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# Photochromic dihetarylethenes

## 11.* Synthesis and photochromic properties of diarylethenes containing furan or furopyrimidine bridges

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Procedures were developed for the synthesis of substituted bis(2,5-dimethyl-3-thienyl)furans based on 1,2-bis(2,5-dimethyl-3-thienyl)-2-hydroxyethanone. Dithienylethene structures in which the ethene fragment is involved in the furan or furopyrimidine system possess photochromic properties and their open forms exhibit fluorescence.

**Key words:** furan, furopyrimidines, α-hydroxyketone, photochromes, 1,2-dithienylethenes, fluorescence.

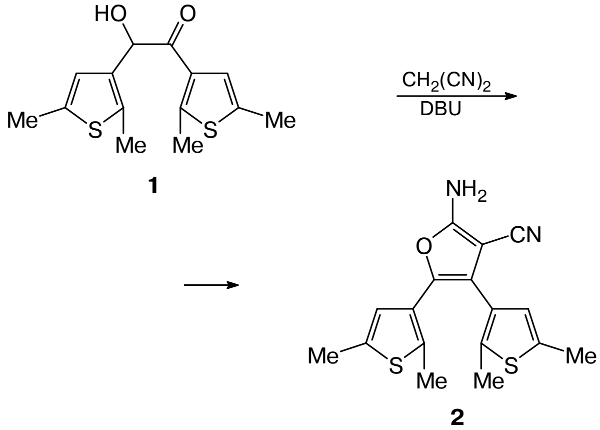
Photochromic thermally irreversible dihetarylethenes are being extensively studied as elements of optical memory, photoswitches, dosimeters, *etc.*[2,3] Previously, we have synthesized dithienylethenes containing triazine[4] or azole[5] bridges and demonstrated that the former compounds do not possess photochromic properties, whereas the azole derivatives bearing electron-donating substituents are photochromes. As part of continuing studies aimed at searching for new readily accessible compounds exhibiting photochromic activity, we developed procedures for the synthesis of substituted bis(2,5-dimethyl-3-thienyl)furans in which the ethene bridges are involved in the furan or furopyrimidine systems.

Structures of this type are often synthesized with the use of 1,2-bifunctional compounds.[6,7] In the present work, we used thenoin **1**, *viz.*, 1,2-bis(2,5-dimethyl-3-thienyl)-2-hydroxyethanone, as the starting compound. Its synthesis has been reported previously.[4]

### Results and Discussion

The reaction of thenoin **1** with malononitrile in the presence of DBU afforded furan derivative **2** (Scheme 1).

**Scheme 1**



Treatment of compound **2** with formamide or formic acid gave rise to the amino or oxo derivatives of furopyrimidine (**3** or **4**), respectively, in good yields (Scheme 2).

By analogy with the known procedure,[6] we used compound **2** for the synthesis of amidine **5**, whose reaction with hydroxylamine yielded aminofuropyrimidine *N*-oxide **6** (Scheme 3).

Treatment of compound **2** with dimedone produced enaminone **7**. According to a procedure developed by us previously,[8] the reaction of the latter compound with arylmethylidenemalononitrile afforded furopyrimidoquinoline **8** (Scheme 4).

We examined the photochromic and spectroscopic characteristics of compounds **2**—**4**, **6**, and **8** (solutions in MeCN). In the absorption spectra of the open forms of compounds **2**, **3**, **6**, and **8**, the long-wavelength bands are observed in the narrow range of 304—310 nm. The spectrum of hydroxypyrimidine **4** has the analogous band at 375 nm, *i.e.*, it is shifted bathochromically by ~65 nm. The conversion of aminopyrimidine **3** into

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* For Part 10, see Ref. 1.

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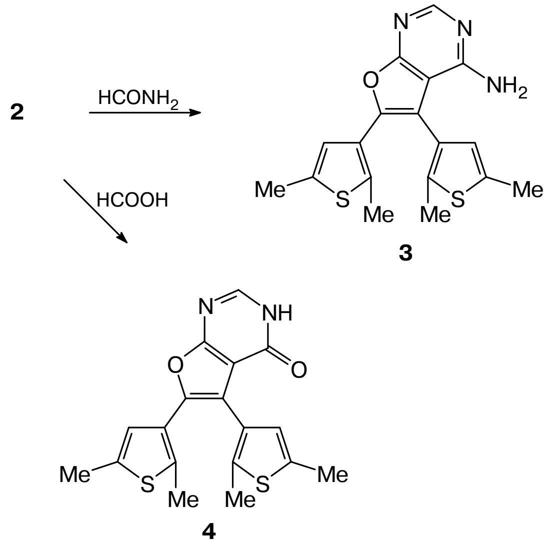
**Scheme 2**

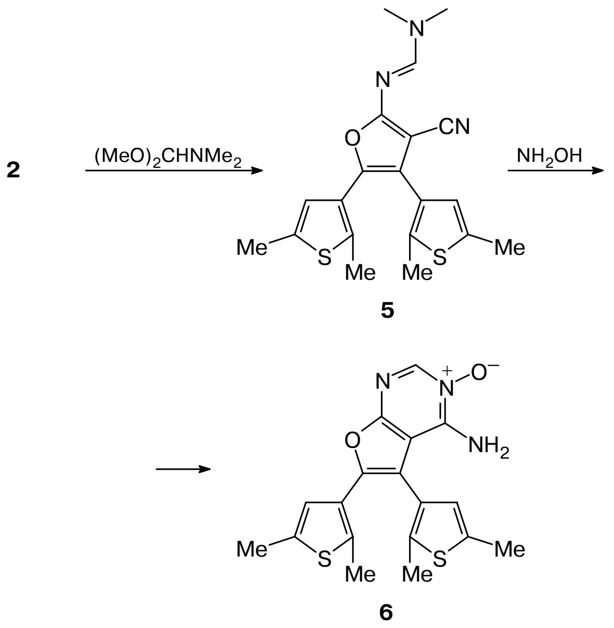


*N*-oxide **6** is accompanied by the hypsochromic shift of the long-wavelength band in the absorption spectrum of the cyclic form by 10 nm.

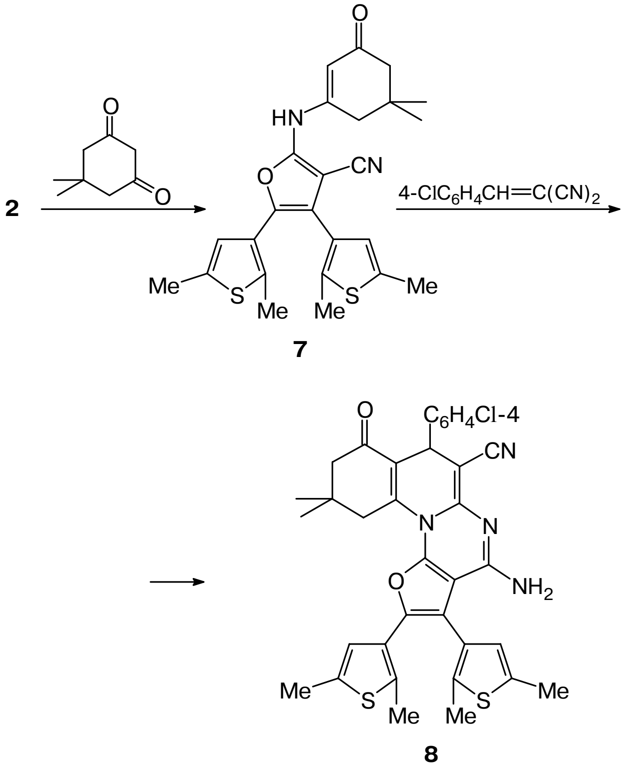
All products, except for furopyrimidoquinoline **8**, exhibit photochromic properties (Scheme 5; Table 1).

The cyclic forms of the photochromes appeared to be unstable. After storage at room temperature for one day, their optical densities in the maximum of the long-wavelength absorption band were halved. Fatigue resistance[2,3] of these compounds is rather low. Thus after three—five transitions from the open to the cyclic form and back (on irradiation), the optical density of the cyclic form was recovered by, at most, 80%. Taking into account the results obtained previously,[5] it can be assumed that low fatigue resistance in solutions is typical of bis(2,5-dimethyl-3-thienyl)ethenes.

**Scheme 3**



**Scheme 4**



**Scheme 5**

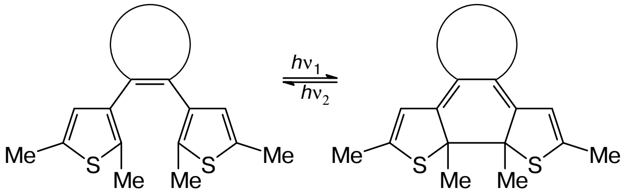


**Table 1.** Maxima of the long-wavelength bands of the electronic absorption spectra ($\lambda_{max}$/nm) and the fluorescence spectra ($\lambda_{fl}$/nm) for the open (**A**) and cyclic (**B**) forms of compounds **2—4**, **6**, and **8**

| Compound | $\lambda_{max}$ |  | $\lambda_{fl}$(**A**) |
|---|---|---|---|
|  | **A** | **B** |  |
| **2** | 304 | 483 | 405 |
| **3** | 307 | 505 | 380 |
| **4** | 375 | 506 | 510 |
| **6** | 310 | 515 | 415 |
| **8** | 304 | — | — |

Earlier, we have demonstrated[9,10] that the fluorescence properties of dithienylethene photochromes are favored by the presence of benzooxazole- or oxadiazole-containing substituents in the thiophene rings as well as by the formation of thienothiophenes. Although the structures of compounds **2**—**4** and **6** do not contain the above-mentioned aromatic fragments, their open forms fluoresce in acetonitrile solutions. It should be emphasized that this is the first example of fluorescence of dithienylethenes resulting from the characteristic structural features of the ethene bridge. The quantum yield of fluorescence is low (<0.1). Based on the measurements of the lifetime of the excited state, the observed fluorescence can be assigned to emission from the $\pi$—$\pi^*$ state. The cyclic forms of the photochromes under study do not exhibit fluorescence.

To summarize, we have developed procedures for the synthesis of substituted bis(2,5-dimethyl-3-thienyl)ethenes in which the ethene fragment is involved in the furan or furopyrimidine systems. It was found for the first time that dihetarylethenes containing the 2,5-dimethylthienyl fragments fluoresce due to the characteristic features of the heterocyclic bridging system.

## Experimental

The $^1$H NMR spectra were recorded on Bruker AM-300 (300.13 MHz) and Bruker WM-250 (250.13 MHz) instruments in DMSO-d$_6$ and CDCl$_3$. The melting points were measured on a Boetius heating stage and were not corrected. The mass spectrum (EI) was obtained on a Kratos MS-30 instrument with direct inlet of the sample into the ion source; the energy of ionizing electrons was 70 eV. The course of the reactions and the purities of the products were monitored by TLC on Silica gel 60 F$_{254}$ plates (Merck) using an AcOEt—hexane solvent system.

The photochromic characteristics of compounds **2**—**4**, **6**, and **8** were examined for solutions in MeCN. Acetonitrile of special-purity grade was used in the measurements. Samples were irradiated with a DRSh-500 mercury lamp using light filters to separate lines of the mercury spectrum ($\lambda$ = 313, 546, and 578 nm). The intensity of radiation of the mercury lamp was determined using an F4 photodetector calibrated using a ferrioxalate actinometer[11] for $\lambda$ = 313 nm and using an actinometer based on the Reinecke salt[12] for $\lambda$ = 546 and 578 nm. The electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. The fluorescence spectra were measured on an Elyumin-2M spectrofluorometer with excitation in the maximum of the absorption spectrum of the compound under study. Since the fluorescence excitation spectra of the open forms corrected for the intensity of the exciting light are identical with the electronic absorption spectra of these forms, the observed fluorescence is attributable to emission of the open forms of the compounds under study.

**2-Amino-4,5-bis(2,5-dimethyl-3-thienyl)furan-3-carbonitrile (2).** Diazabicycloundecene (DBU) (0.228 g, 1.5 mmol) was added to a solution of thenoin **1**[4] (0.280 g, 1 mmol) and malononitrile (0.110 g, 1.66 mmol) in EtOH (3 mL). The reaction mixture was heated with stirring at 65—70 °C for 4 h and then cooled. Water (3 mL) was added and the precipitate that formed was filtered off. The product was recrystallized from aqueous EtOH and compound **2** was obtained in a yield of 0.267 g (81%), m.p. 186—187 °C. Found (%): C, 61.85; H, 5.06; N, 8.12; S, 19.97. $C_{17}H_{16}N_2OS_2$. Calculated (%): C, 62.17; H, 4.91; N, 8.53; S, 19.52. $^1$H NMR (DMSO-d$_6$), $\delta$: 1.98, 2.04, 2.30, and 2.39 (all s, 3 H each, Me); 6.46 and 6.61 (both s, 1 H each, CH); 7.50 (s, 2 H, NH$_2$).

**4-Amino-5,6-bis(2,5-dimethyl-3-thienyl)furo[2,3-*d*]pyrimidine (3).** One—two drops of Ac$_2$O were added to a solution of compound **2** (0.130 g, 0.4 mmol) in HCONH$_2$ (2 mL). The reaction mixture was refluxed for 4 h and then cooled. Water (5 mL) was added and the precipitate that formed was filtered off. The product was recrystallized from dioxane and compound **3** was obtained in a yield of 0.090 g (63%), m.p. 211—212 °C. Found (%): C, 60.43; H, 4.95; N, 12.20; S, 18.59. $C_{18}H_{17}N_3OS_2$. Calculated (%): C, 60.82; H, 4.82; N, 11.82; S, 18.04. $^1$H NMR (DMSO-d$_6$), $\delta$: 2.02, 2.21, 2.32, and 2.44 (all s, 3 H each, Me); 6.53 (s, 1 H, CH); 6.62 (br.s, 2 H, NH$_2$); 6.75 (s, 1 H, CH); 8.23 (s, 1 H, CH arom.).

**5,6-Bis(2,5-dimethyl-3-thienyl)-3,4-dihydrofuro[2,3-*d*]pyrimidin-4-one (4).** A mixture of compound **2** (0.164 g, 0.5 mmol) and HCOOH (2 mL) was refluxed for 8 h and then cooled. Water (5 mL) was added and the precipitate that formed was filtered off. The product was recrystallized from dioxane and compound **4** was obtained in a yield of 0.098 g (55%), m.p. 143—144 °C. Found (%): C, 60.28; H, 4.47; N, 8.09; S, 18.32. $C_{18}H_{16}N_2O_2S_2$. Calculated (%): C, 60.65; H, 4.52; N, 7.86; S, 17.99. $^1$H NMR (DMSO-d$_6$), $\delta$: 1.96, 2.03, 2.34, and 2.38 (all s, 3 H each, Me); 6.59 and 6.62 (both s, 1 H each, CH); 8.14 (d, 1 H, CH arom., $J$ = 2.1 Hz); 12.62 (br.s, 1 H, NH).

***N*-[3-Cyano-4,5-bis(2,5-dimethyl-3-thienyl)-2-furyl]-*N*,*N*′-dimethylformimidamide (5).** A mixture of compound **2** (0.450 g, 1.4 mmol) and (MeO)$_2$CHNMe$_2$ (0.245 g, 2.1 mmol) in anhydrous MeOH (2 mL) was refluxed with stirring for 2 h and then cooled. Water (3 mL) was added and the precipitate was filtered off. The product was recrystallized from aqueous EtOH and compound **5** was obtained in a yield of 0.455 g (85%), m.p. 93—94 °C. Found (%): C, 62.41; H, 5.64; N, 11.23; S, 16.89. $C_{20}H_{21}N_3OS_2$. Calculated (%): C, 62.63; H, 5.52; N, 10.96; S, 16.72. $^1$H NMR (DMSO-d$_6$), $\delta$: 2.01, 2.08, 2.31, 2.39, 3.04, and 3.15 (all s, 3 H each, Me); 6.54 and 6.63 (both s, 1 H each, CH); 8.32 (s, 1 H, N=CH).

**4-Amino-5,6-bis(2,5-dimethyl-3-thienyl)furo[2,3-*d*]pyrimidine 3-oxide (6).** A mixture of compound **5** (0.100 g, 0.3 mmol) and NH$_2$OH $\cdot$ HCl (0.070 g, 1 mmol) in EtOH (1.5 mL) was refluxed for 5—6 h and then cooled. Water (5 mL) was added and the precipitate was filtered off. The product was recrystallized from EtOH and compound **6** was obtained in a yield of 0.085 g (76%), m.p. 109—110 °C. Found (%): C, 57.97; H, 4.54; N, 11.64; S, 16.88. $C_{18}H_{17}N_3O_2S_2$. Calculated (%): C, 58.20; H, 4.61; N, 11.31; S, 17.26. $^1$H NMR (DMSO-d$_6$), $\delta$: 2.03, 2.23, 2.32, and 2.44 (all s, 3 H each, Me); 6.51 and 6.71 (both s, 1 H each, CH); 7.09 (br.s, 2 H, NH$_2$); 8.69 (s, 1 H, CH arom.). MS, $m/z$ ($I_{\text{rel}}$ (%)): 371 [M$^+$] (20).

**2-[(5,5-Dimethyl-3-oxocyclohex-1-enyl)amino]-4,5-bis(2,5-dimethyl-3-thienyl)furan-3-carbonitrile (7).** A solution of dimedone (0.140 g, 1 mmol), compound **2** (0.329 g, 1 mmol), and *p*-toluenesulfonic acid (0.02 g, 0.0001 mol) in benzene (5 mL) was refluxed with the use of a Dean—Stark trap for 5 h. Then the reaction mixture was cooled and the precipitate of the product that formed was filtered off and washed on a filter with a small amount of benzene. Enaminoketone **7** was obtained in a yield of 0.328 g (73%), m.p. 88—89 °C. Found (%): C, 66.78; H, 5.71; N, 6.51; S, 14.01. $C_{25}H_{26}N_2O_2S_2$. Calculated (%): C, 66.64; H, 5.82; N, 6.22; S, 14.23. $^1$H NMR (DMSO-d$_6$), $\delta$: 1.06 (s, 6 H, 2 Me); 2.01 and 2.11 (both s, 3 H each, Me); 2.15 (s, 2 H, CH$_2$); 2.31 and 2.42 (both s, 3 H each, Me); 2.45 (s, 2 H, $CH_2$); 5.69, 6.51, and 6.69 (all s, 1 H each, CH); 10.32 (s, 1 H, NH).

**4-Amino-7-(4-chlorophenyl)-10,10-dimethyl-2,3-bis(2,5-dimethyl-3-thienyl)-8-oxo-8,9,10,11-tetrahydro-7*H*-furo[3′,2′:5,6]pyrimido[1,2-*a*]quinoline-6-carbonitrile (8).** Several drops of DBU were added to a solution of enaminoketone **7** (0.292 g, 0.65 mmol) and *p*-chlorobenzylidenemalononitrile (0.123 g, 0.65 mmol) in EtOH (3 mL). The reaction mixture was refluxed for 4 h and then cooled. The precipitate that formed was filtered off and washed on a filter with a small amount of EtOH. Furopyrimidoquinoline **8** was obtained in a yield of 0.162 g (39%), m.p. 262—263 °C. Found (%): C, 65.52; H, 4.81; Cl, 5.73; N, 8.94; S, 9.76. $C_{35}H_{31}ClN_4O_2S_2$. Calculated (%): C, 65.76; H, 4.89; Cl, 5.55; N, 8.76; S, 10.03. $^1$H NMR (DMSO-$d_6$), δ: 1.00, 1.15, 2.05, and 2.17 (all s, 3 H each, Me); 2.25—2.48 (m, 9 H, Me + $CH_2$); 2.85 (d, 1 H, $CH_2$, $J$ = 18 Hz); 4.68 (s, 1 H, CH); 5.17 (br.s, 1 H, NH); 6.31 and 6.70 (both br.s, 1 H each, CH); 7.29 (m, 4 H, H arom.); 8.10 (br.s, 1 H, NH).

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