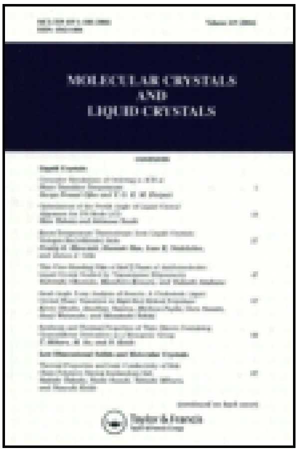

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Y. Haramoto [a] & H. Kamogawa [a]

[a] Department of Applied Chemistry, Yamanashi University, Takeda 4, Kofu, 400, Japan

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Optical Properties of New Ferroelectric Liquid Crystal Materials: (+)-4-(2-Methylbutyloxycarbonyl) 4-(5-alkyl-1,3-dioxan-2-yl)benzoate

Y. HARAMOTO and H. KAMOGAWA
Department of Applied Chemistry, Yamanashi University, Takeda 4, Kofu 400, Japan

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New ferroelectric Liquid Crystal Compounds: (+)-4-(2-Methylbutyloxycarbonyl) 4-(5-alkyl-1,3-dioxan-2-yl)benzoate were synthesized. Some physical properties of these materials were measured and compared with those of (*s*)-2-methylbutyl *p*-(*p*-decyloxybenzylideneamino)cinnamate (DOBAMBC). The principal features of these new ferroelectric liquid crystal compounds are: (1) wider temperature range of the ferroelectric liquid crystalline phase; (2) longer helical pitches; and (3) lower rotational viscosity coefficient.

Keywords: Ferroelectric liquid crystal, 1,3-dioxane, optical property

INTRODUCTION

In recent years, 2,5-disubstituted 1,3-dioxanes, 1,3-oxathianes, and 1,3-dithianes were synthesized as a new type of nematic liquid crystalline materials.[1–10] Subsequently, the basic structures of optically active liquid-crystalline compounds with 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane rings have been synthesized.[11–14]

In our previous paper,[13] the syntheses of new ferroelectric liquid-crystalline compounds with 1,3-dioxane ring was reported. In this paper, we wish to present some of the physical properties of these compounds and compare them with those of (*s*)-2-methylbutyl *p*-(*p*-decyloxybenzylideneamino)cinnamate (DOBAMBC).

RESULTS AND DISCUSSION

The compounds, (+)-4-[(2-Methylbutyloxycarbonyl)phenyl] 4-(5-alkyl-1,3-dioxane-2-yl)-benzoates were synthesized via the following route.

The phenols 2 were prepared by the esterification of *p*-hydroxybenzoic acid with (+)-2-methyl-1-butanol in the presence of an acid catalyst, using a Dean-Stark trap. It was necessary to run the reaction for 48 h to gain a sufficient yield. In the step [(1)+(2)]$\mapsto$(3), 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) was used as a base.

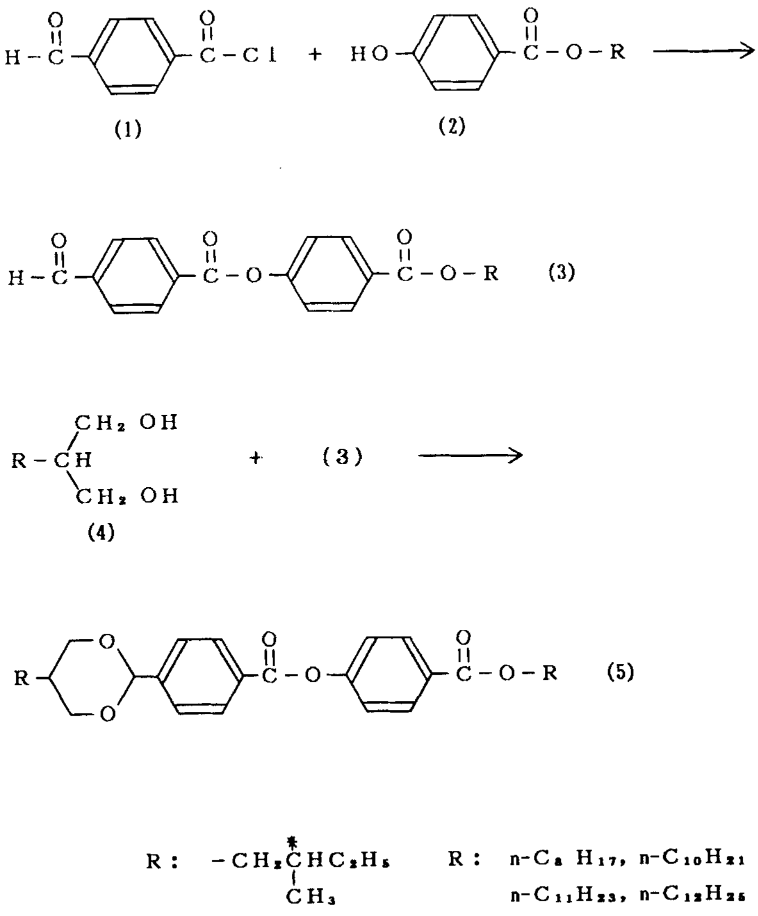


FIGURE 1

Since compounds (3) were soluble in hexane, they were extracted into this solvent. Compounds 5 were synthesized by acid catalyzed acetalization with the diol 4. Both *trans* and *cis* isomers on the 1,3-dioxane ring were produced. Therefore, this material was chromatographed on silica gel, recrystallized several times from hexane, and then chromatographed on prep T.L.C. to give the pure *trans* isomer.

Identification of *trans* isomers was made by using ^{1}H-NMR. In the NMR spectrum for the 1,3-dioxane compounds, the C-2 proton signals of the 1,3-dioxane ring for the *trans* and *cis* isomers were separated by a chemical shift of about 0.05 ppm. That is, the C-2 proton signal of the *trans* isomer absorbs at 5.50 ppm, and that of the *cis* isomer at 5.55 ppm.

Mesomorphic properties were determined using a micro melting-point apparatus equipped with polarizers and a differential scanning calorimeter (D.S.C.). Optical studies were done on an Olympus polarizing microscope in conjunction with a Mettler FP-82 hot stage and a control unit using a function generator on a Hewlett Packard 3310 B and a SONY-TECTRONICS 468 oscilloscope. The helical pitch lengths of the chiral smectic C phases were measured in thick cells (350 μm), whereas other optical data were measured in thin cells (2 μm).

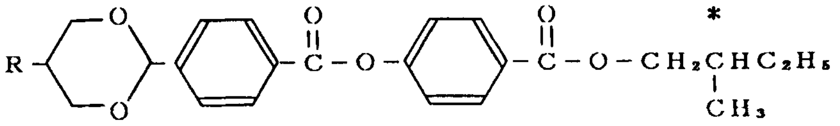
Mesomorphic properties of the synthesized compounds are given in Table I. Phase identification was done by comparing the observed textures with those found in the literature.[15,16] The transition temperatures of smectic to isotropic increase as the number of alkyl carbon atoms decrease. On the contrary, the transition temperatures of the Smectic C* to the Smectic A phase tends to decrease as the number of alykyl carbon atoms decreases. The temperature ranges of the SmC* phase are around room temperature.

Other properties of these ferroelectric liquid crystal compounds are given in Table II.

The spontaneous polarization is about 1.5 nC/cm^2. These values are smaller than those for (*s*)-2-methylbutyl *p*-(*p*-decyloxybenzylideneamino)cinnamate (DOBAMBC). The response times (Tr) of the optical transmission of these compounds were somewhat longer than those of DOBAMBC. Generally, Tr is proportional to η/Ps. (η = rotational viscosity coefficient, Ps = the strength of spontaneous polarization). The strength of spontaneous polarization (Ps) for DOBAMBC is about six times as large as those for compounds 5 and the Tr of DOBAMBC is twice as short as those of compounds 5. Therefore, η of compounds 5 must be smaller than that of DOBAMBC.

TABLE I

Mesomorphic ranges for compounds 5



	R	mesomorphic ranges (°C)[a]
5 − 1	n-C_8H_{17}	$\mathrm{C} \underset{27}{\overset{51}{\rightleftarrows}} \mathrm{SmC^*} \underset{69}{\overset{69}{\rightleftarrows}} \mathrm{SmA} \underset{141}{\overset{141}{\rightleftarrows}} \mathrm{I}$
5 − 2	n-$C_{10}H_{21}$	$\mathrm{C} \underset{14}{\overset{59}{\rightleftarrows}} \mathrm{SmC^*} \underset{93}{\overset{93}{\rightleftarrows}} \mathrm{SmA} \underset{137}{\overset{137}{\rightleftarrows}} \mathrm{I}$
5 − 3	n-$C_{11}H_{23}$	$\mathrm{C} \underset{-4}{\overset{62}{\rightleftarrows}} \mathrm{SmC^*} \underset{94}{\overset{94}{\rightleftarrows}} \mathrm{SmA} \underset{136}{\overset{136}{\rightleftarrows}} \mathrm{I}$
5 − 4	n-$C_{12}H_{25}$	$\mathrm{C} \underset{30}{\overset{66}{\rightleftarrows}} \mathrm{SmC^*} \underset{95}{\overset{95}{\rightleftarrows}} \mathrm{SmA} \underset{135}{\overset{135}{\rightleftarrows}} \mathrm{I}$

[a] C: crystal, Sm: smectic, I: isotropic.

TABLE II

Electro-optic and other relevant properties for compounds 5 and DOBAMBC

Compound R	Ps[a] (nC/cm^2)	Tr[b] (μs)	2θ[c] (°)	pitch (μm)	T_{A-C^*}[d] (°C)
5-1 n-C_8H_{17}	1.6	112	22	28	69
5-2 n-$C_{10}H_{21}$	1.1	179	20	14	93
5-3 n-$C_{11}H_{23}$	1.6	105	28	5	94
5-4 n-$C_{12}H_{25}$	1.3	61	27	14	95
DOBAMBC	9.6	51	37	4	91

[a] Ps: spontaneous polarization
[b] Tr: response time
[c] 2: tilt angle
[d] T_{A-C^*}: transition temperature of smectic A to smectic C*.

Although the Tr for compound 5-1 was measured at a temperature about 20°C lower than those for other members of compounds 5, the value was almost the same as those for others. For example, the Tr for compounds 5-1 and 5-3 are 112 and 105 μs, respectively. The Ps of these compounds are almost equal. Therefore, the rotational viscosity coefficient of 5-1 is almost the same as that of 5-3. This must mean that the initial molecular arrangements of the chiral smectic C phase which is produced from the SmA phase must resemble each other in compounds 5. They also seem to have a similar extent of η. From this initial molecular arrangements of SmC*, decreased temperature make them to the more stabilized state having a larger η. Therefore, it is thinkable that both η of compound 5-1 at 59°C and η of 5-3 at 84°C are nearly equal. The tilt angles of compounds 5 are narrower than that for DOBAMBC.

Helical pitches of the SmC* phases for compounds 5 are longer than that of DOBAMBC. The principal features of these new ferroelectric liquid crystal compounds are: (1) wider ferroelectric liquid crystal phase range; (2) longer helical pitches; and (3) lower rotational viscosity coefficient.

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References

1. Y. Haramoto and H. Kamogawa, *J. Chem. Soc., Chem. Commun.*, **75**, (1983).
2. Y. Haramoto, A. Nobe and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **57**, 1966 (1984).
3. Y. Haramoto, K. Akazawa and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **57**, 3173 (1984).
4. Y. Haramoto and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **58**, 477 (1985).
5. Y. Haramoto and H. Kamogawa, *Chem. Lett.*, **79**, (1985).
6. Y. Haramoto and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **58**, 1821 (1985).
7. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **131**, 101 (1985).
8. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **131**, 201 (1985).

9. Y. Haramoto and M. Sano, and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **59**, 1337 (1986).
10. D. Demus and H. Zaschke, (to V.E.W. Kombinat Microelectronic), Japan Pat. Appl. No. 54-160916, Dec. (1979).
11. Y. Haramoto, Y. Tomita and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **59**, 3877 (1986).
12. Y. Haramoto and H. Kamogawa, *Chem. Lett.*, **755** (1987).
13. Y. Haramoto and K. Kawashima, and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **61**, 431 (1988).
14. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst. Lett.*, **5**, No. 4, 117 (1988).
15. D. Demus and L. Richter, "Textures of Liquid Crystals," Verlag Chemie, Weinheim, New York (1978).
16. G. W. Gray and J. W. Goodby, "Smectic Liquid Crystals Textures and Structures," Heyden & Son Inc., Philadelphia (1984).