

Spectral, Conformational and Photochemical Analyses of Photochromic Dithienylethene: *cis*-1,2-Dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene Revisited

Firealem G. Erko,^[a] Jérôme Berthet,^[a] Abhijit Patra,^{[b][‡]} Régis Guillot,^[c] Keitaro Nakatani,^[b] Rémi Métivier,^[b] and Stéphanie Delbaere^{*[a]}

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The conformational equilibrium and thermodynamic parameters of *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (**1a**) and its *trans* derivative **1c** are presented. Irradiation of both compounds was carried out by using 365 nm light, which affects the *cis/trans* isomerisation process, whereas irradiation with 405 nm light preferentially promotes the for-

Introduction

Since their discovery in 1988, 1,2-dithienylethene derivatives have emerged as a unique class of photochromic functional materials.^[1,2] They have received great attention due to their fascinating properties, such as thermal stability, fatigue resistance, high sensitivity and short response times. Active research has subsequently developed due to their promising applications in an extensive range of technologies, from optical data storage to sensors and switches.^[3-27] The photochromic reaction of cis-1,2-dithienylethenes is a reversible phototransformation between 1,3,5-hexatriene and cyclohexadiene by a conrotatory mechanism according to the Woodward-Hoffmann rules.^[28] Absorption of light induces not only photocyclisation but also a cisltrans isomerisation of the double bond joining the thienyl groups. The latter reaction could be avoided by introducing a perfluorocyclopentene or maleic anhydride group, which prohibits the cis/trans photoisomerisation, which may compete with the photocyclisation reaction.^[2] cis-1,2-Dicyano-1,2bis(2,4,5-trimethyl-3-thienyl)ethene (1a; Scheme 1) was the first bistable dithienylethene molecule to be found that ex-

- 61 av. Président Wilson, 94235 Cachan cedex, France
- [c] Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR8182 CNRS, Université Paris-Sud, Bât 420, 91405 Orsay Cedex, France
- [‡] Present address: Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal 462030, Madhva Pradesh, India
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mation of the cyclised product. Prolonged irradiation of **1a** at 365 nm leads to the formation of a new derivative showing photochromic properties. Evidence for the formation of the novel derivative is presented, and details of its photochromic properties were investigated; a tentative mechanism has also been proposed.

hibited reversible photoisomerisation upon light irradiation.^[2] Its reversible photocyclisation induced with 405 nm light involves an open-ring isomer (open form 1a) and a closed-ring isomer (closed form 1b, see Scheme 1). The open form exists in two conformations, namely the parallel and the antiparallel conformers. The former conformer has both thienyl groups in mirror symmetry, whereas the latter conformer has C_2 symmetry, which is the only form able to photocyclize according to the Woodward–Hoffmann rules.



Scheme 1. Photochromic reactions of *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene in its open *cis* isomer (1a), closed isomer (1b), and open *trans* isomer (1c).

The photochromism of **1a** has been investigated by UV/ Vis and IR spectroscopy,^[29] cyclic voltammetry, fast-sweep voltammetry and in situ electrochemical absorptiometry,^[30] in colloidal solutions and amorphous films,^[18] in amorphous solids,^[31] polymer matrices,^[32] and in nanoscale thin layers^[33,34] to construct photoswitchable materials.

 [[]a] Université Lille Nord de France, UDSL, CNRS UMR 8516, BP83, 59006 Lille, France E-mail: stephanie.delbaere@univ-lille2.fr http://lasir.univ-lille1.fr

[[]b] PPSM, ENS Cachan, CNRS, UMR8531,

NMR spectroscopic analysis of **1a** in CCl₄ was reported by Irie,^[2] before photoirradiation and at the photostationary state under irradiation with 405 nm light. The six lines observed before photoirradiation indicate the existence of two conformations in the compound. The broadening of the six methyl signals is explained by the interconversion of the two conformers, which is induced by rotation of the thiophene rings. The conversion of the *cis* form into the cyclised form (**1b**) in the photostationary state was observed to be 60% and the *cis* (**1a**) into the *trans* (**1c**, Scheme 1) isomerisation was considered to be rather negligible under these irradiation conditions.

In this paper, we detail the structural, conformational and photochemical properties of the three isomers **1a**, **1b**, and **1c** by a combination of UV/Vis, X-ray diffraction and NMR spectroscopy. In addition to the expected photochromic behaviour, upon extended irradiation, the formation of a new photoproduct, being also photochromic, has been underlined and characterised.

Results and Discussion

To obtain a preliminary insight into the rotation behaviour of the thienyl units, ¹H NMR spectra were carefully examined. At room temp., **1a** (300 MHz, CD_3CN , Figure 1a) displays six broad resonances due to the coexistence of the antiparallel and parallel conformations. Compound **1c** exhibits three resonances at ambient temperature (Figure 1b) that are split upon decreasing the temperature (300 MHz, CD_3CN). Repeating the measurement of **1c** in [D₈]toluene at room temp. revealed the existence of five broad signals for six methyl groups (two signals are at the same position), thus indicating the existence of two conformers, observed separately by NMR spectroscopy.



Figure 1. ¹H NMR spectra of (a) pure **1a**, (b) pure **1c**, and (c) mixture after irradiation with 405 nm light.

Variable-temperature NMR studies of **1a** and **1c** were conducted to determine the rates of rotation of the thienyl units. NMR spectra were recorded in the range 229–333 K for **1a**. The coalescence temperatures of 303 and 292 K (300 MHz, CD₃CN) were deduced for **1a** and **1c**, respectively. The rate of rotation of the thienyl groups was deter-

mined from the simulation of the spectra by using DNMR software.^[35,36] Simulated spectra with the corresponding rate constants, along with matching experimental spectra at different temperatures, are shown in the Supporting Information. The rate constant found from the DNMR software is the rate of exchange between the parallel and antiparallel forms and is represented as $k = k_{\text{parallel}} + k_{\text{antiparallel}}$. Since the concentration ratio of parallel vs. antiparallel conformers was found to be independent of the temperature (1:1.03, parallel/antiparallel), the rate constant for both is approximately equal, with $k_{\text{parallel}} = k_{\text{antiparallel}} = k/2$. Then the k values can be used to calculate the activation energy by using the Eyring plot and the Arrhenius plot. The activation parameters for the rotation of the thienyl units in 1a were found to be $\Delta H^{\neq} = 71.2 \text{ kJ mol}^{-1}$, $\Delta S^{\neq} =$ +28.4 J mol⁻¹ K⁻¹ and $E_a = 73.5$ kJ mol⁻¹. In 1c, the activation parameters were calculated to be $\Delta H^{\neq} =$ 77.5 kJ mol⁻¹, $\Delta S^{\neq} = +43.1$ J mol⁻¹ K⁻¹ and $E_a =$ 79.9 kJ mol⁻¹. Then, in both molecules, the rotational energy barriers are comparable, and these activation energies for the conformational changes are in complete agreement with values reported by Uchida et al. for benzo derivatives of **1a** (67 and 71 kJ mol⁻¹).^[37]

The UV/Vis absorption spectrum of 1a in chloroform (Figure 2) shows three main bands at 304, 324, and 375 nm. When irradiated at 365 or 405 nm, the 1a isomer (open cis form) is converted into isomer 1b (closed form). The latter is characterised by an extended absorption spectrum from the visible region, with a large band located at λ_{max} = 522 nm, to the UV region, with a band maximum at 359 nm (Figure 2). The ring-closure reaction $1a \rightarrow 1b$ is reversible; when irradiated at 546 nm, the ring-opening reaction $1b \rightarrow$ 1a occurs, and the open *cis* isomer is fully recovered. However, UV irradiation of 1a in chloroform (365 or 405 nm) does not produce solely the 1b isomer. Indeed, a noticeable proportion of open *trans* isomer **1c** is present at the photostationary state (PSS), as observed by simple thin-layer chromatography. Separation and purification of isomer 1c by column chromatography allowed its absorption spectrum to be recorded, which showed two main bands at 325 and 380 nm. Determination of its absorption coefficient



Figure 2. Molar absorption coefficient curves (ε in L mol⁻¹ cm⁻¹) of **1a**, **1b** and **1c** isomers in CHCl₃.

provided a value that was slightly lower than that of isomer **1a** ($\varepsilon_{325nm} = 5600 \text{ Lmol}^{-1} \text{ cm}^{-1}$ for **1c** vs. $\varepsilon_{304nm} = 7600 \text{ Lmol}^{-1} \text{ cm}^{-1}$ for **1a**).

The X-ray diffraction of single-crystals of 1a, 1b, and 1c provided the structures of the three isomers, as depicted in Figure 3. In the crystalline state, the open *cis* form 1a is in the antiparallel conformation. The distance between the two carbon atoms involved in the cyclisation is 3.496 Å, which is in agreement with the distance required for photochromism in the solid state. Compound 1b has a typical, more planar structure that is compatible with an extended π -conjugated system, and 1c shows thienyl rings tilted from the plane of the ethene bridge, with dihedral angles of 121.38° and 126.90° for the two thiophene rings.



Figure 3. ORTEP views of **1a**, **1b** and **1c** (ellipsoid probability at 50% level, hydrogen atoms have been omitted).

The photochemical behaviour of **1a** and **1c** was then investigated by NMR spectroscopy. Figure 4 shows the concentration/time profiles of **1a** under photoirradiation with 365 and 405 nm light, followed by ¹H NMR spectroscopy. Irradiations led to a decrease in the initial amount of **1a** and the formation of two sets of resonances, assigned to the closed isomer **1b** (Figure 1c) and to the *trans* isomer **1c**. Under our conditions, 62% of the cyclised form **1b** and 20% of the *trans* isomer **1c** (Scheme 1) were reached upon irradiation with 405 nm light, whereas 10% **1b** and 30% **1c** were produced upon irradiation with 365 nm light.



The same procedure was applied by starting from a solution of *trans* isomer 1c, irradiated with 365 and 405 nm light (Figure 5). Similarly, 45% of the cyclised form 1b and 18% of *trans* isomer 1c were formed upon 405 nm irradiation, and 10% of 1b and 20% of 1c were obtained upon 365 nm irradiation. It can then be confirmed that the *cis/trans* photoisomerisation is favoured with 365 nm light, whereas 405 nm irradiation preferentially induces the cyclisation.

During the photochemical investigation of **1a** with 365 nm light, we extended the time of irradiation and were intrigued to observe the formation of a new product designated as **1d** (Figure 6a).

We isolated an appreciable amount of compound 1d by irradiation at 365 nm of a 300 mL solution of CHCl₃ containing 30 mg of compound 1a for 6 h (by means of a closed-loop recirculation system equipped with a suitable 2 mm quartz cell) and further purified by column chromatography. Mass analysis allowed a formula of C₁₈H₁₈N₂O₂S to be determined. ¹H NMR spectra, recorded in CDCl₃, showed six methyl signals for 1d from δ = 1.50 to 2.70 ppm (Figure 6b). Of the signals of the 18 carbon atoms observed in the ¹³C NMR spectrum, two showed high chemical shift values ($\delta = 200.9$ and 208.2 ppm) that were not observed in either of the previously characterised open (1a) or closed form (1b). This indicates that two carbonyl groups might be present in 1d. ¹H-¹³C HMBC spectra were recorded with an optimised coupling constant of 8 Hz $({}^{2}J{}^{-3}J)$ and 1 Hz $({}^{4}J)$. These signals underlined the ${}^{2}J$ correlation between a CH₃ group (δ = 2.69 ppm) and of a highly deshielded carbon atom (δ = 200.9 ppm). In addition, the second deshielded carbon atom (δ = 208.2 ppm) correlated with a CH₃ group (δ = 2.31 ppm) and a second CH₃ group ($\delta = 1.75$ ppm). Two carbon atoms resonating at $\delta = 62.8$ and 64.5 ppm were also detected, which were characterised as bridged sp³ carbon



Figure 4. Time-evolution concentration of 1a upon irradiation with 365 nm (left) and 405 nm light (right). Circles: 1a; squares: 1b; diamonds: 1c.



Figure 5. Time-evolution concentration of 1c upon irradiation with 365 nm (left) and 405 nm light (right). Circles: 1a; squares: 1b; diamonds: 1c.



Figure 6. ¹H NMR spectra of (a) a mixture after 365 nm irradiation of **1a** at room temp. for 30 min; (b) pure **1d**; (c) **1d** after irradiation with 546 nm light; (d) **1a** after irradiation with 365 nm at 253 K for 2 h.

atoms in a configuration of the cyclohexadiene. All these observations are in agreement with the structure of **1d** displayed in Scheme 2. Because **1d** contains a 1,3-cyclohexadiene, it is expected to be opened if a suitable wavelength of irradiation is applied. The absorption spectrum of **1d** shows a band maximum in the visible range (475 nm), characteristic of closed diarylethenes (Figure 7). Irradiation at 546 nm of **1d** at room temp. for 5 min resulted in the formation of a new product that was fully characterised by 1D and 2D NMR spectroscopy as the colourless open form, namely **1e** (see Scheme 2 and Figure 6c). Subsequent irradiation at 365 nm of a sample containing **1e**, led to its conversion into closed **1d**, thus revealing further photochromic properties.



Scheme 2. Photochromic reaction of **1d** and **1e** derivatives; ¹H and ¹³C NMR chemical shifts.



Figure 7. UV/Vis spectra of 1d and 1e in acetonitrile.

To understand the mechanistic pathway leading to the formation of 1d, a fresh sample of 1a was irradiated for 120 min, in periods of 10 min; between each irradiation step, NMR spectra were recorded (Figure 6d). The presence of two additional sets of signals characterising two photoproducts (I_1 and I_2), which thermally evolved towards 1d, was underlined. Cooling of the solution enabled 2D NMR spectra to be recorded to assign these signals to two isomers

of peroxy intermediates, as depicted in Scheme 3. This assignment is in agreement with the suggestion of endoperoxide formation on the thiophene cycle reported by Taniguchi et al.^[38]



Scheme 3. Structures of the two intermediates I_1 (top) and I_2 (bottom) with ¹H and ¹³C NMR chemical shifts.



Scheme 4. Proposed mechanism for the photoreaction from **1a** to **1d** under irradiation at 365 nm.



The presence of two peroxy intermediates is suggested to result from singlet oxygen approaching the thiophene ring from *endo* and *exo* sides. The similarities between the NMR spectroscopic data of the two intermediates are a further indication that the two peroxy derivatives have similar chemical linkages. Thus, considering the experimental evidence, and also that they contain 1,3-cyclohexadiene, it is possible to devise a plausible mechanism for the formation of 1d from 1a (Scheme 4). However, in the course of our studies, we did not succeed in detecting the presence of the two peroxy derivatives with open diarylethenes (I_1' and I_2'), which are expected to be the respective precursor of the two peroxy derivatives with cyclised diarylethenes (I_1 and I_2). The peroxides thermally decompose to 1d with extrusion of sulfur, as previously reported by some authors.^[39–41]

Conclusions

The equilibrium between parallel and antiparallel conformations of *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (**1a**) and its *trans* derivative (**1c**) has been quantified with the determination of the thermodynamics parameters. The photochromic reaction was studied by using two irradiation wavelengths. At 405 nm, the main reaction is the photocyclisation into **1b**, whereas irradiation at 365 nm favours *cis/trans* isomerisation between **1a** and **1c**. The three structures were characterised by NMR and X-ray analyses.

In addition to the conventional photochromic reactions occurring with dithienylethene derivatives (ring-opening/ ring-closure reactions, cis/trans isomerisation), we have obtained evidence for the formation under 365 nm light irradiation of a new coloured compound, 1d, showing its own photochromic properties. This species has been fully identified and could be decyclised with visible light into the colourless compound 1e, which is able to yield back compound 1d. The formation of 1d from 1a upon extended irradiation time involved two peroxy derivatives that are thermally converted into 1d. A plausible mechanism was proposed. The intricate reaction pathways of the 1a derivative under light activation, involving open cis, open trans, closed isomers, and, additionally, these latter photoproducts 1d and 1e, result in a very complex photochromic pattern. Although this dithienylethene compound is used in a wide range of applications, such properties were not described until now. Multiple photochromic routes that depend on the irradiation wavelengths, as described for this simple compound, could be advantageously employed to reach several molecular states by a light trigger, with reversible or irreversible locking/unlocking behaviour, in the field of organic electronic devices.

Experimental Section

NMR spectra (¹H, ¹³C, HMBC and HSQC) were recorded with Bruker 500 or 300 MHz spectrometers equipped with TXI or QNP probes. Samples were irradiated directly in the NMR tube (5 mm) by using a 1000 W Xe-Hg high-pressure filtered short-arc lamp (Oriel), equipped with suitable filters. Monochromatic UV light was obtained by passing the light through a first filter (Schott 11FG09: $259 < \lambda < 388$ nm with $\lambda_{max} = 330$ nm, T = 79%), then through an interferential filter ($\lambda = 365$ nm and T = 30%). Monochromatic visible light was obtained by passing the light through a first filter (Schott SCFIKG1503: $295 < \lambda < 800$ nm with T = 50% at $\lambda = 330$ and 700 nm), then through an interferential filter ($\lambda = 49\%$, $\lambda = 546$ nm and T = 15%).

UV/Vis absorption spectra were recorded with a Cary 5000 spectrophotometer from Agilent Technologies. Production of **1d** in large amounts was performed by using a circulation system with a Mesterflex peristaltic pump, PTFE tube and a circulation quartz cuvette under in situ continuous irradiation by means of an Hg/Xe lamp (Hamamatsu, LC6 Lightningcure, 200 W) equipped with a narrow-band interference filter (Semrock Hg01-365-25 for λ_{irr} = 365 nm).

X-ray diffraction data were collected with a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flash-frozen in a nitrogen gas stream at 100 K.

Supporting Information (see footnote on the first page of this article): NMR spectra, details of DNMR, MS, and X-ray data.

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