SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF NITRO-SUBSTITUTED SPIRONAPHTHOOXAZINES

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7-Nitro- and 8-nitroderivatives of 1',3',3'-trimethylspiro[indoline-2',3-3H-naphtho[2,1-b][1,4]oxazine] were synthesized, the last of them being prepared by direct nitration. The introduction of the nitro group stabilizes a bipolar colored form, the highest stability being exhibited when the NO_2 group is the 8-position.

In continuation of our previous investigations [1, 2] of photochromic compounds of the class of spironaphthooxazines (SNO) we synthesized in the present work SNO substituted by a nitro group in the naphthooxazine fragment, and studied the influence of the NO_2 group on their photochromic properties.



 $R^1 = H, R^2 = NO_2(I), R^1 = NO_2, R^2 = H(II).$

Compound (I) was obtained by the usually employed method for the preparation of the SNO condensation of 1,3,3-trimethyl-2-methyleneindoline with 1-nitroso-5-nitro-2-naphthol (III), which in turn was synthesized from 5-nitro-2-naphthol, prepared according to [3]



Compound (II) was obtained by direct nitration according to [4] of 1',3',3'-trimethylspiro[indoline-2',3-3H-naphtho[2,1-b]-[1,4]oxazine] (IV), synthesized according to [5]



It should be noted that this method was used in [4] using four modifications for introducing the NO_2 group into the 5'-position of the indoline fragment of spirobenzopyrans. In the case of SNO, only nitration in concentrated H_2SO_4 leads to (II) in a fair yield, while in the remaining three cases, the photochromic products could not be isolated. Since we could expect that by a direct nitration of (IV) the NO_2 group would be introduced into the 5'-position of the indoline part or into any of the positions of the naphthooxazine fragment, in order to

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Com- pound	CMe₂	NMe	H2	H₄′	H5′	H¢	H7	H2	He	H'	H8	Ħ٩	H ¹⁰
(I)	$\begin{array}{c} 1,34\\ 1,37 \end{array}$	2,78	7,94	7,15	6,87	7,20	6,67	7,34	8,29	_	8,16	7,77	8,98
(11)	$\begin{array}{c}1.34\\1,37\end{array}$	2,79	7,94	7,16	6,88	7,20	6,68	7,29	8,15	8,86	_	8,33	8,73
(IV)	$\begin{array}{c} 1,32\\ 1,35 \end{array}$	2,76	7,83	7,14	6,85	7,17	6,65	7,04	7,78	7 ,82	7,41	7,57	8,5 6

TABLE 1. PMR Spectra of Spironaphthooxazines in Deuterated Acetone (25°C, δ , ppm)

TABLE 2. Spin-Spin Coupling Constants in the Spectra of Spironaphthooxazines, Hz

Com- pound	³J _{4´,5} ′	+J4',8'	⁵ J4',1'	³ J _{5′,8} ′	*J _{5′,7} ′	³ J _{6',7} '	°J _{5,8}	۶J _{7,8}	4J7,9	⁵ J _{7,10}	³J _{8,9}	4J3,16	³ J _{9,10}	⁵ J _{8,10}
(I) (II) (IV)	7,4 7,4 7,2	1,0 1,3 1,3	0,6 0,6 0,6	7,4 7,4 7,2	1,0 1,0 0,9	7,7 7,7 7,7	9,4 9,0 8,8		$\frac{1}{2,4}$	0,8 0,9	7,6 	$\frac{1,0}{1,3}$	8,6 9,2 8,5	$0,8 \\ 0,8 \\ 0,6$

identify a nitrosubstituted SNO, we examined its PMR spectra in acetone- d_6 and for comparison, the PMR spectra of (I) and (IV), the parameters of which are given in Tables 1 and 2. The signals in the spectra were assigned by double resonance experiments, and for (IV), the assignment agrees with the data on the PMR spectra for other solvents [2].

Analysis of the data shows that in the nitration of (IV), only one hydrogen atom in the naphthooxazine part of the molecule of (IV) is substituted (in position 8 or 9). To unequivocally establish the structure of the nitration product, it was necessary to use the literature data. It is known that when the NO_2 group is introduced into the α -position of naphthalene, the signals of the ortho- and peri-protons are maximally shifted to the weak field, and when this group is introduced into the β -position, two ortho-protons are maximally shifted [6].



In accordance with this rule, in the PMR spectrum of (I), the structure of which depends unequivocally on the method of its synthesis, the greatest shift of signals, compared with that of (IV), is observed for H⁶ and H⁸. The overall analysis of the spectra of (IV), (I) and the products of nitration of (IV), with the allowance for the above regularities of the shift of the proton signals during the introduction of an NO₂ group into naphthalene, enables ascribing the structure (II) to this product. This is confirmed by the data for the SSCC (Table 2). It is known that in monosubstituted benzenes, the increase in electronegativity of a substituent X leads to an increase in ${}^{3}J_{2,3}$ [7, 8]. Thus, exchange of NO₂ for H¹ as X increases the ${}^{3}J_{2,3}$ from 7.54 to 8.36 Hz, with practically no influence on ${}^{3}J_{3,4}$. In complete conformity with this, ${}^{3}J_{8,9}$ in (I) has a higher value than in (IV), while the value of ${}^{3}J_{9,10}$ in (II) exceeds that in (IV).

Compounds (I) and (II) in solutions have photochromic properties, i.e., by the action of the UV light they undergo transition from the initial colorless state A into a colored form B, and after the cessation of irradiation become thermally decolorized according to first order kinetics. Thus, in contrast to unsubstituted SNO (IV), which becomes photocolorized in solid matrices only [1, 9], or in solutions at low temperatures [5], compounds (I) and (II) display photochromic properties in liquid solutions at 25°C. However, together with this general property of nitro-substituted SNO, there are substantial differences between (I) and (II), due to the position of the NO_2 group in the naphthooxazine fragment. Figure 1



Fig. 1. Absorption spectra of the initial forms of SNO (I) (1) and (II) (2) and long-wave absorption bands of their colored forms (3, 4) in ethanol at 25°C.

TABLE 3. Photochromic Properties of Nitro-Substituted Spironaphthooxazines at $25^{\circ}C$

Compound		K, sec ⁻¹		λ_{max}^{B} , nm				
oompound	toluene	acetone	ethano1	toluene	acetone	ethano1		
(I) (II)	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c c} 6.19 \cdot 10^{-2} \\ 2.00 \cdot 10^{-2} \end{array}$	$\begin{vmatrix} 1,37 \cdot 10^{-2} \\ 4,47 \cdot 10^{-3} \end{vmatrix}$	605 621	610 620	615 618		

which gives the absorption spectra of forms (A) of (I) and (II) in ethanol at 25°C shows that their spectral properties differ considerably. To interpret these differences, thorough spectral-luminescent investigations are necessary, which we plan to perform and report in future publications.

The same figure also shows the long-wave absorption bands of forms B of (I) and (II) $(\lambda_{\max}{}^B)$ in ethanol. It can be seen that although these bands are similar to one another in their form, the $\lambda_{\max}{}^B$ for (I) is somewhat lower than $\lambda_{\max}{}^B$ for (II). This difference in $\lambda_{\max}{}^B$ increases still more when the polarity of the solvent decreases, since from the data in Table 3 it follows that for form B of (I) a positive, and for form B of (II) a negative solvatochromism is characteristic. Moreover, the rate constant K of the decoloration in the dark of form B of (I) in all solvents is ~3 times higher than the value of the similar constant of form B of (II).

It has previously been shown [2] that form B of (IV) in a nonpolar solvent represents a quinoid structure, while in a polar solvent a slight shift of the equilibrium is observed to a bipolar form



The considerable slowing down of the decoloration reaction of (I) and (II) in the dark, compared with that of (IV), allowing observation of photochromic properties of nitro-substituted SNO in liquid solutions, is possibly due to the fact that this equilibrium is even further shifted in the direction of the bipolar form. However, the value of this shift is different for (I) and (II), as indicated by difference in the values of K and the difference in the character of the solvatochromic effect. These differences in the photochromic behavior of (I) and (II) can be explained by and large by the fact that the bipolar colored form of (II) is additionally stabilized by resonance (see scheme on following page) which is not possible for form B of (I). Thus, introduction of the NO₂ group into the 8-position of the naphthooxazine part of the SNO results in considerable separation of charges in the



colored form, which, as in the case of conventional spirobenzopyrans [10], is manifested in the stabilization of the colored form and a negative solvatochromic effect. Nitro-substitution at the 7-position also stabilizes the form B, but in this case the influence of the NO_2 group is much lower, as indicated by a more rapid, compared with (II), decoloration in the dark, and by the positive, as in (IV) [1, 5] solvatochromism.

EXPERIMENTAL

The PMR spectra were recorded in $(CD_3)_2CO$ on a Bruker WM-400 spectrometer at 25°C, and the absorption spectra on a Specord UV-VIS spectrophotometer. "Spectrally pure" grade toluene, acetone, as well as ethanol were used as solvents. The irradiation of the samples was carried out by light from a DKSSh-200 lamp through an interferential light filter with a transmittance of 365 nm.

<u>1-Nitroso-5-nitro-2-naphthol (III)</u>. A solution of 6.62 g (0.035 mole) of 5-nitro-2naphthol in 160 ml of 50% AcOH was cooled to -2° C and nitrosylated by a NaNO₂ solution [3.0 g (0.035 mole) in 20 ml of water], maintaining a temperature of -2° C. After 2 h, the brown precipitate was filtered, and dried. Yield, 6 g (79%), mp 133-135°C.

<u>1',3',3'-Trimethyl-7-nitrospiro[indoline-2',3-3H-naphtho[2,1-b][1,4]-oxazine] (I).</u> A solution of 6.0 g (0.027 mole) of (III) in 100 ml of absolute alcohol was purged with argon. A solution of 4.67 g (0.027 mole) of 1,3,3-trimethyl-2-methyleneindoline in 50 ml of absolute alcohol was added at the boiling point, and boiling was continued for 2.5 h. The mixture was cooled and filtered. The brown precipitate was dissolved in benzene and chromatographed on a column with silica gel 40/5 in benzene. The fraction with R_f 0.82 (Silufol, benzene: ether = 8:1) was collected. The solvent was evaporated and crystallized from hexane. Yield, 2.04 g (20%), mp 128-129°C.

<u>1',3',3'-Trimethyl-8-nitrospiro[indoline-2',3-3H-naphtho[2,1-b][1,4]-oxazine] (II).</u> A solution of 9.84 g (0.035 mole) of (IV) in 180 ml of conc. H_2SO_4 was cooled to 0°C, 3.36 g of HNO₃ (d 1.35) was added at the same temperature, the mixture was stirred for 1.5 h, and poured onto 500 g of ice. The mixture was then poured into 0.7 liter of a saturated solution of sodium carbonate containing 150 ml of chloroform. The mixture was extracted with chloroform, and the extract was washed with a sodium carbonate solution and then with water, and dried over Na₂SO₄. The solvent was evaporated and the precipitate was dissolved in a benzene:acetone (10:1) mixture. The solution was passed through a column with silica gel, and a fraction with R_f 0.94 was collected (Silufol, benzene:acetone = 10:1). The solvent was evaporated and the residue was crystallized from an acetone:alcohol = 5:1 mixture. Yield, 3.4 g (29%), mp 234-236°C.

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