ISSN 0018-1439, High Energy Chemistry, 2011, Vol. 45, No. 1, pp. 52–56. © Pleiades Publishing, Inc., 2011.
Original Russian Text © L.S. Atabekyan, V.A. Barachevskii, S.A. Melkozerov, G.N. Lipunova, I.G. Perova, I.N. Lipunov, G.I. Sigeikin, 2011, published in Khimiya Vysokikh Energii, 2011, Vol. 45, No. 1, pp. 55–59.

PHOTOCHEMISTRY

# Laser Photolysis Study of 1-Aryl-3-Methyl-5-(Benzothiazole-2-yl) Formazan Phototransformation

**L. S. Atabekyan[a], V. A. Barachevskii[a], S. A. Melkozerov[b], G. N. Lipunova[c], I. G. Perova[b], I. N. Lipunov[b], and G. I. Sigeikin[d]**

[a] *Photochemistry Center, Russian Academy of Sciences, ul. Novatorov 7a, bldg 1, Moscow, 119421 Russia*
[b] *Ural State Forest Engineering University, Sibirskii trakt 37, Yekaterinburg, 620100 Russia*
[c] *Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, ul. Kovalevskoi 22, Yekaterinburg, 620002 Russia*
[d] *Interdepartmental Center of Analytical Research, Presidium of the Russian Academy of Sciences, ul. Vavilova 44, bldg.2, Moscow, 119333 Russia*
*e-mail: barva@photonics.ru*

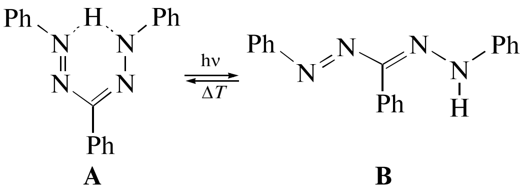
Received June 30, 2010

**Abstract**—Photochromism of 1-aryl-3-methyl-5-(benzothiazole-2-yl)formazans in toluene has been investigated by the laser flash photolysis method. It was established that the photochromic transformations involve the triplet state of the initial chelate form of formazans. The intermediate short-lived products of phototransformation were detected that could be related to one of the conformers or to the tautomers of the formazan molecule.

**DOI:** 10.1134/S0018143911010036

It is known that triarylformazans have photochromic properties in nonpolar solvents, which manifest themselves by reversible color changes of these compounds upon the action of visible irradiation [1–3].

The initial form (A) of these compounds has *EZZ*-configuration stabilized by intramolecular hydrogen bonding. Triphenylformazan and its analogues are the most studied with the phototransformation mechanism involving the photoinduced proton transfer followed by cis–trans isomerization and the formation of the B form (Scheme 1).



**Scheme 1.**

The absorption band of the B form shifts hypsochromically by 90 nm in comparison with the form A absorption band located at 495 nm [4, 5]. Spectral–kinetic investigation of these compounds by the lamp flash photolysis technique revealed that supposedly the form B formation proceeds through the intermediate product resulting from the chelate form after the proton phototransfer due to the *E–Z* isomerization of the –N=N bond [6].

1-Aryl-3-phenyl-5-(benzothiazole-2yl)formazans that exist as *EZZ*-conformers in solution but with a weaker hydrogen bond undergo the similar phototransformations [7].

The results of the laser flash photolysis investigation of the phototransformation of 1-aryl-3-methyl-(benzothiazole-2-yl)formazans FRM 1–FRM 4, investigated earlier by the steady-state excitation technique [8], are presented in this work. The initial

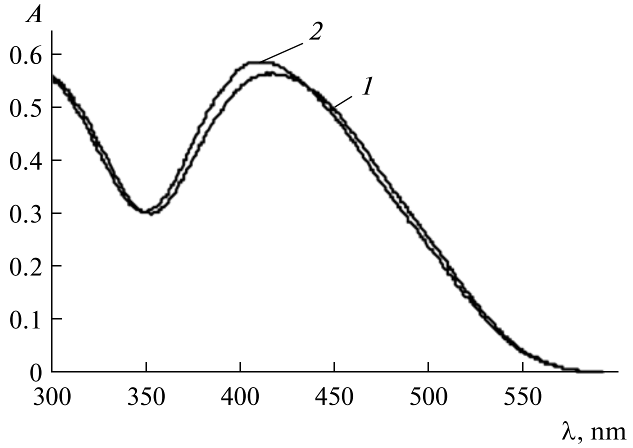


**Fig. 1.** Absorption spectra of FRM 1 formazan in toluene before (*1*) and after (*2*) irradiation ($c = 4 \times 10^{-4}$ mol/l).

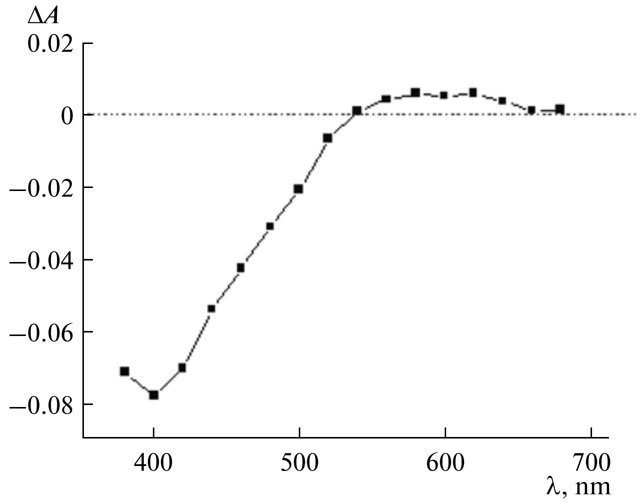
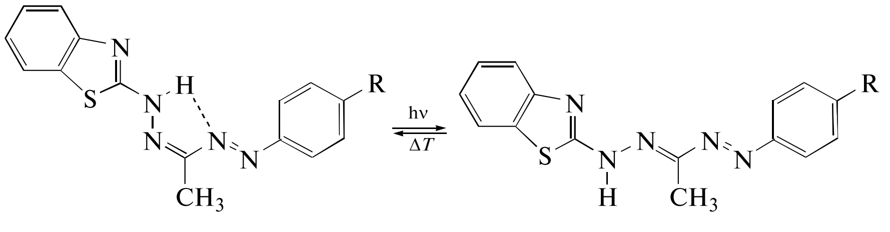


**Fig. 2.** Differential absorption spectrum of the FRM 1 compound in toluene after the excitation with the laser pulse at λ = 354 nm detected after $\tau = 1 \times 10^{-5}$ s after pulse.

form of these compounds is presented as *EEZ*-conformer, and their photochromism is due to the reversible photoinduced isomerization of the C=N bond (Scheme 2).



**A** **B**

FRM 1: R = H; FRM 2: R = $CH_3$; FRM 3: R = Br; FRM 4: R = $NO_2$

**Scheme 2.**

## EXPERIMENTAL

Toluene solutions of the 3-methylbenzothiazolylformazans with different substituents (Scheme 2) were used. The measurements were performed at room temperature in a standard quartz cell 1 × 1 × 4 cm at compound concentrations of $c = (1–2) \times 10^{-5}$ mol/l or in a 1.01-mm quartz cell at concentrations of $c = (1–4) \times 10^{-4}$ mol/l. Bubbling of the solution with nitrogen was used for the removal of air oxygen. Several measurements were performed in the presence of benzophenone.

Absorption spectra of the intermediate products of photoexcitation and kinetics of their transformation were detected using the laser flash photolysis instrument equipped with a neodymium–yttrium Aluminum Garnet laser (Solar, pulse duration of 10 ns, pulse energy 70 mJ, λ = 354 nm). Parametric generator was used for the measurements with the excitation λ = 400 nm that allows to change the wavelength generated by a laser in a wide range. The system for the registration of intermediate products included testing light source—xenon lamp Osram-150 with a power supply block (Applied Biophysics), double monochromator MDR6, emission detector—PMT-84, digital oscilloscope Tektronix 3032B (or oscilloscope on the basis of the Bordo 211 digital board and personal computer).

## RESULTS AND DISCUSSION

Typical absorption spectrum of the initial A form, detected for formazan FRM 1 is presented in Fig. 1.

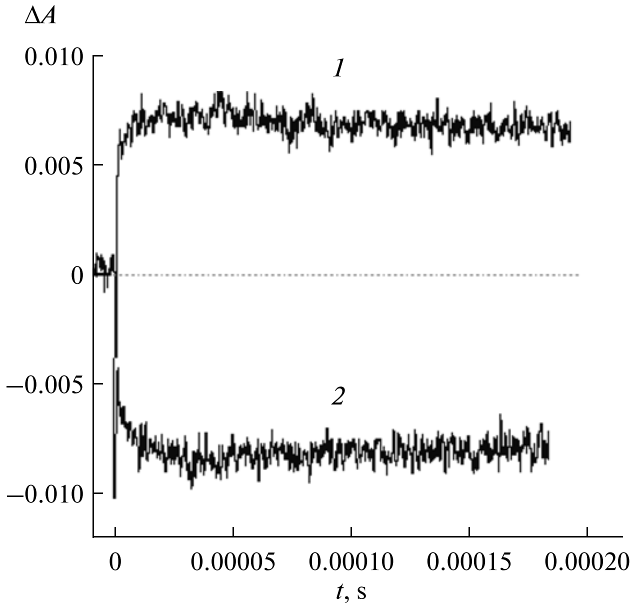


**Fig. 3.** Kinetic curves of the photoinduced optical density changes at 620 nm (*1*) and 520 nm (*2*) for the FRM 1 compound in toluene. $\lambda_{ex} = 354$ nm.

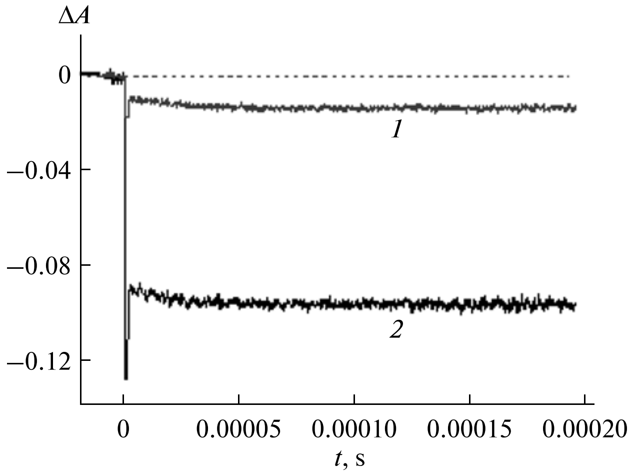


**Fig. 4.** Kinetic curves of the photoinduced optical density decline for the FRM 4 compound in toluene at the wave length $\lambda = 450$ nm for the air-saturated (*1*) and oxygen-free (*2*) solutions. $\lambda_{ex} = 354$ nm.

The similar adsorption spectra were observed for all of the investigated 3-methylbenzothiazolyl formazans.

Absorption band maxima for the initial A form and photoinduced B form are presented in the table.

It should be noted that the absorption band maxima of the photoinduced B form of the 3-methylbenzothiazolylformazans are hypsochromically shifted compared with the absorption bands of the initial chelate form A, similarly to the case of triarylformazans [1–3]. Except that the bands overlap significantly unlike for triarylformazans [8].

A differential spectrum of photoinduced absorption changes in FRM 1 upon laser excitation at 354 nm is presented in Fig. 2.

The similar differential spectrum was observed for the all investigated formazans FRM 1–FRM 4. However, the intensity of the long-wavelength photoinduced absorption band for FRM 2 and FRM 3 was significantly lower than that for FRM 1 and FRM 4.

Absorption band maxima locations for the initial and photoinduced forms of the 3-methylbenzothiazolyl formazans FRM 1–FRM 4 in toluene ($c = 4 \times 10^{-4}$ mol/l)

| Compound | | $\lambda_{max}$, nm | |
|---|---|---|---|
| Designation | R | Form A | Form B |
| FRM 1 | H | 417 | 412 |
| FRM 2 | Br | 423 | 412 |
| FRM 3 | $CH_3$ | 419 | 400 |
| FRM 4 | $NO_2$ | 415 | 402 |

It has been found that the discoloration of the major absorption band ($\lambda_{max} = 417$ nm) occurs upon the action of the laser pulse concurrently with the rise of the absorption band with the maximum at 600 nm. According to the kinetic curves presented in Fig. 3, the photoinduced increase of the optical density at 620 nm is accompanied by a symbatic decline of the optical density in the region of the long wavelength absorption band of the initial A form. The process of the optical density change has two-step kinetics—the jumplike and relatively slow step ($t \approx 20$ μs), which indicates the presence of the short-lived intermediate product of the FRM 1 phototransformation.

It was found that the intensity of the signal decreases significantly in the presence of air oxygen that suggests the involvement of the molecule in triplet state in the process of formazane phototransformation (Fig. 4). The conclusion on the involvement of the interconversion to the triplet state is supported by the observed significant increase of the signal in the presence of the triplet energy donor benzophenone as well as by the established absence of oxidation-reduction reactions of benzothiazolylformazans in nonpolar solvents [7].

The gradual disappearance of the absorption band at 600 nm together with the recovery of the absorption band intensity in the short wavelength spectral region is observed with time.

The kinetics of dark recovery of intensity at the absorption band of FRM 2 in toluene at the different wavelengths has a complex two-step character (Fig. 5).

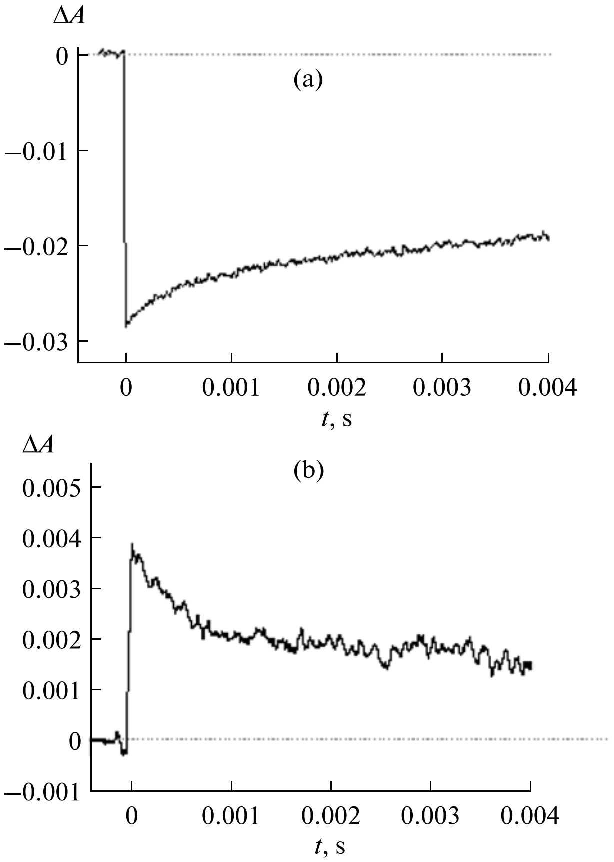


**Fig. 5.** Kinetics of the dark processes of the optical density changes for the FRM 2 compound in toluene at 580 nm (a) and 510 nm (b). $\lambda_{ex} = 354$ nm.

The spectrum of photoinduced changes in the optical density for the solution of the nitrophenyl FRM 4 compound is presented in Fig. 6. As follows from the presented spectrum, the rate of the dark optical density recovery at 400 nm is notably lower than for the process at $\lambda = 480$ nm (insert in Fig. 6), which is indicative of the existence of several forms of the compound with the overlapping spectra. These forms could be assigned to different tautomers of the FRM 4 [9].

Some differences in the differential spectra of the photoinduced absorption changes were observed upon excitation of the photochromic transformation by the laser pulse with $\lambda = 400$ nm (Fig. 7). The existence of several intermediate forms during the dark recovery of the initial absorption of the solution is clearly visible in the presented spectrum.

A comparison of the spectrum of the photoinduced absorption changes for the 3-methyl formazans with their absorption spectrum in the ground state (Figs. 1, 2, table) indicates the shift of the maximum of the discoloration band relative to the maximum of the absorption band. In can be explained much as in [7] by the existence of several forms in the toluene solution of 3-methyl formazans that are present as a mixture of different conformers or tautomer forms at equilibrium. This is also supported by the dependence of the FRM 4 discoloration band maximum on the excitation wave length (Figs. 6, 7). Two-stage character of the photoinduced absorption changes supports this conclusion as well (Figs. 3 and 5).

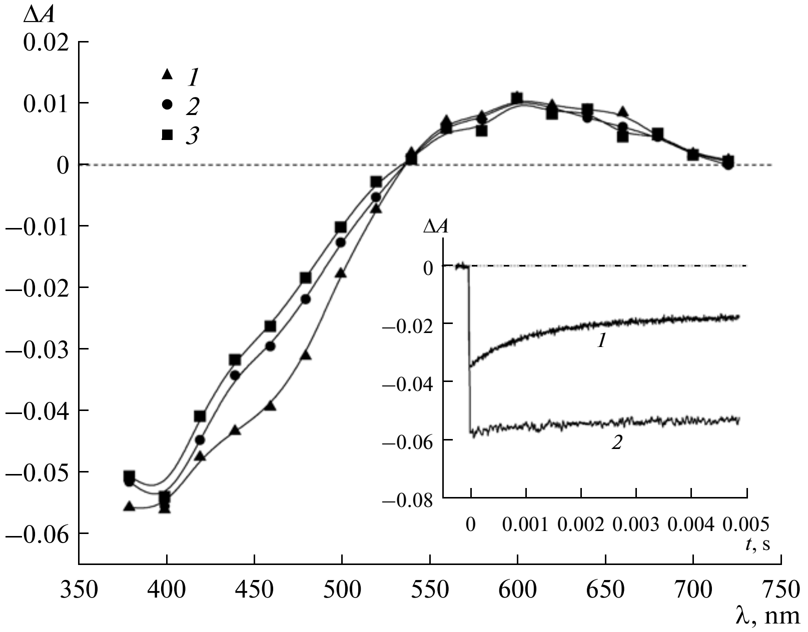


**Fig. 6.** Differential absorption spectra of the FRM 4 compound in toluene measured at the $\tau = 3 \times 10^{-4}$ s (*1*), $1.5 \times 10^{-3}$ s (*2*), and $4 \times 10^{-3}$ s (*3*) after laser pulse. In the insert–kinetic curves of the optical density changes at $\lambda = 480$ (*1*) and 400 nm (*2*). $\lambda_{ex} = 354$ nm.

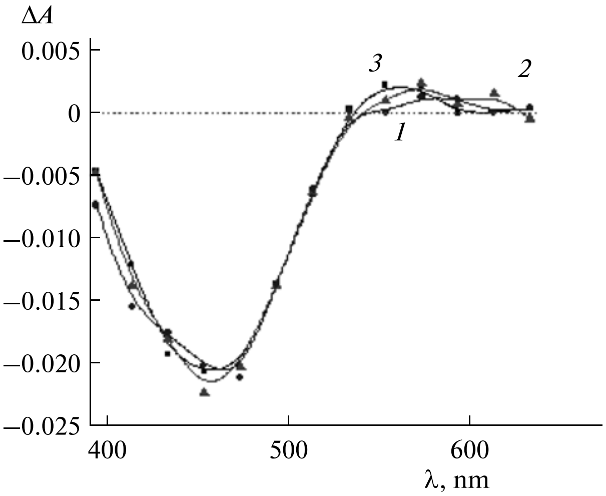


**Fig. 7.** Differential absorption spectra of the FRM 4 in toluene measured at the $\tau = 2 \times 10^{-6}$ (*1*), $1 \times 10^{-5}$ (*2*), and $5 \times 10^{-5}$ s (*3*) after laser pulse. $\lambda_{ex} = 400$ nm.

Hence it was established that the laser-induced phototransformation processes observed for the 3-methylbenzothiazolylformazans solutions indicate the presence of the intermediate products of the photoinduced transformation related to the possible existence of several isomers and tautomeric forms of the benzothiazole formazan molecules. Contrary to the data [6, 7, 9, 10] the influence of oxygen on the intensity of the photoinduced absorption and discoloration bands in toluene was first detected. On this basis we suggest that the process of the 1-aryl-3-methyl-5-(benzothiazole-2-yl)formazans phototransformation in toluene involves the *T*-state of the initial chelate form.

## REFERENCES

1. Buzykin, B.I., Lipunova, G.N., Sysoeva, L.P., and Rusinova, L.I., *Khimiya formazanov* (Chemistry of Formazans), Moscow: Nauka, 1992.
2. *Progress v khimii formazanov. Sintez, svoistva, primenenie*, (Progress in Formazan Chemistry: Synthesis, Properties, and Application) Lipunov, I.N. and Sigeikin, G.I., Eds., Moscow: Nauchnyi Mir, 2009.
3. Barachevskii, V.A., *Zh. Nauchn. Prikladn. Fotogr.*, 2001, vol. 46, no. 2, p. 54.
4. Avramenko, G.V. and Stepanov, B.I., *Zh. Obshch. Khim.*, 1974, vol. 44, p. 1298.
5. Zeif, A.P., Lipunova, G.N., Bednyagina, N.P., Shchegoleva, L.N., and Chernyavskii, L.I., *Zh. Org. Khim.*, 1970, vol. 6, no. 12, p. 2590.
6. Langbein, H., *J. Pract. Chem.*, 1979, vol. 321, p. 655.
7. Tkachenko, L.I., Semenov, E.Yu., Smirnov, V.A., Aldoshin, S.M., Lipunova, G.N., and Sigeikin, G.I., *Izv. Akad. Nauk, Ser. Khim.*, 2002, no. 5, p. 776.
8. Pervova, I.G., Barachevskii, V.A., Melkozerov, S.A., Lipunova, G.N., Sigeikin, G.I., and Lipunov, I.N., *Khim. Vys. Energ.*, 2010, vol. 44, no. 1, p. 16 [*High Energy Chem.*, 2010, vol. 44, no. 1, p. 20].
9. Ponyaev, A.I., Pestov, D.V., and El'tsov, A.V., *Zh. Obshch. Khim.*, 1984, vol. 55, no. 12, p. 2615.
10. El'tsov, A.V., Ol'khovikova, N.B., Ponyaev, A.I., and Lipunova, G.N., *Zh. Obshch. Khim.*, 1990, vol. 60, no. 4, p. 931.