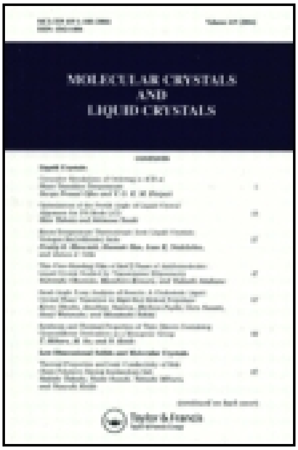

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New Liquid Crystal Materials With Chiral 2-Methylbutyl Group: (+)-2-Methylbutyl 4-(5-alkyl-1,3-dioxan-2-yl) Cinnamate and Benzoate

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New Liquid Crystal Materials with Chiral 2-Methylbutyl Group: (+)-2-Methylbutyl 4-(5-alkyl-1,3-dioxan-2-yl) Cinnamate and Benzoate

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New liquid crystal materials with chiral 2-methylbutyl group: (+)-2-methylbutyl 4-(5-alkyl-1,3-dioxan-2-yl) cinnamate and benzoate were synthesized. The mesomorphic behavior of these compounds were measured, and compared with those of the corresponding 1,3-oxathiane and 1,3-dithiane compounds. Though compounds (7) exhibited a liquid crystal phase, compounds (8) did not. The difference in the chemical structure between (7) and (8) is the existence of CH═CH in the former. So that, CH═CH seems to contribute to exhibit the liquid crystal phase in compound (7). Transition temperatures of the isotropic to the liquid crystal phase decrease in the order: 1,3-dithiane > 1,3-dioxane > 1,3-oxathiane. This result seems to originate in wider molecular width of 1,3-oxathiane compounds and larger dispersion force of 1,3-dithianes.

Keywords: 1,3-dioxane, phase transition

INTRODUCTION

In recent years, we have synthesized new nematic 2,5-disubstituted 1,3-dioxanes, as well as 1,3-oxathianes and 1,3-dithianes as new types of nematic liquid crystal materials.[1-10] Subsequently, the basic structures of optically active liquid-crystal compounds with the 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane ring have also been synthesized.[11-21]

In a previous paper,[11] the syntheses and the mesomorphic behavior of (+)-2-methylbutyl 4-(5-alkyl-1,3-oxathian-2-yl) cinnamates and benzoates and the corresponding 1,3-dithiane type compounds were reported. This paper is related to the corresponding 1,3-dioxane type liquid crystal materials.

RESULTS AND DISCUSSION

The compounds, (+)-2-methylbutyl 4-(5-alkyl-1,3-dioxane-2-yl) cinnamates (7) and benzoates (8) were synthesized via the following route.

As, in the acetalization step, trans and cis isomers were produced which differed at the C5 position of the 1,3-dioxane ring, repeated recrystallizations were required to gain trans isomers. In case trans pure isomers could not be obtained by recrystallizations, a separative TLC (hexane:ether = 2:1) was used. In ^{1}H-NMR of compounds (7) C-2 proton signals of trans and cis isomer appear at $\delta = 5.50$ and 5.55, respectively. (Compounds 8: trans = 5.45 ppm, cis = 5.50 ppm) Therefore, the removal of cis isomer can be checked by the disappearance of the cis isomer's peak.

Measurement of transition temperatures and assignment of the mesophases 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.[22,23] Phase transition temperatures for compounds (7) and (8) and the corresponding 1,3-oxathiane and dithiane compounds are given in the Table I.

Though compounds (7) exhibited the liquid crystal phase, compounds (8) did not. The difference in the chemical structure between (7) and (8) is the existence of CH═CH in (7). That is, the appearence of liquid crystal phase in compounds (7) seems to originate in the existence of CH═CH. The existence of CH═CH seems to contribute to improve the coplanar character in compounds (7). On the other hand, the compound (8′) which has the linear alkyl chain instead of 2-methylbutyl group exhibits a liquid crystal phase. Judging from a molecular model, the width of molecule is decided by the width of core. Therefore, from this point of view molecular width of 8 and 8′ are nearly equal. But the result indicates the width of terminal alkyl part affected to the appearance of liquid crystal phase. In this case, though molecular width are decided principally by the core width, the difference of width at the terminal alkyl part affected to the appearance of liquid crystal phase.

This seem to imply that the narrower width of terminal alkyl part is favorable to exhibit the liquid crystal phase. Therefore, these two factors, i.e., coplanar character and narrower width of terminal alkyl part seem to be necessary to exhibit a liquid crystal phase in compounds (8).

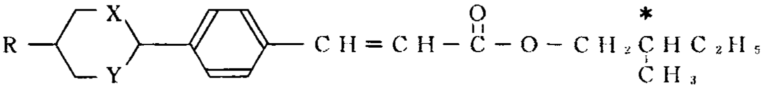
Transition temperatures of the isotropic to the liquid crystal state decrease in the order: 1,3-dithiane > 1,3-dioxane > 1,3-oxathiane. It is said generally that the transition temperature of the isotropic to the liquid crystal state is affected by two factors: molecular width and dispersion force.[24,25] The 1,3-oxathiane compounds are bent at the 1,3-oxathiane ring, caused by a difference in the atomic size between sulfur and oxygen. So that the molecular width of 1,3-oxathiane are wider than those for the corresponding 1,3-dioxane or 1,3-dithiane compounds. Lower transition temperatures of 1,3-oxathiane compounds seem to originate in this effect. The 1,3-dithiane compounds have two sulfur atoms having larger dispersion force. Higher transition temperatures of 1,3-dithiane compounds seem to originate in this effect.

EXPERIMENTAL

IR, ^{1}H-NMR, and mass spectra were obtained with a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi M-80B spectrometer, respec-

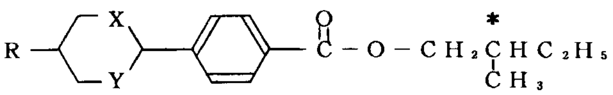
TABLE I

Transition temperatures for compounds 7, 8, 8′, 9, 10, 11, and 12



(7, 9, 10)

	R	X	Y	TRANSITION TEMPERATURES (°C) [a]
7-1	C_8H_{17}	O	O	C $\underset{57}{\overset{67}{\rightleftarrows}}$ SmA $\underset{82}{\overset{82}{\rightleftarrows}}$ I
7-2	$C_{10}H_{21}$	O	O	C $\underset{21}{\overset{45}{\rightleftarrows}}$ SmA $\underset{77}{\overset{77}{\rightleftarrows}}$ I
7-3	$C_{11}H_{23}$	O	O	C $\underset{28}{\overset{58}{\rightleftarrows}}$ SmA $\underset{76}{\overset{76}{\rightleftarrows}}$ I
7-4	$C_{12}H_{25}$	O	O	C $\underset{53}{\overset{67}{\rightleftarrows}}$ SmA $\underset{80}{\overset{80}{\rightleftarrows}}$ I
9-1	$C_{10}H_{21}$	S	O	C $\underset{-50}{\overset{35}{\rightleftarrows}}$ SmA $\underset{71}{\overset{71}{\rightleftarrows}}$ I
9-2	$C_{11}H_{23}$	S	O	C $\underset{-19}{\overset{50}{\rightleftarrows}}$ SmA $\underset{74}{\overset{74}{\rightleftarrows}}$ I
10-1	$C_{10}H_{21}$	S	S	C $\underset{16}{\overset{53}{\rightleftarrows}}$ SmA $\underset{88}{\overset{88}{\rightleftarrows}}$ I
10-2	$C_{11}H_{23}$	S	S	C $\underset{18}{\overset{54}{\rightleftarrows}}$ SmA $\underset{82}{\overset{82}{\rightleftarrows}}$ I

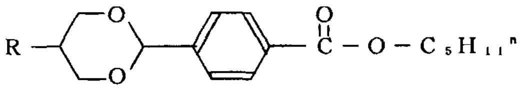


(8, 11, 12)

	R	X	Y	TRANSITION TEMPERATURES (°C) [a]
8-1	C_7H_{15}	O	O	C $\underset{52}{\overset{58}{\rightleftarrows}}$ I
8-2	C_8H_{17}	O	O	C $\underset{43}{\overset{52}{\rightleftarrows}}$ I
8-3	C_9H_{19}	O	O	C $\underset{40}{\overset{44}{\rightleftarrows}}$ I

TABLE I (*Continued*)

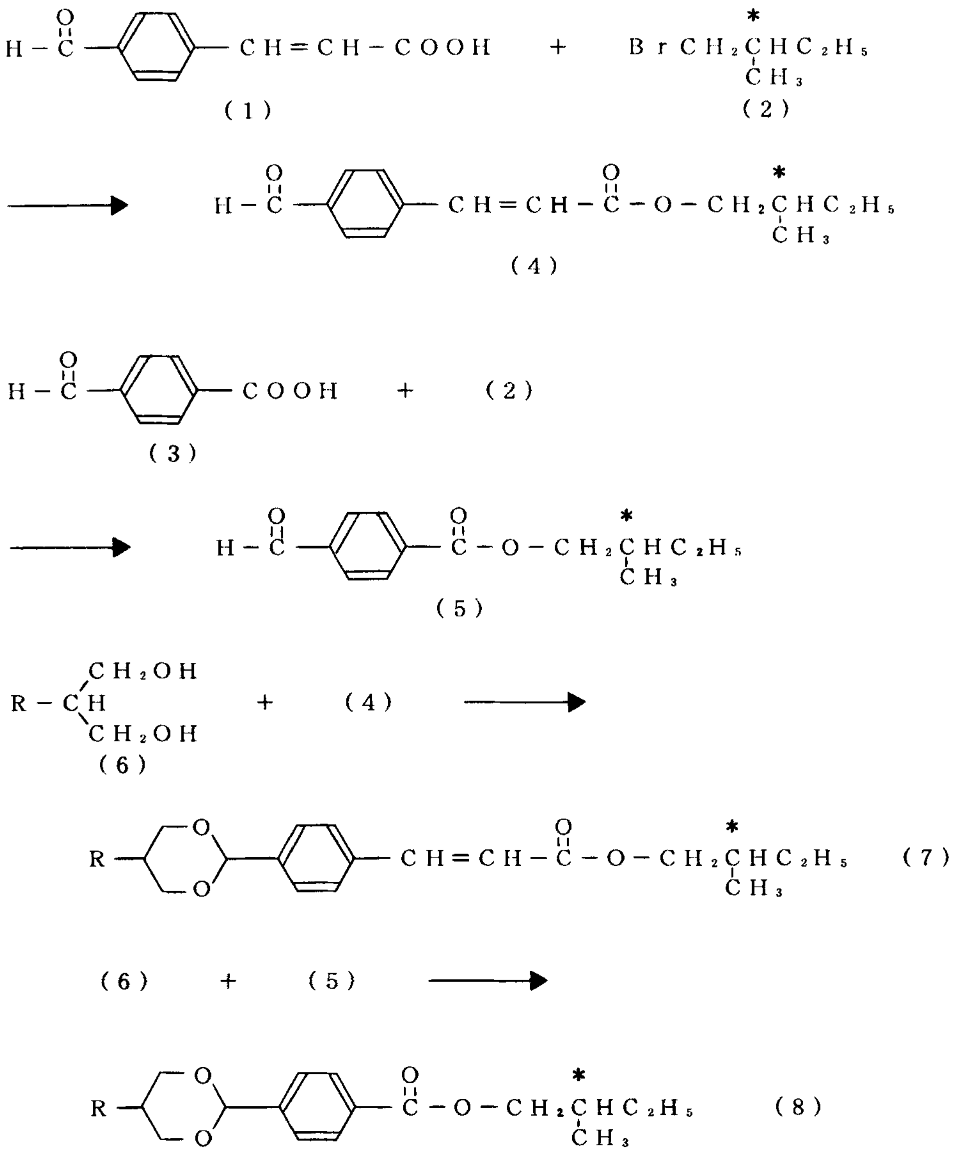
8 − 4	$C_{10}H_{21}$	O	O	$C \underset{45}{\overset{49}{\rightleftarrows}} I$
8 − 5	$C_{11}H_{23}$	O	O	$C \underset{52}{\overset{56}{\rightleftarrows}} I$
8 − 6	$C_{12}H_{25}$	O	O	$C \underset{53}{\overset{57}{\rightleftarrows}} I$
11 − 1	$C_{10}H_{21}$	S	O	$C \underset{11}{\overset{35}{\rightleftarrows}} I$
11 − 2	$C_{11}H_{23}$	S	O	$C \underset{32}{\overset{45}{\rightleftarrows}} I$
11 − 3	$C_{12}H_{25}$	S	O	$C \underset{28}{\overset{37}{\rightleftarrows}} I$
12 − 1	$C_{10}H_{21}$	S	S	$\begin{tikzcd} C \arrow[rr, "46"] & & I \arrow[dl, shift left, "23"] \\ & SmA \arrow[ul, "-15"] \arrow[ur, shift left] & \end{tikzcd}$
12 − 2	$C_{11}H_{23}$	S	S	$\begin{tikzcd} C \arrow[rr, "44"] & & I \arrow[dl, shift left, "28"] \\ & SmA \arrow[ul, "18"] \arrow[ur, shift left] & \end{tikzcd}$
12 − 3	$C_{12}H_{25}$	S	S	$\begin{tikzcd} C \arrow[rr, "56"] & & I \arrow[dl, shift left, "54"] \\ & SmA \arrow[ul, "16"] \arrow[ur, shift left] & \end{tikzcd}$



(8')

	R	TRANSITION TEMPERATURES (°C) [a]
8' − 1	$C_{10}H_{21}$	$\begin{tikzcd} C \arrow[rr, "63"] & & I \arrow[dl, shift left, "47"] \\ & N \arrow[ul, "41"] \arrow[ur, shift left] & \end{tikzcd}$

a) C: Crystal, I: Isotropic,
Sm: Smectic, N: Nematic.



R : $n\text{-}C_7H_{15}$, $n\text{-}C_8H_{16}$, $n\text{-}C_9H_{19}$, $n\text{-}C_{10}H_{21}$, $n\text{-}C_{11}H_{23}$, $n\text{-}C_{12}H_{25}$.

FIGURE 1

tively. 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 Rigaku Denki DSC CN8059LI, CN8208A2, respectively.

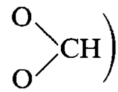
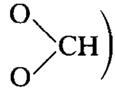
(+)-2-Methylbutyl *p*-formylcinnamate (4)

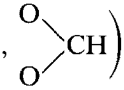
A solution of 4-formylcinnamic acid (0.03 mol) and 1,8-diazabicycro-[5.4.0]-undec-7-ene (0.03 mol) and (+)-2-methylbutylbromide (0.03 mol) in anhyd. DMF (60 ml) was stirred at 80 ~ 90°C for 18 h under a nitrogen atmosphere. The solution was poured into ice water and extracted twice with ether (each 200 ml). The extract was washed with cold 2% aq. HCl, dried over anhyd. Na_2SO_4, and evaporated in vacuo at 30°C. The residue was dissolved in hexane (30 ml) and filtered. The filtrate was evaporated in vacuo at 40°C. A transparent liquid was obtained in 70 ~ 80% yields.

IR ($CHCl_3$) 3000 ~ 2800 (alkyl), 2730 (CHO), 1720 ~ 1680 (C=O) cm^{-1}.
^{1}H-NMR ($CDCl_3$) δ = 0.5–2.0 (m, 9H, $OCH_2\underline{R''}$), 4.1 (d, 2H, OCH_2), 6.6 (d, 1H, =CH), 7.5 ~ 8.1 (q, 5H, CH=, ArH), 10.1 (s, 1H, CHO).
(+)-2-Methlybutyl *p*-formylbenzoate (5)
IR ($CHCl_3$) 3000 ~ 2800 (alkyl), 2730 (CHO), 1720 ~ 1680 (C=O) cm^{-1}.
^{1}H-NMR ($CDCl_3$) δ = 0.6 ~ 2.1 (m, 9H, $OCH_2\underline{R''}$), 4.25 (d, 2H, OCH_2), 8.2 (q, 4H, ArH), 10.2 (s, 1H, CHO).
Butyl *p*-formylbenzoate (5′)
IR ($CHCl_3$) 3000 ~ 2800 (alkyl), 2730 (CHO), 1720 ~ 1680 (C=O) cm^{-1}.
^{1}H-NMR ($CDCl_3$) δ = 0.7 ~ 2.1 (m, 9H, $OCH_2\underline{C_4H_9}$), 4.4 (t, 2H, OCH_2), 8.1 (q, 4H, ArH), 10.2 (s, 1H, CHO).

Alkyl *p*-(5-alkyl-1,3-dioxan-2-yl) cinnamate or benzoate (7, 8)

To a solution of compound (6) (0.004 mol) and 4-substituted benzaldehyde (0.004 mol) in anhyd. $CHCl_3$ (200 ml) cooled in an ice bath were added $BF_3\cdot(C_2H_5)_2O$ (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°C for 16 h. The solution was washed with 10% aq. $NaHCO_3$ (400 ml), then with water (400 ml), dried over anhyd. Na_2SO_4, and evaporated in vacuo at 40°C. The crude product was purified by column chromatography and recrystallizations from hexane. Several compounds in which trans isomers could not be isolated were subjected to a separative T.L.C. to isolate trans isomers.

(+)-2-Methylbutyl *p*-(5-alkyl-1,3-dioxan-2-yl) cinnamate (7)
IR ($CHCl_3$) 3000 ~ 2800 (alkyl), 1710 (C=O), 1600 (Ar) cm^{-1}.
^{1}H-NMR ($CDCl_3$) δ = 0.5 ~ 2.2 (m, $\underline{R—CH}$, OCH_2 $\underline{C_4H_9}$), 3.3 ~ 4.5 (m, 6H, CH_2O), 5.5 (s, 1H,  $\begin{matrix}\text{O}\\ \text{O}\end{matrix}\!\!>\!\text{CH}$), 6.5 (d, 1H, =CH), 7.6 (s, 4H, ArH), 7.75 (d, 1H, CH=).
(+)-2-Methylbutyl *p*-(5-alkyl-1,3-dioxan-2-yl) benzoate (8)
IR ($CHCl_3$) 3000 ~ 2800 (alkykl), 1710 (C=O), 1600 (Ar) cm^{-1}.
^{1}H-NMR ($CDCl_3$) δ = 0.7 ~ 2.1 (m, $\underline{R—CH}$, $OCH_2\underline{C_4H_9}$), 3.3 ~ 4.5 (m, 6H, CH_2O), 5.45 (s, 1H,  $\begin{matrix}\text{O}\\ \text{O}\end{matrix}\!\!>\!\text{CH}$), 7.4 ~ 8.2 (q, 4H, ArH).
Butyl *p*-(5-decyl-1,3-dioxan-2-yl) benzoate (8′)
IR ($CHCl_3$) 3000 ~ 2800 (alkyl), 1710 (C=O), 1600 (Ar) cm^{-1}.

^{1}H-NMR ($CDCl_3$) δ = 0.7 ~ 2.1 (m, 31H, $\underline{C_{10}H_{21}\text{—}CH}$, $OCH_2\underline{C_4H_9}$), 3.3 ~ 4.5 (m, 6H, CH_2O), 5.45  $\left(s, 1H, \begin{matrix} O \diagdown \\ \rangle CH \\ O \diagup \end{matrix}\right)$, 7.4 ~ 8.2 (q, 4H, ArH).

7-1: Yield, 30%. Found: C, 75.23; H, 9.64%. Calcd for $C_{26}H_{40}O_4$: C, 74.96; H, 9.68%. Mass 416 (M^+).

7-2: Yield, 28%. Found: C, 75.66; H, 9.97%. Calcd for $C_{28}H_{44}O_4$: C, 75.63; H, 9.97%. Mass 444 (M^+).

7-3: Yield, 33%. Found: C, 76.26; H, 10.37%. Calcd for $C_{29}H_{46}O_4$: C, 75.94; H, 10.11%. Mass 458 (M^+).

7-4: Yield, 37%. Found: C, 76.73; H, 10.17%. Calcd for $C_{30}H_{48}O_4$: C, 76.22; H, 10.24%. Mass 472 (M^+).

8-1: Yield, 40%. Found: C, 73.76; H, 9.81%. Calcd for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64%. Mass 376 (M^+).

8-2: Yield, 32%. Found: C, 73.60; H, 9.83%. Calcd for $C_{24}H_{38}O_4$: C, 73.80; H, 9.81%. Mass 390 (M^+).

8-3: Yield, 31%. Found: C, 74.22; H, 9.97%. Calcd for $C_{25}H_{40}O_4$: C, 74.21; H, 9.97%. Mass 404 (M^+).

8-4: Yield, 36%. Found: C, 73.89; H, 10.21%. Calcd for $C_{26}H_{42}O_4$: C, 74.60; H, 10.11%. Mass 418 (M^+).

8-5: Yield, 35%. Found: C, 74.89; H, 10.26%. Calcd for $C_{27}H_{44}O_4$: C, 74.95; H, 10.25%. Mass 432 (M^+).

8-6: Yield, 34%. Found: C, 75.81; H, 10.31%. Calcd for $C_{28}H_{46}O_4$: C, 75.29; H, 10.38%. Mass 446 (M^+).

8′-1: Yield, 36%. Found: C, 74.08; H, 10.18%. Calcd for $C_{26}H_{42}O_4$: C, 74.60; H, 10.11%. Mass 418 (M^+).

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