Photochromic and electrochromic properties of 1',3',3'-trimethyl-6-piperidino- and -morpholinospiro[indoline-2',3-3*H*-naphtho[2,1-*b*][1,4]-oxazines]

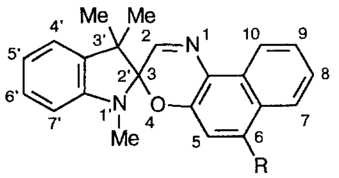
A. E. Kozlovskaya,[a] *V. G. Luchina,*[a] *I. Yu. Sychev,*[a] *and V. S. Marevtsev*[b]*

[a]*Department of the Institute of Solid State Physics and Semiconductors, Academy of Sciences of Belarus',*
210000 Vitebsk, Belarus'
[b]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 938 2156

Electrochromic properties of 1',3',3'-trimethyl-6-piperidino- and -morpholinospiro[indoline-2',3-3*H*-naphtho[2,1-*b*][1,4]-oxazines] resulting from their ionization and the formation of intermediate products were studied. The characteristic features of the photochromic behavior of these compounds are positive solvatochromism for absorption spectra of a colored form and an increase in the rate constant for thermobleaching with increasing solvent polarity.

Key words: electrochromism; photochromism; spirooxazines.

The molecular structure of new, recently obtained photochromic compounds, spironaphthooxazines (SNO),[1] is similar to that of the well-known photochromic indolinospiropyrans (ISP). The latter possess electrochromic properties[2] in solutions of electrolytes when they are excited by an external electric field, *i.e.*, their absorption spectra in the visible region change reversibly due to electrochemical redox reactions. We found that SNO molecules with piperidine (**1**) or morpholine (**2**) substituents in the naphthooxazine fragment also manifest electrochromic properties. In this work, the main photochromic and electrochromic properties of these molecules are described.



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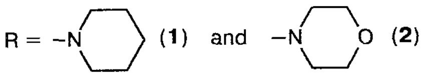

In addition, we studied the electrochromic properties of spironaphthooxazines with the electron-acceptor substituents (R = NO_2, Br) and spiroanthro- and bis-spiroanthrooxazines whose synthesis, structure, and photochromic properties have been studied previously.[3,4]

Experimental

Compounds **1** and **2** were synthesized according to the procedure described previously[5] and purified by recrystallization. All experiments were performed at room temperature. Aprotic solvents (DMF, heptane, and toluene without preliminary purification) and lithium perchlorate (0.1 *M*) as a background electrolyte were used in the studies of the electrochromic properties. Photochromic properties were studied using the same solvents and ethanol ("spectroscopically pure"). The concentration of the compounds studied was maintained in the range 10^{-2}—10^{-3} mol L^{-1}. The prepared composition was cast between two glass plates, on the surface of which transparent conducting coverings of tin dioxide with a resistance of ~50 Ohm per square were applied as electrodes. The width of the gap between the plates was 0.4 mm, and the difference in potentials at the electrodes varied from 2 to 4 V. The photochromic properties of SNO were studied in rectangular quartz cuvettes 1 cm in width. The photocoloring of the solutions was performed by irradiation with a DRSh-1000 mercury lamp through a combination of UFS-1 and NS-1 light filters. The quantum intensity of the photoactivating irradiation was $3 \cdot 10^{-5}$ Einstein (s L)$^{-1}$.

Results and Discussion

Of the compounds studied, only SNO **1** and **2** possess electrochromic properties. When the potential difference $U = 3 \div 4$ V is applied to the electrodes, their solutions in the electrolyte manifest an intense color at the anode. The color disappears gradually when the

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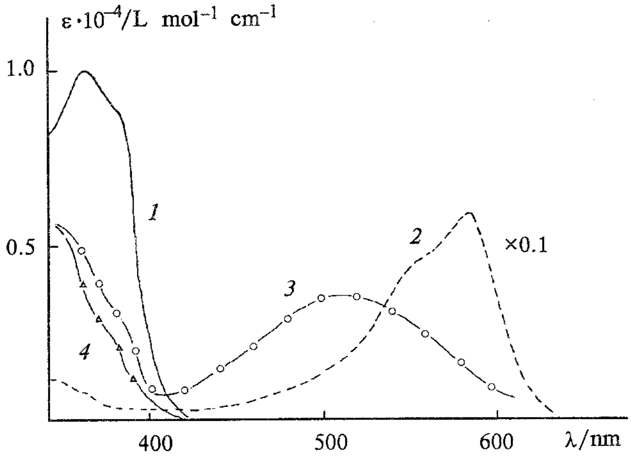

Fig. 1. Absorption spectra of SNO in DMF (*1, 2*) and in the DMF—0.1 *M* $LiClO_4$ system (*1, 3, 4*): (*1*) initial state; (*2*) UV-induced colored state; (*3*) electric field-induced colored state; (*4*) after removal of the electric field.

Table 1. Photochromic characteristics of SNO

Solvent	λ^{B}_{max}/nm	$K_T^{ph}\cdot10^3/s^{-1}$
Heptane	535	50
Toluene	560	114
DMF	580	414
DMF—$LiClO_4$	588	1150
Ethanol	600	1150

voltage is switched off. This process can be performed repeatedly. No electroinduced change in the absorption spectrum was registered under these conditions for the other compounds, although all of them are good photochromes.

The absorption spectra of the solutions of **1** in the initial, photo-, and electrochromic states are presented in Fig. 1. The long-wave absorption band of **1** in DMF in the initial state is observed in the UV-region with λ_{max} = 365 nm. The position and shape of this band are unchanged when 0.1 *M* lithium perchlorate is added to the solution as the background electrolyte.

Compound **1** possesses pronounced photochromic properties, *i.e.*, it is transformed under UV-irradiation from the initial form (**A**) to the colored form (**B**), which becomes decolored with the rate constant K_T^{ph} under dark conditions. Increasing the solvent polarity results in a bathochromic shift of the absorption maximum of form **B** (λ^{B}_{max}) and in a simultaneous increase in K_T^{ph} (Table 1). In such solvents as DMF—$LiClO_4$ and EtOH, K_T^{ph} is so high (because of which, the photo-steady-state optical density does not exceed 0.02 in these media) that the values listed in Table 1 only give the order of magnitude. Compound **2** behaves similarly and therefore will not be further discussed. It should be mentioned that the absorption spectrum of form **A** is completely recovered after dark decoloration of the photoinduced form **B**.

The behavior of SNO **1** differs somewhat in the electrochromic process. Before the application of voltage, the absorption spectrum of the initial form in the DMF—$LiClO_4$ system coincides completely with the spectrum of form **A** in other solvents, while the electroinduced coloring results in the appearance of a new colored form **C** (see Fig. 1, curve *3*), whose spectrum does not correspond to form **B**. In addition, form **C** becomes decolored after removal of the voltage, however, the rate constant of this process K_T^{e} = 0.01 s^{-1} is about 40 times less than K_T^{ph}. The absorption spectrum of the colorless solution (after decoloration of form **C**) does not coincide with that of the initial form **A** (see Fig. 1, curve *4*). This suggests that a new form **D** is formed as a result of the electrochromic cycle. Multiple application and removal of the electric voltage show that only forms **D** and **C** participate in subsequent electrochromic transformations.

The differences between the spectral and kinetic characteristics of photochromic reactions and those of electrochromic reactions may indicate that despite the qualitative similarity of the processes of photo- and electrocoloring, the corresponding mechanisms of the formation of the colored forms are essentially different. The results obtained allow us to state that, like for all of spironaphthooxazines studied previously, the photochromic transition of compound **1** to the colored state is caused by the dissociation of the C—O bond in the naphthooxazine fragment of the molecule to form the planar structure **B** (see Ref. 1), which absorbs in the visible spectral region.

The following considerations can be applied to the electrochromic behavior of **1**. First, we used aprotic solvents in all of the experiments, which excludes electrochemical protonation reactions from consideration. Second, the coloring appears directly at the anode of the electrochemical cell, therefore, the formation of the colored form **C** seems to be caused by the oxidation of the original structure **1**. Third, of all of the SNO studied only **1** and **2** possess electrochromic properties, which most likely reflects the participation of the lone electron pair of the N atom of the substituent in this process.

The available data do not allow us to state unambiguously that the spiro-bond dissociates after oxidation to form a planar structure as has been previously suggested[2] for ISP. More detailed studies are necessary to establish the nature of forms **D** and **C**. The experiments performed have shown that the photochromic processes are caused by the dissociation of the C—O spiro-bond and the electrochromic processes are caused by the ionization of the SNO molecule.

References

1. 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.)].
2. Jpn. Pat. 60-262883, 1985.
3. V. G. Luchina, V. S. Marevtsev, I. Yu. Sychev, T. Ya. Vlasenko, Yu. D. Khamchukov, and M. I. Cherkashin, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 93 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 72 (Engl. Transl.)].
4. V. G. Luchina, I. Yu. Sychev, V. S. Marevtsev, T. Ya. Vlasenko, Yu. D. Khamchukov, and M. I. Cherkashin, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2718 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 2152 (Engl. Transl.)].
5. Eur. Pat. 0245020, 1987.

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