

X-ray Crystallographic Study on Single-Crystalline Photochromism of Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene

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Abstract: The single-crystalline cycloreversion reaction of a photochromic diarylethene, bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene, was studied by X-ray single-crystal structure analysis. The single crystal of the closed-ring form isomer was irradiated with 680 nm light and formation of the open-ring form isomer was followed. The crystal structure analysis revealed that the cycloreversion reaction proceeded in the single crystal in a conrotatory mode.

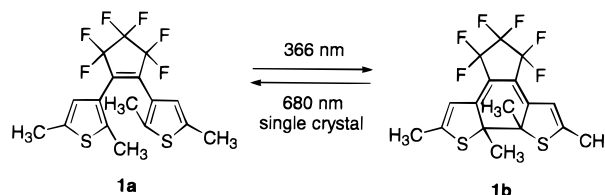
Introduction

Photochromic crystals are useful for rewritable holographic memory^{1,2} as well as nonlinear optics with switching properties.³ Although a great number of photochromic compounds have been reported, compounds which undergo photochromism in a crystalline phase are rare. Typical examples are *N*-salicylideneanilines,⁴ nitrobenzylpyridines,^{5,6} triarylimidazole dimers,⁷ and diarylethenes.^{8–11} Among them diarylethene crystals are promising materials for optical memory and switches, because both states, colorless and colored, are stable even at 100 °C and coloration/decuration cycles can be repeated more than 10 000 times without deterioration.^{9,10}

The diarylethenes undergo a 1,3,5-hexatriene \rightleftharpoons cyclohexadiene type photochromic reaction by alternate irradiation with UV and visible light. According to the Woodward–Hoffmann rule, it is expected that photoinduced cyclization and cycloreversion reactions proceed in a conrotatory mode. In fact the product of the photocyclization reaction of bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**1a**) has only trans configuration for the two methyl groups on the fused ring,¹¹ and the cyclization quantum yield is dependent on the ratio of the antiparallel opening conformation in solution^{12,13} as well as in the crystalline

phase.¹⁰ On the other hand, for the cycloreversion reaction we have not had any direct evidence for the conrotatory mode. In this study we directly detected the conformation of the photo-generated open-ring form isomer in the single crystal of the closed-ring form isomer by X-ray crystallographic analysis.

Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**1a**) undergoes the following photochromism in the crystalline state.¹¹



The open-ring isomer crystal turns to red by irradiation with UV light. X-ray structural analysis of both open- and closed-ring isomers revealed that during the cyclization reaction only sulfur and carbon atoms at reaction points changed their positions and others remained at almost the same positions.¹¹ In this study the movement of the atoms in the single crystal in the cycloreversion reaction process of **1b** was followed by X-ray crystallography.

Result and Discussion

Absorption Spectrum of the Closed-Ring Isomer and Photoirradiation. Figure 1 shows the absorption tail of the single crystal of **1b**. The absorption spectrum extends to 730 nm. Photoirradiation was carried out using monochromatic light of 680 nm. At 680 nm the absorbance of the single crystal (the crystal thickness was ~ 0.2 mm) was less than 0.1. This means that ca. 80% of the irradiated light was passed through the crystal and only 20% was absorbed by the crystal. The crystal was almost homogeneously irradiated with the light. The cycloreversion reaction is considered not to be localized in the surface region but to take place in the whole crystal.

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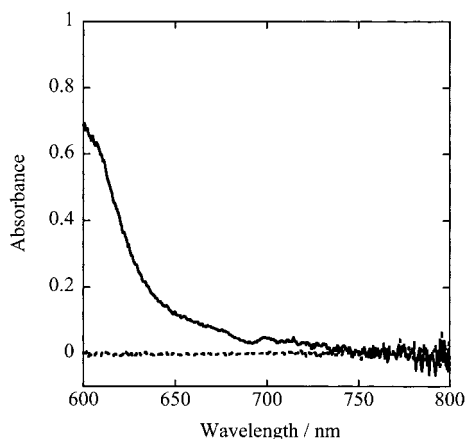


Figure 1. Absorption spectra of the closed-ring form crystal **1b** (solid line) and the open-ring form crystal **1a** (broken line). The crystal thickness was ca. 0.2 mm.

Table 1. Crystallographic Data and Experiment Details

	1b	1b' ^a
empirical formula	C ₁₇ H ₁₄ F ₆ S ₂	
formula weight	396.40	
temperature	123 K	
crystal size	0.5 × 0.4 × 0.2 mm	
crystal system	monoclinic	
space group	P2 ₁ /c	
Z	4	
a/Å	6.2192(9)	6.2674(12)
b/Å	24.520(4)	24.787(5)
c/Å	11.3026(16)	11.381(2)
β/deg	103.667(3)	103.639(3)
V/Å ³	1674.8(4)	1718.2(6)
density calcd/g·cm ⁻³	1.572	1.532
θ range for data collection	1.66 to 27.48°	1.64 to 27.45°
no. of reflns collected	9656	9413
no. of independent reflcs	3585 [R(int) = 0.0297]	3572 [R(int) = 0.0263]
refinement method	full-matrix least-squares on F ²	
no. of restrains/parameters	0/230	67/331
goodness-of-fit on F ²	1.046	1.039
R indices [I > 2σ(I)]	R1 = 0.0395, wR2 = 0.0976	R1 = 0.0433, wR2 = 0.1028
R indices for all data	R1 = 0.0516, wR2 = 0.1022	R1 = 0.0647, wR2 = 0.1106
largest diff peak and hole	0.411 and -0.216 e·Å ⁻³	0.256 and -0.244 e·Å ⁻³

^a Irradiation wavelength: 680 nm, 1.2 × 10⁻⁵ W/cm². The crystal thickness was ca. 0.2 mm.

X-ray Analysis for Crystal 1b before Irradiation. X-ray crystallographic analysis of the closed-ring isomer crystal **1b** was reexamined at 123 K to suppress the thermal motion of the atoms. In a previous paper¹¹ the measurement was carried out at 304 K. The crystal of the closed-ring isomer **1b** has good crystallinity and the molecular structure has no disorder. The crystallographic data are shown in Table 1. The R1 for the reflection with $I > 2\sigma(I)$ and $wR2$ for all data are 0.040 and 0.102, respectively. The highest electron peaks are remaining in the middle of covalent bonds. The heights of the peaks are below 0.41 e·Å⁻³, which indicates the absence of disordered structure in the closed-ring form. The molecular structure of **1b** is shown in Figure 2. The fused ring has a trans configuration. The bond lengths of inner C–S bonds, S1–C1 and S2–C10, were longer (1.835(2) and 1.834(2) Å, respectively) than outer C–S bonds, S1–C4 and S2–C13 (1.756(2) and 1.754(2) Å, respectively). The difference between the C–S bond lengths is due to the hybridization of the carbons.¹⁴ Bond alternation around the fused rings was clearly observed. Bond lengths for

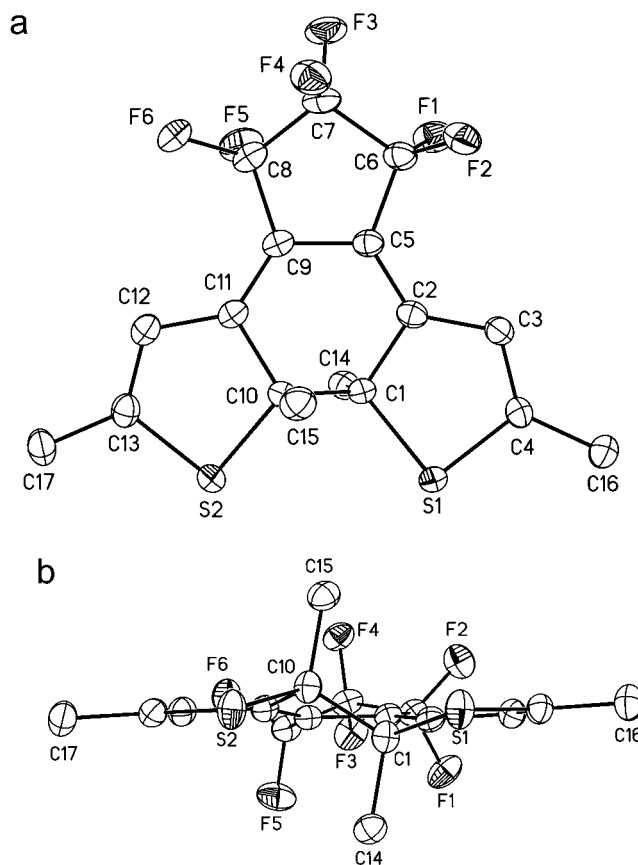


Figure 2. ORTEP drawings of top view (a) and side view (b) of **1b** showing the 50% probability displacement ellipsoids. Hydrogens were omitted for clarity.

double and single bonds are within a range of 1.34 to 1.35 and 1.42 to 1.45 Å, respectively. The mean deviation from the best least-squares plane through atoms C4, C3, C2, C5, C9, C11, C12, and C13 was 0.041 Å, which shows the polyene moiety in the fused ring is almost planar.

X-ray Analysis of Crystal 1b' after Irradiation. The crystallographic data for the crystal **1b'** after 680 nm light irradiation for 100 h are also shown in Table 1. The space group was the same as the crystal before photoirradiation. The *b* axis and the unit cell volume increased as much as 0.267 and 44 Å³, respectively. The crystal structure before irradiation was used as the initial model. After the difference Fourier synthesis, four new peaks, Q1, Q2, Q5, and Q6, appeared around the sulfur and carbon atoms on the fused rings (Figure 3a,b). The heights of peaks Q1 and Q2 were 2.20 and 2.14 e·Å⁻³, which are much larger than other residual peaks (less than 0.68 e·Å⁻³). At the same time negative counter regions were observed at S1 and S2 of the closed-ring isomer. These facts indicate that the S1 and S2 atoms of the closed-ring isomer moved to Q1 and Q2 by irradiation. These peaks were assigned to two sulfur atoms S1B and S2B. Neighboring residual peaks Q5 and Q6 were also assigned to two carbons C1B and C2B at the reaction points of the open-ring isomer. The four peaks existing in the diagonal orientation in Figures 3a and 3b clearly indicated that the open-ring isomer was generated by the conrotatory cycloreversion reaction.

Around the fluorine atoms of the hexafluorocyclopentene ring new electron density peaks appeared. This indicates that hexafluorocyclopentene also changed position during the cycloreversion reaction. Based on these peaks the model of the

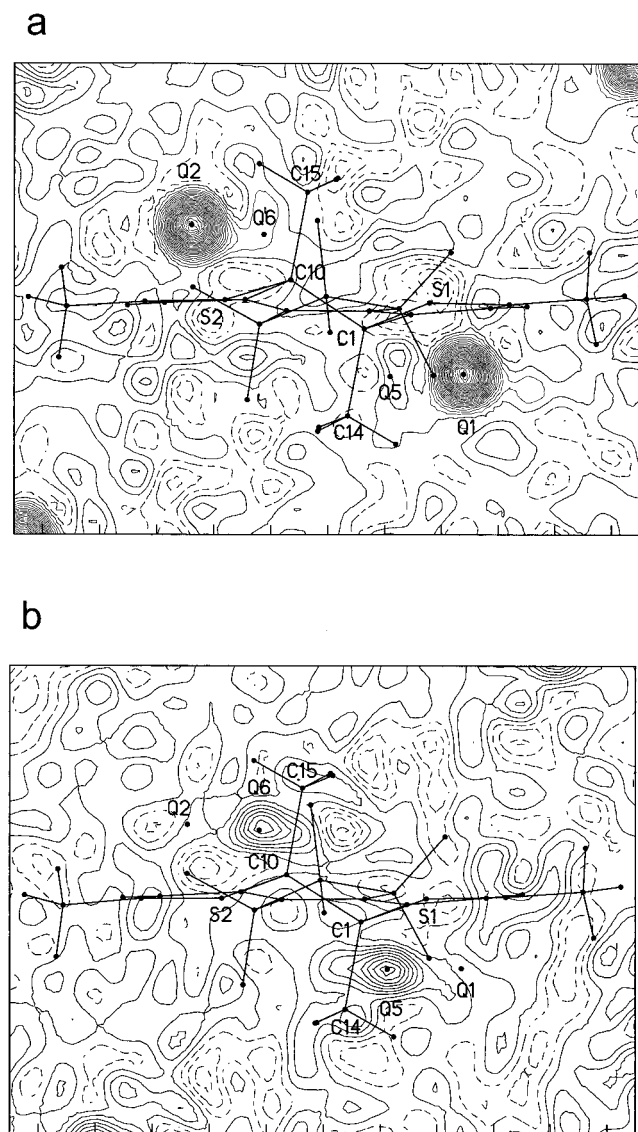


Figure 3. $F_o - F_c$ difference Fourier electron density maps: (a) through peaks Q1 and Q2 and (b) through peaks Q5 and Q6. The data for irradiated crystal **1b'** used as F_o and the coordinates of pure crystal **1b** were used for the calculation of F_c . The solid and broken lines showed positive and negative counter region, respectively.

open-ring isomer was constructed. The $R1$ for the reflection with $I > 2\sigma(I)$ and $wR2$ for all data were 0.043 and 0.111, respectively. The heights of the residual electron peaks were less than $0.256 \text{ e} \cdot \text{\AA}^{-3}$. The molecular structure obtained is shown in Figure 4. The torsion angles C1B–C2B–C5B–C9B and C10B–C11B–C9B–C5B were $42(6)^\circ$, which is slightly smaller than the value of crystal **1a**, $43.8(2)^\circ$. The distance between atoms C1B and C10B was $3.33(3) \text{ \AA}$, which is also slightly shorter than the value for the open-ring isomer crystal **1a**, $3.576(2) \text{ \AA}$. The distance between S1B and S2B was 5.42 \AA , which is smaller than the distance between two sulfur atoms of the open-ring isomer crystal **1a**, 5.96 \AA . The photogenerated open-ring isomer in the closed-ring isomer crystal has a conformation more planar than that in the most stable conformation.¹⁵ Bond angles C1B–C2B–C5B, C10B–C11B–C9B, C2B–C5B–C9B, and C11B–C9B–C5B were $134(3)^\circ$, $130(2)^\circ$, $124(2)^\circ$,

(15) The activation energy for the cycloreversion reaction in a single crystal was smaller than that in solution. Kobatake, S.; Lifca, T.; Irie, M.; Kato, N. Presented at The 3rd International Symposium on Organic Photochromism, Fukuoka, Japan, Nov 1999; Poster P29.

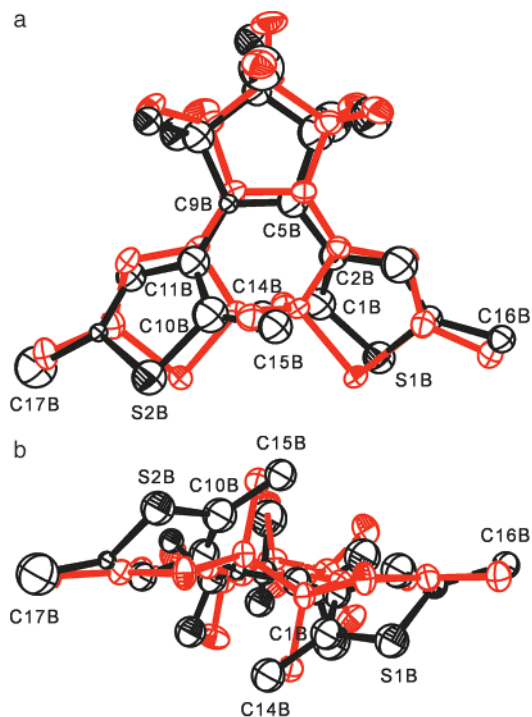


Figure 4. Molecular structure after the irradiation with 680 nm light for 100 h: (a) top view and (b) side view. The closed-ring form **1b** and open-ring form **1a** were drawn by red and black lines, respectively. The ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

and $123(2)^\circ$ and the corresponding values for crystal **1a** were $125.0(1)^\circ$, $125.0(1)^\circ$, $130.7(1)^\circ$, and $130.4(1)^\circ$.

The occupancy factor for the open-ring isomer converged to 0.094(2). This indicates that about 9% of the closed-ring isomers converted to the open-ring isomers by irradiation for 100 h. Since only one open-ring conformer was detected, the cycloreversion reaction proceeded topochemically in a conrotatory mode. In a previous paper,¹¹ we superimposed the molecular structures of **1a** and **1b** and found that the cyclopentene plane slightly tilted during the cyclization reaction. Similar displacement was also observed in the cycloreversion reaction as shown in Figure 4a,b. The center of gravity of photogenerated open-ring isomer **1a** (0.409, 0.382, 0.266) remained at the same position as that of the closed-ring isomer **1b** (0.388, 0.376, 0.269), which corresponds to a movement of less than 0.20 \AA .

Conclusion

This is the first X-ray single crystallographic observation for the cycloreversion reaction of a cyclohexadiene to 1,3,5-hexatriene type photoreaction. The cycloreversion reaction took place to the extent of 9% by irradiation with 680 nm light. After irradiation, new residual peaks appeared around atoms S1, S2, C1, and C10 and around the fluorine atoms. The residual peaks were assigned to the open-ring isomer. This X-ray structure analysis clearly indicated that the photocycloreversion reaction takes place in a conrotatory mode.

Experimental Section

X-ray Crystal Structure Analysis. Preparation and crystallization of compound **1b** were reported previously. A good quality crystal ($0.5 \times 0.4 \times 0.2 \text{ mm}$) 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 crystal was

cooled at 123 K by the cryostat (RIGAKU GN2). 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 s exposure time. The crystal-to-detector distance was 5.118 cm. Crystal decay was monitored by repeating the 50 initial frames at the end 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 was solved by direct methods using SHELXS-86¹⁶ 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. The disordered part with small occupancy was refined isotropically and the bond lengths and geometry should be restrained in the refinement.

Irradiation and Absorption Spectral Measurement. A microscope (Leica DMLP) equipped with a CCD detector (Hamamatsu photonics, PMA-11) was used for the measurement of the absorption spectrum of the single crystal.

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A 500 W Xe lamp (Ushio) was used as the light source. Monochromatic light was obtained by passing the light through the cutoff filters (Toshiba UV-22 and Y-52) and a monochromator (Ritsu MC-10L) (light intensity, 1.2×10^{-5} W/cm²). Crystals were irradiated with 680 nm light for 100 h at room temperature. HPLC measurement was also carried out after dissolving the crystal in hexane to confirm the cycloreversion reaction. After every 25 h of irradiation, X-ray crystallographic analysis was carried out to follow the cycloreversion reaction.

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Supporting Information Available: X-ray structural information on **1b** and **1b'** (PDF). X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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