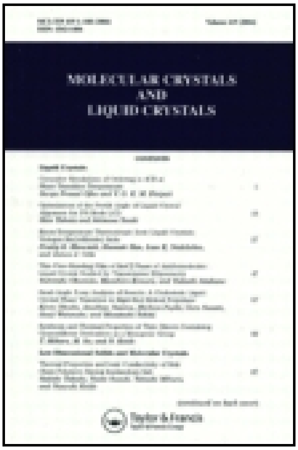

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Photochromism of Diarylethenes in Single-Crystalline Phases

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Photochromism of Diarylethenes in Single-Crystalline Phases

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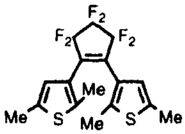
Photochromism of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**1a**) and 1,2-bis(2-methyl-6-nitro-1-benzothiophen-3-yl)perfluorocyclo-pentene (**2a**) in single-crystalline phases was investigated. Upon irradiation with 366 nm light the colorless crystals of **1a** and **2a** turned red and green, respectively. The colored crystals are due to the formation of the closed-ring isomers, **1b** and **2b.** The colored crystals were bleached by irradiation with visible light. The direction of the electronic transition moment of **1b** in crystal was estimated from the absorption anisotropy of 535 nm band. When the photogenerated green colored crystal of **2a** was observed under polarized light, the colored crystal showed dichroism of yellow and blue. The yellow and blue colors were attributed to two perpendicular electronic transitions of **2b** at 465 and 600 nm, respectively.

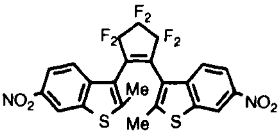
Keywords: diarylethene; crystal; electronic transition moment

INTRODUCTION

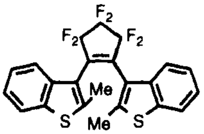
Various types of photochromic compounds have been so far developed[1] in an attempt to apply the compounds to optoelectronic devices, such as optical memory, photo-optical switching and display[2]. Although many photochromic compounds have been reported, compounds which show thermally irreversible photochromic reactivity in the crystalline phases are very rare[3]. Recently, it has been found that some diarylperfluorocyclopentenes having thiophene rings as the aryl groups undergo photochromic reactions in the crystalline phases, and both isomers are thermally stable even at 100°C[4]. In crystals, molecules are regularly oriented and packed in fixed conformations. In many cases free rotation is prohibited. Therefore, photoreactivity in crystalline phases is dependent on the conformation fixed in the crystal lattice. In this paper, we report photochromism of **1a** and **2a** in the single-crystalline phases.



1a



2a



3a

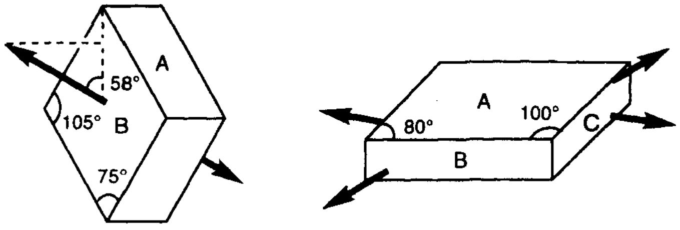
RESULTS AND DISCUSSION

Photochromism of 1a in the single-crystalline phase

A rhombus shape single crystal **1a** was obtained by recrystallization from hexane as shown in Figure 1. Upon irradiation with 366 nm light the colorless crystal of **1a** turned red, and the red color disappeared by irradiation with visible light (λ > 450 nm). The red color is due to the formation of **1b**. When the colored crystal (surface A) was observed under polarized light, the crystal had deep red color at a certain angle, and the color almost disappeared by rotating the crystal as much as 90°. Absorbance at 535 nm in the polarized absorption spectra of the red color dramatically changed by rotating the colored crystal. This indicates that the closed-ring isomers are regularly oriented in the crystal. In other words, the photochromic reaction proceeded in the crystal lattice. The direction of the absorption maximum corresponds to the electronic transition moment vector of the 535 nm band.

The color intensity of the photogenerated colored crystal of the surface B was weaker than that of the surface A. The surface B had pale red color at a certain angle. When the crystal was rotated as much as 90°, the color changed to pale orange, which has an absorption band at 495 nm. The polar plots of absorbances at 495 and 535 nm indicate that the electronic transition moment of the 495 nm band is perpendicular to that of the 535 nm band. The absorption anisotropy of the 535 nm band on the surfaces A and B indicates that the direction of its electronic transition moment of the closed-ring isomer in the crystal can be expressed by the arrow shown in Figure 1. The transition moment vector of the 535 nm band is approximately perpendicular to the surface B. This is the reason why the intensity of the color of the surface B was weak.

The electronic transition moment vector of the longest absorption band (λ_{max} = 535 nm) of **1b** is considered to be in long-axis of the closed-ring isomer **1b** as shown in Figure 2[5]. When the conversion from **1a** to **1b** was low, any crystal shape change was not 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 long-axis of **1a** packed in the crystal. We carried out X-ray crystallographic analysis of crystal **1a** to confirm the relation between the electronic transition of **1b** and the crystal packing of **1a**. The ORTEP drawing of **1a** indicates that **1a** is packed in a photoreactive anti-parallel 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[6]. The direction of the arrow shown in Figure 1 coincides with



crystal **1a** crystal **2a**

FIGURE 1 Shape of crystals **1a** and **2a**. The arrows indicate the direction of electronic transition moments of the closed-ring isomers at the longest absorption.

the direction of long-axis of the open-ring isomer. This result confirms that the photocyclization reaction proceeds in the crystal lattice of the open-ring isomer **1a**.

The molecular structures of **1a** and **1b** were superimposed with keeping the center of gravity by the independent X-ray crystallographic analyses. The results revealed that during the cyclization reaction only four atoms (the reacting carbon and sulfur atoms) changed their positions and others remained at almost similar positions. The result accounts for the rapid cyclization reaction rate (< 10 ps) in the crystalline phase[7].

Photochromism of **2a** in the single-crystalline phase

3a undergoes a thermally irreversible and fatigue resistant photochromic reaction in solution[8]. The benzothiophene aryl groups are effective to provide a fatigue resistant property to photochromic diarylethenes. The compound is, however, photochemically inactive in the crystalline phase.

Single crystal **2a** was obtained by recrystallization from hexane/toluene as a shape shown in Figure 1. Upon irradiation with 366 nm light the single crystal turned green, and the green color disappeared by irradiation with visible light ($\lambda > 450$ nm). The ORTEP drawing of **2a** indicates that **2a** is packed in a photoreactive anti-parallel conformation in the crystal. The distance between the reacting carbon atoms was determined to be 0.384 nm, which is close enough for the reaction[6].

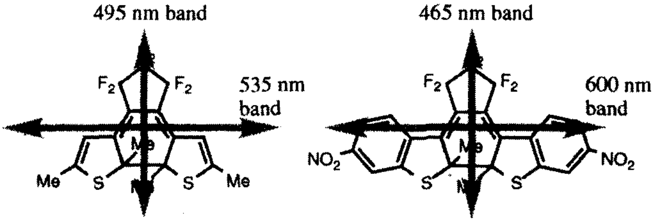
Fatigue resistant characteristic of the crystal **2a** was examined by alternate irradiation with 405 nm light and visible light ($\lambda > 490$ nm). Absorbance at 600 nm reached to ca. 0.8 by irradiation with 405 nm light (9.5 mW) for 5 sec. The 600 nm band disappeared by irradiation with visible light ($\lambda > 490$ nm) for 5 sec. The coloration/decoloration cycles were repeated many times and fatigue resistant property was examined[9]. The absorbance of the closed-ring isomer remained over 90% of the first irradiation cycle even after 10,000 cycles.

The photogenerated colored crystal was observed under polarized light. Before photoirradiation the crystal (surface A) was colorless.

Upon irradiation with 366 nm light the crystal turned yellow at a certain angle. When the crystal was rotated as much as 90°, the color turned blue. The yellow color reappeared at 180°. The clear dichroism from yellow to blue indicates that the closed-ring isomer is regularly oriented in the crystal and the photochromic reaction proceeds in the crystal lattice.

The polarized absorption spectra of the colored crystal were measured. The maximum absorbance of the blue color at 600 nm appeared at 90 and 270°. The maximum absorbance of the yellow color at 465 nm appeared at 0 and 180°. The polar plots of the absorbances at 465 and 600 nm indicate that the two transition moment vectors of the 465 and 600 nm bands are perpendicular to each other on the surface A.

According to the molecular orbital calculation for the closed-ring isomer of **3a**[10], the transition moment vector of the longest absorption band (528 nm, f = 0.162) is in long-axis of the closed-ring isomer and the second band (430 nm, f = 0.101) is perpendicular to that. The electronic transition property is considered to be maintained even when nitro groups were introduced at 6 and 6'-positions of the benzothiophene rings. Therefore, the electronic transition moment vectors of the longest absorption band (λ_{max} = 600 nm) and the second band (λ_{max} = 465 nm) of **2b** are assigned to the long- and short-axes of **2b**, respectively. The X-ray crystallographic analysis of **2a** and the transition moment vector of



1b **2b**

FIGURE 2 Structures of the closed-ring isomers and the electronic transition moments.

2b indicate that **2a** was converted to **2b** with keeping the position of each molecule.

Acknowledgments

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