Synthesis of hybrid photochromes containing fulgimide and salicylidenaniline fragments and study of their properties*

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Fulgimide salicylidenaniline derivatives were synthesized and studied in solutions and solid-phase films. It was found that the compounds obtained exhibit photochromic properties in different aggregate states. Comparative studies showed that the nature of substituents in the aldehyde moiety of the fulgimide azomethine fragments has little effect on the photochromic properties of the compounds obtained.

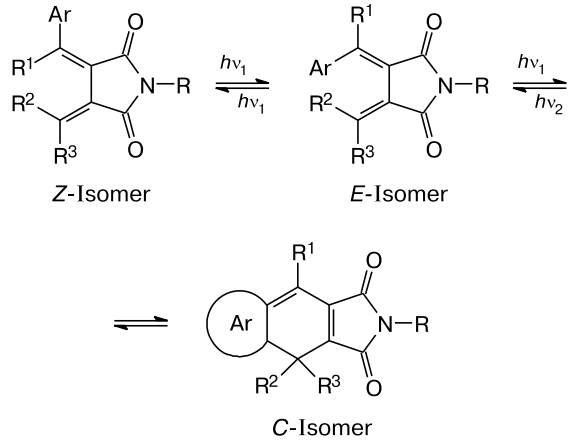
Key words: fulgides, fulgimides, salicylidenanilines, photochromic properties, photocoloring, photobleaching, photodegradation, spectral and kinetic studies, solid-phase layers.

Fulgimides belong to the thermally irreversible photochromic compounds, which are of interest for the development of photochromic registration media for the three-dimensional (3D) optical memory and molecular switches as a basis for the new generation of computational technique for recording, maintaining, and processing large massifs of information.[1] Their both forms possess high thermal stability and high fatigue resistance of photochromic transformations, can be easily transformed to derivatives of related structures, that allows one to extend the range of their functional possibilities.

Upon exposure to the light, fulgimides undergo reversible photoinduced valent isomerization between the open (*E*-isomer) and cyclic (*C*-isomer) isomers, complicated in some cases by *E*—*Z*-photoisomerization (Scheme 1).[2]

Synthetic potential of fulgimides is rather limited.[3—5] We assumed that development of fulgimide "hybrids" with salicylidenanilines would allow us to broaden their synthetic potential, in particular, due to the chelating properties of the latter.[6] One of the processes interesting from the practical point of view, which is accompanied by the change in magnetic properties, is the ligand-driven light-induced spin change (LD-LISC) in coordination compounds.[7] It consists in the fact that photoirradiation of the transition metal complex leads to considerable stereochemical rearrangements of the ligand, which destabilize different spin states of the metal. The LD-LISC has the advantage that it can occur at room temperature on the level of separate molecules. The absence of necessity of cooperative interactions makes possible its exhibiting in solutions, different types of films, and, potentially, in the solid state.

Scheme 1



In this connection, in the present work in continuation of our earlier studies[8] we synthesized a number of hybrid photochromic products containing two fragments in one molecule: the photochromic fulgimide and capable of complexation salicylidenaniline ones, as well as studied their photochromic properties in solutions and solid-phase films.

Results and Discussion

Synthesis of photochromic compounds. The synthesis of hybrid photochromes was performed by the reaction of

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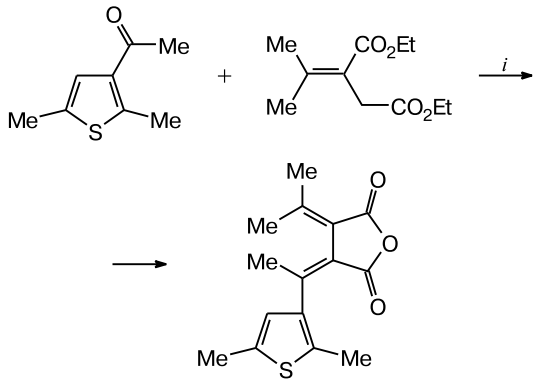
the fulgimide amino derivatives with different salicylaldehydes. 3-[α-(2,5-Dimethyl-3-thienyl)ethylidene]-4-isopropylidenetetrahydrofuran-2,5-dione (**1**) was the starting compound for the synthesis of the fulgimide, which was obtained according to the known procedure[9] in 12% total yield (Scheme 2).

Scheme 2



1

i. 1) Bu^{t}OK; 2) KOH, H_2O—EtOH; 3) AcCl.

Reflux of fulgide **1** with *p*-(*tert*-butoxycarbonylamino)-aniline (**2**) in benzene with subsequent cyclization in the presence of *N*,*N*′-carbonyldiimidazole (CDI) and removal of the Boc protecting group in the formed urethane **3** upon the action of the HCl solution in ethanol afforded *N*-(aminophenyl)fulgimide **4** (see Refs 10 and 11 and Scheme 3).

The reaction of fulgimide **4** with salicylic aldehydes **5a—j** in DMF at room temperature for 5 h furnished the hybrid photochromes **6a—j** (Scheme 4).

The structures of compounds **6a—j** were confirmed by ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis. It is know that *Z*- or *E*-configurations of fulgides and fulgimides can be inferred from the chemical shifts for the methyl groups of the isopropylidene fragment: for *Z*-isomers of fulgides and fulgimides these signals are found in the region δ 1.9—2.5. At the same time, the 1,3,5-hexatriene fragment of *E*-forms of the fulgide molecule is not placed in the plane of the aromatic ring because of steric factors, as a result, the *E*-Me group of the isopropylidene fragment is either over or below its plane and thus is shielded due to the induced magnetic field, giving the signal in the region δ 1.3—1.4.[12,13] The ^{1}H NMR spectra of compounds **6a—j** exhibit signals for the Me groups of the fulgide fragment as singlets in the region δ 1.94—2.49, that indicates the *Z*-configuration of these fragments.

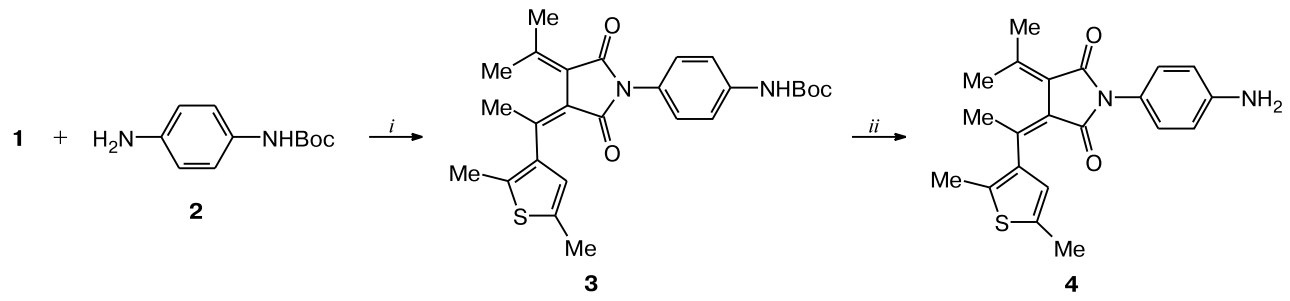
Spectral and kinetic studies. The results of the spectral and kinetic studies of the synthesized hybrid compounds **6a—j** in toluene are given in Table 1. Analysis of the data obtained shows that all of them exhibit photochromic properties intrinsic of fulgimides. The absorption spectra of the open form are structured in most cases (Fig. 1) except compound **6e**, which has the only characteristic absorption band, whose maximum is bathochromically shifted as compared to the absorption maxima of the open forms of other compounds.

Positions of the absorption bands for the cyclic form is virtually independent on the nature of substituents in the hydroxy-substituted phenyl fragment. Nonetheless, from the data in Table 1 it follows that introduction of strong electron-withdrawing groups (compounds **6d**,**f**) leads to a bathochromic displacement of the absorption band for the cyclic form by 2—3 nm. For compounds with less strong electron-withdrawing substituents (**6j**) or with substituents of different nature (**6g**,**i**), virtually no changes in the position of the absorption maximum for the cyclic form are observed (see Table 1). Conversely, in the case of strong electron-releasing substituents (**6b**,**c**,**e**,**h**), a hypsochromic spectral shift by 2—8 nm is observed.

For all the fulgimides studied, only insignificant photoinduced changes of optical density in the absorption band maximum for the cyclic form in the photostationary state were found, which are apparently due to the efficiently proceeding reverse reaction of photobleaching (Table 1).

It is seen from Fig. 2 that introduction of electron-withdrawing substituents causes an increase in the effi-

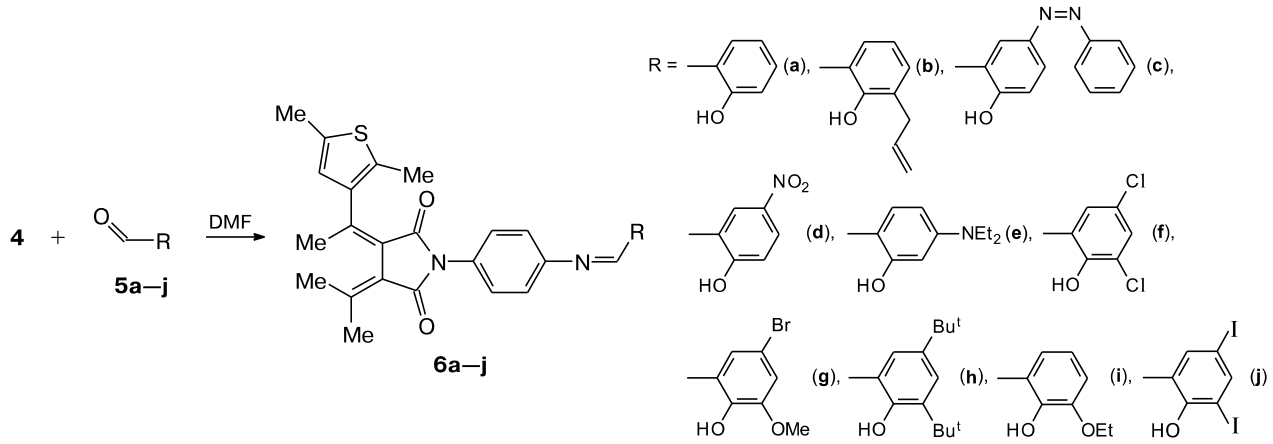
Scheme 3



2 **3** **4**

i. 1) CDI; *ii*. 1) HCl, EtOH; 2) NH_3, MeOH.

Scheme 4



ciency of the photodegradation process. Electron-releasing substituents in a number of cases significantly increase stability of fulgimides to irreversible phototransformations (**6b**,**c**,**e**).

The experimental data obtained allows us to draw a conclusion that the changes in the nature of substituents in the aldehyde moiety of the fulgimide azomethine fragments has insignificant effect on the photochromic properties in solutions.

In addition, photochromic properties of the fulgimides synthesized were studied in the thin (400±90 nm) solid-phase films. The study of the structure of the obtained solid-state films showed that the compounds in the thin solid films are in the amorphous state (Fig. 3).

Table 2 contains the results of the study of photochromic properties of the synthesized compounds in the thin amorphous layers.

Irradiation of the solid-phase samples of fulgimides causes their coloring, whose extent in the photoequilibrium state is low and independent on the structure of compounds under study (Table 2, Fig. 4).

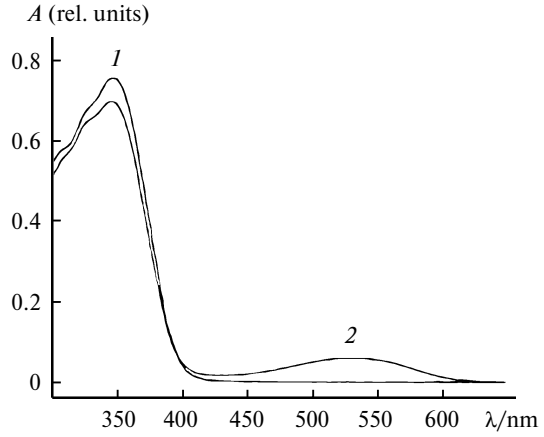


Fig. 1. Absorption spectra of compound **6a** in toluene before (*1*) and after exposure (*2*) to the UV light.

Table 1. Spectral and kinetic characteristics of the synthesized fulgimides **6a—j** in toluene

Compound	λ_A^{max}	λ_B^{max}	A_A^{max}	ΔA_B^{ph}
	nm			
6a	328 sh	530	0.70	0.06
	346		0.77	
6b	331	528	0.93	0.08
	348		0.91	
6c	342	522	1.73	0.09
	370 sh		1.29	
6d	308	533	1.09	0.07
	342		1.10	
6e	381	525	1.82	0.04
6f	325	532	0.63	0.06
	337		0.67	
	356		0.61	
6g	328	530	0.78	0.06
	342 sh		0.72	
	365 sh		0.48	
6h	320	528	0.68	0.06
	332		0.69	
	352		0.63	
6i	328	529	0.67	0.05
	358 sh		0.45	
6j	327	530	0.98	0.08
	340		0.99	
	360 sh		0.79	

Note. Here and in Table 2: λ_A^{max} and λ_B^{max} are the wavelengths of absorption maxima of the open and cyclic forms, respectively; A_A^{max} is the optical density in the absorption maxima of the open form; ΔA_B^{ph} is the maximum photoinduced change in the optical density of the solution in the absorption maximum of the cyclic form in photostationary state.

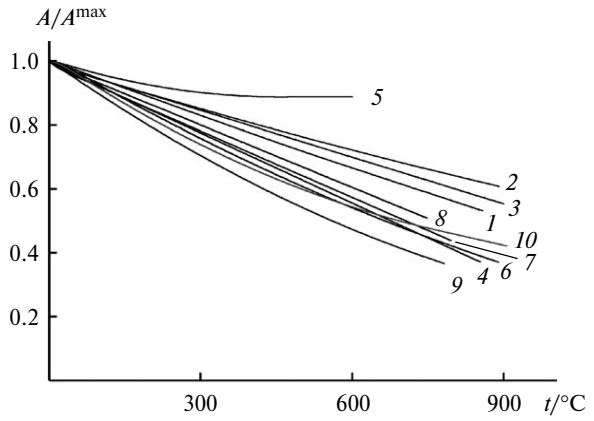


Fig. 2. Normalized kinetic curves of photodecomposition of fulgimides in toluene upon the action of nonfiltered irradiation: **6a** (*1*), **6b** (*2*), **6c** (*3*), **6d** (*4*), **6e** (*5*), **6f** (*6*), **6g** (*7*), **6h** (*8*), **6i** (*9*), and **6j** (*10*).

From the data in Table 2, it follows that, similarly to the case of solutions, introduction of a strong electron-withdrawing substituent (**6d**) leads to a bathochromic shift of the absorption band maximum of the cyclic form. Fulgimides with electron-releasing substituents exhibit hypsochromic shifts of the absorption maxima of the cyclic form, which, however, was less pronounced (see Table 2). The fulgimide with the strongest electron-releasing substituent (**6e**) was an exception. Its hypsochromic shift reached 12 nm (see Table 2).

For the most fulgimides studied, stability in the solid films to irreversible photochemical transformation is higher than in solutions (*cf.* Figs 2 and 5), excluding compounds **6j**, **6e**, and **6d**. Compounds **6c** and **6f** exhibit a unique stability to irreversible phototransformations.

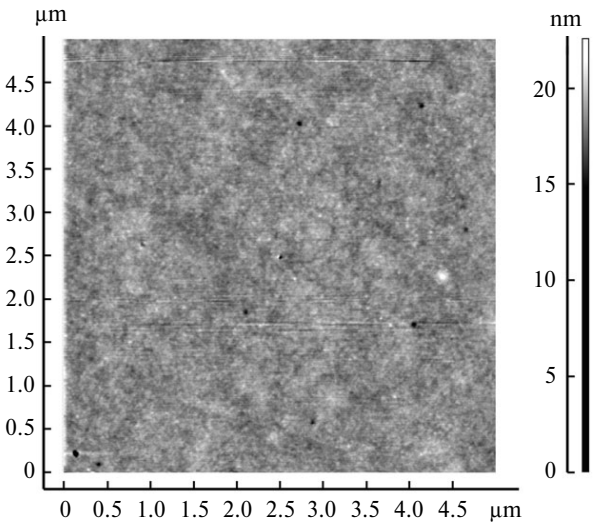


Fig. 3. The typical picture of the amorphous film surface of compound **6h** obtained using a scanning sound microscope (the field of scanning was 5×5 μm, the overfall of heights was 25 nm).

Table 2. Spectral and kinetic characteristics of the amorphous films of fulgimides synthesized

Compound	λ_A^{max}	λ_B^{max}	A_A^{max}	ΔA_B^{ph}
	nm			
6a	276	536	0.70	0.03
	346		0.66	
6b	278	535	1.63	0.05
	330		1.49	
	352		1.39	
6c	236	528	1.98	0.05
	283		1.62	
	338		2.15	
6d	340	432	0.87	0.06
	442	542	0.06	0.03
6e	248	524	0.52	0.02
	272		0.47	
	388		0.60	
6f	230	476	0.55	0.01
	276	528	0.43	0.01
	335		0.40	
	360		0.37	
	465		0.02	
6g	234	494	1.00	0.02
	282	534	0.67	0.02
	326		0.66	
6h	280	492	1.20	0.06
	318		1.09	
	330		1.08	
	352		0.98	
6i	228 sh	533	0.51	0.02
	284		0.37	
	328		0.39	
6j	237	466	1.06	0.02
	284 sh	530 sh	0.66	
	328		0.66	
	342		0.65	
	366		0.53	

However, unlike in solutions, the efficiency of the photodegradation process is independent on the electron-withdrawing and electron-releasing properties of substituents, rather, it is probably determined by the molecular packing in the amorphous layer.

In conclusion, the fulgimides synthesized exhibit photochromic properties not only in solutions, but also in the solid-phase films, which seems important for the planned studies of the LD-LISC-effect in the complexes derived from these compounds. It was found that the solid-phase films have amorphous structure and that the nature of substituents in the hydroxy-substituted phenyl fragment affects spectroscopic characteristics of the isomeric forms and the photodegradation processes.

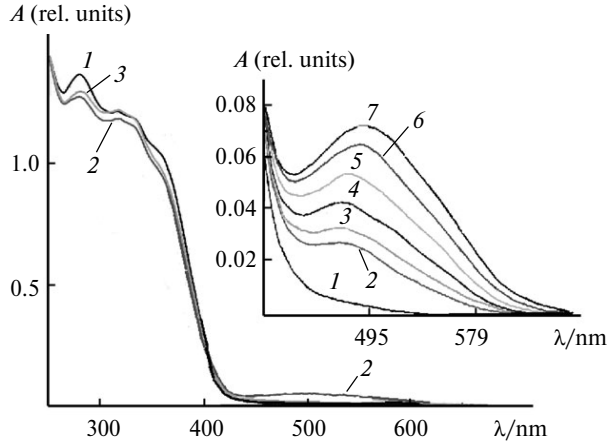


Fig. 4. Absorption spectra of the thin film of compound **6h** before (*1*), after exposure to the UV light through a UFS-1 light filter (*2*) and to the visible light through a ZhS-11 light filter (*3*). In the insertion: an increase in intensity of the absorption band of the cyclic form before (*1*) and after exposure to the UV light through a UFS-1 light filter for 1 (*2*), 2 (*3*), 4 (*4*), 8 (*5*), 15 (*6*), and 30 s (*7*).

Experimental

Spectrophotometric measurements (photostationary spectra), as well as kinetics of the photocoloring, photobleaching, and photodegradation processes of photochromic compounds in solution in toluene were performed on a Cary 50 Bio spectrophotometer (Varian, Australia). The concentration of solutions $C = 2 \cdot 10^{-4}$ mol L^{-1} was chosen as a working one. Cuvettes 10 mm thick were used for spectroscopic studies, whereas for kinetic measurements, 2 mm thick.

Amorphous thin films were obtained by the pouring method, *i.e.* by the even distribution of a given amount of solution of fulgimide in toluene with the working concentration $C = 5 \cdot 10^{-3}$ mol L^{-1} over a quartz glass with subsequent evaporation of the solvent.

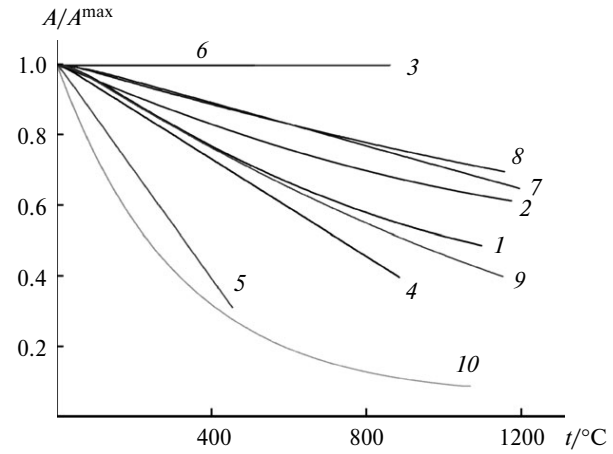


Fig. 5. Normalized kinetic curves of photodecomposition of fulgimides in the solid-phase layers upon exposure to the non-filtered irradiation: **6a** (*1*), **6b** (*2*), **6c** (*3*), **6d** (*4*), **6e** (*5*), **6f** (*6*), **6g** (*7*), **6h** (*8*), **6i** (*9*), and **6j** (*10*).

The films thickness was measured on a Linnik MII-4 microinterferometer (Russia).

The structure of the solid-phase films was studied using a SOLVER BIO scanning sound microscope from NT-MDT (Russia).

Irradiation was produced using an LC4 100-240V-300VA mercury-xenon lamp (50—60 Hz) on a HAMAMATSU lightning cure™ (Japan) and UFS-1 and ZhS-11 color optical filters for photocoloring and photobleaching, respectively.

^{1}H NMR spectra were recorded on Bruker WM-250 (250 MHz) and Bruker AM-300 (300 MHz) spectrometers in $CDCl_3$ and DMSO-d_6. Melting points were determined on a Boetius microscope stage. Reaction progress and purity of compounds obtained were monitored by TLC on Merck 60 F_{254} plates. Merck 60 silica gel (0.040—0.063 mm) was used for flash-chromatography.

We used in the work commercially available salicylic aldehydes **5a—j**, 3-acetyl-2,5-dimethylthiophene, potassium *tert*-butoxide, and *N*,*N*′-carbonyldiimidazole (Acros). Diethyl isopropylidenesuccinate was obtained according to the known procedure[14] by condensation of diethyl succinate and acetone in the presence of potassium *tert*-butoxide; *para*-*N*-Boc-phenylenediamine was obtained according to the known procedure.[15]

Synthesis of Schiff bases 6a—j (general procedure). Fulgimide **4** (0.1 g, 0.0003 mol) and aldehyde **5a—j** (0.0003 mol) were dissolved in DMF (3 mL) with stirring. The reaction mixture was kept at room temperature for 5 h. The crystals that formed were filtered off, washed with ethanol on the filter, and recrystallized.

(3*Z*)-3-[1-(2,5-Dimethyl-3-thienyl)ethylidene]-1-{4-[(2-hydroxybenzylidene)amino]phenyl}-4-(1-methylethylidene)pyrrolidine-2,5-dione (6a). The yield was 94%. Colorless crystals, m.p. 207—208 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ: 2.05 (s, 3 H, Me); 2.13 (s, 3 H, Me); 2.35 (s, 3 H, Me); 2.41 (s, 3 H, Me); 2.49 (s, 3 H, Me); 6.56 (s, 1 H, H_{thioph}); 6.92—7.04 (m, 2 H, H_{arom}); 7.27—7.43 (m, 6 H, H_{arom}); 8.59 (s, 1 H, CH=N); 13.09 (s, 1 H, OH). Found (%): C, 71.41; H, 5.54; N, 5.87. $C_{28}H_{26}N_2O_3S$. Calculated (%): C, 71.47; H, 5.57; N, 5.95.

(3*Z*)-1-{4-[(3-Allyl-2-hydroxybenzylidene)amino]phenyl}-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-(1-methylethylidene)-pyrrolidine-2,5-dione (6b). The yield was 85%. Light yellow crystals, m.p. 168—170 °C (EtOH). ^{1}H NMR (DMSO-d_6), δ: 2.00 (s, 3 H, Me); 2.08 (s, 3 H, Me); 2.25 (s, 3 H, Me); 2.35 (s, 3 H, Me); 2.41 (s, 3 H, Me); 3.41 (d, 2 H, C$\underline{H}_2$—CH=CH_2, J = 6.4 Hz); 5.01—5.11 (m, 2 H, CH_2—CH=C$\underline{H}_2$); 5.96—6.05 (m, 1 H, CH_2—C$\underline{H}$=CH_2); 6.71 (s, 1 H, H_{thioph}); 6.92—6.97 (m, 1 H, H_{arom}); 7.28—7.31 (m, 2 H, H_{arom}); 7.35 (d, 2 H, H_{arom}, J = 8.4 Hz); 7.51 (d, 2 H, H_{arom}, J = 11.9 Hz); 8.99 (s, 1 H, CH=N); 13.58 (s, 1 H, OH). Found (%): C, 72.85; H, 5.90; N, 5.41. $C_{31}H_{30}N_2O_3S$. Calculated (%): C, 72.91; H, 5.92; N, 5.49.

(3*Z*)-3-[1-(2,5-Dimethyl-3-thienyl)ethylidene]-1-[4-({2-hydroxy-5-[(*Z*)-phenyldiazenyl]benzylidene}amino)phenyl]-4-(1-methylethylidene)pyrrolidine-2,5-dione (6c). The yield was 81%. Orange crystals, m.p. 181—183 °C (dioxane). ^{1}H NMR (DMSO-d_6), δ: 2.00 (s, 3 H, CH_3); 2.08 (s, 3 H, Me); 2.25 (s, 3 H, Me); 2.35 (s, 3 H, Me); 2.41 (s, 3 H, Me); 6.71 (s, 1 H, H_{thioph}); 7.16 (d, 1 H, H_{arom}, J = 8.9 Hz); 7.38 (d, 2 H, H_{arom}, J = 8.7 Hz); 7.52—7.61 (m, 5 H, H_{arom}); 7.85—7.88 (m, 2 H, H_{arom}); 8.00—8.04 (m, 1 H, H_{arom}); 8.32 (d, 1 H, H_{arom}, J = 2.2 Hz); 10.37 (s, 1 H, CH=N); 13.64 (s, 1 H, OH). Found (%): C, 71.00; H, 5.23; N, 9.68. $C_{34}H_{30}N_4O_3S$. Calculated (%): C, 71.06; H, 5.26; N, 9.75.

(3*Z*)-3-[1-(2,5-Dimethyl-3-thienyl)ethylidene]-1-{4-[(2-hydroxy-5-nitrobenzylidene)amino]phenyl}-4-(1-methylethylidene)pyrrolidine-2,5-dione (6d). The yield was 88%. Yellow crystals, m.p. 227—230 °C (dioxane). ^{1}H NMR (DMSO-d_6), δ: 2.01 (s, 3 H, Me); 2.08 (s, 3 H, Me); 2.25 (s, 3 H, Me); 2.35 (s, 3 H, Me); 2.41 (s, 3 H, Me); 6.71 (s, 1 H, H_{thioph}); 7.18 (d, 1 H, H_{arom}, J = 9.2 Hz); 7.39 (d, 2 H, H_{arom}, J = 8.5 Hz); 7.51 (d, 2 H, H_{arom}, J = 8.5 Hz); 8.28 (dd, 1 H, H_{arom}, J = 9.2 Hz, J = 2.7 Hz); 8.68 (d, 1 H, H_{arom}, J = 2.7 Hz); 9.17 (s, 1 H, CH=N); 14.15 (s, 1 H, OH). Found (%): C, 65.19; H, 4.87; N, 8.10. $C_{28}H_{25}N_3O_5S$. Calculated (%): C, 65.23; H, 4.89; N, 8.15.

(3*Z*)-1-(4-{[4-(Diethylamino)-2-hydroxybenzylidene]amino}-phenyl)-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-(1-methylethylidene)pyrrolidine-2,5-dione (6e). The yield was 72%. Yellow crystals, m.p. 189—191 °C (EtOH). ^{1}H NMR (DMSO-d_6), δ: 1.10 (t, 6 H, $NCH_2C\underline{H}_3$, J = 7.2 Hz); 2.00 (s, 3 H, CH_3); 2.07 (s, 3 H, CH_3); 2.25 (s, 3 H, Me); 2.35 (s, 3 H, Me); 2.40 (s, 3 H, Me); 3.38 (q, 4 H, $NC\underline{H}_2CH_3$, J = 7.2 Hz); 6.07 (s, 1 H, H_{arom}); 6.32 (d, 1 H, H_{arom}, J = 8.7 Hz); 6.70 (s, 1 H, H_{thioph}); 7.26—7.36 (m, 5 H, H_{arom}); 8.69 (s, 1 H, CH=N); 13.49 (s, 1 H, OH). Found (%): C, 70.92; H, 6.51; N, 7.72. $C_{32}H_{35}N_3O_3S$. Calculated (%): C, 70.95; H, 6.51; N, 7.76.

(3*Z*)-1-{4-[(3,5-Dichloro-2-hydroxybenzylidene)amino]-phenyl}-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-(1-methylethylidene)pyrrolidine-2,5-dione (6f). The yield was 84%. Orange crystals, m.p. 197—199 °C (dioxane). ^{1}H NMR (DMSO-d_6), δ: 2.00 (s, 3 H, Me); 2.08 (s, 3 H, Me); 2.25 (s, 3 H, Me); 2.35 (s, 3 H, Me); 2.41 (s, 3 H, Me); 6.70 (s, 1 H, H_{thioph}); 7.38 (d, 2 H, H_{arom}, J = 8.4 Hz); 7.53 (d, 2 H, H_{arom}, J = 8.4 Hz), 7.74 (s, 2 H, H_{arom}); 9.03 (s, 1 H, CH=N), 14.29 (s, 1 H, OH). Found (%): C, 62.29; H, 4.46; N, 5.14. $C_{28}H_{24}Cl_2N_2O_3S$. Calculated (%): C, 62.34; H, 4.48; N, 5.19.

(3*Z*)-1-{4-[(5-Bromo-2-hydroxy-3-methoxybenzylidene)-amino]phenyl}-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-(1-methylethylidene)pyrrolidine-2,5-dione (6g). The yield was 84%. Orange crystals, m.p. 185—187 °C (dioxane). ^{1}H NMR (DMSO-d_6), δ: 2.00 (s, 3 H, Me); 2.07 (s, 3 H, Me); 2.25 (s, 3 H, Me); 2.35 (s, 3 H, Me); 2.40 (s, 3 H, Me); 6.70 (s, 1 H, H_{thioph}); 7.26 (s, 1 H, H_{arom}); 7.34—7.37 (m, 3 H, H_{arom}); 7.41—7.47 (m, 3 H, H_{arom}); 8.93 (s, 1 H, CH=N); 13.04 (s, 1 H, OH). Found (%): C, 60.06; H, 4.68; N, 4.79. $C_{29}H_{27}BrN_2O_4S$. Calculated (%): C, 60.11; H, 4.70; N, 4.83.

(3*Z*)-1-{4-[(3,5-Di-*tert*-butyl-2-hydroxybenzylidene)amino]-phenyl}-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-(1-methylethylidene)pyrrolidine-2,5-dione (6h). The yield was 43%. Pale yellow crystals, m.p. 131—133 °C (EtOH). ^{1}H NMR (DMSO-d_6), δ: 1.30 (s, 9 H, $C(Me)_3$); 1.42 (s, 9 H, $C(Me)_3$); 2.00 (s, 3 H, Me); 2.08 (s, 3 H, Me); 2.25 (s, 3 H, Me); 2.35 (s, 3 H, Me); 2.41 (s, 3 H, Me); 6.70 (s, 1 H, H_{thioph}); 7.38—7.51 (m, 6 H, H_{arom}); 9.00 (s, 1 H, CH=N); 13.84 (s, 1 H, OH). Found (%): C, 74.13; H, 7.24; N, 4.75. $C_{36}H_{42}N_2O_3S$. Calculated (%): C, 74.19; H, 7.26; N, 4.81.

(3*Z*)-3-[1-(2,5-Dimethyl-3-thienyl)ethylidene]-1-{4-[(3-ethoxy-2-hydroxybenzylidene)amino]phenyl}-4-(1-methylethylidene)pyrrolidine-2,5-dione (6i). The yield was 32%. Cream crystals, m.p. 164—167 °C (EtOH). ^{1}H NMR (DMSO-d_6), δ: 1.35 (t, 3 H, $OCH_2C\underline{H}_3$, J = 6.9 Hz); 2.00 (s, 3 H, Me); 2.08 (s, 3 H, Me); 2.25 (s, 3 H, Me); 2.35 (s, 3 H, Me); 2.41 (s, 3 H, Me); 4.08 (q, 2 H, $OC\underline{H}_2CH_3$, J = 6.9 Hz); 6.71 (s, 1 H, H_{thioph}); 6.87—6.92 (m, 1 H, H_{arom}); 7.12 (dd, 1 H, H_{arom}, J = 4.8 Hz, J = 2.1 Hz); 7.24 (d, 1 H, H_{arom}, J = 16.5 Hz); 7.35 (d, 2 H, H_{arom}, J = 8.4 Hz); 7.47 (d, 2 H, H_{arom}, J = 8.4 Hz); 8.97 (s, 1 H, CH=N); 13.12 (s, 1 H, OH). Found (%): C, 69.95; H, 5.87; N, 5.39. $C_{30}H_{30}N_2O_4S$. Calculated (%): C, 70.02; H, 5.88; N, 5.44.

(3*Z*)-1-{4-[(3,5-Diiodo-2-hydroxybenzylidene)amino]phenyl}-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-(1-methylethylidene)-pyrrolidine-2,5-dione (6j). The yield was 76%. Orange crystals, m.p. 197—199 °C (dioxane). ^{1}H NMR (DMSO-d_6), δ: 2.01 (s, 3 H, Me); 2.08 (s, 3 H, Me); 2.25 (s, 3 H, Me); 2.35 (s, 3 H, Me); 2.41 (s, 3 H, Me); 6.70 (s, 1 H, H_{thioph}); 7.38 (d, 2 H, H_{arom}, J = 8.5 Hz); 7.53 (d, 2 H, H_{arom}, J = 8.5 Hz); 8.01 (s, 1 H, H_{arom}); 8.14 (s, 1 H, H_{arom}); 8.92 (s, 1 H, CH=N); 14.57 (s, 1 H, OH); Found (%): C, 46.52; H, 3.34; N, 3.80. $C_{28}H_{24}I_2N_2O_3S$. Calculated (%): C, 46.56; H, 3.35; N, 3.88.

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