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Mesogenic 4-Acryloyloxy- and 4-(2,3-Epoxypropoxy)phenyl 4-Alkoxybenzoates

E. S. Syrbu[a], O. V. Potemkina[b], I. V. Novikov[a], S. A. Kuvshinova[a], O. I. Koifman[a], V. V. Aleksandriiskii[c], and V. A. Burmistrov[c]

[a]*Research Institute of Macroheterocyclic Compounds at Ivanovo State University of Chemical Engineering, Ivanovo,153000 Russia*
e-mail: sofya.kuv@yandex.ru
[b] *Ivanovo Institute of State Fire Fighting Service of the Russian Emergencies Ministry, Ivanovo, Russia*
[c] *Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia*

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Abstract—Procedures were developed which made it possible to synthesize in good yields homologs of 4-acryloyloxyphenyl 4-alkoxybenzoates (C_3, C_5, C_7, C_8) and of 4-(2,3-epoxypropoxy)phenyl 4-alkoxybenzoates (C_5, C_7). The substituted phenylbenzoates obtained exhibit the enantiotropic nematic mesomorphism in a sufficiently wide temperature range. The studied compounds have absorption maxima in the near UV region and a high temperature of decomposition beginning.

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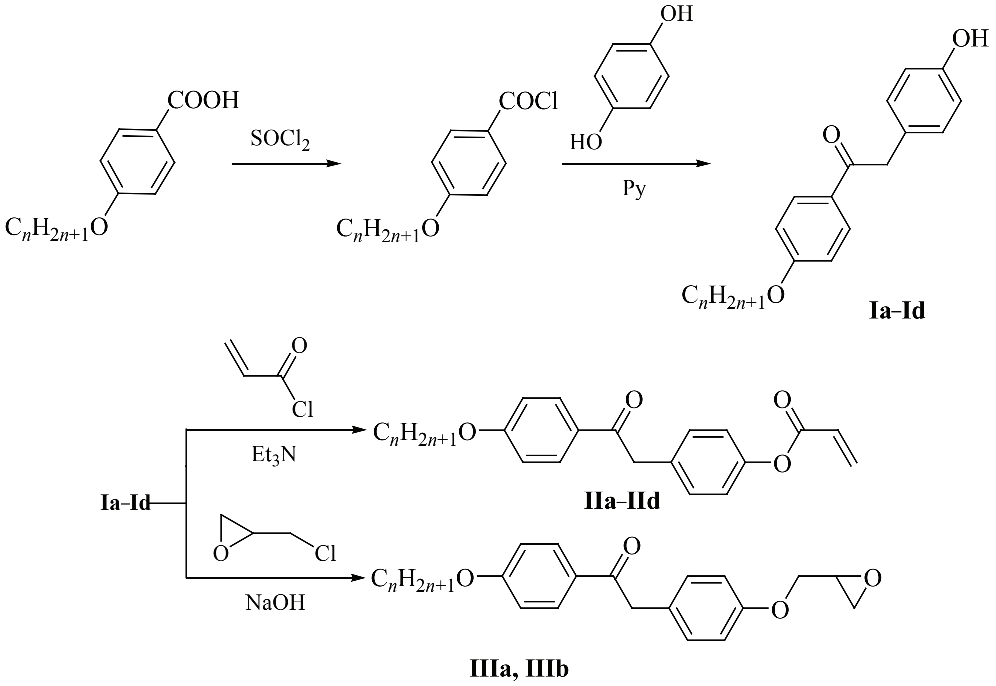
Low-molecular substituted phenyl benzoates owing to their specific properties are promising compounds for practical application. For instance, the liquid crystal compositions based on phenyl benzoates are interesting for application in the information mapping facilities due to the bwide range of the mesophase existence, low viscosity, and high dielectric anisotropy [1]. The interest to substituted phenyl benzoates originates also from the possibility of their application as liquid crystalline stationary phases in GLC for solving versatile analytic problems, first of all, for the separation of spatial isomers of organic substances [2]. Besides the phenyl benzoates with the chemically active substituents are nontoxic and non-coloring light-resistant stabilizers for polyolefins and poly(vinyl chloride) [3]. The introduction into the rigid core of phenyl benzoate of epoxy and acryloyloxy groups followed by polymerization provide a possibility to synthesize liquid crystalline polymers of comb-shaped polymers for the new field of optoelectronics creating flexible electrooptic gadgets, including displays [4].

In this connection the goal of this research was the development of optimum procedures for the synthesis of 4-acryloyloxy- and 4-(2,3-epoxypropoxy)phenyl 4-alkoxybenzoates, the investigation of their mesomorphic properties, and the estimation of the opportunities to use the obtained substances as the stabilizers of polymer materials.

4-Acryloyloxy- (**IIa–IId**) and 4-(2,3-epoxypropoxy) phenyl (**IIIa, IIIb**) 4-alkoxybenzoates were synthesized along the following scheme.

4-Hydroxyphenyl 4-alkoxybenzoates **Ia–Id** were obtained by the reaction of freshly prepared 4-alkoxyphenylcarbonyl chlorides with a five-fold excess of hydroquinone in anhydrous pyridine at 30°C within 10 h [5]. Acryloyloxy-substituted phenyl benzoates **IIa–IId** were synthesized from esters **Ia–Id** by the reaction with acryloyl chloride in the presence of triethylamine as acceptor of the liberating HCl in chloroform at 60°C within 3.5 h. By varying the reagents ratio, amount of the phase transfer catalyst Et_4NBr, concentration of the water solution of NaOH, reaction time and epoxidation temperature we determined the optimum conditions of the preparation of epoxy-substituted phenyl benzoates **IIIa, IIIb**: The ratio of compound **I**–epichlorohydrin–anhydrous sodium hydroxide was 1:30:2, the reaction was carried out at 70°C over 5 h, without catalyst . The obtained substituted phenyl benzoates **IIa–IId, IIIa, IIIb** were recrystallized and dried in a vacuum to the constant temperatures of the

Scheme.



I, **II**, n = 3 (a), 5 (**b**), 7 (**c**), 8 (**d**); **III**, n = 5 (**a**), 7 (**b**).

phase transitions and to the absence of impurity signals in the ^1H NMR spectra.

The composition and the structure of compounds obtained were established from elemental analysis and ^1H NMR spectra. The theoretical calculations of δ values were performed by the method B3LYP/6-311G(O, P) [6], the shielding constants were calculated by GIAO method [7]. The shielding constants were used in calculations of chemical shifts with respect to TMS. It should be noted that for all molecules the theoretical δ values are somewhat larger than the experimental ones. This discrepancy arises from the calculations for isolated molecules in the gas phase without accounting for the effect on the chemical shifts produced by the solvation surrounding. At the same time a stable correlation was observed between the calculated and experimental δ values.

Electron absorption spectra are interesting for the qualitative estimation of the possibility to use the compounds synthesized as modifiers of polymer materials. It has been shown by an example of compounds **IIa, IIIa** that the studied compounds have an inherent absorption in the near UV spectral region (see EXPERIMENTAL), consequently, at their presence in the composition based on macromolecular compounds they shoul screen the polymer matrix in this spectral range which is the most dangerous for the majority of polymers.

The temperatures (°C) of the phase transitions from crystal to nematic phase (C→N) and from nematic phase to isotropic liquid (N→I) of compounds obtained measured by the method of polarization thermomicroscopy are listed in the table.

Compound no.	C↑	N↑
IIa	91.3	116.3
IIb	81.8	106.8
IIc	68.1	97.6
IId	64.8	95.8
IIIa	41.5	67.3
IIIb	42.1	57.8

Consequently phenyl benzoates **IIa–IId, IIIa, IIIb** are enantiotropic liquid crystals, they possess an insignificant thermal stability of the mesophase and a sufficiently large range of its existence. All compounds under investigation above the melting point are melts of low viscosity exhibiting schlieren textures in the polarized light characteristic of the nematic mesaphase. The comparison of the phase transitions of compounds **II** and **III** indicates the stabilization both of nematic and crystal phases at introducing into the structure of the acryloyloxy substituent. Within each series the temperatures of the nematic-isotropic transition regularly decrease with the elongation of the terminal alkyloxy substituents due to the loosening effect of the aliphatic substituents.

Some chemical processes occurring in the substance at heating are known to be accompanied with the change of mass (thermal oxidation, destruction, etc.) [8]. The thermal stability of mesogenes **IIa, IIIa** were estimated by the thermogravimetric analysis. We chose as criteria the temperatures of the decomposition beginning (t_{db}, °C) where the thermogravimetric curves deviate from the initial zero value, and the temperature of the loss of 70% of the sample mass ($t_{70\%}$, °C):

Compound no.	t_{db}	$t_{70\%}$
IIa	337	446
IIIa	362	453

Thus the obtained substituted phenyl benzoates possess a thermal stability exceeding the temperature of the processing of the majority of macromolecular compounds, and consequently, they can be used as modifiers of the polymer materials, in particular, in the compositions underlain by polyolefins and poly(vinyl chloride).

EXPERIMENTAL

Electron absorption spectra were recorded on a spectrophotometer Perkin Elmer Lambda 20 in $CHCl_3$. ^1H NMR spectra were registered in $CDCl_3$ on a spectrometer Bruker Avance III at operating frequency 500 MHz; internal reference TMS. The phase transition temperatures of the compounds obtained were measured and the study of textures was performed on a polarization microscope Polam P211 equipped with a heating block. The accuracy of the measurements of the phase transition temperatures was ±0.2°C. The thermogravimetric analysis was carried out on a NETZSCH instrument in the dynamic mode in an argon flow, heating rate 5 deg min^{-1}, weight of the sample 2–5 mg.

4-Acryloyloxyphenyl 4-propyloxybenzoate (IIa). To a solution of 2.72 g (0.01 mol) of 4-hydroxyphenyl 4-propyloxybenzoate in 50 ml of chloroform was added 1.01 g (0.01 mol) of triethylamine. The solution was stirred for 30 min, afterwards within 1 h was added dropwise 0.9 g (0.01 mol) of acryloyl chloride. The reaction mixture was stirred for 3 h at 40–45°C, cooled, washed thrice with water, the organic layer was separated, dried with Na_2SO_4, the solvent was distilled off, the residue was twice recrystallized from ethanol. Yield 2.48 g (76%), white crystals, mp 91.3°C. UV spectrum, λ_{max}, nm (lgε): 263 (4.01). ^1H NMR spectrum, δ, ppm: 0.95 t (3H, CH_3, *J* 7.41 Hz), 1.50 d (2H, CH_2, *J* 7.04 Hz), 3.95 d (2H, CH_2O, *J* 6.46 Hz), 5.55 d (2H, =CH_2, *J* 10.40 Hz), 5.98 m (1H, CH=), 6.88 d ($2H_{arom}$, *J* 17.97 Hz), 7.09 m ($4H_{arom}$), 7.95 d ($2H_{arom}$, *J* 8.83 Hz). Found, %: C 69.57; H 5.36; O 24.40. $C_{19}H_{18}O_5$. Calculated, %: C 69.94; H 5.52; O 24.54.

Esters **IIb–IId** were obtained similarly.

4-Acryloyloxyphenyl 4-allyloxybenzoate (IIb). Yield 2.76 g (78%), white crystals, mp 81.8°C. ^1H NMR spectrum, δ, ppm: 0.98 t (3H, CH_3, *J* 7.38 Hz), 1.30 m [6H, $(CH_2)_3$], 3.96 d (2H, CH_2O, *J* 6.43 Hz), 5.58 d (2H, =CH_2, *J* 10.38 Hz), 6.01 m (1H, CH=), 6.93 d ($2H_{arom}$, *J* 17.95 Hz), 7.11 m ($4H_{arom}$), 8.09 d ($2H_{arom}$, *J* 8.83 Hz). Found, %: C 70.05; H 6.09; O 21.97. $C_{21}H_{22}O_5$. Calculated, %: C 71.17; H 6.26; O 22.57.

4-Acryloyloxyphenyl 4-heptyloxybenzoate (IIc). Yield 2.86 g (75%), white crystals, mp 68.1°C. ^1H NMR spectrum, δ, ppm: 0.96 t (3H, CH_3, *J* 7.38 Hz), 1.40 m [10H, $(CH_2)_5$], 3.97 d (2H, CH_2O, *J* 6.44 Hz), 5.51 d (2H, =CH_2, *J* 10.37 Hz), 6.01 m (1H, CH=), 6.90 d ($2H_{arom}$, *J* 17.96 Hz), 7.06 m ($4H_{arom}$), 8.03 d ($2H_{arom}$, 8.83 Hz). Found, %: C 72.13; H 6.24; O 20.76. $C_{23}H_{26}O_5$. Calculated, %: C 72.23; H 6.85; O 20.92.

4-Acryloyloxyphenyl 4-octyloxybenzoate (IId). Yield 3.05 g (77%), white crystals. mp 64.8°C. ^1H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3, *J* 7.37 Hz), 1.40 m [12H, $(CH_2)_6$], 3.91 d (2H, CH_2O, *J* 6.45 Hz), 5.50 d. (2H, =CH_2, *J* 10.38 Hz), 6.08 m (1H, CH=), 6.90 d ($2H_{arom}$, *J* 17.97 Hz), 7.01 m ($4H_{arom}$), 7.99 d ($2H_{arom}$, *J* 8.83 Hz). Found, %: C 72.61; H 6.89; O 19.78. $C_{24}H_{28}O_5$. Calculated, %: C 71.73; H 7.07; O 20.20.

4-(2,3-Epoxypropoxy)phenyl 4-allyloxybenzoate (IIIa). A mixture of 3 g (0.01 mol) of 4-hydroxyphenyl 4-allyloxybenzoate, 0.8 g (0.02 mol) of sodium hydroxide, and 27.8 g (0.3 mol) of epichlorohydrin was stirred for 5 h at 60–62°C, the reaction mixture was cooled, filtered, the filtrate was evaporated to dryness. The solid residue was twice recrystallized from ethanol. Yield 2.42 g (68%), white crystals, mp 41.5°C. UV spectrum, λ_{max}, nm (lgε): 272 (4.07). ^1H NMR spectrum, δ, ppm: 0.95 t (3H, CH_3, *J* 6.62 Hz), 1.40 m [6H, $(CH_2)_3$], 2.65 m (2H, Ht), 3.17 m (1H, Ht), 4.05 d (4H, CH_2OAr, OCH_2Ht, *J* 6.46 Hz), 6.93 d ($2H_{arom}$, *J* 8.83 Hz), 7.10 d ($2H_{arom}$, *J* 8.82 Hz), 7.21 d ($2H_{arom}$, *J* 8.84 Hz), 8.13 d ($2H_{arom}$, *J* 8.83 Hz). Found, %: C 70.43; H 6.36; O 22.34. $C_{21}H_{24}O_5$. Calculated, %: C 70.78; H 6.74; O 22.47.

4-(2,3-Epoxypropoxy)phenyl 4-heptyloxybenzoate (IIIb) was obtained similarly. Yield 2.70 g (70%), white crystals, mp 42.1°C. ^1H NMR spectrum, δ, ppm: 0.98 t (3H, CH_3, *J* 6.61 Hz), 1.40 m [10H, $(CH_2)_5$], 2.60 m (2H, Ht), 3.11 m (1H, Ht), 3.97 d (4H, CH_2OAr, OCH_2Ht, *J* 6.45 Hz), 6.88 d ($2H_{arom}$, *J* 8.82 Hz), 7.01 d ($2H_{arom}$, *J* 8.84 Hz), 7.16 d ($2H_{arom}$, *J* 8.83 Hz), 8.09 d ($2H_{arom}$, *J* 8.83 Hz). Found, %: C 71.08; H 7.13; O 20.57. $C_{23}H_{28}O_5$. Calculated, %: C 71.88; H 7.29; O 20.83.

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