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## Liquid Crystals

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# New 1,3-dioxane type ionic liquid crystal materials having a terminal double bond

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New 1,3-dioxane type ionic liquid crystal materials having a terminal double bond were synthesized. The mesomorphic behaviour of these compounds was measured. The principal features of these compounds are a smectic A phase over a very wide range including room temperature, and a low isotropic to mesophase transition temperature (for example, compound **6-1**: Cr-22 SmA 25 I).

## 1. Introduction

There are few reports concerning ionic thermotropic liquid crystal (LC) compounds having two rings in their central core. Some LC polymers with pyridinium side chains [1] or with an alkylammonium salt as a principal chain have been reported [2]. Stilbazole type ionic LCs have also been reported [3–5]. Moreover, we have previously studied 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane type new LC materials [4–17], but ionic LC materials having these structures in their central core have not previously been encountered, although their possibilities are interesting. From this point of view, new LC compounds containing the 1,3-dioxane structure were reported as a Communication [18]. In that report one compound having a terminal double bond exhibited a markedly lower isotropic to smectic transition temperature. Therefore, in this paper we wish to report further on these ionic LC compounds having a terminal double bond.

## 2. Results and discussion

Compounds **6** were synthesized by the route shown in figure 1.

In the syntheses of compounds **5**, both *trans*- and *cis*-isomers were produced, differing at the C-5 position

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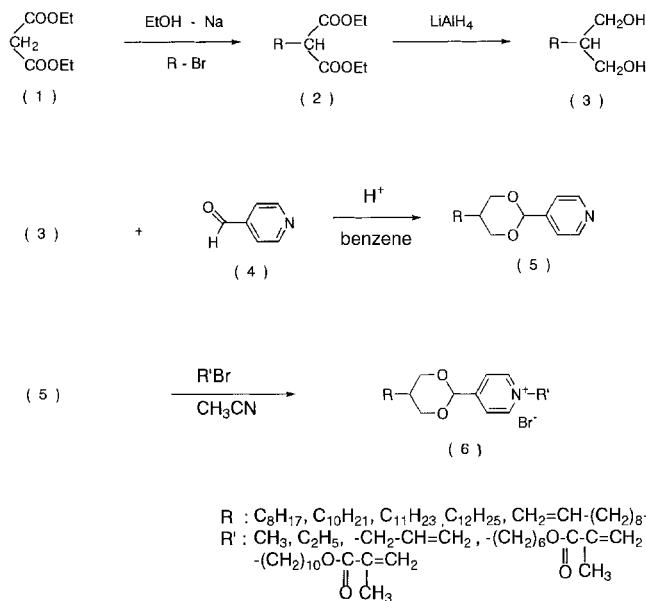


Figure 1. Synthetic pathway for compound **6**.

of the 1,3-dioxane ring. Repeated recrystallization was required to obtain pure *trans*-isomer. In the  $^1\text{H}$  NMR spectra for compounds **5**, the C-2 proton signals for the *trans*- and *cis*-isomer are 5.50 and 5.55 ppm, respectively, therefore removal of the *cis*-isomer could be followed by the disappearance of its peak in the  $^1\text{H}$  NMR spectrum.

The *N*-alkylation caused  $^1\text{H}$  NMR signals for the pyridinium proton and C-2 proton of the 1,3-dioxane ring to be shifted about 0.9 and 0.5 ppm, respectively, to the lower magnetic field. The purity of compounds **6** was checked by the  $^1\text{H}$  NMR data and elemental analyses.

The existence of LC phases, was determined using a micro-melting point apparatus equipped with polarizers: compounds **6** exhibited LC phases, so further detailed measurements were made. The measurement of transition temperatures and assignment of the mesophases were carried out by means of the micro melting point apparatus, differential scanning calorimetry (DSC), and X-ray diffraction. The phase transition temperatures for compounds **6** are given in tables 1 and 2, which also show the full structures for all compounds **6**. All of these compounds exhibited the same smectic A phase texture.

Conoscopic figures and X-ray diffraction supported the assignment of the compound **6** LC phases as smectic A. That is, a uniaxial conoscopic figure was observed, and the diffraction pattern of a typical smectic A phase was also obtained (figure 2). The sharp peak in the small angle region indicated that the layer spacings of the phases of compounds **6-7-6-11** which have a short *R'* group are about 33–35 Å (e.g. compound **6-10**: 34.3 Å). In these cases, the molecules seem to be arranged in a bilayer structure (figure 3). In the case of compounds **6-1-6-6**, the sharp peak in the small-angle region indicated that the layer spacings of about 26–29 Å (e.g. compound **6-6**; 20.0 Å). These values indicate a monolayer molecular structure (figure 4). These latter compounds have two long alkyl chains *R, R'*, and a carbonyl group. The stronger interaction of both terminal groups seems to lead to the monolayer structure.

The isotropic to mesophase transition temperatures of compounds **6** increase with the increasing length of alkyl chain *R*. Also, compounds **6-8** and **6-10**, having a  $-(\text{CH}_2)_8-\text{CH}=\text{CH}_2$  *R* group, instead of the  $-\text{C}_{10}\text{H}_{21}$  *R* group of compounds **6-9** and **6-11**, exhibited lower transition temperatures. In general, isotropic to meso-

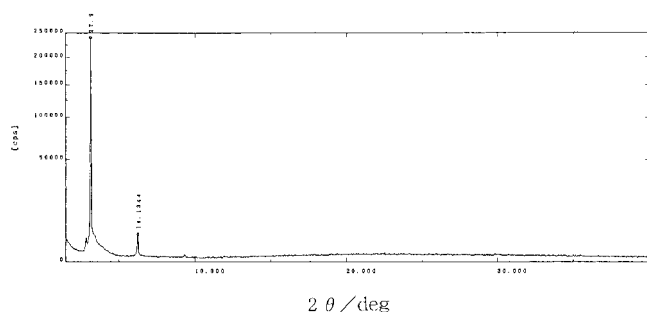


Figure 2. X-Ray diffraction pattern of the smectic phase of compound **6-6**.

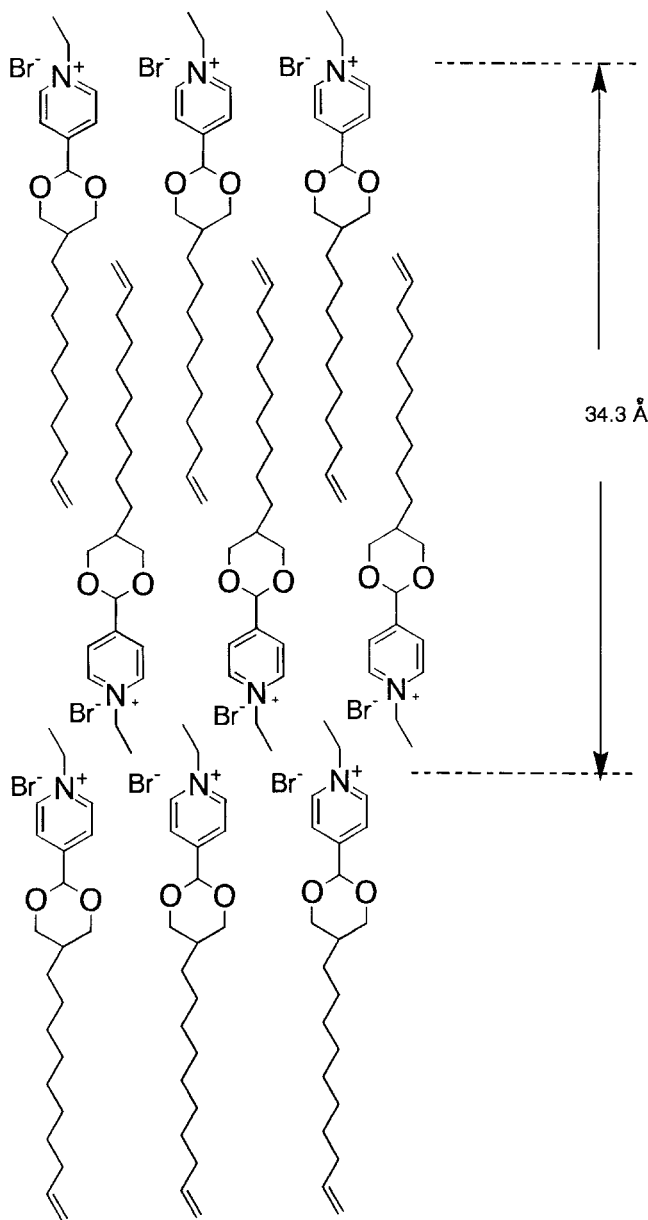
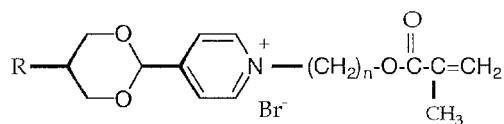


Figure 3. Molecular arrangement of the new ionic liquid crystal compound **6-10**.

phase transition temperatures tend to be decreased by the presence of a terminal double bond in the molecule [19, 20]: this explains our reported observation.

Most ionic LC compounds exhibit a SmA phase above 100°C, stilbazole compounds, for example at about 120–190°C [4]. However, compounds **6** exhibited the SmA phase around ordinary room temperature. The most remarkable feature of these new ionic LC materials having a terminal double bond, is to exhibit a liquid crystalline phase over a very wide temperature range including room temperature (e.g. compound **6-1**: Cr – 22 SmA 25 I).

Table 1. Phase transition temperatures for compounds **6-1-6-6**.

| Compound   | R                               | n  | Phase transition temperatures/°C <sup>a</sup> |
|------------|---------------------------------|----|---|
| <b>6-1</b> | C <sub>8</sub> H <sub>17</sub>  | 6  |   |
| <b>6-2</b> | C <sub>10</sub> H <sub>21</sub> | 6  |   |
| <b>6-3</b> | C <sub>11</sub> H <sub>23</sub> | 6  |   |
| <b>6-4</b> | C <sub>12</sub> H <sub>25</sub> | 6  |   |
| <b>6-5</b> | C <sub>8</sub> H <sub>17</sub>  | 10 |   |
| <b>6-6</b> | C <sub>10</sub> H <sub>21</sub> | 10 |   |

<sup>a</sup> Cr = crystal, SmA = smectic A, I = isotropic.

### 3. Experimental

#### 3.1. Analysis

IR, <sup>1</sup>H NMR, and the mass spectra were obtained with a Hitachi 215 spectrometer, a JNM-PMX 60 spectrometer, and a Hitachi M-80B spectrometer, respectively. Elemental analyses were carried out with a Carlo Erba EA 1108. The transition temperatures and mesomorphic phases were determined by means of a Mitamura Riken micro melting point apparatus equipped with polarizers and a Mac Science DSC 3100 system. X-ray diffraction was performed with a Rigaku Rint 2100 X-ray system.

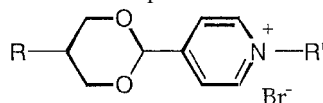
#### 3.2. Synthesis

The identities of starting materials and intermediates are shown in figure 1.

##### 3.2.1. 4-(5-Alkyl-1,3-dioxan-2-yl)pyridine (**5**)

To a solution of compound **3** (0.01 mol) and 4-pyridinecarbaldehyde **4** (0.01 mol) in anhydrous benzene (100 ml) was added *p*-toluenesulfonic acid (10 g). The solution was heated under reflux for 5 h using a Dean–Stark trap. The resulting solution was washed with cold 10% aqueous NaHCO<sub>3</sub> (200 ml), dried over anhydrous

Table 2. Phase transition temperatures for compounds 6-7-6-13.



| Compound | R   | R'                                   | Phase transition temperatures/°C <sup>a</sup>  |
|----------|---|--------------------------------------|--|
| 6-7      | C <sub>10</sub> H <sub>21</sub>                       | -CH <sub>2</sub> -CH=CH <sub>2</sub> | $  \begin{array}{ccc}  & 78 & \\  & \text{Cr} \longrightarrow \text{I} & \\  44 \uparrow & & \downarrow 62 \\  & \text{g} \longleftarrow \text{SmA} & \\  & -19 &   \end{array}  $ |
| 6-8      | CH <sub>2</sub> =CH-(CH <sub>2</sub> ) <sub>8</sub> - | CH <sub>3</sub>                      | Cr 46 SmA 82 I   |
| 6-9      | C <sub>10</sub> H <sub>21</sub>                       | CH <sub>3</sub>                      | Cr 90 SmA 210 dec.   |
| 6-10     | CH <sub>2</sub> =CH-(CH <sub>2</sub> ) <sub>8</sub> - | C <sub>2</sub> H <sub>5</sub>        | $  \begin{array}{ccc}  & 58 & 96 \\  & \text{Cr} \longrightarrow \text{SmA} \longrightarrow \text{I} & \\  & \longleftarrow & \longleftarrow \\  & 15 &   \end{array}  $           |
| 6-11     | C <sub>10</sub> H <sub>21</sub>                       | C <sub>2</sub> H <sub>5</sub>        | g - 24 SmA 152 I   |
| 6-12     | CH <sub>2</sub> =CH-(CH <sub>2</sub> ) <sub>8</sub> - | C <sub>3</sub> H <sub>7</sub>        | Cr 56 I  |
| 6-13     | CH <sub>2</sub> =CH-(CH <sub>2</sub> ) <sub>8</sub> - | C <sub>4</sub> H <sub>9</sub>        | Cr 73 I  |

<sup>a</sup> Cr = crystal, g = glass, SmA = smectic A, I = isotropic.

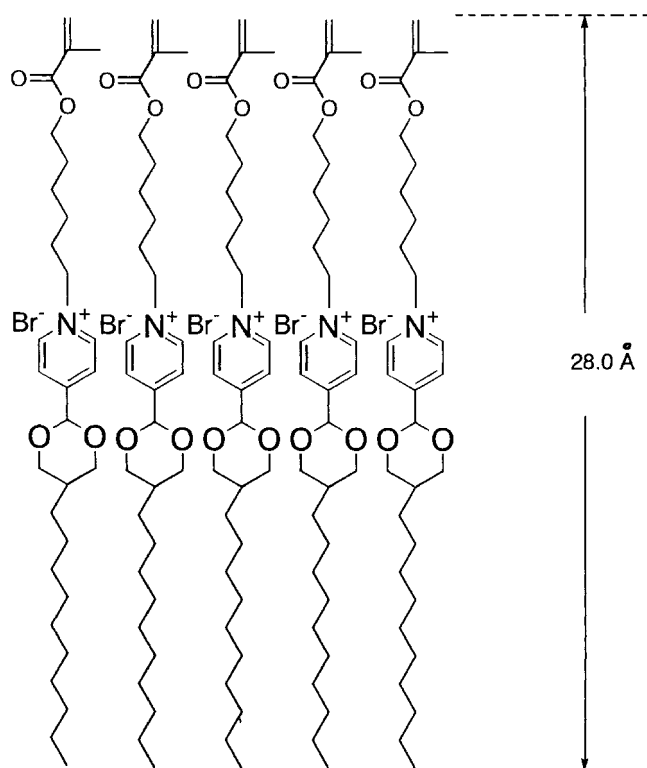


Figure 4. Molecular arrangement of the new ionic liquid crystal compound 6-6.

Na<sub>2</sub>SO<sub>4</sub>, and evaporated *in vacuo* at 40°C. The crude product was purified by column chromatography (Wakogel C-300) and recrystallized, yield 30–40%.

IR (CHCl<sub>3</sub>): 2800–3000 (alkyl), 1600 (pyridine) cm<sup>-1</sup>.  
<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ) 0.6–2.4 (m, R-CH), 3.4–4.5 (m, 4H, CH<sub>2</sub>O), 5.50 (s, 1H, O-CH-O), 7.6, 8.9 (m, 4H, ArH).

### 3.2.2. *N*-Alkyl-4-(5-alkyl-1,3-dioxan-2-yl)pyridinium bromide (6)

A solution of compound 5 (0.004 mol), alkyl bromide (0.08 mol) and phenothiazine (0.05 g) in anhydrous acetonitrile (20 ml) was stirred at 50°C for 72 h under a nitrogen atmosphere. After the reaction was complete, the solution was concentrated under vacuum. The residue was purified by reprecipitations with hexane, yield 60–70%.

IR (CHCl<sub>3</sub>): 2800–3000 (alkyl), 1640 (pyridine) cm<sup>-1</sup>.  
<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ) 0.6–2.6 (m, R-CH, N-CH<sub>2</sub>-R'), 3.5–4.5 (m, 4H, CH<sub>2</sub>-O), 5.3 (2H, N-CH<sub>2</sub>), 5.8 (s, 1H, O-CH-O), 8.5, 10.0 (q, 4H, ArH).

**6-1** Yield, 90%. Found: C, 60.83; H, 8.48; N, 2.45%.  
 Calcd for C<sub>27</sub>H<sub>44</sub>NO<sub>4</sub>Br: C, 61.59; H, 8.42; N, 2.66%. Mass 527 (M<sup>+</sup>).

**6-2** Yield, 89%. Found: C, 62.97; H, 9.16; N, 2.41%.  
 Calcd for C<sub>29</sub>H<sub>48</sub>NO<sub>4</sub>Br: C, 62.80; H, 8.72; N, 2.53%. Mass 555 (M<sup>+</sup>).

- 6-3** Yield, 67%. Found: C, 62.19; H, 9.37; N, 2.42%.  
Calcd for  $C_{30}H_{50}NO_4Br$ : C, 63.37; H, 8.86;  
N, 2.46%. Mass 569 ( $M^+$ ).
- 6-4** Yield, 80%. Found: C, 64.10; H, 9.43; N, 2.43%.  
Calcd for  $C_{31}H_{52}NO_4Br$ : C, 63.90; H, 8.99;  
N, 2.40%. Mass 583 ( $M^+$ ).
- 6-5** Yield, 79%. Found: C, 64.12; H, 9.22; N, 2.33%.  
Calcd for  $C_{31}H_{52}NO_4Br$ : C, 63.90; H, 8.99;  
N, 2.40%. Mass 583 ( $M^+$ ).
- 6-6** Yield, 39%. Found: C, 65.58; H, 9.22; N, 2.27%.  
Calcd for  $C_{33}H_{56}NO_4Br$ : C, 64.90; H, 9.24;  
N, 2.29%. Mass 610 ( $M^+$ ).
- 6-7** Yield, 77%. Found: C, 62.05; H, 9.27; N, 3.23%.  
Calcd for  $C_{22}H_{36}NO_2Br$ : C, 61.96; H, 8.51;  
N, 3.28%. Mass 426 ( $M^+$ ).
- 6-8** Yield, 72%. Found: C, 59.54; H, 8.64; N, 3.35%.  
Calcd for  $C_{20}H_{32}NO_2Br$ : C, 60.30; H, 8.10;  
N, 3.52%. Mass 398 ( $M^+$ ).
- 6-9** Yield, 30%. Found: C, 59.52; H, 8.87; N, 3.24%.  
Calcd for  $C_{20}H_{34}NO_2Br$ : C, 59.99; H, 8.56;  
N, 3.50%. Mass 400 ( $M^+$ ).
- 6-10** Yield, 72%. Found: C, 61.67; H, 9.02; N, 3.40%.  
Calcd for  $C_{21}H_{34}NO_2Br$ : C, 61.16; H, 8.31;  
N, 3.40%. Mass 412 ( $M^+$ ).
- 6-11** Yield, 46%. Found: C, 60.66; H, 8.41; N, 3.49%.  
Calcd for  $C_{21}H_{36}NO_2Br$ : C, 60.86; H, 8.68;  
N, 3.37%. Mass 414 ( $M^+$ ).
- 6-12** Yield, 53%. Found: C, 62.18; H, 9.25; N, 3.27%.  
Calcd for  $C_{22}H_{36}NO_2Br$ : C, 61.95; H, 8.31;  
N, 3.28%. Mass 426 ( $M^+$ ).
- 6-13** Yield, 62%. Found: C, 62.85; H, 9.89; N, 3.17%.  
Calcd for  $C_{23}H_{38}NO_2Br$ : C, 62.71; H, 8.71;  
N, 3.18%. Mass 426 ( $M^+$ ).

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