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Bull. Chem. Soc. Jpn., 73, 2179—2184 (2000) 2179

Headline Articles

X-Ray Crystallographic Study on Single-Crystalline Photochromism of 1,2-Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene

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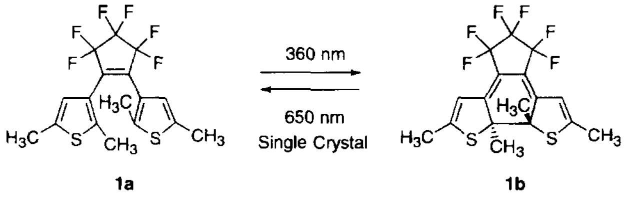
(Received April 3, 2000)

Single-crystalline photochromism of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene was studied by X-ray crystallography. The crystal was irradiated with linearly polarized monochromatic 360 nm light and analyzed with an X-ray diffractometer. The X-Ray crystallographic analysis showed that the conversion from the open-ring to the closed-ring isomers was as much as 8% and that the reaction proceeded in a conrotatory mode. Two sulfur atoms and reactive carbon atoms in the thiophene rings clearly changed their positions. The photogenerated closed-ring isomers completely returned to the initial open-ring isomers in the crystal by irradiation with 650 nm light.

Photochromism has attracted much attention because of potential applications to photonic devices, such as optical memories[1—3] and photo-optical switches.[4—9] Although much effort has been made so far, photochromic compounds still await practical applications. One of the reasons is the lack of suitable compounds, which fulfill the requirements for the applications. Among various compounds so far developed, diarylethenes with heterocyclic aryl groups are the most promising candidates for many applications because of their thermal irreversibility and fatigue resistance.[10,11] The compounds have an additional attractive characteristic, that is crystalline photochromic reactivity.[11—16] Some of diarylethenes undergo crystalline photochromism. When photochromic reactions proceed in crystals, side reactions to produce by-products are strongly suppressed and remarkable improvement of fatigue resistance is expected.[17]

A typical example is 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**1a**), which undergoes single crystalline photochromism, as shown in Scheme 1.[15]

In a previous paper, we reported X-ray crystallographic analysis of the cycloreversion reaction from **1b** to **1a** in the single crystal of the closed-ring isomer **1b**.[16] The photocycloreversion process of the diarylethenes could be followed without too great difficulty. In the visible wavelength region, only the closed-ring isomers have absorption bands, while photogenerated open-ring isomers have no absorption. Therefore, the cycloreversion reaction by irradiation with visible light can proceed without any perturbation of the photogenerated open-ring isomers. To the contrary, it is not easy to follow the cyclization reaction. The conversion from the open-ring isomer **1a** to the closed-ring isomer **1b** isomer is limited, because photogenerated **1b** absorbs at the irradiating ultraviolet wavelength region. Light penetration into the bulk crystal is prohibited by such absorption. The ultraviolet light also induces the cycloreversion reaction. One approach to avoid the absorption (inner filter effect) is to use two-photon excitation.[18] Another convenient method is to irradiate the crystal face, which has the least absorption coefficient, with linearly polarized light.[19] We took the latter method.



Scheme 1.

Results and Discussion

X-Ray Crystallographic Analysis of 1a at 115 K. In a previous paper, we reported the crystal structure of **1a** at room temperature.[15] In order to obtain good reflection intensity data, X-ray intensity measurement was performed at 115(1) K. The crystallographic data are shown in Table 1. At room temperature, crystal **1a** belongs to the triclinic system, the space group, $P\bar{1}$. When the crystal was cooled to 115 K, the crystal system became monoclinic, $P2_1/c$. The highest residual peaks below 0.379 e Å^{-3} were remaining only

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[#] CREST, Japan Science and Technology Corporation.

Table 1. Crystallographic Data and Experiment Details

	1a	**1a**′ a)	**1a**″ b)
Empirical formula	$C_{17}H_{14}F_6S_2$		
Formula weight	396.40		
Temperature	115 K		
Crystal size	0.55 × 0.15 × 0.07 mm		
Crystal system	Monoclinic		
Space group	$P2_1/c$		
Z	4		
a/Å	17.144(1)	17.188(3)	17.159(2)
b/Å	8.772(1)	8.866(1)	8.779(1)
c/Å	11.227(1)	11.230(2)	11.236(1)
β/°	92.949(1)	92.823(3)	92.937(2)
V/Å^3	1686.2(2)	1709.1(5)	1690.5(3)
Density calcd/g cm^{-3}	1.561	1.541	1.558
Theta range (θ) for data collection	1.19 to 27.51°	1.19 to 27.45°	1.19 to 27.48°
Reflections collected	9790	9122	9328
Independent reflections	3620 [R(int) = 0.0158]	3571 [R(int) = 0.0296]	3575 [R(int) = 0.0241]
Refinement method	Full-matrix least-squares on F^2		
No. of restrains/parameters	0/231	151/331	0/231
Goodness-of-fit on F^2	1.049	1.142	1.029
$R1$ [$I > 2\sigma(I)$]	0.0295	0.0521	0.0339
$wR2$ for all data	0.0828	0.1076	0.0876
Largest diff. peak and hole	0.379 and −0.285 e Å^{-3}	0.274 and −0.270 e Å^{-3}	0.363 and −0.275 e Å^{-3}

a) Irradiation wavelength: 360 nm, 0.15 mW cm^{-2}. The crystal thickness was 0.07 mm. b) Irradiation wavelength: 650 nm, 0.61 mW cm^{-2}.

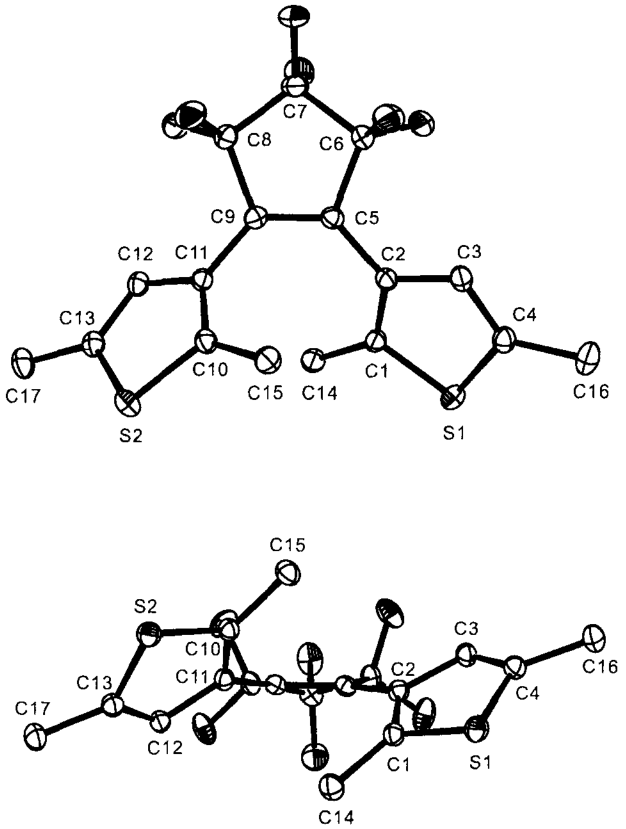

Fig. 1. Molecular structure of **1a** at 115 K. The ellipsoids are drawn at 50% probability level. Hydrogen atoms were omitted for clarity.

in the middle of covalent bonds. This indicates there was no disorder. Figure 1 shows the molecular structure of **1a** with atom numbering. At 115 K, the distance between two reactive terminal carbons of 1,3,5-hexatriene moiety, C1 and C10, was 3.546(2) Å (3.576(2) Å at room temperature). Torsion angles between the perfluorocyclopentene ring and two thiophene rings, C1–C2–C5–C9 and C10–C11–C9–C5, were 37.7(2) and 45.7(2)°, respectively (43.8(2) and 43.9(2)° at room temperature). The disorder due to packering of the perfluorocyclopentene ring observed at room temperature also disappeared. At 115 K, the molecule deviated from the C_2 symmetry.

Absorption Spectrum of the Open-Ring Isomer 1a and Photoirradiation. Thin (ca. 0.1 mm) crystals were obtained by recrystallization from a hexane solution. Two kinds of crystals were obtained; one is rectangular solid-shaped with well-developed (011) crystal face and the other is rhombus-shaped with well-developed (100) crystal face. To find suitable irradiation conditions, UV-visible absorption spectral measurement with linearly polarized light was carried out on each crystal face before and after UV irradiation. The red color intensity of the crystal under polarized light was dramatically changed by rotating the sample as much as 90°. This is because the electronic transition moment of the red color of the photogenerated closed-ring isomer **1b** was regularly arranged in the single crystal.[15]

Figures 2a and 2b show the molecular packing viewed normal to (011) and (100), respectively. The electronic transition moment of the photogenerated **1b** tilted as much as 30° to the a axis and almost agreed with the molecular long axis.[15] Absorption spectra of (011) face of the crystal before and after UV irradiation are shown in Fig. 3. The polarization of the measuring light was set (a) parallel and (b) normal to the molecular long axis. Absorption spectra of crystal **1a**

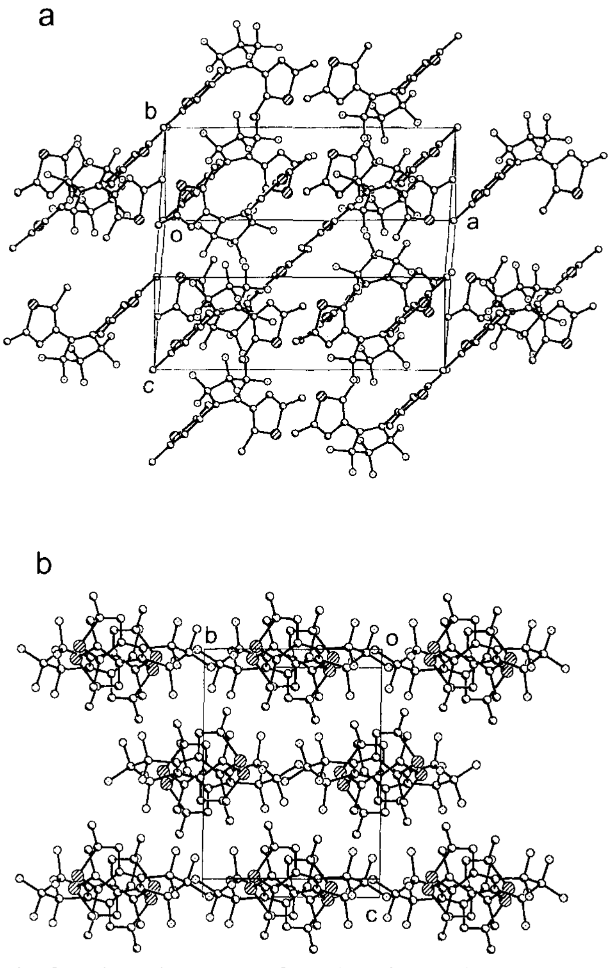

Fig. 2. Crystal structure of **1a** viewed normal to (a) (011) face and (b) (100) face.

extend to about 410 nm. The photoinduced change of the absorption in the direction normal to the molecular long axis was smaller than that in parallel. The crystal face (011) was irradiated with linearly polarized 380 nm light, the direction of which is normal to the molecular long axis. X-Ray analysis after irradiation, however, did not show any structural change. Strong inner filter effect of **1b** at the irradiation wavelength possibly prevented the photoreaction.

Absorption spectra of (100) face of the crystal before and after UV irradiation are shown in Fig. 4. The absorption tail of **1a** extended to 385 nm, which is shorter than that of (011) face. In the ultraviolet region shorter than 400 nm, the photoinduced absorption change observed with linearly polarized light set parallel to the *c* axis (a) is smaller than that normal to the *c* axis (b). To find the best irradiation conditions, the wavelength was scanned from 410 to 350 nm, and 360 nm light was selected. The crystal face (100) was irradiated with linearly polarized 360 nm light, the polarization plane of which was set parallel to the *c* axis, for 24 h. In this case a distinct structural change was observed.

Change of Unit Cell Dimensions at Room Temperature. The change of the unit cell dimension was measured at 298 K during the photocyclization. After every 4-hour irradiation with polarized 360 nm light, the unit cell dimensions were determined on a rhombus-shaped crystal with well-developed (100) face. Table 2 shows *a*, *b*, *c*, and *V* values. As described above, at room temperature the crystal system was triclinic. Although the change was small, all unit cell lengths and unit cell volumes tended to decrease. This corresponds to the decrease of the molecular volume due to transformation from the open-ring isomer to the closed-ring isomer. After 8 h the decrease in unit cell dimensions ceased and the cell dimensions gradually increased. The single-crystallinity is considered to be reduced by accumulation of the photogenerated closed-ring isomers.

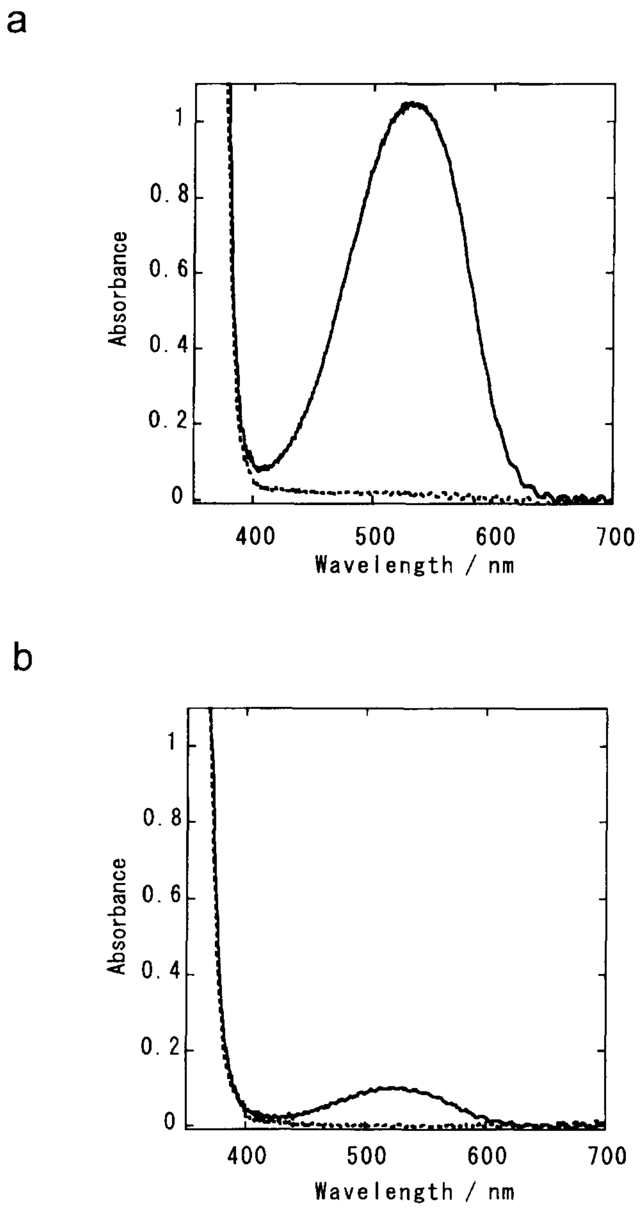

Fig. 3. Absorption spectra of (011) face of crystal **1** before (- - - - -) and after (———) irradiation. The polarization of the measuring light was set to the direction inclined at an angle of (a) 30° and (b) 120° to the *a* axis.

Crystal Structure of 1a′ after 360 nm Irradiation. The single crystal **1a** was irradiated with linearly polarized 360 nm light for 24 h, as described above, and the UV-irradiated

Table 2. Change of Cell Dimensions at Room Temperature[a)]

Irradiation time/h	0	4	8	12	20
a/Å	8.8246(15)	8.8228(17)	8.8189(15)	8.8202(15)	8.8401(14)
b/Å	11.1789(18)	11.1758(22)	11.1663(19)	11.1693(19)	11.1893(17)
c/Å	11.4241(19)	11.4094(22)	11.4062(19)	11.4094(19)	11.4302(18)
V/Å^3	876.54(42)	875.21(51)	873.46(42)	874.24(43)	879.09(41)

a) The crystal system is triclinic as reported previously at room temperature. Interaxisal angles α, β, γ were omitted for clarity.

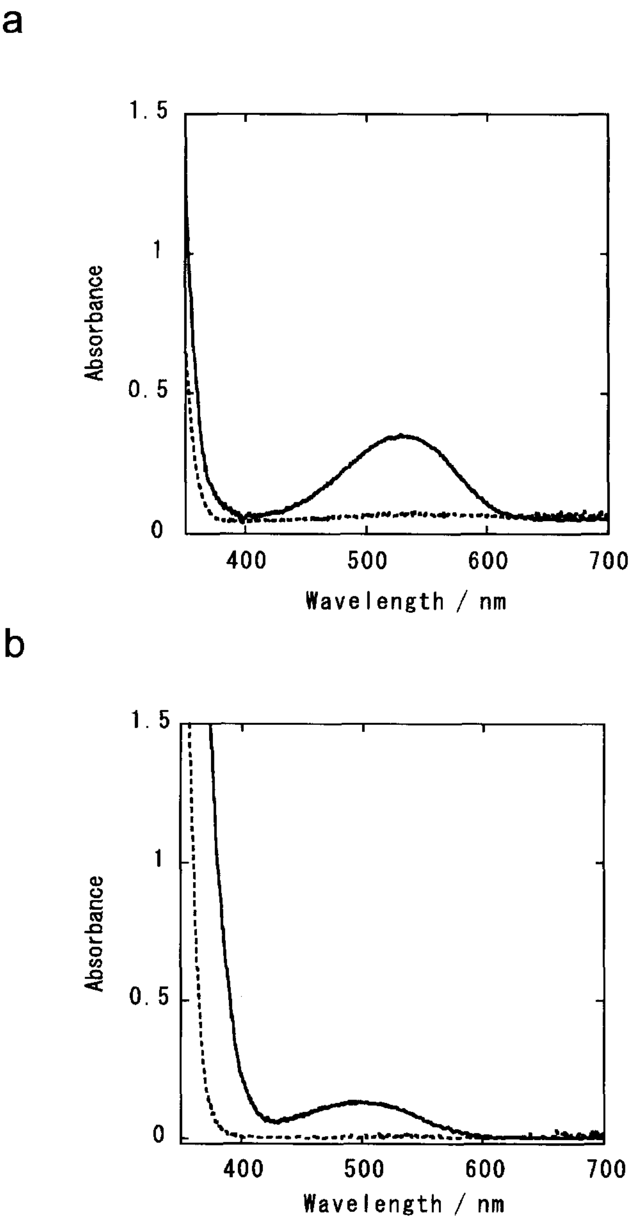

Fig. 4. Absorption spectra of (100) face of crystal **1** before (------) and after irradiation (———). The polarization plane was set (a) parallel and (b) normal to the c axis.

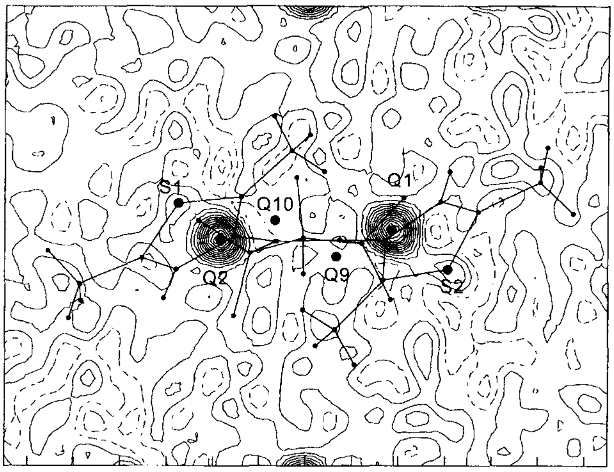

Fig. 5. $F_o - F_c$ Difference Fourier electron density maps through peaks Q1, Q2. Contour interval is 0.2 e Å^{-3}. The data for irradiated crystal **1a′** used as F_o and the coordinates of pure crystal **1a** were used for calculation of F_c. The solid and broken lines showed positive and negative contour region, respectively.

crystal **1a′** was analyzed. The crystallographic data and the difference Fourier electron density map for the crystal **1a′** are shown in Table 1 and Fig. 5, respectively. The space group was the same, $P2_1/c$, as for the crystal before irradiation. The coordinates of the open-ring isomer were used for the initial model for the refinement. After the first least-square refinement, the difference Fourier map showed the existence of two quite high electron density peaks Q1 (2.24 e Å^{-3}) and Q2 (2.22 e Å^{-3}) ascribed to the sulfur atoms of the photogenerated closed-ring isomer. These peaks were apart from the nearest sulfur atoms of the open-ring isomer by 1.52 and 1.21 Å. They are close to positions expected for the closed-ring isomer photogenerated in a conrotatory mode (Fig. 6). The distance between the two peaks was 3.69 Å, which is slightly longer than the length of the closed-ring isomer, 3.56 Å.[16] Electron density peaks corresponding to two carbons at reaction points also appeared. On the map, six new peaks corresponding to fluorine atoms attached to the cyclopentene ring of the photogenerated **1b** appeared beside those of **1a**. According to these peaks, the photogenerated **1b** molecule was composed. Because of the low yield of the photogenerated closed-ring isomer, bond distances were restrained in least-square refinement. The displacement factors of the photogenerated closed-ring isomer were refined isotropically. For the perfluorocyclopentene ring and atoms C2B, C3B, C11B, C12B, C16B, and C17B belonged to the photogenerated closed-ring isomer, the isotropic displacement factors were also restrained softly so as to refer to corresponding atoms of the open-ring isomer because of closeness of the atom positions. Using the model, the full-matrix least-square refinement converged well ($R1$ = 0.052

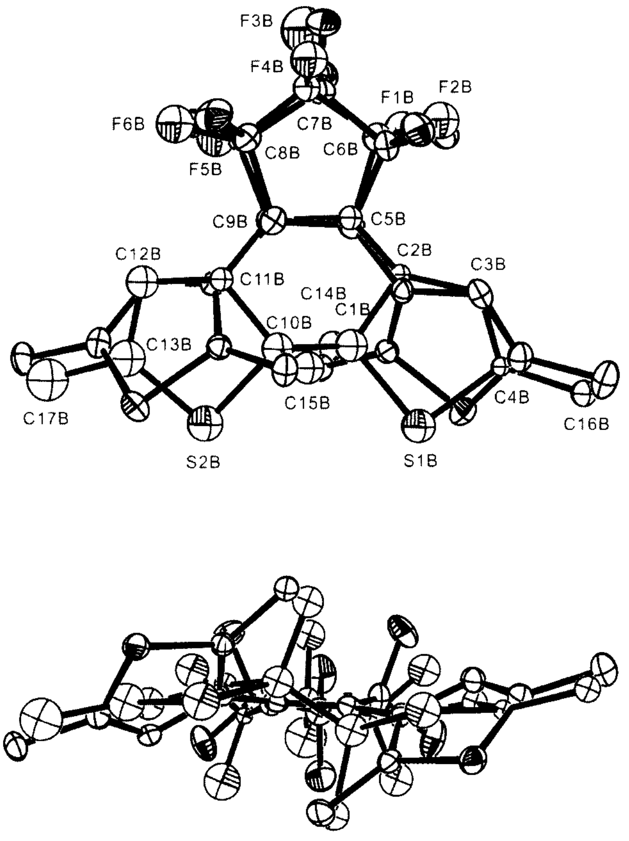

Fig. 6. Molecular structure of **1a**′ after irradiation of 360 nm light for 24 h. The ellipsoids are drawn at 50% probability level. Hydrogen atoms were omitted for clarity. The occupancy of the closed ring isomer was ca. 8%.

for the data with $I > 2\sigma(I)$, $wR2 = 0.108$ for all data, height of the residual electron peak < 0.274 e Å^{-3}). The occupancy factor for the photogenerated closed-ring isomer was 0.084(2), which indicates ca. 8% cyclization reaction took place by the irradiation.

The final molecular structure is shown in Fig. 6. The cyclopentene ring of photogenerated **1b** was inverted. At room temperature, X-ray analysis showed that the cyclopentene ring of **1a** is disordered in the crystal. Therefore it is ambiguous whether the inversion of the cyclopentene ring took place thermally or kinetically.

Crystal Structure after Cycloreversion Reaction. The same crystal used for the above X-ray crystallographic analysis was irradiated with 650 nm light to go back to the open-ring isomer crystal (**1a**″). After irradiation, the red crystal color disappeared and the crystal became transparent.

Table 1 shows the results of X-ray crystal structure analysis of the re-generated open-ring isomer crystal **1a**″. After the least-square refinement, the peaks corresponding to the sulfur atoms of the closed ring isomer and the inversion of the cyclopentene ring disappeared and only open-ring isomer was observed. There were no significant electron peaks on the difference Fourier map. The geometry of the open-ring isomer was not altered from the original one. Although statistics of the diffraction intensity data and R indices slightly changed after the cycloreversion reaction, the geometric change of the photochromic cycle of the dithienylethene **1a** was successfully observed by X-ray crystallography.

Conclusion

X-Ray crystallographic direct observation of the cyclization reaction of photochromic compound **1** was successfully carried out by irradiation with linearly polarized ultraviolet (360 nm) light. X-Ray crystallographic analysis showed that 8% of the open-ring isomer converts to the closed-ring isomer in a conrotatory mode. Two sulfur atoms and reactive carbon atoms in the thiophene rings changed their positions during the photocyclization reaction. The photogenerated closed-ring isomer returned to the initial open-ring isomer by irradiation with 650 nm light.

Experimental

X-Ray Crystal Structure Analysis. Preparation and crystallization of the compound **1a** were reported previously. A good quality crystal (0.55×0.15×0.07 mm) with well-developed (100) crystal face 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 *Kα* radiation. The crystal was cooled at 115(1) K by a 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. 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. SADABS software was used for decay and absorption corrections. The cell constants were calculated by the global refinement. The structure was solved by direct methods using SHELXS-86[20] and refined by full least-squares on F^2 using SHELXL-97.[21] 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 length and geometry were 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 an the deposition numbers 147108-147109. The data also were deposited as Document No. 73057 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Irradiation and Absorption Spectral Measurement. A microscope (JASCO Micro20 with a D2 lamp) equipped with a CCD detector (Hamamatsu photonics, PMA-11) was used for the measurement of the absorption spectrum of the single crystal.

A 500 W Xe lamp (Ushio) was used for the light source. Monochromatic light was obtained by passing the light through cut-off and band-pass filters (Asahi Glass UV-22 and UV-D35 for 360 nm light, UV22 and Y52 for 650 nm light) and a monochromator (Ritsu MC-20L). The light was polarized with a Gram–Tompson polarizer. The light intensity was as follows, 360 nm: 0.15 mW cm^{-2}, 650 nm: 0.61 mW cm^{-2}. For the photocyclization reaction, the crystal face (100) was irradiated with linearly polarized 360 nm light for 24 h at room temperature. The polarization plane of the light was parallel to the *c* axis. For the cycloreversion reaction, the crystal was exposed to non-polarized 650 nm light.

Measurement of Change of Unit Cell Constants. At room temperature the rhombus-shaped crystal with well-developed (100) face was irradiated with UV light, as described above. Unit cell constants were determined by the global refinement after the intensity integration of SAINT6.0 on the data, which covered a full sphere of the crystallographic reciprocal space, collected at 298 K.

The authors thank Drs. Y. Kai, N. Kanehisa, and E. Mochizuki for their helpful discussions. This work was supported by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corporation (JST).

References

1 C. B. McArdle in "Applied Photochromic Polymer Systems," Blackie, Glasgow (1992).

2 M. Hamano and M. Irie, *Jpn. J. Appl. Phys.*, **35**, 1764 (1996).

3 A. Toriumi, S. Kawata, and M. Gu, *Opt. Lett.*, **23**, 1924 (1998).

4 T. Saika, M. Irie, and T. Shimidzu, *J. Chem. Soc., Chem. Commun.*, **1994**, 2123.

5 N. Tanio and M. Irie, *Jpn. J. Appl. Phys.*, **33**, 1550 (1994).

6 F. Ebisawa, M. Hoshino, and K. Sukegawa, *Appl. Phys. Lett.*, **65**, 2919 (1994).

7 S. L. Gilat, S. H. Kawai, and J. -M. Lehn, *Chem. Eur. J.*, **1**, 275 (1995).

8 J. Biteau, F. Chaput, K. Lahlil, J. -P. Boilot, G. M. Tsivgoulis, J. -M. Lehn, B. Darracq, C. Marois, and Y. Lévy, *Chem. Mater.*, **10**, 1945 (1998).

9 K. Matsuda and M. Irie, *Chem. Lett.*, **2000**, 16.

10 M. Irie and M. Mohri, *J. Org. Chem.*, **53**, 803 (1988).

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

12 M. Irie, K. Uchida, T. Eriguchi, and H. Tsuzuki, *Chem. Lett.*, **1995**, 899.

13 M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, **71**, 985 (1998).

14 S. Kobatake, M. Yamada, T. Yamada, and M. Irie, *J. Am. Chem. Soc.*, **121**, 8450 (1999).

15 S. Kobatake, T. Yamada, K. Uchida, N. Kato, and M. Irie, *J. Am. Chem. Soc.*, **121**, 2380 (1999).

16 T. Yamada, S. Kobatake, K. Muto, and M. Irie, *J. Am. Chem. Soc.*, **122**, 1589 (2000).

17 M. Irie, T. Lifka, K. Uchida, S. Kobatake, and Y. Shindo, *Chem. Commn.*, **1999**, 747.

18 J. Harada, H. Uekusa, and Y. Ohashi, *J. Am. Chem. Soc.*, **121**, 5809 (1999).

19 V. Enkelmann and G. Wegner, *J. Am. Chem. Soc.*, **115**, 10390 (1993).

20 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, **46A**, 467 (1990).

21 G. M. Sheldrick, "SHELXL-97, Program for Crystal Structure Refinement," Universität Göttingen, Göttingen (1997).