46-7.43 (t, 1H, ^{3}J8.0Hz, Ar-H), 7.23-7.21 (m, 3H, Ar-H), 7.02-7.00 (d, 2H, ^{3}J9Hz, Ar-H), 4.04-4.02 (t, 2H, ^{3}J6.5Hz, Ar-O-CH$_2$-), 1.82-1.77 (quin, 2H, ^{3}J7.0Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.53-1.29 (m, 26H, 13 x -CH$_2$-), 0.89-0.86 (t, 3H, ^{3}J6.7Hz, -CH$_3$). Elemental analysis: $C_{36}H_{46}O_6$ requires C, 75.23; H, 8.07%; found C, 75.25; H, 8.22%.

4-*n*-Hexadecyloxyphenyl-4-[3-(4-benzyloxybenzoyloxy)benzoyloxy]benzoate, 5.e (*n*=16)

Yield, 78%; m.p. 119-119.7°C; ν (nujol): 2920,2850, 1734, 1605, 1512 cm^{-1}; δ_H: 8.29-8.27 (d, 2H, ^{3}J8.48Hz, Ar-H), 8.19-8.17 (d, 2H, ^{3}J8.48Hz, Ar-H), 8.14-8.12 (d, 1H, ^{3}J7.64Hz, Ar-H), 8.06 (s, 1H, Ar-H), 7.62-7.58 (t, 1H, ^{3}J7.96Hz, Ar-H), 7.54-7.52 (m, 1H, Ar-H), 7.46-7.36 (m, 7H, Ar-H), 7.13-7.11 (d, 2H, ^{3}J8.8Hz, Ar-H), 7.09-7.07 (d, 2H, ^{3}J8.68Hz, Ar-H), 6.94-6.92 (d, 2H, ^{3}J8.76Hz, Ar-H), 5.18 (s, 2H, -O-CH$_2$-Ar), 3.98-3.95 (t, 2H, ^{3}J6.5Hz, Ar-O-CH$_2$-), 1.83-1.76 (quin, 2H, ^{3}J7.0Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.54-1.27 (m, 26H, 13 x -CH$_2$-), 0.9-0.87 (t, 3H, ^{3}J6.5Hz, -CH$_3$). Elemental analysis: $C_{50}H_{56}O_8$ requires C, 76.50; H, 7.19%; found C, 76.72; H, 7.50%.

4-*n*-Hexadecyloxyphenyl-4-[3-(4-hydroxybenzoyloxy)benzoyloxy]benzoate, 5f (*n*=16)

Yield, 73%; m.p. 173-174.0°C; ν_{max} (nujol): 3285,2920,2850, 1732, 1608, 1510 cm^{-1}; δ_H (CD_3COCD_3): 9.8 (s, 1H, Ar-OH, exchangeable with D_2O), 8.30-8.28 (d, 2H, ^{3}J8.56Hz, Ar-H), 8.15-8.13 (m, 4H, Ar-H), 7.75-7.71 (t, 1H, ^{3}J7.8Hz, Ar-H), 7.68-7.66 (m, 1H, Ar-H), 7.59-7.56 (d, 2H, ^{3}J8.56Hz, Ar-H), 7.23-7.21 (d, 2H, ^{3}J8.84Hz, Ar-H), 7.04-7.02 (m, 4H, Ar-H), 4.04-4.01 (t, 2H, ^{3}J6.44Hz, Ar-O-CH_2-), 1.81-1.76 (quin, 2H, ^{3}J7Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.51-1.26 (m, 26H, 13 x -CH_2-), 0.88-0.86 (t, 3H, ^{3}J6.76Hz, -CH_3). Elemental analysis: $C_{43}H_{50}O_8$ requires C, 74.33; H, 7.25%; found C, 74.74; H, 7.41%.

4-*n*-Hexadecyloxyphenyl-4-[3-(2-fluoro-4-benzyloxybenzoyloxy)benzoyloxy]benzoate, 5.g (*n*=16, Y=F, Z=H)

Yield, 71%; m.p. 114-115°C; ν_{max} (nujol): 2920, 2850, 1744, 1730, 1620, 1512 cm^{-1}; δ_H: 8.30-8.28 (d, 2H, ^{3}J8.76Hz, Ar-H), 8.15-8.07 (m, 3H, Ar-H), 7.63-7.59 (t, 1H, ^{3}J8.0Hz, Ar-H), 7.54-7.52 (m, 1H, Ar-H), 7.46-7.36 (m, 7H, Ar-H), 7.13-7.11 (d, 2H, ^{3}J9.0Hz, Ar-H), 7.09-7.07 (d, 2H, ^{3}J9.04Hz, Ar-H), 6.95-6.93 (dd, 1H, ^{3}J9.04Hz, ^{4}J2.2Hz, Ar-H), 6.90-6.87 (dd, 1H, ^{3}J8.92Hz, ^{4}J2.28Hz, Ar-H), 5.16 (s, 2H, -O-CH_2-Ar), 3.98-3.95 (t, 2H, ^{3}J6.52Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^{3}J7.0Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.52-1.27 (m, 26H, 13 x -CH_2-), 0.9-0.87 (t, 3H, ^{3}J6.6Hz, -CH_3).

4-*n*-Hexadecyloxyphenyl-4-[3-(3-fluoro-4-benzyloxybenzoyloxy)benzoyloxy]benzoate, 5.g (*n*=16, Y=H, Z=F)

Yield, 69%; m.p. 124.5-125.5°C; ν_{max} (nujol): 2918, 2850, 1730, 1728, 1618, 1512 cm^{-1}; δ_H: 8.30-8.27 (d, 2H, ^{3}J8.68Hz, Ar-H), 8.15-8.13 (d, 1H, ^{3}J7.68Hz, Ar-H), 8.06 (s, 1H, Ar-H), 7.98-7.93 (m, 2H, Ar-H), 7.62-7.58 (t, 1H, ^{3}J7.96Hz, Ar-H), 7.54-7.52 (m, 1H, Ar-H), 7.48-7.37 (m, 7H, Ar-H), 7.14-7.09 (m, 3H, Ar-H), 6.95-6.92 (d, 2H, ^{3}J8.96Hz, Ar-H), 5.26 (s, 2H, -O-CH_2-Ar), 3.98-3.95 (t, 2H, ^{3}J6.48Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^{3}J6.96Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.52-1.27 (m, 26H, 13 x -CH_2-), 0.9-0.87 (t, 3H, ^{3}J6.6Hz, -CH_3).

4-*n*-Hexadecyloxyphenyl-4-[3-(2-fluoro-4-hydroxybenzoyloxy)benzoyloxy]benzoate, 5.h (*n*=16, Y=F, Z=H)

Yield, 79%; m.p. 167-168°C; ν_{max} (nujol): 3317, 2920, 2851, 1730, 1709, 1620, 1510 cm^{-1}; δ_H (CD_3COCD_3): 9.75 (s, 1H, Ar-OH, exchangeable with D_2O), 8.30-8.28 (d, 2H, ^{3}J8.68Hz, Ar-H), 8.18-8.03 (m, 3H, Ar-H), 7.75-7.71 (t, 1H, ^{3}J8.0Hz, Ar-H), 7.68-7.66 (m, 1H, Ar-H), 7.59-7.56 (d, 2H, ^{3}J9.04Hz, Ar-H), 7.23-7.21 (d, 2H, ^{3}J8.84Hz, Ar-H), 7.04-7.02 (d, 2H, ^{3}J8.96Hz, Ar-H), 6.90-6.86 (dd, 1H, ^{3}J9.0Hz, ^{4}J2.16Hz, Ar-H), 6.80-6.75 (dd, 1H, ^{3}J8.8Hz, ^{4}J2.08Hz, Ar-H), 4.04-4.01 (t, 2H, ^{3}J6.48Hz, Ar-O-CH$_2$-), 1.81-1.76 (quin, 2H, ^{3}J7.04Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.50-1.26 (m, 26H, 13 x -CH$_2$-), 0.92-0.89 (t, 3H, ^{3}J6.88Hz, -CH$_3$).

4-*n*-Hexadecyloxyphenyl-4-[3-(3-fluoro-4-hydroxybenzoyloxy)benzoyloxy]benzoate, 5.h (*n*=16, Y=H, Z=F)

Yield, 81%; m.p. 141-142°C; ν_{max} (nujol): 3545, 3342, 2920, 2850, 1732, 1703, 1600, 1512 cm^{-1}; δ_H (CD$_3$COCD$_3$): 9.6 (s, 1H, Ar-OH, exchangeable with D$_2$O), 8.30-8.28 (d, 2H, ^{3}J8.68Hz, Ar-H), 8.16-8.11 (m, 2H, Ar-H), 7.95-7.91 (m, 2H, Ar-H), 7.75-7.71 (t, 1H, ^{3}J8.0Hz, Ar-H), 7.69-7.67 (m, 1H, Ar-H), 7.59-7.56 (d, 2H, ^{3}J8.68Hz, Ar-H), 7.22-7.18 (m, 3H, Ar-H), 7.01-6.99 (d, 2H, ^{3}J9.0Hz, Ar-H), 4.05-4.02 (t, 2H, ^{3}J6.48Hz, Ar-O-CH$_2$-), 1.83-1.78 (quin, 2H, ^{3}J7.04Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.51-1.26 (m, 26H, 13 x -CH$_2$-), 0.88-0.86 (t, 3H, ^{3}J6.48Hz, -CH$_3$).

4-n-Octadecyloxyphenyl-4-benzyloxybenzoate,5.a (*n*=18)

Yield, 84%; m.p. 118-118.5°C; ν, (nujol): 2918,2849, 1740, 1610, 1456, 1252 cm^{-1}; δ_H: 8.16-8.14 (d, 2H, ^{3}J8.8Hz, Ar-H), 7.46-7.35 (m, 5H, Ar-H), 7.11-7.09 (d, 2H, ^{3}J8.96Hz, Ar-H), 7.06-7.04 (d, 2H, ^{3}J8.84Hz, Ar-H), 6.93-6.91 (d, 2H, ^{3}J8.96Hz, Ar-H), 5.16 (s, 2H, -O-CH$_2$-Ar), 3.97-3.94 (t, 2H, ^{3}J6.52Hz, Ar-O-CH$_2$-), 1.82-1.75 (quin, 2H, ^{3}J7.0Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.48-1.27 (m, 30H, 15 x -CH$_2$-), 0.90-0.87 (t, 3H, ^{3}J6.52Hz, -CH$_3$). Elemental analysis: $C_{38}H_{52}O_4$ requires C, 79.68; H, 9.15%; found C, 80.04; H, 9.45%.

4-n-Octadecyloxyphenyl-4-hydroxybenzoate,5.b (*n*=18)

Yield, 82%; m.p. 132-133°C; ν, (nujol): 3379, 3465, 2918, 2851, 1728, 1709, 1609, 1514 cm^{-1}; δ_H: 9.39 (s, 1H, Ar-OH, exchangeable with D$_2$O), 8.05-8.02 (d, 2H, ^{3}J8.68Hz, Ar-H), 7.14-1.12 (d, 2H, ^{3}J9.0Hz, Ar-H), 7.0-6.95 (m, 4H, Ar-H), 4.03-4.0 (t, 2H, ^{3}J6.36Hz, Ar-O-CH$_2$-), 1.8-1.75 (quin, 2H, ^{3}J7.0Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.49-1.29 (m, 30H, 15 × -CH$_2$-), 0.88-0.86 (t, 3H, ^{3}J6.6Hz, -CH$_3$). Elemental analysis: $C_{31}H_{46}O_4$ requires C, 77.14; H, 9.60%; found C, 76.79; H, 9.83%.

4-*n*-Octadecyloxyphenyl-4-(3-benzyloxybenzoyloxy)benzoate, 5.c (*n*=18)

Yield, 79%; m.p. 101-102°C; ν_{max} (nujol): 2918, 2849, 1742, 1605, 1512, 1463, 1279 cm^{-1}; δ_H: 8.29-8.27 (d, 2H, ^3J8.64Hz, Ar-H), 7.85-7.83 (m, 2H, Ar-H), 7.48-7.26 (m, 9H, Ar-H), 7.13-7.11 (d, 2H, ^3J8.92Hz, Ar-H), 6.96-6.93 (d, 2H, ^3J8.92Hz, Ar-H), 5.16 (s, 2H, -0-CH_2-Ar), 3.99-3.95 (t, 2H, ^3J6.52Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^3J7.04Hz, Ar-O-CH_2-$C\underline{H_2}$-), 1.47-1.29 (m, 30H, 15 × -CH_2-), 0.90-0.87 (t, 3H, ^3J6.52Hz, -CH_3). Elemental analysis: $C_{45}H_{56}O_6$ requires C, 78.00; H, 8.15%; found C, 78.16; H, 8.35%.

4-*n*-Octadecyloxyphenyl-4-(3-hydroxybenzoyloxy)benzoate, 5.d (*n*=18)

Yield, 81%; m.p. 160-160.5°C; ν_{max} (nujol): 3439, 3319, 2920, 2851,1726, 1589, 1508 cm^{-1}; δ_H (CD_3COCD_3): 8.95 (s, 1H, Ar-OH, exchangeable with D_2O), 8.29-8.27 (d, 2H, ^3J8.72Hz, Ar-H), 7.71-7.66 (m, 2H, Ar-H), 7.53-7.51 (d, 2H, ^3J8.68Hz, Ar-H), 7.46-7.42 (t, 1H, ^3J7.96Hz, Ar-H), 7.23-7.21 (m, 3H, Ar-H), 7.02-7.00 (d, 2H, ^3J9.0Hz, Ar-H), 4.04-4.02 (t, 2H, ^3J6.48Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^3J6.96Hz, Ar-O-CH_2-$C\underline{H_2}$-), 1.50-1.29 (m, 30H, 15 x -CH_2-), 0.89-0.86 (t, 3H, ^3J6.52Hz, -CH_3). Elemental analysis: $C_{38}H_{50}O_6$ requires C, 75.72; H, 8.36%; found C, 75.49; H, 8.52%.

4-*n*-Octadecyloxyphenyl-4-[3-(4-benzyloxybenzoyloxy)benzoyloxy]benzoate, 5.e (*n*=18)

Yield, 78%; m.p. 119-119.5°C; ν_{max} (nujol): 2922, 2851, 1736, 1605, 1512, 1250, 1082 cm^{-1}; δ_H: 8.29-8.27 (d, 2H, ^3J8.48Hz, Ar-H), 8.19-8.17 (d, 2H, ^3J8.6Hz, Ar-H), 8.14-8.12 (d, 1H, ^3J7.56Hz, Ar-H), 8.06 (s, 1H, Ar-H), 7.62-7.58 (t, 1H, ^3J7.96Hz, Ar-H), 7.54-7.52 (m, 1H, Ar-H), 7.46-7.36 (m, 7H, Ar-H), 7.13-7.11 (d, 2H, ^3J8.76Hz, Ar-H), 7.09-7.07 (d, 2H, ^3J8.72Hz, Ar-H), 6.95-6.92 (d, 2H, ^3J8.76Hz, Ar-H), 5.18 (s, 2H, -O-CH_2-Ar), 3.98-3.95 (t, 2H, ^3J6.44Hz, Ar-O-CH_2-), 1.83-1.76 (quin, 2H, ^3J6.84Hz, Ar-O-CH_2-$C\underline{H_2}$-), 1.46-1.26 (m, 30H, 15 x -CH_2-), 0.90-0.87 (t, 3H, ^3J6.52Hz, -CH_3). Elemental analysis: $C_{52}H_{60}O_8$ requires C, 76.82; H, 7.44%; found C, 76.78; H, 7.58%.

4-*n*-Octadecyloxyphenyl-4-[3-(4-hydroxybenzoyloxy)benzoyloxy]benzoate, 5.f (*n*=18)

Yield, 75%; m.p. 172-172.5°C; ν_{max} (nujol): 3434, 3285, 2920, 2851, 1732, 1695, 1609, 1510 cm^{-1}; δ_H (CD_3COCD_3): 9.8 (s, 1H, Ar-OH, exchangeable with D_2O), 8.30-8.28 (d, 2H, ^3J8.48Hz, Ar-H), 8.15-8.13 (m, 4H, Ar-H), 7.75-7.71 (t, 1H, ^3J7.8Hz, Ar-H), 7.68-7.66 (m, 1H, Ar-H), 7.58-7.56 (d, 2H, ^3J8.44Hz, Ar-H), 7.23-7.21 (d, 2H, ^3J8.76Hz, Ar-H), 7.04-7.02 (m, 4H, Ar-H), 4.04-4.01 (t, 2H, ^3J6.44Hz, Ar-O-CH_2-), 1.81-1.76 (quin, 2H, ^3J7.0Hz, Ar-O-CH_2-C$\underline{H_2}$-), 1.51-1.26 (m, 30H, 15 x -CH_2-), 0.88-0.86 (t, 3H, ^3J6.6Hz, -CH_3). Elemental analysis: $C_{45}H_{54}O_8$ requires C, 74.77; H, 7.53%; found C, 74.94; H, 7.58%.

Physical constants of the intermediate compounds **5.i** to **5.n** are given in Chapter **6.**

4-*n*-Octyloxyphenyl-4-[3-{4-(4-cyanobenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 5.A.1

This was synthesized following a procedure described for the preparation of compound **5.a** (*n*=8). Quantities: compound **5.f** (*n*=8), (0.15g, 0.26mmol), 4-cyanobenzoic acid, **5.iv**, (X=CN), (0.037g, 0.26mmol), DCC, (0.057g, 0.28mmol), cat. amount of DMAP, dry $CHCl_3$, (10 ml). Yield, 0.018g (65%); m.p. 172.0°C; ν_{max}: 3067, 2929, 2858, 2239, 1743, 1738, 1730, 1605, 1508, 1281, 1076 cm^{-1}; δ_H: 8.35-8.33 (m, 4H, Ar-H), 8.30-8.28 (d, 2H, ^3J8.6Hz, Ar-H), 8.17-8.15 (d, 1H, ^3J7.72Hz, Ar-H), 8.09 (s, 1H, Ar-H), 7.86-7.84 (d, 2H, ^3J8.2Hz, Ar-H), 7.65-7.63 (t, 1H, ^3J7.92Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.43-7.41 (d, 2H, ^3J8.64Hz, Ar-H), 7.39-7.37(d, 2H, ^3J8.6Hz, Ar-H), 7.13-7.11 (d, 2H, ^3J8.84Hz, Ar- H), 6.95-6.92 (d, 2H, ^3J8.92Hz, Ar-H), 3.98-3.95 (t, 2H, ^3J6.4Hz, Ar-O-CH_2-), 1.83-1.75 (quin, 2H, ^3J6.8Hz, Ar-O-CH_2-C$\underline{H_2}$-), 1.49-1.26 (m, 10H, 5 x -CH_2-), 0.90-0.86 (t, 3H, ^3J6.72Hz, -CH_3). Elemental analysis: $C_{43}H_{37}NO_9$ requires C, 72.56; H, 5.24; N, 1.97%; found C, 72.45; H, 5.26; N, 2.01%.

4-*n*-Decyloxyphenyl-4-[3-{4-(4-cyanobenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 5.A.2

Yield, 67%; m.p. 158.0°C; ν_{max}: 3069, 2918, 2853, 2239, 1742, 1736, 1730, 1605, 1508, 1283, 1076 cm^{-1}; δ_H: 8.35-8.33 (m, 4H, Ar-H), 8.30-8.28 (d, 2H, ^3J8.6Hz, Ar-H), 8.17-8.15 (d, 1H, ^3J7.68Hz, Ar-H), 8.09 (s, 1H, Ar-H), 7.86-7.84 (d, 2H, ^3J8.16Hz, Ar-H), 7.65-7.63 (t, 1H, ^3J7.96Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.43-7.41 (d, 2H, ^3J8.6Hz, Ar-H), 7.39-7.37(d, 2H, ^3J8.56Hz, Ar-H), 7.13-7.11 (d, 2H, ^3J8.96Hz, Ar- H), 6.95-6.92 (d, 2H, ^3J8.96Hz, Ar-H), 3.98-3.95 (t, 2H, ^3J6.56Hz, Ar-O-CH_2-), 1.83-1.75 (quin, 2H, ^3J7.04Hz, Ar-O-CH_2-C$\underline{H_2}$-), 1.49-1.26 (m, 14H, 7 x -CH_2-), 0.90-0.86 (t, 3H, ^3J6.68Hz, -CH_3). Elemental analysis: $C_{45}H_{41}NO_9$ requires C, 73.06; H, 5.59; N, 1.89%; found C, 73.39; H, 5.53; N, 1.92%.

4-*n*-Dodecyloxyphenyl-4-[3-{4-(4-cyanobenzoyloxy)benzoyloxy}benzoyloxy]benzoate,

5.A.3

Yield, 70%; m.p. 156.5°C; ν_{max}: 3069, 2918, 2853, 2239, 1748, 1742, 1736, 1730, 1605, 1508, 1281, 1076 cm^{-1}; δ_H: 8.35-8.32 (m, 4H, Ar-H), 8.30-8.28 (d, 2H, ^{3}J8.64Hz, Ar-H), 8.17-8.15 (d, 1H, ^{3}J7.72Hz, Ar-H), 8.09 (s, 1H, Ar-H), 7.86-7.84 (d, 2H, ^{3}J8.16Hz, Ar-H), 7.65-7.63 (t, 1H, ^{3}J8.0Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.43-7.41 (d, 2H, ^{3}J8.68Hz, Ar-H), 7.39-7.37(d, 2H, ^{3}J8.68Hz, Ar-H), 7.13-7.11 (d, 2H, ^{3}J9.04Hz, Ar- H), 6.95-6.92 (d, 2H, ^{3}J9.0Hz, Ar-H), 3.98-3.95 (t, 2H, ^{3}J6.56Hz, Ar-O-CH_2-), 1.83-1.75 (quin, 2H, ^{3}J6.96Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.49-1.26 (m, 18H, 9 x -CH_2-), 0.90-0.86 (t, 3H, ^{3}J6.68Hz, -CH_3). Elemental analysis: $C_{47}H_{45}NO_9$ requires C, 73.52; H, 5.91; N, 1.82%; found C, 73.66; H, 5.91; N, 1.49%.

4-*n*-Tetradecyloxyphenyl-4-[3-{4-(4-cyanobenzoyloxy)benzoyloxy}benzoyloxy]benzoate,

5.A.4

Yield, 69% m.p. 158.0°C; ν_{max}: 3069, 2916, 2849, 2232, 1742, 1736, 1732, 1607, 1510, 1281, 1070 cm^{-1}; δ_H: 8.35-8.32 (m, 4H, Ar-H), 8.30-8.28 (d, 2H, ^{3}J8.72Hz, Ar-H), 8.17-8.15 (d, 1H, ^{3}J7.72Hz, Ar-H), 8.09 (s, 1H, Ar-H), 7.86-7.84 (d, 2H, ^{3}J8.24Hz, Ar-H), 7.65-7.63 (t, 1H, ^{3}J8.04Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.43-7.41 (d, 2H, ^{3}J8.76Hz, Ar-H), 7.39-7.37(d, 2H, ^{3}J8.76Hz, Ar-H), 7.13-7.11 (d, 2H, ^{3}J9.04Hz, Ar- H), 6.95-6.92 (d, 2H, ^{3}J9.04Hz, Ar-H), 3.98-3.95 (t, 2H, ^{3}J6.56Hz, Ar-O-CH_2-), 1.83-1.75 (quin, 2H, ^{3}J6.96Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.49-1.26 (m, 22H, 11 x -CH_2-), 0.90-0.86 (t, 3H, ^{3}J6.72Hz, -CH_3). Elemental analysis: $C_{49}H_{49}NO_9$ requires C, 73.94; H, 6.21; N, 1.76%; found C, 74.36; H, 6.24; N, 1.76%.

4-*n*-Hexadecyloxyphenyl-4-[3-{4-(4-cyanobenzoyloxy)benzoyloxy}benzoyloxy]benzoate,

5.A.5

Yield, 65%; m.p. 161.5°C; ν_{max}: 3072, 2916, 2849, 2237, 1736, 1732, 1605, 1510, 1278, 1078 cm^{-1}; δ_H: 8.35-8.33 (m, 4H, Ar-H), 8.30-8.28 (d, 2H, ^{3}J8.68Hz, Ar-H), 8.17-8.15 (d, 1H, ^{3}J7.72Hz, Ar-H), 8.09 (s, 1H, Ar-H), 7.86-7.84 (d, 2H, ^{3}J8.2Hz, Ar-H), 7.65-7.63 (t, 1H, ^{3}J8.0Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.43-7.41 (d, 2H, ^{3}J8.72Hz, Ar-H), 7.39-7.37(d, 2H, ^{3}J8.72Hz, Ar-H), 7.13-7.11 (d, 2H, ^{3}J9.04Hz, Ar- H), 6.95-6.92 (d, 2H, ^{3}J9.04Hz, Ar-H), 3.98-3.95 (t, 2H, ^{3}J6.52Hz, Ar-O-CH_2-), 1.83-1.75 (quin, 2H, ^{3}J7.0Hz, Ar-O-CH_2-$C\underline{H}_2$-), 1.49-1.26 (m, 26H, 13 x -CH_2-), 0.90-0.86 (t, 3H, ^{3}J6.72Hz, -CH_3).

Elemental analysis: $C_{51}H_{53}NO_9$ requires C, 74.34; H, 6.48; N, 1.71%; found C, 74.02; H, 6.46; N, 1.51%.

4-*n*-Octadecyloxyphenyl-4-[3-{4-(4-cyanobenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 5.A.6

Yield, 71%; m.p. 161.0°C; ν_{max}: 3069, 2916, 2849, 2237, 1736, 1732, 1730, 1605, 1510, 1278, 1078 cm^{-1}; δ_H: 8.35-8.33 (m, 4H, Ar-H), 8.30-8.28 (d, 2H, ^3J8.48Hz, Ar-H), 8.17-8.15 (d, 1H, ^3J7.68Hz, Ar-H), 8.09 (s, 1H, Ar-H), 7.86-7.84 (d, 2H, ^3J8.08Hz, Ar-H), 7.65-7.63 (t, 1H, ^3J8.04Hz, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.43-7.41 (d, 2H, ^3J8.48Hz, Ar-H), 7.39-7.37(d, 2H, ^3J8.56Hz, Ar-H), 7.13-7.11 (d, 2H, ^3J8.88Hz, Ar- H), 6.95-6.92 (d, 2H, ^3J8.84Hz, Ar-H), 3.98-3.95 (t, 2H, ^3J6.52Hz, Ar-0-CHI-), 1.83-1.75 (quin, 2H, ^3J6.96Hz, Ar-0-CHI-c&-), 1.49-1.26 (m, 30H, 15 x -CH_2-), 0.90-0.86 (t, 3H, ^3J6.64Hz, -CH_3). Elemental analysis: $C_{53}H_{57}NO_9$ requires C, 74.71; H, 6.74; N, 1.64%; found C, 74.83; H, 6.84; N, 1.46%.

4-*n*-Octyloxyphenyl-4-[3-{4-(4-nitrobenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 5.B.1

Yield, 61%; m.p. 145.0°C; ν_{max}: 3111, 3080, 2929, 2855, 1738, 1736, 1607, 1508, 1267 cm^{-1}; δ_H: 8.43-8.37 (m, 4H, Ar-H), 8.36-8.34 (d, 2H, ^3J8.76Hz, Ar-H), 8.30-8.28 (d, 2H, ^3J8.76Hz, Ar-H), 8.17-8.15 (d, 1H, ^3J7.72Hz, Ar-H), 8.1 (s, 1H, Ar-H), 7.65-7.63 (t, 1H, ^3J8.04Hz, Ar-H), 7.57-7.55 (m, 1H, Ar-H), 7.45-7.43 (d, 2H, ^3J8.76Hz, Ar-H), 7.39-7.37 (d, 2H, ^3J8.76Hz, Ar-H), 7.13-7.11 (d, 2H, ^3J9.04Hz, Ar- H), 6.94-6.92 (d, 2H, ^3J9.04Hz, Ar-H), 3.98-3.95 (t, 2H, ^3J6.56Hz, Ar-O-CH_2-), 1.83-1.75 (quin, 2H, ^3J6.96Hz, Ar-O-CH_2-$C\underline{H_2}$-), 1.47-1.26 (m, 10H, 5 x -CH_2-), 0.90-0.86 (t, 3H, ^3J6.72Hz, -CH_3). Elemental analysis: $C_{42}H_{37}NO_{11}$ requires C, 68.94; H, 5.10; N, 1.91%; found C, 69.02; H, 5.06; N, 1.65%.

4-*n*-Decyloxyphenyl-4-[3-{4-(4-nitrobenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 5.B.2

Yield, 64%; m.p. 143.5°C; ν_{max}: 3111, 3080, 2920, 2853, 1738, 1736, 1607, 1508, 1267 cm^{-1}; δ_H: 8.43-8.37 (m, 4H, Ar-H), 8.36-8.34 (d, 2H, ^3J8.72Hz, Ar-H), 8.30-8.28 (d, 2H, ^3J8.76Hz, Ar-H), 8.17-8.15 (d, 1H, ^3J7.76Hz, Ar-H), 8.1 (s, 1H, Ar-H), 7.65-7.63 (t, 1H, ^3J8.0Hz, Ar-H), 7.57-7.55 (m, 1H, Ar-H), 7.45-7.43 (d, 2H, ^3J8.76Hz, Ar-H), 7.39-7.37 (d, 2H, ^3J8.72Hz, Ar-H), 7.13-7.11 (d, 2H, ^3J9.0Hz, Ar- H), 6.94-6.92 (d, 2H, ^3J9.04Hz, Ar-H), 3.98-3.95 (t, 2H, ^3J6.52Hz, Ar-0-CHI-), 1.82-1.75 (quin, 2H, ^3J6.96Hz, Ar-O-CH_2-$C\underline{H_2}$-), 1.49-1.26 (m, 14H, 7 x -CH_2-), 0.90-0.86 (t, 3H, ^3J6.6Hz, -CH_3).

Elemental analysis: $C_{44}H_{41}NO_{11}$ requires C, 69.55; H, 5.44; N, 1.84%; found C, 69.09; H, 5.10; N, 1.62%.

4-*n*-Dodecyloxyphenyl-4-[3-{4-(4-nitrobenzoyloxy)benzoyloxy}benzoyloxy]benzoate,

5.B.3

Yield, 70%; m.p. 145.0°C; ν_{max}: 3111, 3080, 2918, 2851, 1738, 1736, 1607, 1508, 1267 cm^{-1}; δ_H: 8.43-8.37 (m, 4H, Ar-H), 8.36-8.34 (d, 2H, ^{3}J8.68Hz, Ar-H), 8.30-8.28 (d, 2H, ^{3}J8.72Hz, Ar-H), 8.17-8.15 (d, 1H, ^{3}J7.72Hz, Ar-H), 8.1 (s, 1H, Ar-H), 7.65-7.63 (t, 1H, ^{3}J7.96Hz, Ar-H), 7.57-7.55 (m, 1H, Ar-H), 7.45-7.43 (d, 2H, ^{3}J8.68Hz, Ar-H), 7.39-7.37 (d, 2H, ^{3}J8.68Hz, Ar-H), 7.13-7.11 (d, 2H, ^{3}J8.96Hz, Ar- H), 6.94-6.92 (d, 2H, ^{3}J8.96Hz, Ar-H), 3.98-3.95 (t, 2H, ^{3}J6.56Hz, Ar-O-CH$_2$-), 1.82-1.75 (quin, 2H, ^{3}J6.96Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.48-1.26 (m, 18H, 9 × -CH$_2$-), 0.90-0.86 (t, 3H, ^{3}J6.6Hz, -CH$_3$). Elemental analysis: $C_{46}H_{45}NO_{11}$ requires C, 70.13; H, 5.76; N, 1.78%; found C, 70.47; H, 5.71; N, 1.71%.

4-n-Tetradecyloxyphenyl-4-[3-{4-(4-nitrobenzoyloxy)benzoyloxy}benzoyloxy]benzoate,

5.B.4

Yield, 65%; m.p. 146.5°C; ν_{max}: 3111, 3080, 2918, 2851, 1736, 1732, 1609, 1510, 1458, 1273 cm^{-1}; δ_H: 8.43-8.37 (m, 4H, Ar-H), 8.36-8.34 (d, 2H, ^{3}J8.48Hz, Ar-H), 8.30-8.28 (d, 2H, ^{3}J8.44Hz, Ar-H), 8.17-8.15 (d, 1H, ^{3}J7.44Hz, Ar-H), 8.1 (s, 1H, Ar-H), 7.65-7.63 (t, 1H, ^{3}J7.92Hz, Ar-H), 7.57-7.55 (m, 1H, Ar-H), 7.45-7.43 (d, 2H, ^{3}J8.48Hz, Ar-H), 7.39-7.37 (d, 2H, ^{3}J8.44Hz, Ar-H), 7.13-7.11 (d, 2H, ^{3}J8.68Hz, Ar- H), 6.94-6.92 (d, 2H, ^{3}J8.80Hz, Ar-H), 3.98-3.95 (t, 2H, ^{3}J6.36Hz, Ar-O-CH$_2$-), 1.82-1.75 (quin, 2H, ^{3}J6.96Hz, Ar-O-CH$_2$-C$\underline{H}_2$-), 1.49-1.26 (m, 22H, 11 x -CH$_2$-), 0.90-0.86 (t, 3H, ^{3}J6.48Hz, -CH$_3$). Elemental analysis: $C_{48}H_{49}NO_{11}$ requires C, 70.66; H, 6.05; N, 1.72%; found C, 71.08; H, 6.0; N, 1.47%.

4-*n*-Hexadecyloxyphenyl-4-[3-{4-(4-nitrobenzoyloxy)benzoyloxy}benzoyloxy]benzoate,

5.B.5

Yield, 62%; m.p. 145.0°C; ν_{max}: 3112, 3082, 2918, 2851, 1736, 1734, 1608, 1510, 1458, 1273 cm^{-1}; δ_H: 8.43-8.37 (m, 4H, Ar-H), 8.36-8.34 (d, 2H, ^{3}J8.64Hz, Ar-H), 8.30-8.28 (d, 2H, ^{3}J8.64Hz, Ar-H), 8.17-8.15 (d, 1H, ^{3}J7.68Hz, Ar-H), 8.1 (s, 1H, Ar-H), 7.65-7.63 (t, 1H, ^{3}J7.96Hz, Ar-H), 7.57-7.55 (m, 1H, Ar-H), 7.45-7.43 (d, 2H, ^{3}J8.68Hz, Ar-H), 7.39-7.37 (d, 2H, ^{3}J8.64Hz, Ar-H), 7.13-7.11 (d, 2H, ^{3}J8.96Hz, Ar- H), 6.94-6.92 (d, 2H, ^{3}J8.96Hz, Ar-

H), 3.98-3.95 (t, 2H, ^3J6.48Hz, Ar-O-CH_2-), 1.82-1.75 (quin, 2H, ^3J7.0Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.50-1.26 (m, 26H, 13 × -CH_2-), 0.90-0.86 (t, 3H, ^3J6.48Hz, -CH_3). Elemental analysis: $C_{50}H_{53}NO_{11}$ requires C, 71.16; H, 6.33; N, 1.66%; found C, 71.47; H, 6.28; N, 1.39%.

4-*n*-Octadecyloxyphenyl-4-[3-{4-(4-nitrobenzoyloxy)benzoyloxy}benzoyloxy]benzoate, 5.B.6

Yield, 71%; m.p. 144.0°C; ν_{max}: 3111, 3080, 2918, 2851, 1736, 1732, 1609, 1510, 1458, 1273 cm^{-1}; δ_H: 8.43-8.37 (m, 4H, Ar-H), 8.36-8.34 (d, 2H, ^3J8.48Hz, Ar-H), 8.30-8.28 (d, 2H, ^3J8.48Hz, Ar-H), 8.17-8.15 (d, 1H, ^3J7.6Hz, Ar-H), 8.1 (s, 1H, Ar-H), 7.65-7.63 (t, 1H, ^3J8.0Hz, Ar-H), 7.57-7.55 (m, 1H, Ar-H), 7.45-7.43 (d, 2H, ^3J8.48Hz, Ar-H), 7.39-7.37 (d, 2H, ^3J8.52Hz, Ar-H), 7.13-7.11 (d, 2H, ^3J8.84Hz, Ar- H), 6.94-6.92 (d, 2H, ^3J8.84Hz, Ar-H), 3.98-3.95 (t, 2H, ^3J6.52Hz, Ar-O-CH_2-), 1.82-1.75 (quin, 2H, ^3J6.92Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.47-1.26 (m, 30H, 15 × -CH_2-), 0.90-0.86 (t, 3H, ^3J6.48Hz, -CH_3). Elemental analysis: $C_{52}H_{57}NO_{11}$ requires C, 71.62; H, 6.59; N, 1.61%; found C, 72.03; H, 6.59; N, 1.58%.

4-*n*-Hexadecyloxyphenyl-4-[3-{4-(4-nitrobenzoyloxy)-2-fluorobenzoylxy}benzoyloxy] benzoate, 5.C.1

Yield, 75%; m.p. 165.0°C; ν_{max}: 3113, 2918, 2851, 1736, 1609, 1510, 1263 cm^{-1}; δ_H: 8.37-8.24 (m, 7H, Ar-H), 8.17-8.15 (d, 1H, ^3J7.64Hz, Ar-H), 8.10 (s, 1H, Ar-H), 7.65-7.63 (t, 1H, ^3J7.96Hz, Ar-H), 7.58-7.56 (m, 1H, Ar-H), 7.39-7.37(d, 2H, ^3J8.48Hz, Ar-H), 7.26-7.24 (m, 2H, Ar-H), 7.13-7.11 (d, 2H, ^3J8.76Hz, Ar- H), 6.95-6.92 (d, 2H, ^3J8.8Hz, Ar-H), 3.98-3.95 (t, 2H, ^3J6.48Hz, Ar-O-CH_2-), 1.83-1.75 (quin, 2H, ^3J6.92Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.49-1.26 (m, 26H, 13 x -CH_2-), 0.90-0.86 (t, 3H, ^3J6.56Hz, -CH_3).

4-*n*-Hexadecyloxyphenyl-4-[3-{4-(4-nitrobenzoyloxy)-3-fluorobenzoyloxy}benzoyloxy] benzoate, 5.D.1

Yield, 68%; m.p. 152.0°C; ν_{max}: 3080, 2918, 2851, 1738, 1736, 1746, 1609, 1510, 1273 cm''; δ_H: 8.44-8.39 (m, 4H, Ar-H), 8.30-8.28 (d, 2H, ^3J8.52Hz, Ar-H), 8.18-8.09 (m, 4H, Ar-H), 7.66-7.62 (t, 1H, ^3J7.92Hz, Ar-H), 7.56-7.48 (m, 2H, Ar-H), 7.40-7.37(d, 2H, ^3J8.56Hz, Ar-H), 7.13-7.11 (d, 2H, ^3J8.84Hz, Ar- H), 6.95-6.92 (d, 2H, ^3J8.84Hz, Ar-H), 3.98-3.95 (t, 2H, ^3J6.48Hz, Ar-O-CH_2-), 1.83-1.75 (quin, 2H, ^3J6.96Hz, Ar-O-CH_2-C$\underline{H}_2$-), 1.49-1.26 (m, 26H, 13 x -CH_2-), 0.90-0.86 (t, 3H, ^3J6.6Hz, -CH_3).

1-[(4-*n*-dodecyloxybenzoyloxy)-4-benzoyloxy)]phenylene-3-[(4-cyanobenzoyloxy)-4-benzoate], 5.E.1

Yield, 71%; m.p. 144.0°C; ν_{max}: 3101, 2920, 2851, 2228, 1747, 1491, 1603, 1508, 1278, 1070 cm^{-1}; δ_H: 8.34-8.27 (m, 6H, Ar-H), 8.17-8.14 (d, 2H, ^{3}J8.76Hz, Ar-H), 7.86-7.84 (d, 2H, ^{3}J8.24Hz, Ar-H), 7.53-7.49 (t, 1H, ^{3}J8.0Hz, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.21-7.18 (m, 3H, Ar-H), 7.0-6.98 (d, 2H, ^{3}J8.8Hz, Ar-H), 4.08-4.04(t, 2H, ^{3}J6.56Hz, Ar-O-CH$_2$-), 1.87-1.80 (quin, 2H, ^{3}J7.0Hz, Ar-O-CH$_2$-C$\underline{H_2}$-), 1.50-1.28 (m, 18H, 9 x -CH$_2$-), 0.90-0.87 (t, 3H, ^{3}J6.68Hz, -CH$_3$). Elemental analysis: $C_{47}H_{45}NO_9$ requires C, 73.52; H, 5.90; N, 1.82%; found C, 73.10; H, 5.84; N, 1.63%.

1-[(4-*n*-dodecyloxybenzoyloxy)-4-benzoyloxy)]phenylene-3-[(4-nitrobenzoyloxy)-4-benzoate], 5.F.1

Yield, 78%; m.p. 150.0°C; ν_{max}: 3111, 2924, 2853, 1747, 1744, 1732, 1603, 1506, 1278, 1070 cm^{-1}; δ_H: 8.43-8.38 (m, 4H, Ar-H), 8.34-8.32 (d, 2H, ^{3}J8.72Hz, Ar-H), 8.30-8.28 (d, 2H, ^{3}J8.72Hz, Ar-H), 8.17-8.15 (d, 2H, ^{3}J8.88Hz, Ar-H), 7.53-7.49 (t, 1H, ^{3}J8.08Hz, Ar-H), 7.43-7.41 (d, 2H, ^{3}J8.72Hz, Ar-H), 7.39-7.37 (d, 2H, ^{3}J8.72Hz, Ar-H), 7.21-7.18 (m, 3H, Ar-H), 7.0-6.98 (d, 2H, ^{3}J8.92Hz, Ar-H), 4.08-4.04 (t, 2H, ^{3}J6.56Hz, Ar-O-CH$_2$-), 1.87-1.80 (quin, 2H, ^{3}J6.96Hz, Ar-O-CH$_2$-C$\underline{H_2}$-), 1.52-1.28 (m, 18H, 9 x -CH$_2$-), 0.91-0.87 (t, 3H, ^{3}J6.56Hz, -CH$_3$). Elemental analysis: $C_{46}H_{45}NO_{11}$ requires C, 70.12; H, 5.76; N, 1.78%; found C, 69.95; H, 5.81; N, 1.68%.

1-[(4-*n*-dodecyloxylbenzoyloxy)-4-benzoyloxy)]phenylene-3-[(4-cyanobiphenyl-carbonyloxy)-4-benzoate], 5.G.1

Yield, 70%; m.p. 167°C; ν; 3080, 2922, 2853, 2224, 1736, 1730, 1603, 1508, 1250, 1059 cm^{-1}; δ_H: 8.34-8.28 (m, 6H, Ar-H), 8.17-8.15 (d, 2H, ^{3}J8.92Hz, Ar-H), 7.81-7.75 (m, 6H, Ar-H), 7.53-7.49 (t, 1H, ^{3}J7.96Hz, Ar-H), 7.43-7.41 (d, 2H, ^{3}J8.76Hz, Ar-H), 7.39-7.37 (d, 2H, ^{3}J8.76Hz, Ar-H), 7.21-7.19 (m, 3H, Ar-H), 7.0- 6.98 (d, 2H, ^{3}J8.8Hz, Ar-H), 4.08-4.04 (t, 2H, ^{3}J6.52Hz, Ar-O-CH$_2$-), 1.87-1.81 (quin, 2H, ^{3}J7.0Hz, Ar-O-CH$_2$-C$\underline{H_2}$-), 1.50-1.28 (m, 18H, 9 x -CH$_2$-), 0.90-0.87 (t, 3H, ^{3}J6.64Hz, -CH$_3$). Elemental analysis: $C_{53}H_{49}NO_9$ requires C, 75.43; H, 5.84; N, 1.66%; found C, 75.00; H, 5.79; N, 1.71%.

1-[(4-*n*-dodecyloxylbenzoyloxy)-4-benzoyloxy)]phenylene-3-[(4-cyanobiphenylcarbonyloxy) 2-fluoro-4-benzoate],5.H.1

Yield, 73%; m.p. 172.0°C; ν_{max}: 3095, 2920, 2226, 1744, 1736, 1732, 1605, 1251, 1161, 1057 cm^{-1}; δ_H: 8.32-8.30 (d, 2H, ^{3}J8.36Hz, Ar-H), 8.29-8.27(d, 2H, ^{3}J8.68Hz, Ar-H), 8.24-8.20 (t, 1H, ^{3}J8.12Hz, Ar-H), 8.17-8.15 (d, 2H, ^{3}J8.76Hz, Ar-H), 7.81-7.75 (m, 7H, Ar-H), 7.53-7.49 (t, 1H, ^{3}J8.12Hz, Ar-H), 7.39-7.37 (d, 2H, ^{3}J8.64Hz, Ar-H), 7.24-7.19 (m, 4H, Ar-H), 7.0-6.98 (d, 2H, ^{3}J8.8Hz, Ar-H), 4.08-4.04 (t, 2H, ^{3}J6.52Hz, Ar-O-CH$_2$-), 1.87-1.80 (quin, 2H, ^{3}J7.08Hz, Ar-O-CH$_2$-C$\underline{\mathrm{H}}_2$-), 1.52-1.28 (m, 18H, 9 x -CH$_2$-), 0.90-0.87 (t, 3H, ^{3}J6.64Hz, -CH$_3$).

1-[(4-*n*-dodecylbenzoyloxy)-4-benzoyloxy)]phenylene-3-[(4-cyanobiphenylcarbonyloxy) 2-fluoro-4-benzoate],5.I.1

Yield, 67%; m.p. 175.0°C; ν_{max}: 3101, 2922, 2851, 2224, 1747, 1740, 1736, 1605, 1242, 1049 cm^{-1}; δ_H: 8.32-8.27 (m, 4H, Ar-H), 8.24-8.20 (t, 1H, ^{3}J8.28Hz, Ar-H), 8.13-8.11 (d, 2H, ^{3}J8.2Hz, Ar-H), 7.81-7.75 (m, 7H, Ar-H), 7.52-7.48 (t, 1H, ^{3}J8.12Hz, Ar-H), 7.40-7.37 (d, 2H, ^{3}J8.76Hz, Ar-H), 7.35-7.33 (d, 2H, ^{3}J8.2Hz, Ar-H), 7.24-7.19 (m, 4H, Ar-H), 2.73-2.69 (t, 2H, ^{3}J7.56Hz, Ar-CH$_2$-), 1.70-1.64 (quin, 2H, ^{3}J7.4Hz, Ar-CH$_2$-C$\underline{\mathrm{H}}_2$-), 1.33-1.27 (m, 18H, 9 x -CH$_2$-), 0.90-0.87 (t, 3H, ^{3}J6.6Hz, -CH$_3$).