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# Crystal Phase Transition and Solid-State Photoisomerization of Benzyl (Z,Z)-Muconate Polymorphs Studied by Direct Observation of Crystal Structure Change

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**ABSTRACT:** We investigated the polymorph structures of benzyl (*Z*,*Z*)-muconate crystals (**ZZ-Bn-** $\alpha$ ,  $\beta$ , and  $\gamma$ ) and their *EZ* photoisomerization behavior in order to clarify the *EZ* isomerization mechanism of diene compounds in the solid state. First, the thermodynamics and crystal phase transition of the polymorphs were investigated by differential scanning calorimetry and X-ray diffraction. A single-crystal-to-single-crystal transition was observed during the change in the polymorph structures from the **ZZ-Bn-** $\beta$  to the  $\alpha$  form. We also observed in situ the migration of the boundary between the different polymorph domains during the phase transition of the **ZZ-Bn-** $\gamma$  to the  $\alpha$  form by optical microscopy. We then investigated the change in the crystal structure of **ZZ-Bn** during the *EZ* photoisomerization in the solid state. The photoisomerization of **ZZ-Bn** to the corresponding *EE* isomer (**EE-Bn**) proceeded according to a bicycle-pedal model via a single-crystal-to-single-crystal topochemical reaction mechanism, which was directly confirmed by an X-ray single-crystal structure analysis. During the photoirradiation of the polymorph crystals of **ZZ-Bn-** $\alpha$  and  $\beta$ , a structural strain was accumulated in the crystal lattice and finally caused a phase transition accompanied by a change in the space group from *P*2<sub>1</sub>/c to *P*2<sub>1</sub>, resulting in a stable crystal structure identical to that of the recrystallized **EE-Bn**. On the other hand, the **ZZ-Bn-** $\gamma$  crystals became amorphous during the photoirradiation because of the greater molecular motions in the crystals. Thus, we have demonstrated the validity of the in situ single-crystal structure analysis for investigating the *EZ* photoisomerization of diene compounds in the solid state.

#### Introduction

The EZ isomerization of polyenes is an important photochemical process for the recognition step of visible light by the visual pigment rhodopsin, which is a protein-coupled receptor containing an 11-cis-retinal chromophore.<sup>1</sup> The fast isomerization process of 11-cis-retinal to the all-trans one is a trigger for the biological activity of rhodopsin. In 1976, Warshel<sup>2</sup> first suggested the bicycle-pedal (BP) model as a volume-conserving reaction mechanism for the achievement of this fast isomerization reaction. The BP model<sup>3</sup> accounts for the two-bond photoisomerization of butadienes,<sup>4</sup> the photochromism of salicylideneanilines,<sup>5</sup> and the conformational changes in azobenzene and polyene compounds in the crystals.<sup>6</sup> Simultaneous two-bond isomerization has also been described as a crankshaft motion in crystals, which was originally introduced to describe the conformational changes in polymer segments.<sup>7</sup> On the other hand, Liu et al.<sup>8</sup> proposed the hula-twist (HT) process to explain the results of the fast reaction of 11-cis-retinal to the all-trans one. This model has been applied to various reactions, including the isomerization of olefins and polyenes with bulky substituents in confined media, such as a viscous fluid, rigid matrix, organic glass, and organic crystals.<sup>9,10</sup> The reactions proceeding according to the BP and HT models require only a small change in the molecular shape of a substrate, differing from the conventional one-bond flip (OBF) or one-bond twist (OBT)<sup>11</sup> motion, which is usually observed during many reactions in solution and other fluid media or in soft materials.<sup>12</sup> The EZ photoisomerization of olefins, dienes, and polyenes in a

glass matrix at a low temperature has been accounted for using different reaction mechanisms. Saltiel et al. reported the BP process as the only photoisomerization pathway of 1,4-diphenyl-1,3-butadienes in the solid state and as a significant pathway competing with the OBF (OBT) pathway in the soft isopentane glass at 77 K, $^{4,13}$  while Liu et al. asserted the HT pathway for the glassy-state reactions<sup>9</sup> and pointed out that the softened glassy state led to the apparent disagreement in the conclusions for the reaction mechanism by two independent research groups.<sup>14</sup>

We have shown that the diene moiety of muconic acid derivatives exhibits a variety of photoreactions in the solid state,<sup>15</sup> including topochemical polymerization,<sup>16</sup> [2 + 2] cyclodimerization,<sup>17</sup> and *EZ* isomerization.<sup>18</sup> Organic reactions performed in the solid state have several interesting features because they proceed in a highly selective manner under crystalline-lattice control; that is, the reaction process significantly depends on the crystal lattice.<sup>19</sup> The solid-state photoisomerization of the muconates has the following characteristics: no formation of the EZ isomer and a one-way reaction from the ZZ to EE form.<sup>18</sup> It is well-known that, in unsaturated compounds, such as olefins, polyenes, and azo compounds, light induces a reversible EZ isomerization to form mixtures of isomers in solution.<sup>12</sup> In contrast, a limited number of EZ isomerizations in the crystalline state had been reported because of the difficulty in the inevitable change in the molecular structure.<sup>20-22</sup> This is because the reactivity in the solid state is determined by the suppressed movement of atoms<sup>23</sup> and stress is accumulated in the crystals.<sup>24</sup> We recently reported preliminary studies for the EZ isomerization of benzyl (Z,Z)-muconate (ZZ-Bn) to benzyl (E,E)-muconate (EE-Bn) (Scheme 1) based on a crystal structure analysis and

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the photoisomerization behavior.<sup>25</sup> Recent advances in crystallography and equipment for such analyses have enabled us to in situ observe a change in the crystal structure during the solid-state reaction.<sup>26</sup> In the present study, we have elucidated the topochemical photoisomerization process of the muconic derivatives in the solid state by monitoring the change in the crystal structure using an in situ X-ray single crystal structure analysis. The solid-state photoisomerization and the polymorph transition are discussed based on the polymorphic structures of **ZZ-Bn**, i.e., the  $\alpha$ ,  $\beta$ , and  $\gamma$  forms and their reaction behavior.

#### **Experimental Section**

General Methods. NMR, IR, and UV-visible spectra were recorded using JEOL JMN A-400, JASCO FT/IR-430, and Shimadzu UV-160 spectrometers, respectively, at room temperature. Single-crystal X-ray diffraction data were collected using a Rigaku RAXIS RAPID imaging plate diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  A) monochromated by graphite at room temperature. 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 nonhydrogen atoms using SHELXL-97.27 A massed void space in the unit cell was estimated using the Free Volume program contained in the Cerius<sup>2</sup> software package (version 4.0). The atomic radii adopted for the calculation are 1.20, 1.70, and 1.60 Å for hydrogen, carbon, and oxygen, respectively. Powder X-ray diffraction profiles were recorded using a Rigaku RINT-2100 with monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54184$  Å, 40 kV, 40 mA, scan speed 2.0°/min, scan range 2-40°) under temperature control, equipped with a high-resolution parallel-beam optics system consisting of a PSA100U parallel slip analyzer and a graded 2960C1 multiplier. Differential scanning calorimetry (DSC) was carried out using a SEIKO DSC-6200 at the heating and cooling rates of 2 °C/min. The melting  $(T_m)$  and phase transition temperature  $(T_1)$  values were determined as the extrapolated onset temperature of the melting or transition, that is, the cross point of the baseline and tangent line at the maximum slope.

**Materials.** The (*Z*,*Z*)- and (*E*,*E*)-muconic acids were purchased from Aldrich Co., Ltd., and used as received. The esters were prepared by the reaction of the muconic acids with the corresponding benzyl bromides according to a previously reported procedure.<sup>28</sup> The NMR data of **ZZ-Bn** and **EE-Bn** are shown in the previous communication.<sup>25</sup> The single crystals of **ZZ-Bn** and **EE-Bn** were obtained during the evaporation of the chloroform and ethanol solutions, respectively, at room temperature.

**Photoreaction.** The photoreaction of **ZZ-Bn** was carried out using an ultrahigh pressure mercury Moritex MUV-250U-L lamp (500 W; 254, 313, 365, 405, 436 nm and others) and an IRA-25S infrared absorption filter after the sample was ground to a powder. The photoreaction of the **ZZ-Bn** single crystal was carried out using the same irradiation apparatus and a UV-D36B band path filter (Asahi Techno Glass Co.) to irradiate light of wavelength in the range 300–400 nm (see Figure S5 in Supporting Information) and supplied for the X-ray structure analysis at specific time intervals. The crystal was exposed to light for which it has a low absorption in order to obtain a homogeneous product throughout the bulk of the crystal and achieve a single-crystal-to-single-crystal reaction.<sup>29</sup> After the photoirradiation, the conversion of the isomer was determined by NMR spectroscopy.

#### **Results and Discussion**

**Crystal Structure of ZZ-Bn Polymorphs.** The **ZZ-Bn** crystals provided three polymorphic forms [**ZZ-Bn**- $\alpha$  (1),  $\beta$  (2), and  $\gamma$  (3)] when they were recrystallized by the evaporation of chloroform as the solvent at room temperature. The form of the crystals depended on the evaporation rate of the solvent.

The 1 crystals with the  $\alpha$ -form frequently appeared when the chloroform was slowly evaporated, while fast evaporation led to the growth of the  $\gamma$ -form crystal. The  $\beta$ -form crystal was rarely obtained under the slow evaporation conditions, and it was difficult to control its appearance. We confirmed that one of the polymorphs was preferentially obtained in a batch without contamination of the other polymorphs during each recrystallization process. Because these polymorphs had a similar crystal shape and habit, we checked the crystal structure for each recrystallization batch by powder X-ray diffraction.

The single crystal structures of the **ZZ-Bn** polymorphs were determined at 23 and -150 °C by an X-ray single-crystal structure analysis. The crystallographic data are summarized in Table 1. The packing structures of the **ZZ-Bn** molecules in the crystals are shown in Figure 1. The crystal system of all the **ZZ-Bn** polymorphs, 1–3, is monoclinic. The space group of 1 and 2 is  $P2_1/c$ , and that of 3 is  $P2_1/n$ . The crystals 1–3 had an identical lattice volume (V = 806.6-807.2 Å<sup>3</sup> at -150 °C and V = 833.8-841.7 Å<sup>3</sup> at 23 °C). No solvent was included in all the crystals. The crystal structure of **EE-Bn** (4) was also determined. The 4 molecule has an asymmetric conformation with bent and stretched benzyl ester groups, while the 1–3 molecules have a symmetric molecular conformation with an inversion center in the crystals

The molecular conformations of polymorphs 1-3 are compared in Figure 2. All the carbons of the diene moiety are located in the same plane. The two aromatic rings in the molecules are packed in the crystals in a parallel fashion for all the polymorphs. The conformational structure of the polymorphs is characterized by the torsion angles between the carbonyl and phenyl groups (Table S1 in the Supporting Information); the torsion angles of the C3-O2-C4-C5 unit were 160.0, 175.8, and 173.8°, and those of O2-C4-C5-C6 were -38.7, -0.6, and  $20.4^\circ$ , for 1, 2, and 3, respectively.

Thermodynamics and Phase Transition of the Polymorphs. The thermodynamic stability was investigated by DSC. Based on the heating process, all the crystals showed an endothermic peak  $T_{\rm m}$  at ca. 70 °C with  $\Delta H_{\rm m} = 7.9-8.9$  kJ/mol, as shown in Figure 3. The polymorph crystals **2** and **3** additionally showed a small endothermic peak;  $T_1 = 55.7$  °C ( $\Delta H_1 = 0.4$  kJ/mol) and 50.2 °C ( $\Delta H_1 = 1.1$  kJ/mol) for **2** and **3**, respectively. NMR spectroscopy confirmed that these crystals included no formation of the *EZ* and *EE* isomers during the heating process for the DSC measurement. The DSC results suggest the possibility of a phase transition from **2** and **3** to **1** in the solid state below the  $T_{\rm m}$ . Therefore, we checked for a change in the powder X-ray diffraction profile of the **ZZ-Bn** crystals

	77_Bn_	φ(I)	77_Bo	. ( <b>1</b> )	77_Bn	3	FE_Rn (4)	<b>2</b> after $\frac{1}{1+2}$	1 after $u_{\text{botoirradiation}}^{c}$	<b>2</b> after whotoirradiation <sup>d</sup>	3 after
-						(2)		Gunnon C 11 C		Tommunoroud	
Iormula	$C_{20}H_{18}O_{4}$		$C_{20}H_{18}U_{4}$		$C_{20}H_{18}O_{4}$		$C_{20}H_{18}O_{4}$	$C_{20}H_{18}O_{4}$	$C_{20}H_{18}O_{4}$	$C_{20}H_{18}O_{4}$	$C_{20}H_{18}O_{4}$
formula weight	322.34		322.34		322.34		322.34	322.34	322.34	322.34	322.34
crystal system	monoclinic		monoclinic		monoclinic		monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_{1/c}$		$P2_{1/c}$		$P2_1/n$		$P2_1$	$P2_{1/c}$	$P2_{1/c}$	$P2_1/c$	$P2_{1/n}$
a, Å	10.390(5)	10.332(4)	8.269(4)	8.5739(14)	5.684(5)	5.7625(14)	9.167(3)	10.327(4)	10.328(6)	8.154(9)	5.7566(15)
$b,  m \AA$	5.633(2)	5.682(2)	10.415(6)	10.468(3)	20.015(19)	20.403(5)	5.7038(11)	5.613(3)	5.765(4)	10.567(9)	20.295(6)
$c,  m \AA$	14.520(8)	14.791(7)	9.448(4)	9.359(2)	7.178(8)	7.2285(18)	17.002(5)	14.453(5)	15.005(9)	9.465(11)	7.104(2)
$\beta$ , deg	108.238(18)	105.86(4)	97.55(2)	96.945(11)	98.72(5)	97.975(11)	104.803(4)	108.48(2)	106.00(3)	97.24(5)	99.306(14)
$V, Å^3$	807.0(7)	835.2(6)	806.6(7)	833.8(3)	807.2(14)	841.7(4)	859.5(4)	794.6(5)	858.8(9)	809.0(15)	819.1(4)
Ζ	2	2	2	2	2	2	2	2	2	2	2
$ ho_{ m calc}$ , g/cm <sup>3</sup>	1.326	1.282	1.327	1.284	1.326	1.272	1.246	1.347	1.247	1.323	1.307
refins measured	7070	6512	6641	7791	7432	8026	8154	4648	6993	6598	7076
unique reflns	1854	1877	1786	1882	1846	1900	3569	1776	1933	1849	1872
no. obsd $(I > 2\sigma(I))$	1086	1198	1033	1030	1198	1282	1625	1238	842	834	1238
$R_1$	0.055	0.052	0.052	0.050	0.050	0.044	0.043	0.068	0.071	0.055	0.067
$wR_2$	0.123	0.132	0.140	0.114	0.120	0.111	0.089	0.210	0.229	0.133	0.211
GOF	0.886	1.032	0.931	0.900	0.950	1.028	0.799	1.060	0.942	0.898	1.089
temp, °C	-150	$23^{a}$	-150	23	-150	23	23 <sup>a</sup>	-150	$23^a$	-150	-150
<sup><i>a</i></sup> The crystallograp conversion). <sup><i>e</i></sup> Photoir	hic data determin radiation for 18	ned for 1 and . h (12.7% conv	<b>4</b> at 23 °C are c /ersion).	ited from ref 2:	5. <sup>b</sup> Heating at 5	6 °C in the da	rk for 0.2 h. <sup>c</sup> Ph	otoirradiation f	or 27 h (35.3% convei	sion). <sup>d</sup> Photoirradiatio	on for 25 h (30.8%



Figure 1. Single crystal structures of (a) ZZ-Bn- $\alpha$  (1), (b) ZZ-Bn- $\beta$  (2), (c) ZZ-Bn- $\gamma$  (3), and (d) EE-Bn (4).



Figure 2. Molecular conformation of ZZ-Bn polymorphs: (a) 1, (b) 2, (c) 3, and (d) superposition of them. Molecules 1–3 have crystal-lographically imposed inversion symmetry.

after a single heating to a temperature over the  $T_1$  and then cooling to room temperature (Figure 4). The diffraction profile of 2 after heating over the  $T_1$  was identical to that of 1. A similar phase transition was also observed for 3. The phase transitions of 2 and 3 to 1 were also monitored by IR spectroscopy under temperature control. The characteristic absorptions at 1610 and 1230 cm<sup>-1</sup> due to each polymorph in the IR spectra of 2 and 3, respectively, gradually disappeared during the heating process, and finally the spectrum became identical to the spectrum of 1 (Figures S1 and S2 of the

Table 1. Crystallographic Data for Dibenzyl Muconates

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**Figure 3.** DSC curves of (a) **1**, (b) **2**, and (c) **3** at the heating rate of  $2 \,^{\circ}C/\text{min}$ .  $T_{\rm m} = 68.5 \,^{\circ}C$  and  $\Delta H_{\rm m} = 8.9 \,\text{kJ/mol}$  for **1**,  $T_{\rm 1} = 55.7 \,^{\circ}C$  and  $\Delta H_{\rm 1} = 0.4 \,\text{kJ/mol}$ ,  $T_{\rm m} = 68.9 \,^{\circ}C$  and  $\Delta H_{\rm m} = 7.9 \,\text{kJ/mol}$  for **2**,  $T_{\rm 1} = 50.2 \,^{\circ}C$  and  $\Delta H_{\rm 1} = 1.1 \,\text{kJ/mol}$ ,  $T_{\rm m} = 71.0 \,^{\circ}C$  and  $\Delta H_{\rm m} = 8.5 \,\text{kJ/mol}$  for **3**.



**Figure 4.** Powder X-ray diffraction profiles of (a) 1, (b) 2, (c) 2 after heating over  $T_1$ , (d) 3, and (e) 3 after heating over  $T_1$ . All the profiles were recorded at room temperature.

Supporting Information). Thus, a polymorphic phase transition was found to occur for the  $\beta$ - and  $\gamma$ -forms, producing the most stable  $\alpha$ -form upon heating over the  $T_1$ . These transitions were thermally irreversible. When we determined the crystal structure of **2** after heating at 56 °C for 0.2 h, the crystal structural parameters agreed well with those of **1**, as shown in the data summarized in Table 1. This is clear evidence for the fact that the polymorph transition of **2** to **1** occurs via a singlecrystal-to-single-crystal process.

In-Situ Observation of the Crystal-to-Crystal Phase Transition. We also successfully observed the phase transition process of 3 to 1 by optical microscopy. Figure 5 shows a change in the image of the 3 crystals observed during the heating process at the rate of 1 °C/min. The phase transition started at 52.3 °C from a point located near a crack on the crystal surface, the new crystal phase due to the polymorph 1 appeared, and then its area gradually expanded. The boundary of the 3 and 1 crystal phases was detected by optical microscopy due to the reduced light transparency because the disturbed molecular packing results in a partly disordered



Figure 5. (a) Polymorph transition of 3 to 1 observed by optical microscopy. The heating rate was 1  $^{\circ}$ C/min. (See also the movie in the Supporting Information.) (b) Schematic illustration of the boundary migration between the two polymorphic phases.

molecular domain in the crystals by the different packing structures of crystals 3 and 1. This suggests that the molecules are rearranged at the boundary area via an amorphous or lessordered solid state during the phase transition. The domain of the new phase of 1 expanded in four directions, as shown by the illustrative scheme in Figure 5b. The velocity of the front lines of the phase transition seems to depend on the crystal lattice directions. For example, the velocity for the migration of the transition front in a vertical direction in this figure was greater than that in the horizontal one. A more detailed investigation is required in order to determine the mechanism of the crystal-lattice dependent polymorphic phase transition because the crystal we used was not a defect-free single crystal and the faces of the crystal were not determined in the present study. In Figure 5, the entire part of the crystal is finally occupied by the 1 crystal phase within a few minutes.

In order to discuss the changes in the molecular structure, which are required during the phase transitions of crystals 2 and 3 to crystal 1, we illustrate the crystal structures both before and after the phase transition view along the axes of crystal 1 in Figure 6. The motion of the ZZ-Bn molecules is the least during the transition of 2  $(P2_1/c)$  to 1  $(P2_1/c)$ , resulting in the single-crystal-to-single-crystal polymorph transition, as already described. On the other hand, the change in the molecular packing structure includes the large and complicated movement of atoms during the transition of the crystal **3**  $(P2_1/n)$  to crystal **1**  $(P2_1/c)$ . In the latter case, the single-crystal-structure determination was unsuccessful because of deterioration in the quality of a single crystal after the transition of 3 to 1. However, a greater change in the molecular conformation enabled us to directly observe the migration of the front lines for the phase transition phenomenon in the microphotograph image, as already shown in Figure 5.

Photoisomerization Reactivity in the Solid State. The photoisomerization reactivity of ZZ-Bn in the solid state depends on its polymorphic structure. After the photoirradiation of the powdered 1 and 2 crystals, the conversion to **EE-Bn** was quantitative ( $\sim 100\%$  yield), as shown in the



Figure 6. Crystal structures of 1 viewed along the *a*-, *b*-, and *c*-axes (red) overlaid with the structures of 2 (a-c, blue) and 3 (d-f, green).



**Figure 7.** Time-conversion plots for the photoisomerization of 1 ( $\bigcirc$ ), 2 ( $\square$ ), and 3 ( $\triangle$ ) during UV irradiation at room temperature.

time-conversion plot of Figure 7. In contrast, **3** crystals provided the **EE-Bn** in only a low yield, and prolonged irradiation resulted in the formation of an amorphous polymer (Figure S3 in the Supporting Information). In all cases, no EZ isomer was detected during the photoirradiation. Figure 8 shows the distribution of the void space for the polymorphic crystals determined using a free volume program on the basis of the single crystal structures. The calculated total volumes of the void spaces in each unit cell



Figure 8. Drawing of the void space in the unit cell for (a) 1, (b) 2, and (c) 3.

were 51.8, 61.2, and 83.6 Å<sup>3</sup> for 1, 2, and 3, respectively, while the average density was the same for all the crystals (see Table 1). A void space exists around the benzyl moiety in all three crystals but not around the diene moiety. The fact that the molecular packing structures of 1 and 2 crystals are similar to that of 4 (Figure 1) is relevant to the fast isomerization reaching a 100% conversion. The isomerization rate of 2 is slightly higher than that of 1 due to the larger void space in the 2 crystal. On the other hand, the transition of the 3 crystal to the 4 crystal requires much greater motions of the molecules, resulting in the collapse of the crystals and a low isomerization yield.



Figure 9. ORTEP drawings of (a) 2 before photoirradiation, (b) 2 after 25-h photoirradiation (conversion to *EE* isomer 30.8%), and (c) 3 after 18-h of photoirradiation (conversion to *EE* isomer 12.7%). The hydrogen atoms are omitted for clarity. The thermal ellipsoids are plotted at the 50% probability level. The crystal structures were determined at -150 °C.



**Figure 10.** Three reaction models for the photoisomerization mechanism of (Z,Z)-muconate to the (E,E)-muconate via one-bondflip (OBF), bicycle-pedal (BP), and hula-twist (HT) models. The OBF and HT models include two-step reactions, while the BP reaction provides the product by a one-step reaction.

Change in Single Crystal Structures during Photoisomerization. In the present study, we successfully monitored the change in the single-crystal structures of ZZ-Bn(1-3) during the solid-state EZ photoisomerization via a single-crystal-tosingle-crystal reaction process. The lattice parameters gradually changed from the structure of 1 or 2 to the structure of the *EE* isomer as the product (Figure S4 in the Supporting Information). For the reaction of 3, the single-crystal structure remained during the initial stage of the photoisomerization (to 12.7% conversion after 18-h of irradiation), but further photoirradiation resulted in the collapse of the single crystals. The packing structures of the starting crystals, that is, the space groups of  $P2_1/c$  for 1 and 2 and  $P2_1/n$  for 3, were retained after the isomerization (Table 1). These crystal forms differ from that for the crystal of  $4 (P2_1)$ . For the crystal structure after photoirradiation, a disordered structure was observed around the diene moiety. The ORTEP drawings for the crystals of 2 and 3 after the photoirradiation are shown in Figure 9. The disordered structures contain both the **ZZ-Bn** and EE-Bn molecules. A similar result was reported for 1 in our previous communication.<sup>25</sup> The conversions after the photoirradiation were estimated to be 35.3, 30.8, and 12.7% for crystals 1, 2, and 3, respectively, from the site occupancy factor of the produced EE-Bn in the crystals. Observation of the crystal structure directly reveals the change in the ZZ isomer to the EE isomer, consistent with the BP model.



**Figure 11.** Change in the powder X-ray diffraction profiles of 1 (a-d) and 2 (e-g) during the photoisomerization at room temperature. Irradiation time: (a) 0, (b) 10, (c) 30, and (d) 55 h for 1, and (e) 0, (f) 10, and (g) 30 h for 2. (h) 4 prepared by recrystallization.

The EZ photoisomerization processes of the (Z,Z)-muconates to (E,E)-muconates via the three reaction models are illustrated in Figure 10. The BP model provides the (E,E)product by the one-step reaction, while the HT and OBF models include successive reactions. The ZZ-Bn molecules imply an s-cis conformation for the carbonyl and alkene groups in crystals. The s-cis relationship is retained during the singlecrystal-to-single-crystal isomerization process in Figure 9. Both the BP and HT models as a volume-conserving reaction mechanism are candidates for explaining the ZZ-to-EE isomerization of the muconates in the solid state. The sequential HT processes including the fast second-step reaction can provide the (E,E)-product, similar to the reaction via the BP model reaction. However, the HT process is always accompanied by a change in the s-cis/trans conformation during rotation around the double bond and the adjacent single bond. As a result, the HT model provides an *s*-trans product in this case. Actually, the product (E,E)-muconates have the *s*-*cis* conformation. We have confirmed the EZ isomerization process of the muconates in the crystals via the BP model. Thus, the single crystal structure analysis provides clear-cut evidence for elucidating the solid-state photoreaction pathway.

Crystal Phase Transition during Photoisomerization. For all the polymorph crystals, no single crystal structure could be determined for longer photoirradiation times because of the collapse in the single crystal structures. Therefore, a structural change in the ZZ-Bn crystals at a higher conversion was investigated based on a powder X-ray diffraction analysis. The X-ray diffraction lines after the reaction agreed well with those for the recrystallized 4 (Figure 11). The molecular conformation of 4 includes an asymmetric structure with a bent benzyl moiety, as shown in Figure 1d, being different from the symmetric conformation of the ZZ-Bn molecules in crystals 1-3. The crystal symmetry changed from an achiral  $P2_1/c$  for 1 and 2 to a chiral  $P2_1$  for 4, although the reason why the crystals lose symmetry is not yet clarified. The simultaneous crystal structure transition was observed for the photoisomerization of the other muconates; for example, the space group of the crystal of di(n-butylammonium) muconate changed from  $P2_1/n$  to P(-1).<sup>18b</sup> Crystal 3 with the  $P2_1/n$  symmetry became amorphous during the prolonged irradiation (Figure S3).

The **EE-Bn** molecules change their conformation in the solid state using the void space around the benzyl moiety

shown in Figure 8. During the photoisomerization of **ZZ-Bn** to **EE-Bn**, a structural strain is produced by a mismatch in the structures of the *ZZ* and *EE* derivatives in the crystal lattice. When the **EE-Bn** molecules are produced in the crystal lattice of the **ZZ-Bn** molecules during the solid-state reaction, a structural strain is accumulated in the **EE-Bn** molecules as a strained molecular conformation, rather than the remaining **ZZ-Bn** molecules. We previously evaluated the geometric parameters for the **ZZ-Bn** and **EE-Bn** molecules in each crystal and the cocrystals obtained during the photoisomerization.<sup>25</sup> The obtained geometric parameters suggested a small change in the molecular structure of **ZZ-Bn** in the crystal during the isomerization, while a structural strain became concentrated at the bond angles in the produced EE molecules.

The reaction mechanism for the photoisomerization of ZZ-Bn to EE-Bn is summarized as follows. The isomerization initially proceeds via a topochemical reaction process according to a bicycle-pedal model, which requires no significant movement of atoms. Structural strain is accumulated during the reaction due to the formation of the EE-Bn molecules in the original crystal lattice of **ZZ-Bn**, and this accumulated structural strain then causes a phase transition from the strained EE-Bn crystal structure to the EE-Bn crystals with a molecular packing structure identical to that of the recrystallized EE-Bn. At the same time, the space group changes from  $P2_1/c$  to  $P2_1$  during the phase transition of 1 and 2, in which the void space included in the crystals plays an important role. The greater molecular motion of 3 causes collapse of the crystals, which become amorphous during irradiation.

### Conclusions

In the present study, we investigated the EZ photoisomerization of the muconates as the 1,3-diene compounds in the solid state. We showed that **ZZ-Bn** provides three kinds of polymorphic crystals by recrystallization from a chloroform solution and produces an EE isomer in the solid state with a different reactivity depending on the molecular packing structure in the polymorphic crystals. Based on the results of the X-ray single-crystal structure analysis, it has been demonstrated that the EZ isomerization from the ZZ to EEderivatives proceeds according to a bicycle-pedal model with minimum movement of the atoms in the solid state. During irradiation, a structural strain accumulated in the crystal lattice and caused a phase transition accompanied by a change in the space group, resulting in the stable crystal structure. The polymorphic phase transition was also successfully monitored by a single crystal structure analysis and microscopic observation in the present study. The fundamental investigation using crystallographic approaches for elucidating the mechanism for the isomerization in a constrained state, such as the crystalline state, would help with the understanding of the reaction mechanism of other complicated systems, because X-ray single crystal structure analysis provides credible experimental results with a high accuracy and a vast amount of information.

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Supporting Information Available: X-ray crystallographic information files (CIF), bond lengths and angles, IR and UV-vis spectra, powder X-ray diffractions, crystal lattice parameters, and movie for polymoph transition. This material is available free of charge via the Internet at http://pubs.acs.org.

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