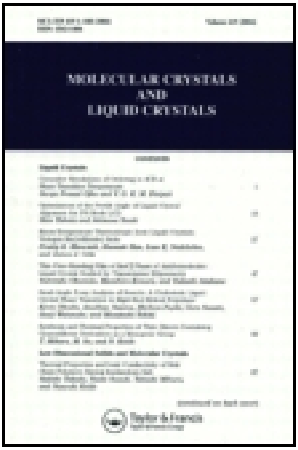

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Direct Nitration Reactions of Photochromic Spirooxazines

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Direct Nitration Reactions of Photochromic Spirooxazines

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A direct nitration of photochromic spirooxazines was carried out by three different methods. The molecular structure of main products was determined by NMR ^{1}H and ^{13}C spectra. The nitration mechanisms were proposed. It was shown that only nitration by mixture of nitric and sulfuric acids gives photochromic compounds with nitrogroup in aryloxazine ring.

Keywords: nitration; NMR; photochromism

Photochromic spirooxazines (SO) are very promising objects from both scientific and practical points of view. However, the fact that well-known multiple-step synthesis of SO is rather laborious gave us an impetus to the development of procedures for modifying SO structures by direct chemical reactions. Present work describes the results of our study of direct nitration reactions of photochromic compounds **1–3**.

All these compounds synthesized by methods [1–3] were nitrated by mixture of nitric and sulfuric acids [2,4] yielding corresponding photochromic mononitroderivatives **4** (8-nitro-**1**), **5** (8-nitro-**2**) and **6** (7-nitro-**3**). In the case of **2** dinitrosubstituted photochromic compound **7** (7′,8-dinitro-**2**) was isolated too.

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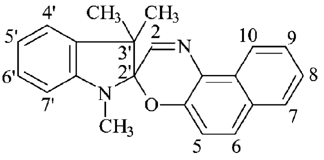

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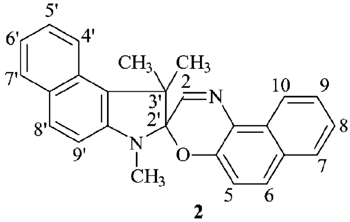

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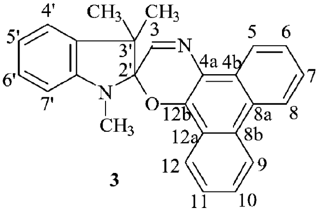
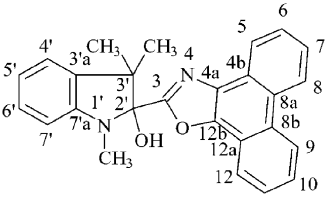


3

Two other methods of nitration, namely by action of $Cu(NO_3)_2$ in acetic anhydride (method 2) [5] and by means of $NaNO_2$ in acetic acid (method 3) [6] were additionally used for **3**, but only nonphotochromic compounds **8** and **9** were obtained under these conditions.



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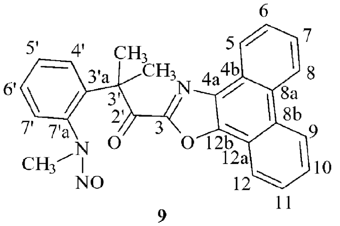


9

The structures of the resulting compounds were established using ^1H and ^{13}C NMR spectroscopy, Table 1 lists ^1H NMR spectral parameters, Table 2 – ^{13}C NMR spectral data for SOs studied. The complete signal assignment in NMR spectra of the starting SO **1–3** has been made previously [2–4].

Analysis of the ^1H NMR spectrum of **4** shows that one hydrogen atom of naphthoxazine fragment of the molecule is substituted by NO_2 group. The presence of three-proton spin system of AKX type with spin-spin coupling constants $^3J_{AK} = 9{,}2\,Hz$ and $^4J_{KX} = 2{,}4\,Hz$ shows that substitution takes place at position 8 or 9. It is known [7] that the presence of NO_2 group in the position 2 of naphthalene leads to the downfield shift of the signals for H(1) and H(3) protons by 0,93 and 0,78 ppm, respectively, compared to those observed in the spectrum of unsubstituted naphthalene. In this case the spin-spin coupling constant $^3J_{3,4}$ increases from 7,54 to 8,36 Hz. As it can be seen from Tables 1, the position of the signals for H(9) and H(10) protons and

TABLE 1 ^{1}H NMR Spectra of Compounds 1–9 in CDCl$_3$

	δ, ppm															
Compound	C(CH$_3$)$_2$	NCH$_3$	H(4′)	H(5′)	H(6′)	H(7′)	H(8′)	H(9′)	H(2)	H(5)	H(6)	H(7)	H(8)	H(9)	H(10)	H(11)	H(12)
1*	1,32 1,35	2,76	7,14	6,85	7,17	6,65	–	–	7,83	7,04	7,78	7,82	7,41	7,57	8,56	–	–
2*	1,58 1,59	2,87	7,94	7,44	7,27	7,76	7,80	7,02	7,86	7,00	7,68	7,84	7,42	7,60	8,60	–	
3	1,40 1,42	2,79	7,13	6,95	7,26	6,61	–	–	7,85*	8,70	7,71	7,60	8,61	8,63	7,65	7,52	8,12
4	1,34 1,37	2,79	7,16	6,88	7,20	6,68	–	–	7,94	7,29	8,15	8,86	–	9,33	8,73	–	–
5	1,59 1,72	2,86	7,90	7,43	7,27	7,79	7,83	7,02	7,90	7,14	7,83	8,70	–	8,32	8,69	–	–
6	1,40 1,42	2,80	7,13	6,96	7,26	6,63	–	–	7,86*	8,80	8,45	–	9,51	8,69	7,76	7,61	8,14
7	1,57 1,69	2,88	8,16	7,48	7,90	–	8,41	7,18	7,88	7,11	7,85	8,71	–	8,34	8,69	–	–
8	1,11 1,60	2,92	7,11	6,89	7,23	6,66	–	–	–	8,61	7,75	7,73	8,74	8,76	7,72		8,22
9	1,85	3,03	7,92	7,65	7,42	7,02	–	–	–	8,21	7,63–7,68		8,64	8,67	7,69–7,73		8,26

*in (CH$_3$)$_2$CO.
**H(3).

TABLE 2 ^{13}C NMR Spectra of Compounds 3, 6, 8 and 9 in $CDCl_3$

Compound	**3**	**6**	**8**	**9**
Carbon atom				
$\mathrm{C-CH_3}$	20,9; 25,5	20,7; 26,2	27,7	20,7; 25,5
$\mathrm{N-CH_3}$	29,6	29,7	36,1	29,6
2′	99,0	99,0	189,2	99,8
3′	51,5	50,1	50,5	51,9
3′a	136,1	135,9	142,9	135,7
4′	121,6	121,7	128,6	121,6
5′	119,8	119,3	129,7	120,2
6′	128,0	128,0	128,0	128,1
7′	107,2	107,4	127,2	107,3
7′a	147,6	148,3	140,4	147,3
3	150,3	165,0	155,4	151,0
4a	120,0	133,7	134,4	119,5
4b	129,4	126,1	125,8	134,1
5	122,2	123,0	122,8	123,4
6	127,4	127,6	127,6	121,1
7	124,9	126,4	126,8	144,8
8	122,5	123,4	123,4	119,0
8a	126,4	128,9	129,2	125,7
8b	131,4	129,4	130,7	131,3
9	122,7	123,7	123,8	123,9
10	127,7	126,8	127,6	128,9
11	126,7	127,3	128,0	128,0
12	122,7	121,0	122,1	123,0
12a	124,3	120,2	120,5	124,8
12b	139,4	145,7	145,3	142,9

increase of spin-spin coupling constant $^3J_{9,10}$ from 8,6 Hz in **1** to 9,2 Hz in **4** are in complete agreement with above-mentioned rule, indicating that NO_2 group is located at position 8.

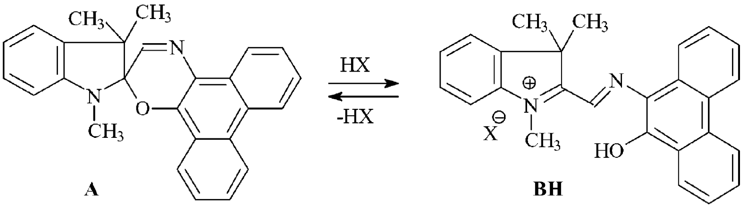
The same situation is observed in ^{1}H NMR spectrum of **5**. All spectral parameters of naphthoxazine fragment of this compound coincide with those for **4**.

Analysis of ^{1}H NMR spectrum of **6** shows that NO_2 group takes one of the following positions – 6,7,10 or 11 – in the phenanthrene fragment. Full analysis of ^{1}H and ^{13}C NMR spectra using standard heteronuclear double resonance techniques evidences the NO_2 group location in position 7.

In the case of dinitrosubstituted **7**, one of the NO_2 groups is located at the position 8 as in the **5**, and the second one is at positions 4′ or 7′ of the benzindoline fragment. Above-mentioned data on the influence of NO_2 group in naphthalene on chemical shifts and coupling constants of the neighboring protons ($^3J_{5',6'}$ is equal 6,7 Hz in **2** and 7,6 Hz in **7**) indicate on the structure **7**.

The structures of nonphotochromic compounds **8** and **9** were established by analysis of ^1H and ^{13}C NMR spectra using COSY, NOESY, HSQC and HMBE techniques.

Now let us discuss some peculiarities of mechanisms of described nitration reactions. Nitration by mixture of nitric and sulfuric acids is a reaction of electrophilic substitution. Since the equilibrium between initial closed form **A** and opened colored form **B** (**A** ↔ **B**) for SOs is known to exist in any solvent and nitration by method 1 is carried out in a strongly acidic medium, where **B** is transformed into the salt form **BH**.



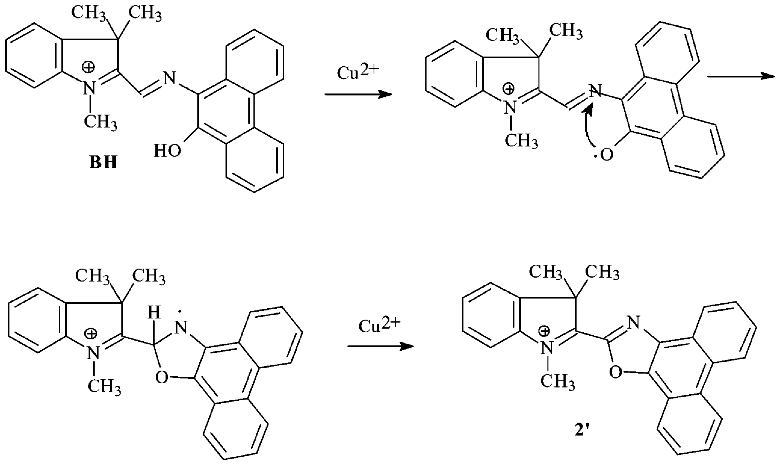
It is reasonable to propose that precisely this form participates in nitration reaction. Then the positions 5, 8, 10 for **1**, **2** and positions 5, 7, 9, 11 for **3** appear to become the most reactive for electrophilic substitution due to activating effect of the OH group. Nitration at the positions 5 and 10 is strongly hindered and therefore nitration of **1** and **2** occurs mainly at position 8, and of **3** – at position 7.

We failed to find the dinitrosubstituted products of **1** and **3**, although the methods for their nitration were similar with that for **2**. This fact can probably be explained by deactivation of the benzene ring in the indoline heterocycle of **1** and **3** by the positively charged quaternary N atom. Introduction of one more benzene ring into compound **2** decreases this effect. Since it is well known that the α-positions in naphthalene are the most reactive, nitration of **2** occurs at position 7′ because position 4′ is shielded by methyl group.

Two other nitration methods were selected for **3** on the base of literature data [3] and because they yield nitrosubstituted derivatives in more soft conditions and without gumming. But contrary to the case of spirobenzopyrans [6] these methods gave no photochromic SOs. In both these methods the initial substance acts as a salt form **BH**. In the nitration method 2 the amount of crystallohydrate water in the salt $Cu(NO_3)_2{\cdot}6H_2O$ is evidently sufficient for nitric acid formation in the reaction medium leading to formation of **BH**.

Then an oxidizing ring-formation showed takes place with high yields in both nitration methods. Cu^{2+} ions act as an oxidant in the second method. HNO_2 and O_2 are the oxidants in the third one.

$$Cu(NO_3)_2 + H_2O \rightleftharpoons Cu(NO_3)(OH) + HNO_3$$



It should be noted that analogue of **8** was earlier obtained [8] as one of the products of SO photo destruction process.

In the method 3 formation of **8** is not the end of the reaction, indoline cycle then opens and is nitrosated at "former indoline" N atom, yielding N-nitrosocompound **9**.

TABLE 3 Photochromic Properties of SO 1–7 at 295 K

	Toluene		Acetone		Ethanol	
Compound	λ_B/nm	$k_B \cdot 10^2/s^{-1}$	λ_B/nm	$k_B \cdot 10^2/s^{-1}$	λ_B/nm	$k_B \cdot 10^2/s^{-1}$
1	592	28,0	596	99,0	610	61,0
2	621	30,0	624	68,0	629[a]	44,0[a]
3	592	0,3[b]	616	1,4[b]	625	3,3[b]
4	621	7,3	620	2,0	618	0,4
5	645	1,5	640	0,7	637[a]	0,1[a]
6	640	14,0	638	7,4	630	4,2[c]
7	616	2,0[d]	612	0,7[d]	615	0,6[d]

[a] In BuOH.
[b] At 253 K.
[c] In acetonitrile.
[d] At 273 K.

Compounds **4–7** have pronounced photochromic properties in solutions, i.e., they undergo transition from the uncolored form **A** to the colored form **B** under UV radiation and then thermally bleached after irradiation cessation. The long wave bands λ_{B} in the absorption spectra of **4–7** in toluene and other solvents and rate constants k_B of dark bleaching are listed in Table 3. From these data it is clear that nitrosubstituted SOs exhibit negative solvatochromism due to bipolar structure of their form **B** contrary to the unsubstituted compounds, which have quinoid structure of form **B** in non-polar solvents and therefore demonstrate positive solvatochromism. Moreover, increase in the medium polarity leads to the acceleration of the unsubstituted SOs bleaching and hindrance of this process for nitrosubstituted compounds due to stronger solvatation of their bipolar molecules by polar solvents.

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