Brief Communications

Synthesis and properties of a novel photochromic luminophore

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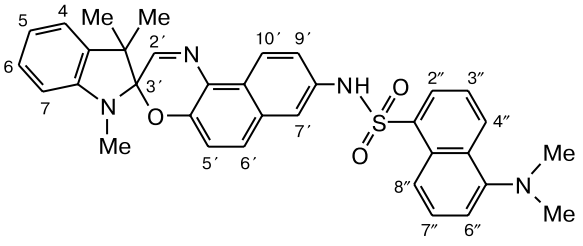
A photochemically bifunctional compound was obtained. Its molecule includes the spironaphthoxazine and dansylamino fragments. This compound exhibits both photochromic and luminescent properties. Its spectroscopic characteristics were studied in different solvents. The electronic systems of two constituent fragments do not interact with each other.

Key words: photochromism, luminescence, spironaphthoxazines, dansylamide.

In the present work, the synthesis and study of photochemically bifunctional compounds[1,2] was extended to 8´-(5-dimethylaminonaphthylsulfonylamino)-1,3,3-trimethyl-2,3-dihydrospiro[2*H*-indole-2,3´-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (**1**). Compound **1** was obtained by a reaction of dansyl chloride with 8´-amino-1,3,3-trimethyl-1,3-dihydrospiro[2*H*-indole-2,3´-[3*H*]naphtho[2,1-*b*][1,4]oxazine] prepared as described earlier.[3]



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Interest in bifunctional compounds, which can undergo fundamentally different transformations when exposed to light, is due to the possibility of controlling the course of those photochemical processes. Compound **1** consists of two fragments: the spironaphthoxazine one, in which a photochromic process can occur, and the dansylamino one, which is known[4] to be a good luminophore. Thus, light absorption can induce two competitive pro-

† Deceased.

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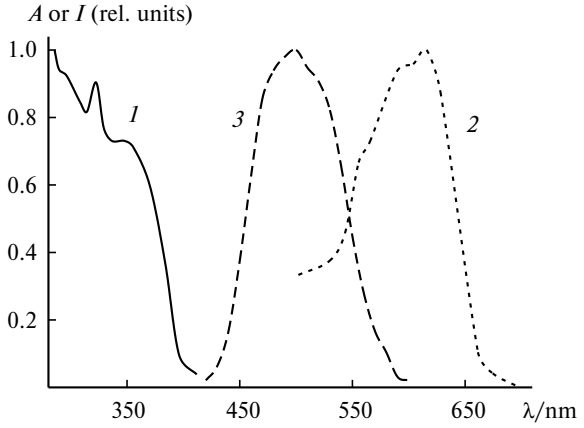


Fig. 1. Absorption spectra of compound **1** before (*1*) and after UV irradiation (*2*) at −10 °C and the luminescence spectrum of the starting form (*3*) at λ_{exc} = 350 nm in toluene.

cesses in compound **1**, namely, dissociation of the spiro C—O bond of the form **A** followed by the formation of a photoinduced colored form **B** or luminescence emission by the dansylamino fragment.

Indeed, compound **1** exhibit both the photochromic properties and intense fluorescence (Fig. 1).

When exposed to UV light, solutions of compound **1** turned colored, which suggests the formation of photoinduced form **B**. The colored form of photochromic spiro compounds is known[5] to exist as the quinonoid ($\mathbf{B_q}$) and bipolar structures ($\mathbf{B_b}$) in mesomeric equilibrium (Scheme 1); the presence of electron-donating or -withdrawing substituents is substantial for the position of the equilibrium.

For colored form **1**, the long-wavelength band ($\lambda_\mathbf{B}$) in the absorption spectrum experiences a bathochromic shift with an increase in the solvent polarity (positive solvatochromism) (Table 1), which provides evidence for quinonoid structure $\mathbf{B_q}$.

Table 1. Spectroscopic and kinetic characteristics of compound **1**

Solvent	$\lambda_\mathbf{B}$	λ_{lum}*	$k_\mathbf{B}$** /s^{-1}
	nm		
Toluene	615	500	$2.2 \cdot 10^{-2}$
Acetone	624	520	$1.6 \cdot 10^{-2}$
Ethanol	635	530	$5.0 \cdot 10^{-3}$

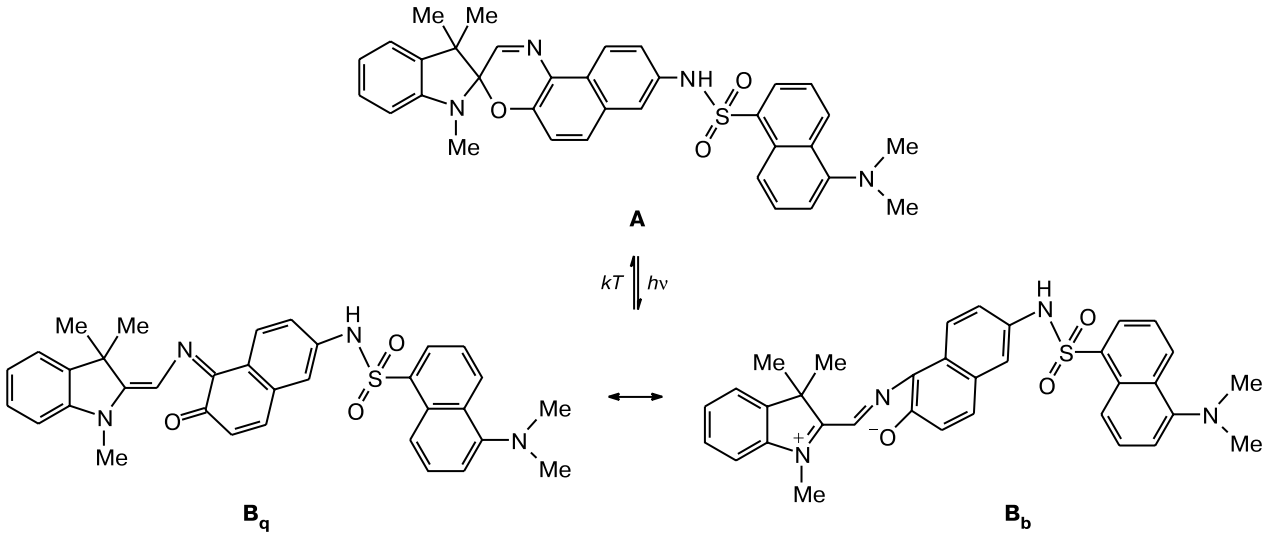
* The luminescence wavelengths.
** At −15 °C.

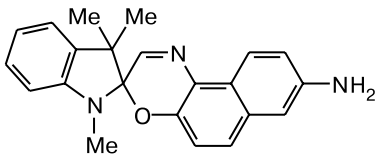
After the irradiation was stopped, the solutions underwent dark decoloration governed by the monoexponential kinetics with the rate constant $k_\mathbf{B}$ (see Table 1). In more polar solvents, $k_\mathbf{B}$ is naturally lower since the formation of structure **B** involves *cis—trans* isomerization hindered by the solvation shell in a polar solvent.

To find out whether two fragments in the original compound **1** interact with each other, we recorded absorption spectra of compound **1** and an equimolar mixture of compounds simulating its naphthoxazine and dansylamino fragments. Aminospironaphthoxazine **2** prepared as described earlier[3] served as a model of the photochromic fragment. The luminescent fragment was simulated by compound **3** specially synthesized for this purpose.

The spectra recorded are shown in Fig. 2. It can be seen that these spectra are in satisfactory agreement. Some observed differences may be due to both insufficiently accurate simulation of the photochromic and luminescent fragments of structure **1** by compounds **2** and **3** and to a difference in solvation between model compounds **2** and **3** and bifunctional compound **1**. The absorption spec-

Scheme 1





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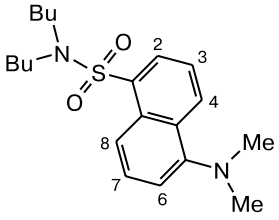

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trum of compound **1** contains no additional long-wavelength bands compared to the spectrum of the mixture, which suggests the absence of interactions between the two fragments in structure **1**. In addition, the luminescence spectra of model (**3**) and bifunctional compounds (**1**) proved to be identical but the relative quantum yield of the luminescence for compound **3** is approximately double that of compound **1**. These data suggest that light is absorbed independently by two fragments of compound **1**; *i.e.*, light absorption by the naphthooxazine fragment causes a photochromic reaction, while light absorption by the dansylamino fragment results in luminescence.

This conclusion was confirmed by HF/6-31G calculations. Optimization of structure **1** by the Hartree—Fock method using the Gaussian program[6] showed (Fig. 3) that the planes of the naphthooxazine and dansylamino fragments in forms **A** and $\mathbf{B_q}$ are virtually perpendicular to each other, which precludes their interaction.

Such a structure of compound **1** allows control of a photochemical process in oriented media by exposing to

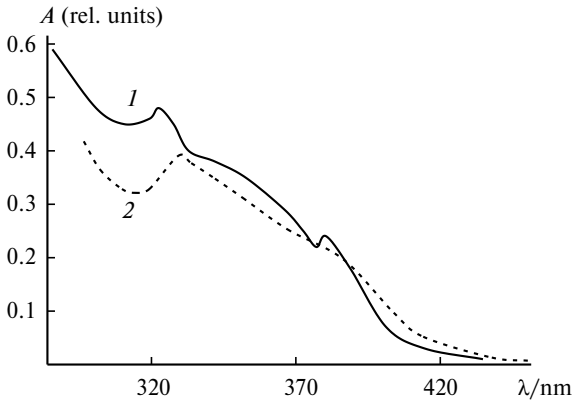

Fig. 2. Absorption spectra of compound **1** (*1*) and an equimolar mixture of compounds **2** and **3** (*2*) in ethanol at room temperature (for either compound, $c = 6.2 \cdot 10^{-5}$ mol L^{-1}).

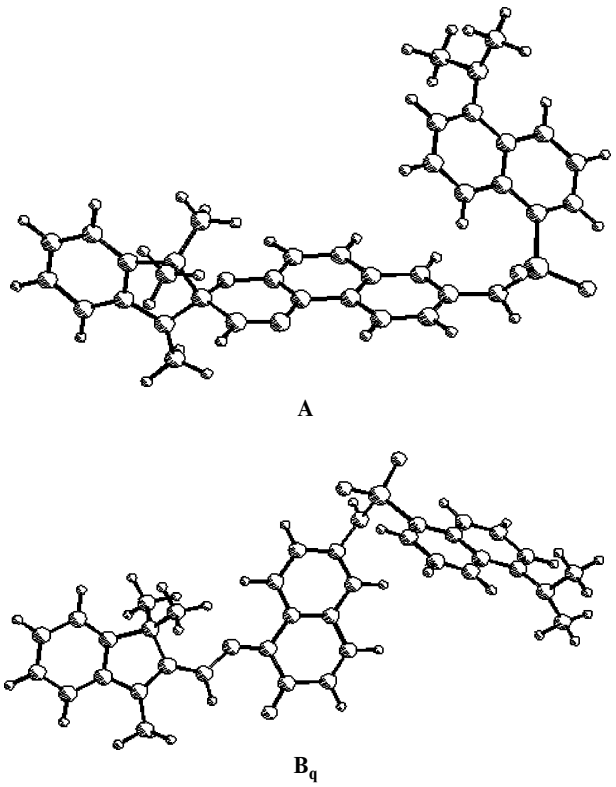

Fig. 3. PM3-optimized structure **1**.

light either the naphthooxazine or dansylamino fragment, which will be a subject of further investigations.

Experimental

NMR spectra were recorded on a Bruker WM-400 spectrometer at 25 °C in $CDCl_3$. Absorption spectra were recorded on a Specord UV—Vis spectrophotometer and luminescence spectra on a Jobin Yvon JY-3 spectrofluorimeter. Spectroscopically pure toluene, acetone, and ethanol were used as solvents. Samples were irradiated with light from a DKSSh-120 lamp through an interference light filter with $\lambda = 365$ nm. TLC analysis was carried out on silica gel plates (Merck) with chloroform—acetone (9 : 1) as an eluent.

8′-(5-Dimethylaminonaphthylsulfonylamino)-1,3,3-trimethyl-2,3-dihydrospiro[2*H*-indole-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (1). A solution of dansyl chloride (110 mg, 0.41 mmol) in anhydrous pyridine (2 mL) was added dropwise to a stirred solution of compound **2** (140 mg, 0.41 mmol) in anhydrous pyridine (3 mL). After 18 h, water (5 mL) and benzene (10 mL) were added. The mixture was shaken in a separatory funnel and the benzene layer was separated. The product from the aqueous layer was extracted with benzene (2×10 mL). The combined solution in benzene was repeatedly washed with a solution of $CuSO_4$ (until the dark blue color disappeared) and dried with anhydrous Na_2SO_4. The solvent was removed in a rotary evaporator. The product was purified by column chromatography on silica gel (40—70 μm; Aldrich) in benzene with a concentration gradient of acetone

from 0 to 5%. A fraction with R_f 0.65 was collected and concentrated. The residue was recrystallized from cyclohexane—methylene chloride to give compound **1** (110 mg, 43%) as light gray crystals, m.p. 225—227 °C. Found (%): C, 78.45; H, 5.82; N, 8.34. $C_{33}H_{27}N_3O_2$. Calculated (%): C, 78.26; H, 5.53; N, 8.30. ^{1}H NMR (400 MHz), δ: 1.29, 1.31 (both s, 3 H each, CMe_2); 2.70 (s, 3 H, NMe); 6.55 (d, 1 H, H(7), $^3J_{6,7}$ = 7.7 Hz); 6.89 (t, 1 H, H(5), $^3J_{4,5}$ = 7.3 Hz, $^3J_{5,6}$ = 7.3 Hz); 6.93 (d, 1 H, H(5′), $^3J_{5',6'}$ = 9.0 Hz); 7.00 (s, 1 H, NH); 7.06 (d, 1 H, H(4), $^3J_{4,5}$ = 7.3 Hz); 7.07 (dd, 1 H, H(9′), $^3J_{9',10'}$ = 9.0 Hz, $^4J_{7',9'}$ = 2.2 Hz); 7.19 (dd, 1 H, H(6″), $^3J_{6'',7''}$ = 7.6 Hz, $^4J_{6'',8''}$ = 1.1 Hz); 7.21 (dd, 1 H, H(6), $^3J_{5,6}$ = 7.3 Hz, $^3J_{6,7}$ = 7.7 Hz); 7.35 (d, 1 H, H(7), $^4J_{7',9'}$ = 2.2 Hz); 7.38 (dd, 1 H, H(7″), $^3J_{5'',7''}$ = 7.2 Hz, $^3J_{7'',8''}$ = 8.6 Hz); 7.43 (d, 1 H, H(6′), $^3J_{5',6'}$ = 9.0 Hz); 7.61 (m, 1 H, H(3″), $^3J_{2'',3'}$ = 8.6 Hz, $^3J_{3'',4''}$ = 8.6 Hz); 8.16 (dd, 1 H, H(8″), $^3J_{7',8''}$ = 7.4 Hz, $^4J_{8'',6''}$ = 1.1 Hz); 8.28 (d, 1 H, H(10′), $^3J_{9',10'}$ = 9.0 Hz); 8.40 (d, 1 H, H(4″), $^3J_{3'',4''}$ = 8.6 Hz); 8.46 (d, 1 H, H(2′), $^3J_{2'',3''}$ = 8.6 Hz).

***N,N*-Dibutyl-5-dimethylaminonaphthalene-1-sulfonamide (3).** A solution of dansyl chloride (100 mg, 0.37 mmol) in anhydrous pyridine (2 mL) was added dropwise at room temperature to a stirred solution of dibutylamine (100 mg, 0.78 mmol) in anhydrous acetonitrile (2 mL). The mixture was kept at room temperature for 18 h and then water (5 mL) and benzene (18 mL) were added. After shaking in a separatory funnel, the benzene layer was separated. The product from the aqueous layer was extracted with benzene (20 mL) and the combined solution in benzene was washed with saturated aqueous $CuSO_4$ and dried over Na_2SO_4. The extract was filtered and concentrated in a rotary evaporator. The residue was chromatographed on silica gel (40—70 μm; Aldrich) in benzene. Fractions with a yellow luminophore (R_f 0.78) were collected and concentrated to give compound **3** (90 mg, 67%) as a light yellow syrup. Found (%): C, 66.32; H, 8.31; N, 7.76. $C_{20}H_{30}N_2O_2S$. Calculated (%): C, 66.26; H, 8.34; N, 7.73. ^{1}H NMR (400 MHz), δ: 0.79 (m, 6 H, $NCH_2CH_2CH_2C\underline{H}_3$, ^3J = 7.4 Hz); 1.16 (q, 4 H, $NCH_2CH_2C\underline{H}_2CH_3$, ^3J = 7.5 Hz, ^3J = 7.4 Hz); 1.44 (m, 4 H, $NCH_2C\underline{H}_2CH_2CH_3$); 2.89 (s, 3 H, NMe); 3.26 (m, 4 H, NCH_2, ^3J = 7.5 Hz); 7.18 (d, 1 H, H(6), $^3J_{6,7}$ = 7.2 Hz); 7.52 (m, 1 H, H(7), $^3J_{6,7}$ = 7.2 Hz, $^3J_{7,8}$ = 7.4 Hz); 7.54 (m, 1 H, H(3), $^3J_{2,3}$ = 7.0 Hz, $^3J_{3,4}$ = 8.6 Hz); 8.17 (d, 1 H, H(8), $^3J_{7,8}$ = 7.4 Hz); 8.29 (d, 1 H, H(4), $^3J_{3,4}$ = 8.4 Hz); 8.53 (d, 1 H, H(2), $^3J_{2,3}$ = 7.0 Hz).

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