SYNTHESIS AND PROPERTIES OF PHOTOCHROMIC 6-METHACRYLYLAMINOBENZOTHIAZOLINOSPIROPYRANS*

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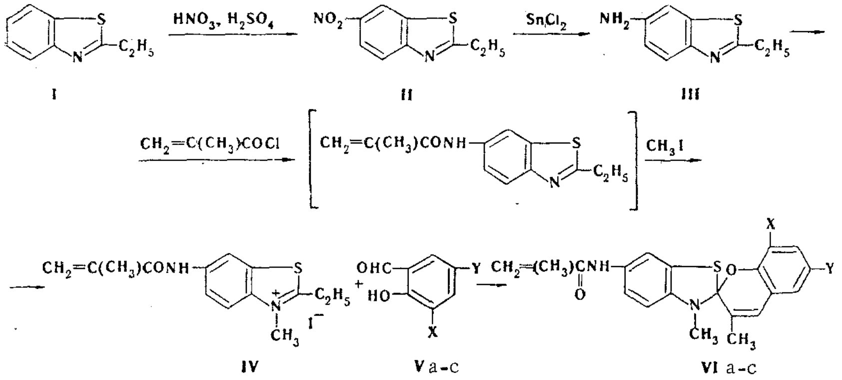
The reaction of 2-ethyl-6-aminobenzothiazole with methacrylyl chloride was used to synthesize the corresponding amide, which was then converted, without isolation, to 2-ethyl-3-methyl-6-methacrylylaminobenzothiazolium iodide. The reaction of the quaternary salt with nitro derivatives of salicylaldehyde leads to benzothiazolinospiropyrans containing a methacrylyl grouping. A copolymer of 3,3'-dimethyl-6-methacrylylamino-6'-nitrospiro-(benzothiazoline-2,2'-[2H-1]benzopyran) with methyl methacrylate was obtained. The photochromic properties of the synthesized benzothiazolinospiropyrans were investigated.

Spiropyrans of the benzothiazoline series, including those containing vinyl groupings, are among the photochromic materials currently under extensive investigation [2, 3]; these compounds seem of interest as monomers for polymerization. It seemed expedient to us to obtain new vinyl monomers of the benzothiazoline series in order to study the photochromic properties of these compounds and of polymers obtained from them.

The benzothiazolinospiropyrans were synthesized via the following scheme:



V, VI a X = H, Y = NO_2; b X = NO_2, Y = H; cX = OCH_3, Y = NO_2

It is known that benzothiazole and its 2-substituted derivatives are nitrated in the 6 position [4-8]. We carried out the nitration of 2-ethylbenzothiazole (I) at various temperatures (0-60°C) and established, by means of gas-chromatographic analysis (with nitrilosiloxane rubber as the stationary phase), that the composition of the nitration products is practically independent of the reaction temperature and that the percentage of 2-ethylnitrobenzothiazole (II) varies over narrow limits from 70 to 80%. Two crystallizations

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of the nitration product from alcohol lead to I with a purity of 99%. The use of other phases – fluorosilicone and polymethylphenylsilicone rubbers – gives similar results.

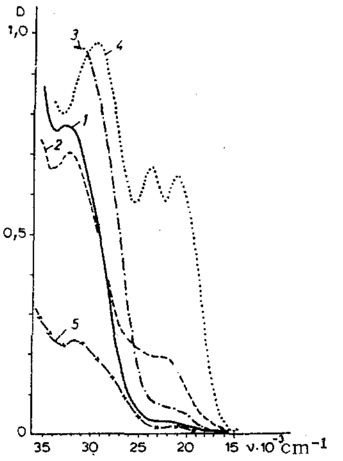

Fig. 1. Absorption spectra of spiropyrans (alcohol, 23°C, L = 0.2 cm): 1) VIa, c $2.18 \cdot 10^{-4}$ M; 2) VIa (after irradiation), c $2.18 \cdot 10^{-4}$ M; 3) VIc, c $2.76 \cdot 10^{-4}$ M; 4) VIc (after irradiation), c $2.60 \cdot 10^{-4}$ M; 5) VIb, c $1.80 \cdot 10^{-4}$ M.

The 2-ethylaminobenzothiazole structure (III) was determined by means of the PMR spectra.* The spectrum of III in the region of phenyl protons is an ABC system with the following parameters: chemical shifts (δ) of 7.58, 6.76, and 7.04 ppm and spin–spin coupling constants (J) of 8.6, 0.4, and 2.2 Hz. The δ and J values found practically coincide with the values obtained for 2-methyl-5(or 6)-aminobenzothiazoles [9]; substitution in the 4 and 7 positions is completely excluded.

Benzothiazolinospiropyrans VIa-c were synthesized by heating quaternary salt IV with 5-nitro- (Va), 3-nitro- (Vb), and 3-methoxy-5-nitrosalicylaldehyde (Vc) in the presence of piperidine.

Copolymer VIIa containing ~1.1 mole % spiropyran links was obtained by copolymerization of spiropyran VIa with methyl methacrylate in benzene in the presence of azobisisobutyronitrile.

Solutions of spiropyrans VIa-c have photochromic properties. When alcohol solutions of spiropyrans VIa, c are irradiated with UV light (303-313 nm) at room temperature, they slowly turn yellow and orange, respectively; the color of the solutions vanishes very slowly when the light source is switched off. Irradiation of the colored alcohol solutions with visible light (546 nm) leads to rapid decolorization of them. The absorption spectra of spiropyrans VIa-c in alcohol solutions before and after irradiation with UV light for 5 min are presented in Fig. 1; the photocoloration and dark-decolorization processes in toluene solutions are accelerated sharply as compared with the processes in alcohol solutions. Brief irradiation of cooled (to −30°) toluene solutions of VIa, c with UV light induces the appearance of a stable color, while prolonged irradiation leads to the formation of a colored precipitate (the solution concentrations were 10^{-4} M). At −30°, the solutions are not decolorized by the action of visible light and have intense fluorescence (fluorescence is not observed at room temperature). An increase in the fluorescence intensity is also detected when the alcohol solutions of the spiropyrans are cooled.

A qualitative comparison of the photochromic properties of spiropyrans VIa, c and spiropyrans of the indoline series [1, 10] reveals a certain similarity between them. For example, the scheme of photochromic transformations $A \underset{KT,\, h\nu}{\overset{h\nu}{\rightleftarrows}} B$ is valid for both indolinospiropyrans and benzothiazolinospiropyrans. The photochromic properties change analogously when the solvent is changed, a decrease in temperature leads to a decrease in the efficiency of the decolorization processes, etc. However, one should note two peculiarities in the behavior of benzothiazolinospiropyrans: 1) the low degree of coloration of the solutions as compared with solutions of indolinospiropyrans of the same concentration under similar irradiation conditions; 2) an increase in the fluorescence intensity of spiropyran solutions on cooling, accompanied by a sharp decrease in the efficiency of the photodecolorization of colored solutions. The first fact is evidence that the photoequilibrium in alcohol solutions of benzothiazolinospiropyrans is shifted to favor uncolored form A to a greater degree than in the case of indolinospiropyrans. It is unlikely that the extinction coefficients of the colored forms for the longest-wave absorption maxima would differ significantly from one another in the case of benzothiazolino- and indolinospiropyrans. The low degree of coloration of the benzothiazolinospiropyran solutions is most probably associated with the fact that the photocoloration of these spiropyrans proceeds with a much lower efficiency than photodecolorization. The rates of these processes are commensurable in the case of indolinospiropyrans.

The increase in the fluorescence intensity and the decrease in the efficiency of photodecolorization as the temperature decreases apparently constitute evidence that the transition of the molecules of colored form B from the singlet excited state to the photochemically active state requires surmounting of the potential barrier.

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The photochromic properties of copolymer VIIa in benzene and toluene solutions are practically the same as the photochromic properties of corresponding solutions of spiropyran VIa.

EXPERIMENTAL

Gas-chromatographic analysis was accomplished with a Tsvet-1 chromatograph (with a katharometer) on a nitrilosiloxane rubber (NSKT, 10%) applied to Chromaton N-AW (the column was 3 m long and 4 mm in diameter, the vaporizer temperature was 250°, the column temperature was 212°, and the carrier-gas (helium) flow rate was 30 cm^3/min). The samples were introduced in benzene solution.

The PMR spectrum of a dimethyl sulfoxide solution was recorded at 24° with a C-60-HL spectrometer with hexamethyldisiloxane (HMDS) as the internal standard. The UV spectra were recorded with a Unicam SP-700 spectrophotometer.

2-Ethyl-6-nitrobenzothiazole (II). This compound was obtained by nitration of 2-ethylbenzothiazole (I) with fuming nitric acid–concentrated sulfuric acid via the method described in [11] and had mp 120-121° (from alcohol) (mp 125-126° [6, 11]).

2-Ethyl-6-aminobenzothiazole (III). This compound was obtained by reduction of thiazole II by the method in [12]. The reaction solution was treated with 10% potassium hydroxide until it was alkaline, and it was then extracted with ether. The ether extracts were dried over magnesium sulfate, and the ether was removed by vacuum distillation. The amine was purified by two methods.

1. A solution of the impure amine in benzene was filtered through a column filled with activity-III-IV aluminum oxide, and the column was eluted with benzene to give 50% of white crystals of amine III with mp 78-79° (from hexane) (mp 72-73° [6, 12]).

2. A 0.4-g sample of the impure amine was separated by preparative thin-layer chromatography on hydrated silicic acid (23 g, 220-by-260 plate) in ether–carbon tetrachloride (1:9) with elution by methanol to give amine III with mp 78-79° in ~60% yield. The purity of the amine was confirmed by GLC.

2-Ethyl-3-methyl-6-methacrylylaminobenzothiazolinium Iodide (IV). A 0.71-g (4 mmole) sample of 2-ethyl-6-aminobenzothiazole was dissolved by heating in 5 ml of absolute benzene, after which 0.4 g (4 mmole) of triethylamine and 0.41 g (4 mmole) of methacrylyl chloride [13] were added successively. A white precipitate formed during the addition. After 12 h, 5 ml of benzene was added to the mixture, and it was heated to 50° to dissolve the bulk of the precipitate. It was then filtered to remove the triethylamine hydrochloride. The heated filtrate was transferred to a glass ampul and washed with 5 ml of benzene, after which 1 g (8 mmole) of methyl iodide was added, and the ampul was sealed and heated at 80° for 24 h. The quaternary salt was removed by filtration and washed successively with benzene and acetone to give 0.76 g (60%) of white crystals of IV with mp 226-227° (dec., from absolute alcohol). Found: C 43.2; H 4.5; N 6.7%. $C_{14}H_{17}IN_2OS$. Calculated: C 43.3; H 4.4; N 7.2%.

3,3'-Dimethyl-6-methacrylylamino-6'-nitrospiro(benzothiazoline-2,2'-[2H-1]benzopyran) (VIa). A 0.32-g (1.9 mmole) sample of 5-nitrosalicylaldehyde and 0.19 ml of piperidine were added to a solution of 0.75 g (1.9 mmole) of impure salt IV in 1.9 ml of absolute methanol, and the mixture was refluxed for ~2 min and evaporated at 50-55° (10 mm). The residue was treated with water until the mass began to solidify, and the solid was dried in a vacuum desiccator. The resulting powder was extracted repeatedly with absolute benzene at 50-60° until an almost colorless extract was obtained. The extracts were evaporated to 5 ml, and the liquid was filtered through a column containing hydrated silicic acid; spiropyran VIa was eluted initially with benzene and then with benzene–ether (95:5) to give 0.44 g (55.5%) of rust-colored crystals with mp 118.5-119.5° (dec., reprecipitated from benzene solution by the addition of hexane) and R_f 0.42.* Found: C 61.6; H 4.7; N 10.1; S 7.8%. $C_{21}H_{19}N_3O_4S$. Calculated: C 61.6; H 4.7; N 10.2; S 7.8%.

3,3'-Dimethyl-6-methacrylylamino-8'-nitrospiro(benzothiazoline-2,2'-[2H-1]benzopyran) (VIb). This compound was similarly obtained as described above from 0.31 g (0.8 mmole) of salt IV and 0.13 g (0.8 mmole) of 3-nitrosalicylaldehyde in 0.8 ml of absolute methanol in the presence of 0.08 ml of piperidine by refluxing for 20 min. The yield of rust-colored crystals of spiropyran VIb with mp 108-109° (dec., reprecipitated from benzene solution by the addition of hexane) and R_f 0.41 was 0.1 g (30%). Found: C 61.4; H 4.7; N 9.8; S 7.7%. $C_{21}H_{19}N_3O_4S$. Calculated: C 61.6; H 4.7; N 10.2; S 7.8%.

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* The R_f values were obtained on glass plates coated with silicic acid in benzene–ether (17:3) (spiropyran VIa) and benzene–ether (13:7) (spiropyrans VIb, c) systems. The chromatograms were developed with iodine vapors.

3,3'-Dimethyl-6-methacrylylamino-8'-methoxy-6'-nitrospiro(benzothiazoline-2,2'-[2H-1]benzopyran) (VIc). This compound was similarly obtained from 0.31 g (0.8 mmole) of salt IV and 0.16 g (0.8 mmole) of Vc in 0.8 ml of methanol in the presence of 0.08 ml of piperidine by refluxing for 15 min. The yield of yellow crystals of spiropyran VIc with mp 177-178° and R_f 0.48 was 0.22 g (75%). Found: C 60.4; H 4.8; N 8.7; S 7.3%. $C_{22}H_{21}N_3O_5S$. Calculated: C 60.2; H 4.8; N 9.5; S 7.3%.

Copolymer of Spiropyran VI and Methyl Methacrylate. A 0.1951-g (0.476 mmole) sample of VIa, 0.0138 g (0.083 mmole) of azobisisobutyronitrile, 1.85 g (18.5 mmole) of methyl methacrylate, and 6 ml of benzene were placed in a glass ampul, and the ampul was degassed, sealed off at 10^{-4} mm, and heated at 65° for 7 h. The polymer was isolated as a light-yellow powder by precipitation with alcohol and was then reprecipitated from benzene solution by the addition of alcohol and dried at 60-70° (10^{-2} mm) to give a product with molecular weight of ~67,600 (determined by viscometry) in ~50% yield. The copolymer contained 1.1 mole % photochromic groupings (determined spectrophotometrically, ε_{CH} $1.7 \cdot 10^4$ liter/mole · cm, λ 330 nm).

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