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Photoinduced Rapid and Explosive Fragmentation of Diarylethene Crystals Having Urethane Bonding

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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. 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. In the research of photoresponsive molecular crystals, we have focused on the photomechanical response of diarylethene crystals. 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. 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. 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. In particular, the bending is the most common motion and the mechanical works using bending motion, such as a gearwheel rotation, lifting up heavy metal balls having the 200~600 times weight of the crystal, and current switching, 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. The photosalient effect is well investigated by Naumov group and the phenomenon is seemed to be very rare. 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. 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-(phenylcarbarylmethyl)phenyl)-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (1a) and 1-(2-methyl-5-(4-(benzylcarbarylmethyl)phenyl)-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (2a),

Scheme 1. Diarylethenes used in this work.
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 solution 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 (Φo→c), the photocycloreversion quantum yield (Φc→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.46 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 hydrogen bonding extends along to the c-axis.

### 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).

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

### Table 1. Optical properties of diarylethenes in dichloromethane

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<tr>
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<th>open-ring isomer (a)</th>
<th>closed-ring isomer (b)</th>
<th>Φo→c a)</th>
<th>Φc→o b)</th>
<th>Conv./% c)</th>
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<tr>
<td>2</td>
<td>290</td>
<td>42000</td>
<td>587</td>
<td>20000</td>
<td>0.51</td>
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</table>

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.
The diarylethene molecules are more fragmentation 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. 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 5i. Figure 4a shows a histogram of the initial speed 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 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.

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 3.2×10⁻¹⁵ 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 0.50×10⁻¹⁵ 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 09 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.

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 diarylene 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 10.1021/acs.org.

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Notes
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