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Banana-shaped mesogens: effect of 2-methylresorcinol as the central unit on the mesomorphic properties of five-ring esters

S. SHUBASHREE, B. K. SADASHIVA* and SURAJIT DHARA

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

Three homologous series of banana-shaped five-ring esters and one series of seven-ring esters derived from 2-methylresorcinol have been synthesized. This has been carried out to understand the effect of chemical structure on the mesomorphic properties of such compounds. It is shown that the 2-methyl substituent in the central phenyl ring destabilizes the mesophases when they are compared with those of the analogous unsubstituted compounds. Replacement of a phenyl ring by a biphenyl moiety (seven-ring esters) in the two arms of the bent-core molecule enhances the thermal range of the mesophases as well as the clearing temperatures. The mesophases have been characterized using techniques such as polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction, and by electro-optical investigations. In the 32 compounds investigated, two mesophases, B_1 and B_2, have been identified.

1. Introduction

Thermotropic mesomorphism has been observed in compounds with three different basic molecular shapes. These are compounds with rod-like molecules or disc-like molecules or banana-shaped molecules. There has been great interest in compounds with banana-shaped molecules as some of these have been reported to exhibit ferroelectric [1] and antiferroelectric properties [2], though the molecules themselves are achiral. As a matter of fact, it was Vorländer who discovered long ago that compounds with non-linear structures exhibit mesophases though the exact nature of these was reported much later [3, 4]. In the last few years several hundred compounds with a bent molecular shape and exhibiting mesomorphic properties have been synthesized [5–15] with a view to understanding the relationship between the molecular structure and the mesophases they exhibit. There have been several studies in which the central phenyl ring has been substituted by chloro [16–18], bromo [15], cyano [19] and nitro [20] substituents. In all these compounds, which are derivatives of resorcinol, the exact position of the substituent has an influence on the nature of the mesophase obtained. The results obtained with various substituents on the central phenyl ring have been summarized in a recent publication [21].

The mesomorphic properties of the derivatives of 2-methylresorcinol have not been studied in detail. A few of the Schiff's base esters reported earlier [22] showed a phase transition from B_2 to B_5 as the isotropic phases

were cooled. The interesting observation was that both of these mesophases are electro-optically switchable. The other unusual observation for these derivatives was that on attaching a fluorine to the outer phenyl ring *ortho* to the terminal alkoxy chain, three different unidentified mesophases were obtained [21]. Interestingly, the replacement of fluorine by chlorine appears not only to depress the melting point but also to eliminate two of the mesophases.

With a view to examining the effect of 2-methyl-resorcinol as the central unit on the mesomorphic properties of compounds which are not Schiff's base derivatives, we have synthesized four homologous series of compounds having the general structure A shown below:
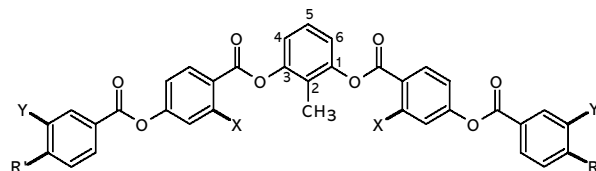
Structure A

X = F, Y = H, R' = OC$_n$H$_{2n+1}$		Series I
X = F, Y = H, R' = C$_n$H$_{2n+1}$		Series II
X = H, Y = F, R' = OC$_n$H$_{2n+1}$		Series III
X = F, Y = H, R' = -C$_6$H$_4$-C$_n$H$_{2n+1}$		Series IV

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

We have also compared the mesomorphic properties of these compounds with those of the unsubstituted parent compounds and report here our results.

2. Synthesis

The banana-shaped compounds belonging to the three series I, II and IV were synthesized following the general scheme shown in figure 1 and those belonging to series III were prepared following the general pathway shown in figure 2. The commercially obtained 2-methylresorcinol was purified before use. The 4-*n*-alkyl and 4-*n*-alkoxybenzoic acids were prepared following procedures described in the literature [23, 24]. 4-Benzyloxybenzoic acid was prepared by first reacting ethyl 4-hydroxybenzoate 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-hydroxybenzoic acid and 3-fluoro-4-hydroxy benzoic acid were synthesized as described earlier [25]. 2-Fluoro-4-benzyloxybenzoic acid and 3-fluoro-4-benzyloxybenzoic acid were prepared following a procedure described previously [26]. 4-*n*-Alkylbiphenyl-4′-carboxylic acids were prepared following a procedure described by us [27]. A typical and standard procedure for the synthesis and characterization of one of the compounds under investigation is given below.
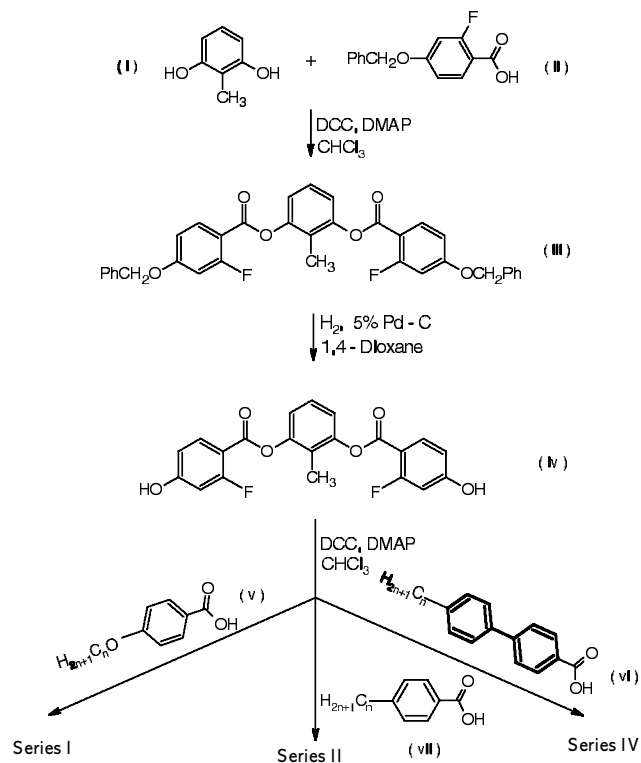

Figure 1. Synthetic pathway for the preparation of the compounds of series I, II and IV.
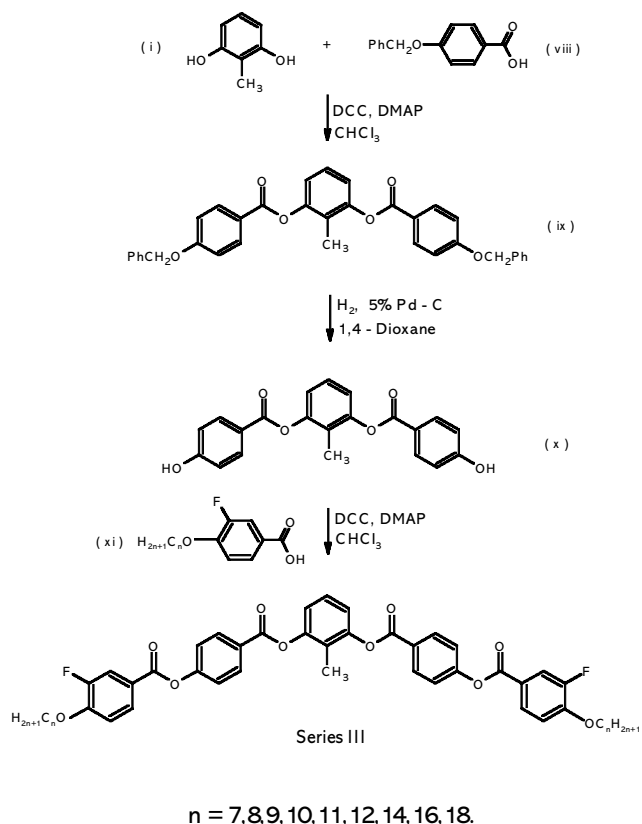

n = 7, 8, 9, 10, 11, 12, 14, 16, 18.

Figure 2. Synthetic pathway for the preparation of the compounds of series III.

2.1. *2-Methyl-1,3-phenylene bis[2-fluoro 4-benzyloxybenzoate] (iii)*

A mixture of 2-fluoro-4-benzyloxybenzoic acid (3 g, 12 mmol), 2-methylresorcinol (0.76 g, 6.11 mmol), *N,N*-dimethylaminopyridine (DMAP, 0.15 g, 1.2 mmol) and dry dichloromethane (50 ml) was stirred for 5 min. To this mixture was added *N,N*-dicyclohexylcarbodiimide (DCC, 27.77 g, 12.1 mmol) and stirring was continued overnight at room temperature. The *N,N*-dicyclohexylurea formed was filtered off and the filtrate diluted with dichloromethane (50 ml). The resultant solution was washed with 5% aqueous acetic acid (2 × 20 ml) and water (3 × 30 ml) and then dried over anhydrous sodium sulphate. 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 a white material which was crystallized from a mixture of chloroform and petroleum ether (b.p. 60–80°C). Yield 2.74 g (78%); m.p. 149–149.5°C; ν_{max} (nujol): 2950, 1740, 1720, 1620, 1580, 1470, 1340, 1260, 1120 and 1070 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 2.12 (s, 3H, ArCH$_3$), 5.14 (s, 4H, ArOCH$_2$)$_2$, 6.76–8.1 (m, 19H, ArH).

2.2. *2-Methyl-1,3-phenylene bis(2-fluoro-4-hydroxybenzoate)* (*iv*)

A mixture of 2-methyl-1,3-phenylene bis(2-fluoro-4-benzyloxybenzoate) (2 g, 3.4 mmol), 5% Pd-C catalyst (0.5 g) and 1,4-dioxane (50 ml) was stirred at 55°C in an atmosphere of hydrogen until the calculated quantity of hydrogen was absorbed. The reaction mixture was then filtered and removal of the solvent gave a residue which was crystallized from ethyl acetate. Yield 1.3 g (94%); m.p. 258–260°C (d); ν_{max} (nujol): 3400, 2950, 1710, 1620, 1460, 1260, 1110, 1080 and 1060 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 2.18 (s, 3H, ArCH$_3$), 3.4 [s, 2H, (ArOH)$_2$], 6.87–8.2 (m, 9H, ArH).

2.3. *2-Methyl-1,3-phenylene bis[4-(4-n-octa-decyloxybenzoyloxy)-2-fluorobenzoate]* (*8*)

This was synthesized following the procedure used for the preparation of compound **iii**; the quantities used were: 2-methyl-1,3-phenylene bis(2-fluoro-4-hydroxy-benzoate) (0.1 g, 0.25 mmol), 4-*n*-octadecyloxybenzoic acid (0.195 g, 0.5 mmol), DCC (0.114 g, 0.55 mmol), DMAP (0.006 g, 0.05 mmol) and anhydrous chloroform (5 ml). The product was crystallized from a butan-2-one-acetonitrile mixture. Yield 77%; m.p 110°C; ν_{max} (nujol): 2900, 1740, 1720, 1600, 1470, 1240, 1120, 1160 and 1060 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.86–0.89 (t, 6H, 2 × CH$_3$), 1.2–1.57 (m, 64H, 32 × CH$_2$), 2.17 (s, 3H, ArCH$_3$), 4.04–4.07 [t, 4H, (ArOCH$_2$)$_2$], 6.98–8.2 (m, ArH, 17H).

All the compounds were purified by chromatographic techniques and by repeated crystallization using suitable solvents. The chemical structures of all the compounds were confirmed by ^{1}H NMR spectroscopy (Bruker AMX 400 spectrometer) using tetramethylsilane as internal standard, by infrared spectroscopy (Shimadzu FTIR-8400 spectrophotometer) and by elemental analysis (Carlo-Erba 1106 analyser).

3. Experimental

The thermal behaviour of the homologous series of compounds was examined by polarizing optical micro-scopy (POM) (Leitz Laborlux 12 POL) using a heating stage and controller (Mettler FP52 and FP5, respectively). Differential scanning calorimetry (DSC) (Perkin-Elmer, Pyris ID) was employed to determine the transition temperatures, as well as the enthalpies of transition. This instrument was calibrated using indium as standard. The thermograms were generally recorded at a scanning rate of 5°C min^{-1} and the enthalpies are quoted in kJ mol^{-1}. Phase identification was made by observation of the optical textures. This was confirmed by X-ray diffraction (XRD) studies using CuK$_\alpha$ radiation from a rotating anode generator with a flat graphite crystal mono-chromator. These diffraction studies were performed on

powder samples in Lindemann capillaries and diffraction patterns were collected on an image plate (Marresearch). The electro-optical studies were carried out employing a standard experimental set-up wherein the sample was mounted between ITO coated glass plates and viewed by POM. The d.c. field was generated using a suitable power supply. The switching current response was obtained using the triangular voltage method.

4. Results and discussion

The transition temperatures together with the associated enthalpies for the homologous compounds of series I, are summarized in table 1. As can be seen, compounds **1**, **2**, and **3** are non-mesomorphic, while the remaining compounds exhibit a monotropic mesophase. The optical microscopic textures of these compounds were examined as thin films obtained by sandwiching the samples between a glass slide and a cover slip and viewed by POM. All the compounds show similar textures, which look like leaves; sometimes a schlieren texture is also obtained. A typical photomicrograph of the texture exhibited by compound **8** is shown in figure 3. This is similar to that observed for the antiferroelectric B$_2$ phase and, as we shall see later, this mesophase has been con-firmed as a B$_2$ phase. The clearing transition enthalpies for compounds **7** and **8** are of the order of 24 kJ mol^{-1}. A plot of the transition temperatures as a function of

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}), in italics, for compounds of series I. Key: Cr = crystalline phase; B$_2$ = antiferroelectric banana phase 2; I = isotropic phase; B$_1$ = two dimensional banana phase 1; ● phase exists; — phase does not exist. () indicates a monotropic transition.

Compound	n	Cr		B$_2$		I
1	10	●	109.5 *94.9*[a]	—	—	●
2	11	●	117.0 *55.7*	—	—	●
3	12	●	119.5 *60.8*	—	—	●
4	13	●	118.0 *65.9*	(●	103.0) [b]	●
5	14	●	115.0 *116.7*[a]	(●	105.0) [b]	●
6	15	●	115.5 *118.9*[a]	(●	107.0) [b]	●
7	16	●	114.0 *137.0*[a]	(●	108.0) *23.3*	●
8	18	●	110.0 *147.2*[a]	(●	109.5) *24.8*	●

[a] Total enthalpy including any other crystal–crystal transition.
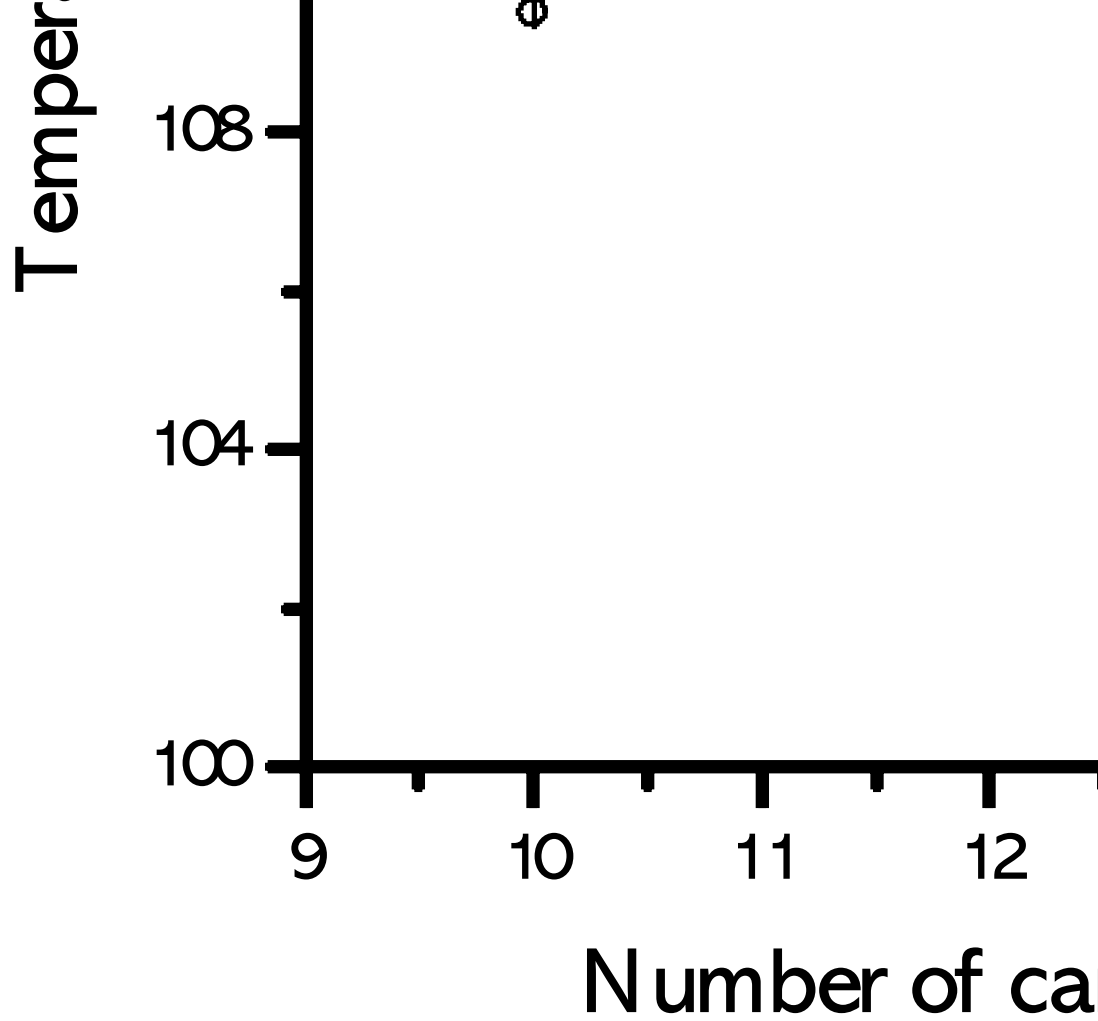[b] The enthalpy could not be measured as the sample crystallizes immediately.

Figure 4. Plot of transiti...
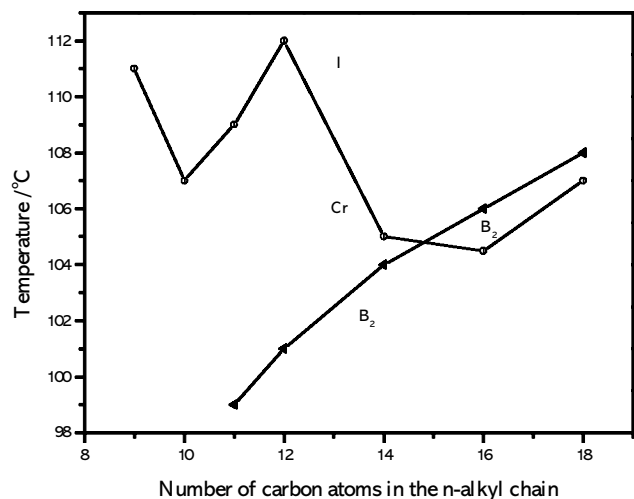of carbon atoms in th...
series I.

Figure 5. Plot of transition temperatures versus the number of carbon atoms in the *n*-alkyl chain for compounds of series II.

smooth curve with a rising trend on ascending the series. As mentioned earlier, this is the typical trend observed for B_2 phase–isotropic liquid transition points. Replacement of the terminal *n*-alkoxy chain in series I by the *n*-alkyl chain has a marginal effect on the mesomorphism. For comparison purposes, the transition temperatures and the corresponding enthalpies for the parent compounds [28] are shown in table 4. The parent compounds **22** and **23** are non-mesomorphic as also are the corresponding 2-methyl substituted compounds **15** and **16**. However, compounds **24** to **27** give enantiotropic phases

while the analogous mesophases for **17**, **18** and **19** are monotropic. It can also be seen that in the 2-methyl substituted compounds there is a reduction in the thermal range of the enantiotropic B_2 phase. For example, compound **27** has a thermal range of 14°C while the corresponding analogous compound **20** has a range of only 1.5°C. Again, this clearly indicates that the 2-methyl substituent suppresses the thermal range of the mesophase.

The compounds containing a fluoro substituent *ortho* to a terminal *n*-alkoxy chain (homologues of series III) show a marked difference. All the compounds of this series are non-mesomorphic and the melting points, along with the associated enthalpies, are collected in table 5. In contrast, the parent compounds show interesting phase behaviour [28]. Therefore the 2-methyl substituent totally suppresses the mesophase in these compounds. To sum up, the 2-methyl substituent destabilizes the mesophases in all these series of compounds.

We have reported [12] earlier that by employing a biphenyl moiety on the side arms of the bent-core molecules, the thermal range of the mesophase can be enhanced considerably. Since the thermal range of the mesophase of the five-ring esters is some what small, we decided to examine the influence of the 2-methyl substituent on such compounds containing a biphenyl moiety. The transition temperatures and the associated enthalpies for these compounds (series IV) are summarized in table 6. All the compounds have fairly wide thermal ranges of the mesophase. Compounds **37**, **38** and **39** exhibit only one mesophase. When a sample of these as a thin film was examined by POM highly

Table 4. Transition temperatures (°C) and enthalpies (kJ mol^{-1}), in italics, for compounds of the following series [28]. For key see table 1.

Compound	n	Cr		B_2		I
22	9	●	100.5 *53.3*	—	—	●
23	10	●	102.5 *49.2*	—	—	●
24	11	●	101.5 *28.5*	●	104.0 *22.2*	●
25	12	●	99.5 *31.22*	●	105.5 *23.9*	●
26	14	●	97.5 *55.1*	●	108.5 *25.9*	●
27	16	●	96.5 *42.5*	●	110.5 *26.6*	●

Table 5. Transition temperatures (°C) and enthalpies (kJ mol^{-1}), in italics, for compounds of series III. For key see table 1.

Compound	n	Cr		I
28	7	●	154.0 *85.2*[a]	●
29	8	●	148.0 *84.3*[a]	●
30	9	●	144.5 *53.9*[a]	●
31	10	●	143.0 *60.1*[a]	●
32	11	●	142.0 *51.2*[a]	●
33	12	●	141.0 *59.2*[a]	●
34	14	●	140.0 *71.2*[a]	●
35	16	●	139.0 *87.4*[a]	●
36	18	●	138.5 *89.8*[a]	●

[a] See table 1.

Table 6. Transition temperatures (°C) and enthalpies (kJ mol^{-1}), in italics, for compounds of series IV. For key see table 1.

Compound	n	Cr			B$_2$		B$_1$		I
37	8	●	168.0 *28.5*	—			●	208.0^c b	●
38	9	●	150.0 *29.1*	—			●	197.0^c b	●
39	10	●	147.8 *38.4^a*	—			●	194.2^c b	●
40	11	●	147.6 *43.5^a*	●	192.0^c b	—			●
41	12	●	136.0 *43.3^a*	●	193.0^c b	—			●
42	14	●	135.8 *48.6^a*	●	194.5^c b	—			●
43	16	●	132.0 *56.8^a*	●	194.0 b	—			●
44	18	●	127.5 *44.0*	●	192.5^c b	—			●

^{a,b} See table 1.
^{c} Beyond this temperature the compound decomposes.

colourful spherulitic growth could be seen as the isotropic liquid was cooled. As the temperature was lowered further, the spherulites coalesced to form a mosaic-like texture. A typical photomicrograph of the texture exhibited by compound **39** at 150°C is shown in figure 6. From this, as well as XRD studies, this mesophase has been characterized as a B$_1$ phase. The remaining compounds **40** to **44** of the series show a mesophase that has been characterized as B$_2$. A comparison of the mesomorphic behaviour of these compounds with that of three of the parent compounds [12] reveals the following. While all three parent compounds exhibit a B$_2$ phase with fairly large thermal range, the analogous 2-methyl substituted compounds show a slightly different behaviour. Compound **39** with a *n*-decyl chain shows a B$_1$ phase while the corresponding parent compound exhibits a B$_2$ phase. However, compounds **40** and **41** show a B$_2$ phase
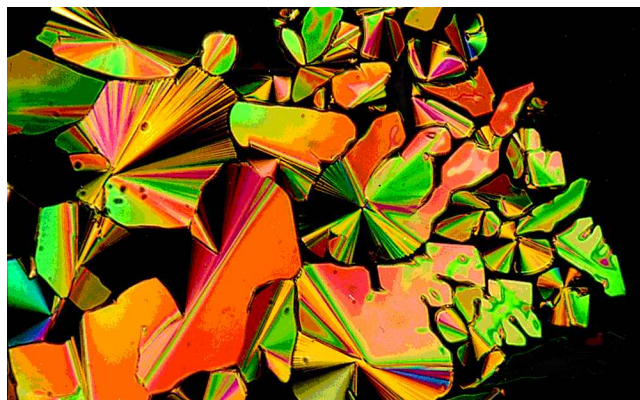
similarly to the parent compounds. The main difference is that the methyl substituted compounds have higher melting points and tend to decompose at the clearing points, while the parent compounds have lower melting points and do not decompose. It is also interesting to note that despite all this, the clearing temperatures are about the same for these six compounds.

5. X-ray diffraction studies

The XRD studies were carried out on non-oriented samples. The sample was generally filled into a 0.5 mm diameter Lindemann capillary tube in the isotropic phase and the ends of the tube were flame sealed. The diffraction patterns were collected on an image plate with an effective pixel size of 100 μm, procured from Marresearch. The diffraction pattern was recorded on cooling the sample into the mesophase. A typical diffraction pattern obtained for compound **8** at 107°C is shown in figure 7. As can be seen this shows four reflections in the small angle region with spacings 42.1, 21.4, 14.3 and 10.7 Å which can be indexed as (0 0 1), (0 0 2), (0 0 3) and (0 0 4) reflections. The periodicities 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 can also be seen. The X-ray angular intensity profile depicted in figure 7 is identical to that observed for the B$_2$ phase [12]. Based on these results, as well as on the microscopic textural observation, this mesophase has been identified as B$_2$. The lamellar spacing of 42.1 Å obtained for compound **8** corresponds to a tilt angle of 56.3° which is calculated assuming the molecule has the conformation shown in figure 8 in which the methylene units of the chains are in a fully extended all *trans*-conformation.
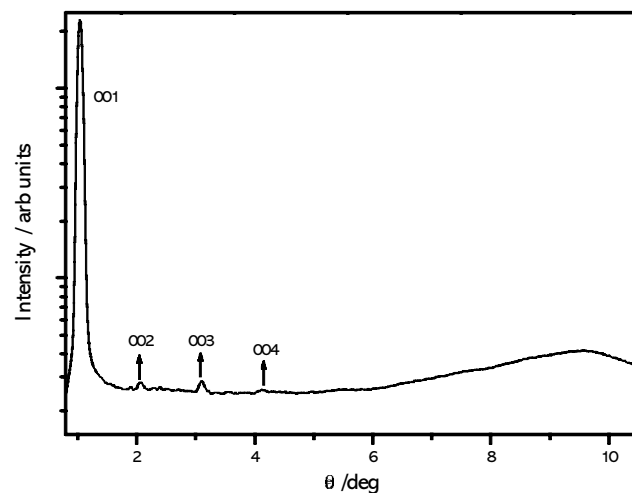

Figure 6. Photomicrograph of the two-dimensional B$_1$ phase of compound **39** at 150°C.

Figure 7. X-ray angular intensity profile of the B$_2$ phase of compound **8** at 107°C.

Figure 8. Molecular model of compound **8** in which the chains are in a fully extended all *trans*-conformation.

Similar diffraction patterns were obtained for the mesophases of compounds **4**–**7** of this series, compounds **11**–**15** in series II and compounds **28**–**32** in series IV. Hence, all these mesophases have been identified as B_2.

The XRD pattern of the mesophase exhibited by compounds **37**, **38** and **39** are identical. The angular intensity profile of the mesophase of compound **39** at 150°C is shown in figure 9. This shows three reflections in the small angle region at 32.5, 24.78 and 14.1 Å which could be indexed as (0 0 2), (1 0 1) and (2 0 0) reflections, respectively, of a centred rectangular two-dimensional lattice as observed before for the B_1 phase [5, 12]. The lattice parameters are $a = 26.8$ Å and $b = 65.0$ Å. Based on these data the mesophase has been identified as B_1. The mesophases of compounds **37** and **38**, which gave similar results, have also been identified as B_1.

6. Electrooptical studies

The effect of a d.c. electric field on the B_2 phase of compound **7** has been studied. The sample was held in a 5 μm thick cell made with conducting plates (ITO coated glass plates), treated with polyimide and unidirectionally rubbed. The sample was viewed between crossed polarizers in the polarizing microscope. As the sample was cooled at a slow rate of 0.1°C min^{-1} under a d.c. field of 4.2 V μm^{-1}, circular domains with characteristic

extinction brushes were formed. In the applied field, the brushes were oriented at an angle of ∼45° with respect to the orientation directions of the crossed polarizers. On reversing the polarity of the applied field, the brushes rotated in the same direction, i.e. the rotation of the brushes in this case occurred in only one direction independent of the sign of the applied field. On switching

(a)

(b)

(c)

Figure 10. Photomicrographs illustrating the effect of a d.c. electric field on compound **7**; rubbed polyimide coated plates at 105°C; (*a*) + 21.3 V, (*b*) 0 V, (*c*) − 21.3 V.
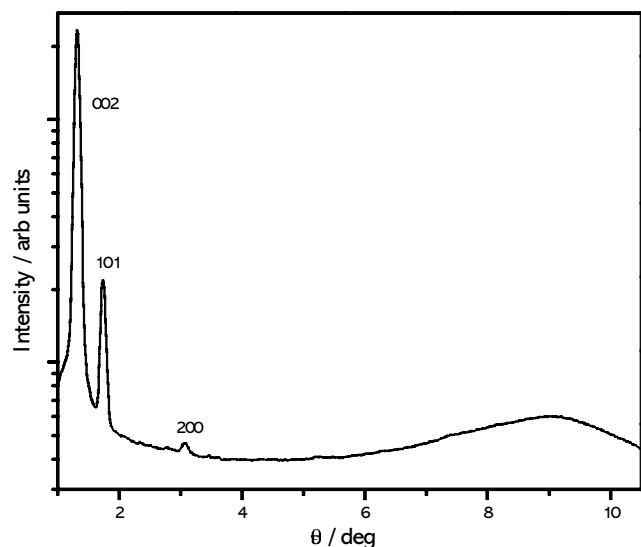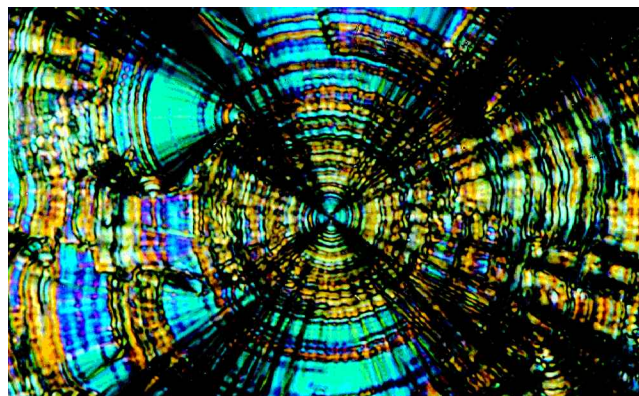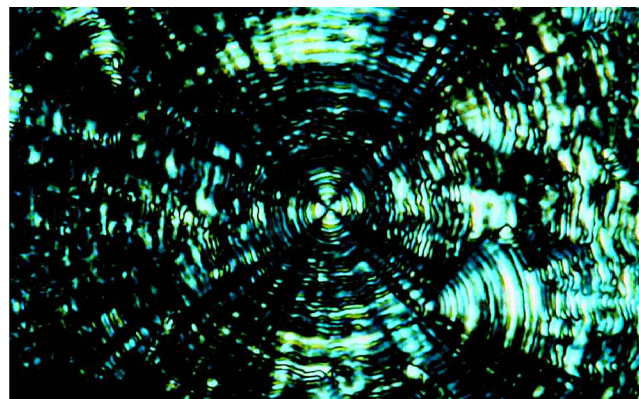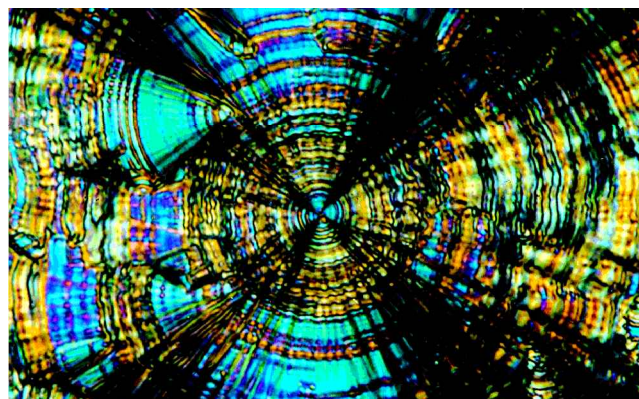

Figure 9. X-ray angular intensity profile of the B_1 phase of compound **39** at 150°C.

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 racemic ground state [29] of the B_2 phase. Figures 10 (*a*, *b*, *c*) show the textures of compound **7** in the presence and absence of the electric field.

Under low d.c. fields the stripes become birefringent and they begin to disappear as the voltage is increased. For this compound the stripes remain up to 23 V after which they begin to disappear. These observations indicate a racemic ground state in this compound which is characterized by synclinic interlayer correlation with an antiferroelectric order from layer to layer.

In order to establish conclusively the antiferroelectric nature of this phase, a switching current response profile was obtained under a triangular wave voltage for compound **20**. The sample was filled in its isotropic state into a cell (ITO coated and etched to give a precise area of $0.8\,cm^2$) of $45\,\mu m$ thickness and treated for homogenous alignment. When a triangular wave with a peak-to-peak voltage of 173 V and a frequency of 65 Hz at 105.5°C was applied, two fairly sharp peaks were recorded during a half period indicating an antiferroelectric switching behaviour. Figure 11 depicts a typical current response profile for this compound. The spontaneous polarization determined by integrating the switching current peaks amounts to about $410\,nC\,cm^{-2}$.

7. Conclusions

Thirty-two compounds having banana-shaped molecules derived from 2-methylresorcinol have been synthesized and their mesomorphic properties examined. The antiferroelectric B_2 phase or the two-dimensional B_1 phase has been observed in many of the compounds. In one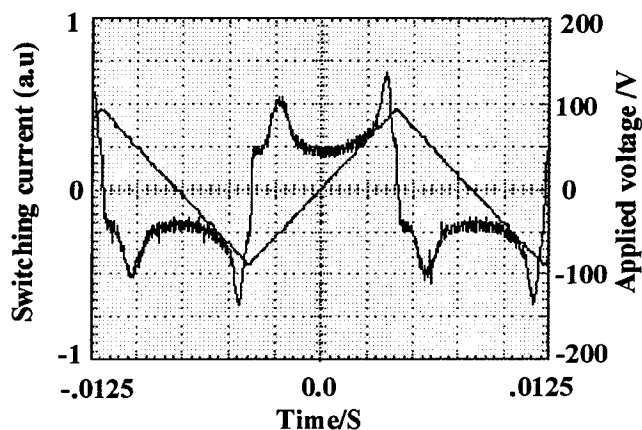 series containing a fluorine atom on the outer phenyl ring, no mesophase could be obtained. The influence of 2-methylresorcinol as the central unit on the mesomorphic properties in the four homologous series has been examined and it is concluded that this central unit has a destabilizing effect on the mesophases.

Figure 11. Switching current response in the B_2 phase of compound **20** on applying a triangular voltage (173 V_{PP}, 65 Hz, 105.5°C).

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