Fatigue Mechanism of Photochromic 1,2-Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene#

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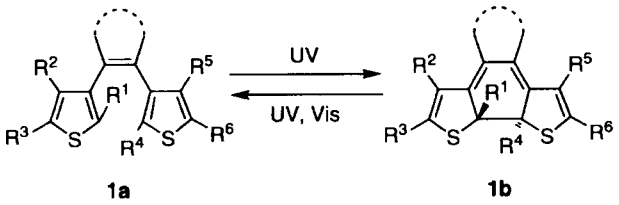
(Received March 13, 2000)

The fatigue mechanism of photochromic 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene was studied in hexane solution. Upon irradiation with ultraviolet light, two kinds of by-products were produced in addition to normal photochromic reactions. The major by-product was isolated by HPLC, and was characterized by ^{1}H NMR and absorption spectroscopies and X-ray crystallographic analysis. A minor by-product was also isolated and analyzed with a mass spectrometer. Based on the molecular structural analysis a possible photofatigue mechanism of the dithienylethene was proposed.

Light-induced reversible isomerization between two forms having different absorption spectra is referred to as photochromism,[1] and compounds capable of these reactions are called photochromic compounds. Various types of photochromic compounds have been developed in an attempt to apply the compounds to optoelectronic devices such as optical memory, photo-optical switching, and displays. Although enormous numbers of photochromic compounds have been reported, the applications of photochromic compounds to practical use are limited.[2] One of the reasons is the lack of fatigue resistance. Photochromic compounds which can repeat photoinduced coloration/decoloration cycles more than 1000 times are very rare. Exceptional examples are spirooxazines and diarylethenes, which have been reported to undergo fatigue-resistant photochromic reactions and the former are now commercially used for ophthalmic plastic lens.[2,3] For optical memories and photo-optical switching devices, diarylethenes with heterocyclic aryl groups are the most promising photochromic compounds because of their thermal irreversibility.[4]

Diarylethenes undergo the following photochromic reactions (Scheme 1).[3,4] Upon irradiation with ultraviolet light, the open-ring form isomer **1a** converts to the closed-ring form isomer **1b**. Although diarylethenes with 1-benzothiophene aryl groups, such as 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene **2** and 2,3-bis(2-methyl-1-benzothiophen-3-yl)maleic anhydride **3**, undergo fatigue resistant photochromic reactions (more than 10000 coloration/decoloration cycles) without any destruction of their structures,[5] some diarylethenes with thiophene rings, such as 2,3-di(2,3,5-trimethylthiophen-3-yl)maleic anhydride **4**, cease their photochromic cycles in less than several hundred cycles even in the absence of oxygen (Chart 1).[3,6]



Scheme 1.

In order to improve fatigue-resistant properties of diarylethenes, it is essential to understand the fatigue mechanism. In this research we isolated and analyzed photogenerated by-products to elucidate the photofatigue mechanism of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene **5**. Compound **5** is known to undergo photochromic cyclization/cycloreversion reactions in solution as well as in the single-

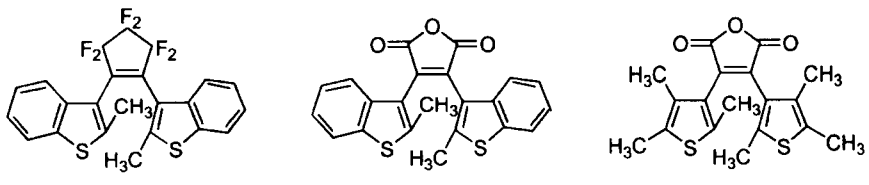


Chart 1. Chemical structures of compounds **2**, **3**, and **4**.

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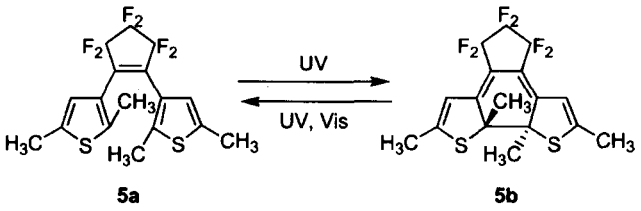
crystalline phase (Scheme 2).[7,8]

Results and Discussion

Characterization of Major By-Product. Figure 1 shows the photoinduced spectral change of **5a** in hexane. Upon irradiation with 254 nm light for 1 min, the colorless solution of **5a** turned red; here a visible absorption band was observed at 503 nm. The red color is due to the closed-ring isomer **5b**.[7] Figure 1 also shows the spectrum of isolated closed-ring isomer **5b**. The conversion from **5a** to **5b** in the photostationary state under irradiation with 254 nm light was 72%. The red color completely disappeared by irradiation with visible light (> 400 nm). However, when the irradiation time with 254 nm light was prolonged to 20 min, a photostable product was produced, which could not be bleached by visible (> 400 nm) light. The absorption spectrum of the by-product is also shown in Fig. 1.

The stable by-product could be isolated by HPLC and was found by molecular mass determination to be isomeric with compound **5**. The molar absorption coefficient value ($\epsilon_{487} = 3.1\times10^3$ M^{-1} cm^{-1}, M = mol dm^{-3}) in the visible region was 40% of the closed-ring form isomer **5b**. ^{1}H NMR spectrum of the by-product has three kinds of methyl groups (2 : 1 : 1) at 1.93, 2.46, and 2.48 ppm, and one olefinic proton at 6.09 ppm. The structure of the by-product could not be determined conclusively by ^{1}H NMR spectroscopy. Therefore, X-ray crystallographic analysis of the single crystal was carried out. A rhombus-shaped red single crystal was obtained by recrystallization from MeOH–H_2O solution. Figure 2 and Table 1 show the molecular structure of the by-product and the structural data, respectively. The thiophene rings no longer exist. It has a condensed system with two six-membered heterocyclic rings. The polyene structure is similar to the closed-ring isomer **5b**. This is the reason why the by-product has a similar absorption spectrum. The condensed ring structure is the same as the by-product,which was produced in the case of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene.[9]



5a **5b**

Scheme 2.

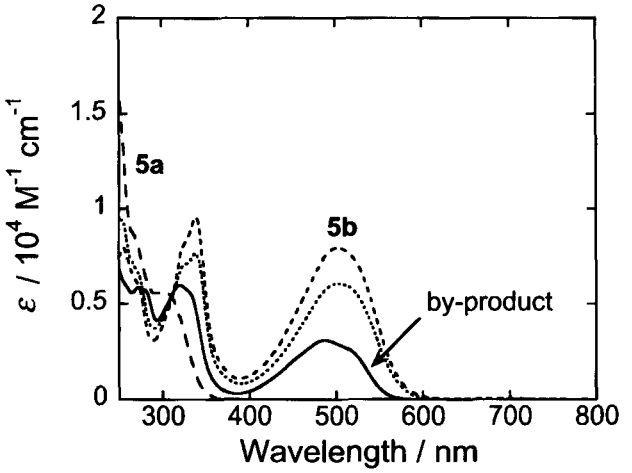


Fig. 1. Absorption spectra of **5a** (- - -), **5b** (····), **5** in the photostationary state (····), and by-product (—) in hexane.

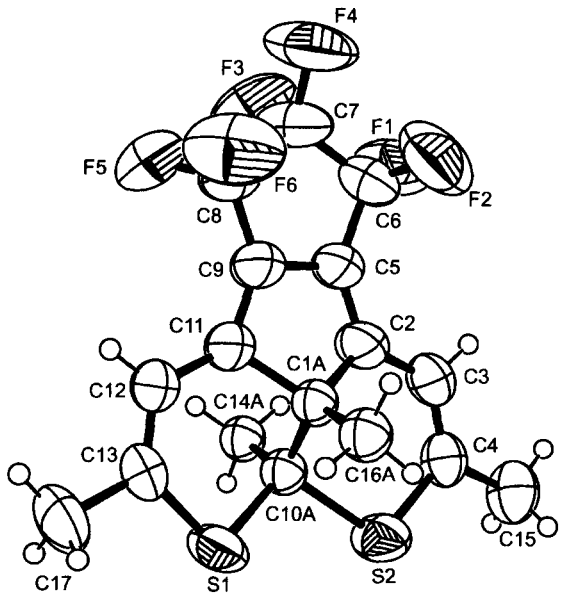


Fig. 2. ORTEP drawing of the major by-product showing 50% probability displacement ellipsoids. Methyl groups and quaternary C atom in the center of the molecule were disordered. Therefore, one side was omitted for clarity.

Table 1. Crystallographic Parameters for the By-Product

Formula	$C_{17}H_{14}F_6S_2$
Formula weight	396.40
Crystal color	Red
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	6.7297(14)
b/Å	23.925(5)
c/Å	11.446(2)
β/°	105.316(4)
V/Å^3	1777.6(6)
Z	4
D_{calcd}/g cm^{-3}	1.481
R_1	0.0722
wR_2	0.2167

The Effect of Irradiation Wavelengths on the By-Product Formation. In order to know the formation mechanism of the by-product, irradiation time dependence of the by-product formation from **5a** and from isolated **5b** was followed, as shown in Figs. 3a and 3b, respectively. Hexane solutions containing **5a** (2.0 mM) and **5b** (2.0 mM) were irradiated with 254 nm and the concentration changes of **5a**, **5b**, and the by-product were measured by HPLC. Although there existed some induction period in the formation of the by-product from **5a** (Fig. 3a), the by-product was produced

from **5b** from the beginning of irradiation (Fig. 3b).

The effect of irradiation wavelength on the by-product formation was also studied, as shown in Fig. 4. The solution containing only **5b** (2.0 mM in hexane) was irradiated with visible light (546 nm). In this case, formation of the by-product was not observed at all. It is inferred from the above results that the by-product is produced by photolysis of **5b** with ultraviolet light.

Formation of By-Product in the Single-Crystalline Phase. Compound **5** undergoes the photochromic reaction in the single-crystalline phase.[7,8] Formation of the by-product was also examined in the photoreaction in the single-crystalline phase. Ultraviolet light (254 nm) was irradiated for a long time to reach the conversion up to 6% in the single-crystalline phase. Then, the crystal was dissolved in hexane and formation of by-products was examined by HPLC. No by-product formation was detected.

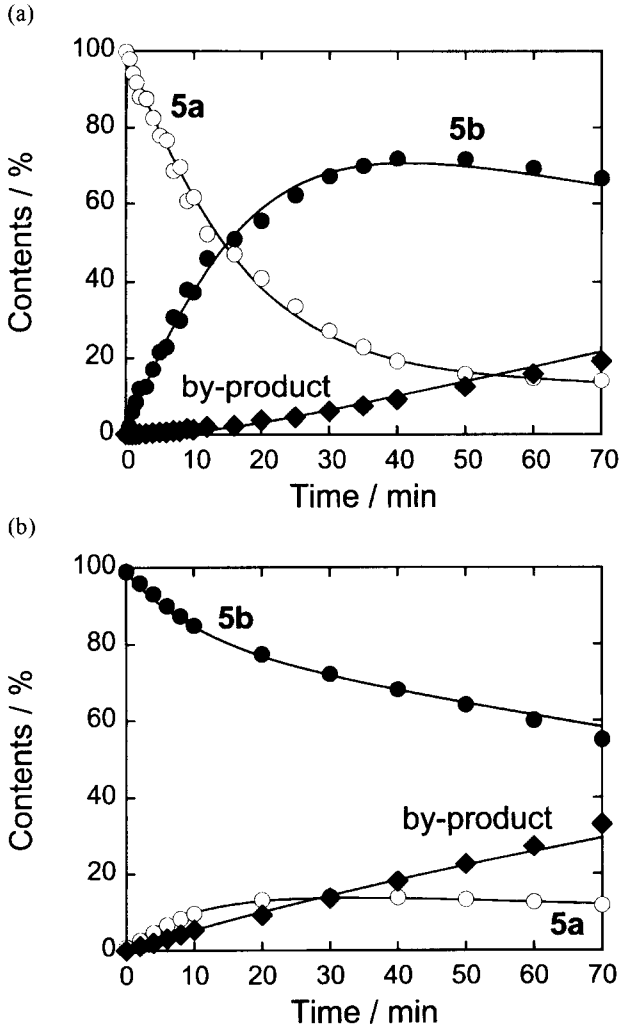


Fig. 3. (a) Decay of **5a** and formation of **5b** and by-product upon irradiation with 254 nm light. The initial concentration of **5a** was 2.0 mM. (b) Decay of **5b** and formation of **5a** and by-product upon irradiation with 254 nm light. The initial concentration of **5b** was 2.0 mM. The solid lines in (a) and (b) were least square fits of the concentration of **5a**, **5b**, and by-product calculated based on Eqs. 1, 2, and 3 (see text).

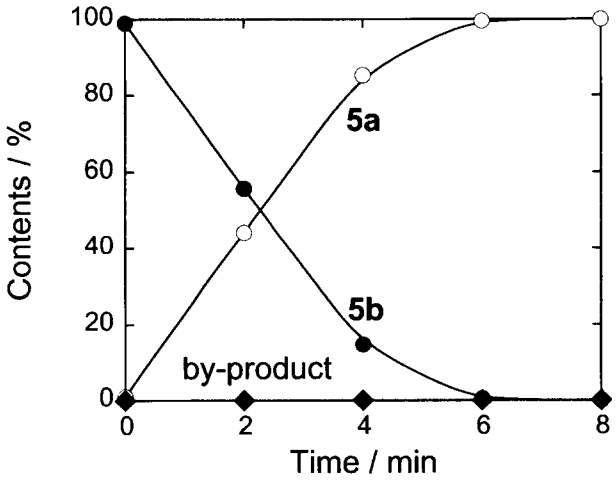


Fig. 4. Decay of **5b** and formation of **5a** upon irradiation with 546 nm light. The initial concentration of **5b** was 2.0 mM.

Kinetic Study. The data shown in Figs. 3a and 3b were analyzed based on the assumption that the by-product was formed directly from **5b** by ultraviolet irradiation (Scheme 3).

$$\frac{dC_{5a}}{dt} = (-k_{5a-5b}C_{5a} + k_{5b-5a}C_{5b})F \quad (1)$$

$$\frac{dC_{5b}}{dt} = (-k_{5b-5a}C_{5b} - k_{5b-p}C_{5b} + k_{5a-5b}C_{5a})F \quad (2)$$

$$\frac{dC_{p}}{dt} = (k_{5b-p}C_{5b})F \quad (3)$$

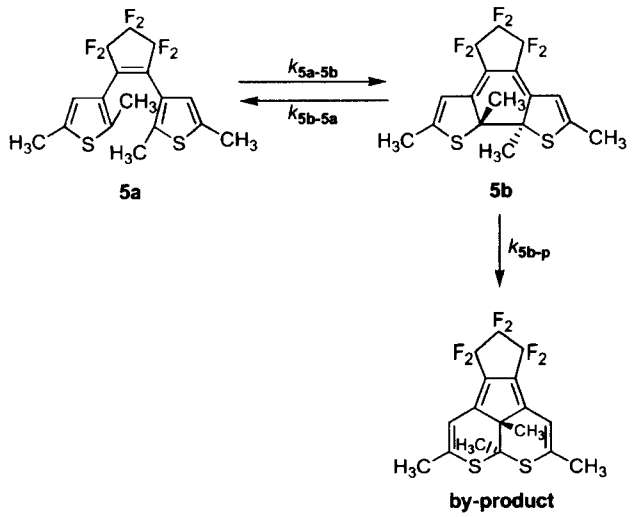
$$F = \frac{1-10^{-A}}{A} \qquad A = \epsilon_{5a}C_{5a} + \epsilon_{5b}C_{5b} + \epsilon_{p}C_{p}$$

$$k_{5a-5b} = \epsilon_{5a}\Phi_{5a-5b}I_0$$

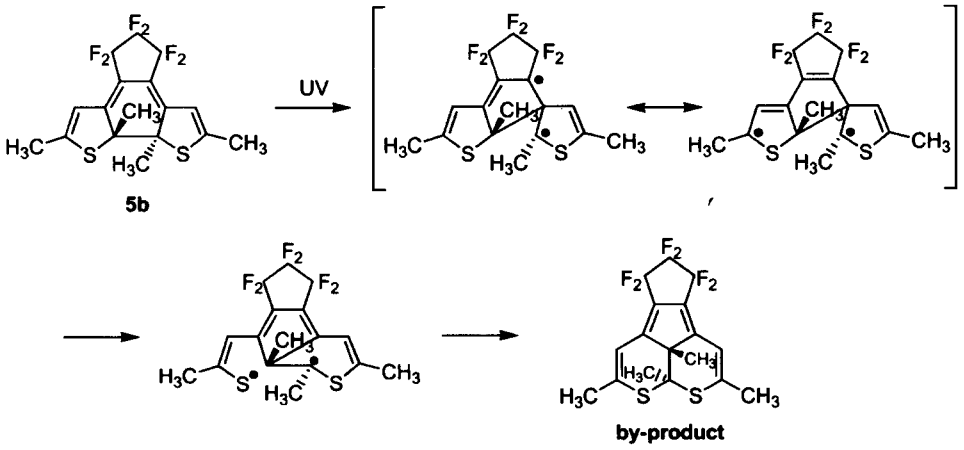
$$k_{5b-5a} = \epsilon_{5b}\Phi_{5b-5a}I_0$$

$$k_{5b-p} = \epsilon_{5b}\Phi_{5b-p}I_0$$

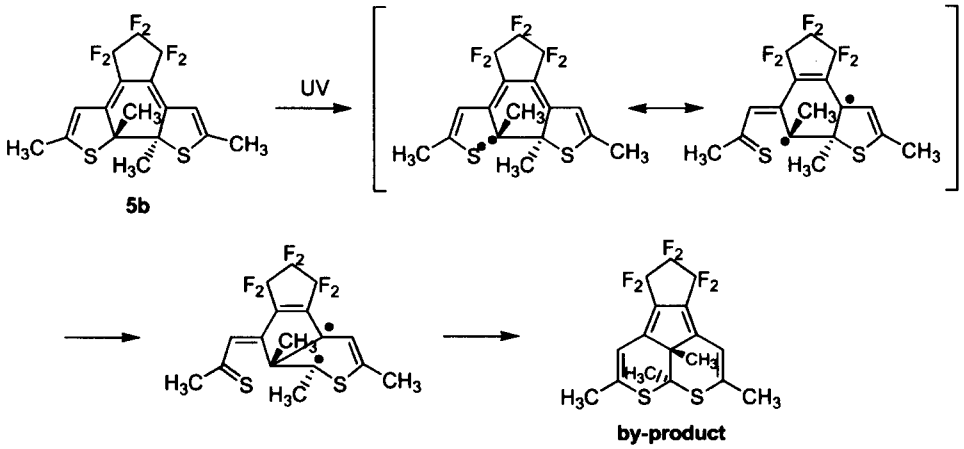
In these differential equations, I_0 is the intensity of irradiation light; Φ_{5a-5b}, Φ_{5b-5a}, and Φ_{5b-p} are reaction quantum yields of **5a** to **5b**, **5b** to **5a**, and **5b** to by-product, respectively. ϵ_{5a},



Scheme 3.



Scheme 4.



Scheme 5.

ϵ_{5b}, and ϵ_p are molar absorption coefficients of **5a**, **5b**, and by-product at the wavelength of ultraviolet irradiation. C_{5a}, C_{5b}, and C_p are concentrations of **5a**, **5b**, and by-product.

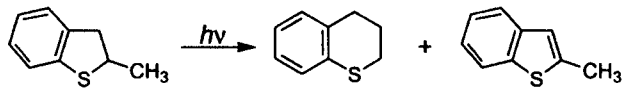
These differential equations were numerically solved and the results were fitted to the experimental data of Figs. 3a and 3b. The best-fitted curves were shown as solid lines in the figures. The parameters used for reproduction of Fig. 3 were as follows: $k_{5a-5b} = 1.29$, $k_{5b-5a} = 0.249$, $k_{5b-p} = 0.0976$ einstein $M^{-1}\,cm^{-1}\,min^{-1}$; $\epsilon_{5a} = 1.4\times10^4$, $\epsilon_{5b} = 7.9\times10^3$, $\epsilon_p = 6.1\times10^3$ $M^{-1}\,cm^{-1}$. The ratio $\Phi_{5a-5b} : \Phi_{5b-5a} : \Phi_{5b-p}$ was calculated to be 1 : 0.34 : 0.13. The quantum yield of the by-product formation was 38% of the cycloreversion quantum yield.

We also carried out a simulation based on the assumption that the by-product is produced directly from **5a**. On this assumption we could not reproduce the experimental results at all.

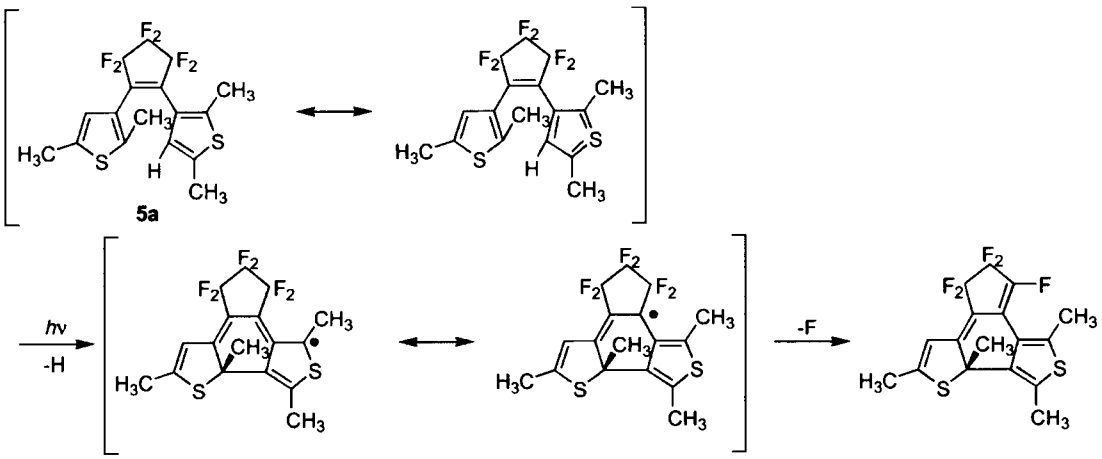
Mechanism of the By-Product Formation. There are several possible reaction routes to produce the by-product from the closed-ring isomer **5b** by photoirradiation. Schemes 4 and 5 show two possible routes. It is known that photoexcited cyclohexadiene has a channel to produce five-membered ring formation.[10] The radical migration in the π-conjugation system and bond-formation and cleavage finally produce the condensed-ring by-product (Scheme 4).

Another possible route is shown in Scheme 5. C–S bond length in the closed-ring isomer **5b** was determined to be 1.829 Å which is fairly long in comparison with the normal length of 1.719 Å.[7] Such a long bond length facilitates the C–S bond cleavage by photoexcitation. Similar band cleavage has been reported for 2-methyl-2,3-dihydro-1-benzothiophene **6**.[11] Compound **6** converts to thiochroman **7** (3, 4-dihydro-2H-1-benzothiine) by C–S bond cleavage in the photoexcited state (Scheme 6). Scheme 5 shows the route starting from the C–S bond cleavage. The radical migration and five-membered ring formation result in the condensed-ring structure.

In order to confirm which mechanism is more probable, we carried out radical scavenger experiments.[12] $(n\text{-Bu})_3SnH$ was added to the hexane solution containing **5a** and the solution was irradiated with 245 nm light. Although, the by-product yield decreased by the addition of $(n\text{-Bu})_3SnH$, we failed to isolate the quenched products. The latter mechanism is



Scheme 6.



Scheme 7.

more probable, but we could not conclude which mechanism works in the present by-product formation.

The by-product formation was not observed for 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene **2** even after prolonged irradiation more than 10 h. The absence of by-product formation can be interpreted from the above mechanisms. In the bis(benzothienyl) derivatives, radical migration to and from the sulfur atom is strongly suppressed because of the condensed phenyl ring. The benzothiophene moiety stabilizes the radical and prevents the radical migration. This is one of the reasons for the absence of the by-product formation and high fatigue-resistant character of the bis(benzothienyl)ethenes.

Minor By-Product. When we continue irradiation for longer time, one more by-product formation was detected by HPLC. Because of the small amount of the isolated product we just measured the mass spectrum. The mass number suggested the elimination of HF from the parent molecule. Scheme 7 shows a possible structure of the minor by-product and the formation mechanism.[13] The scheme is based on the experimental result that the unsymmetrical closed-ring isomer was produced from 1,2-bis(3-thienyl)perfluorocyclopentene.[14] Kellogg et al. also reported the formation of such an unsymmetrical closed-ring isomer from 1-(2-thienyl)-2-(3-thienyl)ethene.[15] Although the mechanism is still speculative, the formations of these by-products are the main fatigue processes of diarylethenes.

Experimental

Photochemical Reaction. Hexane of spectroscopic grade was distilled before use. Absorption spectra were measured with a Hitachi U-3500 absorption spectrometer. Photoirradiation was carried out using a Ushio USH-500D 500W high-pressure mercury lamp or a Spectroline ENF-240C/J low-pressure mercury lamp as the light source. Monochromatic light was obtained by passing the light through a Ritsu MC-20L monochromator.

X-Ray Crystallography. X-Ray crystallographic analysis was carried out using a Bruker SMART CCD X-ray diffractometer. A good quality crystal (0.5×0.2×0.1 mm) was selected for the X-ray diffraction study. The data collection was performed on a Bruker SMART1000 CCD-based diffractometer (50 kV, 40 mA) with Mo $K\alpha$ radiation. The data collection was performed as follows: The data covered a hemisphere of the reciprocal space by combining four sets of runs; each frame covered 0.3° in ω for 30 seconds exposure time. The crystal-to-detector distance was 5.118 cm. Crystal decay was monitored by repeating the 50 initial frames at the end of data collection and analyzing the duplicate reflections. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects, and decay. The cell constants were calculated by the global refinement. The structure solved by direct methods using SHELXS-86[16] and refined by full least-squares on F^2 using SHELXL-97.[17] The positions of all hydrogen atoms were calculated geometrically and refined by the riding model. Disordered part with small occupancy was refined isotropically and the bond lengths and geometry should be restrained in the refinement. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 147144. The data are also deposited as Document No. 73051 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Synthesis and Characterization of the Compounds. ^{1}H NMR spectrum was recorded on a Varian Gemini 200 spectrometer (200 MHz). Tetramethylsilane (TMS) was used as an internal standard. The melting point was measured by using a Laboratory Devices MEL-TEMP II. Mass spectrum was taken with a JEOL JMS-HX110A mass spectrometer.

1,2-Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene open-ring form isomer (**5a**) and closed-ring form isomer (**5b**) were prepared according to the reported procedure.[7]

The major by-product was separated by HPLC (hexane with silica gel column) from hexane solution containing **5a**, which was irradiated with 313 nm for 1 d. By-product: Mp = 101.9—103.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.93 (s, 6 H, $-CH_3$), 2.46 (s, 3 H, $-CH_3$), 2.48 (s, 3 H, $-CH_3$), 6.09 (s, 2 H, –H). HRMS Found: *m/z* 396.0441 (M^+). Calcd for $C_{17}H_{14}F_6S_2$: M, 396.0441.

This work was supported by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corp. (JST).

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