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R. Amaranatha Reddy[a]; B. K. Sadashiva[a]
[a] Raman Research Institute, C. V. Raman Avenue, Sadashivanagar, Bangalore 560 080, India,

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Occurrence of the B_7 mesophase in two homologous series of seven-ring achiral compounds composed of banana-shaped molecules

R. AMARANATHA REDDY and B. K. SADASHIVA*

Raman Research Institute, C. V. Raman Avenue, Sadashivanagar,
Bangalore 560 080, India

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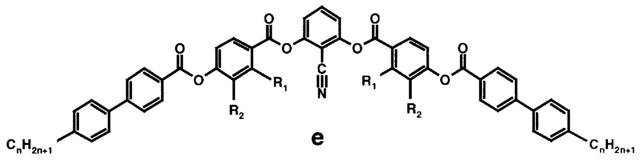
The synthesis and mesomorphic behaviour of twenty compounds belonging to two new series of seven-ring esters derived from 2-cyanoresorcinol are reported. Many homologues of both series exhibit the B_7 mesophase. In addition, some of the lower homologues exhibit a mesophase which shows textural features similar to that of the two-dimensional B_1 phase. The characterization of the mesophases has been carried out using polarizing optical microscopy, differential scanning calorimetry, X-ray diffraction, miscibility studies and electro-optical investigations. The first example of a plot of the B_7–isotropic phase transition temperature as a function of the alkyl chain length is also reported.

1. Introduction

One of the most interesting features of liquid crystalline phases is the fascinating and beautiful optical textures that they exhibit. The different textural characteristics have been used to identify the mesophases of compounds made up of rod-like and disk-like molecules. These include compounds composed of both chiral and achiral molecules. Since the discovery of optical switching in compounds composed of bent-core or banana-shaped molecules [1], there has been renewed interest in the study of such materials, which has formed the basis for a new sub-field of liquid crystals. In recent years, several hundred compounds composed of banana-shaped molecules have been synthesized and their mesophases studied [2–10]. At least seven B phases have been well characterized and only five of them are mesomorphic. The structures of the B_1, B_2, B_5 and B_6 mesophases have been well understood through X-ray diffraction (XRD) studies on oriented samples. The B_3 and B_4 phases have been shown to be crystalline in nature.

The B_7 mesophase was first reported [11, 12] for some Schiff's base derivatives of 2-nitroresorcinol. This mesophase exhibits several beautiful textures when cooled slowly from the isotropic phase and none of these variants are seen in any of the other banana phases. One such characteristic texture of this phase are helical or spiral filaments resembling telephone wires [12]. Such filamentary growth patterns have been observed in some novel sulphur-containing banana-shaped compounds [13, 14], a liquid crystal conglomerate composed of racemic molecules [15], some novel halogen-substituted banana-shaped mesogens [16, 17, 18] and a salicyladimine ester derived from resorcinol [19]. None of these compounds are derivatives of 2-nitroresorcinol, and based on the observation of spiral growth domains in the samples, the symbol B_7 has been assigned to the different mesophases. However, the fluorine-substituted compounds [16] do exhibit other two-dimensional periodic patterns and this mesophase does switch electro-optically.

In a recent communication [20], we reported the characterization of the mesophase of four homologues of a new series of achiral banana-shaped compounds derived from 2-cyanoresorcinol. We have shown that the mesosphase exhibited by these four compounds is indeed the B_7 phase. In this paper, we report the detailed synthetic procedures as well as the mesomorphic behaviour of two homologous series (series I and II) of compounds including the four homologues reported earlier. These symmetrical seven-ring compounds have the general molecular structure **e**, in which a strongly polar cyano substituent is attached in the 2-position of the central phenyl ring.



e

R_1=F, R_2=H Series I

R_1=H, R_2=F Series II

n=5,6..............12,14,16,18

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*Author for correspondence; e-mail: sadashiv@rri.res.in

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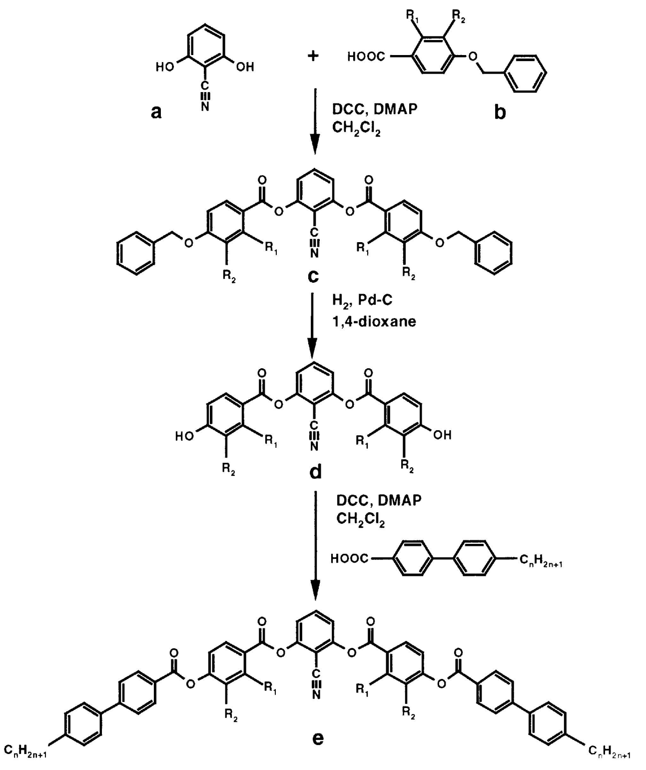
2. Experimental

2.1. *Synthesis*

The synthesis of the two homologous series of seven-ring ester compounds composed of achiral symmetrical bent-core molecules, containing a cyano substituent in the central phenyl ring and a fluoro substituent on the phenyl rings adjacent to it, is shown in the scheme. 2-Cyanoresorcinol was prepared from commercial 2,6-dimethoxybenzonitrile. 2-Fluoro-4-hydroxybenzoic and 3-fluoro-4-hydroxybenzoic acids were synthesized from 3-fluoroanisole and 2-fluoroanisole, respectively according to a procedure described in the literature [21]. 2-Fluoro-4-benzyloxybenzoic and 3-fluoro-4-benzyloxybenzoic acids were synthesized following procedures described previously [21, 22]. 4-*n*-Alkylbiphenyl-4-carboxylic acids were synthesized following a procedure described earlier [23]; their transition temperatures obtained agree with literature values. A detailed synthetic procedure for one of the target compounds under investigation is given.

2.1.1. *2-Cyanoresorcinol* ***a***

A solution of 2,6-dimethoxybenzonitrile (3.0 g, 18.75 mmol) in dry dichloromethane (20 ml) was cooled to −78°C. To this, a solution of boron tribromide (18.78 g, 75 mmol) in dichloromethane (20 ml) was added dropwise over a period of 1 h; the temperature was maintained for 2–3 h, then allowed slowly to attain room temperature. The reaction mixture was then stirred for about 10 h at room temperature and heated at reflux for a further 10 h. Excess of boron tribromide was decomposed carefully by the addition of moist chloroform; removal of solvent then gave a crude product, which was passed through a column of silica gel using 5% acetone in chloroform as eluent. The light brown solid obtained was crystallized using a mixture of chloroform and acetonitrile; yield 1.9 g (77%), m.p. 206–208°C (dec.). ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 9.89 (s, 2H, 2 × Ar–OH, exchangeable with D$_2$O), 7.39–7.35 (t, 1H, $^3J = 8.28$ Hz, Ar–H), 6.65–6.63 (d, 2H, $^3J = 8.28$ Hz, Ar–H). IR (KBr) $\nu_{\max}$: 3452, 3331, 2226, 2239, 1612, 1472, 1022 cm^{-1}. Elemental analysis: $C_7H_5O_2N$ requires C 62.22, H 3.73, N 10.37; found C 62.13, H 3.71, N 10.43%.



n=5,6...........12,14,16,18

Scheme. Synthetic pathway for the preparation of the banana-shaped compounds.

2.1.2. *2-Cyano-1,3-phenylene bis(2-fluoro-4-benzyloxybenzoate)* ***c*** *($R_1 = F$, $R_2 = H$)*

A mixture of compound **a** (1.35 g, 10 mmol), 2-fluoro-4-benzyloxybenzoic acid **b** (4.92 g, 20 mmol), *N*,*N′*-dicyclohexylcarbodiimide (DCC) (4.53 g, 22 mmol) and a catalytic quantity of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) was stirred for about 12 h. The precipitated *N*,*N′*-dicyclohexylurea was filtered off and washed with an excess of dichloromethane. The combined organic solution was washed with ice-cold aqueous 5% sodium hydroxide (2 × 50 ml), 5% aqueous acetic acid (2 × 50 ml) and water (3 × 50 ml) and then dried (anhydrous sodium sulphate). The residue obtained on removal of solvent was chromatographed on silica gel and eluted with chloroform. The material obtained on removal of solvent was crystallized from acetonitrile; yield 4.14 g (70%), m.p. 165–166°C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 8.15–8.11 (t, $^3J = 8.6$ Hz, 2H, Ar–H), 7.71–7.67 (t, $^3J = 8.4$ Hz, 1H, Ar–H), 7.47–7.35 (m, 12H, Ar–H), 6.9–6.87 (dd, $^3J = 8.9$ Hz, $^4J = 2.4$ Hz, 2H, Ar–H), 6.81–6.78 (dd, $^3J = 12.5$ Hz, $^4J = 2.4$ Hz, 2H, Ar–H), 5.15 (s, 4H, 2 × ArCH$_2$O–). IR (Nujol) $\nu_{\max}$: 2235, 1751, 1622, 1600 cm^{-1}.

2.1.3. *2-Cyano-1,3-phenylene bis(2-fluoro-4-hydroxybenzoate)* ***d*** *($R_1 = F$, $R_2 = H$)*

A mixture of compound **c** (4 g) dissolved in 1,4-dioxane (50 ml) and 5% Pd-C catalyst (0.8 g) was stirred in an atmosphere of hydrogen until the required quantity of hydrogen was absorbed. The resulting mixture was filtered hot and the solvent removed under reduced pressure. The solid material obtained was crystallized using a mixture of butan-2-one and petroleum ether (b.p. 60–80°C); yield 2.5 g (91%), m.p. 230–232°C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.3 (s, 2H, 2 × Ar–OH, exchangeable with D_2O), 8.25–8.20 (t, $^3J = 8.7$ Hz, 2H, Ar–H), 7.08–7.04 (t, $^3J = 8.5$ Hz, 1H, Ar–H), 7.69–7.67 (d, $^3J = 8.4$ Hz, 2H, Ar–H), 7.04–7.01 (dd, $^3J = 8.8$ Hz, $^4J = 2.2$ Hz, 2H, Ar–H), 6.94–6.90 (dd, $^3J = 12.8$ Hz, $^4J = 2.3$ Hz, 2H, Ar–H). IR (Nujol) ν_{max}: 3329, 2243, 1755, 1740, 1626 cm^{-1}.

2.1.4. *2-Cyano-1,3-phenylene bis[4-(4-n-dodecylbiphenyl-4′-carbonyloxy)-2-fluorobenzoate)]* ***e*** *($R_1 = F$, $R_2 = H$, $n = 12$)*

A mixture of compound **d** (0.2 g, 0.49 mmol), 4-*n*-dodecylbiphenyl-4-carboxylic acid (0.36 g, 0.98 mmol), DCC (0.22 g, 1 mmol) and a catalytic quantity of DMAP was stirred for about 24 h. The solvent was removed and the residue purified by column chromatography on silica gel using chloroform as eluent. Removal of solvent from the eluate afforded a residue which was recrystallized from butan-2-one; yield 0.19 g (36%), m.p. 134.5°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.32–8.24 (m, 4H, Ar–H), 7.77–7.73 (m, 6H, A–H), 7.6–7.58 (m, 4H, Ar–H), 7.49–7.43 (m, 4H, Ar–H), 7.32–7.30 (m, 7H, Ar–H), 2.69–2.65 (t, $^3J = 7.6$ Hz, 4H, 2 × Ar–CH_2–), 1.66–1.64 (quin, $^3J = 6.5$ Hz, 4H, 2 × Ar–CH_2–$C\underline{H}_2$–), 1.37–1.26 (m, 36H, 18 × –$C\underline{H}_2$), 0.89–0.86 (t, $^3J = 6.4$ Hz, 6H, 2 × –CH_2–$C\underline{H}_3$). IR (Nujol) ν_{max}: 2227, 1755, 1738, 1607 cm^{-1}.

2.2. *Measurements*

All the compounds reported were purified by column chromatography on silica gel, (ACME, 60–120 mesh) and eluted using appropriate solvents. The purities of all the intermediates and the final esters were checked by thin layer chromatography using silica gel (Merck Kieselgel $60F_{254}$) coated aluminium cards with a fluorescent indicator. Normal phase high performance liquid chromatography was carried out for the final esters with a µ-porasil column (3.9 × 300 mm^2, Waters Associates Inc.) using 1% acetone in dichloromethane as eluent. The chemical structure of all the compounds was confirmed by a combination of NMR spectroscopy (Bruker AMX 400, tetramethylsilane as internal standard) and IR spectroscopy (Shimadzu FTIR-8400).

The transition temperatures and associated enthalpies were determined from differential scanning calorimetry (DSC) (Perkin-Elmer, Model Pyris 1D) using indium as a standard. The mesophase behaviour of all the final esters was studied using polarizing optical microscopy (POM) (Leitz Laborlux 12 POL/Olympus BX 50 attached to a FP 82HT heating stage and FP 90 central processor). XRD studies of the non-oriented powder samples were carried out using a 4 kW rotating anode X-ray source (Rigaku Ultrax-18) and graphite monochromated CuK_α radiation (1.54 Å). The diffraction patterns were collected on a two-dimensional detector (imaging plate system, Marresearch).

The electro-optical switching behaviour of the mesophases was studied using polyimide-coated ITO glass cells. The triangular waves were generated by a waveform generator (Wavetek, Model 39), fitted with a Trek Model 601B-3 amplifier. The current was measured across a 10 kΩ resistor and the waveforms recorded using a Tektronix Oscilloscope (TDS 220). The d.c. field experiments were carried out using a Regulated Dual d.c. Power Supply (Aplab, LD 6401).

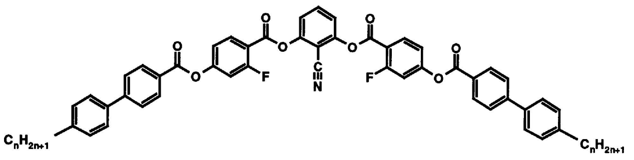
3. Experimental results

3.1. *Microscopic investigations*

The phase transition temperatures and associated enthalpy changes for the two homologous series (I and II) of compounds symmetrically substituted about a central phenyl ring are summarized in tables 1 and 2, respectively. In series I, a fluorine is substituted *ortho* to the carbonyl group while in series II it is in the *meta*-position. Of the twenty compounds synthesized and investigated, eighteen are monomesomorphic, one is dimesomorphic and one compound shows no mesophase. Compounds **1** to **4** are monotropic, compounds **13** and **14** are enantiotropic and all six compounds exhibit the same type of mesophase. On cooling the isotropic liquid of these compounds, as thin films between two glass plates and observed under POM, coloured circular domains appear which grow in size and coalesce. Typical textures obtained for compound **14** are shown in figure 1. The enthalpy of the clearing transition for this mesophase is about 20 kJ mol^{-1}. This mesophase resembles the two-dimensional B_1 phase and the XRD studies indicate a large tilt of the molecules in the lattice (see § 3.2).

The mesophases of compounds **5** to **11** and **15** to **20** exhibit several different textures similar to those observed for the 2-nitro-1,3-phenylene bis[4-(4-*n*-alkoxyphenyliminomethyl)benzoates] (*n*-OPIMB-NO_2) [12] for which the symbol B_7 has been assigned and which represent the standard materials for such a mesophase. As we shall see later, the mesophase of the higher homologues of our two series of compounds is indeed B_7. It is interesting to note that in both series the temperature range of the B_7 phase increases on ascending the series. Also, this thermal range is larger for the *meta* fluorine-substituted compounds (series II) with compound **20** having a B_7 range of about 42.5°C. The clearing transition enthalpy values obtained for this mesophase in both the series is quite high (about 25 to 30 kJ mol^{-1}) when compared with other known B-phases. Plots of transition temperatures as a function of the number of carbon atoms in the *n*-alkyl chain for the series I and II

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1} *in italics*) for compounds of series I. Cr = crystalline phase; B_7 = two-dimensional banana phase with helical superstructure; B_x = unidentified two-dimensional banana phase; B_1 = two-dimensional banana phase; I = isotropic phase; ● phase exists; — phase does not exist.

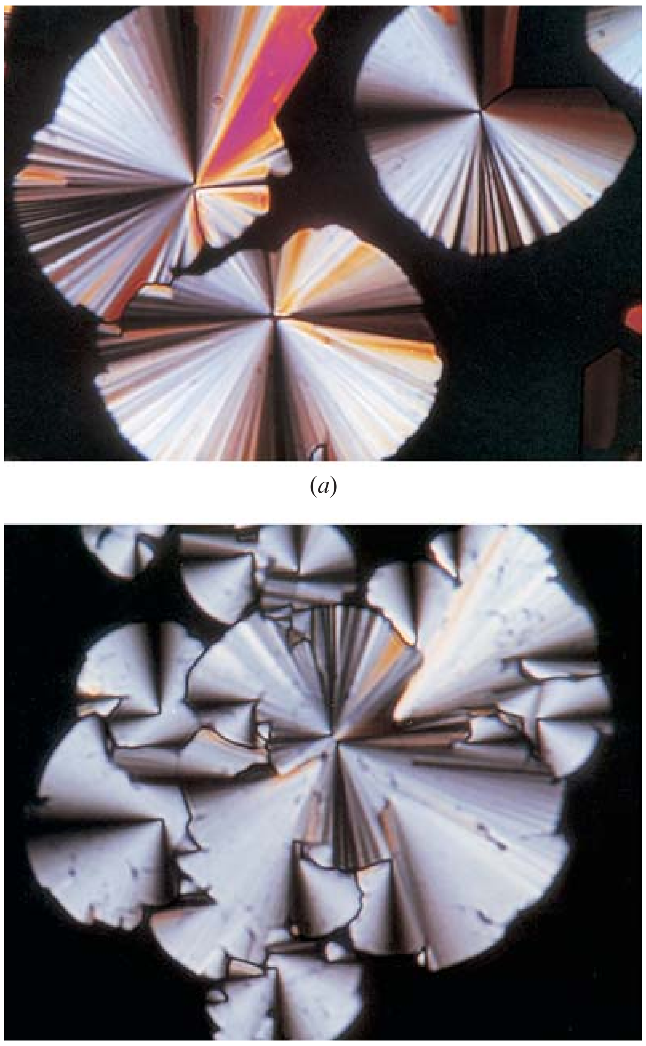


Compound	n	Cr		B_7		B_1		I
1	5	●	149.0 *39.0*	—		(●	143.0)[b]	●
2	6	●	144.0 *41.8*	—		(●	140.0) *17.0*	●
3	7	●	146.0 *53.7*	—		(●	138.0) *19.4*	●
4	8	●	141.5 *52.5*	—		(●	134.5) *21.3*	●
5	9	●	136.5 *30.2*	●	137.5 *23.4*	—		●
6	10	●	130.5 *33.7*	●	141.0 *25.0*	—		●
7	11	●	138.0 *38.5*	●	144.5 *26.6*	—		●
8	12	●	134.5 *36.7*	●	146.0 *26.7*	—		●
9	14	●	131.0 *40.0*	●	148.0 *28.5*	—		●
10	16[a]	●	124.0 *58.6*	●	149.0 *28.7*	—		●
11	18[a]	●	123.0 *59.4*	●	149.5 *30.2*	—		●

[a] Compound has crystal–crystal transition; enthalpy denoted is the sum of all previous transitions.

[b] Temperature obtained on cooling; enthalpy could not be determined as the sample crystallizes immediately.

are shown in figures 2 and 3, respectively. While the clearing points for the B_1 phase show a decreasing trend in both series, those for the B_7 clearing points rise initially and appear to level off as the chain length is increased. These two plots perhaps represent the first examples of B_7–isotropic transition point curves. Interestingly compound **15** shows a highly metastable phase on supercooling the B_7 phase at 95°C. Since the textural changes at the transition are minimal, it is difficult to observe this under POM, but this transition can be clearly seen on a DSC thermogram as the change is accompanied by a small enthalpy change (1.3 kJ mol^{-1}). Since the phase is metastable and we are unable to obtain a perfectly oriented sample for XRD studies, it has therefore been difficult to characterize this mesophase completely; hence we have designated it as a B_x phase.


(*a*)

(*b*)

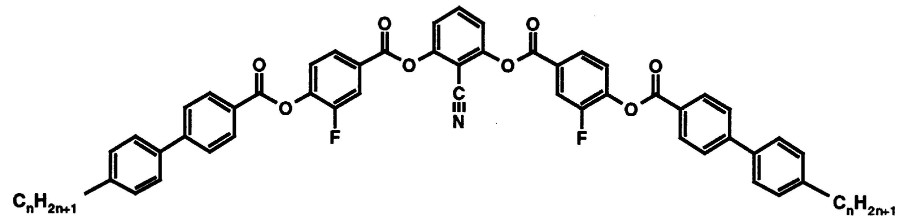
Figure 1. (*a*, *b*) Photomicrographs of the growth of circular domains of the mesophase of compound **14** at 145°C.

The microscopic textures of the B_7 phase exhibited by these compounds are fascinating. When a thin film of the isotropic liquid of compound **15** is cooled slowly, several different textural variants can be seen. One of the common textural features seen for this mesophase is the growth of spiral domains; a photomicrograph of this is shown in figure 4. The various other textures that are obtained for this B_7 mesophase are shown in figures 5 (*a*–*e*). The textural variants observed in these two series of compounds are very similar to those reported for the B_7 mesophase of the standard *n*-OPIMB-NO_2 series of compounds.

3.2. *X-ray investigations*

As mentioned above, we observed three different mesophases in the two series of compounds and have carried out XRD studies on these. The mesophase

Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1} *in italics*) for compounds of series II.



Compound	*n*	Cr		B_x		B_7		B_1		I
12	5	●	162.0 *47.8*	—		—		—		●
13	8	●	142.0 *24.6*	—		—		●	147.0 *20.9*	●
14	9	●	140.5 *45.6*	—		—		●	146.0 *21.8*	●
15	10	●	125.0 *31.2*	(●	95.0) *1.3*	●	148.0 *25.2*	—		●
16	11	●	128.0 *28.1*	—		●	151.0 *25.7*	—		●
17	12	●	131.0 *44.6*	—		●	152.5 *26.6*	—		●
18	14	●	122.5 *35.9*	—		●	154.0 *27.4*	—		●
19	16	●	117.0 *47.5*	—		●	155.0 *29.1*	—		●
20	18	●	112.0 *38.6*	—		●	154.5 *29.9*	—		●

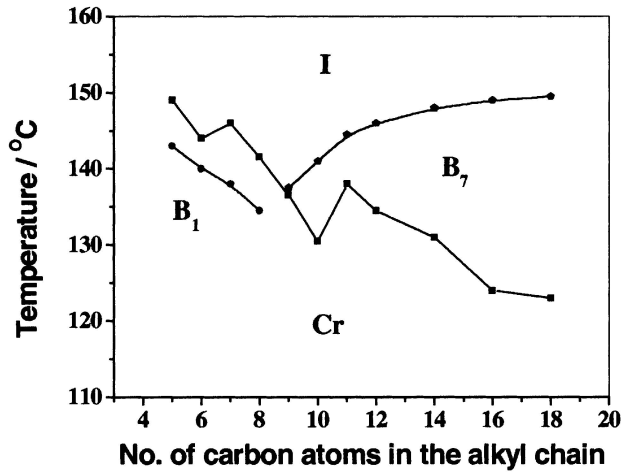


Figure 2. Transition temperatures versus the number of carbon atoms in the *n*-alkyl chain for series **I**.

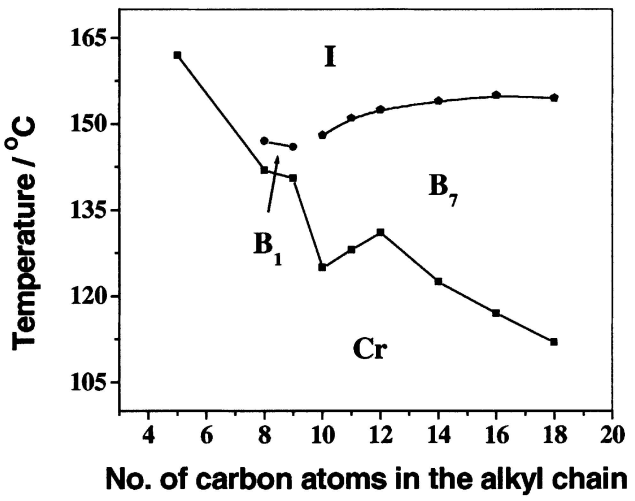


Figure 3. Transition temperatures versus the number of carbon atoms in the *n*-alkyl chain for series II.

of compound **14** (142°C) shows diffuse scattering in the wide angle region at 4.7 Å, indicating a liquid-like in-plane order. In the small angle region three sharp reflections at $d_1 = 31.8$ Å, $d_2 = 20.2$ Å and $d_3 = 15.9$ Å were obtained. These cannot be indexed as reflections from a simple layered structure but are indicative of a two-dimensional structure. The reflection at $d_1 = 31.8$ Å can be safely excluded as due to half the molecular length of this compound, assuming that the chains are in all-*trans* conformations (58 Å). If we assume that the second reflection $d_2 = 20.2$ Å is due to half the molecular length (0 0 2), then the other two reflections d_1 and d_3

Figure 4. Photomicrograph of the characteristic growth of a spiral domain on slow cooling of the isotropic liquid of compound **15**, 146°C.

can be indexed as (1 0 1) and (2 0 2), respectively, for a B_1 phase with a two-dimensional rectangular lattice. From this assumption, the obtained lattice parameters are $a = 51.5$ Å and $b = 40.4$ Å. However, this would mean a very large tilt of the molecules (tilt angle 45°) in the B_1 phase and such a large tilt has not been observed in the usual two-dimensional rectangular B_1 phase reported for a number of other compounds. The angular intensity profile of the mesophase of this compound is shown in figure 6. It has not been possible to obtain a perfectly oriented monodomain sample to confirm the exact structure of this mesophase.

The XRD pattern of an unoriented sample of compound **8** at 138°C shows a number of reflections. In the wide angle region a diffuse peak at 4.8 Å was seen, indicative of the absence of in-plane order. In the small angle region five reflections were obtained; these are $d_1 = 57.8$ Å, $d_2 = 37.6$ Å, $d_3 = 18.8$ Å, $d_4 = 12.6$ Å and $d_5 = 7.7$ Å. This complex pattern rules out a lamellar structure and indicates a two- or three-dimensional ordering for the mesophase. The angular intensity profile of the mesophase of this compound is shown in figure 7. Similar XRD patterns have been obtained for the B_7 phase of some *n*-OPIMB-NO_2 derivatives [24]. In consequence, and given the characteristic textural features, we have identified the mesophases of compounds **5–11** and **15–20** as B_7, see table 3. Since perfectly oriented samples are difficult to obtain, the exact structural features of the B_7 phase are not completely understood.

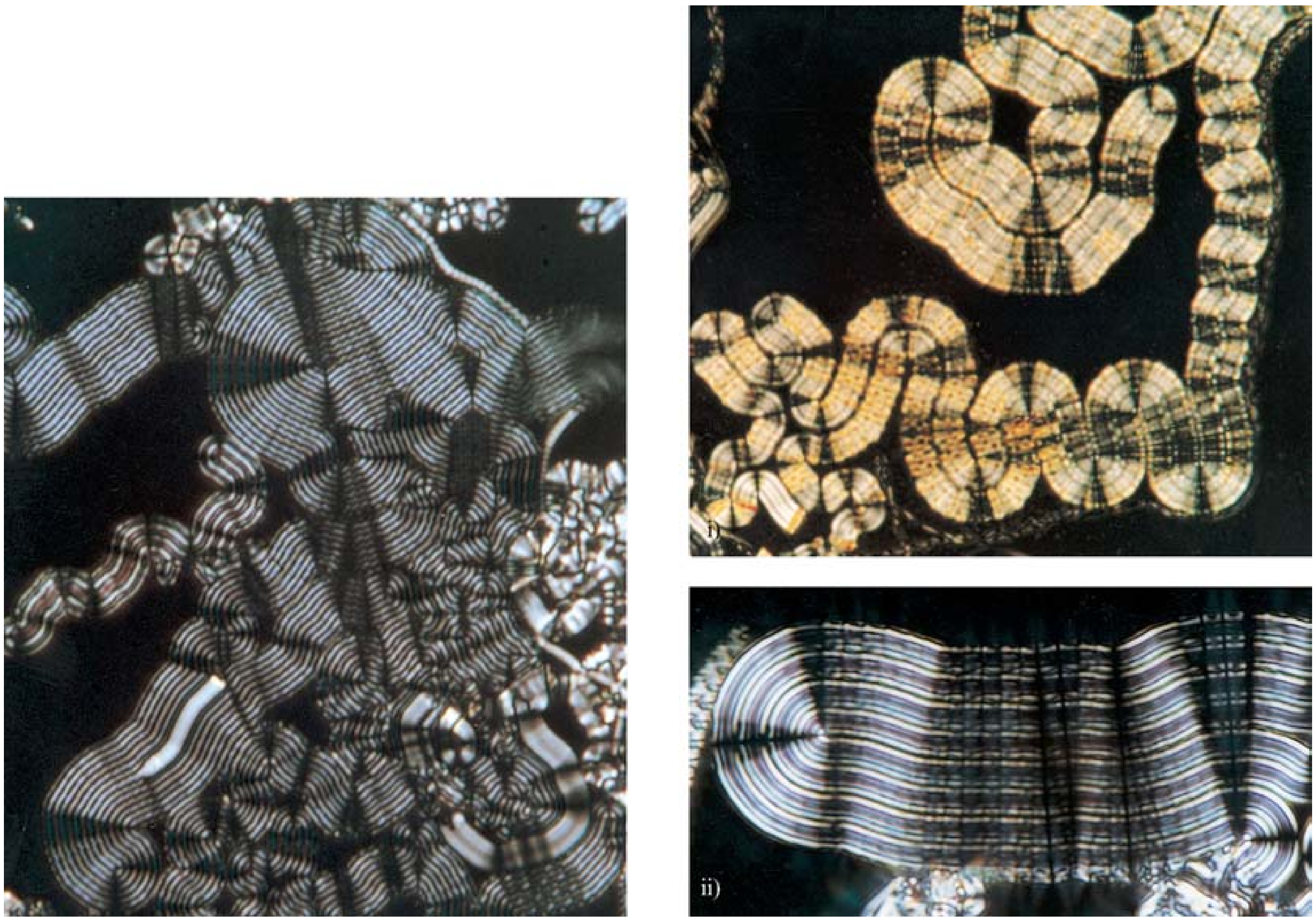
On cooling the B_7 phase of compound **15** to 95°C, a phase transition takes place with no significant change in the texture when viewed under POM. The XRD pattern of this highly metastable phase shows the following reflections. Thus, the wide angle peak at 4.8 Å is retained while a change in the pattern at the small angle is seen. The reflections at the small angle region correspond to $d_1 = 45$ Å, $d_2 = 34$ Å, $d_3 = 22.6$ Å, $d_4 = 11.4$ Å, $d_5 = 7.3$ Å and $d_6 = 6.9$ Å. Since the structure of the higher temperature B_7 phase itself has not been understood, it is difficult to speculate on the structure of this higher ordered mesophase. Hence we have designated this as the B_x phase. Surprisingly this B_x phase has been obtained in only one homologue.

3.3. *Miscibility studies*

In order to confirm that the mesophase exhibited by the higher homologues of the two series (compounds **5–11** and **15–20**) is the same, we have carried out miscibility studies with a standard material, namely 2-nitro-1,3-phenylene bis[4-(4-*n*-dodecyloxyphenyliminomethyl)-benzoate] (12-OPIMB-NO_2). This compound was synthesized and has the following transition temperatures: Cr 85.5 B_7 173.0 I (°C); these temperatures agree well

Table 3. The measured spacings in the small angle region for the compounds exhibiting the B_7 mesophase; *L* is the calculated molecular length.

	Measured spacings from X-ray/Å						
Compound	d_1	d_2	d_3	d_4	d_5	d_6	Calculated molecular length *L*/Å
5	49.9	33.1	22.1	17.4	16.2	7.7	58
8	57.8	37.6	18.8	12.6	7.7	—	65
10	59.7	41.9	20.6	14.0	—	—	75
15	57.8	35.0	25.7	18.6	17.6	—	60
17	65.3	52.2	38.9	19.5	13.0	7.7	65
18	65.2	40.6	20.3	13.5	10.8	7.7	70
20	64.1	45.1	22.9	15.3	11.5	7.7	80



(*a*) (*b*)

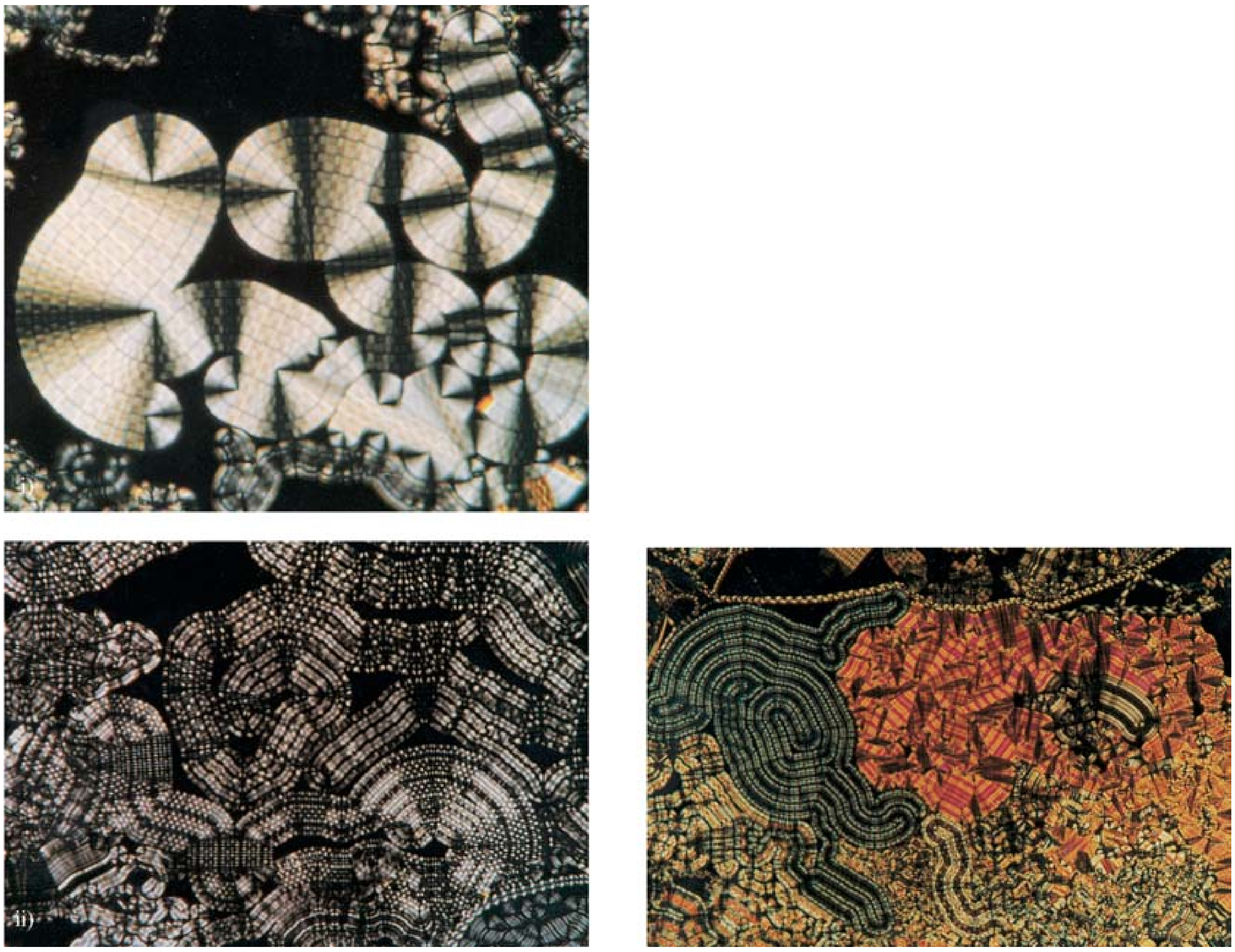
Figure 5. Photomicrographs of the growth of different domains in the B_7 mesophase. (*a*) Ribbons with equidistant stripes; (*b*, i & ii) myelinic textures; (*c*, i & ii) texture with two-dimensional periodic patterns; (*d*) various patterns in the same sample; (*e*, i & ii) other variants of the texture normally obtained for the present series of compounds.

with the literature values [2]. Compound **17** and the standard material were well mixed in the isotropic phase in a range of wt % compositions and the mixtures investigated using POM, DSC and XRD. The isomorphous binary phase diagram thus obtained is shown in figure 8. One can see that the clearing temperatures are not very sharp and vary in width from 1°C to about 8°C. This is probably due to the incompatibility of the two systems which contain either five or seven phenyl rings. Also, the standard compound is a Schiff's base ester while compound **17** is an ester. The eutectic temperature is obtained for about 60 wt % of compound **17**. Apart from this, it is clear from this diagram that there is complete miscibility between the mesophases of the two compounds over the entire composition range, indicating that the mesophase exhibited by compound **17** is indeed B_7.

3.4. *Electro-optical studies*

We have carried out electric field experiments on the B_7 mesophase of the two series of compounds under investigation. For example, compound **17** was placed in a cell (thickness 6.5 μm) constructed using ITO deposited glass plates coated with polyimide and unidirectionally rubbed. On application of a triangular wave electric field up to $\pm 40\ \mathrm{V\,\mu m^{-1}}$, no evidence of switching was seen under POM. This was carried out at different temperatures in the mesophase and varying frequencies from 1 to 100 Hz. Similarly, when a d.c. electric field was applied to the same cell, up to $16\ \mathrm{V\,\mu m^{-1}}$, no change either in the position of the dark brushes or the colour of the circular domains was visible.

In order to verify whether the B_7 mesophase does switch, we carried out triangular wave electric field experiments with one of the standard compounds,



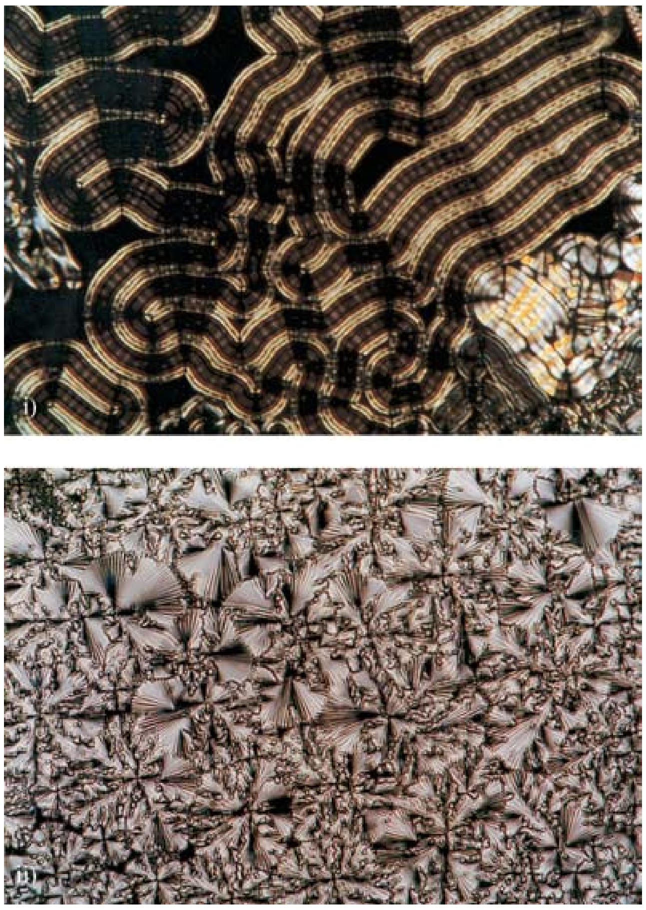
(*c*) (*d*)

Figure 5. (*Continued.*)

12-OPIMB-NO_2 using the same experimental procedure. We observed no switching up to ±40 V μm^{-1}. This supports our view that the mesophases exhibited by compounds of the *n*-OPIMB-NO_2 series [2] as well as by the present series of compounds (**5–11** and **15–20**) containing a strongly polar cyano group in the 2-position in the central phenyl ring, belong to the same mesophase type. In contrast, however, Jakli *et al.* [25] have reported evidence for optical switching in 2-nitro-1,3-phenylene bis[4-(4-*n*-octyloxyphenyliminomethyl)benzoate.

4. Discussion

It is appropriate to consider the mesophases of different compounds which have been assigned the symbol B_7. Since the observation of the fascinating helical textures and other two-dimensional patterns by Pelzl *et al.* [12] in the *n*-OPIMB-NO_2 compounds, attempts have been made to understand the structure of this phase. Single and double spiral domains have been observed by a number of groups in different types of compounds. Heppke *et al.* [13, 14] studied the mesomorphic properties of a series of novel sulphur-containing banana-shaped liquid crystals. These materials exhibit spiral-domain textures indicating the chiral nature of the mesophase and they speculated that this smectic mesophase is B_7. From electro-optic investigations, they have proposed that the mesophase is antiferroelectric in nature. Walba *et al.* [15] have described a ferroelectric liquid crystal composed of racemic molecules, and based on characteristic textural features have indicated that the mesophase of this Schiff's base ester is indeed B_7. Bedel *et al.* [16] reported the synthesis and characterization of a



(*e*)

Figure 5. (*Continued.*)

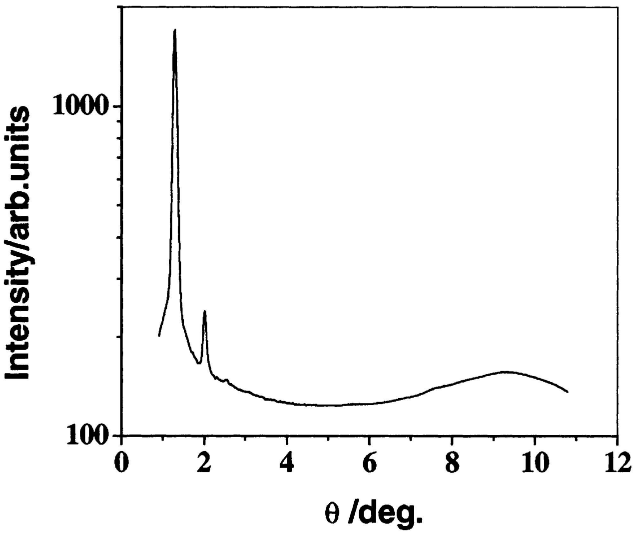


Figure 6. X-ray angular intensity profile of the B_1 phase of compound **14** at 142°C.

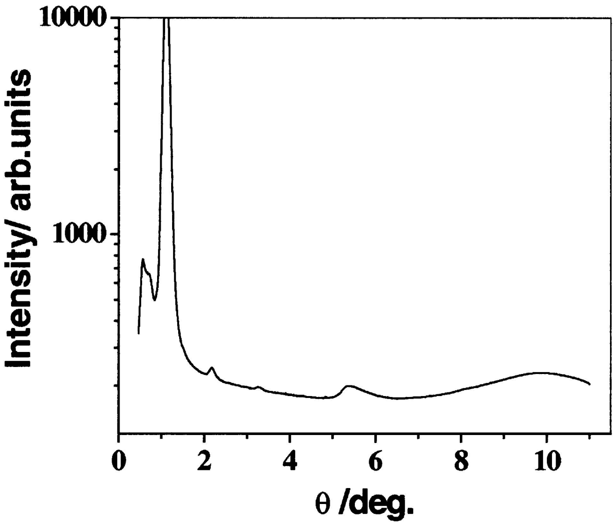


Figure 7. X-ray angular intensity profile of the B_7 phase of compound **8** at 138°C.

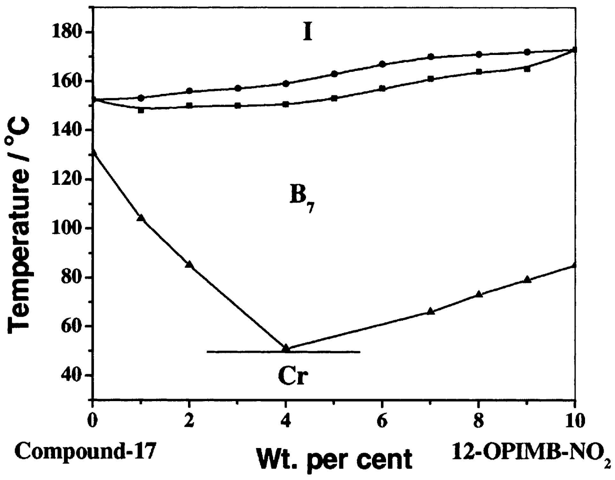


Figure 8. Phase diagram of binary mixtures of compound **17** and the standard compound 12-OPIMB-NO_2.

homologous series of Schiff's base achiral banana-shaped mesogens. The compounds contain a lateral fluorine substituent on the outer phenyl ring *ortho* to the terminal *n*-alkoxy chain. The higher homologues of this series (*n*-alkoxy chain ⩾ *n*-nonyloxy) show microscopic textures as well as XRD patterns similar to those of the B_7 phase of the standard *n*-OPIMB-NO_2 compounds. The electro-optic studies show that this phase is ferroelectric.

Over the last year or so, Shankar Rao *et al.* [19] describe the mesomorphic behaviour of a salicylaldimine derivative which exhibited spiral domains. No other textural variants have been reported for this two-dimensional antiferroelectric phase and the symbol B_7 was assigned to the mesophase. Also, Dierking *et al.*

[18] observed spiral filamentary growth patterns in a Schiff's base containing a fluorine substituent *ortho* to the terminal *n*-alkoxy chain. The phase ordering process was investigated by means of fractal dimensional analysis and the mesophase has been assigned the symbol B_7.

Lee *et al.* [17] reported a switchable banana phase of a Schiff's base containing a chlorine substituent *ortho* to the terminal *n*-alkoxy chain and assigned the symbol B_7 to the mesophase. From XRD data, they showed the mesophase to be lamellar, and from electro-optic switching experiments it has been characterized as ferroelectric. A reexamination of the mesophase of one of these compounds by Weissflog *et al.* [24] showed that the mesophase does switch weakly and that it is not a B_7 phase.

From these reports it is clear that for the mesophase which has been assigned the symbol B_7, both ferroelectric and antiferroelectric switching properties are claimed. However, the standard B_7 compounds, namely the *n*-OPIMB-NO_2 derivatives, do not switch, at least up to about $\pm 40\,\mathrm{V}\,\mu\mathrm{m}^{-1}$, although Jakli *et al.* [25] report a small optical effect under an electric field for one of these compounds. They also suggest that this effect is too complex for any quantitative conclusions to be drawn. Very recently, Clark *et al.* [26] have shown that the phase structure of the B_7 phase is either two- or three-dimensional using synchrotron based XRD and freeze fracture electron microscopy measurements on a B_7 material synthesized by the Halle group. Hence, one can rule out a simple lamellar structure for a B_7 phase as reported, for example, for the sulphur-containing compounds [13, 14]. One common feature in all the above cases is the observation of the growth of helical or spiral domains as the isotropic liquid is cooled slowly. Therefore, the optical textures and the switching behaviour (ferro- or antiferro-electric) provide insufficient proof for the assignment of the B_7 phase. Obviously, careful high resolution XRD measurements coupled with other physical investigations are necessary to arrive unambiguously at the structure of this fascinating B_7 mesophase.

5. Conclusions

Two new homologous series of symmetrically substituted compounds composed of banana-shaped molecules derived from 2-cyanoresorcinol are reported. The textural features, the XRD patterns and the electro-optic switching behaviour of the higher homologues of the two series of compounds are similar to those observed for the mesophase of the *n*-OPIMB-NO_2 standard compounds for which the symbol B_7 has been assigned. We conclude that a strongly polar substituent such as a nitro or a cyano group in the 2-position of the central phenyl ring is responsible for the occurrence of the B_7 mesophase. Furthermore, in these strongly polar compounds, the two-dimensional B_1 phase appears to have a fairly large tilt of the molecules.

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