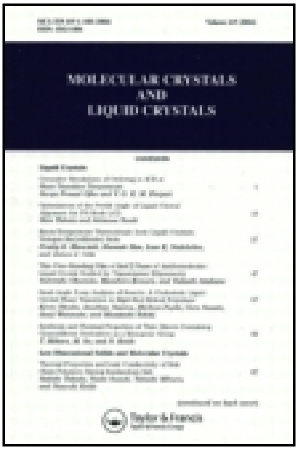

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New Liquid Crystal Materials with a Terminal Alkyl Sulfonic Acid Unit

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New Liquid Crystal Materials with a Terminal Alkyl Sulfonic Acid Unit

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New liquid crystal materials with a terminal alkyl sulfonic acid group were synthesized. The mesomorphic behavior of these compounds was evaluated. These compounds generate the SmA phase, and in the SmA phase, the molecules seem to be able to transport protons. At the temperature of the smectic phase, the proton current increased sharply. The proton transport ability increases about 700 times by forming a smectic molecular order.

Keywords: liquid crystal; proton transport; sulfonic acid

INTRODUCTION

There are many reports concerning thermotropic liquid crystal compounds containing an acidic group, but most of them concern aromatic carboxylic acid compounds [1,2]. There are no reports concerning the transport of protons in the thermotropic liquid crystal materials having a terminal alkyl sulfonic acid group and two rings in their central core.

On the other hand, new proton transport materials have been of interest as the electrolyte of fuel cells. Interestingly, ordered transport of protons seems to be advantageous to increase efficiency and permanence. Therefore in this communication, we report a new class of

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liquid crystal compounds with a terminal alkyl sulfonic acid group that have the possibility of proton transport.

RESULTS AND DISCUSSION

Compounds 6 were synthesized by the route shown in Fig. 1.

In the syntheses of compounds **3**, both mono- and diethers were produced.

As diether is soluble in hexane, it is easy to remove. Compounds **6** were synthesized by etherification of compound **3** and **4** or **3** and **5**. In the etherification of **3** and **4**, 1,8-diazabicyclo[5,4,0]undec-7-ene

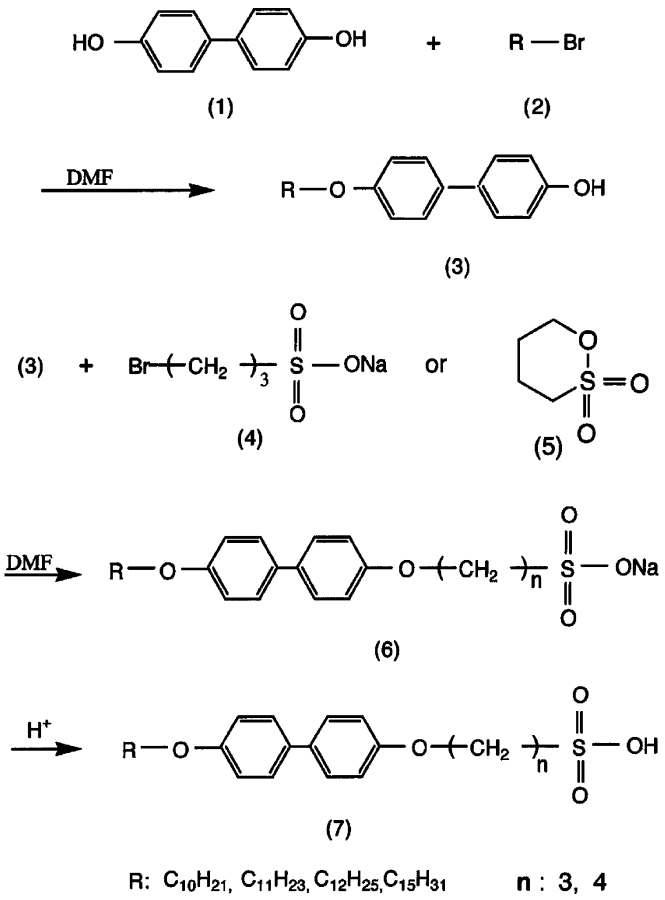

FIGURE 1 Synthetic pathway for the liquid crystalline compounds **7**.

TABLE 1 Phase Transition Temperatures for Compounds **7**

Compound	R	*n*	Phase transition temperatures/°C[a]				
7a	$C_{10}H_{21}$	3	C	114	SmA	132	I
7b	$C_{11}H_{23}$	3	C	127	SmA	134	I
7c	$C_{12}H_{25}$	3	C	135	SmA	158	I
7d	$C_{15}H_{31}$	3	C	137	SmA	170	I
7e	$C_{10}H_{23}$	4	C	115	SmA	145	I
7f	$C_{12}H_{25}$	4	C	119	SmA	148	I

[a] C: Crystal, SmA: Smectic A, I: Isotropic.

(DBU) was used as a base. In the case of **3** and **5**, sodium methoxyde was used as a base.

Crude product **6** was obtained as sodium salt, and 6N-HCl was used to gain sulfonic acid (**7**). Because sulfonic compounds **7** are soluble in 1,4-dioxane solubent, 1,4-dioxane was used in the separation of **6** and **7**. The purity of compounds **7** was checked by the ^{1}H NMR data and elemental analyses.

To judge the existence of liquid crystal phases, a micro-melting-point apparatus equipped with polarizers was employed. Compounds **7a** exhibited a liquid crystal phase, so that further detailed measurements were made. Measurement of transition temperatures and assignment of the mesophases were carried out by means of a polarization microscope equipped with Mettler FP90-FP82HT heating stage and temperature controller, a differential scanning calorimeter (DSC), and an X-ray diffraction instrument. Phase transition temperatures for compounds **7** are given in Table 1. Observation of texture indicates that these

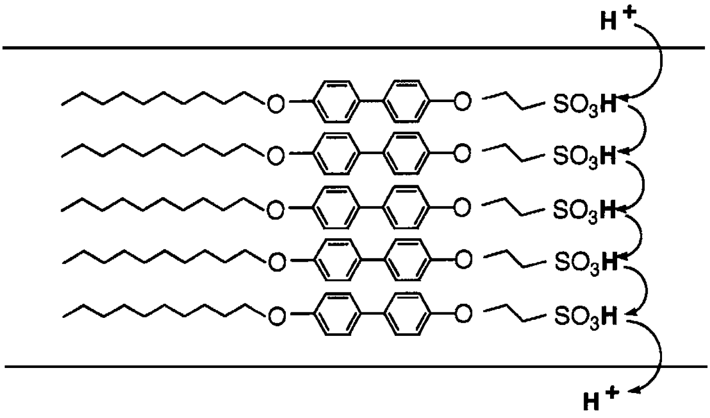

FIGURE 2 Transport of protons in the smectic liquid crystalline phase.

compounds exhibit the same texture of smectic A phase. To confirm this result, conoscopic figures and X-ray diffraction were measured for the phase of compound **7a** (Fig. 2). These results also support the assignment of the liquid crystal phase as smectic A. That is, a uniaxial conoscopic figure was observed for the smectic A phase, and the diffraction pattern of a typical smectic A phase was also obtained. The peaks in the small-angle region indicate that the layer spacings of these phases of the compound **7a** are 51.3 A for the smectic A phase. The layer spacing of 51.3 A is longer than the molecular length of compound **7a**. Therefore, in the smectic A phase, molecules seem to be arranged in the bilayer packing of Fig. 3. Transition temperatures of smectic to isotropic liquid of compounds **7** increase with the increasing length of alkyl

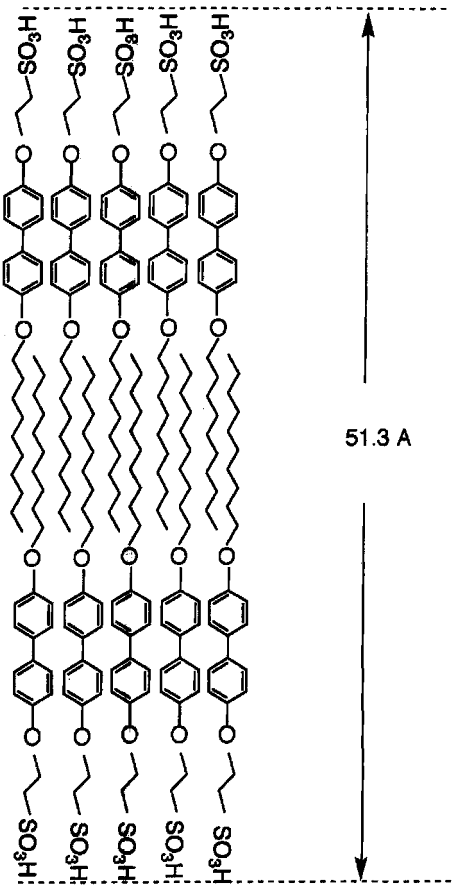

FIGURE 3 Molecular arrangement of the new liquid crystal compound **7a**.

TABLE 2 Proton Transport Ability of Compounds **7**

			Electrical proton current (μA/cm^2)	
Compound	R	*n*	Applied voltage: 0.5 V	Cell gap: 15 μm
7a	$C_{10}H_{21}$	3	0.01 (40°C)	4.84 (120°C)[a]
7c	$C_{12}H_{23}$	3	0.01 (40°C)	1.17 (140°C)[a]
7d	$C_{15}H_{31}$	3	0.01 (40°C)	7.41 (160°C)[a]
7f	$C_{12}H_{23}$	4	0.01 (40°C)	3.52 (130°C)[a]

[a] Maximum electrical proton current in the SMA phase.

chain (R). Transition temperatures of isotropic liquid to mesophase for compounds with a C_4H_8 chain between the core and sulfonic group (**7e**, **7f**) are the same as those for the corresponding compounds with a C_3H_6 chain (**7a**, **7c**).

The electrical proton current of 1-[4-(9-decenyloxy)phenyl]-4-alkyl piperazine was measured for the homogeneous alignment in the liquid cystalline cell (cell spacing: 15 μm, effective area of electrode is 0.16 cm^2) using Advantest 8340 A and Mettler FP90 control processor. (Table 2) Compound **7d** exhibited a proton current of 7.4 μA/cm^2 at 160°C (applied voltage: 0.5 V). At 40°C, the current is 0.01 μA/cm^2. The current increases gradually at 130°C and increases sharply at 155°C, then decreases at 170°C. Generally, normal liquid crystalline compounds exhibit less than 0.0001 μA/cm^2. Though at 40°C these compounds do not have any liquid crystalline order, these compounds seem to have the proton current. At the temperature of the smectic phase, the proton current increased sharply. The proton transport ability increases about 700 times by forming a smectic molecular order. As in this system, no protons are available; therefore, in the case of an abundant supply of protons, it may be possible to get better data.

EXPERIMENTAL

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 using a Carbo Erba EA 1108. The 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. X-ray diffraction was performed with a Rigaku Rint 2100 X-ray system.

Synthesis

Compounds (6), (7), n = 3

A solution of compounds (**3**) (0.02 mol) and (**4**) and 1,8-diazabi cyclo[5.4.0]undec-7-ene (DBU) in anhydrous DMF (20 ml) was stirred at 60°C for 48 h under a nitrogen atmosphere. After the reaction, the solution was concentrated on an evaporator. Diethylether (100 ml) was added to the residue. The precipitate was purified with water and diethylether.

HCl (8 ml) and then tetrahydrofuran (50 ml) were added to the compound (**6**). The solution was stirred 1 h. Then the solution was concentrated to yield the precipitate.

The precipitate was purified by dioxane solvent.

n = 4

A solution of compound (**5**) (0.008 mol) and methanol (20 ml) was added to a solution of methanol (50 ml) and NaOH (0.008 mol). The solution was stirred at 40°C for 2 h under a nitrogen atmosphere. After the reaction, the solution was concentrated on an evaporator. Diethylether (100 ml) was added to the residue. The precipitate was purified with water and diethylether.

HCl (8 ml) and then tetrahydrofuran (50 ml) were added to the compound (**6**). The solution was stirred 1 h. Then the solution was concentrated to yield the precipitate.

The precipitate was purified by dioxane solvent.

IR (KBr) 2800–3000 (alkyl), 1502, 1608 (phenyl), 1178 (S=O). ^{1}H NMR ($CDCl_3$, δ) 0.8–1.8 (m, alkyl), 2.0, 2.6 (m, 2H, $CH_2CH_2{-}S$), 3.9, 4.1 (t, 4H, $O{-}CH_2$), 6.8, 7.5 (m, 8H, ArH).

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