Photochromism of an *N*-aminofulgimide-derived Schiff base

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A Schiff base was synthesized from 5-methoxysalicylaldehyde and *N*-aminofulgimide, *viz.*, 1-amino-3-[1-(2,5-dimethylthiophen-3-yl)ethylidene]-4-isopropylidenepyrrolidine-2,5-dione. The compound synthesized undergoes photochromic transformations typical of those of *N*-aminofulgimide studied earlier. A bathochromic shift of the absorption bands of the open and cyclic forms of the obtained Schiff base compared to the starting *N*-aminofulgimide was observed.

Key words: photochromism, fulgimides, absorption spectra, phototransformations.

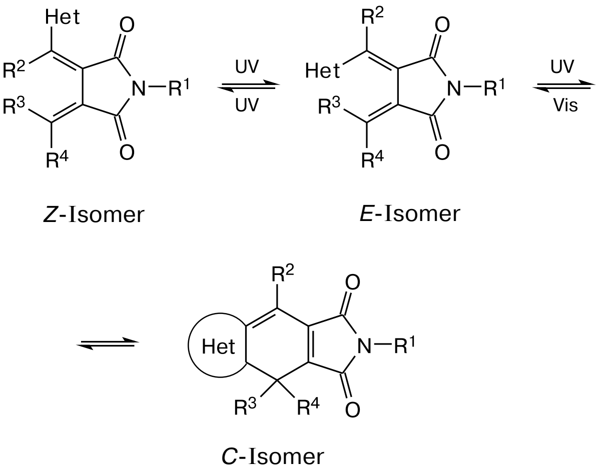
Fulgimide derivatives[1—8] along with fulgides are regarded as possible photosensitive components of the photochromic optical memory devices.[7,8] They usually undergo transformations that are irreversible thermally, but reversible photochemically, between two forms, *viz.*, the colorless open (*E*-isomer) and colored cyclic (*C*-isomer) forms (Scheme 1).

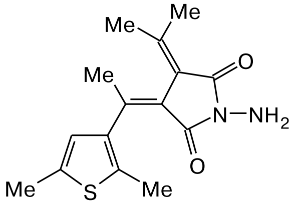
However, as for some fulgides, these transformations may be complicated by reversible *E*—*Z*-photoisomerization on exposure to UV light. In this case, the spectal changes are generally exhibited in the UV region.

Photochromic fulgimides, *viz.*, the earlier[9] synthesized *N*-aminofulgimide **1** and a derived Schiff base **2** obtained by the reaction with 5-methoxysalicylaldehyde, served as the subjects of research.

The aim of the present work was to study the photochromic properties of the Schiff base **2** and their comparison with those of the precursor *N*-aminofulgimide **1**.

Scheme 1





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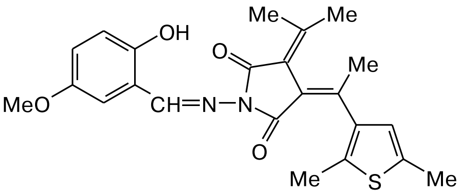

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Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2345—2347, December, 2009.

1066-5285/09/5812-2423 © 2009 Springer Science+Business Media, Inc.

Results and Discussion

Photoinduced spectral changes for a solution of compound **1** in toluene are presented in Fig. 1. The open form of fulgimide **1** is characterised by a long-wavelength absorption band with a maximum at 327 nm (see Fig. 1, curve *1*). Under UV excitation, the intensity of this absorption band is lowered and, at the same time, the absorption band in the visible region at 518 nm appears (see Fig. 1, curve *2*). This is evidence of the formation of a cyclic form, which has been shown by the examples of other fulgimides.[7] We established that this form is thermally stable. On storage of the irradiated solutions for 5 days in the dark, the absorption band intensity is decreased by 16% for a solution in toluene and by 1.4% for a solution in acetonitrile. However, on exposure to light, the cyclic form is again transformed into the open one (see Fig. 1, curve *3*). One isosbestic point is observed, which suggests the occurence of interconversions between two isomeric forms, *i.e.*, between the open (*E*) and cyclic (*C*) forms. Possible *E—Z*-photoisomerization was not spectroscopically observed.

The spectral characteristics of compound **2** significantly differ from those of the above-considered fulgimide (Fig. 2). The absorption band of the open form is shifted to long-wavelengths by 38 nm, its absorption maximum is 365 nm (see Fig. 2, curve *1*). The absorption band of the photoinduced cyclic form that is observed in the visible region, is also bathochromically shifted by 25 nm (λ_{max} = 543 nm) (see Fig. 2, curve *2*). As with compound **1**, the absorption band intensity of the open form (365 nm) decreases with simultaneous appearance of the absorption band of the cyclic form at 543 nm (see Fig. 2, curve *2*). However, in contrast to compound **1**, the absorption band intensity of the open form of compound **2** is not restored, but decreases upon irradiation of the photocolored solutions with visible light (see Fig. 2, curves *3* and *4*). In the case of compound **2**, two isosbestic points are observed.

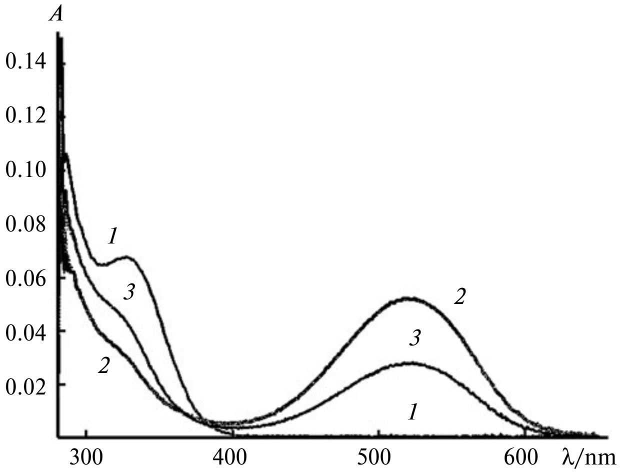

Fig. 1. Absorption spectra of a solution of compound **1** in toluene prior to (*1*) and after irradiation for 30 s with a mercury-xenon lamp through a UFS-8 light filter (*2*), as well as after irradiation for 45 s with the same lamp through a ZhS-10 light filter (*3*).

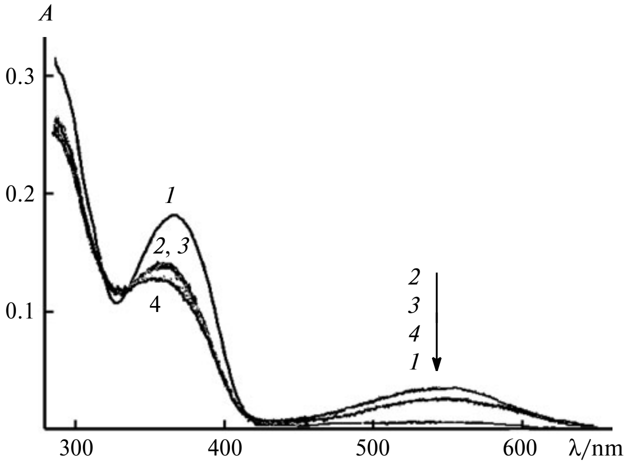

Fig. 2. Absorption spectra of a solution of compound **2** in toluene prior to (*1*) and after irradiation for 20 s with a mercury-xenon lamp through a UFS-8 light filter (*2*), as well as after irradiation for 6 (*3*) and 40 s (*4*) through a ZhS-10 light filter.

A small value of the bathocromic shift of the long-wavelenth absorption bands of the open and cyclic forms of Schiff base **2** is determined by the weak conjugation between the π-systems of the salycilic and fulgimide fragments through the nitrogen atom of the five-membered maleimide ring. This is evidenced by the minor, as against compound **1**, decrease in the absorption band intensity of the open form upon UV irradiation.

The thermal stability of the cyclic form of Schiff base **2** is lower than that of compound **1**, which is evidenced by somewhat faster, spontaneous decoloration of the cyclic form of compound **2** in both toluene (by 85.87% in 12 days) and acetonitrile (by 14.5% in 10 days). As in the case of compound **1**, the rate of spontaneous decoloration in toluene is higher than that in acetonitrile.

The fact that the absorption band intensity of the open form in the case of solution of compound **2** is not restored to the initial value on exposure to visible light, taking into account the presence of two isosbestic points in a series of the photoinduced absorption spectra, can be explained not only by the photocyclization processes, but also by the *E—Z*-photoisomerization reaction, apparently, of the fulgimide and/or imine fragment, as well as by irreversible photodecomposition of compound **2**, which requires further studies.

Thus, as a result of this work, a novel representative of fulgimides is synthesized, which exhibits the photochromical properties close to those of *N*-aminofulgimide with the bathochromically shifted absorption bands of the open and cyclic forms.

Experimental

1-Amino-3-[1-(2,5-dimethylthiophen-3-yl)ethyllidene]-4-isopropylidenepyrrolidine-2,5-dione (**1**) was synthesized according to a known procedure.[9]

1-[(2-Hydroxy-5-methoxybenzylidene)amino]-3-[1-(2,5-dimethylthiophen-3-yl)ethylidene]-4-isopropylidenepyrrolidine-2,5-dione (2). To a boiling solution of compound **1** (0.29 g, 0.001 mol) in ethanol (5 mL), a hot solution of 5-methoxysalicylaldehyde (0.152 g, 0.001 mol) in ethanol (2 mL) was added. The solution was refluxed for 2 h and left for 24 h. The yellow crystalline precipitate that formed was separated, washed with a minimum amount of cold ethanol and recrystallized from ethanol. The yield was 0.39 g (80%), m.p. 160—161 °C. Found (%): C, 65.2; H, 5.5; N, 6.7. $C_{23}H_{24}N_2O_4S$. Calculated (%): C, 65.12; H, 5.66; N, 6.60. ^1H NMR (DMSO-d_6), δ: 2.00, 2.08, 2.28, 2.42, 2.49 (all s, 3 H each, Me); 3.73 (s, 3 H, OMe); 6.57 (s, 1 H, H of thienyl); 6.81 (d, 1 H, H(3) arom., J = 8.93 Hz); 6.88 (dd, 1 H, H(4) arom., J = 2.93 Hz, J = 8.93 Hz); 7.10 (d, 1 H, H(6) arom., J = 2.93 Hz); 9.29 (s, 1 H, CH=N); 10.33 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 424 $[M]^+$ (35), 409 $[M - CH_3]^+$ (35), 274 $[\text{fulgimide}]^+$ (35), 260 (50), 246 (12), 231 (43), 217 (43), 203 (50), 193 (28), 189 (100), 174 (35), 161 (48), 149 (88), 136 (85), 115 (18), 111 $[\text{thiophenyl}]^+$ (28), 106 (31).

Spectral studies for solutions were performed on a Cary 50 Bio (Varian) spectrophotometer in the range of 200—800 nm in a 2-mm cell (KU-1 quartz glass). Toluene (Scharlau, analyt. grade) was used as the solvent. The concentration of compounds in solution was $1 \cdot 10^{-4}$ mol L^{-1}. The ^1H NMR spectra of solutions of compounds in DMSO-d_6 were recorded on a Varian Unity-300 (300 MHz) spectrometer using Me_4Si as the internal standard.

Photocoloration of solutions was induced by UV irradiation with the mercury-xenon lamp (Hamamatsu) through UFS-5 and UFS-8 light filters. Photodecoloration of the colored solutions was performed by irradiation of the solution with visible light through a ZhS-10 light filter.

This work was financially supported by the Division of Chemistry and Materials Science of the Russian Academy of Sciences (Program No. 1) and Southern Federal University.

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Received September 10, 2007;
in revised form March 26, 2008