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New 1,3-oxathiane type ionic liquid crystal compounds

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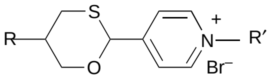
New pyridinium type thermotropic ionic liquid crystal materials having a 1,3-oxathiane ring in the central core, *N*-ethyl-4-(5-alkyl-1,3-oxathian-2-yl)pyridinium bromides **8**, were synthesized. These compounds exhibited a smectic A phase over a very wide range including room temperature (for example **8c**: G −30 S_A 21 I).

There are not many reports concerning ionic thermotropic liquid crystal compounds having two rings in the central core. Some liquid crystal polymers with pyridinium side chains[1] and *N*-alkylpyridinium halides have been reported,[2–4] as have stilbazole (styrylpyridine) type metal-containing liquid crystals.[5] On the other hand, we have studied 1,3-dioxane, 1,3-oxathiane and 1,3-dithiane type new liquid crystal materials.[6–15] Ionic liquid crystal materials having these structures in the central core have not been encountered to date and their possibilities as liquid crystal materials are interesting. In the last year the first of these compounds with a 1,3-dioxane structure was reported.[16] We wish to report a new system of pyridinium type ionic liquid crystal compounds having a 1,3-oxathiane ring in the principal structure.



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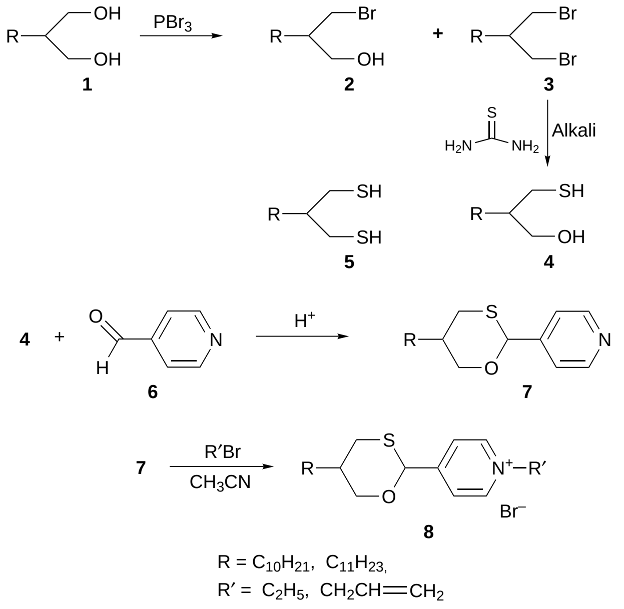
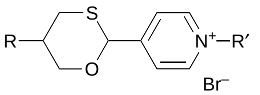
N-Alkyl-4(5-alkyl-1,3-oxathian-2-yl)pyridinium bromides **8** were synthesized by the route shown in Scheme 1. In the bromination of compounds **1**, both mono- and di-bromides were produced. This mixture was used for the syntheses of compounds **4** and **5**. The monothiol **4** and dithiol **5** were separated by column chromatography, in which **4** and **5** were eluted with diethyl ether and hexane, respectively. In the syntheses of compounds **7**, both *trans* and *cis* isomers were produced which differed at the C-5 position of the 1,3-oxathiane ring. Repeated recrystallizations were required to obtain only the *trans* isomers. In the ^{1}H NMR spectra for compounds **7**, the C-2 proton signals for the *trans* and *cis* isomer are at 5.75 and 5.80 ppm, respectively. Therefore, removal of the *cis* isomer can be checked by the disappearance of its peak in the ^{1}H NMR spectrum. On *N*-alkylation, ^{1}H NMR signals for the pyridinium proton and the C-2 proton of the 1,3-oxathiane ring were shifted downfield about 0.8 and 0.45 ppm, respectively. The purity of compounds **8** was checked by ^{1}H NMR spectroscopy and elemental analyses. Good data were obtained for these compounds. To determine the existence of liquid crystal phases, observation was performed using a micro-melting point apparatus equipped with polarizers. Compounds **8** exhibited a liquid crystal phase, so 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 X-ray diffraction. Phase transition temperatures for compounds **8** are given in Table 1.



R = $C_{10}H_{21}$, $C_{11}H_{23}$,
R′ = C_2H_5, $CH_2CH{=}CH_2$

Scheme 1



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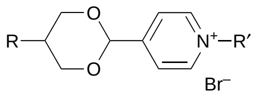

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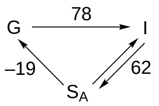
Table 1 Phase transition temperatures for compounds **8** and the corresponding 1,3-dioxanes **9**

	R	R′	phase transition temperatures/°C[a]				
8a	$C_{10}H_{21}$	C_2H_5	K	45	S_A	166	I
8b	$C_{11}H_{23}$	C_2H_5	K	50	S_A	192	I
8c	$C_{10}H_{21}$	$CH_2CH{=}CH_2$	G	−30	S_A	21	I
9a	$C_{10}H_{21}$	C_2H_5	G	−24	S_A	152	I
9b	$C_{11}H_{23}$	C_2H_5	G	−9	S_A	181	I
9c	$C_{10}H_{21}$	$CH_2CH{=}CH_2$	 G 78 I –19 62 S_A				

[a]K: Crystal, G: Glass, S_A: Smectic A, I: Isotropic.

Observation of the textures indicates that these compounds exhibited a smectic A phase. To confirm this result, conoscopic figures and X-ray diffraction were measured for the phase of

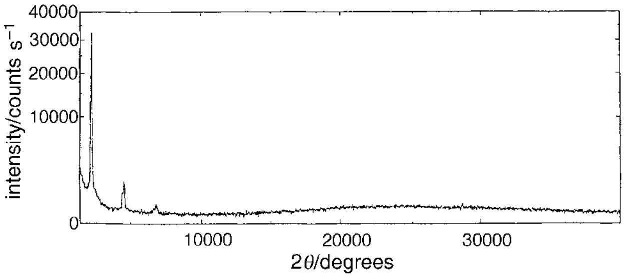


Fig. 1 X-Ray diffraction pattern of the smectic phase of compound **8a**

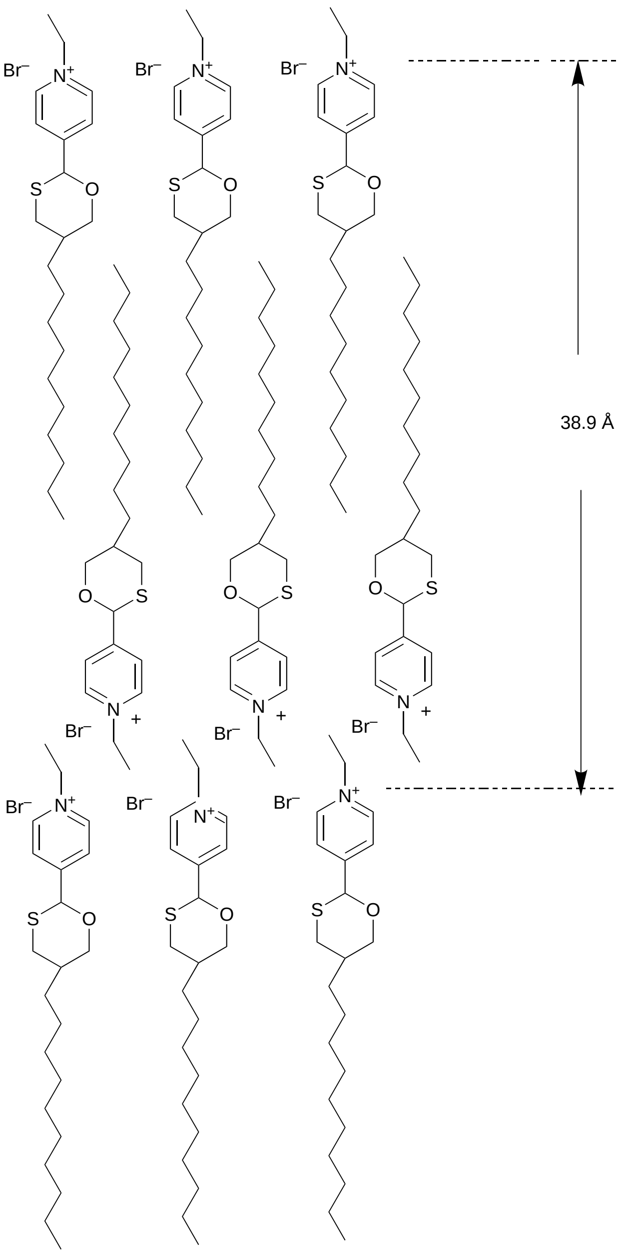


Fig. 2 Molecular arrangement of the new ionic liquid crystal compound **8**

compound **8a** (Fig. 1). 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 indicates that the layer spacing of this phase is 38.9 Å. This value is somewhat larger than that of the corresponding 1,3-dioxane type ionic liquid crystal compound (34.3 Å). From the value of the layer spacing and the peculiar properties of ionic liquid crystal compounds, the molecular arrangement in the smectic A phase may be as shown in Fig. 2. 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 temperature of the isotropic to mesophase transition of compound **8c** having a terminal double bond is lower than those of compounds **8a** or **8b**. This is the same tendency as that observed for 1,3-dioxane type compounds (Table 1). The compound having a $(CH_2)_8CH{=}CH_2$ group instead of the $C_{10}H_{21}$ group of compound **9a** also exhibited a lower isotropic to mesophase transition temperature.[16] 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.[17,18] Therefore, this effect seems to originate in the presence of the terminal double bond.

The most remarkable feature of these new ionic liquid crystal materials is that they exhibit a liquid crystal phase over a very wide range including ordinary room temperature (*e.g.* **8c**: G -30 S_A 21 I).

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