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Phase Transition of (+)-Alkyl *p*-[5-(2-Methylbutyl)-1,3-Dioxan-2-yl]-Cinnamate and the Corresponding 1,3-Oxathiane and 1,3-Dithiane Compounds

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In our search for new ferroelectric liquid crystal compounds (+)-Alkyl-*p*-[5-(2-methylbutyl)-1,3-dioxan-2-yl]cinnamates (8), (+)-Alkyl *p*-[5-(2-methylbutyl)-1,3-oxathian-2-yl]cinnamates (9), and (+)-Alkyl *p*-[5-(2-methylbutyl)-1, 3-dithian-2-yl]cinnamates (11) were synthesized, their transition temperatures determined and compared with those for (+)-2-methylbutyl 4-(5-alkyl-1,3-dioxan-2-yl)cinnamates (11), (+)-2-methylbutyl-4-(5-alkyl-1,3-oxathian-2-yl)cinnamates (12), and (+)-2-methylbutyl 4-(5-alkyl-1,3-dithian-2-yl)cinnamates (13). Compounds (8), (9), (10) have the two terminal substituents of (11), (12), (13) exchanged. Though compounds (11), (12), (13) exhibited a SmA phase, compounds (8), (9), (10) did not show any liquid crystal phases. To better understand the reason for this result, decyl *p*-(5-pentyl-1,3-dioxan-2-yl)cinnamate (14-1), decyl *p*-(5-pentyl-1,3-oxathian-2-yl)cinnamate (14-2) and decyl *p*-(5-pentyl-1,3-dithian-2-yl)cinnamate (14-3) were synthesized. These compounds have a normal pentyl group instead of the bulky 2-methyl-butyl group of compounds (8), (9), (10). All these compounds exhibited a nematic liquid crystal phase. In compounds (8), (9), (10), the 2-methylbutyl group is attached to the heterocyclic ring directly. This causes more steric hindrance between the terminal chain and the ring which increases the molecular width of these molecules giving a structure which is less favorable for forming liquid crystal phases.

Keywords: 1,3-dioxane, 1,3-oxathiane, 1,3-dithiane, phase transition, liquid crystal

1. INTRODUCTION

Various derivatives of 2,5-disubstituted-1,3-dioxanes, -1,3-oxathianes, and 1,3-dithianes have been reported to have nematic liquid crystal phases of interest as display materials.[1–11] More recently, ferroelectric liquid crystal materials have been of interest as display materials because of their faster response speed. Accordingly, various optically active liquid crystal materials with the 1,3-dioxane, 1,3-oxathiane, or 1,3-dithiane ring have been synthesized.[12–23] In a previous paper,[12] the syntheses and the mesomorphic behavior of (+)-2-methylbutyl 4-(5-alkyl-1,3-dioxan-2-yl)cinnamates, (+)-2-methylbutyl 4-(5-alkyl-1,3-oxathian-2-yl)cinnamates, and (+)-2-methylbutyl 4-(5-alkyl-1,3-dithian-2-yl)cinnamates were reported. In this paper,

we wish to report the synthesis and mesomorphic properties for the compounds in which the two terminal substituents of these compounds are exchanged.

2. RESULTS AND DISCUSSION

The cinnamates containing 1,3-dioxane (8), 1,3-oxathiane (9), and 1,3-dithiane (10) rings were synthesized via the following route shown in Figure 1.

The diols (1) were synthesized by treating the appropriate bromide with diethylmalonate. In the bromination of these diols, both the mono and dibromides were produced. This mixture was used for the syntheses of the thiols (4) and (5). Esterification of the cinnamic acid (6) with an alkylbromide in the presence of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) gave the cinnamates (7). These were then treated with the diol (1) or the thiols (4) and (5) to give the heterocyclic cinnamates (8), (9), and (10). In the cyclization step, both trans and cis isomers were produced which differed at the C5 position of the 1,3-dioxane ring. Repeated recrystallizations were required to obtain only the trans isomers. When this separation was not achieved by recrystallization, preparative TLC (hexane:ether = 2:1) was used. In ^{1}H-NMR spectra for compounds (8), (9), and (10), the C-2 proton for the trans isomers appear at δ = 5.45, 5.75, and 5.20, respectively. Whereas those for the cis isomers appear at δ = 5.50, 5.80, and 5.15, respectively. Therefore, removal of the cis isomer can be checked by the disappearance of its peak in a NMR spectrum. Measurement of transition temperatures and assignment of 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.[24,25] Phase transition temperatures for compounds (8), (9), (10), and the related compounds (11), (12), 13), and (14) are given in Table I.

Though compounds (11), (12), and (13) exhibited the liquid crystal phase, compounds (8), (9), and (10) did not. Compounds (8), (9), and (10) have a chemical structure in which two terminal substituents of (11), (12), and (13) are exchanged. The major difference in the chemical structure between compounds (8), (9), (10), and (11), (12), (13) is the location of the 2-methylbutyl group. In the former compounds, the bulky 2-methylbutyl group is located close to the equally bulky heterocyclic ring, so that steric hindrance occurs between these two groups. This hindrance might prevent the 2-methylbutyl group from taking a conformation required for the appearance of liquid crystal phase. In order to better understand these results, decyl *p*-(5-pentyl-1,3-dioxan-2-yl)cinnamate (14-1), decyl *p*-(5-pentyl-1,3-oxathian-2-yl)cinnamate (14-2), and decyl *p*-(5-pentyl-1,3-dithian-2-yl)cinnamate (14-3) were synthesized. These compounds have a normal pentyl group instead of the 2-methylbutyl group of compounds (8), (9), and (10). All of these compounds exhibited a nematic liquid crystal phase with the enantiotropic phase transition. This supports the idea that the steric hinderance between the 2-methylbutyl group and the heterocyclic group prevents the formation of liquid crystal phase in compounds (8), (9), and (10).

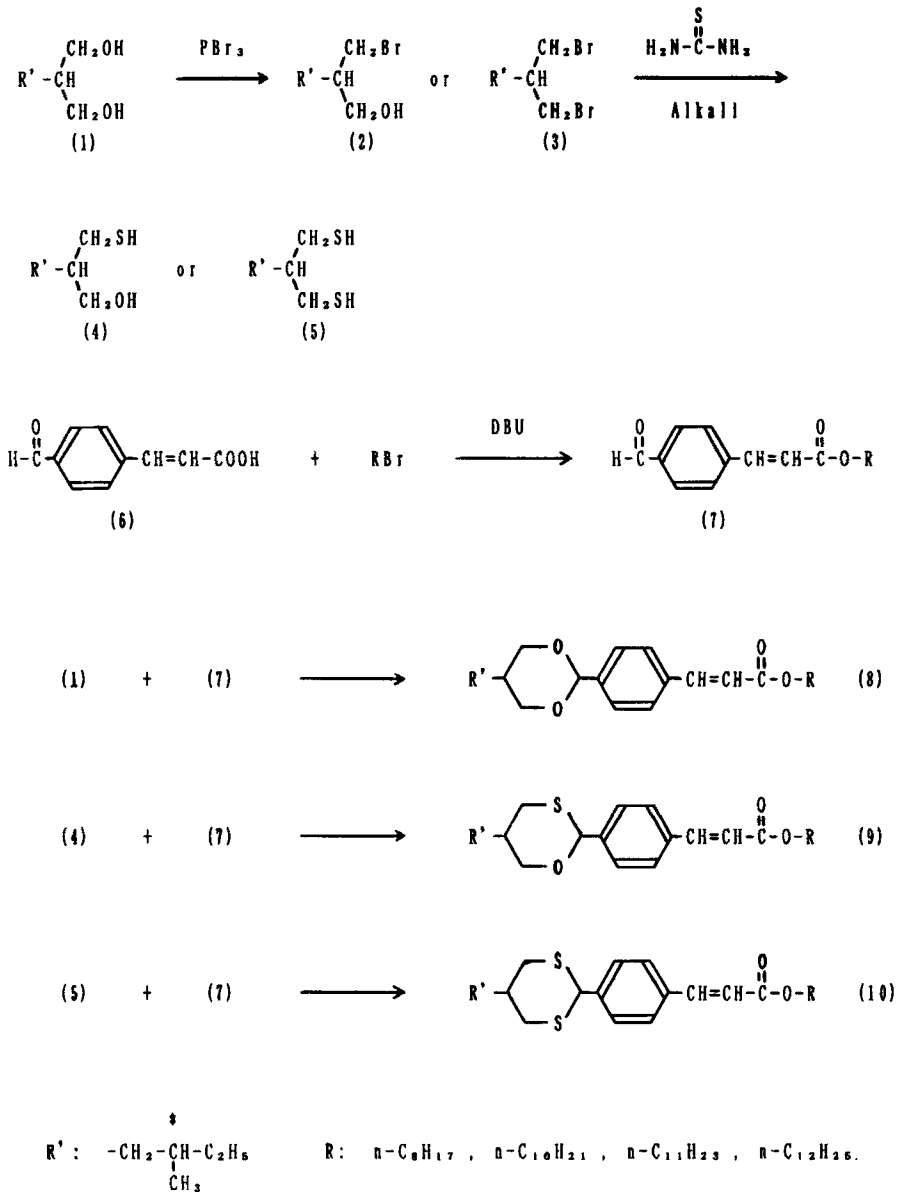


FIGURE 1

3. 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, 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

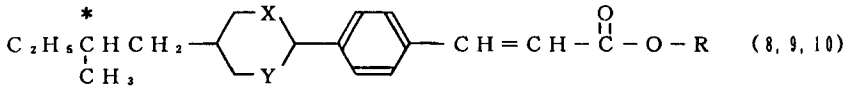
Rigaku Denkl DSC CN8059LI, CN8208A2, respectively. Heating and cooling rates were 3°C/min.

(+)-2-(2-methylbutyl)-1,3-propanediol (1). The same procedure as that in the previous paper[2] was used. A transparent liquid was obtained in a 60 ~ 70% yields.

(+)-2-(2-methylbutyl)-3-mercapto-1-propanol (4), and (+)-2-(2-methylbutyl)-1,3-

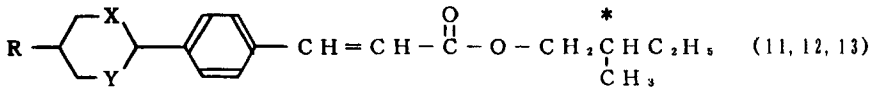
TABLE I

Transition temperatures for compounds 8, 9, 10 and the corresponding compounds 11, 12, 13, 14.



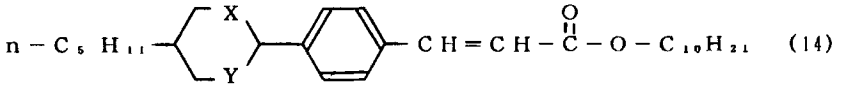
	R	X	Y	TRANSITION TEMPERATURES (°C) a)
8-1	C_8H_{17}	O	O	C $\underset{27}{\overset{62}{\rightleftarrows}}$ I
8-2	$C_{10}H_{21}$	O	O	C $\underset{20}{\overset{45}{\rightleftarrows}}$ I
8-3	$C_{11}H_{23}$	O	O	C $\underset{30}{\overset{46}{\rightleftarrows}}$ I
8-4	$C_{12}H_{25}$	O	O	C $\underset{32}{\overset{43}{\rightleftarrows}}$ I
9-1	$C_{10}H_{21}$	S	O	C $\underset{31}{\overset{43}{\rightleftarrows}}$ I
9-2	$C_{11}H_{23}$	S	O	C $\underset{25}{\overset{46}{\rightleftarrows}}$ I
10-1	C_8H_{17}	S	S	C $\underset{57}{\overset{81}{\rightleftarrows}}$ I
10-2	$C_{10}H_{21}$	S	S	C $\underset{41}{\overset{73}{\rightleftarrows}}$ I
10-3	$C_{11}H_{23}$	S	S	C $\underset{48}{\overset{68}{\rightleftarrows}}$ I
10-4	$C_{12}H_{25}$	S	S	C $\underset{57}{\overset{61}{\rightleftarrows}}$ I

TABLE I (*Continued*)



(11, 12, 13)

	R	X	Y	TRANSITION TEMPERATURES (°C) [a]
11-1	$C_{10}H_{21}$	O	O	C $\underset{21}{\overset{45}{\rightleftharpoons}}$ SmA $\underset{77}{\overset{77}{\rightleftharpoons}}$ I
11-2	$C_{11}H_{23}$	O	O	C $\underset{28}{\overset{58}{\rightleftharpoons}}$ SmA $\underset{76}{\overset{76}{\rightleftharpoons}}$ I
12-1	$C_{10}H_{21}$	S	O	C $\underset{-50}{\overset{35}{\rightleftharpoons}}$ SmA $\underset{71}{\overset{71}{\rightleftharpoons}}$ I
12-2	$C_{11}H_{23}$	S	O	C $\underset{-19}{\overset{50}{\rightleftharpoons}}$ SmA $\underset{74}{\overset{74}{\rightleftharpoons}}$ I
13-1	$C_{10}H_{21}$	S	S	C $\underset{16}{\overset{53}{\rightleftharpoons}}$ SmA $\underset{88}{\overset{88}{\rightleftharpoons}}$ I
13-2	$C_{11}H_{23}$	S	S	C $\underset{18}{\overset{54}{\rightleftharpoons}}$ SmA $\underset{82}{\overset{82}{\rightleftharpoons}}$ I



(14)

	X	Y	TRANSITION TEMPERATURES (°C) [a]
14-1	O	O	C $\underset{25}{\overset{57}{\rightleftharpoons}}$ N $\underset{86}{\overset{86}{\rightleftharpoons}}$ I
14-2	S	O	C $\underset{24}{\overset{49}{\rightleftharpoons}}$ N $\underset{70}{\overset{70}{\rightleftharpoons}}$ I
14-3	S	S	C $\underset{52}{\overset{58}{\rightleftharpoons}}$ N $\underset{77}{\overset{77}{\rightleftharpoons}}$ I

a) C, crystal ; Sm, Smectic ; N, Nematic ; I, Isotropic.

propanedithiol (5). To a solution of thiourèa (0.15 mol) in triethylene glycol (15 ml) kept at 75°C was added a mixture of compounds (2) and (3) (0.04 mol) in a nitrogen atmosphere, followed by stirring at 75°C for 18 hr. Then, tetraethylene-pentamine (0.05 mol) was added at 75°C and stirred for 2 hr under a nitrogen atmosphere. The reaction mixture was poured into cold 5% HCl water (300 ml), stirred and extracted twice with ether (each 300 ml). The organic extract was washed with cold water (100 ml), dried over anhyd. Na_2SO_4, filtered and the filtrate evaporated in vacuo at 30°C. The residue contained both (4) and (5). Compounds (4) and (5) were separated by column chromatography, that is, (5) eluted with hexane and (4) with ether, respectively.

IR ($CHCl_3$) Compound (4): 3500 (OH), 2950–2800 (alkyl) cm^{-1}.

Compounds (5): 2950–2800 (alkyl) cm^{-1}.

^{1}H-NMR ($CDCL_3$) Compound (4): δ 0.5–2.0 (m. 13H, C_5H_{11}—CH, SH), 2.6–3.0 (m, 2H, CH_2S), 3.6–4.5 (m, 3H, CH_2OH). Compound (5): δ 0.5–2.0 (m, 14H, C_5H_{11}—CH, SH), 2.6–3.0 (m, 4H, CH_2S).

Alkyl *p*-formylcinnamate (7). A solution of *p*-formylcinnamic acid (0.015 mol) and 1,8-diazabicycro-[5.4.0] undec-7-ene (0.015 mol) and *n*-alkylbromide (0.015 mol) in anhyd. DMF (30 ml) was stirred at 80 ~ 90°C [or 18 hr 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 filtered and the filtrate evaporated in vacuo. The residue was dissolved in hexane (100 ml), and filtered and the filtrate evaporated in vacuo to give a transparent brown liquid in 50 ~ 60% yield:

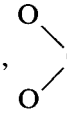
IR ($CHCl_3$) 2700 ~ 2950 (alkyl), 1700 (C=O), 1600 (Ar), 965 (C=C) cm^{-1}.

^{1}H-NMR ($CDCl_3$) δ 0.6–2.0 (m, $OCH_2\underline{C_nH_{2n+1}}$), 4.2 (t, 2H, OCH_2), 6.5 (d, 1H, =CH), 7.5–8.0 (q, 5H, CH=, ArH), 10.0 (s, 1H, CHO).

(+)-Alkyl *p*-[5-(2-methylbutyl)-1,3-dioxan-2-yl]cinnnnamate (8). To a solution of compound (1) (0.004 mol) and compound (7) (0.004 mol) in anhyd. $CHCl_3$ (300 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 hr, and then at 20 ~ 25°C for 16 hr. The solution was washed with 5% aq. $NaHCO_3$ (400 ml), dried over anhyd. Na_2SO_4, filtered and the filtrate evaporated in vacuo. The residue was purified by column chromatography followed by recrystallization from hexane, and then chromatographed on prep. T.L.C. to obtain the trans isomer.

IR ($CHCl_3$) 3000–2800 (alkyl), 1720 (C=O), 1600 (Ar), 980 (C=C).

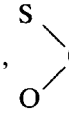
^{1}H-NMR ($CDCl_3$) δ 0.5–2.3 (m, $C_5H_{11}CH$, O—$CH_2\underline{R}$), 3.3–4.5 (m, 6H, CH_2O),



5.45 (s, 1H, CH), 6.5–7.8 (m, 6H, CH=CH, ArH).

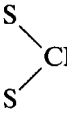
(+)-Alkyl *p*-[5-(2-methylbutyl)-1,3-oxathian-2-yl]cinnamate (9). These compounds (9) were synthesized using this same procedure: that for compounds (8).

IR ($CHCl_3$) 3000–2800 (alkyl), 1720 (C=O), 1600 (Ar), 980 (C=C).

^{1}H-NMR ($CDCl_3$) δ 0.5–2.2 (m, $C_5H_{11}CH$, OCH_2R), 2.8 (d, 2H, CH_2S), 3.0–4.4 (m, 4H, OCH_2), 5.75 (s, 1H, ), 6.2–7.8 (m, 6H, CH=CH, ArH).

(+)-Alkyl *p*-[5-(2-methylbutyl)-1,3-dithian-2-yl]cinnamate (10). The compounds (10) were synthesized according to the same procedures as that for compounds (8).

IR ($CHCl_3$) 3000–2800 (alkyl), 1720 (C=O), 1600 (Ar), 980 (C=C).

^{1}H-NMR ($CDCl_3$) δ 0.5–2.1 (m, $C_5H_{11}CH$, OCH_2R), 2.7–2.9 (m, 4H, CH_2S), 4.2 (t, 2H, OCH_2), 5.20 (s, 1H, ), 6.3–7.9 (m, 6H, CH=CH, ArH).

8-1: Yield, 36%, Found: C, 75.35; H, 9.63%. Calcd for $C_{26}H_{40}O_4$: C, 74.96; H, 9.68%. Mass (m/e) 416 (M^+).

8-2: Yield, 34%. Found: C, 75.77; H, 9.95%. Calcd for $C_{28}H_{44}O_4$: C, 75.63; H, 9.97%. Mass (m/e) 444 (M^+).

8-3: Yield, 27%. Found: C, 75.81; H, 10.18%. Calcd for $C_{29}H_{46}O_4$: C, 75.94; H, 10.11%. Mass (m/e) 458 (M^+).

8-4: Yield, 37%. Found: C, 76.51; H, 10.20%. Calcd for $C_{30}H_{48}O_4$: C, 76.22; H, 10.24%. Mass (m/e) 472 (M^+).

9-1: Yield, 22%. Found: C, 72.51; H, 9.69%. Calcd for $C_{28}H_{44}O_3S$: C, 72.99; H, 9.63%. Mass (m/e) 460 (M^+).

9-2: Yield, 32%. Found: C, 73.81; H, 9.71%. Calcd for $C_{20}H_{46}O_3S$: C, 73.37; H, 9.77%. Mass (m/e) 474 (M^+).

10-1: Yield, 34%. Found: C, 69.24; H, 9.04%. Calcd for $C_{26}H_{40}O_2S_2$: C, 69.59; H, 8.99%. Mass (m/e) 448 (M^+).

10-2: Yield, 37%. Found: C, 70.37; H, 9.32%. Calcd for $C_{28}H_{44}O_2S_2$: C, 70.54; H, 9.30%. Mass (m/e) 476 (M^+).

10-3: Yield, 26%. Found: C, 71.07; H, 9.44%. Calcd for $C_{29}H_{46}O_2S_2$: C, 70.97; H, 9.45%. Mass (m/e) 490 (M^+).

10-4: Yield, 25%. Found: C, 71.29; H, 9.59%. Calcd for $C_{30}H_{48}O_2S_2$: C, 71.37; H, 9.58%. Mass (m/e) 504 (M^+).

14-1: Yield, 28%. Found: C, 75.72; H, 9.96%. Calcd for $C_{28}H_{44}O_4$: C, 75.63; H, 9.97%. Mass (m/e) 444 (M^+).

14-2: Yield, 38%. Found: C, 73.39; H, 9.53%. Calcd for $C_{28}H_{44}O_3S$: C, 72.99; H, 9.63%. Mass (m/e) 460 (M^+).

14-3: Yield, 31%. Found: C, 70.36; H, 9.16%. Calcd for $C_{28}H_{44}O_2S_2$: C, 70.54; H, 9.30%. Mass (m/e) 476 (M^+).

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