Amino-substituted spirooxazine and fulgimide for the nanostructurized photochromic systems

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Comparative spectral kinetic studies of the photochromic properties of a novel *N*-aminofulgimide and the previously synthesized aminospirooxazine intended for the synthesis of ogranic-inorganic photochromic systems based on cyclotriphosphazene were performed. The results from the spectral kinetic studies evidence the fundamental suitability of these compounds for design of the multifunctional photochromic systems based on cyclotriphosphazene. Computer molecular models of aminospirooxazine and *N*-aminofulgimide were developed and optimization of geometric parameters was performed by the semiempirical quantum chemical method AM1.

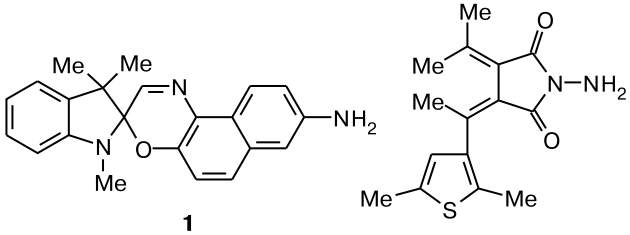
Key words: photochromism, spirooxazine, fulgimide, absorption spectra, phototransformation kinetics, quantum chemical simulation.

In recent years, the interest in studying nanosized structures for various application fields,[1] in particular, for different-type optical sensors[2] and photochromic aggregated structures for nonlinear optical transformation of laser light, is enhanced.[3] One of the problems of application of photosensitive materials, including photochromic substances, for these purposes is design of systems with a high concentration of photosensitive elements. One of the ways for design of such systems is the synthesis of polymers containing the fragments of photochromic compounds. Another way is covalent addition of photochromes to the hybrid organic-inorganic matrices. For example, it seems promising to apply as a matrix cyclotriphosphazenes (CTP) capable of supramolecular interactions.[4] Cyclotriphosphazenes are widely applied for design of various multifunctional systems.[5]

In this regard, we performed studies of the spectral kinetic properties of two photochromic compounds, namely, the thermally irreversible *N*-aminofulgimide and thermally relaxing *C*-aminospirooxazine, in order to determine the possibility of their application as photosensitive fragments for the nanostructurized photochromic systems. We also developed computer structural models of the above-mentioned photochromic compounds.

Results and Discussion

As the subjects of present research, we chose the photochromic *C*-aminospirooxazine **1** and *N*-aminofulgimide **2**.



Synthesis of photochromic compounds. Spirooxazine **1** was synthesized according to a known procedure.[6]

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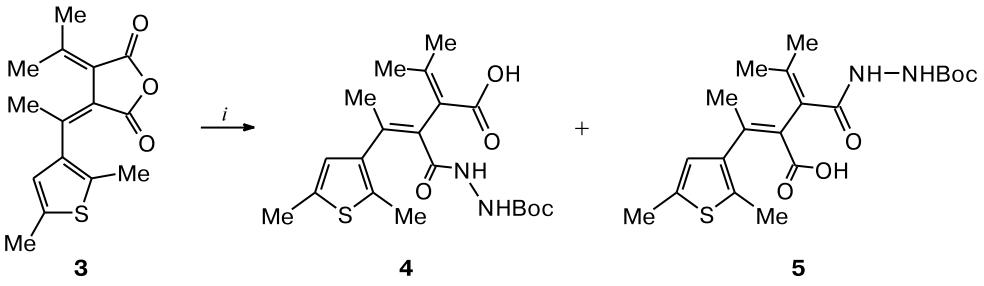
Scheme 1



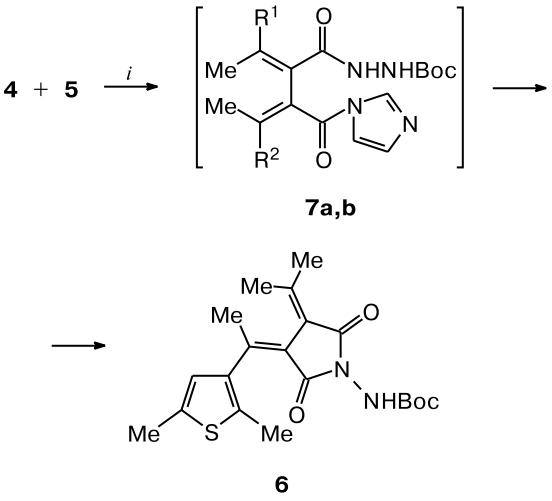
i. $H_2NNHBoc$, PhH, 80 °C, 10 h.

N-Aminofulgimide **2** was prepared from fulgide **3** in three steps. The reaction of fulgide **3** with *N*-(*tert*-butoxycarbonyl)hydrazine in refluxing benzene for 10 h resulted in the formation of a mixture of hydrazido acids **4** and **5** in a yield of 82% (Scheme 1).

Chromatographic separation of acids **4** and **5** was impossible due to the close R_f values. In addition, separation of acids **4** and **5** makes no sense in view of the fact that, upon cyclization, both acids will afford one product, *viz.*, *N*-(*tert*-butoxycarbonyl)aminofulgimide **6**. Therefore, their mixture was used in all further experiments. The structures of hydrazido acids **4** and **5** were confirmed by the data from ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis. The ^{1}H NMR spectrum of a mixture of acids **4** and **5** displays the singlet signals for the *tert*-butyl groups at δ 1.31 and 1.39, respectively. The protons of the CH_3 groups appear as singlets in the region of δ 1.72—2.35. The signals for the protons of amide and urethane NH groups are the broadened singlets at δ 8.65 and 9.35, respectively. According to the ^{1}H NMR spectral data, the ratio of **4** : **5** in the mixture is 1 : 1, which is evidenced by the equal intensities of the proton signals for the thiophene rings of compounds **4** and **5** at δ 6.51 and 6.52, respectively. The mass spectrum of a mixture of compounds **4** and **5** contains the peak of molecular ion at *m*/*z* 408.

Then we studied cyclization of the obtained mixture of hydrazido acids into *N*-(*tert*-butoxycarbonyl)aminofulgimide **6**. The complexity of conducting this reaction is that the reagents usually applied for cyclization of amido acids into imides, such as acetyl chloride or acetic anhydride, were unacceptable, since their use would result in unavoidable elimination of the Boc group under the action of the acids formed during the reaction and subsequent transformations (acylation) of the hydrazido group. When selecting the cyclization conditions, we turned attention to *N*,*N*′-carbonyldiimidazole (CDI). It is known[7] that CDI reacts with carboxylic acids to form imidazolides, *i.e.*, active acylating agents, which allows one to use CDI for cyclization of amido acids into imides. Indeed, the reaction of a mixture of acids **4** and **5** with CDI in THF at room temperature for 12 h resulted in the formation of the target compound **6** in a yield of 82%. The formation of the imide ring proceeds, apparently, *via* intermediates **7a,b**, which are cyclized to eliminate imidazole (Scheme 2).

Scheme 2



7: R^1 = 2,5-dimethyl-3-thienyl, R^2 = Me (**a**), R^1 = Me, R^2 = 2,5-dimethyl-3-thienyl (**b**)

i. CDI, THF, 20 °C, 12 h.

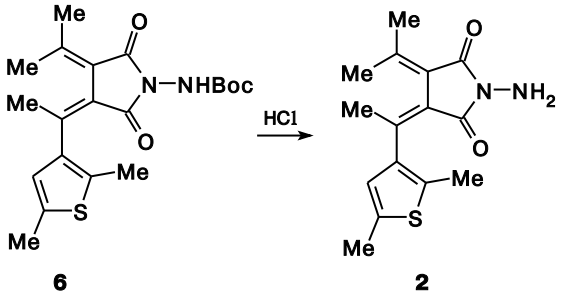
Fulgimide **6** affords in an alcoholic solution of HCl the target *N*-aminofulgimide **2** in a yield of 97% as light-yellow crystals (Scheme 3).

Study of the photochromic properties of amino-substituted spirooxazine and fulgimide. It is known[6] that, on exposure to UV and visible light, spirooxazine **1** undergoes reversible phototransformations between the initial spirooxazine form (**A**) and photoinduced merocyanine form (**B**) (Scheme 4).

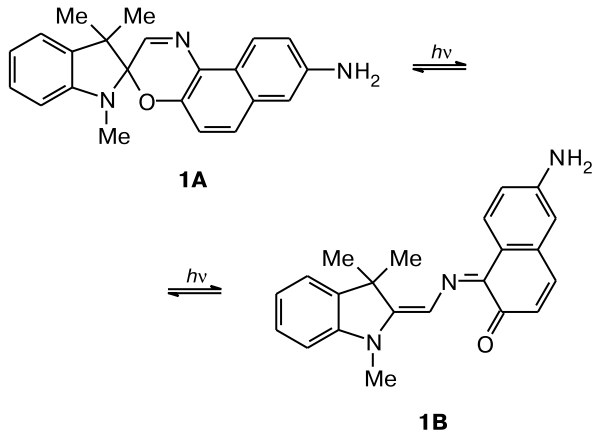
The results of the spectral kinetic study of this compounds are given in Table 1 and Figs 1 and 2.

Figure 1 shows the absorption spectra of initial (**1A**) and photoinduced (**1B**) forms of spirooxazine **1** in dimethyl-

Scheme 3



Scheme 4



formamide and tetrahydrofuran. The absorption band maxima of the merocyanine form **B** of compounds **1** in DMF and THF are observed at 635 and 610 nm, respectively. Thus, upon increase in the solvent polarity, the bathochromic shift of the absorption band maximum of the photoinduced merocyanine form **B** of compound **1** containing the electron-donating substituent in the oxazine fragment is observed, which suggests the quinoid character of this structure.[8]

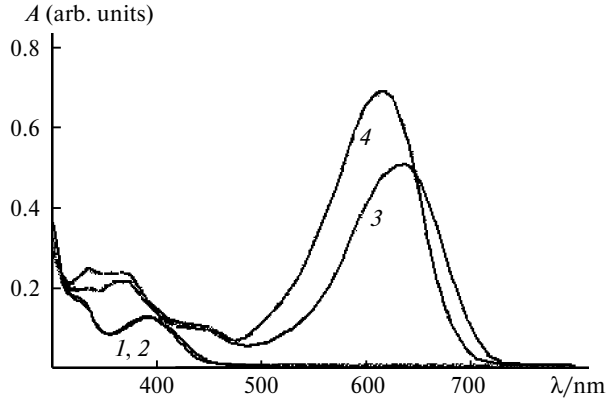


Fig. 1. The absorption spectra of solutions of spirooxazine **1** ($C = 1.10^{-4}$ mol L^{-1}) in THF (*1*, *4*) and DMF (*2*, *3*) before (*1*, *2*) and after (*3*, *4*) irradiation with the unfiltered light of a mercury-xenon lamp for 20 s.

The photoinduced colored form **B** of compound **1** disappears spontaneously in both solvents after termination of irradiation in less than 0.2 min and transforms into the colorless spiro form **A**. The rate constants of dark discoloration in THF and DMF differ slightly, but the rate of dark discoloration in the non-polar solvent is higher (see Table 1).

On long-term exposure to the activating unfiltered irradiation, photodegradation of compound **1** is observed in both solvents (see Fig. 2), the efficiency of photodegradation in the polar solvent (DMF) being higher than in the nonpolar solvent (THF).

Analogously to other fulgimide compounds, *N*-aminofulgimide **2** synthesized by us undergoes reversible valence photoisomerization[9,10] and transforms from the open form (*E*-isomer) to the cyclic form (*C*-isomer) under irradiation with UV and visible light, respectively (Scheme 5).

Table 1. The results of the spectral kinetic study of solutions of spirooxazine **1** and fulgimide **2** in solvents with different polarities ($C = 1.10^{-4}$ mol L^{-1})

Compound	Solvent	ε	λ_{max} /nm	$\lambda^{ph}{}_{max}$ /nm	A^{ph}	$A^{ph}{}_{max}$	k^{ddc} /s^{-1}	$\tau_{0.5}{}^{pd}$ /min
1	THF	7.4	388	610	0.125	0.66	0.82	0.6
	DMF	36.7	388	635	0.125	0.65	0.68	0.4
2	THF	7.4	<350	510	—	0.21	—	14.5
	DMF	36.7	<350	520	—	0.17	—	4.6

Note: ε is the dielectric constant of solvents; λ_{max} and $\lambda^{ph}{}_{max}$ are the absorption band maxima of the initial and photoinduced forms, respectively; A^{ph} is the optical density at the absorption maximum of the initial form; $A^{ph}{}_{max}$ is the photoinduced optical density at the wave length of the absorption band maximum of the photoinduced form in the photoequilibrium state; k^{ddc} is the rate constant of dark discoloration; $\tau_{0.5}{}^{pd}$ is the time for which the maximum photoinduced optical density of a solution at the absorption band maximum of the photoinduced form decreases twofold due to photodegradation of a compound.

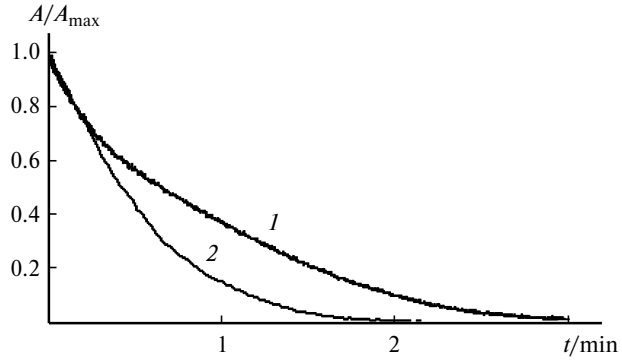


Fig. 2. The kinetic curves of photodegradation of solutions of spirooxazine **1** ($C = 1.10^{-4}$ mol L^{-1}) in THF (*1*) and DMF (*2*) under irradiation with the unfiltered light of a mercury-xenon lamp, which were recorded at the wave lengths of the absorption band maxima of the photoinduced form at 610 and 635 nm, respectively.

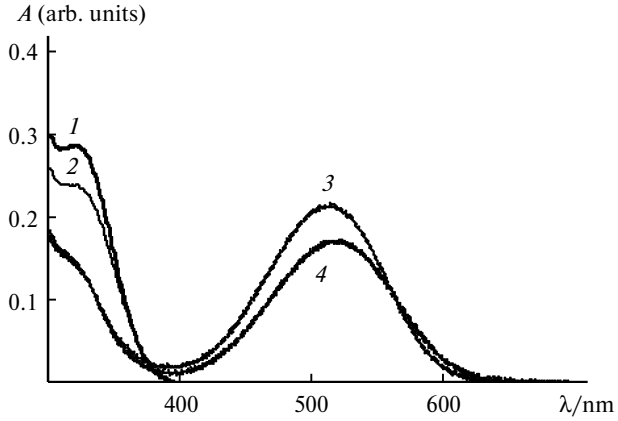


Fig. 3. The absorption spectra of solutions of fulgimide **2** ($C = 1.10^{-4}$ mol L^{-1}) in THF (*1*, *3*) and DMF (*2*, *4*) before (*1*, *2*) and after (*3*, *4*) UV irradiation for 40 s using a UFS-1 light filter.

In addition, reversible *Z*—*E*-isomerization is also possible on exposure to UV light.

The results from the spectral kinetic study of photochromic transformations of the amino-substituted fulgimide **2** are given in Table 1 and Figs 3—5. The absorption band maxima of the merocyanine form of fulgimide **2** in DMF and THF are different and positioned at 520 and 510 nm, respectively (Fig. 3). Thus, on going from a less polar solvent to a more polar one the bathochromic shift of the absorption band maximum is observed as in the case of spirooxazine **1**.

It was found that the photoinduced *C*-isomer is thermally stable in both solvents (Fig. 4).

The results of investigation of the photocoloration and photodecoloration processes of the photochromic fulgimide **2** in the solvents with different polarities (DMF and THF) evidence the reversibility of phototransformations of the thermally stable *E*-form and *C*-form. As for spirooxazine **1**, fulgimide **2** is more stable toward photodegradation in a THF solution compared to a solution in DMF (see Fig. 5 and Table 1).

The analysis of experimental data shows that the solvent polarity has a negligible impact on the positions of

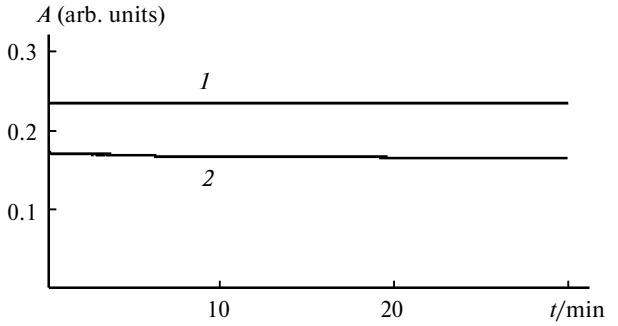
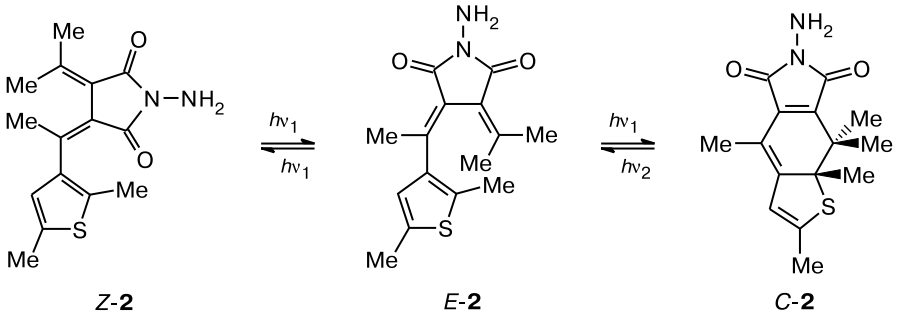


Fig. 4. The dark relaxation kinetics of the photoinduced cyclic form of compound **2** ($C = 1.10^{-4}$ mol L^{-1}) in THF (*1*) and DMF (*2*).

the absorption bands of cyclic form. Compound **2** is characterized by the high stability of the *C*-isomer toward dark relaxation in both THF and DMF, as well as by more efficient photodegradation in DMF compared to THF. Thus, the studied compounds **1** and **2** exhibit the well-defined photochromic properties and can be applied for the synthesis of the photochromic compounds based on CTP.

Scheme 5



Z-**2** *E*-**2** *C*-**2**

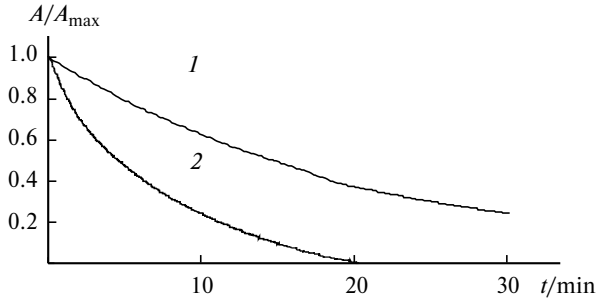


Fig. 5. The kinetic curves of photodegradation of solutions of compound **2** ($C = 1.10^{-4}$ mol L^{-1}) under irradiation with the unfiltered light of a mercury-xenon lamp in THF (*1*) and DMF (*2*), which were recorded at 510 and 520 nm, respectively.

Computer simulation of the structures of photochromic compounds. In order to determine the geometries of the molecules under study, we performed simulation of the structures of photochromic compounds **1** and **2**. Geometry optimization of the low-molecular weight photochromic compounds was performed by the semiempirical quantum chemical method AM1.

Figure 6 shows the optimized structures of spiropyran **A** (see Fig. 6, *a*, *b*) and merocyanine **B** (see Fig. 6, *c*, *d*) molecular forms of spirooxazine **1**. The spyropyran form **1A** is a rigid structure, whose fragments lie in two mutually perpendicular planes. The photoinduced merocyanine form **1B** has a planar structure and a degree of freedom, *i.e.*, the possibility of internal rotation around the C—N ordinary bond.

As compared with the molecule of aminospirooxazine **1**, the open form of fulgimide **2** is considerably more flexible (Fig. 7, *a*) and the cyclic form is characterized by a rigid structure (see Fig. 7, *b*, *c*).

Thus, the study of photochromic properties of *C*-aminospirooxazine and *N*-aminofulgimide showed that spirooxazine undergoes thermally reversible photochromic transformations and fulgimide is characterized by the ther-

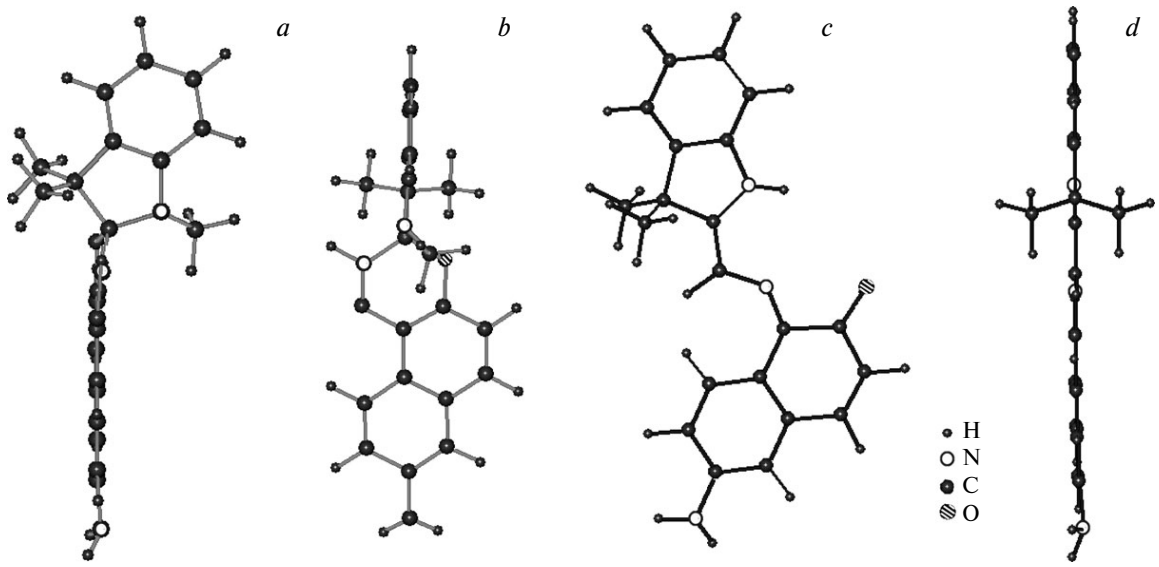


Fig. 6. The optimized structures of the spirooxazine form **1A** (*a*, *b*) and the merocyanine form **1B** (*c, d*) of compound **1** (two projections). The indoline fragment is parallel (*a*, *c*) and perpendicular (*b*, *d*) to the figure plane.

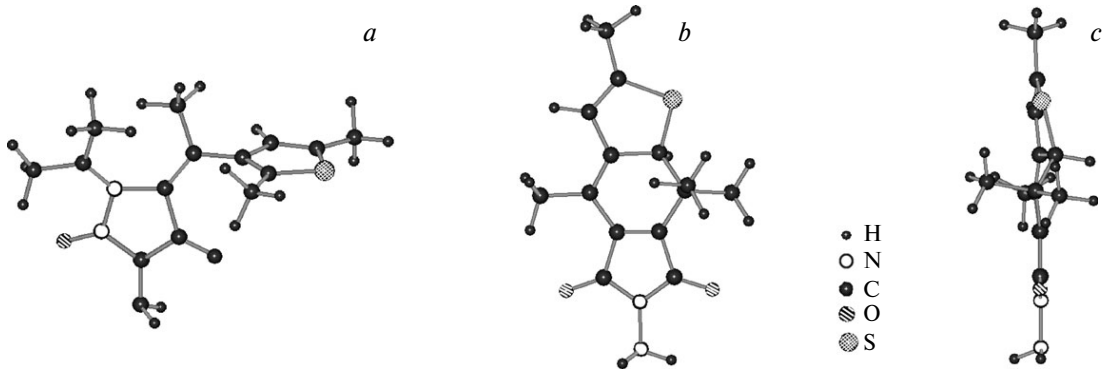


Fig. 7. The optimized structures of the open (*a*) and cyclic (*b*, *c* two projections) forms of fulgimide **2**.

mal stability of two isomers, which undergo reversible interconversions only under irradiation with UV and visible light. Both compounds under study exhibit the practically interesting spectral kinetic properties and can be used for the synthesis of the photochromic compounds based on CTP. The quantum chemical calculations of the structures of the photochromic compounds studied show that *N*-aminofulgimide has a considerably more flexible structure compared to *C*-aminospiroxazine.

Experimental

Spectral studies were performed in solutions of *N,N*-dimethylformamide (Khimmed, chemically pure) and anhydrous tetrahydrofuran (Aldrich, 99.9%). The concentrations of compounds in a solution were 110^{-4} mol L^{-1}.

Absorption spectra were measured on a Cary Bio 50 (Varian) spectrophotometer in a spectral range of 200—800 nm. Photocoloration of solutions of spirooxazine **1** in THF and DMF was performed by unfiltered irradiation using a mercury-xenon lamp (Hamamatsu LC-4) with a power of 470 mW cm^{-2}. In the case of solutions of fulgimide **2**, photocoloration was performed by identical irradiation using a UFS-1 glass light filter and photodecoloration of colored solutions was performed using a ZhS-11 light filter. Spectral measurements were carried out in a cell with a thickness of 2 mm.

The phototransformation kinetics of photochromic compounds was studied on the wavelength of the absroption band maximum of the photoinduced form. Photodecomposition of solutions is characterized by the time for which the photoinduced optical density that is achieved in the photo-steady state at the absorption band maximum of the photoinduced form decreases twofold under sustained irradiation of solutions of spirooxazine and fulgimide with unfiltered light. The kinetic curves of spontaneous relaxation of the photoinduced form of spirooxazine **1** and the cyclic form of compound **2** in solutions were obtained by periodic measurement of the absorption spectra of solutions. During the time between measurements, solutions was stored in the shadowed cell chamber of a spectrophotometer. All kinetic studies were performed at 23 °C.

Geometry optimization of compounds **1** and **2** was performed by the semiempirical quantum chemical method AM1 using the GAMESS program.[11]

^{1}H NMR spectra were recorded on Bruker WM-250 (250 MHz) and Bruker AM-300 (300 MHz) spectrometers. Mass spectra (EI) were obtained on a Kratos MS-30 instrument (direct inlet of a sample), the ionizing voltage was 70 eV, the emission current is 0.1 mA, and the temperature in the ionization chamber is 250 °C. Melting points were measured on a Boetius apparatus and not corrected. The course of reaction and the purity of products were monitored by TLC on Merck 60 F_{254} plates. (3-*Z*)-[1-(2,5-Dimethyl-3-thienyl)ethylidene]-4-isopropylidenefuran-2,5-dione (**3**) was prepared according to a known procedure by condensation of 2,5-dimethyl-3-acetylthiophene with diethyl isopropylidenesuccinate.[12]

(3-*Z*)-3-[(*tert*-Butoxycarbonyl)amino]carbonyl-2-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-methyl-3-pentenoic acid (4) and (2-*Z*)-3-[(*tert*-butoxycarbonyl)amino]carbonyl-2-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-methyl-3-pentenoic acid (5). A solution of compound **3** (2 g, 7.2 mmol) and *N*-(*tert*-butoxycarbonyl)hydrazine (1 g, 7.5 mmol) in benzene (30 mL) was refluxed for 10 h. Benzene was evaporated and the product was isolated by flash chromatography on a SiO_2 column using a hexane—ethyl acetate (2 : 1) mixture and then pure ethyl acetate as eluents. A 1 : 1 mixture of acids **4** and **5** was obtained in a yield of 2.5 g (84%), m.p. 153—156 °C. Found (%): C, 58.62; H, 6.55; N, 6.74. $C_{20}H_{28}N_2O_5S$. Calculated (%): C, 58.80; H, 6.91; N, 6.86. MS of a mixture of **4** and **5**, *m/z* (I_{rel} (%)): 408 (3) $[M]^+$, 319 (34), 277 (68), 275 (86), 261 (97), 231 (66), 217 (78), 203 (67), 189 (100), 91 (80).

Acid **4**. ^{1}H NMR (250 MHz, DMSO-d_6), δ: 1.31 (s, 9 H, CMe_3); 1.72 (s, 3 H, Me); 1.83 (s, 3 H, Me); 2.01 (s, 3 H, Me); 2.18 (s, 3 H, Me); 2.35 (s, 3 H, Me); 6.51 (s, 1 H, H_{thioph}); 8.65 (s, 1 H, NH); 9.35 (s, 1 H, NH).

Acid **5**. ^{1}H NMR (250 MHz, DMSO-d_6), δ: 1.39 (s, 9 H, CMe_3); 1.74 (s, 3 H, Me); 1.84 (s, 3 H, Me); 2.11 (s, 3 H, Me); 2.19 (s, 3 H, Me); 2.35 (s, 3 H, Me); 6.52 (s, 1 H, H_{thioph}); 8.65 (s, 1 H, NH); 9.35 (s, 1 H, NH).

1-[*N*-(*tert*-Butoxycarbonyl)amino]-3-[(*Z*-1)-(2,5-dimethyl-3-thienyl)ethylidene]-4-isopropylidenepyrrolidine-2,5-dione (6). To a solution of hydrazido acids **4** and **5** (2.38 g, 5.8 mmol) in THF (50 mL), *N,N′*-carbonyldiimidazole (1.04 g, 6.41 mmol) was added. The reaction mixture was stirred for 2 h at room temperature and stored for 16 h. The solvent was evaporated and the residue was subjected to flash chromatorgaphy on a SiO_2 column using a hexane—ethyl acetate (5 : 1) mixture as an eluent to yield compound **6** (1.87 g, 82%) as light-yellow crystals, m.p. 178—180 °C. Found (%): C, 61.44; H, 6.94; N, 7.25. $C_{20}H_{26}N_2O_4S$. Calculated (%): C, 61.52; H, 6.71; N, 7.17. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 1.45 (s, 9 H, CMe_3); 1.98 (s, 3 H, Me); 2.08 (s, 3 H, Me); 2.30 (s, 3 H, Me); 2.41 (s, 3 H, Me); 2.44 (s, 3 H, Me); 6.31 (s, 1 H, NH); 6.51 (s, 1 H, H_{thioph}). MS, *m/z* (I_{rel} (%)): 391 (3) [M + 1], 390 (13) $[M]^+$, 319 (32), 290 (39), 275 (100), 260 (86), 217 (83), 203 (45), 189 (63), 137 (74), 112 (65).

1-Amino-3-[(*Z*-1)-(2,5-dimethyl-3-thienyl)ethylidene]-4-isopropylidenepyrrolidine-2,5-dione (2). Compound **6** (0.5 g, 1.3 mmol) was dissolved with stirring in a 5 *M* alcoholic solution of HCl (75 mL) and the resulted solution was stored for 12 h at room temperature. The reaction mixture was evaporated to dryness on a rotary evaporator, the residue was dissolved in methanol (30 mL), and a 5 *N* solution (10 mL) of NH_3 in methanol was added to the mixture. The mixture was again evaporated to dryness and diethyl ether (30 mL) was added to the residue. The precipitate that formed was filtered off and washed with diethyl ether (2×20 mL). The filtrate was evaporated on a rotary evaporator to yield compound **2** (0.36 g, 97%) as light-yellow crystals, m.p. 172—173 °C. Found (%): C, 62.25; H, 6.44; N, 9.55. $C_{15}H_{18}N_2O_2S$. Calculated (%): C, 62.04; H, 6.25; N, 9.65. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.96 (s, 3 H, Me), 2.06 (s, 3 H, Me); 2.29 (s, 3 H, Me); 2.39 (s, 3 H, Me); 2.42 (s, 3 H, Me); 4.18 (s, 2 H, NH_2); 6.50 (s, 1 H, H_{thioph}). MS, *m/z* (I_{rel} (%)): 291 (2) [M + 1], 290 (14) $[M]^+$, 275 (100), 260 (25), 258 (44), 231 (55), 217 (68), 203 (70), 189 (63).

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