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Liquid crystal properties of new ionic liquid crystal compounds having a 1,3-dioxane ring

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New pyridinium type chiral ionic liquid crystal materials having a 1,3-dioxane ring in the central core, (+)-*N*-2-methylbutyl-4-(5-alkyl-1,3-dioxan-2-yl)pyridinium bromides (**6**), were synthesized. Mixture A was made by adding 5.9 wt % of compound **6-3** to the ferroelectric liquid crystal mixture Merck 4655-100; its phase transitions and some liquid crystal properties were measured. In spite of a large decrease of $\mathbf{P}_s$ for mixture A, its response time A was the same as that of Merck 4655-100. The dielectric constants perpendicular to the molecular axis for the smectic C* and smectic A phases were measured for the mixture and Merck 4655-100: in the smectic C phase, these dielectric constants were almost the same (4.5 ~ 5.5), but in the smectic A phase, the perpendicular dielectric constant of the mixture was 47.0 and that of Merck 4655-100 was 4.5.

1. Introduction

There are few reports of ionic thermotropic liquid crystal (LC) compounds having two rings in the central core. Some stilbazole type metal-containing LCs have been reported [1–3], and we have studied 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane type new LC materials [4–15]. Ionic liquid crystal materials having these structures at the central core had not previously been encountered; their possibilities as LC materials are interesting, and we reported the first compounds with a 1,3-dioxane structure as a communication [16].

In pyridinium type ionic LC compounds, the pyridinium cation and counter anion must cause a large electric charge separation, apparently perpendicular to the molecular axis. We now wish to report the phase transition behaviour of these compounds and some LC properties of a mixture containing compound **6-3**. This is the first paper to report the ferroelectric response of a mixture containing an ionic organic compound having a ferroelectric LC structure.

2. Results and discussion

Compounds **6** were synthesized by the route shown in the scheme. In the syntheses of compounds **5** both *trans*- and *cis*-isomers were produced, differing at the C-5 position of the 1,3-dioxane ring. Repeated recrystallizations were required to isolate the *trans*-isomers. In the ^{1}H NMR spectra for 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 can be checked by the disappearance of the *cis*-isomer peak in a ^{1}H NMR spectrum. After *N*-alkylation of compounds **5**, ^{1}H NMR signals for the pyridinium proton and C-2 proton of the hetero-ring were shifted about 1.2 and 0.6 ppm to the lower magnetic field, respectively. The purity of compounds **6** was checked by the ^{1}H NMR data and elemental analysis; satisfactory data were obtained for these compounds. The observation of LC phases, was performed using a micro-melting point apparatus equipped with polarizers. Compounds **6** in the pure form exhibited no LC phases; this may be due to the greater molecular width arising from the presence of the 2-methylbutyl group.

Compounds **6** were mixed with several ferroelectric liquid crystal mixtures; the Merck 4655-100 mixture was selected for this study. Mixture A containing 5.9 wt % of compound **6-3** was made by adding compound **6-3** to Merck 4655-100; mixture A behaved as a ferroelectric LC in the thin cell. Temperatures of the SmA–Cho and SmC*–SmA transitions for mixture A were the same as those for Merck 4655-100, but the temperature for the

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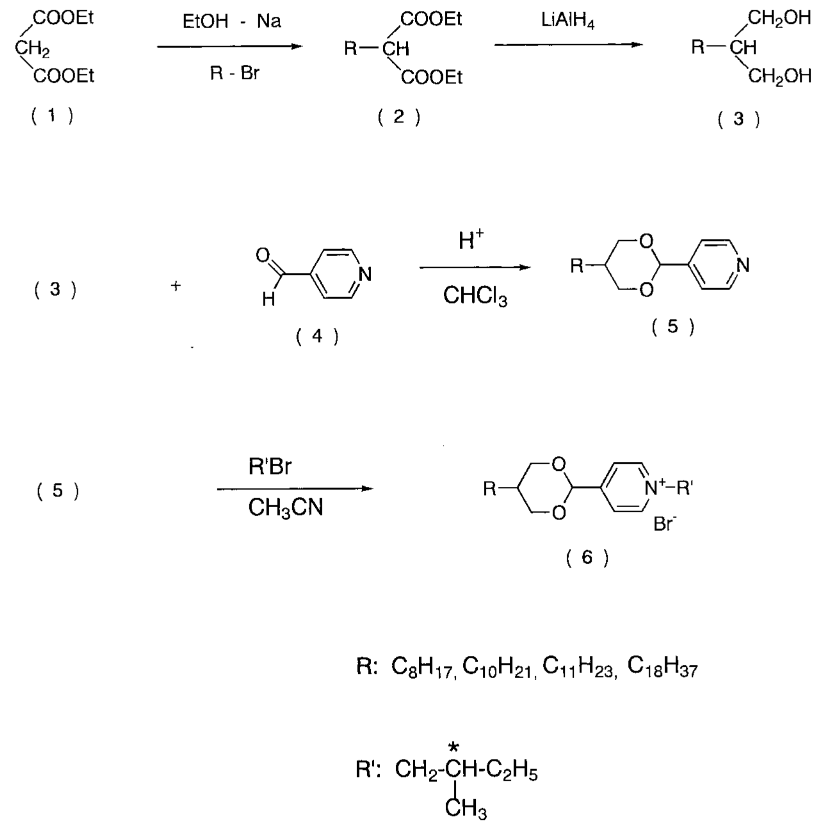

Scheme. Synthetic pathway for the compounds **6**.

Table 1. Transition temperatures (°C) of mixture A and Merck 4655-100. Cr = crystal, SmC* = smectic C*, SmA = smectic A, Cho = cholesteric, I = isotropic phase.

Sample	Cr↔SmC*	SmC*↔SmA	SmA↔Cho	Cho↔I
Mixture A	3	61	72	75
Merck 4655-100	−10<	61	72	76

Cr–SmC* transition in mixture A was higher than that for Merck 4655-100 (table 1). Tilt angles of mixture A were almost the same as those of Merck 4655-100 (table 2). Spontaneous polarizations ($\mathbf{P}_s$) for the mixture A were smaller than those for Merck 4655-100 (table 3). At high temperature the difference is particularly large; at 52°C the $\mathbf{P}_s$ of Merck 4655-100 is more than 10 times as large as that of mixture A. However, at 52°C the response time of mixture A is 25.6 μs (table 4); this value is somewhat smaller than that of Merck 4655-100. Generally, response time is inversely proportional to $\mathbf{P}_s$ and proportional to viscosity, therefore the formulation of mixture A may have resulted in a large decrease of viscosity.

Table 2. Tilt angles (°) of mixture A and Merck 4655-100.

Temperature/°C	Mixture A	Merck 4655-100
52	18.4	18.5
42	21.6	21.6
32	23.4	23.4
22	24.5	24.7
12	25.5	25.8

Table 3. $\mathbf{P}_s$ (nc cm^{-2}) of mixture A and Merck 4655-100.

Temperature/°C	Mixture A	Merck 4655-100
52	—	12.9
42	6.2	17.9
32	10.2	21.2
22	11.8	24.4
12	16.1	27.7

Dielectric constants perpendicular to the molecular axis of mixture A and Merck 4655-100 were measured with varying temperature (table 5). In the SmC* phase

Table 4. Response times (μs) of mixture A and Merck 4655-100.

Temperature/°C	Mixture A	Merck 4655-100
52	25.6	27.4
42	45.2	40.8
32	73.0	62.4
22	110.0	105.0
12	214.0	218.0

Table 5. Dielectric constants perpendicular to the molecular axis of mixture A and Merck 4655-100.

Temperature/°C	Mixture A	Merck 4655-100
30	5.17	5.01
35	5.15	4.95
40	5.15	4.86
45	5.16	4.83
50	5.20	4.78
55	5.38	4.73
60	5.90	4.68
65	31.37	4.79
70	47.06	4.54
75	32.38	4.36

they are somewhat larger than those of the Merck 4655-100, but in the SmA phase the values for mixture A are about 10 times as large as those of Merck 4655-100 (e.g. at 70°C, 4.54 for Merck 4655-100, 47.06 for mixture A). This might mean that in the SmA phase the direction of N+ --Br- in the compound **6-3** is ordered by the surrounding SmA molecules.

The principal features of mixture A are: (1) though the $\mathbf{P}_s$ is small, the response times of mixture A are almost the same as those of Merck 4655-100; (2) in the SmA phase, dielectric constants perpendicular to the molecular axis of mixture A are about 10 times as large as those of the Merck 4655-100.

3. Experimental

3.1. *Characterization*

IR, ^{1}H NMR, and mass spectra were obtained using Hitachi 215, a JNM-PMX 60, and a Hitachi M-80B spectrometers, respectively. Elemental analyses were carried out with a Carbo Erba EA 1108 instrument. 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. Dielectric constants perpendicular to the molecular axis of the smectic A phase were measured by impedance analyser Hewlett Packard 4140B with a Mettler FP80 hot stage. The cell spacing was around 3 μm. Spontaneous polarizations and response times were measured by a Wavetek model 75A with a Mettler FP80; the cell spacing was around 8 μm. The $\mathbf{P}_s$ was measured by the triangular wave method: a triangular voltage waveform of $\pm 5\ V_{p\text{-}p}$ was applied at a frequency of 5 Hz. Tilt angles were measured in thin cells with 1.4 μm spacing. The impedances of the mixture were $2.2 \times 10^9\ \Omega$ cm in the homeotropic cell, and $6.7 \times 10^8\ \Omega$ cm in the homogeneous cell (200 Hz).

3.2. *Synthesis*

3.2.1. *4-(5-Alkyl-1,3-dioxane-2-yl)pyridine (5)*

To a solution of the alkyl compound **3** (0.01 mol) and 4-formylpyridine (0.01 mol) in anhydrous benzene (100 ml) were added *p*-toluenesulphonic acid (10 g), and 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 ($CHCl_3$, cm^{-1}) 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).

3.2.2. *(+)-N-2-Methylbutyl-4-(5-alkyl-1,3-dioxan-2-yl)-pyridinium bromides (6)*

A solution of the compound **5** (0.004 mol) and (+)-2-methylbutyl bromide (0.08 mol) in anhydrous acetonitrile (20 ml) was stirred at 50°C for 72 h under nitrogen. The solution was then concentrated on an evaporator and the residue purified by reprecipitation with hexane/ether (1/1). IR ($CHCl_3$, cm^{-1}) 2800–3000 (alkyl), 1640 (pyridine). ^{1}H NMR ($CDCl_3$, δ) 0.6–2.6 (m, $\underline{R\text{−}CH}$, $N\text{−}CH_2\text{−}\underline{R'}$), 3.4–4.5 (m, 4H, CH_2−O), 5.0 (d, 2H, $N\text{−}CH_2$), 5.7 (s, 1H, O−CH−O), 8.2, 9.8 (q, 4H, ArH).

6-1 yield 48%, m.p. 11°C. Found C 62.06, H 9.37, N 3.11; calcd for $C_{22}H_{38}NO_2Br$ C 61.67, H 8.94, N 3.27%.

6-2 yield 40%, m.p. 50°C. Found C 63.71, H 9.63, N 2.93; calcd for $C_{24}H_{42}NO_2Br$ C 63.14, H 9.27, N 3.07%.

6-3 yield 45%, m.p. 54°C. Found C 60.23, H 9.06, N 3.56; calcd for $C_{25}H_{44}NO_2Br$ C 59.06, H 8.35, N 3.63%.

6-4 yield 28%, m.p. 73°C. Found C 67.20, H 10.58, N 2.00; calcd for $C_{32}H_{58}NO_2Br$ C 67.58, H 10.28, N 2.46%.

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