

Synthesis of photochromic derivatives of cyclobutene-1,2-dione

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The photochromic properties of thienyl- and thieno[3,2-*b*]thiophenyl-substituted cyclobutene-1,2-diones were examined.

During the last decade the chemistry of thermally irreversible photochromic dithienylethenes was developed extensively.^{1,2} These compounds include as a rule one of three kinds of ethene bridges: perfluorocyclopentene, maleic anhydride and maleimide fragments. The synthesis and properties of diarylethenes including different ethene bridges such as dihydrothiophene,³ tetrathiafulvalene,⁴ cyclohexa-2,5-diene-1,4-dione,⁵ hexa-1,3,5-triene system,⁶ cyclopentene⁷ and various aromatic and non-aromatic heterocyclic systems were described.^{8,9} Recently, we have developed a novel approach to the synthesis of photochromic derivatives of maleic anhydride involving, at the first stage, the preparation of dithienylcyclobutenediones.^{10,11} However, 3,4-bis(2,5-dimethylthiophen-3-yl)cyclobut-3-ene-1,2-dione **1**, a potentially photochromic cyclobutene-1,2-dione was found to be non-photochromic.¹⁰

The aim of this work was to study this phenomenon and to design cyclobutenedione derivatives possessing photochromic properties due to an extended conjugation chain and changes in the electronic nature of substituents in hetaryl fragments. The structure of compound **1** was elucidated by X-ray diffraction analysis.¹⁰ Thiophene rings in the product are turned with respect to one another, and the distance between α -carbon atoms is equal to 5.03 Å, which is much longer than the normal van der Waals contact (3.55 Å) (Figure 1). In other words, in the crystalline state, there are no steric grounds for the conversion of 3,4-bis(2,5-dimethylthiophen-3-yl)cyclobut-3-ene-1,2-dione to cyclic form **B**. The rigidity of the structure is responsible for the observed difficulties in the cyclization of compound **1** in heptane, chloroform and ethanol solutions. Our efforts to fix form **B** for this compound by steady-state irradiation with light at 313 nm or by flash photolysis at 254 nm were unsuccessful: in all solvents except for ethanol, only insignificant destruction of 3,4-bis(2,5-dimethylthiophen-3-yl)cyclobut-3-ene-1,2-dione was observed (in ethanol after UV irradiation for 1 h, the compound was completely transformed into a mixture of maleic, succinic and fumaric acid derivatives).

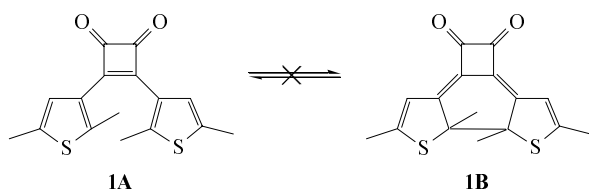


Figure 1 Molecular structure of 3,4-bis(2,5-dimethylthiophen-3-yl)cyclobut-3-en-1,2-dione **1**.

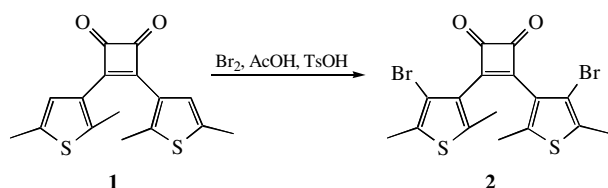
The electronic factors in the photochromic transformations would also be expected to play a significant role. The 6 π -electron aromatic systems of two thiophene rings are disturbed in transformations of the type **1A** \rightleftharpoons **1B**, and the conjugated system including four C=C bonds arises. The above dearomatization is not compensated by the gain from the appearance of a tetraenic fragment. Therefore, we decided to replace one or both thienyl substituents with thieno[3,2-*b*]thiophene residues: in this case, a conjugated tetraene fragment is originated and one or two 10 π -electronic systems transform into 6 π -electronic ones, which keep aromaticity.

For this purpose, we synthesised dithienothiophenylcyclobutenediones **8** and **9** (Scheme 2) and studied their photochromic properties. The starting methyl 5-methylthieno[3,2-*b*]thiophene-2-carboxylate¹² was prepared from 5-methylthiophene-2-carbaldehyde **3** in four steps in total 30–35% yield using the published procedure,¹³ which was modified [the oxidation of 3-(5-methyl-2-thienyl)-2-mercaptoacrylic acid **5**¹⁴ was carried out using *N*-bromosuccinimide in dichloroethane at 60 °C].

Compound **7** was acylated with squaric acid dichloride in the presence of AlCl₃ in dichloroethane–heptane mixtures. The acylation of thiophene and thienothiophene derivatives with squaric acid dichloride was described elsewhere.¹⁰

The study of compound **8** showed that it is a photochrome, viz., on irradiation by UV light ($\lambda = 313$ nm) it forms thermally

We proposed that the introduction of bromine atoms at the 4- and 4'-positions of thiophene rings allows the structure to become a sterically more convenient conformation for the formation of cyclic form **B**. However, these efforts were unsuccessful: product **2** (Scheme 1)[†] did not show photochromic properties.



Scheme 1

[†] 3,4-Bis(4-bromo-2,5-dimethylthiophen-3-yl)cyclobut-3-ene-1,2-dione **2**. To a suspension of 3,4-bis(2,5-dimethylthiophen-3-yl)cyclobut-3-ene-1,2-dione **1** (1.51 g, 0.005 mol) in acetic acid (10 ml), bromine (1.65 g, 0.0103 mol) was added dropwise with stirring. The reaction mixture was heated at 60–80 °C for 30–40 min until complete dissolution of the starting compound. *p*-Toluenesulfonyl chloride monohydrate (0.1 g, 0.0005 mol) was added, and the mixture was stirred at 20 °C for 20 h. The yellow crystals precipitated were filtered off, washed on the filter with cold water and then with cooled petroleum ether, and dried in a Fischer apparatus over P₂O₅. The yield of **2** was 1.89 g (82%). Mp 157–159 °C (from 80% ethanol). ¹H NMR spectrum (CDCl₃), δ : 2.42 (s, 6H, Me), 2.46 (s, 6H, Me). MS (EI), *m/z* (%): 462 (5.01) [M]⁺, 460 (9.91) [M]⁺, 406 (57.56) [M – 2CO]⁺, 404 (100) [M – 2CO]⁺, 381 (36.54) [M – Br]⁺, 379 (40.94) [M – Br]⁺, 300 (89.99) [M – 2Br]⁺. Found (%): C, 41.41; H, 2.72; Br, 33.98; S, 13.63. Calc. for C₁₆H₁₂Br₂O₂S₂ (%): C, 41.76; H, 2.63; Br, 34.73; S, 13.93.

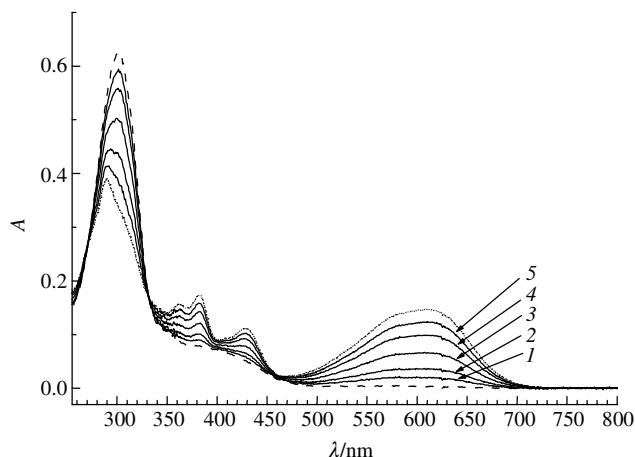


Figure 2 Absorption spectra of 3,4-bis(2-methyl-5-methoxycarbonylthieno[3,2-*b*]thiophen-3-yl)cyclobut-3-ene-1,2-dione **8**: dashed line, before irradiation (open form), and on irradiation at 313 nm, exposure times: (1) 10, (2) 25, (3) 45, (4) 75 and (5) 120 s; dotted line, 180 s (photostationary state).

stable (in the dark) form **B** and returns on irradiation by visible light ($\lambda = 578$ nm) to form **A** (Figure 2).[‡]

Non-symmetrical dihetarylcylobutenedione **9** also displays photochromic properties: cyclic form **B** forms on irradiation by light at 313 nm (Figure 3). Note that cyclic form **B** of dihetaryl-

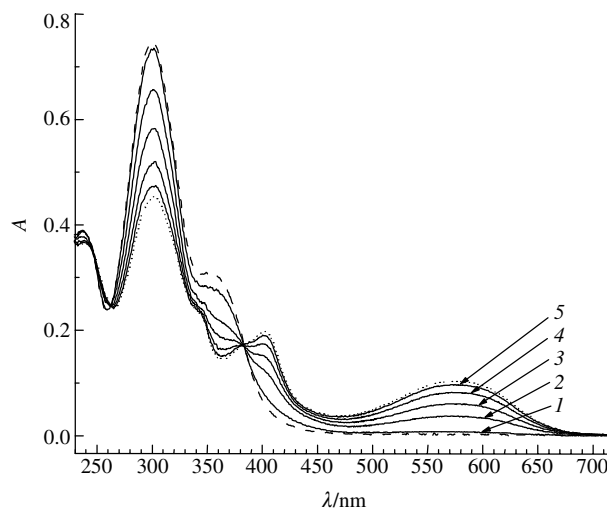
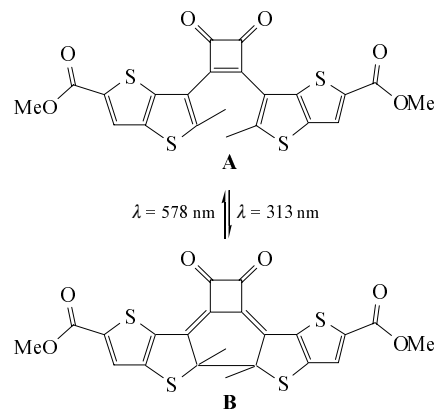
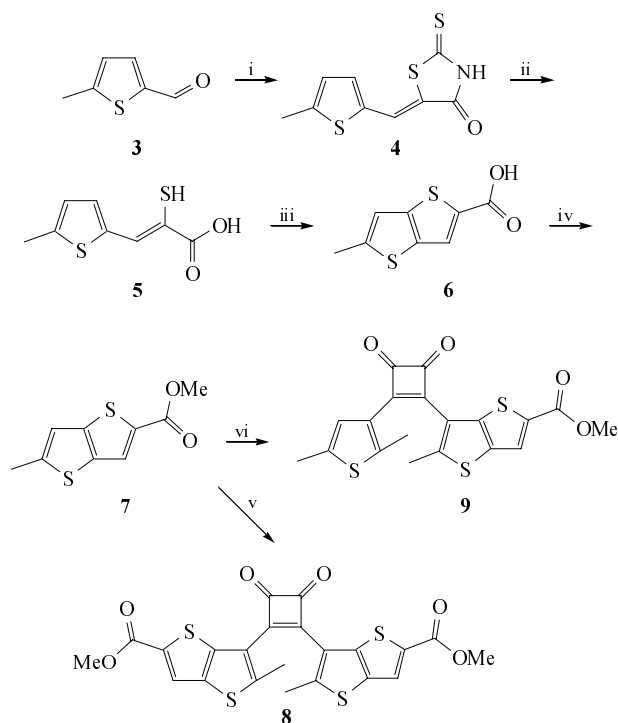


Figure 3 Absorption spectra of 3-(2,5-dimethyl-3-thienyl)-4-(2-methyl-5-methoxycarbonylthieno[3,2-*b*]thiophen-3-yl)cyclobut-3-ene-1,2-dione **9**: dashed line, before irradiation (open form), and on irradiation at 313 nm, exposure times (1) 5, (2) 35, (3) 80, (4) 140, (5) 200 s; dotted line, 260 s (photostationary state).



Scheme 2 Reagents and conditions: i, rhodamine, AcONa, AcOH; ii, NaOH, H₂O; iii, NBS, dichloroethane; iv, MeOH, H₂SO₄; v, 3,4-dichlorocyclobut-3-ene-1,2-dione, AlCl₃, dichloroethane, heptane; vi, 3,4-dichlorocyclobut-3-ene-1,2-dione, 2,5-dimethylthiophene, AlCl₃, dichloroethane, heptane.

[‡] Study of the photochromism of compounds **1**, **2**, **8** and **9** (general procedure). Samples were irradiated with a DRSh-500 mercury lamp using filters for the separation of lines (313 and 578 nm) of the mercury spectrum. The intensity of radiation was determined using a F4 photoelement calibrated with a ferrioxalate actinometer¹⁵ for $\lambda = 313$ nm and an actinometer based on the Reinecke salt¹⁶ for $\lambda = 578$ nm. Absorption spectra were measured on a Shimadzu UV-2101PC spectrophotometer.

Irradiation of compounds **1** and **2** was carried out in hexane, ethanol and acetonitrile; the photochromic characteristics of compounds **8** and **9** were studied in an acetonitrile solution. Changes in the content of cyclic forms of photochromic compounds **8** and **9** on exposure in the dark (the study of thermal stability) were checked by the absorbance of the absorption maxima of long-wave bands of these species.

ethene **9** is thermally stable in the dark, and it was transformed into form **A** only on irradiation with visible light ($\lambda = 580$ nm).

In our opinion, the photochromism of compounds **8** and **9** is due to the fact that, in contrast to thiophene derivatives, their aromaticity loses not completely but partially: one of the thiophene rings of the fused system takes part in the formation of a cyclohexadiene ring but the other ring retains aromaticity. At the same time, the closed form contains a long conjugation chain including in compound **8B**, eight C=C and two C=O bonds or, in **9B**, five C=C bonds and one C=O bond. The transformation of dihetarylcylobutenediones **1** and **2** into closed forms should lead to the complete loss of aromaticity in the heterocycle and to a conjugation system including four C=C bonds, which is energetically less profitable in comparison with their analogues with thieno[3,2-*b*]thiophene residues.

Thus, we synthesised various dihetarylcylobutenediones and studied their photochromic properties. Dithienylcylobutenediones, in contrast to the thieno[3,2-*b*]thiophene derivatives of cyclobutene-1,2-dione, do not exhibit photochromic properties. The presence of only one thieno[3,2-*b*]thiophene fragment in a dihetarylcylobutenedione molecule makes the cyclization on UV irradiation possible.

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