Synthesis of Tripod-shaped Liquid Crystals with sp³ Nitrogen at the Apex

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Tripod-shaped liquid crystals with sp³ nitrogen at the apex were prepared from triethanolamine. Their physical properties were investigated by using optical microscopy, differential scanning calorimetry, and X-ray diffraction measurements. The XRD study suggests that the tripod-shaped molecules show the 2D-ordered phase of either the frustrated smectic layer structure or discotic columnar phases.

Key Words: Liquid crystals, Tripod, Two-dimensional order

Introduction

Liquid crystals have received much attention in diverse application in the fields of materials and bio-related science. Conventional liquid crystalline materials consist of molecules having rod-like or disc-like rigid core with flexible chains attached. Recent advance in LC research has been stimulated by the new concept in designing nonconventional molecules such as banana-shaped molecules, ball-like or hollow cone shaped molecules, and badminton shuttlecock-shaped molecules.

We described herein the synthesis and mesomorphic properties of tripod-shaped liquid crystals with sp³ nitrogen at the apex. Liquid crystals with heteroatom at the apex are quite rare. Some of the works have intended to apply these molecules for application such as self-assembled polar structures, photoluminescence, and electric-field-induced switching. Some of the tripod-shaped liquid crystals with polyacetylene chains could form a disc to assemble columns. The new concept in designing nonconventional molecules such as banana-shaped molecules, bowl-like or hollow cone shaped molecules, and badminton shuttlecock-shaped molecules was added as an an} amine

Experimental Section

Measurements. 1H NMR and 13C NMR spectral data were obtained on Varian Gemini-300 (300 MHz) spectrometer. The textural observation was made under crossed polarizers using an Olympus BX50 polarizing optical microscope (POM) equipped with a temperature controlled by Mettler Toledo FP82 hot stage. Transition temperatures were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 7 calorimeter. X-ray diffraction measurements were performed using a Rigaku-Rint-2000 diffractometer with CuKα radiation.

Synthesis. Tris[2-[4-(4-alkyloxyphenyliminomethyl)]benzoyloxy]ethan]amine 5: A solution of trisaldehyde 3 (52 mg, 0.095 mmol) and p-octyloxyaniline (4a, 53 mg, 0.29 mmol) in chloroform (2 mL) was stirred at room temperature for 40 h. To the cold mixture ethanol was added dropwise. The resulting precipitates were filtered, washed with ethanol and stirred under vacuum to give 88 mg (80%) of 5a. 5a: 1H NMR δ 3.08 (t, 6 H, J = 5.1 Hz), 1.75 (m, 36 H), 1.56 (m, 48 H), 3.11 (t, 6 H, J = 8.9 Hz), 7.83 (d, 6 H, J = 7.8 Hz), 8.02 (d, 6 H, J = 7.8 Hz), 8.44 (s, 3 H); 13C NMR δ 13.4, 22.9, 26.3, 29.4, 29.55, 29.63, 31.2, 53.6, 63.4, 68.5, 115.2, 122.7, 128.6, 130.1, 140.6, 144.2, 156.6, 158.6, 166.3.

Compounds 5b-f were similarly prepared in 79, 79, 90, 48, and 73% yield, respectively. 5b: 1H NMR δ 0.88 (t, 9 H, J = 6.9 Hz), 1.28 ~ 1.46 (m, 36 H), 1.76 ~ 1.81 (m, 6 H), 3.10 (t, 6 H, J = 5.1 Hz), 3.95 (t, 6 H, J = 6.6 Hz), 4.46 (t, 6 H, J = 5.1 Hz), 6.88 (d, 6 H, J = 8.7 Hz), 7.20 (d, 6 H, J = 8.7 Hz), 7.82 (d, 6 H, J = 8.3 Hz), 8.01 (d, 6 H, J = 8.3 Hz), 8.44 (s, 3 H); 13C NMR δ 14.3, 22.9, 26.3, 29.5, 29.6, 29.8, 32.06, 32.12, 53.6, 63.4, 68.5, 115.2, 122.7, 128.6, 130.1, 132.0, 140.6, 144.2, 156.6, 158.6, 166.3.

5c: 1H NMR δ 0.88 (t, 9 H, J = 6.6 Hz), 1.27 ~ 1.43 (m, 42 H), 1.70 ~ 1.84 (m, 6 H), 3.14 (t, 6 H, J = 5.4 Hz), 3.95 (t, 6 H, J = 6.6 Hz), 4.48 (t, 6 H, J = 5.4 Hz), 7.05 (d, 6 H, J = 8.9 Hz), 7.21 (d, 6 H, J = 8.9 Hz), 7.83 (d, 6 H, J = 8.4 Hz), 8.02 (d, 6 H, J = 8.4 Hz), 8.44 (s, 3 H); 13C NMR δ 14.4, 22.9, 24.3, 26.3, 29.6, 29.7, 29.8, 32.1, 53.6, 63.4, 68.5, 115.2, 122.7, 128.6, 130.1, 132.0, 140.6, 144.2, 156.6, 158.6, 166.3.

5d: 1H NMR δ 0.88 (t, 9 H, J = 6.6 Hz), 1.27 ~ 1.56 (m, 48 H), 1.74 ~ 1.81 (m, 6 H), 3.11 (t, 6 H, J = 5.4 Hz), 3.95 (t, 6 H, J = 6.6 Hz).
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6.6 Hz), 4.46 (t, 6 H, J = 5.4 Hz), 6.88 (d, 6 H, J = 8.4 Hz), 7.24 (d, 6 H, J = 8.4 Hz), 7.83 (d, 6 H, J = 8.1 Hz), 8.19 (d, 6 H, J = 8.1 Hz), 8.44 (s, 3 H), 13C NMR δ 14.3, 22.9, 24.15, 24.20, 26.3, 29.6, 29.7, 29.8, 32.1, 53.7, 63.4, 68.5, 115.2, 122.6, 128.5, 130.1, 132.0, 140.6, 144.2, 156.6, 158.6, 166.2.

5e: 1H NMR δ 0.88 (t, 9 H, J = 6.6 Hz), 1.27 ~ 1.56 (m, 48 H), 1.74 ~ 1.81 (m, 6 H), 3.11 (t, 6 H, J = 5.4 Hz), 3.95 (t, 6 H, J = 6.6 Hz), 4.46 (t, 6 H, J = 5.4 Hz), 6.88 (d, 6 H, J = 8.4 Hz), 7.24 (d, 6 H, J = 8.4 Hz), 8.19 (d, 6 H, J = 8.1 Hz), 8.44 (s, 3 H), 13C NMR δ 14.3, 22.9, 24.15, 24.20, 26.3, 29.6, 29.7, 29.8, 32.1, 53.7, 63.4, 68.5, 115.2, 122.6, 128.5, 130.1, 132.0, 140.6, 144.2, 156.6, 158.6, 166.2.

5f: 1H NMR δ 0.88 (t, 9 H, J = 7.2 Hz), 0.90 (d, 9 H, J = 6.9 Hz), 1.09 ~ 1.90 (m, 33 H), 3.19 (dd, 3 H, J = 9.3, 6.9 Hz), 3.28 (dd, 3 H, J = 9.3, 6.3 Hz), 3.47 (t, 6 H, J = 6.3 Hz), 3.99 (t, 6 H, J = 6.3 Hz), 6.89 (d, 6 H, J = 9.0 Hz), 7.22 (d, 6 H, J = 9.0 Hz), 7.84 (d, 6 H, J = 8.4 Hz), 8.02 (d, 6 H, J = 8.4 Hz), 8.45 (s, 3 H); 13C NMR δ 11.6, 16.8, 26.4, 26.5, 26.6, 35.2, 53.6, 63.4, 68.2, 70.7, 76.5, 115.2, 122.6, 128.5, 130.1, 131.7, 140.5, 144.2, 156.6, 158.5, 166.2.

Scheme 2.

Results and Discussion

New tripod-shaped liquid crystals with achiral (5, Cn, n = 8, 9, 10 and 11) and chiral terminal groups (5, Cn, n = 9 and 10) were synthesized and their mesomorphic properties were investigated. The synthetic route leading to the compound 5 is shown in Scheme 1.

Aniline carrying chiral chains 4e and 4f were prepared from the mono oxyalkylation of ditosylate 7 with (S)-2-methyl-1-butoxide, followed alkylation and hydrolysis as shown in Scheme 2.

The mesophase transition temperatures and enthalpies of the new liquid crystal 5 were determined by DSC in conjunction with POM (Table 1). All achiral compounds (C8 ~ C11) enantiotropically exhibit the smectic phases, and their crystallization temperatures decrease as chain length of the terminal alkyl increases.

Chiral compounds C9° and C10° show enantiotropical transitions, their transition temperatures are much lower than those of achiral compounds, Cn. This might be due to the effect of branching methyl group in the chiral terminal chain as was observed in the banana-shaped liquid crystals.7

When the cell was slowly (0.1 °C min−1) cooled from the isotropic phase, colorful mosaic-like texture appeared with a fan-shaped domain in some regions, and quickly changed to the red color domain, as shown in Figure 1.

Chiral compounds C9° and C10° did not show the fan-shaped
Table 1. Transition temperatures (°C) and enthalpies (ΔH, kJ mol⁻¹) (in italics) of tripod-shaped molecules measured on cooling at a rate of 10 °C min⁻¹

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Sm</th>
<th>Iso</th>
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<tbody>
<tr>
<td>C8</td>
<td>175.5</td>
<td>136.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.1</td>
<td>44.4</td>
<td></td>
</tr>
<tr>
<td>C9</td>
<td>172.9</td>
<td>130.5</td>
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</tr>
<tr>
<td></td>
<td>24.8</td>
<td>43.3</td>
<td></td>
</tr>
<tr>
<td>C10</td>
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<td>127.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>23.3</td>
<td>43.0</td>
<td></td>
</tr>
<tr>
<td>C11</td>
<td>169.2</td>
<td>123.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22.5</td>
<td>48.6</td>
<td></td>
</tr>
<tr>
<td>C9*</td>
<td>134.0</td>
<td>74.6</td>
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</tr>
<tr>
<td></td>
<td>16.6</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>C10*</td>
<td>135.0</td>
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</tr>
<tr>
<td></td>
<td>18.9</td>
<td>23.7</td>
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</table>

domain observed for those compounds carrying achiral straight chains, but showed more characteristic mosaic-like textures as shown in Figure 2. Any special effect by chirality was not observed.

The X-ray pattern was obtained by using X-ray beam perpendicular to cells sandwiched between thin glasses. The results for C8 are shown in Figure 3: (a) Sm and (b) Cryst. In addition to two sharp inner reflections, 42.7 Å and 30.8 Å, a broad outer reflection with a spacing of around 4.5 Å were observed in the Sm phase, indicating intralayer liquid-like order. These characteristics of the diffraction properties are similar to those observed for the 2-dimentional (2D) frustrated smectic phase, and if the original and additional diffractions correspond to (001) and (101), the diffraction geometry of the frustrated phase can be explained by 2D lattice with a = 43.4 Å and c = 42.7 Å, as shown in Figure 4(a). Here c is equivalent to the smectic layer spacing.

Generally frustrated phase exhibits additional small-angle Bragg peaks away from the meridian. The frustrate phase was observed in mesogens having strongly polar end groups, but it was reported later that other types of molecular asymmetry such as steric effects can also induce the same structures.¹

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(a) C9* (124.0 °C) and (b) C10* (133.5 °C).

Figure 2. Microphotographs of Sm phases observed for (a) C9* and (b) C10*.

44.6 Å (▲)
26.9 Å (□)

Figure 5. Calculated molecular length of C8 by Spartan’02.

(a) (b)

Figure 3. Non-oriented X-ray diffraction patterns for the (a) Sm phase and (b) crystal phase of compound C8.

(a) Frustrated smectic phase and (b) discotic columnar phase.

Figure 4. Possible molecular orientational structures in a unit cell. (a) Frustrated smectic phase and (b) discotic columnar phase.

Similar mesomorphic properties were also reported in the bent-shaped molecules, in which the bent-shaped molecules with shorter terminal alkyl chains is more favorable to form the frustrated structure due to the strong core-core interaction.

Molecular length (44.6 Å) on the most extended chains of C8 was also calculated by the spartan’02 program, as shown in Figure 5. This is slightly larger than the layer spacing. This result may indicate that the molecules are tilted to the layer normal. However, because of the flexibility of center of molecular, it is very difficult to predict the accurate structure within layer. For example, these molecules may have the structure of dimeric bent-shaped molecules, in which layer spacing will be narrower than calculated molecular length although molecules do not tilt with respect to the layer normal.

Because the lattice is quite close to a square lattice, we can also suggest a discotic columnar phase, in which disc- or tripod-shaped molecules are stacked to form columns, as shown in Figure 4(b). Detailed study for the structures of molecular assemblies are necessary.

C9, C10, and C11 also showed the similar microscope textures. The layer spacings increased as the length of the alkyl terminal chain increased, i.e., 44.2 Å, 45.8 Å, and 47.8 Å for C9, C10, and C11, respectively, as shown in Figure 6 (closed squares). Special odd-even performance did not appear. Calculated molecular lengths (see Figure 5) are also shown in Figure 6 (closed triangles and closed circles). They give the same ten-
dency as the experimental observation of the layer thickness.

In summary, the tripod-shaped molecules studied show the 2D-ordered phase, either of the frustrated smectic layer structure or discotic columnar phase, but it is difficult to conclude the real well-defined structure because of a flexible central core. Thus, more comprehensive data including small-angle X-ray diffraction of aligned samples are necessary for the discussion of detailed mesophase structure, and will be reported in due course.

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References


