# Synthesis of polymerizable photochromic spironaphthoxazines

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Hydrogenation of 8-nitrospironaphthoxazine (**1**) resulted in the corresponding amine (**2**). Acylation of compound **2** yielded the *N*-methacryloyl derivative (**3**). Radical polymerization of the latter resulted in its copolymers with styrene, which possess photochromic properties.

**Key words:** spironaphthoxazine, photochromism; radical polymerization.

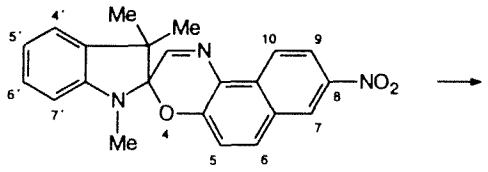
Photochromic spironaphthoxazines[1,2] (SNO) are of great interest as light-sensitive organic compounds with elevated photostability[3] compared to the well-studied spiropyrans.[4] The known methods for the synthesis of SNO are multi-stage and rather labor-consuming. In this connection, the search for direct reactions with SNO to obtain new photochromic compounds promising in their applications is a quite important problem.

Previously we studied the nitration of indoline[1] and benz[*e*]indoline[2] SNO and obtained a series of new photochromic nitro-substituted spironaphthoxazines.[2]

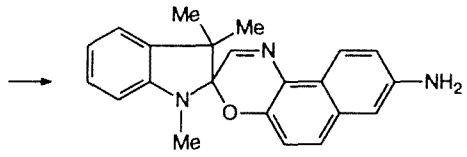
This work deals with the reduction of 8-nitrospironaphthoxazine (**1**)[1] with hydrazine hydrate on Raney Ni according to a modified procedure[5] to obtain the corresponding amine **2** (yield 83 %). Amide **3** was obtained in a 69 % yield by acylation of amine **2** with methacryl chloride[6] (Scheme 1), and its copolymerization with styrene was performed. The photochromic polymers synthesized by us, which contain, as side suspension groups, spironaphthoxazine fragments chemically bonded with the macromolecule, have not hitherto been described.

The structures of products **2** and **3** were confirmed by the data of $^1$H NMR spectroscopy (Table 1). For comparison, Table 1 shows the spectral parameters of SNO **1** (see Ref. 1). Conclusions regarding the structures of

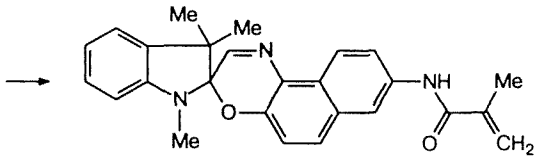
**Scheme 1**




**1**




**2**




**3**

**Table 1.** $^1$H NMR spectra of spironaphthoxazines (acetone-$d_6$, 25 °C)

| Compound | δ | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $CMe_2$ | NMe | H(4′) (d) | H(5′) (t) | H(6′) (t) | H(7′) (d) | H(2) (s) | H(5) (d) | H(6) (d) | H(7) (d) | H(9) (d) | H(10) (d) | Other signals |
| **1** | 1.34, 1.36 | 2.76 | 7.08 | 6.91 | 7.21 | 6.58 | 7.78 | 7.15 | 7.82 | 8.69 | 8.30 | 8.66 | — |
| **2** | 1.30, 1.32 | 2.73 | 7.11 | 6.83 | 7.16 | 6.61 | 7.75 | 6.85 | 7.42 | 6.91 | 7.10 | 8.31 | 4.77 ($NH_2$) |
| **3** | 1.32, 1.35 | 2.75 | 7.13 | 6.85 | 7.17 | 6.64 | 7.85 | 7.02 | 7.70 | 8.36 | 7.80 | 8.48 | 9.24 (NH); 2.04 (Me); 5.50, 5.89 ($CH_2$) |

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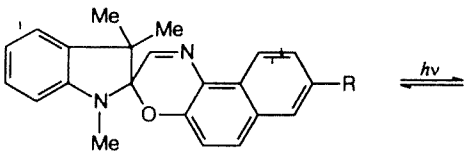
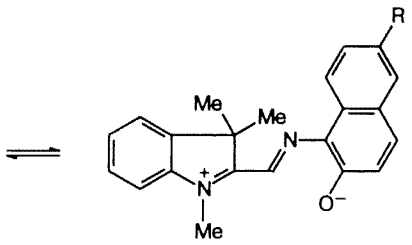
compounds **2** and **3** were made on the basis of literature data concerning changes in chemical shifts depending on the type of substituent.

Compounds **2** and **3** possess markedly pronounced photochromic properties. Thus, when UV-irradiated, they change from the colorless form **A** into the colored planar merocyanine form **B**.




**A**




**B**

The reverse transition **B** → **A** is realized either thermically or under the action of visible light. Figure 1 displays the electronic absorption spectra of SNO **2** and **3** before and after UV irradiation. A comparison of the spectral parameters of compounds **2** and **3** with the data for SNO containing an electron-acceptor group ($NO_2$) at different positions[1,2] and an electron-donor substituent (*N*-piperidyl)[8] at position 6 of the naphthoxazine fragment, as well as with corresponding data for unsubstituted SNO, shows that the electronic absorption spectra of form **A** are defined completely by the donor-acceptor properties of the substituents, whereas the spectra of colored form **B** depend on the structure of its molecule[1,8] as well (on the position and the nature of the substituents). A detailed analysis of these data will be published separately.

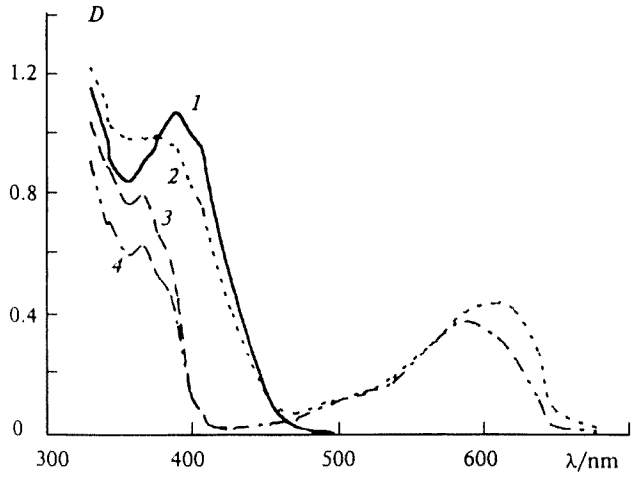



**Fig. 1.** Electronic absorption spectra of compounds **2** (*1*, *2*) and **3** (*3*, *4*) before (*1*, *3*) and after (*2*, *4*) irradiation with UV-light in toluene at 12 °C.

An attempt to synthesize a homopolymer of compound **3** failed. However, using radical polymerization, we succeeded in obtaining its copolymers with styrene (St) with relative contents of starting comonomer **3** equal to 1 and 5 wt. %. The polymerization conditions and the molecular weights of the copolymers obtained are given in Table 2. Both of the copolymers synthesized are photochromic; they become colored under the action of UV light like compounds **2** and **3**. This photocoloring ability confirms the chemical bonding of the photochromic moiety with the macromolecule because it is maintained completely for 8 h after extraction of the powders of the copolymers with methanol. After a similar extraction of a mixture of the powders of the corresponding polymers and compound **3**, the photocoloring ability is reduced by a factor of approximately 10.

As can be seen from the data presented in Table 2, an increase in the relative content of SNO **3** leads to a significant decrease in the average molecular weight. As in the case of polymerizable indolinespiropyrans,[9,10] this seems to be caused by the loss in reactivity of a growing radical when the chain is transfered to the photochromic molecule. Probably, this is the reason why homopolymer **3** is not obtained. Then it would appear natural that only one photochromic molecule is included in the macromolecule of the copolymer, and the reaction results in a mixture of homopolymer St and copolymer St—**3**. However, an alternative situation can take place when several molecules of compound **3** are included in the copolymer. Our further publications will be devoted to the solution of this problem as well as to investigations of the influence of the nature of the comonomers and the polymerization conditions.

The absorption spectra of benzene solutions of compound **3** coincide very closely with those of its copolymers with styrene in the visible area (see Fig. 1). In the dark, a thermal bleaching occurs. When the concentrations of the copolymers are equal to 10 g $L^{-1}$, decolorization proceeds in a monoexponential manner with a rate constant slightly depending on the initial concentration of SNO **3** (0.12 and 0.10 $s^{-1}$ at 12 °C for copolymers St with 1 % and 5 % of starting compound **3**, respectively).

**Table 2.** Copolymerization conditions and average molecular weights of the copolymers

| Monomer | | $M_1 : M_2$ | $M_2$ : AIBN | Solvent | $M_n$ |
|---|---|---|---|---|---|
| $M_1$ | $M_2$ | (mol/mol) | | | |
| St | **3** | 400 : 1 | 0.75 | $C_6H_6$ | 72000 |
| St | **3** | 80 : 1 | 3.75 | $C_6H_6$ | 32000 |
| — | **3** | — | 40 : 1 | $C_6H_6$ | — |

## Experimental

$^1$H NMR spectra were recorded on a Bruker WM-400 spectrometer in acetone-$d_6$ at 25 °C; electronic absorption spectra were recorded with temperature-controlled cells on a Specord UV-Vis spectrophotometer. Specimens were irradiated with the light from a DRSh-1000 high pressure Hg lamp through an interference light filter ($\lambda$ = 365 nm). Determination of the average molecular weights of the copolymers synthesized was performed by measurements of the heat effects of condensation.[11]

**1',3',3'-Trimethyl-8-aminospiro(indoline-2,3'-3*H*-naphtho-[2,1-*b*][1,4]oxazine) (2).** Anhydrous benzene (316 mL), compound **1** (4 g), and Raney nickel (5.5 g) activated with alkali and washed with water and MeOH were placed in a 0.5 L flask. Then a solution of hydrazine hydrate (7.4 mL) in 5 mL of MeOH was added dropwise with intense stirring. The mixture was stirred at 35 °C for 2 h until starting compound **1** disappeared (TLC-monitoring, Silufol, $CHCl_3$). After the catalyst was removed, the filtrate was evaporated to dryness, and the viscous residue was twice recrystallized from a MeOH—$Me_2CO$ (5 : 1) mixture. Product **2** (3.05 g, 83 %) was obtained, m.p. 198—199 °C. Found (%): C, 76.78; H, 6.21; N, 12.34. $C_{22}H_{21}N_3O$. Calculated (%): C, 76.94; H, 6.16; N, 12.24.

**1',3',3'-Trimethyl-8-methacryloylaminospiro(indoline-2,3'-3*H*-naphtho-[2,1-*b*][1,4]oxazine) (3).** Compound **2** (1.2 g, 3.5 mmol) and $Et_3N$ (0.52 mL, 3.8 mmol) in 40 mL of anhydrous benzene were stirred at 35 °C until compound **2** was completely dissolved. Then a solution of methacryl chloride (0.34 mL, 3.5 mmol) in 20 mL of anhydrous benzene was added, and the mixture was stirred at 45 °C for ~2 h until starting compound **2** disappeared completely (TLC-monitoring, Silufol, $CHCl_3$). The precipitate of the salt was separated by filtration, and the filtrate was concentrated to a 1/3 part of the initial volume. An equal amount of hot hexane was added, and the product was crystallized. Compound **3** (0.98 g, 69 %) was obtained, m.p. 190—192 °C.

**Copolymers 3 with styrene.** Monomers taken in the ratio given in Table 2 were dissolved in anhydrous benzene, a corresponding amount of the initiator, 2,2'-azobisisobutyronitrile (AIBN), was added, and the mixture was placed into ampules and degased three times using a high vacuum setup. Then the ampules were sealed and left in a thermostat at 80 °C for 12 h. The contents of the ampules was poured into a tenfold excess of MeOH, and the precipitates were isolated. The copolymers obtained were purified by reprecipitation from a 2 % solution of benzene with a tenfold excess of MeOH and dried *in vacuo*.

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