Synthesis and Properties of New Liquid Crystals Containing Trifluoromethylamino Group

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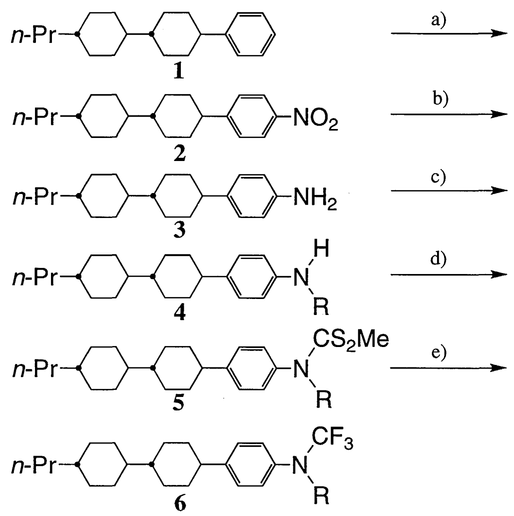
Liquid crystalline compounds containing trifluoromethylamino group were conveniently prepared and shown to exhibit mainly smectic phase in a wide range of temperatures. Their properties as a component of nematic liquid crystals are discussed.

Liquid crystals containing fluorine, trifluoromethyl or trifluoromethoxy group have attracted much attention because of their high polarity, chemical stability and low viscosity.[1,2] We have recently shown that oxidative desulfurization-fluorination of organosulfur compounds is a convenient entry to compounds having such fluorine-containing functionality. According to this method, trifluoromethyl ethers and trifluoromethylamines are readily prepared from the corresponding xanthates and dithiocarbamates, respectively.[3]

Thanks to strongly electron-withdrawing nature of trifluoromethyl group, trifluoromethylamines are expected to show low viscosity, low basicity, high thermal and chemical stability, as compared with ordinary methylamines which can not be used as a component of liquid crystalline materials due to their highly basicity. Thus, we expected that trifluoromethylamines might be used as liquid crystalline materials[4] and/or as inert additives for nematic liquid crystals. Herein we report the synthesis and electro-optical properties of unprecedented liquid crystals containing trifluoromethylamino group.[5]

Scheme 1.



R = Me: **4a**, 28%; **5a**, 71%; **6a**, quant.
R = Et: **4b**, 79%; **5b**, 94%; **6b**, quant.
R = *n*-Pr: **4c**, 80%; **5c**, 81%; **6c**, 94%.

a) H_2SO_4/HNO_3, CH_2Cl_2, 0 °C to r.t., 2 h, 81% yield.
b) Pd/C, H_2, EtOH, r.t., 3.5 h, 90% yield.
c) i) *n*-BuLi (1.0 mol), -78 to 0 °C, ii) RI (1.0 mol).
d) *n*-BuLi (1.0 mol), CS_2 (2.0 mol), MeI (2.0 mol).
e) $TBAH_2F_3$ (5.0 mol), DBH (4.0 mol), CH_2Cl_2, 0 °C, 1 h.

Synthesis of *N*-alkyl-*N*-trifluoromethylaniline derivative **6** was carried out through the route shown in Scheme 1. Commercially available compound **1** was nitrated under the standard conditions to give **2** regioselectively. The nitro group was reduced to give aniline derivative **3**. *N*-Alkylation of **3** was easily achieved with *n*-BuLi and an alkyl iodide. Treatment of **4** with *n*-BuLi, CS_2, and MeI gave dithiocarbamate **5** in high yield. Trifluoromethylation of **5** was effected by use of tetrabutylammonium dihydrogentrifluoride ($TBAH_2F_3$, 5 mol) and 1,3-dibromo-5,5-dimethylhydantoin (DBH, 4 mol) in CH_2Cl_2 at 0 °C, and the desired product **6** was isolated in nearly quantitative yield.[6]

All of **6a-c** showed smectic B (SB) phase[7] in a wide range of temperatures as measured with an optical polarizing microscope equipped with a hot stage and a differential scanning calorimeter system (Table 1).

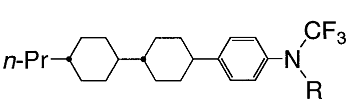
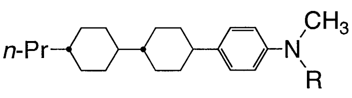
When the carbon number of R was changed from 1 to 3, the temperature range of SB became narrower, and the SB-Iso phase transition temperature was found to be lowered. Long alkyl side-chain appears to destabilize the mesophase, probably because the steric repulsion is induced between trifluoromethyl and alkyl groups to expand the intermolecular space within a layer of SB phase.

In contrast, the corresponding methylamine derivatives **7b** and **7c**[8] did not show any liquid crystalline phase; these exhibited high melting points only.

We next studied the electro-optical properties of trifluoromethylamines **6** as an additive of nematic liquid crystals. Each trifluoromethylamine was added to a mixture of host nematic liquid crystals,[9] and various properties of the resulting mixtures were measured as shown in Table 2.

When **6a** and **6b** was compared, the substitutent effect was obvious. For example, nematic-isotropic phase transition

Table 1. Phase Transition Temperatures of **6** and **7**

		R	Phase Transition Temperatures[a]/°C
	**6a**	Me	< 20 S_B 173 Iso
	6b	Et	Cr 35 S_B 141 Iso
	6c[b]	*n*-Pr	Cr 57 S_B 109 Iso
	**7a**	Me	Cr 59 S_B 189 Iso
	7b	Et	Cr 181 Iso
	7c	*n*-Pr	Cr 168 Iso

[a]Cr: crystalline phase, S_B: smectic B phase, Iso: isotropic phase.
[b]ΔH (Cr to S_B) = 21 KJ/mol, ΔH (S_B to Iso) = 6.9 KJ/mol.

temperature (T_{NI}) of **6a**-containing mixture was higher than that of the host, whereas T_{NI} of **6b**-containing mixture was lower. Thus, **6a** apparently stabilizes nematic phase of the host.

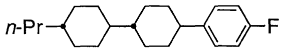
We calculated extrapolation constant ($\Delta\varepsilon_0$) of the dielectric anisotropy ($\Delta\varepsilon$) and found $\Delta\varepsilon_0$ of **6b**-containing mixture was estimated to be 0.10, much smaller than that of **6a**- or **7b**-containing mixture. Thus, the trifluoromethyl substitutent of **6b** appears to be directed perpendicular to the molecular long axis. As a consequence, $\Delta\varepsilon_0$ became very small. When we compare $\Delta\varepsilon_0$ of **6a**-containing mixture with that of **8**-containing mixture, -N(CF_3)Me group appears to influence $\Delta\varepsilon$ equally to or slightly less than F.

When **6a** was added to the host liquid crystals mixture,[9] T_{NI} became slightly higher without change of threshold voltage (V_{th}) (compare **host** and **6a**). Since the phase transition temperatures did not change at all after heating at 100 °C for 50 h, trifluoromethylamines **6** can be used as thermally stable components. In particular, the **6a**-containing mixture, being kept at -20 °C for 7 days, did not cause precipitation or phase separation. Thus, trifluoromethylamines **6a**-**c** have excellent solubility in nematic liquid crystals.

Table 2. Physical and Electro-optical Properties of Nematic Liquid Crystal Mixtures [a]

	host	6a	6b	7b	8
T_{NI}/°C	55	59	49	68	73
V_{th}/V[b]	1.60	1.62	1.46	1.84	1.91
$\Delta\varepsilon$	6.7	5.92	5.38	6.59	6.31
$\Delta\varepsilon_0$[c]	----	2.8	0.10	6.1	4.75
Δn[d]	0.092	0.091	0.104	0.100	0.096
$\eta_{20°C}$/cP[e]	21.0	----	28.6	----	----
$\eta_{0°C}$/cP[e]	62.0	----	90.2	----	----
τ/ms[b,f]	39.2	46.4	65.3	53.9	----
Applied Voltage/V	3.2	3.6	3.2	4.0	----

[a]The mixtures consist of 80% the host mixture and 20% of **6a**, **6b**, **7b** or **8**.
[b]A 6 μm thick cell was used. [c]Extrapolated from $\Delta\varepsilon$.
[d]Δn: anisotropy of refractive index.
[e]$\eta_{20°C}$, $\eta_{0°C}$: viscosity at 20 °C and 0 °C respectively. [f]τ: response time.



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In conclusion, we have reported that trifluoromethylamines show SB phase in a wide range of temperatures and can be used as stable components of nematic liquid crystals mixture. We are further exploring the possibility of novel liquid crystals having trifluoromethylamino group.

References and Notes

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4 M. Kuroboshi, K. Mizuno, K. Kanie, and T. Hiyama, *Tetrahedron Lett.*, **36**, 563 (1995).

5 Smectic liquid crystals containing *N*,*N*-bis(trifluoromethyl)amino group were reported by E. Hayashi, Y. Hayakawa, H. Fukaya, T. Abe, K. Ohomori, and K. Murai, at the 20th Symposium on Liquid Crystals, 2G407, Nagoya, 1994.

6 Compound **6a**: ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3 H), 0.78-1.55 (m, 15 H), 1.68-2.00 (m, 8 H), 2.43 (tt, *J* = 3.3, 12.0 Hz, 1 H), 3.00 (q, *J* = 1.2 Hz, 3 H), 7.17 (s, 4 H). ^{19}F-NMR ($CDCl_3$) δ -61.23 (m). Compound **6b**: ^{1}H-NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.1 Hz, 3 H), 1.07 (t, *J* = 7.2 Hz, 3 H), 0.80-1.56 (m, 15 H), 1.68-2.01 (m, 8 H), 2.44 (tt, *J* = 3.4, 11.4 Hz, 1 H), 3.37 (q, *J* = 7.2 Hz, 2 H), 7.17 (s, 4 H). ^{19}F-NMR ($CDCl_3$) δ -58.22 (m). Compound **6c**: ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.3 Hz, 6 H), 0.77-1.55 (m, 17 H), 1.64-2.00 (m, 8 H), 2.42 (tt, *J* = 3.3, 11.9 Hz, 1 H), 3.25 (dt, *J* = 0.9, 7.3 Hz, 2 H), 7.16 (s, 4 H). ^{19}F-NMR ($CDCl_3$) δ -58.39 (m).

7 Miscibility test revealed that the texture was smectic B (hexatic) phase.

8 Compounds **7a-c** were synthesized by methylation of **4**.

9 The host nematic liquid crystals mixture was composed of 3 types of 4'-alkyl-4-cyanobiphenyls and 6 types of 4'-alkoxyphenyl *trans*-4-alkyl-cyclohexane-1-carboxylates.