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New Ionic Liquid Crystal Compounds Having a 1,3-Oxathiane or 1,3-Dioxane Ring

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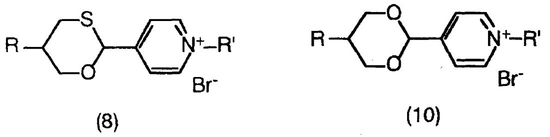
New pyridinium type thermotropic ionic liquid crystal materials bearing a 1,3-oxathiane ring in their central core: N-substituted 4-(5-alkyl-1,3-oxathian-2-yl)pyridinium bromides (**8**) and corresponding 1,3-dioxane analogs (**10**) were synthesized. And the mesomorphic behaviors of these two systems are compared. The principal feature of these compounds is to exhibit a smectic A phase over a very wide temperature range including room temperature [for example **8-4**: G -7 SmA 166 I; **10-4**: G -24 SmA 152 I (°C)].

There are not many reports concerning ionic thermotropic liquid crystal compounds having two rings in their central core. Some liquid crystal polymers with pyridinium side chain[1] and those with alkylammonium salt as a principal chain were reported.[2] Stilbazole type ionic liquid crystals were also reported.[3—5] On the other hand, we have studied 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane type new liquid crystal materials.[4—17] And ionic liquid crystal materials having these structures in their central core had not been encountered to date. Their possibilities as liquid crystal materials are interesting. For example, when a voltage is applied to the ionic liquid crystal molecules, the large separation of ionic charge may generate a big force and it may be able to drive the molecules very fast. From such a point of view, the first compounds with 1,3-dioxane structure were reported as a communication.[18] Then more recently those with 1,3-oxathiane structure were reported as a communication.[19] In this paper, we wish to report in detail two new systems of pyridinium-type ionic liquid crystal compounds having a 1,3-oxathiane ring or 1,3-dioxane ring in the principal structure (Fig. 1).

Results and Discussion

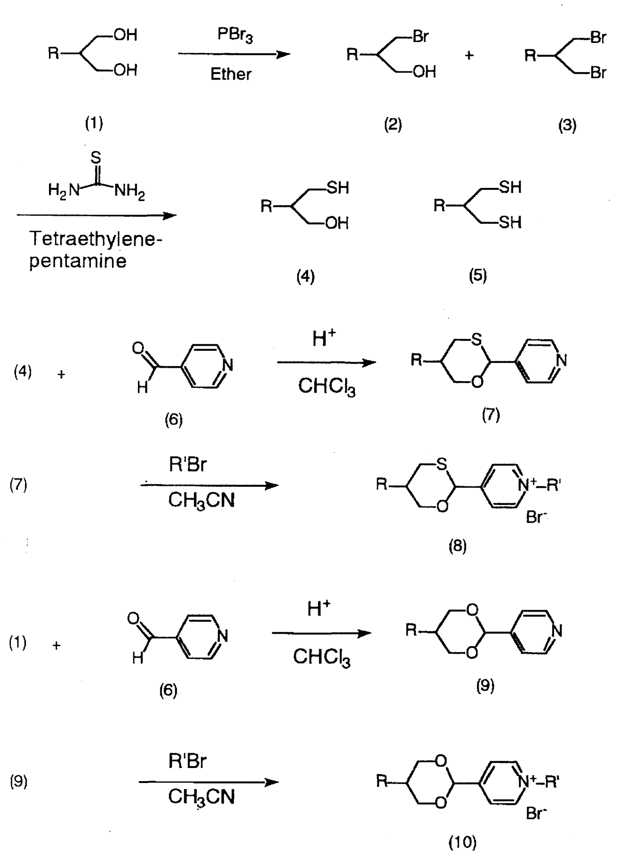
Compounds **8** and **10** were synthesized by the route shown in Fig. 2.



(8) (10)

Fig. 1. Chemical structure of new ionic liquid crystal compounds.

By the bromination of compounds **1**, corresponding mono- and dibromides were produced. This mixture was used for the preparation of monothiols **4** and dithiols **5**. Their separations were attained by column chromatography, where **4** and **5** were eluted with ether and hexane, respectively. In the syntheses of compounds **7** or **9**, both *trans* and *cis* isomers were produced, which differed at the C-5 position of the 1,3-oxathiane ring or 1,3-dioxane ring. Repeated recrystallizations were required to obtain each sole *trans* isomer. In the ^{1}H NMR spectra for the compounds **7**, the C-2 proton signals for the *trans* and *cis* isomer are 5.75 and 5.80 ppm, respectively. In the same way, in the ^{1}H NMR spectra for the compounds **9**, 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 its peak in a ^{1}H NMR spectrum. By the *N*-alkylation, ^{1}H NMR signals for the pyridinium proton and C-2 proton of the 1,3-oxathiane ring or 1,3-dioxane ring were shifted about 0.9 and 0.5 ppm to the lower magnetic field, respectively. The purity of compounds **8** or **10** was checked by the ^{1}H NMR data and elemental analyses. To judge the existence of liquid crystal phases, a micro-melting point apparatus equipped with polarizers was employed. Compounds **8** exhibited a liquid crystal phase, so that further detailed measurements were made. Measurement of 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 a X-ray diffraction instrument. Phase transition temperatures for compounds **8** and **10** are given in Table 1. Observation of these textures indicates that these compounds exhibited the same texture of



R : C_6H_{13}, C_7H_{15}, C_8H_{17}, C_9H_{19}, $C_{10}H_{21}$, $C_{11}H_2$
R' : C_2H_5, $-CH_2-CH=CH_2$

Fig. 2. Synthetic pathway for the compounds **8** and **10**.

smectic A phase. To confirm this result, conoscopic figures and X-ray diffraction were measured for the phase of compound **8-4** (Fig. 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 sharp peak in the small-angle region indicated that the layer spacing of this phase is 38.9 Å. The value of the layer spacing and the peculiarity as an ionic liquid crystal compound suggest the molecular arrangement in the smectic A phase shown in Fig. 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 value of layer spacing of the corresponding 1,3-dioxane type liquid crystal is 38.0 Å (Compound **10-4**). Therefore, the value for 1,3-oxathiane type is somewhat larger than that for 1,3-dioxane type.

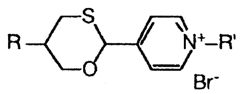
Transition temperatures of isotropic to mesophase for 1,3-oxathiane type compounds **8** are higher than those for the corresponding 1,3-dioxane type compounds **10**. In the case of non ionic liquid crystals, this tendency is reversed. That is, transition temperatures of isotropic to mesophase for 1,3-oxathiane type are lower than those for 1,3-dioxane type. In the case of non ionic liquid crystals, the molecular bending by the size difference between the oxygen atom and the sulfur atom makes the distances between molecules wider. But in this case, the bending of 1,3-oxathiane molecules might have the same direction in the smectic A phase.

The transition temperature of isotropic to mesophase of compound **8-6** having a terminal double bond is lower than those of the other compounds **8**. This is the same tendency as in the case of 1,3-dioxane type compounds (Table 1). And

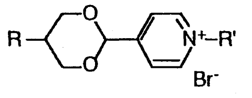
Table 1. Phase Transition Temperatures for Compounds **8** and **10**

	R	R′	Transition temperature (°C)[a]				
8-1	C_6H_{13}	C_2H_5	G	−22			I
8-2	C_7H_{15}	C_2H_5	G	10	SmA	57	I
8-3	C_9H_{19}	C_2H_5	G	−19	SmA	121	I
8-4	$C_{10}H_{21}$	C_2H_5	G	−7	SmA	166	I
8-5	$C_{11}H_{23}$	C_2H_5	G	−3	SmA	192	I
8-6	$C_{10}H_{21}$	$-CH_2-CH=CH_2$	G	−30	SmA	21	I
10-1	C_6H_{13}	C_2H_5	G	−16			I
10-2	C_7H_{15}	C_2H_5	G	−9	SmA	30	I
10-3	C_9H_{19}	C_2H_5	G	−1	SmA	107	I
10-4	$C_{10}H_{21}$	C_2H_5	G	−24	SmA	152	I
10-5	$C_{11}H_{23}$	C_2H_5	G	−9	SmA	181	I
10-6	$C_{10}H_{21}$	$-CH_2-CH=CH_2$	$\begin{tikzcd} G \arrow[rr, "78"] & & I \arrow[dl, shift left] \\ & SmA \arrow[ul, "-19"] \arrow[ur, shift left, "62"'] & \end{tikzcd}$				

a) G: Glass, SmA: Smectic A, I: Isotropic.



(**8**)



(**10**)

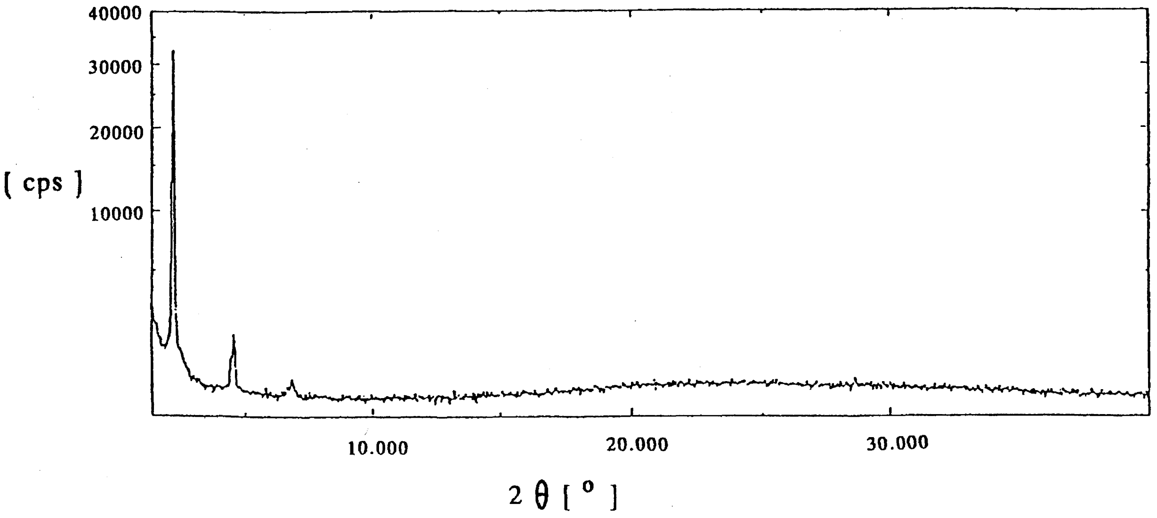


Fig. 3. X-Ray diffraction pattern of new ionic liquid crystal compound **8-4**.

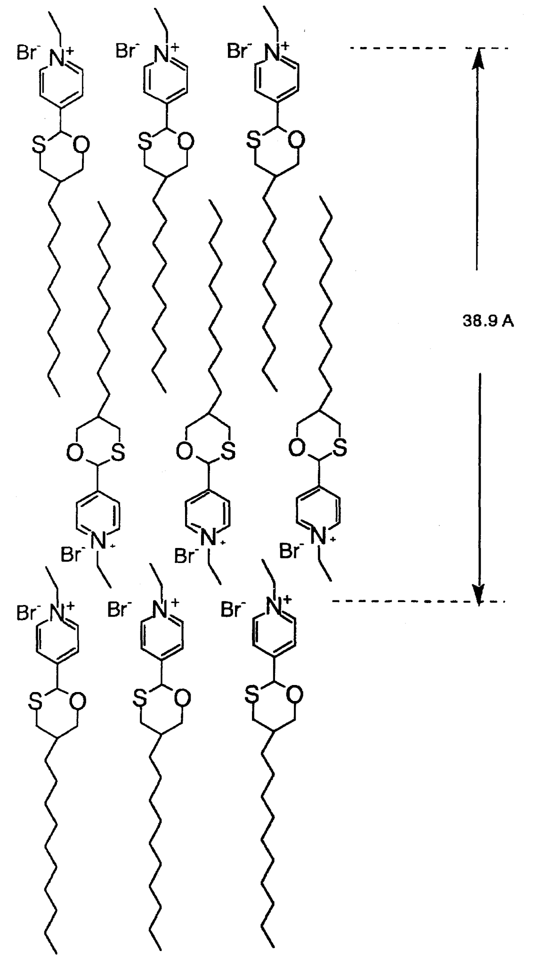


Fig. 4. Molecular arrangement of the new ionic liquid crystal compound **8**.

the compound having a $-(CH_2)_8-CH=CH_2$ group instead of the $-C_{10}H_{21}$ group of compound **10-4** also exhibited a lower transition temperature of isotropic to mesophase.[18] Generally, the transition temperatures of the isotropic to mesophase transition tend to be decreased by the existence of a terminal double bond in the molecule.[20,21] Therefore, this seems to originate in the presence of the terminal double bond.

Transition temperatures of isotropic to mesophase of compounds **8** and **10** increase with the increasing length of alkyl chain.

The $\Delta H_{\mathrm{SmA-I}}$ of these ionic compounds are very much smaller than those of general non-ionic liquid crystal compounds. For example $\Delta H_{\mathrm{SmA-I}}$ of compound **10-4** is 0.54 kJ mol^{-1} and that of compound **8-4** is 0.51 kJ mol^{-1}. These values may imply that SmA phases of these compounds are unstable.

Though stilbazole type ionic liquid crystal compounds exhibit SmA phase about 120—190 °C[4], 1,3-oxathiane type and 1,3-dioxane type ionic liquid crystal compounds exhibit SmA phase around ordinary room temperature. Therefore, the most remarkable feature of these new ionic liquid crystal materials is to exhibit liquid crystal phase over a very wide range including ordinary room temperature (e.g. **8-3**: G −30 SmA 21 I; **10-6**: G −19 SmA 62 I).

Experimental

Analysis. IR, ^{1}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 Carbo 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.

Synthesis. 2-Alkyl-3-mercapto-1-propanol (4). To a solution of thiourea (0.2 mol) in triethylene glycol (20 ml) kept at 75 °C was added a mixture of compounds **2** and **3** (about 0.05 mol) in a nitrogen atmosphere, followed by stirring at 75 °C for 18 h. Tetraethylenepentamine (0.05 mol) was then added, and the mixture was stirred at 75 °C for 2 h under a nitrogen atmosphere. The reaction mixture was then poured into ice water (300 g), and extracted twice with ether (each 300 ml). The extract was dried over anhydrous Na_2SO_4, and concentrated on an evaporator at 30 °C. The separation of compounds **4** and **5** was carried out by column chromatography (Wakogel C-300). Compounds **4** were obtained as transparent liquids.

IR ($CHCl_3$) 2800—3000 (alkyl). ^{1}H NMR ($CDCl_3$) δ = 0.6—2.2 (m, R–CH, SH, OH), 2.5—2.9 (m, 2H, –CH_2S), 3.5—3.8 (m, 2H, –CH_2O).

4-(5-Alkyl-1,3-oxathian-2-yl)pyridine (7). To a solution of compound (**4**) (0.01 mol) and 4-pyridinecarboxaldehyde (**6**) (0.01 mol) in anhydrous benzene (100 ml) were added *p*-toluenesulfonic acid (10 g). 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—2.2 (m, R–CH), 2.8—3.0 (m, 2H, CH_2S), 3.3—4.4 (m, 2H, CH_2O), 5.75 (s, 1H, O–CH–S), 7.6 (d, 2H, ArH), 8.8 (d, 2H, ArH).

***N*-Alkyl-4-(5-Alkyl-1,3-oxathian-2-yl)pyidinium Bromide (8).** A solution of compound (**7**) (0.004 mol) and alkyl bromide (0.08 mol) in anhydrous acetonitrile (20 ml) was stirred at 50 °C for 72 h under a nitrogen atmosphere. After the reaction, the solution was concentrated on an evaporator. The residue was purified by reprecipitations with hexane. Yield 50—60 %.

IR ($CHCl_3$) 2800—3000 (alkyl), 1640 (pyridine). ^{1}H NMR ($CDCl_3$) δ = 0.6—2.6 (m, R–CH, N–CH_2–CH_3), 2.8—3.2 (m, 2H, CH_2–S), 3.3-4.6 (m, 2H, CH_2O), 5.3 (2H, N–CH_2), 6.25 (s, 1H, O–CH–S), 8.3 (d, 2H, ArH), 9.9 (d, 2H, ArH).

8-1: Yield, 60%. Found: C, 53.40; H, 7.66; N, 3.58%. Calcd for $C_{17}H_{28}NOSBr$: C, 54.54; H, 7.54; N, 3.74%.

8-2: Yield, 46%. Found: C, 53.50; H, 7.98; N, 3.23%. Calcd for $C_{18}H_{30}NOSBr$: C, 55.66; H, 7.79; N, 3.61%.

8-3: Yield, 59%. Found: C, 58.05; H, 8.32; N, 3.39%. Calcd for $C_{20}H_{34}NOSBr$: C, 57.68; H, 8.23; N, 3.36%.

8-4: Yield, 20%. Found: C, 59.59; H, 8.98; N, 3.20%. Calcd for $C_{21}H_{36}NOSBr$: C, 58.59; H, 8.43; N, 3.25%.

8-5: Yield, 36%. Found: C, 60.07; H, 8.92; N, 3.02%. Calcd for $C_{22}H_{38}NOSBr$: C, 59.44; H, 8.62; N, 3.15%.

8-6: Yield, 73%. Found: C, 59.72; H, 8.20; N, 3.17%. Calcd for $C_{22}H_{36}NOSBr$: C, 56.48; H, 8.55; N, 3.36%.

4-(5-Alkyl-1,3-dioxan-2-yl)pyridine (9). To a solution of compound (**1**) (0.01 mol) and 4-pyridinecarboxaldehyde (**6**) (0.01 mol) in anhydrous benzene (100 ml) were added *p*-toluenesulfonic acid (10 g). The solution was refluxed for 5 h using 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*-Alkyl-4-(5-alkyl-1,3-dioxan-2-yl)pyidinium Bromide (10).** A solution of compound (**9**) (0.004 mol) and Alkyl bromide (0.08 mol) in anhydrous acetonitrile (20 ml) was stirred at 50 °C for 72 h under a nitrogen atmosphere. After the reaction, the solution was concentrated on an evaporator. The residue was purified by reprecipitations with hexane. Yield 60—70%.

IR ($CHCl_3$) 2800—3000 (alkyl), 1640 (pyridine). ^{1}H NMR ($CDCl_3$) δ = 0.6—2.6 (m, R–CH, N–CH_2–*R'*), 3.5—4.5 (m, 4H, CH_2–O), 5.3 (2H, N–CH_2), 5.8 (s, 1H, O–CH–O), 8.5, 10.0 (q, 4H, ArH).

10-1: Yield, 72%. Found: C, 57.38; H, 8.07; N, 3.88%. Calcd for $C_{17}H_{28}NO_2Br$: C, 56.98; H, 7.88; N, 3.91%.

10-2: Yield, 62%. Found: C, 57.71; H, 8.25; N, 3.69%. Calcd for $C_{18}H_{30}NO_2Br$: C, 58.10; H, 8.06; N, 3.76%.

10-3: Yield, 73%. Found: C, 60.34; H, 8.38; N, 3.49%. Calcd for $C_{20}H_{34}NO_2Br$: C, 60.03; H, 8.49; N, 3.50%.

10-4: Yield, 60%. 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%.

10-5: Yield, 85%. Found: C, 61.23; H, 9.01; N, 3.26%. Calcd for $C_{22}H_{38}NO_2Br$: C, 61.72; H, 8.87; N, 3.27%.

10-6: Yield, 77%. Found: C, 62.05; H, 9.27; N, 3.23%. Calcd for $C_{22}H_{36}NO_2Br$: C, 60.86; H, 8.68; N, 3.37%.

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