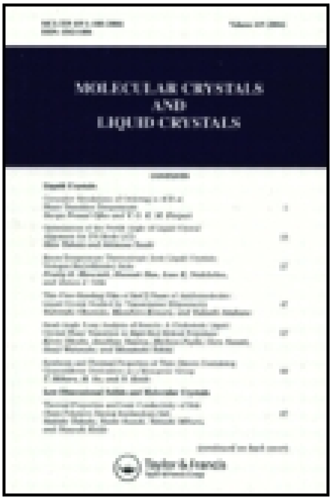

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New 1,3-Dioxane Type Ionic Liquid Crystal Compounds Having a Different Counter Anion

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New 1,3-Dioxane Type Ionic Liquid Crystal Compounds Having a Different Counter Anion

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New pyridinium type thermotropic ionic liquid crystal materials having a 1,3-dioxane ring in their central core: N-substituted-4-(5-alkyl-1,3-dioxan-2-yl)pyridinium halides (**6**) were synthesized. These componds exhibited a smectic A phase over a very wide temperature range including room temperature [for example **6–5**: G −24 SmA 152 I (°C)]. The size of the counter anion affected the transition temperatures between the isotropic state and the smectic A phase.

Keywords: 1; 3-Dioxane; thermotropic ionic liquid crystal; counter ion

1. INTRODUCTION

There are not many reports concerning ionic thermotropic liquid crystal compounds having two rings in their central core. Some stilbazole type metal-containing liquid crystals were reported. 1)-3)On the other hand, we have studied 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane type new liquid crystal materials. 4)-18) Ionic liquid crystal materials having these structures in their central core have not been encountered to date and their possibilities as liquid crystal materials are interesting. From such a point of view, the first compounds with 1,3-dioxane struc-

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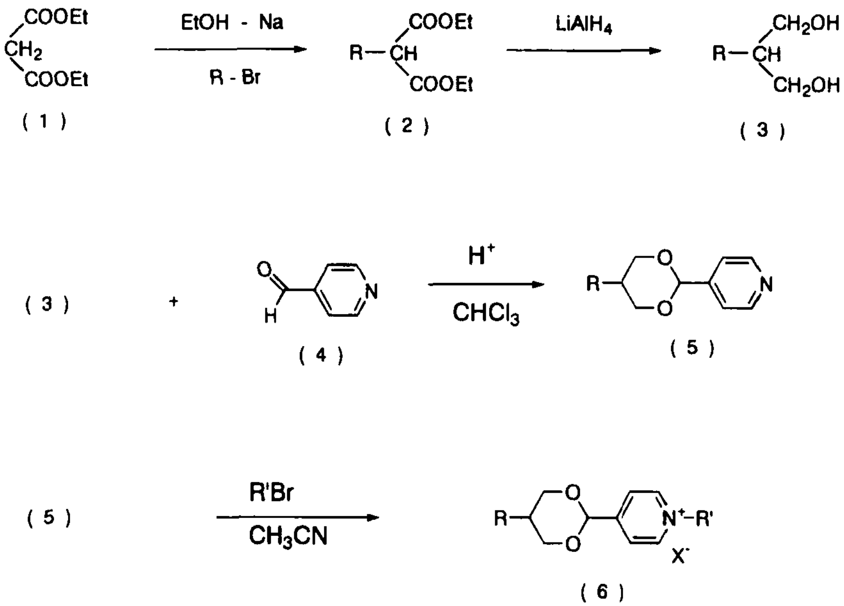
ture were reported as a communication.[16)] In this paper, we wish to report 1,3-dioxane type ionic liquid crystal compounds having a different counter anion.

2. RESULTS AND DISCUSSION

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



R: $C_{10}H_{21}$, $-(CH_2)_8CH=CH_2$

X⁻: Cl^-, Br^-, I^-

FIGURE 1 Synthetic pathway for the compounds 6

In the syntheses of compounds **5** both trans and cis isomers were produced which differed at 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 the 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 these peaks in a ^{1}H-NMR spectrum. To get the compound with different counter anion, in the syntheses of compounds **6**, alkyl chloride or alkyl bromide or alkyl iodide were used, respectively. By the N-alkylation, ^{1}H-NMR signals for the pyridinium proton and C-2 proton of the hetero ring were shifted about 1.2 and 0.6 ppm to a lower magnetic field, respectively. The purity of compounds **6** in the series was checked by ^{1}H-NMR data 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 **6** exhibited liquid crystal phases, so that further detailed measurements were made. Phase transition temperatures for compounds **6** are given in Table I. Observation on these textures indicates that these compounds exhibited the same texture of a smectic A phase. To confirm this result, conoscopic figures and X-ray diffraction data were taken for the phases of compounds **6**. 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 patterns of the typical smectic A phase were also obtained. For example, in the compound **6–1**, a sharp peak in the small-angle region indicated that the layer spacing of this phase is 35.1 Å. (Figure 2) 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 3. In this model, cationic pyridinium ions and anionic chloride ions stabilize each other, and the long alkyl chains orient to form the smectic phase. The value of layer spacing of the compound **6** with chloride counter anion (**6–1**), bromide counter anion (**6–2**) and that with iodide counter anion (**6–3**) are 35.1 Å, 34.3 Å, and 33.4Å, respectively. (Table II) Therefore in this case, the bigger the size of counter anion, the shorter the length of the layer spacing. This might be caused by the strength of molecular side intheractions. That is, the larger iodide atoms make the molecular width wider, which makes the lateral interaction of liquid crystal molecules **6–3** weak, so that alkyl chains can penetrate each other. By the increase of the size of the counter anion, transition temperatures of isotropic to mesophase for compounds **6** decrease. This result also seems to be caused by the strength of the molecular side interaction which is weakened by the wider molecular width of the larger counter anion.

The isotropic to mesophase transition temperatures of compounds **6–1**, **6–2**, and **6–3** having a terminal double bond are lower than those of compounds **6–4**, **6–5**, **6–6**. Generally, the transition temperatures of the isotropic to mesophase transitions tend to be decreased by the existence of a terminal double bond in the molecule.19),20) Therefore, this effect seems to originate with the presence of the terminal double bond.

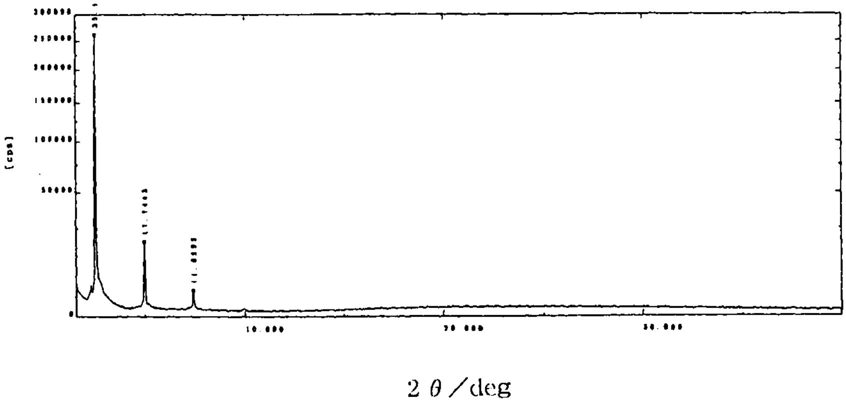
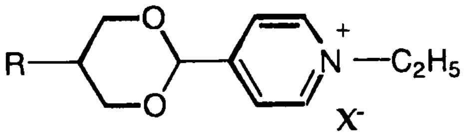
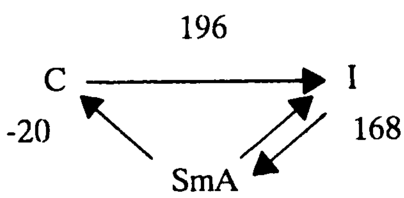
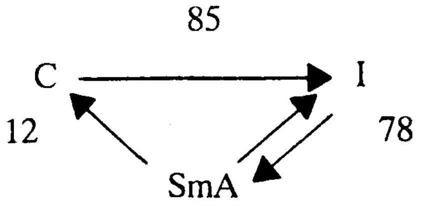


FIGURE 2 X-Ray diffraction pattern of the smectic phase of **compound 6–1**

TABLE I Phase transition temperatures for compounds 6

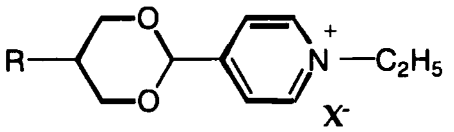

(6)

	R	*X*	*Phase transition temperatures /°C*[a]				
6 – 1	CH_2=CH-$(CH_2)_8$-	Cl	G	–40	SmA	105	I
6 – 2	CH_2=CH-$(CH_2)_8$-	Br	$C \underset{15}{\overset{58}{\rightleftarrows}} SmA \overset{96}{\longleftrightarrow} I$				
6 – 3	CH_2=CH-$(CH_2)_8$-	I	C	65	SmA	75	I
6 – 4	$C_{10}H_{21}$	Cl					

6 - 5	$C_{10}H_{21}$	Br	G	−24	SmA	152	I
6 - 6	$C_{10}H_{21}$	I					

a. C: Crystal, G: Glass, SmA: Smectic A, I: Isotropic.

TABLE II The length of layer spacing of SmA phase of compounds 6



(6)

	R	X	*Layer spacing (A)*
6 - 1	$CH_2{=}CH\text{-}(CH_2)_8\text{-}$	Cl	35.1
6 - 2	$CH_2{=}CH\text{-}(CH_2)_8\text{-}$	Br	34.3
6 - 3	$CH_2{=}CH\text{-}(CH_2)_8\text{-}$	I	33.4
6 - 4	$C_{10}H_{21}$	Cl	38.6
6 - 5	$C_{10}H_{21}$	Br	38.4
6 - 6	$C_{10}H_{21}$	I	36.3

The remarkable features of these new ionic liquid crystal materials are their ability to exhibit a liquid crystal phase over a very wide temperature range including ordinary room temperature [e.g. compound **6–1**: G −40 SmA 105 I (°C)]. The bigger the size of counter anion, the shorter the length of the layer spacing.

3. EXPERIMENTAL

3–1 Analysis

IR, 1H-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 Carbo Erba EA 1108. The transition temperatures and mesomorphic phases were determined by means of a

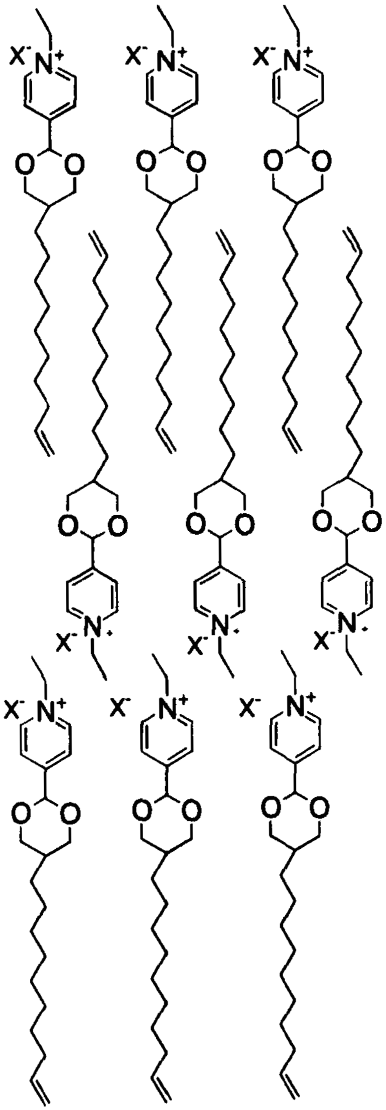


FIGURE 3 Molecular arrangement of the new ionic liquid crystal compound 6

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

4-(5-Alkyl-1,3-dioxan-2-yl)pyridine (5)

To a solution of compound (3) (0.01 mol) and 4-formylpyridine (4) (0.01 mol) in anhydrous benzene (100ml) were added p-toluenesulfonic Acid (10g). The solution was refluxed for 5 h useing a Dean-Stark trap. The solution was washed with cold 10% aqueous $NaHCO_3$(200 ml), dried over anhydrous Na_2SO_4, and evaporated in vacuo at 40 °C. The crude product was purified by column chromatography (Wakogel C-300) and recrystallized. Yield 30–40%.

IR ($CHCl_3$) 2800–3000 (alkyl), 1600 (pyridine). ^{1}H-NMR ($CDCl_3$, δ) 0.6–2.4 (m, R-CH), 3.4–4.5 (m, 4H, CH_2O), 5.50 (s, 1H, O-CH-O), 7.6, 8.9 (m, 4H, ArH).

N-Ethyl-4-(5-Alkyl-1,3-dioxan-2-yl)pyidinium halide (6)

A solution of compound (5) (0.004mol) and Alkyl halide (0.08 mol) in anhydrous acetonitrile (20ml) was stirred at 50 °C for 72h under a nitrogen atmosphere. After the reaction the solution was concentrated on an evaporator. The residue was purified by reprecipitation with hexane. Yield 60–70%

IR ($CHCl_3$) 2800–3000 (alkyl), 1640 (pyridine).

N-Ethyl-4-[5-(9-Decenyl)-1,3-dioxan-2-yl]pyidiniumchloride (6–1)

^{1}H-NMR ($CDCl_3$, δ) 0.6–2.6 (m, 20H, $CH_2{=}CH\text{-}(\underline{CH_2})_8\text{-}\underline{CH}$, $N\text{-}CH_2\text{-}\underline{CH_3}$), 3.5–4.5 (m, 4H, CH_2-O), 4.8–6.3(m, 6H, N-CH_2, CH_2=CH-, O-CH-O), 8.4, 10.3 (q, 4H, ArH).

N-Ethyl-4-[5-(9-Decenyl)-1,3-dioxan-2-yl]pyidiniumbromide (6–2)

^{1}H-NMR ($CDCl_3$, δ) 0.6–2.6 (m, 20H, $CH_2{=}CH\text{-}(\underline{CH_2})_8\text{-}\underline{CH}$, $N\text{-}CH_2\text{-}\underline{CH_3}$), 3.5–4.5 (m, 4H, CH_2-O), 4.8–6.3 (m, 6H, N-CH_2, CH_2=CH-, O-CH-O),, 8.2, 9.8 (q, 4H, ArH).

N-Ethyl-4-[5-(9-Decenyl)-1,3-dioxan-2-yl]pyidiniumiodide (6–3)

^{1}H-NMR ($CDCl_3$, δ) 0.6–2.6 (m, 20H, $CH_2{=}CH\text{-}(\underline{CH_2})_8\text{-}\underline{CH}$, $N\text{-}CH_2\text{-}\underline{CH_3}$), 3.5–4.5 (m, 4H, CH_2-O), 4.8–6.3 (m, 6H, N-CH_2, CH_2=CH-, O-CH-O), 8.2, 9.6 (q, 4H, ArH).

N-Ethyl-4-(5-Decyl-1,3-dioxan-2-yl)pyidiniumchloride (6–4)

^{1}H-NMR ($CDCl_3$, δ) 0.6–2.6 (m, 25H, $\underline{C_{10}H_{21}}\text{-}\underline{CH}$, $N\text{-}CH_2\text{-}\underline{CH_3}$), 3.5–4.5 (m, 4H, CH_2-O), 5.3 (q, 2H, N-CH_2), 5.8 (s, 1H, O-CH-O), 8.4, 10.3 (q, 4H, ArH).

N-Ethyl-4-(5-Decyl-1,3-dioxan-2-yl)pyidiniumbromide (6–5)

^{1}H-NMR ($CDCl_3$, δ) 0.6–2.6 (m, 25H, $\underline{C}_{10}\underline{H}_{21}$-$\underline{CH}$, N-$CH_2$-$\underline{CH}_3$), 3.5–4.5 (m, 4H, CH_2-O), 5.2 (q, 2H, N-CH_2), 5.8 (s, 1H, O-CH-O), 8.2, 9.8 (q, 4H, ArH).

N-Ethyl-4-(5-Decyl-1,3-dioxan-2-yl)pyidiniumiodide (6–6)

^{1}H-NMR ($CDCl_3$, δ) 0.6–2.6 (m, 25H, $\underline{C}_{10}\underline{H}_{21}$-$\underline{CH}$, N-$CH_2$-$\underline{CH}_3$), 3.5–4.5 (m, 4H, CH_2-O), 5.1 (q, 2H, N-CH_2), 5.8 (s, 1H, O-CH-O), 8.2, 9.6 (q, 4H, ArH).

6–1: Yield, 49%. Found: C, 69.12; H, 10.09; N, 3.78%. Calcd for $C_{21}H_{34}NO_2Cl$: C, 68.55; H, 9.31; N, 3.81%.

6–2: Yield, 63%. Found: C, 61.67; H, 9.02; N, 3.37%. Calcd for $C_{21}H_{34}NO_2Br$: C, 61.16; H, 8.31; N, 3.40%.

6–3: Yield, 41%. Found: C, 55.84; H, 9.13; N, 3.04%. Calcd for $C_{21}H_{34}NO_2I$: C, 54.90; H, 7.46; N, 3.05%.

6–4: Yield, 30%. Found: C, 69.30; H, 9.90; N, 3.71%. Calcd for $C_{21}H_{36}NO_2Cl$: C, 68.17; H, 9.81; N, 3.79%.

6–5: Yield, 83%. 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%.

6–6: Yield, 28%. Found: C, 54.33; H, 8.41; N, 3.07%. Calcd for $C_{21}H_{36}NO_2I$: C, 54.66; H, 7.86; N, 3.04%.

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