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Synthesis and Properties of Pyranose Derivatives with Trifluoromethyl Group Used as Chiral Dopants for Ferroelectric Liquid Crystals

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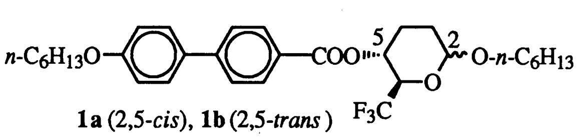
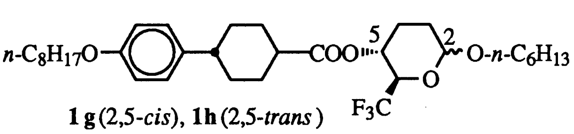
A variety of pyranose derivatives with a trifluoromethyl group were synthesized and found to be excellent chiral dopants for ferroelectric liquid crystals. Relationships between molecular structures and induced ferroelectric properties were discussed.

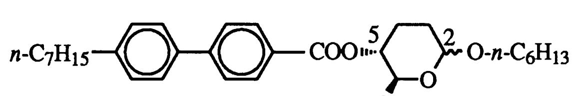
Since the proposal of quick response electro-optical device using ferroelectric liquid crystals (FLCs) in 1980,1) many new FLCs have been synthesized to realize a large size display. In order to obtain quick response FLCs, it is the common way to dope chiral compounds inducing large spontaneous polarization (Ps) to the achiral host liquid crystals which have a smectic C phase (SmC) and low viscosity.

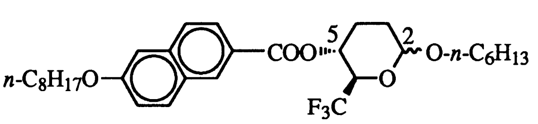
Recently many compounds which have a cyclic chiral part have been reported to show large spontaneous polarization when they were doped to the host SmC mixtures.2-10) Five-membered γ-lactones2-5) and Six-memberd δ-valerolactones6-9) are typical examples for this. It is considered that fixing the lateral dipole moment in the ring structure and inhibiting the free rotation of the chiral part around the long axis by the steric hindrance might be the reason for large Ps. Based on this concept, we have developed novel pyranose derivatives which have a trifluoromethyl group possessing large electronegativity. In this study we would like to report the synthesis of chiral pyranose compounds **1** and their induced ferroelectric properties.

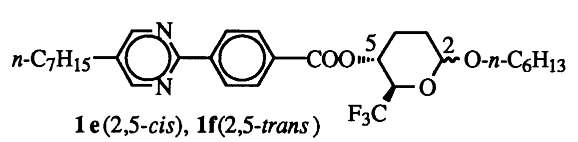
As shown in scheme 1, chiral pyranoses **3** were prepared from a chiral butenolide **2** in several steps according to the method previously reported.11-13) Usual glycosilation of **3** with 1-hexanol followed by the

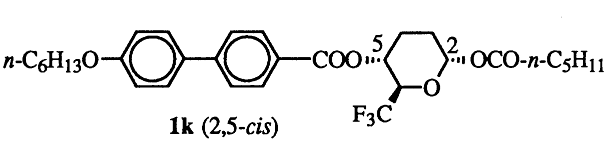

1a (2,5-*cis*), **1b** (2,5-*trans*)

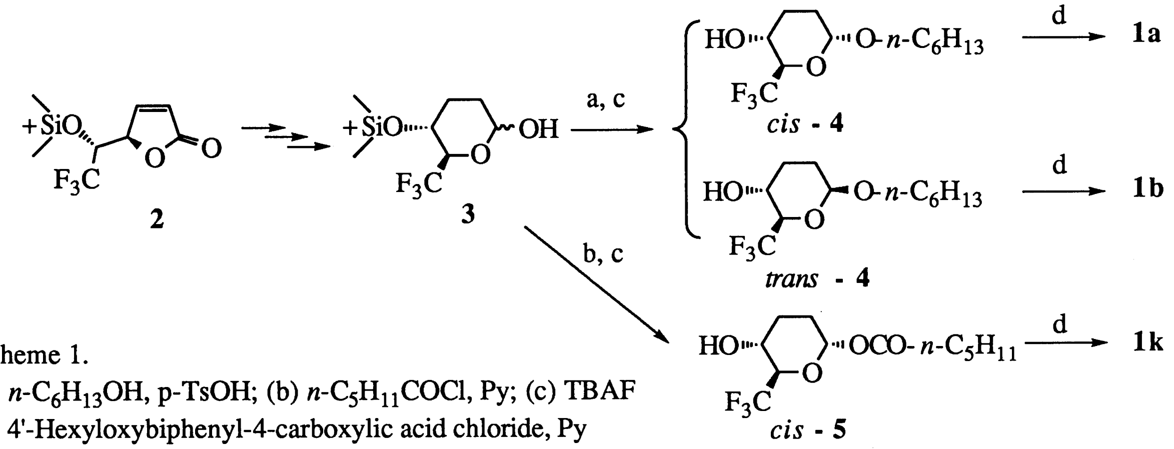

1g (2,5-*cis*), **1h** (2,5-*trans*)


1c (2,5-*cis*), **1d** (2,5-*trans*)


1i (2,5-*cis*), **1j** (2,5-*trans*)


1e (2,5-*cis*), **1f** (2,5-*trans*)


1k (2,5-*cis*)



Scheme 1.
(a) n-$C_6H_{13}OH$, p-TsOH; (b) n-$C_5H_{11}COCl$, Py; (c) TBAF
(d) 4'-Hexyloxybiphenyl-4-carboxylic acid chloride, Py

treatment with TBAF (tetrabutylammonium fluoride) afforded alcohols **4** as a mixture of diastereomers (*cis* : *trans* = 3 : 7). Then, *cis*- and *trans*-alcohols **4** were separated by silica gel column chromatography and esterified with 4'-hexyloxybiphenyl-4-carboxylic acid chloride to give the desired compounds **1a** and **1b**, respectively.[14] Compounds **1c** to **1j** were synthesized from *cis*- and *trans*-alcohols **4** by esterifing with corresponding acid chloride in the same manner.[15] Reaction of lactol **3** with hexanoyl chloride followed by the deprotection with TBAF afforded alcohol **5**, whose stereochemistry at the anomeric position was found to exclusively contain 2,5-*cis* relationship. Then, *cis*-**5** was esterified with 4'-hexyloxybiphenyl-4-carboxylic acid chloride to give the target compound **1k**.

The synthesized pyranose compounds from **1a** to **1k** did not exhibit any mesophase. So the ferroelectric liquid crystals were prepared by doping 2 wt% of chiral pyranose compound to the achiral host mixture.[16] Evaluation was done using 2 μm thickness cell at 30 °C. Induced ferroelectric properties and measured electro-optical properties are shown in Table 1. The phase transition temperature from smectic A (SmA) to smectic C phase (SmC) of the host liquid crystal was lowered a few degrees when *cis* compounds (**1a**, **1c**, **1e**, **1j**, **1k**) were added, while it was hardly reduced when *trans* compounds (**1b**, **1d**, **1f**, **1h**, **1j**) were employed. This may be due to the shape of the molecules: thus the *cis* isomer possessed a bent structure at their chiral part, while the *trans* ones had better linearity. Also the compounds **1g** and **1h** had little tendency for lowering the transition temperature from SmA to SmC* compared with other compounds. These compounds showed very fast response time shorter than 100 μs, and *cis* compounds generally exhibited quicker response time than the corresponding *trans* ones even though they had smaller Ps value. This may be attributed to the smaller tilt angles of the mixtures containing *cis* compounds.

The induced spontaneous polarization was quite large (2.1-4.6 nC/cm^2) considering the small quantity of additives. The reason for the large Ps induced by the pyranoses is supposed that the dipole moments of an ether oxygen and a trifluoromethyl group, both fixed in a ring structure, cooperated effectively. On the contrary to the previous report on δ-valerolactone,[8] however, *cis* compounds generally showed smaller Ps than the corresponding *trans* ones. The reason for this is not yet clear from molecular mechanics but it was partially due to the smaller tilt angles of the mixtures containing *cis* compounds. It was also found that *cis* compounds had opposite helical sense in the chiral nematic phase (N*) and exhibited rather long helical pitch compared with corresponding *trans* ones. Especially, compounds **1e** and **1i** exhibited very long helical pitch (over 80 μm). So the combination of *cis* and *trans* conformers enable us to compensate the helical pitch of the N* of the mixture, resulting in a good alignment quality. Also, it is noted that the helical sense of N* is opposite between **1a** and **1k**, which are different by an alkyl chain at the chiral part, even though they had the same *cis* configuration.

There were not so large differences in induced ferroelectric properties by changing the core structures. However, it can be seen that changing the core structure from biphenyl (**1a, 1b, 1c, 1d**) to phenylpyrimidine (**1e, 1f**), phenylcyclohexane (**1g, 1h**) and naphthalene (**1i, 1j**) caused relatively small Ps and longer response time. Among all, biphenyl type core structure gave the best results.

This study demonstrates that newly synthesized pyranose compounds are excellent chiral dopants for FLCs. They induced large spontaneous polarization and the mixtures doped with them by a small quantity showed quick response. The reason for this is attributed to the unique structure of the pyranose compounds which have a trifluoromethyl group possessing very large electronegativity. Further modification of the pyranose compounds are now in progress.

Table 1. Physical properties of FLC mixtures containing 2 wt% of compound **1**

Compound	Phase transition temp a)/℃							Response time b)	Ps c)	Tilt angle	N* pitch	helical sense d)
	SmC*		SmA		N*		Iso	μs	nC cm^{-2}	deg	μm	
1a	•	45	•	62	•	67	•	74	-3.7	17	14	RH
1b	•	49	•	63	•	69	•	86	-4.3	20	8	LH
1c	•	46	•	62	•	68	•	72	-3.3	18	20	RH
1d	•	49	•	62	•	68	•	75	-4.6	20	7	LH
1e	•	43	•	63	•	68	•	84	-2.2	16	80	RH
1f	•	47	•	62	•	68	•	103	-2.2	18	8	LH
1g	•	48	•	61	•	67	•	92	-3.3	19	24	RH
1h	•	51	•	62	•	67	•	97	-2.3	21	34	LH
1i	•	44	•	61	•	67	•	95	-2.1	17	>90	RH
1j	•	48	•	61	•	67	•	102	-3.2	20	7	LH
1k	•	44	•	62	•	67	•	94	-3.7	17	10	LH

a) SmC*: chiral smectic C phase, SmA: smectic A phase, N*: chiral nematic phase, Iso: Isotropic liquid phase. b) Response time was defined as the change of light-transmission from 0 to 50 % under the voltage of 10 Vpp/μm at 30 ℃. c) Ps was measured by the triangular wave method17) d) Helical sense of N* was defined as that right handed (RH) helix induced l(-) optical rotation.

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15) Spectroscopic data for **1c** and **1d** were given as follows: **1c**; $[\alpha]^{27}{}_{D}$ = +68.7° ($CHCl_3$, C=1.08); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.82–0.89 (m, 6H), 1.20-1.47 (m, 14H), 1.53-1.71 (m, 4H), 1.87-2.25 (m, 4H), 2.65 (t, 2H, J=7.7 Hz), 3.48 (dt, 1H, J=9.6, 6.7 Hz), 3.75 (dt, 1H, J=9.7, 6.8 Hz), 4.30 (dq, 1H, J=9.8, 6.3 Hz), 4.95 (m, 1H), 5.26 (ddd, 1H, J=5.3, 9.7, 9.8 Hz), 7.28 (d, 2H, J=8.2 Hz), 7.54 (d, 2H, J=8.2 Hz), 7.65 (d, 2H, J=8.4 Hz), 8.08 (d, 2H, J=8.4 Hz); ^{19}F-NMR (235 MHz, $CDCl_3$) δ -75.98 (d, J=6.3 Hz); IR (cm^{-1}, KBr) 1730, 1610, 1500, 1260, 1175; MS m/e (M+) calcd 548.3114, found 548.3126: **1d**; $[\alpha]^{27}{}_{D}$ = -14.5° ($CHCl_3$, C=1.02); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.83–0.98 (m, 6H), 1.22-2.08 (m, 21H), 2.39-2.50 (m, 1H), 2.66 (t, 2H, J=7.7 Hz), 3.50 (dt, 1H, J=9.4, 6.9 Hz), 3.92 (dt, 1H, J=9.4, 6.7 Hz), 4.08 (dq, 1H, J=8.8, 6.3 Hz), 4.65 (dd, 1H, J=2.0, 8.1Hz), 5.23 (ddd, 1H, J=5.0, 9.0, 9.3 Hz), 7.28 (d, 2H, J=8.1 Hz), 7.54 (d, 2H, J=8.1 Hz), 7.65 (d, 2H, J=8.4 Hz), 8.06 (d, 2H, J=8.4 Hz); ^{19}F-NMR (235 MHz, $CDCl_3$) δ -75.76 (d, J=6.3 Hz); IR (cm^{-1}, KBr) 1710, 1610, 1495, 1260, 1180, 1050; MS m/e (M+) calcd 548.3114, found 548.3126.

16) The host SmC mixture is composed of 2-(4-nonyloxyphenyl)-5-heptylpyrimidine (25 wt%), 2-(4-octyloxyphenyl)-5-octylpyrimidine (25 wt%), 2-(4-decyloxyphenyl)-5-octylpyrimidine (25 wt%), and 2-(4-hexyloxyphenyl)-5-nonylpyrimidine (25 wt%). Cry 8 SmC 51 SmA 64 N 70 Iso (°C).

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