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SHORT COMMUNICATIONS

New Mesogenic Monomer for Liquid-Crystalline Polymers Based on 3,4-Dihydroxybenzophenone

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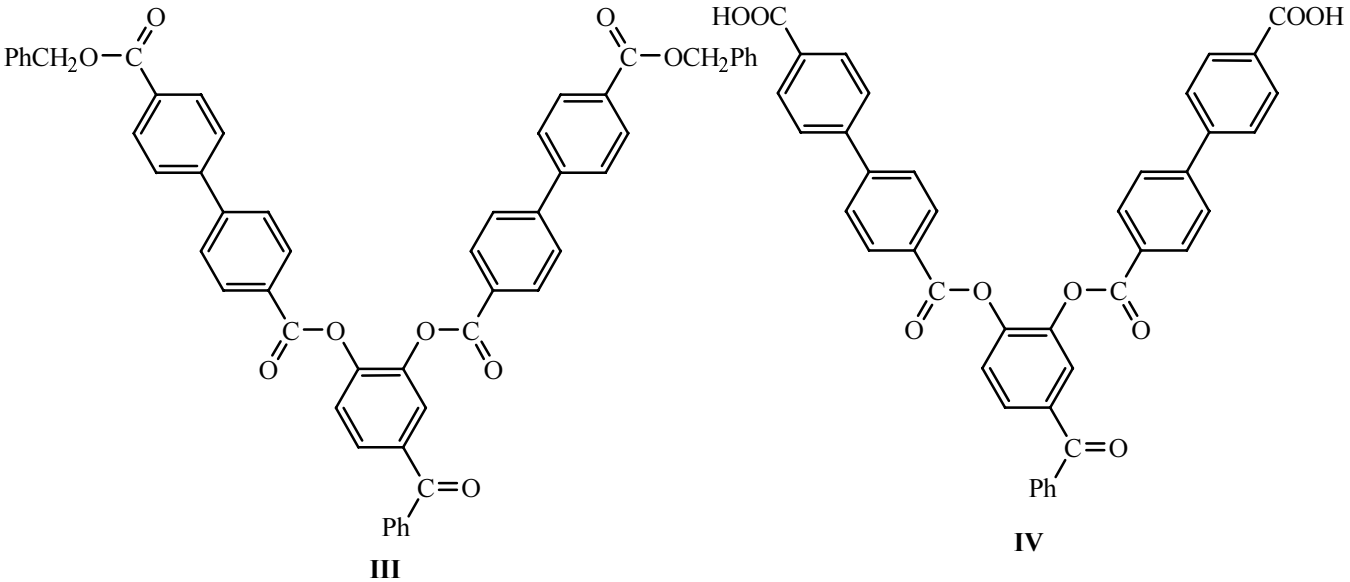
The acylation of 3,4-dihydroxybenzophenone (**I**) [1, 2] with 4-methoxycarbonyl-4'-biphenylcarbonyl chloride (**II**) in a water-organic medium under the conditions of the phase-transfer catalysis (CH_2Cl_2, 2% water solution of NaOH, phase-transfer catalysts[$N(C_4H_9)_4$]Br and [$N(CH_3)_3C_{16}H_{33}$)]Cl) yielded dibenzyl 4-benzoyl-1,2-phenylenebis-[4'-(oxycarbonyl)biphenyl-4-carboxylate] (**III**). The debenzylation of ester **III** effected by HBr, CH_3COOH, or CF_3COOH [3, 4] led to the formation of 4-benzoyl-1,2-phenylenebis[4'-(oxycarbonyl)biphenyl-4-carboxylic acid] (**IV**), a new V-shaped monomer with a photoactive and reactive carbonyl group.

Dibenzyl 4-benzoyl-1,2-phenylenebis-[4'-(oxycarbonyl)biphenyl-4-carboxylate] (III). To a solution containing 1.83 g (8.5 mmol) of 3,4-dihydroxybenzophenone, 71 ml of 2.5% NaOH solution, 0.069 g of [$N(C_4H_9)_4$]Br and 0.0443 g of [$N(CH_3)_3C_{16}H_{33}$]Br was added 3 ml of CH_2Cl_2. The mixture was stirred for 10 min, then 6.58 g (17.94 mmol) of biphenylcarbonyl chloride **II** in 60 ml of anhydrous dichloromethane was added thereto. The mixture was stirred for 1 h at room temperature under an inert gas atmosohere. The organic layer was separated, washed with water, dried with $CaCl_2$, and then poured into 100 ml of petroleum ether.



III **IV**

The separated precipitate was filtered off and dried in a thermostat. Yield 3.83 g (50%), mp 57–58°C, R_f 0.67 (eluent ethyl acetate–toluene, 1:6). IR spectrum, cm^{-1}: 2921, 2951 (CH_2), 1744, 1718 (C=O of ester), 1660 (C=O of ketone). Found, %: C 74.03, 74.10; H 4.06, 4.00. $C_{55}H_{38}O_9$. Calculated, %: C 74.31; H 3.96.

4-Benzoyl-1,2-phenylenebis[4'-(oxycarbonyl)-biphenyl-4-carboxylic acid] (IV). To a solution of 3.83 g (4.54 mmol) of compound **III** in 55 ml (84.43 g, 0.741 mol) of trifluoroacetic acid was added at stirring 6.05 g of acetic acid containing 1.98 g (2.447 mmol) of HBr. The reaction mixture was left standing for 24 h, the separated precipitate was filtered off and washed with 2-propanol and acetone till the removal of the characteristic odor of benzyl bromide. The precipitate was dried in air, and then in a thermostat. Yield 2.23 g (60%), mp >320°C, R_f 0.66 (eluent toluene–ethyl acetate, 1:1). IR spectrum, cm^{-1}: 3064, 3003 (O–H), 1743 (C=O of ester), 1660 (C=O of ketone). ^{1}H NMR spectrum, δ, ppm: 7.0–8.3 (group of signals), 4.2 (COOH). Found, %: C 74.44, 74.40; H 4.10, 4.00. $C_{29}H_{26}O_9$. Calculated, %: C 74.31; H 3.96.

IR spectra were recorded on FTIR-8400S SHIMADZU instrument from samples pelletized with KBr. ^{1}H NMR spectra from solutions in DMSO-d_6 were registered on a spectrometer Bruker AC-200. The elemental analysis was carried out on an automatic Perkin-Elmer analyzer. The reaction progress was monitored by TLC on Silufol UV-254 plates.

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