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B. K. Sadashiva^a; H. N. Shreenivasa Murthy^a; Surajit Dhara^a

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

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Preliminary communication

Effect of lateral substituents on the mesophases formed by some achiral banana-shaped molecules

B. K. SADASHIVA*, H. N. SHREENIVASA MURTHY and SURAJIT DHARA

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

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Several compounds composed of banana-shaped molecules and exhibiting mesophases are reported. The effect of different lateral substituents on the type of mesophase formed is examined and a comparison made with unsubstituted compounds. The mesophases have been characterized using techniques such as polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction. The B_2 phase shows antiferroelectric switching behaviour.

Following the observation of a ferroelectric phase in achiral compounds composed of banana-shaped molecules by Niori *et al.* [1], there has been increased interest in synthesizing new materials and studying their physical properties. Recently, a number of such compounds have been synthesized [2–12] and so far, five different mesophases have been clearly identified. Amongst these, two mesophases, viz. B_1 and B_2 , have been well characterized. The B_1 phase is a two-dimensional phase with a rectangular lattice similar to those observed in rectangular columnar mesophases of disc-like molecules. The B_2 phase is a fluid lamellar phase with antiferroelectric switchable characteristics [13]. Although these two mesophases have been observed in a relatively large number of compounds, the relationship between molecular structure and their liquid crystalline properties is not well understood.

In this preliminary communication, we examine the effects of a number of lateral substituents on the mesophases formed by compounds composed of achiral banana-shaped molecules. To our knowledge such a study has not been undertaken before, and such studies should throw more light on our understanding of structure–property relationships in these bent-core compounds. All the compounds are esters and are thermally stable; they are derived from resorcinol and contain seven aryl rings. All the compounds were prepared following the general synthetic pathway shown in figure 1; the detailed procedure for the preparation of compound **10** has been described previously [11]. The compounds were purified by chromatographic techniques. The structure of each compound was confirmed by spectroscopic methods.

A preliminary identification of the liquid crystalline phases were made by polarizing optical microscopy (POM) using a Leitz Laborlux 12 POL equipped with a Mettler 52 heating stage and FP5 controller. The phase transition temperatures and associated enthalpies were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer Pyris 1 D. The calorimeter was calibrated using pure indium as a standard. The phase structures were determined by X-ray diffraction (XRD) experiments 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 temperature was controlled to better than $\pm 0.1^\circ\text{C}$. Electro-optical investigations were carried out with $4\ \mu\text{m}$ thick polyimide coated ITO cells by applying a triangular voltage using a function generator, Wavetek Model 39, and an amplifier, Trek Model 601-2.

The mesophases exhibited by all the compounds could be easily identified from their characteristic textures. All the compounds display only one banana phase. The transition temperatures together with the associated enthalpies for the unsubstituted parent compounds (series I) and the various substituted derivatives (series II) are summarized in tables 1 and 2, respectively. Compounds **1** to **4** are enantiotropic and exhibit the same type of mesophase. This shows a mosaic texture; a typical texture obtained on slow cooling of the isotropic liquid of compound **3** is shown in figure 2. The clearing enthalpy is fairly high at about $23\ \text{kJ mol}^{-1}$. This mesophase shows the characteristic behaviour of the B_1 phase. Compounds **5** and **6** show a different type of mesophase:

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

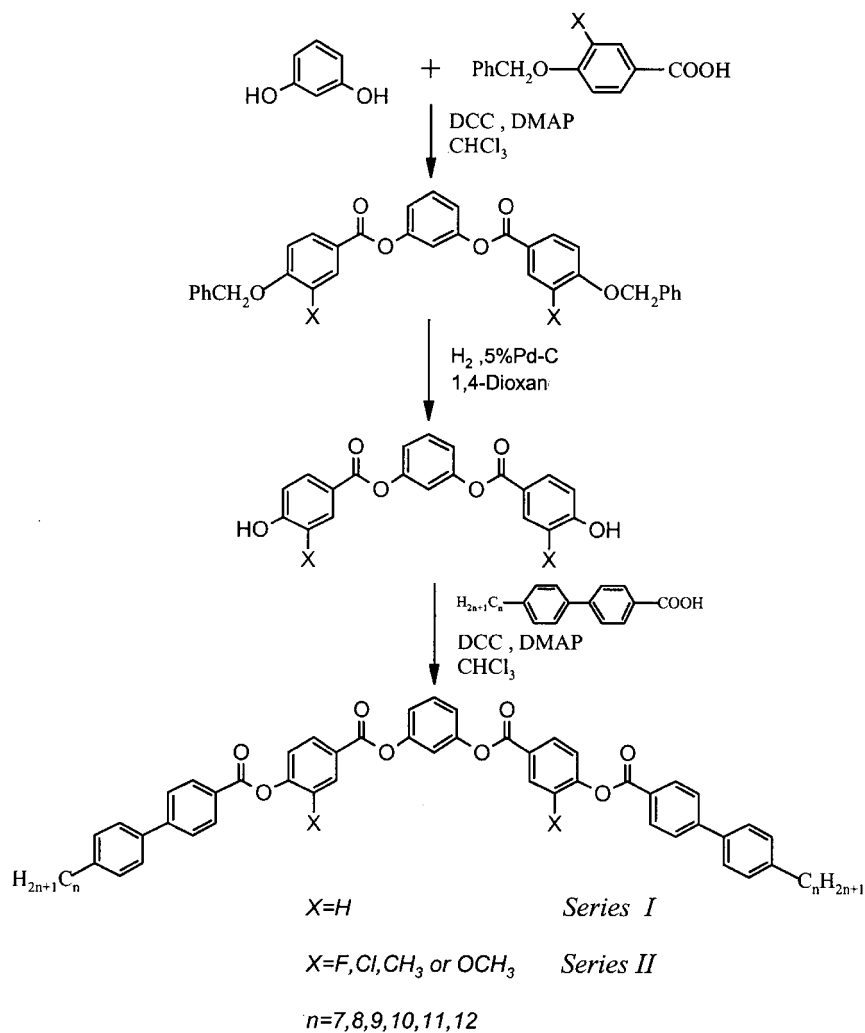


Figure 1. Synthetic pathway used to obtain the banana-shaped mesogens.

Table 1. Transition temperatures ($^{\circ}C$) and enthalpy values ($kJ\ mol^{-1}$) (in italics) for compounds of series I. Cr = crystal, I = isotropic; the nomenclature of the mesophases B_1 and B_2 are those suggested at the Workshop on 'Banana-shaped liquid crystals: Chirality by Achiral Molecules', December 1997, Berlin.

Compound	n	Cr	B_2	B_1	I
1	7	•	163.5 ^a	—	• 235.0
			<i>50.56</i>		• <i>23.46</i>
2	8	•	153.5	—	• 226.0
			<i>36.14</i>		• <i>23.81</i>
3	9	•	141.0	—	• 219.0
			<i>50.98</i>		• <i>24.24</i>
4	10	•	159.0	—	• 211.0
			<i>42.87</i>		• <i>23.76</i>
5	11	•	151.0 ^a	• 209.0	—
			<i>61.42</i>	• <i>25.45</i>	
6	12	•	121.0 ^a	• 209.0	—
			<i>53.14</i>	• <i>26.99</i>	

^a crystal-crystal transition; enthalpy denoted is the sum of all transitions.

on cooling the isotropic liquid of these compounds, an unspecified finger-print texture is obtained and a typical texture for compound **6** is shown in figure 3. This mesophase is less viscous than those of the lower homologues. The mesophase exhibited by compounds **5** and **6** has been identified as the B_2 phase. The clearing enthalpies of all six compounds in table 1 are comparable.

In order to confirm the identity of these mesophases XRD measurements have been carried out. The diffraction pattern of an unoriented sample of the mesophase of compound **3** shows a diffuse peak in the wide angle region with $d \sim 4.7\text{ \AA}$, indicating a liquid-like in-plane order. In the small angle region two reflections at $d_1 = 32.7\text{ \AA}$ and $d_2 = 24.8\text{ \AA}$ were obtained which could be indexed as the (1 1) and (0 2) reflections from a rectangular lattice with $a = 43.5\text{ \AA}$ and $b = 49.7\text{ \AA}$. A typical diffraction pattern obtained for this compound is shown in figure 4. This is similar to the patterns observed for the standard material [2, 3] as well as our own observations [11, 12]. Based on these we have identified this mesophase to be B_1 in nature. The XRD pattern of an unoriented sample

Table 2. Transition temperatures ($^{\circ}\text{C}$) and enthalpy values (kJ mol^{-1}) (in italics) for compounds of series II. (See table 1 for explanation of symbols.)

Compound	n	X	Cr		B_2		B_1		I
7	10	F	•	141.5 <i>27.96</i>	—		•	197.0 <i>22.70</i>	•
8	11	F	•	142.0 <i>35.86</i>	—		•	191.0 <i>22.13</i>	•
9	12	F	•	146.0 <i>40.04</i>	—		•	185.5 <i>22.07</i>	•
10	10	Cl	•	132.0 <i>20.2</i>	—		•	156.5 <i>16.05</i>	•
11	11	Cl	•	128.0 <i>15.91</i>	—		•	153.0 <i>15.36</i>	•
12	12	Cl	•	131.0 <i>15.15</i>	—		•	148.0 <i>14.34</i>	•
13	10	CH_3	•	139.0 <i>68.23</i>	—		(•)	127.5) ^a <i>13.87</i>	•
14	11	CH_3	•	138.5 <i>74.35</i>	(•)	124.0) ^a <i>15.42</i>	—		•
15	12	CH_3	•	114.0 <i>56.38</i>	•	128.5 <i>16.27</i>	—		•
16	10	OCH_3	•	124.0 <i>46.32</i>	—		(•)	119.5) ^a <i>15.0</i>	•
17	11	OCH_3	•	124.0 <i>52.0</i>	(•)	123.5) ^a <i>17.6</i>	—		•
18	12	OCH_3	•	130.5 <i>62.12</i>	(•)	127.5) ^a <i>18.5</i>	—		•

^a Monotropic transition

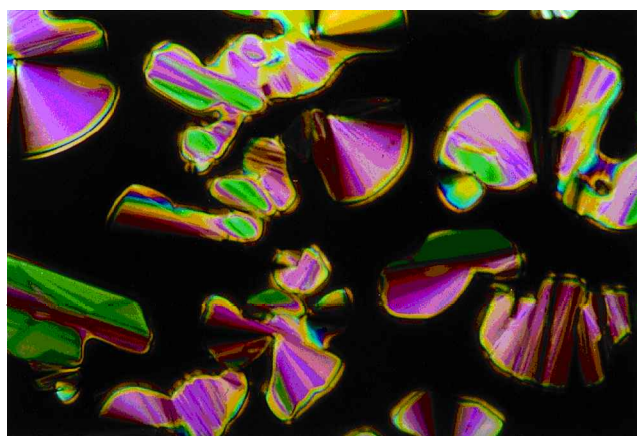


Figure 2. Optical photomicrograph of the B_1 phase developing from the isotropic liquid of compound **3** at 217°C .

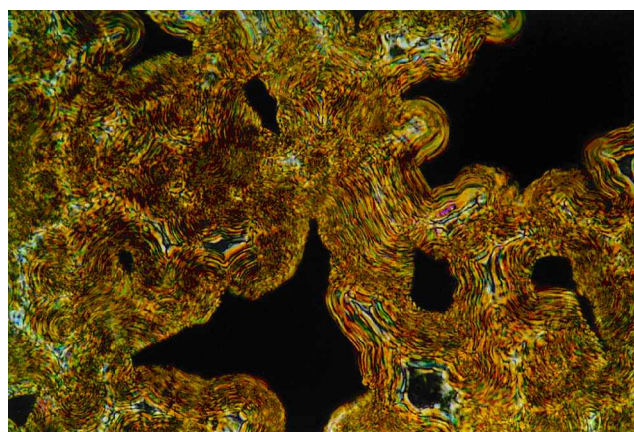


Figure 3. Optical photomicrograph of the B_2 phase developing from the isotropic liquid of compound **6** at 208°C .

of compound **6** also displayed a diffuse peak in the wide angle region, with $d \sim 4.6 \text{ \AA}$, indicative of a liquid-like in-plane order. In addition, four orders of lamellar reflections (in the ratio 1:2:3:4) could be seen. The angular intensity profile of this mesophase is shown in figure 5. From these data and the textural characteristics, we have identified this mesophase to be a B_2 phase.

The switching behaviour of the B_2 phase was observed using electro-optical measurements as well as by simultaneously viewing the sample under a polarizing

microscope. A cell of $4 \mu\text{m}$ thickness was prepared for homogeneous alignment of the sample, and was filled in the isotropic phase and cooled slowly. After the transition to the mesophase, the applied field was gradually increased to get better alignment and saturated current peaks. By applying a sufficiently high ($200 V_{pp}$) triangular voltage, a current response peak per half period could be seen on the oscilloscope screen. A typical switching current response obtained for compound **6** is shown in figure 6. The current was measured across a

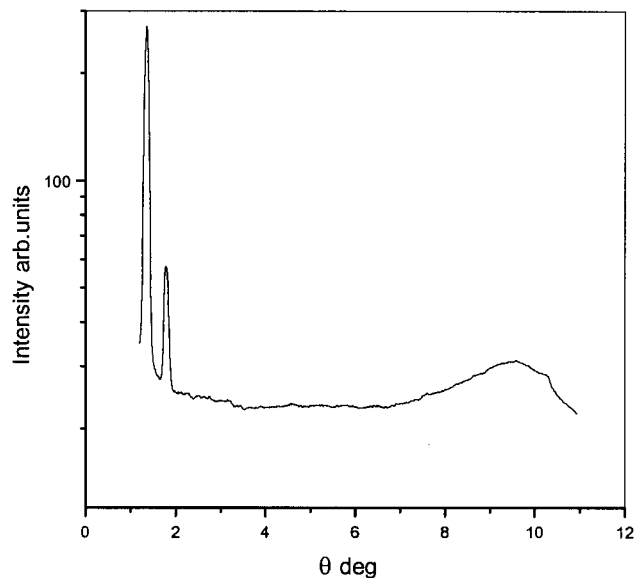


Figure 4. X-ray intensity profile of an unoriented sample of compound **3** at 155°C.

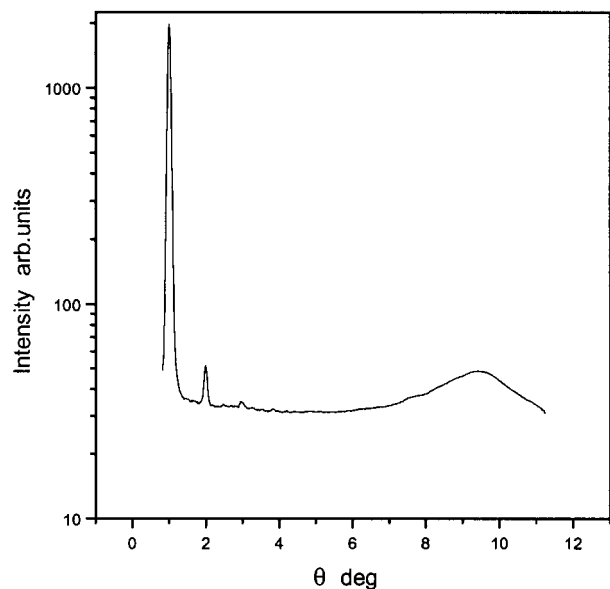


Figure 5. X-ray intensity profile of an unoriented sample of compound **6** at 150°C.

10 k Ω resistance. The apparent 'saturated polarization' P_S was derived from the area under the peaks to be about 760 nC cm $^{-2}$ and is nearly temperature independent except close to the clearing point. The electro-optical response of this sample was also observed under a polarizing microscope. On cooling the sample slowly from the isotropic liquid under an a.c. electric field, a striped focal-conic texture appears when the transition to the mesophase occurs. On increasing the voltage further, the stripes become clearer and sharper. We have observed similar behaviour for the B $_2$ phase of com-

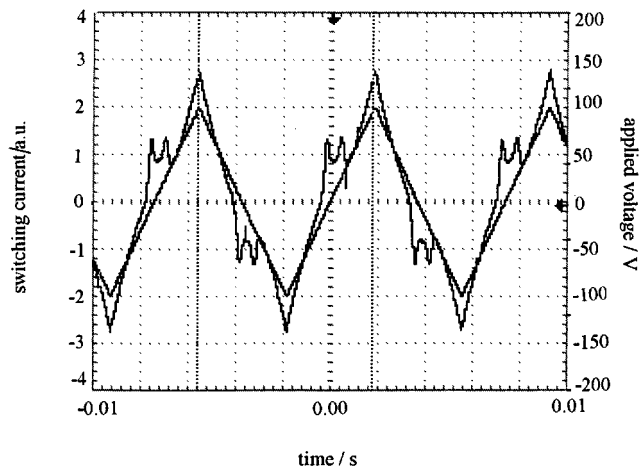


Figure 6. Switching current response in the B $_2$ phase of compound **6** obtained by applying a triangular voltage (200 Vpp): sample thickness 4 μ m, temperature 150°C, polarization \sim 760 nC cm $^{-2}$.

pound **15** [11]. These observations clearly indicate that the mesophase is antiferroelectric in character.

We have examined the effects of some lateral substituents on the mesophases formed by these banana-shaped compounds. The substituents used are fluoro, chloro, methyl and methoxy groups. The same three homologues, viz. $n = 10, 11, 12$ with each of these groups in the same position, were studied. A comparison of the mesophase types and transition temperatures of the unsubstituted parent compounds **4**, **5** and **6** and the differently substituted compounds **7** to **18** (see tables 1 and 2) indicates the following. In all cases, from the small fluoro substituent to the large, bulky methoxy group, there is a reduction of the clearing temperatures. Except for compounds **9**, **12** and **18**, there is also a general decrease in the melting points.

The introduction of a fluoro substituent increases the molecular lateral dimension marginally with a small associated increase in the steric interactions. Since the fluoro substituent is strongly electronegative, it also affects the polarity of the system, and hence the dipolar interactions between neighbouring molecules will be considerable. Indeed, there will be a competition between steric and dipolar interactions whenever a ring hydrogen is replaced by any substituent. Compound **4** shows a B $_1$ phase while compounds **5** and **6** exhibit the B $_2$ phase. The corresponding fluoro-substituted compounds **7**, **8** and **9** show only the B $_1$ phase, eliminating the B $_2$ phase completely. Similar behaviour was observed for the chloro-substituted compounds **10**, **11** and **12**. However, in the case of the methyl substituted derivatives **13**, **14** and **15**, the phases present in the parent compounds are retained although with considerable reductions in the transition temperatures. In the case of the bulky methoxy

substituent, compounds **16**, **17** and **18**, the enantiotropic mesophases present in the parent compounds are replaced by monotropic behaviour but without affecting the nature of the mesophases. As one proceeds from fluoro to chloro, methyl and methoxy groups, their size increases gradually. This results in the lowering of the clearing temperatures, in that order. Although the size of the chloro and methyl groups are about the same, there is a difference in the way they affect the mesophases of the parent compounds. The main difference between these two substituents is that their dipoles are in opposing directions. Also, both fluoro and chloro substituents eliminate the B₂ phase present in the parent compounds. This suggests that dipolar effects are significant when compared with steric factors in these compounds.

A number of other compounds with substituents in different positions have been prepared and the results of studies on these will be presented in a forthcoming publication.

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