

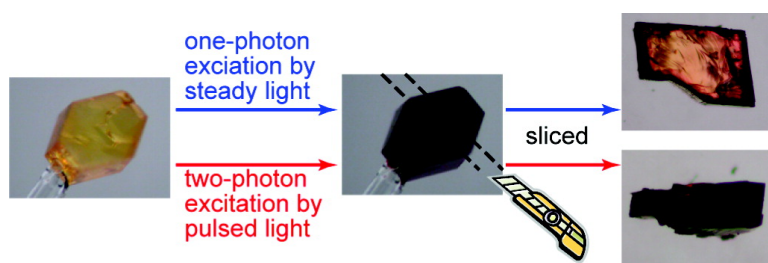
Article

X-ray Diffraction Analysis of Photochromic Reaction of Fulgides: Crystalline State Reaction Induced by Two-Photon Excitation

Jun Harada, Ryo Nakajima, and Keiichiro Ogawa

J. Am. Chem. Soc., **2008**, 130 (22), 7085-7091 • DOI: 10.1021/ja800353u • Publication Date (Web): 09 May 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

X-ray Diffraction Analysis of Photochromic Reaction of Fulgides: Crystalline State Reaction Induced by Two-Photon Excitation

Jun Harada,* Ryo Nakajima, and Keiichiro Ogawa*

Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8902, Japan

Received January 15, 2008; E-mail: harada@ramie.c.u-tokyo.ac.jp; ogawa@ramie.c.u-tokyo.ac.jp

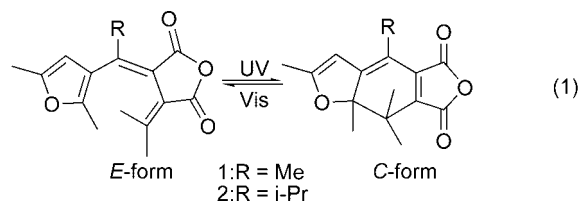
Abstract: Although most fulgides show their photochromism in the solid state, crystal structure changes accompanying the photochromism have not been previously observed. The photochromic reactions have been so far considered to take place on surfaces or at defects of the crystals or to proceed with destruction of the crystals. In this study we have succeeded in observing crystal structure changes accompanying the photochromism of fulgides using X-ray diffraction analysis. Detection of the photoproducts in the crystal structures was not possible when the single crystals of the fulgides were irradiated with steady UV light. Two-photon excitation by pulsed laser light was essential to produce a sufficient amount of the photoproducts without significant deterioration in the quality of the crystals.

Introduction

Light-induced reversible color change of substances is known as photochromism and has attracted much attention from various fields of chemistry.¹ Many physicochemical studies on photochromism have been carried out from scientific viewpoints, in order to elucidate the mechanisms of the photoprocesses, and determination of the molecular structures of uncolored and colored species. From a practical point of view, photochromic compounds have recently attracted increasing attention for their existing (e.g., ophthalmic lenses) or potential applications (e.g., optical information storage, optical switches).

Fulgides, which are derivatives of dimethylene-succinic anhydride, belong to one of the most important classes of photochromic compounds. Since the first report by Stobbe more than a century ago,² many studies have been carried out on the photochromism of the compounds.³ In 1981, Heller succeeded in inventing some highly promising fulgides, i.e., furylfulgides.⁴ UV light irradiation of the furylfulgides changes the stable *E*-form,⁵ which is palely colored, typically yellow, to the deeply colored, typically red, closed *C*-form [eq 1]. The colored *C*-form

reverts back to the original *E*-form by irradiation with visible light. The *E*-form can be photoconverted to the *C*-form almost quantitatively. The furylfulgides do not show thermal interconversion and are fatigue resistant. The advent of the highly promising compounds stimulated interest in the photochromism of fulgides, and many studies have subsequently been carried out.



Most photochromic compounds exhibit their photochromism in many environments, such as solutions, polymer matrices, sol-gel matrices, and the solid state. Photochromism in crystals, in particular, that of diarylethene crystals, has been studied extensively.⁶ Photochromism in crystals has some advantages over that in other media, e.g., higher quantum yields of

- (1) (a) *Photochromism. Techniques of Chemistry*; Brown, G. H., Ed; Wiley-Interscience: New York, 1971; Vol. III. (b) *Photochromism. Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990. (c) *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Topics in Applied Chemistry: Vol. 1, Photochromic Families, Vol. 2, Physicochemical Studies, Biological Applications, and Thermochromism; Plenum Press, New York, 1999. (d) Photochromism: Memories and Switches, Special issue of: *Chem. Rev.* **2000**, *100*, 1683–1890.
- (2) Stobbe, H. *Ber.* **1904**, *37*, 2236–2240.
- (3) (a) For reviews, see: Whittall, J. in reference 1b, chapter 9. (b) Fan, M.-G.; Yu, L.; Zhao, W. in reference 1c, vol. 1 chapter 4. (c) Yokoyama, Y. *Chem. Rev.* **2000**, *100*, 1717–1739.
- (4) (a) Darcy, P. J.; Heller, H. G.; Strydom, P. J.; Whittall, J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 202–205. (b) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341–343.
- (5) In the *E*-form, one of the carbonyl groups of the acid anhydride moiety and the furan ring are in the *E* configuration.

- (6) (a) Kobatake, S.; Yamada, T.; Uchida, K.; Kato, N.; Irie, M. *J. Am. Chem. Soc.* **1999**, *121*, 2380–2386. (b) Kobatake, S.; Yamada, M.; Yamada, T.; Irie, M. *J. Am. Chem. Soc.* **1999**, *121*, 8450–8456. (c) Yamada, T.; Kobatake, S.; Muto, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 1589–1592. (d) Irie, M.; Lifka, T.; Kobatake, S.; Kato, N. *J. Am. Chem. Soc.* **2000**, *122*, 4871–4876. (e) Kodani, T.; Matsuda, K.; Yamada, T.; Kobatake, S.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 9631–9637. (f) Kobatake, S.; Shibata, K.; Uchida, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 12135–12141. (g) Yamada, T.; Kobatake, S.; Irie, M. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2179–2184. (h) Irie, M.; Kobatake, S.; Horichi, M. *Science* **2001**, *291*, 1769–1772. (i) Morimoto, M.; Kobatake, S.; Irie, M. *J. Am. Chem. Soc.* **2003**, *125*, 11080–11087. (j) Kobatake, S.; Irie, M. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 195–210. (k) Morimoto, M.; Irie, M. *Chem. Commun.* **2005**, 3895–3905. (l) Takami, S.; Kuroki, L.; K.; Irie, M. *J. Am. Chem. Soc.* **2007**, *129*, 7319–7326. (m) Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. *Nature* **2007**, *446*, 778–781.

photocoloration processes and restriction of unfavorable side reactions. Moreover, in cases where the reactions take place in the crystalline state, X-ray crystal structure analysis can provide detailed insights into the mechanism of the reactions.^{7,8}

Fulgides also show their photochromism in crystals, where the major side reaction, i.e., the *E*–*Z* photoisomerization, hardly takes place. The photochromism of fulgide crystals, however, has not been thoroughly investigated, which contrasts with that of diarylethene crystals.⁶ Although a few spectroscopic studies on photochromism in fulgide crystals have been reported,⁹ X-ray diffraction analysis has not succeeded in demonstrating the structural changes accompanying the photochromism in crystals.¹⁰

To detect the photoproducts using X-ray diffraction analysis, their yields in the crystals should be at least a few percent, preferably more. The accumulation of the photoproducts without destruction of the crystal is often very difficult, especially for organic photochromic crystals. Therefore, crystal structure changes in only a few classes of photochromic compounds have been reported so far.^{6–8}

In this study we investigated the photochromic reactions in the single crystals of fulgides (*E*)-2-[1-(2,5-dimethyl-3-furyl)-ethylidene]-3-isopropylidenesuccinic anhydride (**1**) and (*E*)-2-[1-(2,5-dimethyl-3-furyl)-2-methylpropylidene]-3-isopropylidenesuccinic anhydride (**2**). When the photoreactions in the crystals were carried out by irradiation with steady UV light, X-ray diffraction analysis of the reaction was not successful. Only when the reactions were induced through two-photon excitation by a pulsed laser light did we succeed in observing the crystal structural changes accompanying the photochromic reactions.

In this paper, first we will present our experimental results. Then we will describe what problems we often have in observing the crystal structure changes using X-ray diffraction analysis. We will elaborate on how the photoreactions proceed in crystals, substantiating it with some experimental data. Finally we will show how we have resolved these problems using a two-photon excitation technique.

Experimental Section

Sample Preparation. Melting points were determined on a micro hot stage apparatus and are uncorrected. The compounds **1** and **2** were prepared according to the method described in the literature.^{4a} Slow evaporation of hexane solutions of the compounds gave good quality single crystals. Yellow crystals of **1** (mp 124.5–125.5 °C) and **2** (mp 126.0–126.5 °C) were used for X-ray diffraction analysis.

Spectral Measurements. Diffuse UV–vis reflectance spectra were measured on a Jasco V-550 spectrometer equipped with an integrating sphere accessory. NaCl powder (MERCK Suprapur) was ground and used as the diluent and the reference. The ground sample crystals of **1** and the NaCl powder were put in a glass vial and mixed together by rolling and shaking the vial by hand. The mixed powder was used as the sample.

Photoirradiation. A Nd:YAG pumped optical parametric oscillator (Quanta-Ray Pro 250 and MOPO SL, a 5 ns pulse duration, 10 Hz repetition rate) was used for laser irradiation of the crystals. The laser beam was depolarized to minimize the effects of presumed optical anisotropy. For steady light irradiation, a SAN-EI UVF-352S high pressure mercury lamp was used for the photocoloration of crystals. Each emission line of 365, 405 nm was isolated by using a corresponding band-pass filter (ASAHI Spectra MX0365, MX0405) and a heat absorption filter. A SAN-EI UVF-202S mercury–xenon lamp with a HOYA Y52 filter and a heat absorption filter was used for the bleaching reaction of the colored crystal.

Single Crystal X-ray Diffraction Analysis. All of the diffraction measurements were carried out using a Bruker SMART 1000 CCD area detector system with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The temperature of the crystals was controlled using a Cryostream (Oxford Cryosystems) open-flow gas cryostat. The temperature in the nozzle was held constant within $\pm 0.2 \text{ K}$ during the measurement. Approximately 2500 frames of data were collected for each data set using a narrow-frame method with scan widths of 0.3° in ω and 5 s exposure times. The frames were integrated with Bruker SAINT V6.45A ($2\theta_{\text{max}} = 60.0^\circ$). Unit cell parameters were determined by least-squares refinement of the three-dimensional centroids of several thousand reflections. The intensities were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied to the data using the SADABS program. The structure was solved by a direct method with SHELXS-97.¹¹ Structures were refined by full-matrix least-squares on F^2 using SHELXL-97.¹² For nondisordered crystals, all H atoms were located from difference Fourier electron density maps and refined isotropically, and all C and O atoms were refined anisotropically. The difference Fourier maps were drawn using SHELXTL. Details of the structure refinement of the disordered crystals have been deposited as Supporting Information. The crystal and experimental data are summarized in Tables 1 and 2.

Determination of the Reaction Yields in Single Crystals. The photochromic reaction yields in the single crystals of **1** and **2** were determined based on the fact that UV light irradiation of the toluene solution of the compounds converts the *E*-form into the *C*-form quantitatively.^{4a,13b} After the photoreaction in a single crystal, the UV–vis spectrum of the toluene solution of the crystal was measured. The solution was then irradiated with 365 nm light until the spectrum of the reacted solution did not show any further change. The spectrum of the final solution is that of the *C*-form. The absorbance at the λ_{max} of the *C*-forms (ca. 495 nm) in the spectra is proportional to the amount of the *C*-form in the solution. Thus the percentage of the *C*-form in the crystal, which is equal to that in the initial solution, is calculated from the ratio of the absorbances of the initial and the final spectra. UV–vis absorption spectra of solutions were measured on a Jasco V-560 spectrometer or on a Jasco Ubest50 spectrometer. Spectroscopic-grade toluene (Spectrosol, Dojin) was used as received.

Results

Photochromism of Fulgide Crystals with Steady Light.

Compound **1** is the best-known photochromic fulgide, which undergoes quantitative conversion into the *C*-form in solution upon irradiation with UV light.⁴ The compound shows no thermal reaction, and the *C*-form is stable even at 100 °C in solution. Compound **2**, which has an isopropyl group substituted for a methyl group of **1**, exhibits photochromic properties similar to those of **1** with a higher quantum yield for the coloring reaction.¹³ Although the spectroscopic studies of the single crystals of **1** and **2** suggested that the photoreactions took place in the bulk of the crystals,⁹ X-ray diffraction analysis has not

(7) Harada, J.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 5809–5810.

(8) Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 8106–8107.

(9) (a) Tayu, T.; Kurita, S. *J. Phys. Chem. Solids* **1996**, *57*, 475–482. (b) Tayu, T.; Fujisawa, M.; Kurita, S. *J. Electron Spectrosc. Relat. Phenom.* **1996**, *78*, 411–414. (c) Kobatake, S.; Irie, M. *Chem. Lett.* **2004**, *33*, 904–905.

(10) (a) Kaftory, M. *Acta Crystallogr.* **1984**, *C40*, 1015–1019. (b) Kumar, V. A.; Venkatesan, K. *Acta Crystallogr.* **1993**, *B49*, 896–900. (c) Khedhiri, L.; Corval, A.; Casalegno, R.; Rzaigui, M. *J. Phys. Chem. A* **2004**, *108*, 7473–7478.

Table 1. Crystal Data and Structure Refinements for Compound 1

compound	1 (before irradiation)	1 (irradiated with 365 nm light)	1 (irradiated with 405 nm light)	1 (irradiated with 742 nm laser light)	1 (irradiated with 742 nm laser light then visible light)
crystal size (mm ³)	0.80 × 0.80 × 0.30	0.70 × 0.50 × 0.40	0.50 × 0.50 × 0.40	0.40 × 0.40 × 0.20	0.40 × 0.40 × 0.20
empirical formula			C ₁₅ H ₁₆ O ₄		
formula weight			260.28		
temperature (K)			90		
crystal system			monoclinic		
space group			<i>P</i> 2 ₁ / <i>n</i>		
<i>a</i> (Å)	12.5389(8)	12.5365(9)	12.5388(9)	12.5342(12)	12.5318(14)
<i>b</i> (Å)	7.6203(5)	7.6211(6)	7.6194(6)	7.6101(8)	7.6226(8)
<i>c</i> (Å)	14.5275(9)	14.5294(11)	14.5373(11)	14.5653(14)	14.5394(16)
β (deg)	109.201(1)	109.180(1)	109.245(1)	108.621(2)	109.285(2)
<i>V</i> (Å ³)	1310.89(14)	1311.11(17)	1311.25(17)	1316.6(2)	1310.9(2)
<i>Z</i>			4		
reflections collected	19 574	19 736	19 233	18 470	17 184
independent reflections	3815	3829	3825	3814	3783
<i>R</i> _{int}	0.0213	0.0182	0.0184	0.0359	0.0378
data/restraints/parameters	3815/0/236	3829/0/236	3825/0/236	3814/0/199	3873/0/236
goodness-of-fit on <i>F</i> ²	1.027	1.018	1.046	1.099	1.046
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0387	0.0374	0.0412	0.0624	0.0466
<i>wR</i> (<i>F</i> ²) (all data)	0.1101	0.1067	0.1176	0.1721	0.1248
δ_{\min} (e Å ⁻³)	-0.258	-0.187	-0.178	-0.235	-0.209
δ_{\max} (e Å ⁻³)	0.398	0.422	0.516	0.623	0.443

Table 2. Crystal Data and Structure Refinements for Compound 2

compound	2 (before irradiation)	2 (irradiated with 365 nm light)	2 (irradiated with 742 nm laser light)	2 (irradiated with 742 nm laser light then visible light)
crystal size (mm ³)	0.80 × 0.50 × 0.30	0.70 × 0.50 × 0.20	0.50 × 0.40 × 0.40	0.50 × 0.40 × 0.40
empirical formula			C ₁₇ H ₂₀ O ₄	
formula weight			288.33	
temperature (K)			90	
crystal system			monoclinic	
space group			<i>P</i> 2 ₁ / <i>c</i>	
<i>a</i> (Å)	8.1636(5)	8.1659(7)	8.2761(10)	8.1632(5)
<i>b</i> (Å)	18.8195(12)	18.8346(17)	18.741(2)	18.8242(12)
<i>c</i> (Å)	10.5104(7)	10.5061(9)	10.5382(13)	10.5207(7)
β (deg)	110.805(1)	110.755(2)	111.036(2)	110.749(1)
<i>V</i> (Å ³)	1509.47(17)	1511.0(2)	1525.6(3)	1511.82(17)
<i>Z</i>			4	
reflections collected	23 092	22 973	21 557	21 350
independent reflections	4408	4423	4456	4401
<i>R</i> _{int}	0.0204	0.0241	0.0565	0.0445
data/restraints/parameters	4408/0/270	4423/0/270	4456/0/241	4401/0/270
goodness-of-fit on <i>F</i> ²	1.058	1.061	1.103	1.042
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0377	0.0415	0.0769	0.0483
<i>wR</i> (<i>F</i> ²) (all data)	0.1052	0.1157	0.1900	0.1237
δ_{\min} (e Å ⁻³)	-0.157	-0.163	-0.344	-0.241
δ_{\max} (e Å ⁻³)	0.439	0.468	0.391	0.416

yet succeeded in demonstrating the structural changes accompanying the reactions.^{10c}

Figure 1 shows the diffuse reflectance spectra of a powder sample of **1**. Only absorption bands of *E*-form ($\lambda_{\max} = 288$ and 345 nm) were observed before irradiation. After irradiation with UV light of a Hg lamp (365 nm, 28 mJ/cm², 1 min) the band intensities of the *E*-form decreased greatly, and the bands of the *C*-form ($\lambda_{\max} = 272$ and 512 nm) developed in the spectrum. These spectral changes accompanying the photoreaction are similar to those in the hexane solution^{4a} and show that the photocoloration in the solid state solution can proceed in fairly good yields.

- (11) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.
 (12) Sheldrick, G. M. *SHELXL-97; program for crystal structure refinement*; Universität Göttingen:Göttingen, 1997.
 (13) (a) Yokoyama, Y.; Goto, T.; Inoue, T.; Yokoyama, M.; Kurita, Y. *Chem. Lett.* **1988**, 1049–1052. (b) Yokoyama, Y.; Inoue, T.; Yokoyama, M.; Goto, T.; Iwai, T.; Kera, N.; Hitomi, I.; Kurita, Y. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3297–3303.

The irradiation of steady UV light (365 nm, 25 mW/cm², 3 h at room temperature) on a single crystal of **1** changed its color from yellow to dark red. X-ray diffraction analysis of the

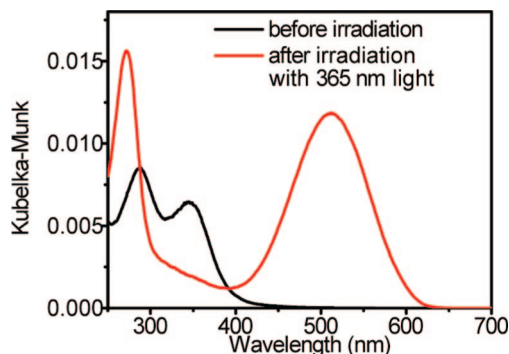


Figure 1. Kubelka–Munk spectra of (*E*)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride (**1**) in NaCl (0.005 wt %) before and after irradiation at 365 nm.

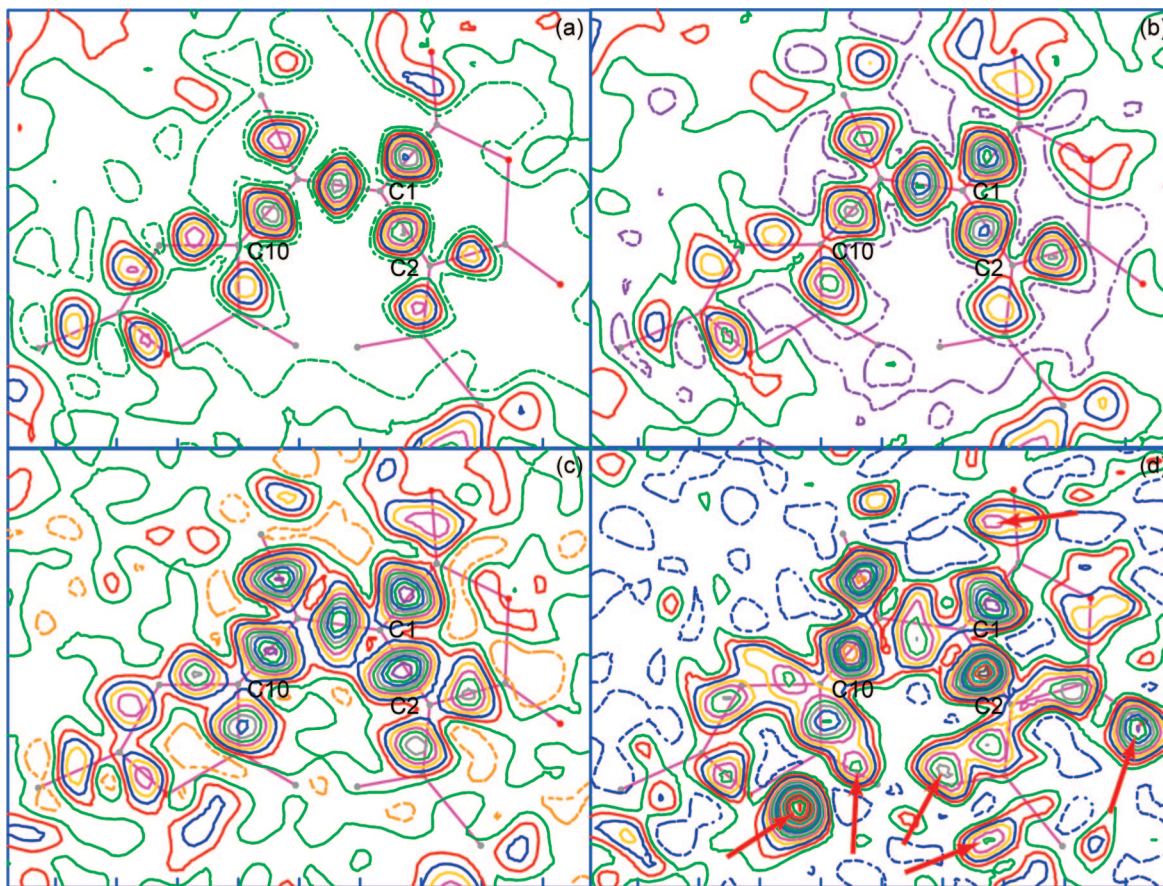


Figure 2. Difference Fourier maps of (*E*)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride (**1**). The section of each map contains C1, C2, and C10. The contour lines are at $0.05 \text{ e } \text{\AA}^{-3}$ intervals. Negative contours are indicated by broken lines. (a) Before irradiation; (b) after irradiated at 365 nm; (c) after irradiated at 405 nm; (d) after irradiated at 742 nm (pulsed light). The peaks corresponding to the photoproduct are indicated by arrows.

irradiated crystal was carried out.¹⁴ For comparison, the crystal structure of a nonirradiated crystal of **1** was also determined,¹⁵ and a difference electron density map was shown in Figure 2a. The lattice parameters of the nonirradiated and UV-irradiated crystals showed no significant differences (Table 1). In the difference electron density map of the irradiated crystal, there were no significant residual peaks that would be expected for the photoinduced *C*-form (Figure 2b). The irradiation of another crystal of **1** with longer wavelength light (405 nm, 54 mW/cm², 5 h at room temperature) and subsequent X-ray analysis of the crystal at 90 K also failed to locate the *C*-form in the crystal (Table 1 and Figure 2c).

Steady UV light irradiation to single crystals of **2** and subsequent X-ray diffraction analysis of them gave results similar to those for **1**. The irradiation of steady UV light (365 nm, 120 mW/cm², 2 h at room temperature) on a single crystal of **2** changed its color from orange to dark red.¹⁶ Any structural

changes were not observed by diffraction analysis of the reacted crystal: The lattice parameters of the nonirradiated and irradiated crystals¹⁷ showed no significant differences (Table 2). The difference maps of both crystals gave no significant residual peaks ascribable to the *C*-form (Supporting Information).

Photochromism of Fulgide Crystals with Pulsed Laser Light. The above results show that the *C*-forms in the crystals produced by irradiation with steady UV light cannot be observed by X-ray diffraction analysis. The following results show that the *C*-forms produced through two-photon excitation by a pulsed laser can be easily observed by X-ray diffraction analysis. The differences between the photoreactions in single crystals induced by steady UV light irradiation and by two-photon excitation will also be discussed in a later section.

A single crystal of **1** was irradiated at room temperature with a high-power output of a pulsed laser (300 mJ/cm² per pulse, 90 min) with a wavelength of ca. 742 nm, which is approximately twice the λ_{max} of the *E*-form. The color of the crystal changed from yellow to dark red, almost black. X-ray diffraction analysis of the laser irradiated crystal was carried out at 90 K. Figure 2d shows the difference electron density map of the laser irradiated **1**. There appeared several new peaks that were not observed in the maps of the nonirradiated or the steady light irradiated crystals. Those peaks can be assigned to six atoms of the *C*-form produced in the crystal. The refinement was

(14) In order to obtain good quality data, all of the X-ray diffraction measurements were carried out at 90 K after the photoreactions at room temperature.

(15) The crystal structure of **1** at 90 K is essentially identical to that at other temperatures reported in the literature. (a) Yoshioka, Y.; Tanaka, T.; Sawada, M.; Irie, M. *Chem. Lett.* **1989**, 19–22. (b) Ulrich, K.; Port, H. *J. Mol. Struct.* **1990**, 218, 45–50. (c) Yokoyama, Y.; Ogawa, K.; Iwai, T.; Shimazaki, K.; Kajihara, Y.; Goto, T.; Yokoyama, Y.; Kurita, Y. *Bull. Chem. Soc. Jpn.* **1996**, 69, 1605–1612. References 9c and 10c.

(16) Crystals of **2** are more photoreactive than those of **1**. The yellow crystals of **2** easily turn orange under indoor lighting.

(17) The crystal structure of **2** at 90 K is essentially identical to that at room temperature reported in the literature. Reference 15c.

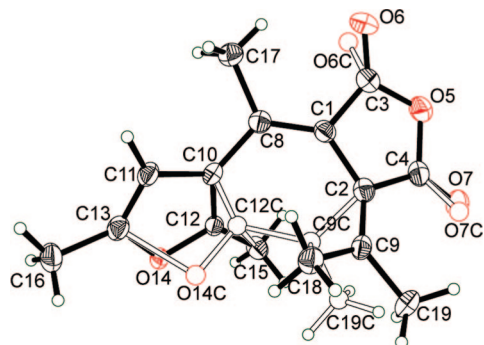


Figure 3. Crystal structure of (*E*)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride (**1**) after laser light irradiation. The photoinduced *C*-form is drawn with open bonds.

carried out with a disordered model, and the population of the *C*-form was determined to be 5.5(3) % (Figure 3). The same crystal was irradiated with visible light (500 nm) at room temperature. The crystal returned to its original yellow color. X-ray diffraction analysis of the crystal was then carried out at 90 K. Only the *E*-form was observed, and the above-mentioned residual peaks of the *C*-form were not detected. This is the first observation of crystal structural changes accompanying the photochromism of fulgides. Although the quality of the crystals deteriorated after prolonged laser irradiation, and X-ray analysis of crystals with larger population of the *C*-form has not yet succeeded, the above results show that the photochromic reaction in the crystal of **1**, which was suggested to induce a loss of crystalline order,^{10c} does take place in the crystal lattice and that the reversible changes of the molecular structure can be observed by X-ray diffraction analysis.

Photoreactions and X-ray diffraction analysis of the crystal of **2** were also carried out similarly to those of **1**. A single crystal of **2** was irradiated with laser light (742 nm, 100 mJ/cm² per pulse, 75 min) at room temperature. X-ray diffraction analysis of the crystal gave the structure of the *C*-form, and its population was refined to be 27.8(2)% (Figure 4a).

The overlapping structures of the *E*- and *C*-forms (Figure 4a) confirmed that the photochromic reaction took place through the 6 π -electrocyclization of the hexatriene moiety (C9, C2, C1, C8, C10, and C12), and the moiety became more planar in the *C*-form (Figure 4b).

The *E*-form of **2** in the crystal has a helical chirality, and the *C*-form has an asymmetric carbon atom (C12C). Each crystal consists of 1:1 racemates of the *E*- and *C*-forms, because of its centrosymmetric space group (*P*2₁/*c*). Thus the photoreaction converted the racemic *E*-forms into the racemic *C*-forms in the crystal as a whole. However, the observed molecular structure of the *C*-form overlapping with the *E*-form shows that the photocyclization in the crystal took place enantioselectively.

It is also notable that the produced *C*-form overlaps fairly well with the original *E*-form in the crystal. This means that the reaction took place without large atomic movements that are inhibited by the surrounding molecules in crystals. This should be the reason why the photochromic reaction proceeded in good yields even in the solid state, as shown in Figure 1.

The same crystal of **2** was irradiated with visible light ($\lambda > 500$ nm) at room temperature, and the color of the crystal returned to the original color. X-ray diffraction of the crystal showed that the photoinduced *C*-form disappeared and that only the original *E*-form existed in the crystal. These results show that we succeeded in demonstrating the reversible structure

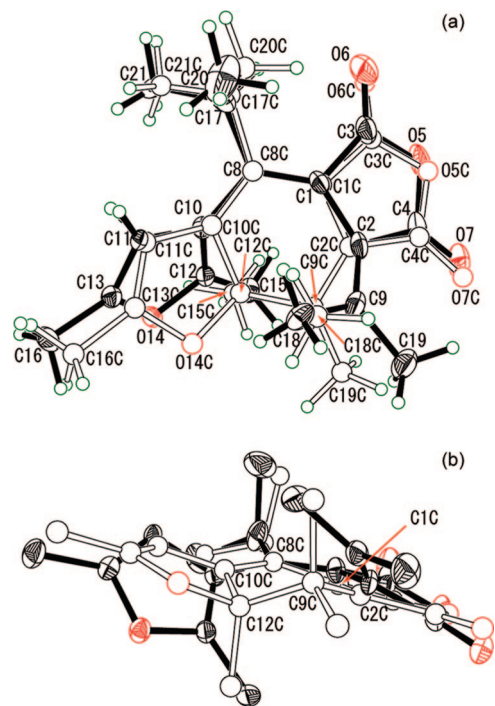


Figure 4. Crystal structure of (*E*)-2-[1-(2,5-dimethyl-3-furyl)-2-methyl-propylidene]-3-isopropylidenesuccinic anhydride (**2**) after laser light irradiation. The photoinduced *C*-form is drawn with open bonds. (a) Top view. (b) Side view. The hydrogen atoms in the side view were omitted for clarity.

changes accompanying the photochromic reactions of fulgide **2** in the crystal lattice.

Discussion

Advantages of Two-Photon Excitation for Crystal Structural Analysis of Photochromism. Now we will explain the reasons why the photochromic crystal structural changes of the fulgides could not be observed when they were induced by steady UV light irradiation. Then we will present the reasons why the photoreactions induced by two-photon excitation led to the successful determination of the crystal structural changes.

To observe the crystal structure changes accompanying photochromic reactions, there seem to be two major obstacles: insufficient yields of the photoproducts and the destruction of crystals with the progress of the reactions. The difficulty in accumulating a sufficient amount of the colored species in crystals is caused by insufficient penetration of incident light and backward photoreactions. A high density of molecules in crystals makes the incident light drop off drastically when it goes through the crystals. Accordingly, the light can hardly penetrate into the bulk of the crystals. When the photoreaction is carried out by irradiating strongly absorbed light, the reaction thus takes place only near the surface of the crystals. Although light with a much longer wavelength corresponding to the absorption tail of the compounds could penetrate into the crystals,^{18,19} such light usually causes backward photochromic reactions and erases the colored photoproducts in the crystals. As a result, there seems to be no wavelength of light that could

(18) (a) Enkelmann, V.; Wegner, G.; Novak, K.; Wagener, K. B. *J. Am. Chem. Soc.* **1993**, *115*, 10390–10391. (b) Novak, K.; Enkelmann, V.; Wegner, G.; Wagener, K. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1614–1616.

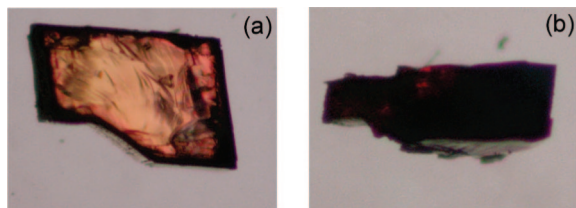


Figure 5. Photographs of cross sections of the photoreacted single crystals of (*E*)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride (**1**). (a) Irradiated with 405 nm steady light; (b) irradiated with 742 nm pulsed laser light.

be expected to produce a sufficient amount of the photoproducts to be detected by X-ray diffraction analysis.

The fulgides studied in the present work, however, photoreacted in fairly good yields even in their single crystals. As described above, X-ray diffraction analysis of the single crystal of **1** irradiated with 405 nm light showed no sign of the *C*-form, but a UV–vis spectrum of the same crystal dissolved in toluene showed that the crystal contained approximately 10% of the *C*-form. A similar result was obtained for the single crystal of **2** irradiated with 365 nm light. Although X-ray diffraction analysis using the crystal gave no sign of the *C*-form, approximately 13% of the *C*-form was found to exist in the crystal.

The fact that the UV irradiation of the single crystals of **1** and **2** yielded a considerable amount of colored species can be explained as follows. When the single crystals were irradiated with UV light, the incident light could initially penetrate only near the surfaces of the crystals. The irradiated molecules in the crystals were converted to the colored species almost quantitatively, and the absorbance of the reacted part of the crystals decreased drastically, as expected from Figure 1. The incident light could then penetrate farther inside the crystals, where the photoreaction proceeded further. By repeating these processes, a substantial amount of the molecules in the crystals were converted to the colored species.²⁰

If the reactions in the single crystals of **1** and **2** follow the above steps, the molecules near the crystal surfaces are converted to the *C*-forms, and those in the bulk of the crystals are almost intact. This picture of the reaction is supported by Figure 5a, which is a photograph of a slice of a single crystal of **1** irradiated with 405 nm light.²¹ Figure 5a shows that the photocoloration by 405 nm irradiation is limited to the region only near the surfaces of the crystal and that the internal region of the crystal remained unreacted. The distribution of the colored species in the single crystal is consistent with the above-mentioned processes of the reaction.

In cases of the crystals of **1** and **2**, the *C*-forms could not be detected by X-ray diffraction analysis, despite the fact that the

populations of the *C*-forms were larger than 10%. This can be explained in terms of the deterioration of the crystals with progress of the reaction, although the reacted crystals gave sharp Bragg reflections in X-ray diffraction and did not show apparent disintegration. When the single crystals of the fulgides were irradiated with UV light, the concentrations of the *C*-forms near their surfaces became so high that the crystals could not accommodate the products in their original lattices. Thus the highly reacted regions could not maintain the crystal lattices and did not contribute to the Bragg reflections. Only the inner regions of the crystals, where the reactions scarcely proceeded, kept the crystal lattices and contributed to the Bragg reflections. Therefore, X-ray diffraction analysis of the reacted crystals gave the same lattice parameters as those of the unreacted ones, and only the structures of the unreacted molecules were observed, even when a substantial amount of the products existed in the crystals. We therefore conclude that the reason why X-ray diffraction analysis failed to detect the *C*-forms in the UV light irradiated crystals of **1** and **2** is not because there were not a sufficient amount of the *C*-forms but because the photoreactions did not proceed with maintaining the crystal lattices.

On the other hand, when the crystals were irradiated with pulsed laser light, X-ray diffraction analysis easily detected the reaction products in the crystals. It should be noted that the *C*-form with only 5% population in the laser-irradiated single crystal was observed but that the *C*-form with 10% population in the UV light irradiated crystal could not be detected. The sharp contrast between the results brought about by the steady and pulsed laser light irradiation should be caused by the difference in distribution of the products in the crystals. Figure 5b shows the photograph of a slice of a single crystal of **1** irradiated with pulsed laser light (742 nm). Compared to the steady light irradiated crystal (Figure 5a), the colored species distribute much more homogeneously. This means that the photoreaction induced by pulsed laser light took place more evenly throughout the crystal.

When the products distributed homogeneously in the crystals, X-ray diffraction analysis of the photoproducts is possible, if we use the crystals where the conversions were low enough to maintain the crystal lattice but high enough for the products to be detected. UV light irradiated crystals were reacted heterogeneously and had only regions where the concentrations of the products were too high or too low. We therefore conclude that homogeneous photoreaction and product distribution are prerequisites for detecting the products by crystal structure analysis.

For a photoreaction to take place homogeneously in crystals, the intensity of the incident light should not decrease drastically inside the crystals. The light should therefore be absorbed extremely weakly by the molecules in the crystals. Irradiation with pulsed laser light with a longer wavelength facilitates fulfillment of this reaction condition. The pulsed laser light with a wavelength of 742 nm used in this study is absorbed by the crystals of **1** and **2** through two-photon absorption,²² because the *E*-forms of both compounds do not show any one-photon absorption at that wavelength. Two-photon excitation by 742 nm light gives the molecule the same energy as that given by one-photon excitation at 371 nm and causes the same

- (19) (a) Some of the recent applications of the long wavelength irradiation to single crystal photoreactions. Zouev, I.; Lavy, T.; Kaftory, M. *Eur. J. Org. Chem.* **2006**, 416, 4–4169. (b) Turowska-Tyrk, I.; Trzop, E.; Scheffer, J. R.; Chen, S. *Acta Crystallogr.* **2006**, B62, 128–134. (c) Turowska-Tyrk, I.; Bkowiec, J.; Scheffer, J. R. *Acta Crystallogr.* **2007**, B63, 933–940. (d) Zheng, S.-L.; Vande Velde, C. M. L.; Messerschmidt, M.; Volkov, A.; Gembicky, M.; Coppens, P. *Chem.—Eur. J.* **2008**, 14, 706–713.
- (20) The photoconversion of **1** into its *C*-form is nearly quantitative even in highly concentrated solutions. This is because the colored form does not act as an internal filter for the activating radiation. Heller, H. G. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Soon, P.-S., Eds.; CRC Press: Boca Raton, FL, 1995; pp 173–183.
- (21) This piece of crystal was sliced off from the single crystal used for the X-ray diffraction analysis shown in Table 1 as “**1** irradiated with 405 nm”.

- (22) Two-photon absorption mentioned here is simultaneous absorption of two photons by individual molecules and does not mean two sequential one-photon absorption events.

photoreaction.^{23,24} The probability of two-photon excitation is much smaller than that of the one-photon excitation, and thus the light is absorbed only weakly by the crystals. By using this two-photon excitation technique, one of the authors has already succeeded in observing crystal structure changes accompanying the photochromism of salicylideneaniline.⁷ The present results support the idea that this technique can be applicable to various types of photochromic compounds.

Summary

In this study we have succeeded in observing the structural changes accompanying the photochromic reactions of fulgides in crystals. This is the first successful X-ray crystal structure analysis of photochromic reactions of fulgides. When single crystals were irradiated with steady UV light, X-ray diffraction analysis of the photoproducts was not successful despite the fact that the photochromic reactions proceeded considerably. Two-photon excitation by pulsed laser light enabled the detection of the photoproducts in the single crystals.

It is often the case that the molecular structural changes accompanying photoreactions in crystals can not be detected

by X-ray diffraction analysis, even when the spectral or color changes of the crystals are substantial. In such occasions, the following explanations have often been proposed: the reactions took place only on the surfaces or at the defects of the crystals. In fact, the failure of X-ray diffraction analysis of the photochromic reactions of fulgide crystals has been explained as above.^{10a,b} The results shown in this paper confirmed that the photochromic reactions of fulgides **1** and **2** take place in the crystal lattices at least to some extent, which was suggested by the spectroscopic studies.⁹

The present study shows that if the conditions of the photoreactions are changed, it could be possible to observe crystal structure changes, which are seemingly impossible under ordinary conditions. Two-photon excitation by pulsed laser light is a promising method for this purpose and could be applicable to many other photoreactive crystals.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Details of the structure refinement of the disordered crystals; ORTEP diagrams and difference electron density maps for **1** and **2** (PDF); X-ray crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA800353U

(23) The IR spectra of the reacted crystals confirmed that the product obtained by the laser light irradiation was identical to that obtained by steady UV light irradiation.

(24) Photochromic reaction by means of two-photon excitation was reported to take place in polymer matrix of **1**. Parthenopoulos, D. A.; Rentzepis, P. M. *J. Appl. Phys.* **1990**, *68*, 5814–5818.