

# Synthesis and Properties of Banana-Shaped Mesogen Containing Isomeric Naphthalene Central Unit

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## Abstract

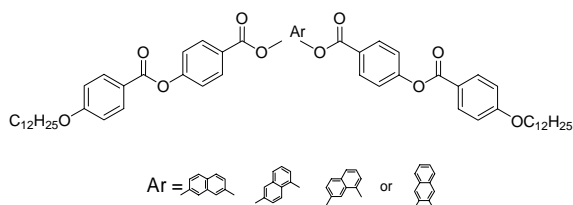
Four bent-core compounds were synthesized introducing ester linking group into mesogenic unit, varying the central unit with 1,6-, 1,7-, 2,3-, and 2,7-naphthylenes, and placing the dodecyloxy group in the terminal flexible unit. The structures of four compounds were identified by FT-IR and <sup>1</sup>H NMR spectroscopy, and the results were in accordance with expected molecular formula. The mesomorphic properties were investigated by differential scanning calorimetry and polarizing optical microscopy.

## 1. Introduction

Over the past few years, a number of studies have been made on establishing the relationship between the structure and properties for the azomethine-type banana-shaped molecules. On the other hand, less report has been given to the ester-type banana-shaped molecules.

As already reported, the ferroelectric and antiferroelectric liquid crystals can be observed in the achiral banana-shaped molecules. The mesomorphic properties of the banana-shape molecules are affected by the angle of the central bent unit and the length of terminal flexible chains.

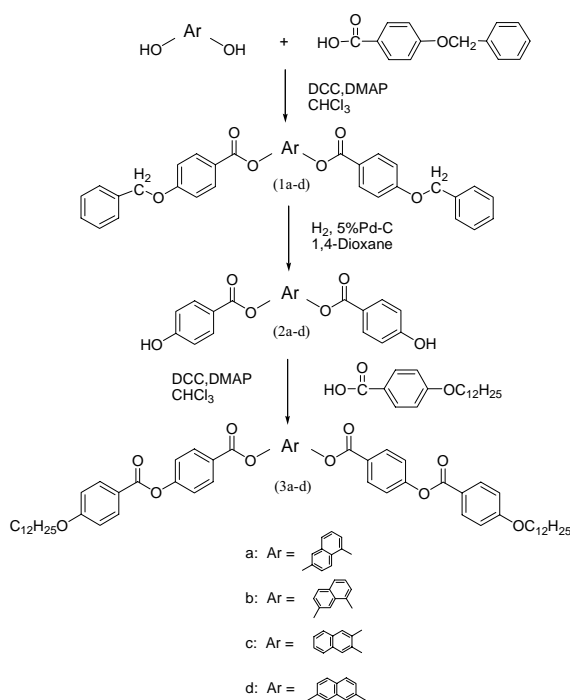
In this study, we synthesized four compounds with different central bent unit, and investigated their mesomorphic properties. All the compounds have the general structure as shown below:



## 2. Experimental

**Synthesis:** Synthetic route is shown in Scheme 1. The  $\alpha,\omega$ -dihydroxynaphthalene reacted with 4-benzyloxybenzoic acid at the presence of 4-dimethylaminopyridine (DMAP) and *N,N'*-dicyclohexylcarbodiimide (DCC), to give the  $\alpha,\omega$ -naphthylene bis(4-benzyloxybenzoate), which reacted with hydrogen at the presence of 10% Pd-C catalyst, to give the  $\alpha,\omega$ -naphthylene bis(4-hydroxybenzoate). The final products were obtained by the reaction of  $\alpha,\omega$ -naphthylene bis(4-hydroxybenzoate) and 4-(dodecyloxy)benzoic acid with DMAP and DCC.

**Synthesis of Compound 3a.** Yield: 21.6%. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3050  $\text{cm}^{-1}$  (aromatic C-H, stretch), 2800-3000  $\text{cm}^{-1}$  (alkane C-H stretch), 1720  $\text{cm}^{-1}$  (conj. C=O stretch), 1610  $\text{cm}^{-1}$  (aromatic C=C stretch), 1250  $\text{cm}^{-1}$  (C-O-C symmetry stretch), and 1130  $\text{cm}^{-1}$  (C-O-C asymmetry stretch). <sup>1</sup>H NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm): 8.42 (4H, Ar-H), 8.22 (5H, Ar-H), 7.53 (4H, Ar-H), 7.31 (2H, Ar-H), 7.03 (7H, Ar-H), 4.12 (4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 1.95 (4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.48 (32H, Ar-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>), and 1.02 (10H, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>3</sub>).



Scheme 1. Synthetic route to banana-shaped ester mesogens.

**Synthesis of Compound 3b.** Yield: 52.9%. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3080 $\text{cm}^{-1}$  (aromatic C-H, stretch), 2900 $\text{cm}^{-1}$  (alkane C-H stretch), 1740 $\text{cm}^{-1}$  (conj. C=O stretch), 1560 $\text{cm}^{-1}$  (aromatic C=C stretch), 1320 $\text{cm}^{-1}$  (C-O-C symmetry stretch), and 1080 $\text{cm}^{-1}$  (C-O-C asymmetry stretch).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm): 8.38 (4H, Ar-H), 8.21 (4H, Ar-H), 7.72 (1H, Ar-H), 7.45 (6H, Ar-H), 7.03 (7H, Ar-H), 4.15 (4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 1.89 (4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.46 (32H, Ar-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>), and 0.92 (10H, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>3</sub>).

**Synthesis of Compound 3c.** Yield: 22.5%. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3050-3150 $\text{cm}^{-1}$  (aromatic C-H, stretch), 2850-3000 $\text{cm}^{-1}$  (alkane C-H stretch), 1740 $\text{cm}^{-1}$  (conj. C=O stretch), 1590 $\text{cm}^{-1}$  (aromatic C=C stretch), 1259 $\text{cm}^{-1}$  (C-O-C symmetry stretch), and 1160 $\text{cm}^{-1}$  (C-O-C asymmetry stretch).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm): 8.19(4H, Ar-H), 7.99(4H, Ar-H), 7.52(2H, Ar-H), 7.30(4H, Ar-H), 7.06(8H, Ar-H), 4.12(4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 1.91(4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.28(32H, Ar-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>), and 0.92-1.02 (10H, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>3</sub>).

**Synthesis of Compound 3d.** Yield: 32.3%. IR (KBr pellet,  $\text{cm}^{-1}$ ): 2820  $\text{cm}^{-1}$  (aromatic C-H, stretch), 2830 $\text{cm}^{-1}$  (alkane C-H stretch), 1350 $\text{cm}^{-1}$  (conj. C=O stretch), 1250 $\text{cm}^{-1}$  (aromatic C=C stretch), 11700 $\text{cm}^{-1}$  (C-O-C symmetry stretch), and 960 $\text{cm}^{-1}$  (C-O-C asymmetry stretch).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm): 8.25-8.35(4H, Ar-H), 8.05(4H, Ar-H), 7.75(2H, Ar-H), 7.49(4H, Ar-H), 7.08(8H, Ar-H), 4.16(4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 1.88(4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.32(32H, Ar-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>), and 0.98 (10H, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>3</sub>).

**Characterization.** IR spectra were recorded using a Jasco 300E FT-IR spectrometer.  $^1\text{H}$ -NMR spectra were recorded using a Bruker DPX 200MHz NMR spectrometer. For  $^1\text{H}$  NMR spectra, the chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. The liquid crystalline behavior and thermal properties were investigated by using an optical polarizing microscope (Zeiss Uenapol) and differential scanning calorimetry (NETZSCH DSC 200 F3) with heating and cooling rates of 10  $^{\circ}\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere..

### 3. Result and Discussion

**Synthesis of Banana-Shaped Compounds.** Four banana-shaped compounds with ester linking group were synthesized: the central structure was varied with 1,6-, 1,7-, 2,3-, and 2,7-naphthylene, and the carbon number of the terminal flexible group was fixed to 12. The synthetic route for the compounds was quite straightforward. The structures of compounds were characterized by  $^1\text{H}$  NMR and FT-IR spectroscopy. The spectral dates were in accordance with the expected molecular formulas.

**Thermal Properties and Optical Textures.** The transition temperatures and enthalpy changes on the 1st heating were summarized in table 1, and Figure 1 displayed the DSC curves of four compounds on the second heating. Compound 3a which has an asymmetric structure, and bend angle of central unit is 120 $^{\circ}$  showed one mesophase. Among the four compounds, the compound 3a showed the lowest

melting temperature of 110.1 °C with the enthalpy change of 21.68 J/g. The isotropic transition temperature of compound 3a was 143.1 °C with enthalpy change of 18.33 J/g. Figure 2 shows the mesophase texture of compound 3a at 107.7 °C on cooling. Compound 3b which has an asymmetric structure, and the bend angle of central unit is 60° could not produce any liquid crystal phase. Nevertheless, the compound 3b showed the highest melting temperature of 163.6 °C with the enthalpy change of 70.34 J/g. Compound 3c and 3d have symmetric structures and the bend angles of central units are 60° and 120°, respectively. The compound 3c exhibited two mesophases: one is smectic phase, and the other is nematic phase. For compound 3c, the melting temperature and the enthalpy change were 134.2 °C and 51.47 J/g, the transition temperature for smectic to nematic phase and the enthalpy change were 211.6 °C and 2.8275 J/g, and the isotropic transition temperature and the enthalpy change were 217.4 °C and 0.7785 J/g. The optical microscopic textures of compound 3c were shown in Figure 3. Texture (a) showed the smectic phase at 143.5 °C on heating, and helical ribbons texture appeared, which was designated as B<sub>7</sub> phase. On cooling, at 215.7 °C, the texture shown in Figure 3(b) appeared in the nematic phase. Compound 3d exhibited one mesophase. The melting temperature and the enthalpy change of compound 3d were 133.6 °C and 22.09 J/g, and isotropic transition temperature and the enthalpy change were 166.1 °C and 14.22 J/g. Figure 4 showed the optical texture for the liquid crystal phase of the compound 3d at 157.3 °C on heating.

#### 4. Conclusions

1. Four bent-core compounds with ester linking group were synthesized, the central unit was varied with 1,6-, 1,7-, 2,3-, and 2,7-naphthylenes, and the carbon number of the terminal flexible group was fixed to 12.

2. The molecular structures were identified by FT/IR and <sup>1</sup>H NMR spectroscopy, and the results were in accordance with the expected molecular

formulas.

3. All of these four compounds with bent-core mesogen were soluble in chloroform.

4. The melting temperature was in the range of 110-160 °C.

5. Of these four compounds, three compounds except one with 1,7-naphthylene central unit were thermotropic liquid crystal.

6. Interestingly, the compound having the 2,3-naphthylene unit as a central unit showed the two mesophases of B<sub>7</sub> and nematic phase.

Table 1. Transition Temperatures (°C) and Enthalpy Changes (J/g) (in Parentheses)<sup>a</sup>

Polymer	Phase behavior
3a	Cr 110.1 (21.68) SmX 143.1 I
3b	Cr 163.6 (70.34) I
3c	Cr 134.2 (51.47) SmX 211.6 N 217.4 I
3d	Cr 133.6 (22.09) SmX 166.1 I

<sup>a</sup> Cr = Crystalline phase; N = nematic phase; SmX = smectic phase.

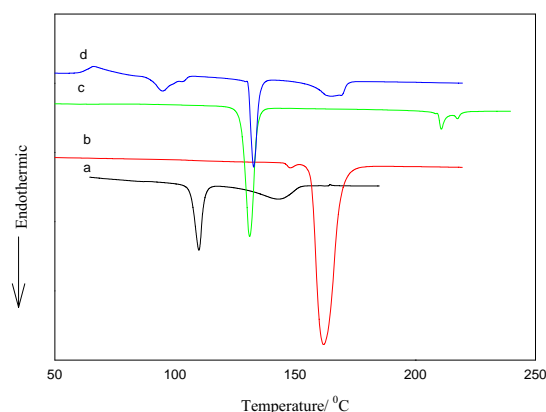


Figure 1. DSC thermograms for compounds on second heating: (a) compound 3a, (b) compound 3b, (c) compound 3c, and (d) compound 3d.

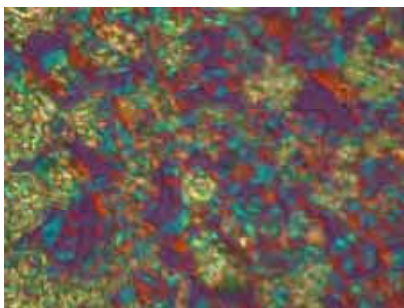
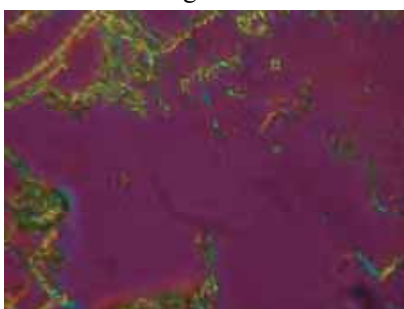
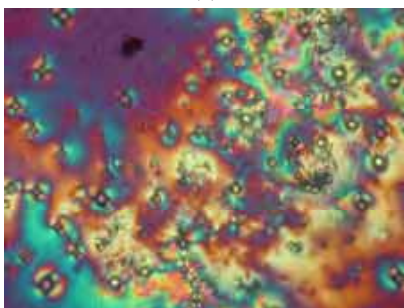


Figure 2: Optical microscopic texture of compound 3a at 107.7 °C on cooling.



(a)



(b)

Figure 3: Optical microscopic textures of compound 3c: (a) at 143.5 °C on heating, and (b) at 215.7 °C on cooling.

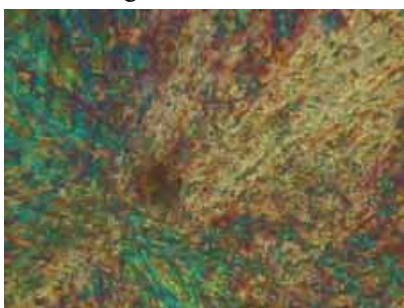


Figure 4: Optical microscopic texture of compound 3d at 157.3 °C on heating.

## 5. Acknowledgement

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## 6. References

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