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# Synthesis and properties of optically active 1,3-diols and their derivatives as chiral dopants for ferroelectric liquid crystals

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New chiral dopants *β*-hydroxy ketones **1**, 1,3-diols **2**, 1,3-dioxanes **3** and 1,3-dioxan-2-ones **4** were designed and synthesized. Reaction of (*R*)-1,2-epoxyoctane with carbanions derived from 2-(4-substituted phenyl)-1,3-dithianes followed by hydrolysis of the resulting hydroxy dithianes afforded **1**. Reduction of **1** gave the diols **2**, which yielded **3** upon acetalization and **4** upon carbonation. The *syn* isomers of **2**, **3**, and **4** exhibited larger spontaneous polarizations, when applied as chiral dopants, than the *anti* isomers or hydroxy ketones **1**.

## 1. Introduction

Since Clark and Lagerwall suggested in 1980 that ferroelectric liquid crystals (FLCs) may be applied in fast-switching liquid crystal displays [1], FLCs have attracted extensive attention as display materials for the future. The switching time of FLC displays is proportional roughly to the viscosity of the material and to the reciprocal of the spontaneous polarization ($P_s$). To search for chiral dopants with large $P_s$, various optically active compounds have been designed and synthesized [2–4]. We have disclosed that chiral dopants having an optically active ring structure such as cyanocyclopropanes, *cis*-*γ*-lactones, and oxazolidin-2-ones show extremely large $P_s$ values [5–8]. In an extension of this study of optically active ring structures, we have prepared the new chiral dopants **1**–**4** containing six-membered rings and report herein their synthesis and electro-optical properties.

## 2. Preparation of materials

Compounds **1**–**4** (see figure 1) were prepared according to the routes shown in schemes 1 to 4. The dithiane **5a** was easily prepared from 4′-octyloxybiphenyl-4-carboxaldehyde with 1,3-propanedithiol in quantitative yield. On the other hand, the phenylpyrimidine type dithianes **5b** or **5c** were prepared by the reaction of 4-(2,6-dithiacyclohexyl)benzamidine, obtained through the reaction of 2-(4-cyanophenyl)-1,3-dithiane with HCl and ethanol followed by reaction with $NH_3$, with 1-(*N*,*N*-

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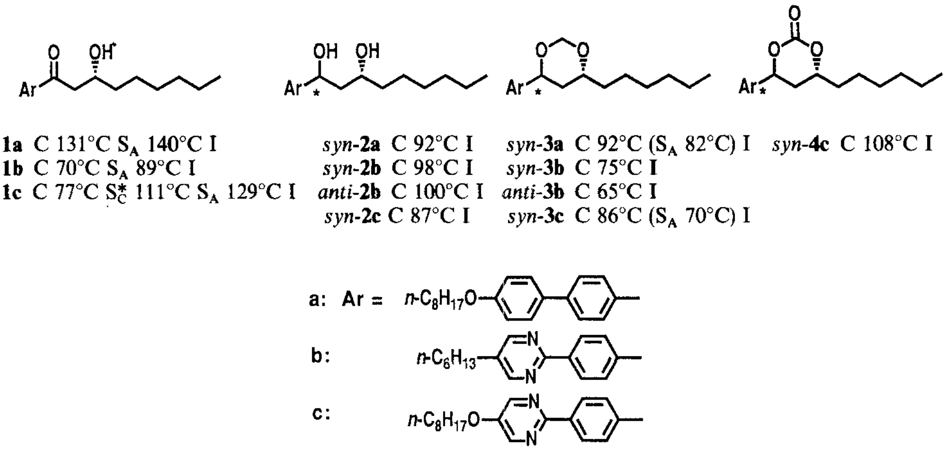
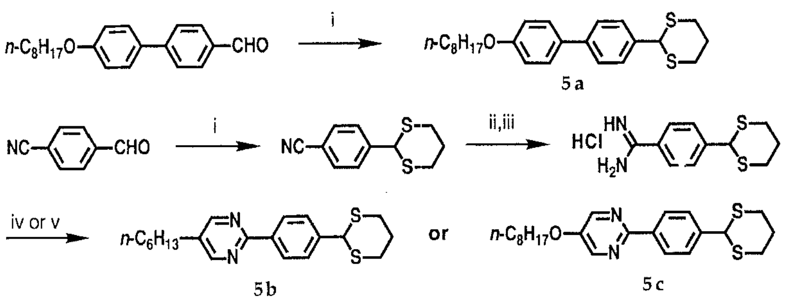


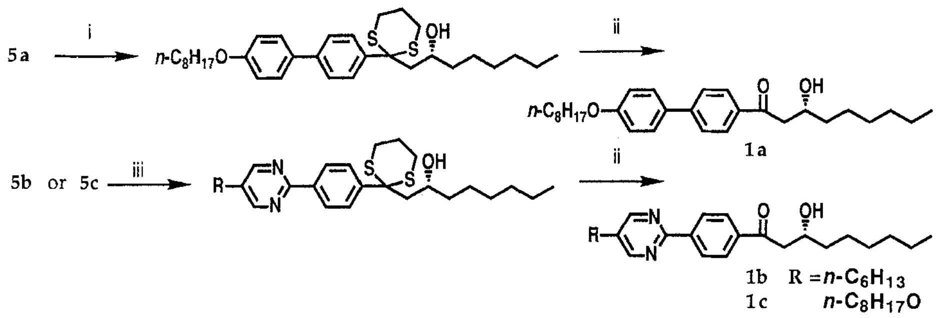
| | | | |
|---|---|---|---|
| **1a** C 131°C $S_A$ 140°C I | *syn*-**2a** C 92°C I | *syn*-**3a** C 92°C ($S_A$ 82°C) I | *syn*-**4c** C 108°C I |
| **1b** C 70°C $S_A$ 89°C I | *syn*-**2b** C 98°C I | *syn*-**3b** C 75°C I | |
| **1c** C 77°C $S_C^*$ 111°C $S_A$ 129°C I | *anti*-**2b** C 100°C I | *anti*-**3b** C 65°C I | |
| | *syn*-**2c** C 87°C I | *syn*-**3c** C 86°C ($S_A$ 70°C) I | |

Figure 1. New chiral dopants **1–4** and their phase transition temperatures.

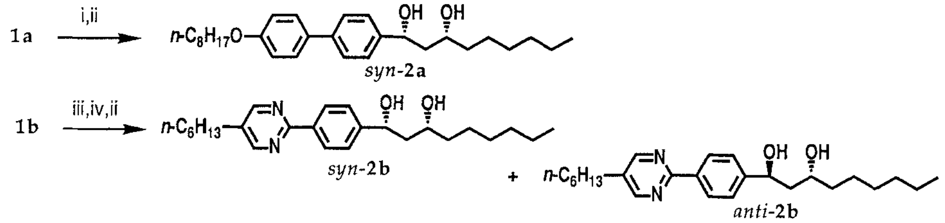
dimethylamino)-2-formyl-1-octene or 3-(*N*,*N*-dimethylamino)-2-octyloxy-2-propenal (see scheme 1). Reaction of the carbanion of **5a** with (*R*)-1,2-epoxyoctane [9] followed by hydrolysis of the resulting hydroxy dithiane using the *N*-chlorosuccinimide (NCS)-$AgNO_3$ reagent system afforded **1a** (86 per cent, 92 per cent *ee*) [10]. In a similar manner, **1b** (91 per cent *ee*) and **1c** (94 per cent *ee* after recrystallization) were synthesized from **5b** and **5c**, respectively, using lithium diisopropylamide (LDA) as a base (see scheme 2). Although *syn*-**2a** was selectively obtained by reduction of **1a** with $Et_2BOMe$–$NaBH_4$ (65 per cent yield, >99 per cent *de*, 98 per cent *ee* after recrystallization) [11] (see scheme 3), about a 1 : 1 or 1 : 2 mixture of *syn*- and *anti*-**2b** (>99 per cent *de*, 99 per cent *ee* and >99 per cent *de*, 94 per cent *ee* respectively after recrystallization) resulted by reduction of **1b** with $Et_2BOMe$–$NaBH_4$ or $NaBH_4$. Each isomer was separated by column chromatography. Similarly, *syn*-**2c** (60 per cent, >99 per cent *de*, 99 per cent *ee*) and *anti*-**2c** were prepared from **1c**. Each of *syn*-**2a**, *syn*-**2b**, *anti*-**2b**, and *syn*-**2c** was transformed to its formaldehyde acetal with dimethoxymethane and 4-toluenesulphonic acid catalyst to give *syn*-**3a** (81 per cent), *syn*-**3b** (73 per cent), *anti*-**3b** (41 per cent), and *syn*-**3c** (78 per cent), respectively. Carbonation of *syn*-**2c** with trichloromethyl chloroformate gave *syn*-**4c** (93 per cent) (see scheme 4).



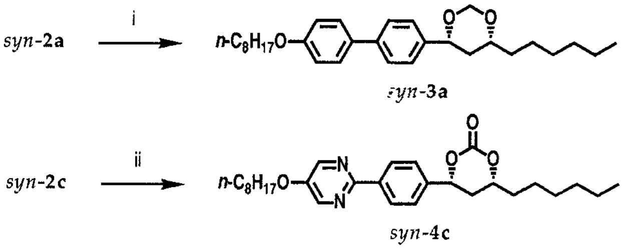
Scheme 1. (i) $HSCH_2CH_2CH_2SH$, Trimethylsilyl polyphosphate; (ii) HCl, EtOH; (iii) $NH_3$; (iv) $n$-$C_6H_{13}C(CHO)$=$CHNMe_2$, MeONa, MeOH; (v) $n$-$C_8H_{17}OC(CHO)$=$CHNMe_2$, MeONa, MeOH.



Scheme 2. (i) $n$-BuLi, ($R$)-1,2-Epoxyoctane; (ii) NCS, $AgNO_3$, $H_2O$, MeCOMe, $CH_3CN$; (iii) LDA, ($R$)-1,2-Epoxyoctane.



Scheme 3. (i) $Et_2BOMe$, $NaBH_4$; (ii) recrystallization; (iii) $NaBH_4$; (iv) separation.



Scheme 4. (i) $CH_2(OMe)_2$, 4-$MeC_6H_4SO_3H$; (ii) $ClCOOCCl_3$.

## 3. Results and discussion

Of the compounds prepared, **1c** exhibited a chiral smectic C ($S_C^*$) phase: the $P_s$ values of **1c** at 95°C and 60°C were $+3{\cdot}8\,nC\,cm^{-2}$ and $+12{\cdot}4\,nC\,cm^{-2}$, respectively. These are unexpectedly small. Thus, each of **1–4** was added to an achiral host liquid crystal mixture A [12], and the electro-optical properties of the resulting mixtures were measured as summarized in the table. The mixtures containing 5 or 10 wt% of $\beta$-hydroxy ketones **1a–c** exhibited very small $P_s$. Among the 1,3-diols prepared, a mixture containing 10 wt% of *syn*-**2a** showed a large $P_s$ value ($+12{\cdot}8\,nC\,cm^{-2}$) and a short response time (96 $\mu$s). It is believed that the hydroxyl group increases the viscosity of liquid crystals. Thus our findings are in sharp contrast to common observations. Probably the viscosity of *syn*-**2a** is not so high due to intramolecular hydrogen bonding. The phenylpyrimidines *syn*-**2b** and *syn*-**2c** exhibited as high as $P_s$ ($+11{\cdot}2$ and $+12{\cdot}1\,nC\,cm^{-2}$, respectively) at only 5 wt% addition. In contrast, *anti*-**2b** showed a small $P_s$ compared with *syn*-**2b**. The observed $P_s$ values of acetal **3** proved to be slightly

Phase transition temperatures and electro-optical properties of **1**–**4** in host A at 25°C. (*a*)

| Chiral dopant (wt %) | | Phase transition temperatures/°C | | | | | | | | Response | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $S_C^*$ | | $S_A$ | | N* | | I | $P_s$/nC cm$^{-2}$ (*b*) | time/$\mu$s (*c*) | $\theta$/° |
| **1a** | (5) | ● | 55 | ● | 69 | ● | 71 | ● | +(~0) | 1008 | 13 |
| | (10) | ● | 48 | ● | — | — | 79 | ● | +(~0) | 237 | 6 |
| **1b** | (5) | ● | 42 | ● | 69 | ● | 71 | ● | +0·2 | 525 | 14 |
| **1c** | (10) | ● | 38 | ● | — | — | 76 | ● | +(~0) | 2200 | 11 |
| *syn*-**2a** | (10) | ● | 50 | ● | — | — | 70 | ● | +12·8 | 96 | 18 |
| *syn*-**2b** | (5) | ● | 50 | ● | 67 | ● | 70 | ● | +11·2 | 112 | 21 |
| | (10) | ● | 46 | ● | 67 | ● | 70 | ● | +19·4 | 122 | 17 |
| *anti*-**2b** | (5) | ● | 54 | ● | 64 | ● | 69 | ● | −2·0 | 594 | 22 |
| | (10) | ● | 52 | ● | 62 | ● | 67 | ● | −5·6 | 196 | 19 |
| *syn*-**2c** | (5) | ● | 54 | ● | 64 | ● | 69 | ● | +12·1 | 99 | 23 |
| *syn*-**3a** | (5) | ● | 56 | ● | 66 | ● | 71 | ● | +2·4 | 199 | 21 |
| | (10) | ● | 56 | ● | 66 | ● | 70 | ● | +7·1 | 120 | 23 |
| *syn*-**3b** | (10) | ● | 48 | ● | 61 | ● | 67 | ● | +8·7 | 119 | 22 |
| *anti*-**3b** | (10) | ● | 50 | ● | 63 | ● | 68 | ● | −0·1 | 820 | 16 |
| *syn*-**3c** | (5) | ● | 55 | ● | 66 | ● | 70 | ● | +2·2 | 261 | 20 |
| | (10) | ● | 53 | ● | 67 | ● | 69 | ● | +6·5 | 141 | 28 |
| | (15) | ● | 53 | ● | 68 | ● | 70 | ● | +10·1 | 93 | 22 |
| *syn*-**4c** | (5) | ● | 55 | ● | 67 | ● | 70 | ● | +16·6 | 99 | 24 |
| | (10) | ● | 55 | ● | 67 | ● | 69 | ● | +34·8 | 139 | 23 |
| | (15) | ● | 56 | ● | 68 | ● | 69 | ● | +52·9 | 102 | 20 |

(*a*) A liquid crystal mixture was sealed in a polyimide rubbed cell of 2 $\mu$m thickness, and a square wave of 10 $V_{p-p}$ $\mu$m$^{-1}$ was applied to the cell.

(*b*) $P_s$ was measured by the triangular wave method.

(*c*) Related to the change in transmittance from 0 to 90%.

smaller than those of **2**, but again *syn*-isomers exhibited larger $P_s$ than *anti*-isomers. The stereochemistry–$P_s$ relationship is similar to that for $\gamma$-lactones [6, 13, 14]. Optically active *cis*-$\gamma$-lactones induce very large $P_s$ values; *trans*-$\gamma$-lactones almost zero. Special attention should be paid to the carbonate *syn*-**4c** which, upon addition to host A at 5, 10 or 15 wt %, exhibited $P_s$ of +16·6, +34·8 or +52·9 nC cm$^{-2}$, respectively. Although these are large $P_s$ values, the response times of the mixtures could not be shortened below 100 $\mu$s.

The stereochemistry–$P_s$ relationship may be understood in terms of the conformation of each of the chiral dopants. The most stable conformation of each of the model compounds **6**–**11** was suggested by molecular orbital calculations (MOPAC Ver. 6/PM3) [15] based on the zig-zag model [16–18] and is shown in figure 2. The dipole of the hydroxyl and carbonyl groups of hydroxy ketone **6** apparently point in almost different directions. In the case of *anti*-diol **8**, the dipole moment of the benzylic hydroxyl group directs *anti*-parallel to that of the 3-hydroxyl group, whereas the two hydroxyl groups of the *syn*-diol **7** are disposed nearly parallel and perpendicular to the plane composed of the core aromatic ring and the alkyl side chain (namely the plane of the paper). This conformation could be responsible for the large $P_s$ of *syn*-**2**. The dipole of the acetal oxygens of the *syn*- and *anti*-dioxanes **9** and **10**, respectively, appears to be arranged parallel to the plane composed of the core aromatic ring and the alkyl side

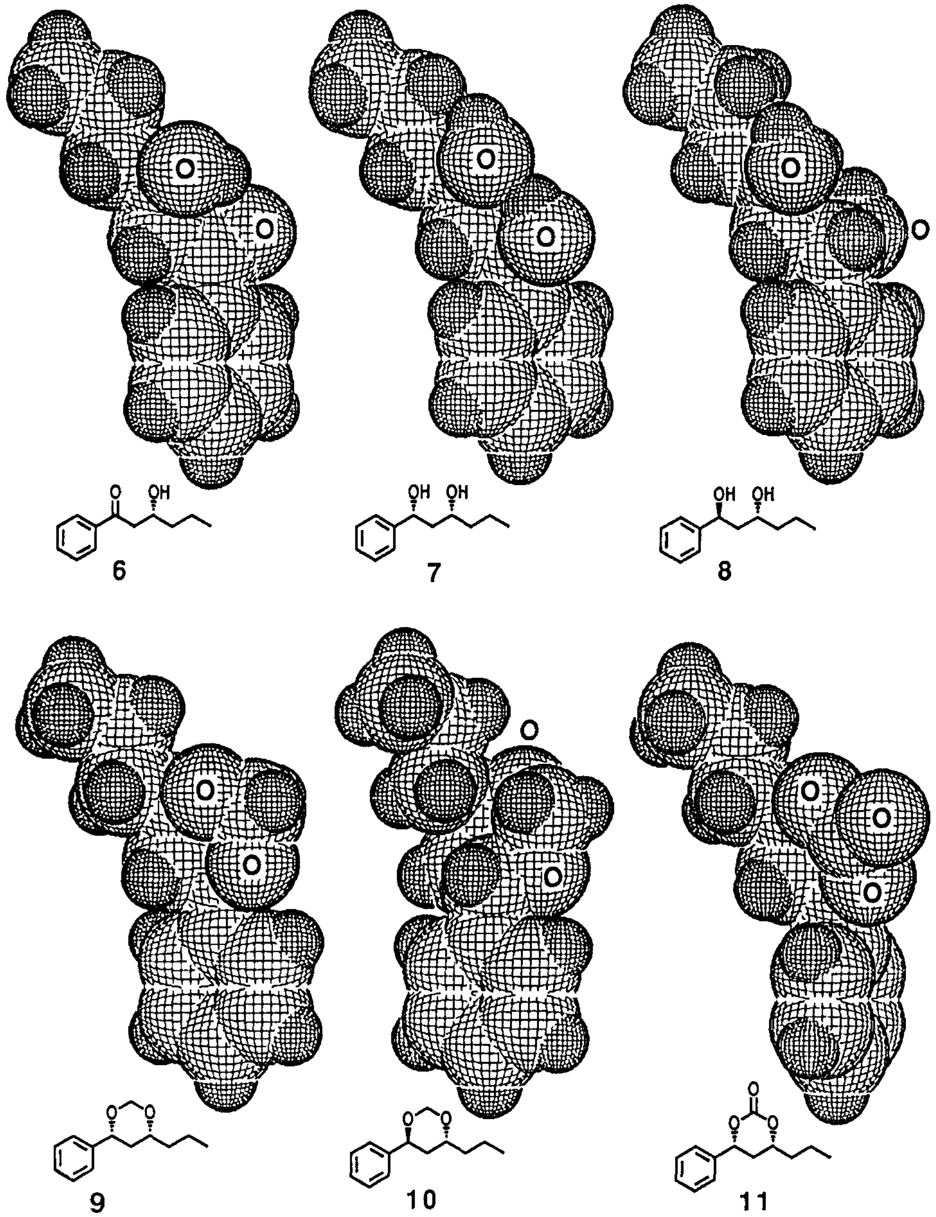


Figure 2. The conformations of **6**–**10**, models of **1**–**4**.

chain. This conformation may cause both *syn*-**3** and *anti*-**3** to induce less $P_s$ than *syn*-**2**. Noteworthy is that the dipole of the carbonyl group of **11** directs nearly perpendicular to the plane. The relationship between the direction of the dipole and the plane composed of the core aromatic ring and the alkyl side chain observed here is fully consistent with our previous observation [6, 8].

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[9] (*R*)-1,2-Epoxyoctane (90 per cent *ee*) was purchased from Nippon Mining Co., Ltd and used directly.

[10] The optical purity of each compound was estimated by HPLC (Daicel Chiralcel OD or Chiralpak AD).

[11] The diastereomer ratio of each compound was determined by HPLC (Silica-60) and $^1$H NMR (400 MHz).

[12] 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 were C 13°C $S_C^*$ 56°C $S_A$ 65°C N 70°C I.

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