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Synthesis and Electro-Optical Properties of 3-Fluoroalkyl-Substituted Phenylpyrimidines as Chiral Dopants for Ferroelectric Liquid Crystals

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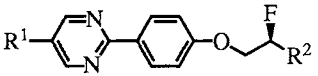
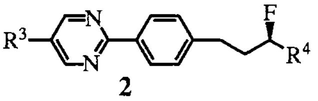
Starting with (*R*)-1,2-epoxyalkanes, (*S*)-5-alkyl(or -alkyloxy)-2-[4-(3-fluoroalkyl)-phenyl]pyrimidines and (*S*)-5-(3-fluoroalkyl)-2-(4-alkyloxyphenyl)pyrimidines were synthesized and shown to be good chiral dopants for achieving fast response of ferroelectric liquid crystals mixtures.

Ferroelectric liquid crystals (FLCs) are materials expected to be applicable to high speed display device.1) The most important requirement for FLC materials is fast switching over a wide range of temperatures including room temperatures. The response time appears to be roughly proportional to the viscosity of the material and inversely proportional both to the spontaneous polarization (Ps) and the intensity of electric field. Recently, a number of chiral compounds have been designed and synthesized for realizing large Ps.2,3) In contrast, Nohira *et al.* have been studying fluorine substituted compounds as less viscous materials and reported that 5-alkyl-2-[4-(2-fluoroalkyloxy)phenyl]pyrimidines (*cf.* **1**) exhibit chiral smectic C (SmC*) phase and achieve short response time.4,5) In order to study in details the effect of fluorine and ethereal oxygen, we designed **2**, a carbon analog of **1**, and **3**,6) a regioisomer of **2**, both containing a chiral 3-fluoroalkyl substituent.7,8) Herein we report their synthesis and electro-optical properties.



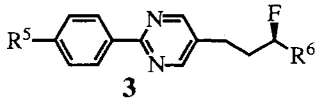
1

a: R^1 = n-$C_{10}H_{21}$ R^2 = n-C_6H_{13} Cr 60 (SmX 49 SmC* 58) SmA 68 Iso9)



2

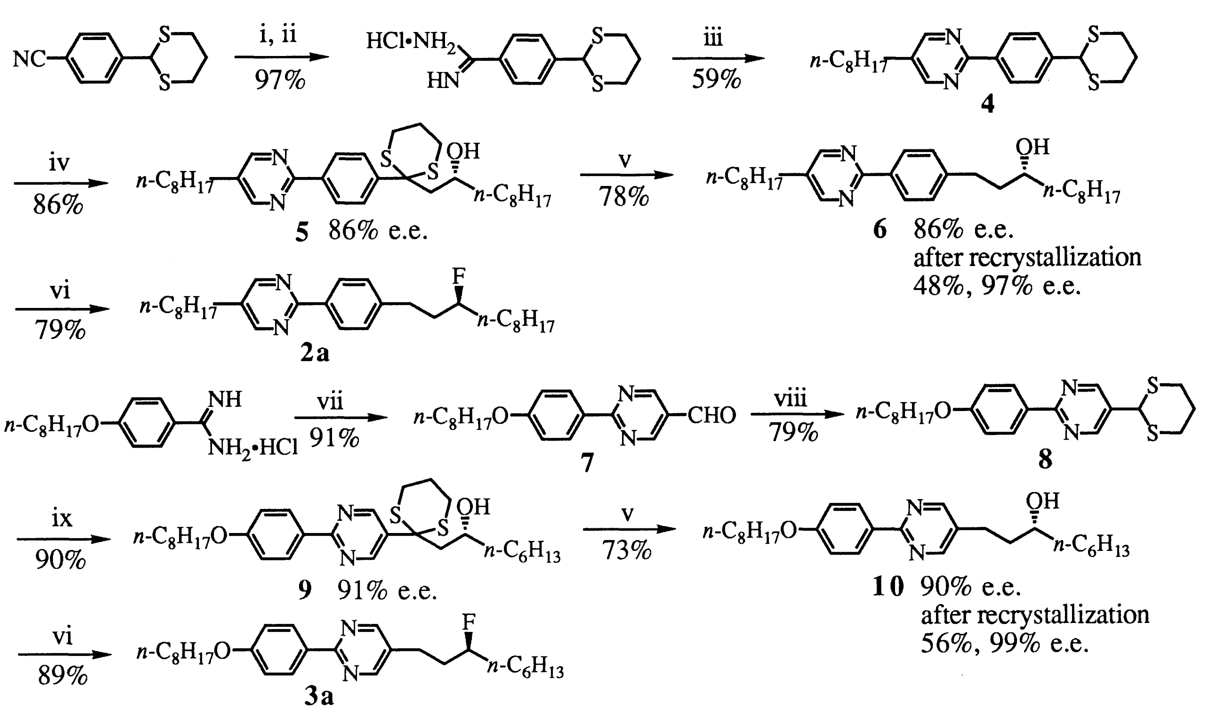
a: R^3 = n-C_8H_{17} R^4 = n-C_8H_{17} Cr 37 SmA 47 Iso
b: n-$C_8H_{17}O$ n-C_6H_{13} Cr 35 SmA 82 Iso



3

a: R^5 = n-$C_8H_{17}O$ R^6 = n-C_6H_{13} Cr 74 SmA 82 Iso
b: n-$C_{10}H_{21}O$ n-C_8H_{17} Cr 85 (SmC* 84) SmA 86 Iso
c: n-$C_{12}H_{25}O$ n-C_6H_{13} Cr 74 SmA 82 Iso

Chiral 2-[4-(3-fluoroundecyl)phenyl]pyrimidine **2a** was prepared according to the route shown in Scheme 1. The dithiane **4**10) was prepared by the reaction of 2-(*N,N*-dimethylaminomethylidene)decanal with 4-(1,3-dithian-2-yl)benzamidine obtained through the reaction of 2-(4-cyanophenyl)-1,3-dithiane with HCl and ethanol



i: HCl, EtOH; ii: NH_3; iii: $n\text{-}C_8H_{17}C(CHO){=}CHNMe_2$, MeONa, MeOH; iv: LDA, (*R*)-1,2-epoxydecane; v: Raney Ni (W-4); vi: DAST; vii: $Me_2NCH{=}C(CHO)_2$, MeONa, MeOH; viii: $HSCH_2CH_2CH_2SH$, trimethylsilyl polyphosphate; ix: LDA, (*R*)-1,2-epoxyoctane.

Scheme 1.

followed by reaction with NH_3. Alkylation of **4** with (*R*)-1,2-epoxydecane[11] and lithium diisopropylamide (LDA) as a base followed by desulfurization of the resulting hydroxy dithiane **5**[12] with Raney Ni afforded **6**.[12] Fluorination of the hydroxyl group of **6** using Et_2NSF_3 (DAST) gave **2a**. Use of 3-(*N*,*N*-dimethylamino)-2-octyloxypropenal and (*R*)-1,2-epoxyoctane[11] at step iii and step iv respectively gave **2b**. 5-(3-Fluorononyl)-pyrimidine **3a** was synthesized from formylpyrimidine **7** obtained through the reaction of 4-octyloxybenzamidine with $Me_2NCH{=}C(CHO)_2$.[13] Triformylmethane[13] also was applicable to this pyrimidine synthesis[14] but with lower yields and poor reproducibility. Dithioacetalization of **7** gave **8** which was allowed to react with (*R*)-1,2-epoxyoctane to give **9**.[12] Desulfurization followed by fluorination afforded **3a**. In a similar manner, **3b** and **3c** were obtained.

Of the compounds we prepared, **3b** only exhibited SmC* phase: Ps, response time and tilt angle of **3b** at 80 °C (4 °C below the SmC*-SmA transition temperature) were -24.2 nC cm^{-2}, 46 μs and 13°, respectively,[15] the response time being shorter than **1a** (-35.6 nC cm^{-2}, 72 μs, 12° at 55 °C (3 °C below the SmC*-SmA transition temperature)).[16] We next added each of **1**, **2**, and **3** to an achiral host liquid crystal mixture (Host A)[17] and measured the electro-optical properties of the resulting mixtures as summarized in Table 1. The mixtures containing **2a** and **2b** exhibited smaller Ps's and slower response than those of **1a** at 10 wt% concentration (-4.5 nC cm^{-2}, 149 μs; -3.6 nC cm^{-2}, 157 μs *vs* -5.4 nC cm^{-2}, 110 μs), but the response times of the mixtures containing 20 wt% of **2a** and **2b** were 76 and 90 μs, shorter than that of **1a** (104 μs). Shorter response times of the mixtures with **2a** and **2b** should be ascribed to lower viscosity of the chiral dopants. Both **2a** and **2b** tend to lower the SmC*-SmA transition temperatures and reduce the tilt angles. Upon 10 wt% addition of **3a**, **3b**, or **3c** to Host A, phase transition temperatures, Ps's and tilt angles remained almost the same as those of **1a**, but response times were found to be longer than that of **1a** (164, 176 or 169 *vs* 110 μs), whereas the mixtures containing 20 wt% of **3a**-**3c** showed properties similar to **1a**: SmC*-SmA transition temperatures, >55 °C, Ps's, >10 nC cm^{-2}; response times, ~100 μs; tilt angles, >20°. Worthy to note is that all Ps's of **1**-**3** are negative, while **2** and **3** induce left handed helix in contrast to **1a** which shows right handed helix at N* phase when mixed in Host A. These results may suggest mixed use of **1** and **2** (or **3**) as chiral dopants induce both large Ps and long helical pitch of N* phase.[18)]

Table 1. Phase transition temperature and electro-optical properties of **1**, **2** and **3** in Host A at 25 °C[a)]

Chiral dopant	(wt%)	Phase transition temperatures[b)]/°C				Ps/nC cm^{-2}	Response time/μs	Tilt angle/°
		SmC*	SmA	N*	Iso			
1a	(10)	• 55	• 67	• 70	•	-5.4	110	22
	(20)	• 51	• 68	• 69	•	-12.7	104	21
2a	(10)	• 47	• 64	• 66	•	-4.5	149	19
	(20)	• 37	• 63	•[c)] 63	•	-7.7	76	14
2b	(10)	• 48	• 70	• 71	•	-3.6	157	18
	(20)	• 42	• 63	-- --	•	-6.8	90	12
3a	(10)	• 57	• 67	• 69	•	-5.0	164	25
	(20)	• 58	• 69	• 70	•	-12.6	93	25
3b	(10)	• 56	• 68	• 69	•	-3.6	176	21
	(20)	• 58	• 69	• 70	•	-10.9	101	22
3c	(10)	• 56	• 68	• 71	•	-5.1	169	22
	(20)	• 55	• 69	• 71	•	-11.9	108	21

a) See reference 15. b) See reference 9. c) N* phase appeared within a range of 0.5 °C.

In summary, we have demonstrated new phenylpyrimidine type chiral dopants having a chiral 3-fluoroalkyl group as a side chain achieve fast response thanks to their low viscosity of the materials.

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9) Cr: crystal phase; SmX: unidentified higher order smectic phase: SmC*: chiral smectic C phase; SmA: smectic A phase; Iso: isotropic liquid phase; N*: chiral nematic phase. Figures in parentheses indicate monotropic phase transition temperatures.

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11) (*R*)-1,2-Epoxyoctane (90% e.e.) and (*R*)-1,2-epoxydecane (86% e.e.) were purchased from Nikko Kyodo Co. Ltd. and used directly.

12) The optical purity of each compound (**5**, **6**, **9**, and **10**) was estimated by HPLC (Daicel, CHIRALCEL OD or CHIRALPAK AD).

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15) Each of **1a**, **3b**, and liquid crystal mixtures was sealed in a polyimide rubbing cell of 2 μm thickness, and a rectangular wave (10 $V_{p\text{-}p}$/mm, 50 Hz) was applied to the cell. Ps was measured by the triangular wave method. The change of transmittance (from 0 to 90%) of light was measured and expressed as response time.

16) Properties of **1a** (Cr 61 (SmX 49 SmC* 62) SmA 71 Iso; 57 °C, 42 nC cm^{-2}, 12 μs) were reported. See reference 4.

17) Host A consists of 2-(4-nonyloxyphenyl)-5-heptylpyrimidine (30 wt%), 2-(4-octyloxyphenyl)-5-octylpyrimidine (20 wt%), 2-(4-decyloxyphenyl)-5-octylpyrimidine (30 wt%), and 2-(4-octyloxyphenyl)-5-nonylpyrimidine (20 wt%). The phase transition temperatures (T/°C) were Cr 13 SmC 56 SmA 65 N 70 Iso (SmC: smectic C phase; N: nematic phase).

18) Long helical pitch of N* phase is required to attain good alignment of liquid crystalline molecules.

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