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Preliminary Communications

New pyridinium type ionic liquid crystal compounds with a 1,3-dioxane ring in the principal structure

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A new pyridinium type ionic thermotropic liquid crystal system having two rings in it's central core has been synthesized. These compounds exhibited a smectic A phase over a very wide range including room temperature (for example **5–1**: Cr -24 S_A 150 I).

There are not many reports concerning ionic thermotropic liquid crystals. Those reported include some liquid crystal polymers with pyridinium side chains [1] and with alkyl ammonium salts as principal chains [2], and stilbazole-type metal-containing liquid crystals [3]. On the other hand, we have studied 1,3-dioxane, 1,3-oxathiane and 1,3-dithiane-type liquid crystal materials [4–14]. Ionic liquid crystalline materials having these structures in their central core have not been encountered to date and their possibilities as liquid crystal materials are interesting.

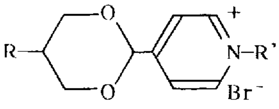

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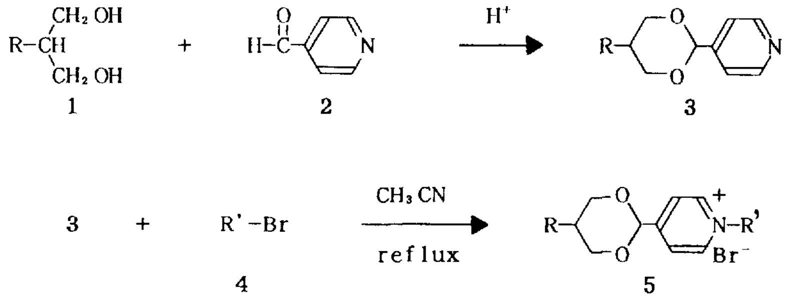
Figure 1. Chemical structure of new ionic liquid crystal compound **5**.

From this point of view, *N*-ethyl-4-(5-alkyl-1,3-dioxan-2-yl) pyridiniumbromide **5** was synthesized. In this preliminary communication, we wish to report the new type of thermotropic ionic liquid crystalline material having the two rings in it's central core (see figure 1).

Compounds **5** were synthesized by the route shown in figure 2.

Compounds **5–2** and **5–3** have a terminal vinyl group. Generally, the transition temperatures of the isotropic to mesophase transition tend to be decreased by the terminal double bond in the molecule [15, 16]. For the purpose of lowering these temperatures, **5–2** and **5–3** were synthesized.

In the syntheses of compounds **5**, both *trans*- and



R : $C_{10}H_{21}-$, $CH_2=CH-(CH_2)_8-$
R' : $-C_2H_5$, $-CH_2-CH=CH_2$

Figure 2. Synthetic pathway for the compounds **5**.

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cis-isomers were produced, which differ in the C-5 position of the 1,3-dioxane ring. Repeated recrystallizations were required to obtain only the *trans*-isomers. In the ^{1}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 can be checked by the disappearance of the peak in the ^{1}H NMR spectrum. By the *N*-alkylation, ^{1}H NMR signals for the pridinium proton and acetal proton (C-2 proton of the 1,3-dioxane ring) were shifted about 0·8 and 0·3 ppm to the lower magnetic field, respectively. The purity of compounds **5** was checked by ^{1}H NMR and elemental analysis. Good data were obtained for these compounds. To judge the existence of liquid crystal phases, observation was performed by a micro-melting point apparatus equipped with polarizers. Compounds **5** exhibited liquid crystal phases and further detailed measurements were made. Measurement of the transition temperatures and assignment of the mesophases were carried out by means of a micro-melting point apparatus equipped with polarizers, a differential scanning calorimeter (DSC), and X-ray diffraction. Phase transition temperatures for compounds **5** are given in the table.

Observation of these textures indicated that these

Table. Phase transition temperatures for compounds **5**.

	R	*R'*	Phase transition temperatures/°C
5-1	$C_{10}H_{21}$	C_2H_5	$\mathrm{Cr} \underset{-29}{\overset{-24}{\rightleftarrows}} \mathrm{S_A} \overset{150}{\longleftrightarrow} \mathrm{I}$
5-2	$C_{10}H_{21}$	$-CH_2-CH=CH_2$	$\begin{array}{ccc} \mathrm{Cr} & \xrightarrow{78} & \mathrm{I} \\ 44\uparrow & & \updownarrow 62 \\ \mathrm{G} & \xleftarrow[-19]{} & \mathrm{S_A} \end{array}$
5-3	$CH_2=CH-(CH_2)_8-$	C_2H_5	$\mathrm{Cr} \underset{15}{\overset{58}{\rightleftarrows}} \mathrm{S_A} \overset{96}{\longleftrightarrow} \mathrm{I}$

Cr: Crystal; G: Glass; S_A: Smectic A; I: Isotropic.

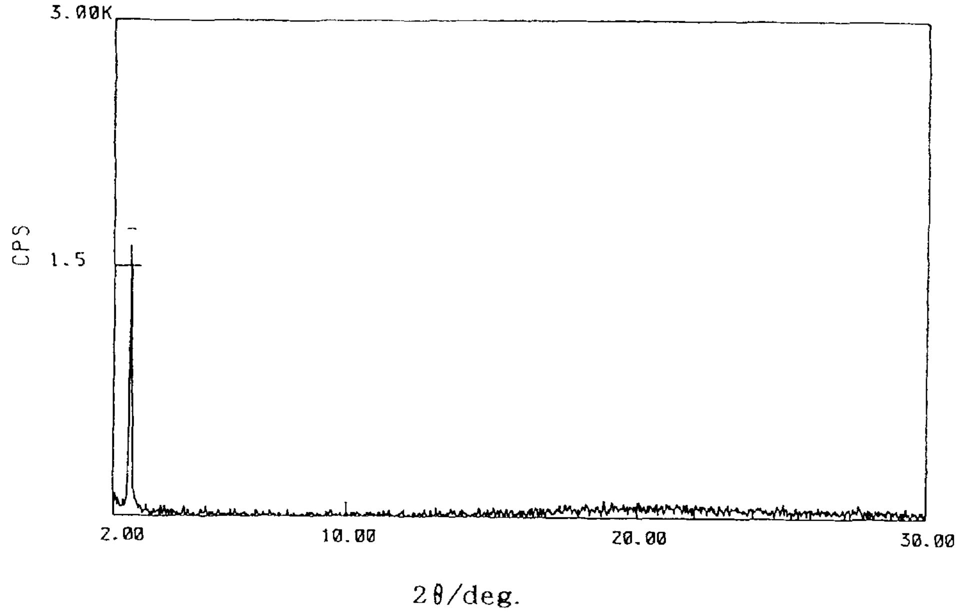

Figure 3. X-ray diffraction pattern of new ionic liquid crystal compound 5–3.

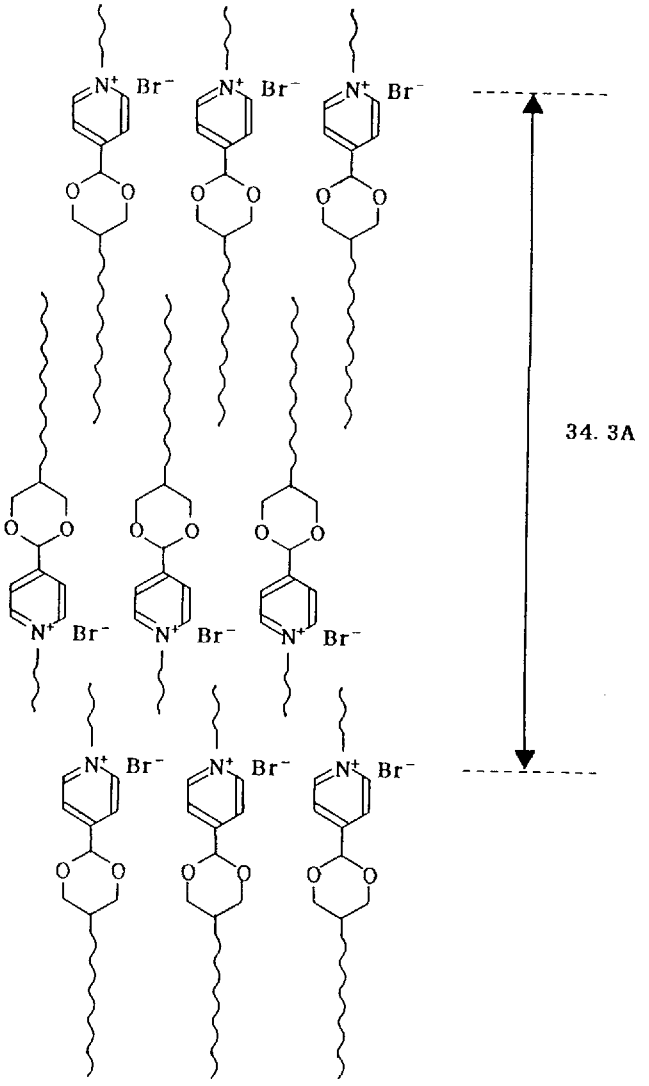

Figure 4. Molecular arrangement of new ionic liquid crystal compound 5.

compounds exhibited the texture of the smectic A phase. To confirm this result, conoscopic figures and X-ray diffraction data were obtained for compound **5–3** (see figure 3). These results also support the assignment of the liquid crystal phase as smectic A. That is, a uniaxial conoscopic figure was observed, and the diffraction pattern of the typical smectic A phase was also obtained.

The only sharp peak in the small-angle region indicated that the layer spacing of this phase is 34·3 Å. From the value of the layer spacing and the peculiarity as an ionic liquid crystal compound, the molecular arrangement in the smectic A phase may be as shown in figure 4. In this model, cationic pyridinium ions and anionic bromide ions stabilize each other, and the long alkyl chains orient to form the smectic phase.

The isotropic to mesophase transition temperatures of compounds **5–2** and **5–3** are lower than that of compound **5–1**. This seems to originate in the presence of the terminal double bonds in compounds **5–2** and **5–3**.

The most remarkable feature of these new ionic liquid crystalline materials is the wide temperature range of liquid crystallinity including room temperature (for example, **5–1**: Cr -24 S_A 150 I).

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