CHAPTER 4

Synthesis and mesomorphic properties of compounds composed of bent-core molecules.

4.0 Historical developments:

Although classical thermotropic liquid crystals are commonly composed of **rod**like (calamitic liquid crystals) or disc-shaped molecules (discotic liquid crystals), there are many types of low molecular weight compounds with unconventional molecular structures which can form nematic **and/or** smectic phases [1]. Since chemical structure is known to have a significant effect on the mesophases formed by a compound, it can be modified in different ways giving rise to various structural features (ie., polycatenar liquid crystals, sanidic liquid crystals). **Vorländer** [2,3] was in fact the first to synthesize a mesogenic compound of non-linear molecular structure, *viz.* 1,2-phenylene **bis**[4-(4-ethoxyphenylazoxy)benzoate] (compound **4.1**). Demus [1] classified this compound under fused twins and identified its mesophase as nematic phase.



Cr 164 N 213 I (**4.1**)

Later, interesting examples of unconventional molecular structure which can form mesophases were studied and reported [1], and of these the banana- shaped molecules or mesogenic compounds with a bend in the middle of the molecule have now attracted much interest. Back in 1925 Schroter [4] synthesized five-ring diesters of isophthalic acid (compounds 4.2 and **4.3**), which were found to exhibit a mesophase above **250°C**. But the type of the mesophase was not identified.



n = 1 : Cr 259 M 266 I. (4.2) n = 2 : Cr 252 M 256 I. (4.3) M : unidentified mesophase.

The current interest in the liquid crystalline behaviour of banana-shaped or bentcore molecules has been stimulated by the synthetic work of Matsunaga and coworkers [5,6,7]. They synthesized compound 4.4 and its homologues [5] and identified the highest temperature phase in all these compounds as a Sm C phase.



(M = more ordered mesophase)(4.4)

They used x-ray layer spacing measurements of the homologous series to argue that the tails are nearly normal to the smectic layers whereas the cores are tilted. They found the core thickness to be 18.5Å and assuming a core conformation giving a 27.5Å spacing between the alkoxy oxygens of 4.4, obtained a core tilt of 48° [5]. No further detailed analysis of the structure and properties of these mesophases have been reported.

In the year 1996 Niori *et* al., [8] synthesized and studied the alkyl homologues of compound **4.5**. From the optical and switching current measurements they concluded that the highest temperature smectic phase had untilted cores and there was ferroelectric ordering of the molecular bows (bent core, figure 4.1), with their arrows (direction of the dipoles) pointing in a particular direction that could be switched by an electric field.



Cr 98 S₂ 156 S₁ 161 I (S₁ and S₂ are smectic phases) (4.5)



Fig 4.1

This very important discovery of ferroelectricity and chirality in achiral molecules has attracted many research groups to study such banana-shaped molecules [9,10]. Heppke *et* al., [11] also observed ferroelectric switching current dynamics in several other homologues of **4.4** and **4.5**.

Chirality has been recognized as an important feature of liquid crystals since the time of their discovery. The influence of chirality on phase behaviour and macroscopic helical structure is of interest in liquid crystal science, stimulated in part by the discoveries of the blue phases [12] and of chiral smectic ferroelectric [13], antiferroelectric [14] and twist grain boundary [15] phases. In all these chiral liquid

crystalline phases, the chirality is of molecular origin and is essentially permanent. It was believed that chirality of the molecules in association with tilting of molecules in smectic layers thereby reducing the overall symmetry of the liquid crystals was essential for conventional ferroelectric liquid crystals [16]. However, since the essential requirement is the introduction of polar symmetry in the system, ferroelectric liquid crystals need not necessarily be chiral. For this reason, a great deal of attention has been directed, theoretically and experimentally, towards non-chiral ferroelectric systems [17-23]. Tournilhac et al., have claimed the first example of achiral molecules showing ferroelectric properties [22]. They synthesized polyphilic molecules comprising three or more chemically different subunits, and found that these achiral molecules can form ferroelectric smectic liquid crystals as a result of the segregation of their units into homogeneous microdomains. Followed by this observation, Watanabe *et* al., [23] reported that a ferroelectric smectic phase may be formed from some main-chain liquid crystal polymers by incorporating two different aliphatic spacers with odd numbers of carbon atoms into the backbone in a regularly alternating fashion. Although several attempts were made to achieve polar order with achiral molecules, it was only when Niori et al. presented evidence for ferroelectric switching in a layered liquid crystalline phase comprising of achiral bent-core molecules [8] that polar order in fluids in the absence of chirality became the focus of interest again.

The origin of the spontaneous polarization in these novel systems is believed to be a combination of the following three factors: (i) the highly polar character of the molecules. (ii) the packing arrangement of the molecules in smectic layers (with the dipoles facing in a common direction within the layers). (iii) the tilt of the molecules with respect to the smectic layer normal [9,10]. All the three factors together can lead to a chiral layer symmetry, although the molecules themselves are not chiral.

Recent investigations on the switching properties of the original materials, initially speculated as being ferrroelectric by Niori *et* al. [8], have provided strong evidence to support the postulation that the materials are actually antiferroelectric in nature [9,10,24-26]. This led to a model with an untilted core structure and antiferroelectric ordering of the molecular bows. Link *et* al., [9] confirmed the antiferroelectric behaviour by electrooptical investigations on freestanding films and on sandwich

preparations. They proposed a structural model [9] based on the spontaneous formation of chiral layers in a liquid crystalline phase consisting of achiral molecules.

The molecular structure of the banana-shaped liquid crystals can be regarded as composed of three units: (i) an angular central unit **A**, (ii) two linear rigid cores B and (iii) the terminal alkyl chains (figure 4.2).



Fig 4.2 : General molecular structural requirements of banana-shaped liquid crystals.

The central unit A can be a resorcinol or substituted resorcinol [27-32], 2,7-[33-35], 3,4'-disubstituted dihydroxynaphthalene biphenyl [36], 1,3-bis(4hydroxyphenyl)benzene [34], 2,6-bis(4-hydroxyphenyl)pyridine [34], 2,6-bis(4hydroxyphenyl)-2-nitrobenzene [34] or diphenyl acetylene [34]. Apart from these, compounds having odd numbered alkylene chain [37] as the central unit also have been investigated. In most cases, Schiff's base containing units are employed as rigid cores [27-32,35]. However, compounds having non-Schiff's base rigid cores such as 4-substituted phenyl rings, biphenyls, 2-phenylpyrimidines or phenylbenzoates connected to the central unit via ester linkages are also known [34]. The major drawback of the Schiff's base (rigid core) containing compounds is their limited thermal and photochemical stability.

Miscibility studies show that the smectic phases formed by banana-shaped molecules are not miscible with any of the smectic phases of calamitic liquid crystals. Therefore this class of compounds represent a new sub-field of liquid crystals and in view of the banana or bow shape of the molecules, the mesophases formed by them are designated as B_1 , B_2 ,*etc.*, in the sequence of their discovery. These new mesophases are interesting not only from the structural point of view but also with respect to some unusual physical properties they exhibit. Up to now about seven mesophases (B_1 to B_7) have been claimed to be observed experimentally. Of these

only the structure of B_2 phase is well characterized and the structure of all the other mesophases are still unclear. Also, the B_3 and B_4 phases have been classified as crystalline phases. The structural details that have been proposed for the different banana phases have already been discussed in chapter 1.

One of the liquid crystalline phases designated as B_2 revealed an antiferroelectric switching behaviour. It was shown that the liquid-like smectic layers of these molecules have a polar structure provided by the dense packing of the bent-core molecules [9,29,25,38]. For this antiferroelectric switchable phase, it was proposed that [9] the molecules arrange in layers whereby the layer polarization alternates from layer to layer (antiferroelectric structure) giving rise to a biaxial smectic phase with the optic axis being tilted relative to the layer normal. By applying an electric field the molecules can be switched into corresponding ferroelectric states. One clear potential area of application of materials possessing this **phase/property** is in electronic nonlinear optics [39]. Initially it was believed that a rigid core comprising a Schiff's base unit was necessary to obtain this unusual **B**₂ mesophase. However, recently a significant number of compounds with non-Schiff's base rigid cores exhibiting **B**₂ phase have been synthesized [36,40]. A survey of the literature shows that compounds with lateral fluoro substitution on the rigid core and exhibiting **B**₂ phase are few in number [40].

The exact molecular structural requirements for the occurrence of the banana phases are not clear. We have carried out the synthesis of four homologous series of compounds (4.6, **4.7**, **4.8** and 4.9) and have studied the effect of 2-methyl substituent of the resorcinol moiety (central unit) on the occurrence and stabilization of B_2 phase.



n = 10, 11, 12, 13, 14, 15, 16, 18.



n = 9,10,11,12,14,16,18.

(4.7)



n = 9,10,11,12,14,16,18.

(4.8)



n = 7,8,9,10,11,12,14,16,18.

(4.9)

4.1 Results and discussion:

The synthetic schemes for the preparation of the above four series of compounds are shown in figures 4.3 and 4.4.



Fig 4.3 : Synthetic scheme for the preparation of compounds of series 4.6, 4.7 and 4.8.



n = 7,8,9,10,11,12,14,16,18.

Fig 4.4 : Synthetic scheme for the preparation of compounds of series 4.9.

The 4-n-alkyl- and 4-n-alkoxybenzoic acids were prepared following a procedure described by Weygand and Gabler [41] and Gray and Jones [42] respectively. The 4n-alkylbiphenyl-4'-carboxylic acids were prepared following a procedure described earlier [43]. 4-Benzyloxybenzoic acid was prepared by first reacting ethyl 4hydroxybenzoate with benzyl chloride in the presence of anhydrous potassium carbonate in butan-2-one followed by hydrolysis of the resulting ester with aqueous alkali. **2-Fluoro-4-benzyloxybenzoic** acid was prepared following the above procedure. The 3-fluoro-4-n-alkoxybenzoic acids were prepared following a procedure described in chapter 2. The phenols **4.16** and **4.17** were prepared by first esterifying 2-methylresocinol with appropriate 4-benzyloxybenzoic acids in the presence of DCC as dehydrating agent and DMAP as a catalyst followed by deprotection of the phenols using palladium catalyzed hydrogenolysis reaction. The final esters were obtained by carrying out a similar esterification reaction of the phenols 4.16 and 4.17 with appropriate benzoic/biphenyl carboxylic acids. 2-Methylresorcinol was obtained commercially and purified.

The optical microscopic textures of the materials were examined using a polarizing microscope equipped with a heating stage. Thin films of samples were obtained by sandwiching them between a glass plate and a cover slip. On cooling the isotropic liquid of compound **8** of series **4.6**, a **leaf/petal-like** texture with uniform coloured stripes or a fringe texture or a schlieren texture identical to that exhibited by the compound (standard) reported by Niori et al. [8] which has been identified [33] as B_2 was observed. Typical photomicrographs of this texture are shown in plates 4.1 and 4.2 respectively.



Plate 4.1 : Photomicrograph of B₂ phase of compound 8 of series 4.6 at 107°C.

This compound exhibited only one mesophase and is monotropic. Compounds 4 to 7 of this series, compounds **3** to 7 of series **4.7** and compounds **4** to **8** of series **4.8** also exhibited similar textures and all of them showed only one mesophase.



Plate 4.2 : Photomicrograph of B₂ phase of compound 8 of series 4.6 at 107°C.

When the isotropic liquid of compound 3 of series 4.8 was cooled, a highly coloured mosaic texture, which is identical to the one observed for the B_1 phase [34] developed. Plate 4.3 depicts a photomicrograph of this texture.



Plate 4.3 : Photomicrograph of B_1 phase of compound 3 of series 4.8 at 150°C.

We observed a similar texture for compounds 1 and 2 of this series.

On cooling the isotropic liquid of compounds belonging to series 4.9, some irregular patterns typical of a crystalline phase began to grow. The texture did not resemble those obtained for any of the known banana phases. Also this phase was not fluid enough for the cover slip to be displaced. Since this phase did not exhibit any characteristics of a mesophase, from the preliminary microscopic observations one can probably conclude that it is a crystalline phase. The non-mesomorphic nature of the compounds belonging to this series has been confirmed by the x-ray diffraction studies and this will be discussed later.

The transition temperatures together with the associated enthalpies of the four homologous series of compounds are summarized in tables **4.1**, **4.2**, **4.3** and **4.4** respectively.

Compound	n	Cr		B ₂		Ι
number						
1	10		109.5	-	-	
			⁸ 94.9			
2	11		117.0	-	-	
			55.7			
3	12		119.5	-	-	
			60.8			
4	13		118.0	(.	103.0)	
			65.9		†	
5	14		115.0	(.	105.0)	
			^{&} 116.7		†	
6	15		115.5	(.	107.0)	-
			⁸ 118.9		ţ	
7	16		114.0	(.	108.0)	-
			^{&} 137.0		23.3	
8	18		110.0	(.	109.5)	
			^{&} 147.2		<i>24.8</i>	

Table 4.1 : Transition temperatures (''C) and enthalpies (kJ mol⁻¹) for the
compounds of series 4.6.

 \dagger : The enthalpy could not be measured as the sample crystallizes immediately; \otimes : Total enthalpy including any other crystal-crystal transition; () : Indicates a monotropic transition.

Compound	n	Cr		B ₂		Ι
number						
1	9	•	111.0	-	-	
			'76.4			
2	10		107.0		-	
			'75.0			
3	11		109.0	(.	99.0)	
			⁸ 97.6		+	
4	12		112.0	(.	101.0)	
			'98.7		23.6	
5	14		104.5	(.	104.0)	
			⁸ 96.2		24.5	
6	16		104.5		106.0	
			33.6		24.5	
7	18		107.0		108.0	
			'91.9		26.1	

Table 4.2 : Transition temperatures (°C) and enthalpies (kJ mol'') for the compounds of series 4.7.

 \dagger : The enthalpy could not be measured as the sample crystallizes immediately; \otimes : Total enthalpy including any other crystal-crystal transition; () : Indicates a monotropic transition.

Table 4.3 : Transition temperatures (°C) and enthalpies (kJ mol ⁻	¹) for the
compounds of series 4.8.	

Compound number	n	Cr		B ₂		\mathbf{B}_1		Ι
1	8		168.0	-			208.0*	
			28.5				t	
2	9		150.0	-			197.0*	
			29.1				ŧ	
3	10	•	147.8	-			194.2*	
			^{&} 38.4				†	
4	11		147.6	•	192.0*	-		
			[∞] 43.5		t			
5	12		136.0		193.0*	-		
			* 43.3		Ť			
6	14	•	135.8	-	194.5*	-		
_			°48.6		†			
7	16	•	132.0		194.0*	-		
	10		°56.8		T			
8	18	-	127.5	•	192.5*	-		
			44.0		ŧ.			

 \dagger : The enthalpy could not be measured; \star : Beyond this temperature the compound decomposes; \otimes : Total enthalpy including any other crystal-crystal transition.

Compound	n	Cr		· I
number				
1	7		154.0	
			⁸ 85.2	
2	8		148.0	
			[∞] 84.3	
3	9		144.5	
			'53.9	
4	10		143.0	
			⁸ 60.1	
5	11		142.0	
			^{&} 51.2	
6	12		141.0	
			^{&} 59.2	
7	14		140.0	
			⁸ 71.2	
8	16		139.0	
			⁸ 87.4	
9	18		138.5	
			'89.8	

Table 4.4 : Melting points (°C) and enthalpies (kJ mol'') for the compounds of series 4.9.

 \otimes : Total enthalpy including any other crystal-crystal transition.

From the tables it is seen that in series **4.6**, compounds 4 to 8 show a monotropic B_2 phase while the lower homologues (compounds 1 to 3) are nonmesomorphic. The higher homologues (compounds 6 and 7) of series **4.7** exhibit an enantiotropic B_2 phase over a short thermal range (1-2°C) and compounds 3 to 5 show a monotropic B_2 phase. The lower homologues (compounds 1 and 2) are again nonmesomorphic. All the compounds of series **4.8** are mesomorphic and the mesophases exhibited by them are all enantiotropic. The lower homologues (compounds 1 to 3) exhibit B_1 phase and the rest of the compounds (4 to 8) show a B_2 phase. All the compounds belonging to this series have very high clearing temperatures and were found to undergo thermal decomposition at this temperature. The compounds of series **4.9** are all non-mesomorphic.

Figures 4.5 and 4.6 show the plots of transition temperatures as a function of number of n-alkoxy/alkyl chain length for the series **4.6** and 4.7 respectively.



Fig 4.5 : Plot of transition temperatures as a function of n-alkoxy chain length for series 4.6.



Fig 4.6 : Plot of transition temperatures *versus* n-alkyl chain length for series 4.7.

From the plots it can be seen that in both the series (4.6 and 4.7) the clearing temperatures increase with increase in the number of carbon atoms in the n-alkoxy/alkyl chain. The plots show a smooth curve for these transitions. Compounds 4 to 8 of series 4.6 show a monotropic B_2 phase, which gets eliminated as the chain length is reduced (compounds 1 to 3). In series 4.7, B_2 phase is enantiotropic and exists over a very short temperature range (1-2°C) for the higher homologues (compounds 6 and 7). It becomes monotropic for compounds 3 to 5 and disappears in the lower homologues (compounds 1 and 2). Since compounds of series 4.8 undergo thermal decomposition at the clearing temperature, the exact clearing temperature could not be determined and hence plot of clearing temperatures versus number of carbon atoms in the n-alkyl chain could not be obtained for this homologous series of compounds.

4.1.1 Effect of 2-methyl substituent of resorcinol moiety (central unit) on the occurrence and stabilization of the B₂ phase:

Consider the following homologous series of compounds [44,40] with unsubstituted resorcinol moiety as the central unit.



n = 10, 11, 12, 14, 16, 18.

(4.10) [44]



n = 9, 10, 11, 12, 14, 16.

(4.11) [44]



Mesomorphic properties of the above series of compounds are briefly summarized below.

All the compounds of series 4.10 are mesomorphic and show enantiotropic B_2 phase with a thermal range of about 1.5 to 18°C. The lower homologues of series 4.11 (n = 9,10) are non-mesomorphic and the rest of the homologues show an enantiotropic B_2 phase having a temperature range of 6 to 14°C. In series 4.12 homologues n = 7 to 11 do not exhibit any mesophase, homologues n = 12 to 18 show an unidentified smectic phase. The thermal range of the enantiotropic smectic phase in this series is about 4 to 11°C. All the three homologues of series 4.13 exhibit an enantiotropic B_2 phase with a wide range of temperature ($\approx 88°C$).

In order to examine the influence of 2-methyl substituent of the central unit on the occurrence of B_2 phase, the mesomorphic behaviour of compounds belonging to series **4.6**, **4.7**, **4.8** and 4.9 can be compared with those of the above four homologous series of compounds.

Comparison of the mesomorphic properties of series 4.6 with those of series 4.10 indicates that in the former series due to the presence of a 2-methyl substituent, B_2 phase which is enantiotropic in series 4.10 completely disappears in compounds 1, 2 and 3 and exists as a monotropic phase in compounds 4 to 8.

A similar comparison can be made between series 4.7-4.11 and series 4.9-4.12. It is seen that like in series 4.11 the lower homologues of series 4.7 (compounds 1 and 2) are non-mesomorphic. The B_2 phase of homologues (n =11, 12 and 14) which are enantiotropic in series 4.11 becomes monotropic in series 4.7 and a drastic reduction (from 14 to 2°C) in the thermal range of the enantiotropic B_2 phase is observed in the higher homologues (compounds 6 and 7) of this series as compared to series 4.11. The effect of 2-methyl substituent is remarkable in series 4.9. Unlike series 4.12 in which the higher homologues exhibit a smectic phase (unidentified), all the homologues of series 4.9 are non-mesomorphic.

A comparison of compounds 3, 4 and 5 of series 4.8 with series 4.13 shows that unlike compound 3 (series 4.8) which shows a B_1 phase, its analogue (n = 10) in series 4.13 shows a B_2 phase. There is no change in the mesomorphic behaviour of compounds 4 and 5 of series 4.8 when compared to those of their analogues (n = 11 and 12) of series 4.13, except for a reduction in the B_2 phase temperature range by about 30°C.

From the above results it can be concluded that incorporation of a 2-methyl substituent in the resorcinol moiety (central unit) does not favour the formation of B_2 phase in particular and other mesophases in general.

The intermediates and the final compounds were characterized by employing similar techniques mentioned in chapter 2. The DSC scan of compound 6 (series 4.7) is shown in figure 4.7. The sample was heated and cooled at the rates of 5 and 0.5°C/min. Since the enantiotropic range of the B_2 phase is short ($\approx 2^{\circ}$ C) the melting and clearing temperatures could not be well resolved. Figures 4.8 and 4.9 represent the ¹H NMR and IR spectra of compounds 6 (series 4.7) and 5 (series 4.6) respectively.



Fig 4.7 : DSC thermogram of compound 6 (series 4.7).



Fig 4.8 : H¹ NMR spectrum of compound 6 of series 4.7.



Fig 4.9 : IR spectrum of compound 5 of series 4.6.

4.1.2 X-ray diffraction studies:

In order to understand the nature of the mesophase and to conclusively establish the type of mesophase exhibited by the three homologous series of compounds (4.6, 4.7 and **4.8**), x-ray diffraction studies were carried out on non-oriented samples. In the powder x-ray diffraction technique, the sample was filled into a **0.5mm** diameter Lindemann capillary tube in the isotropic phase and the ends of the capillary were flame sealed. The sample was then mounted in a computer-controlled oven. The Cu K_{α} radiation from a rotating anode generator (**Rigaku** Ultrax 18) with a flat Graphite crystal monochromator was collimated using a double-slit arrangement so as to have a cross section of roughly 0.5 X **0.5mm** at the sample. The diffraction patterns were collected on an image plate with an effective pixel size of **100µm**, procured from Marresearch. The sample to detector distance was calculated accurately using a standard sample. **A** schematic representation of the x-ray diffraction set-up is shown in figure 4.10.



Fig 4.10 : A schematic diagram showing the x-ray diffraction set-up

The sample was first heated to the isotropic phase and the temperature was maintained constant for about ten minutes. The diffraction pattern was recorded on cooling the sample into the mesophase. The exposure time varied from one hour to three hours. The x-ray diffraction patterns of some of the compounds are discussed below.

Compound 8 of series 4.6 showed a monotropic phase whose textures are shown in plates 4.1 and 4.2. From the preliminary microscopic observation it was identified as a B_2 phase. The x-ray pattern of this mesophase at 107°C showed four reflections in the small angle region with spacings 42.1Å, 21.4 Å, 14.28 Å and 10.7 Å which can be indexed as (001), (002), (003) and (004) reflections. The periodicity of the structure spacing are in the ratio 1:1/2:1/3:1/4. This clearly indicates a layered structure. In addition to these reflections a broad diffuse wide angle reflection at about 4.74 Å due to the alkoxy chain was also seen. A typical diffraction pattern obtained for this sample is shown in figure 4.11.



Fig 4.11 : X-ray angular intensity profile of the B_2 phase of compound 8 (series 4.6) at 107°C.

The pattern depicted in figure 4.11 is identical to the one observed for B_2 phase [31]. Therefore on the basis of this data as well as microscopic texture this mesophase has been identified as B_2 phase. The lamellar spacing 42.1 Å corresponds to a tilt of 56.3" which is calculated assuming the molecule in a conformation as shown in figure 4.12.



Similar diffraction patterns were obtained for compounds 3 to 7 of series **4.7** and 4 **to** 8 of series **4.8**. In view of these it can be concluded that the mesophase exhibited by **all** these compounds is indeed a B_2 phase. Figures 4.13, 4.14 and 4.15 represent the x-ray diffraction patterns for compounds 6 and 7 of series **4.7** and 8 of **series 4.8** respectively.



Fig 4.13 : X-ray angular intensity profile of the B_2 phase of compound 7 (series 4.7) at 107°C.



Fig 4.14 : X-ray angular intensity profile of the B_2 phase of compound 6 (series 4.7) at 105°C.



Fig 4.15 : X-ray angular intensity profile of the B₂ phase of compound 8 (series 4.8) at 130°C.

Table 4.5 shows the lamellar spacing of the reflections in the small angle region for the above compounds.

Series	Compound	dı	d ₂	d ₃	d4		
	number	(A)	(A)	(A)	(A)		
4.6	6	39.6	20.1	13.5	10.2		
4.6	7	42.1	21.4	14.2	10.7		
4.7	8	47.7	24.0	16.5	12.4		

Table 4.5

The x-ray diffraction pattern of compound 3 (series 4.8) showed three reflections in the small angle region at 32.5Å, 24.78Å and 14.1Å which could be indexed as (002), (101) and (200) reflections respectively, of a centered rectangular twodimensional lattice as found for the B_1 phase [45]. The lattice parameters are a = 26.8Å and c = 65.0Å. Figure 4.16 shows the diffraction pattern obtained for this mesophase.



Fig 4.16 : X-ray angular intensity profile of the B₁ phase of compound 3 (series 4.8) at 150°C.

Compounds 1 and 2 belonging to the same series also showed similar results. From these and the microscopic texture we have concluded that compounds 1 to **3** (series **4.8**) exhibit the B_1 phase.

X-ray pattern of the phase obtained on cooling the isotropic liquid of compound 9 of series **4.9** showed several sharp reflections in the small angle and wide angle regions which clearly indicates a three-dimensionally ordered structure. Figure 4.17 depicts the x-ray pattern of this phase.



Fig 4.17 : **X-ray angular intensity profile of the crystalline phase of compound 9** (series 4.9) at **137°C; enlarged version of the reflections in the wide angle region is shown in the inset.**

This pattern was not very much different from the one obtained at $30^{\circ}C$ (crystal). On the basis of this result as well as the microscopic texture we identify this phase to be a crystalline phase. Other homologues of this series also show similar results. Therefore, we believe that all the homologues of this series are non-mesomorphic.

4.1.3 Electrooptical studies:

The effect of a DC electric field on the B₂ phase of compound 7 (series 4.6) has been studied. The sample was taken in a 5pm thick cell made with conducting plates (ITO coated glass plates), coated with polyimide and rubbed. The sample was viewed between crossed polarizers under a microscope. As the sample was cooled at a slow rate (0.1°C/min.) under a DC field of 21.3V/ μ m, circular domains with characteristic extinction brushes were formed. Under the field the brushes were oriented at an angle of $\approx 45^{\circ}$ with respect to the orientation direction of the crossed polarizers. On reversing the polarity of the applied field, the brushes rotated in the same direction ie., the rotation of the brushes in this case occurred in only one direction independent of the sign of the applied field. On switching off the field the orientation of the dark brushes remained unaffected and the resultant texture had uniform periodic stripes on the circular domain. This texture is characteristic of the phase that is obtained at racemic ground state [36]. Plates 4.4 a, b, c show the textures of compound 7 in the presence and absence of the electric field.









(c)

Plate 4.4 : Photomicrographs illustrating the effect of DC electric field on compound 7 (series 4.6) taken between rubbed **polyimide** coated plates at 105°C. (a) +21.3V, (b) OV, (c) -21.3V.

Under low DC fields the stripes become **birefringent** and are retained and they begin to disappear when voltage is increased. For this compound the stripes remain up to 23V after which they begin to disappear. The above observations indicate a **racemic** ground state in this compound which is characterized by **synclinic** interlayer correlation with an antiferroelectric order from layer to layer. The stripe formation in this case (in the ground state) may be a consequence of the equivalence of the tilt directions.

In order to conclusively establish the antiferroelectric switching in the B_2 phase, a switching current response **profile** was **obtained** under a triangular wave voltage for compound 7 of series 4.6. The sample was **filled** in its isotropic state into a cell (ITO coated and etched to give a precise area of 0.8cm^2) of $7.2 \mu \text{m}$ thickness and treated for homogeneous alignment. When a triangular wave with a peak-to-peak voltage of $160V_{pp}$ and a frequency of 17Hz at 106.2°C was applied, two sharp peaks were

recorded during a half period indicating an antiferroelectric switching behaviour. Figure **4.18** depicts a typical current response profile of this compound.



Fig 4.18 : Switching current response in the B₂ phase of compound 7 (series 4.6).

The spontaneous polarization determined by integrating the switching current peaks amounts to about 684 nC/cm^2 .

4.2 Experimental:

The 2-fluoro-4-benzyloxybenzoic acid was prepared following a procedure described in chapter 2. The 4-n-alkyl- [42], 4-n-alkoxybenzoic acids [43] and 4-n-alkylbiphenyl-4'-carboxylic acids [44] were prepared following a procedure described earlier. The procedure for preparation of 3-fluoro-4-n-alkoxybenzoic acids is described in chapter 2.

2-Methyl-1,3-phenylene bis[2'-fluoro-4'-benzyloxybenzoate], (4.14)

This was prepared following an esterification procedure of Hassner and Alexanian [46]. Thus, a mixture of 2-fluoro-4-benzyloxybenzoic acid (3g, 12.1mrnol), 2methylresorcinol (0.76g, 6.1 mmol), DMAP (0.15g, **1.2mmol**) and dry dichloromethane (20ml) was stirred for five minutes. To this mixture, was added DCC (2.77g, 12.1mmol) and stirring continued overnight at room temperature. The N,N'-dicyclohexylurea formed was filtered off and the filtrate diluted with dichloromethane (50ml). The resultant solution was washed with 5% aqueous acetic acid (2X20ml), water (3X30ml) and dried over Na₂SO₄. The solvent was removed from the filtered solution to yield a residue which was purified by column chromatography on silica gel using chloroform as eluent to yield pure 2-methyl-1,3phenylene bis[2'-fluoro-4'-benzyloxybenzoate] as a white solid which was crystallized from chloroform/petroleum ether mixture (2.74g, 78.2%); m.p. 149-149.5°C; v_{max} (nujol): 2950, 1720, 1740, 1620, 1580, 1470, 1340, 1260, 1120 and 1070 cm⁻¹; 6: 2.12 (3H, s, ArCH₃), 5.14 (4H, s, (ArOCH₂)₂), 6.76-8.1 (19H, m, ArH).

2-Methyl-1,3-phenylene bis[4'-benzyloxybenzoate], (4.15)

This was prepared following a procedure similar to the one described above (4.14) using 4-benzyloxybenzoic acid and 2-methylresorcinol. Yield, 80%; m.p. 159.7-160°C; v_{max} (nujol): 2950, 1740, 1610, 1480, 1260, 1180 and 1100 cm⁻¹; 6: 2.02 (3H, s, ArCH₃), 5.1 (4H, s, (ArOCH₂)₂), 6.99-8.12 (21H, m, ArH). Elemental analysis: Found, C, 77.23; H, 5.20% C₃₄H₂₈O₆ requires C, 77.19; H, 5.18%

2-Methyl-1,3-phenylene bis[2'-fluoro-4'-hydroxybenzoate], (4.16)

A mixture of 2-methyl-1,3-phenylene bis[2'-fluoro-4'-benzyloxybenzoate] (2g, 3.4mmol) in 1,4-dioxane (20ml) and 5% Pd-C catalyst (0.5g) was stirred at 55°C in an atmosphere of hydrogen till the calculated quantity of hydrogen was absorbed. The reaction mixture was then filtered and removal of the solvent under reduced pressure yielded a white solid which was crystallized from ethylacetate (1.3g, 94.33%); m.p 258-260°C (decomposes); v_{max} (nujol): 3400, 2950, 1710, 1620, 1460, 1260, 1110, 1080 and 1060 cm⁻¹; δ : 2.18 (3H, s, ArCH₃), 3.4 (2H, s, (ArOH)₂), 6.87-8.2 (9H, m, ArH).

2-Methyl-1,3-phenylene bis[4'-hydroxybenzoate], (4.17)

This was prepared following a procedure similar to the one described above (4.16) using 2-methyl-1,3-phenylene bis[4'-benzyloxybenzoate]. Yield, 93.5%; m.p. 250-252°C (decomposes); v_{max} (nujol): 3400,2950, 1700, 1590, 1460, 1260, 1140, 1160 and 1080 cm⁻¹; 6: 2.18 (3H, s, ArCH₃), 3.08 (2H, s, (ArOH)₂), 7.13-8.24 (11H, m, ArH).

Elemental analysis: Found, C, 69.25; H, 4.41% $C_{34}H_{16}O_{6}$ requires C, 69.22; H, 4.42%

2-Methyl-1,3-phenylene bis[4'(4"-n-octadecyloxybenzoyloxy)-2'-fluorobenzoate]

This was prepared by esterifying compound 4.16 with 4-n-octadecyloxybenzoic acid following a procedure described for compound 4.14. Yield, 77%; m.p. 110.0°C; v_{max} (nujol): 2900, 1720, 1740, 1600, 1470,1240, 1120, 1160 and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.89 (6H, t, 2XCH₃); 1.2-1.57 (64H, m, 32XCH₂); 4.04-4.07 (4H, t, (ArOCH₂-)₂), 6.98-8.2 (17H, m, ArH).

The physical data of the cognate preparations of the other 2-methyl-1,3-phenylene bis[4'(4"-n-alkoxybenzoyloxy)-2'-fluorobenzoates] are given below.

2-Methyl-1,3-phenylene bis[4'(4"-n-hexadecyloxybenzoyloxy)-2'-fluorobenzoate]

Yield, 79.2%; m.p. 114.0°C; v_{max} (nujol): 2900, 1720, 1740, 1600, 1470, 1240, 1120, 1160 and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.89 (6H, t, 2XCH₃); 1.2-1.57 (56H, m, 28XCH₂); 4.04-4.07 (4H, t, (ArOCH₂-)₂), 6.98-8.2 (17H, m, ArH).

2-Methyl-1, 3-phenylene bis[4'(4"-n-pentadecyloxybenzoyloxy)-2'-fluoro benzoate]

Yield, 75.0%; m.p. 115.5°C; v_{max} (nujol): 2900, 1720, 1740, 1600, 1470, 1240, 1120, 1160 and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.89 (6H, t, 2XCH₃); 1.2-1.57 (52H, m, 26XCH₂); 4.04-4.07 (4H, t, (ArOCH₂-)₂), 6.98-8.2 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4"-n-tetradecyloxybenzoyloxy)-2'-fluorobenzoate]

Yield, 82.1%; m.p. 115.0°C; v_{max} (nujol): 2900, 1720, 1740, 1600, 1470, 1240, 1120, 1160 and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.89 (6H, t, 2XCH₃); 1.2-1.57 (48H, m, 24XCH₂); 4.04-4.07 (4H, t, (ArOCH₂-)₂), 6.98-8.2 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4"-n-tridecyloxybenzoyloxy)-2'-fluorobenzoate]

Yield, 80.7%; m.p. 118.0°C; v_{max} (nujol): 2900, 1720, 1740, 1600, 1470, 1240, 1120, 1160 and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.89 (6H, t, 2XCH₃); 1.2-1.57 (44H, m, 22XCH₂); 4.04-4.07 (4H, t, (ArOCH₂-)₂), 6.98-8.2 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4"-n-dodecyloxybenzoyloxy)-2'-fluorobenzoate]

Yield, 80.0%; m.p. 119.5°C; v_{max} (nujol): 2900, 1720, 1740, 1600, 1470, 1240, 1120, 1160 and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.89 (6H, t, 2XCH₃); 1.2-1.57 (40H, m, 20XCH₂); 4.04-4.07 (4H, t, (ArOCH₂-)₂), 6.98-8.2 (17H, m, ArH).

2-Methyl-1, 3-phenylene bis[4'(4"-n-undecyloxybenzoyloxy)-2'-fluorobenzoate]

Yield, 81.0%; m.p. 117.0°C; v_{max} (nujol): 2900, 1720, 1740, 1600, 1470, 1240, 1120, 1160 and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.89 (6H, t, 2XCH₃); 1.2-1.57 (36H, m, 18XCH₂); 4.04-4.07 (4H, t, (ArOCH₂-)₂), 6.98-8.2 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4"-n-decyloxybenzoyloxy)-2'-fluorobenzoate]

Yield, 89.0%; m.p. 109.5°C; v_{max} (nujol): 2900, 1720, 1740, 1600, 1470, 1240, 1120, 1160 and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.89 (6H, t, 2XCH₃); 1.2-1.57 (32H, m, 16XCH₂); 4.04-4.07 (4H, t, (ArOCH₂-)₂), 6.98-8.2 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4"-n-hexadecylbenzoyloxy)-2'-fluorobenzoate]

This was prepared by carrying out **an** esterification reaction between compound 4.16 and 4-n-hexadecylbenzoic acid following a procedure similar to the one described for compound 4.14. Yield, 82.0%; **m.p.** 104.5°C; y (nujol): 2950, 1730, 1610, 1460, 1250, 1280, 1120, and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.90 (6H, t, 2XCH₃); 1.2-1.6 (56H, m, 28XCH₂); 2.69-2.73 (4H, t, (ArCH₂-)₂), 7.1-8.24 (17H, m, ArH).

The physical data of the cognate preparations of the other 2-methyl-1,3-phenylene bis[4'(4"-n-alkylbenzoyloxy)-2-fluorobenzoates] are given below.

2-Methyl-1,3-phenylene bis[4'(4"-n-octadecylbenzoyloxy)-2'-fluorobenzoate]

Yield, 78.0%; m.p. 107.0°C; v_{max} (nujol): 2950, 1730, 1610, 1460, 1250, 1280, 1120, and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.90 (6H, t, 2XCH₃); 1.2-1.6 (64H, m, 32XCH₂); 2.69-2.73 (4H, t, (ArCH₂-)₂), 7.1-8.24 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4"-n-tetradecylbenzoyloxy)-2'-fluorobenzoate]

Yield, 90.0%; m.p. 104.5°C; ν_{max} (nujol): 2950, 1730, 1610, 1460, 1250, 1280, 1120, and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.90 (6H, t, 2XCH₃); 1.2-1.6 (48H, m, 24XCH₂); 2.69-2.73 (4H, t, (ArCH₂-)₂), 7.1-8.24 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4"-n-dodecylbenzoyloxy)-2'-fluorobenzoate]

Yield, 81.5%; m.p. 112.0°C; v_{max} (nujol): 2950, 1730, 1610, 1460, 1250, 1280, 1120, and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.90 (6H, t, 2XCH₃); 1.2-1.6 (40H, m, 20XCH₂); 2.69-2.73 (4H, t, (ArCH₂-)₂), 7.1-8.24 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4"-n-undecylbenzoyloxy)-2'-fluorobenzoate]

Yield, 85.0%; m.p. 109.0°C; v_{max} (nujol): 2950, 1730, 1610, 1460, 1250, 1280, 1120, and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.90 (6H, t, 2XCH₃); 1.2-1.6 (36H, m, 18XCH₂); 2.69-2.73 (4H, t, (ArCH₂-)₂), 7.1-8.24 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4"-n-decylbenzoyloxy)-2'-fluorobenzoate]

Yield, 81.0%; m.p. 107.0°C; ν_{max} (nujol): 2950, 1730, 1610, 1460, 1250, 1280, 1120, and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.90 (6H, t, 2XCH₃); 1.2-1.6 (32H, m, 16XCH₂); 2.69-2.73 (4H, t, (ArCH₂-)₂), 7.1-8.24 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4"-n-nonylbenzoyloxy)-2'-fluorobenzoate]

Yield, 83.0%; m.p. 111.0°C; v_{max} (nujol): 2950, 1730, 1610, 1460, 1250, 1280, 1120, and 1060 cm⁻¹; 6: 2.17 (3H, s, ArCH₃), 0.86-0.90 (6H, t, 2XCH₃); 1.2-1.6 (30H, m, 15XCH₂); 2.69-2.73 (4H, t, (ArCH₂-)₂), 7.1-8.24 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4'''-n-decylbiphenyl-4"-carbonoyloxy)-2'-fluoro benzoate]

This was prepared by esterifying the phenol 4.16 with 4'-n-decylbiphenyl-4carboxylic acid following a procedure described above (4.14). Yield, 80.0%; m.p. 147.8°C; ν_{max} (nujol): 2950, 1740, 1620, 1470, 1380, 1260, 1280, 1130, and 1080 cm⁻¹; 6: 2.19 (3H, s, ArCH₃), 0.87-0.91 (6H, t, 2XCH₃); 1.28-1.7 (32H, m, 16XCH₂); 2.65-2.69 (4H, t, (ArCH₂-)₂), 7.17-8.27 (25H, m, ArH).

The physical data of the cognate preparations of the other 2-methyl-1,3-phenylene bis[4'(4'''-n-alkylbiphenyl-4''-carbonoyloxy)-2-fluorobenzoates] are given below.

2-Methyl-1,3-phenylene bis[4'(4'''-n-octadecylbiphenyl-4"-carbonoyloxy)-2'-fluorobenzoate]

Yield, 75.0%; m.p. 127.5°C; v_{max} (nujol): 2950, 1740, 1620, 1470, 1380, 1260, 1280, 1130, and 1080 cm⁻¹; 6: 2.19 (3H, s, ArCH₃), 0.87-0.91 (6H, t, 2XCH₃); 1.28-1.7 (64H, m, 32XCH₂); 2.65-2.69 (4H, t, (ArCH₂-)₂), 7.17-8.27 (25H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4'''-n-hexadecylbiphenyl-4"-carbonoyloxy)-2'-fluorobenzoate]

Yield, 77.0%; m.p. 132.0°C; v_{max} (nujol): 2950, 1740, 1620, 1470, 1380, 1260, 1280, 1130, and 1080 cm⁻¹; 6: 2.19 (3H, s, ArCH₃), 0.87-0.91 (6H, t, 2XCH₃); 1.28-1.7 (56H, m, 28XCH₂); 2.65-2.69 (4H, t, (ArCH₂-)₂), 7.17-8.27 (25H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4'''-n-tetradecylbiphenyl-4"-carbonoyloxy)-2'-fluorobenzoate]

Yield, 76.0%; m.p. 127.5°C; v_{max} (nujol): 2950, 1740, 1620, 1470, 1380, 1260, 1280, 1130, and 1080 cm⁻¹; 6: 2.19 (3H, s, ArCH₃), 0.87-0.91 (6H, t, 2XCH₃); 1.28-1.7 (48H, m, 24XCH₂); 2.65-2.69 (4H, t, (ArCH₂-)₂), 7.17-8.27 (25H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4'''-n-dodecylbiphenyl-4"-carbonoyloxy)-2'-fluorobenzoate] Yield, 75.0%; m.p. 136.0°C; v_{max} (nujol): 2950, 1740, 1620, 1470, 1380, 1260, 1280, 1130, and 1080 cm⁻¹; 6: 2.19 (3H, s, ArCH₃), 0.87-0.91 (6H, t, 2XCH₃); 1.28-1.7 (40H, m, 20XCH₂); 2.65-2.69 (4H, t, (ArCH₂-)₂), 7.17-8.27 (25H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4'''-n-undecylbiphenyl-4"-carbonoyloxy)-2'-fluorobenzoate]

Yield, 78.0%; m.p. 147.6°C; v_{max} (nujol): 2950, 1740, 1620, 1470, 1380, 1260, 1280, 1130, and 1080 cm⁻¹; 6: 2.19 (3H, s, ArCH₃), 0.87-0.91 (6H, t, 2XCH₃); 1.28-1.7 (36H, m, 18XCH₂); 2.65-2.69 (4H, t, (ArCH₂-)₂), 7.17-8.27 (25H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4'''-n-nonylbiphenyl-4"-carbonoyloxy)-2'-fluorobenzoate]

Yield, 79.0%; m.p. 150.0°C; v_{max} (nujol): 2950, 1740, 1620, 1470, 1380, 1260, 1280, 1130, and 1080 cm⁻¹; 6: 2.19 (3H, s, ArCH₃), 0.87-0.91 (6H, t, 2XCH₃); 1.28-1.7 (30H, m, 15XCH₂); 2.65-2.69 (4H, t, (ArCH₂-)₂), 7.17-8.27 (25H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(4'''-n-octylbiphenyl-4"-carbonoyloxy)-2'-fluorobenzoate]

Yield, 78.5%; m.p. 168.0°C; v_{max} (nujol): 2950, 1740, 1620, 1470, 1380, 1260, 1280, 1130, and 1080 cm⁻¹; 6: 2.19 (3H, s, ArCH₃), 0.87-0.91 (6H, t, 2XCH₃); 1.28-1.7 (28H, m, 14XCH₂); 2.65-2.69 (4H, t, (ArCH₂-)₂), 7.17-8.27 (25H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(3"-fluoro-4"-n-tetradecyloxybenzoyloxy) benzoate]

This was prepared by esterifying the phenol 4.17 with 3-fluoro-4-n-tetradecyloxybenzoic acid following a procedure described above (4.14). Yield, 80.1%; m.p. 140.0°C; v_{max} (nujol): 2950, 1720, 1730, 1610, 1460, 1380, 1280, 1120, and 1080 cm⁻¹; 6: 2.12 (3H, s, ArCH₃), 0.88-0.92 (6H, t, 2XCH₃); 1.2-1.9 (48H, m, 24XCH₂); 4.11-4.15 (4H, t, (ArOCH₂-)₂), 7.0-8.32 (17H, m, ArH).

The physical data of the cognate preparations of the other 2-methyl-1,3-phenylene bis[4'(3"-fluoro-4"-n-alkoxybenzoyloxy)benzoates] are given below.

2-Methyl-1,3-phenylene bis[4'(3"-fluoro-4"-n-octadecyloxybenzoyloxy)benzoate]

Yield, 85.1%; m.p. 138.5°C; v_{max} (nujol): 2950, 1720, 1730, 1610, '1460, 1380, 1280, 1120, and 1080 cm⁻¹; 6: 2.12 (3H, s, ArCH₃), 0.88-0.92 (6H, t, 2XCH₃); 1.2-1.9 (64H, m, 32XCH₂); 4.11-4.15 (4H, t, (ArOCH₂-)₂), 7.0-8.32 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(3"-fluoro-4"-n-hexadecyloxybenzoyloxy)benzoate]

Yield, 83.5%; m.p. 139.0°C; v_{max} (nujol): 2950, 1720, 1730, 1610, 1460, 1380, 1280, 1120, and 1080 cm⁻¹; 6: 2.12 (3H, s, ArCH₃), 0.88-0.92 (6H, t, 2XCH₃); 1.2-1.9 (56H, m, 28XCH₂); 4.11-4.15 (4H, t, (ArOCH₂-)₂), 7.0-8.32 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(3"-fluoro-4"-n-dodecyloxybenzoyloxy)benzoate]

Yield, 81.2%; m.p. 141.0°C; v_{max} (nujol): 2950, 1720, 1730, 1610, 1460, 1380, 1280, 1120, and 1080 cm⁻¹; 6: 2.12 (3H, s, ArCH₃), 0.88-0.92 (6H, t, 2XCH₃); 1.2-1.9 (40H, m, 20XCH₂); 4.11-4.15 (4H, t, (ArOCH₂-)₂), 7.0-8.32 (17H, m, ArH).

2-Methyl-1, 3-phenylene bis[4'(3"-fluoro-4"-n-undecyloxybenzoyloxy)benzoate]

Yield, 80.0%; m.p. 142.0°C; v_{max} (nujol): 2950, 1720, 1730, 1610, 1460, 1380, 1280, 1120, and 1080 cm⁻¹; 6: 2.12 (3H, s, ArCH₃), 0.88-0.92 (6H, t, 2XCH₃);

1.2-1.9 (36H, m, 18XCH₂); 4.11-4.15 (4H, t, (ArOCH₂-)₂), 7.0-8.32 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(3"-fluoro-4"-n-decyloxybenzoyloxy)benzoate]

Yield, 82.0%; m.p. 143.0°C; v_{max} (nujol): 2950, 1720, 1730, 1610, 1460, 1380, 1280, 1120, and 1080 cm⁻¹; δ : 2.12 (3H, s, ArCH₃), 0.88-0.92 (6H, t, 2XCH₃); 1.2-1.9 (32H, m, 16XCH₂); 4.11-4.15 (4H, t, (ArOCH₂-)₂), 7.0-8.32 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(3"-fluoro-4"-n-nonyloxybenzoyloxy)benzoate]

Yield, 84.0%; m.p. 144.5°C; ν_{max} (nujol): 2950, 1720, 1730, 1610, 1460, 1380, 1280, 1120, and 1080 cm⁻¹; 6: 2.12 (3H, s, ArCH₃), 0.88-0.92 (6H, t, 2XCH₃); 1.2-1.9 (30H, m, 15XCH₂); 4.11-4.15 (4H, t, (ArOCH₂-)₂), 7.0-8.32 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(3"-fluoro-4"-n-octyloxybenzoyloxy)benzoate]

Yield, 82.5%; m.p. 148.0°C; v_{max} (nujol): 2950, 1720, 1730, 1610, 1460, 1380, 1280, 1120, and 1080 cm⁻¹; 6: 2.12 (3H, s, ArCH₃), 0.88-0.92 (6H, t, 2XCH₃); 1.2-1.9 (28H, m, 14XCH₂); 4.11-4.15 (4H, t, (ArOCH₂-)₂), 7.0-8.32 (17H, m, ArH).

2-Methyl-1,3-phenylene bis[4'(3"-fluoro-4"-n-heptyloxybenzoyloxy)benzoate]

Yield, 83.0%; m.p. 154.0°C; v_{max} (nujol): 2950, 1720, 1730, 1610, 1460, 1380, 1280, 1120, and 1080 cm⁻¹; 6: 2.12 (3H, s, ArCH₃), 0.88-0.92 (6H, t, 2XCH₃); 1.2-1.9 (26H, m, 13XCH₂); 4.11-4.15 (4H, t, (ArOCH₂-)₂), 7.0-8.32 (17H, m, ArH).

REFERENCES

- [1] D.Demus, Liq. Cryst., 5, 75 (1989).
- [2] D.Vorländer, Ber. Dtsch. Chem. Ges., 65,2831 (1929).
- [3] D.Vorländer and A.Apel, *Ber*. Dtsch. Chem. Ges., 65, 1101 (1932).
- [4] E.Schröter, Thesis, *Halle/S.*, (1925).
- [5] T.Agutagawa, Y.Matsunaga, and K.Yasuhara, Liq. Cryst., 17,659 (1994).
- [6] Y.Matsunaga and S.Miyamoto, Mol. Cryst. Liq. Cryst., 237, 311 (1993).
- [7] H.Matsuzaki and Y.Matsunaga, Liq. Cryst., 14, 105 (1993).
- [8] T.Niori, T.Sekine, J.Watanabe, T.Furukawa and H.Takezoe, J. Mater. Chem., 6, 1231 (1996).
- [9] D.R.Link, G.Natale, R.Shao, J.E.Maclennan, N.A.Clark, E.Körblova and D.M. Walba, *Science*, 278, 1924 (1997).
- [10] G.Heppke and D.Moro, Science, 279, 1872 (1998).
- [11] G.Heppke et al., in Abstracts, European Conference on Liquid Crystals, Zakopane, Poland, ISBN 83-91181-8-1, 34 (1997).
- [12] D.Armitage and F.P.Price, J. Phys (Pans 36 coloque C-1)., C1-133 (1975).
- [13] R.B.Meyer, L.Liebert, L.Strzelecki, and P.Keller, J. Phys (Paris)., 36, L69 (1975).
- [14] A.Fukuda, Y.Takanashi, T.Isozaki, K.Ishikawa and H.Takezoe, J. Mater. Chem., 4,997 (1994).
- [15] S.R.Renn and T.C.Lubensky, Phys. Rev. A., 38,2132 (1988).
- [16] R.B.Meyer, Mol. Cryst. Liq. Cryst., 40, 33 (1977).
- [17] R.G.Petschek and K.M.Wiefling, Phys. Rev. Lett., 59, 343 (1988).
- [18] R.H.Tredgold, J. Phys. D: Appl. Phys., 23, 119 (1990).
- [19] F.Biscarini, C.Zannoni, C.Chiccoli and P.Pasini, Mol. Phys., 73,439 (1991).
- [20] J.Lee and S.D.Lee, Mol. Cryst. Liq. Cryst., 254,395 (1994).
- [21] P.E.Cladis and H.R.Brand, Liq. Cryst., 14, 1327 (1993).
- [22] F.Tournilhac, L.M.Blinov, J.Simon and S.V.Yablonsky, Nature, 359, 621 (1992).
- [23] J.Watanabe, Y.Nakata and K.Shimizu, J. Phys. II (France)., 4, 581 (1994).
- [24] W.Weissflog et al., in Abstracts, European Conference on Liquid Crystals, Zakopane, Poland, ISBN 83-91181-8-1,201 (1997).

- [25] A.Jákli, S.Rauch, D.Lötzsch and G.Heppke, Phys. Rev. E., 57,6737 (1998).
- [26] R.Macdonald, F.Kentischer, P.Warnick and G.Heppke, Phys. Rev. Lett., 81, 4408 (1998).
- [27] T.Sekine, T.Niori, M.Sone, J.Watanabe, S.W.Choi, Y.Takanishi and H.Takezoe, Jpn. J. Appl. Phys., 36,6455 (1997).
- [28] G.Heppke, D.Krüerke, C.Löhning, D.Lötzsch, S.Rauch and N.K.Sharma, Freiburger Arbeitstagung *Flüssige Kristalle*, Freiburg (poster P70) (1997).
- [29] S.Diele, S.Grande, H.Kruth, C.Lischka, G.Pelzl, W.Weissflog and I.Wirth, Ferroelectrics, 212, 169 (1998).
- [30] W.Weissflog, C.Lischka, I.Benné, T.Scharf, G.Pelzl, S. Diele and H.Kruth, Proc. SPIE: Int. Soc. Opt. Eng., 3319, 14 (1998).
- [31] G.Pelzl, S.Diele, S.Grande, A.Jákli, C.Lischka, H.Kresse, H.Schmalfuss, I.Wirth and W.Weissflog, Liq. Cryst., 26,401 (1999).
- [32] G.Pelzl, S.Diele, A.Jákli, C.Lischka, I.Wirth and W.Weissflog, Liq. Cryst., 26, 135 (1999).
- [33] G.Pelzl, S.Diele and W.Weissflog, Adv. Muter., 11, 707 (1999).
- [34] D.Shen, S.Diele, G.Pelzl, I.Wirth and C.Tschierske, J. Mater. Chem., 9, 661 (1999).
- [35] J.Thisayukta, H.Kamee, S.Kawauchi and J.Watanabe, Mol. Cryst. Liq. Cryst., 346, 63 (2000).
- [36] D.Shen, A.Pegenau, S.Diele, I.Wirth and C.Tschierske, J. Am. Chem. Soc., 122, 1593 (2000).
- [37] J.Watanabe, T.Niori, S.W.Choi, Y.Takanishi and H.Takazoe, Jpn. J. Appl. Phys., 37, L401 (1998).
- [38] H.R.Brand, P.E.Cladis and H.Pleiner, Eur. J. Phys. B., 6, 347 (1998).
- [39] F.Kentischer, R.Macdonald, P.Warnick and G.Heppke, Liq. Cryst., 25, 341 (1998).
- [40] B.K.Sadashiva, V.A.Raghunathan and R.Pratibha, Ferroelectrics, 243, 249 (2000).
- [41] C.Weygand and R.Gabler, Z. Phys. Chem., B46, 270 (1940).
- [42] G.W.Gray and B.Jones, J. Chem. Soc., 4179 (1953).
- [43] B.K.Sadashiva and G.S.R.Subba Rao, Mol. Cryst. Liq. Cryst., 38,703 (1977).
- [44] R.Amarnatha Reddy and B.K.Sadashiva, (To be published).

- [45] J.Watanabe, T.Niori, F.Sekine and H.Takezoe, Jpn. J. Appl. Phys., 37, L139 (1998).
- [46] A.Hassner and V.Alexanian, Tetrahedron Lett., 4475 (1978).