Biaxial Nematic Phase Derived From Banana-Shaped Molecules Containing Naphthylene Central Unit

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Abstract

Banana-shaped molecules were synthesized introducing ester linking group into mesogenic unit, varying the central unit with 1,6-, 2,3-naphthylenes, and introducing the hexyloxy group as the terminal flexible unit. The properties of the compounds were characterized by FT-IR, NMR spectroscopy, DSC, polarizing optical microscopy, and X-ray diffractometry.

1. Introduction

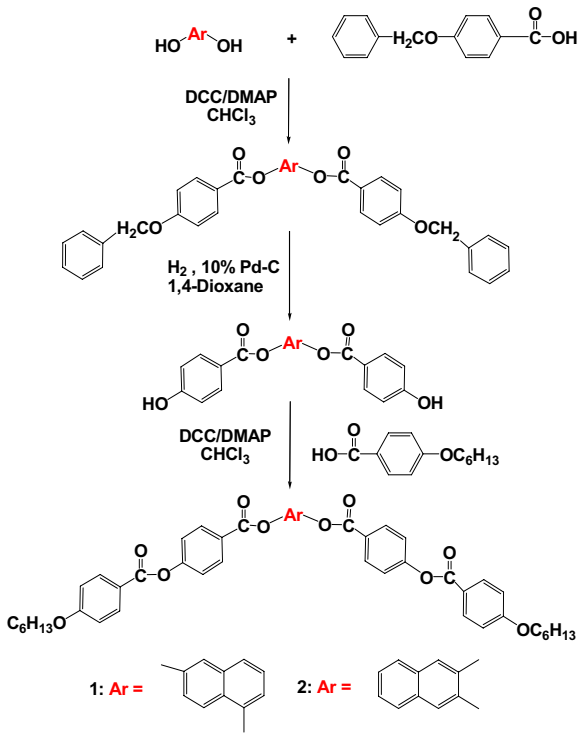
Classical thermotropic liquid crystals are commonly composed of linear molecules, because their structural linearities can give an advantage in the formation of mesophases. However, recently, many unconventional liquid crystals with non-linear structures have been reported by a number of research groups.[1] In 1996, Niori et al.[2] observed the first obvious example of ferroelectricity in a smectic phase formed by achiral banana-shaped molecules. It was known that even when the bent-core mesogens do not contain achiral unit, their tilted smectic mesophases can show the chirality due to decrease of molecular symmetry and the ferroelectricity due to spontaneous polarization. The bent-core mesogens with higher than 140° bend angle can form calamitic phase, whereas the bent-core mesogens with 110° to 140° bend angle can form B-phase.[3] In this study, we have synthesized banana-shaped molecules containing a naphthylene central core, all ester linking groups and relatively short alkyl terminal groups, and their mesomorphic properties were investigated.

2. Experimental

Synthesis. The synthetic route to compounds followed the Scheme 1. First, 1,6-naphthylene bis(benzyloxy benzoate) was prepared by reaction of 4-benzyloxy benzoic acid and 1,6-dihydroxy naphthalene using dicyclohexylcarbodimide (DCC) in chloroform. Then, 1,6-naphthalene bis(4-hydroxy benzoate) was obtained by hydrogenation of 1,6-naphthylene bis(benzyloxy benzoate) with Pd/C in EtOH. Finally, 1,6-naphthalene bis[(4-(4-hexyloxy)benoyloxy)benzoate] was prepared by reaction of 1,6-naphthalene bis(4-hydroxybenzoate) and 4-(hexyloxy)benzoic acid using DCC in chloroform.

FT-IR (KBr Pellet, cm^{-1}): 3050 (Aromatic C-H, stretch), 2800 (Aliphatic C-H stretch), 1720 (Conj. C=O stretch), 1610 (Aromatic C=C stretch), 1250 (C-O-C symmetry stretch), 1130 (C-O-C asymmetry stretch). ^{1}H NMR (S = Acetone-d, δ 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_2CH_2), 1.95 (4H, $OCH_2CH_2CH_2$), 1.48 (8H, Ar-$OCH_2CH_2(CH_2)_2$), 1.02 (6H, $OCH_2CH_2(CH_2)_2CH_2CH_3$).

Characterization. IR and NMR spectra were obtained by Jasco 300E FT/IR and Bruker DPX 400 MHz NMR spectrometers, respectively. The phase transition temperatures were determined by DSC (NETZSCH DSC 200 F3), which were performed in a N_2 atmosphere, and the heating and cooling rates were 10℃/min. Optical textures were observed by the polarizing optical microscope (POM) equipped with a camera and thermo-controller (Mettler FP82HT).



Scheme 1. Synthetic route to compounds.

3. Results and discussion

Figure 1 displays the DSC thermograms of compound 2 with 2,3-naphthylene central core. On the DSC heating scan, compound 2 shows three endothermic peaks, corresponding to melting, mesophase 1-to-2, and isotropization. The transition temperature and the enthalpies changes for the two compounds were summarized in Table 1. Compound 1 with 1,6-naphthylene central core could form a smectic phase reversibly. Compound 2 could form a smectic phase at the lower temperature and a nematic phase at the higher temperature, reversibly. In addition, compound 1 shows the solid-solid transition at 114.9℃ with enthalpy change of 41.24 J/g. Figure 2 displays the optical textures of the compounds. In Figure 2(a), compound 1 shows a Col_r phase on cooling from the isotropic liquid, and on further cooling it was crystallized. In Figure 2(b), compound 2 shows a nematic threaded texture on cooling from the isotropic liquid, and further cooling led to the formation of a smectic texture.

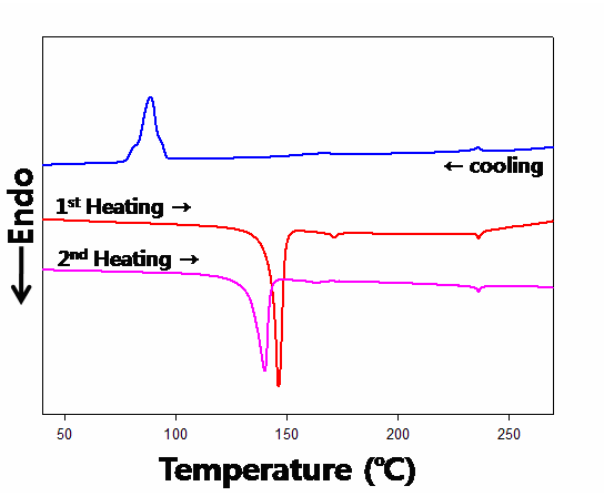
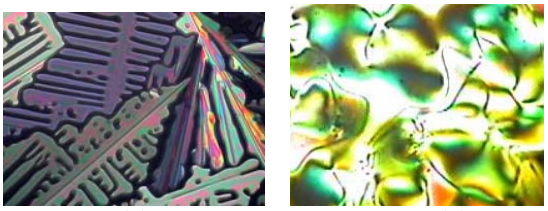


Figure 1. DSC thermograms of compound 2 (Heating and cooling rates = 10℃/min).

Table 1. Transition temperature (℃) and enthalpy changes (in parenthesis, J/g) for compounds[a]

Compound	DSC[b]	Cr	SmX	N	I
1	H	• 158.5 (39.96)	• 167.9 (29.54)		•
	C	• 105.7 (31.19)	• 162.7 (29.97)		•
2	H	• 146.3 (49.67)	• 171.2 (1.01)	• 236.6 (0.696)	•
	C	• 102.1 (38.65)	• 168,8 (0.56)	• 234.6 (0.849)	•

[a]Cr = crystalline phase; SmX = smectic X phase; N = nematic phase; I = isotropic phase; The symbol "•" indicates the occurrence of the phase. [b]H and C stand for the heating and cooling DSC scan, respectively.



(a) (b)

Figure 2. Cross-polarized optical micrographs (magnification of x250): (a) Col_r phase of compound 1 at 165℃, and (b) nematic phase of compound 2 at 200℃.

The structure of the liquid crystal phases has been confirmed by XRD studies as shown in Figure 3. At 140℃, compound 1 showed sharp peaks in the small-angle region and a broad diffuse reflection in the wide angle region. This is indicative of smectic mesophase.

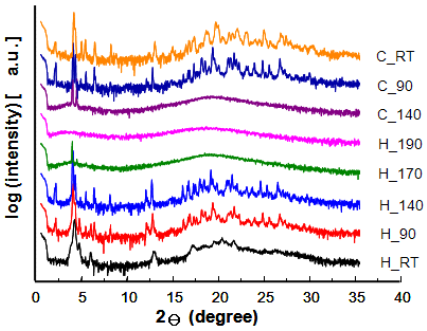


Figure 3. X-ray diffraction patterns of compound 1 at given temperatures (H: heating; C: cooling).

4. Summary

Two new banana-shaped molecules with the naphthalene central core, all-ester linking groups, and short alkyl chain have been synthesized and characterized. The molecular structures of compounds were identified by FT/IR- and NMR-spectroscopy. The compound 1 with asymmetric naphthylene central core with the bending angle of 120° could form a Col_r phase phase, and the compound 2 with symmetric naphthylene central core with the bending angle of 60° could form a nematic phase as well as a smectic phase.

5. Acknowledgements

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6. References

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