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Synthesis and Mesomorphic Properties of Ferroelectric Liquid Crystals with a Fluorinated Asymmetric Frame (2)

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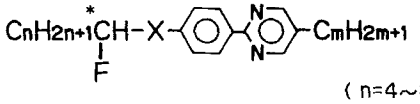
Two new series of ferroelectric liquid crystals with a fluorinated asymmetric frame were synthesized by utilizing optically active S-(−)-2-fluoroalkanols or S-(−)-2-fluoroalkanoic acids, and their mesomorphic and physical properties were studied. 5-Alkyl-2-[*p*-(2-fluoroalkyloxy)phenyl]pyrimidines (5, $n \geq 6$, $m = 12$) exhibited enantiotropic chiral smectic C phase, and their spontaneous polarizations were more than 34nC/cm^2 (except for $n = 4$). The values of response time were short (on the order of 10 μ sec) and were found to be shorter by decreasing the value of n. 5-Alkyl-2-[*p*-(2-fluoroalkanoyloxy)phenyl]pyrimidines (6) exhibited the monotropic chiral smectic C phase characterized by an extremely short response time of 4.2 μ sec.

INTRODUCTION

Recently, we reported the synthesis and mesomorphic and physical properties of several new ferroelectric liquid crystals having new fluorinated chiral frames derived from S-(−)-fluoroalkanoles (1) and phenyl benzoate or biphenyl-phenyl frames as the mesogenic cores.[1]

In this paper, we report on the preparation of new types of optically active compounds, S-(−)-2-fluoroalkanoic acids and the synthesis of two types of new series of ferroelectric liquid crystals (5 and 6) and describe their mesomorphic and physical properties, such as phase behavior, spontaneous polarization and response time.



(n=4∼8, m=8∼12)

5 (X=CH2O)

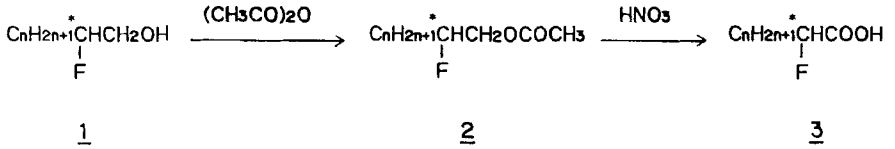
6 (X=COO)

FLCs 5 and 6

RESULTS AND DISCUSSION

Synthesis of S-(−)-2-fluoroalkanoic acids 3

The synthetic route of 3 is given in Scheme I.

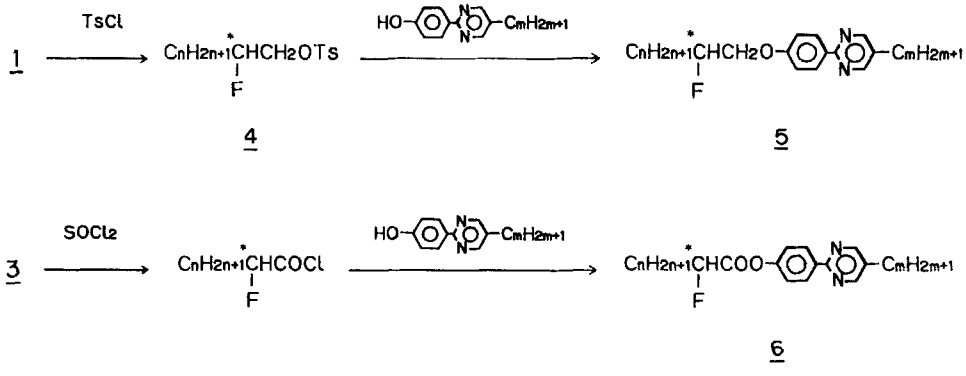


SCHEME I

S-(−)-2-Fluoroalkanols (1) were acetylated with anhydrous acetic acid to give the corresponding acetates (2), which were subsequently oxidized by 16M nitric acid[2] yielding (−)-2-fluoroalkanoic acids (3). Yields and physical properties of 2 and 3 are summarized in Table I and II, respectively. Their optical purity was determined by the method reported previously.[1]

Synthesis of liquid crystals

The synthesis of liquid crystals was carried out as outlined in Scheme II.



SCHEME II

(−)-2-Fluoroalkanols (1) were converted into tosylates (4), which were treated with 5-alkyl-2-(*p*-hydroxyphenyl)pyrimidines in the presence of a base to give (+)-5-alkyl-2-[*p*-(2-fluoroalkyloxy)phenyl]pyrimidins (5). (−)-2-Fluoroalkanoic acids (3) were converted into the corresponding acyl chlorides by a treatment with thionyl

TABLE I

Yields and physical properties of (+)-2-fluoroalkyl acetates (2)

n	Yield (%)	bp (℃ / torr)	$[\alpha]_D$ (c1, Et_2O)
4	70	88 - 89 / 35	+ 3.3 °
5	75	111 - 113 / 33	+ 3.1 °
6	77	114 - 117 / 27	+ 3.9 °
7	86	138 - 140 / 90	+ 2.1 °
8	88	146 - 148 / 33	+ 2.6 °

chloride and subsequently coupled with 5-alkyl-2-(*p*-hydroxyphenyl)pyrimidines to give (+)-5-alkyl-2-[*p*-(2-fluoroalkanoyl)phenyl]pyrimidins (6).

Phase behavior

The phase behavior for 5 is given in Table III.

The phase transition temperatures and the phase stability were shown as a function of the length of the side chains. All 5 have the mesomorphic phase, and exhibit enantiotropic or monotropic S_C^* for the values of $m \geqq 10$. The compounds with the values of $n \geqq 6$, $m = 12$ exhibit the thermodynamically stable S_C^* in the temperature range of approximately 14, and the compound ($n = 6$, $m = 12$) has

TABLE II

Yields and physical properties of (−)-2-fluoroalkanoic acids (3)

n	Yield (%)	bp (℃ / torr)	$[\alpha]_D$ (c1, Et_2O)	O.P. (% e.e.)
4	62	74 - 75 / 3	- 11.6 °	66 [b]
5	51	122 - 125 / 17	- 12.9 °	94 [b]
6	69	105 - 120 / 6	- 13.6 °	91 [a]
7	57	102 - 105 / 3	- 10.5 °	89 [b]
8	50	114 - 120 / 3	- 9.7 °	86 [b]

a) Optical purity determined by HPLC after leading 2 to its amide of 1-(1-naphthyl) ethyl amine.
b) Optical purity of the corresponding epoxides used.[3]

TABLE III

Phase behavior of compounds 5

n	m	C	S_4	S_3	S_C^*	S_A	I
5	8	· 24				· 35	·
6	8	· 62				(· 59)	·
6	9	· 63				· 67	·
4	10	· 48			(· 43)	· 66	·
5	10	· 49			· 60	· 66	·
6	10	· 61		(· 49)	(· 62)	· 71	·
7	10	· 57	(· 29)	· 66*	(· 65)	· 72	·
8	10	· 69			· 73		·
4	12	· 59	(· 37)	(· 39)	(· 43)	· 71	·
5	12	· 60		(· 49)	(· 61)	· 72	·
6	12	· 56			· 70	· 74	·
7	12	· 62			· 74		·
8	12	· 56	(· 40)	· 61	· 76		·

C: crystal, S_c^*: chiral smectic C phase, S_A: smectic A phase, I: isotropic liquid, S_3, S_4: unidentified smectic phase

Temperatures are degrees Celsius. ( ): monotropic transition

the smectic A phase (S_A) above the S_C^*. Each phase stability is strongly influenced by two numbers of carbon atoms (n, m). When $m = 12$, as the value of n increased, S_A diminished and S_C^* appeared. Thus, when $n = 8$, S_A disappeared completely and the smectic phase of a higher order (S_3) appeared. On the other hand, when $n = 6$, as the value of m increased, the liquid crystalline phase extended and the thermodynamically stable S_C^* appeared.

The phase behavior of 6 is given in Table IV.

Two compounds ($n = 8$, $m = 8$) and ($n = 5$, $m = 10$) are not liquid crystals. Although most of 6 also exhibits no mesomorphic phase on heating, those are monotropic liquid crystals having a mesomorphic phase which appears in a supper-cooling state. Four compounds ($n = 6$, $m = 10$), ($n = 8$, $m = 10$), ($n = 4$, $m = 12$) and ($n = 6$, $m = 12$) exhibit S_C^*. It seems that the compounds ($m = 12$) tend to exhibit an even-odd effect which was pronounced at melting point. Namely, the compounds with an even number of n have a higher melting point, and in particular this effect appears remarkably on the short length of the side chain.

By comparing the phase behavior of 5 with that of 6, it was found that the thermodynamically stable S_C^* prefered —CH_2O— to —COO— as a spacer group in the phenylpyrimidine framework with a fluorinated asymmetric carbon center.

TABLE IV

Phase behavior of compounds 6

n	m	C	S_3	S_C^*	S_A	Ch	I
6	8	· 56	(· 38)				·
8	8	· 55					·
6	9	· 53			(· 46)		·
8	9	· 64			(· 46)		·
4	10	· 46	(· 30)		· 49		·
5	10	· 67					·
6	10	· 57	(· 32)	(· 45)			·
7	10	· 59			(· 46)		·
8	10	· 59		(· 43)	(· 46)	(· 48)	·
4	12	· 59		(· 45)	(· 52)		·
5	12	· 14	· 63		(· 50)		·
6	12	· 62		(· 52)			·
7	12	· 22	· 70		(· 61)		·
8	12	· 23	· 87				·

C: crystal, S_C^*: chiral smectic C phase, S_A: smectic A phase, Ch: cholesteric phase, I: isotropic liquid, S_3: unidentified smectic phase

Temperatures are degrees Celsius. ( ): monotropic transition

Spontaneous polarization and response time

The spontaneous polarization and the response time at $T_C - T$ for 5 and 6 are shown in Table V.

The magnitude of spontaneous polarization is more than 34nC/cm^2 in 5 and 6 except for the compounds ($n = 4$). It seems that the comparatively small values of the spontaneous polarization for the compounds ($n = 4$) are attributable to the low optical purity of the chiral part (66% e.e.). The response time was found to be on the order of 10 μ sec or less except for 5 ($n = 8$, $m = 10$) at an applied AC voltage of 4V/μm. With regard to 5 ($m = 12$), the response time closely relates to the n value. The response time is shorter when decreasing the n value. Namely, the compound possessing the shorter chiral terminal group has the faster response speed. It was found that 6 with the values of $n = 4$, $m = 12$ substantially gave the best value (4.2 μsec) of response time among the compounds synthesized in this study. The spontaneous polarization and the response time measured as function of reduced temperature ($T_C - T$) for 5 ($n = 6$, $m = 12$) are shown in Figure 1 and Figure 2, respectively.

TABLE V

Spontaneous polarization and response time of compounds 5 and 6

No.	n	m	Ps (nC / cm²)	τ a) (μsec)	Tc - T (℃)
5	4	10	6	13.0	8
5	5	10	61	12.0	7
5	6	10	42	11.5	5
5	7	10	43	11.0	5
5	8	10	34	21.0	3
5	4	12	19	5.8	3
5	5	12	40	8.0	5
5	6	12	45	10.5	5
5	7	12	38	12.5	5
5	8	12	40	17.0	5
6	6	10	44	13.0	5
6	4	12	26	4.2	1

T_c: the upper limit of S_c*
a) applied AC square waves of 4V/μm

EXPERIMENTAL

The structures of the products prepared were confirmed by the spectroscopic methods of ^{1}H-NMR(JEOL-PMX60si) and IR(JASCO IRA-302). The values of specific rotation were measured on a JASCO DIP-360 digital polarimeter. The phase transition temperatures and the identification of the phases for the compounds were determined by the same method reported previously.[1] The values of spontaneous polarization and the response time were measured by the triangular-waves method[4] and the field-reversal method,[5] respectively.

Preparation of (+)-2-fluorooctyl acetate (2, *n* = 6)

A mixture of (l−)-2-fluorooctanol (2.22 g, 15.0 mmol), acetic anhydride (1.61 g, 15.8 mmol) and sodium acetate (0.56 g, 6.8 mmol) in benzene was stirred at 90°C for four hours. It was quenched with water and then extracted with benzene. The combined extract was washed with water and dried over anhydrous sodium sulfate. After the benzene was evaported in vacua, (+)-2-fluorooctyl acetate was purified by distillation under reduced pressure, bp 114°C–117°C/27 torr. The yield was 2.19 g (11.5 mmol), 77%. $[\alpha]_D$ +3.9° (cl.12, Et_2O), ^{1}H-NMR (CCl_4)δ 0.90(t, 3H), 1.37(m, 10H), 2.00(s, 3H), 4.07(dd, 2H, J = 12Hz, J = 1.5Hz, 4.50(dm, 1H, J = 24), IR(neat)2900, 2850, 1740, 1460, 1360, 1220, 1040, 900, 720, 600 cm^{-1}

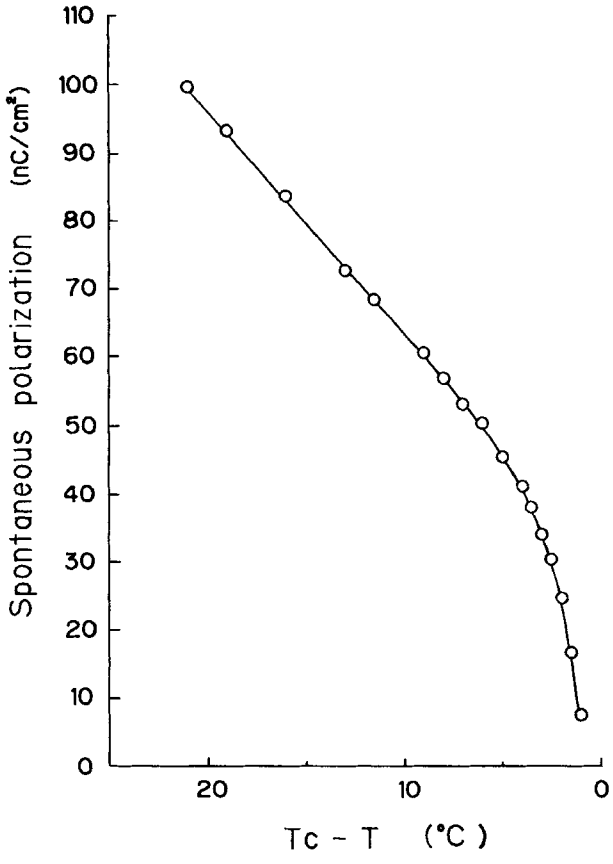


FIGURE 1 Temperature dependence of the spontaneouse polarization of 5 ($n=6$, $m=12$).

Preparation of S-(−)-2-fluorooctanoic acid (3, n = 6)

A mixture of (+)-2-fluorooctyl acetate (2.14 g, 11.3 mmol), acetic acid (5.6 ml), and 16M nitric acid (6.8 ml) was stirred at 55°C–60°C for 24 hours. The mixture was quenched with ice water and extracted with ether. To the combined extract was carefully added 2M sodium bicarbonate solution. The aqueous alkaline solution was extracted with ether. The aqueous solution was neutralized with 6M hydrochloric acid and extracted with ether. The combined extract was washed with water, dried over anhydrous sodium sulfate and evaported in vacua. S-(−)-2-Fluorooctanoic acid was purified by distillation under reduced pressure, bp 105°C–120°C/6 torr. The yield was 1.26 g (7.78 mmol), 69%. $[\alpha]_D$ −13.6° (cl.06, Et_2O), ^{1}H-NMR(CCl_4)δ 0.90 (t, 3H), 1.37(m, 10H), 4.73(dt, 1H, J = 24Hz), 11.07(s, 1H), IR(neat)3000, 2900, 2850, 1730, 1460, 1430, 1240, 1110, 1080, 900, 720, 650, 540 cm^{-1}

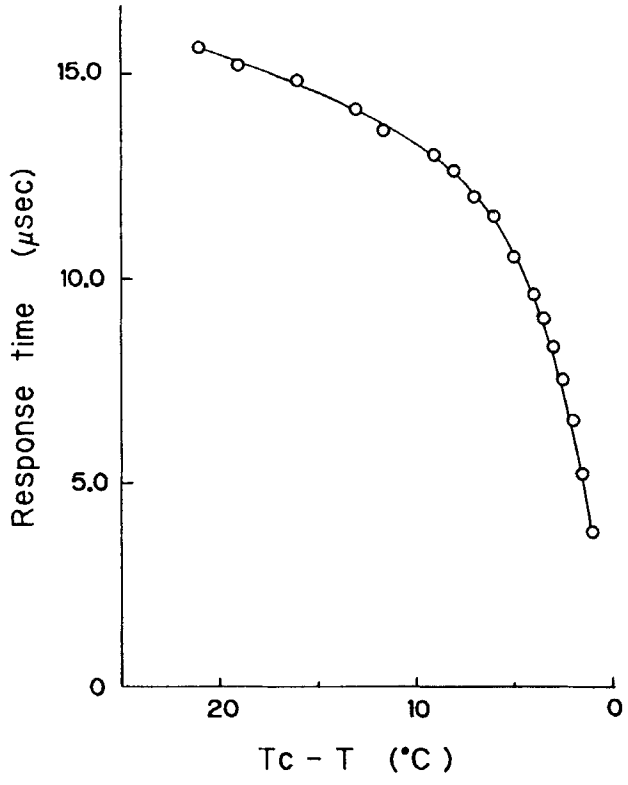


FIGURE 2 Temperature dependence of the response time of 5 ($n=$, $m=12$).

Preparation of (+)-2-fluorooctyl *p*-toluenesulfonate (4, *n* = 6)

S-(−)-2-fluorooctanol (1.66 g, 11.2 mmol) in pyridine was stirred for ten minutes under nitrogen. To this solution was added *p*-toluenesulfonyl chloride (2.35 g, 12.3 mmol) in an ice water bath. After being stirred at room temperature for six hours, the reaction mixture was quenched with 2M hydrochloric acid and extracted with ether. The combined extract was washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 3.83 g of crude product. (+)-2-Fluorooctyl *p*-toluenesulfonate was purified by a column chromatography on silica gel using a mixture of benzene-hexane (2:1) as an eluent. The yield was 2.40 g (7.9 mmol), 71%. $[\alpha]_D$ + 11.5° (cl.05, C_6H_6), ^{1}H-NMR(CCl_4)δ 0.87(t, 3H), 1.30(m, 10H), 2.43(s, 3H), 3.97(dd, 2H, J = 11Hz, J = 2Hz), 4.50(dm, 1H, J = 24Hz), 7.23(d, 2H, J = 4Hz), 7.70(d, 2H, J = 4Hz), IR(neat)2920, 2850, 1600, 1460, 1360, 1180, 1100, 980, 820, 660, 560 cm^{-1}

Preparation of (+)-5-dodecyl-2-[*p*-(2-fluorooctyloxy)phenyl]pyrimidine (5, *n* = 6, *m* = 12)

To a suspension of sodium hydride (0.04 g, 1.00 mmol, 60% dispersion in oil, washed one time with dry benzene) in N,N-dimethyl formamide was added

5-dodecyl-2-(*p*-hydroxyphenyl)pyrimidine (0.27 g, 0.80 mmol), and the mixture was stirred at room temperature for thirty minutes. (+)-2-Fluorooctyl *p*-toluenesulfonate (0.24 g, 0.80 mmol) dissolved in N,N-dimethylformamide was added to the reaction mixture. After being stirred at 100°C for six hours, the mixture was quenched with water and extracted with ether. The combined extract was dried over anhydrous sodium sulfate and evaported in vacua. (+)-5-Dodecyl-2-[*p*-(2-fluorooctyloxy)phenyl]pyrimidine was purified by column chromatography and thin layer chromatography on silica gel using benzene as an eluent. The yield was 0.30 g (0.64 mmol), 80%. $[\alpha]_D$ +2.7° (c0.98,CH_2Cl_2), ^{1}H-NMR($CDCl_3$) δ 0.90(m, 6H), 1.23(m, 30H), 2.53(t, 2H), 4.03(dd, 2H, J = 10Hz, J = 2.5Hz), 4.73(dm, 1H, J = 24Hz), 6.82(d, 2H, J = 4.5Hz), 8.28(d, 2H, 4.5Hz), 8.37(s, 2H), IR(KBr)2930, 2860, 1610, 1590, 1550, 1450, 1260, 1180, 1100, 880, 840, 800, 720, 620 cm^{-1}

Preparation of (+)-5-decyl-2-[*p*-(2-fluorooctanoyloxy)phenyl]pyrimidine (6, *n* = 6, *m* = 10)

A solution of 2-fluorooctanoic acid (0.24 g, 1.5 mmol) and thionyl chloride (2 ml) was stirred at 90°C. After two hours, the excess thionyl chloride was removed by evaporation. To this acid chloride was added a mixture of 5-decyl-2-(*p*-hydroxyphenyl)pyrimidine (0.47 g, 1.5 mmol) and triethylenediamine (0. 34 g, 3.0 mmol) in dry benzene. The mixture was stirred at 50°C for two hours and sodium hydride (0.06 g, 1.5 mmol, 60% dispersion in oil, washed several times in dry benzene) was added to the reaction mixture. After being stirred at 90°C for an additional two hours, the mixture was quenched with 2M hydrochloric acid. The benzene layer was dried over anhydrous sodium sulfate and the solvent was evaported in vacua. (+)-5-Decyl-2-[*p*-(2-fluorooctanoyloxy)phenyl]pyrimidine was purified by column chromatography on silica gel using benzene as an eluent and recrystallized from hexane. The yield was 0.44 g (0.96 mmol), 64%. $[\alpha]_D$ +3.1° (cl.01, CH_2Cl_2) ^{1}H-NMR($CDCl_3$) δ 0.92(m, 6H), 1.27(m, 26), 2.57(t, 2H), 4.98(dt, 1H, J = 4Hz), 7.13(d, 2H, J = 4Hz), 8.47(d, 2H, J = 4Hz), 8.48(s, 2H), IR(KBr)2930, 2860, 1780, 1590, 1550, 1470, 1430, 1200, 1170, 1140, 1090, 1010, 960, 860, 800, 720, 650 cm^{-1}

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