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SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF ASYMMETRIC DIHETARYLETHENES BASED ON 5-METHOXY-1,2-DIMETHYLINDOLE AND 5-(4-BROMOPHENYL)-2-METHYLTHIOPHENE

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We report the synthesis of new asymmetric dihetarylethenes – 4-[5-(4-bromophenyl)-2-methylthiophen-3-yl]-3-(5-methoxy-1,2-dimethyl-1H-indol-3-yl)furan-2,5-dione and 1-alkyl(phenyl)-3-(5-methoxy-1,2-dimethyl-1H-indol-3-yl)-4-[5-(4-bromophenyl)-2-methylthiophen-3-yl]-1H-pyrrole-2,5-diones, which exhibit photochromic and fluorescent properties in solution. Thermally stable photoinduced cyclic isomers were observed for dihetarylethenes derived from 5-methoxy-1,2-dimethylindole and 5-(4-bromophenyl)-2-methylthiophene, unlike for their structural analogs based on 5-methoxy-1,2-dimethylindole and unsubstituted thiophene. Changing the thiophene fragment of dihetarylethenes to a 5-(4-bromophenyl)-2-methylthiophene fragment gave rise to photochromic properties in furan-2,5-dione derivatives.

Keywords: dihetarylethene, furan-2,5-dione, indole, pyrrole-2,5-dione, thiophene, fluorescence, photochromism.

Photochromic heterocyclic compounds have been the objects of comprehensive study due to the possibility of creating new polyfunctional materials for molecular electronics, optical molecular memory, photodynamic chemosensors, and biosensors based on such compounds [1, 2].

Particularly interesting members of this series are dihetarylethenes, which have isomeric forms with high thermal and photostability. Methods have been optimized for the synthesis of dihetarylethenes containing maleic anhydride or maleimide linkers, which offer access to a series of molecular structures with a broad range of spectral-kinetic characteristics [3-4]. The introduction of various substituents opens the possibility of creating polyfunctional photochromic molecular systems having fluorescent [5-7], magnetic [8], and complexing [9-10] properties. Symmetric dihetarylethenes have been previously prepared with cycloalkene [11-13] or perfluorocycloalkene linkers [14], containing thiophene fragments with 5-aryl substituents. Asymmetric dihetarylethenes most frequently include an unsubstituted or 5-alkyl-substituted thiophene ring [15-19].

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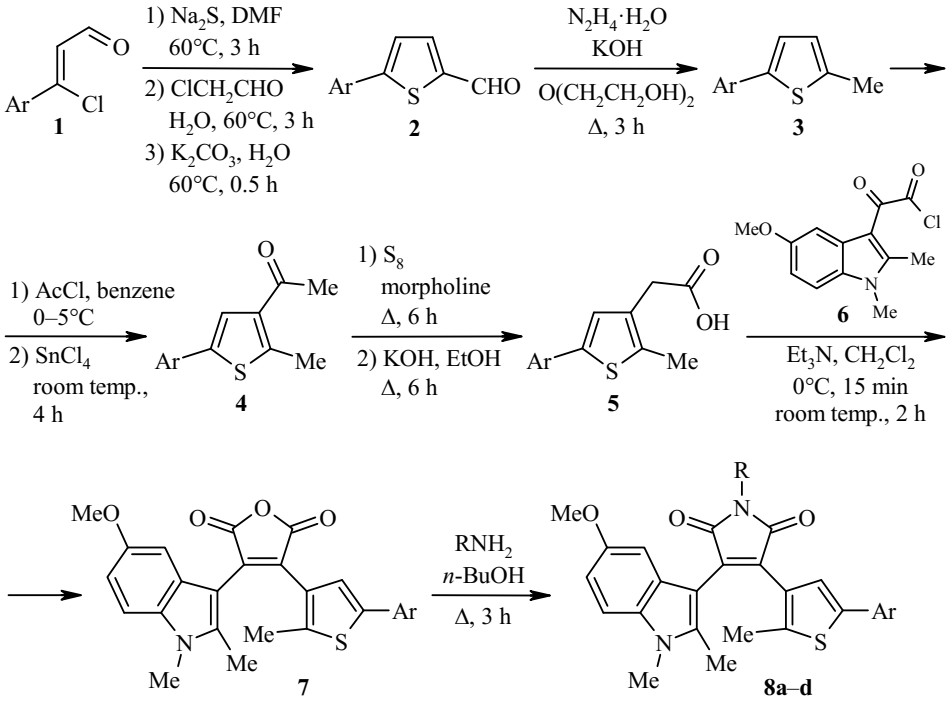
While continuing our research towards the synthesis of photochromic dihetarylethenes [17-23] as potential molecular switches with fluorescent signal function, we synthesized asymmetric ethenes (furan- and pyrrolediones), including indole and 5-aryl-substituted thiophene rings as hetaryl fragments.

4-[5-(4-Bromophenyl)-2-methylthiophen-3-yl]-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)furan(pyrrole)-2,5-diones **7**, **8a-d** containing a 4-bromophenyl substituent at position 5 of the thiophene ring were obtained by the following scheme.



Ar = 4-BrC_6H_4; **8 a** R = *i*-Pr, **b** R = *cyclo*-C_5H_9, **c** R = Bn, **d** R = Ph

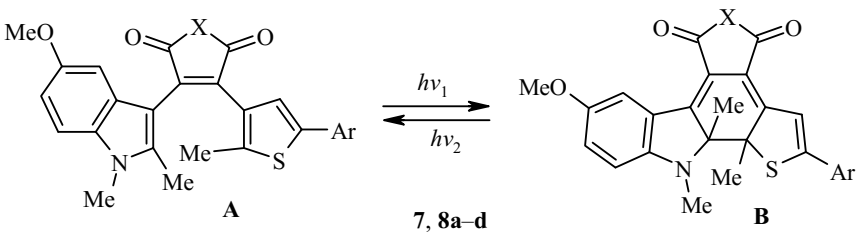
The interaction of 3-(4-bromophenyl)-3-chloropropenal (**1**) with sodium sulfide and chloroacetaldehyde produced 5-(4-bromophenyl)thiophene-2-carbaldehyde (**2**), which was reduced with hydrazine hydrate in a Wolff-Kishner reaction [24], resulting in isolation of 5-(4-bromophenyl)-2-methylthiophene (**3**). This method was used for the first time to prepare compound **3**. The acylation of thiophene **3** allowed to synthesize the previously unknown 1-[5-(4-bromophenyl)-2-methylthiophen-3-yl]ethanone (**4**), which was transformed by Willgerodt-Kindler reaction [25] with sulfur and morpholine to [5-(4-bromophenyl)-2-methylthiophen-3-yl]-acetic acid (**5**). Acylation of 5-methoxy-1,2-dimethylindole with oxalyl chloride gave the acyl chloride **6**, and its subsequent treatment with a solution of thienylacetic acid **5** in the presence of triethylamine led to 4-[5-(4-bromophenyl)-2-methylthiophen-3-yl]-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)furan-2,5-dione (**7**). The action of alkylamines or aniline on compound **7** resulted in 1-alkyl(phenyl)-3-(1-benzyl-5-methoxy-2-methyl-1*H*-indol-3-yl)-4-(3-thienyl)-1*H*-pyrrole-2,5-diones **8a-d**.

The structure of the obtained compounds was confirmed by IR, as well as ^{1}H and ^{13}C NMR spectroscopy.

The ^{1}H NMR spectrum of compound **3** in $CDCl_3$ contained an upfield three-proton singlet of 2-methyl group at 2.51 ppm, the singlets of two thiophene fragment protons ar 6.72 and 7.08 ppm, as well as a four proton multiplet of the *para*-bromophenyl substituent. The ^{1}H NMR spectrum of compounds **4** and **5** in $CDCl_3$ solution lacked a thiophene proton singlet at 6.72 ppm, in contrast to the spectrum of compound **3**, while the rest of the signals were still present. This observation confirmed the fact of acylation at position 3 of thiophene.

The ^{1}H NMR spectra of compounds **7** and **8a-d** in $CDCl_3$ contained four three-proton signals (mainly singlets) in the upfield region at 1.69-1.82 (2-CH_3 indole), 2.36-2.44 (2-CH_3 thiophene), 3.40-3.46 (OCH_3), and

3.65-3.72 ppm (NCH_3). There were three aromatic proton signals due to the indole ring and four proton signals of the bromophenyl group in the downfield region of 6.71-7.50 ppm, and the thiophene ring H-4 proton signal at 6.30-6.40 ppm.



The spectral and photochromic properties of compounds **7**, **8a-d** were studied in toluene at 293 K, with the results presented in Table 1.

The electronic absorption spectra of open forms **A** of the dihetarylethenes **7**, **8a-d** were characterized by long-wave absorption bands of similar shapes and positions (further referred to as absorption bands) with the maxima at 458-468 nm and molar extinction coefficients of 7750-13300 $l \cdot mol^{-1} \cdot cm^{-1}$ (Table 1). The change from 1-alkyl-substituted pyrrole diones **8a-c** to the 1-phenyl-substituted derivative **8d** was associated with an insignificant bathochromic shift of absorption band maxima by 5-10 nm.

Solutions of dihetarylethenes **7** and **8a-d** exhibited fluorescence in the visible spectrum: the fluorescence bands for toluene solutions of the studied compounds were in the range of 560-573 nm, and also exhibited a bathochromic shift by 7-13 nm in the series of **8a-d** (Table 1, Fig. 1).

The pyrrolediones **8a-d** exhibited fluorescence effectiveness that was 4-6 times higher than for furandione **7**, for which the fluorescence quantum yield was 0.01 (Table 1).

The correlation between the molecular structure, absorption and fluorescence properties of the asymmetric dihetarylethenes **7**, **8a-d** based on 5-methoxy-1,2-dimethylindole and 5-(4-bromophenyl)-2-methylthiophene matched that previously established by us [17] for analogous dihetarylethenes based on 5-methoxy-1,2-dimethylindole and unsubstituted thiophene. We should note that dihetarylethenes based on 5-(4-bromophenyl)-2-methylthiophene exhibited a longer wavelength absorption (5-10 nm) and fluorescence (20-30 nm), compared to their structural analogs based on unsubstituted thiophene, but the fluorescence was 2-4 times less effective [17].

TABLE 1. The Spectral Characteristics of Absorption and Fluorescence of the Dihetarylethene **7**, **8a-d** Isomeric Forms in Toluene*, *T* 293 K

Compound	Initial form **A**			Photoinduced form **B**	
	Absorption	Fluorescence		Absorption	
	λ^{abs}, nm ($\varepsilon \cdot 10^{-3}$)	λ^{em}, nm (λ^{ex}, nm)	φ	λ^{abs}, nm	*A*
7	463 (13.3)	560 (463)	0.01	677	0.078
8a	458 (7.75)	560 (459)	0.05	622	0.101
8b	460 (8.95)	562 (462)	0.06	622	0.110
8c	463 (9.35)	566 (463)	0.05	623	0.121
8d	468 (10.48)	573 (469)	0.04	635	0.105

*λ^{abs}, λ^{em} and λ^{ex} – the maxima of absorption, fluorescence, and fluorescence excitation bands, respectively; *A* – optical density parameter at the absorption band maximum for the protoinduced form **B** in photostationary state upon irradiation with 436 nm light; φ – quantum yield of fluorescence.

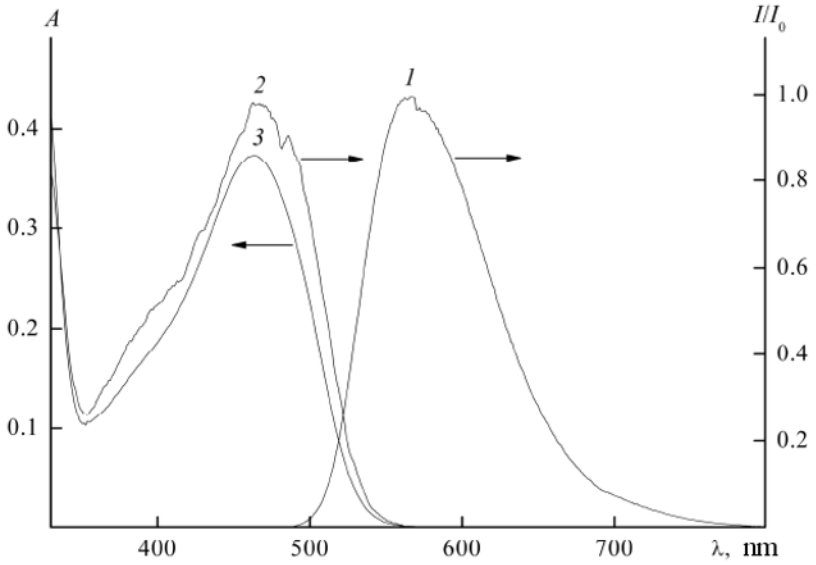


Fig. 1. Fluorescence (*1*), fluorescence excitation (*2*), and absorption spectra (*3*) for solution of compound **8c** in toluene (c $4\cdot10^{-5}$ M, l 1 cm, T 293 K).

In contrast to the previously investigated [17] photochemically inactive 3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-(3-thienyl)furan-2,5-dione, all dihetarylethenes studied in this work, including 4-[5-(4-bromophenyl)-2-methylthiophen-3-yl]-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)furan-2,5-dione (**7**), exhibited photochromic properties in solution.

The irradiation of furan(pyrrole)diones **7**, **8a**–**d** (open form **A**) as toluene solutions with 436 nm wavelength light resulted in color change linked to the appearance of visible spectrum absorption bands with maxima at 622-677 nm (Table 1, Fig. 2). Such absorption is characteristic of the cyclic isomeric forms **B** of dihetarylethenes [2, 17-23].

The longest wavelength absorption was found for the cyclic form **B** of furandione **7** (677 nm). Structural modification of dihetarylethenes, associated with the change from maleic anhydride fragment to maleimide led to a 42-55 nm hypsochromic shift in the absorption spectra of the cyclic form **B** of dihetarylethenes **8a**-**d**.

The effect of substituents at the maleimide nitrogen atom of dihetarylethenes **8a**-**d** on the spectral characteristics of cyclic isomers **B** was manifested to a similar extent as for the open forms **A**. Thus, the fluorescence band maxima of 1-alkyl-substituted pyrrolediones **8a**-**c**, compared to the 1-phenyl derivative **8d**, showed a 19-20 nm hypsochromic shift (Table 1).

Unlike the initial forms **A**, photoisomers **B** did not exhibit fluorescence.

The photoconversion of the initial form **A** to the cyclic form **B** was incomplete for dihetarylethenes **7** and **8a**-**d**. Prolonged irradiation at 436 nm wavelength resulted in a photostationary state, as evidenced by the relatively intense fluorescence of the open forms **A** under the conditions when further irradiation did not change the electronic absorption spectrum (Fig. 3).

The comparison of absorption spectra of compounds **7**, **8a**-**d** with the excitation spectra of the observed fluorescence indicated a good match, clearly supporting the hypothesis that fluorescence was caused by the open isomers **A** (Table 1, Fig. 1).

The irradiation of previously colored dihetarylethene solutions at 578 nm wavelength resulted in complete bleaching due to the reverse photoreaction of ring opening (**B**→**A**).

Dihetarylethenes **7**, **8a**-**d** were stable against photodegradation and could survive at least 20 cycles of photocoloration–photobleaching without reduction of solution optical density at the absorption maximum of cyclic form **B** (Table 1) in the photostationary state.

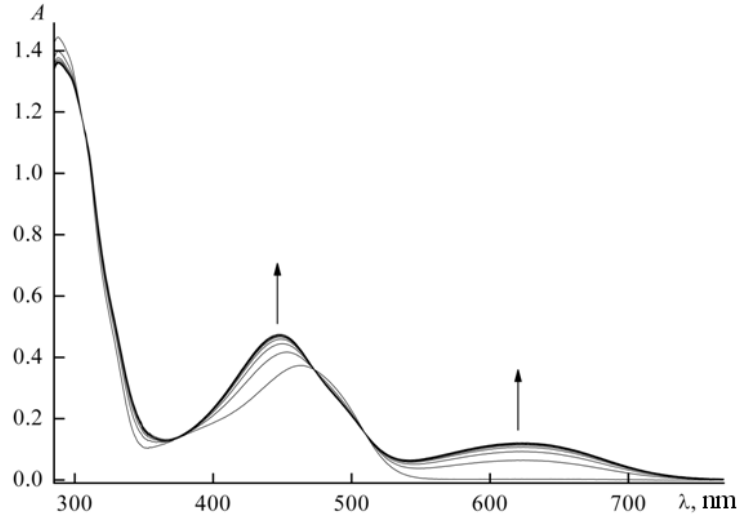


Fig. 2. The color change of dihetarylethene **8c** in toluene (c $4 \cdot 10^{-5}$ M, l 1 cm, T 293 K) after irradiation at λ 436 nm, with 1 min intervals between spectra.

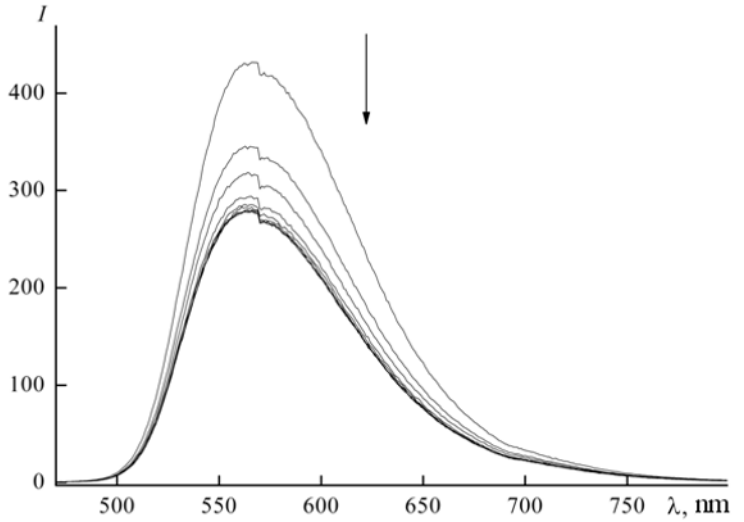


Fig. 3. The decrease of fluorescence intensity observed for dihetarylethene **8c** solution in toluene (c $4 \cdot 10^{-5}$ M, l 1 cm, T 293 K) upon irradiation at λ 436 nm, with 1 min interval between the spectra.

Asymmetric dihetarylethenes based on 5-methoxy-1,2-dimethylindole and 5-(4-bromophenyl)-2-methylthiophene, in contrast to their structural analogs based on 5-methoxy-1,2-dimethylindole and thiophene [17], demonstrated thermal stability of the photoinduced cyclic isomers: the cyclic form **B** of dihetarylethenes **7**, **8a**-**d** was stable at room temperature for at least 5 days in the absence of light (in darkness).

Thus, we have prepared new photochromic asymmetric dihetarylethenes: 4-[5-(4-bromophenyl)-2-methyl-thiophen-3-yl]-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)furan-2,5-dione and 1-alkyl(phenyl)-3-(5-methoxy-1,2-di-methyl-1*H*-indol-3-yl)-4-[5-(4-bromophenyl)-2-methylthiophen-3-yl]-1*H*-pyrrole-2,5-diones that have the properties of molecular switches with fluorescent signal function.

EXPERIMENTAL

Electronic absorption spectra were recorded on a Varian Cary 100 spectrophotometer. Fluorescence measurements were performed on a Varian CaryEclipse spectrofluorimeter. Solution photolysis was performed by DRSh-250 mercury lamp equipped with an interference light filter for isolating the 436 nm (10MLF10-436 Newport) and 578 nm (10MLF10-578 Newport) lines of mercury spectrum. The stability of dihetarylethenes towards photodegradation was studied by performing 20 cycles of photocoloration (irradiation with λ 436 nm light for 8 min) – photobleaching (irradiation with λ 578 nm light for 9 min); the optical density of compounds **7**, **8a-d** as toluene solutions was measured at the maximum of cyclic form **B** absorption band (Table 1) in the photostationary state. The photostationary state (corresponding to photocoloration) was achieved by irradiating the solutions of studied dihetarylethenes at λ 436 nm until further irradiation caused no changes in the electronic absorption spectrum. The fluorescence quantum yields were determined by Parker-Rees method [26] using 3-methoxybenzanthrone in toluene (φ 0.1, λ 365 nm) as standard luminophore [27]. Spectral grade toluene from Sigma-Aldrich was used for the preparation of solutions. IR spectra were recorded on a VarianExcalibur 3100 FTIR instrument using the ATR method. ^{1}H NMR spectra were acquired on a VarianUnity 300 instrument (300 MHz), ^{13}C NMR spectra were acquired on a Bruker Avance 600 instrument. The solvent for all NMR spectra was $CDCl_3$; the residual solvent proton signal was used as internal standard for ^{1}H NMR spectra (7.24 ppm), while the ^{13}C signal of $CDCl_3$ served as internal standard for ^{13}C NMR spectra (77.0 ppm). Elemental analysis was performed on a KOVO CHN-analyzer. Melting points were determined on a Boetius hot stage. Mass spectra were recorded on a Shimadzu GCMS-QP2010SE instrument with direct sample introduction into the ion source (EI, 70 eV).

5-(4-Bromophenyl)thiophene-2-carbaldehyde (2). A suspension of $Na_2S·9H_2O$ (9.3 g, 33 mmol) in freshly distilled DMF (40 ml) was treated by dropwise addition of 3-(4-bromophenyl)-3-chloropropenal (**1**) (7.9 g, 32 mmol) solution in freshly distilled DMF (100 ml) over 1 h at 60°C, followed by heating the reaction mixture for 2 h at the same temperature. Then 50% aqueous solution of chloroacetaldehyde (6 ml, 36 mmol) was added dropwise; the reaction mixture was stirred for 3 h at 60°C and treated with K_2CO_3 (8.3 g, 60 mmol) solution in minimum amount of H_2O. The mixture was heated for additional 30 min and poured into a tenfold excess of H_2O. The precipitate formed was filtered off and recrystallized from EtOH with the addition of activated carbon. Yield 3.2 g (37%), pale-yellow crystals, mp 110-112°C (mp 111-112°C [28]). IR spectrum, ν, cm^{-1}: 1659 (C=O), 1629 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.38 (1H, d, *J* = 3.9, H-4 thiophene); 7.55-7.66 (4H, m, H Ar); 7.73 (1H, d, *J* = 3.9, H-3 thiophene); 9.89 (1H, s, CHO). Found, %: C 49.10; H 2.70. $C_{11}H_7BrOS$. Calculated, %: C 49.46; H 2.64.

5-(4-Bromophenyl)-2-methylthiophene (3). A mixture of aldehyde **2** (2.72 g, 10.2 mmol), KOH (4.28 g, 75.0 mmol), 85% $N_2H_4·H_2O$ (8 ml, 135.0 mmol), and diethylene glycol (50 ml) was refluxed for 3 h. The solution was diluted with H_2O (50 ml), the precipitated product was filtered off, dried, and recrystallized from EtOH. Yield 1.34 g (52%), colorless crystals, mp 126-128°C (lit. 127-128°C [29]). ^{1}H NMR spectrum, δ, ppm: 2.51 (3H, s, CH_3); 6.72 (1H, s, H-3 thiophene); 7.08 (1H, s, H-4 thiophene); 7.38-7.49 (4H, m, H Ar). Found, %: C 52.39; H 3.46. $C_{11}H_9BrS$. Calculated, %: C 52.19; H 3.58.

1-[5-(4-Bromophenyl)-2-methylthiophen-3-yl]ethanone (4). Thiophene **3** (1.520 g, 6.0 mmol) was dissolved in anhydrous benzene (25 ml), cooled to 0-5°C, and AcCl (0.52 ml, 0.572 g, 7.3 mmol) was added with stirring. The obtained mixture was then treated with $SnCl_4$ (0.85 ml, 1.890 g, 7.3 mmol). The reaction mixture was stirred for 4 h at room temperature, then cooled and quenched with 10% HCl (10 ml). The obtained mixture was extracted with $CHCl_3$ (3×20 ml), the organic layer was separated, dried over anhydrous Na_2SO_4, the solvent was removed on rotary evaporator, and the residue was recrystallized from EtOH. Yield 1.12 g (63%), pale-yellow crystals, mp 113-114°C. IR spectrum, ν, cm^{-1}: 1750 (C=C), 1800 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.54 (3H, s, 2-CH_3); 2.75 (3H, s, $COCH_3$); 7.40-7.45 (2H, m, H Ar); 7.50-7.60 (3H, m, H Ar). Mass spectrum, *m*/*z*: 295 $[M]^+$. Found, %: C 53.00; H 3.56. $C_{13}H_{11}BrOS$. Calculated, %: C 52.89; H 3.76.

[5-(4-Bromophenyl)-2-methylthiophen-3-yl]acetic Acid (5). A mixture of ketone **4** (0.59 g, 2 mmol), sulfur (0.13 g, 4 mmol), and morpholine (0.35 ml, 4 mmol) was refluxed for 6 h. The mixture was cooled, treated with EtOH (2 ml), after 1 h the precipitate was filtered off, transferred to 50% KOH solution (1.5 ml) and treated with additional 3 ml of EtOH. The obtained mixture was refluxed for 6 h, treated with H_2O (5 ml), and acidified with conc. HCl. After 30 min, the precipitate was filtered off, washed with H_2O, air-dried, and recrystallized from CCl_4. Yield 0.39 g (63%), pale-brown crystals, mp 161-162°C. IR spectrum, ν, cm^{-1}: 3063, 2558, 1701. ^{1}H NMR spectrum, δ, ppm: 2.41-2.43 (3H, m, CH_3); 3.58 (2H, s, CH_2); 7.11-7.48 (5H, m, H Ar); 10.50-11.60 (1H, br. s, OH). Mass spectrum, *m*/*z*: 311 $[M]^+$. Found, %: C 50.00; H 3.56. $C_{13}H_{11}BrO_2S$. Calculated, %: C 50.18; H 3.56.

4-[5-(4-Bromophenyl)-2-methylthiophen-3-yl]-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)furan-2,5-dione (7). A solution of 5-methoxy-1,2-dimethylindole (0.21 g, 1.2 mmol) in CH_2Cl_2 (5 ml) was cooled to 0°C and treated by dropwise addition of oxalyl chloride (0.11 ml, 0.15 g, 1.2 mmol). The reaction mixture was maintained for 30 min, the solvent was then removed on rotary evaporator. A solution of acid **5** (0.38 g, 1.2 mmol) and Et_3N (0.40 ml, 1.5 mmol) in CH_2Cl_2 (7 ml) was added to the dry residue from evaporation, i.e., (5-methoxy-1,2-dimethylindol-3-yl)oxoacetyl chloride (**6**), stirred for 15 min at 0°C, then for 2 h at room temperature. The precipitate that formed was filtered off. Solvent was removed by distillation at reduced pressure and the product was purified by silica gel column chromatography (eluent $CHCl_3$). Yield 0.15 g (24%), red crystals, mp 259-260°C. IR spectrum, ν, cm^{-1}: 1752 (C=O), 1616 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.82 (3H, s, 2-CH_3 indole); 2.43 (3H, s, 2-CH_3 thiophene); 3.44 (3H, s, OCH_3); 3.72 (3H, s, NCH_3); 6.30-6.31 (1H, m, H-4 thiophene); 6.76-6.82 (1H, m, H Ar); 7.15-7.18 (1H, m, H Ar); 7.26-7.50 (5H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 12.9; 15.3; 30.3; 55.3; 101.3; 102.7; 110.3; 112.9; 121.7; 124.4; 125.6; 127.1; 128.1; 129.3; 132.1; 134.5; 135.6; 140.5; 140.9; 142.5; 155.1; 165.5; 165.6. Mass spectrum, *m*/*z*: 523 $[M]^+$. Found, %: C 59.75; H 4.00; N 2.52. $C_{26}H_{20}BrNO_4S$. Calculated, %: C 59.78; H 3.86; N 2.68.

1-Substituted 4-[5-(4-Bromophenyl)-2-methylthiophen-3-yl]-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-1*H*-pyrrole-2,5-diones 8a-d (General Method). A solution of compound **7** (50 mg, 0.096 mmol) in *n*-BuOH (5 ml) was treated with the corresponding amine (0.200 mmol). The reaction mixture was refluxed for 3 h, then cooled, the solvent was removed under reduced pressure, the products were purified by chromatography on alumina column (eluent $CHCl_3$).

4-[5-(4-Bromophenyl)-2-methylthiophen-3-yl]-1-isopropyl-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-1*H*-pyrrole-2,5-dione (8a). Yield 39 mg (74%), orange crystals, mp 254-255°C. IR spectrum, ν, cm^{-1}: 1696 (C=O), 1616 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.48-1.51 (6H, m, $CH(C\underline{H}_3)_2$); 1.71 (3H, s, 2-CH_3 indole); 2.36 (3H, s, 2-CH_3 thiophene); 3.40-3.43 (3H, m, OCH_3); 3.65-3.67 (3H, m, NCH_3); 4.46-4.51 (1H, m, $NC\underline{H}Me_2$); 6.33-6.34 (1H, m, H-4 thiophene); 6.79-6.80 (1H, m, H Ar); 7.15-7.18 (1H, m, H Ar); 7.26-7.50 (5H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 12.9; 15.2; 20.3; 30.1; 43.3; 52.3; 101.5; 103.1; 109.7; 112.1; 121.2; 125.0; 126.0; 127.0; 128.9; 129.3; 131.9; 133.7; 139.4; 139.6; 140.9; 154.6; 170.9; 171.5. Mass spectrum, *m*/*z*: 563 $[M]^+$. Found, %: C 61.75; H 5.00; N 4.72. $C_{29}H_{27}BrN_2O_3S$. Calculated, %: C 61.81; H 4.83; N 4.97.

4-[5-(4-Bromophenyl)-2-methylthiophen-3-yl]-1-cyclopentyl-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-1*H*-pyrrole-2,5-dione (8b). Yield 31 mg (24%), red crystals, mp 236-237°C. IR spectrum, ν, cm^{-1}: 1695 (C=O), 1616 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.56-2.15 (11H, m, $(CH_2)_4$, 2-CH_3 indole); 2.37 (3H, s, 2-CH_3 thiophene); 3.43 (3H, s, OCH_3); 3.67 (3H, s, NCH_3); 4.55-4.61 (1H, m, $NC\underline{H}(CH_2)_4$); 6.33-6.34 (1H, m, H-4 thiophene); 6.71-6.75 (1H, m, H Ar); 7.09-7.12 (1H, m, H Ar); 7.24-7.46 (5H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 12.9; 15.2; 24.9; 29.6; 30.1; 51.4; 55.3; 101.4; 103.1; 109.7; 112.1; 121.2; 125.0; 126.0; 127.0; 128.9; 129.3; 131.9; 132.1; 132.9; 133.8; 139.4; 139.6; 140.9; 154.6; 171.0; 171.5. Mass spectrum, *m*/*z*: 589 $[M]^+$. Found, %: C 63.35; H 5.00; N 4.72. $C_{31}H_{29}BrN_2O_3S$. Calculated, %: C 63.16; H 4.96; N 4.75.

1-Benzyl-4-[5-(4-bromophenyl)-2-methylthiophen-3-yl]-3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-1*H*-pyrrole-2,5-dione (8c). Yield 54 mg (92%), red crystals, mp 223-224°C. IR spectrum, ν, cm^{-1}: 1691 (C=O), 1616 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.69 (3H, s, 2-CH_3 indole); 2.36 (3H, s, 2-CH_3 thiophene); 3.41 (3H, s, OCH_3); 3.66 (3H, s, NCH_3); 4.82 (2H, s, $NC\underline{H}_2Ph$); 6.31-6.32 (1H, m, H-4 thiophene); 6.71-6.75 (1H, m, H Ar); 7.09-7.12 (1H, m, H Ar); 7.24-7.35 (5H, m, H Ar); 7.42-7.50 (5H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 12.9; 15.2; 25.4; 30.1; 42.0; 55.3; 64.4; 101.4; 103.1; 109.8; 112.2; 121.2; 124.9; 125.9; 127.0; 127.7; 128.7; 128.9; 129.2; 131.9; 132.1; 132.9; 133.9; 136.8; 139.6; 139.7; 141.1; 154.6; 170.8; 171.2. Mass spectrum, *m*/*z*: 611 $[M]^+$. Found, %: C 64.75; H 4.50; N 4.42. $C_{33}H_{27}BrN_2O_3S$. Calculated, %: C 64.81; H 4.45; N 4.58.

4-[5-(4-Bromophenyl)-2-methylthiophen-3-yl]-3-(5-methoxy-1,2-dimethyl-1H-indol-3-yl)-1-phenyl-1*H*-pyrrole-2,5-dione (8d). Yield 37 mg (65%), red crystals, mp 223-224°C. IR spectrum, ν, cm^{-1}: 1700 (C=O), 1616 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.81 (3H, s, 2-CH_3 indole); 2.44 (3H, s, 2-CH_3 thiophene); 3.46 (3H, s, OCH_3); 3.71 (3H, s, NCH_3); 6.39-6.40 (1H, m, H-4 thiophene); 6.79-6.80 (1H, m, H Ar); 7.14-7.18 (1H, m, H Ar); 7.24-7.46 (10H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 13.0; 15.3; 30.1; 55.3; 101.4; 103.0; 109.9; 112.3; 121.3; 125.0; 126.0; 127.0; 127.5; 128.8; 129.0; 129.1; 132.0; 132.1; 132.2; 132.3; 132.9; 134.0; 139.8; 139.9; 141.4; 154.8; 169.8; 170.2. Mass spectrum, *m*/*z*: 597 $[M]^+$. Found, %: C 64.55; H 4.50; N 4.42. $C_{32}H_{25}BrN_2O_3S$. Calculated, %: C 64.32; H 4.22; N 4.69.

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