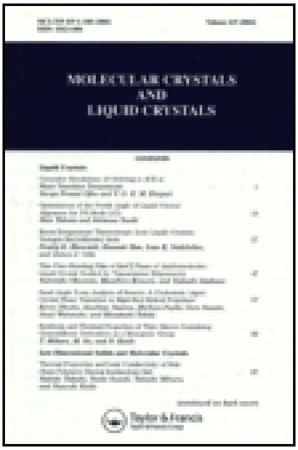

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Synthesis and Photochromic Properties of Functional Diarylethenes with a [1,3]dithiol-2-one (Thione) Bridging Unit

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Synthesis and Photochromic Properties of Functional Diarylethenes with a [1,3]dithiol-2-one (Thione) Bridging Unit

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In designing new photochromic compounds for optical data storage and photoswitching devices, the synthesis of a series of 4,5-diaryl-1,3-dithiol-2-one and 4,5-diaryl-1,3-dithiol-2-thione, which are suitable building blocks for incorporation with fluorophore, is herein reported. Our strategy needs the preliminary preparation of diarylalkynes, obtained by successive Sonogashira-Hagihara coupling-reactions in good yields (63–92%). A combination of these synthetic precursors with diisopropylxanthogen disulfide leads to the corresponding 4,5-diaryl-1,3-dithiol-2-ones under radical conditions with excellent yields (54–70%). The thionation of these compounds is obtained nearly quantitatively with phosphorous pentasulfide.

Keywords: 1,2-diarylalkynes; 4,5-diaryl-1,3-dithiol-2-one; 4,5-diaryl-1,3-dithiol-2-thione; photochromism; synthesis

INTRODUCTION

In the last few years, the increasing demand for optical data storage [1] and photoswitching devices [2] has led to the development of new photochromic compounds. Among the many known photochromic systems, 1,2-diarylethenes derivatives [3] have received the most

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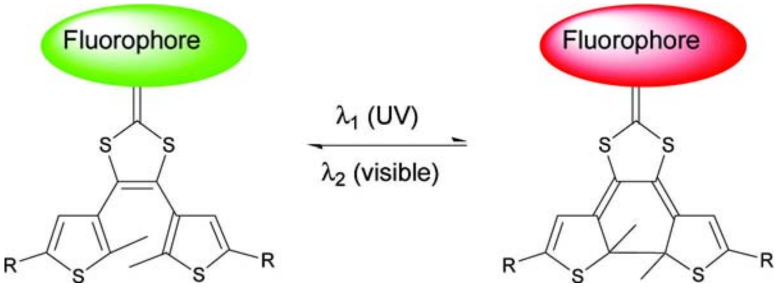
attention because of their remarkable fatigue resistance, thermal and chemical stability. To prevent *cis–trans* photoisomerization, the most common 1,2-diarylethenes, containing maleic anhydride [4], maleimide [5], perfluorocyclopentene and cyclopentene units [6], include a five-membered cycloalkene.

Each bridging unit has its advantages and disadvantages. The two first systems are readily accessible but are sensitive to acidic conditions and exhibit degradation in the presence of oxygen [7]. Although the photochromic properties of the diarylperfluorocyclopentenes are highly attractive, their synthesis are not trivial and the expensive volatile starting material octafluorocyclopentene is a major disadvantage.

Branda's group [8–10] and Irie's group [11] described supramolecular photochromic switches based on bis(thienyl)ethene where the thiophene rings are linked to fluorescent unit. The reversible property changes during the photoisomerization reaction, such as the refractive index [12], dielectric constant, redox potential and luminescence [13] can be used to achieve a non-destructive readout [10]. Further development of new systems based on the 1,2-diarylethene is warranted.

Working from the assumption that 4,5-diaryl-1,3-dithiol-2-one (thione) photoswitch moiety fused with fluorophores could regulate the fluorescence property (Scheme 1), we herein present a new series of diarylethenes based on the 1,3-dithiol-2-one (thione) bridging unit. We conclude with preliminary data on the photochromic properties of these compounds.

The radical methodology used in constructing the 1,3-dithiol-2-one moiety, represents a significant addition to the current literature methodology.



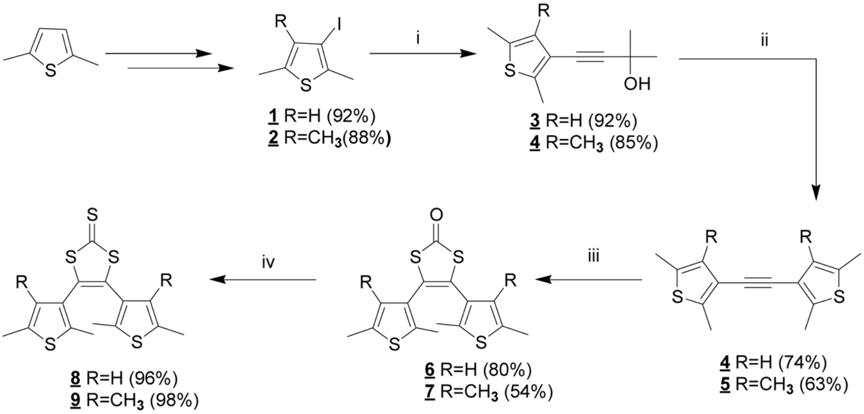
SCHEME 1

RESULTS AND DISCUSSION

Synthesis

Among the various methods for introducing alkynyl groups on aromatic nuclei, the most powerful and useful is the Pd-catalyzed cross-coupling reaction of halogenoarenes with terminal alkynes, which was reported for the first time by *Sonogashira-Hagihara* [14] and *Cassar* [15] in 1975. A variation of this synthetic procedure involves the use of protecting groups [16]. Coupling of halogenoarenes with the commercially available 2-methylbut-3-yn-2-ol provides the 3-arylalkynol [17]. This compound generates '*in situ*' a terminal arylacetylene moiety (by removal of the protecting group), which can be involved in an other *Sonogashira* coupling to afford diarylalkynes [18]. This approach was used to the efficient preparation of bisthienylethynes **4** and **5** as illustrated in Scheme 2.

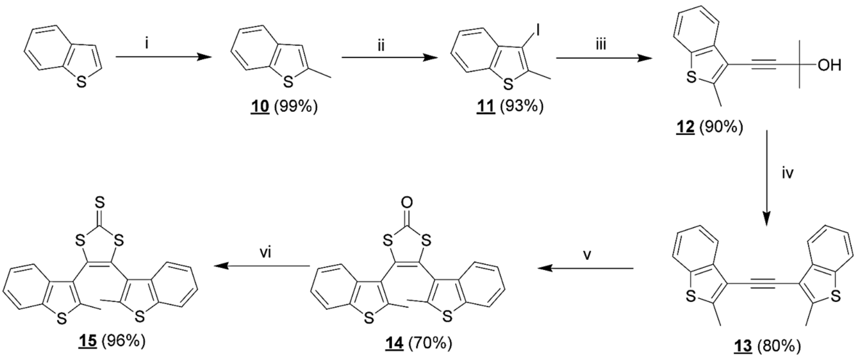
The synthesis of iodothiophene **1** and **2** was accomplished by using the procedure described by *Gronowitz* [19]. In the presence of a catalytic amount of [$PdCl_2(PPh_3)_2$] and CuI, the classic *Sonogashira* reaction of **1** and **2** with the commercially available 2-methylbut-3-yn-2-ol in Et_2NH (room temperature, 15 h) afforded **3** and **4** in 92% and 85% yield respectively. A modified version of the *Sonogashira* coupling carried out under phase-transfer condition [20], allowed the synthesis of compound **4** and **5**. Reaction of **3** and **4** with their respective precursors



SCHEME 2 Reagents and conditions: (i) [$PdCl_2(PPh_3)_2$], CuI, Et_2NH, $HC{\equiv}CC(CH_3)_3OH$, 20°C, 15 h; (ii) [$Pd(PPh_3)_4$], CuI, benzene, aq. 5.5 N NaOH, $PhCH_2Net_3{}^+Cl$, reflux, 20 h; (iii) isopropylxanthic disulfide, AIBN, toluene, reflux; (iv) P_4S_{10}, toluene, reflux.

1 and **2** at 70°C for 20 h, in the presence of benzyltriethylammonium chloride as phase-transfer agent, aqueous 5.5 N NaOH as base, benzene as solvent, and a mixture of $[Pd(PPh_3)_4]$ and CuI as catalysts, gave **4** and **5** in 74% and 63% yield respectively. The formation of the 1,3-dithiol-2-ones is obtained in only one step from commercially available diisopropylxanthogen disulfide and alkynes **4** and **5** under radical conditions. Conversion of **4** and **5** to **6** and **7**, was efficiently accomplished by treatement with diisopropylxanthogen disulfide and AIBN, in refluxing benzene [21]. The buildings blocks **6** and **7** were isolated after chromatography in 80% and 54%. Phosphorus pentasulfide (P_4S_{10}) has been employed for effecting the conversion of carbonyl group to thiocarbonyl group [22]. Treatement of the 1,3-dithiol-2-one **6** and **7** with P_4S_{10}, in refluxing toluene, allowed their nearly quantitative conversion to the corresponding 1,3-dithiol-2-thione **8** and **9** (96% and 98% respectively). This synthetic strategy was extended to prepare a dithianaphthene derivative. Then, the synthesis of photochromic targets **14** and **15** were realized according to the Scheme 3.

The 2-lithiobenzo[*b*]thiophene, obtained in *situ* from the reaction of commercial benzo[*b*]thiophene with *n*-butyllithium, was trapped with iodomethane to give 2-methylbenzo[*b*]thiophene **10** in quantitive yield. Treatment of **10** with iodine in presence of iodic acid in acid conditions afforded **11** in 93%. A *Sonogashira* coupling of **11** with an excess of 2-methyl-3-yn-ol afforded **12** in 90%. Another *Sonogashira* reaction,



SCHEME 3 Reagents and conditions: (i) 2.1 eq n-Buli, Et_2O, $-78°C \rightarrow 20°C$, then CH_3I $-78°C \rightarrow$ rt; (ii) I_2, HIO_3, CH_3COOH, H_2O, H_2SO_4, 70°C, 3 h; (iii) $[PdCI_2(PPh_3)_2]$, CuI, Et_2NH, $HC{\equiv}CC(CH_3)_2OH$, 20°C, 4 days; (iv) KOH, MeOH, Toluene, reflux, 6 h; (v) **14**, $[PdCI_2(PPh_3)_2]$, CuI, EtN_2H, 60°C, 20 h; (vi) isopropylxanthic disulfide, AIBN, toluene, reflux; (vii) P_4S_{10}, toluene, reflux.

carried out under phase transfer conditions [20], of **12** with its precursor **11**, gives **13** in 80%. The radical addition of the diisopropylxanthogen disulfide [21] onto **13**, gives the 1,3-dithiol-2-one **14** in good yield (70%). The thionation of **14** using P_4S_{10} in refluxing toluene [22] afforded **15** in excellent yield (96%).

Photochromic Behavior

An example is given with compound **15**. The photocyclization of **15** was achieved by irradiation of a cyclohexane solution (3.10^{-5}) in presence of air at wavelength corresponding to the absorption band of the open-ring isomer (Fig. 1).

At the photostationary state obtained in about 4 min, the absorption of the colored form is 522 nm. Several cycles photocoloration/photodecoloration (respectively using 374 nm and 522 nm wavelengths) have been achieved, showing the good reversibility of the

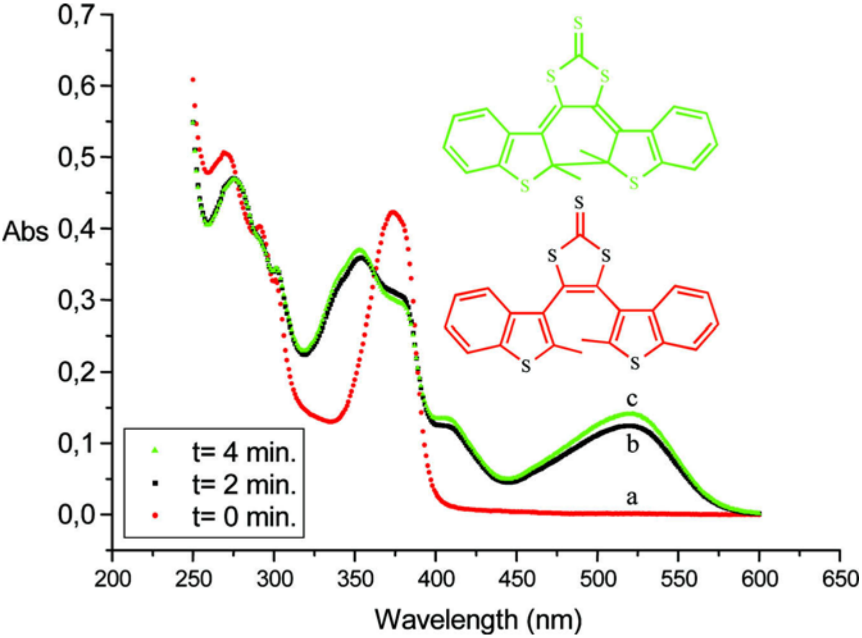


FIGURE 1 UV-Vis absorption spectra change of **15** (3.10^{-5} M in cyclohexane) measured at room temperature, at different stages of the photochromic reaction. Continuous irrdiation (374 nm). (a) starting open-ring isomer, (b) after irradiadiation for 2 minutes, (c) 4 minutes.

system. A more extended study of the photochemical properties of these systems is in progress.

CONCLUSION

We have described a synthetic strategy for the preparation of a series of new photochromic 4,5-diaryl-1,3-dithiol-2-ones and 4,5-diaryl-1,3-dithiol-2-thiones. They constitue good building blocks for the design of photochromic-fluorophore compounds. 1,3-thiole-2-thiones were synthetized too for that aim.

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