Russian Chemical Bulletin, International Edition, Vol. 60, No. 9, pp. 1899—1905, September, 2011

Synthesis and photochromic properties of new nonsymmetric dihetarylethenes — indole and thiophene derivatives

N. I. Makarova,[a] P. V. Levchenko,[a] E. N. Shepelenko,[b] A. V. Metelitsa,[a]★ V. S. Kozyrev,[a] V. P. Rybalkin,[b] V. A. Bren´,[a] and V. I. Minkin[a,b]

[a]*Institute of Physical and Organic Chemistry, Southern Federal University,*
194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation.
Fax: +7 (863) 243 4667. E-mail: photo@ipoc.rsu.ru
[b]*Southern Scientific Center, Russian Academy of Sciences,*
41 prosp. Chekhova, 344006 Rostov-on-Don, Russian Federation

New nonsymmetric dihetarylethenes were synthesized: 3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)furan-2,5-dione and photochromic 1-alkyl-(1-aryl)-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)-1(*H*)-pyrrole-2,5-diones. The absence of benzo-annulation in the indole moiety results in the enhancement of the efficiencies of fluorescence and photocyclization of noncyclic isomers compared to the benzoindole derivatives.

Key words: indole, thiophene, furan-2,5-dione, pyrrole-2,5-dione dihetarylethene, synthesis, photochromism, fluorescence, photocolorability, molecular switches.

Interest in preparing new photochromic dihetarylethenes is due to their ability to exist as two thermally stable forms, which determines diverse possibilities of their use, including that for manufacture of materials of optical information recording and molecular switches.[1—3] A special role among dihetarylethenes belongs to the compounds based on derivatives of maleic anhydride, *viz.*, maleinimides, which, unlike perfluorocyclopentene derivatives of diarylethenes, assume various structure functionalization without a substantial change in the spectral and kinetic characteristics predominantly determined by heterocyclic moieties. The possibility of substitution in the bridging moiety considerably extends areas of practical use of dihetarylethenes with retention of the best photochromic characteristics attained by the modification of heterocyclic moieties. In particular, introduction of cationic moieties is interesting for the development of hybrid supramolecular structures including paramagnetic anions of heteropolyacids and polyfunctional materials with photomodulated magnetic characteristics. The inclusion of long-chain alkyl substituents is necessary for the formation of the Langmuir—Blodgett films, and the production of photochromic polymers is possible using substitution by groups that make it possible to carry out dihetarylethene copolymerization.

Various derivatives of maleic anhydride and maleinimides containing thiophene,[4—6] selenophene, indole,[7] benzothiophene,[8,9] thienopyrrole,[10] and coumarin[11] fragments were synthesized, and nonsymmetric dihetarylethenes exhibit the most interesting properties. Earlier[12] obtained 3-(5-methoxy-1,2-dimethyl-1*H*-benzo[*g*]indol-3-yl)-4-(3-thienyl)-1(*H*)-pyrrole-2,5-diones substituted by position 1 manifest fluorescence of noncyclic isomers along with photochromism. However, both the fluorescence and photocyclization of these compounds are lowly efficient. The purpose of the present work was to enhance the efficiency of photoinitiated processes in molecules of nonsymmetric dihetarylethenes due to the structural modification of the compounds aimed at replacing the benzoindole moiety by indole.

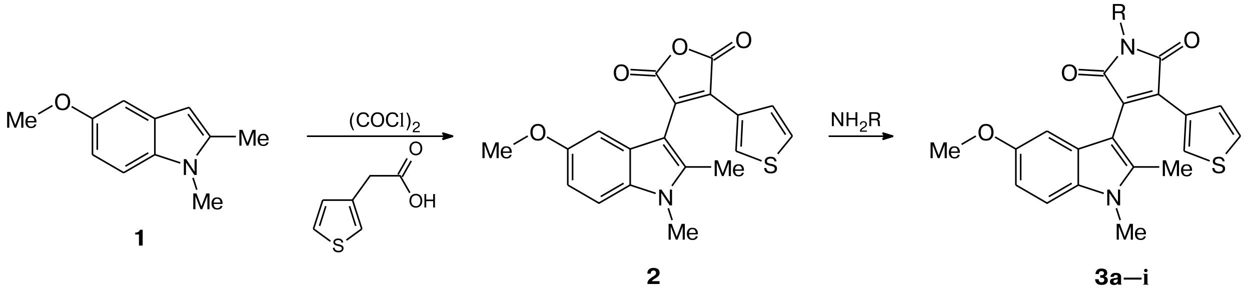
Results and Discussion

The starting 5-methoxy-1,2-dimethylindole (**1**) was synthesized using a known procedure.[13] 3-(5-Dimethoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)furan-2,5-dione (**2**) was obtained by the acylation of indole **1** with oxalyl chloride followed by the treatment with a solution of 3-thienylacetic acid in the presence of triethylamine (similarly to the method described previously[9]). Pyrrole-2,5-diones **3a—i** were synthesized by the action of alkyl- and arylamines on furan-2,5-dione **2** (Scheme 1).

The carbonyl groups of the furan-2,5-dione moiety of dihetarylethene **2** appear in the IR spectra as stretching vibration bands at 1750 and 1820 cm^{-1}. The IR spectra of 3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)-1*H*-pyrrole-2,5-diones **3** substituted in position 1 exhibit the characteristic stretching vibration bands of the carbonyl groups of the imide moiety in the region 1689—1704 cm^{-1}.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1866—1872, September, 2011.

Scheme 1



3: R = Ph (**a**), 4-MeC$_6$H$_4$ (**b**), 4-MeOC$_6$H$_4$ (**c**), 4-ClC$_6$H$_4$ (**d**), Bn (**e**), Bu^i (**f**), *cyclo*-C$_5$H$_9$ (**g**), *cyclo*-C$_7$H$_{13}$ (**h**), *cyclo*-C$_{12}$H$_{23}$ (**i**)

The ^{1}H NMR spectra of solutions of compounds **2** and **3** in the strong field contain three three-proton singlet signals of the indole moiety: of the 2-methyl (δ ~2.40, *N*-methyl (δ ~3.50), and 5-methoxy groups (δ ~3.72).

The downfield regions of these spectra exhibit signals of three aromatic protons of the indole cycle in positions 4, 6, and 7 at δ ~6.35, ~6.80, and 7.20, respectively, with the chemical shifts and spin-spin coupling constants (*J*) characteristic of the 5-methoxyindole substituent; the signals of protons of the thiophene ring in positions 4 and 5 are observed in the region δ 7.10—7.30, and the signals of those in position 2 are observed in the region of 8.00 ppm. Their chemical shifts and *J* constants are also characteristic of thiophene substituted in position 3, which allows one to ascribe the structure of open form **A** to these dihetarylethenes (Scheme 2). In addition, the signals of protons of the substituents at the pyrrolic nitrogen atom are detected in the ^{1}H NMR spectra of solutions of compounds **3a—i**. Thus, compound **2** has the structure of 3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)furan-2,5-dione, and compounds **3a—i** are 3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)-1*H*-pyrrole-2,5-diones substituted at the pyrrolic nitrogen atom (see Scheme 2).

The electronic absorption spectra (EAS) of the synthesized nonsymmetric dihetarylethenes are characterized by long-wavelength absorption bands with maxima at 453—461 nm. The molar absorption coefficients at the absorption band maxima take values of (6.08—9.59) • 10^3 L mol^{-1} cm^{-1}. The hypsochromic shift of the long-wavelength absorption band maxima, whose value is 7—8 nm, is observed in the series of pyrroledione derivatives **3a—i** on going from compounds **3a—d** with *N*-aryl substituents to dihetarylethenes **3f—i** with *N*-alkyl substituents (Table 1). The characteristics of the EAS of furandione **2** are similar to the corresponding parameters of *N*-alkyl-substituted pyrolediones (see Table 1).

The mentioned correlations between the structure and absorption properties of dihetarylethenes based on 5-methoxyindole coincide with those determined earlier[12] for analogous dihetarylethenes based on 5-methoxy-1*H*-benzo[*g*]indole. It should be mentioned that benzoannulation in the indole moiety results in the hypsochromic shift of the long-wavelength absorption band maxima by ~10 nm in nonsymmetric dihetarylethenes based on both furandione and pyrroledione.

Dihetarylethenes **2** and **3a—i** possess fluorescence with band maxima at 533—555 nm. The fluorescence excitation spectra are well consistent with the absorption spectra, evidencing unambiguously that the observed fluorescence belongs to noncyclic isomers **A** of dihetarylethenes **2** and **3a—i** (Fig. 1, see Table 1).

The fluorescence efficiency of compounds **2** and **3a—i** vary in wide ranges depending on the structure (see Table 1). The highest fluorescence quantum yields attaining values of 0.20—0.22 are observed for *N*-alkyl pyrolediones **3e—i**.

Scheme 2

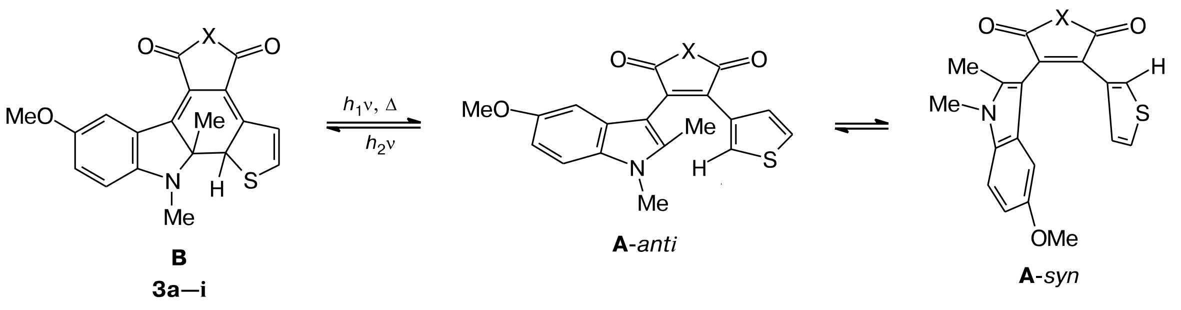


Table 1. Spectral absorption and spectral fluorescence characteristics of isomeric forms of dihetarylethenes **2** and **3a**—**i** in heptane at 293 K

Compound	Initial form, **A**				Photoinduced form, **B**, absorbance, λ_{max}/nm
	Absorbance, λ_{max}/nm ($\varepsilon \cdot 10^{-3}$)	Fluorescence			
		Excitation, λ_{max}/nm	Emission, λ_{max}/nm	Quantum yield, ϕ	
2	453 (7.40)	462	540	0.02	—
3a	461 (6.08)	463	551	0.12	563
3b	461 (6.67)	462	552	0.04	563
3c	461 (7.22)	458	550	0.001	563 sh
3d	467 (8.29)	468	555	0.13	572
3e	458 (7.33)	459	534	0.20	553
3f	453 (9.59)	455	533	0.20	552
3g	454 (7.40)	455	534	0.20	551
3h	453 (9.00)	454	533	0.22	551
3i	453 (7.70)	455	534	0.21	552

Among the *N*-aryl derivatives, the fluorescence quantum yields vary from 0.001—0.04 for compounds **3b,c** with electron-releasing substituents in the phenyl ring to 0.12 and 0.13 for unsubstituted dihetarylethene **3a** and 4-chloro-substituted compound **3d**, respectively. A comparison of the fluorescence efficiency of the indole derivatives considered in the present work and the corresponding benzoindole derivatives of nonsymmetric dihetarylethenes studied earlier[12] makes it possible to draw an important conclusion: benzoannulation to the indole moiety of nonsymmetric dihetarylethenes based on furandione and pyrroledione decreases the fluorescence quantum yields of the open isomers by a factor of 10—30.

The differences caused by the ethene ring structure are observed upon irradiation of solutions of dihetarylethenes **2** and **3a**—**i** in hexane. The irradiation of furandione derivative **2** does result in any visible changes in the EAS. On the contrary, photolysis of solutions of pyrrolediones induces their coloration accompanied by the appearance and growth of absorption bands in the long-wavelength region of the EAS and also by a decrease in the characteristic bands of transitions $S_0 \rightarrow S_1$ of dihetarylethenes (Fig. 2). The long-wavelength absorption band maxima lie in the region 551—572 nm (see Table 1). This behavior is characteristic of the photocyclization of dihetarylethenes **A** → **B**.[1]

The influence of structural peculiarities of dihetarylethenes on the positions of the long-wavelength absorption band maxima of closed isomers **B** is manifested to the same extent as for open forms **A** (see Table 1).

Unlike the starting forms **A**, closed isomers **B** have no fluorescence.

For the quantitative characterization of the phototransformations, we determined the values of "colorability" representing the product of the quantum yield of the photo-

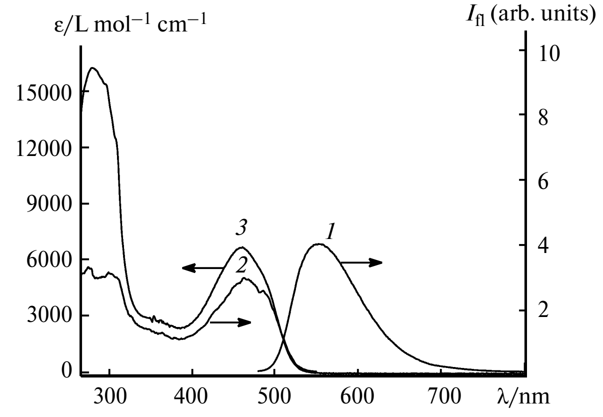


Fig. 1. Fluorescence (*1*) (λ_{exc} = 460 nm), fluorescence excitation (*2*) (λ_{app} = 560 nm), and absorption (*3*) spectra of a solution of compound **3b** in heptane (T = 293 K).

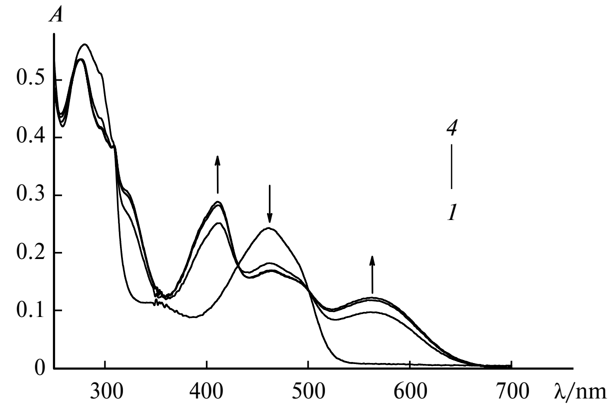


Fig. 2. Electronic absorption spectra of a solution of dihetarylethene **3a** in heptane before (*1*) and after consecutive irradiation with λ = 436 nm (*2—4*) recorded at an interval of 2 min ($C = 4 \cdot 10^{-5}$ mol L^{-1}, l = 1 cm, T = 293 K).

Table 2. Characteristics of photochromic transformations of dihetarylethenes **3a—i** in heptane at 293 K

Compound	Photochemical processes: Coloration, $\Phi_{AB} \cdot \varepsilon_{max}{}^{B} \cdot 10^3$ / L mol^{-1} cm^{-1}	Bleaching, $\Phi_{BA} \cdot \varepsilon_{max}{}^{B} \cdot 10^3$ / L mol^{-1} cm^{-1}	Φ_{AB}/Φ_{BA}	Thermobleaching, $k_{BA} \cdot 10^{-5}$/s^{-1}
3a	1.7	2.2	0.77	14.0
3b	2.2	2.3	0.96	17.3
3c	—	—	—	12.8
3d	1.9	2.0	0.95	9.8
3e	1.6	2.8	0.57	2.6
3f	2.3	2.4	0.96	6.6
3g	2.1	2.6	0.81	1.4
3h	1.9	2.8	0.68	1.7
3i	2.6	2.8	0.93	1.9

reaction (Φ) on the value of molar absorption coefficient at the long-wavelength absorption band maximum of the photoinduced form ($\varepsilon_{max}{}^{B}$). The efficiencies of cyclization photoreactions expressed in terms of "colorability" ($\Phi_{AB} \cdot \varepsilon_{max}{}^{B}$) are listed in Table 2. The values obtained for colorabilities of dihetarylethenes **3a**—**i** based on 5-methoxyindole exceed the colorability of dihetarylethenes based on 5-methoxy-1*H*-benzoindole by a factor of 3—4.[12] The estimation of the quantum yields of photocyclization Φ_{AB} of pyrolediones of the indole series at the averaged value of molar extinction coefficient $\varepsilon_{max}{}^{B} = 10\,000$ L mol^{-1} cm^{-1} taken from the literature data[14—19] gives the values 0.16—0.26. It is noteworthy that in the case of methoxy-substituted dihetarylethene **3c** the level of photocoloration is ultimately low, which does not allow one to estimate quantitatively the efficiency of photocyclization.

The established dependence of the efficiencies of photoinitiated processes, *viz.*, fluorescence and photocyclization, in molecules of nonsymmetric dihetarylethenes on the benzoannulation of the indole moiety can be related to the influence of these structural modifications on the position of conformational equilibrium of the noncyclic isomers. It is most likely that the benzoannulation of the indole fragment increases the content of isomers existing in the "inactive" parallel conformation (**A**-*syn*) and thus decreases the fluorescence and photocyclization efficiencies.

After irradiation was stopped, the very low (at 293 K) backward thermal recyclization **B** → **A** is observed, whose kinetics obeys the multiexponential law. The rate constants of dark reactions **B** → **A** in heptane (see Table 2) are $(1.4—17.3) \cdot 10^{-5} \cdot \mathrm{s}^{-1}$. Thermal recyclization of *N*-aryl derivatives of dihetarylethenes **3a**—**d** is faster than that for *N*-alkyl compounds **3e**—**i**. This is probably caused by the additional stabilization of the closed form in the latter due to more pronounced electron-donor properties of the alkyl substituents.

Closed isomers **B** of dihetarylethenes **3a**—**i** exhibit photochemical activity related to photoinduced ring opening resulting in the formation of the starting forms **A** of dihetarylethenes. The values obtained for efficiencies of photocyclization reactions **B** → **A**, estimated using parameter $\Phi_{BA} \cdot \varepsilon_{max}$, depend on the substituent at the nitrogen atom of the pyrroledione moiety: they are higher in the case of alkyl substituents of compounds **3e**—**i** (see Table 2). The ratio of quantum yields of the forward and backward photoreactions (Φ_{AB}/Φ_{BA}) for compounds **3a**—**i** is 0.57—0.96 and indicates that the efficiencies of the cyclization and ring opening photoreactions are approximately equal in the most part of cases, unlike the benzoindole derivatives for which the ratio is 0.19—0.28 (see Table 2).[12] The estimated values of quantum yields for photoreactions **B** → **A** of dihetarylethenes **3a**—**i** are 0.20—0.28 as in the case of the benzoindole analogs.

No complete photoconversion of the initial form **A** to cyclic form **B** is observed for compounds **3a**—**i**. Prolonged irradiation results in the establishment of the photostationary state, which is indicated by a rather high level of the relative fluorescence intensity of cyclic forms **A** under the conditions where UV irradiation does not already induce changes in the EAS (Fig. 3). The photostationary state exists due to the very low rate constants of backward thermal processes, which is evidently caused by the strong overlapping of the absorption bands attributed to transition $S_0 \rightarrow S_1$ of the initial form **A** and transition $S_0 \rightarrow S_2$ of photoinduced isomer **B**, which inevitably leads to the excitation of form **B** upon the excitation of form **A**. The low yield of photocoloration of 4-methoxyphenyl-substituted dihetarylethene **3c** can be a consequence of the appearance of the photostationary state with an insignificant content of cyclic isomers **B**.

Dihetarylethenes **3a**—**i** are resistant to photodegradation. For instance, no decrease in the absorbance of the photostationary state was observed within 10 cycles photocoloration—photobleaching (Fig. 4).

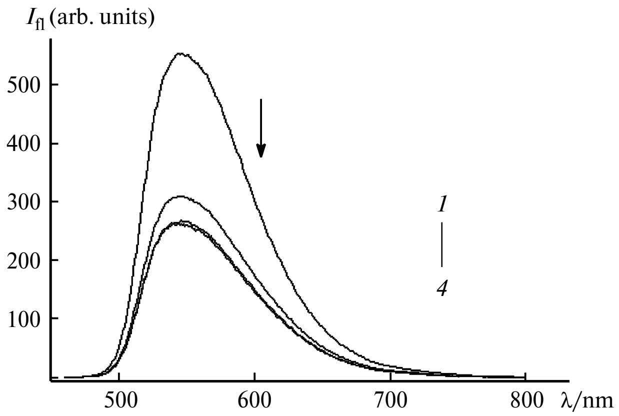


Fig. 3. Fluorescence spectra of a solution of dihetarylethene **3a** in heptane ($C = 4 \cdot 10^{-5}$ mol L^{-1}) before (*1*) and after consecutive irradiation with λ = 436 nm (*2—4*) recorded at an interval of 2 min at the excitation wavelength 420 nm, 293 K, and a layer thickness of 1 cm.

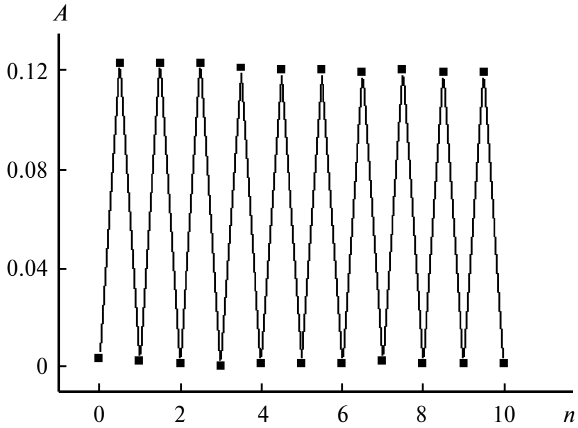


Fig. 4. Change in the absorbance of a solution of dihetarylethene **3a** in heptane at the absorption band maximum of form **B** (564 nm) upon the repetition of photocoloration cycles (irradiation with λ = 436 nm for 6 min)—photobleaching (irradiation with λ = 546 nm for 6 min); *n* is the number of cycles.

Thus, we synthesized the new representatives of the class of nonsymmetric dihetarylethenes: photochemically inactive 3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)furan-2,5-dione and photochromic 1-alkyl-(1-aryl)-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)-1(*H*)-pyrrole-2,5-diones. The absence of benzoannulation in the indole moiety results in the enhancement of the fluorescence and photocyclization efficiencies of the noncyclic isomers. Recyclization processes of the products of photolysis of pyrolediones occur in both the ground and excited states.

Experimental

Electronic absorption spectra were obtained on a Cary 100 spectrophotometer (Varian). Fluorescence was measured on a Cary Eclipse fluorimeter (Varian). The fluorescence quantum yields were determined by the Parker—Rice method[20] using 3-methoxybenzanthrone in toluene (φ = 0.1, λ = 365 nm) as a standard luminophore.[21] The solutions were irradiated with a DRSh-250 mercury lamp using a set of interferential light filters to pick out mercury spectral lines in a quartz cell (l = 1 cm). The kinetic photocoloration curves of dihetarylethene solutions were recorded directly during irradiation on a Cary 50 spectrophotometer with an attachment for thermostatic control of the samples. A xenon lamp with a monochromator for picking out narrow spectral lines (Newport) was used as a radiation source. The absorbance intensity was determined using a Newport 2935 power meter for 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. The slope ratio of the tangent at the initial time moment was calculated from the kinetic photocoloration and photobleaching curves to determine parameters $\Phi_{\mathbf{AB}} \cdot \varepsilon_{\max}{}^{\mathbf{B}}$ and $\Phi_{\mathbf{BA}} \cdot \varepsilon_{\max}{}^{\mathbf{B}}$. In experiments on the determination of $\Phi_{\mathbf{AB}} \cdot \varepsilon_{\max}{}^{\mathbf{B}}$ and $\Phi_{\mathbf{BA}} \cdot \varepsilon_{\max}{}^{\mathbf{B}}$, the absorbance of solutions of the dihetarylethenes studied at the irradiation wavelengths was selected to be equal. The ^{1}H NMR spectra were obtained on a Varian Unity-300 spectrometer (300 MHz) in $CDCl_3$ and DMSO-d$_6$ using HMDS as an external standard. Vibrational spectra were detected on a Varian Excalibur 3100 FT-IR by the frustrated total internal reflection (FTIR) method.

5-Methoxy-1,2-dimethylindole (1) was synthesized according to a procedure described earlier,[13] m.p. 67—68 °C.

3-(5-Methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)furan-2,5-dione (2). Oxalyl chloride (0.26 mL, 3 mmol) was added dropwise to a solution of compound **1** (0.5 g, 3 mmol) in 1,2-dichloroethane (5 mL) at 0 °C. The reaction mixture was stored for 30 min, then the solvent was distilled off, and a solution of 3-thiopheneacetic acid (0.43 g, 3 mmol) and triethylamine (2.1 mL, 15 mmol) in 1,2-dichloroethane (7 mL) was added to the dry residue. The mixture was stored for 15 min at 0 °C and then refluxed for 1 h and cooled. The precipitate that formed was filtered off, the solvent was distilled off, the product was purified by column chromatography (silica gel—chloroform), and chloroform was distilled off. The product was recrystallized from MeOH. The yield was 0.2 g (18.9%), red crystals, m.p. 203—204 °C. IR, ν/cm^{-1}: 1750, 1820 (C=O). ^{1}H NMR ($CDCl_3$), δ: 2.42, 3.53, 3.75 (all s, 3 H each, Me, NMe, OMe); 6.32 (d, 1 H, H(4) of indole, J = 2.3 Hz); 6.84 (dd, 1 H, H(6) of indole, J_1 = 2.3 Hz, J_2 = 8.8 Hz); 7.20—7.26 (m, 3 H, H(4) of thiophene, H(7) of indole, H(5) of thiophene); 8.11 (dd, 1 H, H(2) of thiophene, J_1 = 2.9 Hz, J_2 = 1.3 Hz). Found (%): C, 64.01; H, 4.05; N, 3.83. $C_{19}H_{15}NO_4S$. Calculated (%): C, 64.58; H, 4.28; N, 3.96.

Synthesis of 1-aryl-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)-1*H*-pyrrole-2,5-diones 3a—d (general procedure). The corresponding arylamine (0.42 mmol) was added to a solution of compound **2** (0.28 mmol) in AcOH (4 mL). The reaction mixture was refluxed for 2 h and then cooled, the solvent was evaporated to 2 mL, the precipitate that formed was filtered off, and the obtained product was recrystallized from BuOH.

3-(5-Methoxy-1,2-dimethyl-1*H*-indol-3-yl)-1-phenyl-4-(3-thienyl)-1*H*-pyrrole-2,5-dione (3a). The yield was 0.1 g (83%), orange crystals, m.p. 200—201 °C. IR, ν/cm^{-1}: 1706 (C=O). ^{1}H NMR ($CDCl_3$), δ: 2.39, 3.52, 3.72 (all s, 3 H each, Me, NMe, OMe); 6.40 (d, 1 H, H(4) of indole, J = 2.3 Hz); 6.79 (dd, 1 H, H(6) of indole, J_1 = 2.3 Hz, J_2 = 8.8 Hz); 7.15 (dd, 1 H, H(4) of thiophene, J_1 = 2.9 Hz, J_2 = 5.1 Hz); 7.18 (d, 1 H, H(7) of indole, J = 8.8 Hz); 7.22 (dd, 1 H, H(5) of thiophene, J_1 = 1.3 Hz, J_2 = 5.1 Hz); 7.28—7.58 (m, 5 H, Ar); 8.08 (dd, 1 H, H(2) of thiophene, J_1 = 2.9 Hz, J_2 = 1.3 Hz). Found (%): C, 70.07; H, 4.61; N, 6.50. $C_{25}H_{20}N_2O_3S$. Calculated (%): C, 70.07; H, 4.70; N, 6.54.

3-(5-Methoxy-1,2-dimethyl-1*H*-indol-3-yl)-1-(4-methylphenyl)-4-(3-thienyl)-1*H*-pyrrole-2,5-dione (3b). The yield was 0.1 g (81%), orange crystals, m.p. 202—203 °C. IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR (CDCl$_3$), δ: 2.38, 2.39 (both s, 3 H, Me); 3.51, 3.71 (both s, 3 H each, NMe, OMe); 6.39 (d, 1 H, H(4) of indole, J = 2.3 Hz); 6.79 (dd, 1 H, H(6) of indole, J_1 = 2.3 Hz, J_2 = 8.8 Hz); 7.14 (dd, 1 H, H(4) of thiophene, J_1 = 2.9 Hz, J_2 = 5.1 Hz); 7.17 (d, 1 H, H(7) of indole, J = 8.8 Hz); 7.22 (dd, 1 H, H(5) of thiophene, J_1 = 1.2 Hz, J_2 = 5.1 Hz); 7.24—7.39 (m, 4 H, Ar); 8.08 (dd, 1 H, H(2) of thiophene, J_1 = 2.9 Hz, J_2 = 1.2 Hz). Found (%): C, 70.49; H, 4.98; N, 6.29. $C_{26}H_{22}N_2O_3S$. Calculated (%): C, 70.57; H, 5.01; N, 6.33.

3-(5-Methoxy-1,2-dimethyl-1*H*-indol-3-yl)-1-(4-methoxyphenyl)-4-(3-thienyl)-1*H*-pyrrole-2,5-dione (3c). The yield was 0.1 g (81%), orange crystals, m.p. 161—162 °C. IR, ν/cm^{-1}: 1704 (C=O). ^{1}H NMR (CDCl$_3$), δ: 2.39, 3.51, 3.71, 3.82 (all s, 3 H each, C(2)Me, NMe, OMe, OMe); 6.39 (d, 1 H, H(4) of indole, J = 2.4 Hz); 6.79 (dd, 1 H, H(6) of indole, J_1 = 2.4 Hz, J_2 = 8.8 Hz); 6.94—7.02 (m, 2 H, Ar); 7.14 (dd, 1 H, H(4) of thiophene, J_1 = 2.9 Hz, J_2 = 5.1 Hz); 7.17 (d, 1 H, H(7) of indole, J = 8.8 Hz); 7.21 (dd, 1 H, H(5) of thiophene, J_1 = 1.2 Hz, J_2 = 5.1 Hz); 7.28—7.38 (m, 2 H, Ar); 8.07 (dd, 1 H, H(2) of thiophene, J_1 = 2.9 Hz, J_2 = 1.2 Hz). Found (%): C, 68.03; H, 4.78; N, 6.09. $C_{26}H_{22}N_2O_4S$. Calculated (%): C, 68.11; H, 4.84; N, 6.11.

1-(4-Chlorophenyl)-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)-1*H*-pyrrole-2,5-dione (3d). The yield was 0.11 g (87%), orange crystals, m.p. 199—200 °C. IR, ν/cm^{-1}: 1702 (C=O). ^{1}H NMR (CDCl$_3$), δ: 2.39, 3.51, 3.72, (all s, 3 H each, Me, NMe, OMe); 6.38 (d, 1 H, H(4) of indole, J = 2.5 Hz); 6.79 (dd, 1 H, H(6) of indole, J_1 = 2.5 Hz, J_2 = 8.9 Hz); 7.15 (dd, 1 H, H(4) of thiophene, J_1 = 2.9 Hz, J_2 = 5.1 Hz); 7.18 (d, 1 H, H(7) of indole, J = 8.9 Hz); 7.21 (dd, 1 H, H(5) of thiophene, J_1 = 1.2 Hz, J_2 = 5.1 Hz); 7.44 (m, 4 H, Ar); 8.07 (dd, 1 H, H(2) of thiophene, J_1 = 2.9 Hz, J_2 = 1.2 Hz). Found (%): C, 64.62; H, 4.25; N, 5.89. $C_{25}H_{19}ClN_2O_3S$. Calculated (%): C, 64.86; H, 4.14; N, 6.05.

Synthesis of 1-alkyl-3-(5-dimethoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)-1*H*-pyrrole-2,5-diones 3e—i (general procedure). The corresponding alkylamine (0.42 mmol) and DMAP (4 mg) were added to a solution of compound **2** (0.28 mmol) in butanol (10 mL). The obtained reaction mixture was refluxed for 3 h and then cooled. The solvent was evaporated to 2 mL, and the precipitate that formed was filtered off and washed with MeOH. The product obtained was recrystallized from butanol.

1-Benzyl-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)-1*H*-pyrrole-2,5-dione (3e). The yield was 0.11 g (89%), orange crystals, m.p. 149—150 °C. IR, ν/cm^{-1}: 1702 (C=O). ^{1}H NMR (CDCl$_3$), δ: 2.34, 3.49, 3.69 (all s, 3 H each, Me, NMe, OMe); 4.80 (s, 2 H, CH$_2$); 6.33 (d, 1 H, H(4) of indole, J = 2.4 Hz); 6.77 (dd, 1 H, H(6) of indole, J_1 = 2.4 Hz, J_2 = = 8.8 Hz); 7.07—7.18 (m, 3 H, H(4) of thiophene, H(7) of indole, H(5) of thiophene); 7.24—7.50 (m, 5 H, Ar); 8.01 (dd, 1 H, H(2) of thiophene, J_1 = 2.8 Hz, J_2 = 1.2 Hz). Found (%): C, 70.57; H, 4.95; N, 6.29. $C_{26}H_{22}N_2O_3S$. Calculated (%): C, 70.57; H, 5.01; N, 6.33.

1-(*iso*-Butyl)-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)-1*H*-pyrrole-2,5-dione (3f). The yield was 0.09 g (64%), orange crystals, m.p. 138—139 °C. IR, ν/cm^{-1}: 1702 (C=O). ^{1}H NMR (CDCl$_3$), δ: 0.95 (d, 6 H, Me, J = 6.8 Hz); 2.10 (m, 1 H, CH); 2.34 (s, 3 H, Me); 3.40—3.48 (m, 2 H, NCH$_2$); 3.51 (s, 3 H, NMe); 3.70 (s, 3 H, OMe); 6.35 (d, 1 H, H(4) of indole, J = 2.3 Hz); 6.78 (dd, 1 H, H(6) of indole, J_1 = 2.3 Hz, J_2 = 8.8 Hz); 7.12 (dd, 1 H, H(4) of thiophene, J_1 = 2.9 Hz, J_2 = 5.1 Hz); 7.15 (d, 1 H, H(7) of indole, J = 8.8 Hz); 7.17 (dd, 1 H, H(5) of thiophene, J_1 = 1.3 Hz, J_2 = 5.1 Hz); 8.02 (dd, 1 H, H(2) of thiophene, J_1 = 2.9 Hz, J_2 = 1.3 Hz). Found (%): C, 67.57; H, 5.88; N, 6.79. $C_{23}H_{24}N_2O_3S$. Calculated (%): C, 67.62; H, 5.92; N, 6.86.

1-Cyclopentyl-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)-1*H*-pyrrole-2,5-dione (3g). The yield was 0.11 g (94%), orange crystals, m.p. 199—200 °C. IR, ν/cm^{-1}: 1702 (C=O). ^{1}H NMR (CDCl$_3$), δ: 1.48—1.72 (m, 2 H, CH$_2$); 1.82—2.20 (m, 6 H, CH$_2$); 2.34, 3.51, 3.69 (all s, 3 H each, Me, NMe, OMe); 4.56 (m, 1 H, NCH); 6.36 (d, 1 H, H(4) of indole, J = 2.3 Hz); 6.77 (dd, 1 H, H(6) of indole, J_1 = 2.3 Hz, J_2 = 8.8 Hz); 7.07—7.18 (m, 3 H, H(4) of thiophene, H(7) of indole, H(5) of thiophene); 8.01 (m, 1 H, H(2) of thiophene). Found (%): C, 68.51; H, 5.71; N, 6.59. $C_{24}H_{24}N_2O_3S$. Calculated (%): C, 68.55; H, 5.75; N, 6.66.

1-Cycloheptyl-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)-1*H*-pyrrole-2,5-dione (3h). The yield was 0.12 g (96%), orange crystals, m.p. 158—159 °C. IR, ν/cm^{-1}: 1702 (C=O). ^{1}H NMR (CDCl$_3$), δ: 1.40—1.75 (m, 6 H, CH$_2$); 1.75—1.90 (m, 4 H, CH$_2$); 2.14—2.32 (m, 2 H, CH$_2$); 2.34, 3.51, 3.69 (all s, 3 H each, Me, NMe, OMe); 4.12—4.26 (m, 1 H, CH); 6.34 (d, 1 H, H(4) of indole, J = 2.5 Hz); 6.77 (dd, 1 H, H(6) of indole, J_1 = 2.5 Hz, J_2 = 8.8 Hz); 7.07—7.18 (m, 3 H, H(4) of thiophene, H(7) of indole, H(5) of thiophene); 8.00 (m, 1 H, H(2) of thiophene). Found (%): C, 69.58; H, 6.24; N, 6.19. $C_{26}H_{28}N_2O_3S$. Calculated (%): C, 69.62; H, 6.29; N, 6.24.

1-Cyclododecyl-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)-1*H*-pyrrole-2,5-dione (3i). The yield was 0.13 g (90%), orange crystals, m.p. 139—140 °C. IR, ν/cm^{-1}: 1702 (C=O). ^{1}H NMR (CDCl$_3$), δ: 1.15—2.20 (m, 22 H, CH$_2$); 2.34, 3.51, 3.69 (all s, 3 H each, Me, NMe, OMe); 4.39 (m, 1 H, NCH); 6.35 (d, 1 H, H(4) of indole, J = 2.4 Hz); 6.77 (dd, 1 H, H(6) of indole, J_1 = 2.4 Hz, J_2 = 8.9 Hz); 7.11 (dd, 1 H, H(4) of thiophene, J_1 = 2.9 Hz, J_2 = 5.1 Hz); 7.15 (d, 1 H, H(7) of indole, J = 8.9 Hz); 7.16 (dd, 1 H, H(5) of thiophene, J_1 = 1.3 Hz, J_2 = 5.1 Hz); 8.02 (dd, 1 H, H(2) of thiophene, J_1 = 2.9 Hz, J_2 = 1.3 Hz) Found (%): C, 71.72; H, 7.35; N, 5.38. $C_{31}H_{38}N_2O_3S$. Calculated (%): C, 71.78; H, 7.38; N, 5.40.

This work was financially supported by the Federal Target Program "Scientific and Scientific—Pedagogical Personnel of the Innovative Russia in 2009—2013" (State Contract No. P2260).

References

1. M. Irie, *Chem. Rev.*, 2000, **100**, 1685.
2. V. I. Minkin, *Chem. Rev.*, 2004, **104**, 2751.

3. V. A. Barachevskii, M. M. Krayushkin, *Izv. Akad. Nauk*, *Ser. Khim.*, 2008, 853 [*Russ. Chem. Bull., Int. Ed.*, 2008, **57**, 867].
4. M. Irie, M. Mohri, *J. Org. Chem.*, 1988, **53**, 803.
5. M. M. Krayushkin, V. Z. Shirinyan, L. I. Belen´kii, A. A. Shimkin, A. Yu. Martynkin, B. M. Uzhinov, *Zh. Org. Khim.*, 2002, **38**, 1390 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2002, **38**, No. 9].
6. T. Yamaguchi, M. Irie, *Chem. Lett.*, 2004, **33**, 1398.
7. Y. Nakayama, K. Hayashi, M. Irie, *J. Org. Chem.*, 1990, **55**, 2592.
8. T. Yamaguchi, K. Uchida, M. Irie, *J. Am. Chem. Soc.*, 1997, **119**, 6066.
9. T. Yamaguchi, M. Irie, *Chem. Lett.*, 2005, **34**, 64.
10. M. M. Krayushkin, V. N. Yarovenko, S. L. Semenov, V. Z. Shirinyan, F. Yu. Martynkin, B. M. Uzhinov, *Zh. Org. Khim.*, 2002, **38**, 1386 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2002, Vol. **38**, No. 9].
11. V. F. Traven, A. Yu. Bochkov, M. M. Krayushkin, V. N. Yarovenko, V. A. Barachevsky, I. P. Beletskaya, *Mendeleev Commun.*, 2010, **20**, 22.
12. A. V. Metelitsa, V. P. Rybalkin, N. I. Makarova, P. V. Levchenko, V. S. Kozyrev, E. N. Shepelenko, L. L. Popova, V. A. Bren´, V. I. Minkin, *Izv. Akad. Nauk*, *Ser. Khim.*, 2010, 1596 [*Russ. Chem. Bull.*, *Int. Ed.*, 2010, **59**, 1631].
13. G. I. Zhungietu, V. A. Budylin, A. N. Kost, *Preparativnaya khimiya indola* [*Preparative Chemistry of Indole*], Shtiintsa, Chisinau, 1975, 28 pp. (in Russian).
14. S. Pu, M. Li, C. Fan, G. Liu, L. Shen, *J. Mol. Struct.*, 2009, **919**, 100.
15. Y.-C. Jeong, D. G. Park, I. S. Lee, S. I. Yang, K.-H. Ahn, *J. Mater. Chem.*, 2009, **19**, 97.
16. M. Ohsumi, T. Fukaminato, M. Irie, *Chem. Commun.*, 2005, 3921.
17. C. Fan, S. Pu, G. Liu, T. Yang, *J. Photochem. Photobiol. A: Chem.*, 2008, **194**, 333.
18. C. Fan, S. Pu, G. Liu, T. Yang, *J. Photochem. Photobiol. A: Chem.*, 2008, **197**, 415.
19. M. Takeshita, M. Ogava, K. Miyata, T. Yamato, *J. Phys. Org. Chem.*, 2003, **16**, 148.
20. C. A. Parker, *Photoluminescence of Solutions. With Applications to Photochemistry and Analytical Chemistry,* Elsevier Publishing Co., Amsterdam—London—New York, 1968.
21. B. M. Krasovitskii, B. M. Bolotin, *Organicheskie lyuminofory* [*Organic Luminophores*], Khimiya, Moscow, 1984, p. 292 (in Russian).

Received October 14, 2010;
in revised form March 28, 2011