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Photochromism of 1,2-Bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene in a Single-Crystalline Phase. Conrotatory Thermal Cycloreversion of the Closed-Ring Isomer

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Abstract: 1,2-Bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**) was found to undergo a thermally reversible photochromic reaction in solution as well as in the single-crystalline phase. Upon irradiation with ultraviolet light the hexane or toluene solution containing **1a** and single-crystal **1a** turned blue along with the formation of closed-ring isomer (**1b**). The blue solution and single crystal returned colorless by irradiation with visible light ($\lambda > 500$ nm) or heating above 100 °C. The bleaching is due to the cycloreversion of **1b** to **1a**. The thermal cycloreversion activation energies were measured in the toluene solution and in the single-crystalline phase above 100 °C. The activation energy from photogenerated **1b** to **1a** in the solution was 128 kJ mol^{-1}, while it decreased to 120 kJ mol^{-1} in the crystal of the open-ring isomer **1a**. In the crystal of the closed-ring isomer **1b** the energy increased to 137 kJ mol^{-1}. The cycloreversion reaction was found to be controlled by the environmental conditions. The thermal cycloreversion reaction in the crystal was directly followed by X-ray crystallography and revealed to proceed in a conrotatory mode, which is opposed to the general Woodward−Hoffmann rules.

Introduction

Various types of photochromic compounds have been so far developed in an attempt to apply the compounds to optoelectronic devices.[1−4] For the applications, such as optical memories and photooptical switches, the compounds are required to undergo thermally irreversible and fatigue-resistant photochromic reactions. In most photochromic compounds, however, photogenerated isomers are thermally unstable and return to the initial isomers in the dark. Recently, three types of thermally irreversible photochromic compounds, furylfulgide,[5] diarylethenes,[6] and phenoxynaphthacenequinones,[7] have been developed. Among the compounds, the diarylethenes are the most promising photochromic compounds for the applications because of their fatigue-resistant character.[4]

The thermal stability of the diarylethenes depends on the aryl groups.[8] When the aryl groups are thiophene or benzothiophene groups, such as 2,3-bis(2-methyl-1-benzothiophen-3-yl)maleic anhydride, the closed-ring isomers are thermally stable, while the closed-ring isomers of diarylethenes having phenyl, pyrrolyl, or indolyl groups, such as 2,3-bis(1,2-dimethyl-3-indolyl)maleic anhydride, are thermally unstable (half-life time at 80 °C, 3 h).[8−11] The thermal stability difference is not due to the steric hindrance in the thermal disrotatory cycloreversion reaction as proposed by Heller et al. for furylfulgide,[5] because the steric effect is similar between the above bisbenzothienylethene and bisindolylethene. The difference is ascribed to the electronic structural difference. When the aryl groups have low aromatic stabilization energies, the energy difference between the open- and closed-ring isomers becomes small and the energy barrier in the cycloreversion reaction becomes large, such as bisbenzothienylethene. On the contrary, when the aryl groups have aromatic stabilization energies, the closed-ring isomers become thermally unstable, such as bisindolylethene.

The above discussion assumes that the cycloreversion reactions proceed in a conrotatory mode. The conrotatory thermal cycloreversion process is opposite to the general Woodward−Hoffmann rules[12] of electrocyclic reactions of 6-π electronic

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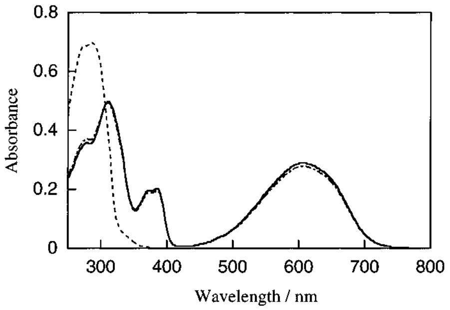
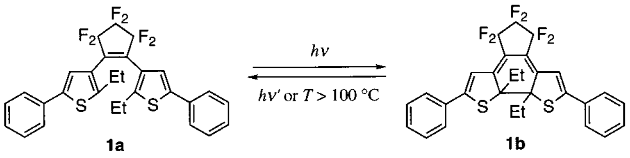


Figure 1. Absorption spectral change of **1** in hexane (1.7×10^{-5} M) by photoirradiation: **1a** (- - -), **1** in the photostationary state under irradiation with 290 nm light (— - —), and **1b** (—).

systems. It is indispensable to confirm the conrotatory thermal cycloreversion process to determine which mechanism, steric or electronic, plays a role in the thermal stability of the closed-ring isomers of diarylethenes. In this paper we report on the photochromism of 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**) in solution and in a single-crystalline phase. The thermal stability of the closed-ring isomer **1b** was measured above 100 °C, and the effect of the environment on the rate was examined. In addition, the thermal cycloreversion process was directly followed by X-ray crystallography to elucidate which mode, conrotatory or disrotatory, takes place.



Results and Discussion

Photochromism in Solution. Figure 1 shows the absorption spectral change of **1a** by irradiation with 290 nm light. **1a** has the absorption maximum at 286 nm ($\epsilon = 4.0 \times 10^{4}$ $\mathrm{M^{-1}\ cm^{-1}}$) in hexane. Upon irradiation with 290 nm light, the colorless hexane solution of **1a** turned blue, in which a visible absorption band was observed at 600 nm. The blue photoproduct was isolated by HPLC (silica gel; hexane as the eluent), and the structure was analyzed by mass spectrum, ^{1}H NMR spectrum, elemental analysis, and X-ray structural analysis. The mass number and elemental analysis were the same as for **1a**. This indicates that the blue material is an isomer of **1a**. The ethyl protons in the ^{1}H NMR spectrum shifted to lower magnetic field and the thienyl proton shifted to higher magnetic field, in comparison with those of **1a**. This result indicates that this product is the closed-ring isomer **1b**. The X-ray crystallographic analysis also confirmed that the product is **1b** having ethyl groups in a trans configuration (see Table 3 and Figure 8).

The absorption spectrum of **1b** is also shown in Figure 1. The spectrum was almost the same as that of the solution in the photostationary state upon 290 nm light irradiation, indicating high conversion from **1a** to **1b**. The ϵ value of **1b** at 600 nm was determined to be 1.7×10^{4} $\mathrm{M^{-1}\ cm^{-1}}$. The conversion from **1a** to **1b** in the photostationary state under irradiation with 290 nm light was 96%. The blue color disappeared upon irradiation with visible light ($\lambda > 500$ nm), and the absorption spectrum returned to that of **1a**.

The cyclization and cycloreversion quantum yields were determined to be 0.52 (286 nm) and 0.0081 (600 nm), respectively. The cyclization quantum yield of **1a** was slightly lower than that of the methyl substituent dithienylethene (**2a**) (0.59[13]).

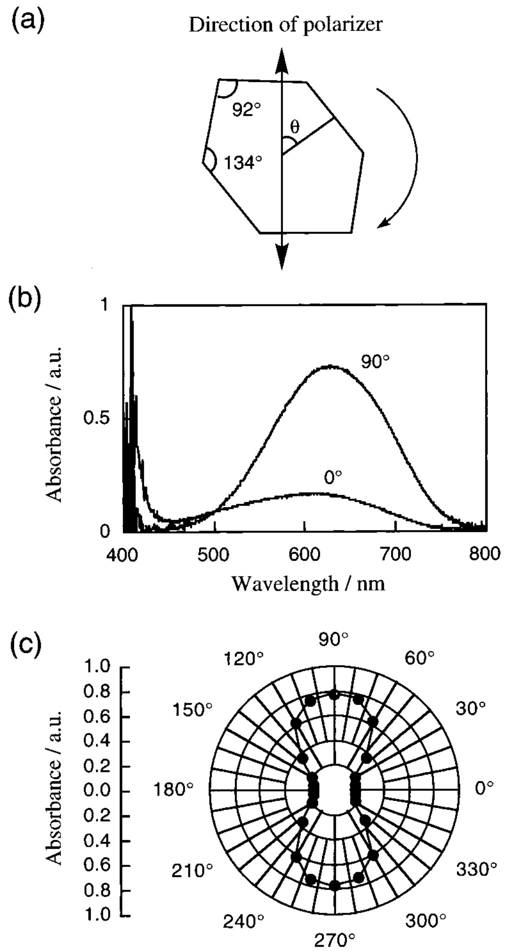
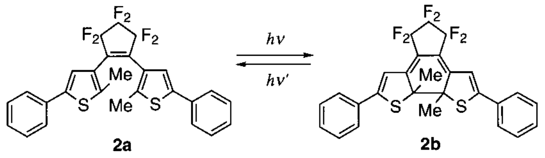


Figure 2. Polarized absorption spectra of the photogenerated blue crystal: (a) direction of polarizer, (b) polarized absorption spectra, and (c) the polar plots of the absorbance at 630 nm.



Photochromism in a Single-Crystalline Phase. A plate single crystal having a hexagonal surface was obtained by recrystallization of **1a** from hexane. The hexagonal surface had angles of two 92° and four 134°, as shown in Figure 2a. Single-crystal **1a** turned blue upon irradiation with 366 nm light. The light could penetrate the crystal as deep as 400 μm and change the color, as shown in Figure 3. The photogenerated blue crystal was dissolved into hexane and the absorption spectrum was measured. The absorption maximum in the visible region was the same as that of **1b** shown in Figure 1. The crystal of the isolated colored photoproduct was confirmed to be **1b** having ethyl groups in a trans configuration by X-ray crystallographic analysis. This indicates that the blue color is due to the formation of **1b**. The blue color of the crystal disappeared upon irradiation with visible light ($\lambda > 500$ nm).

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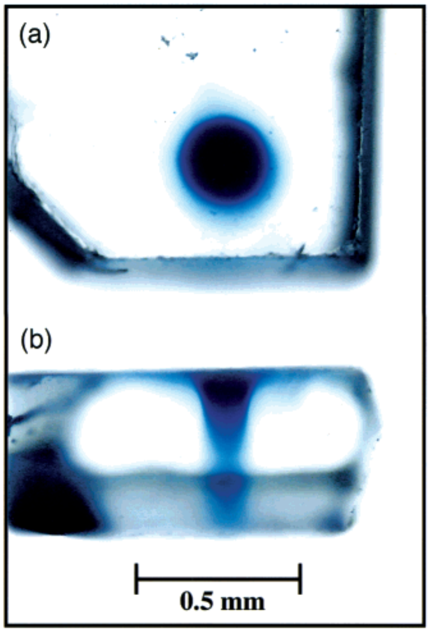

Figure 3. Photographs of top (a) and side (b) views of crystal **1a** irradiated with 366 nm light.

Table 1. Crystal Data and Structure Refinement for **1a**

empirical formula	$C_{29}H_{22}F_6S_2$
formula weight	548.59
temperature	80(2) K
crystal system	orthorhombic
space group	*Pbcn*
unit cell dimensions	$a = 22.277(3)$ Å $b = 10.951(2)$ Å $c = 10.569(2)$ Å
volume	2578.3(7) Å^3
Z	4
density (calculated)	1.413 g/cm^3
goodness-of-fit on F^2	1.092
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.050$ w$R2 = 0.120$
R indices (all data)	$R1 = 0.066$ w$R2 = 0.127$

To confirm that the photochromic reaction proceeds in the crystal lattice, the coloration of the crystal was observed under linearly polarized light, as shown in Figure 2b. Before photoirradiation the crystal was colorless. Upon irradiation with 366 nm light, the crystal turned blue at a certain angle ($\theta = 90°$). When the crystal was rotated as much as 90°, the color almost disappeared. The blue color intensity at 630 nm changed by rotating the crystal sample, as shown in Figure 2c. This indicates that the closed-ring isomers are regularly oriented in the crystal. In other words, the photochromic reaction proceeds in the crystal lattice. If the cyclization reaction proceeded in an amorphous phase, the color intensity change should not be observed.

X-ray Crystallographic Analysis of 1a. Table 1 shows the X-ray crystallographic analysis data of **1a**. Figure 4 shows the ORTEP drawings of **1a**. In solution diarylethenes have two conformations, parallel and antiparallel, and they interconvert. In crystals, on the other hand, there is no exchange between the two conformers. The ORTEP drawing of **1a** indicates that **1a** is packed in an antiparallel conformation in the crystal. The distance between the reacting carbon atoms was estimated to be 0.371 nm, which is close enough for the reaction.[14]

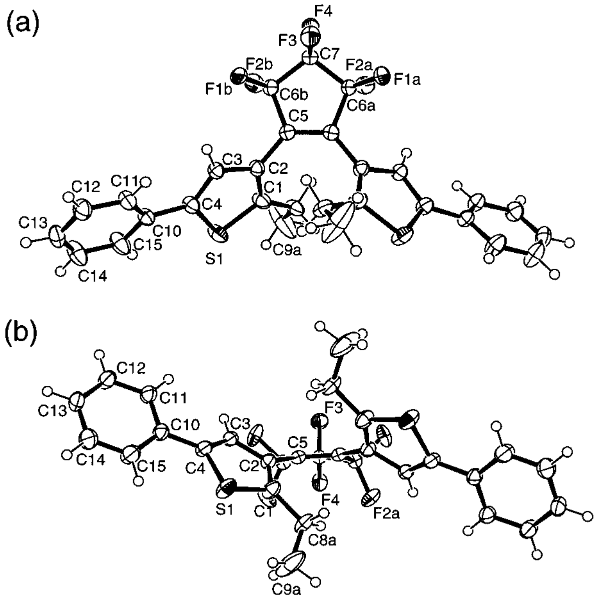

Figure 4. ORTEP drawings of top (a) and side (b) views of **1a** showing 50% probability displacement ellipsoids. Only a half of the molecule is independent. The CF_2 groups in the cyclopentene ring were disordered equally. The ethyl groups were also disordered in the ratio of 76:24. Only the major structure is illustrated for clarity.

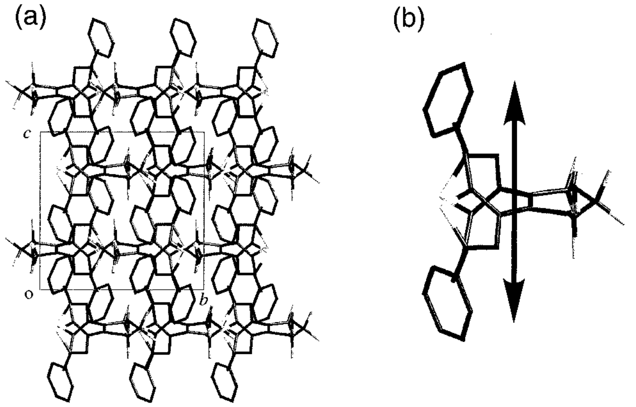

Figure 5. Packing diagram of **1a** (a) and the typical molecular structure of packed **1a** (b). The arrow showed the maximum direction of the polar plots shown in Figure 2.

The hexagonal surface corresponds to the (100) plane. Figure 5a shows the molecular packing of **1a** viewed from the hexagonal surface. The arrow in Figure 5b shows the maximum direction of the 630 nm absorption band of the closed-ring isomer estimated from the absorption anisotropy. The direction of the arrow coincides with the direction of the long axis of the open-ring isomer. The photocyclization reaction proceeded in the crystal lattice of the open-ring isomer **1a** without changing the center of gravity of the molecule.[15]

Thermal Stability of 1b. Diarylethenes having 2-methylthiophene or benzothiophene aryl groups undergo thermally irreversible photochromic reactions even at 100 °C. In a previous paper[13] the half-life time of the closed-ring isomer of **2a** was estimated to be 1900 years at 30 °C. Introduction of bulky substituents at the 2- and 2′-positions of the thiophene or benzothiophene aryl groups is expected to change the thermal stability of the closed-ring isomer. Introduction of isopropyl substituents at the 2- and 2′-positions of benzothiophene aryl groups decreased the thermal stability.[16] **1a** has ethyl substituents

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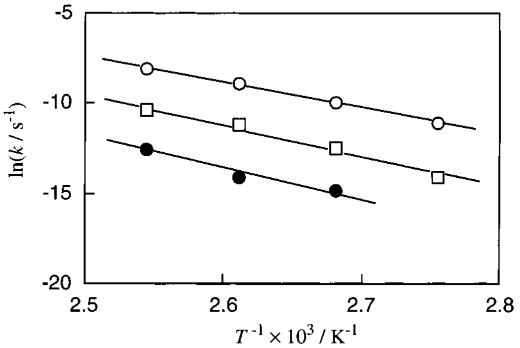

Figure 6. Temperature dependence of thermal cycloreversion reaction rates of **1b** in toluene (□), **1b** photogenerated in crystal **1a** (○), and **1b** in crystal **1b** (●).

Table 2. Arrhenius Parameters of Thermal Cycloreversions from **1b** to **1a**

	E_a/kJ mol^{-1}	A/s^{-1}
in crystal **1a**	120	2.7×10^{12}
in toluene	128	4.0×10^{12}
in crystal **1b**	137	5.3×10^{12}

at the 2- and 2′-positions of thiophene groups. It is of interest to investigate the thermal stability of **1b**.

First, **1b** was heated in toluene for 50 h at 120 °C. The blue color of the solution was bleached. The absorption spectrum of the bleached solution was the same as that of the open-ring isomer **1a**. This clearly indicates that at 120 °C **1b** thermally returned to the open-ring isomer **1a**. The thermal cycloreversion reaction rates of **1b** were followed at various temperatures by the absorption spectral measurement. The half-life time at 100 °C was estimated to be 52 h. Figure 6 shows the temperature dependence of the bleaching. From the plots, the activation energy (E_a) and frequency factor (A) in toluene were determined to be 128 kJ mol^{-1} and 4.0×10^{12} s^{-1}, respectively.

Next, the thermal stability of the closed-ring isomers photogenerated in crystal **1a** was measured. The thermal cycloreversion rate was faster than that observed in toluene. Figure 6 also shows the temperature dependence of the thermal cycloreversion reaction rate in the crystal. The E_a and A values for the photogenerated **1b** in crystal **1a** were determined to be 120 kJ mol^{-1} and 2.7×10^{12} s^{-1}, respectively. The E_a value was smaller than that in toluene. This indicates that **1b** in crystal **1a** is less stable than **1b** in toluene.

Finally, the thermal stability of the closed-ring isomers in crystal **1b** was measured. Crystal **1b** was heated for 110 h at 130 °C, and the bleached product was measured by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum indicated that the bleached product was **1a** and any byproduct was not formed. The thermal cycloreversion rate was much slower than that of **1b** photogenerated in crystal **1a**. Figure 6 shows the temperature dependence of the thermal cycloreversion rate of crystal **1b**. The E_a and A values for the **1b** crystal were determined to be 137 kJ mol^{-1} and 5.3×10^{12} s^{-1}, respectively. The E_a value was much larger than that in toluene. Table 2 summarizes the Arrhenius parameters in toluene, in crystal **1a**, and in crystal **1b**.

From the above kinetic studies the energy diagrams for the reactions of **1** in the ground state can be deduced as shown in Figure 7. In the diagrams it was assumed that the energy levels or the conformations of the molecules in the crystalline phase reflect the levels or conformations in solution. The energy level of the open-ring isomer in crystal **1a** is similar to that in toluene and that of the closed-ring isomer in crystal **1b** is also similar to that in toluene, as shown in Figure 7. On the other hand, the closed-ring isomer photogenerated in crystal **1a** is considered to be less stable than the closed-ring isomer in toluene and in crystal **1b**. Also, the open-ring isomer produced by the thermal cycloreversion reaction is less stable than the open-ring isomer in toluene and in crystal **1a**. In a previous paper it was confirmed that the open-ring isomer photogenerated in the closed-ring crystal has a constrained conformation.[17] The thermally generated open-ring isomer is also considered to be in the constrained conformation (see next section and Figure 10).

Table 3. Crystal Data and Structure Refinement for **1b** and **1b′**

	1b	**1b′**
empirical formula	$C_{29}H_{22}F_6S_2$	
formula weight	548.59	
temperature	123(2) K	
crystal system	monoclinic	
space group	$C2/c$	
unit cell dimensions	$a = 29.762(6)$ Å	$a = 29.804(4)$ Å
	$b = 12.427(2)$ Å	$b = 12.391(2)$ Å
	$c = 13.424(3)$ Å	$c = 13.489(2)$ Å
	$\beta = 100.719(3)°$	$\beta = 101.289(3)°$
volume	4878.2(16) Å^3	4885.0(12) Å^3
Z	8	8
density (calculated)	1.494 g/cm^3	1.492 g/cm^3
goodness-of-fit on F^2	0.969	1.017
final R indices [$I > 2\sigma(I)$]	$R1 = 0.041$	$R1 = 0.046$
	$wR2 = 0.095$	$wR2 = 0.111$
R indices (all data)	$R1 = 0.068$	$R1 = 0.077$
	$wR2 = 0.106$	$wR2 = 0.128$

Mechanism of the Thermal Cycloreversion Reaction. The crystal was not shattered even after the photocyclization/thermal cycloreversion reactions were repeated many times. This means that the photogenerated colored crystal returned to the initial crystal by the thermal cycloreversion reaction. The photocyclization reactions of diarylethenes in crystals proceed in a conrotatory mode.[15,18,19] This means that photogenerated closed-ring isomer **1b** returns to the open-ring isomer **1a** in a conrotatory mode by the thermal cycloreversion reaction.

To confirm the conrotatory thermal cycloreversion reaction of **1b** to **1a**, X-ray crystallographic analysis was carried out before and after the thermal cycloreversion reaction. The crystalline data of **1b** are shown in Table 3. The $R1$ value for the reflection with $I > 2\sigma(I)$ and the $wR2$ value for all data were 0.041 and 0.106, respectively. The residual highest electron peaks remain in the middle of covalent bonds. The heights of the peaks are below 0.463 e Å^{-3}, which indicates the absence of disordered structure in the closed-ring isomer. Figure 8 shows ORTEP drawings of **1b**. Bond lengths for double and single bonds are within a range of 1.355−1.360 and 1.415−1.449 Å, respectively. The three five-membered rings are almost coplanar in the closed-ring isomer.

The crystallographic data for crystal **1b′** after heating at 100 °C for 256 h are also shown in Table 3. The space group was the same as that of crystal **1b**. The crystal structure **1b** was used as the initial model. After the difference Fourier synthesis, two new peaks, Q1 and Q2, appeared around the sulfur atoms as shown in Figure 9. The heights of the peaks Q1 and Q2 were 1.13 and 1.00 e Å^{-3}, respectively, which are much larger than other residual peaks (less than 0.47 e Å^{-3}). At the same time negative counter regions were observed at S1 and S2 of the closed-ring isomer. This indicates that the S1 and S2 atoms of

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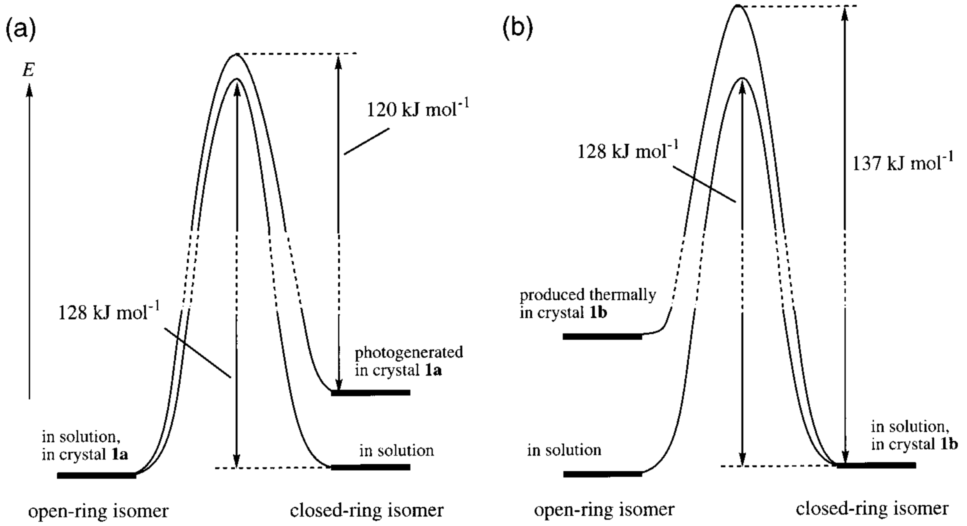

Figure 7. Energy diagram of open- and closed-ring isomers.

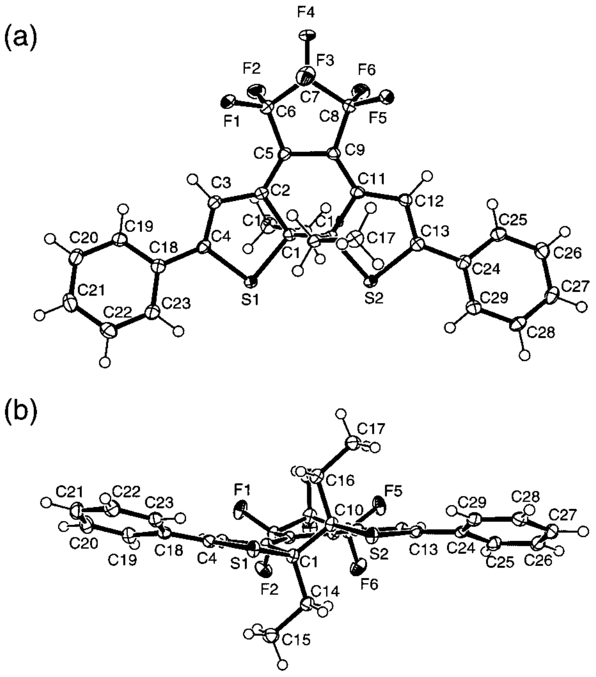

Figure 8. ORTEP drawings of top (a) and side (b) views of **1b** showing 50% probability displacement ellipsoids.

the closed-ring isomer moved to Q1 and Q2 by heating. These peaks were assigned to two sulfur atoms S1B and S2B. The S1B and S2B were refined as disordered atoms of S1 and S2, respectively. Furthermore, two new peaks appeared around the carbon atoms of C1 and C10, respectivelty. The new peaks were also assigned to two carbons C1B and C10B at the reacting points of the open-ring isomer. The C1B and C10B were refined isotropically. The heights of the residual peaks were below 0.43 e Å^{-3}. The $R1$ for the reflection with $I > 2\sigma(I)$ and the $wR2$ for all data were 0.046 and 0.111, respectively. The occupancy factor for the open-ring isomer converged to 0.078, which means that around 8% of the closed-ring isomers thermally converted to the open-ring isomers.

Figure 10 shows ORTEP drawings of the open-ring isomer, which was thermally generated in the closed-ring isomer crystal. The four peaks, S1B, S2B, C1B, and C10B, clearly indicated that the thermal cycloreversion reaction proceeded in a conrotatory mode. The reason the disrotatory cycloreversion was not observed is that the reaction was sterically prohibited by the presence of ethyl groups at the reactive carbons. The distance between C1B and C10B of the open-ring isomer generated by thermal cycloreversion reaction in the crystal was 2.81 Å, which is shorter than the value for the most stable open-ring isomer in the open-ring isomer crystal **1a**, 3.71 Å, which is shown in Figure 10c. The distance between S1B and S2B was 5.46 Å, which is smaller than the distance between two sulfur atoms of the stable open-ring isomer, 6.07 Å. The open-ring isomer (Figure 10b) generated by thermal cycloreversion reaction in the closed-ring isomer crystal has a conformation more planar than the most stable open-ring isomer (Figure 10c). This confirms that the thermally generated open-ring isomer had a constrained conformation. This is the reason the open-ring isomer generated thermally in crystal **1b** is less stable than the open-ring isomer in solution.

Conclusions

It has been demonstrated that 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**) undergoes a thermally reversible photochromic reaction in solution as well as in the single-crystalline phase. Upon irradiation with ultraviolet light the colorless toluene solution containing **1a** and the single crystal **1a** turned blue, and the blue color disappeared upon heating above 100 °C. The activation energies of the thermal cycloreversion reaction from **1b** to **1a** were determined to be 128 kJ mol^{-1} in toluene, 120 kJ mol^{-1} in the crystal of **1a**, and 137 kJ mol^{-1} in the crystal of **1b**. The activation energies and thermal cycloreversion rates depended on the environmental conditions. The X-ray crystallography of crystal **1b** during the thermal reaction indicated that the thermal cycloreversion reaction proceeded in the conrotatory mode.

Experimental Section

General. Solvents used were spectroscopic grade and purified by distillation before use. ^{1}H NMR spectra were recorded on a Varian Gemini 200 spectrometer (200 MHz). Tetramethylsilane was used as an internal standard. Mass spectra were taken with a Shimadzu GCMS-QP5050A gas chromatograph−mass spectrometer. The melting points were measured by using a Perkin-Elmer Pyris 1 differential scanning calorimeter. Absorption spectra in solution were measured with a Hitachi U-3410 absorption spectrophotometer. Absorption spectra in the single-crystalline phase were measured by using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 photodetector. Polarizer and analyzer were set in parallel to each other. A Mettler-Toledo FP82HT hot stage was used to maintain constant

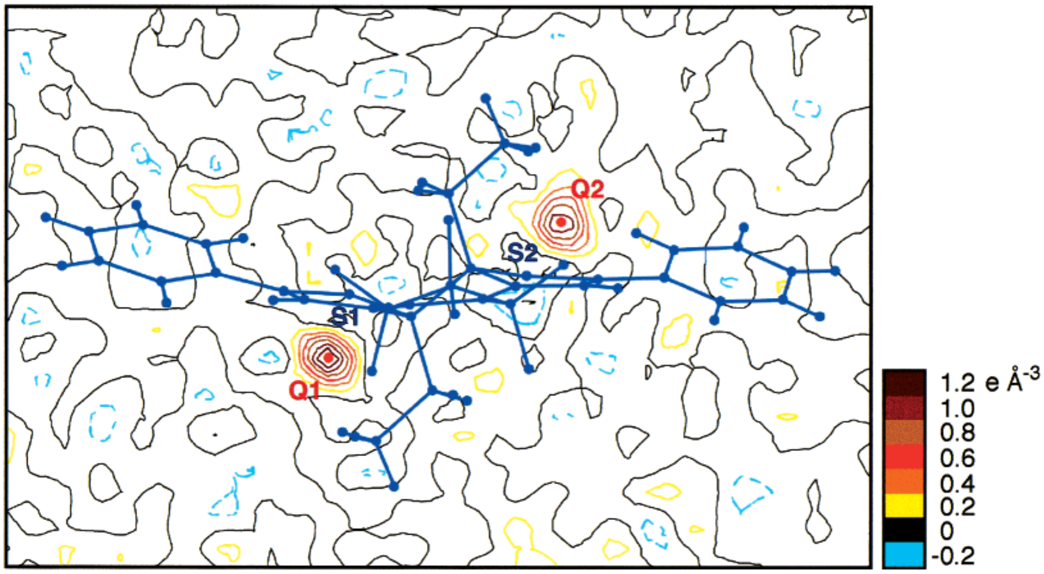

Figure 9. $F_o - F_c$ difference Fourier electron density maps through peaks Q1 and Q2.

temperature of the crystal. Photoirradiation was carried out using a Ushio 500 W super-high-pressure mercury lamp or a Ushio 500 W xenon lamp as the light sources. Monochromic light was obtained by passing the light through a monochromator (Ritsu MV-10N). X-ray crystallographic analysis was carried out with a Bruker SMART1000 CCD-based diffractometer (50 kV, 40 mA) with Mo Kα radiation. The data collection was performed using SAINT, SHELXS-86,[20] and SHELXL-97.[21]

2,4-Dibromo-5-ethylthiophene (3). Bromine (25 mL; 0.49 mol) was added slowly into a flask containing 2-ethylthiophene (25 g; 0.22 mol) and acetic acid (500 mL). The reaction mixture was stirred overnight at room temperature. The mixture was neutralized and extracted with ether. The ether extract was dried over $MgSO_4$, filtrated, and evaporated. The residue was purified by silica gel column chromatography using hexane as the eluent. **3** was obtained as a colorless oil of 39 g (65% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25 (t, $J = 7.5$ Hz, 3H), 2.75 (q, $J = 7.5$ Hz, 2H), 6.86 (s, 1H); MS m/z (M^+) 268, 270, 272. Anal. Calcd for $C_6H_6Br_2S$: C, 26.69; H, 2.24. Found: C, 26.61; H, 2.22.

3-Bromo-2-ethyl-5-phenylthiophene (4). To 340 mL of dry ether containing **3** (20 g; 0.074 mol) was added 49 mL of 15% *n*-BuLi hexane solution (0.080 mol) at −78 °C under nitrogen atmosphere, and the solution was stirred for 1 h at the low temperature. Tri-*n*-butylborate (30 mL; 0.11 mol) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 2 h at that temperature and then overnight at room temperature. The reaction mixture was neutralized with concentrated HCl and then extracted with ether. The ether solution was extracted with aqueous sodium HCl. The aqueous layer was acidified with concentrated hydroxide. The resulting precipitate was filtrated. The solid material (3-bromo-2-ethyl-5-thiopheneboronic acid) (12 g; 0.051 mol) was added into a flask containing THF (300 mL), 20 wt % Na_2CO_3(aq) (100 mL), and iodobenzene (9.6 g; 0.047 mol). The mixture was refluxed for 5 h at 70 °C. The product was extracted with ether. The organic layer was dried over $MgSO_4$, filtrated, and concentrated. The residue was purified by silica gel column chromatography using hexane as the eluent to give 9.1 g of **4** in 46% yield as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31 (t, $J = 7.5$ Hz, 3H), 2.82 (q, $J = 7.5$ Hz, 2H), 7.12 (s, 1H), 7.2−7.7 (m, 5H); MS m/z (M^+) 266, 268. Anal. Calcd for $C_{12}H_{11}BrS$: C, 53.95; H, 4.15. Found: C, 53.97; H, 4.19.

1,2-Bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (1a). To 80 mL of dry THF solution containing **4** (9.0 g; 0.034 mol) was added 24 mL of 15% *n*-BuLi hexane solution (0.039 mol) at −78 °C under nitrogen atmosphere, and the solution was stirred for 2 h at that low

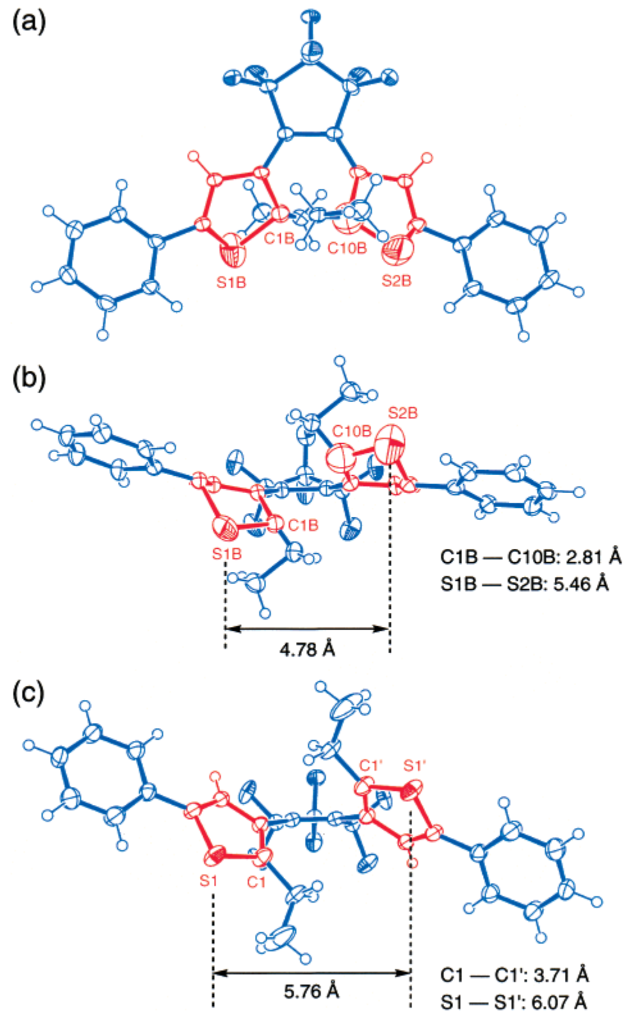

Figure 10. ORTEP drawings of top (a) and side (b) views of the thermally generated open-ring isomer showing 50% probability displacement ellipsoids. The reaction was carried out at 100 °C for 256 h. C1B, C10B, S1B, and S2B were determined based on difference Fourier synthesis and other atoms based on the structure before photoirradiation. (c) ORTEP drawing of the open-ring isomer in the open-ring isomer crystal **1a**. The perfluorocyclopentene rings in parts b and c were horizontally placed. The thiophene rings are red for clarity.

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(21) Sheldrick, C. M. SHELXL-97, Program for Crystal Structure Refinement; Universität Göttingen: Göttingen, 1997.

temperature. Perfluorocyclopentene (2.3 mL; 0.017 mol, Nippon Zeon) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 3 h at that temperature. The reaction was stopped by the addition of methanol. The product was extracted with ether. The organic layer was dried over $MgSO_4$, filtrated, and concentrated. The residue was purified by column chromatography on silica gel using hexane as the eluent and by recrystallization from hexane to give 6.3 g of **1a** in 68% yield as a colorless crystal: mp 164 °C (DSC); ^1H NMR (200 MHz, $CDCl_3$) δ 0.98 (t, $J = 7.4$ Hz, 6H), 2.33 (q, $J = 7.4$ Hz, 4H), 7.20 (s, 2H), 7.2−7.6 (m, 10H); MS *m/z* (M^+) 548. Anal. Calcd for $C_{29}H_{22}F_6S_2$: C, 63.49; H, 4.04. Found: C, 63.51; H, 4.04.

Closed-Ring Isomer of 1a (1b). 1b was isolated by passing a photostationary solution containing **1a** and **1b** through a HPLC (Shimadzu LC-6AD) pump system equipped with Shimadzu SPD-10AV detector and silica gel column (Wako, Wakosil 5SIL) with hexane as the eluent: mp 170 °C (DSC); ^1H NMR (200 MHz, $CDCl_3$) δ 1.16 (t, $J = 7.3$ and 7.5 Hz, 6H), 2.54 (dq, $J = 7.5$ and 13.8 Hz, 2H), 3.04 (dq, $J = 7.3$, 13.8 Hz, 2H), 6.64 (s, 2H), 7.3−7.7 (m, 10H); MS *m/z* (M^+) 548. Anal. Calcd for $C_{29}H_{22}F_6S_2$: C, 63.49; H, 4.04. Found: C, 63.46; H, 4.05.

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

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