

1,2-Bis[5-(1,3-dioxolan-2-yl)-2-ethyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopent-1-ene, a photochromic dithienylethene

Shou-Zhi Pu,^{a*} Tian-She Yang,^a Ru-Ji Wang^b and Jing-Kun Xu^a

^aJiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, People's Republic of China, and

^bDepartment of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

Correspondence e-mail: pushouzhi@tsinghua.org.cn

Received 28 July 2005

Accepted 11 August 2005

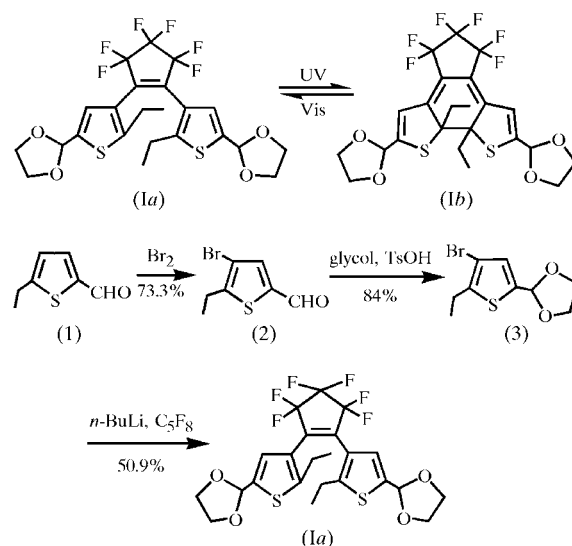
Online 31 August 2005

The title compound, C₂₃H₂₂F₆O₄S₂, a photochromic dithienylethene, is a promising material for optical storage and other optoelectrical devices. The molecule adopts a photoactive antiparallel conformation in the crystalline state. The distance between the two reactive C atoms which are involved in potential ring closure is 3.829 (4) Å. The dihedral angles between the central cyclopentene ring and the adjacent thiophene rings are 55.38 (7) and 54.81 (9)°. The colourless crystals turn magenta when exposed to UV radiation and the process is reversible.

Comment

Photochromic compounds have been extensively investigated for their possible application in optoelectronics, *viz.* as optical memories, photoswitches and waveguides (Fan *et al.*, 1999). Among all photochromic systems, diarylethene derivatives are the most promising candidates for optical memories and other optoelectronic devices because of the good thermal stability of the two isomers and their high sensitivity, fast response and high fatigue resistance (Irie, 2000; Tian & Yang, 2004). Generally, diarylethenes with thiophene heterocyclic rings have two interconverting conformations in almost equal amounts in solution, *i.e.* antiparallel and parallel conformations (Irie & Mohri, 1988; Uchida *et al.*, 1990); only antiparallel conformations can undergo effective photocyclization reactions by a conrotatory mechanism, while the parallel conformations are photochemically inactive (Yamada *et al.*, 2000). However, there is no interconversion between the two conformers in the crystalline phase of diarylethenes and the molecules are regularly oriented in a fixed conformation (Pu *et al.*, 2003, 2004, 2005), except for one example (Kobatake *et al.*, 2005) where there are two independent molecules with different conformations in the asymmetric unit. In addition,

photochromic diarylethene crystals with an antiparallel conformation can reversibly turn various colours (yellow, red, blue or green) from colourless, depending on their molecular structure, upon irradiation with UV and appropriate wavelength visible light (Kobatake & Irie, 2004). These crystals also exhibit good thermal stability of the two isomers and remarkable fatigue resistance. Crystals of diarylethenes in the antiparallel conformation are thus very promising for practical applications.



In the present work, the title photochromic diarylethene, (Ia), was synthesized. We have previously reported the structure of the 2-methyl analogue, (II), of this compound (Pu *et al.*, 2002). In order to investigate systematically the substituent effect at the 2-position of the thiophene of diarylethenes on their photochemical properties, we have now determined the structure of (Ia). The 2-methyl and 2-ethyl compounds differ from each other, not only in their crystal structures but also in their various photochemical properties, such as absorption maxima, ease of cyclization, cycloreversion quantum yield and oxidation–reduction potentials.

The molecular structure of (Ia) is shown in Fig. 1, a packing diagram is shown in Fig. 2 and selected geometric parameters are given in Table 1. As shown in Fig. 1(a), the molecule has approximate twofold symmetry, with the two thiophene rings in a photoactive antiparallel conformation. The hexafluorocyclopentene ring adopts a C4-envelope conformation, with the flap atom (C4) equally disordered over two sites (C4 and C4') and concomitant disorder of the attached F atoms [see Fig. 1(b), with details in the *Experimental* section]. In the cyclopent-1-ene ring, the C1–C2 bond is clearly a double bond, and the other bonds from C1 and C2 (Table 1) are clearly single bonds.

The two independent planar thiophene ring systems have essentially identical geometries and the dihedral angles between the central cyclopent-1-ene ring and the adjacent thiophene rings are 55.38 (7) and 54.81 (9)°. The corresponding values in the methyl analogue, (II), are both 49°. This conformation leads to a C12...C22 separation of

3.829 (4) Å [compared with 3.67 Å in (II)], which is short enough, theoretically, for a ring-closure reaction to take place in the crystalline phase (Ramamurthy & Venkatesan, 1987) to generate compound (Ib) (see scheme). The orientations of the ethyl groups at C12 and C22 are defined by the torsion angles C13–C12–C16–C17 [$-139.8(4)^\circ$] and C23–C22–C26–C27 [$120.8(4)^\circ$].

The two terminal 1,3-dioxolane rings both have envelope conformations; the O31/C32/O33/C34/C35 ring has a C32-envelope conformation, while the O41/C42/O43/C44/C45 ring adopts an O41-envelope form. Their orientations relative to the thiophene rings are presumably largely determined by crystal-packing considerations and lead to the torsion angles H32–C32–C15–S11 = 166° and H42–C42–C25–S21 = -176° .

In the crystal structure, molecules related by a 2_1 screw axis are linked by weak C–H...F intermolecular interactions from one of the dioxolane C–H groups to generate chains extending along the *b* direction, as shown in Fig. 2 (details are given in Table 2).

Crystals of (Ia) showed photochromic reaction, in accordance with the expected ring closure, to form (Ib). Upon irradiation with light of wavelength 254 nm, the colourless crystals of (Ia) quickly became magenta-coloured, as shown in Fig. 3. When observed under polarized light, the intensity of

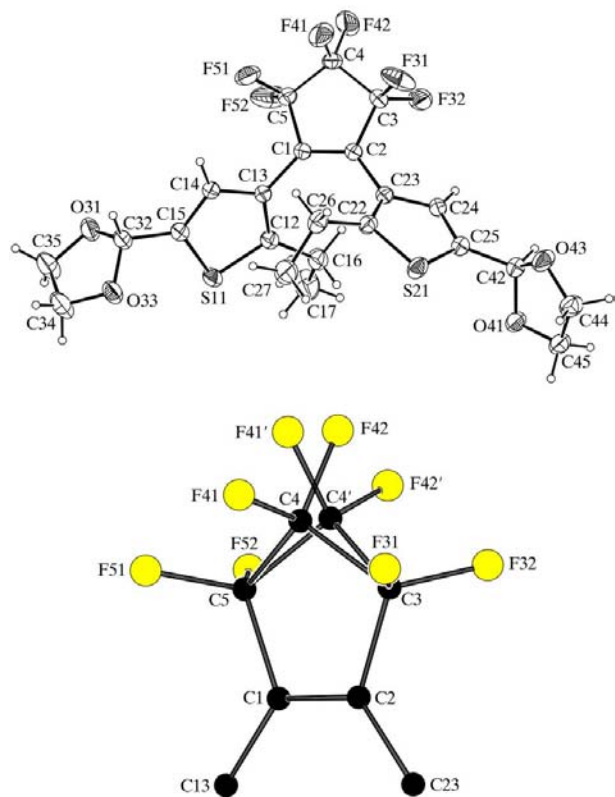


Figure 1

(a) The structure of the title compound, shown with 20% probability displacement ellipsoids. For clarity, only one orientation of the disordered cyclopent-1-ene ring is shown. (b) A ball-and-stick diagram, showing the disorder at C4 in the cyclopent-1-ene ring.

the magenta colour changed on rotation of the crystalline sample. This phenomenon suggests that the closed-ring molecules of (Ib) are packed regularly in the crystal, but we have not been able to establish the crystal structure of (Ib). When the magenta crystal was dissolved in hexane, the solution was magenta-coloured and the absorption maximum was observed at 542 nm, consistent with the presence of the closed-ring isomer (Ib). The magenta colour disappeared upon irradiation with light of wavelength 510 nm or daylight, and the absorption spectrum of the solution containing the colourless material was the same as that of solutions of the open-ring isomer (Ia).

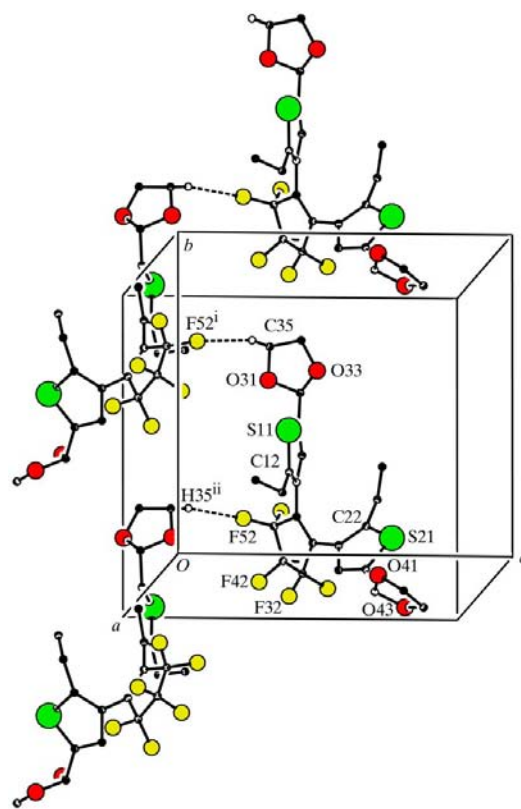


Figure 2

A view along the *b* direction, showing the C–H...F interactions in (Ia) (dashed lines). [Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.]

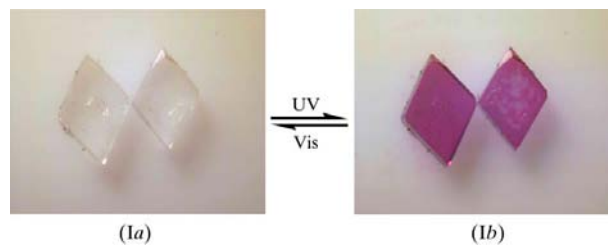


Figure 3

A view of crystals of the colourless compound, (Ia), and the same crystals after exposure to UV radiation, *viz.* (Ib).

Experimental

The title diarylethene, (Ia), was originally derived from 5-ethylthiophene-2-carbaldehyde, (1). First, 4-bromo-5-ethylthiophene-2-carbaldehyde, (2), was afforded in 73.3% yield by brominating compound (1) in acetic acid at room temperature. The dioxolane acetal, (3), was then prepared in 84.0% yield by refluxing under Dean–Stark conditions in the presence of compound (2), glycol and *p*-toluenesulfonic acid (TsOH) in benzene. Finally, to a stirred solution of compound (3) (2.296 g, 8.73 mmol) in tetrahydrofuran (50 ml) was added dropwise a 2.5 M *n*-BuLi solution in hexane (3.5 ml, 8.75 mmol) at 195 K under a nitrogen atmosphere. Stirring was continued for 30 min and then octafluorocyclopentene (0.59 ml, 4.36 mmol) was added slowly to the reaction mixture. The mixture was then stirred for 2.5 h at 195 K. The reaction was quenched by the addition of water. After a series of routine operations, the title compound, (Ia) (1.2 g, 2.2 mmol), was obtained in 50.9% yield by column chromatography on SiO₂ using CHCl₃ as eluent. The compound was crystallized from chloroform–hexane (1:2 *v/v*) at room temperature and produced crystals suitable for X-ray analysis. The crystals of (Ia) had the following elemental analysis and NMR data: m.p. 400.4–400.6 K; analysis calculated for C₂₃H₂₂F₆O₄S₂: C 51.11, H 4.10%; found: C 51.23, H 4.20%; ¹H NMR (400 MHz, CDCl₃): δ 0.924–0.961 (*t*, 6H, *J* = 7.8 Hz, –CH₃), 2.192–2.248 (*q*, 4H, *J* = 7.5 Hz, –CH₂), 4.002–4.036 (*t*, 4H, *J* = 6.8 Hz, –CH₂), 4.101–4.136 (*t*, 4H, *J* = 7.0 Hz, –CH₂), 6.021 (*s*, 2H, –CH), 7.094 (*s*, 2H, thiophene-H).

Crystal data

| | |
|--|--|
| C ₂₃ H ₂₂ F ₆ O ₄ S ₂ | <i>D</i> _x = 1.489 Mg m ^{−3} |
| <i>M</i> _r = 540.53 | Mo <i>K</i> α radiation |
| Monoclinic, <i>P</i> 2 ₁ / <i>n</i> | Cell parameters from 24 reflections |
| <i>a</i> = 13.353 (2) Å | <i>θ</i> = 4.9–12.9° |
| <i>b</i> = 13.370 (2) Å | <i>μ</i> = 0.30 mm ^{−1} |
| <i>c</i> = 13.600 (3) Å | <i>T</i> = 295 (2) K |
| <i>β</i> = 96.796 (11)° | Grain, colourless |
| <i>V</i> = 2411.0 (7) Å ³ | 0.5 × 0.5 × 0.4 mm |
| <i>Z</i> = 4 | |

Data collection

| | |
|---|------------------------|
| Bruker <i>P</i> 4 diffractometer | <i>h</i> = −1 → 15 |
| <i>ω</i> scans | <i>k</i> = −1 → 15 |
| 5323 measured reflections | <i>l</i> = −16 → 16 |
| 4231 independent reflections | 3 standard reflections |
| 3377 reflections with <i>I</i> > 2σ(<i>I</i>) | every 97 reflections |
| <i>R</i> _{int} = 0.026 | intensity decay: none |
| <i>θ</i> _{max} = 25.0° | |

Refinement

| | |
|---|---|
| Refinement on <i>F</i> ² | <i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0639 <i>P</i>) ² + 1.2878 <i>P</i>] |
| <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.049 | where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3 |
| <i>wR</i> (<i>F</i> ²) = 0.144 | (Δ/σ) _{max} < 0.001 |
| <i>S</i> = 1.05 | Δρ _{max} = 0.39 e Å ^{−3} |
| 4231 reflections | Δρ _{min} = −0.29 e Å ^{−3} |
| 340 parameters | Extinction correction: <i>SHELXTL</i> (Bruker, 1997) |
| H-atom parameters constrained | Extinction coefficient: 0.0021 (7) |

Table 1

Selected bond lengths (Å).

| | | | |
|---------|-----------|--------|------------|
| S11–C15 | 1.713 (3) | C2–C23 | 1.472 (3) |
| S11–C12 | 1.719 (3) | C2–C3 | 1.496 (3) |
| S21–C25 | 1.717 (3) | C3–C4' | 1.523 (11) |
| S21–C22 | 1.724 (3) | C3–C4 | 1.528 (12) |
| C1–C2 | 1.344 (3) | C4–C5 | 1.498 (11) |
| C1–C13 | 1.467 (3) | C4'–C5 | 1.529 (12) |
| C1–C5 | 1.505 (3) | | |

Table 2

Hydrogen-bond geometry (Å, °).

| <i>D</i> –H... <i>A</i> | <i>D</i> –H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> –H... <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| C35–H35A...F52 ⁱ | 0.97 | 2.45 | 3.361 (5) | 157 |

Symmetry code: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

It was obvious from electron-density maps that the CF₂ group at C4 was disordered, corresponding with two orientations of the cyclopent-1-ene ring in a C4-envelope conformation. This disorder was readily modelled with atom C4 disordered over two sites (C4 and C4'), with F atoms F41/F41' and F42/F42'. DFIX restraints were used to keep the C4–F, C4'–F and F...F separations in agreement with the observed C–F geometry at the C3 and C5 sites. Initially, the two disordered orientations were refined with tied occupancy parameters, but as these refined occupancy values were not significantly different from 0.5, the occupancies were then fixed at 0.5 for the final refinement cycles. All H atoms were clearly defined in difference maps and were allowed for as riding atoms, with C–H distances in the range 0.96–0.98 Å and with *U*_{iso}(H) = 1.2 and 1.5*U*_{eq}(C).

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

This work was financially supported by the Science Funds of the Education Office of Jiangxi, China (grant No. [2005] 140), and by the Natural Science Foundation of Jiangxi, China (grant No. 050017).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1872). Services for accessing these data are described at the back of the journal.

References

Bruker (1997). *XSCANS* (Version 2.2) and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Fan, M. G., Yu, L. & Zhao, W. (1999). *Organic Photochromic and Thermochromic Compounds*, edited by J. C. Crano & R. Guglielmetti, Vol. 1, pp. 195–197. New York: Plenum Press.

Irie, M. (2000). *Chem. Rev.* **100**, 1685–1716.

Irie, M. & Mohri, M. (1988). *J. Org. Chem.* **53**, 803–808.

Kobatake, S. & Irie, M. (2004). *Bull. Chem. Soc. Jpn.* **77**, 195–210.

Kobatake, S., Matsumoto, Y. & Irie, M. (2005). *Angew. Chem. Int. Ed.* **44**, 2148–2151.

Pu, S.-Z., Xu, J.-K., Shen, L., Xiao, Q., Yang, T.-S. & Liu, G. (2005). *Tetrahedron Lett.* **46**, 871–875.

Pu, S.-Z., Zhang, F.-S., Fan, S., Wang, R.-J., Zhou, X.-H. & Chan, S.-K. (2003). *Tetrahedron Lett.* **44**, 1011–1015.

Pu, S.-Z., Zhang, F.-S., Wang, R.-J. & Liang, Q. (2004). *Acta Cryst.* **C60**, o305–o307.

Pu, S.-Z., Zhang, F.-S., Zhou, X.-H., Sun, F., Guo, H.-B., Chan, S.-K. & Wang, R.-J. (2002). *Z. Kristallogr. New Cryst. Struct.* **217**, 413–414.

Ramamurthy, V. & Venkatesan, K. (1987). *Chem. Rev.* **87**, 433–481.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Tian, H. & Yang, S.-J. (2004). *Chem. Soc. Rev.* **33**, 85–97.

Uchida, K., Nakayama, Y. & Irie, M. (1990). *Bull. Chem. Soc. Jpn.* **63**, 1311–1315.

Yamada, T., Muto, S. K. & Irie, M. (2000). *J. Am. Chem. Soc.* **122**, 1589–1592.