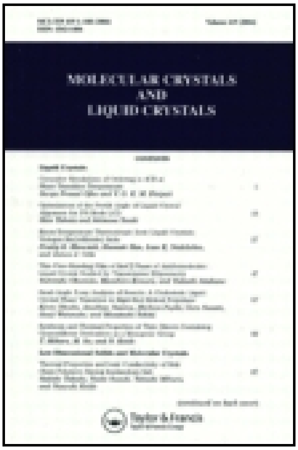

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Synthesis and Photochromism of Dihetarylethenes and Spiro Compounds based on Thiophene Derivatives

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Synthesis and Photochromism of Dihetarylethenes and Spiro Compounds based on Thiophene Derivatives

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Different types of diarylethenes bearing thiophene derivatives were synthesized by a short way and its photchromic properties were examined. It has been demonstrated for the first time that the photochromism of diarylcyclobutenediones depends on aryl substituents and dithienylcyclobutenediones in contrast to the annulated thiophene derivatives of cyclobutenedione, do not exhibit photochromic properties. An efficient approach for the synthesis of spiro compounds of the thieno[3,2-b]pyrrole series was developed starting from easily accessible substituted thienylhydrazine.

Keywords: dithienylethenes, photochromism, spirooxazine, spiropyrane, thiophene

INTRODUCTION

The design and synthesis of photochromic molecules is an intense research area because of their potential applications for optoelectronic devices [1]. Rapid development of computer technology in the last decade has stimulated vast studies in the field of photochromes. It has been synthesized the numerous organic photochromic compounds and its photochromic properties have been examined extensively [2–5].

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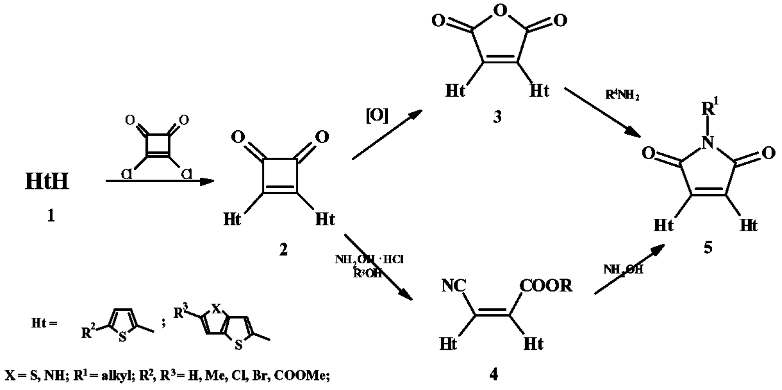
The promising compounds among of them are the photochromes based on thiophene derivatives. However, up to now, their synthesis was quite laborious and low efficient (the overall yields of the products were poor) [6–8]. In this work, we present the synthesis and photochromic properties of new dithienylethenes and spiro compounds based on thieno[3,2-*b*]pyrrole.

SYNTHESIS OF DITHIENYLETHENES

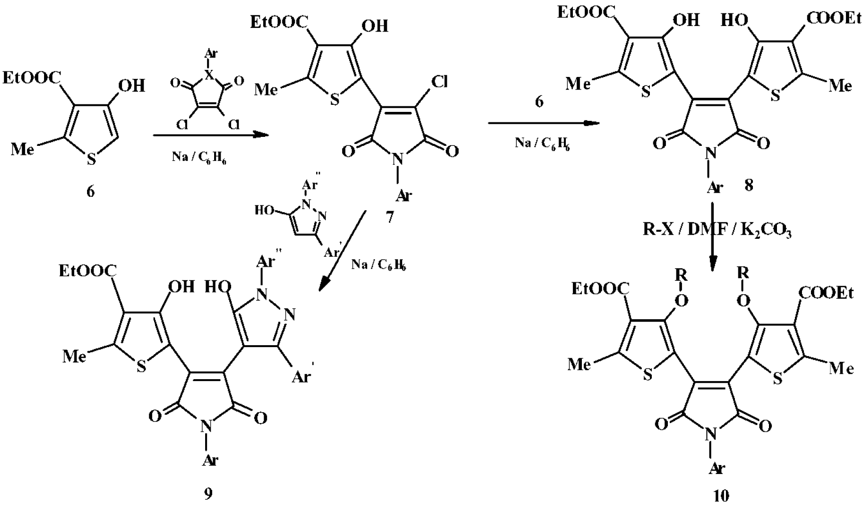
The synthesis of the dithienylethenes involves two main approaches: the first route includes the Friedel-Crafts reaction of the starting thiophene with the dichloride of squaric acid, subsequent oxidation of the condensation products according to Baeyer-Villiger, and the treatment of the latter with primary amines [9]. The second is an electrophilic substitution of the ethers of *β*-hydroxythiophene by dichloride of the N-substituted maleinimides and subsequent alkylation of the condensation products with different alkyl halides [10].

The key stage of the first approach is the synthesis of dithienyl substituted cyclobuten-1,2-diones **2** [11,12]. Then these compounds were applied for the preparation of the target photochromic dithienylethenes based on maleic anhydride **3** [13,14], acrylic acid **4** [15] and maleimides **5** [9,16].



We have synthesized a various symmetrical and unsymmetrical cyclobutene-1.2-diones derivatives bearing thiophene, thieno[3,2-*b*]thiophene and thieno[3,2-*b*]pyrroles fragments as substituents [12,14]. The structures of these dihetarylethenes were confirmed by the data from ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, elemental analysis and X-ray diffraction study. The ^{13}C NMR spectra of dihetarylcyclobutenediones are characterized by signals for the *C* atoms of the keto groups of the cyclobutenedione ring (δ 190—195) and signals for the *C* atoms of the double bond of the cyclobutenedione ring (δ 180—186), which agrees with the known data for various substituted diarylcyclobutenediones [17]. The dithienylethenes **3** were prepared by Baeyer-Villiger oxidation of cyclobutenediones **2** in good yields. The reaction of **2** with hydroxylamine hydrochloride in alcohol leads to dithienyl derivatives of cyanacrylic acid. The maleimides **5** were synthesized under mild conditions by treatment of dithienylethenes **3** and **4** with primary amines in ethanol.

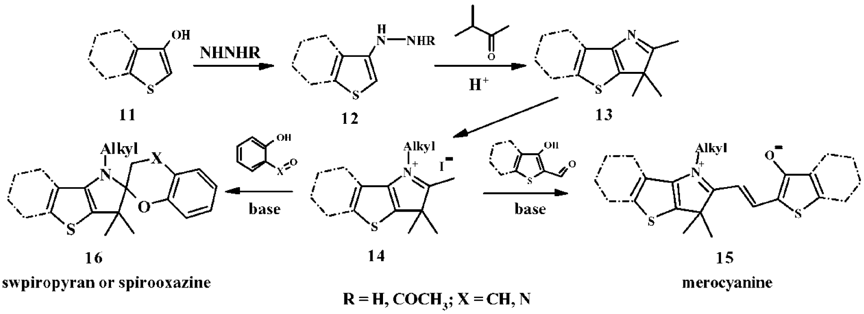
The development of the second pathway allowed us to synthesize different dithienyl maleimide derivatives containing the oxygen atom in the third position of the thiophene cycle. We have found that the reactions of alkyl 4-hydroxy-2-methylthiophene-3-carboxylates **6** with dichloride of maleimides in benzene at 10 to 25°C in the presence of metallic sodium exclusively yields *C*-alkylation products **8** and **9**. *O* – Alkylation of compounds **8** with different alkyl halides in dimethylformamide leads to the target dithienylethenes **10** in high yields [10].



$Ar = Ar' = Ar'' = C_6H_5$, 4-Cl-C_6H_4, 4-MeO-C_6H_4; R = Alkyl; X = Br, I

SYNTHESIS OF SPIRO COMPOUNDS

The most of the known photochromic spiro compounds are indole derivatives. It seemed of interest to synthesize close analogs of these substances containing thieno[3,2-*b*]pyrrole fragments instead of indole ones. Such a replacement of the benzene ring by the thiophene cycle in photochromic systems might induce new useful properties and cause the subsequent chemical modification of the products. The key stage of this synthesis is the preparation of thienopyrrolenine **13**, which has been synthesized by the condensation of thienylhydrazine derivatives **12** with methyl isopropyl ketone. The cyclization is took place in the presence of dry hydrochloric acid in the Fischer reaction. And subsequent alkylation of thienopyrrolenine **13** leads to salt **14**. The reaction of the latter with 2-hydroxybenzaldehyde derivatives or 1-nitroso-2-naphthol yields target spiro compounds **16**. The condensation of the salt **14** with thiophene isoster of salicylaldehyde leads to open merocyanine forms of **15**.



The structures of the synthesized compounds were proved by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry and confirmed by elemental analysis. In the ^{1}H NMR spectrum of spiropyrans, signals from protons of the pyran ring are presented by the AB-quartet with $\delta_A = 5.89$ and $\delta_B = 6.83$ ($J_{AB} = 10.0\,\mathrm{Hz}$) [18]. The spin-spin coupling constants correspond to the published data [19] for spiropyrans of the indole series and indirectly confirm the structures of the obtained spiro compounds.

PHOTOCHROMIC PROPERTIES

The photochromic properties of these new compounds bearing thiophene ring have been studied. Most of the examined dithienylethenes belong to the thermally irreversible photochromic compounds [9,13,16,20]. As expected, dithienylethenes **3–5** turned out to be capable of undergoing reversible isomerization under UV irradiation. Figure 1 illustrates variation of a typical absorption spectrum of compounds **5** under UV irradiation ($\lambda = 365\,\mathrm{nm}$).

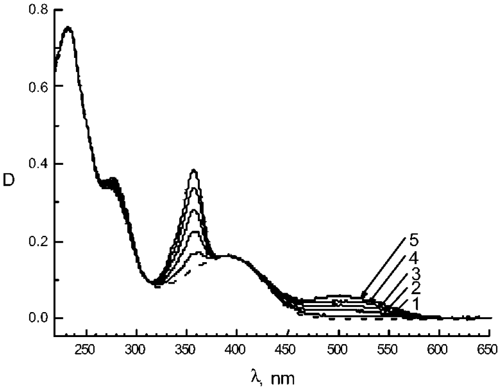


FIGURE 1 Electron absorption spectra of 3,4-bis(2,5-dimethyl-3-thienyl)-1-(2-hydroxyethyl)pyrrole-2,5-dione.

But we have found that the photochromic properties of dihetarylcyclobutenediones **2** depend on hetaryl substituents. So, dithienylcyclobutenediones, in contrast to the thieno[3,2-*b*]thiophene and thieno[3,2-*b*]pyrrole derivatives of cyclobutenedione, do not exhibit photochromic properties. In our opinion, the photochromism of the latter is to the fact that, in contrast to thiophene derivatives, their aromaticity is lost not completetely but partially. We have also found that the compounds **8–10** do not display photochromism, however these compounds are fluorescent and the characteristic fluorescence bands at 525–580 nm are typical for the dithienylethenes **8–10** (Fig. 2).

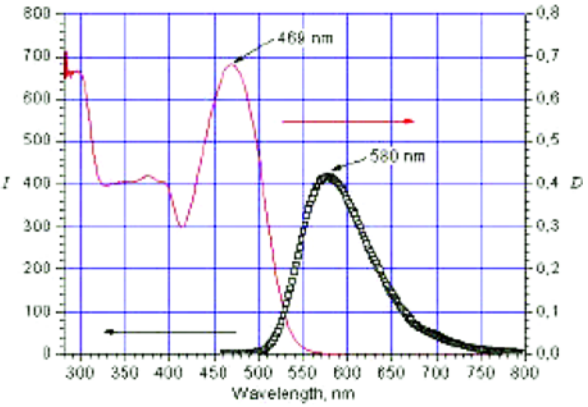


FIGURE 2 Absorption (—) and fluorescence (–□–) spectra.

The photochromic properties of new spiro compounds of the thieno[3,2-*b*]pyrrole series have been examined in various solvents (toluene, acetonitrile and ethanol). The absorption maxima for the 2,4,6,6-tetramethylspiro(thieno[3,2-*b*]pyrroline-5,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine are dependent on solvent: 612 nm in toluene, 565 nm in acetonitrile and 541 nm in ethanol. The colored photogenerated merocyanine form of spironaphthoxazine or spiropyran **16** is thermally unstable and fades immediately. The compounds **15**, containing in chromen part thiophene ring, in contrast to the spiropyran or spirooxazine series **16**, do not exhibit ring closure photoreaction, but they demonstrate *cis–trans* isomerisation process.

CONCLUSION

Thus, the convenient approaches for the preparation of different kinds of dithienylethene were developed and its photochromic properties were examined. In terms of the developed approaches, such fairly promising photochromic systems have become accessible. An effective route for the synthesis of new photochromic spiro compounds based on thieno[3,2-*b*]pyrrole, in spiropyran or spirooxazine series was described.

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