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Communications

Generation of Stable Calamitic Liquid-Crystal Phases with Lateral Intermolecular Hydrogen Bonding

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In mesophases, hydrogen bonding is effective for organizing highly ordered suprastructures.^{1–5} In preceding papers, dimers² and molecular networks^{3–5} were reported in liquid-crystal phases of rodlike molecules possessing a hydrogen-bonding site at their terminals. The directions of their intermolecular hydrogen bond-

ings are parallel to their long axes. However, lateral intermolecular hydrogen bonding has not been applied to rodlike molecules except for a few examples^{4,5} because the spinning of the rod is suppressed by the lateral intermolecular hydrogen bonding to lead to destabilization of the mesophase. In this paper, we describe synthesis of liquid-crystalline compounds **1** and investigation of their thermodynamic behaviors and layer structures. As a result, we have established a novel methodology to generate stable calamitic liquid-crystal phases with lateral intermolecular hydrogen bonding.

The designed molecule has “anchoring” and “spinning” parts (Scheme 1). In the smectic phases, spinning of the anchoring part is strongly suppressed by its *m*-alkoxy chain to stabilize the lateral intermolecular hydrogen bonding, while the spinning part rotates independently to stabilize the liquid-crystal phase. Thus, it was expected that the molecules maintained the intermolecular hydrogen bonding even in the mesophase.

Compounds **1** were prepared from 4-alkoxybenzoyl chloride and *N*-(3-alkoxyphenyl)-4-hydroxybenzoyloxy-

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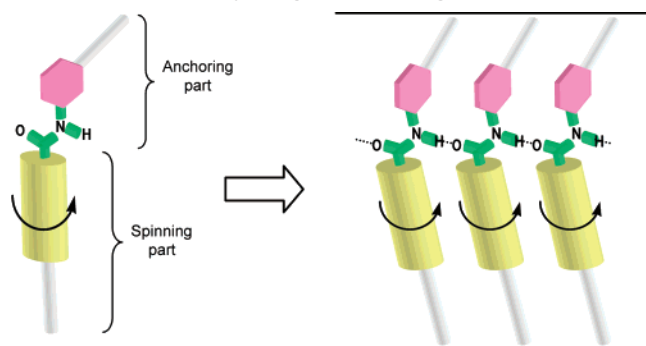
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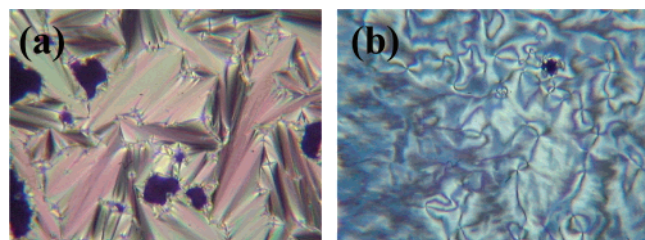
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Scheme 1. Molecular Design and Molecular Organization Generated by Intermolecular Hydrogen Bonding**Table 1. Behaviors of Compounds 1**

$\mathbf{1a}$: $\text{R}^1 = \text{R}^2 = n\text{-C}_4\text{H}_9$
 $\mathbf{1b}$: $\text{R}^1 = n\text{-C}_4\text{H}_9, \text{R}^2 = n\text{-C}_{12}\text{H}_{25}$
 $\mathbf{1c}$: $\text{R}^1 = n\text{-C}_{12}\text{H}_{25}, \text{R}^2 = n\text{-C}_4\text{H}_9$
 $\mathbf{1d}$: $\text{R}^1 = \text{R}^2 = n\text{-C}_{12}\text{H}_{25}$

compound		behavior ^a			
1a	Cr	$\frac{185(8.5)}{164(-8.5)}$	SmA	$\frac{216(1.0)}{216(-1.0)}$	Iso
1b	Cr	$\frac{170(9.7)}{148(-8.5)}$	SmC	$\frac{190(0.079)}{189(-^b)}$	SmA $\frac{211(1.4)}{210(-1.6)}$ Iso
1c	Cr	$\frac{166(12.1)}{154(-12.1)}$	SmA	$\frac{217(2.4)}{217(-2.4)}$	Iso
1d	Cr	$\frac{169(9.7)}{152(-9.7)}$	SmC	$\frac{185(-^b)}{183(-^b)}$	SmA $\frac{189(1.2)}{189(-1.1)}$ Iso

^a The transition temperatures (°C) and enthalpies (in parentheses, kcal/mol) were determined by DSC (5 °C/min) and are given above and below the arrows. Cr, SmA, SmC, and Iso indicate crystal, smectic A, smectic C, and isotropic phases, respectively. ^b The lateral line in parentheses indicates that the enthalpy is too small to be measured.

**Figure 1.** Polarized light micrographs of **1b**: (a) Fan-shaped textures at 200 °C in the smectic A phase; (b) Schlieren textures (all 4-brushes) at 180 °C in the smectic C phase.

benzamide, which were synthesized from 3-alkoxy-aniline in four steps.⁶

The behaviors of liquid-crystalline compounds **1** are shown in Table 1. Compounds **1a** and **1c** only exhibited smectic A phases, while **1b** and **1d** showed both smectic A and smectic C phases. In Figure 1, the compounds exhibited fan-shaped textures in their smectic A phases⁷ and schlieren textures with four brushes in their smectic C phases.⁸ The alkoxy chains (OR²) of **1a** and **1c** are shorter than those of **1b** and **1d**. Thus, the length of R²

Table 2. *d*(100) Peaks in XRD Data of 1^a

compound	molecular length, Å	temp, °C	<i>d</i> (100), Å	phase	<i>d</i> / <i>l</i>	tilt angle, deg
1a	34.0	185	36.5	SmA	1.08 ^b	—
		195	36.5			
		210	36.5			
1b	44.6	170	39.2	SmC	0.88	29
		185	39.2			
1c	40.3	185	42.9	SmA	0.96	—
		210	46.0	SmA	1.14 ^b	—
1d	50.6	170	42.8	SmC	0.81	36
		185	44.6	SmA	0.88	—

^a The XRD was measured by a capillary method on heating. ^b It means that the layer distance is longer than the molecular length.

seems to play an important role in generation of the phase transitions.

To investigate layer distances of the smectic phases of **1**, one- and two-dimensional X-ray diffraction (XRD) was performed. In Table 2, the *d*(100) values of **1a** and **1c** (36.5 and 46.0 Å) in the smectic A phases were longer than their molecular lengths (*l* = 34.0 and 40.3 Å) calculated by MM2. These *d*/*l* ratios were 1.08 and 1.14, respectively. The ratios > 1 mean time-averaged dimerization of the molecules is predominant in an antiparallel manner, while the *d*(100) values of **1b** and **1d** (42.9 and 44.6 Å) in the smectic A phases were slightly shorter than their molecular lengths (*l* = 44.6 and 50.6 Å), and the *d*/*l* ratios were 0.96 and 0.88, respectively. It can be deduced that the dimerization does not occur in the smectic A phases of **1b** and **1d**. In each of the smectic C phases of **1b** and **1d**, the layer distance was observed as one bright spot at both the left and right sides of the X-ray beam spot and the tilted halos at the wide-angle region corresponding to the spinning core were obtained by 2D-XRD.⁹ Additionally, the layer distances (39.2 and 42.8 Å) became shorter than those in the smectic A phases. The arccosines of their *d*/*l* ratios (0.88 and 0.81) gave 29 and 36° as their tilt angles, respectively. If the N–H and C=O (amide) bonds are parallel to the layer plane, the tilt angle is approximately 30° and is most suitable for the lateral hydrogen bonding between N–H and C=O (amide). From their tilt angles (**1b**: 29° and **1d**: 36°) in the layer of the smectic C phases, the intermolecular hydrogen bonding of the N–H with C=O (amide) seems to be more important than that with C=O (ester).

To investigate the intermolecular hydrogen bonding in the mesophase, the temperature-variable FT-IR spectra⁴ of **1d** was measured (Figure 2). The typical wavenumber of N–H stretching vibrations of amides in the crystal state is around 3350 cm^{−1} and that in the isotropic liquid phase is around 3400 cm^{−1}.¹⁰ The N–H wavenumber of **1d** measured at 170 °C was 3382 cm^{−1} in the smectic C phase. It increased to 3387 cm^{−1} during the transition from the smectic C to the smectic A phase, while it slightly increased during the transition from the smectic A to the isotropic phase. These shifts indicated that the intermolecular hydrogen bonding interacted in the smectic C phase, while it was absent

(6) The synthesis is written in the Supporting Information.

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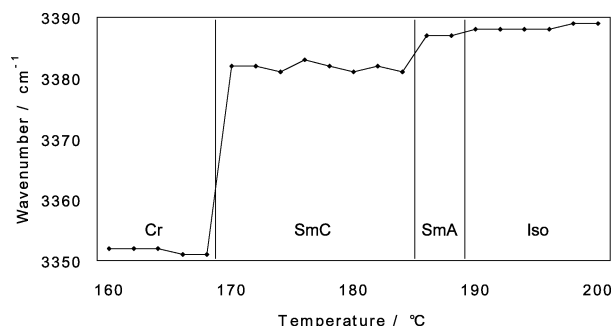
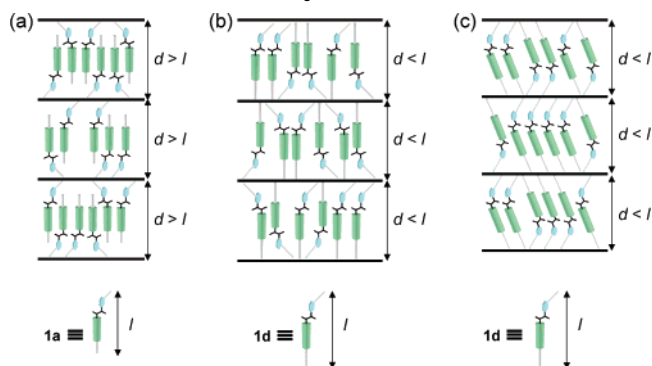


Figure 2. N–H stretching vibration of **1d** in temperature-variable FT-IR spectroscopy. Cr, SmC, SmA, and Iso indicate crystal, smectic C, smectic A, and isotropic phase, respectively.

or very weak in the smectic A phase. Owing to this intermolecular hydrogen bonding, the free rotation of the anchoring part was restricted in the smectic C phase. On the other hand, the molecule could rotate freely in the smectic A phase.

From these considerations, the layer structures of **1a** and **1d** were proposed as depicted in Scheme 2. In the case of **1a** (Scheme 2a, smectic A phase), the molecules dimerize in the antiparallel arrangement to cancel out their large molecular dipoles¹¹ (7 D, in AM1 calculation) and to interact between the spinning cores, which stabilizes the smectic A phase. On the other hand, in the case of **1d** (Scheme 2b, smectic A phase), the dimerization was suppressed by the large intermolecular steric repulsion between OR¹ and OR² in the side-by-side antiparallel arrangement. Additionally, in the smectic C phase (Scheme 2c), the synparallel arrange-

Scheme 2. Layer Structure of 1



(a) Compound **1a** in the smectic A phase dimerized in an antiparallel manner by the dipole–dipole interaction; (b) compound **1d** in the smectic A phase arranged in a parallel manner; (c) compound **1d** in the smectic C phase organized in a synparallel manner by the intermolecular hydrogen bonding. (d = layer distance, l = molecular length).

ment led to generation of the lateral intermolecular hydrogen bonding.

In summary, we demonstrated that the liquid-crystalline compounds consisting of the spinning and anchoring parts could generate stable mesophases effectively with lateral intermolecular hydrogen bonding. The methodology, separation of the spinning and anchoring parts in a molecule, is useful for stabilizing an intermolecularly hydrogen-bonded suprastructure in the mesophase.

Supporting Information Available: Synthesis of **1**, **2**, and **3**, and 1D- and 2D-powder X-ray diffraction charts of **1a** and **1b** and FT-IR spectra of **1d**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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