

Lamellar To Lamellar Phase Transition Driven by Conformation Change of an Amphiphilic Liquid Crystal Oligomer

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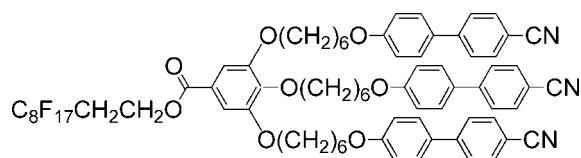
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After preparing a novel amphiphilic liquid crystal hexamer possessing six cyanobiphenyl moieties and a semiperfluorinated alkyl chain, we used optical microscopy, differential scanning calorimetry, and X-ray diffraction to investigate its physical properties. The liquid crystal oligomer, 1, 10-bis{3, 4, 5-tris[6-(4'-cyanobiphenyl-4-yloxy)hexyloxy]benzoyloxy}-1H,1H,10H,10H-heptadecafluorodecane, was found to exhibit a bilayer smectic A to intercalated smectic A transition accompanying a discontinuous decrease in layer spacings. The transition is attributable to a change in its molecular conformation from a folded (or bent) to a linear structure.

Introduction

Smectic liquid crystals have attracted much attention because of their characteristic molecular assembly, structural analogy to biological membranes, and applications in electro-optical devices.^{1,2} Since the discovery of the first smectic A–smectic A transition by Sigaud et al.,³ frustrated smectic phases have been observed in pure compounds and in binary mixtures of polar molecules. The dipoles readily form pairs of antiparallel molecules, and the long-range organization of the position of the polar heads generates different forms of smectic A phases, e.g., monolayer SmA₁, bilayer SmA₂, partially bilayer SmA_d, and the smectic A antiphase, which has a transverse modulation of the structure.^{4–6} Incommensurate smectic phases were proposed in which SmA_d and either SmA₁ or SmA₂ periodic density waves coexist along the layer normal.⁷ Experimental observations of the incommensurate phases have been reported.^{8–11} Recently, a bilayer



1: Cry 83 Cub 141 SmA 155 Iso

Figure 1. Molecular structures and transition temperatures (°C) of amphiphilic oligomer **1**.

SmA to monolayer SmA phase transition was observed in liquid crystal glycolipids.¹² Liquid crystalline systems with an unusual lamellar structure have been important contemporary research topics.

We reported an amphiphilic liquid-crystalline oligomer that comprises cyanobiphenyl mesogenic moieties and a semiperfluorinated alkyl chain (Figure 1).^{13a} The amphiphilic liquid-crystalline oligomer exhibited a phase sequence of smectic A–bicontinuous cubic (Cub_v). In fact, X-ray diffractometry (XRD) measurements of the compound suggest that the SmA phase has an undulating layer structure. Competition of two different molecular packings might give rise to that fluctuation (Figure 2): (a) a segregation effect attributable to incompatibility between a semiperfluorinated moiety and cyanobiphenyl mesogens; and (b) a steric effect attributable to a pronounced taper shape of compound **1**.^{13a} On the other hand, an undulatory deformation mode for a nonequilibrium lamellar structure is known to exist as an

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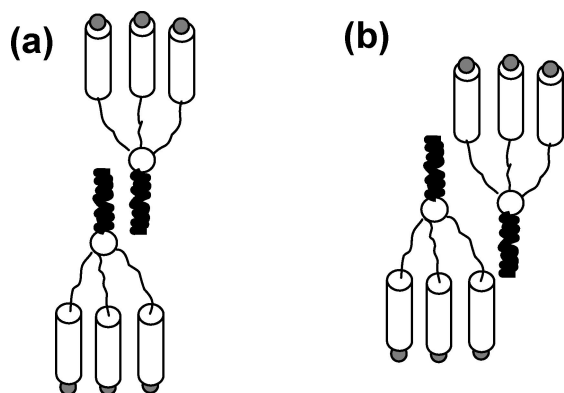


Figure 2. Molecular packings by (a) segregation effect attributable to incompatibility between a semiperfluorinated moiety and cyanobiphenyl mesogens and (b) steric effect attributable to its pronounced tapered shape.

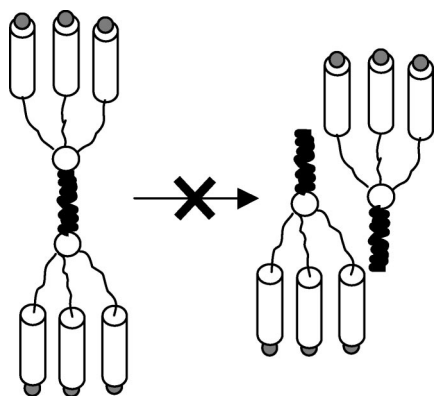


Figure 3. Schematic representation of the novel dumbbell liquid crystal.

unstable transient state between the lamellar and the Cub_V (Gyroid with a space group $Ia3d$) phases in some diblock copolymers.¹⁴ The fluctuated lamellar structure in the SmA phase of compound **1** is thought to be stabilized by antiparallel dipole–dipole interactions between the cyanobiphenyl groups in adjacent layers.^{13b}

For the present study, we designed a novel amphiphilic liquid crystal hexamer possessing six cyanobiphenyl moieties and a semiperfluorinated alkyl chain. The compound corresponds to a dimer of compound **1**. Fluctuation of a lamellar structure observed for compound **1** is thought to be restricted; therefore, a phase transition with discontinuous change in the lamellar structure is expected to occur (see Figure 3).

Experimental Section

Preparation of Materials. The final compound's purity was verified using HPLC (LC9101, JAIGEL-1H column; Japan Analytical Industry Co., Ltd.). Chloroform was used as eluent. Detection of a product was achieved by UV irradiation (254 nm wavelength). The structure of the final product was elucidated using infrared (IR) spectroscopy (FTS-30; Bio-Rad Laboratories, Inc.), proton nuclear magnetic resonance (1H NMR) spectroscopy (JNM-A400;

JEOL), and ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy (JNM-ECA500; JEOL). Analyses of the structure of the product using spectroscopic methods showed the predicted structure.

1,10-Bis{3,4,5-tris[6-(4'-cyanobiphenyl-4-yloxy)hexyloxy]benzoyloxy}-1H,1H,10H,10H-heptadecafluorodecane (2). A mixture of 3,4,5-tris[6-(4'-cyanobiphenyl-4-yloxy)hexyloxy]benzoic acid¹⁵ (500 mg, 0.5 mmol) and thionyl chloride (12 mL) was stirred at room temperature for 7 h. Thionyl chloride was then removed by evaporation under reduced pressure, leaving an off-white solid. The product was dissolved in 1,4-dioxane (7 mL). DMAP (61 mg, 0.5 mmol) and 1H,1H,10H,10H-perfluoro-1,10-decanediol (116 mg, 0.25 mmol) dissolved in 1,4-dioxane (7 mL) were then added, and the resulting mixture was stirred at 80 °C for 5 h. The reaction mixture was dissolved in chloroform. Water was then added to the mixture. The organic solution was separated, dried over sodium sulfate, and filtered. The resultant solution was purified using column chromatography on silica gel with a dichloromethane and ethyl acetate (20/1) mixture as the eluent, and then purified using HPLC. The obtained solid was then reprecipitated using chloroform/ethanol (1/10) to give the desired product. Yield: 30 mg (5%) of a white solid. Inductive effect of fluorine atoms of 1H,1H,10H,10H-perfluoro-1,10-decanediol is thought to reduce reactivity of the final esterification. 1H NMR (400 MHz, $CDCl_3$): δ 7.69–7.65 (m, 12H, Ar-H), 7.63–7.59 (m, 12H, Ar-H), 7.51–7.47 (m, 12H, Ar-H), 7.28 (s, 4H, Ar-H), 6.98–6.93 (m, 12H, Ar-H), 4.80 (t, $J = 6.4$ Hz, 4H, CF_2CH_2OCO), 4.09–3.96 (m, 24H, OCH_2), 1.87–1.54 (m, 48H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.7 (C=O), 159.8 (C_{Ar-O}), 152.9 (C_{Ar-O}), 145.2 (C_{Ar-O}), 143.2 ($C_{Ar-C_{Ar}}$), 132.6 (C_{Ar-H}), 131.4 (C_{Ar-H}), 128.3 (C_{Ar-H}), 127.1 (C_{Ar-H}), 122.9 ($C_{Ar-C=O}$), 119.1 (CN), 115.5 (CF_2), 115.1 (C_{Ar-H}), 114.8 (CF_2), 111.3 (CF_2), 111.1 (CF_2), 110.9 (CF_2), 110.1 (C_{Ar-CN}), 108.5 (C_{Ar-H}), 73.4 (C-O), 69.1 (C-O), 68.0 (C-O), 60.7 (CF_2-C-O), 60.2 (CF_2-C-O), 30.2 (C-H), 29.2 (C-H), 25.9 (C-H). IR (KBr): 2935, 2869, 2225, 1724, 1609, 1248, 1207, 815 cm^{-1} . HPLC, 100%.

Liquid-Crystalline and Physical Properties. The initial phase assignments and corresponding transition temperatures for the final product were determined by optical polarized light microscopy using a polarizing microscope (Optiphot-pol; Nikon Corp.) equipped with a hot stage and FP80 control processor (FP82; Mettler Inst. Corp.). The heating and cooling rates were 5 °C min^{-1} . Photomicrographs were taken using a camera (Olympus Digital Camera C-5050 ZOOM; Olympus Optical Co. Ltd.) with a polarizing microscope (Optiphot-pol; Nikon Corp.). Temperatures and enthalpies of transition were investigated using differential scanning calorimetry (DSC) with a calorimeter (DSC6200; Seiko Instruments Inc.). The materials were studied at a scanning rate of 5 °C min^{-1} after being encapsulated in aluminum pans. The XRD patterns of the sample on cooling process were obtained using a real-time X-ray diffractometer (D8 Discover; Bruker AXS GmbH) equipped with a hot stage and a temperature-control processor. A sample was put on a convex lens, which was placed in a custom-made temperature stabilized holder (stability within ± 0.1 °C). The X-ray apparatus was equipped with a cross-coupled Göbel mirror on a platform system with a two-dimensional position-sensitive proportional counter (PSPC) detector (HI-Star; Bruker AXS GmbH). X-rays were generated at 40 kV and 40 mA; a parallel $Cu K\alpha$ X-ray beam was used to irradiate the sample. Each diffraction pattern was obtained using the PSPC detector at a camera distance of 150 mm for a short counting time of 30 s.

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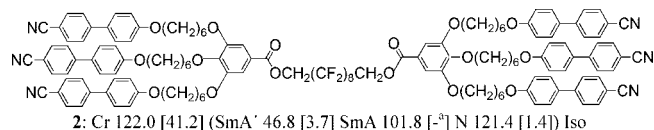


Figure 4. Molecular structure, phase transition temperatures ($^{\circ}\text{C}$), and associated transition enthalpies (kJ mol^{-1} in square brackets) of compound **2**. Brackets indicate monotropic phase transitions. "Too small to be detected."

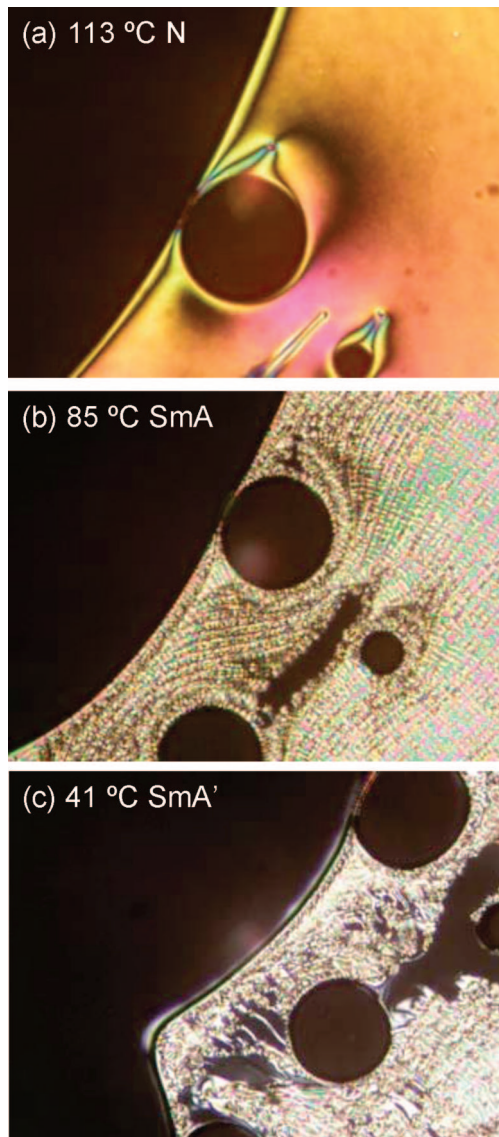


Figure 5. Optical textures of (a) the N phase at 113°C , (b) the SmA phase at 85°C , and (c) the SmA' phase at 41°C for compound **2**.

Results and Discussion

The molecular structure, phase transition temperatures ($^{\circ}\text{C}$), and associated transition enthalpies (kJ mol^{-1} in square brackets) of newly designed and prepared compound **2** are shown in Figure 4.

Compound **2** has a dimeric structure in which two tapered moieties of compound **1** are connected via a semiperfluorinated alkyl spacer. Therefore, molecular packing by the steric effect attributable to a pronounced tapering is considered to be inhibited (Figure 3). Compound **2** exhibited monotropic N and two SmA phases, designated as SmA and SmA', but

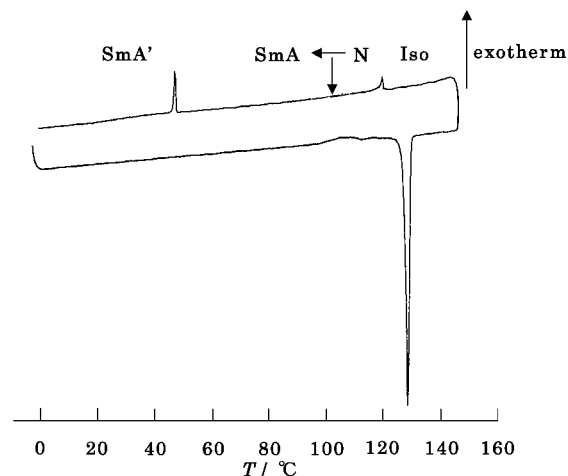


Figure 6. DSC thermogram of compound **2** at a scanning rate of $5^{\circ}\text{C min}^{-1}$.

not the Cub_V phase. Figures 5 and 6 show optical textures in an untreated glass plate and a DSC thermogram of compound **2**, respectively. A Schlieren texture was observed in the N phase as usual (Figure 5a). On cooling from the N phase, the N phase changed to the SmA phase (Figure 5b). On further cooling, the optical texture of the SmA phase almost did not change, but the fringed shape of the borderlines between the substances and air bubbles changed at the transition from the SmA to the SmA' phase, indicating an increase in viscosity at the phase transition (Figure 5b). The SmA and SmA' phases in the homeotropic region showed a dark texture, indicating that the two phases are uniaxial. When differential scanning calorimetry was used on cooling, however, an enthalpy change corresponding to the N–SmA phase transition was not detected, whereas a peak associated with an enthalpy change of 3.7 kJ mol^{-1} was obtained at the SmA–SmA' phase transition (Figure 6). The thermal behavior is reproducible over several heating and cooling cycles.

Figure 7 shows X-ray diffraction patterns in the small angle region for compound **2** on cooling from the isotropic liquid to the SmA' phase. In the N phase at 110°C , a very weak and broad peak was observed around $2\theta = 2^{\circ}$, which are typical characteristics for the N phase. After further cooling, the peak became sharpened slightly at 100°C . This result suggests the formation of the cybotactic cluster, which is observed close to a nematic to smectic phase transition. Molecules are thought to start aggregating into a cluster with a layer structure in the N phase before the transition to the SmA phase, resulting in a small energy difference between the orientational order of the N and SmA phases. Consequently, the formation of such clusters in the N phase might explain the disappearance of the enthalpy change at the N to SmA phase transition. In the SmA phase at 85°C , a sharp peak was observed around $2\theta = 2^{\circ}$, corresponding to the layer spacing of 44.3 \AA . On cooling to 45°C near the SmA to SmA' phase transition, the peak became broad and weak, and in the SmA' phase at 39°C , the peak disappeared and a new weak peak appeared around $2\theta = 4.9^{\circ}$, corresponding to the layer spacing of 17.9 \AA .

Figure 8 shows the expected elongated molecular conformation and length calculated using the MM2 method. The

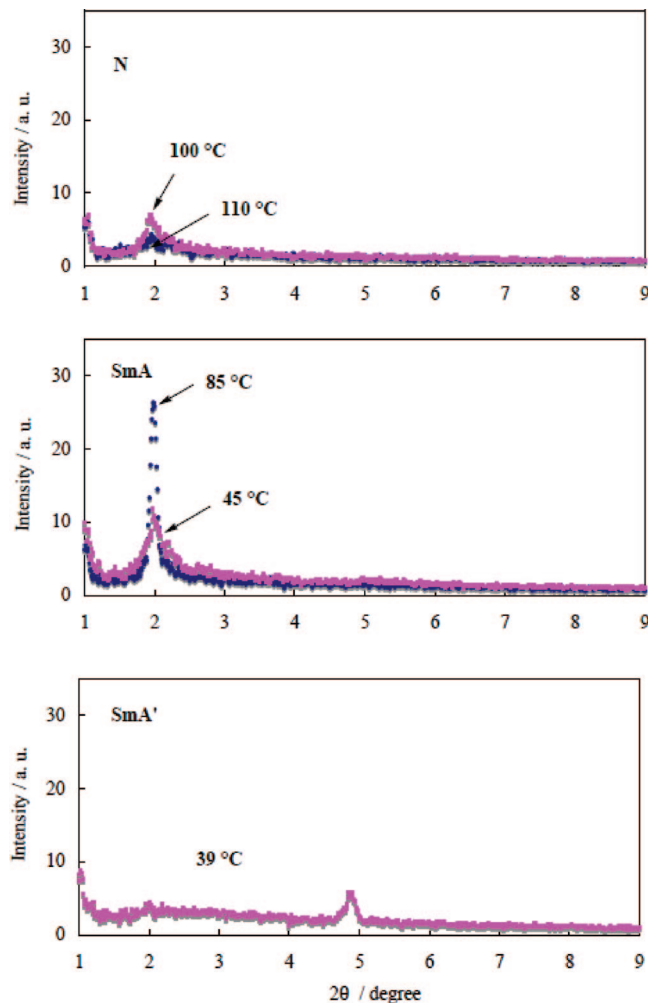


Figure 7. X-ray diffraction patterns for compound 2.

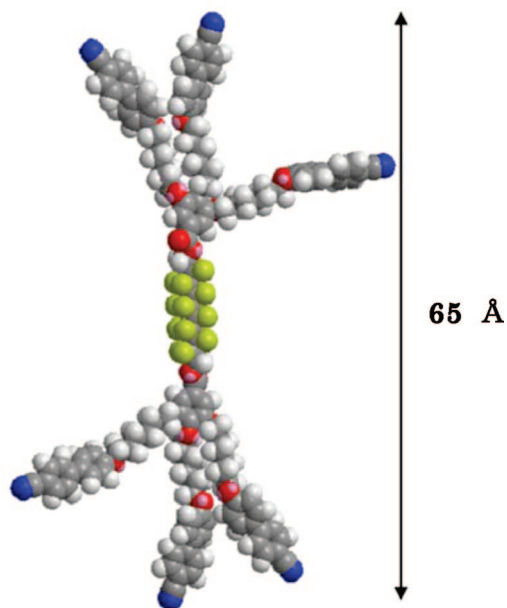


Figure 8. Expected elongated molecular conformation.

molecular length was estimated as 65 Å. Any diffraction peak around $2\theta = 1.3^\circ$ corresponding to the layer spacing of 65 Å was not observed in the SmA and SmA' phases. The observed layer spacing in the SmA phase is shorter than the molecular

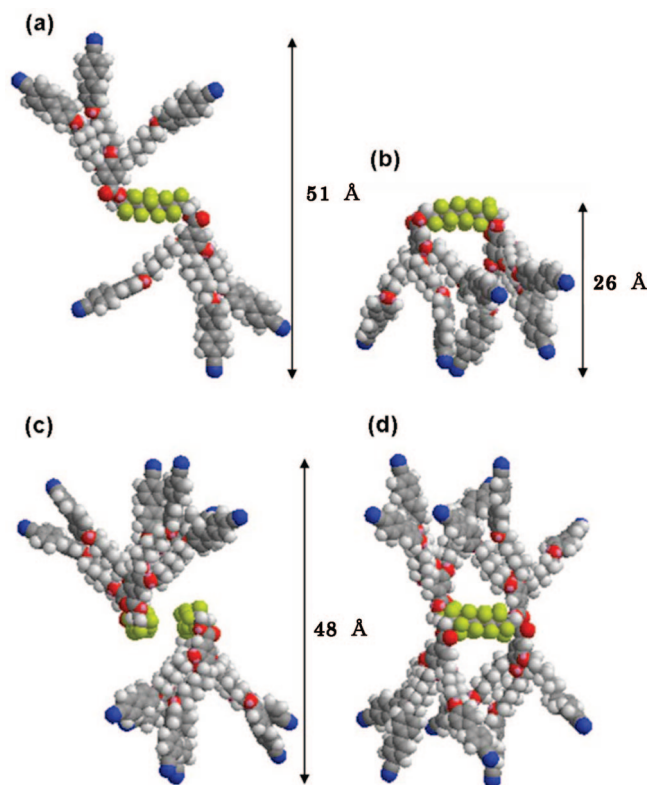


Figure 9. Two different expected (a) bent and (b) folded molecular conformations, and (c) side and (d) front views of a bilayer packing by the folded molecules.

length, but longer than a layer spacing of the possible intercalated structures. For that reason, we must consider other different molecular conformations. Parts a and b in Figure 9 depict the bent and folded molecular conformations, respectively. The molecular lengths were estimated as about 51 Å for the bent and 26 Å for the folded structure using the MM2 method. Furthermore, considering bilayer packing by the folded molecules, the length for the bilayer spacing was estimated to be about 48 Å (Figure 9c, side view; Figure 9d, front view). The minimum steric energies of the bent and folded conformations were calculated as 82.3 and 81.3 kcal mol⁻¹, respectively. The nearly identical energies indicate that two molecular conformations might coexist. Therefore, we might assume a bilayer structure in which the bent and folded molecules coexist for the SmA phase of compound 2 (Figure 10a). The molecular structures shown in Figure 9 are just the minimized energy conformations of an isolated molecule and in a condensed phase it is likely that the mesogenic units would adopt a more oriented alignment that would allow better packing in the SmA phase. Cyanobiphenyl mesogens are known to form an antiparallel dimer by a strong dipole–dipole interaction between cyanobiphenyl groups in the N and SmA phases. The shorter layer spacing (44.3 Å) than molecular length (51 Å or 48 Å), as discussed above, suggests that the intercalation of terminal cyanobiphenyl parts would occur to some extent in each layer. The semiperfluorinated alkyl spacers aggregate in the interface regions between adjacent layers in the SmA phase. If the molecules are assumed to have an extended conformation in the N phase, the bending and folding of molecules are thought to associate a measurable enthalpy change at the

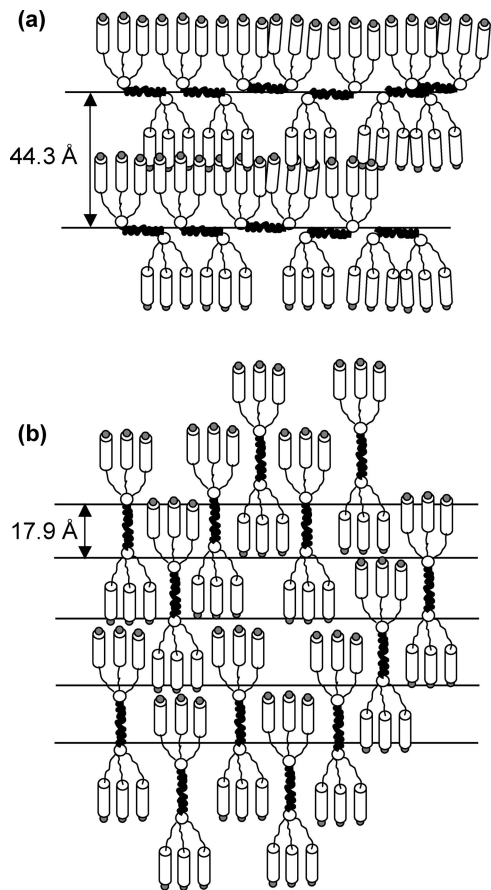


Figure 10. Possible molecular arrangements in the (a) SmA and (b) SmA' phases.

N–SmA transition. On the other hand, the formation of the cybotactic cluster in the N phase as discussed above is accelerated by microsegregation. Therefore, the molecules can form the bent or folded conformation in the N phase. At present, we do not have enough explanation for the undetectable enthalpy change at the N–SmA, and further investigation is necessary.

In the case of the SmA' phase, the elongated molecular length (65 Å) is greater than three times longer than the layer spacing (17.9 Å). Recently, Imrie et al. reported that nonsymmetric liquid crystal trimers containing three different mesogenic units exhibit a new smectic modification, the triply intercalated alternating smectic C phase, in which the layer spacing is close to one-third that of the estimated all-trans molecular length of the most extended conformation.¹⁶ Figure 10b shows a possible molecular arrangement in the SmA' phase of compound **2**. Herein, it is noteworthy that the elongated molecule has a dumbbell shape, i.e., volumes of both the terminal cyanobiphenyl mesogenic units are much larger than that of the central fluorinated spacer. This mismatch of volumes might engender the intercalated structure, as shown in Figure 10b, in which the two incompatible parts, a semiperfluorinated spacer and cyanobiphenyl mesogenic units, intercalate and compensate their mutually different volumes. The peak observed in the small-angle region is weak and broad, and the peak intensity

resembles that observed at 100 °C in the N phase, indicating that the SmA' has a weak layer periodicity. Tschierske et al. reported that calamitic bolaamphiphiles with lateral alkyl chains exhibit a mesophase with a strongly distorted structure (SmA⁺), which is typical SmA-like optical texture and by an X-ray diffraction pattern in which a diffuse scattering in the small-angle region appears adjacent to or instead of the sharp layer reflection.¹⁷ Therein, the space requirement of the lateral chains disturbs the original layer structure. On the other hand, we reported that a novel frustrated phase, which appears at lower temperature of the SmA phase, but which has no layer structure by XRD measurement, is produced by a binary system of nonsymmetric liquid crystal dimers because of frustration between core–core interactions and molecular packing.¹⁸ In the case of the SmA' phase under consideration, some voids that cannot be compensated are thought to remain, and the intercalated perfluorinated alkyl chains disturb the core–core interactions, thereby engendering the loose molecular packing and distortion of the layer ordering. Therefore, the SmA–SmA' transition was thought to be the phase transition from a bilayer to an intercalated structure with a discontinuous decrease in layer spacings. It is interesting that the discontinuous SmA–SmA' transition produces little changes in the optical texture. On the other hand, Molinier et al. reported that the glycolipids exhibit phase transitions within the SmA phase, in which the layer spacing changes continuously.¹² They proposed an explanation for the phase transition: a change is visible in the molecular conformation from a folded to a linear structure. For the folded structure, the molecules would be expected to be organized with their polar groups in uninterrupted sublayers, and their aliphatic chains intercalated.

In conventional liquid crystal dimers, a bent or U-shaped conformation is not assumed to be energetically favorable. We cannot exclude that the SmA–SmA' transition involves an unfolding of the molecules. If Figure 10a was redrawn with the mesogenic units more side by side rather than with just their ends intercalated, and with an extended flexible spacer, the layer spacing would be 46 Å as shown in Figure 11. However, there are unfavorable free volumes in the structure; therefore, the model is unrealistic.

Compound **2** was found to exhibit two SmA phases: one bilayer, the other intercalated. At the higher temperature, the segregation effect is dominant; therefore the molecules are thought to adopt bent and/or folded conformations in which methylene units at the end of the spacer are a gauche conformation. The molecules are organized into a layer structure in which the cyanobiphenyl mesogenic units and the semiperfluorinated unit are segregated into different sublayers. At the lower temperature, the freedom and flexibility of the methylene units decrease: they adopt a trans conformation, with the result that the molecule has an

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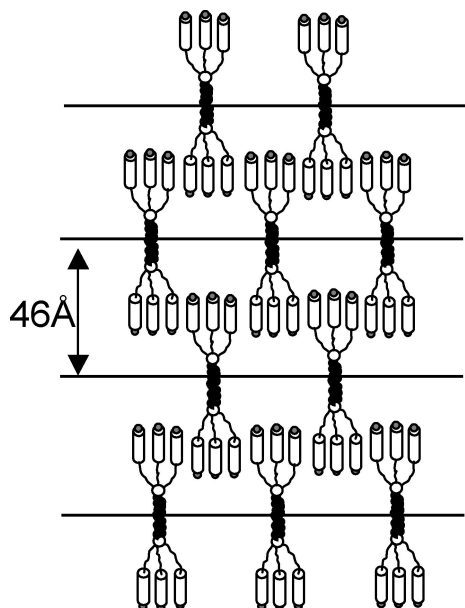


Figure 11. Possible molecular arrangement in the SmA phase organized by the extended molecules.

elongated conformation. Consequently, the steric effect is dominant, and the molecules form the intercalated layer structure.

Conclusions

We prepared an amphiphilic liquid crystal in which two taper units possessing three cyanobiphenyl moieties are each connected via a semiperfluorinated alkyl chain. The novel dumbbell molecule was found to exhibit a bilayer SmA to the intercalated SmA phase transition with a discontinuous decrease in layer spacings. The phase transition is attributable to a change in the molecular conformation from a folded (or bent) structure, stabilized by the segregation effect to a linear structure by the steric effect.

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