

Synthesis and Electro-optical Properties of Novel Liquid Crystals Having a Cyclohexyl Trifluoromethyl Ether Moiety

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A convenient synthetic method is described for new type liquid crystals (LCs) containing a cyclohexyl trifluoromethyl ether moiety. The novel LCs are shown to exhibit mesophases and decrease birefringence and threshold voltage of host LCs upon mixing by 20 wt%.

High chemical and thermal stability and low viscosity of organofluorine compounds have attracted much attention in material science.¹ For example, replacing a methoxyl group of organic materials by a trifluoromethoxyl group decreases the viscosity of the parent materials.² Although aryl trifluoromethyl ethers³ are used as materials for TFT-display due to their low viscosity and small birefringence, we considered that the corresponding cyclohexyl trifluoromethyl ethers would further improve these properties.⁴ Thus, we undertook the synthesis of liquid crystals (LCs) containing the novel polar functionality through the oxidative desulfurization-fluorination reaction,⁵ which allows us to convert the xanthates derived from not only phenols but also primary and secondary alcohols into the corresponding trifluoromethyl ethers under mild conditions.^{6,7} Especially, LCs of secondary alkyl trifluoromethyl ethers are unprecedented,⁸ though these are expected to be better materials than LCs of aryl trifluoromethyl ethers.

Herein we report the synthesis, phase transition behaviors and electro-optical properties of LCs containing a cyclohexyl

trifluoromethyl ether moiety. We also compare these properties of LCs with the corresponding methyl ether moiety and a phenyl trifluoromethyl ether functionality.

Synthesis of cyclohexyl trifluoromethyl ether **4** was carried out through the route shown in Scheme 1. Reduction of cyclohexanone **1** with LiAlH₄ followed by separation by silica gel column chromatography and/or recrystallization gave *trans*-cyclohexanol **2**, which was transformed to xanthate **3** in high yields by treatment with NaH (or *n*-BuLi), CS₂, and MeI. Treatment of **3** with 50% hydrogen fluoride-pyridine (HF-py, 40 mol; prepared by neutralization of 70% HF-py with pyridine) and *N*-bromosuccinimide (NBS, 5.0 mol) in CH₂Cl₂ at 0 °C gave trifluoromethyl ether **4** in moderate yields.⁹ The yields are summarized in Table 1.

Phase transition temperatures of **4** as well as methyl ether **5**¹⁰ were measured by differential scanning calorimetry (DSC) and the textures of liquid crystalline phase were observed with an optical polarizing microscope equipped with a hot stage (Table 2). Although **4a** was an oil and **4d** showed a melting point only, trifluoromethyl ethers **4b** and **4c** exhibited nematic phase and smectic A phase, respectively, in a wide range of temperatures. DSC of **4b** showed four endothermic peaks at 44, 112, 147, and 189 °C with enthalpy of 7.3, 2.7, 5.8, and 0.8 kJ/mol, respectively, on heating. These peaks correspond to the phase transitions of C-to-S_X, S_X-to-S_B, S_B-to-N, and N-to-I, respectively. In general, trifluoromethyl ether **4** seems to exhibit better liquid-crystallinity than methyl ether **5**.

Scheme 1. Synthesis of cyclohexyl trifluoromethyl ethers **4**

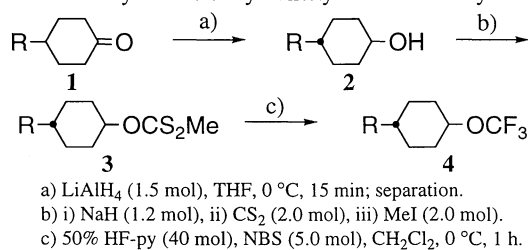


Table 1. Yields of **2**, **3**, and **4** according to Scheme 1

R	yields/%		
	2	3	4
Pr-	63 (2a)	79 (3a)	40 (4a)
Pr-	36 (2b)	73 (3b) ^a	34 (4b)
Pr-	65 (2c)	95 (3c)	25 (4c)
F-	86 (2d)	86 (3d)	42 (4d)

^aPrepared using *n*-BuLi in lieu of NaH.

Table 2. Phase transition temperatures of **4** and **5**

	phase transition temp./°C ^a
Pr--X (4a)	oil
Pr--X (5a)	oil
Pr--X (4b)	C 44 S _X 112 S _B 147 N 189 I
Pr--X (5b)	C 207 S _B 211 I
Pr--X (4c)	C 90 S _X 104 S _A 129 I
Pr--X (5c)	C 45 S _X 88 N 128 I
F--X (4d)	C 43 I ^b
F--X (5d)	C 68 I ^b

C: crystal, S_X: higher order smectic, S_B: smectic B,

S_A: smectic A, N: nematic, I: isotropic liquid.

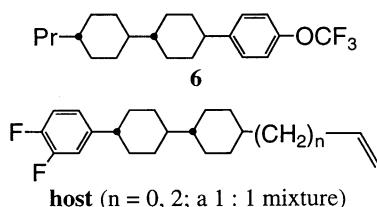
^aMeasured by DSC on heating.

^bObserved with an optical polarizing microscope.

We next studied physical and electro-optical properties of cyclohexyl trifluoromethyl ether **4** as an additive of nematic LCs and compared the properties with those of methyl ether **5** and aryl trifluoromethyl ether **6**. These compounds were added by 20

Table 3. Physical and electro-optical properties^a of **4**, **5** and **6** as added by 20 wt% to **host**

Compound	host	4a	5a	4b	5b	6 ^f
$T_{NI}/^{\circ}\text{C}$	116.7	90.1	93.5	130.2	137.3	122.4
$\Delta\epsilon$	4.8	5.2	3.6	4.7	3.4	5.1
$\Delta\epsilon^b$	----	6.7	-1.2	4.3	-2.2	6.5
V_{th}/V	2.14	1.86	2.20	2.10	2.43	2.19
Δn	0.090	0.078	0.077	0.084	0.084	0.089
Δn^c	----	0.030	0.025	0.060	0.060	0.087
$\tau^d(\tau_r=\tau_d)/\text{ms}^e$	25.3	34.3	36.3	37.0	44.1	----
applied voltage/V	5.1	4.3	4.9	4.6	5.1	----

^aMeasured at 20 °C. ^bExtrapolated from $\Delta\epsilon$. ^cExtrapolated from Δn .^dResponse time. ^eCorrected for 6.0 μm cell. ^fInterpolated from 30 wt%.

wt% to **host**, and the properties of the resulting mixtures are summarized in Table 3.

Extrapolation of dielectric anisotropy ($\Delta\epsilon$) to 100% allowed us to estimate $\Delta\epsilon'$, which showed that trifluoromethyl ether **4** would be p-type LCs ($\Delta\epsilon' > 0$), whereas methyl ether **5** would form n-type LCs ($\Delta\epsilon' < 0$). In accord with the sign of $\Delta\epsilon'$, trifluoromethyl ether **4** lowers threshold voltage (V_{th}) of **host**, whereas **5** raises V_{th} of **host**. Thus, a trifluoromethoxy group on a cyclohexane mesogen improves these properties of **host** compared with methyl ether **5**. Because both **4** and **5** had equally low $\Delta n'$ as estimated by extrapolation of birefringence (Δn), the effect may be ascribed to the mesogen structure rather than the polar functional groups. It is evident that cyclohexyl trifluoromethyl ether **4b** raises transition point from nematic to isotropic phase (T_{NI}) of **host** compared with phenyl trifluoromethyl ether **6**.¹¹ It is worth noting that **4** induced small Δn in comparison with relatively large $\Delta\epsilon'$ value. Since T_{NI} of the mixture of **4a** and **host** did not change at all after heating at 80 °C for 10 h, cyclohexyl trifluoromethyl ethers **4** are demonstrated to be thermally stable LC materials.

In conclusion, unprecedented LCs with a cyclohexyl trifluoromethyl ether moiety were prepared for the first time using a reagent system consisting of 50% HF/py and NBS.¹² These compounds exhibited nematic and/or smectic phase in a wide range temperatures and were shown to be p-type LCs, which, upon mixing in **host**, decrease V_{th} and Δn of **host**. These properties should be favorable for the materials of displays currently spread in the market.

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- 9 Following procedure is representative. Pyridine (0.46 mL) and then 70% HF-py (1.0 mL, 4.4 mmol, 40 mmol of F) were added dropwise to a dichloromethane (2.5 mL) suspension of NBS (5.0 mmol) at -42 °C. The resulting mixture was stirred at room temperature for 5 min and cooled to 0 °C. A dichloromethane (1.5 mL) solution of xanthate **3d** (1.0 mmol) was added dropwise at 0 °C. The whole was stirred at 0 °C for 1 h and poured into a buffer solution (pH = 10; NaHCO_3 , NaHSO_3 and NaOH). The aqueous layer was extracted with diethyl ether. The ethereal layer was dried over MgSO_4 , filtered and concentrated under reduced pressure. Flash column chromatography (cyclohexane) afforded *trans*-4-[*trans*-4-(3,4-difluorophenyl)cyclohexyl]cyclohexyl-trifluoromethyl ether (**4d**) in 42% yield. ¹H-NMR (200 MHz, CDCl_3): δ 0.96-1.26 (m, 6H), 1.30-1.62 (m, 4H), 1.72-1.96 (m, 6H), 2.06-2.20 (m, 2H), 2.41 (tt, $J = 3, 12$ Hz, 1H), 4.09 (tt, $J = 5, 11$ Hz, 1H), 6.82-7.18 (m, 3H); ¹⁹F-NMR (188 MHz, CDCl_3): δ -58.1 (s, 3F), 139.1 (dddd, $J = 1, 8, 12, 21$ Hz, 1F), -142.9 (dddd, $J = 3, 7, 12, 21$ Hz, 1F).
- 10 Prepared by treatment of **2** with a base (NaH or *n*-BuLi) and MeI. Products (% yield) are **5a** (99), **5b** (42), **5c** (90), and **5d** (100).
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