

SHORT
COMMUNICATIONS

Synthesis of 1,2-Bis(3-methylbenzo[*b*]furan-2-yl)cyclopentene and 1,2-Bis(3-methylbenzo[*b*]furan-2-yl)cyclohexene

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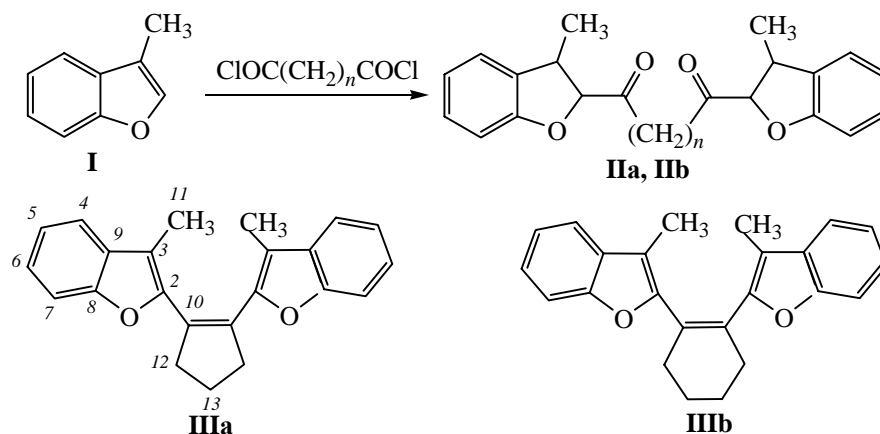
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Bistable photochromic compounds, whose initial and photoinduced forms possess thermal stability, are subjected to comprehensive studies due to the recently discovered possibility to apply them in the field of informational technology [1]. A special place among them belongs to diheterylethenes that are regarded as light-sensitive components of materials for three-dimensional fixation of information [2]. The main problem consists now in preparation of such compounds of this class that alongside the bistability characteristic are endowed with fluorescence of the initial or, better, of the photoinduced colored form.

In order to look for a sensible way of preparation of new diheterylethenes containing in the molecule

benzo[*b*]furan fragments we synthesized 1,2-bis(3-methylbenzo[*b*]furan-2-yl)cyclopentene (**IIIa**) and 1,2-bis(3-methylbenzo[*b*]furan-2-yl)cyclohexene (**IIIb**). The application of diheterylethenes with an ethane fragment attached to the position 2 of the heterocycle may result in appearance of fluorescence in a cyclic form, as, for example, in a related class of photochromic compounds, indolyl-2 fulgides [3].

As an initial heterocyclic compound we used the 3-methylbenzo[*b*]furan (**I**), that by acylation with glutaryl dichloride and adipoyl chloride gave the corresponding diketones **IIa** and **IIb** which were reduced into ethenes **IIIa** and **IIIb** by McMurry procedure [4].



$n = 1$ (a), 2 (b).

The composition and structure of synthesized compounds **II** and **III** were established from elemental analysis, IR, ^1H and ^{13}C spectroscopy. Electron absorption spectra of diheterylethenes **IIIa** and **IIIb** solutions in hexane, toluene, and acetonitrile contain characteristic absorption bands in the longwave region with maxima at 315–330 nm. Stationary irradiation with a light of a mercury lamp through a filter of dilute solutions of compounds **IIIa** and **IIIb** ($c \sim 10^{-5}$ mol l $^{-1}$ in hexane, toluene, and acetonitrile) resulted in irreversible changes in their electronic spectra, noticeable by the sharp intensity decrease in the longwave absorption bands. No absorption band were observed in the visible spectral range characteristic of cyclic colored isomers of diheterylethenes indicating the lack of photochromic qualities under the given conditions in diheterylethenes **IIIa** and **IIIb**.

1,5-Bis(3-methylbenzo[*b*]furan-2-yl)pentane-1,5-dione (IIa). To a suspension of 5 g (0.019 mol) of AlCl_3 in 50 ml of anhydrous dichloroethane was added dropwise a solution 2.5 ml (0.02 mol) glutaryl dichloride in 10 ml of anhydrous dichloroethane at 0–10°C, and the mixture was kept at this temperature for 0.5 h; then dropwise was added a solution of 5 g (0.038 mol) of 3-methylbenzo[*b*]furan in 20 ml of anhydrous dichloroethane. The reaction mixture was stirred at room temperature for 2 h, then it was poured on ice, acidified with HCl, the dichloroethane layer was separated, the water phase was extracted with dichloroethane (3×20 ml). The combined dichloroethane solutions were washed with water, dried over CaCl_2 , dichloroethane was distilled off, and compound **IIa** obtained was twice recrystallized from 1-butanol. Yield 5.4 g (73%), colorless crystals, mp 110°C. IR spectrum, cm^{-1} : 1680 (C=O), 1570 (C=O), 1465 (CH_3). ^1H NMR spectrum (CDCl_3), δ , ppm: 2.23 quintet (2H, CH_2 , J 7.2 Hz), 2.62 s (6H, 2 CH_3), 3.17 t (4H, 2 CH_2 , J 7.2 Hz), 7.25–7.35 m (2 H_{arom}), 7.41–7.49 m (4 H_{arom}), 7.62–7.67 m (2 H_{arom}). Found, %: C 76.6; H 5.5. $\text{C}_{23}\text{H}_{20}\text{O}_4$. Calculated, %: C 76.65; H 5.59.

1,6-Bis(3-methylbenzo[*b*]furan-2-yl)hexane-1,6-dione (IIb) was prepared similarly from 3-methylbenzo[*b*]furan and adipoyl chloride. Yield 3.6 g (50%), colorless crystals, mp 134°C. IR spectrum, cm^{-1} : 1660 (C=O), 1565 (C=O), 1445 (CH_3). ^1H NMR spectrum (CDCl_3), δ , ppm: 1.88 m (4H, 2 CH_2), 2.60 s (6H, 2 CH_3), 3.08 m (4H, 2 CH_2), 7.25–7.35 m (4 H_{arom}), 7.62–7.67 m

(2 H_{arom}). Found, %: C 76.6; H 5.8. $\text{C}_{24}\text{H}_{22}\text{O}_4$. Calculated, %: C 76.99; H 5.92.

1,2-Bis(3-methylbenzo[*b*]furan-2-yl)cyclopentene (IIIa). To a suspension of 2.2 g (0.04 mol) of NaAlH_4 in 70 ml of anhydrous THF was added dropwise in an argon flow 9.5 g (0.05 mol) of TiCl_4 at 0–2°C, and the mixture was kept for 1 h. To a black solution obtained was added dropwise a solution of 4.16 g (0.012 mol) of compound **IIa** in 20 ml of anhydrous THF, and the mixture was stirred at room temperature for 1 h. Then the reaction mixture was heated on a water bath at 60°C for 4 h, then it was cooled, poured into 200 ml of 10% solution of K_2CO_3 , the reaction product was extracted into chloroform. The extract was dried over CaCl_2 , chloroform was distilled off in a vacuum, and the residue was recrystallized from acetonitrile. Yield 43%, colorless crystals, mp 79°C. IR spectrum, cm^{-1} : 1450 (C=C, CH_3). UV spectrum (acetonitrile), λ_{max} , nm (log ϵ): 213 (4.24), 265 (4.17), 330 (4.18). ^1H NMR spectrum (CDCl_3), δ , ppm: 1.73 s (6H, 2 CH_3), 2.16 quintet (2H, CH_2 , J 7.6 Hz), 3.05 t (4H, 2 CH_2 , J 7.6 Hz), 7.14–7.30 m (4 H_{arom}), 7.36–7.44 m (4 H_{arom}). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 8.89 q (C^{11} , J 127.7 Hz), 22.61 t (C^{13} , J 130.7 Hz), 36.61 t (C^{12} , J 131.9 Hz), 110.71 m (C^7), 113.13 m (C^3), 119.22 m (C^4), 122.13 m (C^6), 124.09 m (C^5), 130.24 m (C^9), 131.49 m (C^{10}), 149.76 q (C^2 , J 5.4 Hz), 154.25 m (C^8). Found, %: C 84.01; H 6.01. $\text{C}_{23}\text{H}_{20}\text{O}_2$. Calculated, %: C 84.12; H 6.14.

1,2-Bis(3-methylbenzo[*b*]furan-2-yl)cyclohexene (IIIb) was obtained in the same way. Yield 47%, colorless crystals, mp 152°C. IR spectrum, cm^{-1} : 1445 (C=C, CH_3). UV spectrum (acetonitrile), λ_{max} , nm (log ϵ): 213 (4.36), 261 (4.30), 316 (4.17). ^1H NMR spectrum (CDCl_3), δ , ppm: 1.54 s (6H, 2 CH_3), 1.80–1.94 m (4H, 2 CH_2), 2.55–2.70 m (4H, 2 CH_2), 7.11–7.31 m (4 H_{arom}), 7.33–7.42 m (4 H_{arom}). Found, %: C 84.01; H 6.21. $\text{C}_{24}\text{H}_{22}\text{O}_2$. Calculated, %: C 84.18; H 6.48.

IR spectra of samples as mulls in mineral oil were recorded on a spectrophotometer Specord 75IR, ^1H and ^{13}C NMR spectra of solutions in CDCl_3 were registered on a spectrometer Varian Unity-300 (300 MHz). Electron absorption spectra were taken on a spectrophotometer Varian Carry-100. Photolysis of the solution was carried out with a mercury lamp DRSh-250 equipped with a set of interference filters for isolating the lines of mercury spectrum.

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