

Synthesis and photochromic properties of novel nonsymmetric dihetarylethenes based on benzindole and thiophene

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Novel nonsymmetric dihetarylethenes 3-(5-methoxy-1,2-dimethyl-1*H*-benzo[g]indol-3-yl)-4-(3-thienyl)furan-2,5-dione and 1-alkyl- and 1-aryl-3-(5-methoxy-1,2-dimethyl-1*H*-benzo[g]indol-3-yl)-4-(3-thienyl)-1(*H*)-pyrrole-2,5-diones were synthesized. The substitution of the furandione moiety for pyrroledione gives rise to the radiation and photochemical channels of deactivation of the electron excitation energy of dihetarylethenes. The products of photolysis of pyrrolediones undergo recyclization in both the ground and excited states.

Key words: benzo[g]indole, dihetarylethene, maleimide, synthesis, photochromism, fluorescence, photocolorability, molecular switches.

In recent decades, demands of optoelectronics, molecular electronics, and chemosensor engineering of novel polyfunctional materials became a powerful stimulus for the creation of various types of photochromic compounds,^{1–5} among which dihetarylethenes can be first distinguished due to high thermal stability of their isomeric forms and resistance to photodegradation.^{4,6} Fluorescence of one of the isomeric forms provides possibilities for optical information recording and creation of molecular switches with the fluorescent signal function.^{5,7} Many dihetarylethenes with various heterocyclic substituents, such as thiophene, benzothiophene, furan, benzofuran, thiazole, indole, pyrazole, and pyrrole moieties, have been synthesized to the present time. In the most part of cases, these are symmetric systems. With the purpose to extend the range of structural types of dihetarylethenes and to study their reactivity and photochromism, we synthesized and studied nonsymmetric ethenes (furan- and pyrrolediones) containing the thiophene and benzo[g]indole moieties as hetaryl residues.

Results and Discussion

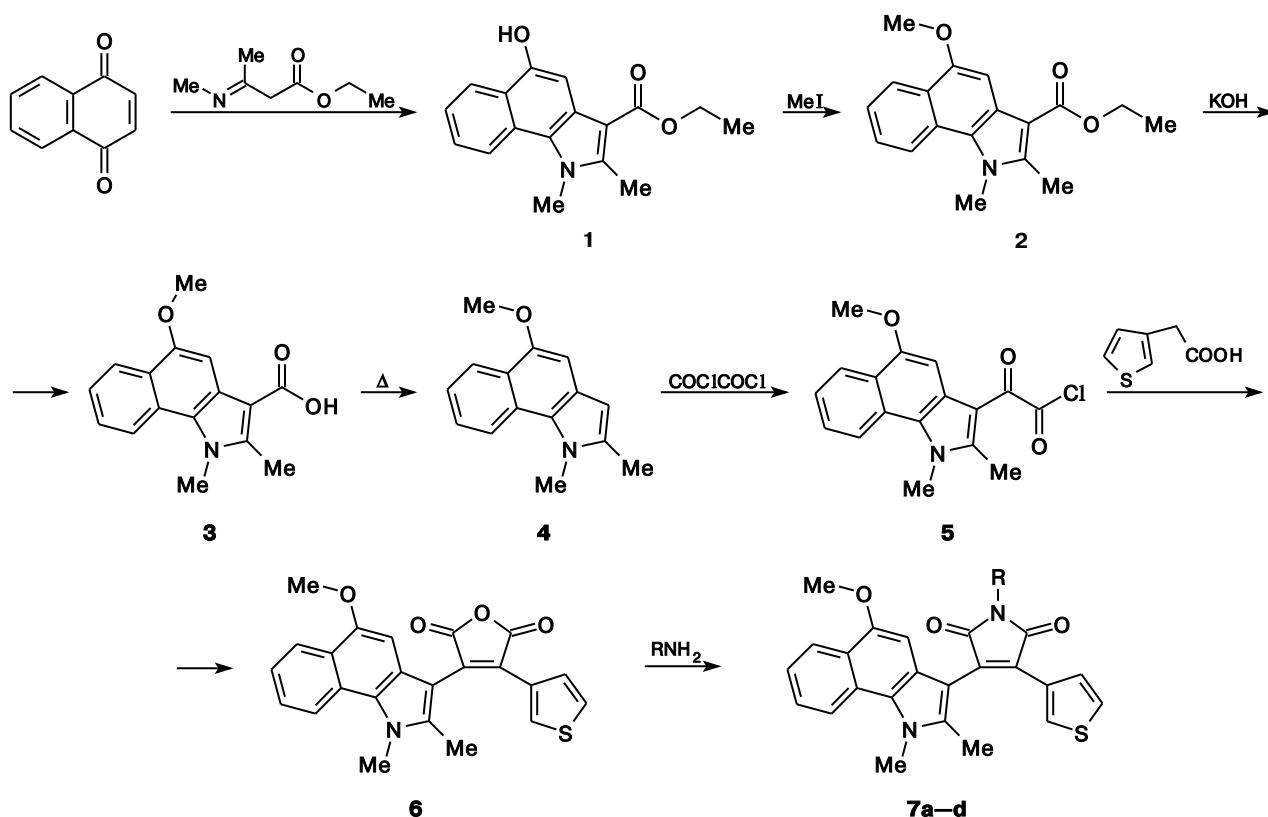
The methylation of ethyl 5-hydroxy-1,2-dimethyl-1*H*-indole-3-carboxylate (**1**)⁸ yielded ethyl 5-methoxy-1,2-dimethyl-1*H*-benzo[g]indole-3-carboxylate (**2**)⁹ which was hydrolyzed to acid **3**. Benzindole **4** was obtained by the decarboxylation of acid **3**. 2-(5-Methoxy-1,2-dimethyl-1*H*-benzo[g]indol-3-yl)oxoacetyl chloride (**5**) was

formed due to the acylation of compound **4** with oxalyl chloride, and the reaction of acid chloride **5** with 3-thienylacetic acid affords, similarly to the synthesis of indolemaleic anhydrides,¹⁰ 3-(5-methoxy-1,2-dimethyl-1*H*-benzo[g]indol-3-yl)-4-(3-thienyl)furan-2,5-dione (**6**). The reaction of furandione **6** with alkyl- and arylamines gives 1-alkyl- and 1-aryl-3-(5-methoxy-1,2-dimethyl-1*H*-benzo[g]indol-3-yl)-4-(3-thienyl)-1(*H*)-pyrrole-2,5-diones **7a–d** (Scheme 1).

The presence of the anhydride moiety in molecule **6** predetermines the appearance of the IR spectral bands at 1760 and 1830 cm^{−1} in the range of absorption of carbonyl groups. The imide structure of compounds **7a–d** is confirmed by the presence of bands at 1690 and 1750 cm^{−1}. The ¹H NMR spectra of ethenes **6** and **7a–d** contain signals of benzindole and thiophene moieties, whereas for compounds **7a–d** they contain additionally signals of the substituents at the imide nitrogen atom (see Experimental). In addition, no signals of aliphatic protons at the sp³-hybridized carbon atom of the annulated thiophene moiety makes it possible to ascribe the structure of the open form A to compounds **6** and **7a–d** (Scheme 2).

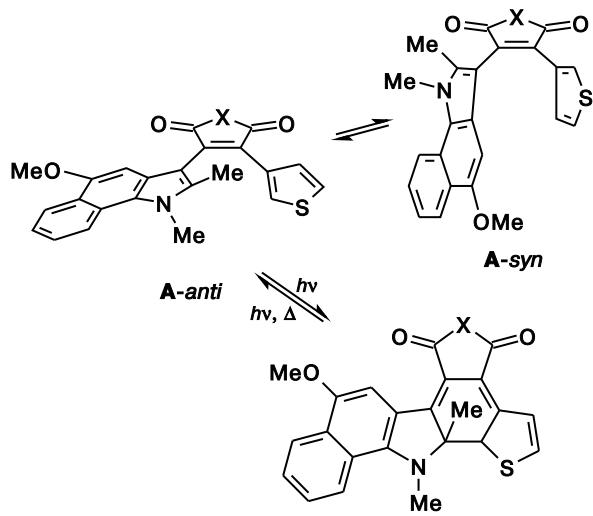
The electronic absorption spectra of dihetarylethenes **6** and **7a–d** (form A) are characterized by long-wavelength absorption bands with maxima in the range from 442 to 451 nm and the molar absorption coefficients 7190–9570 L mol^{−1} cm^{−1} (see Table 1, Fig. 1). An insignificant bathochromic shift of the long-wavelength absorption maxima of pyrrole-2,5-diones **7a**, **7b**, **7c**, and

Scheme 1



7: R = Buⁱ (**a**), CH₂Ph (**b**), Ph (**c**), 3-pyridylmethyl (**d**)

Scheme 2



X = NR

7d compared to the maximum of the corresponding absorption band of furan-2,5-dione **6** by $\Delta\lambda = 2, 5, 9$, and 8 nm, respectively, is observed (see Table 1). In the series

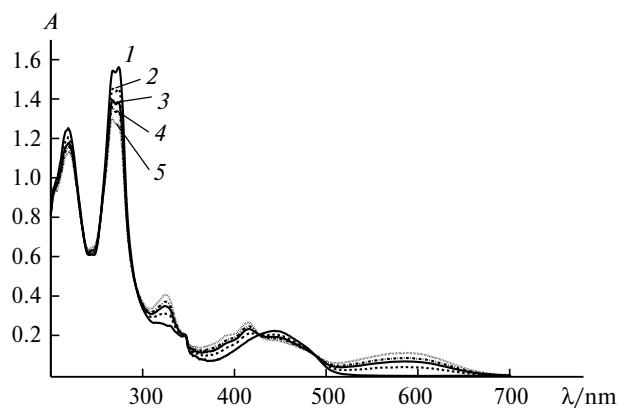
of pyrrolediones **7a–d**, the $\Delta\lambda$ value reflects the contribution of the substituents at the nitrogen atom to the electron density delocalization of the main chromophoric core.

Pyrrole-2,5-dione derivatives **7a–d** in the open form **A** manifest fluorescence properties at room temperature in heptane solutions, unlike furandione **6** that does not fluoresce under these conditions. The fluorescence band maxima of compounds **7a–d** range from 542 to 560 nm. The excitation fluorescence spectra agree well with the long-wavelength absorption bands of pyrrolediones in form **A** (see Table 1). The fluorescence quantum yields of dihetarylethenes **7a,b** several times exceed the values of fluorescence efficiency of compounds **7c,d** (see Table 1).

The irradiation of solutions of furandione **6** at 293 K gives no noticeable changes in the electronic absorption spectra. On the contrary, solutions of pyrrolediones **7a–d** are colored upon photolysis and this is accompanied by spectral changes characteristic of $(2_n+2_n+2_n)$ photocyclization reactions of dihetarylethenes.⁴ For example, the irradiation of solutions of compounds **7a–d** in heptane gives rise to new long-wavelength absorption bands with maxima at 589–603 nm, indicating the formation of cyclic isomers **B** (see Scheme 2, Table 1, Fig. 1). The influence of the substituents at the nitrogen atom of the pyrroledione moiety on the position of the long-wave-

Table 1. Spectral absorption and fluorescence characteristics of the isomeric forms of dihetarylethenes **6** and **7a–d** in heptane at 293 K

Com- ound	Initial form A				Photoinduced form B , absorption, λ_{\max}/nm	
	Absorption		Fluorescence			
	λ_{\max}/nm	$\epsilon_{\max}/\text{L mol}^{-1}\text{cm}^{-1}$	excitation	emission		
6	442	9570	—	—	—	
7a	444	7190	445	542	0.030	
7b	447	7280	445	555	0.020	
7c	451	7300	450	557	0.004	
7d	450	8480	450	560	0.005	

**Fig. 1.** Electronic absorption spectra of a solution of dihetarylethene **7a** in heptane before (1) and after irradiation with the light with the wavelength 436 nm for 1 (2), 2 (3), 3 (4), and 8 s (5) ($c = 3.1 \cdot 10^{-5} \text{ mol L}^{-1}$, $T = 293 \text{ K}$).

length absorption maxima of the forms **B** appears to the same extent as for the noncyclic isomers **A**: the conjugation of the pyrroledione ring with the π -system of the substituent at the nitrogen atom in the series **7a**, **7b**, **7d**, and **7c** leads to the bathochromic shift of the long-wavelength absorption maximum. Unlike the initial forms **A**, the cyclic isomers **B** have no fluorescence. For quantitative characterization of phototransformations, we used the parameter, being the product of the quantum yield of

the photoreaction (Φ) by the molar absorption coefficient value at the long-wavelength absorption maximum of the photoinduced form ($\epsilon_{\max}^{\text{B}}$) corresponding to one of concepts about "photocolorability" (see Ref. 11). The efficiencies of cyclization photoreactions expressed in "photocolorability" terms ($\Phi_{\text{AB}} \cdot \epsilon_{\max}^{\text{B}}$) are given in Table 2. The estimation of the quantum yields of photocyclization Φ_{AB} at the averaged value of the molar absorption coefficient $\epsilon_{\max}^{\text{B}} = 10\,000 \text{ L mol}^{-1} \text{cm}^{-1}$, taken from published data,^{12–17} gives values of 0.04–0.06.

A backward thermal process (very slow at room temperature) returning the system to the initial state is observed after the end of irradiation. The recyclization kinetics obeys the monoexponential law (Fig. 2). The rate constants of thermal reactions **B** → **A** at 293 K in heptane are listed in Table 2 and lie in the range $(0.29–3.63) \cdot 10^{-5} \text{ s}^{-1}$.

The backward photoreaction is characteristic of pyrrolediones **7a–d** along with thermal recyclization. The values obtained for efficiencies for the photorecyclization reaction **B** → **A** are estimated by $\Phi_{\text{BA}} \cdot \epsilon_{\max}^{\text{A}}$ and depend insignificantly on the substituents at the nitrogen atom of the pyrroledione moiety (see Table 2). The ratio of the quantum yields of the direct and backward photoreactions ($\Phi_{\text{AB}}/\Phi_{\text{BA}}$) for compounds **7a–d** is 0.19–0.28 and indicates a substantially higher efficiency of ring opening, which has been observed earlier for the photochromic

Table 2. Characteristics of photochromic transformations of dihetarylethenes **7a–d** in heptane at 293 K

Com- ound	Photochemical processes		Thermal decoloration	
	Coloration, $\Phi_{\text{AB}} \cdot \epsilon_{\max}^{\text{B}} \cdot 10^2$	Decoloration, $\Phi_{\text{BA}} \cdot \epsilon_{\max}^{\text{B}} \cdot 10^2$	$\Phi_{\text{AB}}/\Phi_{\text{BA}}$	$k_{\text{BA}} \cdot 10^{-5}$ $/\text{s}^{-1}$
7a	5.3	22.1	0.24	1.10
7b	6.5	23.0	0.28	0.29
7c	4.2	22.1	0.19	0.89
7d	4.2	20.9	0.20	3.63

* In $\text{L mol}^{-1} \text{cm}^{-1}$.

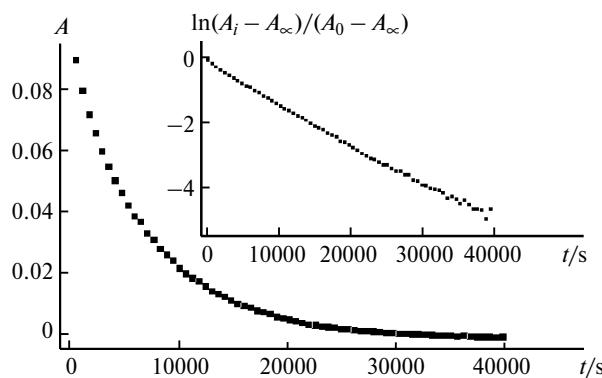


Fig. 2. Kinetic curve of the thermal relaxation of dihetarylethene **7d** in heptane ($c = 3.6 \cdot 10^{-5}$ mol L $^{-1}$, $T = 318$ K). inset: linear anamorphosis of the kinetic curve of thermal relaxation.

rearrangements of bis(2-thienyl)perfluorocyclopentene¹⁸ (see Table 2). The estimated quantum yield values for the photoreactions **B** \rightarrow **A** are 0.21–0.23. The ratios obtained for the quantum yields of direct and backward photoreactions explain the low level of the content of colored isomers in the photostationary state estimated by a low value of absorbances achieved at the absorption band maxima of the photoinduced forms. The appearance of the photostationary state due to very low rate constants of the backward thermal processes is mainly related to the strong overlapping (see Fig. 1) of the absorption bands, which is caused by the transition $S_0 \rightarrow S_1$ of the initial form **A** and the transition $S_0 \rightarrow S_2$ of the photoinduced isomer **B**, which upon the excitation of the form **A** inevitably results in the excitation of the form **B**.

Thus, we developed the procedure of synthesis and synthesized novel representatives of the class of non-symmetric dihetarylenes: 3-(5-methoxy-1,2-dimethyl-1*H*-benzo[g]indol-3-yl)-4-(3-thienyl)furan-2,5-dione and 1-alkyl- and 1-aryl-3-(5-methoxy-1,2-dimethyl-1*H*-benzo[g]indol-3-yl)-4-(3-thienyl)-1(*H*)-pyrrole-2,5-diones. Unlike furandione, pyrrolediones exhibit photochromic and fluorescence properties in solutions. Recyclization processes of the photolysis products of pyrrolediones occur in both the ground and excited states. The quantum yields of photocoloration of pyrrolediones are by 4–5 times lower than the photodecoloration quantum yields.

Experimental

Electronic absorption spectra were recorded on a Cary 100 spectrophotometer (Varian). Fluorescence measurements were carried out on a Cary Eclipse spectrofluorimeter (Varian). Fluorescence quantum yields were determined by the Parker–Reis method¹⁹ using 3-methoxybenzanthrone in toluene ($\phi = 0.1$, $\lambda_{\text{exc}} = 365$ nm) as a standard luminophore.²⁰ Solutions in a quartz cell ($l = 1$ cm) were irradiated with a DRSh-250 mercury lamp with a set of interference light filters to pick out lines of the mercury spectrum. Kinetic curves of photocoloration of dihetaryl-

ethene solutions were detected directly during irradiation on a Cary 50 spectrophotometer equipped with a thermostat. A xenon lamp with the monochromator for picking out narrow spectral lines (Newport) was used as a radiation source. The optical radiation intensity was determined with a Newport 2935 power meter of optical radiation. The optical radiation intensity at the wavelengths used (460 and 580 nm) was $4.17 \cdot 10^{15}$ and $1.33 \cdot 10^{15}$ photon s $^{-1}$, respectively. To determine the parameters $\Phi_{\text{AB}} \cdot \epsilon_{\text{max}}^{\text{B}}$ and $\Phi_{\text{BA}} \cdot \epsilon_{\text{max}}^{\text{B}}$, the slope ratio of the tangent was calculated at the initial time moment from the kinetic photocoloration and photodecoloration curves. Equal absorbances of solutions of the dihetarylenes at the irradiation wavelengths were selected in experiments on the determination of $\Phi_{\text{AB}} \cdot \epsilon_{\text{max}}^{\text{B}}$ and $\Phi_{\text{BA}} \cdot \epsilon_{\text{max}}^{\text{B}}$.

The IR spectra of samples in Nujol were recorded on a Specord 75 IR instrument. The ^1H NMR spectra in CDCl_3 were obtained on a Varian Unity-300 instrument (300 MHz) using HMDS as the external standard.

Ethyl 5-hydroxy-1,2-dimethyl-1*H*-benzo[g]indole-3-carboxylate (1). Acetic acid (20–25 mL) was added to 1,4-naphthoquinone (11 g, 0.07 mol) until an easily stirred mixture was obtained. Then ethyl *N*-methyl β -aminocrotonate (10 mL, 0.007 mol) was added by small portions at 5–10 °C with thorough stirring. The reaction mixture turned pink and gradually thickened. The reaction mixture was stored for ~14 h. A precipitate of acid **1** that formed was filtered off, thoroughly washed with a small amount of acetic acid and then with methanol, and dried in air. Recrystallization from a mixture of butanol (20 mL) and DMF (60 mL) gave pale pink crystals in 93% yield, m.p. 279–280 °C (*cf.* Ref. 8: m.p. 279–280 °C). ^1H NMR (DMSO-d_6 , δ): 1.46 (t, 3 H, Me, $J = 7.1$ Hz); 2.78 (s, 3 H, Me); 4.12 (s, 3 H, NMe); 4.35 (q, 2 H, $J = 7.1$ Hz); 7.30–7.55 (m, 2 H, Ar); 7.64 (s, 1 H, Ar); 8.22–8.30, 8.40–8.48 (both m, 1 H each, Ar); 9.42 (s, 1 H, OH). Found (%): C, 72.19; H, 6.10; N, 4.80. $\text{C}_{17}\text{H}_{17}\text{NO}_3$. Calculated (%): C, 72.07; H, 6.05; N, 4.94.

Ethyl 5-methoxy-1,2-dimethyl-1*H*-benzo[g]indole-3-carboxylate (2). Anhydrous DMSO (23 mL), NaOH thoroughly milled in a mortar (1.84 g, 46 mmol), and 3-carboethoxy-5-hydroxy-1,2-dimethyl-benzo[g]indole (6.51 g) were placed in a 100-mL three-necked flask equipped with a stirrer and a dropping funnel. Benzoindole was partially dissolved, and the reaction mixture turned dark green. At 5 °C CH_3I (7.1 mL, 114 mmol) was added dropwise to this mixture with stirring for 1 h. The reaction mixture gradually became homogeneous and turned pale pink, and a white precipitate began to form. The mixture was stirred for 4 h more and stored for ~14 h. The reaction mixture was poured to 200 mL of water with ice. An oil that formed solidified after trituration with methanol. The precipitate was filtered off, washed with water and recrystallized from a heavy petroleum ether–toluene (1 : 3) mixture. The yield was 70.2%, m.p. 143–145 °C (*cf.* Ref. 9: m.p. 228–229 °C). ^1H NMR, δ : 1.48 (t, 3 H, Me, $J = 7.1$ Hz); 2.82 (s, 3 H, Me); 4.07 (s, 3 H, NMe); 4.15 (s, 3 H, OMe); 4.42 (q, 2 H, CH_2 , $J = 7.1$ Hz); 7.40–7.60 (m, 2 H, Ar); 7.75 (s, 1 H, Ar); 8.37–8.48 (m, 2 H, Ar). Found (%): C, 72.59; H, 6.33; N, 4.80. $\text{C}_{18}\text{H}_{19}\text{NO}_3$. Calculated (%): C, 72.71; H, 6.44; N, 4.71.

5-Methoxy-1,2-dimethyl-1*H*-benzo[g]indole-3-carboxylic acid (3). Ester **2** (8.9 g, 0.03 mol) was added by portions with stirring to a melt of KOH (16.8 g, 0.3 mol) and H_2O (4.2 g) heated to 155–160 °C. The mixture was thoroughly stirred at this temperature for 30 min. Then the melt was heated to

200–210 °C and stirred at this temperature to solidification. After cooling the solid residue was dissolved in water (700 mL). The resulting solution was treated with active carbon, filtered, and acidified with dilute hydrochloric acid to the acidic pH. A precipitate of acid **3** that formed was filtered off, and thoroughly washed with water. The yield was 93%, decomp. temp. 210–220 °C. ¹H NMR (DMSO-d₆), δ: 2.80 (s, 3 H, Me); 4.00 (s, 3 H, NMe); 4.17 (s, 3 H, OMe); 7.32–7.60, 8.13–8.60 (both m, 2 H each, Ar); 7.72 (s, 1 H, Ar); 11.82 (br.s, 1 H, OH). Found (%): C, 71.52; H, 5.83; N, 5.17. C₁₆H₁₅NO₃. Calculated (%): C, 71.36; H, 5.61; N, 5.20.

5-Methoxy-1,2-dimethyl-1H-benzo[g]indole (4). Acid **3** (5 g) was heated at 230–245 °C until carbon dioxide stopped evolving (5–10 min). Upon cooling the resulting solid product was recrystallized from butanol. The yield was 90%, m.p. 123–124 °C. ¹H NMR, δ: 2.50 (s, 3 H, Me); 4.02 (s, 3 H, NMe); 4.13 (s, 3 H, OMe); 6.33, 7.0 (both s, 1 H each, Ar); 7.36–7.58 (m, 2 H, Ar); 8.35–8.50 (m, 2 H, Ar). Found (%): C, 79.7; H, 6.03; N, 6.70. C₁₅H₁₅NO. Calculated (%): C, 79.97; H, 6.71; N, 6.22.

2-(5-Methoxy-1,2-dimethyl-1H-benzo[g]indol-3-yl)oxoacetyl chloride (5). A solution of benzoindole **4** (450 mg, 2 mmol) in diethyl ether (20 mL) was cooled to 0 °C, and oxalyl chloride (0.25 mL) was slowly added dropwise. Orange-yellow needles gradually precipitated from the solution. The mixture was stored for 40 min at ~20 °C. A precipitate of oxoacetyl chloride **5** was filtered off and washed with ether. The yield was 87%. ¹H NMR, δ: 2.74 (s, 3 H, Me); 4.07 (s, 3 H, NMe); 4.19 (s, 3 H, OMe); 7.25–7.45 (m, 3 H, Ar), 8.35–8.48 (m, 2 H, Ar). Found (%): C, 63.47; H, 4.50; N, 4.79. C₁₆H₁₄CINO₃. Calculated (%): C, 63.27; H, 4.65; N, 4.61.

3-(5-Methoxy-1,2-dimethyl-1H-benzo[g]indol-3-yl)-4-(3-thienyl)furan-2,5-dione (6). 3-Thienylacetic acid (142 mg, 1 mmol) and freshly distilled triethylamine (0.3 mL) were added to a solution of oxoacetyl chloride **5** (315 mg, 1 mmol) in anhydrous benzene (8 mL). The solution turned orange-red, and triethylamine hydrochloride precipitated. The reaction mixture was stored for ~14 h. The precipitate was filtered off. Benzene was removed on a rotary evaporator. The yield of furandione **6** was 36.5%. The product obtained was purified by column chromatography (silica gel–chloroform), chloroform was distilled off, and the residue was twice recrystallized from MeCN. Red-orange crystals, m.p. 259–260 °C. IR, v/cm⁻¹: 1760, 1830 (C=O). ¹H NMR, δ: 2.48 (s, 3 H, Me); 3.66 (s, 3 H, NMe); 4.24 (s, 3 H, OMe); 6.30 (s, 1 H, Ar); 7.18–7.28, 7.42–7.66, 8.36–8.52 (all m, 2 H each, Ar); 8.20 (m, 1 H, Ar). Found (%): C, 68.59; H, 4.35; N, 3.41. C₂₃H₁₇NO₄S. Calculated (%): C, 68.47; H, 4.25; N, 3.47.

Synthesis of 3-(5-methoxy-1,2-dimethyl-1H-benzo[g]indol-3-yl)-4-(3-thienyl)-1H-pyrrole-2,5-diones 7a–d (general procedure). The corresponding amine (3.9 mmol) was added to furandione **6** (0.13 mmol), and the mixture was heated for 10 min. Then isopropyl alcohol (10 mL) was poured to the reaction mixture, and the mixture was refluxed for 15 min. The mixture was cooled, and the solvent was distilled off. The pyrrolediones obtained were purified by column chromatography (silica gel–chloroform), and chloroform was distilled off. The products were dried in air. The yields of pyrrolediones were 33–80%.

1-Isobutyl-3-(5-methoxy-1,2-dimethyl-1H-benzo[g]indol-3-yl)-4-(3-thienyl)-1H-pyrrole-2,5-dione (7a) was synthesized

according to the general procedure from furandione **6** and isobutylamine. The yield was 33.3%. Orange crystals, m.p. 150–151 °C. IR, v/cm⁻¹: 1690, 1750 (C=O). ¹H NMR, δ: 1.00 (d, 6 H, Me, J = 7.2 Hz); 2.06–2.24 (m, 1 H, CH); 2.43 (s, 3 H, Me); 3.51 (m, 2 H, CH₂); 3.64 (s, 3 H, NMe); 4.21 (s, 3 H, OMe); 6.40, 8.12 (both s, 1 H each, Ar); 7.04–7.20, 7.40–7.62, 8.36–8.52 (all m, 2 H each, Ar). Found (%): C, 70.69; H, 5.65; N, 6.03. C₂₇H₂₆N₂O₃S. Calculated (%): C, 70.72; H, 5.71; N, 6.11.

1-Benzyl-3-(5-methoxy-1,2-dimethyl-1H-benzo[g]indol-3-yl)-4-(3-thienyl)-1H-pyrrole-2,5-dione (7b) was synthesized from furandione **6** and benzylamine according to the general procedure. The yield was 73.5%. Orange crystals, m.p. 199–200 °C. IR, v/cm⁻¹: 1690, 1750 (C=O). ¹H NMR, δ: 2.43 (s, 3 H, Me); 3.64 (s, 3 H, NMe); 4.21 (s, 3 H, OMe); 4.85 (s, 2 H, CH₂); 7.05–7.30 (m, 10 H, Ar); 8.11 (s, 1 H, Ar); 8.35 (d, 1 H, Ar, J = 8.6 Hz); 8.94 (d, 1 H, Ar, J = 8.9 Hz). Found (%): C, 73.11; H, 4.87; N, 5.61. C₃₀H₂₄N₂O₃S. Calculated (%): C, 73.15; H, 4.91; N, 5.69.

3-(5-Methoxy-1,2-dimethyl-1H-benzo[g]indol-3-yl)-4-(3-thienyl)-1-phenyl-1H-pyrrole-2,5-dione (7c) was synthesized from furandione **6** and aniline according to the general procedure. The yield was 80.7%. Orange crystals, m.p. 235–236 °C. IR, v/cm⁻¹: 1690, 1750 (C=O). ¹H NMR, δ: 2.52 (s, 3 H, Me); 3.66 (s, 3 H, NMe); 4.28 (s, 3 H, OMe); 6.44 (s, 1 H, Ar); 7.10–7.28 (m, 2 H, Ar); 7.36–7.68 (m, 7 H, Ar); 8.21 (m, 1 H, Ar); 8.36–8.52 (m, 2 H, Ar). Found (%): C, 72.71; H, 4.57; N, 5.80. C₂₉H₂₂N₂O₃S. Calculated (%): C, 72.78; H, 4.63; N, 5.85.

3-(5-Methoxy-1,2-dimethyl-1H-benzo[g]indol-3-yl)-1-methylpyridin-3-yl-4-(3-thienyl)-1H-pyrrole-2,5-dione (7d) was synthesized from furandione **6** and 3-pyridylmethylaniline according to the general procedure. The yield was 62.5%. Orange crystals, m.p. 200–201 °C. IR, v/cm⁻¹: 1690, 1750 (C=O). ¹H NMR, δ: 2.44 (s, 3 H, Me); 3.62 (s, 3 H, NMe); 4.20 (s, 3 H, OMe); 4.80–4.98 (m, 2 H, CH₂); 6.38 (s, 1 H, Ar); 7.08–7.20, 7.32–7.48 (both m, 2 H each, Ar); 7.54–7.66, 7.90–7.98, 8.08, 8.80 (all m, 1 H each, Ar); 8.32–8.64 (m, 3 H, Ar). Found (%): C, 70.52; H, 4.66; N, 4.84. C₂₉H₂₃N₃O₃S. Calculated (%): C, 70.57; H, 4.70; N, 4.81.

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