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New 1,3-dioxan-type ionic liquid crystal compounds having a large dielectric constant

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New pyridinium-type thermotropic ionic liquid crystal materials having a 1,3-dioxan ring in its central core: *N*-substituted-4-(5-alkyl-1,3-dioxan-2-yl)pyridinium bromides (**6**) were synthesized. The mesomorphic behaviour of these compounds and dielectric constant perpendicular to the molecular axis were measured. The principal features of these compounds are that they exhibit a smectic A phase over a wide temperature range including room temperature—for example **6f**: g −9 SmA 181 I (°C)—and they have a large dielectric constant perpendicular to the molecular axis.

1. Introduction

There are few reports concerning ionic thermotropic liquid crystal (LC) compounds having two rings in the central core, although some stilbazole-type metal-containing LCs have been reported [1–3]. We have previously studied 1,3-dioxan-, 1,3-oxathian-, and 1,3-dithian-type new LC materials [4–9]; ionic LC materials having these structures at the central core had not been encountered previously but their possibilities were interesting. From this point of view, the first compounds with a 1,3-dioxan structure were reported as a communication [10]. In pyridinium-type ionic LC compounds, the pyridinium cation and counter anion must cause a large electric charge separation whose direction seems to be perpendicular to the molecular axis. In this paper, we wish to report the mesomorphic behaviour of these compounds, and the dielectric constants perpendicular to the molecular axis of this new system of pyridinium-type ionic LC compounds having a 1,3-dioxan ring in the principal structure.

2. Results and discussion

Compounds **6** were synthesized by the route shown in figure 1. In the syntheses of compounds **5** both *trans*- and *cis*-isomers were produced which differed at the C-5 position of the 1,3-dioxan ring. Repeated recrystallizations were required to separate 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 could be followed by the disappearance of the *cis*-isomer peak in a ^{1}H NMR spectrum. Following the *N*-alkylation of the compounds **5**, ^{1}H NMR signals for the pyridinium proton and C-2 proton of the hetero ring were shifted about 1.1 and 0.3 ppm to the lower magnetic field, respectively. The purity of compounds **6** was checked by the ^{1}H NMR data and elemental analysis; good data were obtained for most of these compounds. To observe LC phases, micro-melting point apparatus equipped with polarizers was used. Compounds **6** exhibited a LC phase, so further detailed measurements were made. The measurement of transition temperatures and assignment of the mesophases were carried out by the melting point apparatus, a differential scanning calorimeter (DSC), and X-ray diffraction (XRD). Phase transition temperatures for compounds **6** are given in table 1.

Observation of their textures indicates that these compounds exhibit the same smectic A phase texture. To confirm this result, conoscopic figures and XRD were carried out on the SmA phase of compound **6e**. A uniaxial conoscopic figure was observed, and the diffraction pattern of a typical smectic A phase was obtained. The sharp peak in the small angle region indicated that the layer spacing of this phase is 38.4 Å (figure 2). From

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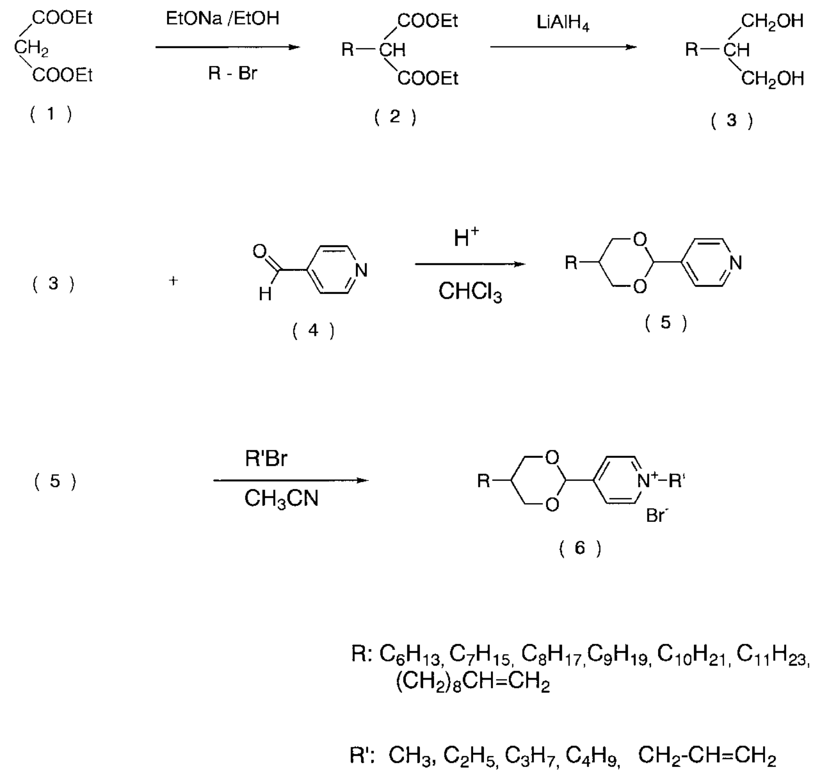

Figure 1. Synthetic pathway for the compounds **6**.

Table 1. Phase transition temperatures for compounds **6**: g = glass, SmA = smectic A, I = isotropic, dec. = decomposed.

Compound	*R*	*R'*	Transition temperature/°C
6a	C_6H_{13}	C_2H_5	g − 16 I
6b	C_7H_{15}	C_2H_5	g − 9 SmA 30 I
6c	C_8H_{17}	C_2H_5	g − 11 SmA 53 I
6d	C_9H_{19}	C_2H_5	g − 1 SmA 107 I
6e	$C_{10}H_{21}$	C_2H_5	g − 24 SmA 152 I
6f	$C_{11}H_{23}$	C_2H_5	g − 9 SmA 181 I
6g	$C_{18}H_{37}$	C_2H_5	g 52 SmA 220 (dec.)
6h	$C_{10}H_{21}$	CH_3	g 11 SmA 220 (dec.)
6i	$C_{10}H_{21}$	C_3H_7	g 30 I
6j	$C_{10}H_{21}$	CH_2=CH–CH_2	$\mathrm{g} \xrightarrow{78} \mathrm{I}$ $\mathrm{I} \xrightarrow{62} \mathrm{SmA} \xrightarrow{-19} \mathrm{g}$
6k	CH_2=CH–$(CH_2)_8$	CH_3	g 46 SmA 82 I
6l	CH_2=CH–$(CH_2)_8$	C_2H_5	$\mathrm{g} \underset{15}{\overset{58}{\rightleftarrows}} \mathrm{SmA} \overset{96}{\rightleftarrows} \mathrm{I}$
6m	CH_2=CH–$(CH_2)_8$	C_3H_7	g 56 I
6n	CH_2=CH–$(CH_2)_8$	C_4H_9	g 73 I
6o	CH_2=CH–$(CH_2)_8$	C_5H_{11}	g 49 I

the value of its layer spacing and its peculiarity as an ionic LC compound, the molecular arrangement in the smectic A phase may be as shown in figure 3. In this model, cationic pyridinium ions and anionic bromide ions stabilize each other, and the long alkyl chains orient to form the smectic phase.

Temperatures of the isotropic to mesophase transition for compounds **6** tend to increase with the length of alkyl chain *R*. The isotropic to mesophase transition temperatures of compounds **6k** and **6j** having a terminal double bond are lower than that of compounds **6h** or **6e**; this is in accord with the general observation that

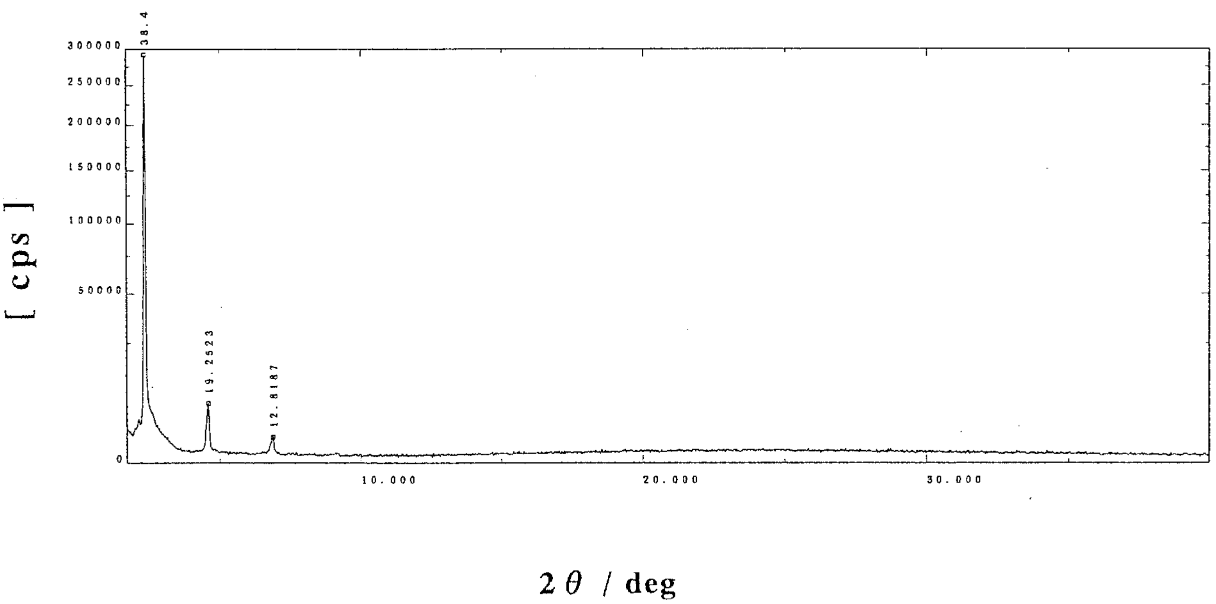

Figure 2. X-ray diffraction pattern of compound **6e**.

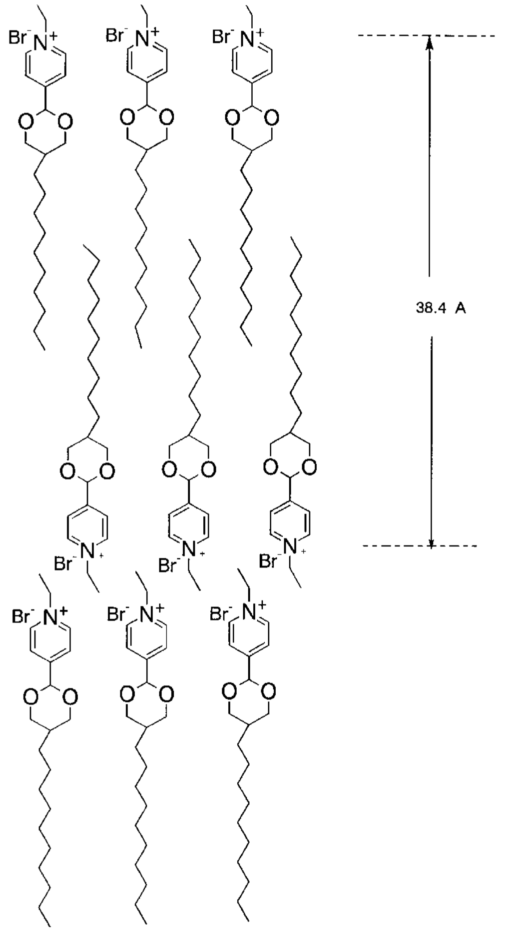

Figure 3. Molecular arrangement of compound **6e**.

the transition temperatures of the isotropic to mesophase transition tend to be decreased by the presence of a terminal double bond in the molecular [11, 12].

10 wt % of compound **6e** was added to the LC formulation Merck 4655-100. The phase transition of this mixture was: Cr – 5 SmC* 61 SmA 72 Ch 75 I (°C). The dielectric constants of the mixture and of Merck 4655-100 were measured separately.

The dielectric constants parallel to the molecular axis of these two samples were almost equal, but the dielectric constant perpendicular to the molecular axis of the mixture (36.0) was larger than that of Merck 4655-100 (7.1). The impedance of the mixture was 600 kΩ cm.

As the pyridinium cation and counter anion must cause a large separation of electric charge, and the direction of charge separation appears to be perpendicular to the molecular axis, the difference in dielectric constants seems to originate in the separation of electric charge in the ionic liquid crystal molecule.

A most remarkable feature of these new ionic LC materials is that they exhibit a LC phase over a very wide temperature range including ordinary room temperature, and they have a large dielectric constant perpendicular to the molecular axis.

3. Experimental

3.1. *Analysis*

IR, ^{1}H NMR, and 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 Carlo Erba EA 1108 instrument. The transition temperatures and

Table 2. Elemental analysis of compounds **6**.

Compound	Yield/%	Found/%			Calculated/%		
		C	H	N	C	H	N
6a	72	57.38	8.07	3.88	56.98	7.88	3.91
6b	62	57.71	8.25	3.69	58.10	8.06	3.76
6c	70	60.23	9.06	3.56	59.06	8.35	3.63
6d	73	60.34	8.38	3.49	60.03	8.49	3.50
6e	60	60.66	8.41	3.49	60.86	8.68	3.37
6f	85	61.23	9.01	3.26	61.72	8,87	3.27
6g	52	66.57	11.07	2.64	66.14	9.95	2.66
6h	30	59.52	8.87	3.24	59.99	8.56	3.50
6i	72	60.95	9.09	2.93	61.67	8.94	3.27
6j	77	62.05	9.27	3.23	61.96	8.51	3.28
6k	72	59.54	8.64	3.35	60.30	8.10	3.52
6l	37	61.67	9.02	3.37	61.16	8.31	3.40
6m	53	62.18	8.95	3.27	61.96	8.51	3.28
6n	62	61.40	9.89	3.10	62.71	8.71	3.18
6o	33	61.81	8.96	3.01	63.41	8.89	3.08

mesomorphic phases were determined by means of a Mitamura Riken micro-melting point apparatus equipped with polarizers and a Mac Science DSC 3100 system. XRD was performed with a Rigaku Rint 2100 X-ray system. The dielectric constants perpendicular to the molecular axis of smectic A phases were measured by the impedance analyser Hewlett Packard 4140B.

3.2. *Synthesis*

3.2.1. *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 (100 ml) was added *p*-toluenesulfonic acid (10 g). The mixture was heated under reflux for 5 h using a Dean–Stark trap to remove water. 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 from hexane:ether (5:1); yield 30–40%. IR ($CHCl_3$, cm^{-1}) 2800–3000 (alkyl), 1600 (pyridine). ^1H 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).

3.2.2. *N-Alkyl-4-(5-alkyl-1,3-dioxan-2-yl)pyridinium bromide (6)*

A solution of compound **5** (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 was complete the solution was concentrated by evaporation, and the residue purified by reprecipitation with hexane:ether (1:1). Yields and analysis are given in table 2. IR ($CHCl_3$, cm^{-1}) 2800–3000 (alkyl), 1640 (pyridine). ^1H NMR ($CDCl_3$, δ) 0.6–2.6 (m, $\underline{R{-}CH}$, $N{-}CH_2{-}\underline{R'}$), 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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