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Photochemically bifunctional compound from the class of spironaphthooxazines

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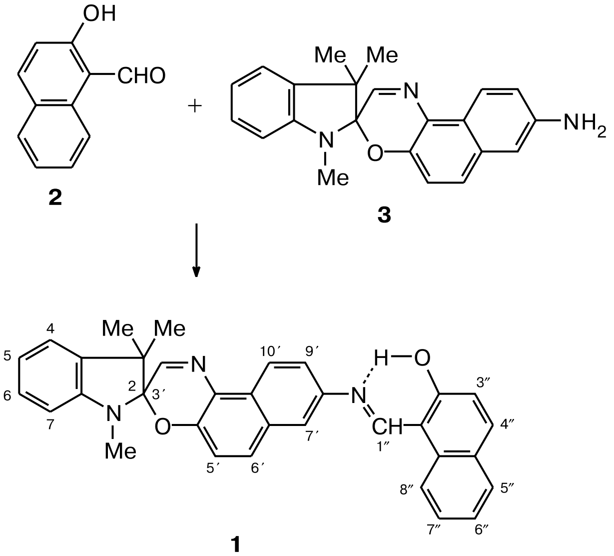
Photochromism is the reversible light change under the light with a certain wavelength. This phenomenon is of great interest from both theoretical and practical points of view. Spirooxazines are of special significance among photochromic compounds, because they are highly photostable compared to other organic photochromes.

Many spirooxazines are presently known. However, all these compounds were synthesized by traditional procedures including many steps, which results, naturally, in low yields of the target products. Therefore, the development of direct chemical reactions of various spirooxazines aimed at the targeted modification of the structures of their molecules seems to be a very important task.

In continuation of the works on the direct chemical reactions of photochromic spirooxazine molecules,[1–4] we synthesized for the first time a new compound: 8´-(2-hydroxy-1-naphthylideneimino)-1,3,3-trimethylspiro[2*H*-indole-2,3´-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (**1**). The molecule of this compound is photochemically bifunctional because contains two functionally different fragments: hydroxynaphthylideneimine in which the intramolecular proton transfer is possible upon electron excitation and spironaphthooxazine in which the C—O spiro bond can dissociate upon UV light absorption.

Compound **1** was synthesized by the reaction of 2-hydroxy-1-naphthaldehyde (**2**) with 8´-amino-1,3,3-trimethylspiro[2*H*-indole-2,3´-[3*H*]naphth[2,1-*b*][1,4]oxazine] (**3**), which was obtained according to a previously described procedure.[3]



Compound **1** is characterized by the photochromic properties: upon UV irradiation a solution of compound **1** in acetonitrile cooled to 0 °C becomes colored (Fig. 1), which is caused by the transition of the molecule from the starting spiran form **A** to photoinduced form **B** with the dissociated spiro C—O bond. After cessation of irradiation, the inverse **B** → **A** transition is observed. It occurs according to a monoexponential law with a rate constant of $3.3 \cdot 10^{-2}$ s^{-1}. In addition, at room temperature compound **1** exhibits weak fluorescence. For example, excitation at 400 nm in dioxane results in the luminescence with a maximum at 490 nm and a shoulder at 520 nm. The fluorescence excitation spectrum of compound **1** coincides with the long-wave part of the absorption spectrum.

The absence of a signal from the NH group in the ^{1}H NMR spectrum indicates that the starting molecule **1** exists in the enolic (without proton transfer) form.

Note that the preliminary studies of compound **1** by laser femtosecond spectroscopy showed its photochemi-

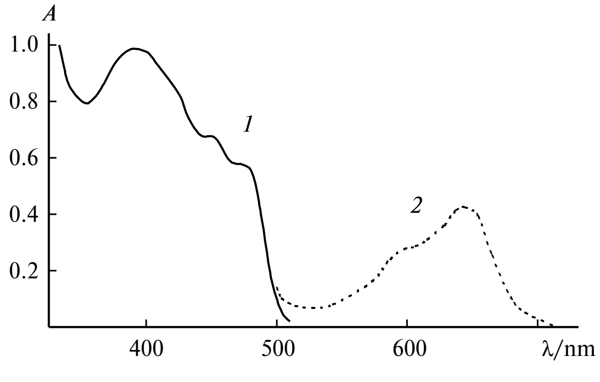


Fig. 1. Absorption spectra of compound **1** in acetonitrile at 0 °C before (*1*) and after (*2*) UV irradiation.

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cal bifunctionality. Two processes were found after the action of a photon with 308 nm: C—O spiro bond opening in the oxazine ring with a characteristic lifetime of 350 fs and the intramolecular proton transfer in the hydroxyazomethine fragment (100 fs). These data will be presented in detail elsewhere.

^{1}H NMR spectra were recorded on a Brucker WM-400 spectrometer at 25 °C in $CDCl_3$. Absorption spectra were measured on a Specord UV-VIS spectrophotometer. Luminescence spectra were obtained on a JY-3 spectrofluorimeter.

8´-(2-Hydroxy-1-naphthylideneimino)-1,3,3-trimethylspiro[2*H*-indole-2,3´-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (1). A mixture of amine **3** (70 mg, 0.2 mmol) and aldehyde **2** (35 mg, 0.2 mmol) was refluxed in anhydrous toluene (20 mL) for 2 h with slow distillation of the solvent (10 mL). The residue was concentrated. The resulting mixture was chromatographed on silica gel, and the fraction with R_f 0.85 (chloroform—acetone, 9 : 1) was collected. The product was crystallized from petroleum ether. Compound **1** as orange crystals was obtained in 65% yield (65 mg), m.p. 242—243 °C. Found: C, 78.45; H, 5.82; N, 8.34. $C_{33}H_{27}N_3O_2 \cdot 1/2(H_2O)$. Calculated: C, 78.26; H, 5.53; N, 8.30. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.37, 1.38 (both s, 3 H each, $C(CH_3)_2$); 2.78 (s, 3 H, NCH_3); 6.59 (d, 1 H, H(7), $^3J_{6,7} = 7.7$ Hz); 6.92 (t, 1 H, H(5), $^3J_{5,6} = 7.3$ Hz); 7.07 (d, 1 H, H(5´), $^3J_{5',6'} = 8.9$ Hz); 7.09 (d, 1 H, H(3″), $^3J_{3'',4''} = 9.2$ Hz); 7.10 (d, 1 H, H(4), $^3J_{4,5} = 6.9$ Hz); 7.23 (td, 1 H, H(6), $^3J_{6,7} = 7.3$ Hz, $^4J_{4,6} = 1.0$ Hz); 7.34 (dd, 1 H, H(6″), $^3J_{5'',6''} = 8.4$ Hz, $^3J_{6'',7''} = 7.4$ Hz); 7.53 (ddd, 1 H, H(7″), $^3J_{7'',8''} = 8.4$ Hz, $^4J_{5'',7''} = 1.2$ Hz, $^3J_{7'',6''} = 7.4$ Hz); 7.66 (dd, 1 H, H(9´), $^3J_{9',10'} = 8.8$ Hz, $^4J_{7',9'} = 2.2$ Hz); 7.68 (d, 1 H, H(7´)); 7.69 (d, 1 H, H(4″)); 7.71 (d, 1 H, H(8″)); 7.78 (s, 1 H, H(2´)); 7.79 (d, 1 H, H(6´)); 8.15 (d, 1 H, H(5´)); 8.64 (d, 1 H, H(10´)); 9.46 (d, 1 H, H(1″), $^3J_{H(1''),OH} = 3.0$ Hz); 13.49 (br.s, 1 H, OH).

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