Fatigue Mechanism of Photochromic 1,2-Bis(3-thienyl)perfluorocyclopentene

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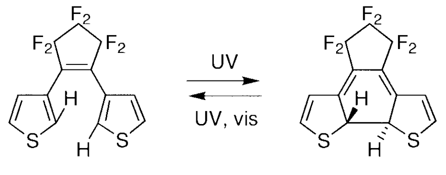
Non-substituted 1,2-bis(3-thienyl)perfluorocyclopentene **1a** was synthesized and its photochromic reactivity was compared with 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene **4a**. Upon irradiation with ultraviolet light **1a** easily decomposed and two kinds of by-products were produced in addition to the normal closed-ring isomer. The structures of the by-products were determined by X-ray crystallographic analysis.

Photochromic compounds, in general, undergo thermally reversible photoreactions.[1] Photogenerated isomers return to the initial isomers in the dark. Such thermally reversible photochromic compounds can not be applied to optoelectronic devices, such as optical memories or switches.[2] Recently three types of thermally irreversible photochromic compounds, furylfulgides,[3] diarylethenes[4] and phenoxynaphthacenequinone,[5] have been developed. Among the compounds, 1,2-diarylethenes with heterocyclic aryl groups are the most promising because of their high fatigue resistance. The fatigue resistance is known to depend on the aryl groups and also the substituents on the aryl groups.[6] Diarylethenes with benzothiophene aryl groups undergo fatigue-resistant photochromic reactions,[7] while some diarylethenes with thiophene rings cease their photochromic cycles in less than several hundred cycles.[6]

Non-substituted 1,2-bis(3-thienyl)perfluorocyclopentene **1a** was synthesized to study the substituent effect on the photochromic reactions of the dithienylethene derivatives.

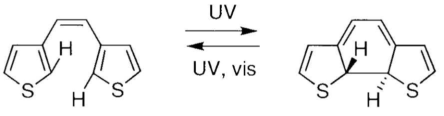
Scheme 1.



1a **1b**

Figure 1 shows the photoinduced spectral change of **1a** in hexane. Upon irradiation with 313 nm light for 1 min, the colorless solution of **1a** turned yellow, in which visible absorption band was observed at 469 nm. The yellow color is assigned the closed-ring isomer **1b**. Kellogg et al. reported that upon UV-irradiation 1,2-di(3-thienyl)ethene **2a** was converted to closed-ring isomer **2b**, which has absorption maximum at 420 nm (Scheme 2).[8] The formation of dehydrogenated phenanthrene-type derivatives was not discerned from both **1b** and **2b**, because of instability of β-thio-substituted radicals.[8] The yellow color was partly bleached by irradiation with visible light (> 400 nm). After irradiation with visible light, there remained absorption bands in the ultraviolet region longer than the absorption of the open-ring isomer **1a**. This indicates the production of photostable by-products.

Scheme 2.



2a **2b**

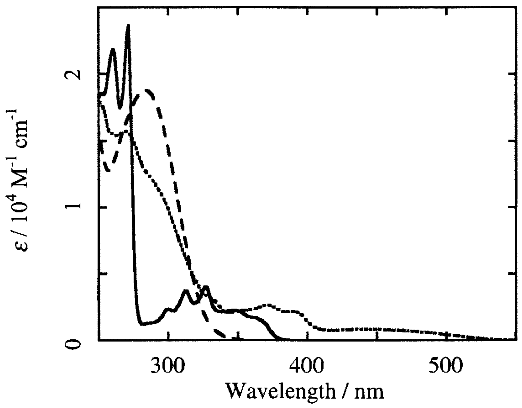
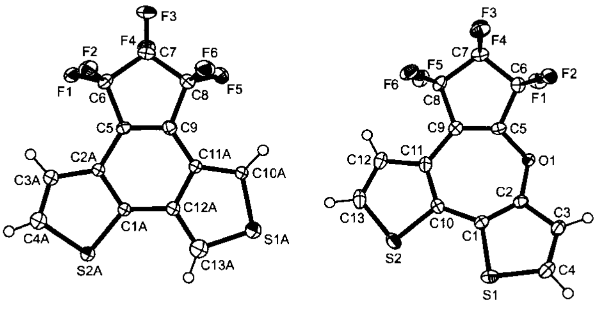


Figure 1. Absorption spectra of open-ring isomer **1a** (- - - -), **1** in the photostationary state (· · · ·), and by-product **3** (——) in hexane.

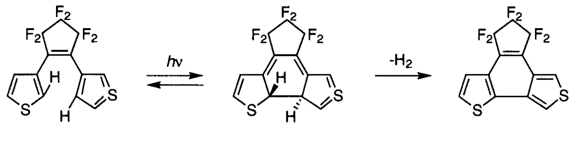
After irradiation with 313 nm light for 24 h a photostable by-product was isolated by HPLC. Almost half of **1a** converted to the by-product. The by-product was analyzed by ^{1}H NMR and mass spectrum. ^{1}H NMR spectrum had four kinds of protons (1:1:1:1) at 7.60, 7.66, 8.03, and 8.25 ppm. This suggests that two thiophene rings were not lost.[9] The mass spectrum indicated the elimination of two protons. To know the exact structure of the by-product X-ray crystallographic analysis was carried out. A needle shape colorless single crystal was obtained by recrystallization from the hexane solution. Figure 2a shows the molecular structure of the by-product.[10] It has a planar π-conjugate system and the absorption spectrum is shown in Figure 1.



(a) (b)

Figure 2. ORTEP drawing with thermal ellipsoids (50% probability). (a) Molecular structure of **3**. Only one conformation of two disordered structure is shown for clarity. (b) Molecular structure of **6**.

Scheme 3.



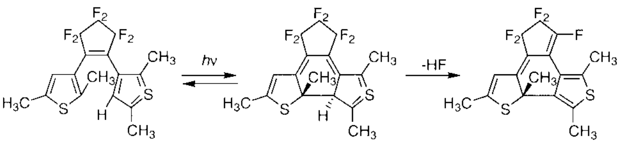
1a **3**

Scheme 3 shows the possible mechanism of the by-product formation. One of the resonance structures of thiophene uses an expanded valence shell of a sulfur atom, as shown in Scheme 3.[11] In the structure a double bond is formed between 3- and 4-positions. Therefore, the molecule has a chance to cyclize in between 2- and 4'-positions of the two thiophene rings. Subsequent dehydrogenation produces the by-product **3**.

Dithienylethenes having methyl groups at 2- and 2'-positions of the thiophene rings, 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene **4a**, did not produce the above by-product **3**. This is due to difficult elimination of the methyl group. In a previous paper[12] we reported that **4** produced a minor by-product, in which HF was eliminated from the parent molecule. The HF elimination mechanism can be explained as shown in Scheme 4 based on the mechanism of by-product **3** formation. Because of difficulty to eliminate the methyl group the intermediate is considered to detach fluorine and hydrogen atoms to produce the minor by-product **5**. When the hydrogen at 4-position of the thiophene ring was substituted with a methyl group, the by-product **5** was not formed.

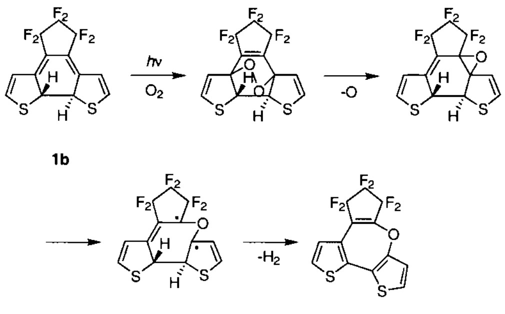
In the presence of oxygen, another minor by-product formation was observed. The by-product was isolated by HPLC and analyzed by X-ray crystallography. A needle shape yellow single crystal was obtained by recrystallization from hexane solution. The structure contains seven-membered heterocyclic ring as shown in Figure 2b.[13] The possible mechanism of the by-product **6** formation is shown in Scheme 5. Upon irradiation with ultraviolet light in the presence of oxygen the closed-ring isomer **1b** is considered to produce epoxide. The epoxide is presumed to be the origin of the by-product.[14] The formation of **6** was not discerned in argon bubbled hexane.

Scheme 4.



4a **5**

Scheme 5.



1b **6**

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9 ^{1}H NMR data for **1a**: δ 7.01 (2H, q, -H^4, J = 4.97, 1.07), 7.34 (2H, q, -H^5, J = 4.97, 2.82), 7.61 (2H, q, -H^2, J = 2.82, 1.07)

10 Crystallographic data for **3**: $C_{13}H_4F_6S_2$, FW = 338.28, triclinic $P\bar{1}$, a = 7.3548(12) Å, b = 8.9543(14) Å, c = 9.7105(16) Å, α = 107.063(2)°, β = 96.109(3)°, γ = 91.092(3)°, V = 607.03(17) Å^3, Z = 2, R_1 = 0.0473, wR_2= 0.1223.

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13 Crystallographic data for **6**: $C_{13}H_4F_6OS_2$, FW = 354.28, monoclinic $P2_1/c$, a = 9.0827(16) Å, b = 4.8100(8) Å, c = 28.515(5) Å, β = 94.558(3)°, V = 1241.8(4) Å^3, Z = 4, R = 0.0456, wR_2= 0.0865.

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