

Photochromism of 1,2-Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene in a Single Crystalline Phase

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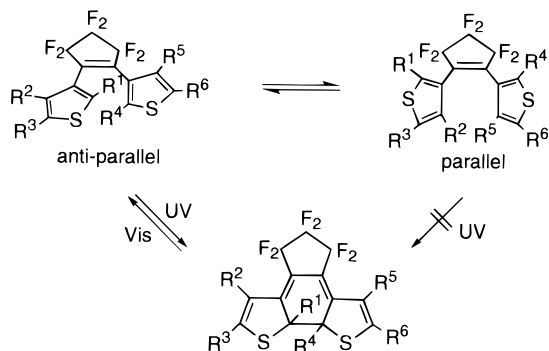
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Abstract: 1,2-Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**1a**) was found to undergo photochromism in a single crystalline phase. Upon irradiation with ultraviolet light the colorless crystal turned red with keeping the crystal shape. The red color is due to the closed-ring form **1b**. The red color was bleached by irradiation with visible light ($\lambda > 450$ nm). The intensity of the red color observed under polarized light dramatically changed by rotating the crystal sample, and the order parameter was as high as 0.84. The high order parameter confirmed that the molecules undergo photochromism in the crystalline lattice. The direction of the electronic transition moment of **1b** estimated from the absorption anisotropy at 535 nm agreed with the long axis of **1a** packed in the crystal, which was determined by X-ray crystallographic analysis. The movement of each atom of the molecule in the crystal during the cyclization reaction was estimated by comparing the structures of **1a** and **1b**, both of which were determined by X-ray analysis.

Introduction

Various types of photochromic compounds have been so far developed in an attempt to apply the compounds to optoelectronic devices.¹ Among the compounds diarylethenes having heterocyclic aryl groups are the most promising photochromic compounds for the application because of their fatigue resistant and thermally irreversible properties.² The diarylethenes undergo the following photochromic reaction:



The open-ring form diarylethenes in solution have two conformations, antiparallel and parallel, and the conrotatory cyclization can proceed only from the antiparallel conformation.³ The photogenerated closed-ring forms have absorption in the visible

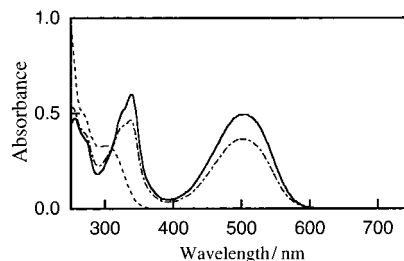


Figure 1. Absorption spectral change of **1** in hexane (6.2×10^{-5} M) by photoirradiation: **1a** (---), **1** in the photostationary state under irradiation with 290 nm light (- · -), and **1b** (—).

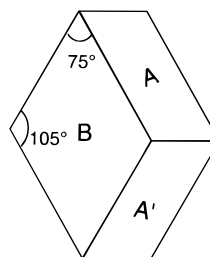


Figure 2. Shape of single crystal **1a**.

region. The closed-ring forms are thermally stable and never return to the initial open-ring forms in the dark. Upon irradiation with visible light the colored closed-ring forms regenerate the open-ring forms.

The cyclization quantum yields depend on the ratio of the two conformations. The high contents of antiparallel conformation lead to high cyclization quantum yields. One approach to increase the ratio of antiparallel conformation is to include the compounds into confined reaction spaces, such as cyclodextrins.

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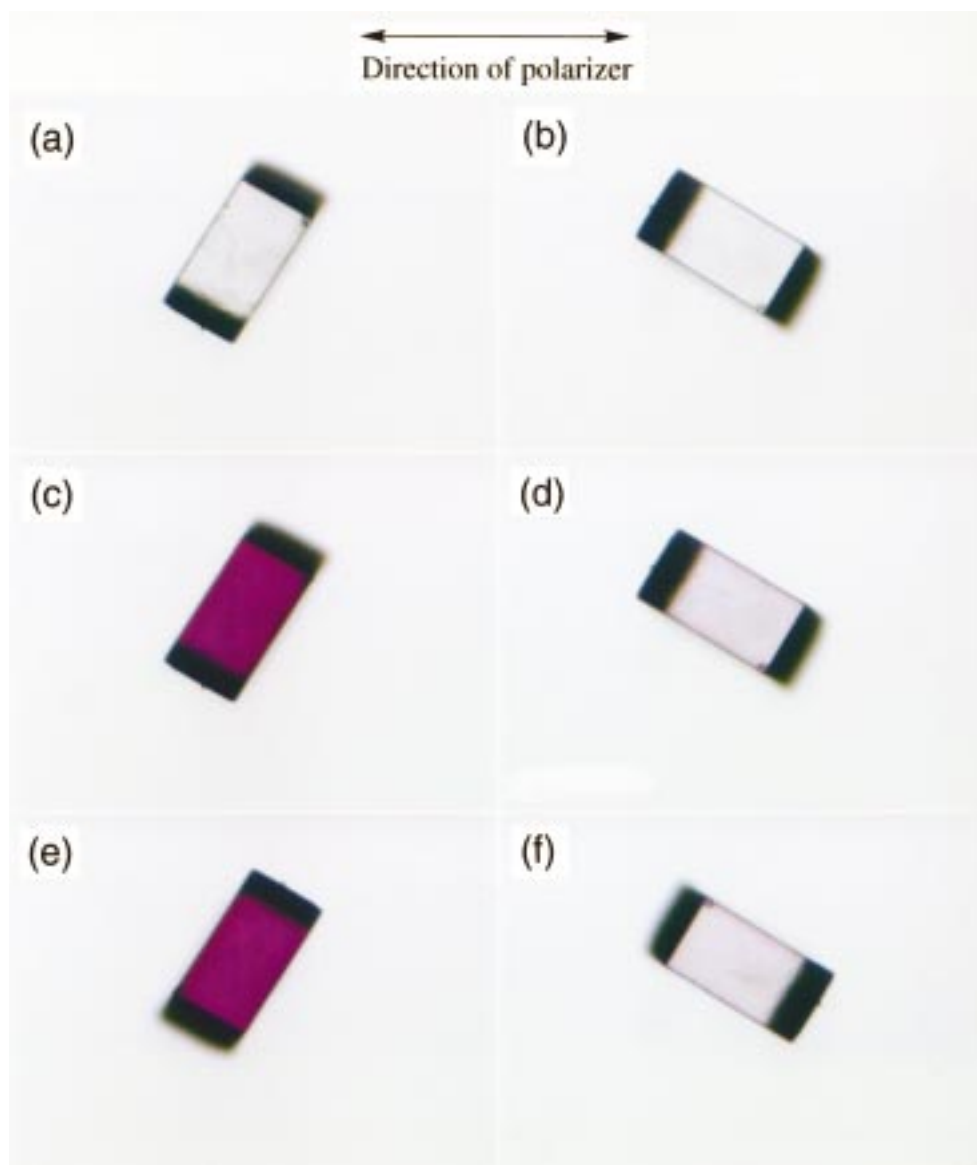


Figure 3. Photographs of single crystal **1a** (surface A) under polarized light before ((a) $\theta = 30^\circ$, (b) $\theta = 120^\circ$) and after ((c) $\theta = 30^\circ$, (d) $\theta = 120^\circ$, (e) $\theta = 210^\circ$, (f) $\theta = 300^\circ$) irradiation with 366 nm light. θ is the rotation angle of the crystal as shown in Figure 4a.

Inclusion of a sodium sulfonate derivative of 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene into β - and γ -cyclodextrin cavities resulted in the increase of the cyclization quantum yields.⁴ Another approach is to fix the conformation in a crystalline phase. Diarylethenes packed in crystals in the antiparallel conformation are expected to show efficient photochromic reactivity.⁵

Although many photochromic compounds have been reported, compounds which show photochromic reactivity in crystalline phases are rare.⁶ Typical examples of crystalline photochromic compounds are paracyclophanes,⁷ triarylimidazole dimer,⁸ diphenylmaleronitrile,⁹ aziridines,¹⁰ 2-(2',4'-dinitrobenzyl)pyridine,¹¹

N-salicylideneanilines,¹² and triazenes.¹³ In most cases, the photogenerated closed-ring forms are thermally unstable. Recently, we have reported that some diarylethenes undergo thermally irreversible photochromic reactions in single crystalline phases.^{2,14,15} The colored forms are stable in the crystals even at 100 °C and never returned to the initial colorless forms in the dark. The thermally irreversible crystalline photochromic materials are potentially applicable to optical memories and switches.

In this paper, we studied photochromism of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**1a**) in the single crystalline phase. The molecular arrangement of **1b** in the single crystal was estimated from the absorption anisotropy under

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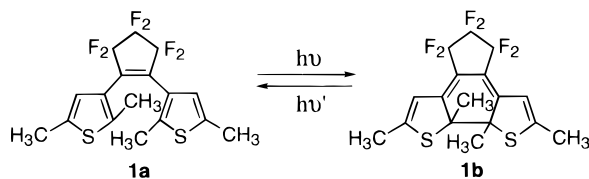
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polarized light and compared with the molecular packing of **1a** determined by X-ray crystallographic analysis.



Results and Discussion

Photochromism in Solution. Compound **1** undergoes photochromism in solution. Figure 1 shows the absorption spectral change of **1a** by irradiation with 290 nm light. **1a** has the absorption shoulder at 303 nm (ϵ , $5.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) in hexane. Upon irradiation with 290 nm light, the colorless solution of **1a** turned red, in which visible absorption band was observed at 505 nm. The red color is due to the closed-ring forms (see below). The conversion from **1a** to **1b** in the photostationary state under irradiation with 290 nm light was 74%. The red color disappeared by irradiation with visible light ($\lambda > 450 \text{ nm}$).

The photoisomerization process in a CDCl_3 solution was followed by ^1H NMR spectroscopy. Upon irradiation with 313 nm light, new peaks appeared at 2.03, 2.19, and 5.99 ppm with the peak intensity of 3:3:1 along with the decrease of the peaks at 1.81, 2.41, and 6.71 ppm. The peaks at 1.81 and 2.41 ppm are assigned to the methyl protons of **1a** at 2- and 5-positions, respectively. The absence of splitting of the peaks indicates that the interconversion of the two conformations, antiparallel and parallel, is very fast.¹⁶ The new peaks at 2.03 and 2.19 ppm are assigned to the methyl protons of the closed-ring form **1b**. The 4-thienyl protons of **1a** at 6.71 ppm shifted to a higher field of 5.99 ppm in the colored form. The higher field shift of the thienyl protons and two singlet peaks of the methyl protons in the NMR spectrum agree with the structure of the closed-ring form.

The colored isomer was isolated by HPLC, and the electronic absorption and NMR spectra were measured. Three peaks at 2.03, 2.19, and 5.99 ppm were observed in the NMR spectrum, and the absorption coefficient (ϵ) at 505 nm was determined to be $8.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The molecular structure of the closed-ring form was also determined by X-ray crystallographic analysis (see Figure 12 and the last section).

Photochromism in a Single Crystalline Phase. A rhombus shape single crystal was obtained by recrystallization of **1a** from hexane as shown in Figure 2. The crystal consists of six surfaces with four rectangles (A and A') and two parallelograms (B). Single crystal **1a** turned red upon irradiation with ultraviolet (366 nm) light. The red color of the crystal is due to the formation of **1b**. The red crystal was dissolved into hexane, and the absorption spectrum was measured. The absorption maximum was the same as that of the closed-ring form shown in Figure 1. The red color of the crystal disappeared by irradiation with visible light ($\lambda > 450 \text{ nm}$), and the coloration/decoloration cycles could be repeated many times ($> 10^4$) with keeping the crystal shape.

The color of the crystal was observed under polarized light. Figure 3 shows the color change of surface A. Before photoirradiation the crystal was colorless (a and b). Upon irradiation with 366 nm light, the crystal turned red. At a certain angle ($\theta = 30^\circ$ shown in Figure 4a) the crystal has a deep red color. When the crystal was rotated as much as 90° , the color almost disappeared. The deep red color reappeared at 210° . The red

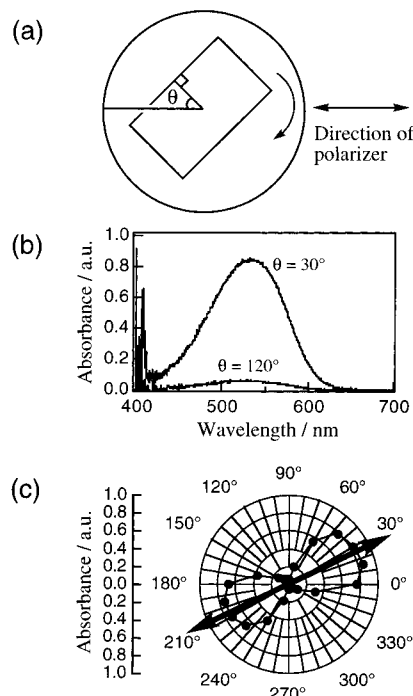


Figure 4. Polarized absorption spectra of the red color of the surface A: (a) direction of polarizer, (b) polarized absorption spectra, and (c) the polar plots at 535 nm.

color intensity change by rotating the crystal sample indicates that the closed-ring isomers are regularly oriented in the crystal. In other words, the photochromic reaction proceeds in the crystal lattice. The color change of surface A' was similar to that of surface A.

Figure 4 shows the polarized absorption spectra of the red color at 30 and 120° and the polar plots at 535 nm. The absorption maximum, 535 nm, did not change by rotation, but the intensity dramatically changed. The order parameter ($(A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$) was calculated to be 0.84. Such a high order parameter confirms that **1a** underwent the photochromic reaction in the single crystalline phase.

Figures 5 and 6 show the color change of crystal surface B and the polarized absorption spectra, respectively. The intensity of the color of surface B was weaker than that of surfaces A and A'. Upon irradiation with 366 nm light surface B turned pale red at a certain angle ($\theta = 0^\circ$ shown in Figure 6a). When the crystal was rotated as much as 90° , the color changed to pale orange. Pale red color reappeared at 180° . The absorption maximum changed from 530 nm ($\theta = 0^\circ$) to 505 nm ($\theta = 90^\circ$) by rotating the crystal. This can be interpreted by assuming two absorption bands, $\lambda_{\text{max}} = 495 \text{ nm}$ (half-width 105 nm) and $\lambda_{\text{max}} = 535 \text{ nm}$ (half-width 105 nm). The absorption spectrum ($\lambda_{\text{max}} = 535 \text{ nm}$) observed on surface A and A' was adopted as one of the absorption bands. The absorption spectra observed at 0° , 45° , 75° , and 90° were well reconstructed by adding two 495 and 535 nm bands in the ratios of 8/92, 34/66, 64/36, and 68/32, respectively. Figure 6c shows the polar plots of the absorbances for the simulated spectra at 495 and 535 nm. The electronic transition moment of 495 nm band is perpendicular to that of 535 nm band.

The absorption anisotropy of the 535 nm band on surfaces A, A', and B indicates that the direction of its electronic transition moment of the closed-ring form in the crystal can be expressed by the arrow shown in Figure 7. The transition moment vector is approximately perpendicular to surface B. This is the reason the intensity of the color of surface B was weak.

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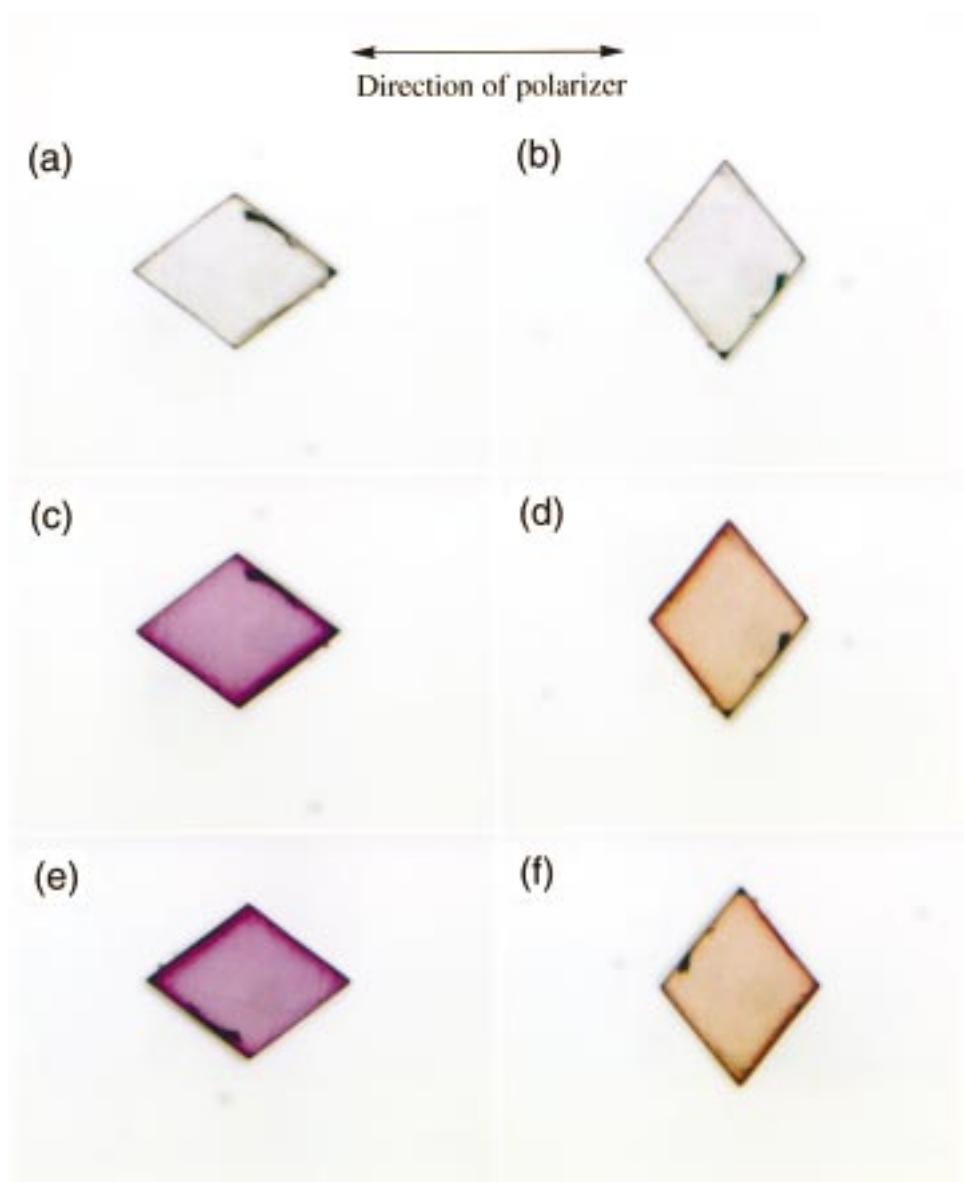


Figure 5. Photographs of single crystal **1a** (surface B) under polarized light before ((a) $\theta = 0^\circ$, (b) $\theta = 90^\circ$) and after ((c) $\theta = 0^\circ$, (d) $\theta = 90^\circ$, (e) $\theta = 180^\circ$, (f) $\theta = 270^\circ$) irradiation with 366 nm light. θ is the rotation angle of the crystal as shown in Figure 6a.

The electronic transition moment vector of the longest absorption band ($\lambda_{\max} = 535$ nm) of **1b** is considered to be in the direction of x axis as shown in Figure 8.^{3,17} Three five-membered rings, two thiophene and cyclopentene rings, are almost coplanar in the closed-ring form **1b**. Therefore, the x direction shown by the arrow corresponds to the long axis of the molecular plane of **1b**. When the conversion from **1a** to **1b** was low, no crystal shape change was observed. This indicates that **1b** was produced from **1a** in the crystal lattice of **1a**. The transition moment vector is expected to coincide approximately with x axis of **1a** packed in the crystal. We carried out X-ray crystallographic analysis of crystal **1a** to confirm the relation between the x axis of **1b** and the crystal packing of **1a**.

X-ray Structural Analysis of 1a. Table 1 shows the results of X-ray crystallographic analysis of **1a**. Figure 9 shows the ORTEP drawings of **1a**. In solution diarylethenes have two conformations, parallel and antiparallel, and they interconvert with each other. In crystals, on the other hand, there is no exchange between 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 0.358 nm, which is close enough for the reaction.¹⁸

The planes of $\{(1-1-1), (-111)\}$ and $\{(100), (-100)\}$ correspond to surfaces A and A', respectively, and the planes of $\{(0-11), (01-1)\}$ correspond to surface B. Parts a and b of Figure 10 show the molecular packing of **1a** viewed from surfaces A and B, respectively. The arrows depicted in Figure 10 show the direction of transition moment of 535 nm absorption band determined from the absorption anisotropy. The direction of the arrow shown in Figure 10b coincides with the direction of x axis of the open-ring form. This result confirms that the photocyclization reaction proceeds in the crystal lattice of the open-ring form **1a**.

To find the relation between the electronic transition direction of **1b** and crystal packing of **1a**, the sectional views of packed **1a** molecules along the transition direction were obtained as shown in Figure 11. In the sectional views, there are two kinds

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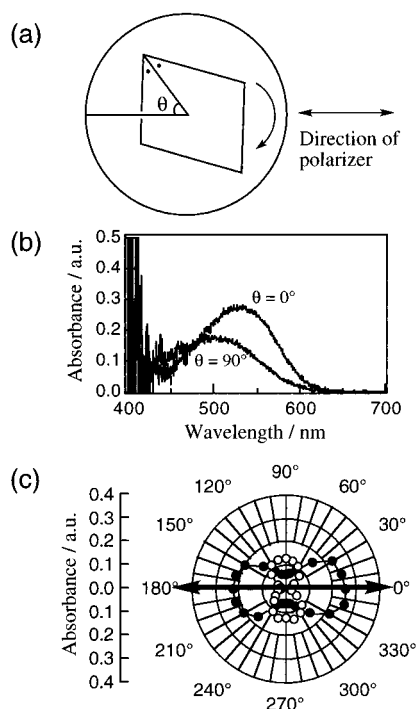


Figure 6. Polarized absorption spectra of the red color of the surface B: (a) direction of polarizer, (b) polarized absorption spectra, and (c) the polar plots at 495 (○) and 535 nm (●).

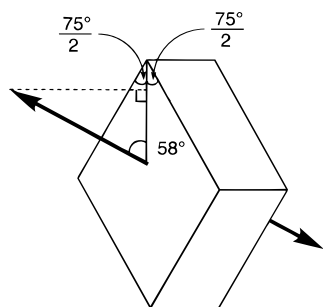


Figure 7. Relationship between the crystal shape of **1a** and the electronic transition moment of **1b** at 535 nm.

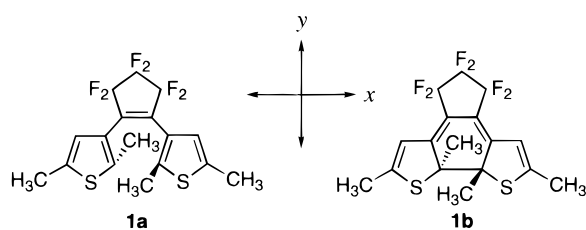


Figure 8. Molecular structures of **1a,b**: *x* and *y* are long and short axes of the molecules, respectively.

of molecules, which have an inversion center. The transition direction indicates that during cyclization reaction the cyclopentene rings scarcely move the position. To know more precisely the movement of each atom of the molecule it is necessary to know the molecular structure of the closed ring form **1b**.

X-ray crystallographic analysis of the closed-ring form crystal was carried out, and the result is shown in Table 2. Figure 12 shows the ORTEP drawings of **1b**. Table 3 and Figure 13 show the movement of each atom during the reaction. The origin corresponds to the center of gravity for **1a,b**. The results indicate

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

formula	C ₁₇ H ₁₄ F ₆ S ₂	
formula wt	396.40	
temp (K)	293(2)	
cryst syst	triclinic	
space group	P $\bar{1}$	
unit cell dimens	<i>a</i> = 8.833(2) Å	α = 100.588(8)°
	<i>b</i> = 11.178(2) Å	β = 112.708(6)°
	<i>c</i> = 11.431(2) Å	γ = 113.218(12)°
volume (Å ³)	878.5(3)	
Z	2	
density (calcd) (g/cm ³)	1.499	
goodness-of-fit on <i>F</i> ²	0.969	
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.034, w <i>R</i> 2 = 0.096	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.050, w <i>R</i> 2 = 0.104	

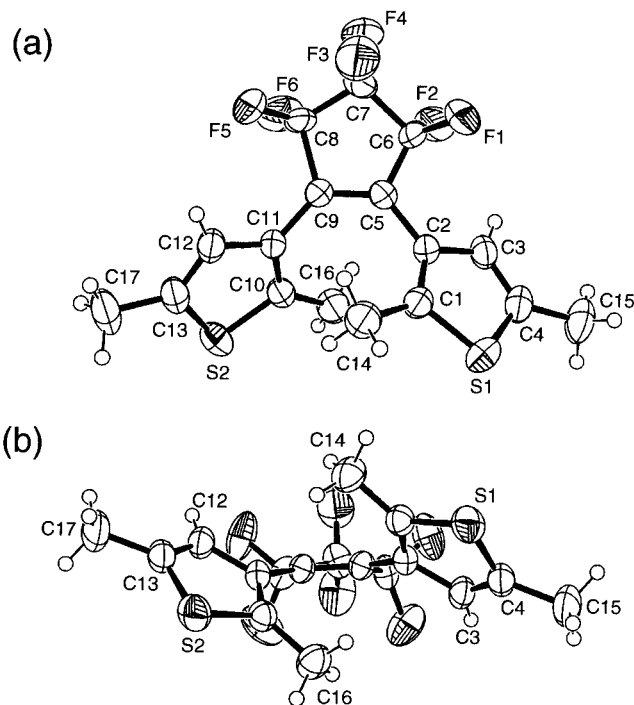


Figure 9. ORTEP drawings of (a) top and (b) side views of **1a** showing 50% probability displacement ellipsoids. The CF₂ groups in cyclopentene ring were disordered. Only a conformer was illustrated for clarity.

that the reacting carbon (C1 and C10) and sulfur atoms (S1 and S2) move a longer distance in comparison with other atoms. In Figure 11b the ethylene bond is not parallel to the transition moment shown by the arrow. When the open-ring form converts to the closed-ring form, the C–C bond becomes parallel to the arrow. The cyclopentene plane slightly tilts during the isomerization as shown in Figure 13b. The closed-ring form produced from **1a** according to the illustration shown in Figure 13 gives the transition moment direction shown in Figure 11. The result indicates that the molecule undergoes the isomerization in the crystal with keeping the center of gravity of the molecule.

Conclusions

It has been demonstrated that 1,2-bis(2,5-dimethyl-3-thienyl)-perfluorocyclopentene undergoes photochromism in the single crystalline phase. Upon irradiation with 366 nm light the colorless open-ring form crystal turned red, and the red color disappeared by irradiation with visible light ($\lambda > 450$ nm). The intensity of the red color observed under polarized light dramatically changed by rotating the crystal sample. The molecular arrangement of the closed-ring forms was estimated

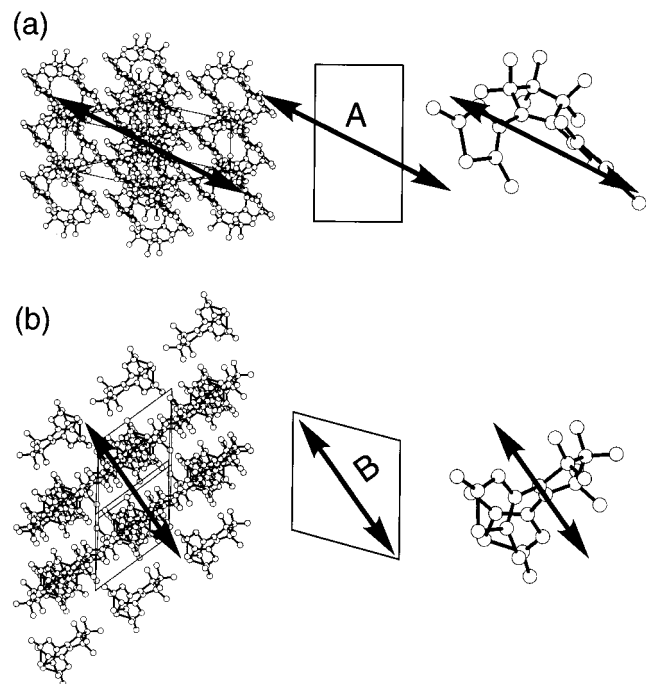


Figure 10. Packing diagram of **1a** and the crystal shape of the (a) surfaces A (-111) and (b) B ($0-11$). The arrows showed the direction of the transition moment of 535 nm absorption. Typical molecular structures of packed **1a** were also shown in the right-hand sides. Hydrogen atoms were omitted for clarity.

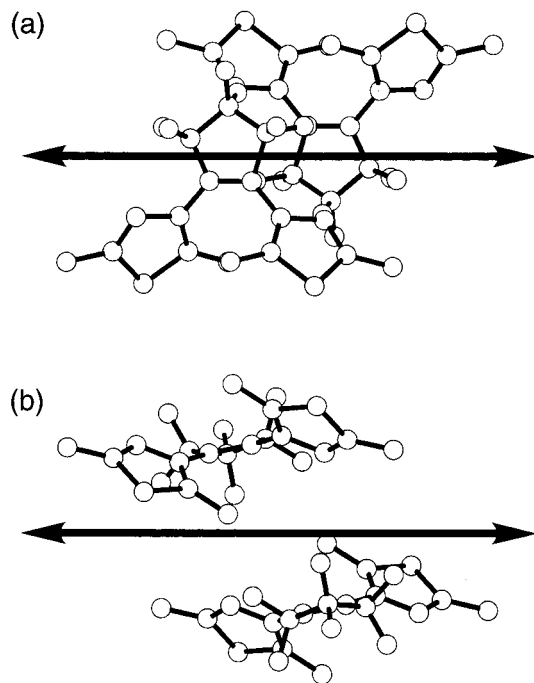


Figure 11. Sectional views of packed **1a** molecules along with the transition moment of 535 nm absorption band: (a) top view and (b) side view. Hydrogen atoms were omitted for clarity.

from the absorption anisotropy under polarized light and compared with the molecular packing of the open-ring forms, which was determined by X-ray crystallographic analysis. X-ray structural analysis of both isomers revealed that during the cyclization reaction only four atoms (C1, C10, S1, and S2) changed their positions and others remained at almost the same positions. The result accounts for the very rapid cyclization reaction rate (<10 ps) in the crystalline phase.⁵

Table 2. Crystal Data and Structure Refinement for **1b**

formula	$C_{17}H_{14}F_6S_2$		
formula wt	396.40		
temp (K)	304(2)		
cryst syst	monoclinic		
space group	$P2_1/c$		
unit cell dims	$a = 6.353(2)$ Å	$\alpha = 90^\circ$	
	$b = 24.750(6)$ Å	$\beta = 104.891(4)^\circ$	
	$c = 11.460(3)$ Å	$\gamma = 90^\circ$	
volume (Å ³)	1741.6(7)		
Z	4		
density (calcd) (g/cm ³)	1.512		
goodness-of-fit on F^2	1.027		
final R indices [$I > 2\sigma(I)$]	R1 = 0.084, wR2 = 0.159		
R indices (all data)	R1 = 0.181, wR2 = 0.192		

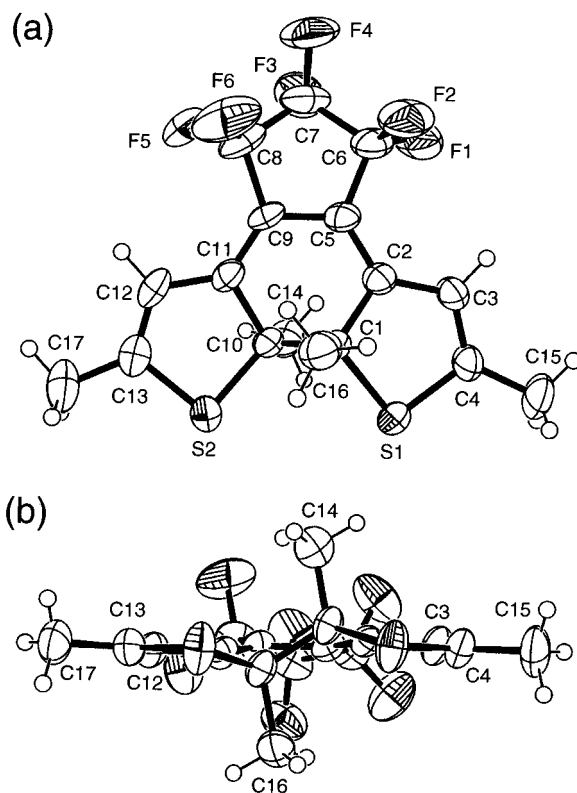


Figure 12. ORTEP drawings of top (a) and side (b) views of **1b** showing 50% probability displacement ellipsoids.

Table 3. Rectangular Coordinates of **1a,b** and Displacement of Each Atom by the Photochromic Reaction^a

	open-ring form (Å)			closed-ring form (Å)			dist (Å)
	x	y	z	x	y	z	
S1	2.703	-2.665	1.258	1.788	-3.029	0.032	1.572
S2	-2.701	-2.666	-1.261	-1.789	-3.026	-0.022	1.579
C1	1.334	-1.630	1.193	0.642	-1.646	0.420	1.038
C2	1.588	-0.563	0.370	1.451	-0.393	0.115	0.336
C3	2.906	-0.612	-0.188	2.845	-0.645	0.032	0.231
C4	3.626	-1.679	0.196	3.167	-1.951	-0.008	0.571
C5	0.665	0.544	0.121	0.721	0.760	0.001	0.254
C9	-0.665	0.545	-0.121	-0.721	0.751	-0.001	0.245
C10	-1.330	-1.632	-1.193	-0.645	-1.669	-0.416	1.037
C11	-1.585	-0.565	-0.370	-1.432	-0.398	-0.129	0.330
C12	-2.903	-0.612	0.190	-2.836	-0.663	-0.070	0.274
C13	-3.622	-1.679	-0.198	-3.173	-1.950	-0.007	0.558
C14	0.122	-1.944	2.006	0.363	-1.652	1.930	0.386
C15	5.041	-2.028	-0.166	4.525	-2.564	-0.057	0.751
C16	-0.119	-1.948	-2.008	-0.350	-1.678	-1.961	0.358
C17	-5.039	-2.027	0.164	-4.521	-2.546	0.084	0.738

^a The origin corresponds to the center of gravity for **1a,b**. Carbon and fluorine atoms of CF_2 groups and hydrogen atoms are omitted.

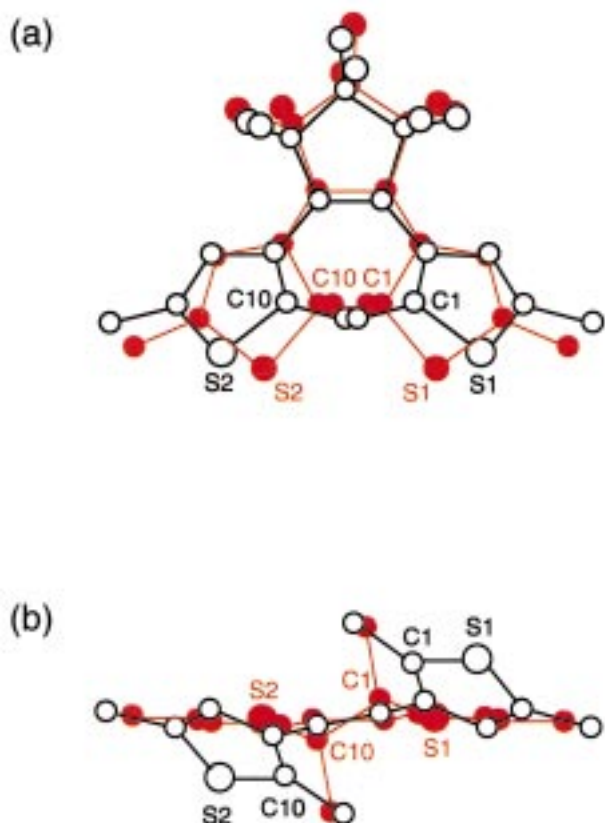


Figure 13. Movement of each atom of **1** in the crystal during photoisomerization and relative atom positions of **1a** (○, open circles) and **1b** (●, red circles): (a) top view and (b) side view.

Experimental Section

General. Solvents used were spectroscopic grade and purified by distillation before use. ^1H NMR spectra were recorded on a Varian Gemini 200 spectrometer (200 MHz). Tetramethylsilane was used as an internal standard. The melting points were measured by using a Perkin-Elmer Pyris 1 differential scanning calorimeter. Mass spectra were taken with a Shimadzu GCMS-QP5050A gas chromatography–mass spectrometer. Absorption spectra in a solution were measured with a Hitachi U-3410 absorption spectrophotometer. Absorption spectra

in single crystalline phases were measured by using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 detector. The polarizer and analyzer were set in parallel to each other. Photoirradiation was carried out using a USIO 500 W high-pressure mercury lamp or a USIO 500 W xenon lamp as the light source. Monochromatic light was obtained by passing the light through a monochromator (Ritsu MV-10N). X-ray crystallographic analysis was carried out using a Bruker SMART CCD X-ray diffractometer.

1,2-Bis(2,5-dimethylthien-3-yl)perfluorocyclopentene (1a). To a 100 mL tetrahydrofuran solution containing 2,5-dimethyl-3-iodothiophene (19 g; 80 mmol) was added 50 mL of a 15% *n*-BuLi hexane solution (82 mmol) at -78 °C under nitrogen atmosphere, and the solution was stirred for 1 h at the low temperature. Perfluorocyclopentene (5.5 mL, 41 mmol) was slowly added to the reaction mixture at -78 °C, and the mixture was stirred for 3 h at the temperature. The reaction was stopped by the addition of methanol. The product was extracted with ether. The organic layer was washed with 1 N HCl aqueous solution and water. The organic layer was dried over MgSO_4 , filtrated, and evaporated. The residue was purified by column chromatography on silica gel using hexane as the eluent and by recrystallization from hexane to give 10 g of **1a** in 63% yield as a colorless crystal: mp = 119 – 119.5 °C; ^1H NMR (200 MHz, CDCl_3) δ 1.81 (s, 6H), 2.41 (s, 6H), 6.71 (s, 2H); MS m/z (M^+) 396. Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{F}_6\text{S}_2$: C, 51.51; H, 3.56. Found: C, 51.64; H, 3.67.

Closed-Ring Form for 1a (1b). **1b** was isolated by passing a photostationary solution containing **1a,b** through HPLC (Hitachi L-6250 HPLC system, silica gel column, hexane as the eluent): mp = 106 °C (DSC); ^1H NMR (200 MHz, CDCl_3) δ 2.03 (s, 6H), 2.19 (s, 6H), 5.99 (s, 2H); MS m/z (M^+) 396.

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

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