Synthesis and photochromic properties of spiro(benzindoline-naphthoxazines)

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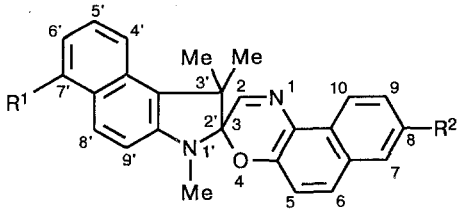
A new photochromic compound belonging to the class of spiro(indoline-naphthoxazines) was synthesized. Nitration of this compound was carried out and the structures of two photochromic nitro-substituted products were determined. The photochromic properties of the products were studied in solvents of different polarity.

Key words: photochromism; spiro(indoline-naphthoxazines), nitration.

Photochromic compounds belonging to the class of spiro(indoline-naphthoxazines) attract special attention because they have greater photostability[1] than the well-studied[2] spiro(indoline-pyrans). The range of the structures of spiro(indoline-naphthoxazines) that has been studied is narrower than that of spiro(indoline-pyrans). This is due mostly to the fact that the synthesis of the former compounds is rather laborious and involves many steps. Therefore, the elaboration of methods for synthesizing various derivatives of spiro(indoline-naphthoxazines) by modifying unsubstituted compounds belonging to this class is of current interest.

In the present work we synthesized a new photochromic spiro(indoline-naphthoxazine), studied its nitration, determined the structure of the photochromic products obtained, and studied their properties in solvents of different polarity.

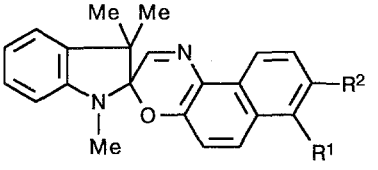
We studied the spiro(indoline-naphthoxazines) with structures **1—3**.



1—3

1: $R^1 = R^2 = H$; **2:** $R^1 = H$, $R^2 = NO_2$; **3:** $R^1 = R^2 = NO_2$

The photochromic properties of compounds **1—3** were analyzed by comparing them with the data for indoline spiro(indoline-naphthoxazines) (structures **4—6**), whose synthesis and properties have been described earlier.[3—5]



4—6

4: $R^1 = R^2 = H$; **5:** $R^1 = H$, $R^2 = NO_2$; **6:** $R^1 = NO_2$, $R^2 = H$

The synthesis of compound **1** involved the preliminary preparation of the corresponding salt of the benzo analog of Fischer's base, 1,2,3,3-tetramethylbenz[*e*]indolinium iodide (**7**), according to Scheme 1. Salt **7** was transformed directly in the reaction mixture by treatment with Et_3N into base **8**, which was then treated with 1-nitroso-2-naphthol to give compound **1**.

Compounds **2** and **3** were obtained by direct nitration of **1** using a procedure similar to that used by us[3] for the synthesis of compound **5**. However, unlike the procedure in Ref. 3, in which nitration of compound **4** afforded only one photochromic product, **5**, (compound **6** was obtained from 1-nitroso-5-nitro-2-naphthol), in this case we managed to isolate two photochromic products, **2** and **3**.

In order to determine the structures of all of the compounds synthesized, we studied their ^1H NMR

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Scheme 1

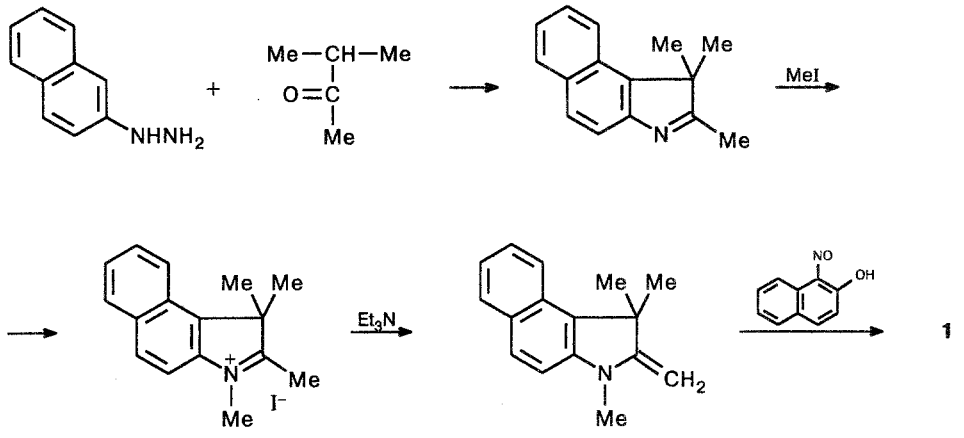


Table 1. ^{1}H NMR spectra of spiro(benzo[*e*]indoline-napthoxazines), δ

Compound	CMe_2	NMe	H(2)	H(4')	H(5')	H(6')	H(7')	H(8')	H(9')	H(5)	H(6)	H(7)	H(8)	H(9)	H(10)
1	1.58 1.59	2.87	7.86	7.94	7.44	7.27	7.76	7.80	7.02	7.00	7.68	7.84	7.42	7.60	8.60
2	1.59 1.72	2.86	7.90	7.90	7.43	7.27	7.79	7.83	7.02	7.14	7.83	8.70	—	8.32	8.69
3	1.57 1.69	2.88	7.88	8.16	7.48	7.90	—	8.41	7.18	7.11	7.85	8.71	—	8.34	8.69

Table 2. Coupling constants in the ^{1}H NMR spectra of spiro(benzo[*e*]indoline-napthoxazines) (*J*/Hz)

Compound	$^3J_{4',5'}$	$^4J_{4',6'}$	$^5J_{4',8'}$	$^3J_{5',6'}$	$^4J_{5',7'}$	$^3J_{6',7'}$	$^3J_{8,9}$	$^3J_{5,6}$	$^5J_{6,10}$	$^3J_{7,8}$	$^4J_{7,9}$	$^3J_{9,10}$	$^4J_{8,10}$
1	8.5	1.8	0.9	6.7	1.2	8.2	8.5	8.9	0.6	8.2	1.5	8.2	1.2
2	8.5	1.1	*	7.3	1.2	8.5	8.5	8.8	*	—	2.4	9.2	—
3	8.9	1.0	0.9	7.6	—	—	9.2	8.9	0.6	—	2.4	9.2	—

* Not determined.

spectra in $CDCl_3$. The spectral parameters are presented in Tables 1 and 2. The signals in the spectra were assigned using the double resonance method. The analysis of the data obtained indicates that in one of the photochromic products of the nitration of compound **1**, only one hydrogen atom of the naphthoxazine fragment, namely that at position 8, is replaced. All of the parameters of the ^{1}H NMR spectrum of the naphthoxazine fragment of this compound coincide with the similar parameters of **5** (see Ref. 3), *i.e.*, this is compound **2**. In the second product, two hydrogen atoms are replaced: one of them at the same position 8, the second one at position 4′ or 7′ of the benzoindoline fragment. In order to determine the position of the substituent in the second product, we used the literature data concerning the influence of the NO_2 group in naphthalene on the chemical shifts and coupling constants of the neighboring protons,[6—8] as in the method that we used[3] for the determination of structure **5**. The analysis of the data obtained and the literature data lead to the conclusion that the second photochromic product is compound **3**.

Compounds **1—3** have pronounced photochromic properties in solutions, *i.e.*, they undergo transition from the uncolored state **A** to the colored form **B** when irradiated by UV-light, and are thermally decolorized after irradiation is finished.

The absorption spectra of forms **A** of compounds **1—3** in the near UV-region are shown in Fig. 1. For comparison, the similar spectra of **4** and **5** are presented in the same figure. A comparison of the spectra of **1** and **4** indicates that benzannelation of the indoline

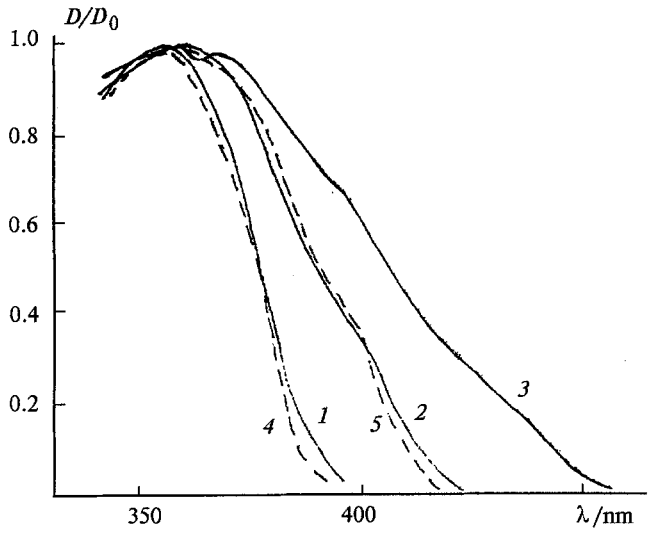


Fig. 1. Absorption spectra of the non-colored forms of spiro(indoline-naphthoxazines) **1** (*1*), **2** (*2*), **3** (*3*), **4** (*4*), and **5** (*5*) in toluene at 295 K.

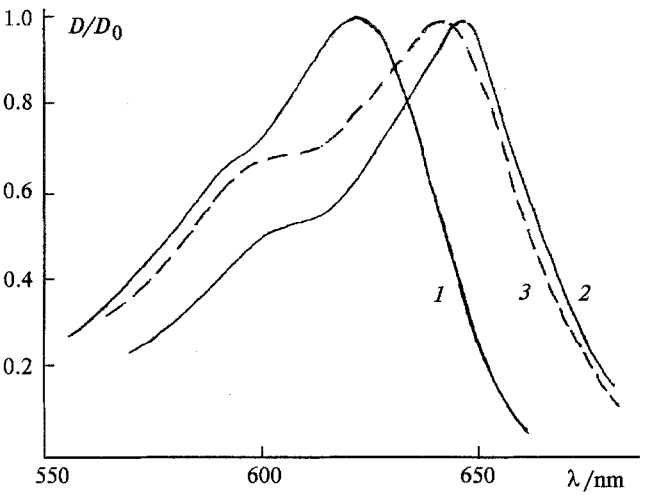
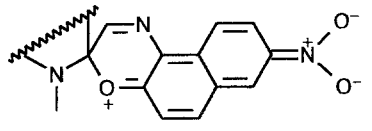


Fig. 2. Long-wave regions of the absorption spectra of the colored forms of spiro(indoline-naphthoxazines) **1** (*1*), **2** (*2*), and **3** (*3*) in toluene at 295 K.

fragment has almost no effect on the absorption spectra, since the bands belonging to the naphthoxazine fragment are located in the region above 300 nm.[5] For the same reason, the absorption spectrum of **2** coincides with that of **5**. As shown previously,[5] the differences between the latter spectra and the spectra of **1** and **4**, respectively, result from the appearance of a new band of intramolecular charge transfer from the oxygen atom to the nitro group with the formation of structure **9**.



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The even greater long-wave shift of the bands in the absorption spectra of compound **3** is probably due to the interference of the additional band of intramolecular charge transfer to the NO_2 group in the benzindoline fragment, which manifests itself in the region of absorption of the naphthoxazine heterocycle.

A more detailed interpretation of the properties of the electronically excited states of these molecules requires spectral, luminescent, and polarization investigations, which we will do in our future work.

The colored form of spiro(indoline-naphthoxazine) **B** is formed after a molecule of **A** absorbs a photon to form an electronically excited state, then dissociation of the C—O spiro-bond and *cis—trans*-isomerization occur. As a result, the left and right heterocycles, which are initially orthogonal to each other (in form **A**), appear to be in the same plane and π-conjunction between them is achieved. The structure of form **B** is in many ways similar to the structure of merocyanine dyes, therefore, its spectral characteristics are well described by known regularities.[10,11]

The long-wave bands in the absorption spectra of **1B—3B** in toluene are shown in Fig. 2. Their absorption maxima (λ_B) in other solvents are given in Table 3; as an example, Table 3 also presents data for **4B** and **5B**. The analysis of these data allows some conclusions to be made.

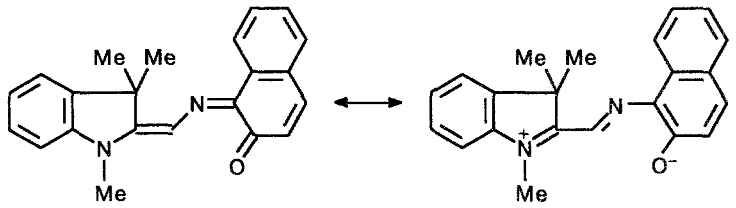
First, it is evident that whereas a positive solvatochromic shift of λ_B is typical of **1B** and **4B**, a negative shift is observed for other spiro(indoline-naphthoxazines). Previously,[12] it has been shown that **4B** has a quinoid structure in non-polar solvents, while a small shift of the equilibrium towards the bipolar form occurs in polar solvents (Scheme 2).

The positive solvatochromism of compound **1** and the absence of donor and acceptor substituents in it, as in **4**, allow us to propose that **1B** also exists mainly in the quinoid form. The fact that $\lambda_{1B} > \lambda_{4B}$ in all solvents is explained by the extension of the π-conjugated system in **1B** by means of benzannelation of the indole heterocycle. This explanation is also valid for the relationship $\lambda_{2B} > \lambda_{4B}$.

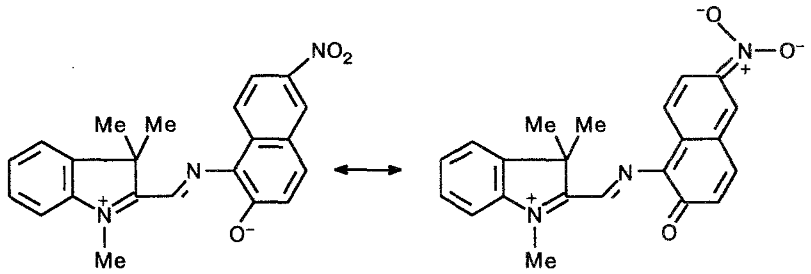
Secondly, by analogy with nitro derivatives **5** and **6** (see Ref. 3), compounds **2B** and **3B** are bipolar ions. The existence of a nitro group exactly at position 8 of the naphthoxazine fragment results in stabilization of the bipolar form due to resonance (Scheme 3).

The colored form of 8-nitro-substituted spiro-(indoline-naphthoxazines) may exist mainly as structure **2B** since the conjugation chain between the auxochrome and the anti-auxochrome in this structure

Scheme 2



Scheme 3



1B **2B**

Table 3. Photochromic parameters of solutions of spiro(indoline-naphthoxazines) at 295 K

Compound	Toluene					Acetone					Ethanol				
	λ_B /nm	$k_1 \cdot 10^2$ /s^{-1}	$k_2 \cdot 10^2$ /s^{-1}	$E_1^{\neq}$ /kcal mol^{-1}	$E_2^{\neq}$ /kcal mol^{-1}	λ_B /nm	$k_1 \cdot 10^2$ /s^{-1}	$k_2 \cdot 10^2$ /s^{-1}	$E_1^{\neq}$ /kcal mol^{-1}	$E_2^{\neq}$ /kcal mol^{-1}	λ_B /nm	$k_1 \cdot 10^2$ /s^{-1}	$k_2 \cdot 10^2$ /s^{-1}	$E_1^{\neq}$ /kcal mol^{-1}	$E_2^{\neq}$ /kcal mol^{-1}
1	621	30.0	—	17.0	—	624	68.0	—	17.4	—	629[a]	44[a]	—	—	—
2	645	1.5	—	20.7	—	640	0.7	—	20.5	—	637[a]	0.1[a]	—	22.6[a]	—
3	640	14.0	1.9	14.5	8.5	638	7.4	0.6	20.8	13.9	630[b]	4.2[b]	0.4[b]	—	—
4[c]	592	28.0	—	—	—	596	99.0	—	—	—	610[d]	61.0[d]	—	20.6[d]	—
5[e]	621	7.3	—	—	—	620	2.0	—	—	—	618[d]	0.45[d]	—	—	—

[a] In Bu^{i}OH. [b] In acetonitrile. [c] See Ref. 9. [d] In EtOH. [e] See Ref. 3.

is longer than that in compound **1B**. This explains the following relationships between λ_B in all the solvents studied: $\lambda_{2B} > \lambda_{1B}$, $\lambda_{3B} > \lambda_{1B}$, $\lambda_{5B} > \lambda_{6B}$. The NO_2 group in compound **6** is at position 7 and the structure similar to **2B** cannot be achieved for its colored form, hence $\lambda_{5B} > \lambda_{6B}$ (see Ref. 3). The presence of an electron-withdrawing NO_2 group in the benzindole fragment of **3B** leads to a lower (as compared to **2B**) effective charge, which oscillates along the chain of the conjugated bonds under the action of light. This results in the following relationship: $\lambda_{2B} > \lambda_{3B}$.

In all of the solvents studied, the kinetics of the dark decoloration of **1B** and **2B**, as well as that of **4B—6B** (see Refs. 3 and 9), are described by first-order equations. Table 3 summarizes the rate constants, *k*, at 295 K and the activation energies $E^{\neq}$ for this process. However, for **3B** the reaction of dark decoloration is not mono-exponential and its kinetics obeys the following equation containing two constants:

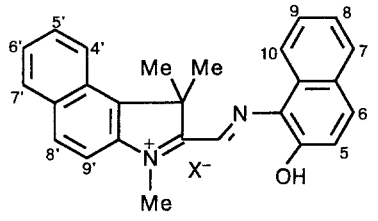
$$D(t) = a\exp(-k_1 t) + b\exp(-k_2 t).$$

As can be seen from Table 3, an increase in the polarity of the medium leads to acceleration of decoloration of **1B** and **4B** and hindrance of this process for **2B**, **3B**, and **5B**. Earlier,[9] an analysis of the rate of decoloration of **4B** in a wide set of solvents showed that in the media that display no specific intermolecular interactions the *k* value is determined by the dielectric constant of the solvent, ε. Since the structures of the colored forms **1B** and **4B** are similar, one may assume that this conclusion is also valid for **6B**. The dependence of *k* on the polarity of the medium in bipolar forms **B** of nitro-substituted spiro(indoline-naphthoxa-

zines) is in fair agreement with that of the well-studied[2] spiro(indoline-pyrans). This is explained by the fact that the dipolar molecules of **B** in a more polar solvent are solvated more strongly, which inhibits the dark decoloration.

The complex kinetics of the dark decoloration of **3B** probably results from the fact that the introduction of the second NO_2 group impairs the solubility of compound **3** to the extent that the molecules of **3** exist as associates in solution. This assumption is indirectly confirmed by the values of $E_1^{\neq}$ and $E_2^{\neq}$, which are lower for **3B** than for the other compounds. This is most clearly illustrated by the values in non-polar media, especially that of $E_2^{\neq}$ ($E_1^{\neq}$ and $E_2^{\neq}$ are the formal activation energies of the bi-exponential kinetic equation).

In conclusion we should note some peculiarities of the nitration mechanism. Since the equilibrium **A** $\rightleftharpoons$ **B** for spiro(indoline-naphthoxazines) and spiro(indoline-pyrans) is known[2,13] to exist in any solvent and the nitration is carried out in a strongly acidic medium, where **B** is irreversibly transformed into the salt form **10** (see Ref. 2), it is reasonable to propose that precisely this form participates in nitration.



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Then, positions 5, 8, and 10 appear to become the most reactive due to the activating effect of the OH group. Nitration at positions 5 and 10 is sterically hindered and, therefore, the nitration of compounds **1** and **4** occurs mainly at position 8.

We failed to find the dinitro-substituted product of **4**,[3] although the methods for nitrating **1** and **4** were similar. This can probably be explained by the deactivation of the benzene ring in the indole heterocycle of **4** by the positively charged quaternary N atom. The introduction of one more benzene ring into compound **1** decreases this effect. Since it is well known that the α-positions in naphthalene are the most reactive, the nitration of **1** occurs at position 7′ because position 4′ is shielded by methyl groups.

Experimental

^{1}H NMR spectra were recorded on a Bruker WM-400 spectrometer at 25 °C in $CDCl_3$. Absorption spectra were obtained on a Specord UV-VIS spectrophotometer in a thermostatted cell. Irradiation of samples was carried out with light from a DRSh-1000 lamp through an interference light filter with transmission at 365 nm. Kinetic measurements and their processing were carried out according to the previously described method.[3–5]

1,2,3,3-Tetramethyl-3*H*-benzo[*e*]indoline iodide (7). Methyl isopropyl ketone (9.00 g, 0.1 mol) was added to a solution of 2-naphthylhydrazine (15.80 g, 0.1 mol) in 250 mL of 70 % AcOH. The mixture was stirred at 20 °C for 0.5 h, and the light emulsion that formed was extracted with ether (5 × 100 mL) and dried with anhydrous Na_2SO_4. The ether was distilled off from the solution, then 100 mL of glacial AcOH was added, and the mixture was refluxed for 2 h. The solution was poured onto ice, and the acid was neutralized with sodium carbonate. The mixture was extracted with ether (3×100 mL), and the extract was washed with water and dried with anhydrous Na_2SO_4. The ether was distilled off. Methyl iodide (14.00 g, 0.1 mol) and 100 mL of benzene were added. The mixture was sealed in an ampule and kept at 85 °C for 5 h. The ampule was cooled and unsealed, and the product was filtered off, washed with benzene (2 × 100 mL) and with cold methanol (1 × 20 mL) to give 31.5 g (90 %) of compound **7**, t.decomp. 240 °C, R_f = 0.25 (Silufol, acetone).

1,3,3-Trimethylspiro(benzo[*e*]indole-2′,3-3*H*-naphtho[2,1-*b*][1,4]oxazine) (1). A mixture of compound **7** (7.00 g, 0.02 mol) and 1-nitroso-2-naphthol (3.40 g, 0.02 mol) in 100 mL of MeOH was heated to boiling in a flask with a reflux condenser, then a solution of Et_3N (3.6 mL, 0.04 mol) in 10 mL of MeOH was added. The mixture was refluxed for 2 h. After cooling, the product was isolated and washed with acetone to give 2.30 g (30 %) of compound **1**, R_f = 0.67 (Silufol, $CHCl_3$), m.p. 149—151 °C. Found (%): C, 82.41; H, 5.98; N, 7.28. Calculated for $C_{26}H_{22}N_2O$ (%): C, 82.51; H, 5.86; N, 7.40.

1,3,3-Trimethyl-8-nitrospiro(benzo[*e*]indole-2′,3-3*H*-naphtho[2,1-*b*][1,4]oxazine) (2). A solution of compound **1** (1.90 g, 0.005 mol) in 50 mL of conc. H_2SO_4 was cooled to 3—5 °C, then 0.46 mL of HNO_3 (d = 1.35 g cm^{-3}) was added, and the reaction mixture was stirred for 2 h. The mixture was poured onto 200 g of ice and then poured into a mixture of saturated $NaHCO_3$ (0.2 L) with $CHCl_3$ (50 mL) and extracted with chloroform (4 × 50 mL). The extract was dried with anhydrous Na_2SO_4, the solvent was evaporated, and the residue was dissolved in $CHCl_3$. The solution was chromatographed on a column with 40 g of silica gel (the column was filled with benzene) using $CHCl_3$ as the eluent. The fraction with R_f = 0.58 (Silufol, $CHCl_3$) was collected. The solvent was evaporated, and the residue was recrystallized from an acetone—ethanol mixture, 5 : 1, to give 0.59 g (29 %) of product **2**, m.p. 263—265 °C (decomp.).

1,3,3-Trimethyl-7,8-dinitrospiro(benzo[*e*]indole-2′,3-3*H*-naphtho[2,1-*b*][1,4]oxazine) (3) was obtained similarly to **2** but the chromatographic fraction with R_f = 0.45 (Silufol, $CHCl_3$) was collected to give 0.25 g (10 %) of product **3**, m.p. 268—270 °C (decomp.).

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