Photochemistry of benzothiazolylformazanes in solutions

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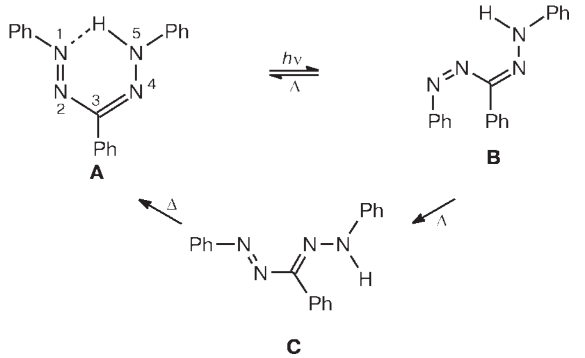
Photochemical transformations of substituted benzothiazolylformazanes were studied by electronic spectroscopy under conditions of steady-state photolysis. The phototransformations were established to be photoreversible *cis—trans*-isomerization, unlike photoirreversible one of triphenylformazane. Electron-donor and electron-acceptor substituents (except for NO_2) in the *para*-position of the phenyl ring of one of the nitrogen atoms retard thermoisomerization.

Key words: photochromism, formazanes, benzothiazolylformazanes, dark isomerization, *cis—trans*-isomerization, quantum yield.

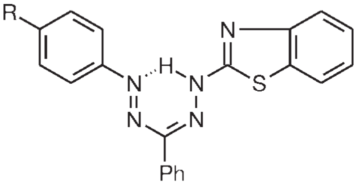
Formazanes ($R^1—N=N—C(R^2)=N—NH—R^3$) contain the mobile π-system, their redox processes, isomerizations, and tautomeric transformations occur easily, and these compounds, especially hetarylformazanes, are characterized by enhanced basicity and acidity. All these properties create prerequisites for search in this series for thermochromic and photosensitive compounds.

The photochromic transformations of formazanes have first been observed for triphenylformazane (TPF).[1] Under the visible light, a solution of its red form was transformed into a solution of the stable yellow form, and in the dark the initial spectrum was recovered. It was assumed that the appearance of the yellow form is caused by the opening of the chelate cycle of the initial structure **A** (Scheme 1) and the formation of the *E* isomer relative to the C=N bond. The color of 1,3,5-triarylformazanes changes reversibly only in nonpolar solvents. In protic and polar aprotic solvents, in the presence of dioxygen, irradiation results in the irreversible decoloration of formazanes due to oxidative destruction.[2] Therefore, toluene was used as a solvent for photochemical studies.

Scheme 1

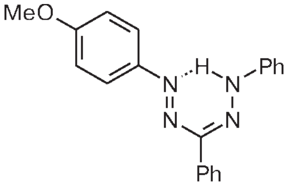


In this work, we present the results of steady-state photolysis studies of the photothermochromic transformations of 1-aryl-5-benzothiazolyl-3-phenylformazanes **1—6** and 1-(4-methoxyphenyl)-3,5-diphenylformazane (**7**), whose rate constant of the dark reaction (*k*´) and activation energy (E_a) are known.[2]



1—6

R = H (**1**), NO_2 (**2**), Cl (**3**), Br (**4**), NMe_2 (**5**), COOMe (**6**)



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Experimental

Formazanes **1—7** were synthesized as described previously.[3] Purity of the synthesized compounds were monitored by TLC.

Absorption spectra were recorded on an Specord M-40 spectrophotometer. Samples were irradiated with the light from a DRSh-1000 mercury lamp using a set of light filters in a standard quartz cell. The duration of irradiation was varied from 1 s to 1 h.

Toluene was treated with H_2SO_4 three times, washed with water, a 10% solution of NaOH, and water again, and dried for several days above sieves 4A. The anhydrous toluene was distilled above sodium. Before experiments, toluene was frozen and defrosted above $LiAlH_4$. The presence or absence of air oxygen in samples had no effect on photochemical transformations under the experimental conditions. The quantum yield of *trans—cis*-isomerization ($\varphi_{t—c}$) was determined relative to stylbene isomerization in EtOH (standard) for which $\varphi_{t—c} = 0.5$ under irradiation with the light with $\lambda = 313$ nm at room temperature. The k' values were estimated from the time of exponential decay of absorbance of the photoproduct under dark conditions.

Results and Discussion

Based on the spectral and X-ray structure studies of TPF,[2] the author showed that the chelate form **A** (see Scheme 1) has the $E^{1,2}Z^{2,3}Z^{3,4}$-configuration of the azohydrazone chain stabilized by the intramolecular hydrogen bond (IMHB). The electronic spectra of TPF contain a long-wave band at $\lambda = 495$ nm from the π—π^*-transition polarized along the long axis of the molecule in the conjugated azohydrazone system including the phenyl fragment bound to the azo group.[4] This band is sensitive to the conformation of the azohydrazone chain. With the chelate ring opening, its position is hypsochromically shifted by 90 nm and the intensity increases.[5] The long-wave band overlaps the low-intensity band from the n—π^*-transition caused by the fragment of the —N= type, which results in the appearance of a shoulder at 546 nm.[4]

The study of TPF photoisomerization is impeded by fast thermal reactions between intermediate isomerization products and a strong influence of traces of acids or bases on the rate of thermal reactions. The study of TPF photochromism in thoroughly purified solvents at low temperatures showed[6] that photoisomerization occurs only at the N=N bond, whereas isomerization at the C=N bond is a thermal reaction. These conclusions were confirmed[7,8] by the Raman spectroscopic data. The results of studying the phototransformations of triarylformazanes (TAF) under flash irradiation indicate[9] that at the first stage, along with *cis—trans*-isomerization at the N=N bond, *s-cis—trans*-isomerization also occurs by the turn at 180° about the simple N(2)—C(3) bond of the formazane chain. It has lately been established that the proton transfer in the excited state can be the primary act in TAF photochromism.[10] The formation of the yellow form of nonsymmetric TAF occurs through the one-stage photoisomerization of the initial chelate form relative to the C=N bond accompanied by the proton transfer in the excited state.[2] The photochromic properties of di-, triarylformazanes, and their derivatives found practical use[11] but the problem concerning the mechanism of phototransformations remains disputable.

Table 1. Spectral and kinetic characteristics of benzothiazolylformazanes **1—6** and triarylformazane **7**

Compound	C^a	λ_{max}/nm		$\varepsilon^b \cdot 10^{-4}$		$k' \cdot 10^4$ /s^{-1}
		I^c	II^d	I^c	II^d	
1	8	484, 609	465	1.2	>2.4	6.7
2	7	560, 595	458	1.2	>3.0	57.0
3	6	490, 625	476	1.8	>4.0	3.2
4	4	490, 625	476	2.1	>5.3	4.6
5	—	434, 500, 529	434, 488	—	—	2.0
6	6	550	455	1.9	>3.8	4.8
7	5	495, 526	404	2.4	>4.8	1.6

[a] Concentration of a toluene solution, $C \cdot 10^5$/mol L^{-1}.
[b] Molar absorption coefficient/L mol^{-1} cm^{-1}.
[c] Initial form.
[d] Photoinduced form.

The spectral and photochemical properties of benzothiazolylformazanes **1—6** are presented in Table 1. It has previously[12] been shown that compound **1** in crystals (according to the X-ray structure analysis data) exists in the $E^{1,2}Z^{2,3}Z^{3,4}$-conformation stabilized by the IMHB (similarly to TPF) with hydrogen localization at the nitrogen atom bound to the heterocycle. In compounds **1—6** the IMHB is weaker than that in TPF, and they exist in a solution as an equilibrium mixture of the $E^{1,2}Z^{2,3}Z^{3,4}$- and $E^{1,2}E^{2,3}Z^{3,4}$-forms with prevailing of the first one.[12] The electronic absorption spectra of freshly prepared solutions of compound **7** in thoroughly purified toluene exhibit two bands at $\lambda_{max} = 495$ and 526 nm (Fig. 1). Under irradiation with the light with $\lambda = 546$ nm, the red form is isomerized to the open yellow form with $\lambda = 404$ nm, and the inverse process occurs in the dark. Such a photochemical process is analogous to the behavior of TPF and associated with the chelate cycle opening and isomeric transformations, which results in the hypsochromic shift of the absorption band of the initial form by 100 nm. The rate constant of the dark reaction (k') is equal to $1.6 \cdot 10^{-4}$ s^{-1} at 18 °C. This compound is characterized by the previously[13] found $k' = 0.78 \cdot 10^{-4}$ s^{-1} and $E_a = 199.31$ kJ mol^{-1} at 45 °C, whereas for TPF k' is equal to $1.27 \cdot 10^{-4}$ and $4.1 \cdot 10^{-4}$ s^{-1} at 21 and 43 °C, respectively.

The replacement of the phenyl fragment in TPF by benzothiazolyl results in the bathochromic shift of the

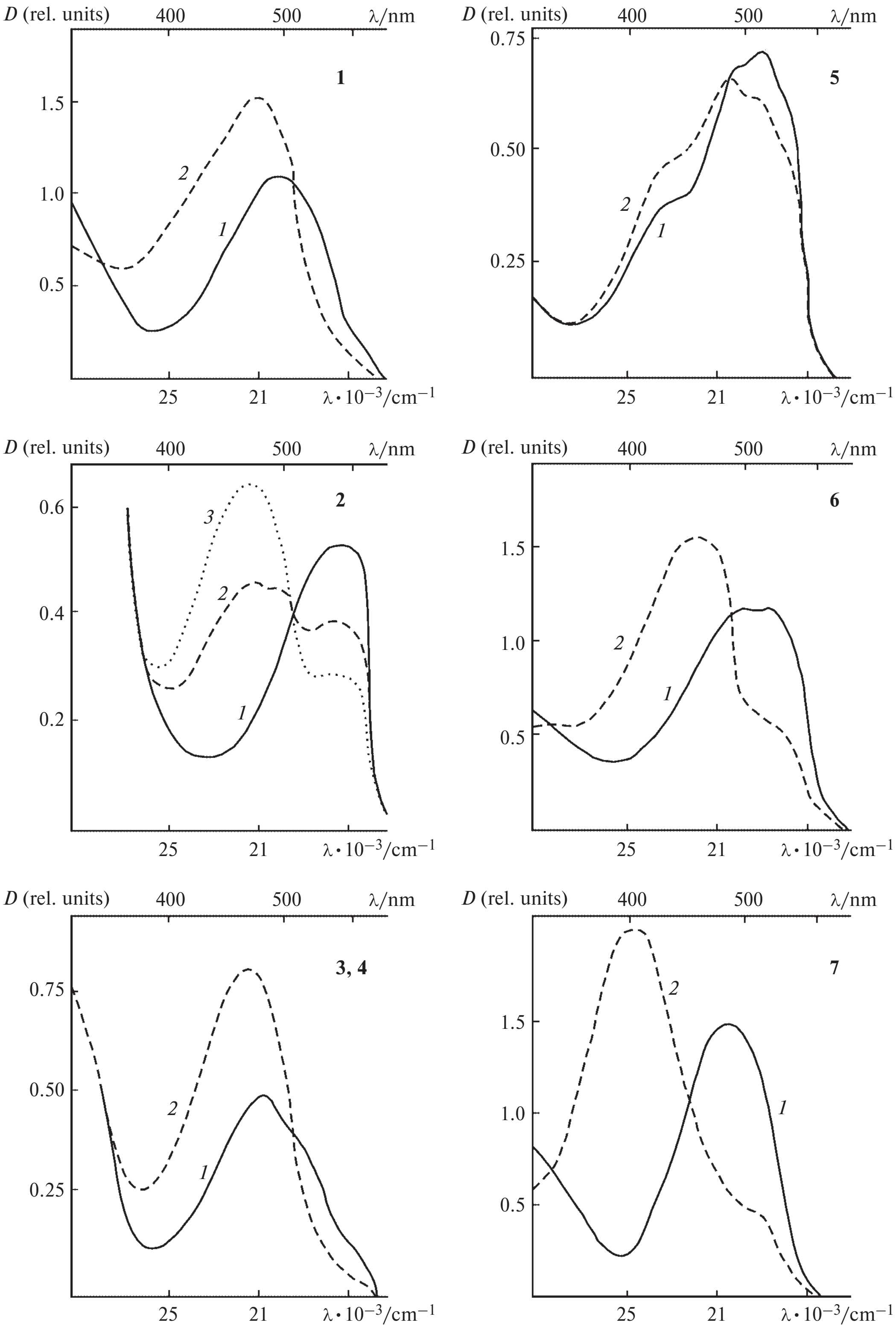


Fig. 1. Absorption spectra of toluene solutions of benzothiazolylformazanes **1—6** and substituted triphenylformazane **7** at 18 °C before (*1*) and after (*2, 3*) irradiation with the light with λ = 578 (**1—6**) and 546 nm (**7**). Irradiation time: 1.5 (**1**), 0.5 (*2*) and 1.0 (*3*) (**2**), 10 (**3** and **4**), 40 (**5**), 8 (**6**), and 0.5 min (**7**).

absorption bands of a non-irradiated toluene solution of compound **1** (see Fig. 1). The electron-donor (NMe_2) and electron-acceptor (especially NO_2 and COOMe) substituents in the *para*-position of the aryl fragment still more enhance this shift (see Fig. 1). When the Cl and Br atoms are introduced as substituents into the benzothiazolylformazane molecule, an insignificant bathochromic shift of absorption bands of the initial form is observed. The spectra of compounds **3** and **4** are indiscernible by the position of the absorption bands before irradiation (see Fig. 1).

Irradiation of toluene solutions of benzothiazolylformazanes **1—6** with the light with λ = 578 nm changes the color from red (compounds **1**, **3**, and **4**) or blue (compounds **2** and **6**) to yellow. The photoinduced form returns to the initial state due to both the dark thermal reaction and irradiation with the light with λ = 436 nm. However, the authors[11,14] reported that a solution of 5-benzothiazolyl-1,3-diphenylformazane (**1**) under steady-state photolysis conditions (PRK-4 and PRK-7 lamps) is photochemically stable but reversible changes in the absorption spectrum were detected under flash photolysis. We believe that this is due to experimental conditions (irradiation of the sample with the non-filtered light and, perhaps, the presence of trace amounts of admixtures in the solvent).

For compound **1** $k' = 6.7 \cdot 10^{-4}$ s^{-1} at 18 °C. In benzothiazolylformazane **1** the symmetric distribution of the electronic density in the formazane chain is distorted compared to TPF, which changes the acid-base properties of the NH and N=N groups and, hence, violates the tautomeric equilibrium. As a result, virtually one tautomer is observed in which a proton is bound to the nitrogen atom at the more withdrawing benzothiazolyl. The intramolecular hydrogen bond is weakened compared to that in TPF. This fixation should increase the localization of the electron density on the N=N and C=N bonds in the chelate form of the initial formazane and, as a consequence, decreases the double bonding of the simple N(2)—C(3) bond, which accelerates thermoisomerization.

The electronic absorption spectrum of a freshly prepared toluene solution of compound **2** contains two bands: at 560 and 595 nm (see Fig. 1). When this solution is irradiated with the visible light with λ = 578 nm, the absorbance in the spectrum of the initial form decreases at 560 and 595 nm and the peak of the yellow form at λ_{max} = 458 nm increases in the spectrum of the initial form. The yellow form decays with $k' = 57 \cdot 10^{-4}$ s^{-1}. The difference in the wavelengths of the initial and photoinduced forms is 100 nm as for compound **7**. In the presence of trace amount of acids in toluene, no photochemical transformations occur under steady-state photolysis because of the substantial acceleration of the thermal reaction in the presence of protons. This is explained, perhaps, by the catalytic influence of protons appeared by the partial dissociation of the forms present in a solution according to the equilibrium $RH \rightleftharpoons R^- + H^+$. This assumption is based on the previously[15] published results, according to which this is precisely the nitro group which affects the acidic properties of hetarylformazanes.

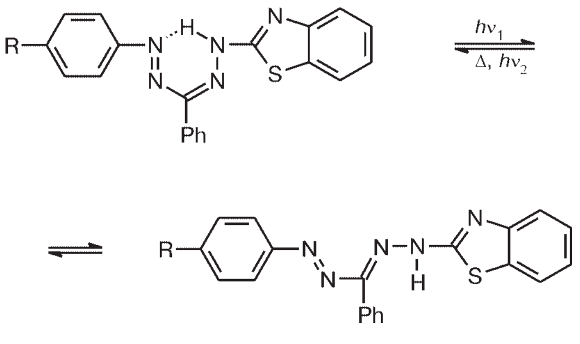
The absorption spectra of the initial and final forms of compound **5** differ slightly (see Fig. 1). The introduction of the electron-donor NMe_2 substituent into the phenyl ring at the nitrogen atom hinders both photochemical and thermal transitions. In compounds with electron-acceptor substituents (Cl, Br, COOMe) these processes also slow down. The introduction of the NO_2 group increases k' by an order of magnitude (see Table 1).

The study of the kinetics of the photo- and thermotransformations of compounds **2**, **6**, and **7** showed isosbestic points in their absorption spectra. This indicates that the lifetimes of the intermediate forms are much shorter than those of the initial compounds and target products. Photothermochromic transformations in compounds **1**, **3**, **4**, and **5** occur with the formation of long-lived intermediates. The quantum yield of transformation of the blue form into the yellow one under the light with λ = 578 nm for compound **6** is $(7\pm1) \cdot 10^{-3}$. For other compounds the superposition of the absorption spectra of the initial and final forms did not allow us to determine the quantum yields of isomerization but we can assume, according to the irradiation time, that the quantum yields are of the same order.

We did not observe photochemical transformations under steady-state conditions for benzothiazolylformazanes with the alkyl substituent at the *meso*-carbon atom.

Thus, benzothiazolylformazanes in liquid toluene solutions under steady-state photolysis undergo reversible photochemical transformations. The main photoreaction is *trans—cis*-isomerization relative to the C=N bond (Scheme 2). The system returns to the initial state under both dark conditions and irradiation.

Scheme 2



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