ORGANIC LETTERS

2003
Vol. 5, No. 9
1435−1437

Synthesis and Photochromic Properties of Functional Diarylethene with a 2,5-Dihydrothiophene Bridging Unit

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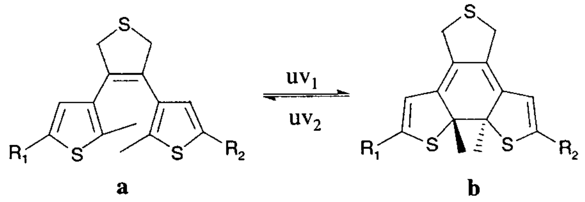
Received January 30, 2003

ABSTRACT



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A novel synthetic route to symmetric and nonsymmetric dithienylethene derivatives with a 2,5-dihydrothiophene bridging unit was described. A class of new functional photochromic compounds was prepared and showed photochromic properties similar to those of known diarylethenes.

Diarylethenes, notably the bis(thien-3-yl) system, display excellent photochromic properties[1] and are the most promising photochromic compounds among various photochromic compounds for photoelectronic applications such as optical memony media[2] and photoswitching devices[3] because of their fatigue resistant[4] and thermally irreversible properties.[5] There are several 1,2-bis(thien-3-yl) systems containing maleic anhydride,[6] maleimide,[7] perfluorocyclopentene,[8] and cyclopentene[9] units that have been employed so far. Each unit has its advantages and disadvantages. Diarylethenes with a perfluorocyclopentene bridging unit, for instance, exhibit excellent photochromic properties. However, the expensive and rather volatile starting material octafluorocyclopentene is a major disadvantage. Both diarylmaleic anhydrides and diarylmaleimides are readily accessible but are sensitive to acidic conditions.

We report herein a new class of diarylethenes with a 2,5-dihydrothiphene unit[10] and a novel synthetic route to preparing symmetric and nonsymmetric functional dithienylethene derivatives. We also present the photochromic properties of

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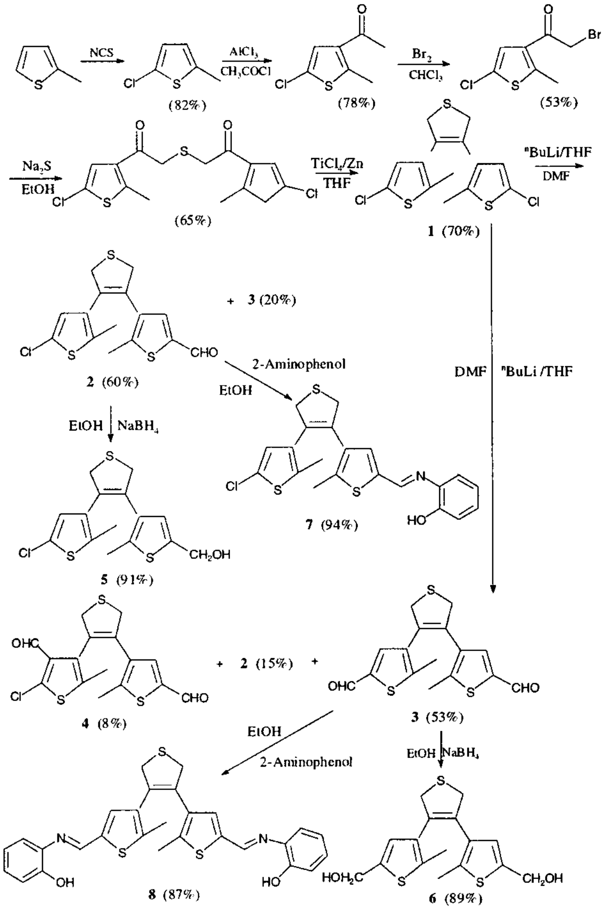
10.1021/ol034166r CCC: $25.00

these new compounds. Compared with reported synthetic methods and properties of diarylethenes, the merits of this paper are based on (1) a class of new diarylethenes with symmetric and nonsymmetric molecular structures, (2) cheap starting materials, and (3) readily accessible dithienylethene derivatives. The synthesis can be performed on a large scale from cheap starting materials (Scheme 1). Compound **1a** was obtained starting from 2-methylthiophene, which was chlorinated at the 5-position with NCS in AcOH, followed by acylation and bromination with CH_3COCl in dichloromethane (DCM) and Br_2 in chloroform, respectively. 1,1′-Bis[3-(5-chloro-2-methyl)-acetylthiophene]-dimethyl sulfide, which was obtained from 3-(5-chloro-2-methyl)-1′-bromine-acetylthiophene with Na_2S in EtOH, was used in the McMurry coupling reaction[11] with $TiCl_4$ and Zn in THF to afford **1a**. Monoaldehyde **2a** and dialdehyde **3a** were synthesized by lithiation of **1a** under different conditions followed by quenching with DMF. It is worth noting that when the ratio of **1a** and $\mathrm{Bu^nLi}$ and DMF was 1:2.5:1.5 (mole), compound **2a** as the major product was obtained in 60% yield, and compound **3a** as the minor product was obtained in 20% yield; when the ratio of **1a** and $\mathrm{Bu^nLi}$ and DMF was 1:5.0:1.5 (mole), compound **3a** as the major product was obtained in 53% yield, and compounds **2a** and **4a** as the minor product were obtained in 15% and 8% yield, respectively. The yields in the coupling step were very good (total yields were about 80%) and the regioselectivity of the aldehydelyzation of compound **1a** was reasonable. The conversion of **5a** and **6a** was performed by reduction of **2a** and **3a** with $NaBH_4$ in EtOH at room temperature, respectively. Schiff base **7a** and **8a** were obtained by treatment of **2a** and **3a** with 2-aminophenol in EtOH under reflux, respectively. This new route provides ready access to a variety of symmetric or nonsymmetric diarylethenes with a 2,5-dihydrothiophene unit.

Scheme 1. Synthetic Route of Functional Diarylethene with a 2,5-Dihydrothiophene Bridging Unit



The photochromic behavior was illustrated by Figures 1 and 2. Figures 1 and 2 represent the changes of absorption of **2a** and **3a** in acetonitrile upon irradiation at 254 nm. In general, the absorption of the ring-open form appears at a shorter wavelength, while the absorption of the ring-closed form takes place at a longer wavelength since π-electrons delocalize throughout the two condensed thiphene rings and further extend to the substituents in the ring-closed form. When **2a** was irradiated, two new absorption bands appeared at 348 and 526 nm, respectively, corresponding to closed form **2b**. A similar result was obtained from Figure 2 when **3a** was irradiated at 254 nm, and the two new absorption

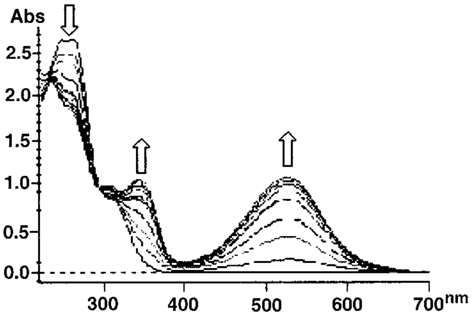


Figure 1. Absorption changes of **2a** in acetonitrile upon irradiation at 254 nm (2×10^{-5} M).

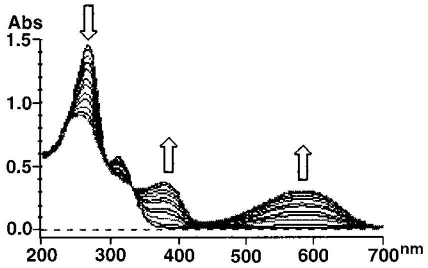


Figure 2. Absorption changes of **3a** in acetonitrile upon irradiation at 254 nm (2×10^{-5}M).

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bands appeared at 389 and 582 nm, respectively, which were ascribed to the closed form isomer **3b**. Both figures showed the typical absorption spectral changes of diarylethene derivatives in solvents.[12] From the figures it could also be seen clearly that an isobestic point appeared in both absorption spectra. That indicated only two isomers existed when the compound underwent the photoisomerization reaction.

The UV–Vis data of other compounds for the open and closed forms are listed in Table 1. Compared to the known diarylethene derivatives, the absorption maximum of **1**, **3**, and **8** in the closed form was almost the same as was reported.[6] Compounds **2**, **4**, **5**, **6**, and **7** also showed the typical absorption spectral changes of photochromic diarylethene derivatives upon irradiation in solvent. From the viewpoint of application to optical memory media, it is desired to develop photochromic compounds that have sensitivity in the wavelength region 530–650 nm (DVD). The effect of substituents on the absorption maximum in actonitrile was examined. When chloro or hydroxy groups were substituted at the 5- and 5′-position of the thiophene rings, the absorption maximum of the ring-closed form (**1b**, **5b**, **6b**) was about 450 nm in acetonitrile. When an electron-withdrawing substituent was introduced into the 5- and 5′-position of the thiophene ring, the absorption maximum of the ring-closed form **3b** was shifted to 582 nm in acetonitrile. However, when an electon-donating substituent was introduced into the 5- and 5′-position of the thiophene ring, the absorption maxium of the ring-closed form **8b** was further shifted to 608 nm in acetonitrile.

Table 1. UV–Vis Data of Compounds in Acetonitrile

compd	λ_{max}/nm (open)	λ_{max}/nm (closed)
1	234	448, 305
2	232[a]	526, 345
3	266[a]	582, 384
4	243[a]	512, 375
5	224	452, 301
6	232	454, 301
7	296, 246	497, 371
8	362, 260	608

[a] Shoulder.

It is interesting to compare the absorption maximum of the ring-open isomer and ring-closed isomer of symmetric and nonsymmetric compounds such as **2** and **3**, **5** and **6**, and **7** and **8**. When the substituent attached at the 5- and 5′-position was neither strongly electron-donating nor strongly electron-withdrawing, the absorption maximum of both ring-opened isomer and ring-closed isomer was just a little bit different for symmetric and nonsymmetric compounds (**5** at 452 nm and **6** at 454 nm, in acetonitrile). However, when the substituents at the 5- and 5′-position were strong electron-donating or electron-withdrawing groups, the absorption maxima of the ring-open isomer and the ring-closed isomer were obviously different. The absorption maximum of **3** was red shifted as much as 34 nm for ring-open isomer and 56 nm for ring-closed isomer in comparison with the absorption maximum of **2** in acetonitrile. More differences in absorption maximum of both isomers were obtained by comparison of **7** and **8**.

The photochromic bleaching was performed with compound **3** and illustrated in Figure 3. It showed **3b** (closed form) could be easily reversed back to open form **3a** upon irradiation (≥450 nm) in solution. There was also an obvious isobestic point at 324 nm, and it indicated the equilibrium of two isomers (open form and closed form) existed in isomerization upon irradiation. This result corresponded with the above. The fatigue resistance experiments also showed that compound **8** performed very well: after eight cycles no degradation was detected by UV–Vis absorption but there was about 10% decrease in absorption (optical density) for compounds **2** and **3** after one cycle. In addition, preliminary investigations showed that all compounds were thermally stable at ambient temperature.

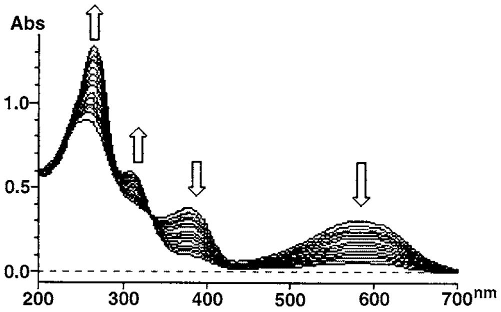

Figure 3. Photochromic bleaching of **3b** in acetonitrile upon irradiation at ≥450 nm.

In conclusion, a facile synthetic route to the preparation of functional dithienylethene derivatives with a 2,5-dihydrothiophene bridging unit has been developed. It can been achieved by obtaining symmetric and nonsymmetric dithienylethene derivatives with a 2,5-dihydrothiophene unit by controlling the ratio of starting material and reagent. All dithienylethene derivatives with a 2,5-dihydrothiophene unit show photochromic behavior and further study of photochromic properties and applications of compounds is in progress.

Acknowledgment. This work was supported by the National Science Foundation of China (NO 60277001) and the National Principal Research Project "973" (G 1999033005).

Supporting Information Available: Experimental procedures and characterization relating to the syntheses of **1a**–**8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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