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New Ferroelectric Liquid Crystal Materials. (+)-4-[(2-Methylbutyloxycarbonyl)phenyl] 4-(5-Alkyl-1,3-dioxan-2-yl)benzoate

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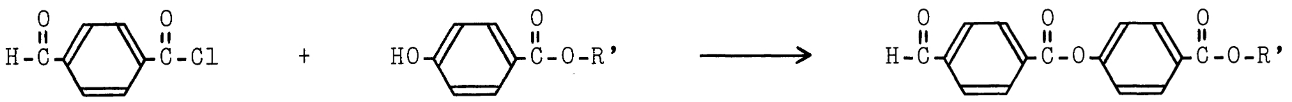
(+)-4- (2-Methylbutyloxycarbonyl)phenyl 4-(5-alkyl-1,3-dioxan-2-yl)benzoate (9) and (+)-4-[(2-methylbutyloxy)phenyl] 4-(5-alkyl-1,3-dioxan-2-yl)benzoate and corresponding dithianes and oxathianes were synthesized. Only compounds 9 exhibited the ferroelectric liquid crystal behavior ($R=n-C_{11}H_{23}$: -4 SmC 93 °C).

In recent years, 2,5-disubstituted 1,3-dioxanes, 1,3-oxathianes, and 1,3-dithianes have been reported as new types of liquid crystal materials.[1 - 11] In proportion to increase in attention given to new types of liquid crystal displays using ferroelectric liquid crystals, various ferroelectric liquid crystal compounds have been synthesized. So, the basic structure of optically active liquid crystal compounds with 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane rings were synthesized.

Among these compounds, only 9 exhibited ferroelectric liquid crystal behavior. Therefore, in this letter, we wish to report the syntheses and mesomorphic behavior of these compounds as well as the relation between the appearance of SmC phase and chemical structure. (+)-4-[(2-Methylbutyloxycarbonyl)phenyl] 4-(5-alkyl-1,3-dioxan-2-yl)benzoate (9), (+)-4 [(2-methylbutyloxy)phenyl] 4-(5-alkyl-1,3-dioxan-2-yl)-benzoate (10), and corresponding 1,3-oxathiane (11, 12) and 1,3-dithiane compounds (13, 14) were synthesized via the following route.



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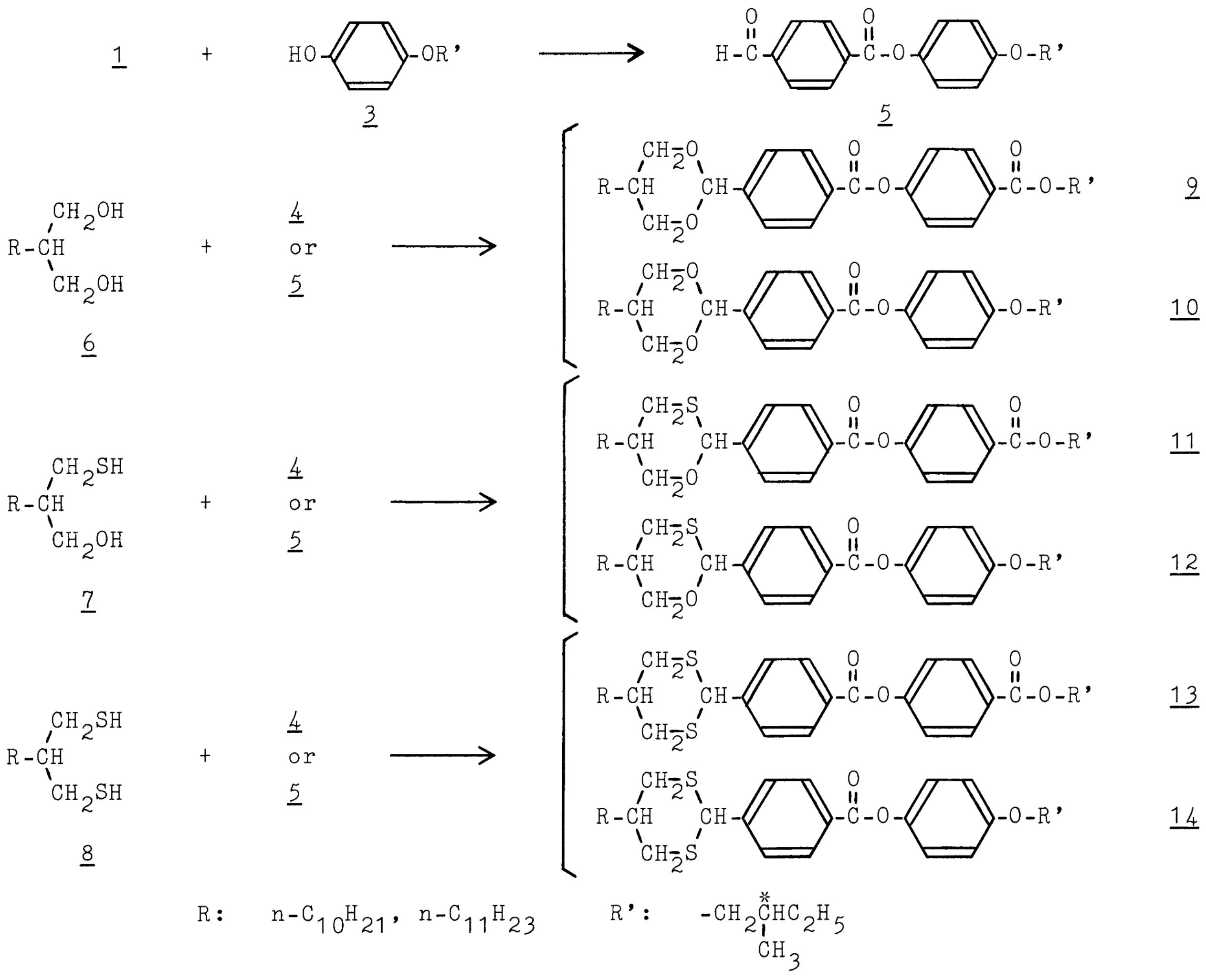

Compound 2 was obtained by the esterification of p-hydroxybenzoic acid and (+)-2-methyl-1-butanol in the presence of acid catalyst by using a Dean-Stark trap. Compound 3 was synthesized by the monoetherification of hydroquinone. Though both diether and monoether were produced, monoether was obtained by the purification using column chromatography. The former was eluted with hexane and the latter with benzene. Compounds 9, 10, 11, 12, 13, and 14 were purified by column chromatography and recrystallized with hexane. The trans isomers of compounds 10, 12, 13, and 14 were isolated by use of TLC (hexane : ether = 5 : 2).

In the ^{1}H-NMR data of 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane compounds, C-2 proton signals of the 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane rings for trans isomers exhibited about 0.05 ppm with a different magnetic field than those for cis isomers. For example, the C-2 proton spectra of the trans isomers appeared at δ=5.50 (compound 9-1), 5.75 (11-1), and 5.20 (13-1) but the corresponding spectra of the cis isomers appeared at δ=5.55, 5.80, and 5.15, respectively.

Measurements of the mesomorphic ranges and assignment of the mesophases were carried out by means of a micro melting point apparatus equipped with polarizers and a differential scanning calorimeter (D.S.C.). To determine the type of smectic phase, smectic phases were compared with the color photographs found in the literature.[12)] Mesomorphic ranges of the synthesized compounds are given in Table 1.

Table 1. Mesomorphic ranges for compounds 9, 10, 11, 12, 13, and 14

	R	Mesomorphic range / °C[a)]		R	Mesomorphic range / °C[a)]
9-1	$C_{10}H_{21}$	C $\underset{11}{\overset{57}{\rightleftarrows}}$ SmC $\underset{80}{\overset{80}{\rightleftarrows}}$ SmA $\underset{137}{\overset{137}{\rightleftarrows}}$ I	12-1	$C_{10}H_{21}$	C $\underset{-50}{\overset{66}{\rightleftarrows}}$ SmB $\underset{111}{\overset{111}{\rightleftarrows}}$ SmA $\underset{134}{\overset{134}{\rightleftarrows}}$ I
9-2	$C_{11}H_{23}$	C $\underset{-4}{\overset{62}{\rightleftarrows}}$ SmC $\underset{93}{\overset{93}{\rightleftarrows}}$ SmA $\underset{136}{\overset{136}{\rightleftarrows}}$ I	12-2	$C_{11}H_{23}$	C $\underset{-50}{\overset{64}{\rightleftarrows}}$ SmB $\underset{111}{\overset{111}{\rightleftarrows}}$ SmA $\underset{132}{\overset{132}{\rightleftarrows}}$ I
10-1	$C_{10}H_{21}$	C $\underset{22}{\overset{66}{\rightleftarrows}}$ SmB $\underset{100}{\overset{100}{\rightleftarrows}}$ SmA $\underset{136}{\overset{136}{\rightleftarrows}}$ I	13-1	$C_{10}H_{21}$	C $\underset{94}{\overset{113}{\rightleftarrows}}$ SmA $\underset{150}{\overset{150}{\rightleftarrows}}$ I
10-2	$C_{11}H_{23}$	C $\underset{94}{\overset{113}{\rightleftarrows}}$ SmA $\underset{137}{\overset{137}{\rightleftarrows}}$ I	13-2	$C_{11}H_{23}$	C $\underset{99}{\overset{117}{\rightleftarrows}}$ SmA $\underset{147}{\overset{147}{\rightleftarrows}}$ I
11-1	$C_{10}H_{21}$	C $\underset{-50}{\overset{89}{\rightleftarrows}}$ SmA $\underset{134}{\overset{134}{\rightleftarrows}}$ I	14-1	$C_{10}H_{21}$	C $\underset{54}{\overset{104}{\rightleftarrows}}$ SmB $\underset{136}{\overset{136}{\rightleftarrows}}$ SmA $\underset{153}{\overset{153}{\rightleftarrows}}$ I
11-2	$C_{11}H_{23}$	C $\underset{-50}{\overset{70}{\rightleftarrows}}$ SmB $\underset{98}{\overset{98}{\rightleftarrows}}$ SmA $\underset{136}{\overset{136}{\rightleftarrows}}$ I	14-2	$C_{11}H_{23}$	C $\underset{63}{\overset{109}{\rightleftarrows}}$ SmB $\underset{140}{\overset{140}{\rightleftarrows}}$ SmA $\underset{153}{\overset{153}{\rightleftarrows}}$ I

a) C: Crystal; S: Smectic; I: Isotropic.

Though smectic C of compounds 9 can be drived in homogenious cells (d=2 μm, applied voltage=20 V), other smectic phases can not. Therefore, compounds 9 are ferroelectric liquid crystal compounds, and others are not.

1,3-Oxathiane and 1,3-dithiane compounds which correspond to the compounds 9 did not exhibit SmC liquid crystal phase. This must imply that 1,3-dioxane compounds are more favorable for transition of SmA to SmC than 1,3-oxathiane or 1,3-dithiane compounds.

Though compounds 9 exhibit SmC phase, compounds 10 do not. The difference of these two compounds lies in the number of the carbonyl group. Accordingly, the carbonyl group having a dipole moment of vertical direction to the molecular axis must contribute to transition from SmA to SmC.

Several properties as a ferroelectric liquid crystal compounds were measured for compound 9-2: the strength of the spontanious polarization=0.53 nC/cm^2 (90 °C), herical pitch length=4 μm, the response of the optical transmission=68 μs (80 °C, 20 V). Though the strength of the spontaneous polarization is smaller than that of (S)-2-methylbutyl p-(p-decyloxybenzylideneamino)cinnamate (DOBAMBC),$^{13)}$ herical pitch length of this compound is longer than that of DOBAMBC. The most remarkable feature of these new ferroelectric liquid crystal compounds is that though they indicate supercooling state, they exhibit the ferroelectric liquid crystal behavior over a very wide range including ordinary room temperature (from 93 to -4 °C).

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