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Mosomorphic Phenyl Benzoate and 1,3-Dioxane Derivatives Bearing Terminal Vinyl Group

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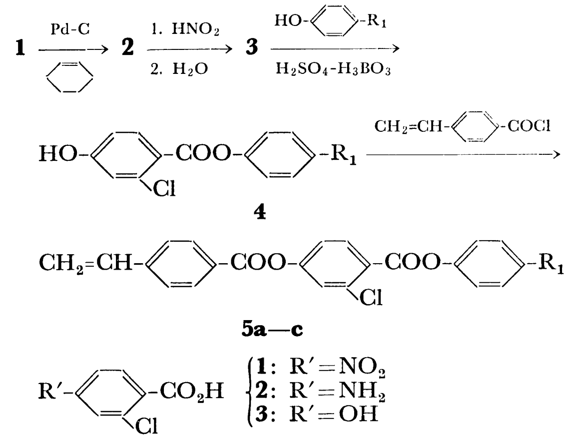
Synopsis. 4-Alkylphenyl 2-chloro-4-(4-vinylbenzoyloxy) benzoates and 2-phenyl-1,3-dioxane derivatives with terminal vinyl groups were synthesized. Most of the novel compounds obtained possess characteristic mesomorphic ranges.

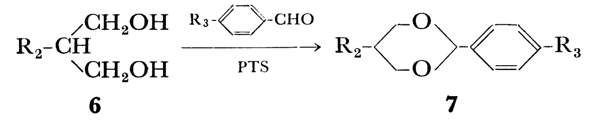
Some efforts have been made to incorporate vinyl groups into nematic liquid crystalline structures with intention of polymerizing the resulting vinyl monomers to obtain polymeric liquid crystals.[1] Besides the potentiality of these monomers as precursors to polymeric liquid crystals, the terminal rigid vinyl group bearing the sp^2-carbon atoms is itself expected to afford liquid-crystalline characteristics different from those of the corresponding compounds with alkyl and related flexible groups. With this intention, two series of novel vinyl compounds were prepared and their liquid-crystalline behavior was compared with that of the corresponding compounds with alkyl and related groups.

Vinyl compounds were prepared as follows:

(a)



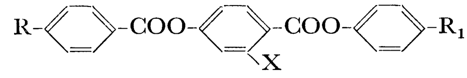
(b)



Tables 1 and 2 summarize the yields and mesomorphic ranges of compounds **5** and **7**, respectively, in comparison with those of the corresponding compounds with alkyl and related groups.

All of the vinyl compounds listed in these tables, among which **5a**—**c** and **7a**—**f** have not been listed in literature as yet, are stable up to the isotropic ranges, presumably due to their long rodlike structures.

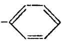
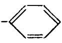
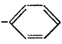
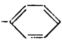
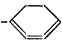
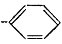
TABLE 1. MESOMORPHIC RANGE OF BENZOATES (**5**)



No.	R	R_1	X	Yield/%	Mesomorphic range/°C[a]
5a	$CH_2{=}CH$-	*s*-C_4H_9	Cl	46	C 50 S 70—72 N 96—99 I
5b	$CH_2{=}CH$-	*n*-C_4H_9	Cl	64	C 45 S 75—78 N 176—179 I
5c	$CH_2{=}CH$-	*n*-C_5H_{11}	Cl	67	C 50 S 71—74 N 171—174 I
5d[b]	$CH_2{=}CH$-	*s*-C_4H_9	H	—	C 88—90 N 169—170 I
5e[b]	$CH_2{=}CH$-	*t*-C_4H_9	H	—	C 115—118 S 128 N 151—154 I
5f[b]	$CH_2{=}CH$-	1,1-$Me_2C_3H_5$	H	—	C 102 N 107 I
5g[b]	$CH_2{=}CH$-	1-MeC_4H_8	H	—	C 79 S 96 N 130 I
5h[c]	*n*-C_3H_7	*n*-C_5H_{11}	H	—	C 78 N 188 I
5i[c]	*n*-C_3H_7	*n*-C_5H_{11}	Cl	—	C 57 N 130 I
5j[c]	*n*-C_4H_9	*n*-C_5H_{11}	H	—	C 75 N 179 I
5k[c]	*n*-C_4H_9	*n*-C_5H_{11}	Cl	—	C 46 N 118 I

a) C: Crystal, S: smectic, N: nematic, I: isotropic. The type of smectic texture is undetermined. b) Ref. 3. c) Ref. 2.

TABLE 2. MESOMORPHIC RANGE OF 1,3-DIOXANES (**7**)

No.	R_2	R_3	Yield/%	Mesomorphic range/°C
7a	$CH_2{=}CH$--CH_2-	CN	26	C 60 N 105 I
7b	$CH_2{=}CH$--CH_2-	*n*-C_3H_7O	30	C 55 S 65 I
7c	$CH_2{=}CH$--CH_2-	*n*-$C_6H_{13}O$	34	C 65 S 75 I
7d	*n*-C_4H_9	$CH_2{=}CH$-	61	Turbid liq. at rt[a]
7e	*n*-C_7H_{15}	$CH_2{=}CH$-	49	Turbid liq. at rt[a]
7f	$CH_2{=}CH$--CH_2-	$CH_2{=}CH$-	3	C 70 S 80 N 90 I
7g	*n*-C_4H_9	CH_3O	87	C 34 S 39 I
7h[b]	*n*-C_4H_9	*n*-C_3H_7O	61	C 43 I
7i[b]	*n*-C_7H_{15}	*n*-$C_6H_{13}O$	53	C 42 N 63 I
7j[b]	*n*-C_4H_9	CN	54	C 30 S 43 I
7k[b]	*n*-C_6H_{13}--	CN	—	C 84 N 151 I
7l[b]	*n*-C_4H_9O--	CN	—	C 121 N 202 I
7m[b]	*n*-C_4H_9O--	*n*-$C_7H_{15}O$	—	C 134 S 166 I
7n[b]	*n*-C_4H_9	*n*-C_4H_9	—	C 44 N (40) I[c]
	n-C_6H_{13}	*n*-C_3H_7	—	C 35 S 41 I

a) rt: room temperature (25 °C). No clearing point could be determined exactly. b) Ref. 4. c) Monotropic.

In the phenyl benzoate series (Table 1), the replacement of the alkyl group as R by the rigid vinyl group generally causes smectic ranges to appear prior to nematic ones with elevation of temperature, which is not general in the conventional **5**-type esters.[2] The absence of smectic textures for compounds **5d** and **5f** having no chlorine atom may indicate that the effects of chain length and branching in R_1 on the smectic alignments of the molecules are predominant in the absence of the chlorine atom. Higher N—I transition temperatures were also recognized for compounds with unbranched R_1 (**5b** and **5c** *vs.* **5i** and **5k**).

In the dioxane series (Table 2), compounds wtih the 4-vinylbenzyl group as R_2, in spite of the presence of the rigid vinyl end, have much lower mesomorphic ranges than those with the alkylphenyl or alkoxyphenyl group (**7a** *vs.* **7k** and **7l**; **7b** and **7c** *vs.* **7m**), although the alkylbenzyl group is required for exact structural comparison. Compounds **7d** and **7e** also have lower melting points (below room temperature) than **7n**, **7o**, **7g**, and **7h**.

These results indicate that the introduction of the terminal rigid vinyl group into these two series of compounds does not interfere with the formation of mesomorphic structures at all, leading to characteristic mesomorphic behavior, when appropriate chemical structures are adopted.

Experimental

Infrared, ^{1}H NMR, and mass spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi RMU-6 spectrometer, respectively, under standard conditions. Elemental analyses were carried out with a Perkin-Elmer 250 instrument. Mesomorphic ranges were determined by means of either a Yamato MP-21 melting point apparatus or an optical microscope, both equipped with crossed polarizers.

2-Chloro-4-hydroxybenzoic Acid (3). A known preparative procedure[2] was modified as follows: 2-Chloro-4-aminobenzoic acid (**2**; mp 205—207 °C; 9 g, 52 mmol), prepared by heating 2-chloro-4-nitrobenzoic acid (**1**) in ethanol under reflux for 2 h in the presence of 5% Pd–C and a large excess of cyclohexene and purified by recrystallization from water, was dissolved in a solution of sodium nitrite (4 g, 58 mmol) and sodium carbonate (4 g, 40 mmol) in water (250 ml). A solution of concd sulfuric acid (30 ml) in water (200 ml) was then added with ice cooling, and the resulting solution was further stirred for 15 min. Urea (1 g) was next added, and stirring was further continued at 50—60 °C for 7 h. The reaction mixture was then extracted with ether (200 ml). The orange organic layer was washed with water, dried over anhyd sodium sulfate, and evaporated *in vacuo* to leave the crude product. Recrystallizations from water provided pure needles (mp 203—206 °C; lit,[2] 206—208 °C) in 50% yield: IR(KBr) 1680 (C=O), 1590, 1570 (aromatic), 1400, 1290, and 1240 (OH) cm^{-1}; NMR ($CDCl_3$+DMSO-d_6) δ=6.8 (m, 2H, ArH) and 7.7—8.7 (m, 3H, ArH+OH+COOH).

4-Butylphenyl 2-Chloro-4-(4-vinylbenzoyloxy)benzoate (5b). 4-Vinylbenzoyl chloride (0.8 g, 5.0 mmol) was added to a solution of 4-butylphenyl 2-chloro-4-hydroxybenzoate (**4**; 1.4 g, 4.7 mmol), prepared from 2-chloro-4-hydroxybenzoic acid (**3**) and 4-butylphenol,[3] and 4-*t*-butylcatechol (50 mg) in dry pyridine (25 ml). After stirring at room temperature for 18 h, the reaction mixture was poured into an ice–water mixture and the product was isolated by filtration. Three-time recrystallizations from ethanol gave pure crystals: Found: C, 71.58; H, 5.32%. Calcd for $C_{26}H_{23}O_4Cl$: C, 71.80; H, 5.33%. IR (KBr) 1740, 1590, 980, and 910 cm^{-1}; NMR ($CDCl_3$+DMSO-d_6) δ=0.9—3.0 (m, 9H, C_4H_9), 5.4 (d, 1H), 5.8 (d, 1H), 6.7 (q, 1H), 7.3 (t, 8H), and 8.1 (d, 3H); MS (rel intensity) 435 (M$^+$, 5) and 298 (100).

Compounds **5a** and **5c** were prepared in the same manner with satisfactory analytical data.

2-Vinylbenzyl-1,3-propanediol (6). To a solution of sodium (2.3 g, 100 mmol) in absolute ethanol (100 ml) was gradually added with ice cooling first diethyl malonate (16.0 g, 100 mmol) and then a mixture of vinylbenzyl chloride (Seibi Chem. Co.; *m*/*p*=60/40; 15.2 g, 100 mmol) and 4-*t*-butylcatechol (1 g) with exclusion of moisture. The mixture was heated under reflux until it became no longer alkaline (about 2 h). The reaction mixture was then purified by distillation under reduced pressure to afford diethyl vinylbenzylmalonate (bp, 135 °C/3 mmHg) (1 mmHg=133.322 Pa) in 22% yield. The malonate (13.8 g, 50 mmol) was then heated under reflux for 2 h in anhyd ether in the presence of $LiAlH_4$ (3.8 g) with exclusion of moisture. The reaction mixture was worked up as usual to afford compound **6** in 93% yield: Found: C, 75.34; H, 8.11%. Calcd for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33%. IR ($CHCl_3$) 3350—3200 (OH), 990 and 900 (vinyl) cm^{-1}; NMR ($CDCl_3$) δ=5.2 (d, CH_2=), 5.7 (d, CH_2=), and 6.7 (q, =CH–).

2-(4-Cyanophenyl)-5-(4-vinylbenzyl)-1,3-dioxane (7a). A solution of compound **6** (1.92 g, 10 mmol), 4-cyanobenzaldehyde (1.31 g, 10 mmol), 4-*t*-butylcatechol (0.1 g), and *p*-toluenesulfonic acid (PTS; 0.1 g) in benzene (100 ml) was heated under reflux for 7 h with a Dean-Stark trap fitted. The reaction mixture was washed with aq Na_2CO_3, then with water, dried over anhyd Na_2SO_4, and concentrated on a rotary evaporator to afford the crude product. Column chromatography (Wakogel C-300) using benzene as eluent and subsequent several recrystallizations from methanol provided colorless needles: Found: C, 78.34; H, 6.53: N, 4.85 %. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59%. IR (KBr) 2220 (CN), 990, 910 (vinyl), and 820 (1,4-disubstitution) cm^{-1}; NMR ($CDCl_3$) δ=2.4 (s, 3H, CH_2, CH), 3.3—4.4 (m, 4H, $2CH_2O$), 5.3 (d, 1H, CH_2=), 5.5 (s, 1H, $-\mathrm{CH}\langle{}^{\mathrm{O-}}_{\mathrm{O-}}$), 5.8 (d, 1H, CH_2=), 6.7 (q, 1H, –CH=), and 6.9—7.9 (8H, ArH); MS 305 (M$^+$).

Compounds **7b** and **7c** were prepared in the same manner with satisfactory analytical data.

2-(4-Vinylphenyl)-5-(4-vinylbenzyl)-1,3-dioxane (7f). The same reaction procedure as that for **7a** was applied to **6** and vinylbezaldehyde, synthesized from vinylbenzyl chloride by the Sommlet reaction,[5] to afford colorless crystals: Found: C, 77.47; H, 6.79%. Calcd for $C_{21}H_{22}O_2$: C, 77.56; H, 6.82%. IR (KBr) 990, 900 (vinyl), and 840 (1,4-disubst.) cm^{-1}; NMR ($CDCl_3$) δ=2.4 (s, 3H, CH_2, CH), 3.3—4.5 (m, 4H, $2CH_2O$), 5.3 (d, 2H, $2CH_2$=), 5.4 (s, 1H, $-\mathrm{CH}\langle{}^{\mathrm{O-}}_{\mathrm{O-}}$), 5.8 (d, 2H, $2CH_2$=), 6.7 (q, 2H, 2–CH=), and 6.9—7.6 (m, 8H, ArH); MS 306 (M$^+$).

Compounds **7d** and **7e** were prepared in the same manner with satisfactory analytical data.

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