Synthesis and photochromic properties of helically locked 1,2-dithienylethenes

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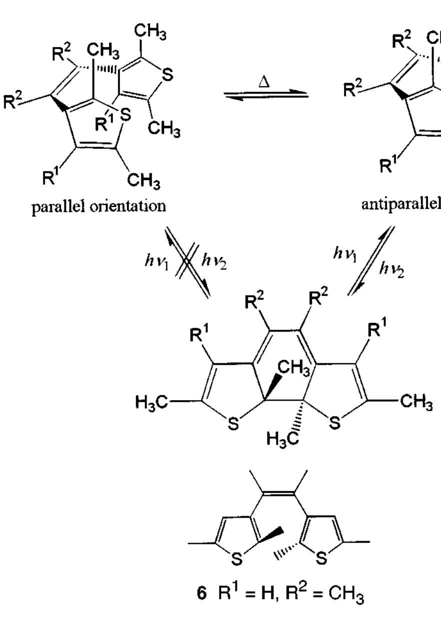
The synthesis of a new family of 1,2-diarylethenes, helically locked 1,2-dithienylethenes, is reported, along with their photochromic properties in solution and as polymeric films.

In recent years a considerable effort has been made towards 1,2-diarylethenes, a class of photochromic compounds known to undergo a reversible ring closing and opening upon irradiation at two different wavelengths. Properties such as thermal stability in isomeric forms, easy preparation and good resistance to repetitive photoisomerization cycles make diarylethenes potential materials for optical data storage.[1] In order to avoid a competing *trans–cis* photoisomerization, the aryl moieties are bound to the double bond of a cycloalkene.[2] To date, all the reported photochromic 1,2-diarylethenes have a five-membered cycloalkene, which can be considered as derivatives of maleic anhydride, maleimide and perfluorocyclopentene. Recently, Feringa *et al.* succeeded in synthesizing a series of 1,2-dithienylethenes based on the cyclopentene moiety and showed that one compound was suitable for multiple photoisomerization cycles.[2]

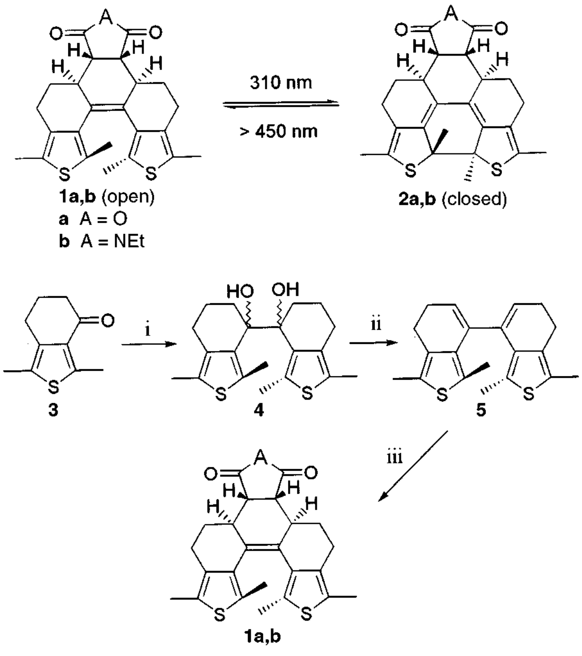
One of features of known 1,2-dithienylethenes is that the aryl rings are able to rotate around the alkene–aryl single bond. As a result, the molecules are distributed between two equally populated conformational states resulting from the parallel and antiparallel orientations of the aryl rings.[3] According to the Woodward–Hoffman rule, photocyclization of a hexa-1,3,5-triene system is allowed only in conrotatory mode. In addition to this, the photocyclization reaction of 1,2-diarylethylenes is restricted to proceed only for molecules that are in the antiparallel orientation (Scheme 1). ^{1}H NMR studies have shown that the full interconversion of the two conformers occurs at temperatures exceeding 40 °C, which is above the temperature limit ideal for most practical applications.[3] Hence, it would be of fundamental interest to design and study a rigid dithienylethene system, in which the two thiophene rings are ‘frozen’ or locked in an antiparallel orientation suitable for efficient cyclization. Such a system can be realized by connecting the R^1 and R^2 groups of the 1,2-dithienylethenes shown in Scheme 1. Herein we report a new class of photochromic compounds: helical 1,2-dithienylethenes **1a**,**b** (Scheme 2) that are built on the rigid frame of $\Delta^{4a(b)}$-dodecahydrophenanthrene. The multi-ring locked structure and the overlapping methyl substituents give rise to a molecular helicity in these compounds, which allows the thiophene rings to adopt an almost an antiparallel orientation. The increase in the molecular rigidity might also provide a stabilizing effect on the isomers **2a**,**b**.



Scheme 1

As shown in Scheme 2, our synthetic approach to these compounds began with commercially available 2,5-dimethylthiophene (Aldrich), which was converted into cyclic ketone **3** using a known method.[4] The McMurry–Mukaiyama coupling[5] of **3** with TiCl$_4$ and Zn in THF gave pinacol **4** in 95% yield. Without further purification, pinacol **4** was dehydrated using POCl$_3$ in pyridine to give the diene **5** in 84% yield. The subsequent steps involved the Diels-Alder reactions of **5** with maleic anhydride or *N*-ethylmaleimide to produce the racemic *endo* adducts **1a**,**b**.

Molecular mechanics calculations indicated that dithienylethenes **1a**,**b** are highly unsymmetrical. Due to the *cis*-fusion of the anhydride and imide moieties, the preferred conformations of **1a**,**b** do not exhibit any C_2 and mirror symmetry elements, as evidenced by the NMR spectral data of **1a**,**b**.[6] The NOESY and COSY NMR data recorded for **1b** were consistent with an *endo* configuration.[7]



Scheme 2 *Reagents and conditions*: i, TiCl$_4$, Zn, THF, 25 °C; ii, POCl$_3$, pyridine, 120 °C; iii, dienophile, xylene, reflux.

At first, the photocyclization of dithienylethenes **1** was examined in solution (Scheme 2). Solutions of **1a** and **1b** in oxygen-free benzene (1×10^{-4} M) were irradiated at wavelengths corresponding to the absorption bands of the open (λ = 310 nm) and closed isomers ($\lambda > 450$ nm). Upon irradiation with UV light (λ = 310 nm, Hg medium pressure lamp), the solutions turned from clear to yellow, as illustrated by the absorption change shown in Fig. 1(*a*). Alternatively, irradiation of the yellow solutions with white light (tungsten lamp) caused the decoloration of the solutions as the closed isomers **2a**,**b** were converted back to **1a**,**b**. The thermal stability of the closed isomers was found to be comparable with that of the closed isomer derived from *cis*-2,3-bis(2,5-dimethyl-3-thienyl)but-2-ene (**6**, R^1 = H, R^2 = CH_3, Scheme 1), a non-helical analogue reported by Irie.[8] A deoxygenated solution of **2b** in benzene was kept at 60 °C for 15 h and no visible change in the UV–VIS absorption spectrum was found.

Previous experiments conducted with diarylethenes in the crystalline state have shown that the photochemical ring closing proceeded reversibly and unrestricted.[9] Thus, it was useful to monitor the photochromic behavior of diarylethenes **1a** and **1b** in an amorphous polymeric film. A polycarbonate film containing **1a** or **1b** was irradiated at 310 and >450 nm, respectively. The photocyclization proceeded readily at ambient temperature, as evidenced by the absorption maximum (λ = 450 nm) of the closed isomer [Fig. 1(*b*)]. Similar to the results of the solution experiment, irradiation of the polycarbonate film containing **2a** or **2b** with white light led to the recovery of **1a** or **1b**, respectively. Therefore, in contrast to some non-helical 1,2-dithienylethenes,[10] the complete switch between **1** and **2** in solution and in the solid polymer film can conceivably be attributed to molecular rigidity (*i.e.* locked rings) and helical conformation (*i.e.* antiparallel orientation) of compound **1**.

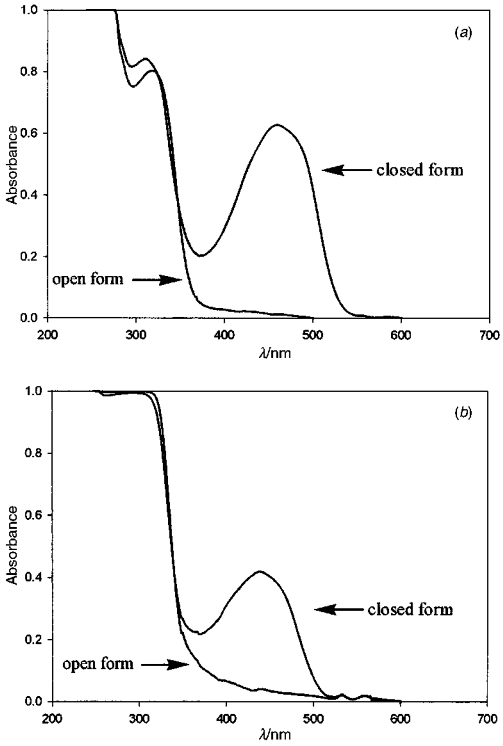


Fig. 1 UV–Visible absorption spectra of (*a*) **1b** in benzene (1×10^{-4} M) in the dark and after irradiation at 310 nm; (*b*) **1b** in polycarbonate film (6.8×10^{-2} mg per mg polymer) in the dark and after irradiation at 310 nm.

The fatigue resistance properties can be determined by the number of colour change cycles over which the color intensity of the photochromic medium decreases to 80% of that of the first cycle.[3] Accordingly, it was found that the fatigue resistance for dithienylethenes **1a**,**b** in benzene in air is about four cycles. A similar cycle number was recorded for **6** (Scheme 1),[8] which has a similar chromophore core (absorption peak corresponding to the closed isomer is 431 nm in benzene). When oxygen was removed from the benzene solution, more than ten switching cycles could be easily achieved without a noticeable decrease in the photochromic intensity.

In conclusion, we have demonstrated a new series of 1,2-dithienylethenes that display distinct photochroism at 310 and 450 nm at ambient temperatures.

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Notes and references

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6 *Selected data* for **1a**: δ_H(400 MHz, $CDCl_3$) 1.36 (s, 3H), 1.37 (s, 3H), 1.75–1.90 (m, 2H), 2.04–2.15 (m, 2H), 2.22 (s, 6H) 2.44 (dt, *J* = 14.0, 3.2, 1H), 2.63 (dd, *J* 8.4, 2.8, 2H), 2.73–2.86 (m, 3H), 3.38–3.47 (m, 2H). For **1b**: δ_H(400 MHz, $CDCl_3$) 1.22 (t, *J* 7.2, 3H), 1.23–1.33 (m, 1H), 1.44 (s, 3H), 1.53 (s, 3H), 1.52–1.60 (m, 1H), 2.22 (q, *J* 13.5, 2H), 2.32 (s, 3H), 2.33 (s, 3H), 2.50–2.55 (m, 1H), 2.61–2.86 (m, 6H), 2.95–3.00 (m, 1H), 3.61 (q, *J* 7.2, 2H).

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