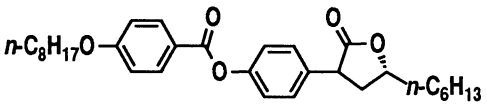
CHEMISTRY LETTERS, pp. 1623 - 1624, 1991.

Synthesis and Properties of Optically Active 3-Aryl-5-alkyloxazolidin-2-ones. New Chiral Dopants for Ferroelectric Liquid Crystals

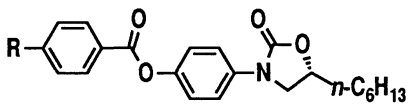
Tetsuo KUSUMOTO, Ken-ichi SATO, Tamejiro HIYAMA,* Sadao TAKEHARA,*†
Masashi OSAWA,† Kayoko NAKAMURA,† and Toru FUJISAWA†
Sagami Chemical Research Center, 4-4-1 Nishiohnuma, Sagamihara, Kanagawa 229
†Central Research Laboratories, Dainippon Ink and Chemicals, Inc., 631 Sakado, Sakura, Chiba 285

New chiral dopants for ferroelectric liquid crystals containing an optically active oxazolidin-2-one moiety, synthesized from (*R*)-1,2-epoxyoctane, exhibit large spontaneous polarization.

Recently synthesis of new type of ferroelectric liquid crystals (FLCs) has been of great interest in connection with their application to fast response display devices.[1] The response time depends on the magnitude of spontaneous polarization (Ps) and viscosity of the FLCs. The FLC materials are made usually of achiral host liquid crystal mixtures of low viscosity and chiral dopants of large Ps. For chiral dopants various optically active compounds have been designed and synthesized. We recently have reported that the optically active *cis*-γ-lactones such as **1a** show extremely large Ps's,[2] but the *trans*-lactone **1b** did not induce any measurable Ps's. The diastereomers had to be separated by silica gel column chromatography and we were a little apprehensive of the epimerization of α-carbon. To avoid separation of stereoisomers and epimerization of γ-lactones, we designed and prepared 3-aryl-5-alkyloxazolidin-2-ones **2a-2c**. Synthetic details and the electro-optical properties of these are reported herein.



1a (*cis*)
1b (*trans*)

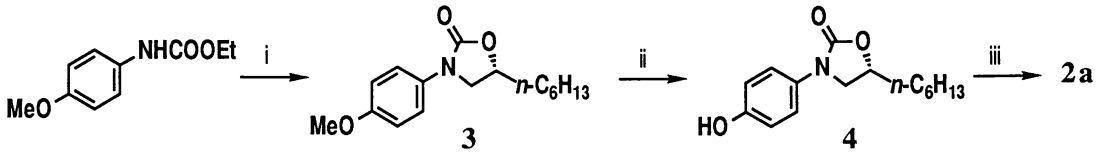


2a R = *n*-$C_8H_{17}O$- Cr 109 S_X 147 I
2b *n*-C_8H_{17}- Cr 108 S_A 127 N* 127.1 I
2c (*S*)-EtCHMeCH$_2$- Cr 93 N* 99 I

The chiral oxazolidinone **2a** was prepared according to the route shown in Scheme 1. N-(4-Methoxyphenyl)ethylurethane was reacted with (*R*)-1,2-epoxyoctane[3] in the presence of triethylamine at 100 °C in a sealed tube to give oxazolidinone **3** (85% yield, 91% ee).[4,5] Demethylation of **3** was effected with BBr_3 to give **4** (76% yield, 91% ee)[5] which was esterified with 4-octyloxybenzoyl chloride to give **2a** (43% yield). In a similar manner, compounds **2b** and **2c** were obtained. Oxazolidinones **2a-2c** were found to show better liquid crystallinity than γ-lactones **1a** or **1b**, exhibiting higher order smectic (S_X), smectic A (S_A), and/or chiral nematic (N^*) phase but no chiral smectic C (S_C^*) phase. Thus, each was added to Host A.[6] The electro-optical properties of the resulting mixtures are listed in Table 1. The mixture containing 5 wt% of **2a** exhibited large Ps

(7.7 nC/cm^2) but this value was about half as compared with that of *cis*-lactone **1a** (14.5 nC/cm^2) and response time was roughly doubled (235 *vs* 119 μs). Use of 10 wt% of **2a** resulted in remarkable enhancement of Ps and decrease of the response time: 26.3 nC/cm^2 and 139 μs respectively. Oxazolidinones **2b** and **2c** also showed large Ps's.

Optically active oxazolidinones reported herein are easily prepared from chiral 1,2-epoxyalkanes and found to be useful chiral dopants.



i: (*R*)-1,2-epoxyoctane, Et_3N; ii: BBr_3; iii: *n*-$C_8H_{17}OC_6H_4COCl$, pyridine.

Scheme 1.

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

Chiral dopant	(wt%)	Ps[b]/nC cm^{-2}	Response time[c]/μs	Tilt angle/deg	Twist sense[d]
1a	(5)	+14.5	119	25	left
2a	(5)	+7.7	235	21	left
2a	(10)	+26.3	139	21	left
2b	(5)	+8.2	178	21	left
2b	(10)	+20.6	121	22	left
2c	(5)	+4.8	181	18	left

a) The liquid crystal mixture was sealed in a polyimide rubbing cell of 2 μm thickness, and a square wave of 10 $V_{p\text{-}p}$/μm was applied to the cell. b) Ps was measured by the triangular wave method. c) The change of transmittance (from 0 to 90%) of light was observed. d) This was observed regarding N^* phase.

References

1) N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).

2) T. Kusumoto, A. Nakayama, K. Sato, K. Nishide, T. Hiyama, S. Takehara, T. Shoji, M. Osawa, T. Kuriyama, K. Nakamura, and T. Fujisawa, *J. Chem. Soc., Chem. Commun.*, **1991**, 311.

3) (*R*)-1,2-Epoxyoctane (ca. 90% ee) was purchased from Nippon Mining Co., Ltd.

4) Y. Iwakura and S. Izawa, *J. Org. Chem.*, **29**, 379 (1964).

5) The optical purities of **3** and **4** were estimated by HPLC (Daicel, Chiralcel OD).

6) Host A consists of 2-(4-decyloxyphenyl)-5-octylpyrimidine (21.4 wt%), 2-(4-nonyloxyphenyl)-5-octylpyrimidine (18.2 wt%), 2-(4-hexyloxyphenyl)-5-octylpyrimidine (9.6 wt%), 2-(4-nonyloxyphenyl)-5-heptylpyrimidine (12.3 wt%), 4-octylphenyl *trans*-4-heptylcyclohexanecarboxylate (8.1 wt%), 4-heptylphenyl *trans*-4-heptylcyclohexanecarboxylate (8.1 wt%), 4-octylphenyl *trans*-4-hexylcyclohexanecarboxylate (4.1 wt%), 2-(2-fluoro-4-octyloxyphenyl)-5-(4-octylphenyl)pyrimidine (7.3 wt%), 2-(2-fluoro-4-octyloxyphenyl)-5-(4-heptylphenyl)pyrimidine (7.3 wt%), 2-(2-fluoro-4-octyloxyphenyl)-5-(4-hexylphenyl)pyrimidine (3.6 wt%). The phase transition temperatures (T/°C) were Cr -3 S_C 43 S_A 65 N 77 I.

(Received June 24, 1991)