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Brief Communications

One-step synthesis of novel photochemically bifunctional compounds of the spiropyran class

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The one-step reaction of 5-amino-1,3,3-trimethyl-2-methylideneindoline with two equivalents of different *ortho*-hydroxy-substituted aromatic aldehydes afforded novel photochemically bifunctional compounds. Molecules of these compounds include two functionally different fragments: the substituted azomethine (salicylideneimine or hydroxynaphthylmethylideneimine) fragment in which intramolecular proton transfer can be induced by electronic excitation and the spiropyran fragment in which the O—C_{spiro} bond can dissociate upon UV-light absorption to form the merocyanine form. No conjugation between the azomethine and pyran fragments is observed in the initial state of the molecule. The compounds synthesized manifest the photochromic properties and luminescence.

Key words: spiropyrans, photobifunctional compounds, photochromism, luminescence, ^{1}H NMR spectroscopy.

Photochromic compounds that undergo reversible phototransformations accompanied by the change in color and other properties are presently intensively investigated due to their use in optical systems of information detection and imaging, molecular switchers, transport systems, dynamic chemisensors and biosensors, *etc.*[1—6] Since possible applications of photochromic compounds are diverse, the range of demands imposed on their characteristics is also rather broad.

We have recently synthesized for the first time photochemically bifunctional compounds (PBC) based on spironaphthoxazines in order to extend their functional properties. A molecule of PBC includes two fragment of different nature in which two different photoprocesses can occur under irradiation.[7—10]

Continuing these works, we developed the one-step method for synthesis of PBC, whose molecules include the spiropyran and substituted azomethine fragments. Molecules of these compounds are photochemically bifunctional, because the excited state intramolecular proton transfer (ESIPT) from the phenolic hydroxy group to the nitrogen atom is possible in the salicylideneimine or hydroxynaphthylmethylideneimine fragment, whereas in the spiropyran fragment the O—C_{spiro} bond can dis-

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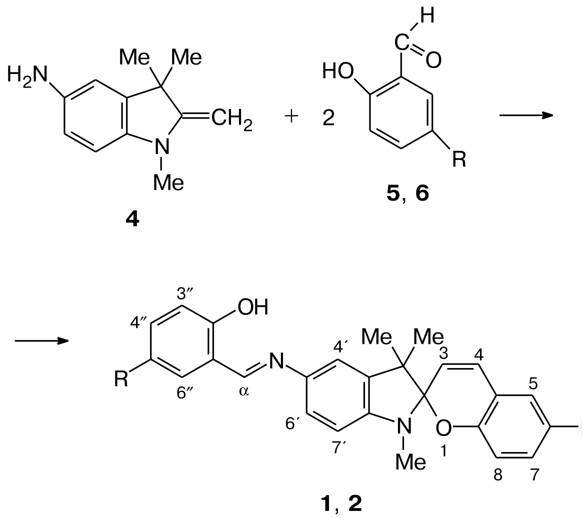
sociate to form the merocyanine form. In this case, no conjugation is observed between the azomethine fragment introduced into the indoline part of the PBC molecules and the benzo- or naphthopyran part in the ground state of the molecule.

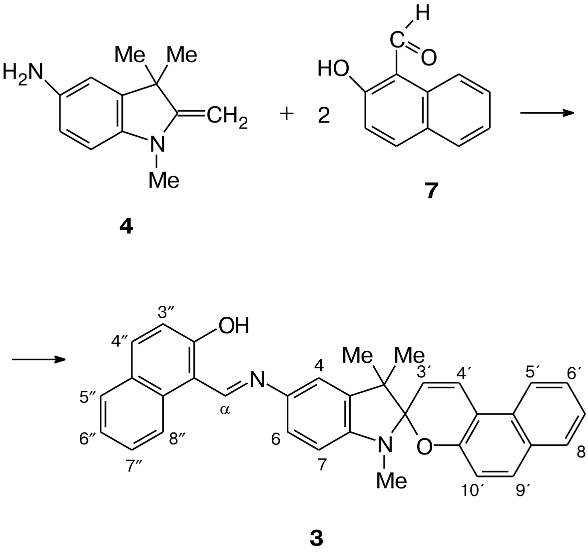
Compounds **1—3** were synthesized by the one-step reaction of 5-amino-1,3,3-trimethyl-2-methylideneindoline (**4**), obtained by an earlier descried procedure,[11] with 5-bromo- and 5-nitrosalicylaldehydes (**5** and **6**) and 1-hydroxy-2-naphthaldehyde (**7**), respectively, at the reactant ratio 1 : 2 (Schemes 1 and 2). This reaction involves the double condensation of *ortho*-hydroxy-substituted aromatic aldehydes at the enamine group and the amino group of synthone **4**.

Scheme 1



R = Br (**1**), NO$_2$ (**2**)

Scheme 2



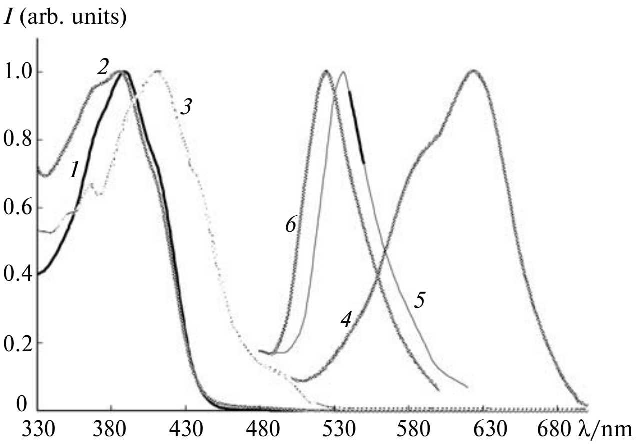


Fig. 1. Absorption spectra of compounds **1—3** (*1—3*) and the open form of compound **2** (*4*) at 20 °C and the luminescence spectra of the initial form of compounds **1** (*5*) and **2**, **3** (*6*) at λ_{exc} = 400 nm in toluene.

The structures of the synthesized compounds were determined by elemental analysis, NMR spectra, and mass spectra (see Experimental). Signals in the ^{1}H NMR spectra were assigned by comparing the data on the products and starting aldehydes, as well as the earlier synthesized PBC.[7,10]

The absorption spectra of compounds **1—3** in toluene are shown in Fig. 1. The spectrum of compound **3** is shifted to the long-wavelength region compared to the spectra of compounds **1** and **2** due to the substitution of the benzo fragment for the naphtho moiety.

Unlike compounds **1** and **3**, compound **2** exhibits the photochromic properties in toluene solutions at room temperature (see Fig. 1), which is due to the stabilization of the merocyanine form by the nitro group (which is a strong electron acceptor) in position 6.[12] In addition, at room temperature in toluene solutions compounds **1—3** fluoresce (see Fig. 1): fluorescence with a maximum at 520—540 nm is observed upon excitation in the region of 400 nm. The fluorescence excitation spectrum of all compounds coincides with the long-wavelength part of the absorption spectrum.

Further the dynamics of the photoprocesses in these compounds will be studied in detail.

Experimental

NMR spectra were detected on a Bruker WM-400 spectrometer at 25 °C in CDCl$_3$. Absorption spectra were recorded on a Genesys-2 spectrophotometer followed by digital processing. samples were irradiated with the light from a DRSh-1000 lamp through an interferentional light filter with transmission at 365 nm. Luminescence spectra were obtained on a Jobin Yvon JY 3 spectrofluorimeter. Mass spectra were measured on a Finnigan MAT INCOS 50 mass spectrometer.

6-Bromo-5´-(5-bromo-2-hydroxybenzylideneimino)-1´,3´,3´-trimethyl-1´,3´-dihydrospiro[(2*H*)-1-benzopyran-2,2´-(2*H*)-indole] (1). 5-Bromosalicylaldehyde (**5**) (0.9 g, 4.48 mmol) was added to a solution of 5-amino-2-methylidene-1,3,3-trimethylindoline (**4**) (0.4 g, 2.1 mmol) in toluene (60 mL), and the mixture was refluxed for 4 h with azeotropic distillation of water. The precipitate was filtered off and washed with petroleum ether (10 mL). The product was isolated by chromatography on the plate coated with silica gel using a chloroform—acetone (19 : 1) mixture as eluent. Compound **1** was obtained (0.96 g, 82%) as brightly yellow crystals with m.p. 176—177 °C. ^{1}H NMR, δ: 1.20; 1.33 (both s, 3 H each, $C(CH_3)_2$); 2.76 (s, 3 H, NCH_3); 5.73 (d, 1 H, H(3); $^3J_{3,4}$ = 10.2 Hz); 6.61 (d, 1 H, H(8), $^3J_{7,8}$ = 9.3 Hz); 6.82 (d, 1 H, H(4); $^3J_{3,4}$ = 10.2 Hz); 7.20 (m, 2 H, H(5), H(7);) 6.54 (d, 1 H, H(7´); $^3J_{6',7'}$ = 8.1 Hz); 6.90 (d, 1 H, H(3″), $^3J_{3'',4''}$ = 8.8 Hz); 7.11 (d, 1 H, H(4´), $^4J_{4',6'}$ = 2.0 Hz); 7.20 (dd, 1 H, H(6´), $^3J_{6',7'}$ = 8.1 Hz; $^4J_{4',6'}$ = 2.0 Hz); 7.39 (dd, 1 H, H(4″), $^3J_{3'',4''}$ = 8.8 Hz; $^4J_{4'',6''}$ = 2.3 Hz); 7.49 (d, 1 H, H(6´), $^4J_{4'',6''}$ = 2.3 Hz); 8.56 (s, 1 H, H(α)); 13.7 (br.s, 1 H, OH). MS, *m/z*: 554 $[M]^+$. Found (%): C, 55.38; H, 3.74; N, 4.91. $C_{26}H_{22}Br_2N_2O_2$. Calculated (%): C, 56.35; H, 4.00; N, 5.06.

5´-(2-Hydroxy-5-nitrobenzylideneimino)-1´,3´,3´-trimethyl-6-nitro-1´,3´-dihydrospiro[(2*H*)-1-benzopyran-2,2´-(2*H*)-indole] (2). 5-Nitrosalicylaldehyde (**6**) (1.086 g, 6.5 mmol) was added to a solution of 5-amino-2-methylidene-1,3,3-trimethylindoline (**4**) (0.4 g, 2.1 mmol) in toluene (60 mL), and the mixture was refluxed for 4 h with azeotropic distillation of water. The precipitate was filtered off and washed with petroleum ether (10 mL). The product was isolated by chromatography on the plate coated with silica gel using a chloroform—acetone (19 : 1) mixture as eluent. Compound **2** was obtained in a yield of 0.85 g (80%) as a brick-red powder with m.p. 232—233 °C. ^{1}H NMR, δ: 1.25; 1.35 (both s, 3 H each, $C(CH_3)_2$); 2.80 (s, 3 H, NCH_3); 5.87 (d, 1 H, H(3); $^3J_{3,4}$ = 10.3 Hz); 6.61 (d, 1 H, H(7´); $^3J_{6',7'}$ = 8.3 Hz); 6.79 (d, 1 H, H(8), $^3J_{7,8}$ = 8.5 Hz); 7.06 (d, 1 H, H(4); $^3J_{3,4}$ = 10.3 Hz); 7.07 (d, 1 H, H(3″), $^3J_{3'',4''}$ = 9.2 Hz); 7.17 (d, 1 H, H(4´), $^4J_{4',6'}$ = 2.2 Hz); 7.26 (dd, 1 H, H(6´), $^3J_{6',7'}$ = 8.3 Hz; $^4J_{4',6'}$ = 2.2 Hz); 8.02 (d, 1 H, H(5) $^4J_{5,7}$ = 2.7 Hz); 8.05 (dd, 1 H, H(7); $^3J_{7,8}$ = 8.5 Hz; $^4J_{5,7}$ = 2.7 Hz); 8.22 (dd, 1 H, H(4″), $^3J_{3'',4''}$ = 9.2 Hz; $^4J_{4'',6''}$ = 2.7 Hz); 8.37 (d, 1 H, H(6″), $^4J_{4'',6''}$ = 2.7 Hz); 8.73 (s, 1 H, H(α)); 14.98 (br.s, 1 H, OH). MS, *m/z*: 486 $[M]^+$. Found (%): C, 63.87; H, 4.49; N, 11.20. $C_{26}H_{22}N_4O_6$. Calculated (%): C, 64.19; H, 4.56; N, 11.52.

5-(2-Hydroxy-1-naphthylmethylideneimino)-1,3,3-trimethyl-1,3-dihydrospiro[(2*H*)-indole-2,2´-(3*H*)-naphtho[2,1-*b*]pyran] (3). 1-Formyl-2-naphthol (**7**) (1.1 g, 6.4 mmol) was added to a solution of 5-amino-1,3,3-trimethyl-2-methylideneindoline (**4**) (0.4 g, 2.1 mmol) in toluene (60 mL), and the mixture was refluxed for 4 h with azeotropic distillation of water. The precipitate was filtered off and washed with benzene (10 mL) and petroleum ether (10 mL). The product was isolated by chromatography on the plate coated with silica gel using a chloroform—acetone (19 : 1) mixture as eluent. Compound **3** was obtained in a yield of 0.81 g (78%) as orange crystals, R_f 0.85 (chloroform—acetone (9 : 1) mixture as eluent), m.p. 206—207 °C. ^{1}H NMR, δ: 1.29; 1.41 (both s, 3 H each, $C(CH_3)_2$); 2.79 (s, 3 H, NCH_3); 5.82 (d, 1 H, H(3´); $^3J_{3',4'}$ = 10.4 Hz); 6.59 (d, 1 H, H(7); $^3J_{6,7}$ = 8.2 Hz); 7.01 (d, 1 H, H(10´), $^3J_{9',10'}$ = 8.9 Hz); 7.13 (d, 1 H, H(3″), $^3J_{3'',4''}$ = 9.1 Hz); 7.19 (d, 1 H, H(4), $^4J_{4,6}$ = 2.2 Hz); 7.27 (dd, 1 H, H(6), $^3J_{6,7}$ = 8.2 Hz; $^4J_{4,6}$ = 2.2 Hz); 7.33 (ddd, 1 H, H(6´) $^3J_{5',6'}$ = 8.4 Hz; $^3J_{6',7'}$ = 6.9 Hz, $^4J_{6',8'}$ = 1.1 Hz); 7.35 (m, 1H, H(6″)); 7.52 (ddd, 1 H, H(7´)) $^3J_{7',8'}$ = 8.4 Hz; $^3J_{6',7'}$ = 6.9 Hz; $^3J_{5',7'}$ = 1.1 Hz; 7.52 (m, 1 H, H(7″)); 7.64 (d, 1 H, H(4´); $^3J_{3',4'}$ = 10.4 Hz); 7.65 (d, 1 H, H(9´), $^3J_{9',10'}$ = 8.9 Hz); 7.73 (d, 1 H, H(8´), $^3J_{7',8'}$ = 8.3 Hz); 7.78 (dd, 1 H, H(4″), $^3J_{3'',4''}$ = 9.1 Hz); 9.34 (s, 1 H, H(α)); 8.05 (d, 1 H, H(5´), $^3J_{5',6'}$ = 8.4 Hz, $^4J_{5',7'}$ = 1.3 Hz); 8.05 (dd, 1 H, H(5″), $^3J_{5'',6''}$ = 8.1 Hz; $^4J_{5'',7''}$ = 1.3 Hz); 8.12 (dd, 1 H, H(8″), $^3J_{7'',8''}$ = 8.4 Hz; $^4J_{6'',8''}$ = 1.1 Hz); 15.97 (br.s, 1 H, OH). MS, *m/z*: 496 $[M]^+$. Found (%): C, 80.36; H, 5.38; N, 5.50. $C_{34}H_{28}N_2O_2$. Calculated (%): C, 82.23; H, 5.68; N, 5.64.

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