

SHORT  
COMMUNICATIONSSynthesis of Photochromic 3,4-Bis(1,2-dimethylindol-3-yl)-  
2,5-dihydrothiopheneV. P. Rybalkin<sup>a</sup>, E. N. Shepelenko<sup>b</sup>, L. L. Popova<sup>a</sup>, A. D. Dubonosov<sup>b</sup>, A. V. Metelitsa<sup>a</sup>,  
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Received November 2, 2005

DOI: 10.1134/S1070428006040257

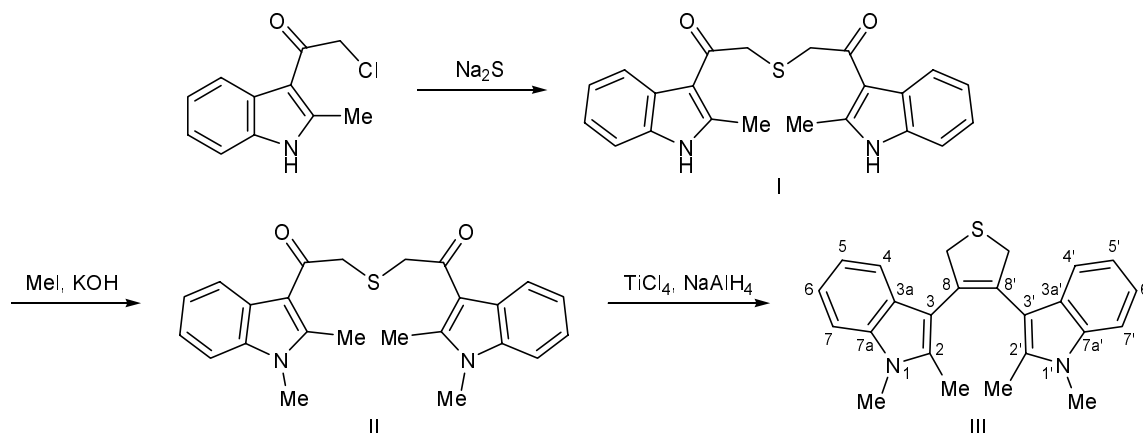
Bistable photochromic compounds attract increasing interest as materials for three-dimensional optical data storage devices and optically controlled molecular switches [1]. From this viewpoint, dihetarylethenes constitute one of the most promising classes of organic photochromes due to thermal stability of both their initial and photoinduced forms [2]. The use of dihetarylethenes with a cyclic bridging moiety makes it possible to avoid *cis-trans* isomerization at the double bond in the excited state, which competes with the photocyclization. The list of cyclic ethene fragments proposed for the synthesis of light- and heat-resistant photochromic diarylethenes is so far short; therefore, new ethene fragments suitable for this purpose attract considerable interest.

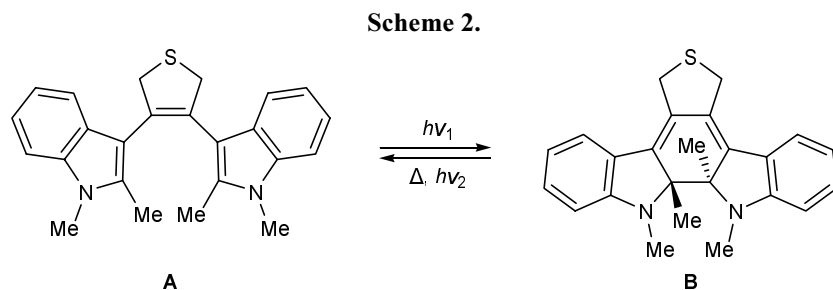
Huang *et al.* [3] proposed a synthetic approach to cyclic ethenes via intramolecular McMurry reaction

[4]. This approach ensured preparation of both 1,2-dihetarylcycloalkenes and 3,4-dihetaryl-2,5-dihydrothiophenes. However, experimental implementation of this reaction is not always simple. For example, the product isolated in [3] was erroneously assigned the structure of 3,4-bis(1,2-dimethyl-1*H*-indol-3-yl)-2,5-dihydrothiophene (**III**), though it showed no photochromic properties. We have developed a procedure for the synthesis of compound **III** (Scheme 1).

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound **III** thus obtained contained signals from both indole and 2,5-dihydrothiophene fragments, primarily a triplet from the olefinic C<sup>8</sup> atoms at δ 131.78 ppm (*J* = 7.8 Hz) in the carbon spectrum. Signals from the methylene protons and protons of the 2-methyl groups in the indole fragments were broadened, indicating the occurrence of conformational transformations charac-

Scheme 1.





terized by a high energy barrier, which is typical of 1,2-dihetarylethenes.

Compound **III** showed photochromic properties both in solution and in the crystalline state. Initial state **A** is characterized by a long-wave absorption band with its maximum at  $\lambda$  287 nm (in toluene;  $\epsilon = 27070 \text{ l mol}^{-1} \text{ cm}^{-1}$ ). Irradiation with a mercury lamp ( $\lambda$  313 nm) induces thermally and photochemically reversible coloration of solutions containing compound **III** due to formation of cyclic isomer **B** with the long-wave absorption maximum located at  $\lambda$  507 nm. The colored solution of isomer **B** is thermally stable; its lifetime at 293 K is as long as  $2.2 \times 10^5$  s. Irradiation of the solution in the visible region ( $\lambda$  546 nm) restores the original absorption spectrum of isomer **A** as a result of photoinduced ring opening **B**  $\rightarrow$  **A** (Scheme 2).

Thus, in contrast to [3], we can state with certainty that we have synthesized a new bistable photochromic dihetarylethene, 3,4-bis(1,2-dimethyl-1*H*-indol-3-yl)-2,5-dihydrothiophene (**III**).

**1,5-Bis(2-methyl-1*H*-indol-3-yl)-3-thiapentane-1,5-dione (I).** Sodium sulfide nonahydrate, 3.8 g (0.015 mol), was added to a solution of 6.2 g (0.03 mol) of 2-chloro-1-(2-methyl-1*H*-indol-3-yl)ethanone in 10 ml of dimethylformamide. The mixture was heated for 3 h at 80–90°C, cooled, and poured into water. The precipitate was filtered off and recrystallized from 1-butanol–DMF (1:1). Yield 61%, colorless crystals, mp 280–282°C; published data [5]: mp 228–232°C (decomp., from dioxane). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3210 (NH), 1615 (CO), 1440.  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 2.68 s (6H, CH<sub>3</sub>), 3.96 s (4H, CH<sub>2</sub>S), 7.02–7.18 m (4H, H<sub>arom</sub>), 7.26–7.34 m (2H, H<sub>arom</sub>), 7.83–8.93 m (2H, H<sub>arom</sub>), 11.72 br.s (2H, NH). Found, %: C 70.63; H 5.52; N 7.22. C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S. Calculated, %: C 70.19; H 5.35; N 7.44.

**1,5-Bis(1,2-dimethyl-1*H*-indol-3-yl)-3-thiapentane-1,5-dione (II).** Sodium hydroxide,\* 0.85 g (0.02 mol), was added to a solution of 6.1 g (0.016 mol)

of sulfide **I** in 30 ml of DMSO, the mixture was stirred for 0.5 h, 1.3 ml (0.02 mol) of methyl iodide was added dropwise under stirring, and the mixture was stirred for 2.5 h and poured into water. The precipitate was filtered off and recrystallized from 1-butanol. Yield 83%, colorless crystals, mp 183–184°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1620 (CO), 1450.  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 2.70 s (6H, CH<sub>3</sub>), 3.70 s (6H, NCH<sub>3</sub>), 4.02 s (4H, SCH<sub>2</sub>), 7.10–7.23 m (4H, H<sub>arom</sub>), 7.36–7.44 m (2H, H<sub>arom</sub>), 7.80–7.90 m (2H, H<sub>arom</sub>). Found, %: C 70.83; H 5.72; N 7.22. C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S. Calculated, %: C 71.26; H 5.98; N 6.92.

**3,4-Bis(1,2-dimethyl-1*H*-indol-3-yl)-2,5-dihydrothiophene (III).** Titanium(IV) chloride, 3.79 g (0.02 mol), was added dropwise to a suspension of 0.81 g (0.015 mol) of NaAlH<sub>4</sub> in 50 ml of anhydrous THF under stirring at 0–2°C in a stream of argon, and the mixture was kept for 1 h. Sulfide **II**, 2.02 g (0.005 mol), was then added in portions to the resulting black solution, and the mixture was stirred for 1 h at room temperature, heated for 8 h at 60°C on a water bath, cooled, poured into 200 ml of a 10% solution of K<sub>2</sub>CO<sub>3</sub>, and extracted with chloroform. The extract was dried over CaCl<sub>2</sub> and evaporated under reduced pressure, and the residue was purified by column chromatography on Al<sub>2</sub>O<sub>3</sub> using chloroform as eluent, followed by recrystallization from acetonitrile. Yield 11%, colorless crystals, mp 142–144°C; published data [3]: mp 106–108.  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 1.80 br.s (6H, CH<sub>3</sub>), 3.47 s (6H, NCH<sub>3</sub>), 3.90–4.80 br (4H, CH<sub>2</sub>), 6.98–7.24 m (6H, H<sub>arom</sub>), 7.48–7.60 m (2H, H<sub>arom</sub>).  $^{13}\text{C}$  NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 11.19 q (CH<sub>3</sub>,  $J = 128.0$  Hz), 29.34 q (NCH<sub>3</sub>,  $J = 137.9$ ), 42.60 t (CH<sub>2</sub>,  $J = 143.0$ ), 108.44 m (C<sup>7</sup>) 108.75 m (C<sup>3</sup>), 118.04 m (C<sup>5</sup>), 118.92 m (C<sup>6</sup>), 119.04 m (C<sup>5</sup>), 120.30 m (C<sup>4</sup>), 126.92 m (C<sup>3a</sup>), 131.78 br.t (C<sup>8</sup>,  $J = 7.8$  Hz), 134.05 m (C<sup>2</sup>), 136.48 m (C<sup>7a</sup>). Found, %: C 77.01; H 6.31; N 7.63. C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>S. Calculated, %: C 77.38; H 6.49; N 7.52.

The electron absorption spectra were measured on a Varian Carry 100 spectrophotometer. Photolysis of

\* As in Russian original.—*Publisher*.

solutions was performed with the use of a DRSh-250 high-pressure mercury lamp equipped with a set of interference filters (to isolate the required line); cell thickness 10 mm; concentration  $2 \times 10^{-5}$  M (toluene). The IR spectra were recorded on a Specord 75IR spectrometer from samples dispersed in mineral oil. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Varian Unity-300 instrument (300 MHz for  $^1\text{H}$ ) using  $\text{DMSO}-d_6$  ( $^1\text{H}$ ) and  $\text{CDCl}_3$  ( $^{13}\text{C}$ ) as solvents.

This study was performed under financial support by the International Scientific and Technical Center (project no. 2117), by the Russian Foundation for Basic Research (project no. 05-03-08087), and by the Ministry of Education and Science of the Russian

Federation (trade research program "Development of the Scientific Potential at Higher School," 2005, project no. 30079).

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