Nitration of photochromic spirophenanthroxazine

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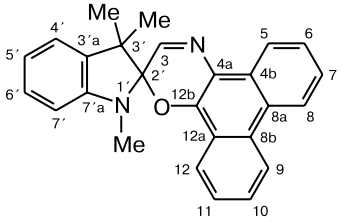
Nitration of photochromic spirophenanthrooxazine with three different reagents (cupric nitrate, $NaNO_2$ in acetic acid, and HNO_3—H_2SO_4) was studied. The major reaction products were specified and characterized by ^1H and ^{13}C NMR and mass spectra. The mechanisms of their formation were proposed. Only the nitration with a mixture of nitric and sulfuric acids yielded a photochromic product containing the nitro group in the phenanthrene fragment.

Key words: nitration, photochromism, spiro compounds, NMR spectroscopy, mass spectrometry, absorption spectra.

At present, a topical problem in information technology is passage from 2D carriers of optical information to 3D recording media, which will give rise to superpowerful information devices, including personal computers. One of the promising approaches to creation of such media is the use of photochromic compounds, among which spirooxazines are of great interest. However, the synthesis of spirooxazines is a rather labor-consuming process, for which reason modification of the spirooxazine structure by direct chemical reactions is under study.[1—6]

Earlier, the nitration of unsubstituted spiro[indoline-naphthoxazine][1] and spiro[benzindolinenaphthooxazine][2] afforded photochromic mono- and dinitro derivatives. It was found that introduction of a nitro group substantially changes the photochromic properties. In addition, the presence of a nitro group in a spiro compound made it possible to reduce it,[3] with subsequent modification of the resulting amino group. The present work was devoted to a investigation of nitration of 1´,3´,3´-trimethylspiro[indoline-2´,2-2*H*-phenanthro[9,10-*b*]-1,4-oxazine] (**1**) and the spectroscopic properties of nitration products.



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Three nitration techniques differing in the nature of the nitrating agent were used. The structures of the products isolated were proved by spectroscopic methods (^1H and ^{13}C NMR spectroscopy and mass spectrometry) and elemental analysis.

Before analyzing the nitration products, let us examine the ^1H and ^{13}C NMR spectra of the starting compound **1**, which can exist in solution as a spiro form (**A**) and a colored form (**B**). For the purpose of comparing spectroscopic data in a more convenient way, the atomic numbering in all products was the same as in the starting compound **1** and is shown for the respective structural formulas. The ^1H NMR spectra of compound **1** were interpreted with the use of homonuclear ^1H—^1H COSY and NOESY 2D procedures. The COSY spectrum revealed three closed four-spin systems belonging to the H(4´)—H(7´), H(5)—H(8), and H(9)—H(12) protons.

Apart from the signals related to these systems, the ^1H NMR spectrum of compound **1** contains three three-proton singlets at δ 1.40, 1.42, and 2.79 and a one-proton singlet at δ 7.85; assignment of these signals to the resonances of two $CC\underline{H}_3$ groups, one $NC\underline{H}_3$ group, and the H(3) proton, respectively, was evident from their chemical shifts. Signals for the spin system of the H(4´)—H(7´) protons were assigned when analyzing the NOESY spectrum showing $CC\underline{H}_3$/H(3),H(4´) and $NC\underline{H}_3$/H(3),H(7´) correlation peaks. To assign signals in the other two systems, heteronuclear ^1H—^{13}C HMBC 2D data were required. The ^{13}C NMR spectrum of compound **1** contains three low-field signals for the quaternary C atoms at δ 136.1, 139.4, and 147.6. Such chemical shifts allowed these signals to be assigned to the C(3´a) and C(7´a) atoms (downfield shifts of the signals because of the

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β-effect of the methyl groups) and the C(12b) atom (owing to the presence of the O atom at this carbon atom). Assignment of the signals at δ 136.1 to C(3´a) and at δ 147.6 to C(7´a) was evident from the presence of correlation peaks at δ_H/δ_C 1.40, 1.42/136.1 ($CC\underline{H}_3$/C(3´a)) and 2.79/147.6 ($NC\underline{H}_3$/C(7´a)) in the HMBC spectrum (see Experimental). Thus, the low-field peak of the quaternary C atom at δ 139.4 should be assigned by exclusion to C(12b). Only the H(12)proton in the two other spin systems can have a considerable constant $^3J_{H,C}$ of the spin-spin coupling with the C(12b) atom. The presence of a correlation peak at δ_H/δ_C 8.12/139.4 allows one to assign a doublet signal at δ 8.12 to the resonance of H(12) and, with the use of the COSY spectrum, interpret signals for the other protons of the H(9)—H(12) system. Signals of the H(5)—H(8) system in the ^{1}H NMR spectrum were assigned on the following grounds. The spatial proximity of the H(9) and H(8) protons in the phenanthrene fragment is sufficient for the nuclear Overhauser effect (NOE) to occur. However, the NOESY spectrum shows no correlation peak for the H(9) proton (δ 8.63, d) with any proton of the H(5)—H(8) system also manifested by a doublet signal. This can be only explained by virtually coincident chemical shifts of the H(9) and H(8) protons, which allows assignment of a doublet signal at δ 8.61 to the resonance of the H(8) proton. The other signals of the H(5)—H(8) system were assigned from the COSY spectrum. The complete assignment of signals in the ^{1}H NMR spectrum of compound **1** (Table 1) allowed us to assign signals for all protonated C atoms with the use of the heteronuclear ^{1}H—^{13}C HSQC spectrum. Signals for the quaternary C atoms were assigned while analyzing the earlier partially interpreted HMBC spectrum. It was taken into account that in aromatic systems, considerable coupling constants (and, consequently, the most intense correlation peaks in the HMBC spectrum) are observed for protons and C atoms separated by three bonds (owing to the dihedral angle 180° or 0° favorable for high $^3J_{H,C}$ values). Usually, a spectrum also contains correlation peaks due to $^2J_{H,C}$ and no peaks due to the long-range coupling constants $^4J_{H,C}$, $^5J_{H,C}$, *etc*. The exception may be a coupling constant $^4J_{H,C}$ detected when a spin-spin coupling between the magnetic nuclei is transmitted along two bond systems simultaneously. For instance, the presence of a weak correlation peak H(3)/C(12b) is due to the spin-spin coupling transmitted across H(3)—N(4)—C(4a)—C(12b) and H(3)—C(2´)—O—C(12b).

Nitration by cupric nitrate

This method was chosen because it allows[7] one to carry out the reaction at low temperatures, without resinification, and to introduce an NO_2 group only into a specified position. We found that the nitration of compound **1** in this way mainly gives nonphotochromic product **2** in 80% yield.

In contrast to the ^{1}H NMR spectrum of the starting reagent, the spectrum of this product contains no singlet

Table 1. Parameters of the ^{1}H NMR spectra of solutions of compounds **1**—**4** in $CDCl_3$

Group, atom	δ (*J*/Hz)			
	1	**2**	**3**	**4**
CMe_2	1.40, 1.42 (both s)	1.11, 1.60 (both s)	1.85 (s)	1.40, 1.42 (both s)
NMe	2.79 (s)	2.92 (s)	3.03 (s)	2.80 (s)
H(4´)	7.13 (dd, *J* = 7.3, *J* = 1.2)	7.11 (d, *J* = 7.3)	7.92 (dd, *J* = 8.1, *J* = 1.3)	7.13 (dd, *J* = 7.3, *J* = 1.1)
H(5´)	6.95 (td, *J* = 7.5, *J* = 0.9)	6.89 (t, *J* = 7.2)	7.65 (m)	6.96 (td, *J* = 7.7, *J* = 0.8)
H(6´)	7.26 (td, *J* = 7.5, *J* = 1.2)	7.23 (td, *J* = 7.7)	7.42 (td, *J* = 7.6, *J* = 1.4)	7.26 (td, *J* = 7.7, *J* = 1.3)
H(7´)	6.61 (d, *J* = 7.5)	6.66 (d, *J* = 7.8)	7.02 (dd, *J* = 7.9, *J* = 1.3)	6.63 (d, *J* = 7.7)
H(3)	7.85 (s)	—	—	7.86 (s)
H(5)	8.70 (dd, *J* = 8.2, *J* = 1.4)	8.61 (dd, *J* = 7.9, *J* = 1.1)	8.21 (v.m)	8.80 (d, *J* = 9.1)
H(6)	7.71 (dd, *J* = 8.3, *J* = 7.0, *J* = 1.2)	7.75 (t, *J* = 7.3)	7.63—7.68	8.45 (dd, *J* = 9.1, *J* = 2.2)
H(7)	7.60 (dd, *J* = 8.3, *J* = 7.0, *J* = 1.3)	7.73 (t, *J* = 7.9, *J* = 1.1)	7.63—7.68	—
H(8)	8.61 (d, *J* = 8.9)	8.74 (d, *J* = 8.3)	8.64 (v.m)	9.51 (d, *J* = 2.2)
H(9)	8.63 (d, *J* = 8.7)	8.76 (v.m)	8.67 (v.m)	8.69 (d, *J* = 8.3)
H(10)	7.65 (td, *J* = 8.4, *J* = 1.5)	7.72 (v.m)	7.69—7.73	7.76 (td, *J* = 8.3, *J* = 7.0, *J* = 1.1)
H(11)	7.52 (td, *J* = 8.1, *J* = 1.1)	7.72 (v.m)	7.69—7.73	7.61 (t, *J* = 8.1, *J* = 7.7, *J* = 1.0)
H(12)	8.12 (dd, *J* = 8.2, *J* = 1.4)	8.22 (v.m)	8.26 (v.m)	8.14 (d, *J* = 8.3, *J* = 1.2)

* *Note:* v.m denotes virtual multiplet.

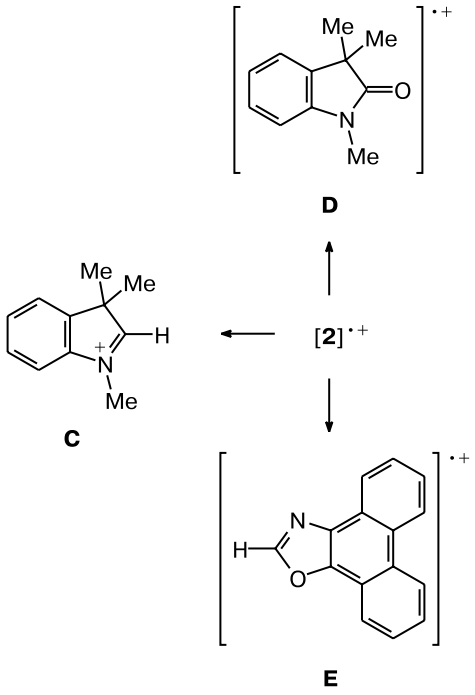
Table 2. Parameters of the ^{13}C NMR spectra of solutions of compounds **1**—**4** in $CDCl_3$

C atom	1	2	3	4
$C\underline{C}H_3$	20.9, 25.5	20.7, 26.2	27.7	20.7, 25.5
NCH_3	29.6	29.7	36.1	29.6
C(2′)	99.0	99.0	189.2	99.8
C(3′)	51.5	50.1	50.5	51.9
C(3′a)	136.1	135.9	142.9	135.7
C(4′)	121.6	121.7	128.6	121.6
C(5′)	119.8	119.3	129.7	120.2
C(6′)	128.0	128.0	128.0	128.1
C(7′)	107.2	107.4	127.2	107.3
C(7′a)	147.6	148.3	140.4	147.3
C(3)	150.3	165.0	155.4	151.0
C(4a)	120.0	133.7	134.4	119.5
C(4b)	129.4	126.1	125.8	134.1
C(5)	122.2	123.0	122.8	123.4
C(6)	127.4	127.6	127.6	121.1
C(7)	124.9	126.4	126.8	144.8
C(8)	122.5	123.4	123.4	119.0
C(8a)	126.4	128.9	129.2	125.7
C(8b)	131.4	129.4	130.7	131.3
C(9)	122.7	123.7	123.8	123.9
C(10)	127.7	126.8	127.6	128.9
C(11)	126.7	127.3	128.0	128.0
C(12)	122.7	121.0	122.1	123.0
C(12a)	124.3	120.2	120.5	124.8
C(12b)	139.4	145.7	145.3	142.9

signal for the H(3) proton but it shows an additional signal at δ 3.87. However, all signals belonging to the protons of the indoline and phenanthrene fragments, appear in the ^1H NMR spectrum of compound **2**. The ^1H and ^{13}C NMR spectra of compound **2** were assigned while analyzing the correlation peaks in the COSY, NOESY, HSQC, and HMBC 2D spectra as was described above for compound **1** (see Tables 1, 2). The differences between the spectra of compounds **1** and **2** were explained as follows. The HSQC spectrum revealed that the proton manifested by a signal at δ 3.87 is not bound to the C atom. In the HMBC spectrum, this proton shows correlation peaks with the C(2′) and C(3′) atoms, which proved its belonging to the hydroxy group localized at the C(2′) atom. Apart from the aforementioned correlation peaks for the hydroxyl proton, the spectrum also contains a peak at δ_H/δ_C 3.80/165.0. Such a low-field signal can belong to the sp^2-hybridized C atom bound to two electronegative atoms, which allows it to be identified as C(3) in the oxazole ring. The contraction of the six-membered ring in compound **1** to a five-membered one in product **2** caused the expected downfield shifts of the resonances of the C(4a) and C(12b) atoms in compound **2** (see Table 1).

Thus, compound **2** is 2-(2′-hydroxy-1′,3′,3′-trimethylindolin-2′-yl)phenanthro[9,10-*d*]oxazole. This assignment was confirmed by mass-spectrometric data. The EI mass spectrum of compound **2** contains a molecular ion peak $[M]^+$ (*m/z* 394) and peaks of ions corresponding to detachment of the CH_3 group (*m/z* 379), CH_4 (*m/z* 378), and CH_3OH (*m/z* 362). In addition, the observed peaks with *m/z* 160, 175, and 219 belong to the indoline (**C**, **D**) and phenanthroxazole (**E**) fragments (Scheme 1).

Scheme 1



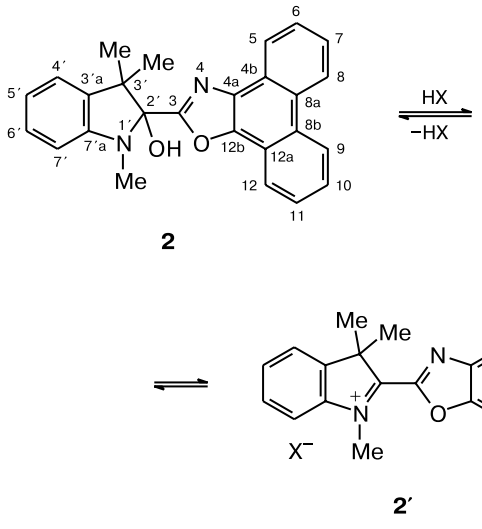
The proposed structure **2** was indirectly confirmed by the formation of deeply colored salt **2′** upon the acid treatment of a solution of compound **2** (Scheme 2, Fig. 1). When treated with a base, salt **2′** changed back into compound **2**.

Note that in the study[8] of photodestruction of spironaphthooxazines, a compound structurally similar to compound **2** was detected among photoreaction products. This suggests that light-initiated oxidation of the molecule is one of the processes resulting in loss of the photochromic properties.

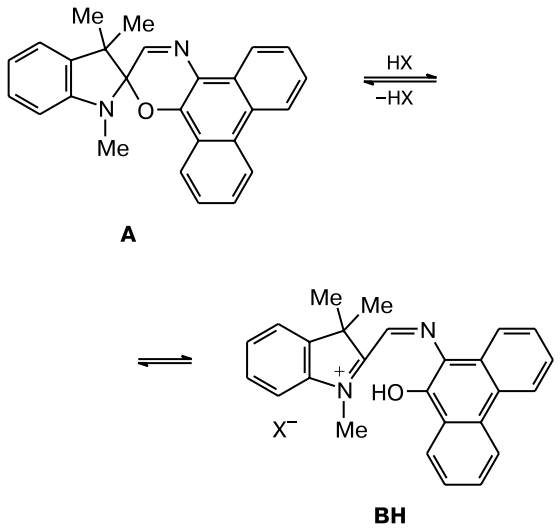
To explain the nitration mechanism, it should be kept in mind that in solutions of compound **1** and other spiro compounds, starting spiro form **A** and colored form **B** are in thermodynamic equilibrium depending on the particular structure, temperature, and the polarity of the medium. In the presence of strong acids,[9] the colored form produces salt **BH** in solution (Scheme 3).

The fact that the nitration by cupric nitrate in acetic anhydride gives the only product **2** suggests that $Cu(NO_3)_2$ acts as an oxidant rather than a nitrating agent. Appar-

Scheme 2



Scheme 3



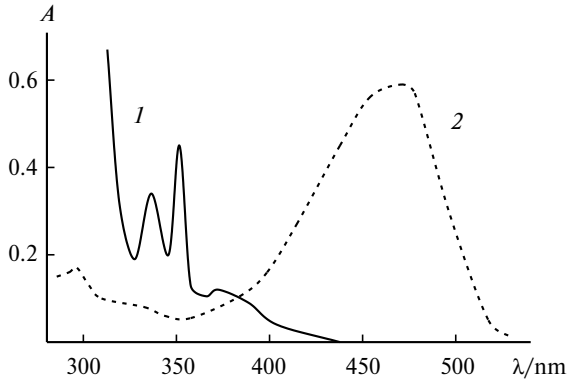


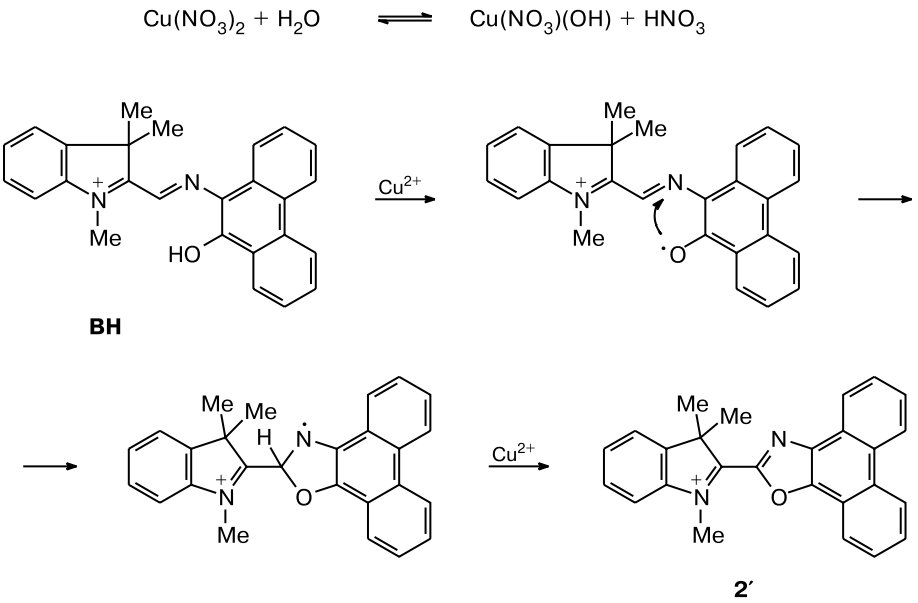
Fig. 1. Absorption spectra of compound **2** in dioxane without (*1*) and with CF_3COOH (*2*).

ently, the presence of the water of crystallization in the copper salt is sufficient for the formation of nitric acid and, consequently, salt **BH** in the system. Then the formation of compound **2** is most likely due to oxidative cyclization of the hydroxyphenanthreneiminomethylene fragment (Scheme 4).

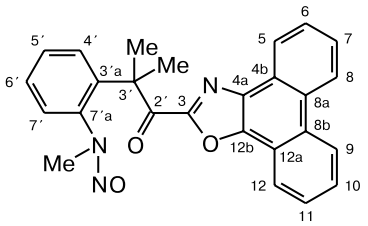
Reaction with sodium nitrite in acetic acid

In the second technique, $NaNO_2$ in acetic acid served as a reagent. Earlier,[10] this technique afforded nitro derivatives of spirobenzopyrans. However, we detected no photochromic compounds among the reaction products.

Scheme 4



The major products were both known compound **2** (30% yield) and novel compound **3** (20%).



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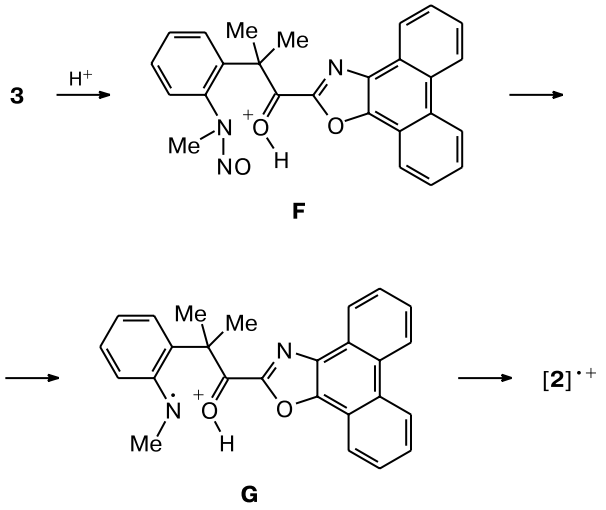
The structure of compound **3** was also proved by NMR spectroscopy and mass spectrometry. Its ^{13}C NMR spectrum contains a low-field signal at δ 189.2 (*i.e.*, with a chemical shift characteristic of a carbonyl C atom). The HMBC spectrum shows a correlation peak between this atom and the $C(C\underline{H}_3)_2$ protons, which allowed this atom to be identified as C(2′). However, the spectrum revealed no correlation with the $NC\underline{H}_3$ protons, which indicates the absence of the N(1′)—C(2′) bond and, consequently, opening of the five-membered indoline ring. In turn, this substantially changed the chemical shifts for H(4′)—H(7′) and for all C atoms in the phenyl residue compared to the shifts for the H and C atoms of the indoline fragment in compounds **1** and **2** (see Tables 1, 2). At the same time, the chemical shifts of the C atoms of the phenanthrene fragment in compound **3** are not very different from those for compound **2**, which suggests that this fragment remains intact. As in the preceding cases, all signals in the ^1H and ^{13}C NMR spectra were assigned from an analysis of correlation peaks in the 2D spectra; only a signal at δ 155.4 was assigned to the C(3) atom by elimination since the HMBC spectrum contains no correlation peaks associated with this atom, in contrast to other quaternary C atoms (see Experimental). Another piece of evidence for the structure given above is the presence of a signal at δ −170 in the ^{15}N NMR spectrum of compound **3**, which appears in the range characteristic of signals for a nitroso group.[11]

The EI mass spectrum of compound **3** contains no molecular ion peak (*m/z* 423); however, it shows intense peaks with *m/z* 394, 219, 175, and 160. These peaks are due to protonation of compound **3**, elimination of the NO group from structure **F** upon EI (**G**, *m/z* 394), recyclization at the carbonyl group yielding compound **2** (Scheme 5), and its subsequent decomposition according to Scheme 1 into the same ions **C**, **D**, and **E**.

The absence of a peak of the protonated molecular ion **F** in the EI mass spectrum of compound **3** (which is probably due to the instability of the nitrosoamino group in this molecule at high ionization energies) caused us to use ESI mass spectrometry. Indeed, in this case, the spectrum contains an intense peak of the pseudomolecular ion $[M + Na]^+$ with *m/z* 446 and a number of other

Scheme 5



peaks. The most intense peaks belong to the ions $[M + Na - NO]^+$ (*m/z* 416), $[M + H - NO]^+$ (*m/z* 394), and $[M + H - NO - OH]^+$ (*m/z* 377).

Thus, the second nitration technique afforded both compound **2** and nitroso derivative **3**. The following considerations can be applied to the reaction mechanism. Acetic acid, in which this reaction is carried out, converts molecules **1** into salt form **BH**, which then yields product **2** according to the mechanism described above, HNO_2 and atmospheric oxygen acting as oxidants instead of Cu^{2+}.

However, in a weakly acid medium, not only can compound **2** exist as cation **2′** but also the indoline ring can undergo opening[12] to give product **2″** (Scheme 6).

In this case, nitrosation of tautomer **2″** at the "former" indole N atom yields the corresponding nitrosoamine **3**.

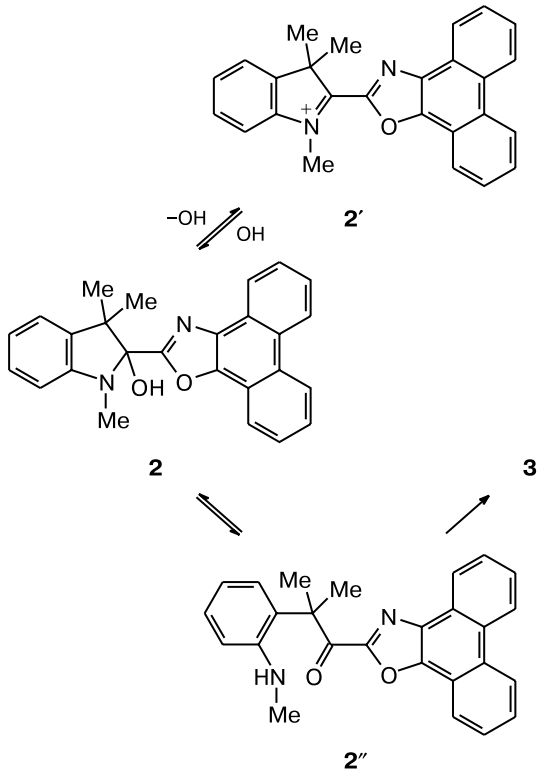
Nitration by nitric acid

This technique with a mixture of HNO_3 and H_2SO_4 as a nitrating agent was used by us earlier[1,2] for nitration of spironaphthoxazines.

In this case, compound **2** (50%) was obtained as the major product, which completely agrees with the mechanism proposed above for its formation. Apparently, atmospheric oxygen and nitrogen oxides serve as oxidants in this reaction. However, under these conditions, the formation of compound **2** from salt **BH** competes with the nitration of compound **1** giving nitro derivative **4** in 10% yield; this is probably due to the significantly higher reactivity of the nitrating mixture compared to other agents.

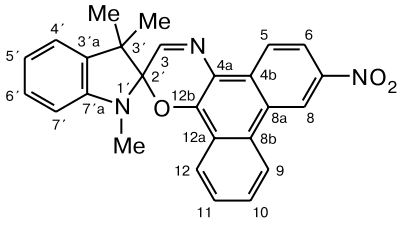
An analysis of the COSY and NOESY spectra of compound **4** revealed that the protons of the indoline moiety of the molecule make a four-spin closed system and the positions of the signals virtually do not differ from those in compound **1**. The ^1H NMR spectrum of the phen-

Scheme 6



anthrene moiety of the molecule shows two closed spin systems: four- and three-proton ones. The latter contains a doublet with a low coupling constant (2.2 Hz) characteristic of proton coupling in aromatic systems separated by four bonds but it contains no signals with large triplet splitting. This indicates a bonding between a nitro group and one of the carbon atoms: C(6), C(7), C(10), or C(11). An analysis of correlation peaks in the HMBC spectrum was decisive for location of the nitro group. The chemical shift of the C(4a) atom (δ_C 119.5) was determined from the correlation peak with the H(3) proton (δ_H 7.86). For the C(4a) atom, the spectrum shows another intense correlation peak with the proton at δ_H 8.80. The presence of this peak can be explained only by correlation between H(5) and C(4a) owing to the three-bond coupling constant. The H(5) proton is manifested by a doublet (J = 9.1 Hz) because of a coupling with the H(6) proton at δ_H 8.45. The doublet of doublets for H(6) and the associated coupling constants (9.1 ($^3J_{H,H}$) and 2.2 Hz ($^4J_{H,H}$)) suggest that the adjacent C(7) atom bears no proton, while the C(8) atom is protonated. Thus, the analysis of the spectra allowed us to locate the nitro group at C(7) in the phenanthrene fragment of compound **4**. Assignment of signals of the three-spin system made it possible to detect a signal for H(9) from the correlation peak H(8)/H(9) in the NOESY spectrum and, in turn, to assign signals for the H(9)—H(12) protons from the correlation peaks in the COSY spectrum. As above, signals in the ^{13}C NMR spectrum were assigned when analyzing the HSQC and HMBC spectra (see Experimental). The changes in the chemical shifts of the protons and the C atoms in compound **4** compared to those for compound **1** agree[13] with the presence of the nitro group at C(7).

Thus, one can state that the nitration of compound **1** according to the third technique affords a 7-nitro derivative of spirooxazine: 1′,3′,3′-trimethyl-7-nitrospiro[indoline-2′,2-2*H*-phenanthro[9,10-*b*]-1,4-oxazine] (**4**).



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This conclusion was confirmed by mass spectrometric data. The EI mass spectrum of compound **4** contains intense peaks of the molecular ion $[M]^+$ (m/z 423) and ions corresponding to the elimination of CH_3 (m/z 408) and NO_2 groups (m/z 377).

Hence, with this technique of nitration of compound **1**, the reaction mixture mainly contains molecules **BH**, which are then converted competitively into either compound **2** or nitro derivative **4**. Since nitration follows the electrophilic substitution mechanism, the positive charge on the indoline N atom deactivates the indoline heterocycle. Under these conditions, electrophilic species of the nitrating agent attack the phenanthrene fragment at the most preferable positions. Quantum-chemical calculations (PM3, Hypercube 6.0) of molecule **BH** showed that the highest negative charge is localized at the C atom in position 7. It was the corresponding product **4** that was obtained in the synthesis.

Compound **4** exhibits photochromic properties. When a solution of compound **4** in dioxane was irradiated with UV light, an intense band appeared in the visible range of its absorption spectrum, which suggests that the starting form **A** had passed into colored form **B** (Fig. 2). After the irradiation was stopped, the solution became colorless.

Thus, we found that the nitration of compound **1** can yield different products, depending on the technique used. However, the major and common (for all three techniques) product was compound **2** formed by oxidation of compound **1**. Photochromic 7-nitro derivative was obtained only in the nitration by a mixture of nitric and sulfuric acids.

Experimental

^{1}H and ^{13}C NMR spectra of compounds **1**—**4** were recorded on a Bruker DRX-500 spectrometer at 25 °C in $CDCl_3$ with

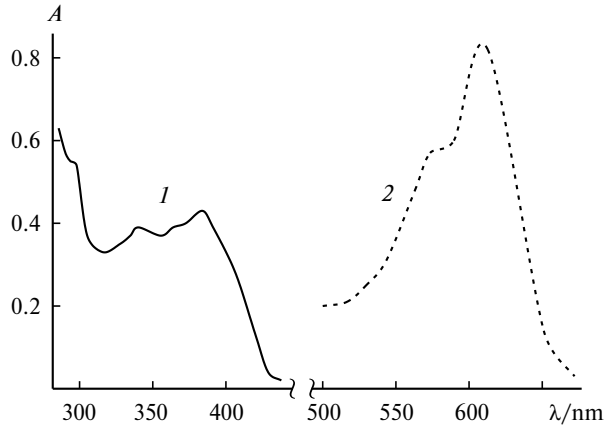

Fig. 2. Absorption spectra of compound **4** in toluene at −12 °C prior to (*1*) and after irradiation with UV light (*2*).

Me_4Si as the internal standard. 2D Spectra were recorded with the use of a standard Bruker procedure. The mixing time in recording gNOESY spectra was 0.5 s; the HMBC experiment was optimized for the coupling constant $J_{H,C}$ = 5 Hz. A ^{15}N NMR spectrum of compound **3** was recorded on a Bruker MW-400 spectrometer in $CDCl_3$ with $CD_3{}^{15}NO_2$ as the external standard.

Mass spectra (EI) were recorded on a Kratos MS-30 instrument (ionizing energy 70 eV, ionization temperature 230 °C, direct inlet probe). A mass spectrum (ESI) was recorded on a Finnigan LCQ instrument (capillary temperature 200 °C, spraying voltage 4.5 kV) with MeCN as a solvent (3 μL min^{-1}). Electronic absorption spectra were recorded on a Specord UV—VIS spectrophotometer. Solutions were irradiated with light of a DKSSh-120 lamp through an interference light filter for 365 nm. Compound **1** was prepared according to a described procedure.[14]

Selected correlation peaks of high (h), medium (m), and low intensities (l) in the HMBC spectrum of compound **1**:

H(4′)/C(6′) (h), H(4′)/C(7′a) (h), H(5′)/C(3′a) (h), H(5′)/C(6′) (l), H(5′)/C(7′) (m), H(6′)/C(7′) (m), H(6′)/C(7′a) (m), H(7′)/C(3′a) (h), H(7′)/C(5′) (h), H(3)/C(2′) (h), H(3)/C(4a) (h), H(3)/C(12b) (l), H(5)/C(4a) (m), H(5)/C(7) (m), H(5)/C(8a) (m), H(6)/C(5) (m), H(6)/C(8) (m), H(6)/C(8a) (m), H(7)/C(5) (m), H(7)/C(8a) (m), H(8)/C(4b) (h), H(8)/C(6) (m), H(8)/C(8b) (h), H(9)/C(8a) (m), H(9)/C(11) (h), H(9)/C(12a) (h), H(10)/C(8b) (m), H(10)/C(12) (h), H(11)/C(9) (h), H(11)/C(12a) (m), H(12)/C(8b) (h), H(12)/C(10) (h), H(12)/C(12b) (h), NMe/C(2′) (h), NMe/C(7′a) (h), CMe_2/C(2′) (h), CMe_2/C(3′) (h), and CMe_2/C(3′a) (h).

2-(2′-Hydroxy-1′,3′,3′-trimethylindolin-2′-yl)phenanthro[9,10-*d*]oxazole (2). A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (1.21 g, 5 mmol) in acetic anhydride (63 mL) was added dropwise at −4 °C to a stirred solution of compound **1** (1.89 g, 5 mmol) in acetic anhydride (90 mL). Then the reaction mixture was slowly warmed to room temperature and poured into ice. The product was extracted with benzene, washed with aqueous sodium carbonate, dried over Na_2SO_4, and filtered. The extract was concentrated and the residue was washed twice with light petroleum and dried. The yield of compound **2** was 1.58 g (80%), m.p. 179 °C. Found (%): C, 78.86; H, 5.66; N, 7.08. $C_{26}H_{22}N_2O_2$. Calculated (%): C, 79.16; H, 5.62; N, 7.10.

Selected correlation peaks of high (h), medium (m), and low intensities (l) in the HMBC spectrum of compound **2**:

H(4′)/C(3′) (m), H(4′)/C(6′) (h), H(4′)/C(7′) (l), H(4′)/C(7′a) (h), H(5′)/C(3′a) (h), H(5′)/C(7′) (h), H(6′)/C(4′) (h), H(6′)/C(7′a) (h), H(7′)/C(3′a) (h), H(7′)/C(5′) (h), H(5)/C(4a) (h), H(5)/C(7) (m), H(5)/C(8a) (h), H(6)/C(4b) (h), H(6)/C(8) (h), H(7)/C(5) (m), H(7)/C(8a) (m), H(8)/C(4a) (l), H(8)/C(4b) (m), H(8)/C(8b) (m), H(9)/C(8a) (l), H(9)/C(11) (m), H(9)/C(12a) (h), H(10)/C(8b) (m), H(10)/C(12) (h), H(10)/C(12a) (m), H(11)/C(9) (m), H(12)/C(8b) (m), H(12)/C(10) (h), H(12)/C(12a) (l), H(12)/C(12b) (m), NMe/C(2′) (h), NMe/C(7′a) (h), CMe_2/C(2′) (h), CMe_2/C(3′) (h), CMe_2/C(3′a) (h), OH/C(3′) (m), and OH/C(3) (m).

2-Methyl-2-[2-(*N*-methyl-*N*-nitrosoamino)phenyl]-1-(phenanthro[9,10-*d*]oxazol-2-yl)propanone (3). Sodium nitrite (0.69 g, 10 mmol) was added to a solution of compound **1** (1.89 g, 5 mmol) in glacial acetic acid (100 mL). The reaction mixture was stirred at room temperature for 30 min and poured into water. The product was extracted with benzene, washed with aqueous sodium carbonate, dried over Na_2SO_4, and filtered. The extract was concentrated and the residue was recrystallized from C_6H_6 to give compound **3** (0.43 g, 20%), m.p. 194 °C, R_f 0.91 ($CHCl_3$—Me_2CO (9 : 1) as an eluent). Found (%): C, 73.61; H, 5.02; N, 9.62. $C_{26}H_{21}N_3O_3$. Calculated (%): C, 73.74; H, 5.00; N, 9.92. ^{15}N NMR (40.53 MHz, $CDCl_3$), δ: −170 (N=O), +129 (Ar—N—N), +139 (N in the heterocycle).

Selected correlation peaks of high (h), medium (m), and low intensities (l) in the HMBC spectrum of compound **3**:

H(4′)/C(3′) (m), H(4′)/C(7′a) (m), H(5′)/C(3′a) (m), H(5′)/C(7′) (l), H(7′)/C(3′a) (m), H(7′)/C(5′) (m), H(7′)/C(7′a) (l), H(5)/C(4a) (h), H(5)/C(7) (l), H(5)/C(8a) (m), H(6)/C(4b) (m), H(8)/C(4b) (m), H(8)/C(6) (m), H(8)/C(8b) (m), H(9)/C(8a) (m), H(9)/C(11) (m), H(9)/C(12a) (m), H(10)/C(8b) (m), H(10)/C(12) (m), H(11)/C(12a) (m), H(12)/C(10) (l), H(12)/C(12b) (l), NMe/C(7′a) (m), CMe_2/C(2′) (h), and CMe_2/C(3′) (h).

1′,3′,3′-Trimethyl-7-nitrospiro[indoline-2′,2-2*H*-phenanthro[9,10-*b*]-1,4-oxazine] (4). Nitric acid (d = 1.41) (0.65 mL) was slowly added dropwise at 0 °C to a stirred solution of compound **1** (3.78 g, 10 mmol) in conc. H_2SO_4 (51.4 mL). After one hour, the reaction mixture was poured into ice (600 cm^3) and neutralized with a solution of Na_2CO_3. The product was extracted with $CHCl_3$ and the extract was washed with water, dried over Na_2SO_4, filtered, and concentrated. The residue was dissolved in benzene and chromatographed on silica gel (100/160) with C_6H_6 as an eluent. A fraction with R_f 0.44 was collected and recrystallized from ethanol to give compound **4** (0.42 g, 10%), m.p. 293 °C. Found (%): C, 73.87; H, 4.89; N, 9.68. $C_{26}H_{21}N_3O_3$. Calculated (%): C, 73.74; H, 5.00; N, 9.92.

Selected correlation peaks of high (h), medium (m), and low intensities (l) in the HMBC spectrum of compound **4**:

H(4′)/C(3′) (l), H(4′)/C(3′a) (m), H(4′)/C(6′) (h), H(4′)/C(7′a) (h), H(5′)/C(3′a) (h), H(6′)/C(7′a) (m), H(7′)/C(3′a) (h), H(7′)/C(5′) (h), H(3)/C(2′) (h), H(3)/C(4a) (h), H(5)/C(4a) (m), H(5)/C(7) (l),

H(5)/C(8a) (m), H(6)/C(4b) (m), H(8)/C(4b) (h), H(8)/C(6) (h), H(8)/C(7) (h), H(8)/C(8b) (m), H(9)/C(8a) (m), H(9)/C(8b) (l), H(9)/C(11) (m), H(9)/C(12a) (h), H(10)/C(8b) (m), H(10)/C(12) (m), H(11)/C(8b) (l), H(11)/C(9) (h), H(11)/C(12a) (h), H(12)/C(8b) (h), H(12)/C(10) (m), H(12)/C(12b) (m), NMe/C(2′) (h), NMe/C(7′a) (h), CMe_2/C(2′) (h), CMe_2/C(3′) (h), and CMe_2/C(3′a) (h).

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References

1. V. Yu. Nedoshivin, A. V. Lyubimov, N. L. Zaichenko, V. S. Marevtsev, and M. I. Cherkashin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2576 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 2363 (Engl. Transl.)].
2. V. Yu. Nedoshivin, N. L. Zaichenko, A. I. Shienok, and V. S. Marevtsev, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 732 [*Russ. Chem. Bull.*, 1995, **44**, 712 (Engl. Transl.)].
3. V. Yu. Nedoshivin, N. L. Zaichenko, N. N. Glagolev, and V. S. Marevtsev, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1243 [*Russ. Chem. Bull.*, 1996, **45**, 1182 (Engl. Transl.)].
4. N. L. Zaichenko, G. S. Kikot′, A. P. Pleshkova, A. I. Shienok, L. S. Kol′tsova, and V. S. Marevtsev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 451 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 470].
5. N. A. Voloshin, A. V. Metelitsa, Zh. K. Misho, E. N. Voloshina, S. O. Bezuglyi, A. V. Vdovenko, N. E. Shelepin, and V. I. Minkin, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1110 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 1172].
6. Zh. K. Misho, N. A. Voloshin, A. V. Metelitsa, E. N. Voloshina, S. O. Bezuglyi, A. V. Vdovenko, N. E. Shelepin, V. I. Minkin, V. V. Tkachev, B. B. Safoklov, and S. A. Aldoshin, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1929 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2038 (Engl. Transl.)].
7. *Preparatyka Organiczna*, Ed. W. Polaczkowa, Panstwowe Wydawnictwa Techniczne, Warszawa, 1954.
8. V. Malatesta, C. Neri, and M. L. Wis, *Mol. Cryst. Liq. Cryst.*, 1997, **298**, 145.
9. L. S. Kol′tsova, N. L. Zaichenko, A. I. Shienok, and V. S. Marevtsev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1157 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1214].
10. N. P. Samoilova and M. A. Gal′bershtam, *Khim. Geterotsikl. Soedin.*, 1977, 1065 [*Chem. Heterocycl. Compd.*, 1977 (Engl. Transl.)].
11. *Nitrogen NMR*, Eds M. Witanowski and G. A. Webb, Plenum Press, London—New York, 1973.
12. P. Aeberly, P. Eden, J. H. Gogerty, W. J. Houlihan, and C. Penberthy, *J. Med. Chem.*, 1975, **18**, 177.
13. E. Pretsh, T. Clerc, J. Seibl, and W. Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds*, Springer-Verlag, Berlin, 1989.
14. P. Tardieu, R. Dubest, I. Aubard, A. Kellmann, F. Tfibel, A. Samat, and R. Guglielmetti, *Helv. Chim. Acta*, 1992, **75**, 1185.

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