

## Synthesis and Mesomorphic Properties of Banana-Shaped Mesogens with All-Ester Linking Group

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### Abstract

*Four banana-shaped compounds have been synthesized introducing ester linking group into mesogenic unit, varying the central core with 1,6-, 1,7-, 2,3-, and 2,7-naphthylene units, and introducing the dodecyloxy group as the terminal flexible unit. All obtained compounds except one with 1,7-naphthylene unit were reversibly thermotropically liquid crystalline. The compound with 1,7-naphthylene unit could not form the mesophase due to its asymmetrical and sharp substitution angle. The compounds with 1,6- and 2,3-naphthylene units showed an antiferroelectric switchable smectic phase, which has been designated B2 phase. Interestingly, the compound with the 2,3-naphthylene unit showed the two mesophases of B2 and nematic phase.*

### 1. Introduction

Since 1996, many attempts have been made by a number of research groups to modified the parent series of banana-shaped molecules, 1,3-phenylene bis[4-(4-n-alkyl-phenyliminomethyl)benzoates] and 1,3-phenylene bis[4-(4-n-alkyloxyphenyliminomethyl)benzoates]. On the other hand, only a few studies have been made on bent-core mesogens containing only ester linking groups.

In 1998, Shen et al.<sup>[1]</sup> attempted to obtain (anti)ferroelectric switchable achiral banana-shaped molecules without Schiff's base units. Their compound contained 1,3-pyridine, 2,7-naphthalene

and m-terphenyl moieties at the center of mesogen. They found that only molecules with seven aromatic rings show liquid crystalline properties. However none of the synthesized compounds exhibit the typical switching behavior in the mesophase known from the Schiff's base derivatives.

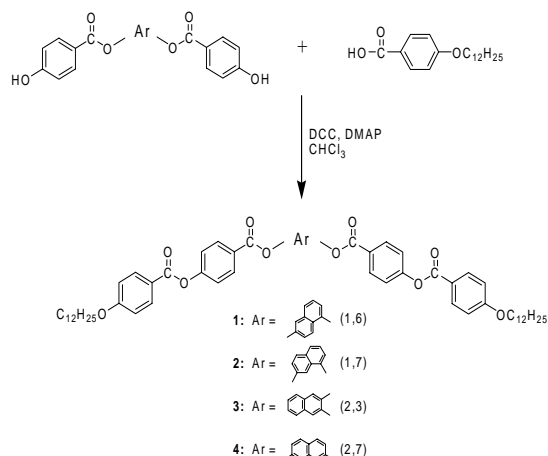
In 2002, Murthy et al.<sup>[3]</sup> reported that banana-shaped mesogens with seven-ring esters. Their compounds containing a biphenyl moiety in the side arms and lateral substituents could form banana phases such as B<sub>1</sub>, B<sub>2</sub> and B<sub>6</sub>. Also, Dantlgraber et al.<sup>[3]</sup> reported the bent-core mesogens with all ester linking groups comprising a central 3,4'-disubstituted biphenyl unit. They found that most compounds exhibited broad regions of antiferroelectrical switchable SmCP<sub>A</sub> phases.

In 2006, Weissflog et al.<sup>[4]</sup> reported that five-ring bent-core mesogens with only ester linking groups. They found that some of the compounds showed polymorphism variants where polar phases occur together with conventional mesophases.

In this study, to know how the structure change in the central unit affect the mesomorphic properties of the bent-core mesogen, four banana-shaped molecules containing only ester linking groups between the aromatic rings were synthesized. The carbon number of the terminal flexible group was fixed to 12, and the central unit was varied with 1,6-, 1,7-, 2,3-, and 2,7-naphthylenes. The properties of mesophase were investigated by differential scanning calorimetry, polarizing optical microscopy, x-ray diffractometry, and electro-optical measurements.

## 2. Experimental

The synthetic route to obtain the banana-shaped molecules used a modified literature procedure<sup>[5]</sup> and is shown in Scheme 1.



**Scheme 1. Synthesis of compounds.**

IR and NMR spectra were obtained by a Jasco 300E FT/IR and a Bruker DPX 200 MHz NMR spectrometers. Elemental analyses were performed with a Thermofinnigan EA1108. The transition behaviors were characterized by DSC (Perkin-Elmer DSC7) and POM (Zeiss, Jenapol). DSC measurements were performed in a N<sub>2</sub> atmosphere with heating and cooling rates of 10°C/min. XRD measurements were performed in transmission mode with synchrotron radiation at the 10C1 x-ray beam line ( $\lambda = 1.54 \text{ \AA}$ ) at Pohang Accelerator Laboratory, Pohang, South Korea. On heating and cooling, the sample sealed with a window of 7  $\mu\text{m}$  thick Kapton film on both sides was held in an aluminum sample holder. The liquid crystals were injected between two ITO glass substrates by a capillary action at isotropic phase (150°C). Each ITO deposited substrate was spin-coated with a commercial polyimide solution of AL1254 (JSR Corp.) and baked for 1 hour at 230°C. The rubbing directions of the upper and lower substrates were antiparallel to each other. The cell gap was 2  $\mu\text{m}$ .

## 3. Results and discussion

In Table 1, obtained compounds show melting and isotropization temperatures at 110-164°C and at

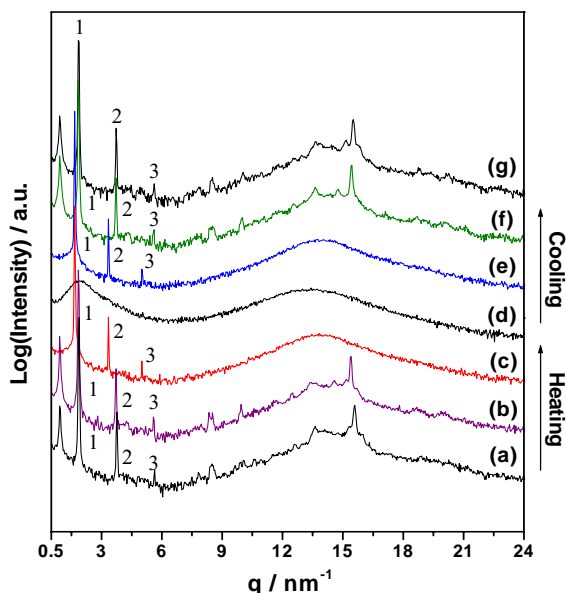
143-217°C, respectively. The melting temperature and the associated enthalpies of compound **2** with unsymmetrical, 60° substitution angle was the highest among four compounds, but could not form a liquid crystalline phase. The mesophase of compound **1** with unsymmetrical, 120° substitution angle and compound **3** with symmetrical, 60° substitution angle showed homeotropic domains in their optical textures. The compounds **1** and **3** showed an antiferroelectric switchable smectic phase, which has been designated B<sub>2</sub> phase. Interestingly, the compound **3** with the 2,3-naphthylene unit showed a smectic mesophase at 212°C as well as a nematic mesophase at 217°C.

**TABLE 1. Transition temperatures (°C) and enthalpies changes (KJ/mol, in parentheses) for the compounds<sup>a</sup>**

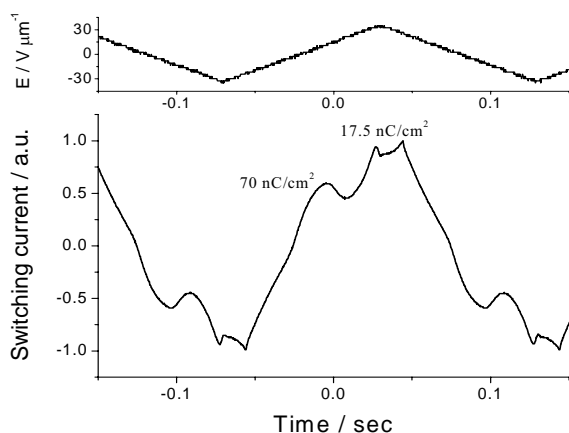
Code	Phase sequence <sup>b</sup>			
	Cr	Sm	N	Iso
<b>1</b> (1,6)	• 110 (21.2)	• 143 (17.9)		•
<b>2</b> (1,7)	• 164 (68.7)			•
<b>3</b> (2,3)	• 134 (50.3)	• 212 (2.76)	• 217 (0.76)	•
<b>4</b> (2,7) <sup>c</sup>	• 134 (21.6)	• 166 (13.9)		•

<sup>a</sup>Cr = crystalline phase; Sm = smectic phase; N = nematic phase; Iso = isotropic phase. <sup>b</sup>The symbol • indicates the occurrence of a phase in a compound. <sup>c</sup>It was known that analogue of compound **4** with dodecyl end group formed B<sub>2</sub> phase<sup>[6]</sup>.

Compound **1** shows crystalline diffraction pattern at room temperature, and as heated to 90°C, the diffraction patterns of small- and wide-angle regions were not changed (Figs. 1a-1b). As heated to 120°C, the peaks in a small-angle region are remained but peaks in a wide-angle region are disappeared (Fig. 1c). As heated to 160°C, the diffraction pattern corresponding to the isotropic liquid phase was observed (Fig. 3d), and it was followed by the cooling process (Figs. 1e-1g). The phase sequence observed in the cooling process was reverse to that observed in the heating process. This indicates that compound **1** can form an enantiotropic smectic mesophase. The *d* value was calculated to be 3.76 nm from the peak at  $q = 1.67 \text{ nm}^{-1}$ . The length of molecule for compound **1** was calculated to be 5.4 nm by assuming the molecular chain to be fully extended in the all-trans-conformation, and the tilt angles ( $\theta$ ) of the mesogen normal to the layer were estimated to be 46°.



**Fig. 1.** X-ray diffraction patterns of compound 1: on heating as-prepared sample, measured at (a) room temperature, (b) 90°C, (c) 120°C, and (d) 160°C; on cooling the isotropic liquid, measured at (e) 110°C, (f) 70°C, and (g) room temperature.



**Fig. 2.** Switching current response in the B2 phase of compound 1 at 120°C on applying a triangular-wave voltage at a frequency of 5 Hz.

The spontaneous polarization of the cell of the smectic mesophases was measured. The cell showed two switching current peaks per every half period when a sufficiently high triangular voltage was applied. This result is a typical experimental evidence to be antiferroelectric B2 phase where the dipole

direction in the bent molecules is antiparallel in adjacent layers at zero field state.

#### 4. Summary

Since 1996, many attempts have been made by a number of research groups to modified the parent series of banana-shaped molecules, 1,3-phenylene bis[4-(4-n-alkyl-phenyliminomethyl)benzoates] and 1,3-phenylene bis[4-(4-n-alkoxyphenyliminomethyl)benzoates]. On the other hand, only a few studies have been made on bent-core mesogens with only ester linking groups. In this study, the mesomorphic properties could be controlled by varying the substitution angle of central naphthylene unit. To date, such mesophase behavior has been observed in only a few classes of bent-core compounds. A remarkable finding is that the bent-core mesogens that possess only ester linking group and unsymmetrical or highly bent central unit can form banana-phase with wide temperature range.

#### Acknowledgements

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