Synthesis and Electro-Optical Properties of Dihydrobenzofurans and Dihydrofuropyridines as Chiral Dopants for Ferroelectric Liquid Crystals

Tetsuo Kusumoto,* Ken-ichi Sato, Tamejiro Hiyama,† Sadao Takehara,†† and Kayoko Ito††
Sagami Chemical Research Center, 4-4-1 Nishiohnuma, Sagamihara, Kanagawa 229
†*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226*
††*Dainippon Ink and Chemicals, Inc., 4472-1 Komuro, Ina-machi, Kita-adachi-gun, Saitama 362*

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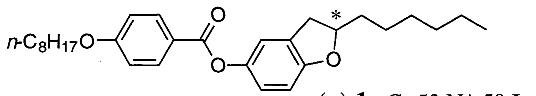
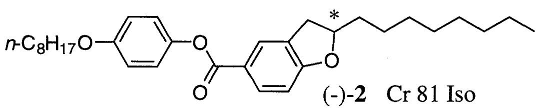
Optically active dihydrobenzofurans and dihydrofuropyridines were synthesized and shown to be good chiral dopants for ferroelectric liquid crystals.

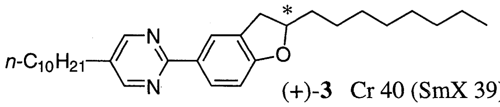
Ferroelectric liquid crystals (FLCs) are materials expected to be applicable to high speed display device.[1] The most important requirement for FLC materials is fast switching over a wide range of temperatures above and below room temperatures. For achieving fast switching, many kinds of optically active compounds have been designed and synthesized.[2-6] In particular, we have shown dihydrobenzofuran **1** is a less viscous chiral dopant.[7] To study in details the effect of core aromatic ring structure of **1**, we designed **2**, **3**, and **4**. Herein we report their synthesis and electro-optical properties.



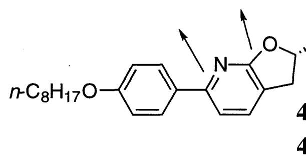
(+)-1 Cr 53 N* 59 Iso



(-)-2 Cr 81 Iso



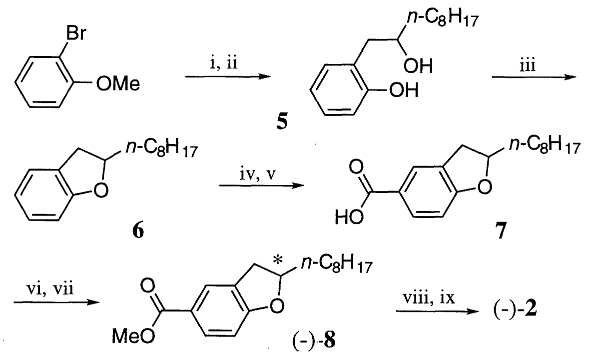
(+)-3 Cr 40 (SmX 39) N* 47 Iso



4a: R = n-C_6H_{13} Cr 68 Iso
4b: n-C_9H_{19} Cr 94 Iso

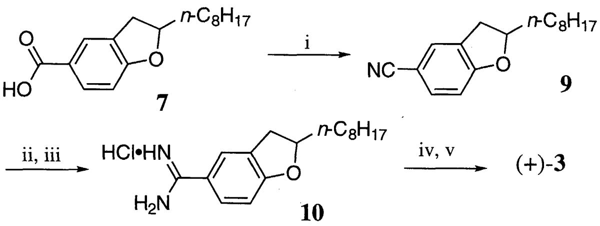
Chiral dihydrobenzofurans **2** and **3** were prepared according to the routes shown in Scheme 1 and Scheme 2 respectively. The dihydrobenzofuran **6** was prepared by the cyclization of diol **5** obtained through the reaction of 2-methoxyphenylmagnesium bromide with 1,2-epoxydecane followed by demethylation with $AlCl_3$ and Me_2S. Acetylation of **6** with Ac_2O and $AlCl_3$ followed by oxidation of the resulting 5-acetoxydihydrobenzofuran with NaOBr afforded carboxylic acid **7**. Esterification of **7** and resolution by HPLC (Daicel, CHIRALCEL OD, hexane / 2-propanol = 40 / 1) afforded (+) and (-)-enantiomers of **8**. Hydrolysis of (-)-**8** gave (-)-**7** which was condensed with 4-octyloxyphenol to give rise to (-)-**2**.

Condensation of **7** with NH_3 in the presence of ethyl polyphosphate was followed by dehydration to give nitrile **9**,[8] which was transformed to amidine **10** by treatment with HCl in ethanol and then with NH_3. Racemic **3** was prepared from **10** with n-$C_{10}H_{21}C(CHO)=CHNMe_2$ and MeONa. Resolution of **3** by HPLC (Daicel, CHIRALCEL OD, hexane / 2-propanol = 9 / 1) gave (+) and (-)-enantiomers of **3**.



i: n-BuLi, CuI, 1,2-epoxydecane; ii: $AlCl_3$, Me_2S; iii: p-$MeC_6H_4SO_3H$; iv: Ac_2O, $AlCl_3$; v: NaOBr, H_2O; iv: CH_2N_2; vii: separation by HPLC (CHIRALCEL OD); viii: KOH; ix: n-$C_8H_{17}OC_6H_4OH$, DCC, DMAP

Scheme 1.

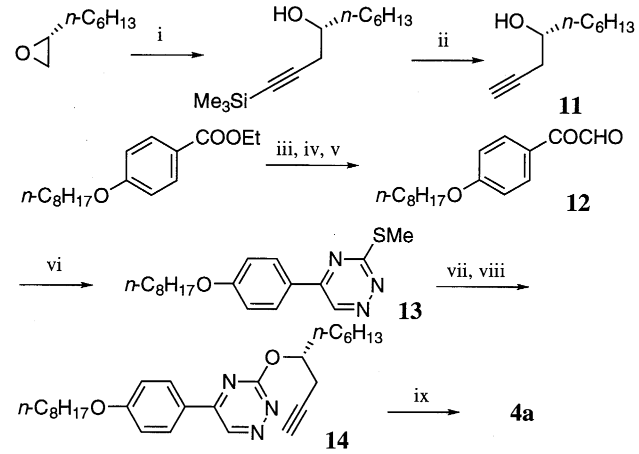


i: ethyl polyphosphate, NH_3; ii: HCl, EtOH; iii: NH_3; iv: n-$C_{10}H_{21}$-$C(CHO)=CHNMe_2$, MeONa; v: separation by HPLC (CHIRALCEL OD)

Scheme 2.

Optically active dihydrofuropyridine **4a** was prepared according to the route shown in Scheme 3. Triazine **13** is available by the reaction of glyoxal **12** with S-methylthiosemicarbazide.[9] Oxidation of **13** with m-chloroperbenzoic acid (m-CPBA) followed by reaction with chiral alcohol **11** prepared from (R)-1,2-epoxyoctane (91% *e.e.*) afforded 3-(1-octyl-3-butynyloxy)-1,2,4-triazine **14**.[10] Heating **14** in refluxing chlorobenzene led, *via* intramolecular cycloaddition and aromatization under elimination of molecular nitrogen, to the desired chiral dihydrofuropyridine **4a** (91% *e.e.* after recrystallization) in good yield.[10] In a similar manner, **4b** (98% *e.e.*) was obtained.

Each of **1**-**4** was added to an achiral host mixture A,[11] and electro-optical properties of the resulting mixtures were measured as summarized in Table 1. The mixture containing 10 wt% of (-)-**2** showed very small Ps and slow response time (~0 nC cm^{-2},



i: LiC≡CSiMe$_3$; ii: KF, MeOH; iii: DMSO, *t*-BuOK; iv: HCl *aq*; v: Cu(OAc)$_2$; vi: NH$_2$NHC(SMe)=NH•HCl; vii: *m*-CPBA; viii: **11**, *n*-BuLi; ix: PhCl, Δ

Scheme 3.

1600 µs). Although Ps of the mixture containing 10 wt% of (+)-**3** was almost the same as that of (+)-**1**, the mixture of (+)-**3** responded faster than that of (+)-**1** (+2.6 nC cm^{-2}, 240 µs *vs* +2.6 nC cm^{-2}, 315 µs). These observations mean that -COO- of (+)-**1** does not affect Ps, but dipole moment of -OCO- of (-)-**2** cancels that of dihydrobenzofuran. Pyrimidine ring of (+)-**3** has no influence on Ps, but shorter response time of the mixture with (+)-**3** should be ascribed to lower viscosity of the core.

On the other hand, the mixtures containing 10 wt% of **4a** or **4b** exhibited larger Ps than those of (+)-**1** or (+)-**3**. This may be attributed to net dipole moment. The dipole moment of dihydrofuropyridine is larger than that of dihydrobenzofuran, because dihydrofuropyridine has pyridine nitrogen whose dipole moment is nearly parallel to that of oxygen. Upon 5 wt% addition of **4a** or **4b** to Host A, Ps was smaller than that of 10 wt% mixture, but the response time remained almost equal to that of 10 wt% mixture. Accordingly, dihydrofuropyridines **4a** and **4b** may be useful chiral dopants for ferroelectric liquid crystals at low content.

In summary, we have synthesized new chiral dopants having a dihydrobenzofuran or dihydrofuropyridine ring structure and demonstrated these exhibit low viscosity and/or large Ps as the chiral dopant. These observations should be useful for design of new chiral dopants of short response times.

Table 1. Electro-optical properties of **1**, **2**, **3** and **4** in Host A at 25 °C[a)]

Dopant (wt%)	Phase transition temperatures/°C[b)]	Ps /nC cm^{-2}	Response time/µs	Tilt angle/°
(+)-**1** (10)	SmC* 49 SmA 58 N* 66 Iso	+2.6	315	18
(-)-**2** (10)	SmC* 52 SmA 62 N* 67 Iso	~0	1600	22
(+)-**3** (10)	SmC* 51 SmA 63 N* 67 Iso	+2.6	240	21
(20)	SmC* 47 SmA 61 N* 65 Iso	+5.5	145	22
4a (5)	SmC* 57 SmA 61 N* 67 Iso	+2.7	250	23
(10)	SmC* 54 N* 64 Iso	+7.6	250	15
4b (5)	SmC* 57 SmA 63 N* 68 Iso	+2.0	180	18
(10)	SmC* 58 SmA 61 N* 66 Iso	+4.4	190	13

a) Each of liquid crystal mixtures was sealed in a polyimide rubbing cell of 2 µm thickness, and a rectangular wave (10 V_{p-p} µm^{-1}, 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. b) SmC*: chiral smectic C phase; SmA: smectic A phase; N*: chiral nematic phase; Iso : isotropic liquid phase.

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11 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 (°C) were Cr 13 SmC 56 SmA 65 N 70 Iso (Cr: crystal phase; SmC: smectic C phase; N: nematic phase).