Photochromism of 1',3',3'-trimethyl-6-piperidinospiro[indoline-2',3-3*H*-naphth[2,1-*b*][1,4]-oxazine]

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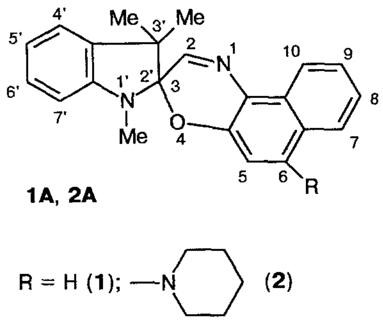
The effect of the piperidine substituent on the spectral and photochromic properties of spiro(indoline-naphthoxazines) (SINO) in different solvents is studied. The introduction of this substituent into the naphthoxazine fragment of SINO results in the appearance of fluorescence of the initial form **A** of SINO at low temperatures. This fluorescence gradually disappears as the temperature increases. The temperature and concentration dependences of the spectral parameters of photoinduced form **B** of SINO make it possible to assume that **B** molecules aggregate in non-polar solvents. In all solvents studied, form **B**, unlike the photoinduced form of the non-substituted spiro naphthoxazine, is stabilized as a bipolar ion with a positive charge on the nitrogen atom of the piperidine substituent. The increase in the rate of thermal decolorization as the medium polarity increases is explained.

Key words: photochromism; spiro oxazines; luminescence.

This work continues the study of the photochromic properties of spiro oxazines,[1—3] and is devoted to studying 1',3',3'-trimethyl-6-piperidinospiro[indoline-2',3-3*H*-naphth[2,1-*b*][1,4]-oxazine]. Previously,[4,5] the effect of the electron-withdrawing NO_2 group at different positions on the photochromic properties of spiro(indoline-naphthoxazines) (SINO) has been studied. In this work, SINO with an electron-donating substituent in the naphthoxazine fragment is studied.

A comparison of the experimental data obtained for this compound and for unsubstituted SINO makes it possible to follow the effect of the piperidine substituent on the spectral and photochromic properties. The structural formulas of the compounds studied (**1, 2**) are presented below.



1A, 2A

Experimental

Compounds **1** and **2** were synthesized and purified by the procedures described previously.[6,7] Ethanol, acetonitrile, DMF, acetone, toluene, butyl acetate, heptane, and petroleum ether purified by the standard procedures were used as solvents. All spectral and photochemical measurements were carried out for optically thin layers in thermostated rectangular quartz cells in the installation and by the procedures described previously.[5] The concentrations of **1** and **2** were varied from 10^{-6} to 10^{-4} *M*. A DRSh-1000 mercury lamp was the source of the photoactivating irradiation in the photochemical studies. The light intensity at the activation wavelength (365 nm) was $3 \cdot 10^{-5}$ Einstein s^{-1} L^{-1}.

Results and Discussion

Compounds **2** and **1** (see Refs. 6 and 8) have pronounced photochromic properties, *i.e.*, the initial form **A** of compound **2** transforms under the action of ultraviolet light into colored form **B**, which returns in the dark to colorless state **A**. The $\mathbf{A} \xrightarrow{h\nu} \mathbf{B}$ transition is related to the dissociation of the spiro C—O bond and to *cis—trans*-isomerization, which result in form **B** with a planar configuration that intensely absorbs light in the visible spectral range.

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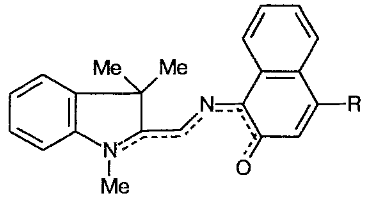


1B, 2B

The presence of the electron-donating substituent in **2** results in the substantial differences in the photochromic parameters of **1** and **2**.

In all of the solvents studied, the absorption spectrum of initial form **2A** lies in a longer-wave range than that of **1A** (Fig. 1), which is probably due not only to the evident bathochromic shift under the effect of the electron-donating substituent,[9,10] but also to the possible appearance of new electronic $n\pi^*$-transitions in **2A** (that are absent in **1A**). This assumption is indirectly confirmed by the fact that molecules **2A** at 77 K are fluorescent in all solvents studied (see Fig. 1), while no fluorescence is observed for **1A** at any temperature.[5,6] The fluorescence observed belongs to molecules **2A**, which is confirmed by the decrease in its intensity during photocolorization and the appearance of the same bands in the excitation spectrum as in the absorption spectrum of **2A**. Some of the differences between the latter two spectra are probably related to the dependence of the quantum yield of the photocolorization on the excitation wavelength. No phosphorescence of **2A** is observed.

It should be mentioned that the shape of the absorption spectrum of **2A** is virtually independent of the concentration and polarity of the medium, while the fluorescence spectra in non-polar heptane and petroleum ether change substantially with concentration (see Fig. 1). This dependence is absent in polar solvents (DMF, EtOH). In addition, the fluorescence intensity gradually decreases as the temperature increases from 77 K and drops to zero when any solvent transforms into the liquid state. The similar effect previously found for spiro anthroxazines (SAO)[2,3] has been explained by the fact that SAO molecules are luminescent only in aggregated states, most probable of which are dimers, whose anthroxazine fragments are arranged under one another along their long axis. However, there is a substantial difference: SAO have luminescence in non-polar solvents even at 300 K, while bis-SAO[2] are luminescent at 300 K in polar solvents as well. Therefore, taking into account that **1A** has no luminescence even at 77 K and the piperidine substituent in **2A** prevents the formation of similar SAO dimers, we believe that the disappearance of the fluorescence of **2A** with temperature is related to the non-radiative internal conversion of the excited state $A^* \rightsquigarrow A$, which is absent in a glass-like or crystalline solvent at low temperatures.[11] Thus, in polar media **2A** exists in the monomeric form even at low temperatures, while aggregation takes place in non-polar ("bad") solvents, which is manifested in the change in the fluorescence spectrum when the concentration is varied.

The results of studying the effect of temperature on the absorption spectra of **2B** in heptane, DMF, and EtOH are presented in Fig. 2. The temperature range of the change depends on the solvent. These ranges are 77 to 300 K for EtOH, which vitrifies at 77 K, and from the melting point to 300 K for crystallizing DMF and heptane. The samples were photocolored by two methods. In the first case, the solutions were irradiated at a low temperature until the maximum value of the optical density in the absorption band range of **2B** was reached

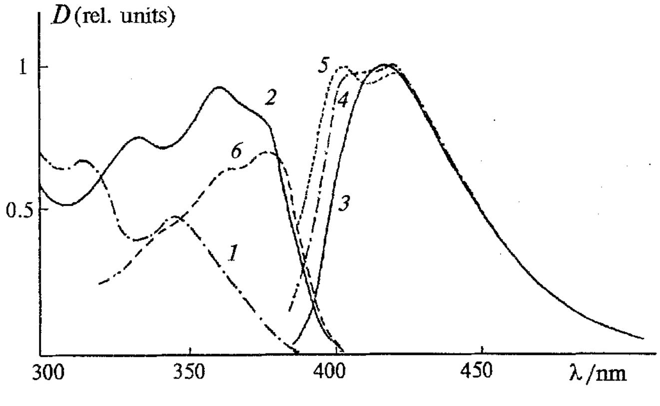


Fig. 1. Spectra of absorption (*1, 2*), luminescence (*3—5*), and luminescence excitation (*6*) for molecules of **1A** (*1*) and **2A** (*2—6*) in heptane at 300 K (*1, 2*) and 77 K (*3—6*). Concentration of **2A**: 10^{-4} (*3*), 10^{-5} (*4*), and 10^{-6} (*5*) *M*.

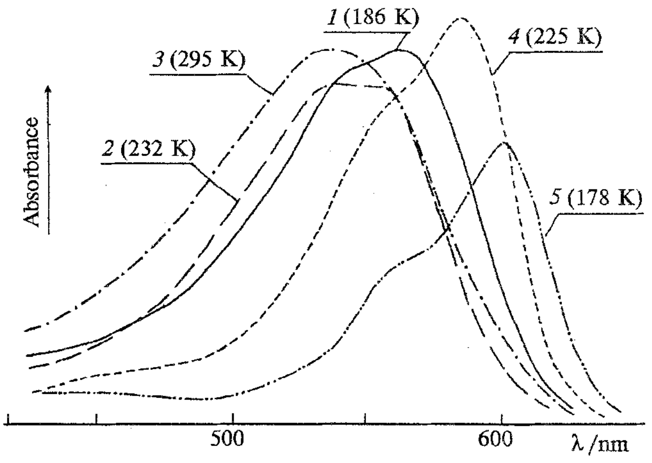


Fig. 2. Absorption spectra of photoinduced form **2B** in heptane (*1—3*), DMF (*4*), and EtOH (*5*). Recording temperature is given in parentheses.

Table 1. Photochromic parameters for compounds **1** and **2** in different solvents

Solvent	**1**			**2**			$E_T{}^c$/ kcal mol^{-1}	ε^c
	ν_B/cm^{-1a}	E_a/ kcal mol^{-1}	$k_T \cdot 10$ /s^{-1b}	ν_B/cm^{-1a}	E_a/ kcal mol^{-1}	$k_T \cdot 10$ /s^{-1b}		
EtOH	16400	20.6	6.1	16600	13.9	19.1	51.9	24.3
Acetonitrile	—	—	—	17120	—	7.5	46.0	37.5
DMF	16530	15.8	10.8	17240	11.9	3.1	43.8	36.7
Acetone	16780	—	9.9	17360	—	3.7	42.2	20.7
Toluene	16890	—	2.8	17860	—	0.7	33.9	2.4
Butyl acetate	17240	—	5.5	18020	—	0.6	—	5.0
Heptane	18020	10.7	1.6	18690	4.2	0.4	30.9	1.9

$^a T = 300$ K. $^b T = 290$ K. ^{c} See Ref. 14. ^{d} The results obtained agree well with the literature data.[17]

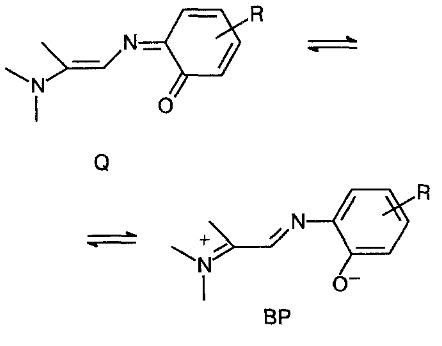
and the spectrum transformation was followed as the temperature increased gradually. In the second case, the freshly prepared solutions were cooled to the specified temperature, then colored until the photostationary state was achieved, and the absorption spectrum was recorded at constant UV irradiation. It was established that the spectral parameters of **2B** at a given temperature are independent of the method of photoinitiation, and only the absorption spectra of the solutions of **2** in heptane change with temperature. For example, at 186 K the spectrum of **2B** consists of two bands with maxima at 560 and 535 nm, but the band at 560 nm gradually disappears as the temperature increases. Since it is impossible to record absorption spectra in heptane below the melting point, the similar measurements were performed for solutions of **2** in petroleum ether, which vitrifies at low temperatures. The long-wave band disappears in the absorption spectrum of **2B** in the range from 77 to 300 K in petroleum ether and heptane. The relative intensity of the long-wave band increases with concentration and the effect of its disappearance with temperature becomes more pronounced.

It is known that absorption spectra of photoinduced forms of indolinospiropyrans (ISP) are temperature-dependent, which is related to the existence of different stereoisomers of form **B**. These stereoisomers have different spectra and are in an equilibrium that depends on the temperature and properties of the surroundings.[12,13] Despite the fact that the transformation of the absorption spectra of **2B** with temperature in non-polar solvents is quantitatively similar to the temperature changes in absorption for ISP, several factors do not allow one to relate this phenomenon to the mutual transformations of stereoisomers of **2B**. First, as mentioned above, the absorption spectrum of **2B** in polar EtOH and DMF is temperature-independent, and it is known[13] that a mixture of ISP stereoisomers can be obtained most easily in these polar solvents and, hence, the temperature dependence of the absorption spectra is more pronounced in these media. Second, if the temperature changes in the absorption spectra of **2B** were caused by different stereoisomers, the relative intensities of the bands in the spectrum at a certain temperature would remain constant as the total concentration of **2** increased. However, for **2** in heptane and petroleum ether, the relative intensity of the band at 560 nm in the low-temperature absorption spectrum of **2B** increases as the concentration increases. Thus, the temperature and concentration dependences of the spectral parameters of **2B** studied make it possible to assume that molecules of **2B** form aggregates in non-polar solvents.

For **1B** and **2B**, a change in the solvent polarity results in a bathochromic shift of the absorption spectrum (Table 1), and the position of the long-wave maximum (ν_B) for both compounds depends on a solvent parameter such as the Dimroth polarity, E_T, used for many dyes.[14] Two facts attracted our attention. First, by analogy with form **A**, it could be expected that the electron-donating substituent in **2B** would also result in the long-wave shift of ν_B compared to **1B**. However, as can be seen from Table 1, in all solvents used ν_{2B} is in a shorter-wave range than ν_{1B}. Second, the absolute shift of ν_{2B} on going from non-polar heptane to polar EtOH is greater than the shift of ν_{1B} (2030 and 1620 cm^{-1}, respectively).

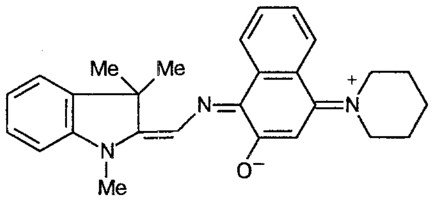
These distinctions in the solvatochromic behavior of **2B** and **1B** are probably due to the differences in their structures.

It is known[15] that the colored forms of photochromic spiro compounds exist as the mesomeric equilibrium between the quinoid (Q) and bipolar (BP) structures.



It has previously been shown[16] that **1B** exists as the Q-form in non-polar solvents and the contribution of the BP-structure becomes noticeable as the polarity of the medium increases. The assumption that the same is true for **2B** is disproved by the fact that $\nu_{2B} > \nu_{1B}$ in all solvents, because the piperidine substituent acts as an electron donor in both structures (Q and BP), which, for initial form **A**, should result in the inverse correlation between ν_{2B} and ν_{1B} (see Refs. 9 and 10).

To explain this fact, we assume that **2B** in all solvents is stabilized as bipolar form BPA, unlike BP.


BPA

It is noteworthy that a similar structure can also be formed for other SINO, if they have a secondary amine as a substituent at positions 6, 7, or 9 of the naphthoxazine fragment. In terms of the model of linear oscillators,[9] whose validity for the colored form of ISP has been previously shown,[12] the long-wave band in the absorption spectrum of a dye is caused by the charge oscillation along the chain of conjugated bonds between an auxochrome and an antiauxochrome and the larger the shift to the red range, the longer this chain. A comparison of structures BP and BPA shows that when both structures have the same auxochrome and antiauxochrome, the BPA molecule should be characterized by absorption in a shorter-wave range, which is observed experimentally.

In addition, the spectrum of bipolar form **2B** should be more sensitive to the polarity of the medium than form Q of compound **1B**, which explains why the ν_{2B} shift is larger than ν_{1B} on going from heptane to EtOH. The positive solvatochromism of **1B** and **2B** is related to the fact that the electron-excited states of these molecules are more polar than the ground states. It is likely that the electron-excited states of both compounds have BP structures.

It is reasonable to expect that the difference in the structures of **1B** and **2B** affects the kinetic parameters of their dark decolorization as well. In fact, despite the fact that the decolorization of **1B** and **2B** is monoexponential, the absolute values of the rate constants k_T^1 and k_T^2, and activation energies E_a^1 and E_a^2, and their dependences on the polarity of the medium differ significantly (see Table 1). It can be seen that the k_T^1 values are determined not by the solvent polarities E_T, but by their dielectric constants ε. For visual demonstration, the dependence of $\ln k_T$ on $1/\varepsilon$, the most frequently used dependence in studying the effects of solvents on the rate of chemical reactions,[14] is presented in Fig. 3. It is evident that the correlation is quite satisfactory for $\ln k_T^1$, while it is completely absent for $\ln k_T^2$. The value of $\ln k_T^2$ in EtOH drops out of the general dependence, and is probably related to specific intermolecular interactions. Let us note that $\ln k_T$ depends linearly on $(\varepsilon-1)/(2\varepsilon+1)$, whereas this dependence is absent for k_T^2.

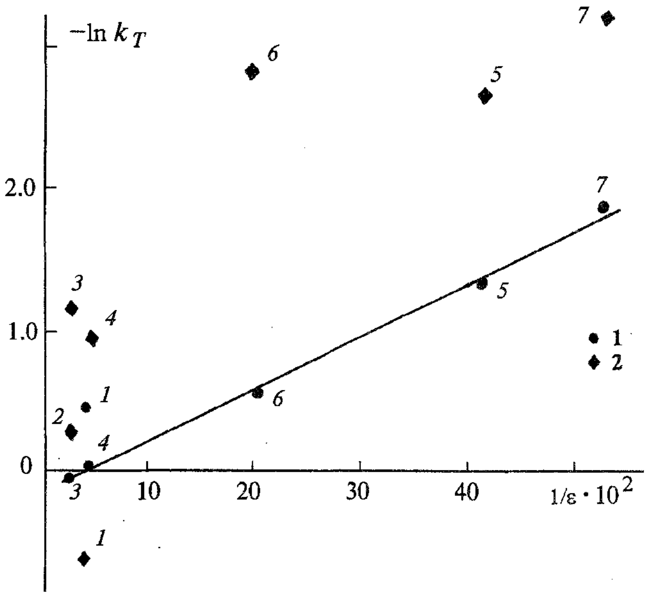
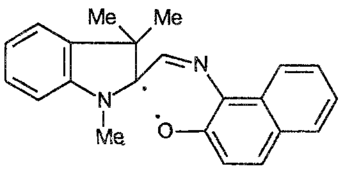
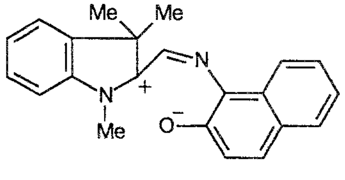


Fig. 3. Dependence of $\ln k_T$ on $1/\varepsilon$ for molecules of **1** and **2** in different solvents: EtOH (*1*); acetonitrile (*2*); DMF (*3*); acetone (*4*); toluene (*5*); butyl acetate (*6*); heptane (*7*).

According to the Hughes—Ingold theory,[14] an increase in the reaction rate as ε of a solvent increases means that the activated complex is more polar than the initial state. If the state of molecules **1B** after the *trans*—*cis*-isomerization and directly before closing of the oxazine cycle is considered to be the activated complex of the reaction of decolorization of molecule **1B**, the structure of this activated complex can be represented by either biradical or bipolar forms.





Since, as shown above, **1B** exists as the non-polar quinoid structure Q, the dependence of k_T^1 on ε should be virtually absent in the case of a non-polar biradical transition state, *i.e.*, it can be assumed that the activated complex is bipolar. This assumption agrees well with the data for ISP obtained previously.[15,18]

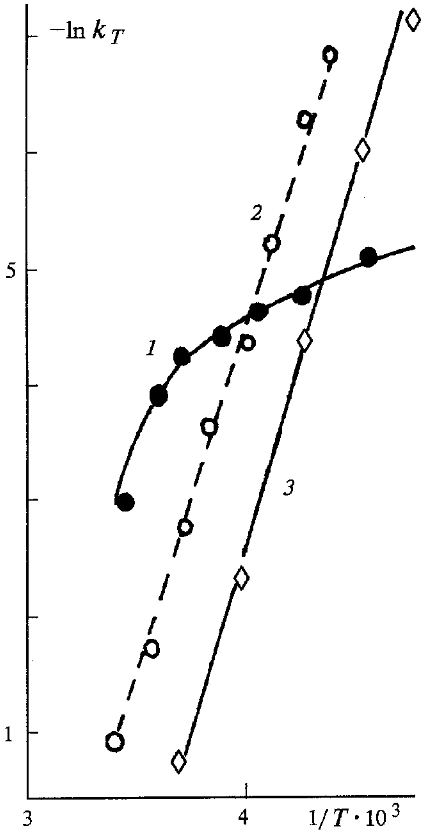


Fig. 4. Arrhenius dependences for the thermal decolorization of molecules of **2B** in different solvents: heptane (*1*), DMF (*2*), EtOH (*3*).

It is likely that the transition state in the decolorization of **2B** is also bipolar, and since the initial state of **2B** is also bipolar (BPA), the dependence of $\ln k_T^2$ on the solvent polarity is complicated.

The difference in the structures of the colored forms of **1B** and **2B** is indirectly confirmed by the values of the activation energies E_a, which differ considerably even in polar media, where the Arrhenius dependence is well fulfilled for both compounds (see Table 1). In non-polar heptane, the dependence of $\ln k_T^2$ on $1/T$ is not linear (Fig. 4), and the value of E_a^2 in this solvent presented in Table 1 is obtained by averaging over the whole temperature range studied. This fact agrees well with the conclusion made above that molecules of **2B** are in an aggregated state in non-polar media and the degree of aggregation depends on temperature.

Thus, the study performed shows that the difference in the photochromic properties of **1** and **2** is related to the nature and position of the piperidine substituent.

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