A Facile Synthesis and Electro-optical Properties of New Liquid Crystals Having a *vic*-Difluoro Olefinic Moiety

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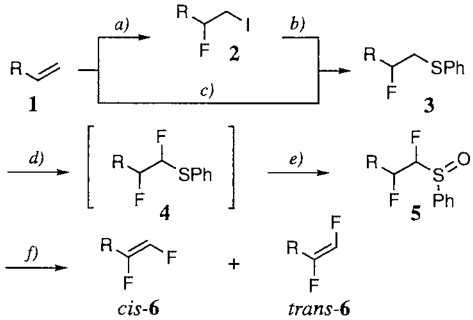
A facile method for the difluorination of olefins was exploited and applied to the synthesis of novel liquid crystals (LCs) having a *vic*-difluoro olefinic moiety. The physical and electro-optical properties of these LCs were compared with those of the corresponding parent olefinic LCs.

Much attention has been directed to synthetic methods of organofluorine compounds[1,2] because of the high thermal and chemical stability and low viscosity of fluorine-containing materials. To assist such exploitation, a novel method has been needed for the efficient, mild and selective fluorination of prevailing materials. This sort of methodology allows us to compare the properties of the fluorinated ones with the parent ones and thus to evaluate the fluorine effect.

Because liquid crystals (LCs) containing an ω-alkenyl side chain induce lower viscosity and threshold voltage than those with an alkyl side chain,[3] the olefinic LCs are utilized as the materials for LC displays. On the other hand, LCs containing a *vic*-difluoro olefinic moiety as a group connecting two mesogens exhibit high polarity and low viscosity.[4] With these precedents, we considered that LCs having an ω-*vic*-difluoroalkenyl group would exhibit unique properties and thus studied a novel fluorination strategy of olefins.[5]

Herein we report a facile method for the synthesis of *vic*-difluoro olefins from the corresponding parent olefins. We also disclose the phase transition behaviors and electro-optical properties of these difluoro olefinic LCs.

Scheme 1. Synthesis of *vic*-difluoro olefins **6**.



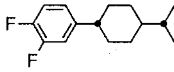
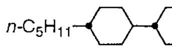
a) TBAH$_2$F$_3$ (3 mol), NIS (1 mol), CH$_2$Cl$_2$, rt
b) PhSH (1.2 mol), NaH (1.1 mol), THF, 0 °C to rt
c) 70% HF/py (10 mol), *N*-PhS-phthalimide (1 mol), CH$_2$Cl$_2$, rt
d) TBAH$_2$F$_3$ (3 mol), DBH (1 mol), CH$_2$Cl$_2$, rt, 30 min
e) *m*CPBA (1.1 mol), CH$_2$Cl$_2$, -30 °C, 3 h
f) *o*-xylene, 170 °C

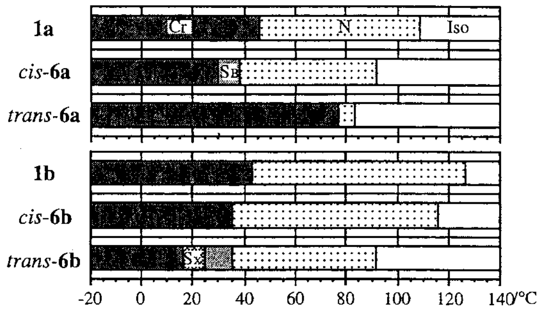
Synthesis of *vic*-difluoro olefins was carried out through a route shown in Scheme 1. Olefins **1** were converted into β-fluoroalkyl phenyl sulfides **3** by an iodo-fluorination using tetrabutylammonium dihydrogentrifluoride (TBAH$_2$F$_3$) and *N*-iodosuccinimide (NIS)[6] followed by a substitution of resulting iodo-fluorination products **2** with a phenythio nucleophile or alternatively by a direct thio-fluorination.[7] Although the thio-fluorination is straightforward, this reaction was not applicable to vinylcyclohexanes **1a** and **1c**. The fluoro-Pummerer rearrangement of **3** using TBAH$_2$F$_3$ and 1,3-dibromo-5,5-dimethylhydantoin (DBH)[8] gave α,β-difluoroalkyl phenyl sulfides **4** in high yields as 1 : 1 diastereomeric mixtures,[9] which without isolation[10] were oxidized to phenyl sulfoxides **5** by treatment with *m*-chloroperbenzoic acid (*m*CPBA). Thermolysis[11] of **5** at 170 °C in xylene (sealed tube) afforded a mixture of *cis*- and *trans*-difluoro olefins **6**.[12] Each isomer was readily isolated by flash column chromatography on silica-gel. The yields of the intermediates and final products are summarized in Table 1.

Phase transition temperatures[13] of *cis*-**6**, *trans*-**6** and **1** as well as the textures[14] of LC phases are summarized in Figure 1 and Figure 2. Although *trans*-**6a** and *trans*-**6b** showed a nematic phase in a temperature range narrower than those of parent compounds **1a** and **1b**, *cis*-**6a** and *cis*-**6b** exhibited a nematic phase in a similar range but at lower temperatures (Figure 1). The LCs having a *trans*-4-pentylcyclohexylcyclohexane mesogen are summarized in Figure 2. Compound *cis*-**6c** exhibited a nematic temperature range much wider than **1c** or *trans*-**6c**, whereas those with a longer side chain diminished or lost the nematic phase. Among *trans*-difluoro olefins, *trans*-**6c** showed little liquid crystallinity; *trans*-**6d** and *trans*-**6e** exhibited an S$_B$ phase on a parallel with **1d** and **1e**. Thus, the fluorine effect was most striking in **6c**.

We mixed each of *cis*- and *trans*-isomers of **6c**-**6e** and parent olefinic LCs **1c**-**1e** by 20 wt% with **host**, a 1 : 1 mixture

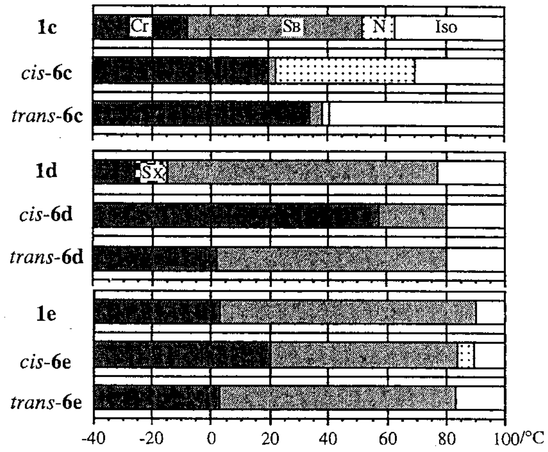
Table 1. Yields of **2**, **3**, **5**, and **6** prepared according to Scheme 1

compound	n	isolated yield/%				
		2	**3**	**5**	*cis*-**6**	*trans*-**6**
	0 (**1a**)	82 (**2a**)	91 (**3a**)	95 (**5a**)	46 (*cis*-**6a**)	16 (*trans*-**6a**)
	2 (**1b**)		77 (**3b**)	94 (**5b**)	33 (*cis*-**6b**)	22 (*trans*-**6b**)
	0 (**1c**)	68 (**2c**)	95 (**3c**)	88 (**5c**)	55 (*cis*-**6c**)	18 (*trans*-**6c**)
	1 (**1d**)		81 (**3d**)	93 (**5d**)	45 (*cis*-**6d**)	29 (*trans*-**6d**)
	2 (**1e**)		78 (**3e**)	87 (**5e**)	39 (*cis*-**6e**)	25 (*trans*-**6e**)



Cr: crystal, Sx: higher order smectic, SB: smectic B, N: nematic, Iso:isotropic liquid.

Figure 1. Phase transition behaviors of **6a** and **6b**.



Cr: crystal, Sx: higher order smectic, SB: smectic B, N: nematic, Iso:isotropic liquid.

Figure 2. Phase transition behaviors of **6c**, **6d**, and **6e**.

Table 2. Physical and electro-optical properties[a] of **1c**-**1e**, *cis*- and *trans*-**6c**-**6e** as mixed by 20 wt% in **host**

compounds	T_{NI}/°C	$\Delta\varepsilon$	$\Delta\varepsilon'$[b]	V_{th}/V[c]	Δn	$\Delta n'$[d]	τ/ms[c, e] (V)[f]
host	116.7	4.8	---	2.14	0.090	---	25.3 (5.1)
1c	102.8	3.6	-1.2	2.29	0.081	0.045	22.4 (5.3)
cis-**6c**	105.1	4.2	1.8	1.99	0.081	0.045	33.3 (4.3)
trans-**6c**	97.7	3.3	-2.7	2.16	0.081	0.045	31.2 (4.7)
1d	94.4	3.1	-3.7	2.08	0.077	0.025	32.6 (4.4)
cis-**6d**	87.4	3.0	-4.2	2.00	0.076	0.020	44.1 (4.2)
trans-**6d**	86.8	3.1	-3.7	2.04	0.075	0.025	43.1 (4.2)
1e	108.3	3.3	-2.7	2.29	0.082	0.050	26.9 (5.0)
cis-**6e**	108.6	4.0	0.8	2.15	0.083	0.055	29.4 (4.7)
trans-**6e**	101.6	3.2	-3.2	2.22	0.081	0.045	34.3 (4.7)

[a]Measured at 20 °C. [b]Extrapolated from $\Delta\varepsilon$. [c]Corrected for 7.0 μm cell. [d]Extrapolated from Δn. [e]Responce time ($\tau_r = \tau_d$). [f]Applied voltage/V.

of **1a** and **1b**, and measured dielectric anisotropy ($\Delta\varepsilon$), threshold voltage (*Vth*), birefringence (Δn), and response time (τ) of the resulting mixtures. The data are summarized in Table 2.

All *trans*-**6** indicated $\Delta\varepsilon$s similar to those of **1**, probably because the dipole moments of the two C-F bonds compensate each other. On the other hand, $\Delta\varepsilon$s of *cis*-**6** varied depending on the kind of a side chain; $\Delta\varepsilon$s of *cis*-**6c** and *cis*-**6e** were much larger than **1c** and **1e**, respectively; $\Delta\varepsilon$ of *cis*-**6d** turned out to be smaller than **1d**. Extrapolation of $\Delta\varepsilon$ to 100% allowed us to estimate $\Delta\varepsilon'$. Since $\Delta\varepsilon'$ of *cis*-**6d** was negative, this compound was proved to be an n-type LC, whereas both *cis*-**6c** and *cis*-**6e** should be p-type LCs ($\Delta\varepsilon' > 0$). All the *vic*-difluoro olefins lowered *Vth* of host LCs upon mixing by 20 wt% as compared with the parent olefins. In particular, the effect of *cis*-**6** was remarkable in comparison with *trans*-**6**. All the difluoro olefins had equally low Δn's as estimated by extrapolation; mixing them with **host** lowered Δn of **host.** Thus, the difluoro olefins should be useful additives for lowering Δn of LC materials. Both *cis*- and *trans*-difluoro olefins are thermally stable, because no decomposition could be observed by heating their xylene solutions at 170 °C for 24 h.[15]

We have reported the synthesis of new type LCs having a *vic*-difluoro olefinic moiety from the corresponding parent optical properties of these compounds led to a conclusion that the properties of LCs having a $(CH_2)_nCF=CHF$ group change strikingly depending on the configuration and the number of n. The difluoro olefinic LCs lower *Vth* and Δn of host LCs upon mixing by 20 wt% more effectively than the corresponding parent olefins.

References and Notes

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5 A prevailing method for the synthesis of *vic*-difluoro olefins involves the reaction of an organometallic reagent with 1,1,2-trifluoro-1-alkenes. See ref. 4.

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9 Determined by integration ratio of ^{19}F NMR spectroscopy.

10 Since compound **4** was not stable in neat liquid, it was necessary to immediately oxidize **4** to **5**.

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12 Following procedure for the preparation of *cis*- and *trans*-**6b** is representative. Compound **5b** (prepared according to ref. 5-7, 2.81 mmol) and *o*-xylene (15 mL) in a thick-walled Pyrex pressure tube was heated at 170 °C for 16 h before concentration in vacuo. To quench a co-produced sulfur compound, the residue was dissolved in CH_2Cl_2 (10 mL) and treated with *m*CPBA (3.08 mmol) in one portion at -30 °C and stirred for 6 h. The excess *m*CPBA was reduced with $NaHSO_3$, and the whole was treated with water. Work-up followed by flash column chromatography (hexane) gave *cis*-**6b** (0.915 mmol, 33% yield; ^{19}F NMR ($CDCl_3$) δ ($CFCl_3$) -135.80 (tdd, J = 19, 18, 11 Hz) and -167.70 (ddt, *J* = 74, 11, 5 Hz)) and *trans*-**6b** (0.627 mmol, 22% yield; ^{19}F NMR ($CDCl_3$) δ ($CFCl_3$) -160.63 (ddt, *J* = 127, 3, 23 Hz) and -184.20 (ddt, J = 127, 77, 5 Hz)).

13 Measured by differential scanning calorimetry (DSC).

14 Observed with an optical polarizing microscope equipped with a hot stage.

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