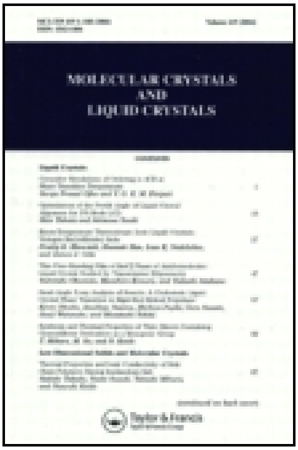

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Calamitic Liquid Crystalline Molecules with Lateral Intermolecular Hydrogen Bonding

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Calamitic Liquid Crystalline Molecules with Lateral Intermolecular Hydrogen Bonding

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*Calamitic liquid crystalline amides **1–3** were synthesized and their thermodynamic behaviors were investigated. Bent-rod shaped compound **1** exhibited a usual smectic C phase. On the other hand, in the case of straight-rod compound **2**, two kinds of smectic C phases (SmC$_x$ and SmC$_y$) were observed above the crystal phase. Although SmC$_y$ phase belonged to general smectic C phases, SmC$_x$ phase exhibited very sharp lines in its schlieren textures. As the packing model of smectic C$_x$ phase, a lateral linear arrangement of the molecules was proposed to explain the difference between these smectic C phases. Additionally, in the case of **3** which has a flexible spacer between its amide group and straight rodlike core, the molecules generated the highly ordered smectic C (**3a**, SmC$_x$) and a chiral cubic phase (**3b**).*

Keywords: amide; chiral cubic; lateral intermolecular hydrogen bonding; liquid crystal; supra-structure

INTRODUCTION

In liquid crystal phases, introduction of hydrogen bonding is effective to organize molecules into supra-structures such as dimers and molecular networks [1]. Especially, intermolecular hydrogen bonding parallel to the molecular long axis is effective for generation of stable mesomorphic supra-structures. However, lateral intermolecular

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hydrogen bonding has not been applied to rodlike molecules except for a few examples [2–6], since it works as a brake to the molecular spinning to lead to destabilization of the mesophase. In this paper, realization of stable mesophases with lateral intermolecular hydrogen bondings is described.

EXPERIMENTAL

Rodlike liquid crystalline compounds **1–3** (Fig. 1) possessing an *N*-(*m*- or *p*-octyloxyphenyl)amide moiety were synthesized. Their purities and structures were confirmed by thin-layer chromatography, NMR spectroscopy, IR spectroscopy, and elemental analysis. Their phase transition behaviors were observed by means of differential scanning calorimetry (DSC) and polarized optical microscopy (POM).

RESULTS AND DISCUSSION

The behaviors of liquid crystalline compounds **1**[7] and **2** are shown in Table 1. Compound **1** exhibited smectic A and smectic C phases. On the other hand, compound **2** exhibited a smectic A and two smectic C phases ($\mathrm{SmC_x}$ and $\mathrm{SmC_y}$). The lines of the schlieren textures [8–10] became slightly sharper without change of the textures during the phase transition from $\mathrm{SmC_y}$ to $\mathrm{SmC_x}$ on cooling. Accordingly, it could be assumed that two smectic C phases had similar layer structures and the difference in the sharpness originated in the difference in their molecular arrangement in the layer. This indicated that the intermolecular interaction (lateral hydrogen bonding) in $\mathrm{SmC_x}$ phase was stronger than that in $\mathrm{SmC_y}$ phase.

The difference in the thermodynamic stabilities of the smectic phases of **1** and **2** was caused by the difference in their molecular shapes. Bent-rod shaped molecule **1** consists of two kinds of parts, "anchoring" and "spinning" parts (Fig. 1). In the smectic phases, rotation of the anchoring part around the long axis is strongly suppressed by steric effect of its lateral alkyl chain and the lateral intermolecular hydrogen bonding. The spinning part is parallel to the long axis and rotates independently to stabilize the liquid crystal phase. It was assumed that the lateral intermolecular hydrogen bonding organized the plural molecules into a laterally linear arrangement in the layers. On the other hand, in the case of straight-rod shaped molecule **2**, the amide group also works as an anchoring part. However, the free rotation of the two spinning parts can suppress the crystallization. Accordingly, it seemed that the melting point of **2** decreased and the more ordered smectic C phase ($\mathrm{SmC_x}$) appeared under the usual smectic C phase ($\mathrm{SmC_y}$).

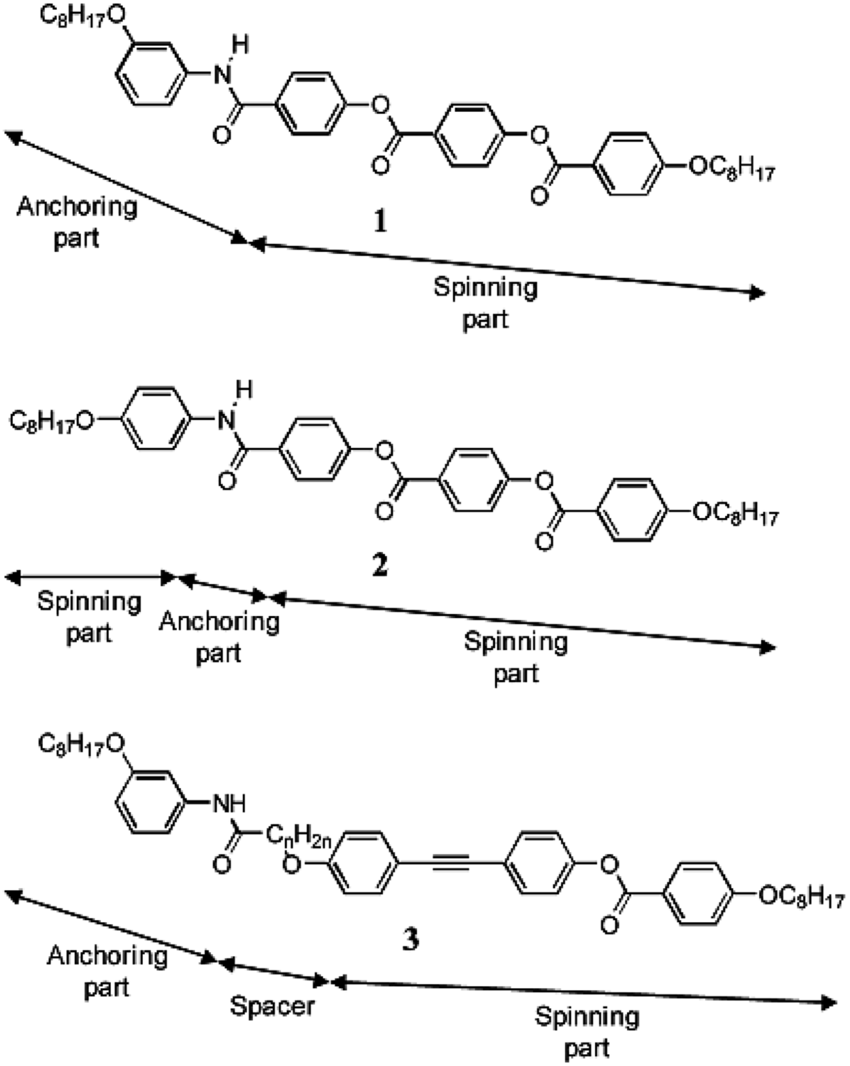

FIGURE 1 Molecular structures of **1–3**.

TABLE 1 Behaviors of Compounds **1** and **2**

Compound	Behavior
1	$\mathrm{Cr} \underset{159}{\overset{174}{\rightleftharpoons}} \mathrm{Smc} \underset{176}{\overset{176}{\rightleftharpoons}} \mathrm{Sma} \underset{197}{\overset{199}{\rightleftharpoons}} \mathrm{Iso}$
2	$\mathrm{Cr} \underset{198}{\overset{202}{\rightleftharpoons}} \mathrm{SmC_x} \underset{206}{\overset{206}{\rightleftharpoons}} \mathrm{SmC_y} \underset{280}{\overset{280}{\rightleftharpoons}} \mathrm{SmA} \xrightarrow{350} \mathrm{decomp}$

TABLE 2 Behaviors of Compounds **3**

Compound	n	Behavior
3a	5	$\begin{tikzcd} \mathrm{Cr} \arrow[rr, "114"] & & \mathrm{SmC_y} \arrow[dl, "91"] \arrow[r, shift left, "132"] & \mathrm{N} \arrow[l, shift left, "121"] \arrow[r, shift left, "145"] & \mathrm{Iso} \arrow[l, shift left, "144"] \\ & \mathrm{SmC_x} \arrow[ul, "84"] & & & \end{tikzcd}$
3b	10	$\begin{tikzcd} \mathrm{Cr} \arrow[rr, "106"] & & \mathrm{SmC} \arrow[dl, shift left, "97"] \arrow[r, shift left, "112"] & \mathrm{N} \arrow[l, shift left, "111"] \arrow[r, shift left, "131"] & \mathrm{Iso} \arrow[l, shift left, "130"] \\ & \mathrm{Cubic} \arrow[ur, shift left, "106"] & & & \end{tikzcd}$

The behaviors of compounds **3** are shown in Table 2. Compound **3a** possessing a rodlike core and the *m*-octyloxyphenylamide unit connected with a short flexible spacer (n = 5), exhibited nematic, smectic $\mathrm{C_y}$, and monotropic smectic $\mathrm{C_x}$ phases. Again, the two smectic C phases ($\mathrm{SmC_x}$ and $\mathrm{SmC_y}$) were observed. These phases were identified in comparison with the textures and phase transition enthalpies of **2**. On the other hand, **3b** which had a long spacer (n = 10) exhibited nematic, smectic C, and cubic phases [11]. Interestingly, mosaic plane textures were observed [12] in the cubic phase in POM. Additionally, the bright area was changed into the dark area and vice versa by clockwise and counterclockwise rotations of the analyzer from the cross-polarization position. This indicated that two different chiral domains existed in the cubic phase. Identification of the molecular packing structure in the cubic phase and investigation of the mechanism for generation of the molecular aggregation are in progress.

CONCLUSION

We synthesized bent- and straight-rod shaped molecules with an amide group and investigated their phase behaviors. They exhibited more ordered smectic C ($\mathrm{SmC_x}$) and chiral cubic phases [13–16]. It was assumed that the molecules generated highly ordered molecular aggregations by introduction of the lateral intermolecular hydrogen bonding. Additionally, it was considered that generation of the chirality in the cubic phase of **3b** related closely to its molecular shape, lateral hydrogen bonding, and lateral polarization.

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