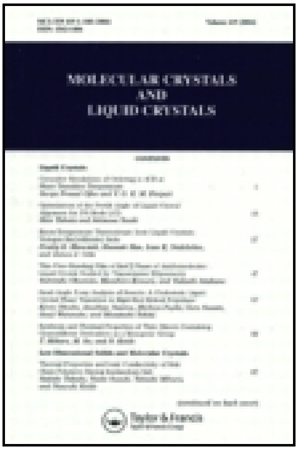

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T. Niori [a], J. Yamamoto [a] & H. Yokoyama [a]

[a] Yokoyama Nano-structured Liquid Crystal Project, Japan Science and Technology Corporation, Ibaraki, Tsukuba, Japan

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SEARCH FOR THE B PHASE IN AN ACHIRAL NON-SYMMETRIC BANANA-SHAPED MATERIALS

T. Niori, J. Yamamoto, and H. Yokoyama
Japan Science and Technology Corporation, Yokoyama
Nano-structured Liquid Crystal Project, 5-9-9 Tokodai,
Tsukuba, Ibaraki 300-2635, JAPAN

We synthesised a series of banana-shaped materials to search for the B phase in an achiral non-symmetric system. Almost compounds were found to exhibit the B phase, B1 and B2. Interestingly some compounds formed the classical mesophases which were observed in usual rod-like molecular system. In this paper we will report the synthesis and the mesophase properties of these materials.

Keywords: B phase; nematic phase; non-symmetric banana-shaped material

INTRODUCTION

Since the discovery of the novel electro-optical properties in an achiral system composed of the banana-shaped material [1], many research groups have been drawn much interests by this field from both the physical and chemical points of view. As consequence of the vigorous works, a large number of compounds have been reported in this last five years [2] and the seven, or maybe more, types of B phase has been discovered. In these B phases, B2 phase is the most interesting and the most investigated one due to not only its electro-optical behaviour but also its variety of the ground state [3]. In the banana-shaped molecular system, the mesophase properties are very much sensitive to the chemical structure. For example, the original banana-shaped compound with terminal octyloxy chain forms B2 phase [4,5], whereas the chloro substitution at the terminal benzene ring [6] or the nitro substitution at the central core [7] with the same terminal chain makes the phase behaviour completely different. These materials show B7 phase. In Addition, it is amazing that the banana-shaped compound can form the conventional mesophases such as smectic A, C

Address correspondence to T. Niori, Japan Science and Technology Corporation, Yokoyama Nano-structured Liquid Crystal Project, 5-9-9 Tokodai, Tsukuba, Ibaraki 300-2635, Japan.

and nematic phases [8,9] as well as B phases. We have already reported the mesophase properties of some achiral non-symmetric banana-shaped compounds [8]. This time we synthesised new series of banana-shaped materials for the purpose of searching for the B phase in the non-symmetric system and investigated their mesophase properties by means of the classical method; DSC, POM, XRD and electro-optical measurement. Almost materials were found to form the B phase (B1 or B2) but some of them exhibited conventional smectic phases. Moreover a nematic phase was observed for some compounds.

MATERIALS

All materials synthesised are listed in Figure 1 and their transition temperatures are summarised in Table 1. The synthetic route of compound 9 is shown in Scheme 1 and each step is described below.

• 3-Chloro-4-n-octyloxybenzoic Acid (I)

Ethyl 3-chloro-4-hydroxybenzoate (0.1 mol) and Potassium carbonate (0.1 mol) was dissolved in 200 ml of Ethanol and the solution was heated. Then 1-Bromooctane (0.15 mol) in 10 ml of Ethanol was gradually added to this solution with vigorously stirring. The final mixture was kept with reflux for 20 hrs. The reaction mixture was cooled down and the precipitated KBr was filtered off. The solvent was reheated and Sodium hydroxide (0.12 mol) in 100 ml of water was added. The mixture was refluxed for further 4 hrs and then cooled down. Then the solution was acidified by HCl and the precipitates were collected. The crude product was recrystallised twice from n-Hexane.

• 4-Nitrophenyl 3′-chloro-4′-n-octyloxybenzoate (II)

4-Nitrophenol (0.05 mol) and 3-Chloro-4-n-octyloxybenzoic acid (0.05 mol) was dissolved in 100 ml of Chloroform and to this solution DCC (0.06 mol) and catalytic amount of DMAP was added. The mixture was kept with stirring for 24 hrs at room temperature. The precipitated urea was filtered off and the solvent was removed under reduced pressure. The residue was recrystallised twice from Ethanol/n-Hexane mixture. The final product was purified by column chromatography (Silica gel, Chloroform as eluent).

• 4-Aminophenyl 3′-chloro-4′-n-octyloxybenzoate (III)

4-Nitrophenyl 3′-chloro-4′-n-octyloxybenzoate (0.03 mol) was dissolved in Ethyl acetate and Ethanol mixture. The solvent was kept with stirring for 24 hrs at room temperature in the presence of Palladium on carbon under

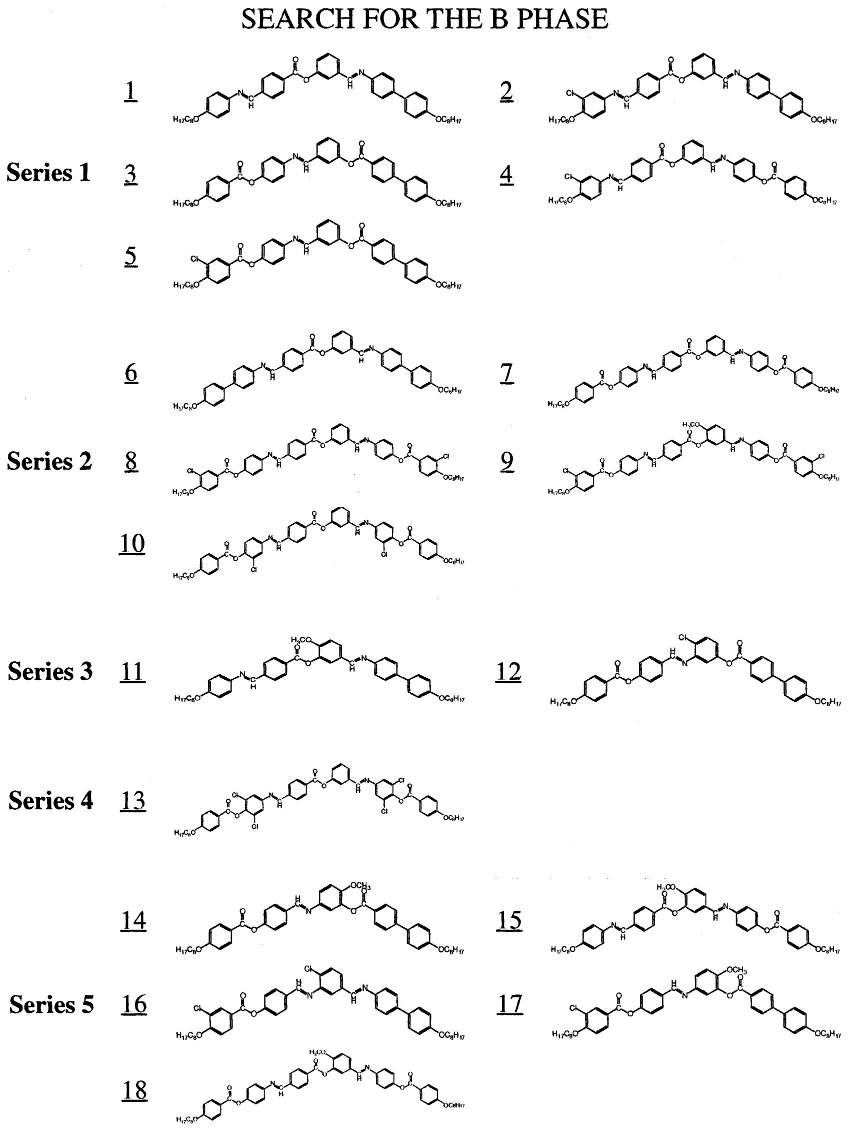


FIGURE 1 Chemical structures of non-symmetric banana-shaped materials.

Hydrogen atmosphere. Then the catalyst was filtered off and the solvent was removed under reduced pressure. The crude product was recrystallised twice from Ethanol/n-Hexane mixture. The final product was purified by column chromatography (Alumina activated, Chloroform as eluent).

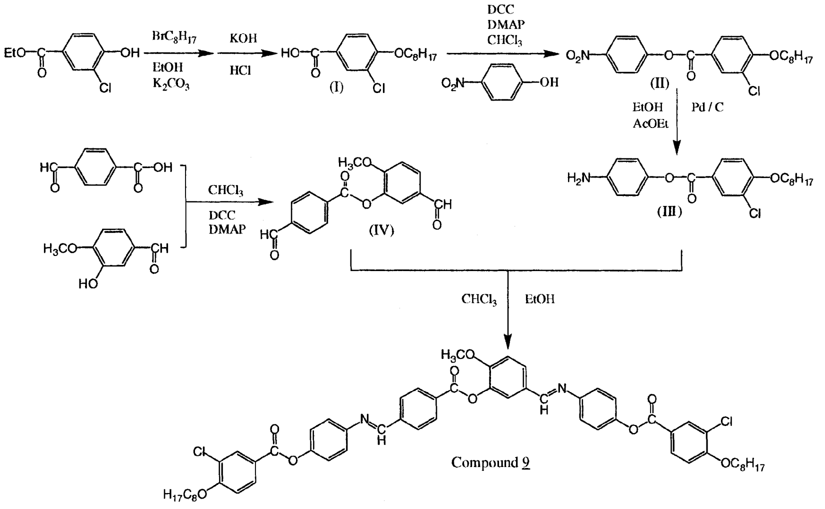
TABLE 1 Phase Transition Temperatures of Series 1,2,3, 4 and 5

Series 1	1	Iso. – 180°C – B2 – 166°C – K
	2	Iso. – 160°C – BXI – 110°C – BX2 – 85°C – K
	3	Iso. – 144°C – B1 – 110°C – K
	4	Iso. – 143°C – B1- 82°C – K
	5	Iso. – 137°C – B2 – 93°C – K
Series 2	6	Iso. – 246°C – B2 – 241°C – K
	7	Iso. – 201°C – B1 – 126°C – K
	8	Iso. – 163°C – B1 – 86°C – K
	9	Iso. – 147°C – B2 – 60°C – G
	10	Iso. – 108°C – B1 – 40°C – G
Series 3	11	Iso. – 223°C – SmA – 199°C – K
	12	Iso. – 205°C – SmA – 114°C – K
Series 4	13	Iso. – 143°C – unique phase – 71°C – K
Series 5	14	Iso. – 116°C – N – 79°C – K
	15	*Iso. – –100°C – –N – –83°C – –SmA – –41°C – –K*
	16	Iso. – 284°C – N – 250°C – SmC – 108°C – K
	17	Iso. – 95°C – N – 79°C – B4
	18	Iso. – 201°C – N – 162°C – B1 – 56°C – K

G : Glass state.

• 2-Methoxy-5-formylphenyl 4′-formylbenzoate (IV)

Terephthalaldehydic acid (0.1 mol) and Isovanillin (0.1 mol) was added to the solution of DCC (0.12 mol) in 200 ml of Chloroform. DMAP was added as catalyst and the mixture was kept with stirring for 24 hrs at room



SCHEME 1

temperature. The precipitates were filtered off and the solvent was removed under reduced pressure. The crude product was recrystallised twice from Ethanol and the final product was purified by column chromatography (Silica gel, Chloroform as eluent).

• Compound 9

3 mmol of (III) and 1.3 mmol of (IV) was dissolved in the mixture of Chloroform/Ethanol (1:4). The solution was refluxed for 5 hrs and the reaction mixture was cooled down. The precipitates were filtered off and the residue was recrystallised from Chloroform/Ethanol mixture. The final product was purified by column chromatography (Alumina activated, Chloroform as eluent).

RESULTS

As can be seen in Table 1, all compounds prepared formed mesophase. They are categorised into five series for convenience. Series 1 and 2 are the materials showing B phases and the former series are composed of 5 benzene rings, whereas the later are of 6 benzene rings. Two compounds in series 3 form SmA phase. Series 4 exhibits unique phase behaviour [10] and series 5 is all nematogenic compounds. We will report here the mesophase properties of series 1,2,3 and compound 15, 18. The rest will be introduced in another report [10]. Almost B phases can be easily identified by the polarised microscopy and confirmed by X-ray diffraction measurement. Up to date, however, two phases observed for compound 2 could not be assigned so that they are temporarily designated as BXI and BX2, respectively. The typical textures of B1, B2 and SmA phases are shown in Figures 2. In general, the texture of B1 phase appears as platelet and coalesces to the mosaic-like texture shown in Figure 2(a). Whereas the grainy texture is usually observed for B2 phase as can be seen in Figure 2(b). In SmA phase, the bâtonnets are initially appeared from the isotropic melt and coalesce to the focal conic fan-shaped domain (see Fig. 2(c)). Shearing the glass plates in the SmA state, homeotropic alignment can be easily achieved and no birefringence is observed under the polarised optical microscope. We have carried out the X-ray investigations for all materials and the results of the layer spacing are listed in Table 2. The layer spacings of B and SmA phases were found to be independent of the temperature. The typical X-ray patterns are shown in Figures 3. It is difficult to orient the molecules in a glass capillary but the unit cell of the B1 phase can be easily estimated by the assumption that the inner and outer sharp reflections are associated with (110) and (200), respectively. The

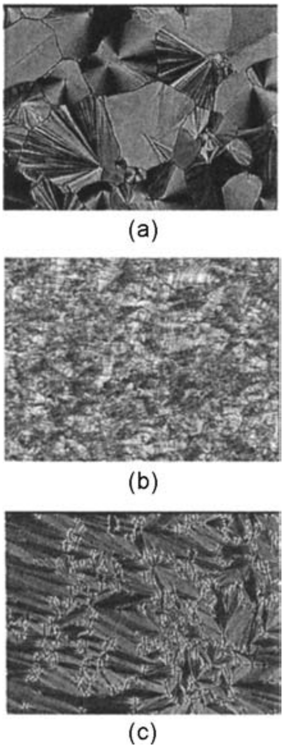


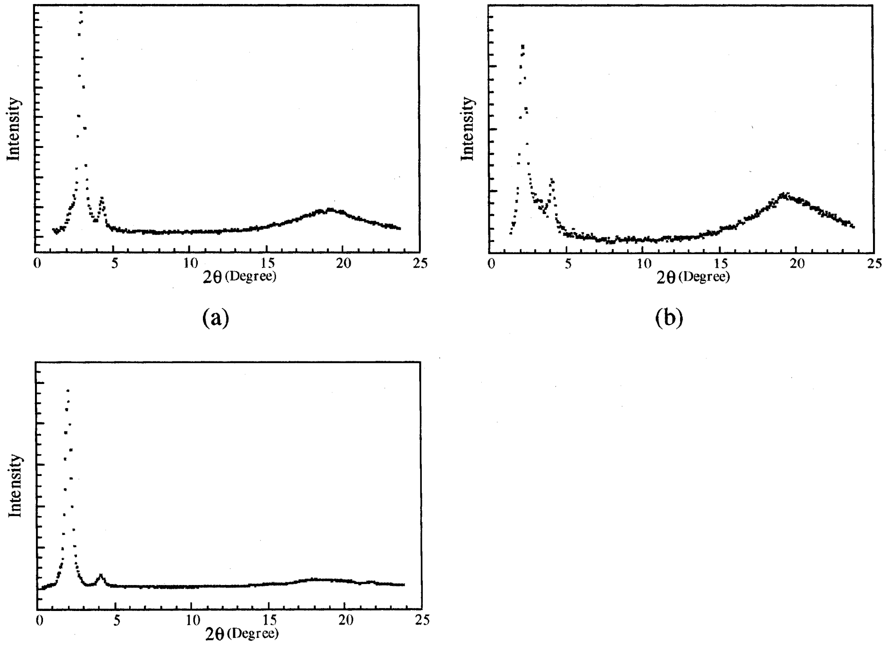
FIGURE 2 Typical textures of (a) B1, (b) B2, and (c) SmA phases.

calculated unit cell parameters a and c, are listed in Table 3 together with the number of the molecule (n) in the unit cell. We are strongly interested in how the molecular shape is in the uniaxial SmA state. However all attempts to obtain the oriented sample were unsuccessful so that the direct evidence of molecular shape is still unclear. Therefore we tried to make a

TABLE 2 List of the Layer Spacing of B Phases and SmA Phase

1	41Å	2	42.3Å (BX1), 43.7Å (BX2)
3	30.1Å, 20.8Å	4	35.6Å, 23.8Å
5	41.6Å	6	——a)
7	33.7Å, 24.0Å	8	42.8Å, 24.0Å
9	42.8Å	10	33.7Å, 24.4Å
11	45.0Å	12	31.5Å
15	41.0Å	18	32.9Å, 26.2Å

a) X-ray measurement could not be carried out due to the narrow temperature range.



(a)

(b)

(c)

FIGURE 3 Typical X-ray patterns of (a) B1 phase for compound 3 at 135°C, (b) B2 phase for compound 5 at 120°C and (c) SmA phase for compound 11 at 215°C.

comparison between the X-ray results and the molecular length calculated from the *all-trans* conformation. In Table 4, the experimental results (d) and the calculated molecular length (L) are summarised. As consequence, the layer spacings of the compound 11 and 15 are comparable to the *all-trans* molecular length. It indicates that the molecular shape in the SmA

TABLE 3 List of the Unit Cell Parameter of B1 Phase

Compound	a(Å)	c(Å)	n
3	41.6	24.4	5.4
4	47.6	28.5	6.3
7	48	47.3	10.5
8	48	94.5	21
10	48.7	27.7	6.2
18	52.4	42.3	9.4

TABLE 4 List of the layer spacing of SmA and the molecular length

Compound	d (Å)	L (Å)
11	45.0	46.9
12	31.5	43.2
15	41.0	47.7

state of these materials may be possibly bent, although the intercalated structure of the linear molecules is also still possible. If the molecule is bent shape in the SmA state, the electrooptical response could be expected even in an achiral system, since the spontaneous polarisation within the layer is probably rotated from one layer to the next just like a SmC* phase (no birefringence in homeotropic). On the other hand, we are not able to explain the observed layer spacing which is much smaller than the molecular length for compound 12. It should be noted here that the introduction of the substitution into the central core sometimes leads the conformational change of the whole molecule [9]. Keeping this in mind, let us look around the chemical structures again. For all compounds exhibited the SmA phase the substitution is introduced into the central core. Therefore the conformational change is also the possibility for SmA phase appearance, although the temperature dependence of the layer spacing could not be detected. In this case, the intercalated smectic phase is the most plausible model.

SUMMARY

We synthesised the new series of achiral non-symmetric bananashaped materials and investigated the mesophase properties. Almost compounds were found to form the B phases but some of them exhibited the conventional mesophase as usually observed in the rodlike molecular system. Especially we are strongly interested in the molecular shape in the classical smectic phase. If the bent shape molecules constitute the SmA phase, the electro-optical response would be expected even in an achiral system.

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