Bromination of photochromic spironaphthoxazines

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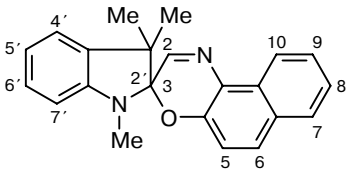
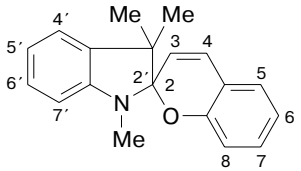
Direct bromination of photochromic compounds of the spironaphthoxazine and spironaphthopyran series was performed using *N*-bromosuccinimide to obtain both photochromic bromine-substituted spiro compounds and nonphotochromic 2-(naphtho[1,2-*d*]oxazol-2-yl)-3*H*-indolium bromides. The structures of the resulting products were established by NMR spectroscopy and mass spectrometry. The mechanism of bromination taking into account the involvement of both closed and open (colored) forms of spiro compounds was proposed.

Key words: photochromism, spironaphthoxazines, spironaphthopyrans, bromination, NMR spectroscopy, mass spectrometry.

Presently, spirooxazines and, in particular, indoline-containing spironaphthoxazines (SNO), are the most promising photochromic compounds for the practical use owing to their higher photostability[1,2] compared to the related well-studied spirobenzopyrans (SBP).



SNO

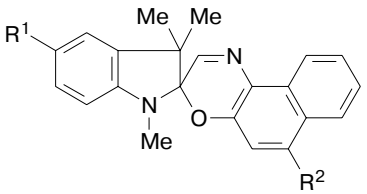


SBP

A known multiple-step synthesis of SNOs is rather laborious, which gave impetus to the development of procedures for modifying the structures of these molecules by direct chemical reactions. Previously, mono- and dinitro-substituted photochromic products have been prepared by nitration of unsubstituted indoline-[3] and benzoindoline-containing[4] SNOs, respectively. Methacryloyl-substituted SNO was synthesized by reduction of the nitro group followed by the replacement of one hydrogen atom in the amino group.[5]

Direct bromination of photochromic compounds has been performed previously[6,7] in the case of indoline-containing SBP. However, data on direct bromination of SNO are lacking in the literature.

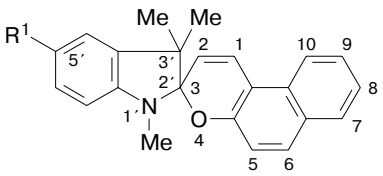
In the present study, we performed direct bromination of photochromic compounds **1**—**3** of the spirooxazine series. For comparison, bromination of spironaphthopyran (SNP) **4** was also performed.



1—**3**, **6**

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

2: $R^1 = Br$, $R^2 = H$ **6:** $R^1 = Br$, $R^2 = Br$



4: $R^1 = H$

8: $R^1 = Br$

It should be noted that the SNO and SNP molecules, like SBP, are present in solutions as colorless (**A**) and colored (**B**) forms existing in the thermodynamical equilibrium, its position being dependent on the polarity of

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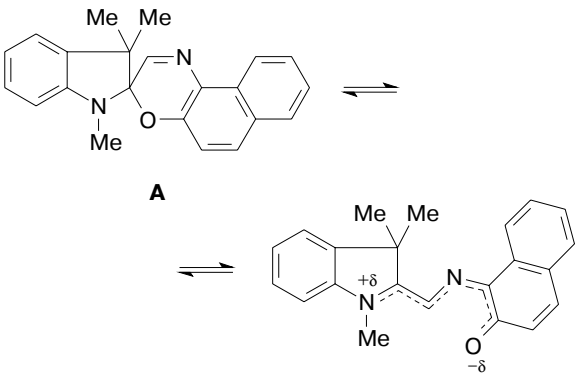
the medium, the temperature, the presence of substituents at particular positions, and their donor-acceptor properties.



All SNOs and SNPs were brominated with *N*-bromosuccinimide (NBS) in chloroform under the same conditions according to a procedure reported previously.[6]

When performing bromination of compound **1**, we isolated monobromo derivative **2** containing the 5′-substitututed indoline heterocycle from the reaction solution in 35% yield, which agrees with the results of bromination of unsubstituted SBP.[6] By-product **5** (its structure is described below) was detected in the precipitate (the yield was 15%).

Bromination of compound **2** also afforded two products, *viz.*, compound **5** (according to the data of NMR spectroscopy and mass spectrometry) and 5′,6-dibromo-substituted SNO **6**, in 45% and 20% yields, respectively.

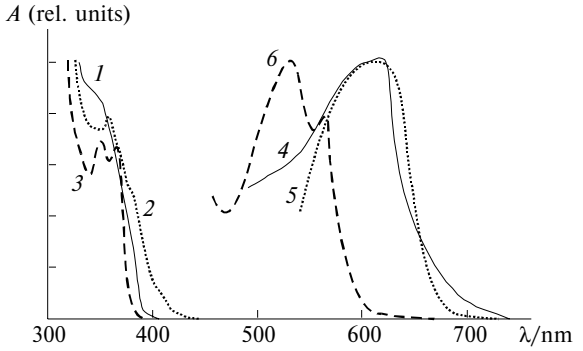


Fig. 1. Absorption spectra of the initial forms **A** (*1*—*3*) (in toluene at 20 °C) and photoinduced forms **B** (*4*—*6*) (in light petroleum at −196 °C) of brominated spiro compounds **2** (*1*, *4*), **6** (*2*, *5*), and **8** (*3*, *6*).

However, bromination of SNO **3** did not give rise to a 5′-bromo-substituted product as would be expected by analogy with bromination of compounds **1** and **2**. In this case, we isolated compound **7** in 50% yield (its structure is described below).

The structures of the resulting compounds were examined by NMR spectroscopy and mass spectrometry. The parameters of the ^{1}H NMR spectra of compounds **1**—**8** are given in Tables 1 and 2. The complete assignment of the signals in the spectrum of the starting SNO **1** has been made previously.[8] Since compounds **2** and **6**,

Table 1. ^{1}H NMR spectra of photochromic spiro compounds at 20 °C

Compound	Solvent	δ												
		CMe_2	NMe	H(2)	H(4′)	H(5′)	H(6′)	H(7′)	H(5)	H(6)	H(7)	H(8)	H(9)	H(10)
1	$CDCl_3$	1.35 s, 1.36 s	2.76 s	7.75 s	7.09 dd	6.90 m	7.21 m	6.58 d	7.01 d	7.66 d	7.74 dd	7.39 m	7.58 m	8.55 dd
2	$CDCl_3$	1.32 s, 1.36 s	2.73 s	7.72 s	7.16 dd	—	7.31 dd	6.45 d	7.02 d	7.68 d	7.75 dd	7.41 m	7.58 m	8.54 dd
	DMSO-d_6	1.24 s, 1.28 s	2.67 s	7.87 s	7.32 dd	—	7.31 dd	6.63 d	7.10 d	7.80 d	7.85 dd	7.42 m	7.58 m	8.45 dd
3[a]	$CDCl_3$	1.36 s, 1.37 s	2.76 s	7.62 s	7.10 dd	6.90 m	7.22 m	6.58 d	6.57 d	—	8.04 dd	7.37 m	7.55 m	8.54 dd
4[b]	$CDCl_3$	1.24 s, 1.37 s	2.76 s	5.82 d	7.11 dd	6.89 m	7.21 dd	6.56 d	7.00 d	7.63 d	7.74 dd	7.35 m	7.53 m	8.05 d
5	DMSO-d_6	2.00 s	4.68 s	—	8.38 d	—	8.00 dd	8.18 d	8.24 d	8.43 d	8.29 dd	7.82 m	7.93 m	8.67 d
6	$CDCl_3$	1.33 s, 1.36 s	2.73 s	7.74 s	7.16 d	—	7.31 dd	6.45 d	7.38 d	—	8.13 dd	7.51 m	7.62 m	8.59 dd
7[c]	$CDCl_3$	2.06 s	4.93 s	—	7.60 — 7.72[f] m			8.04 d	7.38 s	—	8.25 dd	7.70 m	7.79 m	8.60 d
7[d]	DMSO-d_6	1.95 s	4.61 s	—	7.97 dd	7.70—7.75 m		8.13 dd	7.63 s	—	8.38 dd	7.80 m	7.89 m	8.63 dd
8[e]	$CDCl_3$	1.21 s, 1.31 s	2.71 s	5.77 d	7.17 d	—	7.27 dd	6.40 d	6.97 d	7.63 d	7.71 dd	7.35 m	7.52 m	8.02 d

[a] Signals of piperidine: 1.62 s (2 H); 1.81 m (4 H); 3.00 s (4 H).
[b] The signal for H(1): 7.61 d.
[c] Signals of piperidine: 1.76 s (2 H); 1.93 s (4 H); 3.30 s (4 H).
[d] Signals of piperidine: 1.70 s (2 H); 1.85 s (4 H); 3.23 s (4 H).
[e] The signal for H(1): 7.61 d.
[f] A degenerate system.

Table 2. Spin-spin coupling constants in the ^{1}H NMR spectra of spiro compounds (J/Hz) at 20 °C

Compound	Solvent	$^3J_{4',5'}$	$^4J_{4',6'}$	$^3J_{6',7'}$	$^3J_{5,6}$	$^3J_{7,8}$	$^4J_{7,9}$	$^3J_{8,9}$	$^4J_{8,10}$	$^3J_{9,10}$
1	$CDCl_3$	7.4	1.3	8.1	9.4	8.1	1.3	8.1	1.3	8.1
2	$CDCl_3$	—	2.1	8.2	8.9	8.2	1.2	6.7	1.2	8.2
	DMSO-d_6	—	2.0	8.1	8.7	8.1	1.3	6.7	1.3	8.7
3	$CDCl_3$	7.3	1.2	7.6	—	8.2	1.5	6.7	1.2	8.5
4	$CDCl_3$	7.6	1.5	8.1	8.8	8.1	1.5	7.4	*	8.8
5	DMSO-d_6	—	1.9	8.5	9.5	8.2	1.2	7.2	*	7.6
6	$CDCl_3$	—	1.8	8.2	—	8.5	1.2	7.3	1.2	8.5
7	DMSO-d_6	6.2	2.8	6.2	—	8.2	1.2	7.0	1.5	7.8
	$CDCl_3$	*	*	7.9	—	8.5	1.2	7.3	1.2	8.1
8	$CDCl_3$	—	2.2	8.1	8.9	8.1	1.5	6.6	*	8.1

* Constants were not determined.

unlike **5** and **7**, exhibit photochromic properties, *i.e.*, turn colored under UV light and are decolorized in the dark (Fig. 1), let us consider their NMR spectra first.

As can be seen from Table 1, only one hydrogen atom of the indoline fragment in bromide **2** is replaced by the Br atom. A choice between two possible positions (5′ or 6′) was made based on the data[9] on the effect of the Br atom on the chemical shifts of the adjacent protons depending on its position in the benzene ring. The NMR spectrum calculated on the assumption that the Br atom is located at position 5′ is virtually identical with the experimental spectrum of this product. Hence, it can be said with assurance that bromination of compound **1** afforded the 5′-substituted product. Moreover, since the general NMR pattern of this compound is identical with that of SNO **1** and taking into account that the product exhibits photochromic properties, it is reasonably safe to suggest that we obtained SNO **2**. This conclusion is consistent with the results of bromination of indoline-containing SNPs.[6]

The NMR spectrum of photochromic product **6** obtained upon bromination of compound **2** indicates that compound **6** contains the second Br atom at position 5 or 6 of the naphthoxazine fragment. It is known[10] that the presence of the Br atom at position 1 of naphthalene leads to downfield shifts of the signals for the H(7) and H(8) protons by 0.09 and 0.37 ppm, respectively, compared to those observed in the spectrum of unsubstituted naphthalene. In this case, the spin-spin coupling constant $J_{7,8}$ increases from 8.2 to 8.5 Hz. As can be seen from Tables 1 and 2, the positions of the signals for the H(8) and H(7) protons and their spin-spin coupling constants $J_{7,8}$ in the NMR spectra of compounds **2** and **6** are in complete agreement with the above-described rule.

The mass spectra (electron impact) of bromo-substituted spironaphthoxazines **2** and **6** and of compounds **1** and **3** with the known structures were examined (Table 3). Fragmentation of all four spironaphthoxazines proceeds according to a general scheme. Thus, the mass spectra of compounds **1**—**3** and **6** have high intensity peaks of the $[M]^+$ molecular ions. In addition, the most intense peaks in the mass spectra are associated either with the formation of the ions corresponding to the spiro-fused moieties of the molecules (**D** and **E**) or with elimination of the methyl group (**C** and **F**). The major fragmentation paths of these molecules with the assumed structures of ions **C**—**G** are shown in Scheme 1. It should be noted that ions with the structures corresponding to ion **D** were observed upon oxidative destruction of the respective SNO as well.[11,12]

It is known that bromination of aromatic compounds with NBS can proceed either by ionic[13] or radical[14] mechanisms. In the latter case, the reaction should be inhibited by the addition of compounds readily reacting with free radicals. The yield of bromo-substituted product **2** obtained by bromination of compound **1** in the presence of benzoquinone is independent of the presence and concentration of the inhibitor, which is indicative of the electrophilic mechanism of the reaction.

The structures of products **5** and **7** were also investigated by NMR spectroscopy and mass spectrometry (the

Table 3. Mass spectra of spironaphthoxazines

Ion	**1**		**2**		**3**		**6**	
	m/z	I_{rel} (%)	m/z	I_{rel} (%)	m/z	I_{rel} (%)	m/z	I_{rel} (%)
$\mathbf{M}^+$	328	42	406/408	59 : 60	411	100	484/486/488	12 : 23 : 11
C	313	44	391/393	58 : 55	396	83	469/471/473	9 : 16 : 9
D	169	26	169	40	252	80	247/249	14 : 13
E	159	100	237/239	100 : 97	159	46	237/239	100 : 97
F	144	67	222/224	50 : 47	144	36	222/224	38 : 38
G	158	55	236/238	45 : 43	158	49	236/238	58 : 53

Scheme 1

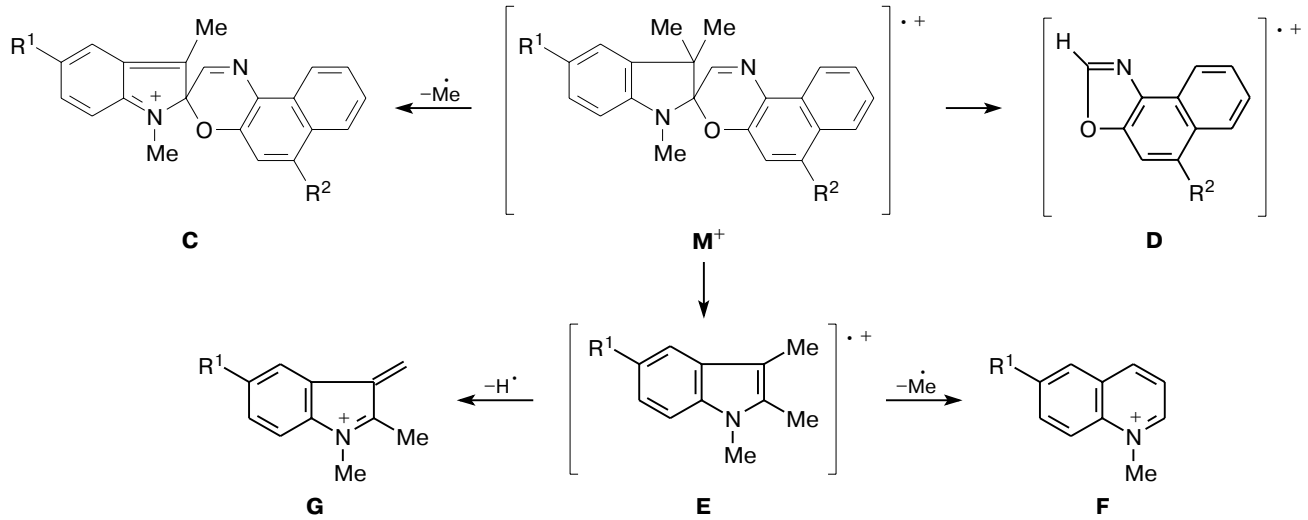
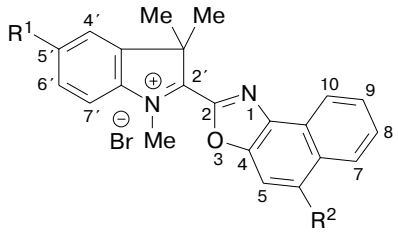


Table 4. Mass spectra of compounds **5** and **7**

Ion	**5**		**7**	
	m/z	I_{rel} (%)	*m/z*	I_{rel} (%)
$[\mathbf{M}]^{\cdot +}$	484/486/488	0	489/491	0
$[HBr]^{\cdot +}$	80/82	100 : 100	80/82	100 : 100
$[MeBr]^{\cdot +}$	94/96	100 : 100	94/96	100 : 100
J	404/406	4 : 3	409	4
K	390/392	100 : 94	395	100

parameters of the spectra are given in Tables 1, 2, and 4). The ^{1}H NMR spectral data provide evidence that both products contain components identical with those of the usual spiro compound, *i.e.*, the indoline and naphthoxazine fragments. The only signal of the CMe_2 group and the low-field signal of the NMe group indicate that molecules **5** and **7** exist in open forms bearing a positive charge on the indoline N atom and posssessing π-conjugation between two heterocycles. This is also evidenced by the absorption spectra of compounds **5** and **7*** (Fig. 2), which have intense bands in the visible region. It would appear reasonable that products **5** and **7** have structures of colored form **B**. In addition, the absence of signals for the H(2) protons in the NMR spectra suggests that the Br atom in both products is located at position 2 of the oxazine ring. However, the fact that compounds **5** and **7** do not exhibit photochromic properties, the poor solubility of compound **5** in organic solvents, and the fact that forms **B** of these compounds can undergo intramolecular cyclization[16—18] cast doubt upon the validity of the interpretation of their structures. Actually, it appeared that the NMR spectra of compounds **5** and **7** (Tables 1 and 2) are virtually identical in positions of the signals and their integral intensities (except for certain details associated with the particular molecular structure) to the NMR spectrum of one of the decomposition products of SNO, which was formed both upon prolonged irradiation of SNO solutions and in their reactions with strong oxidizing agents (TCNQ** or $CuCl_2$).[12,15] Hence, the following structures can be proposed for compounds **5** and **7**:



5: R^1 = Br, R^2 = H

7: R^1 = H, R^2 = 

The mass spectra of compounds **5** and **7** (Scheme 2, Table 4) differ radically from those of compounds **1**—**3** and **6**. The main difference is that no molecular ion peaks are present in the mass spectra of compounds **5**

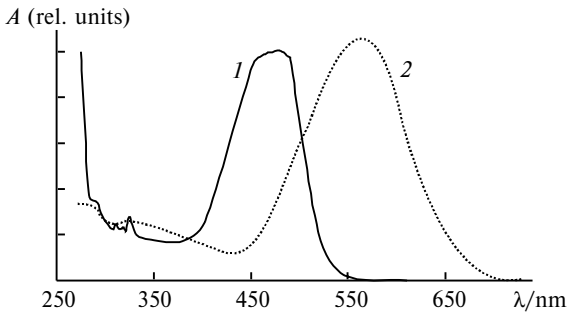


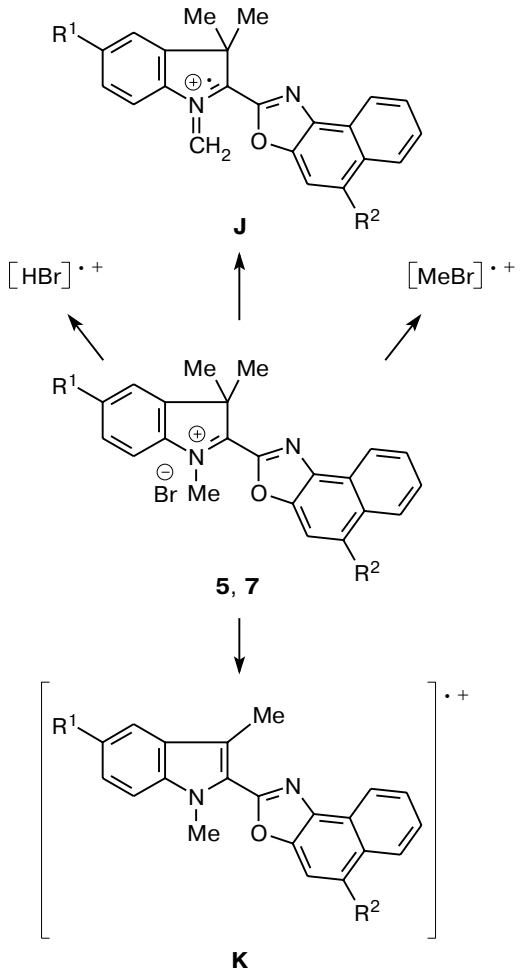
Fig. 2. Absorption spectra of compounds **5** (*1*) and **7** (*2*) in $CHCl_3$ at 20 °C.

* ε_{465} (**5**) = $1.5 \cdot 10^4$ L mol^{-1} cm^{-1}, ε_{570} (**7**) = $2.8 \cdot 10^4$ L mol^{-1} cm^{-1}.

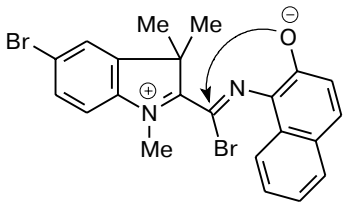
** 7,7,8,8-Tetracyanoquinodimethane.

and **7**. These compounds readily undergo thermal destruction with elimination of HBr and MeBr, respectively. The corresponding peaks at *m/z* 80/82 and 94/96 possess the maximum intensities. The products that formed upon elimination have presumably structures **J** and **K**. The intensity of the peak of ion **J** is rather low due, apparently, to its further efficient decomposition, whereas product **K** is rather stable and its peak has the maximum intensity. Therefore, the mass spectra of compounds **5** and **7** agree well with the assumed molecular structures, which are favorable for elimination of HBr and MeBr due to the fact that the Br^- anion and the methyl group are in close proximity.

Scheme 2



Our results provide an idea of the mechanism of bromination of spironaphthoxazines. As demonstrated above, bromination of SNO with NBS proceeds as electrophilic replacement. Semiempirical quantum-chemical calculations of the electron density performed by the PM3 method* demonstrated that the carbon atoms at positions 5′ and 7′ in form **A** of molecule **1** bear the largest negative charges (−0.16). Since position 7′ is sterically blocked, bromination occurs at position 5′. Apparently, the introduction of the Br atom at this position changes the equilibrium position between forms **A** and **B** and the concentration of the latter form increases. According to these calculations, the maximum negative charge in form **B** of compound **2** is located on the azomethine C atom (−0.36). Evidently, bromination occurs at this position to form intermediate imidoyl bromide.



As mentioned above, the latter compound is very reactive and undergoes intramolecular cyclization according to the mechanism[16–18] of nucleophilic replacement involving the phenoxide O^- atom and the labile C—Br bond to form product **5**.

Therefore, we assumed that in the case of bromination of **1**, photochrome **2** arised from closed form **1**, whereas compound **5** was generated from open (colored) form **2**. Correspondingly, in the case of bromination of compound **2**, compound **5** and dibromo-substituted SNO **6** arised from the colored and starting forms of **2**, respectively. Apparently, we failed to isolate a photochrome containing the Br substituent in the indoline moiety upon bromination of SNO **3** due to the fact that the colored form of this SNO prevailed in the mixture under the reaction conditions. The reaction of this form with NBS gave rise to compound **7** according to the above-described mechanism.

The mechanism proposed for the reaction of SNO with NBS is indirectly supported by the fact that we isolated only 5′-substituted photochrome **8** in 56% yield in the case of bromination of SNP **4**, whereas a product with the structure analogous to that of compound **5** was not detected. Apparently, this is due to the fact that SNP **4** exists in solution only in form **A** because its colored form **B** is very unstable and can be observed only at low temperature even upon photocoloring.[19]

Therefore, bromination of spironaphthoxazines is characterized by the involvement of both the closed and colored forms of photochrome molecules giving rise to different products. Hence, it is believed that the course of the reaction can be controlled by changing the reaction conditions so that the equilibrium between forms **A** and **B** is changed.

Experimental

The ^1H NMR spectra were recorded on a Bruker WM-400 spectrometer at 25 °C. The mass spectra were measured on a KRATOS MS90 instrument; the energy of ionizing electrons was 70 eV, the temperature of the ionization chamber was 200 °C.

* Hyperchem. Release 5.1 Pro for Windows, Hypercube, Inc.

The absorption spectra of the synthesized compounds in solutions were recorded on a Specord UV VIS spectrophotometer.

The results were discussed and the spectra of compounds **1**—**8** were described using the atomic numbering scheme presented in the structural formulas; however, the IUPAC nomenclature was used in the Experimental section.

The solvents were purified according to standard procedures; NBS (analytical grade; the Ural Chemical Plant) was used without additional purification. The syntheses of compounds **1**, **3**, and **4** have been reported previously.[20—22]

5-Bromo-1,3,3-trimethylspiro[indoline-2,3′-3*H*-naphtho[2,1-*b*][1,4]oxazine] (2). A solution of NBS (1.28 g, 7.2 mmol) in $CHCl_3$ (75 mL) was added dropwise with stirring to a solution of compound **1** (2 g, 6 mmol) in $CHCl_3$ (30 mL) upon refluxing for 40 min. Then the reaction mixture was refluxed for 1 h. The precipitate that formed was filtered off, washed three times with water, and dried with Na_2SO_4. The choroform was distilled off. The product was twice recrystallized from 95% EtOH. Sandy-yellow crystals of **2** were obtained in a yield of 0.87 g (35%), m.p. 183—184 °C, R_f 0.64 (Silufol, benzene). Found (%): C, 64.13; H, 5.06; N, 6.98; Br, 20.44. $C_{22}H_{19}BrN_2O$. Calculated (%): C, 64.88; H, 4.70; N, 6.86; Br, 19.62.

5,6′-Dibromo-1,3,3-trimethylspiro[indoline-2,3′-3*H*-naphtho[2,1-*b*][1,4]oxazine] (6) and 5-bromo-1,3,3-trimethyl-2-(naphtho[1,2-*d*]oxazol-2-yl)-3*H*-indolium bromide (5). A solution of NBS (0.47 g, 2.64 mmol) in $CHCl_3$ (30 mL) was added with stirring to a solution of compound **2** (0.908 g, 2.2 mmol) in $CHCl_3$ (60 mL) upon refluxing for 55—60 min. Then the reaction mixture was refluxed for 3 h and filtered. The filtrate was washed three times with water, dried with Na_2SO_4, and concentrated. The residue was dissolved in PhH and chromatographed on a column with silica gel L 100/160 μm. The fraction with R_f 0.83 (Silufol, benzene) was collected. The product was twice recrystallized from aqueous EtOH. Yellow-green crystals of **6** were obtained in a yield of 0.23 g (21%), m.p. 113—114 °C. Found (%): C, 53.83; H, 3.45; N, 5.36; Br, 32.36. $C_{22}H_{18}Br_2N_2O$. Calculated (%): C, 54.35; H, 3.73; N, 5.76; Br, 32.87.

After filtration of the reaction mixture, the precipitate was successively refluxed in CH_2Cl_2 for 1 h and then in MeCN, filtered off, and dried *in vacuo*. A red-brown powder of **5** was obtained in a yield of 0.55 g (18%), m.p. 222—224 °C. R_f 0.66 (Silufol, $CHCl_3$). Found (%): C, 53.93; H, 3.85; N, 5.84; Br, 32.80. $C_{22}H_{18}Br_2N_2O$. Calculated (%): C, 54.35; H, 3.73; N, 5.76; Br, 32.87.

1,3,3-Trimethyl-2-[5-(piperidin-1-yl)naphtho[1,2-*d*]oxazol-2-yl]-3*H*-indolium bromide (7). A solution of NBS (2.14 g, 0.12 mol) in $CHCl_3$ (120 mL) was added with stirring to a solution of compound **3** (4.11 g, 0.01 mol) in $CHCl_3$ (50 mL) upon refluxing for 2 h. Then the reaction mixture was refluxed for 3 h and washed three times with ice water. The organic layer was dried with Na_2SO_4. The chloroform was evaporated and benzene (50 mL) was added. The precipitate that formed was filtered off and recrystallized from benzene. Dark-brown crystalline compound **7** was obtained in a yield of 2.47 g (50.3%), m.p. 184—185 °C. Found (%): C, 63.37; H, 6.18; N, 8.69; Br, 16.45; H_2O (according to Fisher) 3.49. $C_{27}H_{28}N_3OBr \cdot H_2O$. Calculated (%): C, 63.78; H, 5.95; N, 8.26; Br, 15.71; H_2O, 3.54.

5-Bromo-1,3,3-trimethylspiro[indoline-2,3′-3*H*-naphtho[2,1-*b*]pyran] (8). A solution of NBS (0.37 g, 2 mmol) in $CHCl_3$ (22 mL) was added dropwise with stirring to a solution of SNP **4** (0.54 g, 1.7 mmol) in $CHCl_3$ (10 mL) upon refluxing for 30 min. Then the reaction mixture was refluxed for 2 h. The solution was separated from the precipitate by filtration. The filtrate was washed three times with water and dried with Na_2SO_4. The chloroform was distilled off and the residue was chromatographed on a column with silica gel L 100/160 μm in the 1 : 1 CCl_4—CH_2Cl_2 system. The fraction with R_f 0.50 was collected. White crystals of **8** were obtained in a yield of 0.4 g (56%), m.p. 248—250 °C. Found (%): C, 67.90; H, 5.02; N, 3.53; Br, 19.50. $C_{23}H_{20}NOBr$. Calculated (%): C, 67.99; H, 4.96; N, 3.45; Br, 19.67.

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