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Liquid Crystals

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Yuichiro Haramoto; Yoshiharu Akiyama; Ryouichi Segawa; Masato Nanasawa; Andrew B. Holmes; Seiji Ujiie

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New ionic liquid crystal compounds having a 1,3-dithiane or 1,3-dioxane ring

YUICHIRO HARAMOTO*, YOSHIHARU AKIYAMA, RYOUICHI SEGAWA,
MASATO NANASAWA
Department of Applied Chemistry and Biotechnology, Yamanashi University,
Takeda 4, Kofu 400, Japan

SEIJI UJIIE
Department of Chemistry, Shimane University, Nishikawatu, Matsue 690, Japan

and ANDREW B. HOLMES
Melville Laboratory for Polymer Syntheses, Department of Chemistry,
University of Cambridge, Pembroke Street, Cambridge CB2 3RA, UK

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New pyridinium type thermotropic ionic liquid crystal materials having a 1,3-dithiane ring in the central core—N-substituted 4-(5-alkyl-1,3-dithian-2-yl)pyridinium bromides and the corresponding 1,3-dioxanes—were synthesized and their mesomorphic behaviours compared. The principal feature of these compounds is to exhibit a smectic A phase over a very wide temperature range including room temperature.

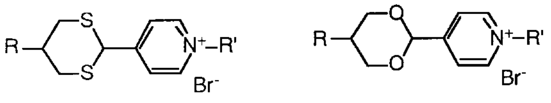
1. Introduction

There are few reports concerning ionic thermotropic liquid crystal (LC) compounds having two rings in their central core. Some LC polymers with pyridinium side chains [1] and those with an alkyl ammonium salt as a principal chain have been reported [2]; stilbazole type metal-containing LCs have also been reported [3]. In addition, we have studied 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane type new LC materials [4–15]. Ionic LC materials having these structures in their central core have been rarely encountered and their possibilities as LC materials are interesting. The first compounds with the 1,3-dioxane structure were reported as a Preliminary Communication [16]. In this paper, we wish to report in detail two new systems of pyridinium type ionic liquid crystal compounds having a 1,3-dithiane ring or 1,3-dioxane ring in the principal structure (figure 1).

2. Results and discussion

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

In the syntheses of intermediate compounds **7** and **9** both *trans*- and *cis*-isomers were produced which differed at the C-5 position of the 1,3-dithiane or 1,3-dioxane 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*-isomers are 5.20 and 5.15 ppm, respectively; for compounds **8**, the C-2 proton signals for the *trans*- and *cis*-isomers are 5.50 and 5.55 ppm, respectively. Therefore, ^{1}H NMR can be used to follow the removal of the *cis*-isomer during purification. In both compounds **8** and **10**, N-alkylation shifted the ^{1}H NMR signals for the pyridinium proton and the C-2 proton of the hetero ring by about 1.2 and 0.6 ppm, respectively, to the lower magnetic field. The purity of compounds **8** and **10** was determined by ^{1}H NMR data and elemental analysis; high levels of purity were established for these compounds. To determine the existence of liquid crystal phases, observations were performed using a micro-melting point apparatus equipped with polarizers. Compounds **8** and **10** exhibited LC phases, and further detailed measurements



(8) (10)

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

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*Author for correspondence; e-mail: haramoto@abll.yamanashi.ac.jp

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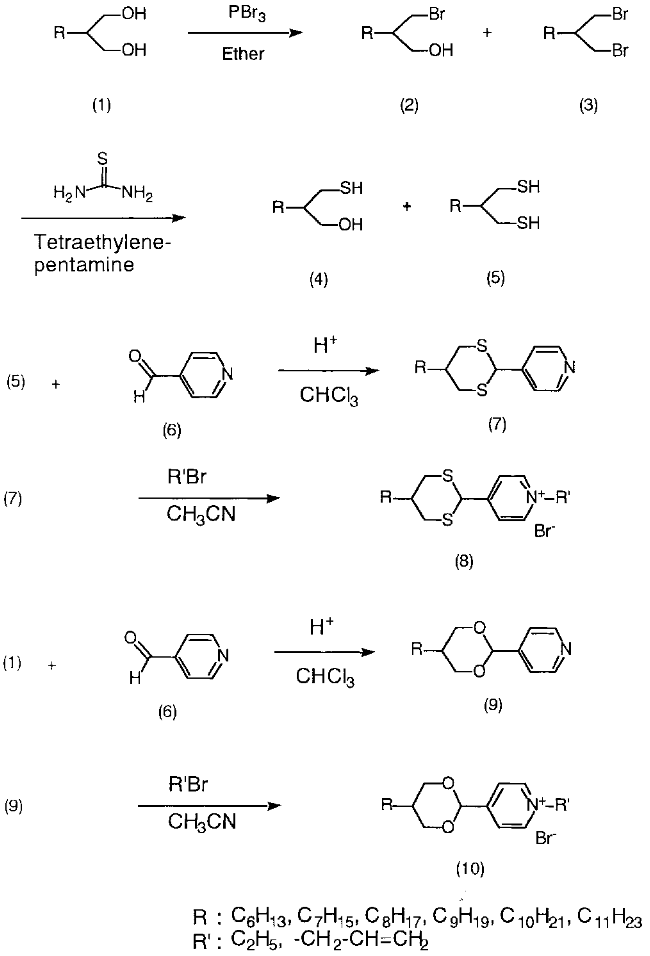


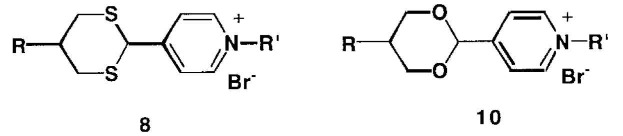
Figure 2. Synthetic pathway for the compounds **8** and **10**.

were made using the melting point apparatus, a differential scanning calorimetry (DSC), and X-ray diffraction. Phase transition temperatures for compounds **8** and **10** are given in the table.

Our observations indicated that these compounds exhibit a smectic A phase texture. To confirm this result, conoscopic figures and X-ray diffraction were obtained for the LC phase of compound **8-4** and **10-4**. These results also support the assignment of the liquid crystal phase as smectic A. That is, a uniaxial conoscopic figure was observed, and a typical smectic A phase diffraction pattern was obtained. For example, in compound **8-4**, the sharp peak in the small angle region indicated that the layer spacing of this phase is 39.4 Å (figure 3). From this value of the layer spacing and the peculiarity of the compound as an ionic liquid crystal, 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 layer spacing in the corresponding 1,3-dioxane type liquid crystal is 38.0 Å (compound **10-4**), i.e. somewhat smaller than for the 1,3-dithiane type. This might originate in the strength of the molecular side interaction, i.e. larger sulphur atoms have a larger dispersion force, strengthening the lateral interaction of the LC molecules, so that alkyl chains can not interdigitate.

Transition temperatures for the isotropic to mesophase transition for 1,3-dithiane type compounds **8** are higher than those for the corresponding 1,3-dioxane type compounds **10**. There is a similar tendency in the case of non-ionic LCs formed of these types of compounds [5]. The difference in chemical structure is only in the hetero atoms: sulphur vs. oxygen. The 1,3-dithiane compounds have two sulphur atoms giving a larger dispersion force; their lighter transition temperatures seem to originate in this effect. The isotropic to mesophase transition temperatures of compound **8-6** and **10-6** (having a terminal double bond) are lower than those of compounds **8-4** or **10-4**. 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 isotropic to mesophase transition temperature [16]. Generally, the temperatures of the isotropic to mesophase transition

Table 1. Phase transition temperatures for compounds **8** and **10**: g = glass, SmA = smectic A, I = isotropic



8 **10**

	R	*R'*	Transition temperature/°C
8-1	C_6H_{13}	C_2H_5	$g \xrightarrow{56} I$ $2 \nwarrow \quad \nearrow\!\swarrow\ 16$ SmA
8-2	C_7H_{15}	C_2H_5	g 6 SmA 75 I
8-3	C_8H_{17}	C_2H_5	g 24 SmA 83 I
8-4	$C_{10}H_{21}$	C_2H_5	g 5 SmA 188 I
8-5	$C_{11}H_{23}$	C_2H_5	g 20 SmA 198 I
8-6	$C_{10}H_{21}$	$-CH_2-CH=CH_2$	g 28 SmA 66 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_8H_{17}	C_2H_5	g − 11 SmA 53 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	$C_{10}H_{21}$	$-CH_2-CH=CH_2$	$g \xrightarrow{78} I$ $-19 \nwarrow \quad \nearrow\!\swarrow\ 62$ SmA

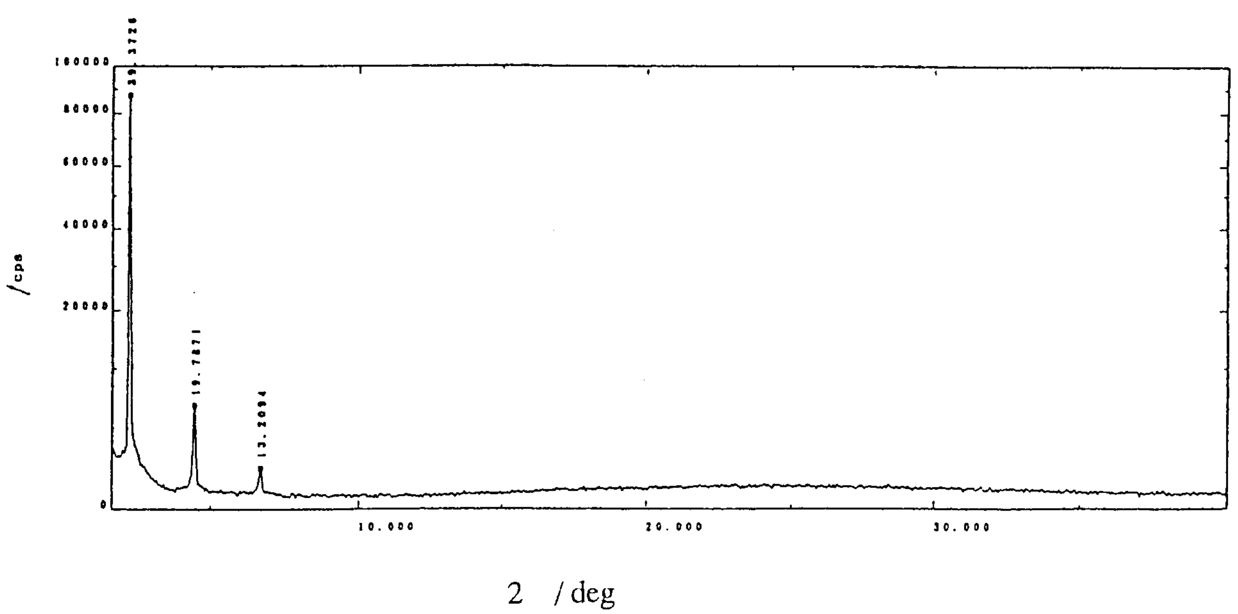


Figure 3. X-ray diffraction pattern of new ionic liquid crystal compound **8-4**.

tend to be lowered by a terminal double bond in the molecule [17, 18].

The most remarkable feature of these new ionic liquid crystal materials is their very wide smectic A temperature range which includes room temperature. For example, compound **8-4**: g 5 SmA 188 I; **10-4**: g – 24 SmA 152 I (°C).

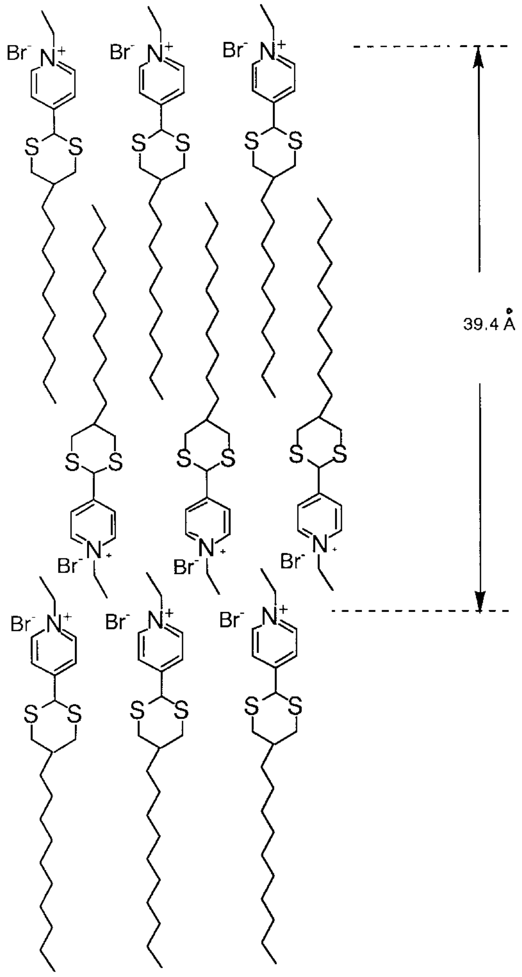


Figure 4. Molecular arrangement of the new liquid crystal compound **8-4**.

3. Experimental

3.1. *Analysis*

IR, ^{1}H NMR and mass spectra were obtained with a Hitachi 215, a JNM-PMX 60, and a Hitachi M-80B spectrometer, respectively. Elemental analyses were carried out with a Carlo Erba EA 1108 instrument. The transition temperatures and mesophases 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.

3.2. *Synthesis*

*2-Alkyl-1,3-propane dithiol (**5**)*

To a solution of thiourea (0.2 mol) in triethyleneglycol (20 ml) at 75°C, was added the pre-synthesized mixture of compounds **2** and **3** (about 0.05 mol) under a nitrogen atmosphere; this was followed by stirring at 75°C for 18 h. Tetraethylenepentamine (0.05 mol) was then added, and the mixture stirred at 75°C for a further 2 h under nitrogen. The reaction mixture was then poured into ice water (300 g), and extracted with ether (2 × 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 **5** were yellow transparent liquids. IR (cm^{-1}) ($CHCl_3$) 2800–3000 (alkyl). ^{1}H NMR ($CDCl_3$, δppm) 0.6–2.0 (m, R–CH, SH), 2.5–2.9 (m, 4H, –CH_2S).

*4-(5-Alkyl-1,3-dithian-2-yl)pyridine (**7**)*

To a solution of compound **5** (0.01 mol) and 4-formylpyridine (**6**) (0.01 mol) in anhydrous benzene (100 ml) was added *p*-toluenesulphonic acid (10 g). The mixture was heated under reflux for 5 h using a Dean–Stark trap. The resulting 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 (Waklogel C-300) and recrystallized. Yield 30–40%. IR (cm^{-1}) ($CHCl_3$) 2800–3000 (alkyl), 1600 (pyridine). ^{1}H NMR ($CDCl_3$, δppm) 0.6–2.2 (m, R–CH), 2.75–3.0 (m, 4H, CH_2S), 5.20 (s, 1H, S–CH–S), 7.55, 8.8 (m, 4H, ArH).

*N-Alkyl-4-(5-alkyl-1,3-dithian-2-yl)pyridinium 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. The solution was then concentrated on an evaporator and the residue purified by reprecipitation with hexane. Yield 50–60%. IR (cm^{-1}) ($CHCl_3$) 2800–3000 (alkyl), 1640 (pyridine). ^{1}H NMR ($CDCl_3$, δppm) 0.6–2.6 (m, $\underline{R\text{–CH}}$, N–CH_2–$\underline{R'}$), 2.8–3.2 (m, 4H, CH_2–S), 5.3 (2H, N–CH_2), 5.8 (s, 1H, S–CH–S), 8.5, 10.05 (q, 4H, ArH).

*4-(5-Alkyl-1,3-dioxan-2-yl)pyridine (**9**)*

To a solution of compound **1** (0.01 mol) and 4-formylpyridine (**6**) (0.01 mol) in anhydrous benzene (100 ml) was added *p*-toluenesulphonic acid (10 g). The mixture was heated under reflux for 5 h using a Dean–Stark trap. The resulting 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 (cm^{-1}) ($CHCl_3$) 2800–3000 (alkyl), 1600 (pyridine). ^{1}H NMR ($CDCl_3$, δppm) 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)pyridinium 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. The solution was then concentrated on an evaporator and the residue purified by reprecipitation with hexane. Yield 60–70%. IR (cm^{-1}) ($CHCl_3$) 2800–3000 (alkyl), 1640 (pyridine). ^{1}H NMR ($CDCl_3$, δppm) 0.6–2.6 (m, $\underline{R\text{–CH}}$, N–CH_2–$\underline{R'}$), 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).

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