Effect of Alkylthio Tail on Phase Behaviors of Bent-shaped Molecules Based on Naphthalene Core

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New bent-shaped molecules with naphthalene central core and alkylthio tail are prepared, and their banana phase structures and properties are discussed in comparison with those of conventional alkoxy molecules.

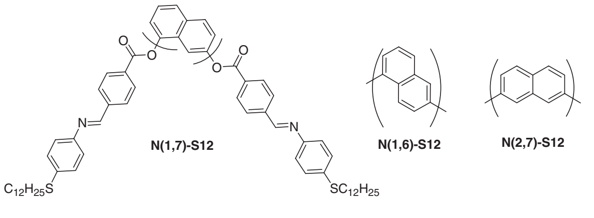
Since the discovery that bent-shaped (or banana) molecules can form banana phases with unique polarity[1] and chirality,[2] a new area in the field of liquid crystal research has opened. A number of bent-shaped molecules have been synthesized and characterized[3–5] to clarify the structure–property relationships and the source of polarity and chirality.

Almost all bent-shaped molecules are designed by using alkoxy or alkyl groups as a terminal chain as the terminal chain plays an important role in determining the phase structure. In this study, we synthesized a new homologous series of bent-shaped molecules with dodecylthio tail and naphthalene central core where typical Schiff-based side wings are substituted on 1,7-, 1,6-, and 2,7-positions.[9] The compounds designated N(*n*,*m*)-S12 are shown in Scheme 1. The effect of the alkylthio tail on their mesomorphic behaviors and phase structures is discussed.

All the compounds show enantiotropic transitions. In Table 1, their transition temperatures and associated enthalpy changes are listed and compared with those of conventional alkoxy compounds, namely, N(*n*,*m*)-O12.[6,7]

N(1,7)-S12 shows the B1 phase as well as the solid B4 phase irrespective of its low bent angle of around 60°. When it is cooled from isotropic phase, mosaic texture of the B1 phase is observed (Figure S1a). This phase does not switch under application of an electric field. In X-ray diffraction measurement, two sharp inner reflections with spacings of 56.3 and 33.2 Å and a broad outer reflection of 4.5 Å are observed, indicating a two-dimensional (2D) frustrated structure with a unit lattice of $a = 106.2$ Å and $c = 66.4$ Å.[8] On further cooling to the B4 phase, two optically active domains with opposite chiralities are observed, in which the brightness is interchanged by positive and negative rotations of polarizer from the cross polarization position (Figure S1b).

In N(1,6)-S12, typical B2 phase is observed as high birefringent circular domains on cooling from isotropic phase. By applying a rectangular-wave field, yellow domains with an extinction direction parallel and perpendicular to the layer normal are observed, whereas dark blue domains with fine stripes are observed in the field-off state (Figure 1a). On applying a triangular-wave electric field, the B2 phase exhibits double switching current peaks in half a circle (Figure 1b), indicating that it has a racemic SmC_SP_A structure as a ground state and that electro-optical switching takes place between SmC_SP_A and SmC_AP_F (Figure 1c). On further cooling from B2 phase, two crystal phases are observed with clear transition peaks on the DSC thermogram. These results are very similar to those of N(1,6)-O12[7] (refer to Table 1).



Scheme 1.

Table 1. Transition temperatures and enthalpies based on DSC cooling data, in alkylthio and alkoxy compounds

	Transition temperature/°C (enthalpy/kJ mol^{-1})
N(1,7)-S12	B4 118.3 (22.8) B1 131.4 (3.2) Iso
N(1,7)-O12	B4 145.7 (27.4) Iso
N(1,6)-S12	Cr_2 81.7 (3.5) Cr_1 110.7 (10.2) B2 (SmC_SP_A) 171.2 (24.0) Iso
N(1,6)-O12	Cr_2 95.8 (2.8) Cr_1 130.1 (9.9) B2 (SmC_SP_A) 193.5 (25.4) Iso
N(2,7)-S12	B4 170.7 (22.8) B2 (SmC_SP_F) 200.4 (11.6) Iso
N(2,7)-O12	B4 170.0 (8.1) B4^f 196.9 (27.7) B2 (SmC_AP_A) 224.0 (18.9) Iso

The B2 phase is also formed from N(2,7)-S12, but its electrooptic switching behavior is different from that of N(1,6)-S12. On applying an electric field for example, the extinction direction of fan-shaped domains rotates in opposite direction on reversing the polarity. On terminating the field, the position of extinction direction is retained (Figure 2a). Moreover, a single switching current peak indicating ferroelectric switching appears in the triangular-wave field (Figure 2b). Thus, a bistable switching occurs between two homochiral ferroelectric SmC_SP_F states (Figure 2c). This homochiral SmC_SP_F in ground state is different from the homochiral antiferroelectric SmC_AP_A in N(2,7)-O12. On further cooling to the lower temperature region, typical B4 phase with two opposite chiral domains is observed.

As mentioned above, variation of the chemical structure in bent-shaped molecules is very important for interlayer interaction, influencing the formation of banana phases. In this study, we used an alkylthio terminal chain that is flexible than conventional alkoxy terminal chains. The flexibility of the alkylthio tail can be understood from Figure 3 which shows the relative energy diagram as a function of dihedral angle around the C–S bond in Phenyl–S and C–O bond in Phenyl–O. Here, dodecylsulfanylbenzene and dodecyloxybenzene were used for simple calculation. Two stable conformations are found in both compounds (dihedral angle: 0 or 180°). But the path from one stable conformer to the other is different. The path for C–O is obstructed by high energy barrier (13.2 kJ mol^{-1}, in position of dihedral angle: 90°). In contrast, the potential barrier for C–S is lower (1.88 kJ mol^{-1}, in position of dihedral angle: 50 and 130°)

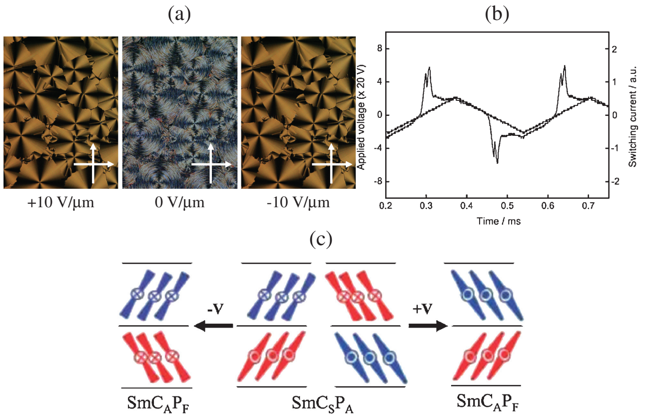


Figure 1. (a) Photomicrographs observed on switching, (b) polarization reversal current in the $\mathrm{SmC_SP_A}$ phase of N(1,6)-S12 under the application of a 240 $\mathrm{V_{pp}}$ triangular wave voltage of 3 Hz, and (c) schematic representation of molecular rearrangement on antiferro-switching (3.0 μm thick cell).

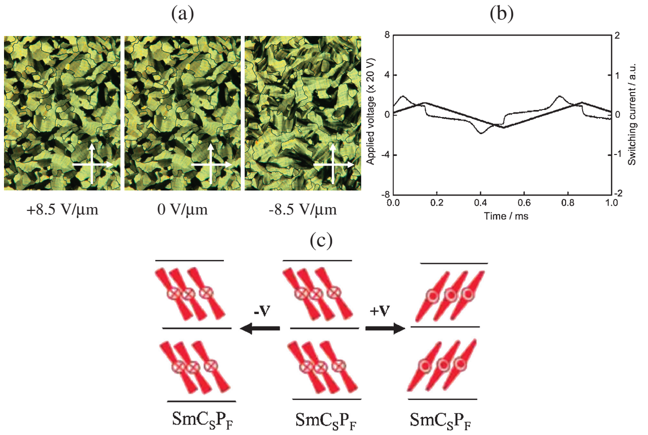


Figure 2. (a) Photomicrographs observed on switching, (b) polarization reversal current in the $\mathrm{SmC_SP_F}$ phase of N(2,7)-S12 under the application of 84 $\mathrm{V_{pp}}$ triangular wave voltage of 1.4 Hz, and (c) schematic representation of molecular rearrangement on ferro-switching (2.2 μm thick cell).

although metastable conformer exists at 90°. These particularly low barriers of the alkylthio terminal chain enable the compound to change the conformation more easily and affect the mesophase structure and properties as follows.

First, the transition temperatures are remarkably affected. All alkylthio compounds show transition temperatures lower by 15–25 °C than alkoxy compounds (Table 1). Second, although the layer spacings of the B4 and crystal are similar, the spacings of the B2 phase in alkylthio compounds are larger than those of alkoxy ones (Table 2). Thus, the molecular lengths are similar, but the tilt angle in the B2 phase of alkylthio compounds is smaller. Since the molecules lie perpendicular to the layer in the B4 phase,[6] for example, tilt angle is calculated as 38° for N(2,7)-O12, while it is 27° for N(2,7)-S12. Finally, $\mathrm{SmC_AP_A}$ in N(2,7)-O12 is altered to the $\mathrm{SmC_SP_F}$ in N(2,7)-S12. Both the phases are homochiral, but the same directionality of polarization becomes maintained through the layers in N(2,7)-S12. Although more comprehensive study will be required, the present result shows the importance of the flexibility of terminal chains on the phase structure and opens up prospects for new molecular designs for bent-shaped molecules.

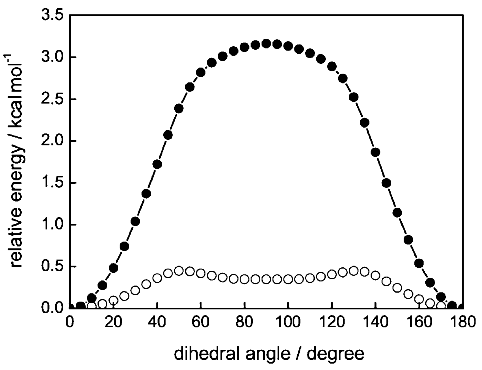


Figure 3. Internal rotational energy against the dihedral angles of phenyl–S (open circles) and phenyl–O (closed circles) bonds (see the text).

Table 2. Layer spacings (Å) of alkylthio and alkoxy compounds

	Cry	B4	B2	B1
N(1,7)-S12		33.4		33.2
N(1,7)-O12		33.2		
N(1,6)-S12	49.7		47.4	
N(1,6)-O12	50.0		44.8	
N(2,7)-S12		54.6	48.6	
N(2,7)-O12		57.3	44.8	

In summary, the mesophase behaviors of new bent-shaped molecules with naphthalene central core and alkylthio tail have been studied. All compounds showed the well-defined fluid smectic mesophase. However, the phase structure is different from the conventional alkoxy tail compounds. This difference may be caused by the flexibility of alkylthio terminal chain.

References and Notes

1 T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe, *J. Mater. Chem.* **1996**, *6*, 1231.
2 D. R. Link, G. Natale, R. Shao, J. E. Maclennan, N. A. Clark, E. Korblova, D. M. Walba, *Science* **1997**, *278*, 1924.
3 G. Pelzl, S. Diele, W. Weissflog, *Adv. Mater.* **1999**, *11*, 707.
4 H. Takezoe, Y. Takanishi, *Jpn. J. Appl. Phys.* **2006**, *45*, 597.
5 R. A. Reddy, C. Tschierske, *J. Mater. Chem.* **2006**, *16*, 907.
6 J. Thisayukta, Y. Nakayana, S. Kawauchi, H. Takezoe, J. Watanabe, *J. Am. Chem. Soc.* **2000**, *122*, 7441.
7 S. K. Lee, Y. Naito, L. Shi, M. Tokita, H. Takezoe, J. Watanabe, *Liq. Cryst.* **2007**, *34*, 935.
8 J. Watanabe, T. Niori, T. Sekine, H. Takezoe, *Jpn. J. Appl. Phys.* **1998**, *37*, L139.
9 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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