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A new class of photochromic 1,2-diarylethenes; synthesis and switching properties of bis(3-thienyl)cyclopentenes

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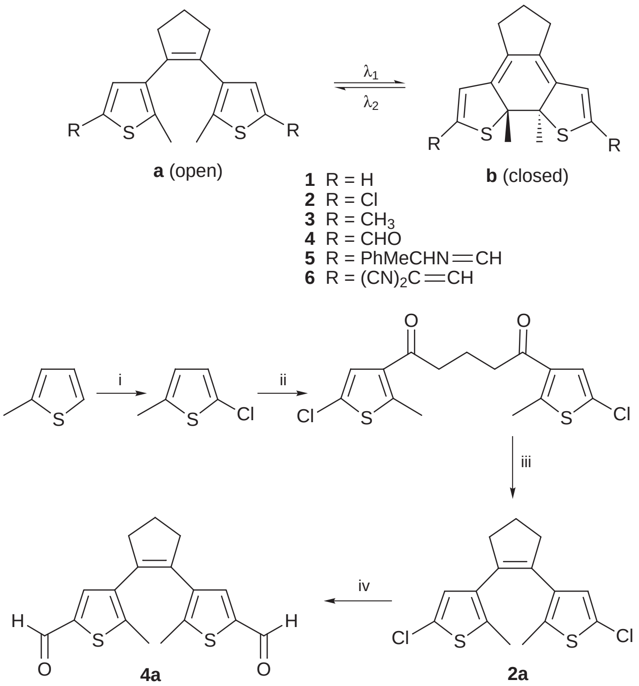
A novel synthetic route to diarylethenes fixed in a cyclopentene based on titanium-mediated carbonyl coupling leads to bis(3-thienyl)cyclopentenes that show photochromic behaviour similar to that of known diarylethenes.

Diarylethenes constitute an important class of photochromic molecules, as they are thermally irreversible and show high fatigue resistance,[1] which are promising features for application in optical data storage[2] and as molecular switches.[3,4] The aryl groups are bound to a cycloalkene to prevent *cis–trans* isomerization, which might compete with photocyclization. 1,2-Bisaryl-substituted maleic anhydride,[5] maleimide[6] and perfluorocyclopentene[7] moieties have been employed so far. Each bridging unit has its advantages and disadvantages. Diarylmaleic anhydrides are readily accessible, but are sensitive to acidic conditions and need certain types of aryl derivatives to maintain their photofatigue resistance in the presence of air.[8] Diarylmaleimides are also sensitive to acidic conditions and furthermore show some degradation in the presence of oxygen.[9] Diarylperfluorocyclopentenes exhibit excellent photochromic behaviour, since up to 80 °C they are stable in the presence of air during cyclization, unless strong electron-donating and −withdrawing substituents are introduced at the 5-position of the thiophene ring.[10] Despite these highly attractive properties the expensive and rather volatile starting material octafluorocyclopentene and the low yields commonly found in double substitution reactions of octafluorocyclopentene with lithiated thiophenes are major disadvantages.

Herewith we present a new class of diarylethenes, the dithienylcyclopentenes, and a novel synthetic route to diarylethenes based on titanium-mediated carbonyl coupling. The synthesis can be performed on a large scale from rather cheap starting materials (Scheme 1). We envisioned that an intramolecular McMurry coupling of a bisthienyl substituted 1,3-dicarbonyl compound would be a feasible route to 1,2-dithienylcyclopentenes. Compounds **1–6**[†] were synthesized starting from 2-methylthiophene, which was chlorinated at the 5-position with NCS in AcOH and benzene, followed by a Friedel–Crafts reaction with $AlCl_3$ and glutaryl chloride at 0 °C. The resulting 1,5-bis(5-chloro-2-methyl-3-thienyl)pentadione was used in a McMurry reaction[11] with $TiCl_3(THF)_3$ and Zn in THF at 40 °C to provide **2a**. Starting from 2,5-dimethylthiophene, **3a** was obtained *via* the same procedure as described above. By using Mg instead of Zn in the McMurry reaction with 1,5-bis(5-chloro-2-methyl-3-thienyl)pentane-1,5-dione, **1a** was obtained.[‡] Dialdehyde **4a** was synthesized by double lithiation of **1a** or **2a** followed by quenching with DMF. The conversion of **4a** to **5a** and **6a** was performed according to published procedures.[10,12] Enantiomerically pure (+)-(*R*)-1-phenylethylamine was used in the synthesis of compound **5**.[12] Although the yields in the low-valent titanium coupling step are still modest, this new route provides ready access to a variety of dithienylcyclopentenes.

The photochromic behaviour was followed by both ^1H NMR and UV spectroscopy. Fig. 1 illustrates the change in absorption of a solution of **4a** in benzene upon irradiation at 313 nm. A new absorption band appeared at 583 nm due to formation of the closed form, which has an extended conjugated structure. Table 1 shows the UV–VIS data for the open and closed forms of the new photochromic compounds. Compared to the known diarylethene derivatives the wavelengths at the absorption maxima of the closed forms show a blue shift; only **6b** measured in benzene showed the same absorption maximum in the closed form as was reported earlier for the perfluorocyclopentene analog.[10] The diarylethenes **1a**, **2a** and **3a** turn yellow upon UV irradiation, which is unusual; no diarylethene compounds showing this behaviour have been described in literature. The



Scheme 1 *Reagents and conditions*: i, NCS, AcOH, benzene, reflux, 80%; ii, $AlCl_3$, glutaryl chloride, CS_2, 0 °C, 94%; iii, $TiCl_3(THF)_3$, Zn, THF, 40 °C, 44%; iv, Bu^nLi, DMF, 39%.

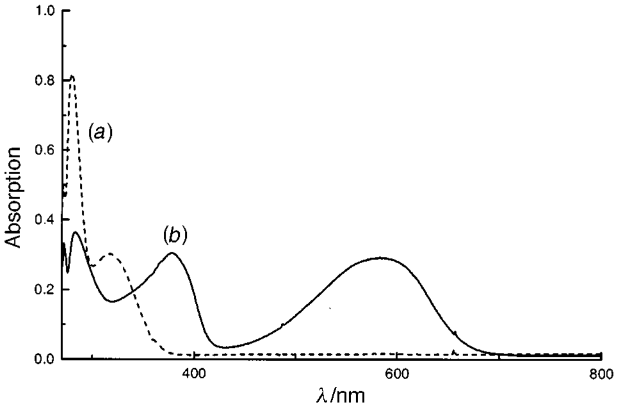


Fig. 1 UV–VIS spectra of **4a** (*a*) before and (*b*) after irradiation for 5 min at 313 nm (2.05×10^{-5} M in benzene).

Table 1 UV–VIS data of the dithienylcyclopentenes

Compound	Solvent	$\lambda_{\max}$/nm	$\varepsilon/10^3 \mathrm{cm}^{-1}\ \mathrm{M}^{-1}$
1a	hexane	268[a]	10.4
1b	hexane	228	15.7
2a	hexane	240	19.01
2b	hexane	444	1.16
3a	hexane	270[a]	9.5
3b	hexane	220	12.6
4a	benzene	318	14.7
4b	benzene	583	14.3
4a	CH_2Cl_2	317	8.3
4b	CH_2Cl_2	580	6.9
5a	hexane	305[a]	23.5
5b	hexane	557	13.1
6a	benzene	391	41.6
6b	benzene	726	29.8
6a	CH_2Cl_2	395	27.6
6b	CH_2Cl_2	734	20.1

[a] Shoulder.

absorption spectra of compounds **1b** and **3b** show no maxima in the visible region. Therefore diarylethenes **1–3** are not suitable for optical switching. Upon photochemical ring closure of **4a**, **5a** (λ = 313 nm) and **6a** (λ = 405 nm), only one methyl signal appeared at high field in their ^{1}H NMR spectra.§ In accordance with the Woodward–Hoffmann rules,[13] we anticipate conrotatory ring closure and a *trans* disposition of the methyl groups.

The half life of the thermal ring opening in benzene at 60 °C of compound **6b** is 4.27 min. Compared to the perfluorocyclopentene analog[10] it shows slower thermal ring opening. Preliminary investigations show that compounds **4b**, **5b** and **6b** are thermally stable under ambient conditions. Finally a number of photochemical bleaching and colouring experiments were performed with compounds **4** and **5**. Dialdehyde **4** showed a ±8% decrease in absorption (UV–VIS) after one cycle, but bisimine derivative **5** performed very well and after ten cycles no degradation was detected. For compounds **1**–**3** it was not possible to perform such switching cycles, because it was impossible to bleach the molecules completely due to a minor difference between the absorption maxima of the open and closed forms of the compounds.

In conclusion a facile synthetic route to a new class of diarylethenes, bis(3-thienyl)cyclopentenes, has been developed. It appears that these bis(3-thienyl)cyclopentenes, which are now readily accessible, show photochromic behaviour, similar to known diarylethenes. Provided the proper substituents are present thermal irreversibility and fatigue resistance are observed. Assessment of the scope of this new methodology and study of applications of these new photochromic compounds is in progress.

Notes and references

† All compounds were fully characterized showing spectroscopic and analytical data in accordance with the structures shown.

‡ Dechlorination occurs during McMurry coupling with low valent titanium prepared using Mg.

§ ^{1}H NMR chemical shift data the CH_3 (thiophene), CH= and CH (thiophene) resonances for the open and closed forms of compounds **4–6**: for **4a**: δ 2.04, 9.74, 7.42; for **4b**: δ 2.17, 9.78, 6.72; for **5a**: δ 1.97, 8.25, 6.95; for **5b**: δ 1.94, 8.15, 7.37; for **6a**: δ 2.14, 7.63, 7.40; for **6b**: δ 2.05, 7.43, 6.56.

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