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New 1,3-dithiane type ionic liquid crystal compounds

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New pyridinium type thermotropic ionic liquid crystal materials having a 1,3-dithiane ring in their central core, *N*-substituted-4-(5-alkyl-1,3-dithian-2-yl)pyridinium bromides (**8**), were synthesized. These compounds exhibited a smectic A phase over a very wide temperature range including room temperature.

1. Introduction

There are few reports concerning ionic thermotropic liquid crystal compounds having two rings in their central core. Some liquid crystal polymers with a pyridinium side chain [1] and those with an alkyl ammonium salt as a principal chain have been reported [2]. Stilbazole type metal-containing liquid crystals were also reported [3]. On the other hand, we have studied 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane type new liquid crystal materials [4–15]. Ionic liquid crystal materials having these structures in their central core have not yet been encountered and their possibilities as liquid crystal materials are interesting. From this point of view, the first compounds with the 1,3-dioxane structure were recently reported [16]. In this letter, we wish to report a new system of pyridinium type ionic liquid crystal compounds having a 1,3-dithiane ring in the principal structure (figure 1).

2. Results and discussion

Compounds **8** were synthesized by the route shown in figure 2. In the bromination of compound **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 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-dithiane ring. Repeated recrystallizations were required to isolate the *trans* isomers. In the ^{1}H NMR spectra for compounds **7**, the C-2 proton signals for the *trans* and *cis* isomers are 5·20 and 5·15 ppm, respectively. Therefore, removal of the *cis* isomers can be followed by the disappearance of its peak in a ^{1}H NMR spectrum.

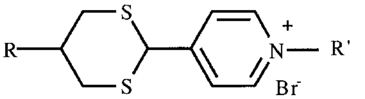

Figure 1. Chemical structure of new ionic liquid crystal compounds **8**.

As a result of the *N*-alkylation, ^{1}H NMR signals for the pyridinium proton and thioacetal proton (C-2 proton of the 1,3-dithiane ring) were shifted about 0·8 and 0·3 ppm to the lower magnetic field, respectively. The purity of compounds **8** was checked by ^{1}H NMR data and elemental analysis. Good data were obtained for these compounds.

To confirm the existence of liquid crystal phases, observations were made using a micro-melting point apparatus equipped with polarizers. Compounds **8** exhibited a liquid crystal phase, so further detailed measurements were made. The measurement of transition temperatures and assignment of mesophases were carried out by means of the micro melting point apparatus, differential scanning calorimetry (DSC), and X-ray diffraction (XRD). Phase transition temperatures for compounds **8** are given in the table.

Observation of their textures indicate that the compounds exhibited a similar texture of smectic A phase. To confirm this result, conoscopic figures and XRD were observed for the LC phase of compound **8-1** (figure 3). These results also supported the assignment of the liquid crystal phase as smectic A, i.e. a uniaxial conoscopic figure was observed, and the diffraction pattern of the typical smectic A phase was obtained. The sharp peak in the small-angle region indicated that the layer spacing of this phase is 39·4 Å. From the value of the layer spacing and the peculiarity as an ionic liquid crystal

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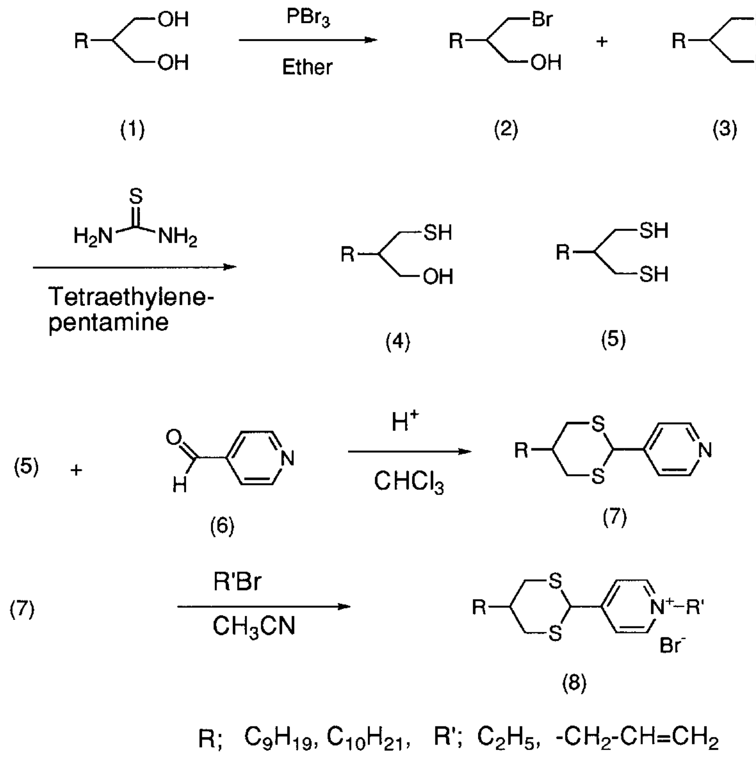
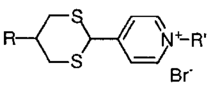
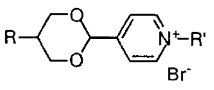


Figure 2. Synthetic pathway for the compounds **8**.

Table. Phase transition temperatures for compounds **8** and the corresponding 1,3-dioxanes **9**. All these compounds are *trans* isomers.


(8)


(9)

Compound	*R*	*R′*	Phase transition temperatures/°C[a]
8-1	$C_{10}H_{21}$	C_2H_5	G 5 SmA 188 I
8-2	C_9H_{19}	C_2H_5	G −3 SmA 146 I
8-3	$C_{10}H_{21}$	$CH_2{-}CH{=}CH_2$	G 28 SmA 66 I
9-1	$C_{10}H_{21}$	C_2H_5	G −24 SmA 152 I
9-2	C_9H_{19}	C_2H_5	G −11 SmA 107 I
9-3	$C_{10}H_{21}$	$CH_2{-}CH{=}CH_2$	$G \xrightarrow{78} I$ $-19 \nwarrow \swarrow 62$ SmA

[a] G: Glass, SmA: Smectic A, I: Isotropic.

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 transition temperatures for isotropic to mesophase for 1,3-dithiane type compounds **8** are higher than those for the corresponding 1,3-dioxane type compounds. There is a similar tendency in the case of non-ionic liquid crystals of these types of compounds [5], the difference in chemical structure being only in the hetero atoms, sulphur and oxygen. The 1,3-dithiane compounds have two sulphur atoms having a larger dispersion force. The higher transition temperatures of 1,3-dithiane compounds seem to originate from this effect. The isotropic to mesophase transition temperature of compound **8-3**, which has a terminal double bond, is lower than that of compounds **8-1** or **8-2**. The same tendency is seen in the case of 1,3-dioxane type compounds (see the table). The compound having a $(CH_2)_8{-}CH{=}CH_2$

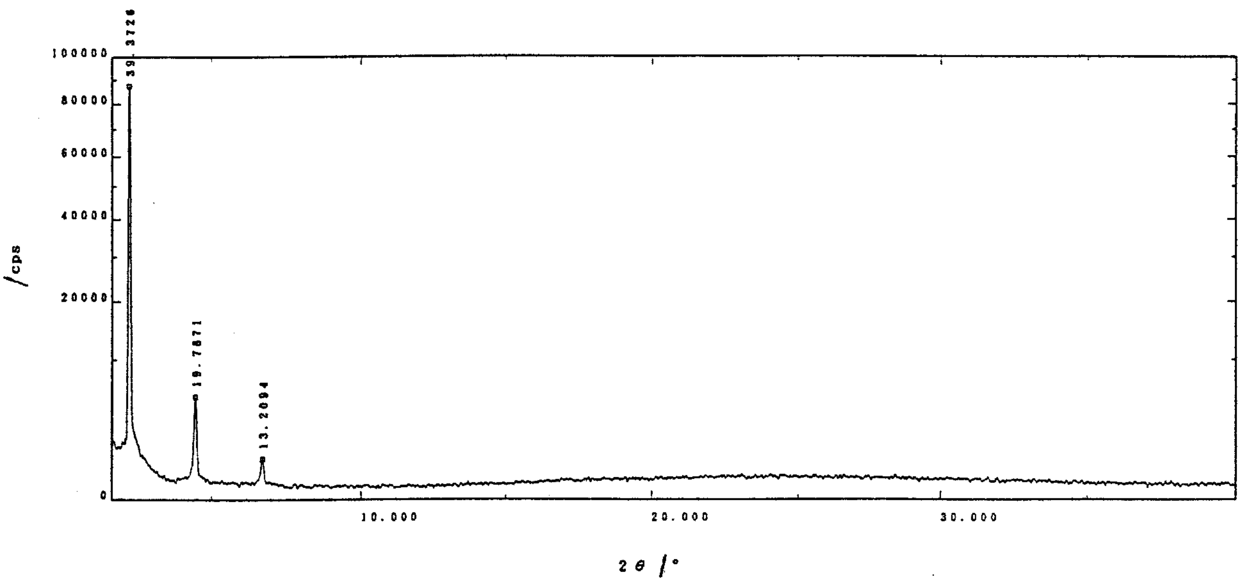


Figure 3. X-ray diffraction pattern of new ionic liquid crystal compound **8-1**.

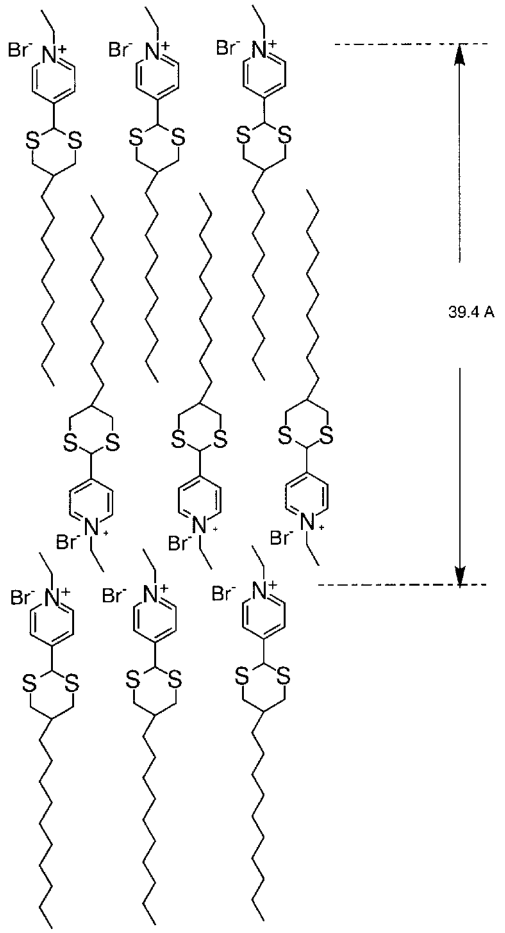


Figure 4. Molecular arrangement of the new liquid crystal compounds **8**.

group instead of the $C_{10}H_{21}$ group of compound **9-1** also exhibited a lower isotropic to mesophase transition temperature [16]. Generally, the temperatures of the isotropic to mesophase transition tend to be decreased by the existence of a terminal double bond in the molecules [17, 18].

The most remarkable feature of these new ionic liquid crystal materials is that they exhibit liquid crystal phases over a very wide temperature range including room temperature, e.g. compound **8-1**: G 5 SmA 188 I (°C).

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