Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Novel Antiferroelectric Liquid Crystals Derived from Trifluoromethylated Pyranoses

Keizou Itoh [a], Tatsushi Ishizuka [a], Mitsunori Takeda [a], Masaaki Namekawa [a], Takashi Yamazaki [b] & Tomoya Kitazume [b]

[a] R&D Dept., Kashima Oil Co., Ltd., 4 Towada, Kamisu-machi, Kashima-gun, Ibaraki, 314-02, Japan

[b] Department of Bioengineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa, 226, Japan

Version of record first published: 04 Oct 2006

To cite this article: Keizou Itoh, Tatsushi Ishizuka, Mitsunori Takeda, Masaaki Namekawa, Takashi Yamazaki & Tomoya Kitazume (1997): Novel Antiferroelectric Liquid Crystals Derived from Trifluoromethylated Pyranoses, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 302:1, 277-288

To link to this article: http://dx.doi.org/10.1080/10587259708041838

Mol. Cryst. Liq. Cryst., 1997, Vol. 302, pp. 277–288
Reprints available directly from the publisher
Photocopying permitted by license only

NOVEL ANTIFERROELECTRIC LIQUID CRYSTALS DERIVED FROM TRIFLUOROMETHYLATED PYRANOSES

KEIZOU ITOH, TATSUSHI ISHIZUKA, MITSUNORI TAKEDA, and MASAAKI NAMEKAWA
R&D Dept., Kashima Oil Co., Ltd., 4 Towada, Kamisu-machi, Kashima-gun, Ibaraki 314-02, Japan
TAKASHI YAMAZAKI and TOMOYA KITAZUME
Department of Bioengineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226, Japan

Abstract A new series of liquid crystals possessing trifluoromethylated pyranoses was synthesized and their mesomorphic properties were investigated. Electro-optical studies showed that some of these compounds exhibited an antiferroelectric chiral smectic C (SmC_A^*) phase. Further, it was found that the appearance of the SmC_A^* phase was strongly dependent on the conformation of the chiral part; *cis* and *trans* configurations of the pyranose ring. Relationship between molecular structures and a propensity to the formation of the SmC_A^* phase was discussed.

INTRODUCTION

Since the discovery of an antiferroelectric chiral smectic C phase (SmC_A^*)[1-2], a lot of work has been done from the standpoint of application in display devices as well as synthesis of new materials. Up to now, several compounds with the SmC_A^* phase have been reported[3-5], however, most of them were synthesized from chiral 2-alkanols or the corresponding 1,1,1-trifluorinated counterparts. Recently, a few compounds showing the SmC_A^* phase derived from other chiral moieties have been reported and their mesomorphic properties were discussed.[6-10] However, the fact that variation of chiral moieties to prepare antiferroelectric liquid crystals (AFLCs) is still so restricted has imposed us the limitation to obtain better understanding on the relationship between molecular structures and the appearance of the SmC_A^* phase. Therefore, we have designed and prepared novel AFLCs derived from chiral trifluoromethylated pyranoses, which were already reported to be useful chiral moieties to prepare chiral dopants for ferroelectric liquid crystals.[11-13] In this paper, we would like to report on the synthesis and characterization of new AFLC materials. The molecular structures of the synthesized compounds are shown in Figure 1.

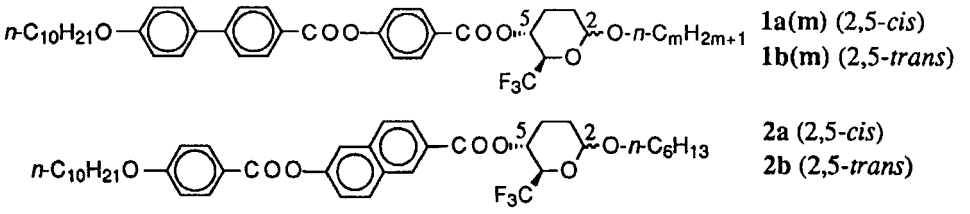


FIGURE 1 Molecular structures of the synthesized pyranose compounds.

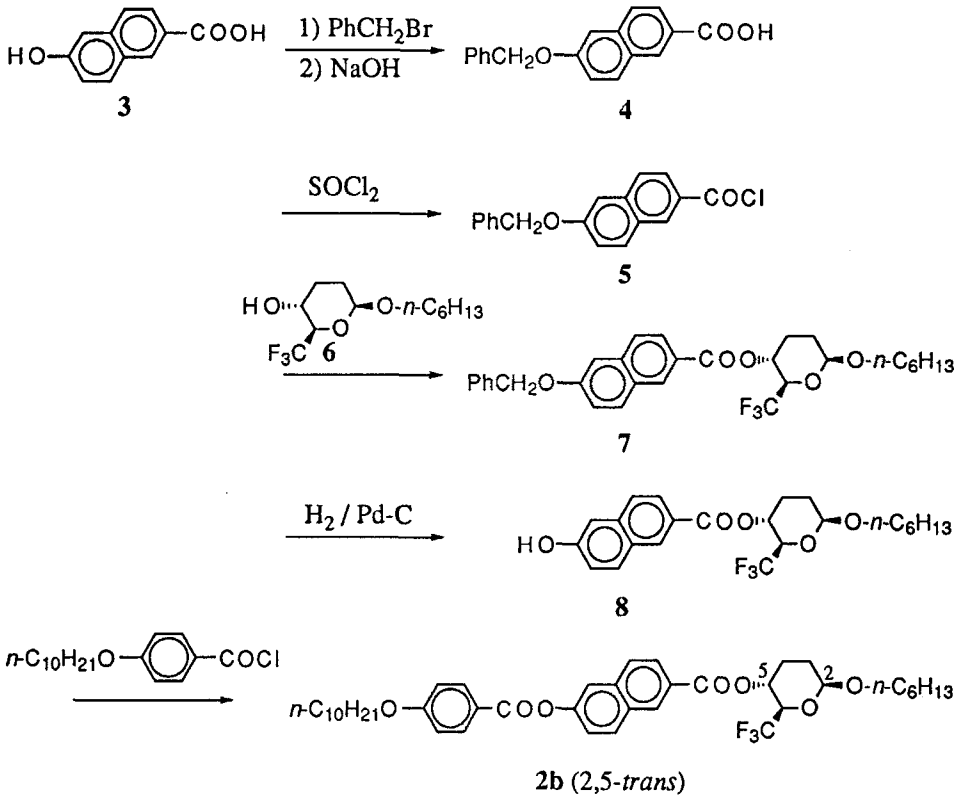
RESULTS AND DISCUSSION

Synthesis of Compounds

Compounds **1(m)** series were synthesized according to the method previously reported.[14] The synthesis of compound **2b** was carried out as outlined in Scheme 1. 6-Benzyloxy-2-naphthoic acid **4**, obtained through a reaction of 6-hydroxy-2-naphthoic acid **3** and benzyl bromide followed by hydrolysis, was converted into the corresponding acid chloride **5** by reacting with $SOCl_2$. Then chiral pyranose compound (*2S,5R,6R*)-tetrahydro-6-trifluoromethyl-2-hexyloxy-5-hydroxypyrane (*trans*-**6**)[11] was esterified with the acid chloride **5** in the presence of pyridine to yield (*2S,5R,6R*)-tetrahydro-5-(6-benzyloxy-2-naphthoyloxy)-6-trifluoromethyl-2-hexyloxypyrane **7**. Deprotection of compound **7** by hydrogenolysis reaction with Pd-C produced (*2S,5R,6R*)-tetrahydro-6-trifluoromethyl-2-hexyloxy-5-(6-hydroxy-2-naphthoyloxy)pyrane **8**, which was esterified with 4-decyloxybenzoyl chloride to give the target compound (*2S,5R,6R*)-tetrahydro-5-[6-(4-decyloxybenzoyloxy)-2-naphthoyloxy]-6-trifluoromethyl-2-hexyloxypyrane **2b**. Compound **2a** was synthesized in a similar manner using *cis* -**6** as a chiral moiety.

Mesomorphic Properties

The transition temperatures of the mesophases were determined by DSC. The mesophases were identified principally by optical microscopy, and further characterized by other electro-optical method. The phase transition temperatures measured for all materials on the cooling stage at a rate of 5 °C·min^{-1} are summarized in Table 1. In the previous communication, we reported that the compounds **1a(6)** and **1b(6)** had an SmC* phase.[14] However, more detailed study revealed that these compounds had an SmC_A* phase. Compounds **1b** (for m = 4, 5, 6, 7) with the *trans* configuration at the pyranose ring exhibited Iso-SmA-SmC*-SmC_A* phase sequence. These compounds showed rather high transition temperature compared with the corresponding *cis* isomers probably due to their



SCHEME 1 Synthetic route to (*2S,5R,6R*)-tetrahydro-5-[6-(4-decyloxybenzoyl-oxy)-2-naphthoyloxy]-6-trifluorometyl-2-hexyloxypyrane.

linear molecular structures. Further, it is noteworthy that the thermal stability of the SmC_A* phase became larger, when the length of peripheral alkyl chain attached to the pyranose became shorter. On the other hand, all of the *cis* compounds **1a** (for m = 4, 5, 6) showed direct phase transition from Iso to the SmC_A* phase, followed by another phase transition to an unidentified smectic phase (SmX_1) around room temperature, resulting in a wide temperature range of the SmC_A* phase. In addition, they exhibited extremely low crystallization points below -20 °C, probably due to their bent molecular structures. These results strongly suggest that *cis* compound **1a** has much higher propensity to form the SmC_A* phase compared with *trans* compound **1b**. Compound **2b** possessing a naphthalene unit in the core part exhibited Iso-SmA-SmC_A* phase sequence and the more stable SmC_A* phase compared with compound **1b** having a biphenyl unit in the core part. Meanwhile, *cis* compound **2a** showed extremely low thermal stability of the mesomorphic phase.

TABLE 1 Phase transition temperatures of the compounds **1(m)** and **2** series.

Compounds	2,5-configuration	m.p.[b]	Phase Transition Temperature[a] / °C						
			Cry	SmX_2	SmX_1	SmC_A*	SmC*	SmA	Iso
1a(4)	*cis*	73	• <-20		• (27)	•		118	•
1b(4)	*trans*	112	• 91			• 127	• 141	• 169	•
1a(5)	*cis*	53	• <-20		• (21)	•		104	•
1b(5)	*trans*	96	• 82			• 122	• 152	• 174	•
1a(6)	*cis*	60	• <-20		• (15)	•		99	•
1b(6)	*trans*	91	• 75			• 96	• 154	• 173	•
1b(7)	*trans*	92	• 68			• (83)	• 150	• 163	•
2a	*cis*	-18	• -18	•				14	•
2b	*trans*	66	• 47			•	80	• 103	•

[a]Taken from DSC thermograms recorded at cooling rates of 5 °C·min^{-1}; Iso: isotropic phase; SmA: smectic A phase; SmC*: chiral smectic C phase; SmC_A*: antiferroelectric chiral smectic C phase; SmX_1, SmX_2: unidentified smectic phase; Cry: crystal phase.
[b]Taken from DSC thermograms recorded at heating rates of 5 °C·min^{-1}.
Parentheses denote a monotropic transition.

The spontaneous polarization (Ps) of the compounds **1a(5)**, **1b(5)**, and **2b** was measured as a function of temperature and illustrated in Figure 2. As has already been reported on compounds **1a(6)** and **1b(6)**,[14] these compounds exhibited a quite large Ps of 600~800 nC·cm^{-2}. Compound **1a(5)** showed fairly large Ps just below the transition temperature(Tc), which increased gradually as the temperature decreased, while compounds **1b(5)** and **2b** showed relatively small Ps just below the Tc, which increased much more than that of **1a(5)**. This phenomenon is attributed to the different phase transition order owing to their phase sequences. The large dipole moment from an ether oxygen and a trifluoromethyl group, both fixed on a pyranose ring and cooperatively

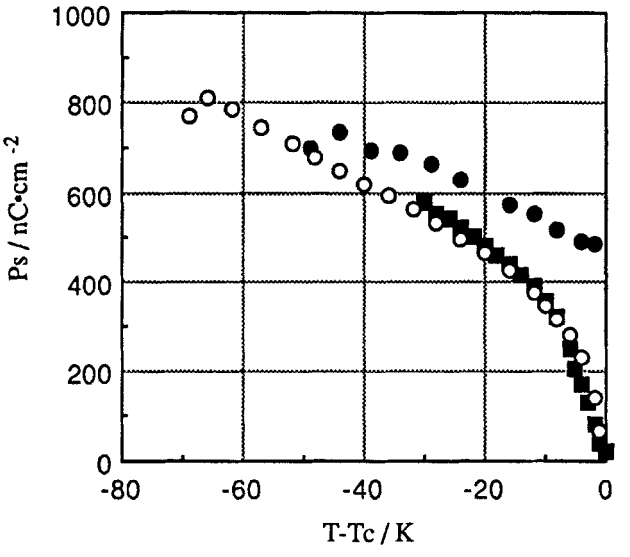


FIGURE 2 Temperature dependence of the spontaneous polarization for the compounds: **1a(5)**(●); **1b(5)**(○); **2b**(■).

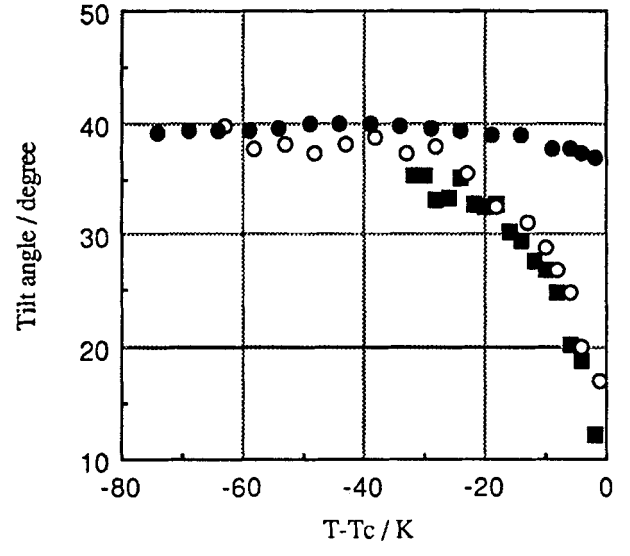


FIGURE 3 Temperature dependence of the optical tilt angle for the compounds: **1a(5)**(●); **1b(5)**(○); **2b**(■).

working, would be responsible for the large Ps of the pyranose derivatives.

The optical tilt angle of the compounds **1a(5)**, **1b(5)** and **2b** was also measured as a function of temperature and illustrated in Figure 3. These compounds exhibited a large tilt angle of 35 ~ 40 degrees. The similar tendency obtained in the Ps was also observed in the temperature dependence of the tilt angle for these compounds. Further, compounds **1b(5)** and **2b** possessing different core structures showed quite similar temperature dependence of the tilt angle as well as the Ps.

Characterization of the SmC_A^* Phase

The antiferroelectric smectic C* phase was identified by optical microscopy and electro-optical measurements. The transmittance (T) - electric field (E) profiles of *trans* compounds were investigated by applying a triangular wave voltage (30 Vpp, 0.1Hz) at several points below transition temperatures. Figure 4 shows a typical example of T - E profile obtained by a homogeneously aligned cell of **2b** at 20 °C below Tc. As clearly seen in Figure 4, a typical double-hysteresis loop which was characteristic of a stable antiferroelectric phase was observed.[15] In addition, a relatively large pretransitional effect was also observed. Further, the corresponding tristable switching between the antiferroelectric and ferroelectric states[1] was confirmed by a polarizing optical microscope.

Because of multi-domain alignment of homogeneously aligned cells of **1a**, we could not measure the optical response of these compounds. Therefore, we studied an electric response of these compounds under triangular wave voltage. There observed two switching- current peaks for all **1a** (for m = 4, 5, 6) at several temperatures below Tc. Figure 5 shows a typical example obtained by homogeneously aligned thin cell of **1a(5)** under 40 Vpp triangular waves of 2 Hz at 10 °C below Tc. This feature is also characteristic of a tristable switching in AFLC; the field-induced transition from antiferroelectric(AF) to ferroelectric(F) phase and from F to AF are associated with a switching current when applying a triangular wave of low frequency. Therefore, this phase of *cis* compounds must be an antiferroelectric phase.

Molecular Structures and Antiferroelectricity

On the appearance of the antiferroelectric phase, a dimerization model of the molecules belonging to the adjacent layers was proposed.[16] In this model, a pairing of transverse dipole moment of the molecules in adjacent layers plays an important role in the emergence of the antiferroelectric order. In our case, *cis* compound **1a** showed a broad temperature range of the SmC_A^* phase compared with *trans* isomers. Based on the results of ^1H NMR analysis, it is estimated that *cis* compounds in a solution have a bent molecular structure at the pyranose ring, whereas the corresponding *trans* isomers have more linear conformation

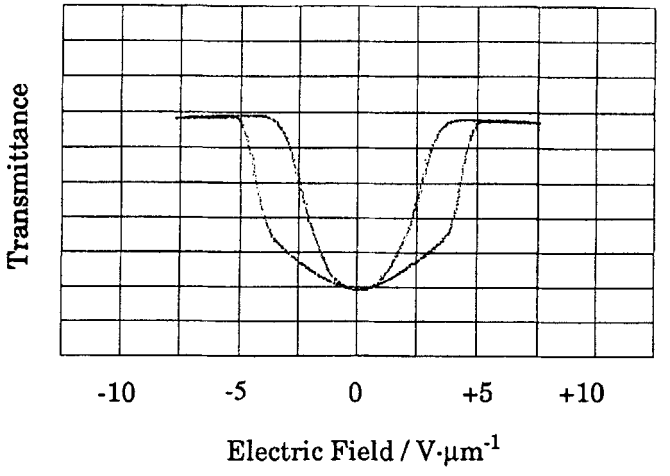


FIGURE 4 T - E profiles observed in a homogeneously aligned cell of compound **2b**.

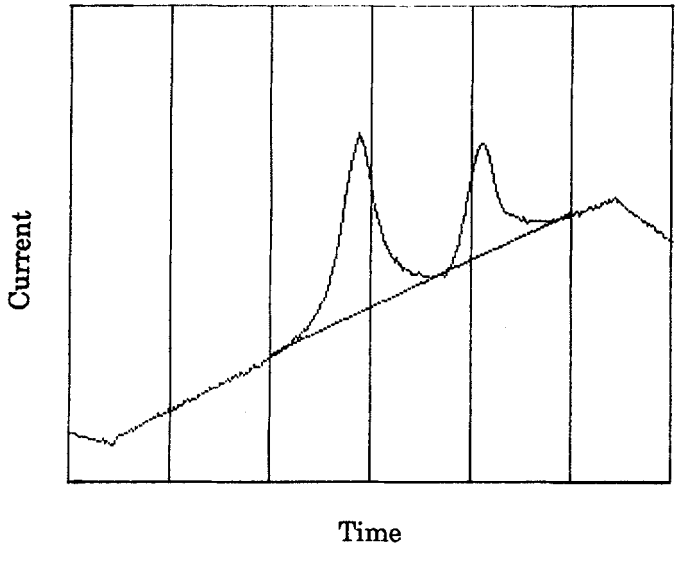


FIGURE 5 Switching current of the compound **1a(5)** under triangular wave voltage.

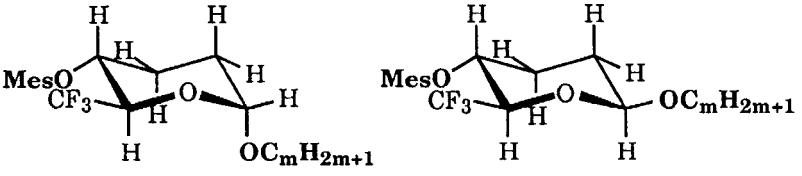


FIGURE 6 Conformational structures of the trifluoromethylated pyranose ring. Mes; 4-(4'-decyloxybiphenyl-4-carboxy)benzoyl or 6-(4-decyloxybenzoyloxy)-2-naphthoyl.

as shown in Figure 6. If it was the case in the liquid-crystalline phase, dipoles of *cis* molecules in adjacent layers would be more closer than those of *trans* molecules. As a result, *cis* molecules in adjacent layers are easy to make pairs of dipoles, resulting in a stable antiferroelectric smectic order.

On the other hand, *trans* compounds showed the following tendency: when the length of the alkyl chain at the chiral end became shorter, the SmC_A^* phase became more stable. This is explained by the same idea that the shorter alkyl chain causes strong dipole-dipole interaction of the molecules in adjacent layers. Therefore, a shorter alkyl chain attached to the pyranose of the *trans* compounds favours the formation of the antiferroelectric order.

For the origin of the occurrence of the SmC_A^* phase, another important factor, the steric factor, was pointed out. Thus the odd-even effect of the alkyl chain at the chiral part on the appearance of the SmC_A^* phase was reported on some compounds.[17] However, this was not the case for our compounds probably due to their large transvers dipole moment at the pyranose, which caused more stronger dipole interaction than the steric effect of the alkyl chain.

CONCLUSIONS

A new series of liquid crystals has been derived from chiral pyranoses with a trifluoromethyl group. All compounds except **2a** displayed an SmC_A^* phase. It was observed that the *cis* configuration of the pyranose was favorable for the formation of the antiferroelectric smectic order compared with the *trans* configuration. In addition, shorter alkyl chain at the chiral end of the *trans* compounds served for the stability of the SmC_A^* phase. These phenomena are explained by the pairing model of the dipoles in adjacent layers on the occurrence of the SmC_A^* phase. Thus it is suggested for the appearance of the SmC_A^* phase that the design of the chiral moiety to strengthen the dipole interaction of the molecules in adjacent layers is important.

EXPERIMENTAL

General Procedure

All final products were purified by column chromatography on silica gel and further purified by recrystallization from ethanol. The structures of the synthesized compounds were determined by spectroscopic data, ^{1}H-NMR and ^{19}F-NMR (BRUKER AC-250), IR (Shimadzu IR-440), mass (JEOL JMX-AX505H) spectrum. The specific optical rotation was measured by using a JASCO DIP-370 digital polarimeter. The phase transition temperatures were determined by DSC (SII DSC22C). Mesophases were identified by optical microscopy using a Nikon OPTIPHOTO-POL polarizing microscope in conjunction with a Mettler FP82 heating stage and a FP80 controller. Sample cells were fabricated by ITO glasses coated with unidirectionally buffed polyimide films, and their gaps were about 2 μm. The magnitude of the spontaneous polarization was measured by the triangular wave method.[18]

Preparation of Materials

(1) (*2S,5R,6R*)-Tetrahydro-5-[6-(4-decyloxybenzoyloxy)-2-naphthoyloxy]-6-trifluoromethyl-2-hexyloxypyrane (**2b**).

To a solution of 6-benzyloxy-2-naphthoyl chloride **5** (1.00 g, 3.5 mmol) in toluene (15 mL) were added triethylamine (0.48 mL, 3.5 mmol) and (*2S,5R,6R*)-tetrahydro-6-trifluoromethyl-2-hexyloxy-5-hydroxypyrane *trans*-**6** (0.78 g, 2.9 mmol) at 0 °C. The mixture was stirred for 15 h at room temperature. After adding 1N HCl, the reaction mixture was extracted with diethyl ether. Then the extract was washed with brine and dried over anhydrous $MgSO_4$. After removing diethyl ether, the residue was purified by column chromatography on silica gel to give the ester compound (*2S,5R,6R*)-tetrahydro-5-(6-benzyloxy-2-naphthoyloxy)-6-trifluoromethyl-2-hexyloxypyrane **7** (1.14 g, 2.2 mmol) in 76 % yield.

To a solution of above **7** in ethanol (15 mL) was added Pd-C (10 %, 0.22 g) under N_2 atmosphere. The mixture was stirred at room temperature for 50 h under H_2 atmosphere. Then the mixture was filtered and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to obtain (*2S,5R,6R*)-tetrahydro-6-trifluoromethyl-2-hexyloxy-5-(6-hydroxy-2-naphthoyloxy) pyrane **8** (0.42 g, 0.94 mmol) in 44 % yield.

To a mixture of compound **8** (0.42 g, 0.94 mmol), 4-decyloxybenzoyl chloride (0.33 g, 1.1 mmol) and toluene (7 mL) was added pyridine (0.1 mL) at 0 °C. After the reaction mixture was stirred at room temperature overnight, 1N HCl was added to quench the reaction. After usual workup, the product was isolated by column chromatography on

silica gel to afford the desired compound (*2S,5R,6R*)-tetrahydro-5-[6-(4-decyloxybenzoyloxy)-2-naphthoyloxy]-6-trifluoromethyl-2-hexyloxypyrane **2b** (0.22 g, 0.31 mmol) in 35 % yield: $[\alpha]^{25}_D$=+0.6 ° ($CHCl_3$, C=1.10); ^1H NMR ($CDCl_3$) δ(ppm) 0.78–1.00 (m, 6H), 1.16-2.12 (m, 27H), 2.40-2.53 (m, 1H), 3.51 (dt, J=9.5, 6.8 Hz, 1H), 3.93 (dt, J=9.5, 6.7 Hz, 1H), 4.05 (t, J=6.5 Hz, 2H), 4.13 (dq, J=8.7, 6.3 Hz, 1H), 4.67 (dd, J=2.1, 7.8 Hz, 1H), 5.23-5.38 (m, 1H), 6.99 (d, J=8.9 Hz, 2H), 7.43 (dd, J=2.2, 8.9 Hz, 1H), 7.73 (d, J=2.1 Hz, 1H), 7.86 (d, J=8.7 Hz, 1H), 8.00 (d, J=8.7 Hz, 1H), 8.03 (dd, J=1.6, 9.1 Hz, 1H), 8.18 (d, J=8.9 Hz, 2H), 8.59 (s, 1H); ^{19}F NMR ($CDCl_3$) δ(ppm) –75.75 (d, J=6.2 Hz); IR (cm^{-1}) 1720, 1610, 1515, 1260, 1170 ; high resolution mass calcd for $C_{40}H_{51}O_7F_3$ 700.3587, found 700.3613.

(2) (*2R,5R,6R*)-Tetrahydro-5-[6-(4-decyloxybenzoyloxy)-2-naphthoyloxy]-6-trifluoromethyl-2-hexyloxypyrane (**2a**).

By using (*2R,5R,6R*)-tetrahydro-6-trifluoromethyl-2-hexyloxy-5-hydroxypyrane (0.58 g, 2.2 mmol), the same procedures described above were carried out to obtain the desired compound **2a** (0.57 g, 0.8 mmol) in 36 % total yield: $[\alpha]^{25}_D$=-46.2 ° ($CHCl_3$, C=1.08); ^1H NMR ($CDCl_3$) δ(ppm) 0.79–1.03 (m, 6H), 1.15-2.30 (m, 28H), 3.49 (dt, J=9.7, 6.5 Hz, 1H), 3.77 (dt, J=9.7, 6.7 Hz, 1H), 4.05 (t, J=6.5 Hz, 2H), 4.29-4.44 (m, 1H), 4.91-4.99 (m, 1H), 5.26-5.37 (m, 1H), 6.99 (d, J=8.9 Hz, 2H), 7.43 (dd, J=2.2, 8.9 Hz, 1H), 7.73 (d, J=2.1 Hz, 1H), 7.86 (d, J=8.7 Hz, 1H), 8.01 (d, J=9.0 Hz, 1H), 8.06 (dd, J=1.6, 8.7 Hz, 1H), 8.18 (d, J=8.9 Hz, 2H), 8.60 (s, 1H); ^{19}F NMR ($CDCl_3$) δ(ppm) –75.95 (d, J=6.3 Hz); IR (cm^{-1}) 1725, 1605, 1510, 1250, 1165 ; high resolution mass calcd for $C_{40}H_{51}O_7F_3$ 700.3587, found 700.3558.

(3) (*2R,5R,6R*)-Tetrahydro-2-butoxy-5-[4-(4'-decyloxybiphenyl-4-carboxy)benzoyloxy]-6-(trifluoromethyl)pyrane (**1a(4)**).

To a mixture of (*2R,5R,6R*)-tetrahydro-2-buthoxy-6-trifluoromethyl-5-hydroxypyrane (0.48 g, 2.0 mmol), 4-benzyloxybenzoyl chloride (0.59 g, 2.4 mmol) and toluene (10 mL) was added pyridine (1 mL) at 0 °C. After the reaction mixture was stirred at room temperature for 24 h, 1N HCl was added to quench the reaction. The organic layer was separated and the water layer was extracted with diethyl ether. The combined organic solution was washed with distilled water and with brine, and then dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give (*2R,5R,6R*)-tetrahydro-2-butoxy-5-(4-benzyloxybenzoyloxy)-6-(trifluoromethyl)pyrane (0.34 g, 0.7 mmol) in 35% yield.

To a mixture of whole product obtained above, toluene (5 mL) and acetic acid (1 mL) was added Pd-C (10 %, 0.1 g) under N_2 atmosphere. The mixture was stirred at room temperature for 120 h under H_2 atmosphere. Then the mixture was filtered and worked up similarly. The product was isolated by column chromatography on silica gel to

afford (*2R,5R,6R*)-tetrahydro-2-butoxy-6-trifluoromethyl-5-(4-hydroxybenzoyloxy) pyrane (0.26 g, 0.7 mmol) in 99% yield.

To a mixture of whole product obtained above, 4'-decyloxybiphenyl-4-carboxylic acid chloride (0.33 g, 0.9 mmol) and toluene (5 mL) was added pyridine (0.5 mL) at 0 °C. After the reaction mixture was stirred at room temperature overnight, 1N HCl was added to quench the reaction. After usual workup, the product was purified by column chromatography on silica gel to give the target compound (*2R,5R,6R*)-tetrahydro-2-butoxy-5-[4-(4'-decyloxybiphenyl-4-carboxy)benzoyloxy]-6-(trifluoromethyl)pyrane **1a(4)** (0.34 g, 0.48 mmol) in 69 % yield: $[\alpha]^{26}_D$=-52.5 ° ($CHCl_3$, C=1.09); ^1H NMR ($CDCl_3$) δ(ppm) 0.89 (t, J=6.5 Hz, 3H), 0.97 (t, J=7.3 Hz, 3H), 1.19-2.26 (m, 24H), 3.49 (dt, J=9.7, 6.4 Hz, 1H), 3.76 (dt, J=9.7, 6.7 Hz, 1H), 4.02 (t, J=6.5 Hz, 2H), 4.29 (dq, J=9.7, 6.3 Hz, 1H), 4.95 (m, 1H), 5.26 (ddd, J=5.4, 9.7, 9.8 Hz, 1H), 7.01 (d, J=8.8 Hz, 2H), 7.33 (d, J=8.7 Hz, 2H), 7.60 (d, J=8.7 Hz, 2H), 7.70 (d, J=8.4 Hz, 2H), 8.12 (d, J=8.7 Hz, 2H), 8.23 (d, J=8.4 Hz, 2H); ^{19}F NMR ($CDCl_3$) δ(ppm) −76.01 (d, J=6.3 Hz); IR (cm^{-1}) 1730, 1720, 1605, 1500, 1270, 1180.

(4) (*2S,5R,6R*)-Tetrahydro-2-butoxy-5-[4-(4'-decyloxybiphenyl-4-carboxy)benzoyloxy]-6-(trifluoromethyl)pyrane (**1b(4)**).

To a mixture of (*2S,5R,6R*)-tetrahydro-2-butoxy-6-trifluoromethyl-5-hydroxy-pyrane (0.48 g, 2.0 mmol), 4-benzyloxybenzoyl chloride (0.59 g, 2.4 mmol) and toluene (10 mL) was added pyridine (1 mL) at 0 °C. After the reaction mixture was stirred at room temperature for 24 h, 1N HCl was added to quench the reaction. After usual workup, the residue was purified by column chromatography on silica gel to give (*2S,5R,6R*)-tetrahydro-2-butoxy-5-(4-benzyloxybenzoyloxy)-6-(trifluoromethyl)pyrane (0.41 g, 0.9 mmol) in 45 % yield.

To a mixture of whole product obtained above, ethanol (5 mL) and acetic acid (1 mL) was added Pd-C (10 %, 0.1 g) under N_2 atmosphere. The mixture was stirred at room temperature for 115 h under H_2 atmosphere. Then the mixture was filtered and worked up similarly. The product was isolated by column chromatography on silica gel to afford (*2S,5R,6R*)-tetrahydro-2-butoxy-6-trifluoromethyl-5-(4-hydroxybenzoyloxy) pyrane (0.30 g, 0.8 mmol) in 89 % yield.

To a mixture of whole product obtained above, 4'-decyloxybiphenyl-4-carboxylic acid chloride (0.37 g, 1.0 mmol) and toluene (5 mL) was added pyridine (0.5 mL) at 0 °C. After the reaction mixture was stirred at room temperature overnight, 1N HCl was added to quench the reaction. After usual workup, the product was purified by column chromatography on silica gel to yield the target compound (*2S,5R,6R*)-tetrahydro-2-butoxy-5-[4-(4'-decyloxybiphenyl-4-carboxy)benzoyloxy]-6-(trifluoromethyl)pyrane **1b(4)** (0.50 g, 0.72 mmol) in 90 % yield: $[\alpha]^{26}_D$=+6.8 ° ($CHCl_3$, C=0.90); ^1H NMR

($CDCl_3$) δ(ppm) 0.85–1.02 (m, 6H), 1.22-2.09 (m, 23H), 2.40-2.52 (m, 1H) 3.51 (dt, J=9.4, 6.8 Hz, 1H), 3.93 (dt, J=9.4, 6.7 Hz, 1H), 4.02 (t, J=6.5 Hz, 2H), 4.00-4.12 (m, 1H), 4.65 (dd, J=2.0, 8.5 Hz, 1H) 5.18-5.30 (m, 1H), 7.01 (d, J=8.6 Hz, 2H), 7.33 (d, J=8.7 Hz, 2H), 7.60 (d, J=8.6 Hz, 2H), 7.70 (d, J=8.3 Hz, 2H), 8.10 (d, J=8.6 Hz, 2H), 8.23 (d, J=8.4 Hz, 2H); ^{19}F NMR ($CDCl_3$) δ(ppm) −75.79 (d, J=6.2 Hz); IR(cm^{-1}) 1735, 1720, 1605, 1505, 1260, 1165, 1075; high resolution mass calcd for $C_{40}H_{49}O_7F_3$ 698.3431, found 698.3442.

REFERENCES

1. A. D. L. Chandani, T. Hagiwara, Y. Suzuki, Y. Ouchi, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys., 27, L729 (1988).
2. A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda, Jpn. J. Appl.Phys., 28, L1265 (1989).
3. Y. Suzuki, T. Hagiwara, I. Kawamura, N. Okamura, T. Kitazume, M. Kakimoto, Y. Imai, Y. Ouchi, H. Takezoe, and A. Fukuda, Liq. Cryst., 6, 167 (1989).
4. S. Inui, T. Suzuki, N. Iimura, H. Iwane, and H. Nohira, Mol. Cryst. Liq. Cryst., 239, 1 (1994).
5. V. Faye, J.C. Rouillon, C. Destrade, and H.T. Nguyen, Liq. Crystals, 19, 47 (1995).
6. I. Nishiyama, A. Yoshizawa, M. Fukumasa, and T. Hirai, Jpn. J. Appl. Phys, 28, L2248 (1989).
7. H. Moritake, N. Sigeno, M. Ozaki, and K. Yoshino, Liq. Crystals, 14, 1283 (1993).
8. S. L. Wu, F. K. Huang, B. J. Uang, W. J. Tsai, and J. J. Liang, Liq. Crystals, 18, 715 (1995).
9. S. L. Wu, D. G. Chen, S. J. Chen, C. Y. Wang, and J. T. Shy, Mol. Cryst. Liq. Cryst., 264, 39 (1995).
10. Y. Aoki and H. Nohira, Liq. Crystals, 19, 15 (1995).
11. K. Itoh, M. Takeda, M. Namekawa, S. Nayuki, Y. Murayama, T. Yamazaki, and T. Kitazume, Ferroelectrics, 148, 85 (1993).
12. K. Itoh, M. Takeda, M. Namekawa, S. Nayuki, Y. Murayama, T. Yamazaki, and T. Kitazume, Chem. Lett., 1994, 839.
13. K. Itoh, M. Takeda, M. Namekawa, Y. Murayama, and S. Watanabe, J. Mater. Sci. Lett., 14, 1002 (1995).
14. K. Itoh, M. Takeda, M. Namekawa, S. Nayuki, Y. Murayama, T. Yamazaki, and T. Kitazume, Chem. Lett., 1995, 641.
15. J. Lee, A. D. L. Chandani, K. Itoh, Y. Ouchi, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys., 29, 1122 (1990).
16. Y. Takanishi, K. Hiraoka, V. K. Agrawal, H. Takezoe, A. Fukuda, and M. Matsushita, Jpn. J. Appl. Phys., 30, 2023 (1991).
17. H. Takezoe, A. Fukuda, A. Ikeda, Y. Takanishi, T. Umemoto, J. Watanabe, H. Iwane, M. Hara, K. Itoh, Ferroelectrics, 122, 167 (1991).
18. K. Miyasato, S. Abe, H. Takezoe, A. Fukuda, and E. Kuze, Jpn. J. Appl. Phys., 22, L661 (1983).