

Article

Quantitative Evaluation of Photoinduced Bending Speed of Diarylethene Crystals

Daichi Kitagawa ¹, Chika Iwaihara ¹, Hiroyasu Nishi ^{1,2} and Seiya Kobatake ^{1,*}

¹ Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan; E-Mail: kitagawa@bioa.eng.osaka-cu.ac.jp (D.K.)

² Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan; E-Mail: nishi-h@iis.u-tokyo.ac.jp

* Author to whom correspondence should be addressed; E-Mail: kobatake@a-chem.eng.osaka-cu.ac.jp; Tel./Fax: +81-6-6605-2797.

Academic Editor: Rui Tamura

Received: 30 August 2015 / Accepted: 30 October 2015 / Published: 6 November 2015

Abstract: We investigated photoinduced crystal bending behavior of various photochromic diarylethenes. In all the diarylethene derivatives we used in this work, the relationship between the initial photoinduced bending speed and the crystal thickness was well explained by the easy-handled Timoshenko's bimetal model. Moreover, we proposed a quantitative analysis method to reveal the relationship between the bending speed and the molecular structure of diarylethenes. These results provide the quantitative evaluation method of the photoinduced crystal bending speed.

Keywords: photochromism; diarylethene; single crystal; photomechanical crystal; bending

1. Introduction

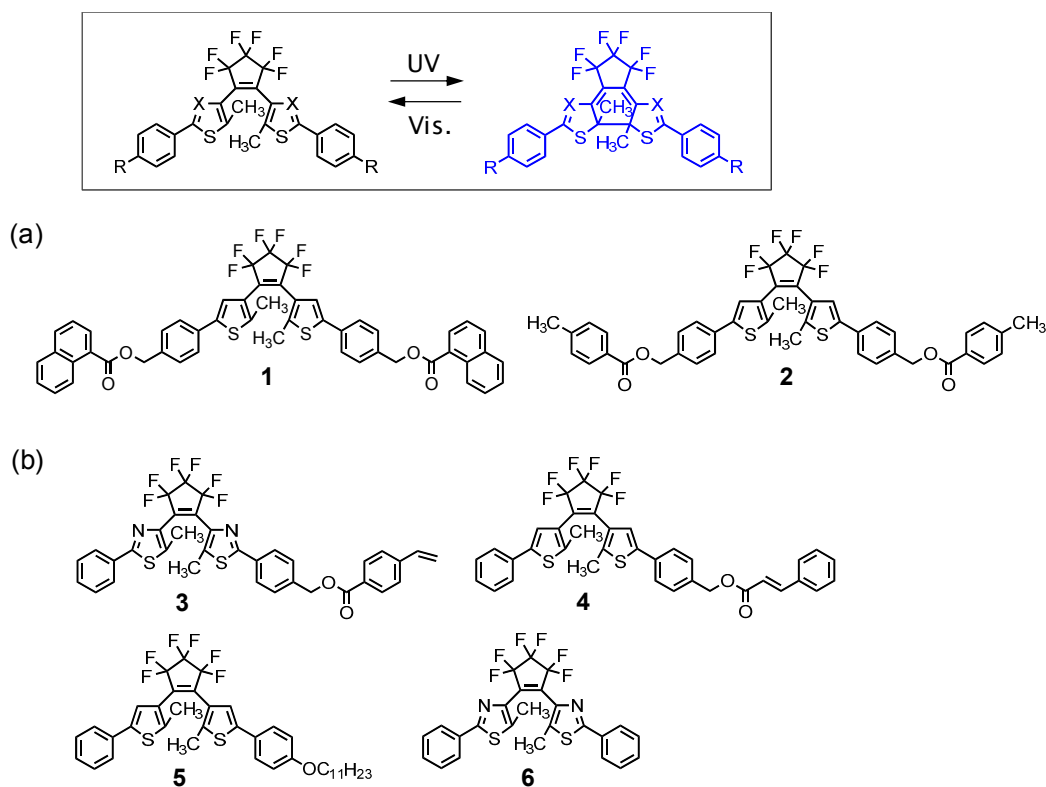
While there are reports on the photomechanical bending induced by linkage isomerism [1–3], valence tautomerism [4], and charge transfer [5–7], Kobatake, Irie, and co-workers have reported the rapid and reversible crystal shape change of photochromic diarylethene crystals in 2007 [8]. The photomechanical crystals have attracted much attention because they can work without any direct contact or electrical wires [9]. Various types of photomechanical behaviors such as contraction [8,10], expansion [11],

bending [8,11–17], separation [18], twisting [19], and rolling [12] have been reported so far. Although photochromic compounds such as diarylethenes [8,19], furylfulgide [20], azobenzene [21,22], anthracene carboxylates [23–28], salicylideneaniline [29], 4-chlorocinnamic acid [30], 1,2-bis(4-pyridyl)ethylene salt [31], benzylidenedimethylimidazolinone [32], and others [33] exhibit photochemical reactions in the crystalline phase, their photomechanical motions in the crystal are almost bending. It is essential for the development of the research field of photomechanical crystals to investigate the crystal bending behavior in detail.

There are two types of bending directions in photoinduced crystal bending: bending away from ultraviolet (UV) light and bending toward UV light. The crystal bending away from UV light is caused by the expansion of the photoreacted crystal layer upon UV irradiation. In contrast, the crystal bending toward UV light is due to the contraction of the irradiated part of the crystal upon irradiation with UV light. In both types, the photoinduced crystal bending is caused by heterogeneous photoisomerization in depth because of high absorption of the crystal in UV region. To analyze and evaluate the photoinduced crystal bending behavior, the development of the easy-handled simplified model is required.

We have reported the crystal thickness dependence of photoinduced crystal bending of diarylethene derivatives [11,15]. It has been experimentally clarified that the initial speed of bending depends on the thickness of the crystal. When the crystal thickness is thin, the crystal bends largely and rapidly. To discuss photoinduced bending behavior in the easy-handled model, we have introduced the Timoshenko's equation known as the simplified bimetal model [34]. The correlation between the initial speed of the curvature change and the crystal thickness was well explained by the Timoshenko's bimetal model in both types of bending, bending away from UV light and bending toward UV light. Naumov and Bardeen have also independently reported the more sophisticated mathematical treatments based on the fact that the concentration of the photoreacted product throughout the crystal continuously changes for other photoreactive compounds [35,36]. Such a rigorous analysis of the experimental fact is necessary for the development of the research field. On the other hand, the quantitative argument of the bending speed among different molecular crystals in easy-handled model is attractive and required to establish the general analysis method that can be widely used by other chemists.

Herein, we report on the quantitative evaluation of photoinduced bending speed among various diarylethene crystals (Scheme 1). All the diarylethenes **1–6** exhibited the photoinduced crystal bending caused by expansion or contraction of the photoreacted crystal layer and their bending speeds depended on the crystal thickness. The correlation between the initial speed of the curvature change and the crystal thickness in all the diarylethene crystals can be well explained by the Timoshenko's bimetal model. Moreover, the normalized relative bending speed in each crystal could be determined by focusing on the relationship between the thickness and the actuation strain of photoreacted layer in bimetal model.



Scheme 1. Diarylethene derivatives used in this work: (a) bending away from UV light; (b) bending toward UV light.

2. Results and Discussion

In all the diarylethenes **1–6**, their rod-like crystals can be crystallized out by slow evaporation of solvents. The space groups of the crystals of **1–6** were $P\bar{1}$, $P2_1/n$, $P2_1/c$, $P2_1/c$, $P\bar{1}$, and $P2_1/n$, respectively. The molecular packing and crystallographic data are summarized in Figures S1–S6 and Table S1. Diarylethene molecules in all the crystals of diarylethenes **1–6** exist in an antiparallel conformation. The distance between the reactive carbons was shorter than 4.2 Å, which is short enough for photoisomerization from the open-ring isomer to the closed-ring isomer to take place in the crystalline phase [37].

Figure 1 shows the photoinduced crystal bending behavior of diarylethene derivatives **1–6** upon irradiation with UV light. UV light irradiation was conducted to the (0 1 0) face (**1**), (0 0 $\bar{1}$) face (**2**), (1 0 0) face (**3**), (0 0 1) face (**4**), (0 1 0) face (**5**), and (0 $\bar{1}$ 0) face (**6**). The crystals of diarylethenes **1** and **2** bend away from the incident UV light, and the crystals of diarylethenes **3–6** bend toward the incident light. The bending direction is determined by either contraction or expansion of the photoirradiated parts in the crystal surface.

The initial velocity of the curvature change (V_{init}) for various samples having different crystal thicknesses was estimated by fitting in a polynomial function to the curvature change against UV irradiation time and the differential of the function at $t = 0$. The dependence property of V_{init} on the crystal thickness in the photoinduced bending was investigated in all the diarylethene crystals. Figure 2 shows the relationship between V_{init} and the crystal thickness of diarylethene derivatives **1–6**. When the crystal thickness is thin, V_{init} becomes large. It can be well explained by the Timoshenko's bimetal

model. The illustration and equation of the Timoshenko's bimetal model are shown in Figure 3 and Equation (1) [34].

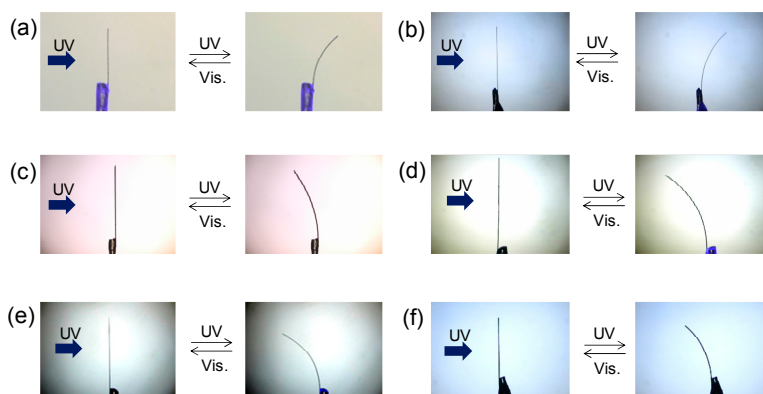


Figure 1. Photoinduced bending behavior of diarylethene (a) 1; (b) 2; (c) 3; (d) 4; (e) 5; and (f) 6, respectively.

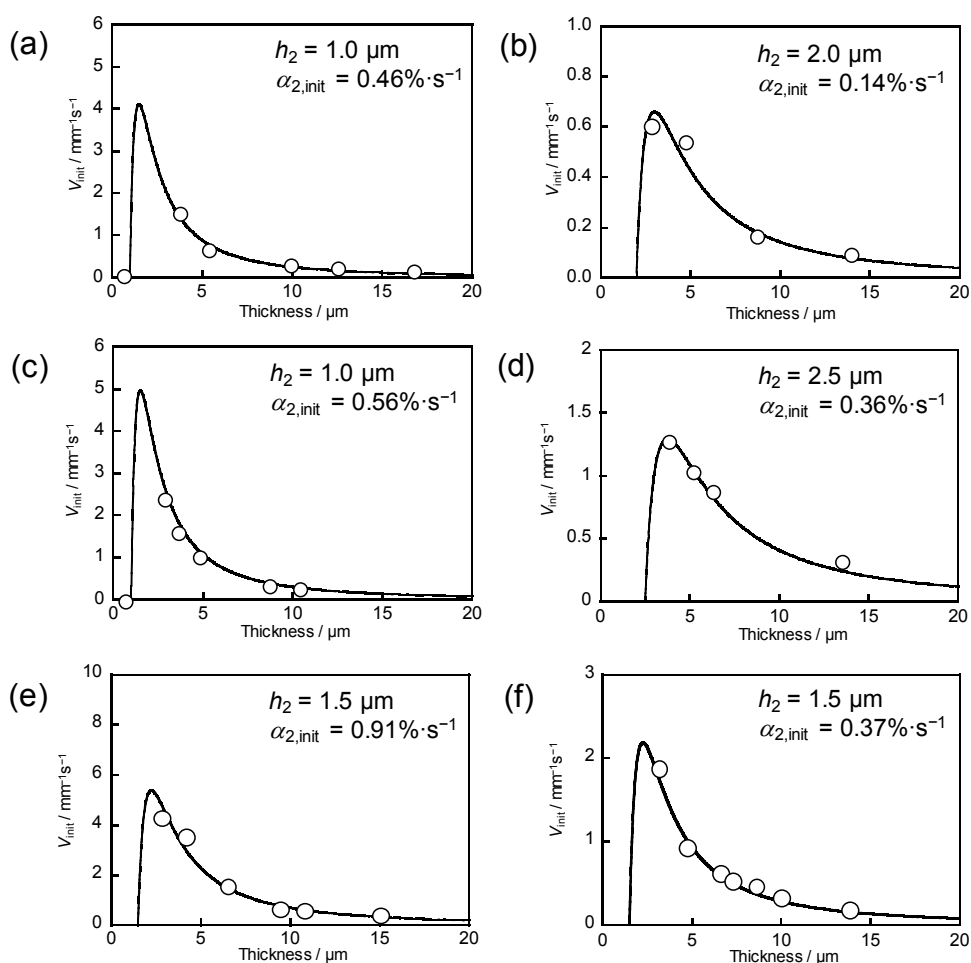


Figure 2. Initial speed of the curvature change relative to the crystal thickness in diarylethene crystals (a) 1; (b) 2; (c) 3; (d) 4; (e) 5; and (f) 6. The solid lines show fitting curve using the bimetal model.

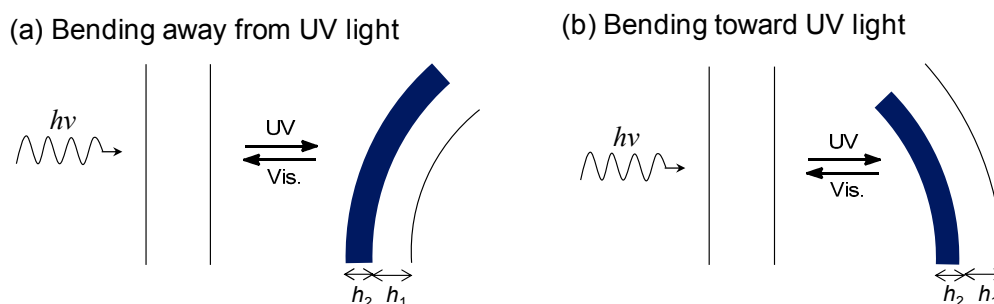


Figure 3. Illustration of Timoshenko's bimetal model in the case of (a) bending away from UV light and (b) bending toward UV light.

$$\text{Curvature} = \frac{1}{R} = \frac{\alpha_2 - \alpha_1}{h_2} \frac{6mn(1+m)}{1+4mn+6m^2n+4m^3n+m^4n^2} \quad (1)$$

$$= \frac{\alpha_2}{h_2} \frac{6m(1+m)}{1+4m+6m^2+4m^3+m^4} \quad (2)$$

where R is the curvature radius, α_i ($i = 1, 2$) are the actuation strains, h_i ($i = 1, 2$) are the layer thicknesses, $m = h_1/h_2$, $n = E_1/E_2$, and E_i ($i = 1, 2$) are the Young's moduli. Actuation strain α means the coefficient of expansion or contraction of the layer in the absence of the other layer upon UV irradiation. In the non-photoreacted layer, the value of actuation strain α_1 is always zero because the layer cannot expand or contract. In the type of bending away from UV light, the value of α_2 is the coefficient of expansion. In contrast, it is the coefficient of contraction when the crystal bends toward UV light. Moreover, the assumption that the Young's modulus E_1 is the same as E_2 is introduced because only a few % of diarylethene molecules in the crystal are converted from the open-ring isomer to the closed-ring isomer in the initial stage of the bending. As a result, the Timoshenko's equation becomes very simple, as shown in Equation (2). This equation can be applied to the explanation of the relationship between the initial velocity of the curvature change of photoinduced bending and the thickness of crystal. That is, the initial velocity of α_2 is expressed as $\alpha_{2,\text{init}}$. The values of h_2 and $\alpha_{2,\text{init}}$ can be obtained by the best fitting curve (Equation (3)) to the experimental data.

$$V_{\text{init}} = \frac{\alpha_{2,\text{init}}}{h_2} \frac{6m(1+m)}{1+4m+6m^2+4m^3+m^4} \quad (3)$$

The values of h_2 and $\alpha_{2,\text{init}}$ in diarylethenes 1–6 are summarized in Table 1. When the depth of photoreaction from the crystal surface (h_2) is the same, a potential capacity of bending in each crystal can be compared by only the value of $\alpha_{2,\text{init}}$. However, the potential capacity of each crystal cannot be compared by only the value of $\alpha_{2,\text{init}}$ when the value of h_2 is different in each crystal. The new analytical method to evaluate the unique value in each crystal is required.

Table 1. Values of $\alpha_{2,\text{init}}$, h_2 , and C for diarylethenes 1–6.

	1(010)	1(001)	2	3	4	5	6
$\alpha_{2,\text{init}}/\% \cdot \text{s}^{-1}$	0.46	0.10	0.14	0.56	0.36	0.91	0.37
$h_2/\mu\text{m}$	1.0	5.0	2.0	1.0	2.5	1.5	1.5
$C/\% \cdot \text{s}^{-1} \cdot \mu\text{m}$ (relative)	0.46 (1)	0.50 (1.0)	0.28 (0.61)	0.56 (1.2)	0.9 (2.0)	1.4 (3.0)	0.56 (1.2)

Here, we have focused on the relationship between h_2 and $\alpha_{2,\text{init}}$ in the same crystal. The value of h_2 in the same crystal depends on the faces irradiated with UV light because of the difference of the absorption coefficient due to the molecular orientation viewed from the faces. The value of $\alpha_{2,\text{init}}$ is proportional to the conversion rate from the open-ring isomer to the closed-ring isomer in the photoreacted layer. The number of photoreacted molecules is the same even when the face irradiated with UV light is different. Therefore, the value of multiplication of $\alpha_{2,\text{init}}$ and h_2 is always constant, as shown in Figure 4 and Equation (4). In other words, the value of $\alpha_{2,\text{init}}$ is proportional to h_2^{-1} , as shown in Equation (5).

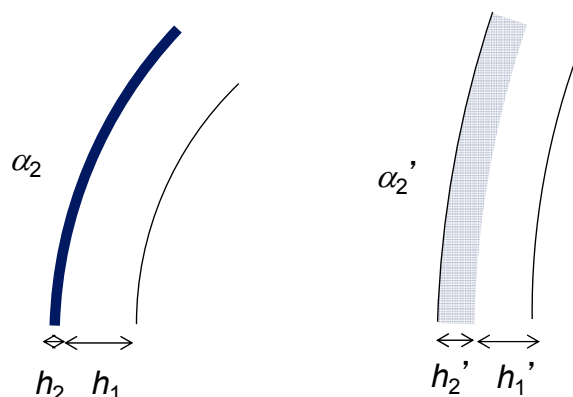


Figure 4. Illustration of the relationship between h_2 and α_2 when the UV light irradiation is conducted to the different face in the same crystal.

$$\alpha_{2,\text{init}} \cdot h_2 = \alpha'_{2,\text{init}} \cdot h'_2 = C \quad (4)$$

$$\alpha_{2,\text{init}} = C \cdot \frac{1}{h_2} \quad (5)$$

To discuss whether Equation (4) is suitable for the crystal of the same compound, the dependence of the photoinduced bending speed on the faces irradiated with UV light was investigated for diarylethene **1**. The face indices of the rod-like crystal of **1** were determined as shown in Figure S1. When the crystal was irradiated from the (0 0 1) face with UV light, the movement of the crystal was small and slow. In contrast, when the crystal was irradiated from the (0 1 0) face, it was bent largely and rapidly [11]. Figure 5 shows the dependence property of the bending speed on the crystal thickness when the UV irradiation was performed to the (0 0 1) and (0 1 0) faces of the crystal of **1**. In the case of irradiation with UV light to the (0 1 0) face, $h_2 = 1.0 \mu\text{m}$ and $\alpha_{2,\text{init}} = 0.46\% \cdot \text{s}^{-1}$ were obtained. On the other hand, $h_2 = 5.0 \mu\text{m}$ and $\alpha_{2,\text{init}} = 0.10\% \cdot \text{s}^{-1}$ were obtained in the case of irradiation with UV light to the (0 0 1) face. This result means that the values of h_2 and $\alpha_{2,\text{init}}$ are different when the face irradiated with UV light is different.

Figure 6 shows the relationship between $\alpha_{2,\text{init}}$ and h_2^{-1} in diarylethenes **1–6**. In the case of irradiation with UV light to the (0 0 1) and (0 1 0) faces of diarylethene **1**, the plots of $\alpha_{2,\text{init}}$ against h_2^{-1} ride on a line through the origin. This result indicates that the value of $\alpha_{2,\text{init}}$ is proportional to h_2^{-1} in experimental. By using this relationship, the effect of h_2 on the value of $\alpha_{2,\text{init}}$ can be normalized. In other words, the slope of a line through the origin is the unique value in each crystal. Here, we introduce the potential capacity of bending speed (C) that normalized the crystal thickness and the

depth of the photochromic reaction from the crystal surface. The C value in each crystal can be calculated from the slope of the line. The relative C values of diarylethenes **1–6** were 1.0, 0.61, 1.2, 2.0, 3.0, and 1.2, respectively, as summarized in Table 1. These values indicate that the potential capacity of diarylethene crystal **5** is the largest value among the six compounds and is three times as large as that of **1**. Thus, we have succeeded in the quantitative evaluation for the potential capacity of photoinduced bending speed among different diarylethene crystals.

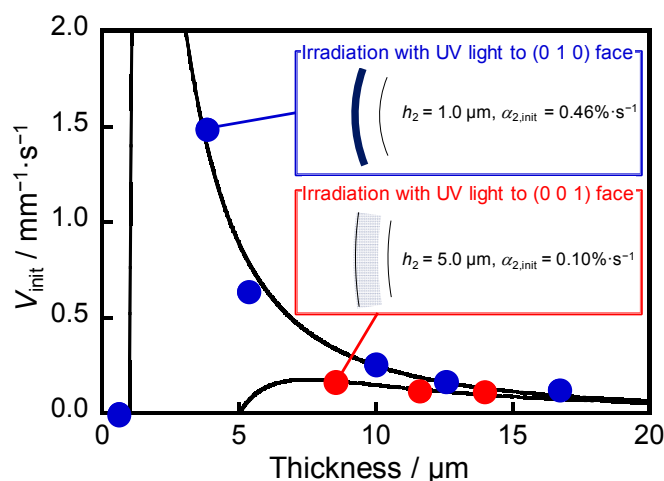


Figure 5. Initial speed of the curvature change relative to the crystal thickness with UV light irradiation to the (0 1 0) face (blue) and the (0 0 1) face (red) of diarylethene **1**. The solid lines show fitting curve using the bimetal model.

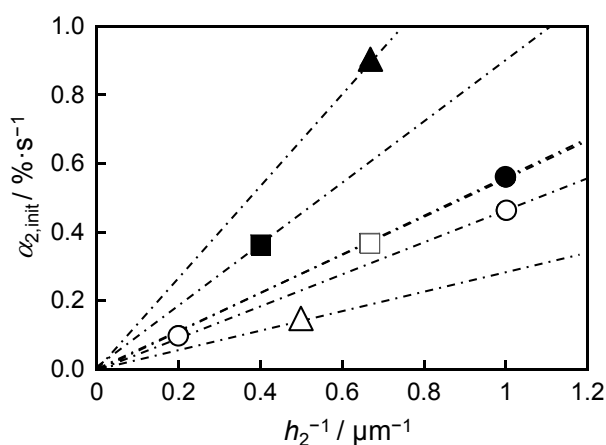


Figure 6. Relationship between $\alpha_{2,\text{init}}$ and h_2^{-1} in diarylethenes **1** ($\circ$), **2** ($\triangle$), **3** ($\bullet$), **4** ($\blacksquare$), **5** ($\blacktriangle$), and **6** ($\square$).

3. Experimental Section

3.1. General

The photoinduced bending behavior of diarylethene crystals was observed using a Keyence VHX-500 digital microscope. UV irradiation was carried out using a Keyence UV-LED UV-400 (365-nm light). The light intensity was $55 \text{ mW}\cdot\text{cm}^{-2}$ on the crystal surface. Visible light irradiation

was carried out using a halogen lamp (100 W). Single crystal X-ray crystallographic analysis was carried out using a Rigaku RAXIS RAPID imaging plate diffraction instrument or a Rigaku VariMax with Saturn CCD single crystal X-ray diffraction instrument with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) monochromated by graphite. The crystal structures were solved by a direct method using SIR92 and refined by the full-matrix least-squares method on F^2 with anisotropic displacement parameters for non-hydrogen atoms using SHELXL-97.

3.2. Determination of the Initial Speed of the Curvature Change

The edge of a rod-like crystal was fixed to a glass capillary, and a fluorescent material was painted on the glass capillary. The fluorescence of the glass capillary shows the onset time of UV irradiation. The value of the curvature against UV irradiation time (t) was fitted by a polynomial function. The initial speed of the curvature change was calculated by the differential of the function at $t = 0$. The error of the initial speed determined by the method was less than 8%. The standard deviation of the repeating experiments using the same crystal was smaller than the error.

3.3. Materials

Diarylethenes **1**, **3**, and **6** were synthesized according to a procedure described in the literature [11,38,39]. Diarylethenes **2**, **4**, and **5** were synthesized as shown in Supporting Information.

4. Conclusions

We have investigated the photoinduced bending behavior of various diarylethene crystals. All the diarylethenes showed the photoinduced crystal bending behavior caused by expansion or contraction of the photoreacted crystal surface. Their bending speeds depended on the crystal thickness. The correlation between the initial bending speed and the crystal thickness in all the diarylethene crystals can be well explained by the Timoshenko's bimetal model. When the thickness of the photoreacted layer (h_2) in the bimetal model is the same even in different diarylethene crystals, the bending speed can be compared quantitatively using the value of $\alpha_{2,\text{init}}$. However, the h_2 values are different depending on the molecular structure and the molecular packing. The multiplication of h_2 and $\alpha_{2,\text{init}}$ led to a constant value of C in the same crystal. By using this relationship, the effect of h_2 on the value of $\alpha_{2,\text{init}}$ can be normalized. Therefore, the value of C means the potential capacity of bending speed.

Acknowledgments

This work was partly supported by a Grant-in-Aid for Scientific Research on Innovative Areas "Photosynergetics" (No. 26107013) from The Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. D.K. appreciates Research Fellowships of the Japan Society for the Promotion of Science (JSPS) for Young Scientists. The authors also thank Nippon Zeon Co., Ltd. for providing octafluorocyclopentene.

Author Contributions

The authors contributed equally to this work.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Boldyreva, E.V. Intramolecular linkage isomerization in the crystals of some Co(III)-ammine complexes—a link between inorganic and organic solid state chemistry. *Mol. Cryst. Liq. Cryst.* **1994**, *242*, 17–52.
2. Boldyreva, E. Structural aspects of intramolecular solid-state linkage isomerization in Co(III) pentaammine nitro/nitrito complexes. *Russ. J. Coord. Chem.* **2001**, *27*, 1–28.
3. Boldyreva, E.V.; Sidelnikov, A.A.; Chupakhin, A.P.; Liakhov, N.Z.; Boldyrev, V.V. Deformation and mechanical destruction of $\text{Co}(\text{NH}_3)_5\text{NO}_2 \cdot \text{X}_2$ crystals ($\text{X} = \text{Cl}^-$, Br^- , NO_3^-) in the course of solid-state photochemical nitro-nitrito linkage isomerization. *Dokl. Akad. Nauk SSSR* **1984**, *277*, 893–896.
4. Abakumov, G.A.; Nevodchikov, V.I. Thermomechanical and photomechanical effects observed on crystals of a free-radical complex. *Dokl. Akad. Nauk SSSR* **1982**, *266*, 1407–1410.
5. Bubnov, M.P.; Nevodchikov, V.I.; Fukin, G.K.; Cherkasov, V.K.; Abakumov, G.A. New dicarbonyl-o-semiquinonato rhodium complexes. *Inorg. Chem. Commun.* **2007**, *10*, 989–992.
6. Lange, C.W.; Foldeaki, M.; Nevodchikov, V.; Cherkasov, K.; Abakumov, G.; Pierpont, C.G. Photomechanical properties of rhodium(I)-semiquinone complexes: The structure, spectroscopy, and magnetism of (3,6-di-*tert*-butyl-1,2-semiquinonato)dicarbonylrhodium(I). *J. Am. Chem. Soc.* **1992**, *114*, 4220–4222.
7. Nath, N.K.; Panda, M.K.; Sahoo, S.C.; Naumov, P. Thermally induced and photoinduced mechanical effects in molecular single crystals—A revival. *CrystEngComm* **2014**, *16*, 1850–1858.
8. Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. Rapid and reversible shape changes of molecular crystals on photoirradiation. *Nature* **2007**, *446*, 778–781.
9. Irie, M.; Fukaminato, T.; Matsuda, K.; Kobatake, S. Photochromism of diarylethene molecules and crystals: Memories, switches, and actuators. *Chem. Rev.* **2014**, *114*, 12174–12277.
10. Kuroki, L.; Takami, S.; Yoza, K.; Morimoto, M.; Irie, M. Photoinduced shape changes of diarylethene single crystals: Correlation between shape changes and molecular packing. *Photochem. Photobiol. Sci.* **2010**, *9*, 221–225.
11. Kitagawa, D.; Kobatake, S. Crystal thickness dependence of photoinduced crystal bending of 1,2-bis(2-methyl-5-(4-(1-naphthoyloxymethyl)phenyl)-3-thienyl)perfluorocyclopentene. *J. Phys. Chem. C* **2013**, *117*, 20887–20892.
12. Uchida, K.; Sukata, S.I.; Matsuzawa, Y.; Akazawa, M.; de Jong, J.J.D.; Katsonis, N.; Kojima, Y.; Nakamura, S.; Areephong, J.; Meetsma, A.; *et al.* Photoresponsive rolling and bending of thin crystals of chiral diarylethenes. *Chem. Commun.* **2008**, doi:10.1039/B71525E.
13. Morimoto, M.; Irie, M. A diarylethene cocrystal that converts light into mechanical work. *J. Am. Chem. Soc.* **2010**, *132*, 14172–14178.

14. Terao, F.; Morimoto, M.; Irie, M. Light-driven molecular-crystal actuators: Rapid and reversible bending of rodlike mixed crystals of diarylethene derivatives. *Angew. Chem. Int. Ed.* **2012**, *51*, 901–904.
15. Kitagawa, D.; Kobatake, S. Crystal thickness dependence of the photoinduced crystal bending of 1-(5-methyl-2-(4-(*p*-vinylbenzoyloxymethyl)phenyl)-4-thiazolyl)-2-(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene. *Photochem. Photobiol. Sci.* **2014**, *13*, 764–769.
16. Kitagawa, D.; Kobatake, S. Photoreversible current on/off switching by the photoinduced bending of gold-coated diarylethene crystals. *Chem. Commun.* **2015**, *51*, 4421–4424.
17. Kitagawa, D.; Tanaka, R.; Kobatake, S. Dependence of photoinduced bending behavior of diarylethene crystals on irradiation wavelength of ultraviolet light. *Phys. Chem. Chem. Phys.* **2015**, *17*, 27300–27305.
18. Kobatake, S.; Hasegawa, H.; Miyamura, K. High-convertible photochromism of a diarylethene single crystal accompanying the crystal shape deformation. *Cryst. Growth Des.* **2011**, *11*, 1223–1229.
19. Kitagawa, D.; Nishi, H.; Kobatake, S. Photoinduced twisting of a photochromic diarylethene crystal. *Angew. Chem. Int. Ed.* **2013**, *52*, 9320–9322.
20. Koshima, H.; Nakaya, H.; Uchimoto, H.; Ojima, N. Photomechanical motion of furylfulgide crystals. *Chem. Lett.* **2012**, *41*, 107–109.
21. Koshima, H.; Ojima, N.; Uchimoto, H. Mechanical motion of azobenzene crystals upon photoirradiation. *J. Am. Chem. Soc.* **2009**, *131*, 6890–6891.
22. Koshima, H.; Ojima, N. Photomechanical bending of 4-aminoazobenzene crystals. *Dyes Pigments* **2012**, *92*, 798–801.
23. Al-Kaysi, R.O.; Mueller, A.M.; Bardeen, C.J. Photochemically driven shape changes of crystalline organic nanorods. *J. Am. Chem. Soc.* **2006**, *128*, 15938–15939.
24. Al-Kaysi, R.O.; Bardeen, C.J. Reversible photoinduced shape changes of crystalline organic nanorods. *Adv. Mater.* **2007**, *19*, 1276–1280.
25. Zhu, L.; Al-Kaysi, R.O.; Dillon, R.J.; Tham, F.S.; Bardeen, C.J. Crystal structures and photophysical properties of 9-anthracene carboxylic acid derivatives for photomechanical applications. *Cryst. Growth Des.* **2011**, *11*, 4975–4983.
26. Zhu, L.; Al-Kaysi, R.O.; Bardeen, C.J. Reversible photoinduced twisting of molecular crystal microribbons. *J. Am. Chem. Soc.* **2011**, *133*, 12569–12575.
27. Zhu, L.; Agarwal, A.; Lai, J.; Al-Kaysi, R.O.; Tham, F.S.; Ghaddar, T.; Mueller, L.; Bardeen, C.J. Solid-state photochemical and photomechanical properties of molecular crystal nanorods composed of anthracene ester derivatives. *J. Mater. Chem.* **2011**, *21*, 6258–6268.
28. Kim, T.; Al-Muhanna, M.K.; Al-Suwaidan, S.D.; Al-Kaysi, R.O.; Bardeen, C.J. Photoinduced curling of organic molecular crystal nanowires. *Angew. Chem. Int. Ed.* **2013**, *52*, 6889–6893.
29. Koshima, H.; Takechi, K.; Uchimoto, H.; Shiro, M.; Hashizume, D. Photomechanical bending of salicylideneaniline crystals. *Chem. Commun.* **2011**, *47*, 11423–11425.
30. Kim, T.; Zhu, L.; Mueller, L.J.; Bardeen, C.J. Dependence of the solid-state photomechanical response of 4-chlorocinnamic acid on crystal shape and size. *Cryst. Eng. Comm.* **2012**, *14*, 7792–7799.

31. Sun, J.K.; Li, W.; Chen, C.; Ren, C.X.; Pan, D.M.; Zhang, J. Photoinduced bending of a large single crystal of a 1,2-bis(4-pyridyl)ethylene-based pyridinium salt powered by a [2+2] cycloaddition. *Angew. Chem. Int. Ed.* **2013**, *52*, 6653–6657.
32. Naumov, P.; Kowalik, J.; Solntsev, K.M.; Baldridge, A.; Moon, J.-S.; Kranz, C.; Tolbert, L.M. Topochemistry and photomechanical effects in crystals of green fluorescent protein-like chromophores: Effects of hydrogen bonding and crystal packing. *J. Am. Chem. Soc.* **2010**, *132*, 5845–5857.
33. Seki, T.; Sakurada, K.; Muromoto, M.; Ito, H. Photoinduced single-crystal-to-single-crystal phase transition and photosalient effect of a gold (i) isocyanide complex with shortening of intermolecular auropilic bonds. *Chem. Sci.* **2015**, *6*, 1491–1497.
34. Timoshenko, S. Analysis of bi-metal thermostats. *J. Opt. Soc. Am.* **1925**, *11*, 233–255.
35. Nath, N.K.; Pejov, L.; Nichols, S.M.; Hu, C.; Saleh, N.; Kahr, B.; Naumov, P. Model for photoinduced bending of slender molecular crystals. *J. Am. Chem. Soc.* **2014**, *136*, 2757–2766.
36. Kim, T.; Zhu, L.; Mueller, L.J.; Bardeen, C.J. Mechanism of photoinduced bending and twisting in crystalline microneedles and microribbons composed of 9-methylantracene. *J. Am. Chem. Soc.* **2014**, *136*, 6617–6625.
37. Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. Single-crystalline photochromism of diarylethenes: Reactivity-structure relationship. *Chem. Commun.* **2002**, doi:10.1039/B208419H.
38. Nishi, H.; Namari, T.; Kobatake, S. Photochromic polymers bearing various diarylethene chromophores as the pendant: Synthesis, optical properties, and multicolor photochromism. *J. Mater. Chem.* **2011**, *21*, 17249–17258.
39. Uchida, K.; Ishikawa, T.; Takeshita, M.; Irie, M. Thermally irreversible photochromic systems. Reversible photocyclization of 1,2-bis(thiazolyl)perfluorocyclopentenes. *Tetrahedron* **1998**, *54*, 6627–6638.