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Photochromic dihetarylethenes
19.* Synthesis of 1,2-dihetarylethenes on the basis of thieno[3,2-*b*]pyrroles linked by a maleimide bridge

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New photochromic 1,2-dihetarylethenes containing maleimide-bridged thieno[3,2-*b*]pyrrole fragments with aliphatic and aromatic substituents at the nitrogen atom were synthesized.

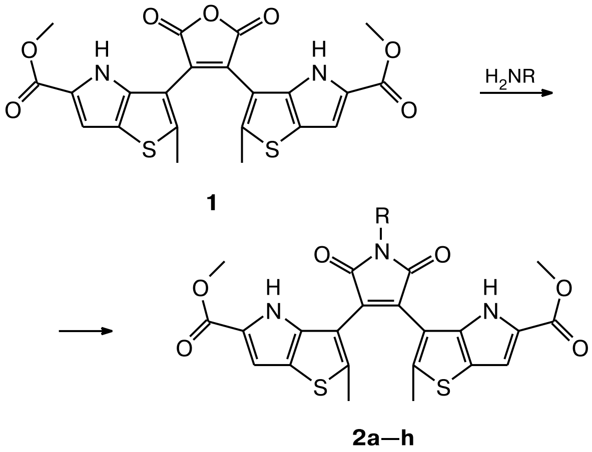
Key words: photochromes, 1,2-dihetarylethenes, thieno[3,2-*b*]pyrroles, maleic anhydride, maleimides.

1,2-Dihetarylethenes are considered as promising carriers of three-dimensional optical memory.[2,3] A rather large number of derivatives of this type have now been obtained; however, the broad range of demands placed on photochromic substances stimulates the synthesis of new compounds of this class. A promising route in the design of these structures is the use of fused heterocycles, because photochromic products based on heterocycles such as benzothiophene, indole, and thieno[3,2-*b*]thiophene are known to possess high fatigue resistance and thermal irreversibility.[3,4]

Previously,[5] we have demonstrated for the first time that thieno[3,2-*b*]pyrroles, close analogs of the above-mentioned heterocycles, can be used in the design of photochromic system **1**, which exhibits a high thermal irreversibility. It is also known that the maleimide fragment is widely used in photochromic 1,2-dihetarylethenes as a bridge. The transformation of 1,2-dihetarylmaleic anhydrides into maleimides containing an unsubstituted nitrogen atom (on treatment with ammonium acetate or hexamethyldisilazane) or into *N*-alkylmaleimides (using aliphatic amines) has been reported; however, no data concerning the use of aromatic amines in these reactions are available.[6,7]

This study is an attempt to construct new photochromic compounds containing thieno[3,2-*b*]pyrrole fragments with *N*-substituted maleimide bridges by the reaction of furandione **1** with a series of aliphatic and aromatic amines. This reaction takes place on refluxing in ethanol for 6—7 h and affords photochromic 1,2-dihetarylethenes **2a—h** in good yields (Scheme 1).

Scheme 1



R = Me (**a**), CH_2CH_2OH (**b**), CH_2Ph (**c**), $CH_2CH=CH_2$ (**d**), $CH_2C(O)Ph$ (**e**), OMe (**f**), 2-pyridyl (**g**), Ph (**h**)

It is worth noting that substituents present at the maleimide nitrogen atom include hydroxyethyl, allyl, and phenacyl groups, capable of further transformations. For example, photochromes **2b,d** can be used in the formation of films or can be grafted to appropriate matrices.

By using *O*-methylhydroxylamine, photochrome **2f**, containing a methoxy group at the nitrogen atom of the maleimide ring, was synthesized for the first time.

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Table 1. Photochemical characteristics of the obtained compounds

Compound	R	λ_{max}/nm		τ*/h
		A	**B**	
2b	CH_2CH_2OH	293	359, 412, 582	>50
2c	CH_2Ph	293	358, 414, 584	>340
2d	$CH_2CH=CH_2$	294	357, 413, 583	>430
2e	CH_2COPh	293	415, 586	>840
2f	OMe	293	414, 548	**
2g	2-Py	293	361, 415, 588	***
2h	Ph	294	339, 414, 590	>1200

* Thermal stability in the absence of irradiation.

** Over a period of 340 h, 4% of the cyclic form decomposes.

*** Over a period of 340 h, 3% of the cyclic form decomposes.

The reaction of the maleic anhydride fragment in 1,2-dihetarylethenes with aromatic amines was also performed for the first time. Photochromic products **2g,h** were isolated in ~70% yields after refluxing compound **1** in ethanol with aniline or 2-aminopyridine for 6—7 h.

The photochromic properties of the compounds obtained were studied in an acetonitrile solution (Table 1); a typical absorption spectrum of compound **2e** is shown in Fig. 1. The absorption spectra of all the studied substances contain isosbestic points. The fact that the positions of these points for the forward and back reactions coincide implies a fully reversible photocyclization and the absence of side processes. The introduction of different in kind substituents to the nitrogen atom of the maleimide bridge does not affect the position of the absorption maxima of the open form (λ = 293—294 nm). The situation observed for the absorption maxima of the cyclic form is virtually the same. For photochromes with aliphatic and aromatic substituents, they occur in a narrow range, 582—590 nm. The only deviation, the reason for which is not entirely clear, is λ = 548 nm found for compound **2f**, containing the OMe group.

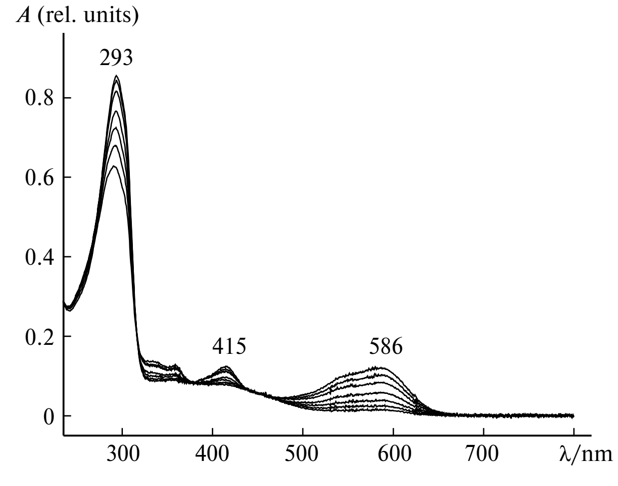

Fig. 1. Variation of the absorption spectra of photochrome **2e** on exposure to light with λ = 313 nm.

The photochromes **2b—h** we synthesized are highly thermally stable (see Table 1), as determined from the variation of the intensity of the absorption bands corresponding to the cyclic forms (**B**). The data concerning the thermal stability indicate that products **2b—e,h** are thermally irreversible over the time periods indicated in Table 1. The cyclic forms of photochromes **2f,g** undergo only insignificant transformations into the open forms (**A**) over a period of 340 h.

Experimental

^{1}H NMR spectra were recorded on Bruker WM-200 (200 MHz) and Bruker WM-250 (250 MHz) instruments in DMSO-d_6 and $CDCl_3$ relative to HMDS. Mass spectra were run on a Varian MAT CH-6 instrument with direct sample injection into the ion source; the ionization energy was 70 eV and the accelerating voltage was 1.75 kV. Melting points were measured on a Boetius hot stage and were not corrected. The reaction mixtures were analyzed and the purity of the isolated products was checked by TLC on Silufol UV-254 plates using an AcOEt—*n*-C_6H_{14} mixture (1 : 3 v/v) as the eluent.

The samples were irradiated with a DRSh-100 mercury lamp using light filters for separation of mercury spectrum lines (313 and 546 nm). The absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. The thermal stability of the cyclic forms was studied at room temperature.

The starting furandione **1** was synthesized by a procedure described previously.^{5}

Synthesis of maleimides (general procedure). Amine (0.11 mmol) and TsOH (0.001 g) were added to furandione **1** (0.05 g, 0.1 mmol) in 2—4 mL of 99.5% ethanol and the mixture was refluxed for 4—8 h (TLC monitoring). The solvent was evaporated *in vacuo* and the product was purified by preparative thin layer chromatography on silica gel and recrystallized from EtOH.

3,4-Bis(5-methoxycarbonyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)-1-methyl-1*H*-pyrrole-2,5-dione (2a). The yield of **2a** was 0.039 g (76%), m.p. 219—221 °C. MS, *m/z*: 497 $[M]^+$. ^{1}H NMR ($CDCl_3$), δ: 1.81 (s, 6 H, 2 Me); 3.82 (s, 6 H, 2 MeO); 7.07 (s, 2 H, 2 CH_{arom}); 9.12 (s, 2 H, 2 NH). Found (%): C, 55.79; H, 3.86; N, 8.60; S, 12.95. $C_{23}H_{19}N_3O_6S_2$. Calculated (%): C, 55.52; H, 3.85; N, 8.45; S, 12.89.

1-(2-Hydroxyethyl)-3,4-bis(5-methoxycarbonyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)-1*H*-pyrrole-2,5-dione (2b). The yield of **2b** was 0.038 g (70%), m.p. 143—145 °C. MS, *m/z*: 527 $[M]^+$. ^{1}H NMR (DMSO-d_6), δ: 1.81 (s, 6 H, 2 Me); 3.40 (s, 2 H, NCH_2); 3.70 (s, 2 H, CH_2OH); 3.82 (s, 6 H, 2 MeO); 7.07 (s, 2 H, 2 CH_{arom}); 11.69 (s, 2 H, 2 NH). Found (%): C, 54.80; H, 4.03; N, 8.07; S, 12.30. $C_{24}H_{21}N_3O_7S_2$. Calculated (%): C, 54.64; H, 4.01; N, 7.96; S, 12.16.

1-Benzyl-3,4-bis(5-methoxycarbonyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)-1*H*-pyrrole-2,5-dione (2c). The yield of **2c** is 0.021 g (35%), m.p. 144—146 °C. MS, *m/z*: 573 $[M]^+$. ^{1}H NMR ($CDCl_3$), δ: 1.93 (s, 6 H, 2 Me); 3.88 (s, 6 H, MeO); 4.87 (s, 2 H, CH_2); 7.06 (s, 2 H, 2 CH_{arom}); 7.30—7.60 (m, 5 H, Ph); 9.18 (s, 2 H, 2 NH). Found (%): C, 60.84; H, 4.05; N, 7.52; S, 11.40. $C_{29}H_{23}N_3O_6S_2$. Calculated (%): C, 60.72; H, 4.04; N, 7.33; S, 11.18.

1-Allyl-3,4-bis(5-methoxycarbonyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)-1*H*-pyrrole-2,5-dione (2d). The yield of **2d** was 0.043 g (80%), m.p. 178—180 °C. MS, *m/z*: 523 $[M]^+$. ^1H NMR ($CDCl_3$), δ: 1.81 (s, 6 H, 2 Me); 3.88 (s, 6 H, 2 MeO); 3.92 (s, 1 H, CH=); 4.33 (d, 2 H, CH_2=, *J* = 5.86 Hz); 5.32 (m, 2 H, CH_2); 7.07 (s, 2 H, 2 CH_{arom}); 9.17 (s, 2 H, 2 NH). Found (%): C, 57.60; H, 4.03; N, 8.07; S, 12.30. $C_{25}H_{21}N_3O_7S_2$. Calculated (%): C, 57.35; H, 4.04; N, 8.03; S, 12.25.

3,4-Bis(5-methoxycarbonyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)-1-(2-oxo-2-phenylethyl)-1*H*-pyrrole-2,5-dione (2e). The yield of **2e** was 0.036 g (63%), m.p. 141—143 °C. MS, *m/z*: 601 $[M]^+$. ^1H NMR ($CDCl_3$), δ: 2.01 (s, 6 H, 2 Me); 3.86 (s, 6 H, 2 MeO); 5.15 (s, 2 H, CH_2); 7.07 (s, 2 H, 2 CH_{arom}); 7.55 (t, 2 H, 2 CH_{arom}, *J* = 7.5 Hz); 7.66 (d, 1 H, CH_{arom}, *J* = 7.25 Hz); 8.04 (d, 1 H, CH_{arom}, *J* = 7.52 Hz); 9.17 (s, 2 H, 2 NH). Found (%): C, 59.97; H, 3.85; N, 7.12; S, 10.82. $C_{30}H_{23}N_3O_7S_2$. Calculated (%): C, 59.89; H, 3.85; N, 6.98; S, 10.66.

1-Methoxy-3,4-bis(5-methoxycarbonyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)-1*H*-pyrrole-2,5-dione (2f). The yield of **2f** was 0.040 g (76%), m.p. 148—150 °C. MS, *m/z*: 513 $[M]^+$. ^1H NMR ($CDCl_3$), δ: 1.97 (s, 6 H, 2 Me); 3.88 (s, 6 H, 2 MeO); 4.15 (s, 3 H, MeON); 7.07 (s, 2 H, 2 CH_{arom}); 9.13 (s, 2 H, 2 NH). Found (%): C, 53.95; H, 3.74; N, 8.32; S, 12.62. $C_{23}H_{19}N_3O_7S_2$. Calculated (%): C, 53.79; H, 3.73; N, 8.18; S, 12.49.

3,4-Bis(5-methoxycarbonyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)-1-pyridin-2-yl-1*H*-pyrrole-2,5-dione (2g). The yield of **2g** was 0.039 g (67%), m.p. 171—173 °C. MS, *m/z*: 560 $[M]^+$. ^1H NMR ($CDCl_3$), δ: 1.98 (s, 6 H, 2 Me); 3.86 (s, 6 H, MeO); 7.08 (s, 2 H, 2 CH_{arom}); 7.43 (t, 1 H, $CH_{pyridine}$, *J* = 6.07 Hz); 7.55 (d, 1 H, $CH_{pyridine}$, *J* = 7.92 Hz); 7.96 (t, 1 H, $CH_{pyridine}$, *J* = 7.46 Hz); 8.72 (d, 1 H, $CH_{pyridine}$, *J* = 4.19 Hz); 9.30 (s, 2 H, 2 NH). Found (%): C, 57.93; H, 3.62; N, 10.15; S, 11.65. $C_{27}H_{20}N_4O_6S_2$. Calculated (%): C, 57.85; H, 3.60; N, 9.99; S, 11.44.

3,4-Bis(5-methoxycarbonyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)-1-phenyl-1*H*-pyrrole-2,5-dione (2h). The yield of **2h** was 0.04 g (69%), m.p. 183—185 °C. MS, *m/z*: 559 $[M]^+$. ^1H NMR (DMSO-d_6), δ: 1.88 (s, 6 H, 2 Me); 3.82 (s, 6 H, 2 MeO); 7.10 (s, 2 H, 2 CH_{arom}); 7.50—7.80 (m, 5 H, Ph); 11.98 (s, 2 H, 2 NH). Found (%): C, 60.25; H, 3.78; N, 7.75; S, 11.62. $C_{28}H_{21}N_3O_6S_2$. Calculated (%): C, 60.09; H, 3.78; N, 7.51; S, 11.46.

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