

Chapter 3

Part-I

Synthesis and mesomorphic properties of

- (i) **2-Cyano-1, 3-phenylene bis[4-(4-*n*-alkoxyphenyliminomethyl)benzoates]**

Series- 3.1

Part-II

Synthesis and mesomorphic properties of

- (i) **2-Nitro-1, 3-phenylene bis[4-(4-*n*-alkoxybenzylideneamino)benzoates]**

Series- 3.11

- (ii) **2-Cyano-1, 3-phenylene bis[4-(4-*n*-alkoxybenzylideneamino)benzoates]**

Series- 3.111

Introduction

One of the interesting features of liquid crystals is the beautiful optical textures they exhibit when the sample of a suitable compound is cooled from the isotropic phase under a polarizing microscope. The mesophases can be distinguished from each other because of their characteristic optical textures. Amongst all the known B phases, the **B**₇ phase exhibits beautiful optical textures, which are unique, and the structure of the mesophase has been resolved to some extent recently [44]. This mesophase was first observed [28, 42] in some five-ring Schiff's base compounds derived from 2-nitroresorcinol. One of the characteristic textures of the **B**₇ mesophase is the growth of spiral filaments, which can be obtained when the isotropic liquid of an appropriate compound is cooled very slowly. In addition, various other two-dimensional patterns are also observed for this phase [42]. The helical filamentary growth patterns have been observed in a number of other systems not derived from 2-nitroresorcinol, and the mesophases of all these compounds have been assigned the symbol **B**₇. It is appropriate to outline the different mesophases labeled as **B**₇ mesophase. The first series of compounds, which were, assigned the symbol **B**₇ exhibit various textural patterns along with spiral filaments [42]. XRD studies on these compounds show several incommensurate reflections in the small angle region. Although there was a claim by Jakli *et al.* [83] about an optical change in these materials, no electric field switching (neither ferro- nor antiferro-electric properties) was observed atleast upto 40 V μm^{-1} . The mesophase of the novel sulphur compounds exhibiting spiral filaments [45, 46] was characterized as smectic and antiferroelectric and assigned the symbol **B**₇. Walba *et al.* [47] described ferroelectric properties in compounds containing racemic octan-2-ol in one of the terminal positions. Based on optical textures they also labeled the mesophase as **B**₇. Some Schiff's base compounds containing a lateral fluorine substituent on the outer phenyl ring *ortho* to the *n*-alkoxy chain exhibiting textural variants similar to standard **B**₇ materials have also been reported [30]. The XRD studies of these compounds match with the standard **B**₇ materials. But the electric field experiments point towards a ferroelectric switching behaviour. Therefore they labeled the mesophase as **B**_{7bis}. The two-dimensional mesophase with antiferroelectric properties are reported [50] in some salicylaldimine compounds and assigned the symbol **B**₇. These compounds do exhibit helical patterns but no other two-dimensional textural variants were observed. The mesophase exhibited by compounds containing fluorine *ortho* to the *n*-alkoxy

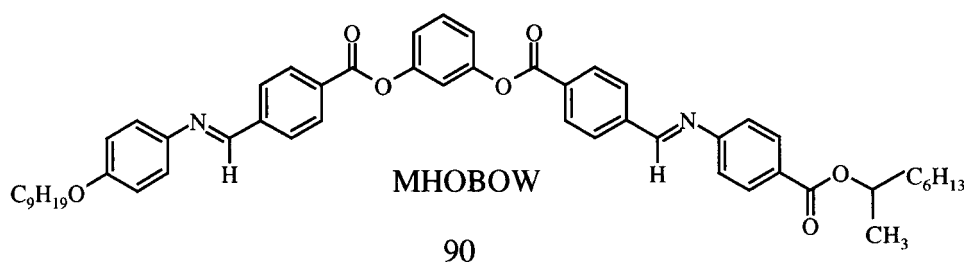
chain was reported as **B₇ mesophase** based on fractal dimension analysis [49]. The **B₇ mesophase** was also reported [48] in compounds containing chlorine *ortho* to n-alkoxy chain. These showed a smectic mesophase with antiferroelectric characteristics. Later Weissflog *et al.* [53] synthesized these compounds and re-examined the mesophase carefully and concluded that it was not a **B₇** phase. Although the standard **B₇** materials do not switch electrically atleast upto about $40\text{V}\mu\text{m}^{-1}$, both ferro- and antiferro- electric properties were reported for some of the mesophases identified as **B₇**.

Two series of symmetrical seven-ring esters derived from 2-cyanoesorcinol and exhibiting the **B₇** phase have been reported [32, 43] from our laboratory. The different textures, the XRD pattern and the electro-optical switching behaviour of the mesophase of these compounds are similar to the **B₇** phase of the standard materials [42].

Recently, Coleman *et al.* [44] have carried out extensive studies on several compounds and mainly on compound MHOBOW. The mesophase of MHOBOW was earlier reported as smectic and ferroelectric and assigned the symbol **B₇**, purely based on spiral growth patterns observed under a polarizing microscope.

Coleman *et al.* [44] have used several experimental techniques such as synchrotron based powder and single-domain micro-beam X-ray, freeze-fracture transmission electron microscopy, and depolarized transmission and reflection light microscopy in arriving at the structure of the mesophase exhibited by compound MHOBOW. Based on these experimental results they have argued that in the mesophase of MHOBOW, local splay prevails in the form of periodic supermolecular scale polarization modulation stripes and are coupled to layer undulation waves. The polar domains are locally chiral and organized into patterns of alternating handedness and polarity. They have also proposed a model, a schematic representation of which is shown in figure 3.1.

They have concluded, "In the mesophase of MHOBOW the local spontaneous polar/chiral ordering drives a larger scale periodic structure of polarization defects. The dominant structure of MHOBOW is the globally 2D-rectangular antiferroelectric racemic phase with splay stripes, exhibiting a striking out of phase alternation of polarization and chirality".



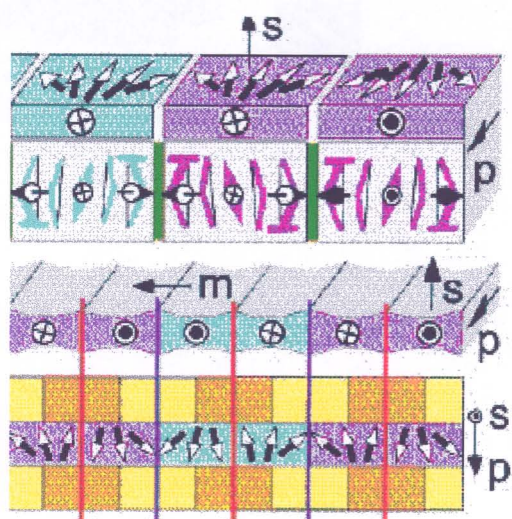


Figure 3.1: The proposed model of modulated structure of B_7 mesophase of compound MHOBOW [44].

They have also carried out experiments on the mesophase of compound W 1044 (*n*-OPIMB-NO₂) [42], for which the symbol B_7 was assigned at the 1997 International Workshop on Banana-shaped mesogens: “Chirality by Achiral Molecules” held in Berlin. In the mesophase of compound W 1044 the layers are interdigitated to provide efficient packing at the polarization splay defects to produce a 2D lattice and it has been suggested that it belongs to B_1 family. A schematic representation of the model proposed for compound W 1044 is shown in figure 3.2.

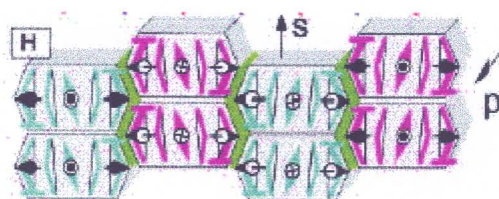
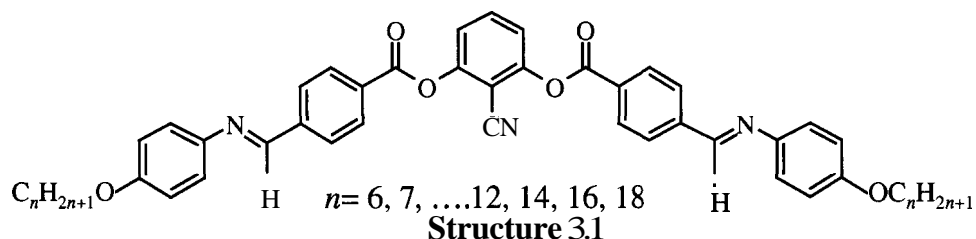


Figure 3.2: The proposed model for a B_7 mesophase of 2-nitroresorcinol derivative [44].

The nomenclature used in this chapter to assign a symbol for this interesting mesophase is B_7 and is based on what was accepted at the above workshop.

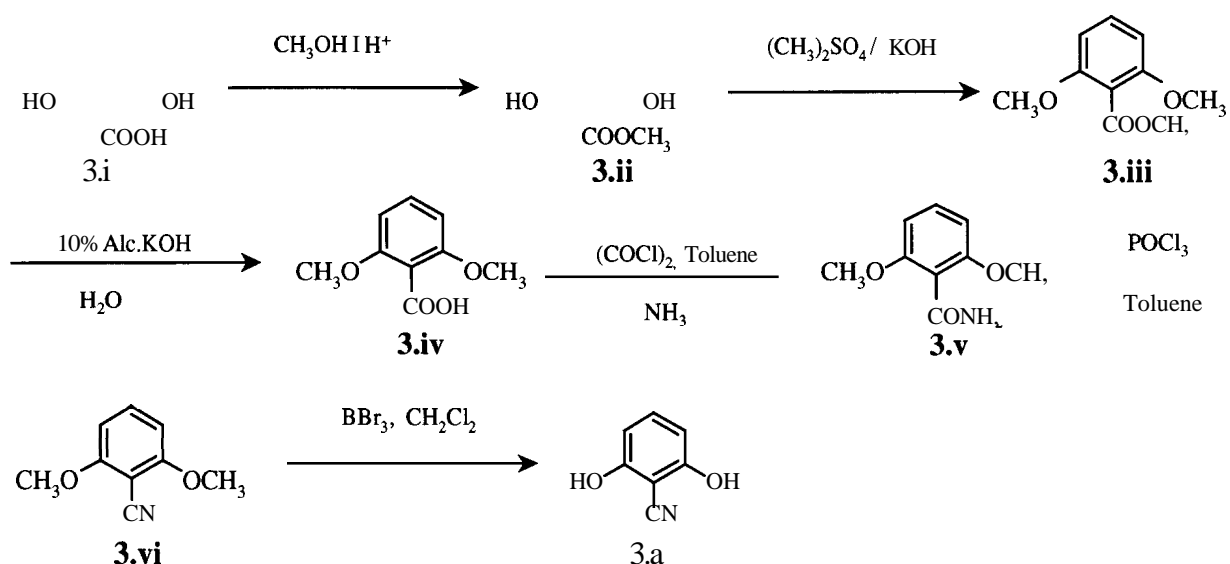
In this chapter, the synthesis and characterization of compounds belonging to three homologous series (series **3.I-3.III**) of Schiff's base esters derived from 2-cyano- and 2-nitro-resorcinol have been described.

In the first part, the synthesis and mesomorphic properties of compounds of series 3.1 are discussed. The general molecular structure of the compounds is shown below (structure 3.1).



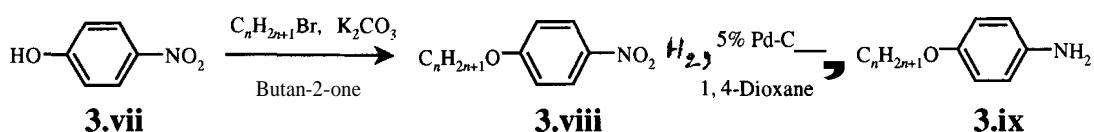
Synthesis

The synthesis of 2-cyanoresorcinol was achieved following a route outlined in scheme 3.1. Methyl 2, 6-dimethoxybenzoate was obtained by esterifying the commercially available 2, 6-dihydroxybenzoic acid followed by methylation using dimethyl sulphate. The ester was hydrolyzed to get 2, 6-dimethoxybenzoic acid. The resultant carboxylic acid was converted into the carboxamide via its acid chloride. The dehydration of the amide in the presence of phosphoryl chloride gave 2, 6-dimethoxybenzonitrile, which was demethylated using boron tribromide to yield the desired 2-cyanoresorcinol.



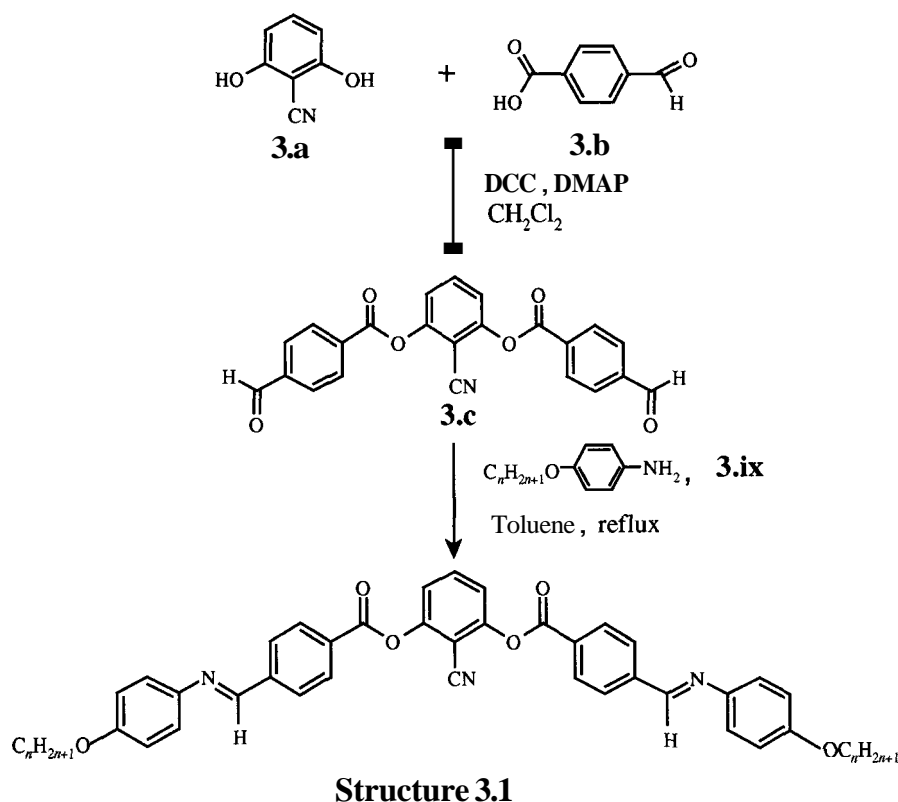
Scheme 3.1: Synthetic pathway used to prepare 2-cyanoresorcinol.

4-Carboxybenzaldehyde was obtained commercially and used without further purification. 4-n-Alkoxyanilines were prepared following a procedure already described in the literature [62]. The synthetic pathway used is shown in scheme 3.2.



Scheme 3.2: Synthetic pathway used to prepare 4-n-alkoxyanilines.

The synthesis of 2-cyano-1, 3-phenylene bis [4-(4-n- alkoxyphenylirminomethyl) benzoates] was carried out as follows. 4-Carboxybenzaldehyde was condensed with 2-cyano-resorcinol in the presence of DCC and DMAP in dry dichloromethane to get 2-cyano-1, 3-phenylene bis-[4-formylbenzoate]. The dialdehyde thus obtained was purified and condensed with appropriate 4-n-alkoxyanilines in a Dean-Stark apparatus using toluene as a solvent. The general synthetic pathway used is given in scheme 3.3.



Scheme 3.3: Synthetic pathway used for obtaining the banana-shaped compounds of series 3.1.

Results and discussion

In table 3.1 the phase transition temperatures together with the associated transition enthalpies for the 2-cyano-1, 3-phenylene bis[4-(4-*n*-alkoxyphenyliminomethyl)benzoates], are summarized. All the compounds show enantiotropic mesomorphic behaviour. Some interesting observations can be made from this data. Compounds 3.A.1 to 3.A.4 have a lower melting enthalpy than the corresponding clearing enthalpy. However for homologues 3.A.5 to 3.A.10, the melting enthalpies are higher. The DSC thermogram obtained for compound 3.A.7 is shown in figure 3.3 and a number of crystal-crystal transitions can be seen. In addition to a gradual increase of the thermal range of the mesophase, there is a reduction in the melting points on ascending the series. In the series, compound 3.A.10 has the largest temperature range for the mesophase, *Ca* 39°C. One of the most interesting features of the **B₇** mesophase is the beautiful optical textures they exhibit. For example, when a thin film of compound 3.A.9 was sandwiched between two glass plates and cooled slowly from the isotropic phase, both single and double winded helices could be seen under a polarizing microscope. Typical textures obtained for this compound is shown in figure 3.4 (a-d). In addition, various other patterns could also be seen to grow in other parts of the same sample. The textural variants include elongated germs, myelinic texture and two-dimensional periodic patterns and these are depicted in figure 3.5 (a-f). All these textures are very typical for the **B₇** mesophase.

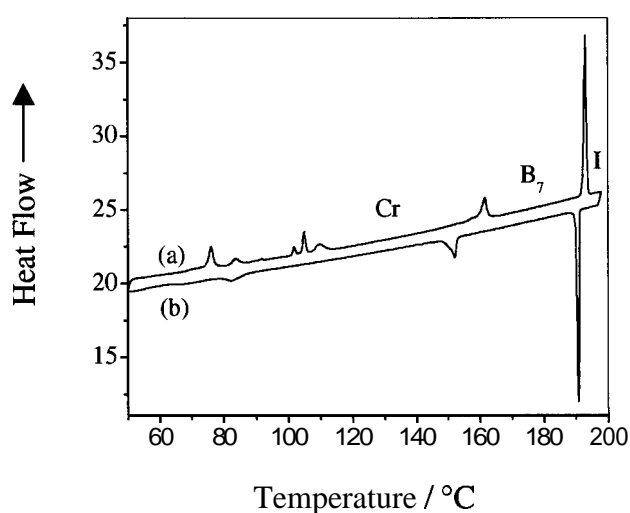
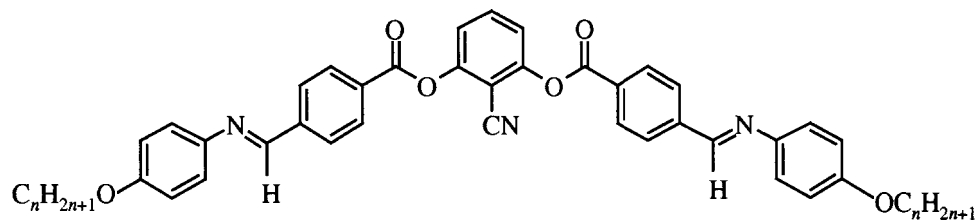


Figure 3.3: A DSC thermogram obtained for compound 3.A.7; (a) heating and (b) cooling cycles; rate, 5°C min⁻¹.

Table 3.1: Transition temperatures (°C) and the associated enthalpy values (kJ mol⁻¹) for the compounds of series 3.1



Compound	n	Cr	B ₇	I
3.A.1	6	. 177.0 14.5	. 190.0 26.7	.
3.A.2	7	. 172.0 17.6	. 192.5 27.4	.
3.A.3	8	. 170.0 14.5	. 193.5 26.9	.
3.A.4	9	. 163.0 16.6	. 193.5 28.2	.
3.A.5	10	. 163.0 35.1	. 193.5 27.9	.
3.A.6	11	. 162.0 42.8	. 193.0 30.8	.
3.A.7	12	. 160.0 33.6	. 192.0 33.6	.
3.A.8	14	. 156.0 43.8	. 190.0 33.9	.
3.A.9	16	. 152.0 52.5	. 188.0 34.7	.
3.A.10	18	. 146.5 58.8	. 185.5 35.3	.

Key: Cr: crystalline phase; B₇: non-switchable non-layered banana phase with helical superstructure; I: isotropic phase.

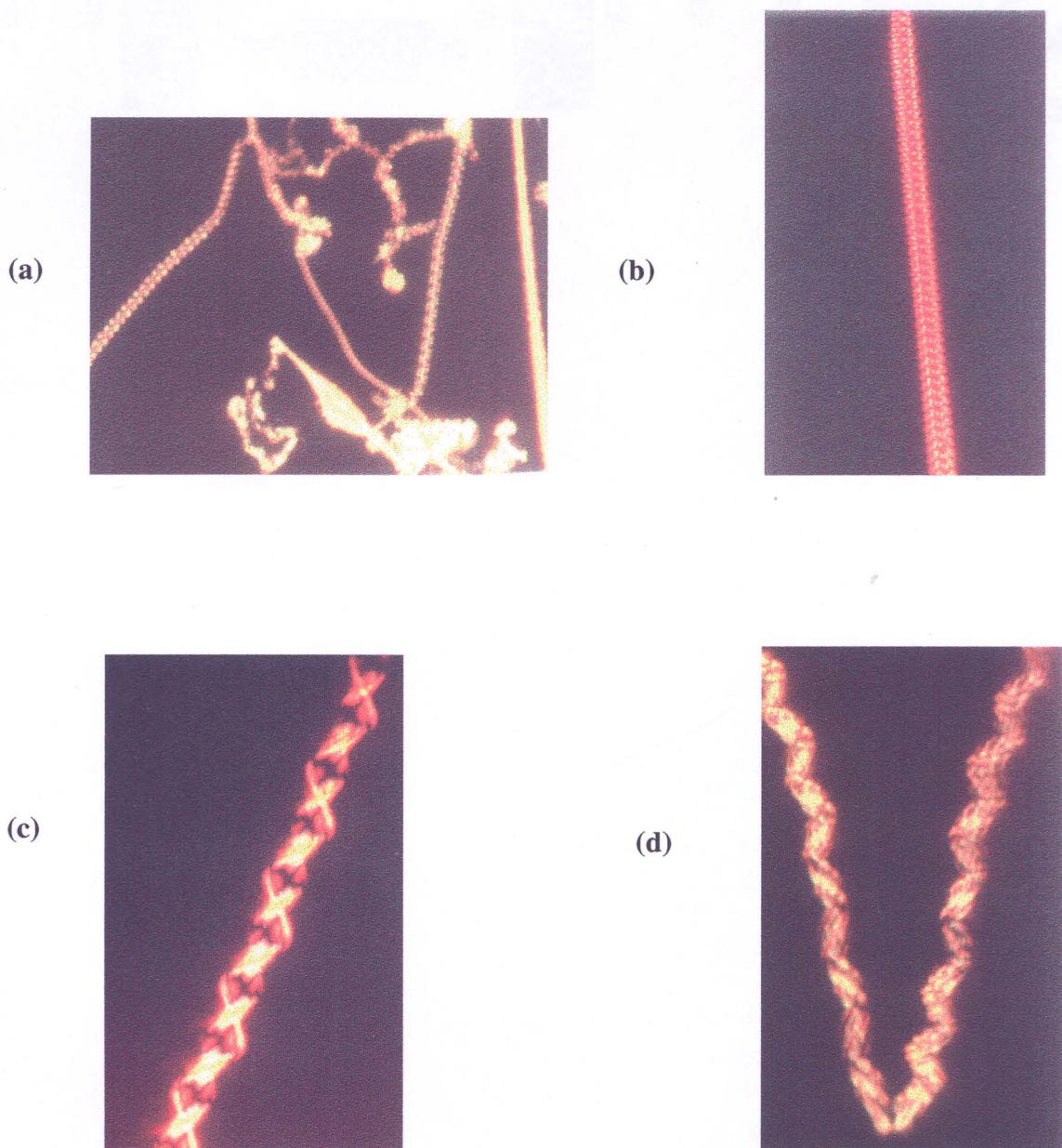
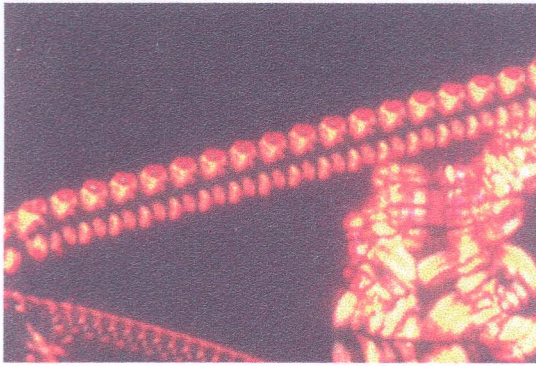
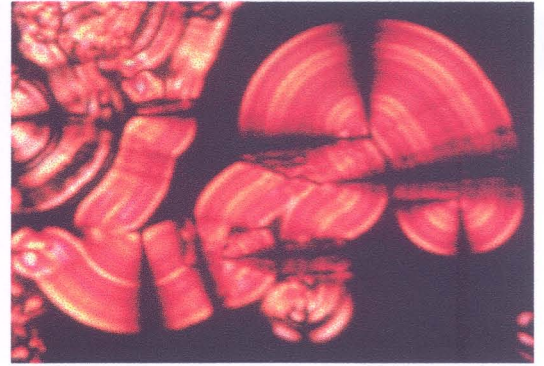


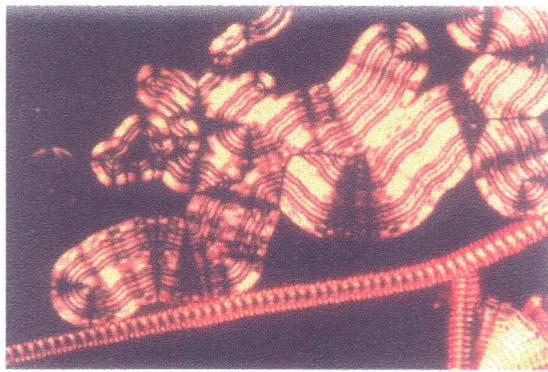
Figure 3.4 (a-d): Optical photomicrographs of the helical patterns obtained for the B₇ mesophase.



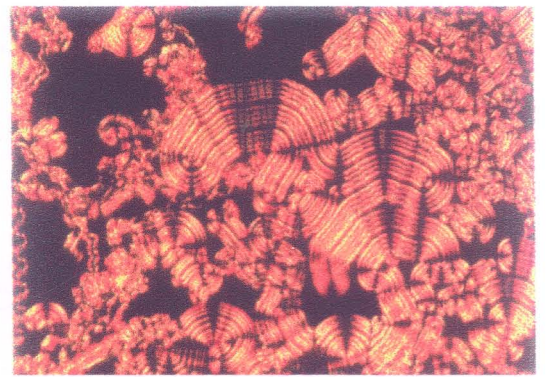
(a)



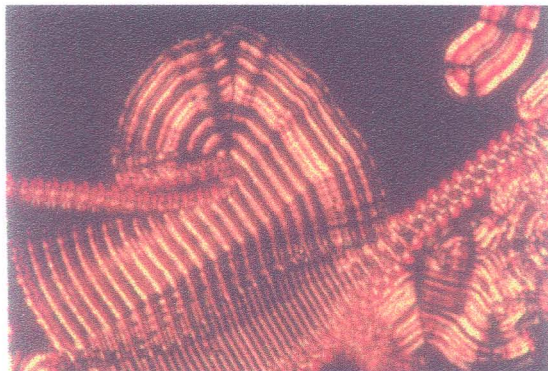
(b)



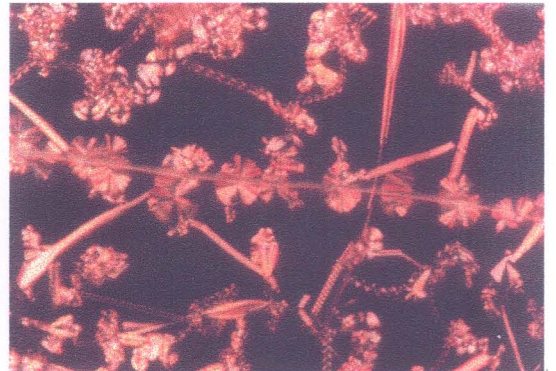
(c)



(d)



(e)



(f)

Figure 3.5 (a-f): Optical photomicrographs of the various patterns obtained for the B₇ mesophase.

A plot of the transition temperatures as a function of the number of carbon atoms in the n-alkoxy chain is shown in figure 3.6. The clearing temperatures fall on a smooth curve as observed for this mesophase in two other series of seven-ring esters [32].

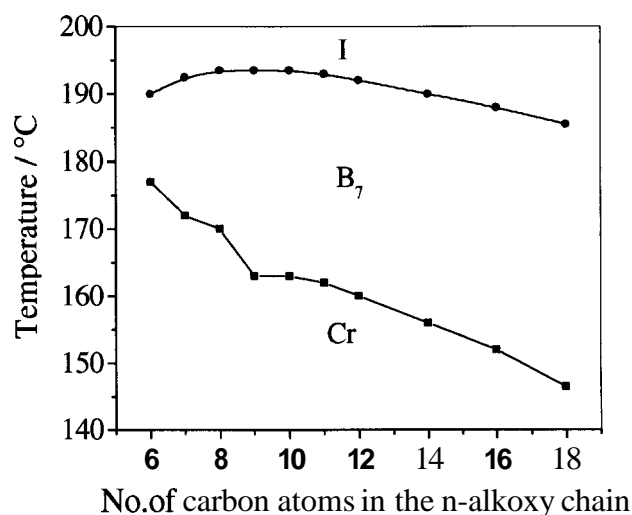


Figure 3.6: A Plot of transition temperatures as a function of the length of the n-alkoxy chain.

In order to confirm the identity of this mesophase, X-ray diffraction experiments were carried out on non-oriented sample using an image plate arrangement. A sample of compound **3.A.10** in the isotropic phase was taken in a Lindemann capillary and cooled slowly to the mesophase. The temperature of the sample was controlled to within $\pm 0.1^\circ\text{C}$. The X-ray angular intensity profile obtained for this compound at 160°C is shown in figure 3.7. The diffuse scattering in the wide-angle region at 4.8 \AA is indicative of the absence of in-plane order. In the small angle region, six reflections could be seen corresponding to $d_1=47.6 \text{ \AA}$, $d_2=27.8 \text{ \AA}$, $d_3=16.7 \text{ \AA}$, $d_4=12.5 \text{ \AA}$, $d_5=9.9 \text{ \AA}$ and $d_6=7.6 \text{ \AA}$. Although these reflections cannot be indexed easily, a simple layered structure for the mesophase can be excluded and perhaps points to a two- or three-dimensional structure. The d-spacings obtained from XRD studies and measured molecular length from molecular models of the compounds are given in table 3.2.

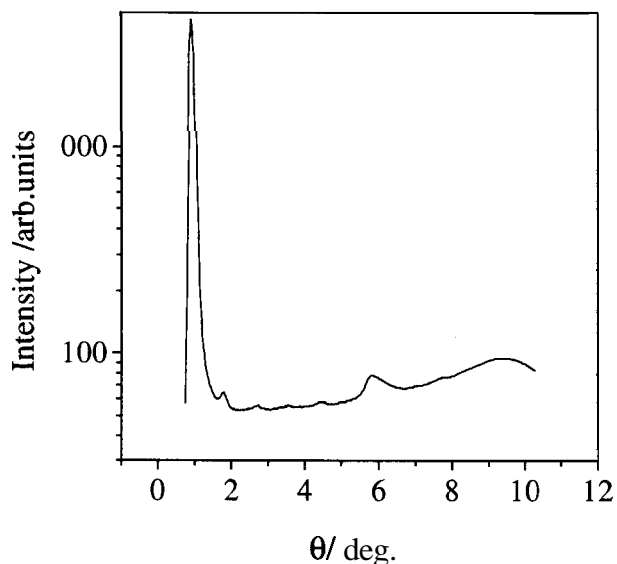


Figure 3.7: The X-ray angular intensity profile obtained for the mesophase of compound **3.A.10** at **160°C**.

Table 3.2: The obtained *d* values from XRD studies and the measured molecular length by considering the methylene units of the *n*-alkoxy chain in an all trans conformation

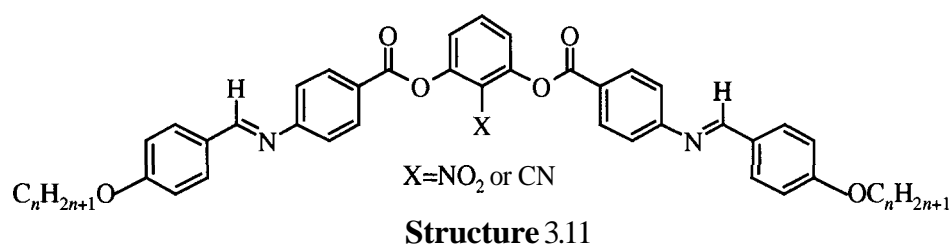
Compound	d spacing / Å						measured molecular length / L / Å
	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	
3.A.3	34.6	17.6	-	11.8	-	7.6	50.4
3.A.7	40.9	20.0	17.3	12.7	-	7.6	57.6
3.A.10	47.6	27.8	16.7	12.5	9.6	7.6	77.8

The electric field experiments on this mesophase were carried out using the triangular-wave method. For example, a sample of compound **3.A.10** was taken in an ITO coated cell with a thickness of 9µm. The inner surfaces was coated with polyimide and unidirectionally rubbed for homogeneous alignment of the sample. On applying a triangular-wave electric field $\pm 44 \text{ V}\mu\text{m}^{-1}$, no evidence of switching could be seen. The various optical textures and X-ray data obtained for the mesophase of compounds presented here can be compared with those obtained for 2-nitroresorcinol derivatives [42] which represent the standard materials for the B₇ mesophase. Moreover no switching behaviour for the mesophase of compounds **3.A.1** to **3.A.10** was

observed like those of the standard materials. Therefore one can safely argue that the mesophase of these compounds is indeed B_7 as suggested at the international Workshop in Berlin. A strongly polar substituent such as a **nitro-** or a **cyano-** group in the 2 position of the central phenyl ring may be responsible for inducing this B_7 mesophase. However, Coleman *et al.* [44] have studied the compound viz. *n*-OPIMB NO₂ (standard materials for B_7 phase) and proposed a model for the B_7 phase. According to that model, the B_7 phase exhibited by the standard compounds belongs to a B_1 family of mesophases.

Part II

In this part, the synthesis and characterization of two homologous series (series 3.11 and series 3.III) of compounds derived from both 2-nitro- and 2-cyano-resorcinol and exhibiting the B₇ phase having the general molecular structure shown below are described.

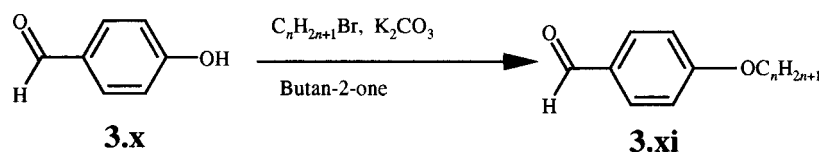


$X = \text{NO}_2$ $n = 7, 9, \dots, 12, 14, 16, 18, 20$ Series- 3.11

$X = \text{CN}$ $n = 7, 9, \dots, 12, 14, 16, 18$ Series-3.111

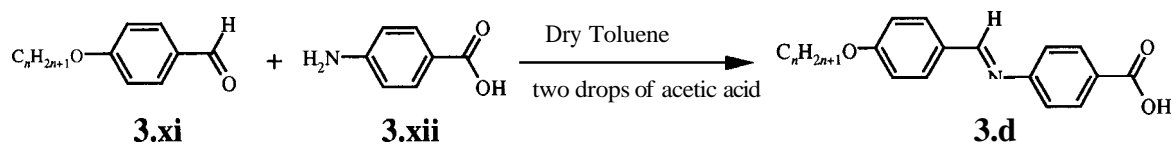
Synthesis

4-n-Alkoxybenzaldehydes were obtained by alkylation of 4-hydroxybenzaldehyde with an appropriate n-alkyl bromide in the presence of anhydrous potassium carbonate [64] as shown in scheme 3.4.

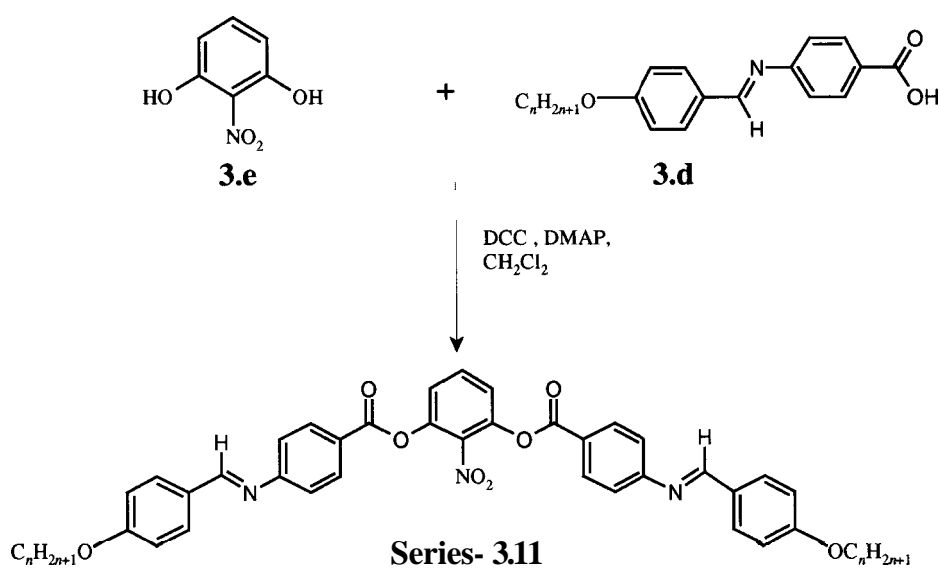


Scheme 3.4: Synthetic pathway used for the preparation of 4-n-alkoxybenzaldehydes.

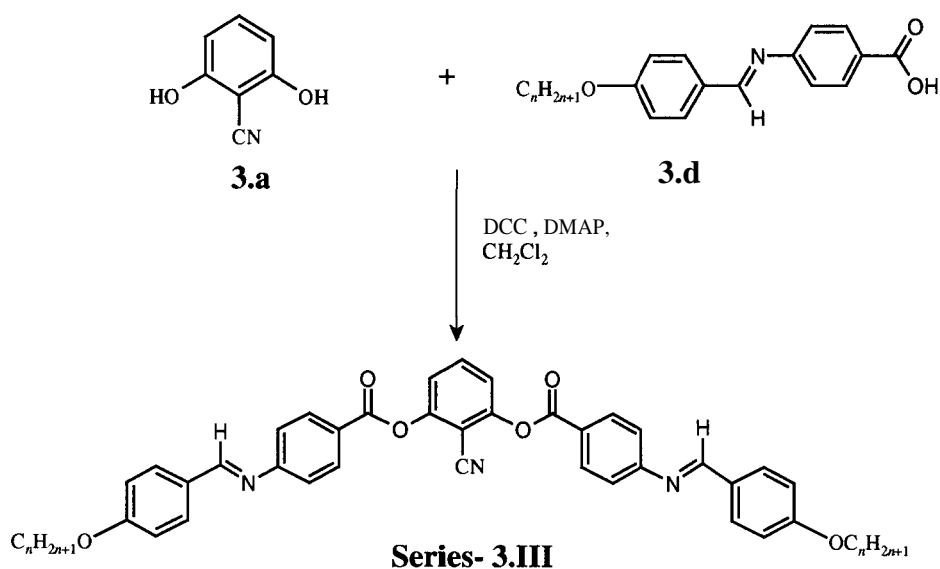
4-Aminobenzoic acid was obtained commercially and used without further purification. **4-n-Alkoxybenzylideneamino-4-benzoic** acids were synthesized by condensation of 4-n-alkoxybenzaldehydes with 4-aminobenzoic acid in toluene using a Dean-Stark apparatus as shown in scheme 3.5. 2-Nitroresorcinol was obtained commercially and used without further purification. The target compounds were obtained by reacting two equivalents of an appropriate **4-n-alkoxybenzylideneamino-4-benzoic** acid, with 2-substituted resorcinol. The synthetic pathway used is depicted in schemes 3.6 and 3.7.



Scheme 3.5: Synthetic pathway used for obtaining the 4-n-alkoxybenzylideneamino-4-benzoic acids.



Scheme 3.6: Synthetic pathway used for obtaining the banana-shaped compounds of series 3.11.

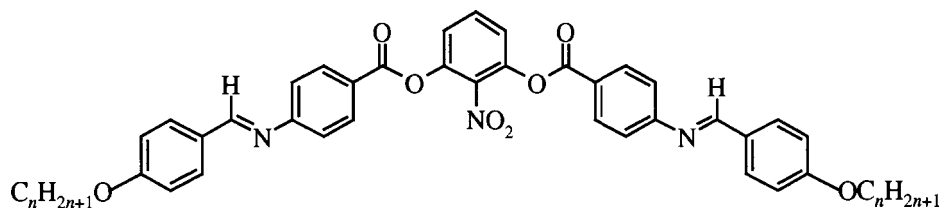


Scheme 3.7: Synthetic pathway used for obtaining the banana-shaped compounds of series 3.II.

Results and discussion

The phase transition temperatures and the associated enthalpy values obtained for the homologous series of compounds derived from 2-nitroresorcinol (series 3.II) are summarized in table 3.3. Compounds 3.B.1 and 3.B.2 are non-mesomorphic and hence the lower homologues were not prepared. The remaining seven compounds 3.B.3 to 3.B.9 are mesomorphic and all of them show similar optical textures when their isotropic liquids are cooled slowly. However, compounds 3.B.7 and 3.B.8 exhibit two additional phases. A DSC thermogram obtained for compound 3.B.7 is shown in figure 3.8. As can be seen, three reversible transitions were obtained. The lower temperature phases have been designated as B_{7AF1} and B_{7AF2} , and the B_{7AF1} phase exists even in compound 3.B.9 as an enantiotropic mesophase over a thermal range of 12°C. Both ferroelectric as well as antiferroelectric switching behaviour have been reported for mesophases for which the symbol B_7 was assigned by several investigators. Hence, we prefer to use the symbol B_7 for a non-switchable, non-layered mesophase derived from either 2-nitro- or 2-cyano-resorcinol and whose X-ray diffraction pattern and textural variants are similar to those of the standard material [28, 42].

Table 3.3: Transition temperatures ($^{\circ}\text{C}$) and the associated enthalpy values (kJ mol^{-1}) for the compounds of series 3.11



Compound	n	Cr	B_{7AF2}	B_{7AF1}	B_7	I
3.B.1	7	. 142.0 71.9	-	-	-	.
3.B.2	9	. 132.0 50.1	-	-	-	.
3.B.3	10	. 112.0 25.1	-	-	. 119.0	.
3.B.4	11	. 107.0 ^a 13.4	-	-	. 120.5	.
3.B.5	12	. 117.0 30.2	-	-	. 121.5	.
3.B.6	14	. 99.0 42.0	-	-	. 123.5	.
3.B.7	16	. 100.5 ^a 66.6	. 104.0 0.2	. 105.5 1.9	. 124.5	.
3.B.8	18	. 100.0 ^a 79.4	(. 97.0)	. 113.0 1.7	. 125.0	.
3.B.9	20	. 103.0 ^a 99.3	-	. 115.0 1.5	. 125.0	.

Key: Cr: crystalline phase, B_7 ; non-switchable non-layered banana phase with helical superstructure, B_{7AF1} and B_{7AF2} : novel two-or three-dimensional antiferroelectric mesophases; I: isotropic liquid, a: sample has crystal-crystal transitions, enthalpy denoted is the sum of all such transitions.

In addition, the transition from this non-switchable B_7 phase to an antiferroelectric phase, which goes over to another antiferroelectric phase was observed and hence these two sub-phases have been assigned the symbols B_{7AF1} and B_{7AF2} respectively. When a thin film of the isotropic liquid of compound **3.B.8** was cooled slowly and viewed under a polarizing microscope, different types of textures could be seen. Though the texture with spiral filaments could be seen, it is not the

dominant feature. Generally, spherulitic domains in which the extinction cross are parallel to polarizer and analyzer, long leaf-like texture and other unusual textures are obtained which are shown in figure 3.9 (a-d).

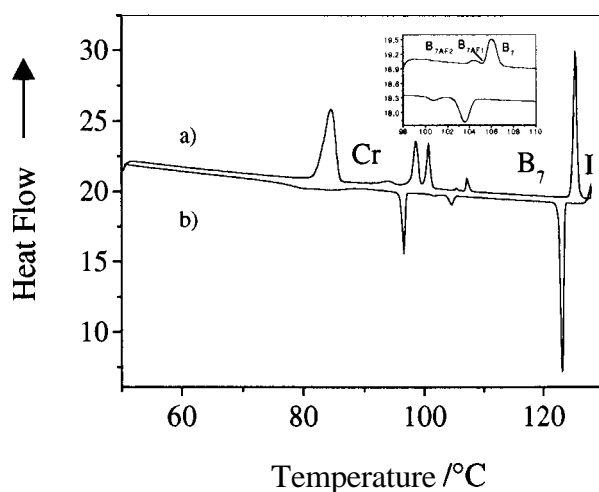


Figure 3.8: A DSC thermogram obtained for compound 3.B.7; (a) heating cycle; (b) cooling cycle; rate $5^{\circ}\text{C min}^{-1}$. Inset shows the expanded region of B_7 , B_{7AF1} and B_{7AF2} phase transitions.

The clearing enthalpy value is in the range of $25\text{-}29\text{ kJ mol}^{-1}$. Based on these as well as other physical measurements (described later) the higher temperature mesophase has been identified as B_7 . On further cooling the B_7 mesophase of compound 3.B.8, a phase transition takes place, which could be clearly seen under a polarizing microscope. The existing fine lines on the spherulites of B_7 phase disappeared and they became smooth. This change in the texture from B_7 phase to B_{7AF1} phase (108°C) is shown in figure 3.10. The transition from B_7 phase to B_{7AF1} phase was accompanied by a small enthalpy change of about $1.5\text{-}1.9\text{ kJ mol}^{-1}$.

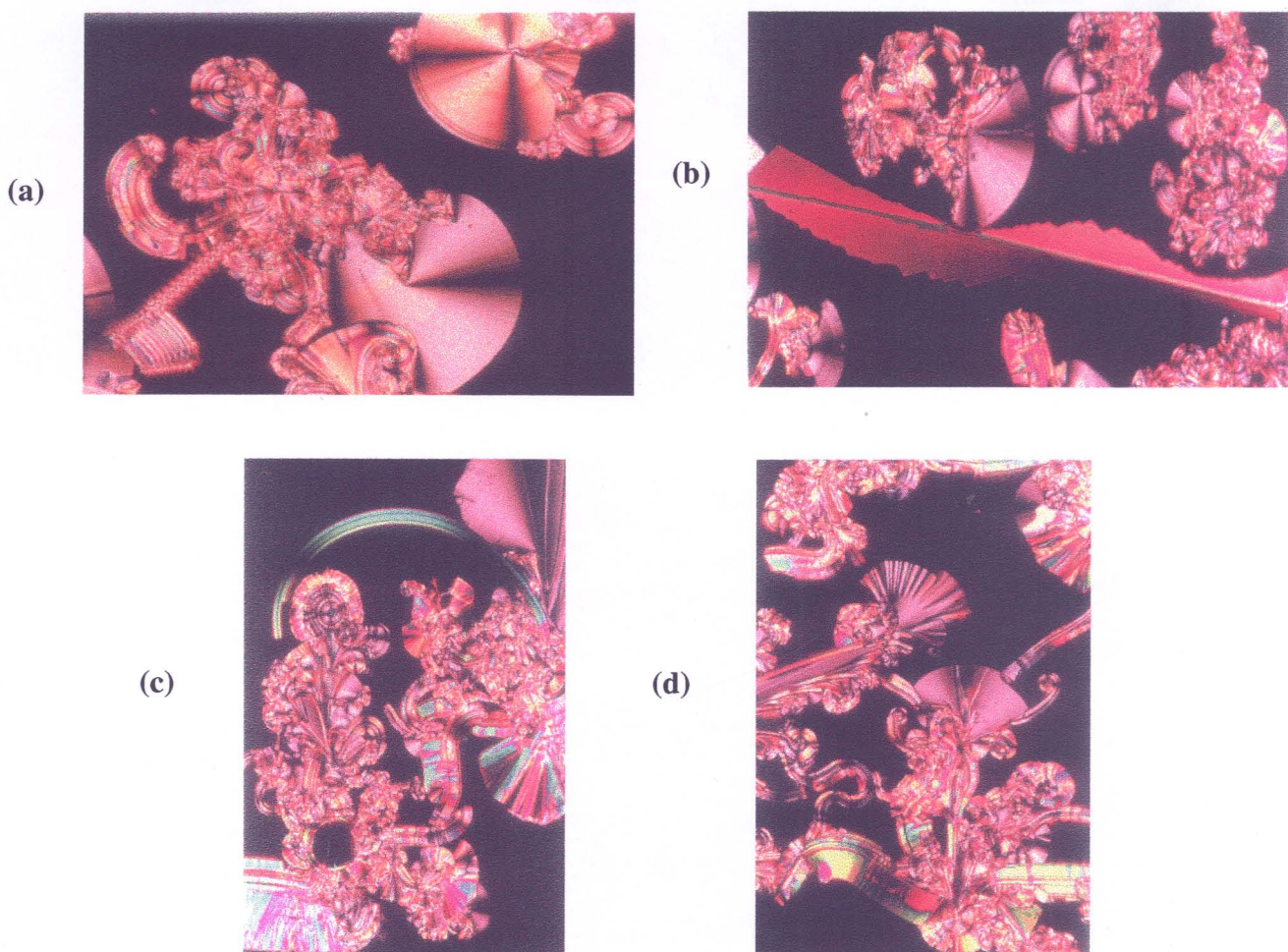


Figure 3.9 (a-d): Optical photomicrographs of various patterns of the B₇ mesophase obtained for compound 3.B.8.

On lowering the temperature further, another phase transition took place at 97°C and although no textural change was visible, a small endothermic peak could be observed on a DSC thermogram and this monotropic phase was designated as B_{7AF2}.

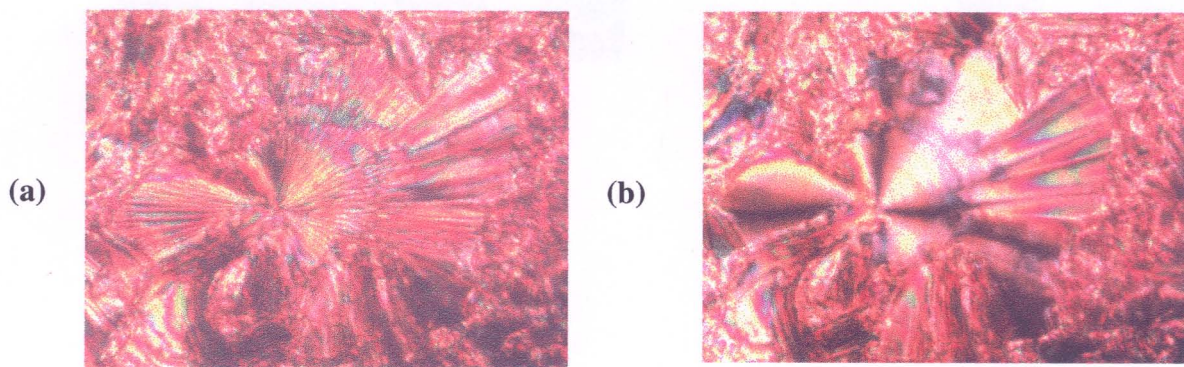


Figure 3.10: Optical photomicrographs showing the textural change from (a) B_7 mesophase to (b) B_{7AF1} mesophase of compound 3.B.8.

A plot of the transition temperatures as a function of number of carbon atoms in the terminal n -alkoxy chain is shown in figure 3.11. One can clearly see a smooth curve for the clearing temperatures.

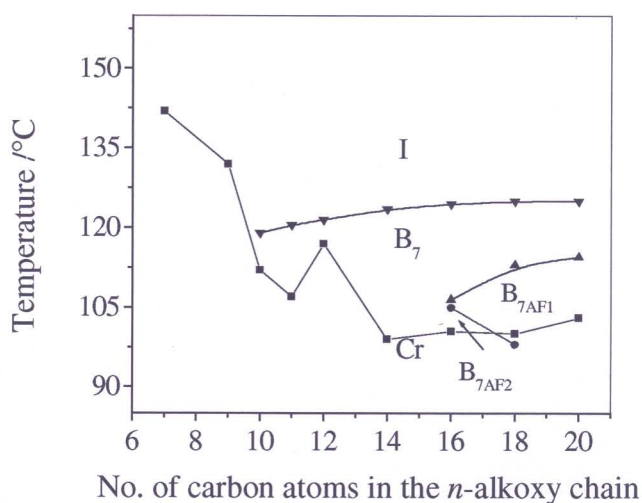
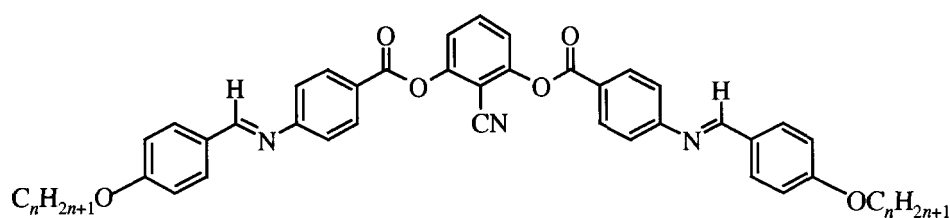


Figure 3.11: A plot of the transition temperatures as a function of number of carbon atoms in the n -alkoxy chain for compounds of series 3.II.

The transition temperatures and the associated enthalpy values for the analogous compounds which are derived from 2-cyanoresorcinol (series 3.III) are summarized in table 3.4. In this series, compound 3.C.1 is non-mesomorphic while the remaining are monomesomorphic.

From the optical textures and clearing enthalpy values, the mesophase of all these strongly polar compounds have been identified as **B₇**. A typical texture developing from the isotropic liquid of compound **3.C.5** is shown in figure **3.12**. A plot of transition temperatures as a function of the terminal n-alkoxy chain length for compounds of series **3.III** is shown in figure **3.13** and the clearing points fall on a smooth curve which is typical for the **B₇** phase.

Table 3.4: Transition temperatures (°C) and the associated enthalpy values (kJ mol⁻¹) for the compounds of series 3.III



Compound	n	Cr	B₇	I
3.C.1	7	.	150.0 69.2	-
3.C.2	9	.	130.0 ^a 55.9	(. 120.0) 19.3
3.C.3	10	.	112.0 35.2	. 122.5 20.5
3.C.4	11	.	99.5 34.7	. 125.0 23.1
3.C.5	12	.	103.5 37.7	. 127.0 23.2
3.C.6	14	.	102.0 ^a 59.4	. 130.0 23.2
3.C.7	16	.	104.0 59.3	. 132.5 25.8
3.C.8	18	.	105.5 ⁿ 81.5	. 132.0 25.6

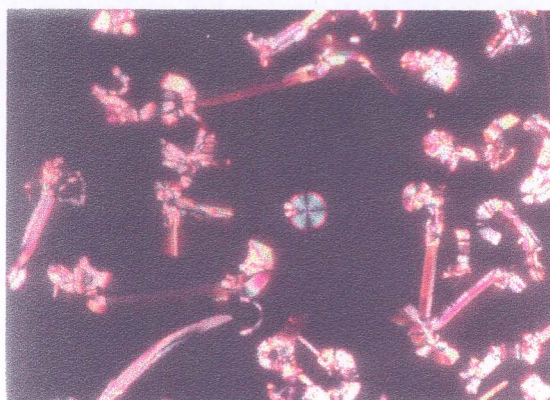


Figure 3.12: A photomicrograph showing lancet as well as spherulitic patterns obtained for the B_7 mesophase of compound 3.C.5.

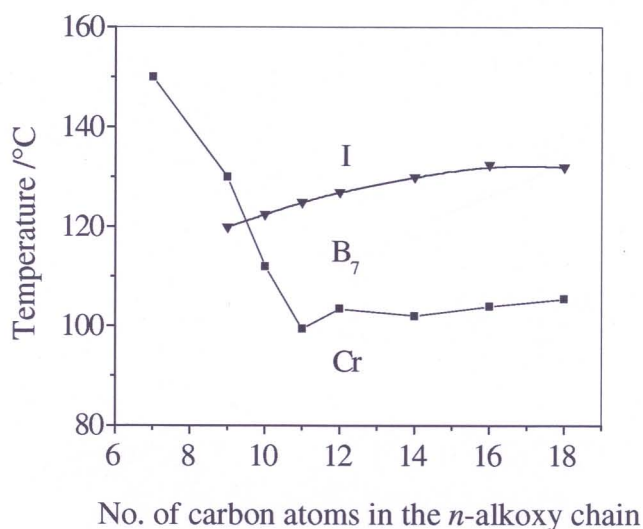


Figure 3.13: A plot of the transition temperatures as a function of number of carbon atoms in the *n*-alkoxy chain for compounds of series 3.III.

In order to investigate the mesophase structure of these newly synthesized materials, X-ray diffraction studies were carried out on non-oriented samples. Generally, the compounds were taken in 0.7 mm diameter Lindemann capillaries and temperature of the heater was controlled to $\pm 0.1^\circ\text{C}$. A typical XRD pattern obtained for the mesophase of compound 3.B.8 gives six incommensurate reflections in the small angle region which rule out the possibility of a simple layered structure. The diffuse wide-angle reflection at about 4.6\AA indicates the absence of

in-plane order. It is interesting to note that a reflection at $d=7.4-7.6\text{\AA}$ is always observed for the B_7 mesophase of all compounds derived from 2-nitro- or 2-cyano- resorcinol [28, 32]. This characteristic peak could be seen even in the solid state of these compounds. This reflection perhaps is from some kind of in-plane periodicity and is independent of whether it is from five-ring Schiff's bases or seven-ring esters. It was also observed that no significant change in the diffraction pattern took place as the sample was cooled from the B_7 phase to the lower temperature B_{7AF1} and B_{7AF2} phases. At this juncture, since the structure of B_7 phase is not clear it is difficult to speculate the structure of these low temperature phases. Perhaps, high resolution experiments such as those reported by Coleman *et al.* [44] would be required to unambiguously arrive at the structure of these phases. The d values obtained for four of the compounds under investigation and the measured molecular length L in their most extended form with an all trans conformation of the n -alkoxy chains are tabulated in table 3.5. The X-ray angular intensity profile obtained in the B_7 mesophase of compound 3.B.8 is shown in figure 3.14.

Table 3.5: The d -spacings of the compounds in the small angle region obtained from XRD studies and the corresponding measured molecular length (L) obtained by considering the methylene units of n -alkoxy chain in an all *trans* conformation

Compound	d spacing / \AA						measured molecular length / $L / \text{\AA}$
	d_1	d_2	d_3	d_4	d_5	d_6	
3.B.5	36.7	29.0	22.1	19.6	-	7.4	62.1
3.B.7	44.7	40.0	31.7	20.8	17.6	7.4	73.1
3.B.8	44.1	34.3	21.8	19.5	14.9	7.4	78.3
3.C.14	67.0	25.8	17.1	-	-	7.6	62.1

The electric field experiments on the B_7 as well as on B_{7AF1} and B_{7AF2} mesophases were carried out using standard triangular-wave method. For example compound 3.B.8 was taken in a cell having a thickness $9.9\mu\text{m}$, the inner surfaces of which were coated with polyimide and

unidirectionally rubbed. On applying a triangular-wave electric field of 550 V_{pp} at 30 Hz, no polarization current peak was observed in the B₇ mesophase.

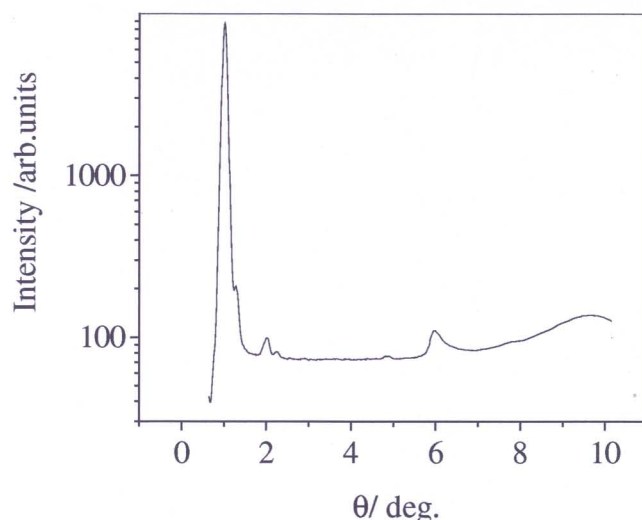


Figure 3.14: The X-ray angular intensity profile obtained for the B₇ mesophase compound 3.B.8 at 118°C.

This is in conformity with what was observed for the B₇ phase of various other compounds. However, on cooling the sample to a low temperature B_{7AF1} phase, two prominent current peaks per half cycle was observed which remained until the sample crystallized well below the melting point. Simultaneously, the sample was observed under a polarizing microscope. The optical textures observed under these conditions for the B₇ and the B_{7AF1} phases are shown in figure 3.15.

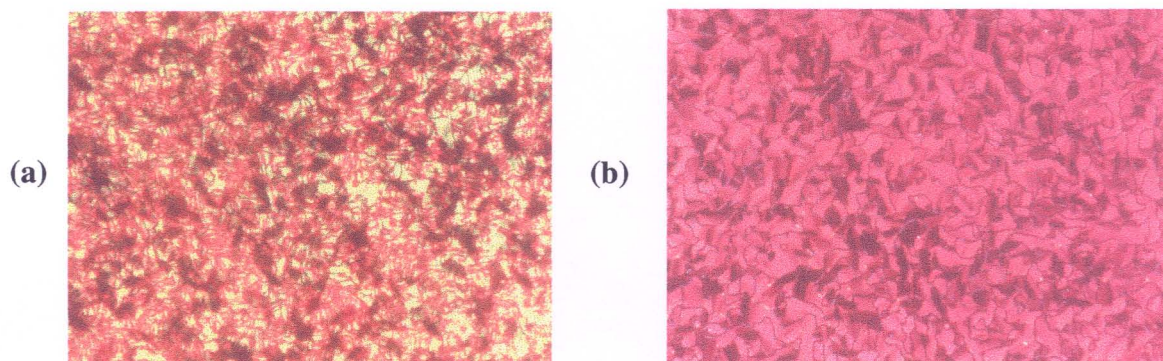


Figure 3.15: Optical photomicrographs of the texture obtained under an a triangular-wave electric field for (a) B₇ mesophase and (b) B_{7AF1} mesophase.

At this high voltage of 550 V_{pp} an apparent third peak which follows the two antiferroelectric peaks was observed. A similar current response was obtained by Heppke *et al.* [46] for the mesophase of some novel sulfur containing compounds. As pointed out by them, this may be due to a combination of switching through the two different types of antiferroelectric phases (homochiral and racemic) in addition to the bistate and tristate switching.

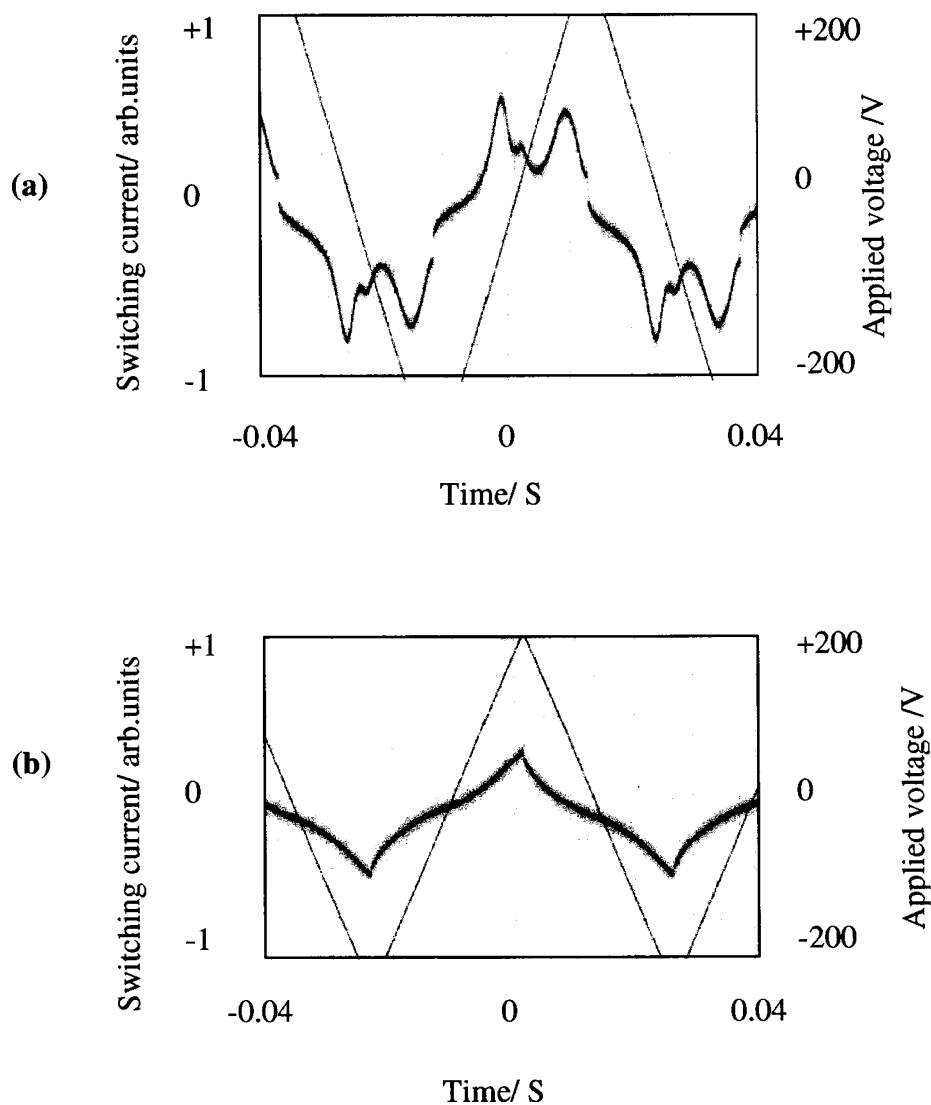


Figure 3.16: The switching current response obtained by applying a triangular-wave electric field of ± 275 V_{pp} for compound 3.B.8; (a) B_{7AF1} phase at a frequency of 20Hz and (b) B₇ phase at a frequency 30Hz.

At this juncture this is only speculative and more work is needed to understand the behaviour. Nevertheless the basic ground state structure of both the B_{7AF1} and B_{7AF2} mesophases is antiferroelectric in nature. Typical switching current responses obtained for the B_{7AF1} and B_7 mesophases of compound 3.B.8 are shown in figure 3.16 (a) and (b) respectively. The polarization value obtained by integrating the area under the current peaks was about 430 nC cm^{-2} . This is the first observation of a direct transition from a non-switchable B_7 phase to an antiferroelectric sub-phase.

All the compounds exhibiting a B_7 mesophase show optical textures, XRD pattern, and electro-optical switching behaviour similar to those of the standard B_7 materials viz. *n*-OPIMB- NO_2 compounds [28, 42].

A comparison of the mesomorphic properties of 2-nitro-1, 3-phenylene bis[4-(4-*n*-alkoxyphenyliminomethyl)benzoates] [42] (standard compounds for B_7 mesophase) and the compounds of series 3.11, viz. 2-nitro-1, 3-phenylene bis[4-(4-*n*-alkoxybenzylideneamino)benzoates], reveal the following interesting points. The two series of compounds differ by the way in which the azomethine linking group is attached. In the case of compounds of series 3.11, the clearing temperatures are reduced by about 50°C although the melting points are enhanced. Thus, the thermal range of the B_7 mesophase has been reduced. In the standard materials [53] for compound *n*=8, an additional B_x phase was observed but this phase has not been characterized. In the compounds of series 3.11 two new antiferroelectric mesophases have been obtained. A comparative plot of the transition temperatures as a function of the terminal chain length is shown in figure 3.17.

A similar comparison can be made between the compounds of series 3.11 and those of series 3.1, viz. 2-cyano-1, 3 phenylene bis[4-(4-*n*-alkoxyphenyliminomethyl)benzoates]. Even here the clearing temperatures of the B_7 phase are reduced by 50°C although no additional mesophase has been observed. A comparative plot of the transition temperatures as a function of the number of carbon atoms in the alkoxy chain is shown in figure 3.18.

Thus, the orientation of the azomethine linking group which affects the polarity of the system, has a bearing not only on the transition temperatures but also on the type of mesophases obtained. It is also interesting to note that in general the unsubstituted compounds viz. 1, 3-phenylene bis [4-(4-*n*-alkoxybenzylideneamino)benzoates] are non-mesomorphic [28], while 2-nitro- or 2-cyano-1, 3-phenylene bis [4-(4-*n*-alkoxybenzylideneamino)benzoates] are

mesomorphic. Thus, a substituent such as nitro or cyano group in position 2 of the central phenyl ring induces a mesophase in these five-ring Schiff's base esters.

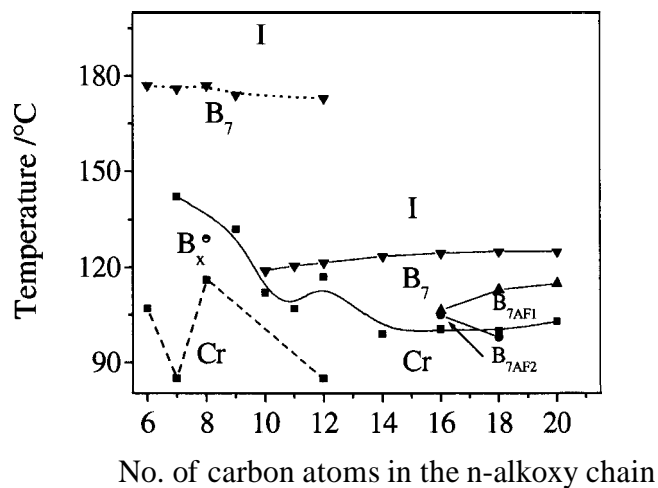


Figure 3.17: A comparative plot of transition temperatures as a function of the number of carbon atoms in the n-alkoxy chain for compounds of series **3.11** (solid line) with those of standard materials **[42]** (dotted lines), showing the effect of orientation of the azomethine linkage group.

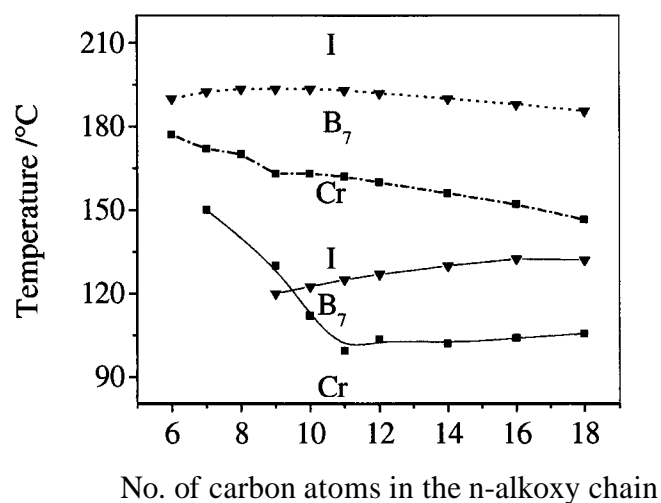


Figure 3.18: A comparative plot of transition temperatures as a function of the number of carbon atoms in the n-alkoxy chain for compounds of series **3.11** (solid line) and series **3.1** (dotted lines), showing the effect of orientation of the azomethine linkage group.

Summary

Three new homologous series of symmetrical Schiff's base esters derived from 2-nitro- and 2-cyano-resorcinol have been synthesized and their mesomorphic properties investigated. Most of the compounds exhibit the fascinating B_7 mesophase. Some of the higher homologues of 2-nitro substituted compounds show two additional antiferroelectric phases, which have been designated as B_{7AF1} and B_{7AF2} . This is the first observation of a direct transition from a non-layered, non-switchable B_7 phase to an antiferroelectric sub-phase (B_{7AF1}). The 2-cyano substituted compounds are thermally more stable and are monomesomorphic, while some of the 2-nitro derivatives are polymesomorphic. In the five-ring Schiff's base esters derived from 2-nitro- and 2-cyano-resorcinol, the orientation of the azomethine linkage group has a strong influence on the mesomorphic behaviour.

Experimental

Methyl-2, 6-dihydroxybenzoate, 3.ii

A mixture of commercial 2, 6-dihydroxybenzoic acid, **3.i** (40g, 0.26mol), methanol (300ml) and concentrated sulphuric acid (3ml) were taken in a one liter RB flask and refluxed for about onehundredtwenty hours and excess methanol was distilled off. The reaction mixture was cooled and poured into ice-cold water and extracted with ether (3 x 300 ml). The combined organic solution was washed with 5% sodium bicarbonate solution (2 x 100 ml), water (2 x 100 ml), and dried over anhydrous sodium sulphate. Removal of the solvent gave a low melting solid, which was purified by column chromatography on silica gel using 5% ethyl acetate in chloroform as eluent. Further, the compound was recrystallized from petroleum ether (b.p. 60-80°C). Yield, 24g (55%); m.p. 67°C (reported 67-68°C [65]).

Methyl-2, 6-dimethoxybenzoate, 3.iii

Methyl-2, 6-dihydroxybenzoate, **3.ii** (22g, 0.13mol) was dissolved in aqueous potassium hydroxide solution (15g in 100ml water) and cooled in an ice-bath. The reaction mixture was stirred and dimethyl sulphate (33g, 0.26mol) was added dropwise over a period of fortyfive min. Stirring was continued for two hours and then the reaction mixture was refluxed for two hours. The reaction mixture was cooled and acidified with sulphuric acid. The organic compound was extracted with solvent ether (3 x 300 ml). The combined organic solution was washed with 5% sodium hydroxide solution (2 x 75 ml), water (2 x 100 ml), and dried over anhydrous sodium sulphate. Removal of solvent gave a low melting solid, which was purified by column chromatography on silica gel using 3:1chloroform-petroleum ether mixture. Further, the required compound was recrystallized from petroleum ether (b.p.60-80°C). Yield, 13g (51%); m.p. 87.5-88.5°C.

2, 6-Dimethoxybenzoic acid, 3.iv

A mixture of Methyl-2, 6-dimethoxybenzoate, **3.iii** (10g, 0.061mol), 10% alcoholic potassium hydroxide solution was refluxed for six hours. Excess ethanol was distilled off, and the reaction mixture was cooled and neutralized with ice-cold hydrochloric acid solution. The white product thus obtained was filtered and washed several times with water and air dried. The

compound was crystallized from aqueous ethanol. Yield, 8g (75%); m.p. 188-189°C (reported 188°C [65]).

2, 6-Dimethoxybenzamide, 3.v

A mixture of 2, 6-dimethoxybenzoic acid, **3.iv** (5.0g, 0.032mol), toluene (30ml) and oxalyl chloride (5ml), was refluxed for eight hours and excess oxalyl chloride and toluene were distilled off. Dry toluene (20 ml) was added to the acid chloride and ammonia was directly bubbled into this solution for a few minutes and left overnight. The white solid thus obtained was filtered, washed thoroughly with water and air dried. The compound was recrystallized from methanol. Yield, 3.0g (60%); m.p. 206-207°C (reported 207-208°C [65]).

2, 6-Dimethoxybenzotrile, 3.vi

2, 6-Dimethoxybenzamide, **3.v** (2.8g, 0.015mol), was dissolved in dry toluene (20 ml), and to this mixture was added freshly distilled phosphorus oxychloride (POCl_3) (15 ml) and refluxed for fifteen hours. Excess phosphorus oxychloride and toluene were distilled off under reduced pressure. The reaction mixture was poured into ice-cold water and extracted with solvent ether (2x 200 ml), which was washed with water (2 x 100ml) and dried over anhydrous sodium sulphate. Removal of solvent gave a yellowish solid, which was recrystallized from a mixture of benzene and petroleum ether (b.p. 60-80°C). Yield, 2.0g (80%); m.p. 119-120°C (reported 118°C [65]).

2, 6-Dihydroxybenzotrile, 3.a

2, 6-Dimethoxybenzotrile, **3.vi** (2.0g, 0.013mol), was dissolved in dry dichloromethane (20 ml) and cooled to -78°C under liquid nitrogen. To this mixture, a solution of boron tribromide (6.5g, 0.026mol) in dichloromethane (10 ml) was added dropwise over a period of one hour and this temperature was maintained for about two to three hours and left to attain the room temperature. The reaction mixture was stirred at room temperature for four hours and refluxed for two hours. The excess boron tribromide was decomposed slowly with moist chloroform. The solvent was removed from the mixture and extracted with acetone using Soxhlet apparatus. The isolated compound thus was purified by column chromatography on silica gel using 10% acetone in chloroform. The compound was then purified by sublimation (145°C at 1.5

mm of Hg). Yield, 1.1g (66%), m.p. 207-208°C (dec), (reported m.p. after sublimation 209°C [66]).

4-*n*-Alkoxyanilines, **3.ix**

These were synthesized according to the procedure given in the literature [62]. The physical constants obtained agreed well with the reported values.

4-*n*-Alkoxybenzaldehydes, **3.xi**

These were synthesized according to the procedure given in the literature [64]. The physical constants obtained agreed well with the reported values.

4-*n*-Alkoxybenzylideneaminobenzoic acid, 3.d

These were synthesized according to the procedure described in the literature [64]. Thus, a mixture of 4-*n*-alkoxybenzaldehyde, **3.xi** and commercial 4-aminobenzoic acid **3.xii** in dry toluene were refluxed for four hours using a Dean-Stark apparatus. The reaction mixture was cooled and filtered. The compound thus obtained was recrystallized from toluene. The physical data of the 4-*n*-alkoxybenzylideneamino benzoic acids are given in table 3.6

Table 3.6: The melting points of 4-*n*-alkoxybenzylideneaminobenzoic acids

No.	<i>n</i>	Observed m.p. °C	Reported m.p. °C [64]
1	7	162.5	163.0
2	9	140.5	137.5
3	10	129.5	131.5
4	11	128.0	-
5	12	130.5	128.0
6	14	124.0	-
7	16	122.0	111.0
8	18	121.0	106.5
9	20	120.0	-

2-Cyano-1, 3-phenylene bis [4-formylbenzoate], 3.c

A mixture of 2-cyanoresorcinol, **3.a** (1.0g, 7.4 mmol), commercial 4-carboxy-benzaldehyde, **3.b** (2.22g, 14.8 mmol), and a catalytic amount of 4-(N, N-dimethylamino)pyridine were stirred in dry dichloromethane (20ml) for ten min. To this mixture N, N'-dicyclohexylcarbodiimide (3.35g, 16.3 mmol) was added and stirred at room temperature overnight. The precipitated N, N'-dicyclohexylurea was filtered off and washed with dichloromethane (10ml). The combined organic solution was washed with ice-cold aqueous 5% sodium hydroxide solution (2 x 30ml), 5% aqueous acetic acid solution (2 x 30ml) and water (3 x 40ml) and dried over anhydrous sodium sulphate. The solvent was removed and the residue was chromatographed on silica gel using a mixture of 2% ethylacetate in chloroform as eluent. The required compound was purified by crystallization using a mixture of chloroform and acetonitrile. Yield, 2.0g (68%), m.p. >265°C. ν (nujol): 2924, 2854, 2232, 1751, 1705 cm^{-1} . δ_{H} : 10.16 (s, 2H, 2 x Ar-CHO), 8.43-8.40 (d, 4H, $^3\text{J}_{8.2\text{Hz}}$, Ar-H), 8.07-8.05 (d, 4H, $^3\text{J}_{8.3\text{Hz}}$, Ar-H), 7.78-7.74 (t, 1H, $^3\text{J}_{8.4\text{Hz}}$, Ar-H), 7.50-7.48 (d, 2H, $^3\text{J}_{8.4\text{Hz}}$, Ar-H). Elemental analysis: $\text{C}_{23}\text{H}_{13}\text{O}_6\text{N}$ requires C, 69.17; H, 3.28; N, 3.51%; found C, 68.92; H, 3.38; N, 3.41%.

2-Cyano 1, 3-phenylene bis [4-(4-n-hexyloxyphenyliminomethyl)benzoate], 3.A.1

A mixture of 2-cyano-1, 3-phenylene bis-[4-formylbenzoate], **3.c**. (0.1g, 0.25 mmol), n-hexyloxyaniline, **3.ix** ($n=6$) (0.097g, 0.5 mmol), toluene (20ml) were refluxed using a Dean-Stark apparatus for four hours. The solution was cooled to room temperature, and the precipitate formed was filtered off. The precipitate was passed through a column of basic alumina using chloroform as an eluent. The product thus obtained was crystallized using a mixture of chloroform and acetonitrile followed by recrystallization from butan-2-one. Yield, 0.091g (48%); m.p. 177.0°C; ν 2927, 2857, 2235, 1736, 1591, 1240, 1105 cm^{-1} ; δ_{H} : 8.59 (s, 2H, 2 x -CH=N-), 8.35-8.33 (d, 4H, $^3\text{J}_{8.32\text{Hz}}$, Ar-H), 8.07-8.05 (d, 4H, $^3\text{J}_{8.36\text{Hz}}$, Ar-H), 7.77-7.73 (t, 1H, $^3\text{J}_{8.48\text{Hz}}$, Ar-H), 7.49-7.47 (d, 2H, $^3\text{J}_{8.4\text{Hz}}$, Ar-H), 7.31-7.29 (d, 4H, $^3\text{J}_{8.8\text{Hz}}$, Ar-H), 6.96-6.94 (d, 4H, $^3\text{J}_{8.8\text{Hz}}$, Ar-H), 4.00-3.98 (t, 4H, $^3\text{J}_{6.56\text{Hz}}$, 2 x Ar-O-CH₂-), 1.84-1.77 (quin, 4H, $^3\text{J}_{7.04\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.48-1.35 (m, 12H, 6 x -CH₂-), 0.94-0.90 (t, 6H, $^3\text{J}_{6.88\text{Hz}}$, 2 x -CH₃). Elemental analysis: $\text{C}_{47}\text{H}_{47}\text{O}_6\text{N}_3$ requires C, 75.28; H, 6.32; N, 5.60%; found C, 75.38; H, 6.61; N, 5.39%.

2-Cyano 1, 3-phenylene bis [4-(4-*n*-heptyloxyphenyliminomethyl)benzoate], 3.A.2

Yield, 45%; m.p. 172.0°C; ν_{\max} : 2924, 2854, 2235, 1736, 1591, 1240, 1105 cm^{-1} ; δ_{H} : 8.59 (s, 2H, 2 \times -CH=N-), 8.35-8.33 (d, 4H, $^3\text{J}_{8.32\text{Hz}}$, Ar-H), 8.07-8.05 (d, 4H, $^3\text{J}_{8.32\text{Hz}}$, Ar-H), 7.77-7.73 (t, 1H, $^3\text{J}_{8.4\text{Hz}}$, Ar-H), 7.49-7.47 (d, 2H, $^3\text{J}_{8.4\text{Hz}}$, Ar-H), 7.31-7.29 (d, 4H, $^3\text{J}_{8.84\text{Hz}}$, Ar-H), 6.96-6.94 (d, 4H, $^3\text{J}_{8.84\text{Hz}}$, Ar-H), 4.00-3.98 (t, 4H, $^3\text{J}_{6.56\text{Hz}}$, 2 \times Ar-O-CH₂-), 1.84-1.77 (quin, 4H, $^3\text{J}_{6.96\text{Hz}}$, 2 \times Ar-O-CH₂-CH₂-), 1.51-1.32 (m, 16H, 8 \times -CH₂-), 0.92-0.88 (t, 6H, $^3\text{J}_{6.68\text{Hz}}$, 2 \times -CH₃). Elemental analysis: C₄₉H₅₁O₆N₃ requires C, 75.65; H, 6.61; N, 5.40%; found C, 75.77; H, 6.81; N, 5.17%.

2-Cyano 1, 3-phenylene bis [4-(4-*n*-octyloxyphenyliminomethyl)benzoate], 3.A.3

Yield, 40%; m.p. 170.0°C; ν_{\max} : 2922, 2853, 2235, 1736, 1591, 1240, 1105 cm^{-1} ; δ_{H} : 8.59 (s, 2H, 2 \times -CH=N-), 8.35-8.33 (d, 4H, $^3\text{J}_{8.28\text{Hz}}$, Ar-H), 8.07-8.05 (d, 4H, $^3\text{J}_{8.28\text{Hz}}$, Ar-H), 7.77-7.73 (t, 1H, $^3\text{J}_{8.36\text{Hz}}$, Ar-H), 7.49-7.47 (d, 2H, $^3\text{J}_{8.4\text{Hz}}$, Ar-H), 7.31-7.29 (d, 4H, $^3\text{J}_{8.76\text{Hz}}$, Ar-H), 6.96-6.94 (d, 4H, $^3\text{J}_{8.8\text{Hz}}$, Ar-H), 4.00-3.98 (t, 4H, $^3\text{J}_{6.56\text{Hz}}$, 2 \times Ar-O-CH₂-), 1.84-1.77 (quin, 4H, $^3\text{J}_{7.0\text{Hz}}$, 2 \times Ar-O-CH₂-CH₂-), 1.47-1.3 (m, 20H, 10 \times -CH₂-), 0.92-0.88 (t, 6H, $^3\text{J}_{6.68\text{Hz}}$, 2 \times -CH₃). Elemental analysis: C₅₁H₅₅O₆N₃ requires C, 76.00; H, 6.88; N, 5.21%; found C, 75.66; H, 7.11; N, 4.98%.

2-Cyano 1, 3-phenylene bis [4-(4-*n*-nonyloxyphenyliminomethyl)benzoate], 3.A.4

Yield, 40%; m.p. 163.0°C; ν_{\max} : 2957, 2922, 2849, 2235, 1736, 1591, 1240, 1105 cm^{-1} ; δ_{H} : 8.59 (s, 2H, 2 \times -CH=N-), 8.35-8.33 (d, 4H, $^3\text{J}_{8.32\text{Hz}}$, Ar-H), 8.07-8.05 (d, 4H, $^3\text{J}_{8.32\text{Hz}}$, Ar-H), 7.77-7.73 (t, 1H, $^3\text{J}_{8.38\text{Hz}}$, Ar-H), 7.49-7.47 (d, 2H, $^3\text{J}_{8.36\text{Hz}}$, Ar-H), 7.31-7.29 (d, 4H, $^3\text{J}_{8.8\text{Hz}}$, Ar-H), 6.96-6.94 (d, 4H, $^3\text{J}_{8.84\text{Hz}}$, Ar-H), 4.00-3.98 (t, 4H, $^3\text{J}_{6.56\text{Hz}}$, Ar-O-CH₂-), 1.84-1.77 (quin, 4H, $^3\text{J}_{6.92\text{Hz}}$, Ar-O-CH₂-CH₂-), 1.47-1.29 (m, 24H, 12 \times -CH₂-), 0.92-0.88 (t, 6H, $^3\text{J}_{6.32\text{Hz}}$, 2 \times -CH₃). Elemental analysis: C₅₃H₅₉O₆N₃ requires C, 76.32; H, 7.13; N, 5.04%; found C, 76.11; H, 7.11; N, 5.25%.

2-Cyano 1, 3-phenylene bis [4-(4-*n*-decyloxyphenyliminomethyl)benzoate], 3.A.5

Yield, 44%; m.p. 163.0°C; ν_{\max} : 2957, 2922, 2851, 2237, 1740, 1734, 1591, 1259, 1244, 1105 cm^{-1} ; δ_{H} : 8.59 (s, 2H, 2 \times -CH=N-), 8.35-8.33 (d, 4H, $^3\text{J}_{8.24\text{Hz}}$, Ar-H), 8.07-8.05 (d, 4H,

$^3\text{J}8.32\text{Hz}$, Ar-H), 7.77-7.73 (t, 1H, $^3\text{J}8.4\text{Hz}$, Ar-H), 7.49-7.47 (d, 2H, $^3\text{J}8.4\text{Hz}$, Ar-H), 7.31-7.29 (d, 4H, $^3\text{J}8.76\text{Hz}$, Ar-H), 6.96-6.94 (d, 4H, $^3\text{J}8.84\text{Hz}$, Ar-H), 4.00-3.98 (t, 4H, $^3\text{J}6.52\text{Hz}$, 2 x Ar-O-CH₂-), 1.84-1.77 (quin, 4H, $^3\text{J}7.0\text{Hz}$, 2 x Ar-O-CH₂-CH₂-), 1.47-1.29 (m, 28H, 14 x -CH₂-), 0.90-0.87 (t, 6H, $^3\text{J}6.32\text{Hz}$, 2 x -CH₃). Elemental analysis: C₅₅H₆₃O₆N₃ requires C, 76.63; H, 7.37; N, 4.87%; found C, 76.21; H, 7.67; N, 4.52%.

2-Cyano 1, 3-phenylene bis [4-(4-*n*-undecyloxyphenyliminomethyl)benzoate], 3.A.6

Yield, 41%; m.p. 162.0°C; ν_{max} : 2957, 2922, 2851, 2237, 1740, 1736, 1591, 1242, 1105 cm⁻¹; δ_{H} : 8.59 (s, 2H, 2 x -CH=N-), 8.35-8.33 (d, 4H, $^3\text{J}8.32\text{Hz}$, Ar-H), 8.07-8.05 (d, 4H, $^3\text{J}8.32\text{Hz}$, Ar-H), 7.77-7.73 (t, 1H, $^3\text{J}8.4\text{Hz}$, Ar-H), 7.49-7.47 (d, 2H, $^3\text{J}8.4\text{Hz}$, Ar-H), 7.31-7.29 (d, 4H, $^3\text{J}8.8\text{Hz}$, Ar-H), 6.96-6.94 (d, 4H, $^3\text{J}8.84\text{Hz}$, Ar-H), 4.00-3.98 (t, 4H, $^3\text{J}6.52\text{Hz}$, 2 x Ar-O-CH₂-), 1.84-1.77 (quin, 4H, $^3\text{J}7.0\text{Hz}$, 2 x Ar-O-CH₂-CH₂-), 1.47-1.28 (m, 32H, 16 x -CH₂-), 0.90-0.87 (t, 6H, $^3\text{J}6.44\text{Hz}$, 2 x -CH₃). Elemental analysis: C₅₇H₆₇O₆N₃ requires C, 76.91; H, 7.59; N, 4.72%; found C, 76.71; H, 7.68; N, 4.63%.

2-Cyano 1, 3-phenylene bis [4-(4-*n*-dodecyloxyphenyliminomethyl)benzoate], 3.A.7

Yield, 40%; m.p. 160.0°C; ν_{max} : 2957, 2914, 2851, 2241, 1740, 1736, 1591, 1244, 1105 cm⁻¹; δ_{H} : 8.59 (s, 2H, 2 x -CH=N-), 8.35-8.33 (d, 4H, $^3\text{J}8.32\text{Hz}$, Ar-H), 8.07-8.05 (d, 4H, $^3\text{J}8.36\text{Hz}$, Ar-H), 7.77-7.73 (t, 1H, $^3\text{J}8.36\text{Hz}$, Ar-H), 7.49-7.47 (d, 2H, $^3\text{J}8.4\text{Hz}$, Ar-H), 7.31-7.29 (d, 4H, $^3\text{J}8.8\text{Hz}$, Ar-H), 6.96-6.94 (d, 4H, $^3\text{J}8.84\text{Hz}$, Ar-H), 4.00-3.98 (t, 4H, $^3\text{J}6.56\text{Hz}$, 2 x Ar-O-CH₂-), 1.84-1.77 (quin, 4H, $^3\text{J}6.96\text{Hz}$, 2 x Ar-O-CH₂-CH₂-), 1.46-1.27 (m, 36H, 18 x -CH₂-), 0.90-0.87 (t, 6H, $^3\text{J}6.44\text{Hz}$, 2 x -CH₃). Elemental analysis: C₅₉H₇₁O₆N₃ requires C, 77.18; H, 7.79; N, 4.58%; found C, 76.78; H, 7.67; N, 4.31%.

2-Cyano 1, 3-phenylene bis [4-(4-*n*-tetradecyloxyphenyliminomethyl)benzoate], 3.A.8

Yield, 48%; m.p. 156.0°C; ν_{max} : 2957, 2916, 2851, 2239, 1740, 1591, 1244, 1107 cm⁻¹; δ_{H} : 8.59 (s, 2H, 2 x -CH=N-), 8.35-8.33 (d, 4H, $^3\text{J}8.32\text{Hz}$, Ar-H), 8.07-8.05 (d, 4H, $^3\text{J}8.32\text{Hz}$, Ar-H), 7.77-7.73 (t, 1H, $^3\text{J}8.32\text{Hz}$, Ar-H), 7.49-7.47 (d, 2H, $^3\text{J}8.4\text{Hz}$, Ar-H), 7.31-7.29 (d, 4H, $^3\text{J}8.8\text{Hz}$, Ar-H), 6.96-6.94 (d, 4H, $^3\text{J}8.84\text{Hz}$, Ar-H), 4.00-3.98 (t, 4H, $^3\text{J}6.56\text{Hz}$, 2 x Ar-O-CH₂-),

1.84-1.77 (quin, 4H, $^3J_{6.96\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.47-1.27 (m, 44H, 22 x -CH₂-), 0.90-0.87 (t, 6H, $^3J_{6.52\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₆₃H₇₉O₆N₃ requires C, 77.66; H, 8.17; N, 4.31%; found C, 77.23; H, 8.23; N, 3.94%.

2-Cyano 1, 3-phenylene bis [4-(4-*n*-hexadecyloxyphenyliminomethyl)benzoate], 3.A.9

Yield, 50%; m.p. 152.0°C; ν_{max} : 2957, 2916, 2851, 2239, 1742, 1740, 1591, 1246, 1107 cm⁻¹; δ_{H} : 8.59 (s, 2H, 2 x -CH=N-), 8.35-8.33 (d, 4H, $^3J_{8.4\text{Hz}}$, Ar-H), 8.07-8.05 (d, 4H, $^3J_{8.44\text{Hz}}$, Ar-H), 7.77-7.73 (t, 1H, $^3J_{8.28\text{Hz}}$, Ar-H), 7.49-7.47 (d, 2H, $^3J_{8.44\text{Hz}}$, Ar-H), 7.31-7.29 (d, 4H, $^3J_{8.88\text{Hz}}$, Ar-H), 6.96-6.94 (d, 4H, $^3J_{8.92\text{Hz}}$, Ar-H), 4.00-3.98 (t, 4H, $^3J_{6.56\text{Hz}}$, 2 x Ar-O-CH₂-), 1.84-1.77(quin, 4H, $^3J_{7.0\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.49-1.26 (m, 52H, 26 x -CH₂-), 0.90-0.87 (t, 6H, $^3J_{6.64\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₆₇H₈₇O₆N₃ requires C, 78.10; H, 8.51; N, 4.08%; found C, 78.46; H, 8.81; N, 3.85%.

2-Cyano 1, 3-phenylene bis [4-(4-*n*-octadecyloxyphenyliminomethyl)benzoate], 3.A.10

Yield, 40%; m.p. 146.5°C; ν_{max} : 2957, 2916, 2851, 2240, 1742, 1738, 1591, 1246, 1107 cm⁻¹; δ_{H} : 8.59 (s, 2H, 2 x -CH=N-), 8.35-8.33 (d, 4H, $^3J_{8.36\text{Hz}}$, Ar-H), 8.07-8.05 (d, 4H, $^3J_{8.4\text{Hz}}$, Ar-H), 7.77-7.73 (t, 1H, $^3J_{8.32\text{Hz}}$, Ar-H), 7.49-7.47 (d, 2H, $^3J_{8.44\text{Hz}}$, Ar-H), 7.31-7.29 (d, 4H, $^3J_{8.84\text{Hz}}$, Ar-H), 6.96-6.94 (d, 4H, $^3J_{8.88\text{Hz}}$, Ar-H), 4.00-3.98 (t, 4H, $^3J_{6.56\text{Hz}}$, 2 x Ar-O-CH₂-), 1.84-1.77 (quin, 4H, $^3J_{7.0\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.49-1.25 (m, 60H, 30 x -CH₂-), 0.90-0.87 (t, 6H, $^3J_{6.64\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₇₁H₉₅O₆N₃ requires C, 78.49; H, 8.81; N, 3.87%; found C, 78.51; H, 9.04; N, 3.62%.

2-Nitro-1, 3-phenylene bis [4-(4-*n*-heptyloxybenzylideneamino)benzoate], 3.B.1

A mixture of 4-*n*-heptyloxybenzylideneamino-4-benzoic acid, **3d** (*n*=7) (0.6g, 1.76mmol), commercial 2-nitroresorcinol, **3e** (0.136g, 0.88mmol), and a cat. amount of 4-(*N,N*-dimethylamino) pyridine (DMAP), in dry dichloromethane were stirred for ten min. To this *N,N*-dicyclohexylcarbodiimide (DCC) (0.40g, 1.9mmol) was added and stirred overnight. The reaction mixture was filtered, the precipitate was washed with chloroform and the solvent from the filtrate was removed to yield a residue. This was purified by column chromatography on basic alumina, and eluted using chloroform as an eluent. Removal of solvent from the eluate

gave a yellow product, which was further purified by repeated crystallization using a mixture of chloroform and acetonitrile. Yield, 0.28g (39%); m.p. 142.0°C; ν_{\max} : 2924, 2855, 1753, 1740, 1589, 1566, 1254, 1227, 1159, 1067 cm^{-1} ; δ_{H} : 8.36 (s, 2H, 2 x -N=CH-), 8.18-8.15 (d, 4H, $^3\text{J}_{8.4\text{Hz}}$, Ar-H), 7.89-7.85 (d, 4H, $^3\text{J}_{8.60\text{Hz}}$, Ar-H), 7.67-7.62 (t, 1H, $^3\text{J}_{8.28\text{Hz}}$, Ar-H), 7.42-7.40 (d, 2H, $^3\text{J}_{8.36\text{Hz}}$, Ar-H), 7.25-7.23 (d, 4H, $^3\text{J}_{8.4\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3\text{J}_{8.64\text{Hz}}$, Ar-H), 4.05-4.02 (t, 4H, $^3\text{J}_{6.52\text{Hz}}$, 2 x Ar-O-CH₂-), 1.85-1.78 (quin, 4H, $^3\text{J}_{6.88\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.50-1.32 (m, 16H, 8 x -CH₂-), 0.92-0.89 (t, 6H, $^3\text{J}_{6.64\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₄₈H₅₁O₈N₃ requires C, 72.25; H, 6.44; N, 5.27%; found C, 72.48; H, 6.49; N, 4.92%.

2-Nitro-1, 3-phenylene bis [4-(4-*n*-nonyloxybenzylideneamino)benzoate], 3.B.2

Yield, 40%; m.p. 132.0°C; ν_{\max} : 2922, 2853, 1740, 1736, 1591, 1572, 1533, 1231, 1256, 1165, 1086 cm^{-1} ; δ_{H} : 8.36 (s, 2H, 2 x -N=CH-), 8.18-8.15 (d, 4H, $^3\text{J}_{8.48\text{Hz}}$, Ar-H), 7.88-7.85 (d, 4H, $^3\text{J}_{8.72\text{Hz}}$, Ar-H), 7.68-7.63 (t, 1H, $^3\text{J}_{8.36\text{Hz}}$, Ar-H), 7.42-7.40 (d, 2H, $^3\text{J}_{8.4\text{Hz}}$, Ar-H), 7.25-7.23 (d, 4H, $^3\text{J}_{8.52\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3\text{J}_{8.72\text{Hz}}$, Ar-H), 4.05-4.02 (t, 4H, $^3\text{J}_{6.52\text{Hz}}$, 2 x Ar-O-CH₂-), 1.85-1.78 (quin, 4H, $^3\text{J}_{6.96\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.51-1.32 (m, 24H, 12 x -CH₂-), 0.91-0.87 (t, 6H, $^3\text{J}_{6.44\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₅₂H₅₉O₈N₃ requires C, 73.13; H, 6.96; N, 4.92%; found C, 73.31; H, 6.88; N, 4.57%.

2-Nitro-1, 3-phenylene bis [4-(4-*n*-decyloxybenzylideneamino)benzoate], 3.B.3

Yield, 42%; m.p. 112.0°C; ν_{\max} : 2992, 2853, 1736, 1591, 1572, 1533, 1254, 1231, 1163, 1074 cm^{-1} ; δ_{H} : 8.36 (s, 2H, 2 x -N=CH-), 8.18-8.15 (d, 4H, $^3\text{J}_{8.48\text{Hz}}$, Ar-H), 7.87-7.85 (d, 4H, $^3\text{J}_{8.68\text{Hz}}$, Ar-H), 7.67-7.63 (t, 1H, $^3\text{J}_{8.32\text{Hz}}$, Ar-H), 7.42-7.40 (d, 2H, $^3\text{J}_{8.36\text{Hz}}$, Ar-H), 7.25-7.23 (d, 4H, $^3\text{J}_{8.52\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3\text{J}_{8.68\text{Hz}}$, Ar-H), 4.05-4.02 (t, 4H, $^3\text{J}_{6.56\text{Hz}}$, 2 x Ar-O-CH₂-), 1.85-1.78 (quin, 4H, $^3\text{J}_{6.96\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.48-1.28 (m, 28H, 14 x -CH₂-), 0.90-0.87 (t, 6H, $^3\text{J}_{6.52\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₅₄H₆₃O₈N₃ requires C, 73.53; H, 7.20; N, 4.76%; found C, 73.17; H, 7.24; N, 4.36%.

2-Nitro-1, 3-phenylene bis [4-(4-*n*-undecyloxybenzylideneamino)benzoate], 3.B.4

Yield, 41%; m.p. 107.0°C; ν_{\max} : 2922, 2853, 1740, 1736, 1591, 1572, 1252, 1238, 1165, 1096 cm^{-1} ; δ_{H} : 8.36 (s, 2H, 2 x -N=CH-), 8.18-8.16 (d, 4H, $^3\text{J}_{8.44\text{Hz}}$, Ar-H), 7.87-7.85 (d, 4H,

$^3J_{8.6\text{Hz}}$, Ar-H), 7.67-7.63 (t, 1H, $^3J_{8.6\text{Hz}}$, Ar-H), 7.42-7.40 (d, 2H, $^3J_{8.4\text{Hz}}$, Ar-H), 7.25-7.23 (d, 4H, $^3J_{8.64\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3J_{8.6\text{Hz}}$, Ar-H), 4.05-4.02 (t, 4H, $^3J_{6.52\text{Hz}}$, 2 x Ar-O-CH₂-), 1.85-1.78 (quin, 4H, $^3J_{7.08\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.48-1.28 (m, 32H, 16 x -CH₂-), 0.90-0.87 (t, 6H, $^3J_{6.5\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₅₆H₆₇O₈N₃ requires C, 73.90; H, 7.42; N, 4.62%; found C, 74.35; H, 7.46; N, 4.37%.

2-Nitro-1, 3-phenylene bis [4-(4-*n*-dodecyloxybenzylideneamino)benzoate], 3.B.5

Yield, 37%; m.p. 117.0°C; ν_{max} : 2922, 2851, 1736, 1734, 1591, 1574, 1532, 1254, 1232, 1165 cm⁻¹; δ_{H} : 8.36 (s, 2H, 2 x -N=CH-), 8.18-8.16 (d, 4H, $^3J_{8.56\text{Hz}}$, Ar-H), 7.87-7.85 (d, 4H, $^3J_{8.72\text{Hz}}$, Ar-H), 7.67-7.63 (t, 1H, $^3J_{8.56\text{Hz}}$, Ar-H), 7.42-7.40 (d, 2H, $^3J_{8.36\text{Hz}}$, Ar-H), 7.25-7.23 (d, 4H, $^3J_{8.56\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3J_{8.76\text{Hz}}$, Ar-H), 4.05-4.02 (t, 4H, $^3J_{6.52\text{Hz}}$, 2 x Ar-O-CH₂-), 1.85-1.78(quin, 4H, $^3J_{7.0\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.49-1.27(m, 36H, 18 x -CH₂-), 0.90-0.87 (t, 6H, $^3J_{6.52\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₅₈H₇₁O₈N₃ requires C, 74.25; H, 7.63; N, 4.48%; found C, 74.67; H, 7.53; N, 4.08%.

2-Nitro-1, 3-phenylene bis [4-(4-*n*-tetradecyloxybenzylideneamino)benzoate], 3.B.6

Yield, 42%; m.p. 99.0°C; ν_{max} : 3121, 2920, 2851, 1736, 1591, 1572, 1251, 1230, 1165, 1084 cm⁻¹; δ_{H} : 8.36 (s, 2H, 2 x -N=CH-), 8.18-8.16 (d, 4H, $^3J_{8.56\text{Hz}}$, Ar-H), 7.87-7.85 (d, 4H, $^3J_{8.72\text{Hz}}$, Ar-H), 7.67-7.63 (t, 1H, $^3J_{8.16\text{Hz}}$, Ar-H), 7.42-7.40 (d, 2H, $^3J_{8.36\text{Hz}}$, Ar-H), 7.25-7.23 (d, 4H, $^3J_{8.48\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3J_{8.72\text{Hz}}$, Ar-H), 4.05-4.02 (t, 4H, $^3J_{6.56\text{Hz}}$, 2 x Ar-O-CH₂-), 1.85-1.78(quin, 4H, $^3J_{7.0\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.50-1.27(m, 44H, 22 x -CH₂-), 0.90-0.87 (t, 6H, $^3J_{6.68\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₆₂H₇₉O₈N₃ requires C, 74.89; H, 8.01; N, 4.22%; found C, 75.29; H, 8.11; N, 3.96%.

2-Nitro-1, 3-phenylene bis [4-(4-*n*-hexadecyloxybenzylideneamino)benzoate], 3.B.7

Yield, 44%; m.p. 100.5°C; ν_{max} : 3122, 2918, 2855, 1751, 1736, 1730, 1591, 1574, 1251, 1231, 1165 cm⁻¹. δ_{H} : 8.36 (s, 2H, 2 x -N=CH-), 8.18-8.16 (d, 4H, $^3J_{8.56\text{Hz}}$, Ar-H), 7.87-7.85 (d, 4H, $^3J_{8.72\text{Hz}}$, Ar-H), 7.67-7.63 (t, 1H, $^3J_{8.36\text{Hz}}$, Ar-H), 7.42-7.40 (d, 2H, $^3J_{8.36\text{Hz}}$, Ar-H), 7.25-7.23 (d, 4H, $^3J_{8.56\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3J_{8.72\text{Hz}}$, Ar-H), 4.05-4.02 (t, 4H, $^3J_{6.56\text{Hz}}$, 2 x Ar-O-CH₂-), 1.85-1.78 (quin, 4H, $^3J_{6.96\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.48-1.27 (m, 52H, 26 x

-CH₂-), 0.90-0.87 (t, 6H, ³J_{6.56}Hz, 2 x -CH₃). δ_C: 163.5, 162.5, 161.3, 158.1, 144.0, 132.0, 131.5, 128.6, 124.6, 121.6, 121.2, 114.9, 68.4, 40.0, 29.7, 29.4, 29.2, 26.0, 22.7, 14.1. Elemental analysis: C₆₆H₈₇O₈N₃ requires C, 75.47; H, 8.35; N, 4.0%; found C, 75.51; H, 8.37; N, 3.73%.

2-Nitro-1, 3-phenylene bis [4-(4-*n*-octadecyloxybenzylideneamino)benzoate], 3.B.8

Yield, 41%; m.p. 100.0°C; v_{max}: 3126,2916,2851, 1751, 1734, 1728, 1591, 1574, 1252, 1234, 1165 cm⁻¹. δ_H: 8.36 (s, 2H, 2 x -N=CH-), 8.18-8.16 (d, 4H, ³J_{8.6}Hz, Ar-H), 7.87-7.85 (d, 4H, ³J_{8.8}Hz, Ar-H), 7.67-7.63 (t, 1H, ³J_{8.4}Hz, Ar-H), 7.42-7.40 (d, 2H, ³J_{8.36}Hz, Ar-H), 7.25-7.23 (d, 4H, ³J_{8.6}Hz, Ar-H), 7.0-6.98 (d, 4H, ³J_{8.8}Hz, Ar-H), 4.05-4.02 (t, 4H, ³J_{6.56}Hz, 2 x Ar-O-CHI-), 1.85-1.78 (quin, 4H, ³J_{7.0}Hz, 2 x Ar-O-CH₂-CH₂-), 1.48-1.27 (m, 60H, 30 x -CH₂-), 0.90-0.87 (t, 6H, ³J_{6.60}Hz, 2 x -CH₃). δ_C: 163.4, 162.5, 161.3, 158.1, 143.9, 132.0, 131.5, 131.0, 128.6, 124.6, 121.6, 121.2, 114.9, 68.3, 40.0, 29.7, 29.4, 29.2, 26.0, 22.7, 14.1. Elemental analysis: C₇₀H₉₅O₈N₃ requires C, 75.98; H, 8.65; N, 3.80%; found C, 75.61; H, 9.02; N, 3.63%.

2-Nitro-1, 3-phenylene bis [4-(4-*n*-eicocyloxybenzylideneamino)benzoate], 3.B.9

Yield, 45%; m.p. 103.0°C; v_{max}: 3126,2916,2851, 1751, 1736, 1728, 1591, 1574, 1252, 1235, 1165 cm⁻¹. δ_H: 8.36 (s, 2H, 2 x -N=CH-), 8.18-8.16 (d, 4H, ³J_{8.52}Hz, Ar-H), 7.87-7.85 (d, 4H, ³J_{8.68}Hz, Ar-H), 7.67-7.63 (t, 1H, ³J_{8.4}Hz, Ar-H), 7.42-7.40 (d, 2H, ³J_{8.36}Hz, Ar-H), 7.25-7.23 (d, 4H, ³J_{8.56}Hz, Ar-H), 7.0-6.98 (d, 4H, ³J_{8.64}Hz, Ar-H), 4.05-4.02 (t, 4H, ³J_{6.52}Hz, 2 x Ar-O-CHI-), 1.85-1.78 (quin, 4H, ³J_{7.0}Hz, Ar-O-CH₂-CH₂-), 1.48-1.26 (m, 68H, 34 x -CH₂-), 0.90-0.87 (t, 6H, ³J_{6.52}Hz, 2 x -CH₃). δ_C: 163.5, 162.6, 161.3, 158.2, 144.0, 132.9, 132.0, 131.2, 128.6, 121.6, 121.2, 115.0, 68.4, 32.0, 29.7, 29.4, 29.2, 29.1, 26.0, 22.7, 14.0. Elemental analysis: C₇₄H₁₀₃O₈N₃ requires C, 76.45, H, 8.93, N, 3.61%; found C, 76.85, H, 9.12; N, 3.22%.

2-Cyano-1, 3-phenylene bis [4-(4-*n*-heptyloxybenzylideneamino)benzoate], 3.C.1

Yield, 42%; m.p. 150.0°C; v_{max}: 3125,2922,2853,2235, 1749, 1740, 1589, 1566, 1257, 1159, 1069 cm⁻¹. δ_H: 8.37 (s, 2H, 2 x -N=CH-), 8.28-8.26 (d, 4H, ³J_{8.52}Hz, Ar-H), 7.88-7.85 (d, 4H, ³J_{8.72}Hz, Ar-H), 7.74-7.70 (t, 1H, ³J_{8.4}Hz, Ar-H), 7.46-7.44 (d, 2H, ³J_{8.4}Hz, Ar-H), 7.28-7.26 (d, 4H, ³J_{8.56}Hz, Ar-H), 7.0-6.98 (d, 4H, ³J_{8.72}Hz, Ar-H), 4.06-4.02 (t, 4H, ³J_{6.56}Hz, 2 x Ar-O-CH₂-), 1.85-1.78 (quin, 4H, ³J_{7.0}Hz, 2 x Ar-O-CH₂-CH₂-), 1.50-1.33 (m, 16H, 8 x -CH₂-),

0.90-0.87 (t, 6H, $^3J_{6.68\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₄₉H₅₁O₆N₃ requires C, 75.65; H, 6.61; N, 5.40%; found C, 75.87; H, 6.51; N, 5.12%.

2-Cyano-1, 3-phenylene bis [4-(4-*n*-nonoxybenzylideneamino)benzoate], 3.C.2

Yield, 46%; m.p. 130.0°C; ν_{max} : 3120, 2922, 2853, 2235, 1740, 1736, 1591, 1572, 1254, 1161, 1076 cm⁻¹. δ_{H} : 8.37 (s, 2H, 2 x -N=CH-), 8.28-8.26 (d, 4H, $^3J_{8.52\text{Hz}}$, Ar-H), 7.88-7.85 (d, 4H, $^3J_{8.72\text{Hz}}$, Ar-H), 7.74-7.70 (t, 1H, $^3J_{8.44\text{Hz}}$, Ar-H), 7.46-7.44 (d, 2H, $^3J_{8.4\text{Hz}}$, Ar-H), 7.28-7.26 (d, 4H, $^3J_{8.4\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3J_{8.68\text{Hz}}$, Ar-H), 4.05-4.02 (t, 4H, $^3J_{6.52\text{Hz}}$, 2 x Ar-O-CH₂-), 1.85-1.78 (quin, 4H, $^3J_{7.0\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.51-1.30 (m, 24H, 12 x -CH₂-), 0.90-0.87 (t, 6H, $^3J_{6.4\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₅₃H₅₉O₆N₃ requires C, 76.32; H, 7.13; N, 5.04%; found C, 76.21; H, 7.01; N, 5.35%.

2-Cyano-1, 3-phenylene bis [4-(4-*n*-decyloxybenzylideneamino)benzoate], 3.C.3

Yield, 48%; m.p. 112.0°C; ν 3060, 2922, 2853, 2237, 1751, 1736, 1591, 1570, 1254, 1161, 1076 cm⁻¹; δ_{H} : 8.37 (s, 2H, 2 x -N=CH-), 8.28-8.26 (d, 4H, $^3J_{8.48\text{Hz}}$, Ar-H), 7.88-7.85 (d, 4H, $^3J_{8.64\text{Hz}}$, Ar-H), 7.74-7.70 (t, 1H, $^3J_{8.52\text{Hz}}$, Ar-H), 7.46-7.44 (d, 2H, $^3J_{8.4\text{Hz}}$, Ar-H), 7.28-7.26 (d, 4H, $^3J_{8.4\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3J_{8.68\text{Hz}}$, Ar-H), 4.05-4.02 (t, 4H, $^3J_{6.52\text{Hz}}$, 2 x Ar-O-CH₂-), 1.85-1.78 (quin, 4H, $^3J_{6.96\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.49-1.28 (m, 28H, 14 x -CH₂-), 0.90-0.87 (t, 6H, $^3J_{6.4\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₅₅H₆₃O₆N₃ requires C, 76.63; H, 7.37; N, 4.87%; found C, 77.02; H, 7.34; N, 4.39%.

2-Cyano-1, 3-phenylene bis [4-(4-*n*-undecyloxybenzylideneamino)benzoate], 3.C.4

Yield, 42%; m.p. 99.5°C; ν 3125, 2920, 2851, 2234, 1738, 1730, 1589, 1570, 1250, 1163, 1090 cm⁻¹; δ_{H} : 8.37 (s, 2H, 2 x -N=CH-), 8.28-8.26 (d, 4H, $^3J_{8.44\text{Hz}}$, Ar-H), 7.88-7.85 (d, 4H, $^3J_{8.64\text{Hz}}$, Ar-H), 7.74-7.70 (t, 1H, $^3J_{8.48\text{Hz}}$, Ar-H), 7.46-7.44 (d, 2H, $^3J_{8.44\text{Hz}}$, Ar-H), 7.28-7.26 (d, 4H, $^3J_{8.48\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3J_{8.64\text{Hz}}$, Ar-H), 4.06-4.02 (t, 4H, $^3J_{6.48\text{Hz}}$, 2 x Ar-O-CH₂-), 1.85-1.78 (quin, 4H, $^3J_{7.08\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.49-1.28 (m, 32H, 16 x -CH₂-), 0.90-0.87 (t, 6H, $^3J_{6.48\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₅₇H₆₇O₆N₃ requires C, 76.91; H, 7.59; N, 4.72%; found C, 76.51; H, 7.73; N, 4.53%.

2-Cyano-1, 3-phenylene bis [4-(4-*n*-dodecyloxybenzylideneamino)benzoate], 3.C.5

Yield, 42%; m.p. 103.5°C; ν_{\max} : 3125, 2920, 2851, 2234, 1740, 1728, 1589, 1570, 1250, 1163, 1090 cm^{-1} ; δ_{H} : 8.37 (s, 2H, 2 x -N=CH-), 8.28-8.26 (d, 4H, $^3\text{J}_{8.52\text{Hz}}$, Ar-H), 7.88-7.85 (d, 4H, $^3\text{J}_{8.76\text{Hz}}$, Ar-H), 7.74-7.70 (t, 1H, $^3\text{J}_{8.24\text{Hz}}$, Ar-H), 7.46-7.44 (d, 2H, $^3\text{J}_{8.4\text{Hz}}$, Ar-H), 7.28-7.26 (d, 4H, $^3\text{J}_{8.56\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3\text{J}_{8.76\text{Hz}}$, Ar-H), 4.06-4.02 (t, 4H, $^3\text{J}_{6.56\text{Hz}}$, 2 x Ar-O-CH₂-), 1.85-1.78 (quin, 4H, $^3\text{J}_{7.0\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.49-1.27 (m, 36H, 18 x -CH₂-), 0.90-0.87 (t, 6H, $^3\text{J}_{6.52\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₅₉H₇₁O₆N₃ requires C, 77.18; H, 7.79; N, 4.58%; found C, 77.11; H, 7.81; N, 4.17%.

2-Cyano-1, 3-phenylene bis [4-(4-*n*-tetradecyloxybenzylideneamino)benzoate], 3.C.6

Yield, 49%; m.p. 102.0°C; ν_{\max} : 3126, 2920, 2851, 2235, 1747, 1732, 1724, 1591, 1251, 1236, 1165, 1090 cm^{-1} ; δ_{H} : 8.37 (s, 2H, 2 x -N=CH-), 8.28-8.26 (d, 4H, $^3\text{J}_{8.48\text{Hz}}$, Ar-H), 7.88-7.85 (d, 4H, $^3\text{J}_{8.68\text{Hz}}$, Ar-H), 7.74-7.70 (t, 1H, $^3\text{J}_{8.24\text{Hz}}$, Ar-H), 7.46-7.44 (d, 2H, $^3\text{J}_{8.4\text{Hz}}$, Ar-H), 7.28-7.26 (d, 4H, $^3\text{J}_{8.48\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3\text{J}_{8.68\text{Hz}}$, Ar-H), 4.05-4.02 (t, 4H, $^3\text{J}_{6.52\text{Hz}}$, 2 x Ar-O-CH₂-), 1.85-1.78 (quin, 4H, $^3\text{J}_{6.96\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.48-1.27 (m, 44H, 22 x -CH₂-), 0.90-0.87 (t, 6H, $^3\text{J}_{6.44\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₆₃H₇₉O₆N₃ requires C, 77.66; H, 8.17; N, 4.31%; found C, 78.11; H, 8.31; N, 4.10%.

2-Cyano-1, 3-phenylene bis [4-(4-*n*-hexadecyloxybenzylideneamino)benzoate], 3.C.7

Yield, 50%; m.p. 104.0°C; ν_{\max} : 3132, 2920, 2851, 2233, 1740, 1730, 1589, 1248, 1165, 1088 cm^{-1} ; δ_{H} : 8.37 (s, 2H, 2 x -N=CH-), 8.28-8.26 (d, 4H, $^3\text{J}_{8.48\text{Hz}}$, Ar-H), 7.88-7.85 (d, 4H, $^3\text{J}_{8.68\text{Hz}}$, Ar-H), 7.74-7.70 (t, 1H, $^3\text{J}_{8.24\text{Hz}}$, Ar-H), 7.46-7.44 (d, 2H, $^3\text{J}_{8.4\text{Hz}}$, Ar-H), 7.28-7.26 (d, 4H, $^3\text{J}_{8.48\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3\text{J}_{8.68\text{Hz}}$, Ar-H), 4.05-4.02 (t, 4H, $^3\text{J}_{6.52\text{Hz}}$, 2 x Ar-O-CH₂-), 1.85-1.78 (quin, 4H, $^3\text{J}_{6.96\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.48-1.27 (m, 52H, 26 x -CH₂-), 0.90-0.87 (t, 6H, $^3\text{J}_{6.44\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₆₇H₈₇O₆N₃ requires C, 78.10; H, 8.51; N, 4.08%; found C, 78.08; H, 8.67; N, 3.76%.

2-Cyano-1, 3-phenylene bis [4-(4-*n*-octadecyloxybenzylideneamino)benzoate], 3.C.8

Yield, 47%; m.p. 105.5°C; ν_{\max} : 3132, 2918, 2849, 2233, 1740, 1730, 1728, 1589, 1252, 1165, 1089 cm^{-1} ; δ_{H} : 8.37 (s, 2H, 2 x -N=CH-), 8.28-8.26 (d, 4H, $^3\text{J}_{8.48\text{Hz}}$, Ar-H), 7.88-7.85 (d, 4H, $^3\text{J}_{8.68\text{Hz}}$, Ar-H), 7.74-7.70 (t, 1H, $^3\text{J}_{8.4\text{Hz}}$, Ar-H), 7.46-7.44 (d, 2H, $^3\text{J}_{8.36\text{Hz}}$, Ar-H), 7.28-7.26 (d, 4H, $^3\text{J}_{8.48\text{Hz}}$, Ar-H), 7.0-6.98 (d, 4H, $^3\text{J}_{8.68\text{Hz}}$, Ar-H), 4.05-4.02 (t, 4H, $^3\text{J}_{6.52\text{Hz}}$, 2 x Ar-O-CH₂-), 1.83-1.78 (quin, 4H, $^3\text{J}_{6.96\text{Hz}}$, 2 x Ar-O-CH₂-CH₂-), 1.48-1.27 (m, 60H, 30 x -CH₂-), 0.90-0.86 (t, 6H, $^3\text{J}_{6.48\text{Hz}}$, 2 x -CH₃). Elemental analysis: C₇₁H₉₅O₆N₃ requires C, 78.49; H, 8.81; N, 3.87%; found C, 78.61; H, 8.94, N, 3.58%.