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Photoinduced Rapid and Explosive Fragmentation of Diarylethene Crystals Having Urethane Bonding

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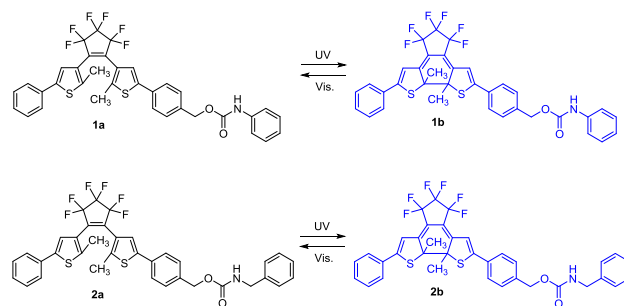
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ABSTRACT: Crystals of diarylethenes having urethane bonding exhibited photoinduced rapid and explosive fragmentation according to the photochromic reaction. The speed of the photogenerated crystal fragments was as fast as a few meters per second. The kinetic energy was independent of size, thickness, and volume of crystals, and depended on the crystal characters, such as crystal density and strength of intermolecular hydrogen bonding.

Mechanically responsive materials induced by light, heat, mechanical force, or other stimuli are of great interest to material science to construct molecular machines, molecular rotors, molecular robots, and artificial muscles.¹⁻⁵ Such mechanically responsive materials, especially induced by light, have been investigated using liquid crystalline polymers and molecular crystals containing photoresponsive molecules, such as azobenzene, spiropyran, anthracene, diarylethene, and so on.⁶⁻¹⁰ In the research of photoresponsive molecular crystals, we have focused on the photomechanical response of diarylethene crystals.¹¹⁻¹⁷ Diarylethene can reversibly undergo photoisomerization between the open-ring isomer and the closed-ring isomer upon alternating irradiation with ultraviolet (UV) and visible light. There are two stable conformations in the open-ring isomer, parallel and antiparallel conformations.¹⁸ Only from antiparallel conformation, the photocyclization reaction from the open-ring isomer to the closed-ring isomer can proceed. When diarylethene molecules exist in an antiparallel conformation and the distance between the reactive carbons is less than 4.2 Å, diarylethenes can undergo a photochromic reaction even in the crystalline phase.¹⁹ The geometrical structure change due to the photoisomerization causes the strain in crystal to result in the macroscopic crystal shape change of the bulk crystal. Various types of photomechanical motion in diarylethene crystals, such as contraction, expansion, bending, twisting, curling, and separation, have been reported.²⁰ In particular, the bending is the most common motion and the mechanical works using bending motion, such as a gearwheel rotation,²¹ lifting up heavy metal balls

having the 200~600 times weight of the crystal,²² and current switching,¹⁵ have been reported.

On the other hand, recently, the “photosalient effect” that means crystal jumping like popping of corn has been reported in other molecular crystals.^{23,24} The photosalient effect is well investigated by Naumov group and the phenomenon is seemed to be very rare.^{25,26} As one of the molecules that exhibit the photosalient effect, crystals of diarylethene, 1,2-bis(5-methyl-2-(2-pyridyl)-3-thiazolyl)-perfluorocyclopentene, have been reported.²⁷ However, further studies have not been so far performed. In the course of study on the photomechanical behavior of various diarylethene crystals, we found that diarylethenes having urethane bonding, 1-(2-methyl-5-(4-(phenylcarbaryl)methyl)phenyl)-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**) and 1-(2-methyl-5-(4-(benzylcarbaryl)methyl)phenyl)-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**2a**),



Scheme 1. Diarylethenes used in this work.

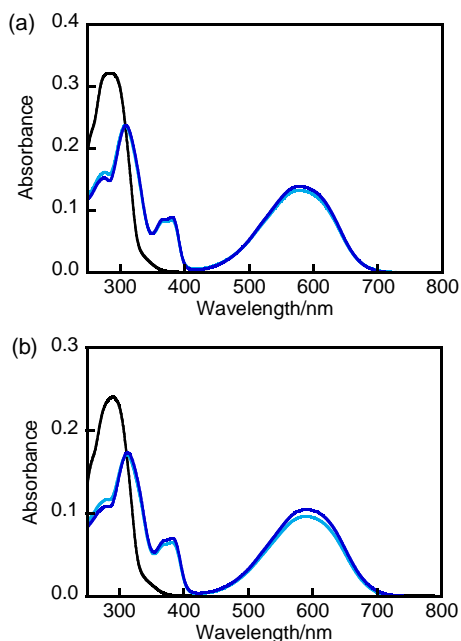


Figure 1. Absorption spectral change of diarylethenes **1a** (7.1×10^{-6} mol L⁻¹) (a) and **2a** (5.7×10^{-6} mol L⁻¹) (b) in dichloromethane: the open-ring isomer (black line), the closed-ring isomer (blue line), the photostationary state upon irradiation with 313 nm light (sky blue).

exhibit the photosalient effect; the photoinduced rapid and explosive fragmentation upon irradiation with 365 nm light. In this work, we investigated the influences of size (area), thickness, and volume of crystals on the fragmentation. Furthermore, the initial speed of fragmentation and the kinetic energy were estimated by the observation of the photoinduced crystal fragmentation behavior using a high-speed camera. The conversion from light energy to kinetic energy was also estimated.

Diarylethenes **1a** and **2a** underwent reversible photoisomerization between the colorless open-ring isomer and the colored closed-ring isomer upon alternating irradiation with ultraviolet (UV) and visible light, as shown in Scheme 1. **Figure 1** shows the absorption spectral changes of **1a** and **2a** in dichloromethane. Upon irradiation with 313 nm light, the colorless solutions of **1a** and **2a** turned blue, in which the visible absorption maxima were observed at 587 nm for both **1b** and **2b**. These spectral changes are ascribed to the photoisomerization from the open-ring isomer to the closed-ring isomer. The blue so-

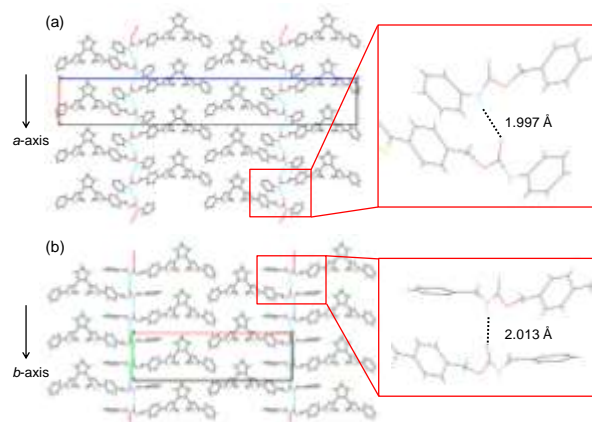


Figure 2. Molecular packings of single crystals of **1a** (a) and **2a** (b).

lution returned to the initial colorless solution upon irradiation with visible light (> 500 nm) and the absorption spectra also returned to those of **1a** and **2a**. The open- and closed-ring isomers were stable at room temperature in the dark. The molar absorption coefficient (ϵ), the photocyclization quantum yield ($\Phi_{o \rightarrow c}$), the photocycloreversion quantum yield ($\Phi_{c \rightarrow o}$), and the conversion from the open-ring isomer to the closed-ring isomer upon irradiation with 313 nm light were determined as shown in **Table 1**.

The photochromic performance of crystal **1a** and **2a** was examined. The crystals of **1a** and **2a** were prepared by recrystallization from acetone/*n*-hexane. To know molecular structure and packings in crystals, single crystal X-ray crystallographic analysis was performed. The crystallographic data are summarized in **Table S1**. The crystal systems of crystals **1a** and **2a** are orthorhombic and monoclinic, respectively. The space groups of **1a** and **2a** are *Pbca* and *P2₁/c*, respectively. Both crystals have one molecule in the asymmetric unit. The diarylethene molecules exist in an antiparallel conformation in both crystals and the distances between the reactive carbons in crystals **1a** and **2a** are 3.537 and 3.567 Å, respectively, which are sufficiently short for photocyclization to take place in the crystalline phase.¹⁹ Furthermore, in both crystals, there is intermolecular hydrogen bonding between the urethane units, as shown in **Figure 2**. In crystal **1a**, the intermolecular hydrogen bonding extends along to the *a*-axis. The distance of O...HN between the urethane units is 1.997 Å. On the other hand, in crystal **2a**, the intermolecular hy-

Table 1. Optical properties of diarylethenes in dichloromethane

	open-ring isomer (a)		closed-ring isomer (b)		$\Phi_{o \rightarrow c}$ ^{a)}	$\Phi_{c \rightarrow o}$ ^{b)}	Conv./% ^{c)}
	λ_{\max}/nm	$\epsilon/M^{-1}\text{cm}^{-1}$	λ_{\max}/nm	$\epsilon/M^{-1}\text{cm}^{-1}$			
1	289	45000	587	22000	0.45	0.0053	95
2	290	42000	587	20000	0.51	0.0043	92

a) Upon irradiation with 313 nm light. b) Upon irradiation with 587 nm light. c) Conversion from the open-ring isomer to the closed-ring isomer upon irradiation with 313 nm light.

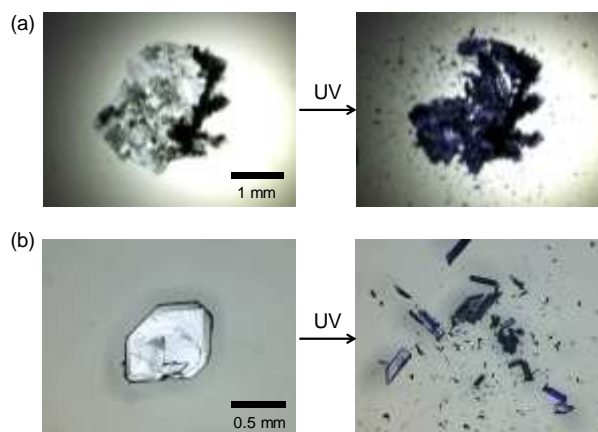


Figure 3. Optical photographs of diarylethene crystals **1a** (a) and **2a** (b) before and after UV irradiation.

drogen bonding extends along to the *b*-axis. The distance of O...HN between the urethane units is 2.013 Å. These results suggest that diarylethene molecules in both crystals are strongly interacted by the hydrogen bonding in intermolecular interaction.

Figure 3 shows the photographs of crystals **1a** and **2a** observed under normal view. Upon irradiation with 365 nm light, the colorless crystals of **1a** and **2a** turned blue as well as in solution. Surprisingly, at the same time, both crystals were rapidly and explosively fragmented as shown in **Movies S1** and **S2**. This is ascribed to the strain generated by the geometrical structure change of diarylethene molecules due to the photochromic reaction from the open-ring isomer to the closed-ring isomer in the crystalline phase. In the crystals **1a** and **2a**, there is intermolecular hydrogen bonding between the urethane units as described above. Such strong intermolecular interaction is considered to cause a large strain when a photochromic reaction takes place in the crystalline phase, which results in the rapid and explosive crystal fragmentation.

Naumov and coworkers have reported the correlation between the latent time and the excitation power or the size of the crystal in the photosalient effect. It means that the photosalient effect can only occur above a certain threshold in the internal strain.²⁶ On the other hand, here, we have examined a distribution of the initial speed of fragmentation. The initial speed of fragmentation was calculated from the moving distance of crystal fragment per unit of time, which was observed by high-speed camera as shown in **Figure S1**. **Figure 4a** shows a histogram of the initial speed of fragmentation of each fragment generated from a piece of crystal of **1a**. **Figure 4b** also shows a histogram of that generated from 17 pieces of crystal of **1a**. Comparing the histogram in both cases, no significant difference in distribution of the initial speed of fragmentation was observed. The average initial speed of fragmentation of **1a** was determined to be 4.7 m s⁻¹. Similar experiments were performed for crystal **2a**. **Figure 4c**

shows a histogram of the initial speed of fragmentation of each fragment generated from a piece of crystal of **2a**. **Figure 4d** also shows a histogram of that generated from 9 pieces of crystal of **2a**. Comparing the histogram in both cases, no significant difference in dispersion of the initial speed of fragmentation was observed as well as in the case of crystal **1a**. The average initial speed of fragmentation of **2a** was determined to be 1.9 m s⁻¹. To examine the effect of size (area), thickness, and volume of crystals on the photoinduced fragmentation, the initial speed of fragmentation was investigated. In various crystals having different size (area), thickness, and volume, major changes in the initial speed of fragmentation was not observed as shown in **Figure 5**. This indicates that the initial speed of fragmentation is independent of such factors.

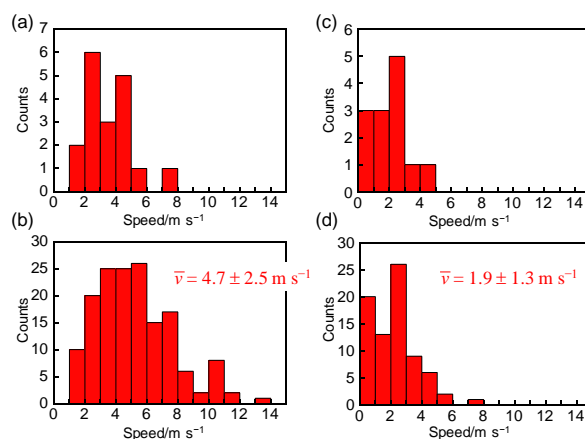


Figure 4. Histogram for the speed of fragments generated from **1a** and **2a**. (a) one sample for **1a**, (b) 17 samples for **1a**, (c) one sample for **2a**, and (d) 9 samples for **2a**. The errors represent the standard deviation.

Next, we focused on the kinetic energy of each crystal fragment. The average volume of fragment of **1a** was determined to be 1.96×10^{-7} mm³ by observation of each fragment using high-speed camera. The density of crystal **1a** is 1.476 g cm⁻³, which is determined by X-ray crystallographic analysis. From these values, the kinetic energy of a crystal fragment of **1a** was calculated to be 3.2×10^{-12} J. The average volume of fragment of **2a** was also determined to be 1.96×10^{-7} mm³. The density of crystal **2a** is 1.417 g cm⁻³. From these values, the kinetic energy of a crystal fragment of **2a** was calculated to be 0.50×10^{-12} J. As one of the causes of such difference in the kinetic energy between the crystals of **1a** and **2a**, the molecular packing can be considered. The diarylethene molecules are more densely packed in crystal **1a** ($d = 1.476$ g cm⁻³) than in crystal **2a** ($d = 1.417$ g cm⁻³). Furthermore, the distance of intermolecular hydrogen bonding in the crystal **1a** (1.997 Å) is also slightly shorter than that in the crystal **2a** (2.013 Å). These results mean that intermolecular interaction in crystal **1a** is stronger than that in crystal **2a**. In addition,

the lattice energy of crystal **1a** and **2a** was calculated using Gaussian 09²⁸ as shown in Supporting Information. It was determined to be 10.95 kJ mol⁻¹ for **1a** and 2.35 kJ mol⁻¹ for **2a**, respectively. This result also indicates that intermolecular interaction in crystal **1a** is stronger than that in crystal **2a**. From such a point of view, the strain caused by photoisomerization from the open-ring isomer to the closed-ring isomer in crystal **1a** is considered to be larger than that in crystal **2a**, which might result in the difference in the kinetic energy between the crystal of **1a** and **2a**.

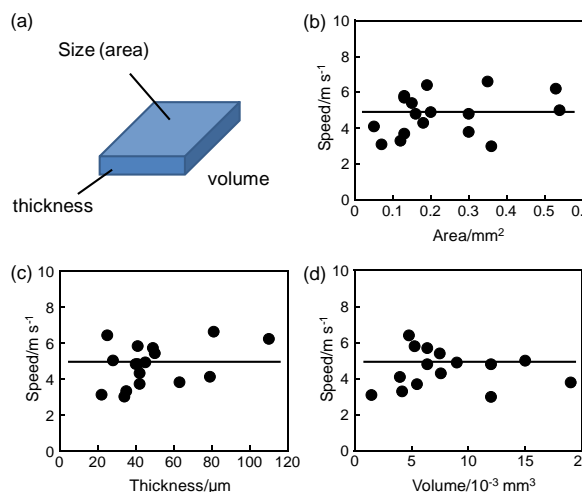


Figure 5. Illustration of crystal (a) and the speed of crystal fragment by area (b), thickness, (c), and volume (d) for crystal **1a**.

Diarylethenes having urethane bonding, **1a** and **2a**, were synthesized and their photomechanical performance was investigated. X-ray crystallographic analysis revealed that the urethane units of the diarylethenes formed the intermolecular hydrogen bonding in both crystals and the diarylethene molecules are strongly interacted by the hydrogen bonding intermolecular interaction. When irradiated with UV light, both crystals exhibited the photoinduced rapid and explosive fragmentation accompanying the color change of crystals from colorless to blue. This may be ascribed to the large strain generated by the photoisomerization of diarylethene molecules from the open-ring isomer to the closed-ring isomer in the rigid crystalline phase. The influence of crystal characters, such as size (area), thickness, and volume on the initial speed of a fragment was not observed. The average speed and the kinetic energy for a crystal fragment were estimated to be 4.7 m s⁻¹ and 3.2 × 10⁻¹² J for **1a** and 1.9 m s⁻¹ and 0.50 × 10⁻¹² J for **2a**, respectively.

ASSOCIATED CONTENT

Supporting Information.

Crystallographic data of **1a** and **2a** in CIF format, Figure of optical photographs taken by high-speed camera, X-ray crystallographic data for diarylethenes **1a** and **2a**, and movies of photoinduced rapid and explosive fragmentation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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