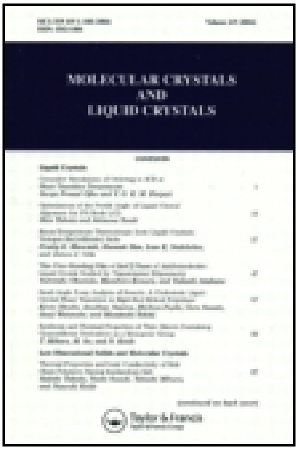


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

New Liquid Crystal Compounds: (+)-4-Alkoxycarbonylphenyl-4-[5-(2-methylbutyl)-1,3-dioxan-2-yl]benzoate

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

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

To cite this article: Y. Haramoto & H. Kamogawa (1991): New Liquid Crystal Compounds: (+)-4-Alkoxycarbonylphenyl-4-[5-(2-methylbutyl)-1,3-dioxan-2-yl]benzoate, Molecular Crystals and Liquid Crystals, 201:1, 161-166

To link to this article: http://dx.doi.org/10.1080/00268949108038645

Mol. Cryst. Liq. Cryst., 1991, Vol. 201, pp. 161–166
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

New Liquid Crystal Compounds: (+)-4-Alkoxycarbonylphenyl-4-[5-(2-methylbutyl)-1,3-dioxan-2-yl]benzoate

Y. HARAMOTO and H. KAMOGAWA

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

(Received September 14, 1990; in final form February 8, 1991)

New Liquid Crystal Compounds: (+)-4-Alkoxycarbonylphenyl-4-[5-(2-methylbutyl)-1,3-dioxan-2-yl]-benzoates (**5**) were synthesized.

The mesomorphic behavior of these compounds is compared with that of (+)-4-(2-methylbutyloxycarbonyl)phenyl 4-(5-alkyl-1,3-dioxan-2-yl)benzoates (**6**).

Compounds **5** exhibited cholesteric and smectic A phases and their transition temperatures to the isotropic state were lower than those of corresponding compounds **6**. These properties are supposed to originate in the greater molecular widths of the formers caused by 2-methylbutyl group at the 5 position of the 1,3-dioxane ring. Though compounds **6** exhibit the ferroelectric behavior, compounds **5** don't. This might mean that a short distance between the carbonyl and chiral group is one factor for the appearance of the SmC* phase.

INTRODUCTION

In recent years, 2,5-disubstituted 1,3-dioxanes, 1,3-oxathianes, and 1,3-dithianes were synthesized as new types of nematic liquid crystal materials.[1–10]

More recently, optically active liquid crystal compounds with 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane rings have been synthesized with the object of attaining ferroelectric characteristic.[11–18] In our previous paper[13,15] the syntheses and optical properties of new ferroelectric liquid crystal compounds: (+)-4-(2-methyl-butyl-oxycarbonyl)-phenyl 4-(5-alkyl-1,3-dioxan-2-yl)-benzoates (**6**) have been reported. The title compounds have the chemical structure in which the two terminal group of compounds **6** are exchanged. In this study, we wish to report the synthesis of the title compounds and comparison of the mesomorphic behavior between these two materials.

RESULT AND DISCUSSION

The compounds, (+)-3-alkoxycarbonylphenyl 4-[5-(2-methylbutyl)-1,3-dioxan-2-yl]benzoate (**5**) were synthesized by the following route.

Compounds **2** were obtained by the esterification of *p*-hydroxybenzoic acid with *n*-alkylalcohol in the presence of an acid catalyst using a Dean-Stark trap. About 48 hours were necessary for the reaction time to gain a sufficient yield.

In the step 1, 2, → 3, 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) was used as a base. Compound **3** could be purified by recrystallization from hexane. If purity was not enough to satisfy, it was further purified by column chromatography.

Compounds **5** were synthesized by the ring formation reaction of compounds **4** with **3**.

The products **5** were purified by column chromatography, followed by recrys-

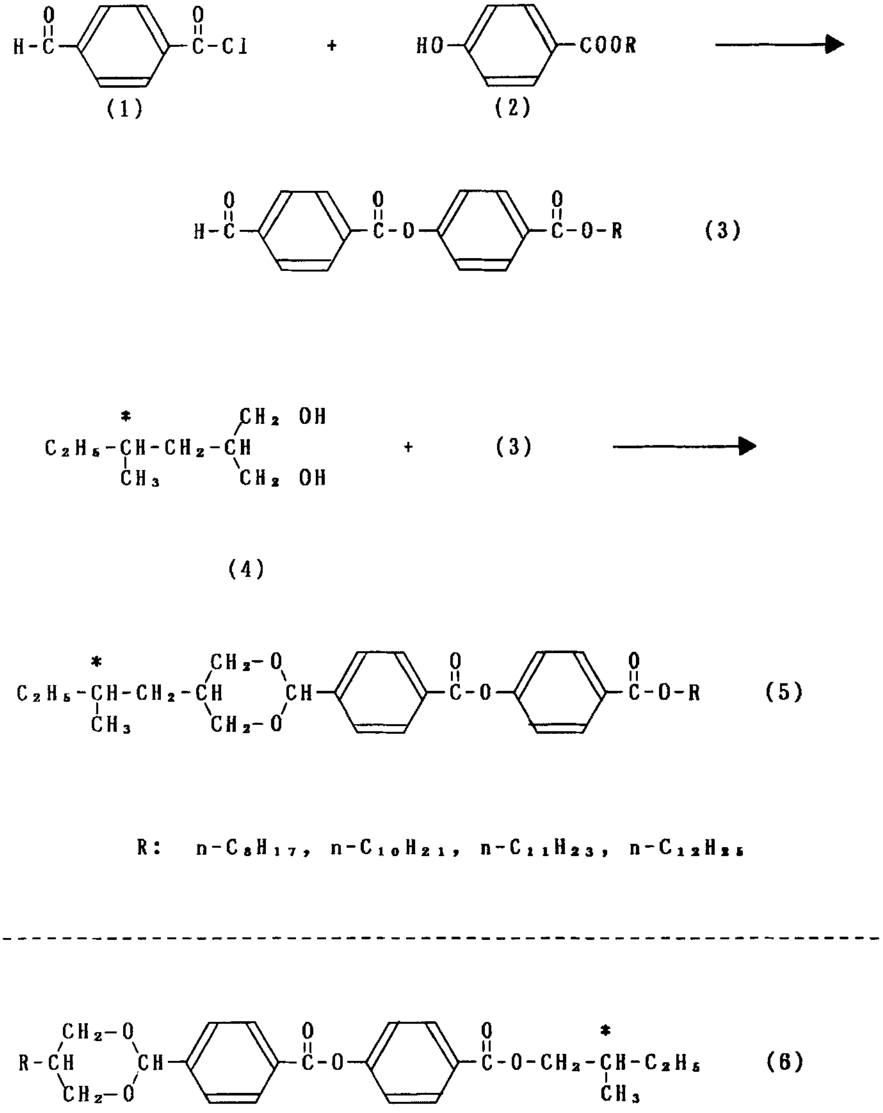


FIGURE 1

tallizations from hexane. Since each product obtained as a white powder contained about 10–20% of cis isomer, it was purified by the preparative thin-layer chromatography to obtain pure trans isomer. In the ^{1}H-NMR data for compounds **5**, the C-2 proton signals of the 1,3-dioxane ring for the trans and cis isomers appeared at $\delta = 5.50$ and 5.55, respectively. Therefore, the removal of cis isomer by purification was checked by the disappearance of the cis isomer's peak.

Measurements of the mesomorphic range and assignment of the mesophase were carried out by means of a micro melting point apparatus equipped with polarizers. Phase identification was made by comparing the observed textures with those in the literature.[19,20] Mesomorphic transition temperatures for compounds **5** and the corresponding compounds **6** are given in Table I.

Though the compounds **6** exhibited smectic A phases on cooling the isotropic state, the compounds **5** exhibited the cholesteric phases. In compounds **5**, the 2-methylbutyl group is combined at the **5** position of the 1,3-dioxane ring, so that 2-methylbutyl group and 1,3-dioxane ring are considered to hinder sterically each other, judging from the result obtained with the molecular model.

This must make the molecular width of compounds **5** greater than that of compounds **6**. Therefore, lateral molecular interactions of compounds **5** may become weaker than those of compounds **6**, so that smectic phases did not appear. The transition temperatures to the isotropic state for compounds **5** are lower than those for compounds **6**. This also may originate in the greater molecular width of the compounds **5**.

Though compounds **6** exhibited the SmC* phase, compounds **5** did not. The latter have the chemical structures in which the two terminal substituents of the formers are exchanged. Namely, in compounds **6**, the carbonyl group is close to the chiral group, whereas, in compounds **5**, they are situated far apart each other. Therefore, in this case, the near-by existence of the chiral group and carbonyl group seems to be necessary for the appearance of the SmC* phase.

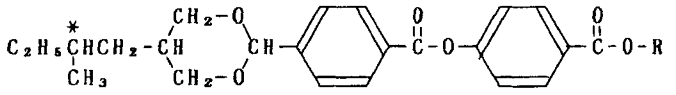
EXPERIMENTAL

IR, ^{1}H-NMR, and mass spectra were obtained with a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi M-80 B spectrometer, respectively. Elemental analyses were carried out with a Perkin-Elmer 250 instrument. Transition temperatures and mesomorphic phases were determined by means of a Mitamura Riken micro melting point apparatus equipped with polarizers and a Rigaku Denki DSC CN8059Li, CN8208A2, respectively.

4-Alkoxycarbonylphenyl 4'-formylbenzoates (**3**). To a solution of compound (**2**) (0.015 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.015 mol) in anhyd. N,N-dimethyl-formamide (30 ml) was added (**1**) (0.015 mol) in a nitrogen atmosphere, followed by stirring at 40°C for 18 h. The solution was poured into ice water and shaken twice with ether (each 200 ml). The extract was washed with cold 5% aq. HCl, dried over anhyd. Na_2SO_4, and evaporated in vacuo at 40°C. The residue was extracted into hexane, and the extract concentrated under reduced pressure. The residue was purified by recrystallization from hexane, then by column chromatography. The white powder was obtained in a 40–50% yield.

TABLE I

Transition temperatures for the compounds **5** and the corresponding compounds **6**



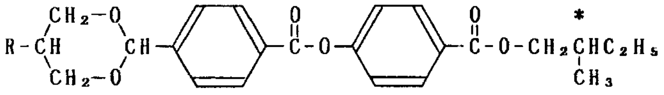
(5)

	R	TRANSITION TEMPERATURE °C a)
5-1	C_8H_{17}	$\begin{tikzcd} C \arrow[rr, "74"] & & I \arrow[dl, shift left, "66"] \\ & cho \arrow[ul, "50"] \arrow[ur, shift left] & \end{tikzcd}$
5-2	$C_{10}H_{21}$	$\begin{tikzcd} C \arrow[r, shift left, "67"] & cho \arrow[l, shift left, "48"] \arrow[r, shift left, "81"] & I \arrow[l, shift left, "81"] \end{tikzcd}$
5-3	$C_{11}H_{23}$	$\begin{tikzcd} C \arrow[r, shift left, "68"] & cho \arrow[l, shift left, "51"] \arrow[r, shift left, "76"] & I \arrow[l, shift left, "76"] \end{tikzcd}$
5-4	$C_{12}H_{25}$	$\begin{tikzcd} C \arrow[r, "68"] & I \arrow[d, shift left, "66"] \\ SmA \arrow[u, "48"] \arrow[r, shift left] & cho \arrow[u, shift left] \arrow[l, shift left, "61"] \end{tikzcd}$

mp: R = C_8H_{17}; 65–66°C, $C_{10}H_{21}$; 71–72°C, $C_{11}H_{23}$; 79–81°C, $C_{12}H_{25}$; 96–97°C.
IR ($CHCl_3$) 2800–3000 (alkyl), 1740, 1680 (C=O), 1600 (Ar) cm^{-1}.
^{1}H-NMR ($CDCl_3$) δ 0.6–2.1 (*m*, OCH_2 *R*), 4.3 (*t*, 2H, OCH_2), 7.2–8.5 (*m*, 8H, ArH), 10.2 (*s*, 1H, CHO).

(+)-4'-Alkoxycarbonylphenyl 4-[5-(2-methylbutyl)-1,3-dioxan-2-yl]-benzoate (**5**). To a solution of compounds (**4**) (0.004 mol) and (**3**) (0.004 mol) in anhyd. $CHCl_3$ (200 ml), cooled in an ice bath were added $BF_3(C_2H_5)_2O$ (0.5 g) and molecular sieves (3A, 1/15; 3 g). The mixture was stirred at 0–5°C for 8 h and then at 20–25°C for 10 h. The solution was washed with 10% aq. $NaHCO_3$ (400 ml), dried over anhyd. Na_2SO_4, and concentrated under reduced pressure at 40°C. The crude product was purified by column chromatography and recrystallizations from hex-

TABLE I (*continued*)



(6)

	R	TRANSITION TEMPERATURE °C [a]
6-1	C_8H_{17}	$C \underset{27}{\overset{51}{\rightleftarrows}} SmC^* \underset{69}{\overset{69}{\rightleftarrows}} SmA \underset{141}{\overset{141}{\rightleftarrows}} I$
6-2	$C_{10}H_{21}$	$C \underset{14}{\overset{59}{\rightleftarrows}} SmC^* \underset{93}{\overset{93}{\rightleftarrows}} SmA \underset{137}{\overset{137}{\rightleftarrows}} I$
6-3	$C_{11}H_{23}$	$C \underset{-4}{\overset{62}{\rightleftarrows}} SmC^* \underset{94}{\overset{94}{\rightleftarrows}} SmA \underset{136}{\overset{136}{\rightleftarrows}} I$
6-4	$C_{12}H_{25}$	$C \underset{30}{\overset{66}{\rightleftarrows}} SmC^* \underset{95}{\overset{95}{\rightleftarrows}} SmA \underset{135}{\overset{135}{\rightleftarrows}} I$

[a] C: Crystal, Cho: Cholesteric, Sm: Smectic, I: Isotropic.

ane, followed by the preparative T.L.C. (silica gel) to remove cis isomer. A white powder was obtained.

IR ($CHCl_3$) 2800–3000 (alkyl), 1710 (C=O), 1600 (Ar), 1110 (ether) cm^{-1}.

^{1}H-NMR ($CDCl_3$) δ 0.6–2.1 (*m*, R′CH, OCH_2 *R*), 3.3–4.5 (*m*, 6H, OCH_2), 5.50 (*s*, 1H, OCH), 7.2–8.4 (*m*, 8H, ArH).

5–1: Yield, 35%. Found: C, 72.83; H, 7.79%. Calc for $C_{30}H_{42}O_5$: C, 72.91; H, 8.29%. Mass 510 (M^+).

5–2: Yield, 23%. Found: C, 74.25; H, 8.59%. Calc for $C_{33}H_{46}O_6$: C, 73.57; H, 8.61%. Mass 538 (M^+).

5–3: Yield, 27%. Found: C, 74.39; H, 8.69%. Calc for $C_{34}H_{48}O_6$: C, 73.88; H, 8.75%. Mass 552 (M^+).

5–4: Yield, 22%. Found: C, 75.11; H, 8.78%. Calc for $C_{35}H_{50}O_6$: C, 74.17; H, 8.89%. Mass 566 (M^+).

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, M. Sano and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **59**, 1337 (1986).
10. D. Demus and H. Zaschke, (to V.E.W. Kombinat Mikroelectronic), 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, K. Kawashima and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **61**, 431 (1988).
14. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst. Lett.*, **5**, 117 (1988).
15. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **173**, 89 (1989).
16. Y. Haramoto and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **63**, 156 (1990).
17. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **182B**, 195 (1990).
18. Y. Haramoto and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, in press.
19. D. Demus and L. Richter, "Textures of Liquid Crystals," Verlag Chemie, Weinheim, New York (1978).
20. G. W. Gray and J. W. Goodby, "Smectic Liquid Crystals Textures and Structures," Leonard Hill, Glasgow and London (1984).