Synthesis of new spirobenzopyrans with two long-chain substituents

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Two new photochromic compounds each containing two substituents with long alkyl chains in different parts of a molecule were synthesized by a sequence of direct reduction, acylation, and nitration reactions of substituted spirobenzopyrans. The structures of the compounds synthesized were determined using the ^{1}H NMR spectra.

Key words: spirobenzopyrans, synthesis, acylation, nitration, photochromism, NMR spectroscopy.

Although new classes of organic photochromes have been synthesized recently, researchers are still interested in spirobenzopyranindolines (SBPs) due to new possible areas of their use based on the previously found photoinduced aggregation of their molecules in the merocyanine form.[1] For example, it was found that the SBPs with two long-chain substituents in a molecule, being irradiated in films obtained by the Langmuir—Blodgett method, formed J-aggregates.[2] These films exhibit nonlinear optical properties, in particular, they provide the generation of the second harmonic of laser radiation,[3] which seems promising for the use of these systems for nonlinear optical transformation of laser radiation.[4] Narrow absorption bands of the J-aggregates that formed can be considered as a basis for frequency-selective optical memory.[5,6]

In the present work, we continue our earlier studies of the properties of the SBP J-aggregates[7] performing a sequence of chemical reactions for the synthesis of two new SBPs **3** and **4**, whose molecules contain two different long-chain substituents, from compound **1** through intermediate SBP **2** (Scheme 1).

Compound **1** was synthesized according to a known procedure.[8] The reduction of compound **1** with hydrazine hydrate in the presence of Raney nickel[9] was used to synthesize compound **2**.

The structure of all the compounds synthesized were determined by ^{1}H NMR spectroscopy and confirmed by

Scheme 1

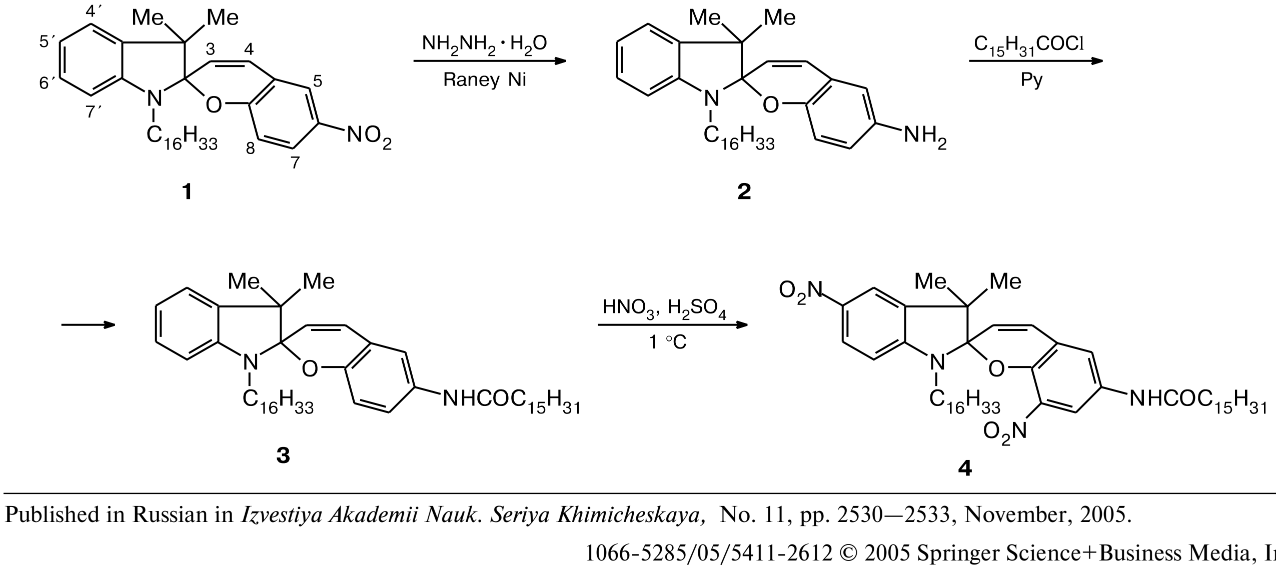

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Table 1. ^{1}H NMR spectra of the photochromic spiro compounds at 25 °C in $CDCl_3$

Compound	δ														
	CMe_2 (s)	H(3) (d)	H(4) (d)	H(5) (d)	H(7)	H(8) (d)	H(4´) (d)	H(5´) (t)	H(6´)	H(7´) (d)	NCH_2	$C(O)CH_2$	$(CH_2)_n$ (m)	CH_3 (t)	NH (s)
1	1.18, 1.23	5.85	6.89	7.98	8.00 (dd)	6.74	7.08	6.86	7.18 (t)	6.56	3.13 (m)	—	1.28 1.55 1.61	0.88	—
2	1.14, 1.41	5.57	6.48	6.00	6.06 (dd)	6.51	7.03	6.88	7.18 (t)	6.57	3.17 (m) 3.32 (m)	—	1.30 1.41 1.69	0.92	2.6
3[a]	1.11, 1.30	5.69	6.78	7.43	6.96 (dd)	6.62	7.05	6.80	6.52 (t)	6.52	3.14 (m) 3.18 (m)	2.33 (m)	1.29 1.60 1.74	0.88	7.43
4	1.20, 11.38	5.84	6.93	7.63	7.87 (d)	—	7.93	—	8.15 (dd)	6.50	3.23 (t)	2.36 (t)	1.25 1.71	0.80	7.21

[a] In C_6D_6.

Table 2. Spin-spin coupling constants in the ^{1}H NMR spectra of the spiro compounds (J/Hz) at 25 °C

Compopund	$^3J_{4',5'}$	$^4J_{4',6'}$	$^3J_{5',6'}$	$^3J_{6',7'}$	$^3J_{3,4}$	$^4J_{5,7}$	$^3J_{7,8}$
1	7.7	1.1	7.4	7.8	10.3	2.7	8.7
2	7.3	1.2	7.2	7.7	10.3	2.5	8.5
3	7.2	1.1	7.7	7.8	10.3	2.6	8.8
4	—	2.3	—	8.7	10.5	2.6	—

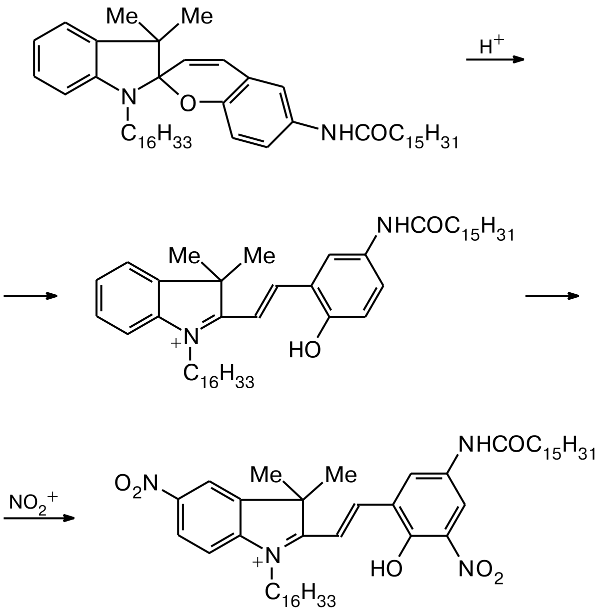
elemental analysis data. The parameters of the NMR spectra for compounds **1**—**4** are given in Tables 1 and 2.

An analysis of the ^{1}H NMR spectrum of compound **4** shows that the nitration of compound **3** resulted in the substitution of two aromatic protons by the NO_2 groups. In this case, in one benzene ring three protons form the ABX system with the *ortho*-constant 8.7 Hz and *meta*-constant 2.3 Hz, and in another ring two protons form the KX system with a *meta*-constant of 2.6 Hz. We considered two possible variants of substitution: (1) both nitro groups are located in the indoline moiety of the molecule (in positions 5´ and 7´ or 4´ and 6´), and the benzopyran fragment remained unchanged; (2) one nitro group is located in the indoline fragment (in position 5´ or 6´), and another one is located in the benzopyran fragment in position 8.

The choice between these variants and further analysis were carried out with allowance for the influence of the NO_2 group in both positions of the benzene ring on chemical shifts of the neighboring protons.[10] The first variant of substitution was excluded immediately, because the chemical shifts of the H(5) and H(7) protons in compound **4** exhibited the downfield shift by approximately 1 ppm as compared to similar signals in the spectrum of mononitro-substituted compound **3**, although no structural changes should occur in this part of the molecule. Thus, we found that one of the NO_2 groups exists in the benzopyran fragment in position 8.

Probably, in this case, the *ortho*-orienting effect of the OH group, which appears upon the nitration of the open salt form of spirobenzopyran, is decisive (Scheme 2).

Scheme 2



When choosing between positions 5´ or 6´ in the indoline moiety for the second NO_2 group, we unambiguously suggested in favor of position 5´ on the basis of the influence of the NO_2 group. This choice was confirmed by the coincidence of the spectrum of the fragment in compound **4** with the data[11] for the 5´-substituted spiro compounds. The spectrum obtained agrees with the data[12] on the nitration of 1,3,3-trimethyl-2-methyleneindoline with a nitrating mixture, which produces almost only the 5-nitro-substituted derivative.

It should be mentioned that only 5´,8-dinitro-substituted compound **4** was formed, in this case, at the equimolar ratio of reactants, contrary to our previous results on the direct nitration of photochromic spirooxazines[13—15] for which the mononitro-substituted product was mainly formed at the same ratio of reactants.

The absorption spectra of compounds **3** and **4** were measured in toluene, acetonitrile, and ethanol. Both compounds synthesized were found to exhibit the photochromic properties. At room temperature, the spectrum of compound **3** containing no nitro substituent in toluene is characterized by a low-intensity absorption band of the photoinduced merocyanine form with a maximum at 600 nm (Fig. 1, *a*). This intensity of photoinduced absorption is caused by a high rate of thermal relaxation of the photoinduced merocyanine form to the initial spiran form, which is characteristic of the SBPs containing no nitro groups.[16] It is known that electron-releasing and electron-withdrawing substituents in different parts of the SBP molecules affect the photochromic properties.[17] The introduction of such a strong electron-withdrawing substituent as an NO_2 group into the benzopyran moiety of the SBP molecule weakens the n_N-σ^*_{CO} interaction in the spiro unit of the molecule and thus facilitates opening of the C(2)—O spiro bond. The resonance bipolar structures of the open form involving the NO_2 group stabilize this form (Scheme 3).

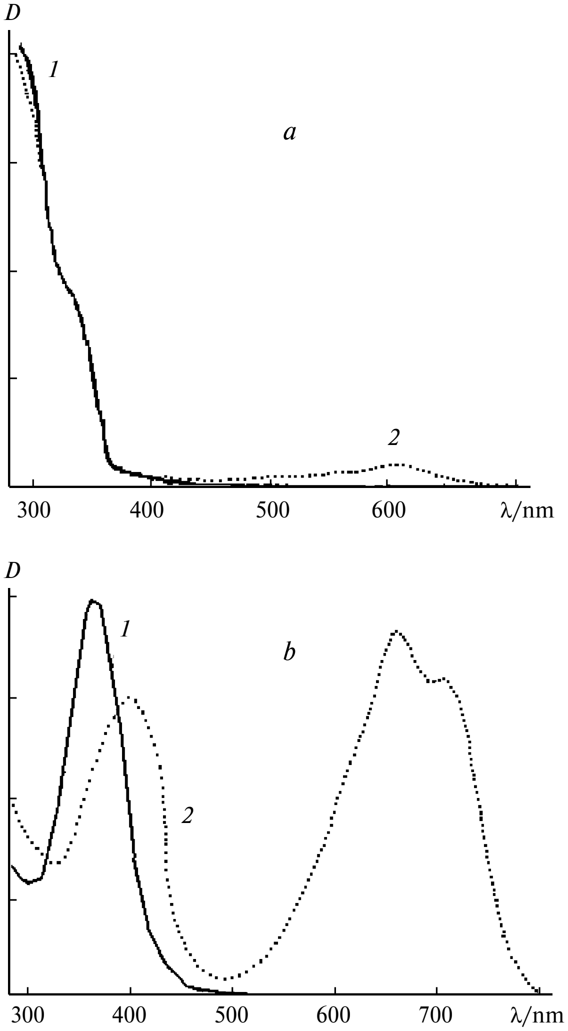
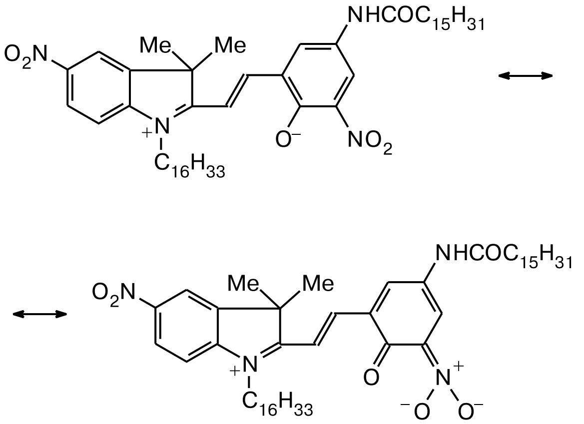


Fig. 1. Absorption spectra of compounds **3** (*a*) and **4** (*b*) in toluene before (*1*) and after (*2*) UV irradiation.

Scheme 3



Therefore, the introduction of the NO_2 substituent provides a high concentration of the merocyanine form and thus enables one to study efficiently the aggregation of these molecules. According to the aforesaid, a new intense structured absorption band with a maximum at 660 nm appears under UV irradiation in the visible spectral region of the absorption spectrum of compound **4** in toluene (Fig. 1, *b*). The colored form of compound **4** exhibits the hypsochromic shift of the long-wave maximum in the absorption spectrum with an increase in the solvent polarity, which indicates that the open form has a bipolar structure.

Thus, two new SBPs were synthesized, each of which contains two long alkyl substituents and can undergo photochromic transformations.

Experimental

^1H NMR spectra were recorded on a Bruker WM-400 spectrometer (400 MHz) at 25 °C. Absorption spectra were obtained on Varian Cary 50 and Specord UV-VIS spectrophotometers using acetonitrile, toluene, and ethanol (spectral purity) as solvents. Samples were irradiated with the light of a DKsSh-120 lamp through an interference light filter of 365 nm.

Raney nickel was prepared using a known procedure.[18] Hydrazine hydrate was concentrated,[19] and palmitoyl chloride and Et_3N (ACROS Organics) were used without additional purification.

1´-Hexadecyl-3´,3´-dimethyl-6-palmitoylamino-1´,3´-dihydrospiro-[2*H*-1-benzopyran-2,2´-(2*H*)-indole] (3). A solution of 98% palmitoyl chloride (0.62 mL, 2 mmol) in benzene (2 mL) was added dropwise to a solution of compound **2** (1 g, 2 mmol) and Et_3N (0.28 mL, 2 mmol) in benzene (20 mL) with cooling to +5 °C. The mixture was stirred at room temperature for 3.5 h. A precipitate of $Et_3N \cdot HCl$ that formed was filtered off, and the solution was concentrated by evaporation. The resulting dark red oil was separated on a preparative TLC plate with silica gel (Analtech), using an acetone—benzene (1 : 19) mixture as eluent. A dark lilac layer with R_f 0.6 was taken from the plate, the substance was washed out with acetone, and the acetone was distilled off. A dark cherry-colored paste was obtained in a yield of 1.03 g (70%), R_f 0.78 (Silufol, acetone—benzene (1 : 9) mixture). Found (%): C, 81.11; H, 10.94; N, 3.68. $C_{50}H_{80}N_2O_2$. Calculated (%): C, 81.02; H, 10.88; N, 3.78.

1´-Hexadecyl-3´,3´-dimethyl-5´,8-dinitro-6-palmitoylamino-1´,3´-dihydrospiro-[2*H*-1-benzopyran-2,2´-(2*H*)-indole] (4). Nitric acid (4 mL, 66.9%, *d* 1.39) was added dropwise with stirring and cooling to +1 °C to a solution of compound **3** (0.88 g, 1.2 mmol) in concentrated H_2SO_4 (13 mL). The mixture was stirred for 2 h, and the temperature of the reaction mixture increased gradually to ambient. The mixture was poured onto ice (40 mL) and stored for 30 min. Chloroform (40 mL) was poured, and concentrated NH_4OH was added to neutral pH. The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$. The combined extracts were washed with water, dried over Na_2SO_4, and filtered. The solvent was distilled off. The residue was dissolved in benzene and chromatographed on a column packed with silica gel L 0.035—0.070 µm, eluting successively with benzene and a benzene—acetone (100 : 2) mixture. A fraction with R_f 0.59 (benzene—acetone, 19 : 1) was collected, and the solvent was evaporated. An orange crystalline substance with m.p. 101 °C was obtained in a yield of 0.51 g (31.4%). Found (%): C, 72.39; H, 9.54; N, 6.54. $C_{50}H_{78}N_4O_6$. Calculated (%): C, 72.25; H, 9.46; N, 6.74.

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