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Locally polar smectic A phase in V-shaped molecules


The first obvious experimental evidence that V-shaped molecules with acute-subtended angle (Ar), in cooperation with a lateral halogen substituent (X), can form the locally polar smectic A phase (SmAP$_n$).
Locally polar smectic A phase in V-shaped molecules


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1. Introduction

Nowadays polar property of mesophase is a hot issue in the research field of liquid crystals because of its potential application in advanced information-display areas of technology. In 1974, it was discovered that if chiral molecules with rod-like mesogen form the tilted smectic phase their mesophases can possess the spontaneous polarization: these mesophases are the polar smectic C phase (SmCP). In 1996, Takezoe and Watanabe’s group reported the first obvious example of a SmCP derived from an achiral molecule with bent-core mesogen. In 1997, Clark and Walba’s group depictedly explained the layer structure of the SmCP using three stereogenic elements such as chirality (+/-), clinicity (S/A) and polarity (F/A) of the adjacent layer: there are four states such as SmC{sub A}, SmC{sub B}, SmC{sub A} and SmC{sub B}. Since then, a large number of studies have been made on the SmCP.

On the other hand, so far limited number of studies on SmAP (the polar semi A phase) for an example, asymmetric banana-shaped molecules can form the SmAP. Recently, Pociecha et al. have reported that SmAP in asymmetric banana-shaped molecules has a layered, nontilted, optically uniaxial and polarly ordered structure with random direction of the layer polarization. To account for the structure of such SmAP, five possible arrangements have been proposed, SmAP{sub E}, SmAP{sub A}, SmAP{sub E}, SmAP{sub A} and SmAP{sub R}. α stands for helicoidally modulated polarization with the short pitch; R stands for a randomly oriented polarization. Moreover, Shimbo et al. reported that such polar SmAP shows the fast polarization orientation and the associated birefringence as an in-plane electronic field was applied to vertically aligned cells, which originate from the cooperative motion of the bent molecules with quasi-long-range order of dipoles based on a two-dimensional Langevin process.

According to the bent angle of central core, the bent-core molecules can be classified into two categories: the V-shaped molecules that have acute angled central core and the banana-shaped molecules that have obtuse angled central core. To date the polar mesophase of the banana-shaped molecules has been an object of study for a long time. However, there is little agreement as to the polar mesophase of the V-shaped molecules. In the beginning of 1990, Japanese groups firstly reported that the V-shaped molecules with 1,2-phenylene central core form conventional nematic, smectic A and smectic B phases depending on the length of flexible terminals. Since then, more studies on this topic have been reported by several research groups. Prasad reported that a series of 1,2-phenylene bis[(4-alkoxyphenyl)benzoates] form nematic, smectic A and crystal E phases. Yelamaggad et al. reported that V-shaped molecules with salicylaldimine segments form nematic and smectic A phases due to the intramolecular hydrogen bonding. Watanabe et al. reported that V-shaped molecules with 1,2-, 1,3-, 1,7- and 2,3-dihydroxyphenylalanine central core form smectic A and B{sub 2} phases. Recently, we reported that a main-chain polymer with a V-shaped mesogen based on 2,3-naphthalene form SmCP and a V-shaped molecule with 2,3-dihydroxyphenylalanine central core forms an electric-field-induced SmAP.

In this paper, four new V-shaped molecules with an acute-angled central core (Ar) and a lateral halogen substituent (X) have been synthesized as shown in Scheme 1. Their mesomorphism properties were investigated by DSC, polarizing microscopy, and X-ray diffraction, and electro-optical measurements. We have described the obvious experimental evidence that our V-shaped molecules can form the SmAP{sub R}.
2.1. Synthesis

The V-shaped molecules (4a-4d) were synthesized by a modification of the procedure previously reported by our group: compound 1 was prepared by the direct esterification,[20] and then compound 4 was prepared by nucleophilic addition followed by dehydration.[19] The purity and structure of the final compound was confirmed by thin-layer chromatography, elemental analysis, and FT/IR and $^1$H NMR spectrometry. The resultant data was in accordance with the expected formula.

Compound 4a. IR (KBr Pellet, cm$^{-1}$): 3074 (aromatic =C-H, st), 2917, 2848 (aliphatic C-H, st), 1737 (C=O, st), 1512, 1488 (aromatic C=C, st), 1628 (C=N, st), 1242, 1106, 1070 (C-O, st). $^1$H NMR (CF$_3$COOD, $\delta$ in ppm): 8.70 (2H, s, N=CH), 8.12 (4H, t, J=6.33Hz OCH$_2$), 1.84-1.66 (4H, m, OCH$_2$CH$_2$), 1.40-0.99 (36H, m, OCH$_2$CH$_2$CH$_2$). Elemental analysis calcd (%) for C$_{85}$H$_{164}$N$_2$O$_6$: C 74.97, H 7.59, N 3.01; found C 75.13, H 7.89, N 3.21.

Compound 4b. IR (KBr Pellet, cm$^{-1}$): 3063 (aromatic =C-H, st), 2928, 2850 (aliphatic C-H, st), 1738 (C=O, st), 1513, 1469 (aromatic C=C, st), 1617 (C=N, st), 1259, 1231, 1055 (C-O, st). $^1$H NMR (CF$_3$COOD, $\delta$ in ppm): 8.44 (2H, s, N=CH), 8.23-6.74 (16H, m, Ar-H), 1.35-0.88 (4H, t, J=6.54Hz OCH$_2$), 1.86-1.76 (4H, m, OCH$_2$CH$_2$), 1.43-1.25 (36H, m, OCH$_2$CH$_2$CH$_2$). Elemental analysis calcd (%) for C$_{85}$H$_{164}$Cl$_2$N$_2$O$_6$: C 72.41, H 7.33, N 2.91; found C 72.60, H 7.53, N 3.03.

2.2. Characterization

**Instruments.** IR and NMR spectra were obtained by a Jasco 3000 FT/IR and a Bruker Avance 400 MHz NMR spectrometer, respectively. Elemental analysis was performed with a Thermo Scientific Flash 2000 Elemental Analyzer. The transition behaviors were characterized by a differential scanning calorimeter (Netzsch DSC 200 F3 Maia). DSC measurements were performed in a N$_2$ atmosphere with heating and cooling rates of 10 and 20 °C/min. Optical texture observation was carried out using a polarizing microscope (Carl Zeiss Axioskop 40) with a heating stage (Mettler FP82HT).

**X-ray Investigation.** XRD measurements were performed in transmission mode with synchrotron radiation ($\lambda$ = 1.54 Å) at the Pohang Accelerator Laboratory. When heating and cooling, the sample, which was sealed on both sides with 7 μm thick Kapton film, was held in an aluminum sample holder. The data are presented as a function of $q = 4\sin\theta/\lambda$ (θ: the scattering angle).

The sample was heated with two cartridge heaters, and its temperature was monitored by a thermocouple placed close to the sample. A background scattering correction was performed by subtracting the scattering from the Kapton film.

**Electro-Optical Measurement.** The LC was injected between two ITO glass substrates by capillary action at 180°C. Each non-patterned ITO glass substrate was spin-coated with a commercial planar alignment regent (AL22620, JSR). The spin-coated alignment layer was pre-baked at 100°C for 10 min to evaporate the solvent, and then cured at 210°C for 1 h to complete imidization reaction. The rubbing directions of the upper and the lower substrates were antiparallel to each other. The cell thickness was maintained using glass spacers of 4.5 μm. The temperature of the cell was maintained with an accuracy of within 0.1°C using a heating stage (FP90, Mettler). The switching current response characteristics were measured by applying a triangle wave voltage ($E = 22$ V μm$^{-1}$, $f = 3$ Hz).
3. Results and Discussion

3.1. Mesogenic Properties

Mesogenic properties have been examined by thermal, optical, and x-ray measurements. In Fig. 1, DSC thermograms of compounds show two distinctive transition temperatures that have been defined as melting ($T_m$) and isotropization ($T_i$), respectively. The transition temperatures and enthalpy changes, defined by DSC are summarized in Table 1. Among four compounds, compound 4e with Ar/X = 2,3-Naph/F exhibits the highest $T_m$ value and compound 4d with Ar/X = 2,3-Naph/Cl exhibited the lowest one. This implies that a highly bent 2,3-phenylene central core with a second ring extruded can play either a constructive or destructive role in molecular packing.

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**Fig. 1.** DSC thermograms obtained with heating and cooling rates of 10 (a-d, f-i, k, m) or 20 °C/min (e, j, l, n): dash-line: 1st cooling; solid-line: 1st heating; dash-dot-line: 2nd heating. (a-c) 4a; (d-g) 4b; (h-j) 4c; (k-n) 4d.

**Table 1.** Transition temperatures (°C) and enthalpy changes (kJ mol⁻¹)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ar/X</th>
<th>DSC scan</th>
<th>$T_m$</th>
<th>$\Delta H_m$</th>
<th>$T_i$</th>
<th>$\Delta H_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>1,2-Phen/F</td>
<td>1-H</td>
<td>95</td>
<td>59.0</td>
<td>150</td>
<td>3.1</td>
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<tr>
<td></td>
<td></td>
<td>1-C</td>
<td>61</td>
<td>7.3</td>
<td>148</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-H</td>
<td>94</td>
<td>58.6</td>
<td>150</td>
<td>3.0</td>
</tr>
<tr>
<td>4b</td>
<td>1,2-Phen/Cl</td>
<td>1-H</td>
<td>83</td>
<td>54.9</td>
<td>133</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1-C</td>
<td>75</td>
<td>3.3</td>
<td>130</td>
<td>2.5</td>
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<tr>
<td></td>
<td></td>
<td>2-H</td>
<td>88</td>
<td>3.0</td>
<td>133</td>
<td>2.5</td>
</tr>
<tr>
<td>4c</td>
<td>2,3-Naph/F</td>
<td>1-H</td>
<td>118</td>
<td>47.1</td>
<td>242</td>
<td>7.6</td>
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<tr>
<td></td>
<td></td>
<td>1-C</td>
<td>42</td>
<td>6.4</td>
<td>234</td>
<td>6.1</td>
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<tr>
<td>4d</td>
<td>2,3-Naph/Cl</td>
<td>1-H</td>
<td>75</td>
<td>3.3</td>
<td>231</td>
<td>9.3</td>
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<tr>
<td></td>
<td></td>
<td>1-C</td>
<td>41</td>
<td>2.5</td>
<td>224</td>
<td>7.1</td>
</tr>
</tbody>
</table>

*Abbreviation: 1-H = 1st heating; 2-H = 2nd heating; 1-C = 1st cooling.

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**Fig. 2.** Synchrotron radiation X-ray diffraction profiles of compounds obtained at given temperatures (°C, in parentheses). Abbreviation: RT = room temperature; H = heating process; C = cooling process.
solid state in cooperation with the lateral halogen substituent. On the other hand, the ΔHf values of compounds 4e and 4d have 2.5 and 3.6 times greater than those of compounds 4a and 4b, respectively. This means that the 2,3-naphthylene central core plays an important role in enhancing directional ordering of mesogens instead of steric hindrance in their mesophase.

In Fig. 1, the melting behavior for compound 4b with X = Cl depends on the thermal history whereas compound 4a with X = F did not show that. The fluorine atom can bestow better packing property due to higher electron negativity, lower molecular cohesive energy and smaller van der Waals radius compared with the chlorine atom. In case of compounds 4e and 4d, the similar result was observed although their Tm are enough high to suffer thermal decomposition (Fig. 1, j and n).

In Fig. 2, the X-ray diffraction patterns obtained during heating and cooling process. The powder samples were mounted between two amorphous Kapton films. At temperatures below Tm defined by DSC, all compounds exhibited many diffraction peaks, indicating a crystalline state. As heated above the Tm, a strong peak was found in the small angle region, while the all peaks in the wide angle region disappeared. This is indicative of the smectic phase. As further heated above Tm defined by DSC, only broad scattering patterns were observed, indicating an isotropic liquid phase. Subsequently, when the isotropic liquid was cooled below the Tm, the smectic phase appeared reversibly in all compounds. As further cooled to room temperature, compound 4a exhibited most distinctive recrystallization, according with the DSC result.

In Table 2, the layer spacing (d) values of the smectic mesophases are in the ranged of 3.77-4.00 nm. In general the d-spacing values show subtle differences not only depending on structure but also temperature. This indicates that bent angles of molecules can be altered by temperature change in the melt state.

To account for a stable conformation, in a similar way with 1,3-phenylene central unit,[21,22] we have postulated that phenyl rings are coplanar when carbonyl groups are attached to them, and alkynoxy groups in all-trans conformation are equiplanar to the benzene rings. Moreover, we assumed that the bent angle is 60° degree and there is no intercalation between chains. Then, we can estimate the length of molecule with the all-trans-conformation to be 3.53 nm by using the PCFF force-field model of martial studio. However, this value is not matched with d values determined by X-ray measurements. Nevertheless, the postulation that the molecules would form tilted smectic mesophase can be excluded because the d-spacing value would be smaller than 3.53 nm. In the mean time, if you assume that bent angles are larger than 60°, the fact that d-values are larger than 3.53 nm can be explained by the formation of smectic A phase. Then, you can calculate the opening angle of arms to be 76.9-82.6 degree corresponding to d = 3.77-4.00 nm.

In Fig. 3 shows cross-polarizing optical micrographs obtained by using a normal slide glass. During heating process, compounds 4a and 4d showed the optical texture shown in Fig. 3a and b, respectively, while compounds 4b and 4c showed homeotropic-like optical texture. When the isotropic liquid was cooled, no birefringence was occurred at the isotropic-to-smectic transition temperatures and then the smectic phases held a homeotropic optical texture until solidification. Note that compounds 4a and 4e showed the Maltese-cross spherulites with homeotropic region as shown in Fig. 3c and d, respectively.

**Fig. 3.** Cross-polarizing optical micrographs obtained at given temperature (x200). On heating: (a) 4a at 127°C; (b) 4d at 225 °C. On cooling: (c) 4a, at 37°C; (d) 4c, at 65°C.

**Fig. 4.** Cross-polarizing optical micrographs obtained using planarly aligned cells at given temperatures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ar: X</th>
<th>Process temp. (°C)</th>
<th>q (nm⁻²)</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>1,2-Phen/F</td>
<td>H(120)</td>
<td>1.64</td>
<td>3.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(140)</td>
<td>1.64</td>
<td>3.83</td>
</tr>
<tr>
<td>4b</td>
<td>1,2-Phen/Cl</td>
<td>H(110)</td>
<td>1.65</td>
<td>3.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(100)</td>
<td>1.64</td>
<td>3.83</td>
</tr>
<tr>
<td>4c</td>
<td>2,3-Naph/F</td>
<td>H(150)</td>
<td>1.67</td>
<td>3.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(220)</td>
<td>1.61</td>
<td>3.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(200)</td>
<td>1.58</td>
<td>3.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(60)</td>
<td>1.57</td>
<td>4.00</td>
</tr>
<tr>
<td>4d</td>
<td>2,3-Naph/Cl</td>
<td>H(200)</td>
<td>1.62</td>
<td>3.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(200)</td>
<td>1.61</td>
<td>3.90</td>
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<tr>
<td></td>
<td></td>
<td>C(60)</td>
<td>1.64</td>
<td>3.83</td>
</tr>
</tbody>
</table>
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Fig. 5. Switching current response for compounds by applying a triangular voltage (E = 22 V μm⁻¹, f = 3 Hz) at given temperatures.

Fig. 6. (a) Peak separations of reverse current curves taken at smectic phase. (b) Temperature dependence of the polarization estimated from 1st peak (●), 2nd peak (♦), and total peak (○) of reverse current.

3.2. Electro-optical Property

For electro-optical investigation, planarly aligned cells were used. The rubbing directions of the upper and the lower substrates were antiparallel to each other. In Fig. 4, the direction of polarizer (P) and analyzer (A) crossing each other make an angle of 45° with the rubbing direction (R). On the planar alignment layers, the optical textures of compounds 4a–4c show the incomplete unidirectional alignment similar to micro-domains. The transmittance differences among these compounds are rather attributed to the different effective retardation: although the cell gaps are almost same, the incomplete uniformity in alignment and different magnitude of birefringence can lead each texture to different brightness and colors. Nonetheless, compound 4d has the totally different textures compared with compounds 4a–4c. This indicates that the former forms a different type of smectic phase from the latter.

Moreover, we have measured the polar property for these smectic mesophases by using current peak evaluation. Fig. 5 shows the switching current response on applying a triangular wave voltage. The reverse current peaks appeared at every half period of applied voltage, indicating a polar switching. In Fig. 6a, the all reverse current peaks are clearly separated by two individual peak functions. In Fig. 6b, the spontaneous polarizations gradually increase as the temperature increases. As a result, we have suggested that the smectic phases of 4a–4c are...
locally polar, SmAP$_R$. But the smectic phase of 4d was conventional.

4. Conclusions

Four V-shaped molecules containing an acute-angled central core (Ar = 1,2-Phen or 2,3-Naph) and a lateral halogen substituent (X = F or Cl) have been synthesized. Their mesomorphic properties were investigated by DSC, polarizing microscopy, X-ray and electro-optical measurements. All compounds were enantiotropically liquid crystalline. In general, compounds showed homeotropic optical texture using a normal slide glass without surface treatment. In contrast, using a planar alignment cell, compounds with Ar/X = 1,2-Phen/F, 1,2-Phen/Cl, and 2,3-Naph/F showed the optical texture with the incomplete unidirectional alignment. According to our experimental data, we have concluded that compounds with Ar/X = 1,2-Phen/F, 1,2-Phen/Cl, and 2,3-Naph/F formed the locally polar smectic A phase, SmAP$_R$. But compound with Ar/X = 2,3-Naph/Cl formed the conventional smectic A phase. From the structural point of view, smectic A phase in these compounds can be compared with smectic C phase in the polymer analogues. This different mesomorphism may be attributed to competition between mesogenic unit’s tendency toward molecular ordering and main chain’s tendency toward stable conformation, which is much greater in the melt state of polymer than that of compound. Meanwhile it is not clear why 4d formed conventional A phase while the other compounds formed the polar smectic A phase. Perhaps the lateral chlorine substitution is less effective to dipolar orientation than the lateral fluorine substituent. Further study is needed to fully understand this subject.

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References