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Synthesis and mesomorphic properties of banana-shaped compounds derived from 2,7-dihydroxynaphthalene

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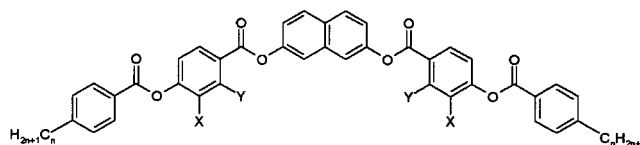
(Received 28 March 2000; accepted 22 May 2000)

Thirty eight compounds composed of achiral banana-shaped molecules belonging to three new homologous series have been synthesized and their mesomorphic properties investigated. The mesophases have been characterized using a combination of polarized light microscopy, differential scanning calorimetry, miscibility methods and X-ray diffraction measurements. All the compounds reported exhibit mesomorphic properties. Most of the homologues in the three series show B_1 and B_2 phases and the transition temperatures of these are lower in the fluoro substituted compounds. Some of the lower homologues of the fluoro substituted derivatives also show the nematic phase.

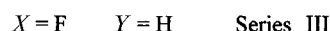
1. Introduction

The occurrence of ferroelectricity and antiferroelectricity in liquid crystals has been observed in certain compounds containing a chiral moiety [1, 2]. A large number of such compounds have been synthesized and investigated from the stand point of both a fundamental understanding of the molecular arrangement within their mesophases and of their technological applications [3, 4]. All these compounds belong to the calamitic type of liquid crystals. However, in 1996, Niori *et al.* [5] showed that achiral compounds composed of banana-shaped molecules exhibit a smectic phase with ferroelectric properties. Later, Link *et al.* [6] demonstrated that chirality in these smectic layers arises due to the tilting of the banana-shaped molecules and the polar molecular orientational ordering about the layer normal; indeed, they showed that an electric field induced a transition from the antiferroelectric to the ferroelectric state. Since then a number of new compounds have been synthesized [7–10] and their mesomorphic properties investigated. Although five related mesophases, viz. B_1 , B_2 , B_5 , B_6 and B_7 , have been reasonably well characterized [7], the B_2 phase has been examined in greatest detail because of its switching characteristics. In the last couple of years, considerable effort has been given by various groups to understanding clearly the relationship between molecular structure and mesomorphic properties, and banana-shaped compounds containing five, six and seven aromatic rings have been shown to exhibit mesomorphic properties [7, 10]. In continuation of our effort [11, 12] to synthesize and examine such compounds

composed of banana-shaped molecules, we report here three homologous series of compounds which have been derived from 2,7-dihydroxynaphthalene. All the compounds are esters having the general structure:



$$n = 1, 2, 3, \dots, 12, 14, 16, 18$$



Of the 38 compounds reported here, 20 exhibit the switchable B_2 mesophase.

2. Synthesis

The compounds belonging to the three series I, II and III were prepared following the general synthetic pathway shown in figure 1. 2,7-Dihydroxynaphthalene from Fluka, Switzerland was purified before use. 2-Fluoro-4-hydroxybenzoic acid and 3-fluoro-4-hydroxybenzoic acid were synthesized according to an earlier report [13]. 4-Benzyloxybenzoic acid, 2-fluoro-4-benzyloxybenzoic acid and 3-fluoro-4-benzyloxybenzoic acid were prepared following a procedure described previously [14]. A typical detailed procedure for the synthesis and characterization of one of the compounds under investigation is given below.

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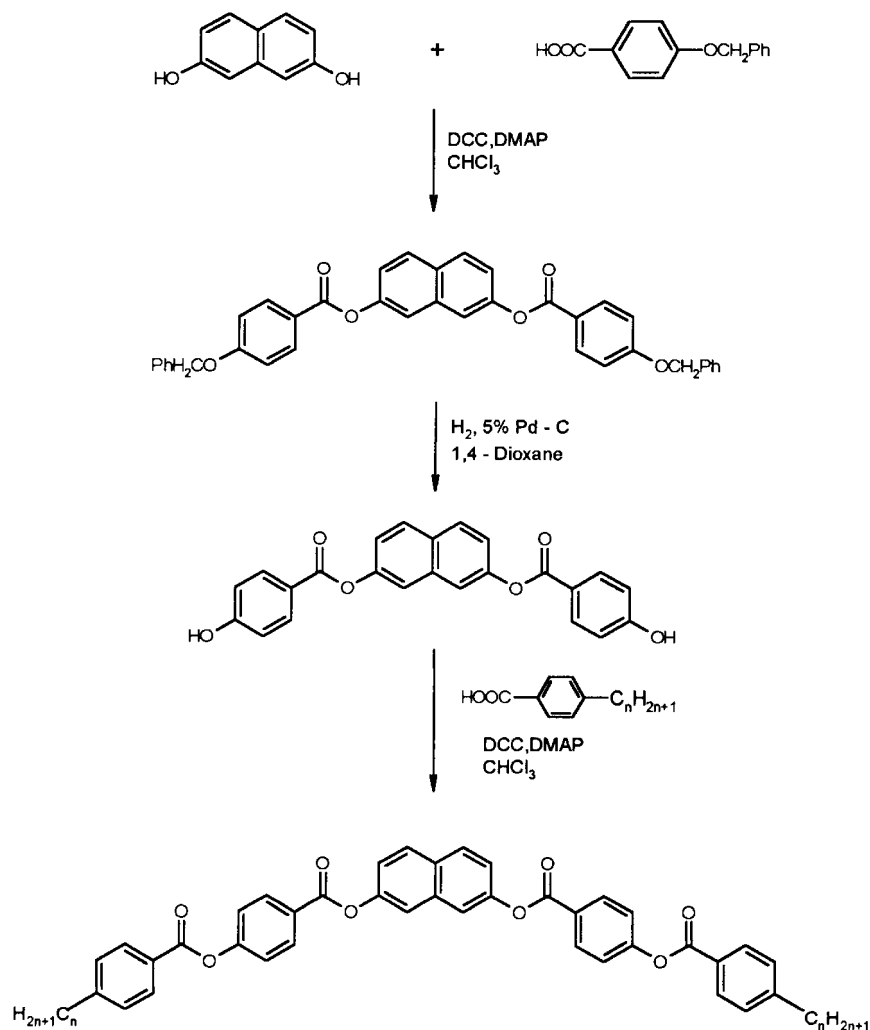


Figure 1. Synthetic pathway for the preparation of the banana-shaped compounds

2.1. 2,7-Naphthylene bis(4-benzyloxybenzoate)

A mixture of 2,7-dihydroxynaphthalene (1.6 g, 10 mmol), 4-benzyloxybenzoic acid (4.56 g, 20 mmol), 4-dimethylaminopyridine (DMAP) (0.4 g, 2 mmol) and dry chloroform (25 ml) was stirred for 10 min. To this mixture, *N,N'*-dicyclohexylcarbodiimide (DCC) (4.12 g, 20 mmol) was added and stirring was continued for 10 h at room temperature. The precipitated *N,N'*-dicyclohexylurea was filtered off and the filtrate diluted with chloroform (100 ml). This solution was washed with 5% aqueous acetic acid (2×50 ml), cold 5% aqueous sodium hydroxide (2×50 ml) and water (3×50 ml), then dried over anhydrous Na_2SO_4 . After the solvent was removed, the residue was purified by column chromatography on silica gel using 2% ethyl acetate in chloroform as eluent. Removal of solvent from the eluate afforded a white solid. This was crystallized from a mixture of chloroform and acetonitrile. Yield 4.8 g (83%), m.p. 217.5–218.5°C. ^1H NMR (CDCl_3) δ : 5.18 (s, 4H, $2 \times \text{ArCH}_2$), 7.07–8.21 (m, 24H, ArH). IR (Nujol) ν_{max} 1730, 1605, 1580, 1500,

1460, 1280, 1120 cm^{-1} . Elemental analysis: found C 78.52, H 4.59; $\text{C}_{38}\text{H}_{28}\text{O}_6$ requires C 78.60, H 4.86%.

2.2. 2,7-Naphthylene bis(4-hydroxybenzoate)

2,7-Naphthylene bis(4-benzyloxybenzoate) (4.5 g, 11.25 mmol) was dissolved in 1,4-dioxane (50 ml) and 5% Pd-C catalyst (1.2 g) was added. The mixture was stirred at 50°C in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. The mixture was filtered and the solvent removed under reduced pressure. The residue was passed through a column of silica gel and eluted with a mixture of 5% acetone in chloroform. Removal of solvent from the eluate gave a white material which was crystallized using a mixture of 1,4-dioxane and petroleum ether. Yield 3.0 g (89%), m.p. > 250°C (d). ^1H NMR (CD_3COCD_3) δ : 3.1 (s, 2H, $2 \times \text{Ar-OH}$), 7.14–8.26 (m, 14H, Ar-H). IR (Nujol) ν_{max} 3330, 1720, 1605, 1280, 1120 cm^{-1} . Elemental analysis: found C 72.43, H 3.97; $\text{C}_{24}\text{H}_{16}\text{O}_6$ requires C 72.06, H 4.03%.

2.3. 2,7-Naphthylene bis[4-(4-*n*-decylbenzoyloxy)-benzoate] (6)

A mixture of 2,7-naphthylene bis(4-hydroxybenzoate) (200 mg, 0.5 mmol), 4-*n*-decylbenzoic acid (290 mg, 1 mmol), DMAP (12 mg, 0.1 mmol) and dry chloroform (5 ml) was stirred for 10 min. To this mixture, DCC (412 mg, 1 mmol) was added and stirring was continued for 10 h at room temperature. The precipitated *N,N'*-dicyclohexylurea was filtered off and the filtrate diluted with chloroform (10 ml). This solution was washed with 5% aqueous acetic acid (2 × 10 ml), cold 5% aqueous sodium hydroxide solution (2 × 10 ml) and water (3 × 10 ml), then dried over anhydrous Na₂SO₄. The solvent was removed and the residue purified by column chromatography on silica gel using chloroform as eluent. The residue obtained after removal of solvent from the eluate was crystallized using a mixture of chloroform and acetonitrile. Yield 352 mg (75%), transitions (°C) Cr 164.5 B₂ 166.5 I. ¹H NMR (CDCl₃) δ; 0.86–0.89 (t, 6H, 2 × CH₃), 1.26–1.66 (m, 32H, 16 × CH₂), 2.69–2.73 (t, 4H, 2 × Ar–CH₂), 7.26–8.39 (m, 24H, ArH). IR Nujol ν_{\max} 1720, 1710, 1605, 1460, 1280, 1120 cm⁻¹. Elemental analysis: found C 78.21, H 7.25%; C₆₂H₇₂O₈ requires C 78.35, H 7.25%.

3. Experimental

In general, the intermediate and final compounds were purified by column chromatography on silica gel using appropriate solvent systems. The purity of all the compounds was checked by thin layer chromatography (Merck Kieselgel 60F₂₅₄ precoated plates) and by normal phase high performance liquid chromatography (μ porasil column, 3.9 mm × 300 mm, Waters Associates Inc.) using 1% ethyl acetate in dichloromethane as the eluent. The yield of the compounds was in the range 65–80%.

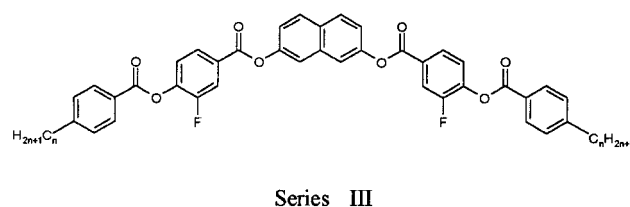
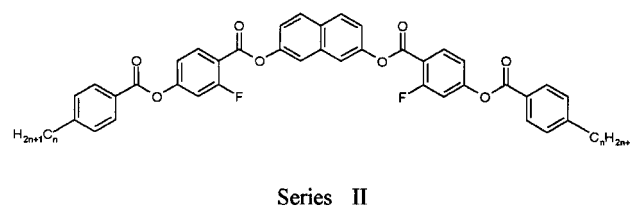
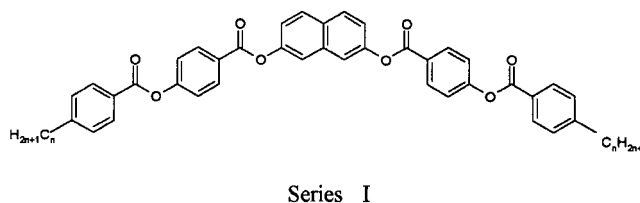
The chemical structure of all the compounds was confirmed by using a combination of ¹H as well as ¹³C nuclear magnetic resonance spectroscopy (Bruker AMX 400 spectrometer) with 1% tetramethylsilane in deuteriochloroform as an internal standard, infrared spectroscopy (Shimadzu IR 435) and elemental analysis (Carlo-Erba 1106 analyser). The phase behaviour of all the compounds was examined by thermal polarized light microscopy using a polarizing microscope (Leitz Laborlux 12 POL) equipped with a heating stage and controller (Mettler FP52 and FP5, respectively) and also from thermograms recorded on a differential scanning calorimeter (Perkin-Elmer, Model Pyris 1D). The enthalpies for the various transitions were also determined using the latter method. The calorimeter was calibrated using pure indium as standard. X-ray diffraction studies were carried out using CuK_α radiation from a rotating anode generator (Rigaku Ultrax 18) with a flat graphite crystal monochromator. The diffraction

patterns were collected on an image plate (Marresearch). Unoriented samples were contained in Lindemann capillaries and the sample temperature was controlled to within ± 0.1°C.

4. Results

4.1. Mesomorphic properties

The phase transition temperatures and the associated enthalpies for the three homologous series of banana-shaped compounds I, II and III are summarized in tables 1, 2 and 3, respectively. The homologues of series I, the parent compounds, have the highest melting and clearing temperatures. Out of 38 compounds reported here, only three are dimesomorphic and the rest exhibit only one mesophase. The majority of the compounds exhibit the B₁ and B₂ mesophases and five show the nematic phase.



As can be seen in table 1, all eleven compounds are monomesomorphic. While compounds 1 and 4 give monotropic phases, compounds 2 and 3 give enantiotropic phases though over a narrow range of temperature. These four compounds exhibit the same type of texture on slow cooling of their isotropic phases. A mosaic texture is usually obtained and sometimes spherulites reminiscent of a columnar mesophase can be seen. The mesophase is highly viscous and birefringent and the clearing enthalpy is rather high at about 16–20 kJ mol⁻¹. This mesophase has been identified as B₁ (see other sections). However, compounds 5 to 11 show a different type of texture. Compound 5 forms a monotropic phase,

Table 1. Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kJ mol^{-1}) for compounds of series I. Cr = Crystalline phase; B_3 = Crystalline phase; B_2 = Banana mesophase 2; B_1 = Banana mesophase 1 (Nomenclature as adopted at the International Workshop on Banana-shaped liquid crystals held in Berlin in December 1997); N = Nematic phase; I = Isotropic phase. • Phase exists; — phase does not exist. Temperatures in parentheses indicate monotropic transitions.

Compound number	<i>n</i>	Cr	B_2	B_1	I
1	5	• 191.0 57.21	—	(• 181.5) 17.58	•
2	6	• 175.0 44.25	—	• 176.5 16.7	•
3	7	• 172.0 43.0	—	• 173.5 17.11	•
4	8	• 168.5 59.0	—	(• 167.0) 19.63	•
5	9	• 167.5 51.6	(• 165.0) 17.86	—	•
6	10	• 164.5 29.8	• 166.5 18.72	—	•
7	11	• 164.5 29.14	• 168.5 20.58	—	•
8	12	• 162.5 28.84	• 169.0 20.77	—	•
9	14	• 159.0 53.22	• 169.5 22.28	—	•
10	16	• 152.0 24.5	• 168.5 22.32	—	•
11	18	• 149.0 25.0	• 167.0 22.57	—	•

while the rest give enantiotropic phases. On slow cooling of the isotropic liquid an undefined texture develops which rapidly fills the entire field of view. A photomicrograph of this typical texture exhibited by compound **6** is shown in figure 2. Sometimes one can also see a schlieren texture. This mesophase is highly mobile and the cover slip can be displaced very easily. The enthalpy

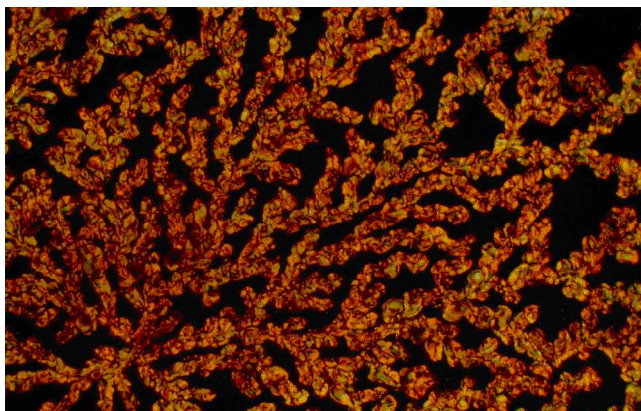


Figure 2. Photomicrograph of the optical texture of the B_2 phase of compound **6** growing from the isotropic phase.

for the mesophase to isotropic liquid transition is about $17\text{--}23 \text{ kJ mol}^{-1}$. This has been characterized as a B_2 mesophase. A plot of the clearing temperatures against the number of carbon atoms in the alkyl chain is shown in figure 3. While there is a steep fall for the B_1 –isotropic transition temperature as the series is ascended, the B_2 –isotropic transition temperature curve rises initially, reaches a maximum and then gradually decreases as the chain is lengthened. In this series, the thermal range of the mesophase increases from about 1.5° for compound **2** to about 18° for compound **11**.

The compounds of series II and III contain a lateral fluoro substituent and their mesomorphic behaviour is somewhat similar. The effect of the fluoro substituent in general is to reduce the melting points as well as the clearing temperatures. In addition, in both series a nematic phase is observed for the lower homologues. Cooling of the isotropic liquid of compound **13** in the polarizing microscope shows the formation of nematic droplets at 170°C which coalesce to form a threaded texture. Further cooling to 137.5°C gives a growth pattern as shown in figure 4. This slowly filled the field of view resulting in a mosaic texture. This texture is similar to that exhibited by the B_1 phase [7, 12]. Indeed this was proved to be the B_1 phase (see later). The higher homologues up to compound **19** also exhibit this phase. Compounds **20** to **26** exhibit a texture similar to that shown by compound **6** that has been characterized as B_2 . The enthalpies of the nematic–isotropic transitions are quite small and comparable to those of calamitic compounds. The clearing enthalpies of the B_1 and B_2 phases are quite comparable. In this series also, the thermal range of the mesophase increases from 3.5° for compound **14** to 41° for compound **26**. A plot of the clearing temperatures as a function of the number of carbon atoms in the alkyl chain is shown in figure 5. While there is evidence for an odd–even effect for the N–I transition temperatures, the B_1 –isotropic transition temperature curve rises sharply initially, reaches a maximum and falls as the series is ascended. However, the clearing temperatures for the B_2 phases lie on a smooth curve.

In series III, compounds **27** and **28** show a metastable nematic phase. Only one compound exhibits an enantiotropic B_1 phase over a narrow range of 3.5° . The remaining compounds **33** to **38** show the B_2 phase. The nature of these mesophases was established on the basis of the texture patterns described for the other two series of compounds. However, compounds **34** and **35** show additional phase transitions, though monotropic. As will be proved later the phase involved has been identified as the crystalline B_3 phase. Figure 6 shows a plot of the clearing temperatures as a function of the number of carbon atoms in the alkyl chain for the compounds

Table 2. Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kJ mol^{-1}) for compounds of series II.

Compound number	n	Cr	B_2	B_1	N	I
12	1	•	217.5 58.81	—	—	(• 201.0) 0.18
13	2	•	188.5 49.71	—	(• 137.5) ^a	(• 170.0) 0.13
14	3	•	171.0 52.68	—	(• 155.0) 10.71	• 174.5 0.20
15	4	•	160.0 48.0	—	(• 159.0) 12.52	—
16	5	•	143.0 35.0	—	• 162.0 13.79	—
17	6	•	150.0 33.78	—	• 155.5 15.15	—
18	7	•	148.0 40.0	—	• 151.0 13.87	—
19	8	•	154.0 50.7	—	(• 143.0) 13.85	—
20	9	•	153.0 51.52	(• 147.0) 18.48	—	—
21	10	•	150.0 61.36	(• 149.5) 18.89	—	—
22	11	•	135.5 41.45	• 152.0 21.29	—	—
23	12	•	133.5 38.95	• 154.0 21.62	—	—
24	14	•	130.0 53.93	• 156.0 22.3	—	—
25	16	•	125.0 62.47	• 156.0 23.42	—	—
26	18	•	114.0 57.97	• 155.0 23.6	—	—

^a Enthalpy could not be determined.

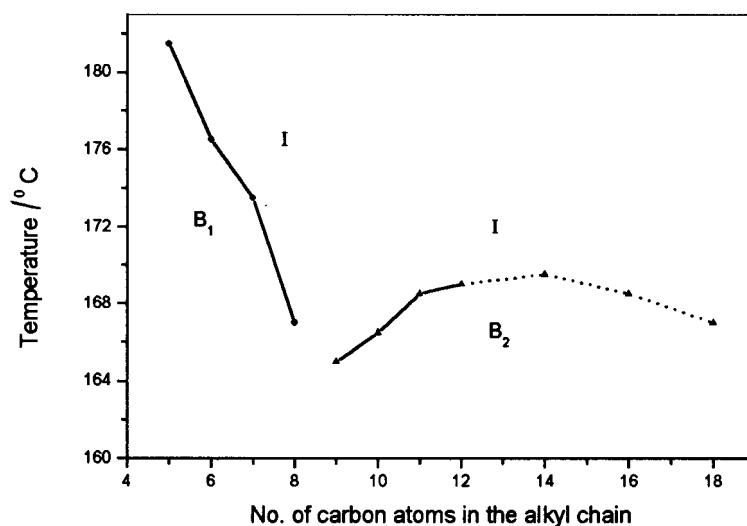


Figure 3. Plot of clearing temperatures against the number of carbon atoms in the alkyl chain for compounds of series I.

of series III. Once again, one can see a falling trend for the B_1 -isotropic transition points and the B_2 -isotropic transition points lie on a smooth curve. The thermal range of the mesophase increases as the series is ascended, similarly to the other two series of compounds.

It was reported recently that 2,7 dihydroxynaphthalene as the central mesogenic unit is unfavourable for providing mesophases [10]. However, using the same unit we have been able to obtain mesophases in a number of compounds.

Table 3. Transition temperatures ($^{\circ}\text{C}$) and *enthalpies* (kJ mol^{-1}) for compounds of series III. For key see caption to table 1.

Compound number	<i>n</i>	Cr	T_{Cr}	ΔH_{Cr}	T_{B_3}	ΔH_{B_3}	T_{B_2}	ΔH_{B_2}	T_{B_1}	ΔH_{B_1}	N	T_{N}	ΔH_{N}	I
27	4	•	185.5	—	—	—	—	—	—	—	(•	154.0)	•	
			50.81	—	—	—	—	—	—	—	(•	0.1)	•	
28	5	•	154.5	—	—	—	—	—	(•	145.5) ^a	(•	150.5)	•	
			44.9	—	—	—	—	—	—	—	(•	0.26)	•	
29	6	•	173.5	—	—	—	—	—	(•	140.5)	—	—	•	
			49.95	—	—	—	—	—	—	—	—	—	•	
30	7	•	161.0	—	—	—	—	—	(•	141.5)	—	—	•	
			49.46	—	—	—	—	—	—	—	—	—	•	
31	8	•	137.0	—	—	—	—	—	(•	137.5)	—	—	•	
			60.96	—	—	—	—	—	—	—	—	—	•	
32	9	•	133.0	—	—	—	—	—	•	136.5	—	—	•	
			48.28	—	—	—	—	—	—	13.65	—	—	•	
33	10	•	128.5	—	•	137.5	—	—	—	—	—	—	•	
			64.0	—	•	15.92	—	—	—	—	—	—	•	
34	11	•	121.5	(•	97.0)	•	140.0	—	—	—	—	—	•	
			54.14	(•	14.45)	•	16.88	—	—	—	—	—	•	
35	12	•	119.0	(•	96.0)	•	141.0	—	—	—	—	—	•	
			76.18	(•	13.62)	•	16.98	—	—	—	—	—	•	
36	14	•	116.0	—	•	143.0	—	—	—	—	—	—	•	
			63.16	—	•	18.22	—	—	—	—	—	—	•	
37	16	•	111.5	—	•	143.5	—	—	—	—	—	—	•	
			95.0	—	•	18.8	—	—	—	—	—	—	•	
38	18	•	111.0	—	•	142.5	—	—	—	—	—	—	•	
			87.57	—	•	19.82	—	—	—	—	—	—	•	

^a Enthalpy could not be determined.

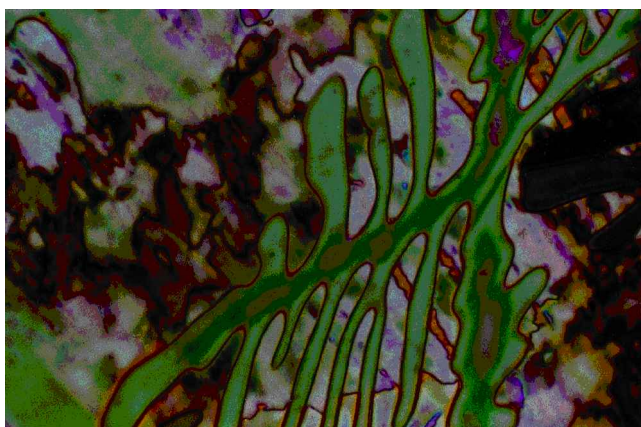


Figure 4. Photomicrograph of the optical texture of compound 13 in which the B_1 phase is developing from the nematic phase at 137.5°C .

A comparison of the three series of compounds indicates that the transition temperatures for the compounds of series III are the lowest. All the three series of compounds exhibit the B_1 and B_2 mesophases. The introduction of the small lateral fluorine substituent reduces the melting as well as the clearing temperatures without drastically affecting the nature of the meso-

phases. The effect of various lateral substituents on the nature and transition temperatures of mesophases exhibited by banana-shaped compounds will be reported elsewhere [15].

4.2. Miscibility studies

In order to confirm the identity of the mesophases exhibited by these compounds, we have carried out miscibility studies with substances whose mesophases have been established. The standard substances used are 1,3-phenylene bis(4-*n*-heptyloxybenzoyloxybenzylidene)-diamine (PBHBD) which is known to exhibit the B_1 phase [16] and 1,3-phenylene bis[4-(4-*n*-octylphenyliminomethyl)benzoate (PBOB) which exhibits the B_2 phase [17, 18]. Figure 7 shows the binary phase diagram of compound 2 with PBHBD. Although compound 2 has a narrow thermal range of 1.5° for the mesophase, it is clear from the phase diagram that this phase is completely miscible over the entire composition range indicating that the mesophase exhibited by compound 2 is B_1 . To verify the identity of those mesophases which have textural similarity in the other two series, binary phase diagrams were constructed as weight% compositions of the compounds using compound 2, as the reference. Figures 8 and 9 show the miscibility diagram

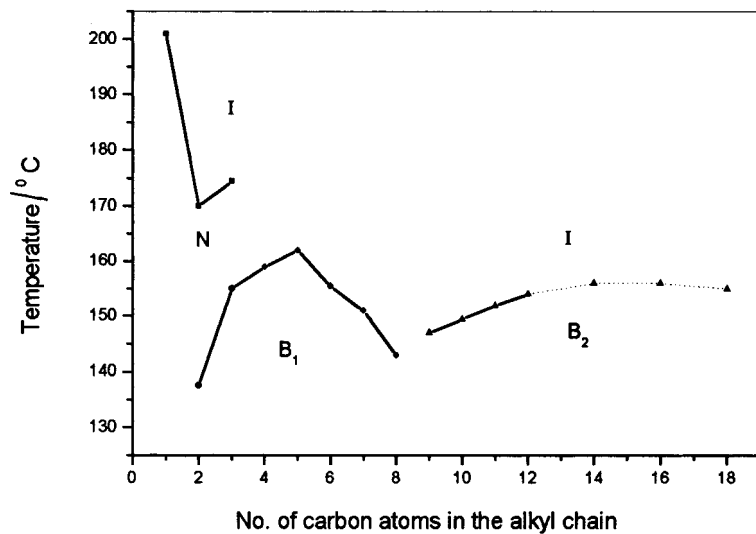


Figure 5. Plot of clearing temperatures against the number of carbon atoms in the alkyl chain for the compounds of series II.

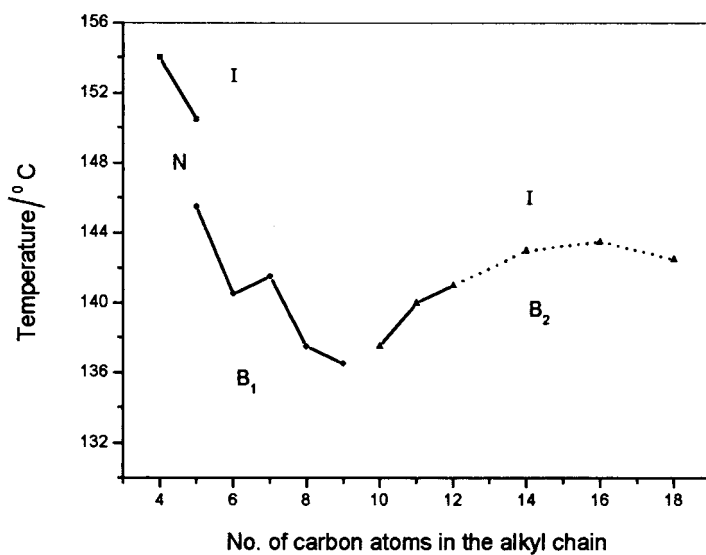


Figure 6. Plot of clearing temperatures against the number of carbon atoms in the alkyl chain for the compounds of series III.

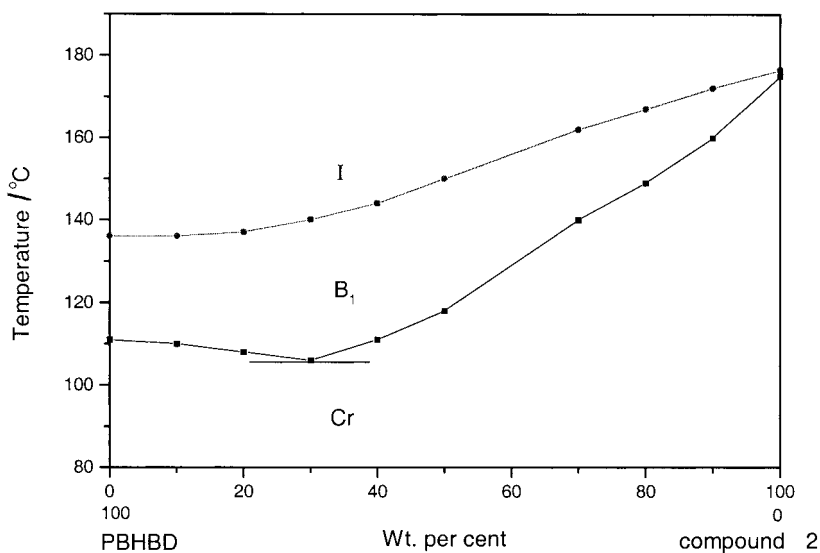


Figure 7. Miscibility diagram of state for binary mixtures between compound 2 and the standard PBHBD.

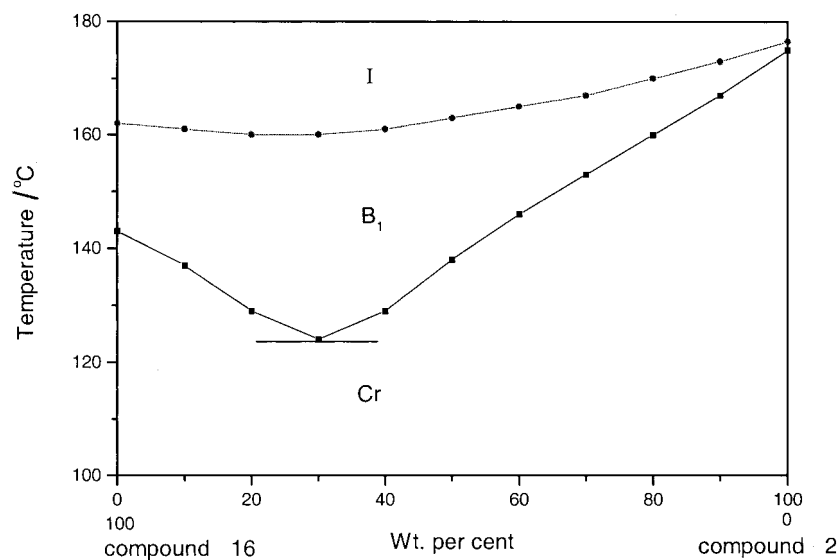


Figure 8. Miscibility diagram of state for binary mixtures between compounds **2** and **16**.

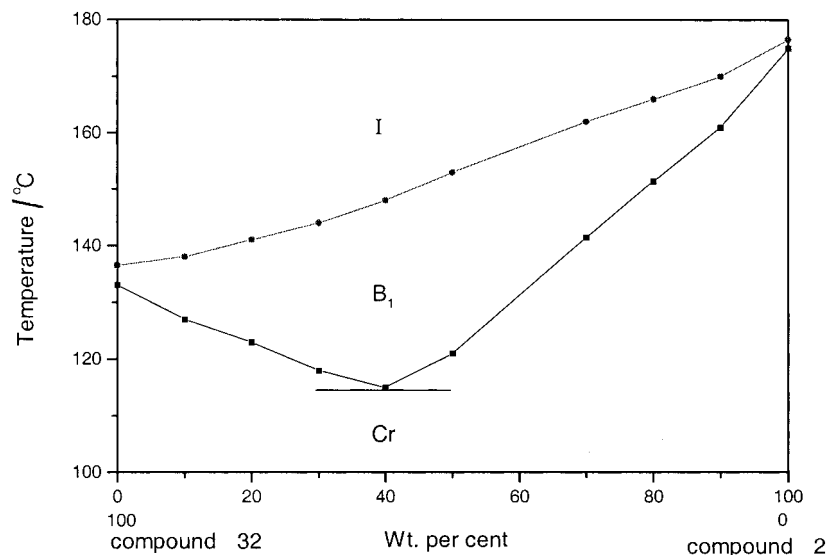


Figure 9. Miscibility diagram of state for binary mixtures between compounds **2** and **32**.

for compounds **16** and **32**, respectively. It is clear from these diagrams that the mesophases of compounds **16** and **32** are continuously miscible over the whole range of concentration, confirming that the phase is indeed B_1 . Similarly, using as reference PBOB, which exhibits the quite fluid B_2 phase, a binary phase diagram was constructed with compound **35**, see figure 10. It is quite clear from this diagram that the two mesophases are the same, as they are completely miscible. Again, higher homologues of series I and II, viz. compounds **8** and **23**, were mixed with compound **35** as weight% compositions with the results shown in figures 11 and 12, respectively. As can be seen, complete miscibility is established indicating that the mesophase is B_2 .

4.3. X-ray diffraction measurements

X-ray diffraction studies were undertaken on the three 'banana phases' B_1 , B_2 and B_3 to prove their identity. The X-ray diffraction pattern for compound **32** showed the following features. A diffuse wide angle peak at about 4.9 \AA indicated a liquid-like in-plane order. In the small angle region two reflections at $d_1 = 30.4 \text{ \AA}$ and $d_2 = 22.5 \text{ \AA}$ were obtained and these could be indexed as the (1 1) and (0 2) reflections from a rectangular lattice with $a = 41.2 \text{ \AA}$ and $b = 45 \text{ \AA}$. A typical diffraction pattern obtained for this compound is shown in figure 13. We also carried out X-ray diffraction studies for the standard compound PBHBD and the diffraction patterns are similar. Based on this and miscibility criterion described

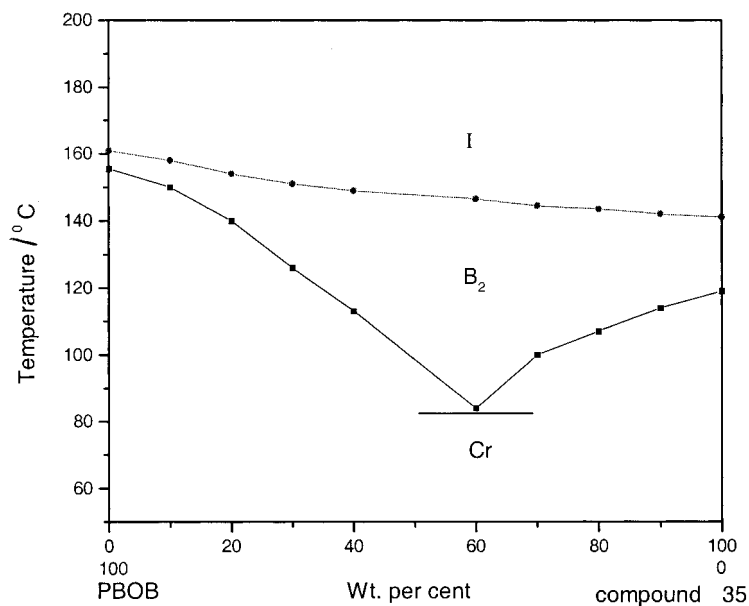


Figure 10. Miscibility diagram of state for binary mixtures between compounds **35** and standard compound PBOB.

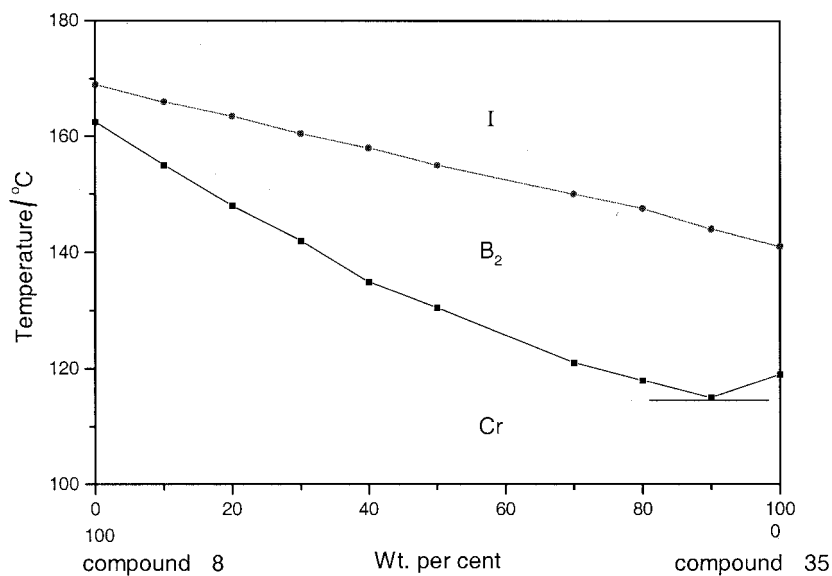


Figure 11. Miscibility diagram of state for binary mixtures between compounds **8** and **35**.

earlier, the nature of the mesophase of compound **32** is proved to be B₁.

Similarly, the X-ray pattern of a non-oriented sample of compound **33** was examined and the angular intensity profile is shown in figure 14. As can be seen, the diffraction pattern shows a diffuse scattering in the wide angle region with a peak around 5 Å which is indicative of a liquid-like in-plane order. In addition, two peaks could be seen in the small angle region at $d_1 = 35.2 \text{ \AA}$ and $d_2 = 17.7 \text{ \AA}$. These correspond to a lamellar ordering with a spacing of 35.2 Å. It was also estimated that the

molecules tilt by about 45° at 136°C. In view of this, the highly fluid phase has been identified as the B₂ phase, taking into consideration also of course the miscibility with the standard material.

In addition to these two mesophases, compounds **34** and **35** exhibit a transition to a monotropic phase which is highly ordered. The cover slip on a microscopic slide could not be displaced. The X-ray angular intensity profile of this phase is shown in figure 15. One can see a number of fairly sharp reflections in the wide angle region which is suggestive of a crystalline structure.

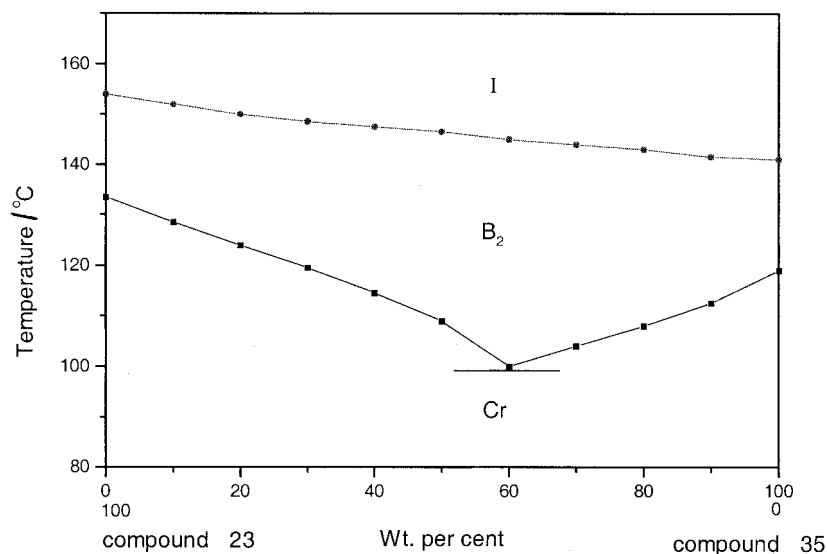


Figure 12. Miscibility diagram of state for binary mixtures between compounds **23** and **35**.

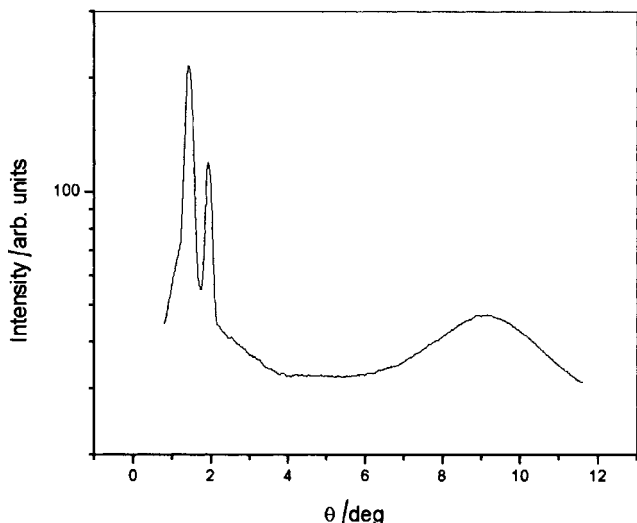


Figure 13. X-ray angular intensity profile of the B₁ phase of compound **32** at 135°C.

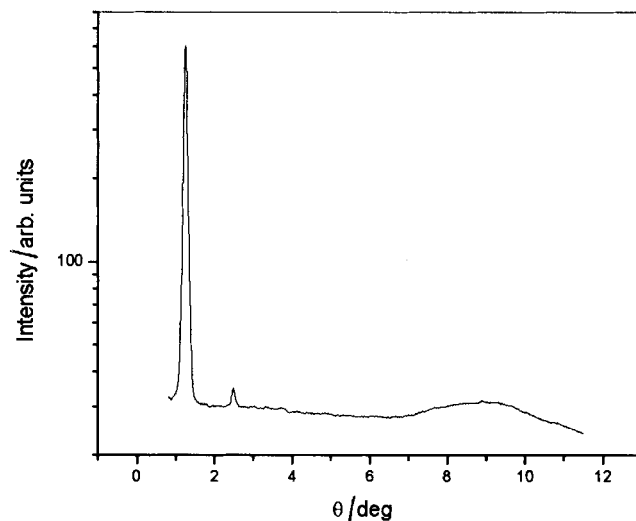


Figure 14. X-ray angular intensity profile of the B₂ phase of compound **33** at 136°C.

Comparison of this X-ray pattern with that obtained for the phase designated as B₃ in the literature [7] clearly shows that the lower temperature phase exhibited by these two compounds is also B₃ and that it is crystalline in nature.

4.4. Effect of a d.c. electric field

The switching behaviour of the B₂ phase of compound **35** under a d.c. electric field has been examined using a polarizing microscope. The sample cell was constructed using conducting glass plates which had been coated with polyimide and unidirectionally rubbed. The thick-

ness of the cell was 4 μm . On cooling the isotropic liquid of this compound under a d.c. electric field of about $\pm 5 \text{ V } \mu\text{m}^{-1}$, which is the threshold, a striped texture (spherulitic growth) appears. On increasing the voltage, colourful stripes dominate the field of view which stabilizes around $\pm 10 \text{ V } \mu\text{m}^{-1}$. Typical photomicrographs of the texture obtained for this compound, with and without the field, are shown in figures 16 and 17, respectively. We have observed [12] a similar effect of a d.c. electric field on the B₂ mesophase from other series of compounds. The detailed electro-optic measurements on this B₂ mesophase are in progress and the results will be reported elsewhere.

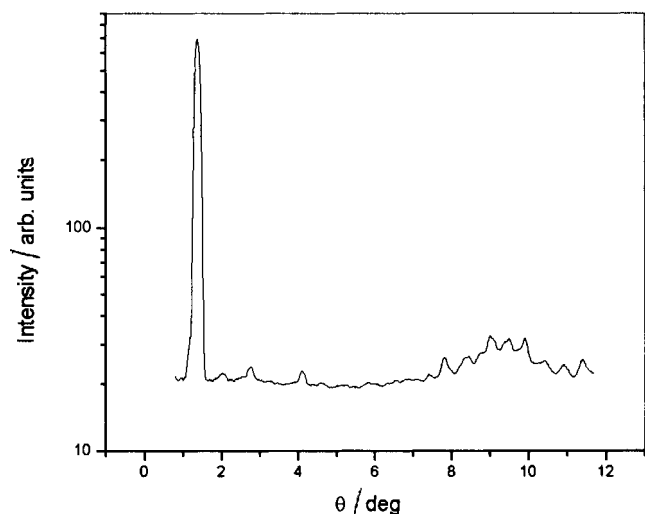


Figure 15. X-ray angular intensity profile of the B₃ phase of compound **34** at 95°C.

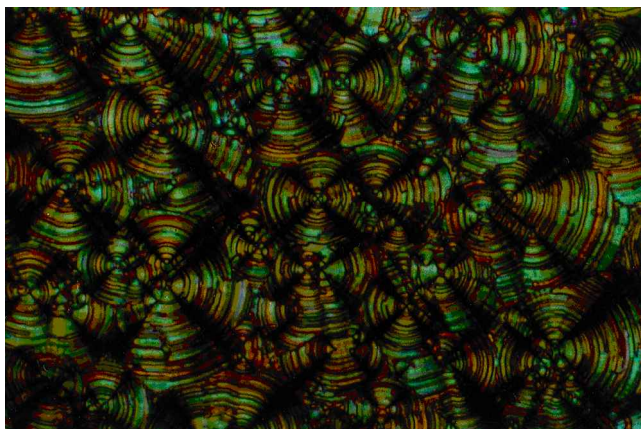


Figure 16. Optical texture of the B₂ phase of compound **35** at 120°C, ± 40 V, spherulites with coloured stripes.

5. Conclusions

In the three homologous series of compounds derived from 2,7-dihydroxynaphthalene, B₁ and B₂ mesophases predominate. In the fluoro substituted compounds, a nematic phase could also be observed. Textural observation, miscibility studies, DSC and X-ray diffraction studies have established the identity of the three different phases. The small lateral fluoro substituent reduces the transition temperatures from those of the parent compounds.

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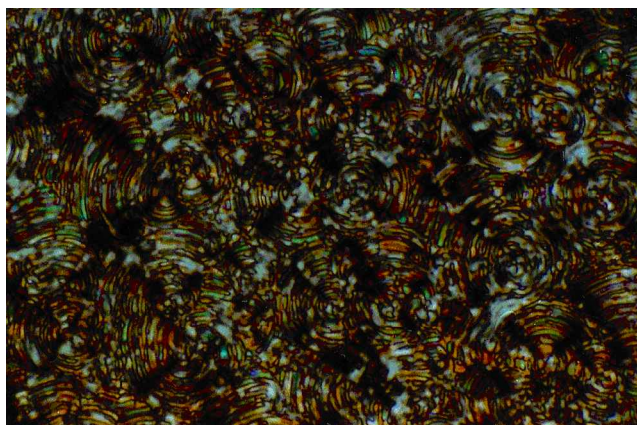


Figure 17. Optical texture of the B₂ phase of compound **35** at 120°C, 0 V, 4 μm cell.

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