Formation and Properties of Ferroelectric Liquid Crystalline Compound Containing -C(O)-S-O- Linkage

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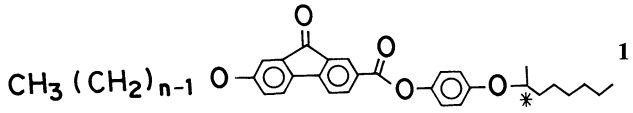
During our investigations of the synthesis of ferroelectric liquid crystal compounds containing a fluorenone nucleus, the formation of a novel compound having a -C(O)-S-O- linkage was discovered as a by-product when a derivative of fluorenone carboxylic acid was treated with thionyl chloride and a phenol. This compound also exhibited ferroelectric liquid crystal properties. Compounds with a -C(O)-S-O- linkage have been little reported; this is the first report concerning a liquid crystalline compound with this type linkage. The thermal stability of the mesophase is reduced upon changing from the -C(O)-O- linkage to the -C(O)-S-O- linkage. The synthesis and properties of this compound are discussed in detail.

The authors previously reported the properties of ferroelectric liquid crystals containing fluorene and fluorenone structures.[2,3] During the synthesis of some fluorenone compounds **1**, small amounts of by-products (compounds **2**) appeared during



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the esterification step. After isolation and purification, compound **2** (n=10) was found to show a liquid crystal phase over a wide range of temperatures under a polarized microscope. For a novel molecular structure of liquid crystalline material and a new reaction, the molecular structure was identified and the properties as a ferroelectric liquid crystal were investigated.

Experimental

Measurements. Measurements of transition temperature and observations of the microscopic texture of the mesophases were carried out using an Olympus polarizing microscope in conjunction with a Mettler FP82 heating stage, a FP80 control unit and a Seikohdenshi differential scanning calorimeter (model DSC 200). ^{1}H NMR spectra were measured using a JEOL JNM-GSX-270 NMR spectrometer for a solution in $CDCl_3$, with tetramethylsilane used as the internal standard. The IR spectra were recorded on a KBr disc with a JASCO Report-100 infrared spectrometer. The purity of each sample was checked by HPLC JASCO TWINCLE and element analysis.

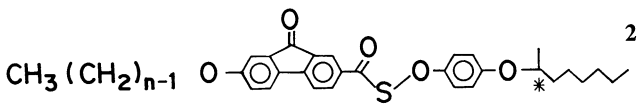
The Synthesis and Purification of Compound 1 (n=10) and Compound 2. 7-Decyloxy-9-oxo-2-fluorenecarboxylic acid (3.00 g, 7.89 mmol) in 35 ml of thionyl chloride was warmed at 70 °C for 2 h. After evaporating the thionyl chloride, 25 ml of dry pyridine was added. Then 4-((*S*)-1-methylheptyloxy)-phenol (2.21 g, 9.95 mmol) in 10 ml of dry pyridine solution was added and the mixture was warmed at 80 °C for 3 h. It was then poured into ice water. After acidification, the precipitate was collected and purified by column chromatography. By recrystallizing the first fraction product from petroleum ether and an ethanol solution, 1.02 g (1.75 mmol, 22%) of yellowish needles were obtained. By recrystallizing the second fraction product from petroleum ether and toluene, 0.84 g (1.29 mmol, 16%) of yellowish needles were obtained.

The molecular structures of these compounds were confirmed using ^{1}H NMR, IR, UV-spectra, and elemental analyses.

Results and Discussion

Formation. The formation of this by-product (compound **2**) has only been confirmed in a few cases. However, in the case of the synthesis of compound **1** (n=10), for example, a good amount of compound **2** (n=10) was obtained. The authors discuss this particular case here and give a detailed description of the conditions in the experimental section.

Molecular Structure. The molecular structure of compound **2** (n=10) was determined by the ^{1}H NMR, IR, UV-spectra, as well as elemental analysis. All of the data are consistent with the molecular structure **2** (n=10), shown below.



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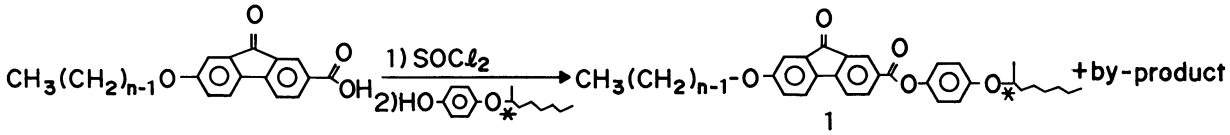

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(n=10 22% 16%)

Scheme 1.

Table 1. NMR Spectra of Compound **1** and Compound **2**

Assignment	Chemical shift δ_H/ppm		Pattern (Integral)
	Compound **1**	Compound **2**	
$-(CH_2)_8CH_3$ and $-C(CH_3)(CH_2)_5CH_3$	1.84—0.86	1.86—0.85	m (35H)
R-CH_2-O-fluorenone	4.03	4.01	t (2H)
Ar-O-CH(Me)R	4.29—4.36	4.32—4.21	m (1H)
-OArO-H-2, 3, 5, and 6	6.95—6.89 7.14—7.08	7.14—6.99	m (4H)
Fluorenone H-3	7.05 J_{5-6}=8.1 Hz J_{6-8}=2.7 Hz	6.81 J_{5-6}=8.1 Hz J_{6-8}=2.7 Hz	dd (1H)
Fluorenone H-1	7.26	7.21	d (1H)
Fluorenone H-4 or H-5	7.51	7.45	d (1H)
Fluorenone H-4 or H-5	7.54	7.47	d (1H)
Fluorenone H-6	8.31 J_{3-4}=8.1 Hz J_{1-3}=2.7 Hz	8.26 J_{3-4}=8.1 Hz J_{1-3}=2.7 Hz	dd (1H)
Fluorenone H-8	8.40	8.33	d (1H)

Table 2. IR and UV-Spectra and Elemental Analysis of Compound **1** and Compound **2**

Compound **1**	IR/cm^{-1} (KBr)	2930, 2860, 1740 (CO), 1720 (CO), 1600, 1510, 1470, 1300, 1270, 1240, 1200, 1090
	λ_{max}/nm (CH_2Cl_2)	435, 339, 325, 283, 252, 231
Compound **2**	IR/cm^{-1} (KBr)	2930, 2860, 1740 (CO), 1720 (CO), 1610, 1490, 1470, 1300, 1260, 1200, 1100
	λ_{max}/nm (CH_2Cl_2)	439, 340, 326, 283, 231
	Elemental analysis/%	C 74.28 (73.99)
	(Calcd for $C_{38}H_{48}O_5S$)	H 7.96 (7.84)
		S 5.44 (5.20)

The ^{1}H NMR spectra of compound **1** (n=10) and **2** (n=10) are shown in Table 1. The assignment of each peak was carried out by a comparison with the data for other fluorenone derivatives.[2,3] The chemical shifts and splitting patterns of compounds **1** (n=10) and **2** (n=10) were almost identical.

IR, UV-spectra, and elemental analyses of compound **1** (n=10) and **2** (n=10) are shown in Table 2. The IR spectrum of compound **2** (n=10) is very similar to that of compound **1** (n=10), except that a strong characteristic peak at 1260 cm^{-1} appears and the peak at 1510 cm^{-1} of compound **1** (n=10) disappears. The UV-spectra of the two fluorenone derivatives are essentially the same in the region above 260 nm. These spectral properties imply that the main structures comprising compound **1** (n=10), such as the fluorenone moiety as well as the phenyl and alkyl groups, remain in compound **2** (n=10).

Compound **2** (n=10) was purified by triple recrystallization, and elemental analysis was carried out at each stage. All of the analytical results were coincident within experimental error with the calculated values for the formula $C_{38}H_{48}O_5S$.

Judging from all of these results, compound **2** (n=10) was determined to have chemical formula of **2** (n=10).

One possible structure which could explain these data is one with the -C(O)-O-S- linkage. Nevertheless, there seems to be no possibility to form this structure, considering the reaction mechanism.

Compounds containing the -C(O)-S-O- linkage structure have been little reported. The author has found those compounds mentioned in only 10 papers among the literature published since 1962.

For example, Haas et al.[4] reported on the formation of $FC(O)SOC(O)CF_3$ by a reaction of fluorocarbonylsulfenic acid chloride (FC(O)SCl) and silver trifluoroacetate ($F_3CC(O)OAg$). Schuphan and Casida[5] showed the formation of $(R)_2NC(O)SOCH_2CCl{=}CH_2$ through a [2,3]sigmatropic rearrangement of *S*-(3-chloroallyl) thiocarbamate sulfoxide ($(R)_2NC(O)S(O)CH_2CCl{=}CH_2$).

Moon and Oh,[6] Islam and Kwart,[7] and U. Hildebrand et al.[8] reported the formation of a compound containing the -C(O)-S-O- linkage by the reaction of acylsulfenyl chloride derivatives with appropriate alcohol derivatives.

There has been no report concerning a compound with the -C(O)-S-O- linkage, which is formed through a reaction of alcohols or phenols with products formed from carboxylic acids and thionyl chloride.

Phase Transition Behavior. The phase transition behavior of compound **2** was observed using a polarized microscope in conjunction with a heating stage and differential scanning calorimeter.

The phase transition behavior of compound **2** (n=10) is shown below, along with that of compound **1** (n=10) for a comparison.

$$\mathrm{Cr} \xrightarrow{93\,^\circ\mathrm{C}} \mathrm{S_{c^*}} \xrightarrow{102\,^\circ\mathrm{C}} \mathrm{ISO} \quad \text{compound } \mathbf{2}\ (n=10)$$

$$\mathrm{Cr} \xrightarrow{81\,^\circ\mathrm{C}} \mathrm{S_{c^*}} \xrightarrow{118\,^\circ\mathrm{C}} \mathrm{S_A} \xrightarrow{127\,^\circ\mathrm{C}} \mathrm{ISO} \quad \text{compound } \mathbf{1}\ (n=10)$$

Compound **2** (n=10) shows no tendency to decompose when heated to 200 °C in air. A phase determination was possible, since it showed the broken fan texture characteristic of the smectic C phase under a polarized microscope. Miscibility tests were carried out with liquid crystalline materials of which the phase transition behavior was already known. The material exhibits a direct transition from isotropic liquid into the chiral smectic C phase. It has a higher melting point and a lower isotropic liquid–liquid crystal transition temperature than does compound **1** (n=10).

The decrease in the mesophase thermal stability (the transition temperature from the liquid crystal phase to the isotropic liquid phase) of compound **2** (n=10), compared with compound **1** (n=10), can be attributed to the fact that the change from the –C(O)–O– linkage to the –C(O)–S–O– linkage increases the molecular width, decreases the linearity of the molecule and increases the flexibility of the linkage. Especially, the disappearance of the smectic A phase in the case of compound **2** (n=10) means a decrease in the lateral attractive intermolecular interaction, due to the factors mentioned above.

After purification by triple recrystallization and checking the purity using elemental analysis and HPLC each time, the sample was sufficiently pure; however, the isotropic and chiral smectic C phases coexisted in equilibrium over several degrees. The authors experienced this phenomenon in liquid crystalline materials which have a direct transition from an isotropic liquid to the smectic C phase.[3)]

Tilt Angle and Spontaneous Polarization. The temperature dependence of the tilt angle and spontaneous polarization for the compound were measured. These measurements were carried out by a previously reported method.[3)] Liquid crystal cells having a 1×1 cm^2 electrode area were used. Alignment was achieved by coating the glass surfaces with polyimide and buffing the surface in one direction. The cell spacing was 2.0 μm, which was obtained using fiber spacers. In Fig. 1, the temperature dependence of the tilt angle for compounds **1** (n=10) and **2** (n=10) are shown.

The tilt angle of compound **1** (n=10) gradually increases with decreasing temperature, a characteristic of a second-order transition. On the other hand, the tilt angle of compound **2** (n=10) increases abruptly to 29 degrees just below the transition from an isotropic liquid to the chiral smectic C phase; no significant change was observed. These are characteristic of a first-order transition.

The temperature dependence of spontaneous polarization of compounds **1** (n=10) and **2** (n=10) are shown in Fig. 2.

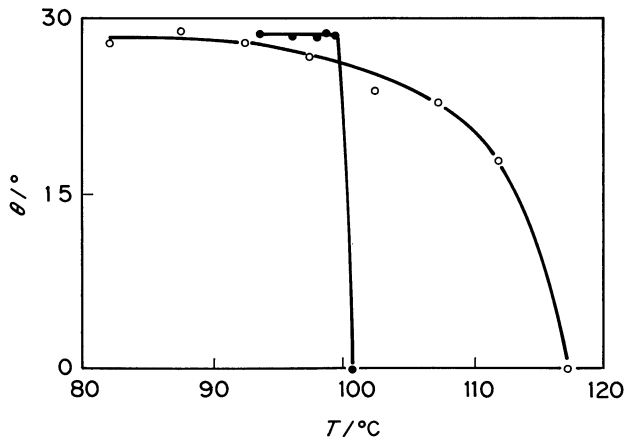

Fig. 1. Tilt angle (θ) temperature dependences of compound (**1**) and compound (**2**). ○ and ● denote compound (**1**) and compound (**2**), respectively.

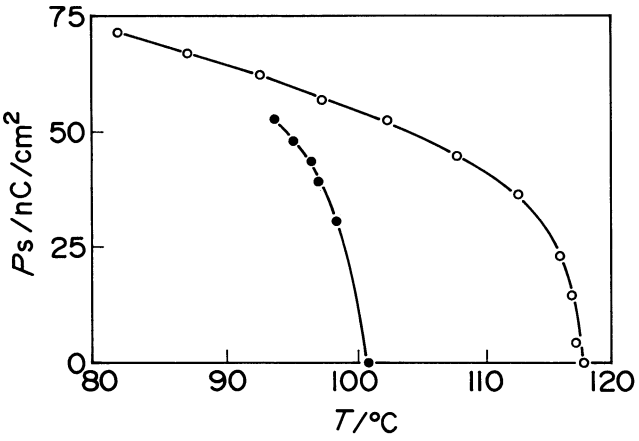

Fig. 2. Spontaneous polarizations (Ps) temperature dependences of compound (**1**) and compound (**2**). ○ and ● denote compound (**1**) and compound (**2**), respectively.

Over the entire temperature range, compound **2** (n=10) shows a lower spontaneous polarization than does compound **1** (n=10). Just below the transition temperature, ths slope of compound **2** (n=10) is steeper than that of compound **1** (n=10) for the ISO-S_{c^*} type first-order transition. However, spontaneous polarization gradually increases with decreasing temperature, in spite of the first-order transition. This could be ascribed to the fact that, in the case of compound **2** (n=10), the transition between the isotropic liquid phase and the chiral smectic C phase is ambiguous and both phases coexist until about 95 °C. From these results, it can be said that the change from the –C(O)–O– linkage to the –C(O)–S–O– linkage does not greatly influence the magnitudes of the tilt angle and spontaneous polarization.

References

1) A part of the results in this paper was presented in the 56th Annual Meeting of the Chemical Society of Japan, 1989, Abstr., 4B IIB 10 138 and the International Liquid Crystal Conference, 1990, Abstr., FER 46P.

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