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Mesomorphic 4-Alkylphenyl 4-Benzoyloxybenzoate Bearing a Terminal Vinyl Group

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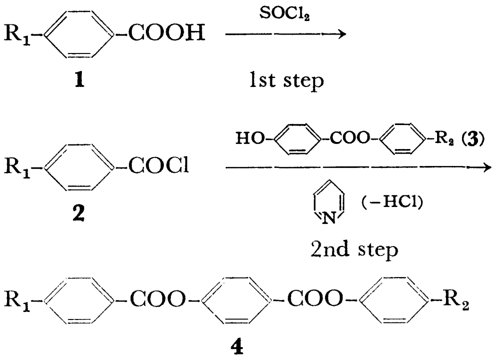
Synopsis. 4-Alkylphenyl 4-(4-vinyl-, methacryloyloxy-, and methacrylamido-benzoyloxy)benzoates have been synthesized by the reactions of 4-alkylphenyl 4-hydroxybenzoates with the corresponding substituted benzoyl chloride in pyridine. The mesomorphic ranges of these novel monomers are highly dependent upon the type of substituent at both ends of the molecules.

Phenyl 4-benzoyloxybenzoates such as 4-hexylphenyl 2-chloro-4-(4-hexylbenzoyloxy)benzoate have been reported[1] to possess low mesomorphic ranges as well as to be more stable against hydrolysis as compared with the Schiff bases commonly used for liquid crystal applications.

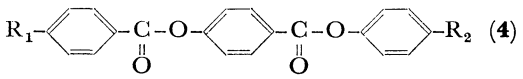
In the course of synthetic studies of mesomorphic organic compounds bearing terminal vinyl groups and their polymers,[2,3] several novel 4-alkylphenyl 4-benzoyloxybenzoates bearing terminal vinyl groups have been synthesized.

The synthetic route adopted was as follows.



The 4-vinyl-, methacryloyloxy-, and methacrylamido-benzoic acids (**1**) synthesized were converted to the respective acyl chlorides (**2**), which were subsequently reacted with 4-alkylphenyl 4-hydroxybenzoate (**3**) in

TABLE 1. MESOMORPHIC RANGE FOR SUBSTITUTED PHENYL 4-BENZOYLOXYBENZOATES


(**4**)

Monomer	R_1	R_2	Yield[a)]/%	Mesomorphic range[b)]/°C
4-1	$CH_2{=}CH{-}$	$CH_3CH_2{-}\underset{\substack{\mid\\ CH_3}}{C}H{-}$	36	C 88—90 N 169—170 I
4-2	$CH_2{=}CH{-}$	$CH_3{-}\overset{\substack{CH_3\\ \mid}}{\underset{\substack{\mid\\ CH_3}}{C}}{-}$	16	C 115—118 S 128 N 151—154 I
4-3	$CH_2{=}CH{-}$	$CH_3{-}\overset{\substack{CH_3\\ \mid}}{\underset{\substack{\mid\\ CH_3}}{C}}{-}CH_2{-}\overset{\substack{CH_3\\ \mid}}{\underset{\substack{\mid\\ CH_3}}{C}}{-}$	52	C 117—118 I
4-4	$CH_2{=}CH{-}$	$CH_3CH_2CH_2{-}\underset{\substack{\mid\\ CH_3}}{C}H{-}$	45	C 79 S 96 N 130 I
4-5	$CH_2{=}CH{-}$	$CH_3CH_2{-}\overset{\substack{CH_3\\ \mid}}{\underset{\substack{\mid\\ CH_3}}{C}}{-}$	19	C 102 N 107 I
4-6	$CH_2{=}\overset{\substack{CH_3\\ \mid}}{C}{-}COO{-}$	$CH_3CH_2{-}\overset{\substack{CH_3\\ \mid}}{C}H{-}$	18	C 125—126 N 134—135 I
4-7	$CH_2{=}\overset{\substack{CH_3\\ \mid}}{C}{-}COO{-}$	$CH_3CH_2CH_2{-}\overset{\substack{CH_3\\ \mid}}{C}H{-}$	9	C 121—122 S 126 N 157—158 I
4-8	$CH_2{=}\overset{\substack{CH_3\\ \mid}}{C}{-}CONH{-}$	$CH_3CH_2{-}\overset{\substack{CH_3\\ \mid}}{C}H{-}$	18	C 162—165 N 175—176 I
4-9	$CH_2{=}\overset{\substack{CH_3\\ \mid}}{C}{-}CONH{-}$	$CH_3CH_2{-}\overset{\substack{CH_3\\ \mid}}{\underset{\substack{\mid\\ CH_3}}{C}}{-}$	20	C 170—171 N 176—177 I

a) For purified products. b) C: crystal; S: smectic; N: nematic; I: isotropic.

anhydrous pyridine to afford the desired product **4**. The yields however were not high. The success of this synthetic route depends on the 2nd step. The nature of R_1 appears to markedly affect the yield and the extent of side reactions, *e.g.*, the use of acryloyloxyl or acrylamido groups as R_1 resulted in little reaction or polymerization. Substitution of *N,N*-dimethylaniline for pyridine as the HCl-acceptor did not give satisfactory results.

The novel vinyl monomers thus synthesized are listed in Table 1, where it may be seen that the effect of R_1 and R_2 on the mesomorphic range is large. It is anticipated that branching in the alkyl group R_2 brings about a narrower mesomorphic range. Normal alkyl groups were however not introduced due to the lack of raw materials. The use of vinyl (**4-1**—**4-5**), methacryloyloxyl (**4-6** and **4-7**), and methacrylamido (**4-8** and **4-9**) as R_1 markedly affected the mesomorphic range. The vinyl group appears to afford the lowest CN or SN transition temperature and the widest nematic range, which appear to be comparable with those with freely rotatable alkyl groups.[1]

The compounds not only indicate mesomorphic ranges as they are, but also they might afford polymers with mesomorphic ranges due to pendant portions by suitable polymerization methods.

Experimental

Mesomorphic ranges were determined by means of a Yamato MP-21 melting point apparatus. 4-Alkylphenyl 4-hydroxybenzoates (**3**) were synthesized according to the reported method.[1]

*4-*s*-Butylphenyl 4-(4-Vinylbenzoyloxy)benzoate (4-1).* To a solution of 4-*s*-butylphenyl 4-hydroxybenzoate (**3**, 1.3 g, 4.7 mmol) and 4-*t*-butylcatechol (50 mg) in anhydrous pyridine (25 ml), 4-vinylbenzoyl chloride (**2**, 0.8 g, 5.0 mmol) prepared by the room temperature reaction of 4-vinylbenzoic acid (**1**) and thionyl chloride was added with ice-cooling. The solution was allowed to stand at room temperature for 18 h with the exclusion of moisture. The reaction mixture was then poured into iced water and the precipitated crude product was recrystallized three times from ethanol to afford colorless crystals (0.7 g, 36% yield). Found: C, 77.49; H, 6.05%. Calcd for $C_{26}H_{24}O_4$: C, 77.98; H, 6.04%. IR (KBr) 1720 (C=O), 995, 900 (vinyl) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.8 (t, 3H, CH_3), 1.2 (d, 3H, CH_3), 1.6 (t, 2H, CH_2), 2.6 (q, 1H, CH), 5.4 (d, 1H, $C\underline{H}_2$=CH–), 5.8 (d, 1H, $C\underline{H}_2$=CH–), 6.7 (q, 1H, CH_2=C$\underline{H}$–), 7.3 (q, 8H, ArH), 8.2 (t, 4H, ArH) ppm. Mass (*m*/*e*) 400 (M$^+$, 6), 131 (100).

The monomers **4-2**—**4-5** were synthesized in the same manner, their analytical data being also satisfactory.

4-(1-Methylbutyl)phenyl 4-[4-(Methacryloyloxy)benzoyloxy]benzoate (4-7). The same procedure as that for monomer **4-1** was applied for **3** (R_2=1-methylbutyl; 1.3 g, 5.0 mmol) prepared from 4-(methacryloyloxy)benzoic acid (**1**), which was itself synthesized by the reaction of sodium 4-hydroxybenzoate with methacryloyl chloride in aqueous solution, to afford colorless crystals (0.2 g, 9% yield). Found: C, 73.74; H, 5.49%. Calcd for $C_{29}H_{28}O_6$: C, 73.69; H, 5.99%. IR (KBr) 1740 (C=O), 950, 885 (CH_2=CCH_3) cm^{-1}. NMR ($CDCl_3$+DMSO-d_6) δ 0.8 (t, 3H, CH_3), 1.3 (d, 3H, CH_3), 1.6 (m, 4H, CH_2CH_2), 2.1 (s, 3H, CH_2=$CC\underline{H}_3$), 2.5 (m, 1H, CH), 5.8 (s, 1H, CH_2=), 6.4 (s, 1H, CH_2=), 7.4 (m, 8H, ArH), 8.3 (d, 4H, ArH) ppm. Mass (*m*/*e*) 472 (M$^+$, 2), 190 (100).

Monomer **4-6** was synthesized in the same manner with satisfactory analytical data.

*4-*t*-Pentylphenyl 4-[4-(Methacrylamido)benzoyloxy]benzoate (4-9).* Compound **3** (R_2=*t*-pentyl; 1.3 g, 4.7 mmol) and 4-(methacrylamido)benzoyl chloride (**2**, 1.1 g, 5.0 mmol), prepared by the reaction of sodium 4-aminobenzoate with methacryloyl chloride in aqueous solution, when subjected to the same reaction procedure as described above, gave colorless crystals (0.4 g, 20% yield). Found: C, 73.80; H, 6.50; N, 3.16%. Calcd for $C_{29}H_{29}NO_5$: C, 73.87; H, 6.20; N, 2.97%. IR (KBr) 1740 (ester), 1680 (amide), 960, 860 (CH_2=CCH_3) cm^{-1}. NMR ($CDCl_3$) δ 0.7 (t, 3H, CH_3), 1.3 (s, 6H, 2 CH_3), 1.6 (t, 2H, CH_2), 2.1 (s, 3H, CH_2=$CC\underline{H}_3$), 5.5 (s, 1H, CH_2=), 5.8 (s, 1H, CH_2=), 7.0—8.3 (m, 13H, ArH+CONH) ppm. Mass (*m*/*e*) 471 (M$^+$, 3), 190 (100).

Monomer **4-8**, synthesized in the same manner, also provided satisfactory analytical data.

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