1214 *Russian Chemical Bulletin, International Edition, Vol. 50, No. 7, pp. 1214—1217, July, 2001*

Merocyanine form of photochromic spirooxazines in acid solutions

L. S. Kol'tsova,**★* ***N. L. Zaichenko, A. I. Shiyonok, and V. S. Marevtsev

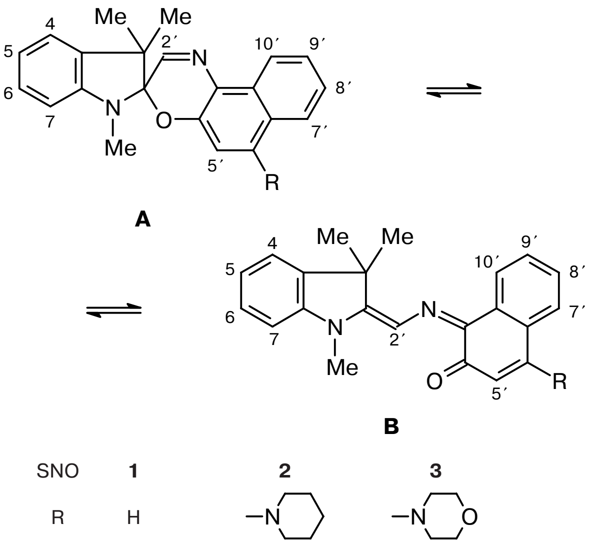
N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 119991 Moscow, Russian Federation.
Fax: +7 (095) 137 8284. E-mail: marvic@polymer.chph.ras.ru

Electronic absorption and NMR spectra of solutions of photochromic spironaphthoxazines (SNOs) were studied. The addition of an acid results in the formation of a salt of the colored form of SNO. For SNOs with nitrogen-containing electron-releasing substituents, the structure of the product that formed depends on the acid concentration being the salt of the mono- or dication.

Key words: photochromism, spironaphthoxazines, acid, merocyanine, electronic absorption spectra, NMR spectroscopy.

Photochromism of spiro compounds is due to the photolytic or thermal cleavage of the C—O bond in the initial colorless state **A** and transition of the molecule to the merocyanine form **B**. Spironaphthoxazines (SNOs), which possess a higher photostability than traditional spirobenzopyranes (SBPs), are of most interest. The photochromic behavior of SBP in both solutions and polymeric matrices depends on the presence of organic or inorganic acids in the system.[1—3] This is a result of the fact that the merocyanine form possessing basic properties is capable of forming BH^+X^- salts with strong acids and complexes having a hydrogen bond B...HX with weak acids. This work is devoted to the study of the influence of acid on the spectral properties of solutions of SNO (**1—3**) and structure elucidation of the products obtained (Scheme 1).

Scheme 1



Experimental

1,3,3-Trimethylspiro(indoline-2,3′-3*H*-naphtho[2,1-*b*][1,4]-oxazine) (**1**), 1,3,3-trimethyl-6′-piperidinospiro(indoline-2,3′-3*H*-naphtho[2,1-*b*][1,4]-oxazine) (**2**), and 1,3,3-trimethyl-6′-morpholinospiro(indoline-2,3′-3*H*-naphtho[2,1-*b*][1,4]-oxazine) (**3**) were synthesized by previously described procedures.[4] Dioxane, acetone, and chloroform ("for UV spectroscopy" trade mark) were used as solvents. The concentration of the photochrome was 10^{-4}—10^{-5} mol L^{-1}. The concentration of acids H_2SO_4 and CF_3COOH was varied in the 6—$6 \cdot 10^{-3}$ mol L^{-1} interval. A required amount of an acid solution was added to a solution of SNO, and the absorption spectrum was immediately recorded on an Specord UV—Vis spectrophotometer. ^1H NMR spectra were recorded on a Bruker WM-400 spectrometer in $CDCl_3$ with an addition of a necessary amount of concentrated CF_3COOH. All measurements were carried out at room temperature.

Results and Discussion

Compounds **1—3** change their color under UV irradiation in solutions and polymeric matrices at room temperature.[5,6] The addition of an acid to nonirradiated solutions of these SNOs results in their coloring almost immediately. The spectral parameters depend on the specific compound, acid, its concentration, solvent, and time. In the case of H_2SO_4, the dependence of the acid concentration was studied only in acetone because this acid is immiscible with $CHCl_3$, while in dioxane at an acid concentration exceeding $1.5 \cdot 10^{-2}$ mol L^{-1} irreversible acidolysis processes occur rapidly.

In the spectrum of compound **1** in dioxane, one absorption band appears with a maximum at 538 nm for H_2SO_4 and 552 nm for CF_3COOH (Fig. 1). At the same concentration of **1** ($1.1 \cdot 10^{-4}$ mol L^{-1}), the absorbance *D* at the absorption maximum is equal to 0.25 at a concentration of H_2SO_4 of $1.5 \cdot 10^{-2}$ mol L^{-1} and only 0.1 for a concentration of CF_3COOH of 1.2 mol L^{-1}.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1157—1160, July, 2001.

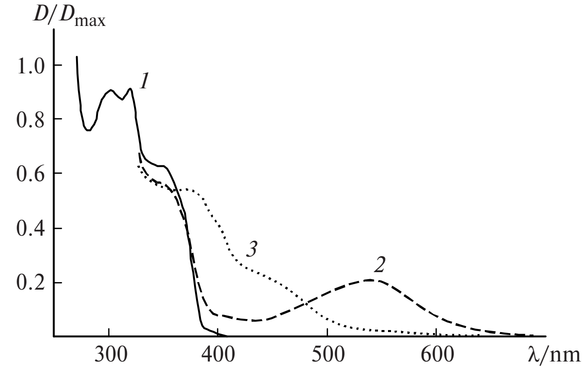


Fig. 1. Absorption spectra of **1** ($9.75 \cdot 10^{-5}$ mol L^{-1}) in dioxane: *1*, without acid; *2*, with addition of H_2SO_4 ($1.5 \cdot 10^{-2}$ mol L^{-1}); and *3*, solution *2* after 5 days.

An increase in the CF_3COOH concentration is not accompanied by the appearance of new absorption bands, only *D* increases and a slight hypsochromic shift related to the solvatochromic effect is observed. The visible band disappears with time (5 days), the solution becomes yellow, its absorption spectrum changes (see Fig. 1), and then the solution loses its photochromic properties. The behavior of **1** in $CHCl_3$ in the presence of CF_3COOH is similar, distinctions being observed only in position of the long-wave maximum (556 nm) and in much lower (compared to a solution in dioxane) acid concentration at which the color appears; for example at a concentration of 0.6 mol L^{-1} *D* is 1.1.

The behavior of compounds **2** and **3** differs substantially from that of SNO **1**. The position of an absorption maximum in the visible spectral region of these compounds depends on the acid concentration. For example, an increase in the CF_3COOH concentration in a solution of **3** in $CHCl_3$ from $6.2 \cdot 10^{-3}$ to 1.2 mol L^{-1} shifts the maximum from 639 to 541 nm (Fig. 2). The spectra are transformed with time. In the case of a low acid concentration, the colored form with a maximum at 639 nm is transformed into the product with the absorption band at 541 nm (Fig. 3). In turn, the spectral form with λ 541 nm, which is formed at a high concentration of the acid, is completely decolorized during 14 days, and the spectrum of the resulting product does not coincide with the initial spectrum, which indicates that irreversible acidolysis reactions occur. A similar behavior is observed in dioxane, however, as for compound **1**, a much higher concentration of the acid than that in a solution in $CHCl_3$ is required. The absorption maxima of the colored forms of **2** and **3** in various solvents and in the presence of various acids are presented in Table 1.

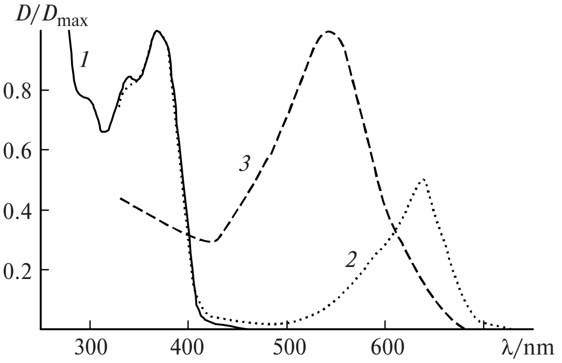


Fig. 2. Absorption spectra of freshly prepared solutions of **3** in $CHCl_3$ without acid (*1*) and in the presence of CF_3COOH (*2, 3*) in concentrations of $6.2 \cdot 10^{-3}$ (*2*) and 1.2 mol L^{-1} (*3*).

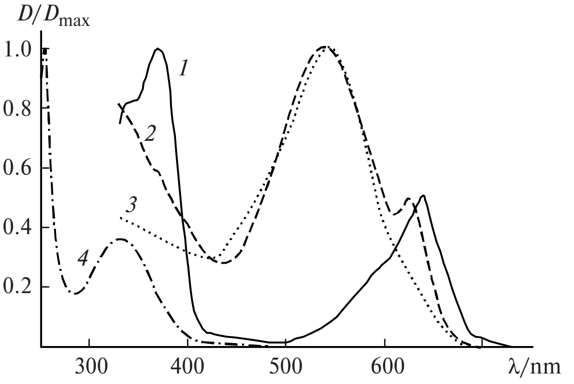


Fig. 3. Absorption spectra of solutions of **3** in $CHCl_3$ in the presence of CF_3COOH at concentrations of $6.2 \cdot 10^{-3}$ mol L^{-1} (*1, 2*) and 1.2 mol L^{-1} (*3, 4*): freshly prepared solutions (*1, 3*) and after storage for 14 days (*2, 4*).

In order to establish the structure of colored compounds formed from SNO by the acid addition. we studied the ^1H NMR spectra, whose parameters for compounds **1** and **2** are presented in Table 2 (the spectra for SNO **3** coincide almost completely with those for **2**, except for signals from the substituent). The

Table 1. Long-wave absorption maxima of SNO solutions in the presence of acids[a]

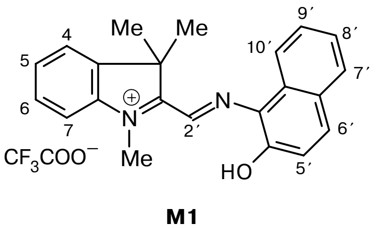
SNO	Solvent	Acid	C^b/mol L^{-1}	λ_{max}/nm
1	Acetone	H_2SO_4	0.26	516
	$CHCl_3$	CF_3COOH	0.6	556
	Dioxane	CF_3COOH	1.2	552
		H_2SO_4	0.015	538
2	Acetone	H_2SO_4	0.006	606
		H_2SO_4	0.39	492
	$CHCl_3$	CF_3COOH	0.006	650
		CF_3COOH	0.6	528
	Dioxane	CF_3COOH	1.2	638
		CF_3COOH	6.2	532
		H_2SO_4	0.015	641
3	Acetone	H_2SO_4	0.004	584
		H_2SO_4	0.43	505
	$CHCl_3$	CF_3COOH	0.006	639
		CF_3COOH	1.2	541
	Dioxane	CF_3COOH	1.2	624
		CF_3COOH	6.2	553
		H_2SO_4	0.015	638

[a] For freshly prepared solutions.
[b] Acid concentration.

Table 2. Parameters of ^{1}H NMR spectra of SNO solutions in $CDCl_3$ in the presence of CF_3COOH

Group	δ				
	1	**M1**	**2**	**M2**	**D2**
NCH_2	—	—	3.00	3.55	3.86
$NCCH_2$	—	—	1.81	1.94	2.25
CH_2	—	—	1.62	1.78	1.90
CMe_2	1.35 s; 1.36 s	1.99 s	1.36 s; 1.37 s	1.94 s	2.00 s
NMe	2.76 s	4.24 s	2.76 s	4.05 s	4.36 s
H(2′)	7.75 s	10.11 s	7.62 s	9.73 s	10.06 s
H(4)	7.09 dd	7.62—7.80	7.10 dd	7.50—7.60	7.70—7.80
H(5)	6.90 m	7.62—7.80	6.90 m	7.50—7.60	7.70—7.80
H(6)	7.21 m	7.62—7.80	7.22 m	7.50—7.60	7.70—7.80
H(7)	6.58 d	7.62—7.80	6.58 d	7.50—7.60	7.70—7.80
H(5′)	7.01 d	7.39 d	6.57 d	7.13 s	7.70—7.80
H(6′)	7.66 d	7.60—7.70	—	—	—
H(7′)	7.74 dd	7.82 dd	8.04 d	7.92 d	8.03 d
H(8′)	7.39 m	7.60—7.70	7.37 m	7.67 m	7.65 m
H(9′)	7.58 m	7.60—7.70	7.55 m	7.80 m	7.70—7.80
H(10′)	8.55 dd	8.46 dd	8.54 dd	8.52 dd	8.56 dd
OH	—	10.0 s	—	10.0 s	10.8 s

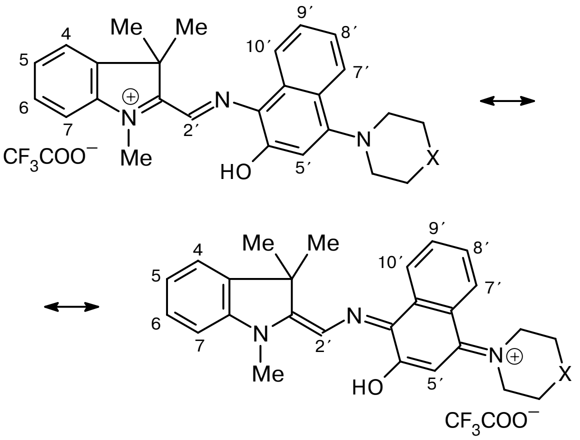
spectrum of compound **1** in the presence of an acid differs substantially from the initial spectrum and is characterized by the singlet signal from the CMe_2 groups, which confirms their equivalence and is typical of the open form **B** of spiro compounds.[7] The signals from the NMe group and H(2′) proton are shifted to the weak field, indicating the appearance of a positive charge on the N atom of the indoline heterocycle and π-conjugation between the primarily orthogonal fragments of the molecule. These data allow one to suggest the structure of the monocation salt (**M1**) for the colored form **1** in the presence of an acid.



M1

The ^{1}H NMR spectrum of SNO **2** in $CDCl_3$, as its absorption spectrum, depends on the concentration of the added acid. In the case of a low concentration corresponding to the absorption spectrum with a maximum at 650 nm, the ^{1}H NMR spectrum of the salt form is similar to the spectrum of **1** in many respects; however, the signals from the NMe group and H(2′) proton lie in a weaker field. In addition, the downfield shift of the signal of the NCH_2 group of the piperidine ring compared to the initial spectrum indicates the appearance of a positive charge on the N atom. Most likely, monocation salts of SNO **2** (**M2**) and **3** (**M3**) have the mesomeric structure, intermediate between two limiting cationic forms (Scheme 2).

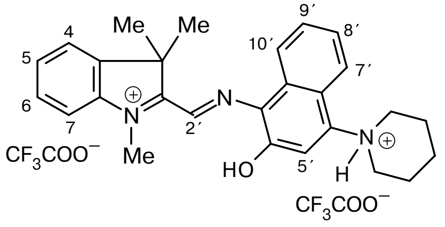
Scheme 2



M2: X = CH_2, **M3:** X = O

The possibility of this mesomerism for photoinduced forms of these compounds has been shown previously.[6]

At a high acid concentration corresponding to the absorption spectrum with a maximum at 528 nm, the ^{1}H NMR spectrum exhibits the further downfield shift of signals from the CMe_2 and NMe groups, H(2′) proton, and protons of the piperidine substituent. The positions of the signals of the first three groups almost coincide with positions of the corresponding signals for **M1**. This implies that positive charges, whose values exceed similar charges in **M2**, are localized on both N atoms. Most likely, the salt of dication **D2** is formed under these conditions.



D2

This assumption is confirmed by the fact that the absorption maximum for **D** is shifted to the short-wave region compared to that for the corresponding **M**. This spectral behavior is due to the fact that **M2** and **M3** contain the electron-donor substituent (piperidyl or morpholyl), which in the **D** form, due to the formation of the quaternary N atom, becomes electron-acceptor, which leads the hypsochromic shift of the absorption maximum.[8,9]

It is known[10] that forms **A** and **B** of spiro compounds exist in a solution at the thermodynamic equilibrium. In the presence of an acid, the concentration of **A** decreases due to the formation of the salt of form **B**. Since even in the case of formation of monocations **M2** and **M3**, the acid concentration exceeds much the concentration of the photochrome, the monocations are transformed with time into the corresponding dications **D2** and **D3**. The dependence of the behavior of SNO on the solvent nature is resulted from the proton-donor capability of the acid in this solvent. It is known[11] that dioxane is referred to the class of aprotic protophilic solvents in which a proton is strongly solvated by a hydrogen bond, and $CHCl_3$ is related to the class of aprotic inert solvents. This implies that dioxane is a stronger base that $CHCl_3$.[12,13] Since on forming the salt form, SNO competes for a proton with the solvent, in a stronger base a lower fraction of SNO is transformed into the protonated form.

When a base (alkali, amine) is added to freshly prepared solutions of mono- and dications of salts of compounds **1**—**3**, the color of solutions disappears, the absorption spectra become similar to the spectra of the initial compounds, and for **2** and **3** this transition, according to the absorption spectra, occurs *via* the stage of formation of the corresponding monocation. UV irradiation of these solutions shows that they possess photochromic properties. Then the scheme of processes can be presented as follows:

$$\mathbf{A} \rightleftharpoons \mathbf{B} \underset{-H}{\overset{+H}{\rightleftharpoons}} \mathbf{M} \underset{-H}{\overset{+H}{\rightleftharpoons}} \mathbf{D} \longrightarrow \mathbf{C},$$

where **C** are the acidolysis products. Naturally, for **1** the stage of dication formation is absent.

Thus, in an acidic medium SNOs form salts of the colored form, and if the photochrome molecule contains a nitrogen-containing electron-donor substituent, either mono- or dications of the merocyanine form characterized by different absorption spectra are formed depending on the concentration and strength of the acid.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-32095).

References

1. L. S. Atabekyan and A. K. Chibisov, *J. Photochem.*, 1985, **31**, 123.
2. V. D. Arsenov, V. S. Marevtsev, I. V. Komlev, M. A. Tavrizov, and M. I. Cherkashin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1019 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 889 (Engl. Transl.)].
3. Ch. D. Gabbutt, J. D. Hepworth, and B. M. Heron, *Dyes and Pigments*, 1999, **42**, 35.
4. Eur. Pat. 0245020, 1987.
5. L. S. Kol′tsova, A. V. Lyubimov, V. S. Marevtsev, and M. I. Cherkashin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2259 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 2032 (Engl. Transl.)].
6. V. G. Luchina, I. Yu. Sychev, A. I. Shienok, N. L. Zaichenko, and V. S. Marevtsev, *J. Photochem. Photobiol., A: Chemistry,* 1996, **93**, 173.
7. N. L. Zaichenko, A. V. Lyubimov, V. S. Marevtsev, and M. I. Cherkashin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1040 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 941 (Engl. Transl.)].
8. R. C. Bertelson, in *Photochromism. Techniques of Chemistry*, Vol. **3**, Ed. G. H. Brown, Wiley-Interscience, New York, 1971, 733.
9. A. N. Terenin, *Fotonika molekul krasitelei* [*Photonics of Dye Molecules*], Nauka, Leningrad, 1967, 616 pp. (in Russian).
10. O. V. Sverdlova, *Elektronnye spektry v organicheskoi khimii* [*Electronic Spectra in Organic Chemistry*], Khimiya, Leningrad, 1985, 248 pp. (in Russian).
11. I. M. Kolthoff, *Anal. Chem.*, 1974, **46**, 1992.
12. C. Reichardt, *Solvents and Solvent Effects in Organic Synthesis*, *2nd ed.*, Weinheim, FRG, 1988, 534 p.
13. M. I. Martin, *Annales de Physique*, 1962, **7**, 35.

Received December 18, 2000;
in revised form March 2, 2001