Fatigue resistant properties of photochromic dithienylethenes: by-product formation

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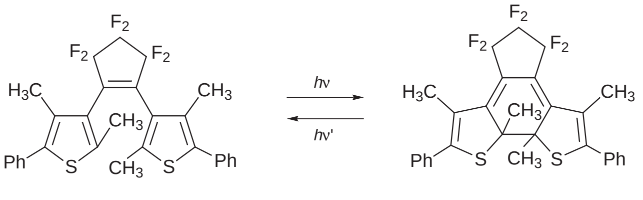
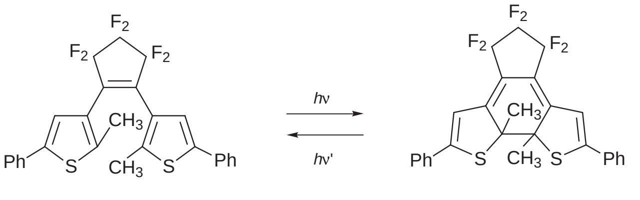
Beside normal cyclization/ring-opening photochromic reactions, a side reaction to produce a photostable by-product took place when 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene was irradiated in deaerated hexane with ultraviolet light.

Light-induced reversible isomerization between two forms having different absorption spectra is referred to photochromism, and compounds capable of these reactions are called photochromic compounds. Various types of photochromic compounds, such as spiropyrans, spirooxazines, fulgides and diarylethenes, have been so far developed[1] in an attempt to apply the compounds to optoelectronic devices,[2,3] such as optical memory, photo-optical switching and displays. Among the compounds, diarylethenes with heterocyclic aryl groups are the most promising photochromic compounds for these applications, because of their fatigue-resistant and thermally-irreversible properties.[4] Although diarylethenes with benzothiophene aryl groups undergo fatigue-resistant photochromic reactions (more than 10 000 coloration/decoloration cycles)[5–7] without any destruction of their structures, some diarylethenes with thiophene rings cease their photochromic cycles in less than several hundred cycles even in the absence of oxygen.[6–9] To know the reason why the thiophene derivatives are easily damaged by photoirradiation, we compared the fatigue-resistant properties of dithienylethenes **1** and **2**.[10,11]

Compound **1**[10] has methyl groups at the 4 and 4′ positions of the thiophene rings, while compound **2**[11]† has no methyl groups at these positions. The cyclization quantum yield of **2a** (Φ = 0.68) is larger than that of **1a** (Φ = 0.46),[10] while the ring-opening quantum yields are similar (Φ = 0.013 and 0.015, respectively).



1a **1b**



2a **2b**

Fig. 1 shows the fatigue resistant behavior of the two compounds in hexane in the absence of oxygen. The absorbance of the two compounds at 313 nm was normalised. In each cycle **1a** and **2a** were converted to **1b** and **2b**, respectively, to give 80% of the photostationary states by irradiation with 313 nm light, and both closed-ring forms, **1b** and **2b**, were completely bleached by irradiation with > 440 nm light. The absorbances of the bleached samples were plotted in Fig. 1. The absorbance of **1a** (λ_{max} 268 nm) remained almost constant even after 800 cycles, while the absorbance of **2a** (λ_{max} 276 nm) gradually declined. At the same time a photostable violet product with an absorption maximum at 547 nm was formed. As can be seen in Fig. 1 the formation process of the by-product coincides with a decrease of the open-ring form **2a**. The saturation tendency after 200 cycles is ascribed to the overlapping of the strong absorption of the by-product at 313 nm (see Fig. 2). In the case of **1** no such colored photoproduct was detected. In the presence of oxygen both **1** and **2** readily decomposed in less than 500 cycles. The decomposition is due to the formation of oxidized products.[7]

The stable photoproduct could be isolated by HPLC (silica gel column, hexane) and was found by elementary analysis and molecular mass determination to be isomeric with compound **2a**. Fig. 2 shows the absorption spectrum of the by-product **3** along with those of **2a** and **2b**. The absorption maximum of the by-product slightly shifted to shorter wavelength and its ε value

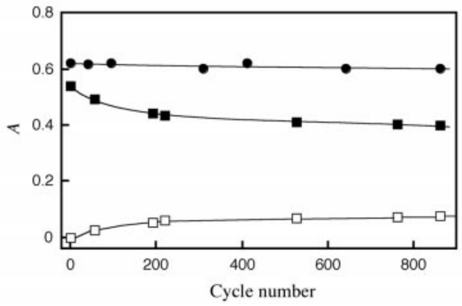


Fig. 1 Fatigue resistant properties of **1** and **2** in deaerated hexane. Absorbances of **1a** (●) and **2a** (■) were plotted after irradiation with visible light. The visible absorbance at 547 nm (□), which still remained after visible irradiation of a hexane solution containing **2**, was also plotted.

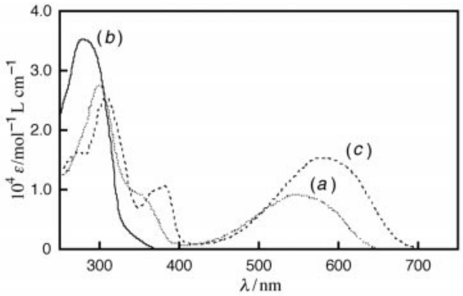
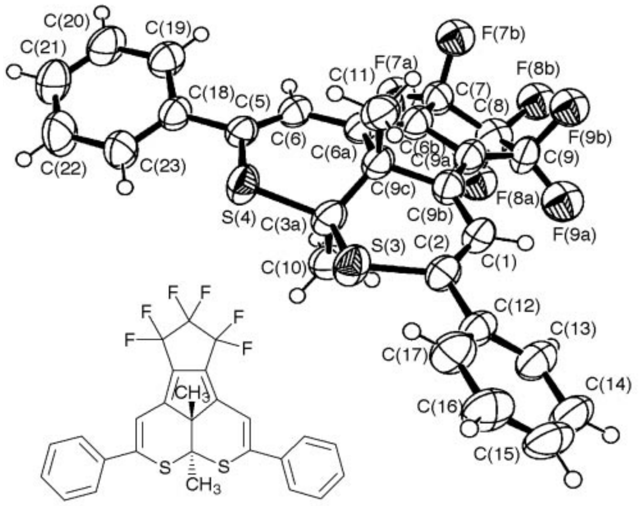


Fig. 2 Absorption spectrum of the (*a*) by-product **3** along with those of (*b*) **2a** and (*c*) **2b** in hexane.



3

Fig. 3 ORTEP view of by-product **3** (50% probability thermal ellipsoids) and its chemical structure. The fluorinated cyclopentane ring was disordered. Only the major structure is illustrated for clarity.

in the visible region was 60% of the closed-ring form.The structure of the by-product could not be determined conclusively by NMR spectroscopy,‡ but was established by X-ray crystallographic analysis of a single crystal (mp 131 °C) from MeOH–hexane.§

Fig. 3 shows the molecular structure of by-product **3**. The thiophene rings no longer exist, having formed a condensed system with two six-membered heterocyclic rings. The polyene structure is similar to the closed-ring form **2b**. This is the reason why the by-product has a similar absorption spectrum. Although the formation mechanism of the by-product has not yet been revealed, the by-product was more efficiently produced from **2b** by ultraviolet irradiation.

Compound **2** underwent photochromism even in the crystalline phase. It is worthwhile to note that the by-product **3** formation was not observed in the crystalline phase. The fatigue resistant characteristics of crystalline **2a** were examined by alternate irradiation with ultraviolet (313 nm) and visible ($\lambda > 440$ nm) light. Any appreciable increase in the visible absorption was not observed for the crystal even after 2000 coloration–decoloration cycles. The transmittance of the crystal decreased to around 80% of the fresh crystal after 10 000 cycles, but the decrease is mainly due to an increasing roughness of the crystal surface and not due to by-product formation.

Notes and references

† *Selected data* for **2a**: 140 °C; δ_H(200 MHz) 7.30–7.75 (m, 10H, CH of Ph), 7.28 (s, 2H, CH of thiophene), 1.97 (s, 6H, Me); δ_C(125 MHz) 142.2, 141.1, 133.3, 109.8 (8C, Cq), 128.9, 127.8, 125.6 (10C, CH of Ph), 122.4 (2C, CH of thiophene), 14.5 (2C, Me); *m/z* 520 (M$^+$, 64%), 505 (100), 490, 472, 385, 121, 77. (Calc. for $C_{27}H_{18}F_6S_2$: C, 62.30; H, 3.49. Found: C, 62.66; H, 3.72%).

‡ *Selected data* for **3**: mp 131 °C; δ_H(200 MHz) 7.36–7.51 (m, 10H, CH of Ph), 6.50 (s, 2H, H at C1/C6), 2.78 (s, 3H, Me at C3a), 2.75 (s, 3H, Me at C9c); δ_C(125 MHz) 144.8 (2C, C2/C5), 144.5 (2C, C6a, C9b), 137.3 (2C, ipso-C of Ph), 130.3 (2C, *p*-C of Ph), 128.7 (4C, *m*-C of Ph), 126.0 (4C, *o*-C of Ph), 123.1 (2C, C6b/C9a), 115.5 (1C, C8), 112.5 (2C, C1/C6), 112.4 (2C, C7/C9), 65.8 (1C, C3a), 59.6 (1C, C9c), 28.2 (1C, Me at C3a), 22.9 (1C, Me at C9c); *m/z* 520 (M$^+$, 63%), 505 (100), 490, 385, 121, 77 (Calc. for $C_{27}H_{18}F_6S_2$: C, 62.30; H, 3.49. Found: C, 62.64; H 3.72%).

§ *Crystal data* for **3**: $C_{27}H_{18}F_6S_2$, T = 293(2) K, M = 520.56, triclinic, space group $P\bar{1}$, a = 11.565(3), b = 11.827(3), c = 10.206(2) Å α = 95.45(2), β = 100.68(2), γ = 60.12(2)°, V = 1189.4(5) Å^3, Z = 2, μ = 2.584 mm^{-1}, 4741 measured, 4506 independent reflections, of which 2932 were considered as observed [$I > 2\sigma(I)$]. Final $R1$ = 0.0778, $wR2$ = 0.2121. CCDC 182/1196. Crystallographic data are available in .cif format from the RSC web site, see: http://www.rsc.org/suppdata/cc/1999/747/

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11 **2a** was prepared by a similar method as used for **1a**. See also S. H. Kawai, S. L. Gilat, R. Ponsinet and J.-M. Lehn, *Chem. Eur. J.*, 1995, **1**, 285.

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