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Crystal Structure−Reactivity Correlation in Single-Crystalline Photochromism of 1,2-Bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene

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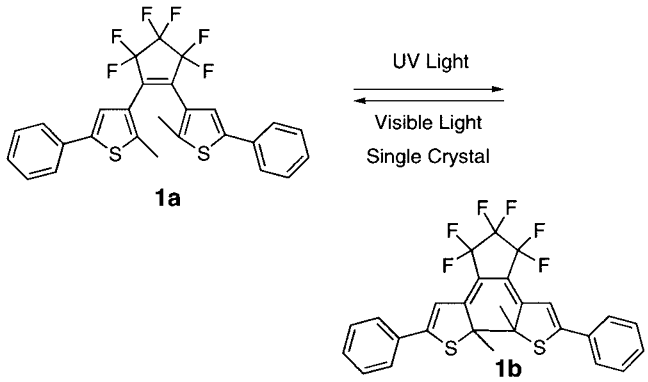
Single-crystalline photochromism of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene **1a** was followed in situ by X-ray crystallographic analysis. The crystal of **1a** has two molecules with different conformations in the crystallographic asymmetric unit. The X-ray analysis of the photoirradiated crystal showed that the photocyclization reaction of the molecule with the shorter distance between the reactive carbons prevails over the reaction of the other molecule. The mechanism has been discussed based on the calculation of the electronic transitions of the two molecules in the different conformations. The photocyclization quantum yield was determined to be 1 (100%) in the crystal.

Introduction

Photochromism has attracted much attention because of their potential applicability to photonic devices, such as optical memories[1−5] and photooptical switches.[6−13] Among a number of photochromic compounds, diarylethene derivatives are the most promising compounds for these applications because of high durability for coloring/decoloring cycles, thermal stability of both isomers, and rapid response.[14−16] Single-crystalline photochromism is also a unique character of diarylethene derivatives. We have reported some 1,2-bis(3-thienyl)-perfluorocyclopentene derivatives that undergo single-crystalline photochromism.[13,17−24] Both photocyclization and photocycloreversion processes of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene crystals have been elucidated in situ by X-ray crystallographic analysis.[21,22]

Scheme 1



In the present paper we describe the study of single-crystalline photochromism of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene **1a** (Scheme 1).[23] This compound undergoes an efficient photocyclization reaction in solution (Φ(cyclization) $= 0.59$, Φ(cycloreversion) $= 0.013$ in hexane),[25] and the activation energy of the photocyclization is zero in solution as well as in the crystalline phase.[23] The crystal of **1a** has two molecules with different conformations in the crystallographic asymmetric unit, and the distance between the reactive carbons in each of the molecules is different. From the

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Table 1. Crystallographic Data of 1a before and after Irradiation

	1a	**1a′** [a,b]	**1a″** [c]
empirical formula		$C_{27}H_{18}F_6S_2$	
formula weight		520.23	
temperature/K		133(2)	
crystal size/mm		0.50 × 0.18 × 0.12	
crystal system		monoclinic	
space group		$P2_1/c$	
Z		8	
a/Å	18.685(2)	18.704(2)	18.720(1)
b/Å	11.812(1)	11.801(1)	11.831(1)
c/Å	21.338(2)	21.338(2)	21.382(2)
β/deg	95.681(2)	95.468(2)	95.673(1)
V/Å^3	4686(1)	4688(1)	4713(1)
density calcd /g cm^{-3}	1.476	1.475	1.467
θ range for data collection	1.10 to 27.51	1.09 to 27.52	1.09 to 27.50
reflections collected	27909	27498	27564
independent reflections	10271	10156	10251
refinement method		full matrix least-squares on F^2	
no. of parameters/restraints	635/0	683/27	635/0
goodness-of-fit on F^2	0.949	0.964	0.934
$R1$ [$I > 2\sigma(I)$]	0.039	0.047	0.040
$wR2$ for all data	0.099	0.126	0.093
largest diff peak and hole	0.39, −0.30	0.39, −0.40	0.38, −0.30

[a] Irradiation wavelength: 390 nm, 0.013 mW cm^{-2}. [b] For molecule A, two sulfurs and two carbons of the photogenerated closed-ring isomer were included in the model. For molecule B, only two sulfurs were included to estimate the conversion yield from the occupancy. [c] Irradiation wavelength: 680 nm, 0.018 mW cm^{-2}.

viewpoint of structure−reactivity correlation, it is of interest to compare the reactivity of the two different molecules with each other in the same crystal.

Results and Discussion

Molecular Structure of 1a at 133 K. The crystal structure at room temperature has been previously reported.[23] To suppress thermal atomic displacement the measurement was carried out at 133 K. The crystallographic data is listed in Table 1. The crystal belongs to a monoclinic system, $P2_1/c$ and $Z = 8$. The crystal has two molecules in the asymmetric unit. These molecules are referred to as molecule A and molecule B in this paper. The crystal structure of **1a** viewed along the b axis is shown in Figure 1. Molecules A and B are depicted by red and blue lines, respectively. Molecules of the same type are arranged in a line along the c axis, and the layers of molecules A and B are stacked alternatively.

Figure 2 shows the structure of molecule A with atom numbering. Some geometrical parameters of the two molecules, A and B, are listed in Table 2. Conformations of the two molecules differ slightly, while both molecules have thiophene rings in a photoreactive antiparallel orientation. Although the torsion angle between the thiophene and the perflurocyclopentene rings, C1−C2−C5−C9, in molecule A (45.8(3)°) is larger than C5−C9−C11−C10 in molecule B (44.6(3)°), the distance between the two reactive carbons C1···C10 of molecules A (3.507(3) Å) is shorter than in molecule B (3.578(3) Å). The difference in the torsion angles (C2−C5−C9−C11) causes the difference in the distances. The plane in molecule A including C2(thiophene), C5(cyclopentene), C9(cyclopentene), and C11(thiophene) atoms is planer (C2−C5−C9−C11 = 3.3(3)°) than the equivalent plane in molecule B (7.1(3)°). Figure 3 shows the difference in the conformation of the two molecules. The crystal was irradiated with UV light to examine whether the structural difference affects the reactivity.

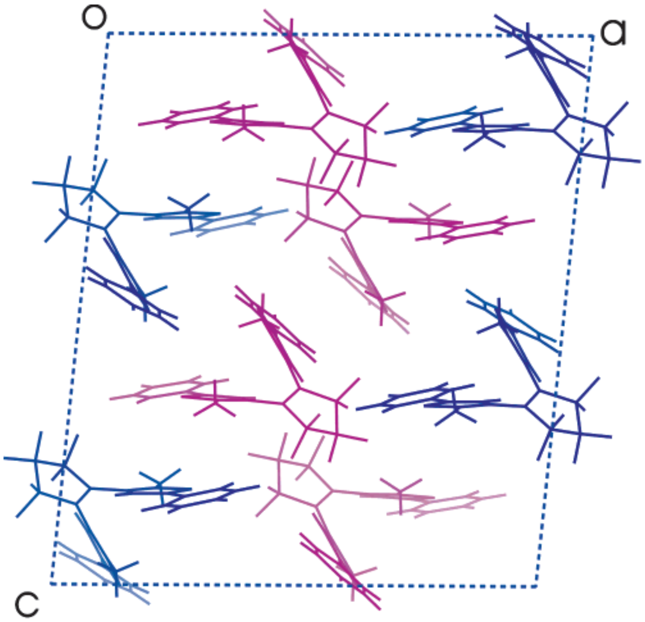


Figure 1. Crystal structure of **1** viewed along the b axis. Crystallographically independent molecule A and molecule B were drawn by red and blue lines, respectively.

Table 2. Geometrical Parameters of Molecule A and B at 133 K

	molecule A	molecule B
C2−C5−C9 (deg)	130.5(2)	130.8(2)
C5 C9−C11 (deg)	129.0(2)	129.7(2)
C1−C2−C5−C9 (deg)	45.8(3)	46.5(3)
C5−C9−C11−C10 (deg)	46.6(3)	44.6(3)
C2−C5−C9−C11 (deg)	3.3(3)	7.1(3)
S1−C4−C16−C17 (deg)	14.0(3)	11.5(2)
S2−C13−C22−C23 (deg)	−19.7(3)	−30.5(3)
C1...C10 (Å)	3.507(3)	3.578(3)

Absorption Spectra of $(\bar{1}01)$ Faces of Crystal of 1a. To search for suitable irradiation conditions, the absorption spectra of the single crystal **1a** were measured. Prismlike crystals were recrystallized from a hexane solution. The crystal had well-developed $(\bar{1}01)$ faces. The absorption spectra were measured under linearly polarized light before and after UV irradiation,

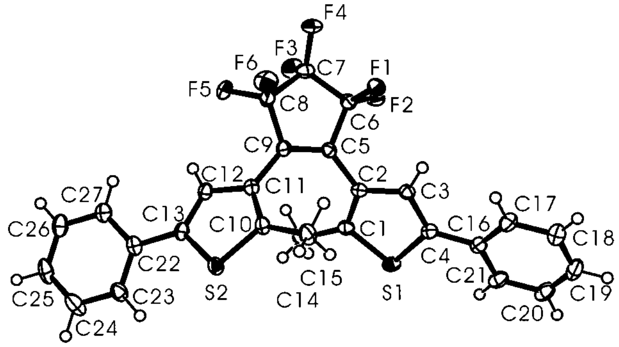


Figure 2. Molecular structure of molecule A in crystal **1** with atom numberings. For clarity, suffix A is omitted. Atom numberings are common to molecule B except for suffix B. The ellipsoids are drawn at 50% probability level.

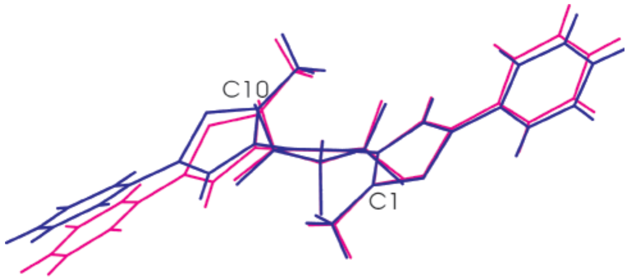
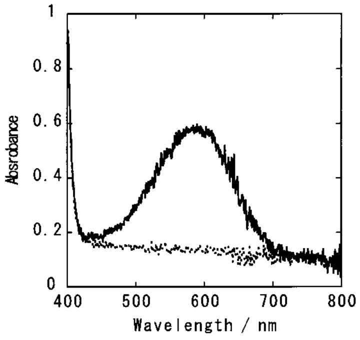


Figure 3. Superimposition of molecule A (red line) and molecule B (blue line). Molecule A has a shorter distance between C1···C10.

a) parallel to b axis



b) normal to b axis

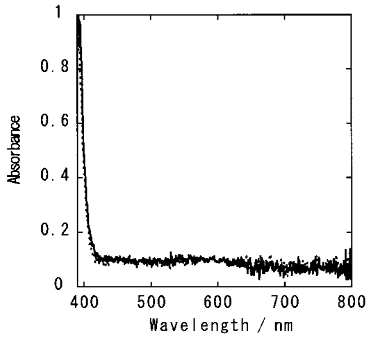


Figure 4. Absorption spectra of (101) face of a thin crystal **1** before (broken line) and after (solid line) UV irradiation. The polarization plane of the incident and detected light is (a) parallel and (b) normal to the *b* axis. Transition moment of the photogenerated closed-ring is along the *b* axis.

as shown in Figure 4. The crystal has the absorption tail at ca. 400 nm before UV irradiation. Upon irradiation with 390 nm light, a strong blue color appeared. The electronic transition moment of the blue absorption is polarized along the *b* axis of the crystal. The anisotropy of the absorption spectrum indicates that the long molecular axis of the photogenerated closed-ring isomers is arranged regularly along the *b* axis and the photocyclization takes place in the crystalline lattice as reported previously.[23] The absorption in visible light region polarized normal to the *b* axis was not observed.

Photoirradiation was carried out using linearly polarized light parallel and normal to the *b* axis, and the conversion to the colored isomer was compared. Irradiation with 390 nm light polarized parallel to the *b* axis gave higher conversion to the colored isomer than that with light polarized normal to the *b* axis. This result suggests that the absorption of the colored isomers at 390 nm is polarized normal to the *b* axis. Direct measurement of the polarized absorption spectrum failed because of the strong overlapping of the absorption of the open-ring isomers.

Molecular Structure after Irradiation with 390 nm Light. The crystal was irradiated with linearly polarized 390 nm light parallel to the *b* axis for 48 h. Intensity measurement of X-ray diffraction of the crystal **1a′** was performed at 133 K to suppress thermal atomic displacement. Crystallographic data are listed in Table 1. The X-ray analysis was carried out in the same way as that reported previously.[21,22] In the first least-squares refinement cycle and the following difference Fourier electron density calculation, the structure of the open-ring form crystal before UV irradiation was used. The least-squares refinement afforded the following values: $R1 = 0.053$ for the data with $I > 2\sigma(I)$, $wR2 = 0.130$ for all data.

For molecule A, the photogenerated sulfur atoms S1C, S2C and carbon atoms C1C, C10C were found in the difference Fourier electron density map (peak heights are 1.08, 1.13 and 0.31, 0.35 eÅ^{-3}, respectively). Because of low conversion, the disordered structures could not be assigned to the phenyl and the cyclopentene groups. The same structures of these groups were used for both the open- and the closed-ring isomers. In the refinement process, S1C′, S2C′ and the disordered fluorine atoms of the perfluorocyclopentene of the closed-ring isomer B were taken into account. For molecule B, only S1C′, S2C′ were observed (peak heights are 0.45 and 0.40 eÅ^{-3}, respectively). The displacement of carbon atoms was not discerned. Using this model, the least-squares refinements converged well: $R1 = 0.047$ for the data with $I > 2\sigma(I)$, $wR2 = 0.126$ for all data, the highest residual electron peak 0.39 eÅ^{-3}. The structure of molecule A is shown in Figure 5. The photocyclization reaction proceeded in a conrotatory mode. From the occupancy factors, the yields of the closed-ring forms of site A and B were estimated to be ca. 4 and 2%, respectively. The reaction of molecule A with the shorter distance between the reactive carbons prevailed over the reaction of molecule B.

In many cases, the distance between the reactive centers controls the reactivity in the crystals.[26] The

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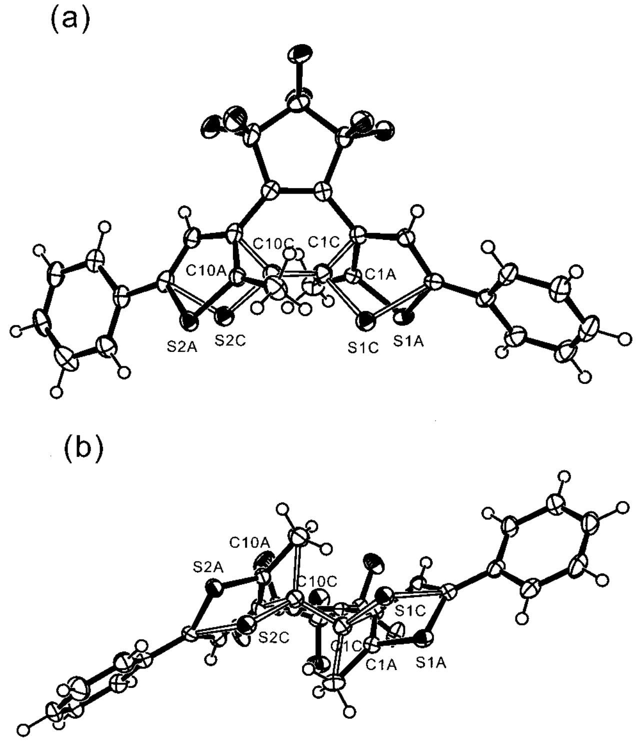

Figure 5. Molecular structure of molecule A in crystal after irradiation with 390 nm light. Open bonds stand for the photogenerated closed ring whose occupancy was estimated at ca. 4% from X-ray structure analysis.

dimerization of cinnamic acid derivatives, for example, scarcely takes place when the distance between the reactive double bonds is longer than the critical distance of 4.2 Å.[27] Although the distance between the reactive carbons of molecule B is slightly longer (∼0.1 Å) than that of molecule A, the distances of both molecules are well below 4.0 Å. This means that such a small distance difference cannot explain the large reactivity difference between molecules A and B.

The photocyclization reaction has no activation energy.[23] The reaction rates in the crystal were the same even if the reaction temperature was changed from 70 to −50 °C. It is inferred from the temperature independence that the cyclization reaction along the downhill potential energy surface[23] readily takes place irrespective of the mobility difference.

The molecular property change associated with the conformational difference is the electronic structure. We carried out molecular orbital calculation to find out the electronic structures of the two molecules. The absorption bands and the electronic transition moments of molecules A and B were calculated using the program MOS−F with CNDO/S method (Fujitsu Co. ltd.). The molecular structures determined at room temperature were employed for the calculation. The three lower energy transitions with strong oscillator strength are listed in Table 3. Although the absolute wavelength is quite different from the observed absorption spectra of **1a**, the calculation shows that the subtle conformational difference causes large spectral changes.

Molecule A has absorption bands at longer wavelengths with high oscillator strengths. The irradiation wavelength of 390 nm is the tail of the absorption bands of the two molecules. Therefore, molecule A more effectively absorbs the light than molecule B by the irradiation of the absorption tail. The selective absorption by molecule A can account for the conversion difference of the two molecules. This result suggests that the energy difference between them is very small. Each photoexcited molecule is considered to readily undergo the efficient cyclization reaction without transferring the energy to neighboring molecules.

Table 3. Calculated Electronic Transition Moments on 1a[a,b]

wavelength (oscillator strength)	
molecule A	molecule B
312.48 nm (0.449)	307.84 nm (0.266)
300.76 nm (0.719)	296.22 nm (0.917)
294.30 nm (0.624)	289.98 nm (0.596)

[a] These values were calculated with MOS-F using CNDO/S on the molecular structures obtained from the X-ray analysis. [b] Twenty molecular orbitals were taken into account for CI calculation.

Cyclization Quantum Yields. To confirm the above interpretation, the photocyclization quantum yield was measured in the crystal. If the reactivity difference between A and B molecules is inherent to the crystal lattice environment, the cyclization quantum yield should be less than 0.75 because the conversion of B molecules is half of that of A molecules. The quantum yield was determined using the same method described before.[28] The absorption coefficient of the photogenerated closed-ring isomer was 1.4 × 10^4 M^{-1} cm^{-1} at 589 nm.[23] The rate of the photocyclization reaction of the crystal was compared with that of furyl fulgide in poly(methyl methacrylate) film as a reference. Based on the absorption coefficient and the rate of the photocyclization reaction, the quantum yield was determined to be 1.01 ± 0.04. The quantum yield of unity confirms that both A and B molecules have inherently extremely high efficiency of photocyclization, and the reactivity difference between A and B molecules is attributable to the selective excitation of A molecules.

Molecular Structure after Irradiation with 680 nm Light. The same crystal used for the above X-ray crystallographic analysis was irradiated with 680 nm light to go back to the open-ring isomer crystal (**1a**″). After irradiation, the blue crystal color disappeared and the crystal became transparent. Table 1 shows the results of the X-ray crystal structure analysis of the regenerated open-ring isomer crystal **1a**″. After the least-squares refinement, the peaks corresponding to the closed ring isomer disappeared and only open-ring isomer was observed. There was no significant electron density peak on the difference Fourier map. The geometry of the open-ring isomer was not altered from the original one. The geometric change of molecule during the single crystalline photochromic cycle was successfully observed by X-ray crystallography.

Conclusion

The crystal of **1a** has two molecules with different conformations in the asymmetric unit. The photocyclization reactivity difference of the two molecules was

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examined by in situ X-ray crystallographic analysis. Molecule A with short distance between reactive carbons more efficiently underwent the photocyclization reaction than the other molecule B. The photocyclization quantum yield was determined to be 1 (100%) in the crystal. The molecular orbital calculation of electronic absorption of the two molecules with different conformations indicated that the difference in the apparent reactivity resulted from the selective excitation of molecule A by the tail irradiation with 390 nm light.

Experimental Section

X-ray Crystal Structure Analysis. 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 133 K by the cryostat (RIGAKU GN2). The data collection was performed as follows: the data covered a hemisphere of the reciprocal space. Each frame data covered 0.3° in ω. The crystal-to-detector distance was 5.127 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 correction. The cell constants were calculated by the global refinement. The structure solved by direct methods using SHELXS-86[29] and refined by full least-squares on F^2 using SHELXL-97.[30] The positions of all hydrogen atoms were calculated geometrically and refined by the riding model. For the minor disordered part, only the positions and occupancy were refined. Their isotropic atomic displacement referred to those of the major part. The bond lengths and geometry were restrained to have ideal values in the refinement.

Irradiation and Absorption Spectral Measurement. The 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 a cutoff filter (Asahi Grass UV-31 and R-65 for 390 and 680 nm light, respectively) and a monochromator (Ritsu MC-20L). The light was polarized with a Gram-Tompson polarizer. The light intensity is 0.13 and 0.18 mW/cm^2 for 390 and 680 nm light, respectively.

Calculation of Electronic Transition Moments and Absorption Spectra. MOS-F (Fujitsu) with CNDO/S method was used for these calculations. Twenty molecular orbitals were taken into account for CI calculation (default value). Coordinates of Molecules A and B in crystal **1** obtained from X-ray crystallographic analysis performed at 298 K were used for the model structure.[23]

Quantum Yield Measurement. A 75 W Xe lamp was used as the light source for photocyclization. The cyclization reaction was carried out upon irradiation with linearly polarized 370 nm light by passing the light through a band-pass filter. The rate of the reaction was measured by monitoring the visible absorbance of the colored closed-ring isomers using a Leica DMLP polarizing microscope connected with the CCD photodetector. A furyl fulgide in poly(methyl methacrylate) film (ca. 4 wt %, thickness = ca. 10 μm) was used as a reference for the measurement of cyclization rates of the crystal. Both the polymer film and the crystal were irradiated with linearly polarized light.

The quantum yields of the single crystal were calculated using the following equation:

$$\frac{\Phi_{\text{fulgide}}\,\varepsilon_{\text{fulgide}}\,(1\text{-}T_{\text{fulgide}})}{\text{Slope}_{\text{fulgide}}} = \frac{\Phi_{\text{crystal}}\,\varepsilon_{\text{crystal}}\,(1\text{-}T_{\text{crystal}})}{\text{Slope}_{\text{crystal}}}$$

where Φ, ϵ, Slope, and T represent the quantum yield of cyclization, the absorption coefficient at the monitoring wavelength, the slope of the relationship between absorbance and time, and the transmittance at 370 nm, respectively. The ϵ value of the closed-ring isomer in crystal was determined using the same method described before.[28]

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Supporting Information Available: Crystallographic data for **1a**, **1a′** and **1a″** (PDF) and the difference Fourier map for **1a′** used for positioning the photogenerated closed-ring isomer. These materials are available free of charge via the Internet at http://pubs.acs.org.

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