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Optically Active *O*-Acyl Cyanohydrins as Chiral Dopants for Ferroelectric Liquid Crystals

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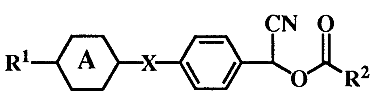
O-Acyl cyanohydrins having a chiral center directly connected to the core aromatic ring were prepared through asymmetric hydrocyanation of 4-substituted benzaldehydes and shown to be excellent chiral dopants for ferroelectric liquid crystals.

Since the display device using ferroelectric liquid crystals (FLCs) was suggested by Clark and Lagerwall in 1980,[1] many liquid crystals or their mixtures having a chiral smectic C phase ($S_C{}^*$) have been investigated.[2] The FLC materials were made usually of achiral host liquid crystal mixtures of low viscosity and a chiral guest dopant having a high spontaneous polarization (Ps) in order to achieve short response time (τ). Chiral dopants so far studied have commonly a chiral center and a polar functional group like -COO-, -O-, -CO-, -F, or $-CF_3$ on the side chain. We anticipated that the FLCs having a chiral center connected directly to both polar group and core aromatic ring should exhibit much improved Ps. Based on this working hypothesis, we prepared 1-(4-substituted phenyl)ethyl ethers,[3] 2-(4-substituted phenyl)propionates,[3] and 4-substituted phenyl sulfoxides[4] and reported these were in fact good chiral dopants for FLCs. Compared with the polar groups involved in these materials, a cyano group has a larger group dipole moment and thus is expected to be a better polar functional group. Accordingly we planned the synthesis of the FLCs having an optically active cyanohydrin group like **1**.[5-7] The details of the synthesis and the opto-electrical properties of the new chiral molecules are reported herein.



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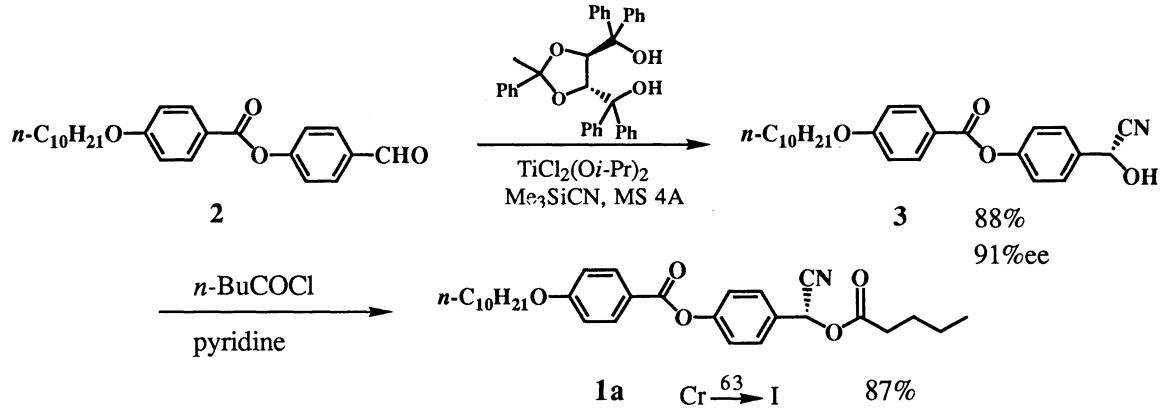
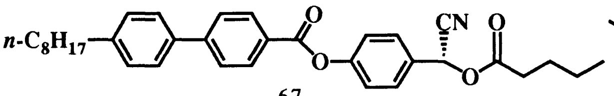
The chiral *O*-acyl cyanohydrin **1a** was prepared according to the route shown in Scheme 1.[8] 4-(4-Decyloxyphenylcarboxy)benzaldehyde (**2**) was allowed to react with trimethylsilyl cyanide in the presence of the Narasaka's chiral titanium catalyst[9] to give the corresponding cyanohydrin **3** with high enantioselectivity.[10] The ester **1a** was obtained by acylation of **3** with pentanoyl chloride.[11] In the similar manner, **1b**-**1i** were synthesized from the corresponding 4-substituted benzaldehydes.[12]

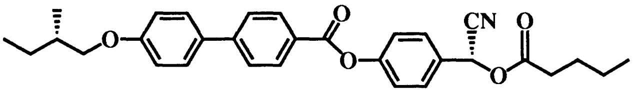


Scheme 1.



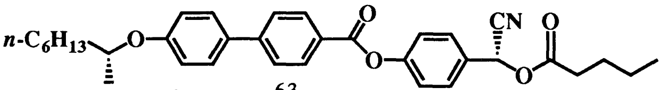
1b $\mathrm{Cr}\xrightarrow{67}\mathrm{I}$

$\mathrm{S_A} \rightleftarrows$ 63

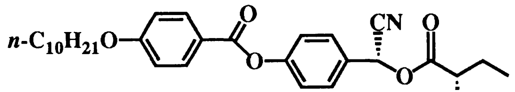


1c $\mathrm{Cr}\xrightarrow{135}\mathrm{I}$

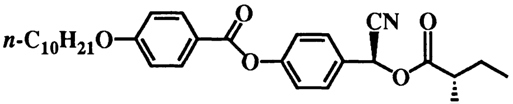
$\mathrm{S_C^*}\xleftarrow{x}\mathrm{S_A} \rightleftarrows$ 78



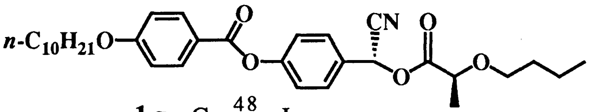
1d $\mathrm{Cr}\xrightarrow{63}\mathrm{I}$



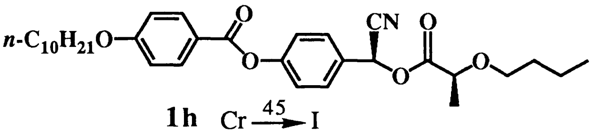
1e $\mathrm{Cr}\xrightarrow{39}\mathrm{I}$



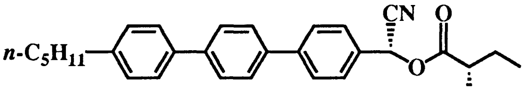
1f $\mathrm{Cr}\xrightarrow{38}\mathrm{I}$



1g $\mathrm{Cr}\xrightarrow{48}\mathrm{I}$



1h $\mathrm{Cr}\xrightarrow{45}\mathrm{I}$



1i $\mathrm{Cr}\xrightarrow{124}\mathrm{I}$

$\mathrm{S_A} \leftarrow$ x

The phase transition temperatures[13] of **1a**-**1i** are shown below each structure. Of the compounds we prepared, **1c** exhibited S_C^* phase, but the Ps of **1c** could not be measured unfortunately. Compounds **1a**-**1i** were found to be good chiral dopants for achiral smectic C liquid crystals. Each was added by 5 wt% to a host liquid crystal mixture A.[14] The electro-optical properties of the resulting mixtures are listed in Table 1. The mixture containing **1a** showed a comparably large Ps (5.6 nC/cm^2) and a short response time (79 μs) at 25 °C. These data are apparently much improved ones compared with those of ArCHMeOR or ArCHMeCOOR[3] type FLCs or slightly better than those of the FLCs derived from chiral sulfoxides.[4] Use of (*R*)-1-methylheptyloxy group on the left side chain resulted in much enhancement of Ps up to 8.2 nC/cm^2 (cf. **1d** *vs.* **1a** or **1c**). On the other hand, introduction of a methyl group on the right side chain did not improve the Ps. For example, the other hand, introduction of a methyl group on the right side chain did not improve the Ps. For example, the cyanohydrin esters **1e** and **1f** derived from (*S*)-2-methylbutanoic acid exhibited smaller Ps than **1a**. The Ps's of **1g** and **1h** also were smaller than that of **1a**. These observations contrast to the opto-electrical behavior of chiral sulfoxides whose Ps's were enhanced by branching of the alkyl side chain.[4)] The FLC mixture derived from **1i** having a terphenylene group as the core exhibited the Ps of 9.1 nC/cm^2. The τ of this mixture was 64 μsec, one of the highest levels now. It should be noted that the sign of Ps[15)] and twist sense are governed decisively by the chirality of the cyanohydrin's chiral center: the (*R*)-configuration correlates to (+) and *left* respectively; (*S*)-configuration to (-) and *right* (cf. **1c**-**1i**). The other chiral centers apparently do not affect this empirical rule.

We have shown that the FLCs of type **1** are excellent chiral dopants and apparently are superior to the FLCs of the other cyanohydrins.[5-7)] The FLCs' cells containing **1** exhibit large Ps and fast response in addition to appropriate tilt angle and thus were shown to be versatile for liquid crystal display device.

Table 1. Properties of the chiral dopant **1** in achiral host crystal mixture A at 25 °C[a)]

Chiral dopant	Phase transition temp[b)] S_C^*	S_A	N^* I	Ps[c)] nC/cm^2	Response time[d)] μs	Tilt angle deg	Twist[e)] sense
1a	56	75	80	+5.6	79	21.5	left
1b	55	80	83	+5.6	88	20.1	left
1c	60	78	83	+5.5	78	13.4	left
1d	62	74	80	+8.2	64	23.7	left
1e	60	75	80	+3.4	134	22.3	left
1f	58	76	80	-5.6	102	21.9	right
1g	56	75	80	+4.4	125	20.6	left
1h	51	76	79	-4.6	113	18.9	---[f)]
1i	57	76	81	-9.1	64	21.5	right

a) The guest chiral dopant was dissolved by 5 wt% in host A. See Ref. 14. b) See Ref. 13. c) See Ref. 15. d) The liquid crystal mixture was sealed in a polyimide rubbing cell of about 2 μm thickness, and a square wave of 10 $V_{p\text{-}p}$/μm was applied to the cell. The change of transmittance (from 10% to 90%) of light was observed. e) The twist sense of chiral nematic phase. f) Not measured due to long helical pitch.

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4) K. Nishide, A. Nakayama, T. Kusumoto, T. Hiyama, S. Takehara, T. Shoji, M. Osawa, T. Kuriyama, K. Nakamura, and T. Fujisawa, *Chem. Lett.*, **1990**, 623.

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6) The FLCs having optically active cyanohydrin aryl ether: D. M. Walba, K. F. Eidman, and R. C. Haltiwanger, *J. Org. Chem.*, **54**, 4939 (1989). See also PCT Int. Appl. WO 87-07890; *Chem. Abstr.*, **110**, 145120 (1989). We observed Ps of (*R*)-4-(1-cyanopentyloxy)phenyl 4-(4-octyloxyphenyl)benzoate (5 wt% in host A) was -1.1 nC/cm^2 at 25 °C.

7) We observed Ps of (*R*)-4-(1-cyano-2-oxa-4-pentenyl)phenyl 4-(4-octyloxyphenyl)benzoate (5 wt% in host A) was +1.5 nC/cm^2 at 25 °C.

8) At first we attempted to prepare **1** by asymmetric hydrocyanation of 4-acetoxybenzaldehyde and acylation, followed by deacetylation. However, the product 2-acyloxy-2-(4-hydroxyphenyl)acetonitrile turned out to be too labile for the subsequent condensation with the left part of **1**.

9) H. Minamikawa, S. Hayakawa, T. Yamada, N. Iwasawa, and K. Narasaka, *Bull. Chem. Soc. Jpn.*, **61**, 4379 (1989).

10) The optically yield was estimated by ^{1}H NMR of its MTP ester.

11) The acylation of the chiral cyanohydrin using the carboxylic acid and *N,N'*-dicyclohexylcarbodiimide or ethyl polyphosphate works equally well without any racemization.

12) Hydrocyanation of 4-[4-(4-octyloxyphenyl)phenylcarboxy]benzaldehyde and 4-(4-octyloxyphenoxycarbonyl)benzaldehyde was unsatisfactory with regard to yield and enantioselectivity.

13) Given in °C. Cr: crystalline phase, S_C*: chiral smectic C phase, S_A: smectic A phase, N*: chiral nematic phase, I: isotropic liquid phase, S_C smectic C phase, N: nematic phase. Temperature X means *not determined*, as the following phase was not stable enough.

14) The host liquid crystal mixture A consists of 2-(4-decyloxyphenyl)-5-octylpyrimidine (28 wt%), 2-(4-nonyloxyphenyl)-5-octylpyrimidine (28 wt%), 2-(4-octyloxyphenyl)-5-octylpyrimidine (24 wt%), and 2-(2-fluoro-4-octyloxyphenyl)-5-(4-heptylphenyl)pyrimidine (20 wt%). The phase transition temperatures of the host A were $\mathrm{Cr} \xrightarrow{13} S_C \xrightarrow{68.5} S_A \xrightarrow{73.5} \mathrm{N} \xrightarrow{83.5} \mathrm{I}$.

15) The sign of Ps of (*S*)-2-methylbutyl 3-[4-(4-decyloxybenzylideneamino)-phenyl]-2-propenoate, the standard compound, is defined to be (-).

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