

Electronic supplementary information for

Direct observation of change in molecular structure of benzyl (Z,Z)-muconate during photoisomerization in the solid state

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Experimental Procedures

General Methods

The powder X-ray diffraction profile was recorded using a Rigaku RINT-2100 with monochromated Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$, 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 parallel slip analyzer PSA100U and a graded multilayer 2960C1. DFT calculation was carried out at (R)B3LYP/6-311G(d) level of theory using a Gaussian program.^{S1} A massed void space in the unit cell was estimated using a Free Volume program contained in the *Cerius*² software package (version 4.0). The atomic radii adopted for the calculation are 1.20, 1.70, and 1.60 \AA for hydrogen, carbon, and oxygen, respectively.

Single-Crystal Structure Analysis

The single-crystal X-ray diffraction data were collected using a Rigaku RAXIS RAPID imaging plate diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) monochromated by graphite at room temperature. The cell constants were calculated by the global refinement. Data reduction was performed using CrystalStructure software. 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.^{S2} The positions of all hydrogen atoms were calculated geometrically and refined by the riding model.

The details of X-ray analysis of crystal **1** after UV light irradiation are as follows: The crystal structure of **1** before photoirradiation was used as the initial model of the refinement. When the C1 and C2 atoms were refined isotropically, two new peaks Q1 and Q2 appeared around C1 and C2 atoms. The heights of peaks Q1 and Q2 were 0.80 and 0.56 e\AA^{-3} , which are much larger than other residual peaks (less than 0.2 e\AA^{-3}). These peaks were assigned to two olefin carbons of EE isomer, C1E and

C2E. Based on these peaks the model of the EE isomer was constructed. The bond lengths and geometry of the phenyl groups in both ZZ and EE isomers were restrained in the refinement. The EE isomer was obtained as a disordered structure. All of non-hydrogen atoms for both isomers were finally refined anisotropically. The R_1 for the reflection with $I > 2\sigma(I)$ and wR_2 for all data were 0.071 and 0.229, respectively. The heights of the residual electron peaks were less than $0.18 \text{ e}\text{\AA}^{-3}$. The occupancy factor for the EE isomer converged to 0.353(15).

Materials

(*Z,Z*)- and (*E,E*)-muconic acids were purchased from Acros Organics and Aldrich Co., Ltd., respectively, and used without further purification. All of the esters were prepared by the reaction of the muconic acids with benzyl bromide according to a previously reported procedure.^{S3} Single crystals were obtained during the evaporation of the *n*-hexane and ethanol solutions of **1** and **2**, respectively, at room temperature.

Benzyl (*Z,Z*)-muconate (**1**): Recrystallized from *n*-hexane; mp 68.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.93 (m, CH=CHCO₂R, 2H), 7.34 (m, Ar, 10H), 6.03 (m, CH=CHCO₂R, 2H), 5.19 (s, OCH₂, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 165.36 (C=O), 138.34 (CH=), 135.64, 128.60, 128.34, and 128.27 (Ar), 124.01 (CH=), 64.29 (OCH₂).

Benzyl (*E,E*)-muconate (**2**): Recrystallized from ethanol; ¹H NMR (400 MHz, CDCl₃) δ 7.36 (m, CH=CHCO₂R, 2H), 7.26 (m, Ar, 10H), 6.24 (m, CH=CHCO₂R, 2H), 5.21 (s, OCH₂, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 165.65 (C=O), 141.18 (CH=), 128.63, 128.41, 128.35, and 128.24 (Ar), 135.58 (CH=), 66.71 (OCH₂).

Photoreaction

The photoreaction of **1** was carried out using an ultra-high pressure mercury Moritex MUV-250U-L lamp (500 W). The photoreaction of the single crystal of **1** for the *in-situ* X-ray analysis was carried out under irradiation at an absorption tail using an infrared absorption filter IRA-25S and a band path filter UV-D36B (Asahi Techno Glass Co.) at specific time intervals in order to maintain a single crystal form by a homogeneous reaction. Very small change was observed in the UV-vis absorption spectrum of the crystals of **1** during photoirradiation, as shown in Fig. S1, because the molecules **1** and **2** have similar absorption properties due to the similar molecular conformation. During photoirradiation of the powdered crystals, only an IRA-25S filter was used to achieve a high conversion. After the photoirradiation, the conversion of the isomer was determined by NMR spectroscopy.

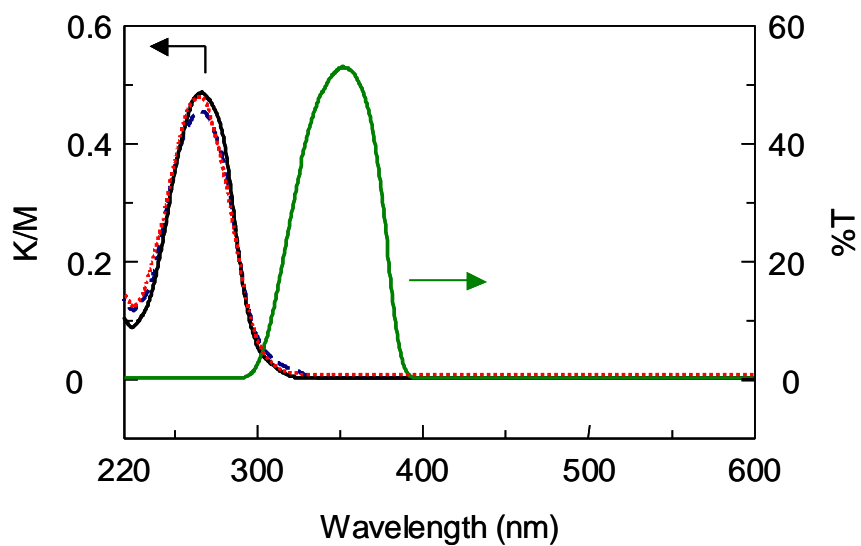


Fig. S1 UV-vis spectra for the crystals of **1** (dotted line in red), the crystals of **1** after 2-h photoirradiation (dashed line in blue), the crystals of **2** recrystallized (solid line in black) and UV-D36B (solid line in green).

Data for Crystal Structure Analysis

Table S1. Crystallographic Data for **1** and **2**^a

	1	1 (after UV irradiation) ^b	2
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁</i>
<i>a</i> , Å	10.332(4)	10.328(6)	9.167(3)
<i>b</i> , Å	5.682(2)	5.765(4)	5.7038(11)
<i>c</i> , Å	14.791(7)	15.005(9)	17.002(5)
β , deg	105.86(4)	106.00(3)	104.803(4)
<i>V</i> , Å ³	835.2(6)	858.8(9)	859.5(4)
<i>Z</i>	2	2	2
ρ_{calc} , g/cm ³	1.282	1.247	1.246
reflns measured	6512	6993	8154
unique reflns	1877	1933	3569
no. obsd ($I > 2\sigma(I)$)	1198	842	1625
<i>R</i> ₁	0.052	0.071	0.043
<i>wR</i> ₂	0.132	0.229	0.089
GOF	1.03	0.94	0.80

^a **1** was recrystallized from *n*-hexane and **2** from ethanol. ^b After the photoirradiation of **1** for 27 h at room temperature using an ultra-high pressure mercury lamp (500W), a band path filter UV-D36B and an infrared absorption filter IRA-25S (A conversion to **2** was 35%).

Table S2. Comparison of Selected Geometrical Parameters for Molecules Included in the Crystals

bond length and angle ^a	1 (recrystal- lized)	1 (calcd) ^b	1 molecule after photo- irradiation of 1 [strain, %]	2 (recrystal- lized)	2 (calcd) ^b	2 molecule after photo- irradiation of 1 [strain, %]
C1-C1 (Å)	1.426(3)	1.45214	1.434(17) [0.6]	1.439(3)	1.44449	1.44(4) [0.1]
C1-C2 (Å)	1.331(2)	1.34870	1.340(10) [0.7]	1.324(3)	1.34336	1.34(2) [1.2]
C2-C3 (Å)	1.461(2)	1.48062	1.527(10) [4.5]	1.467(4)	1.47957	1.47(2) [0.2]
C3-O1 (Å)	1.1941(18)	1.21211	1.193(10) [0.1]	1.195(3)	1.21000	1.11(3) [7.1]
C3-O2 (Å)	1.3368(18)	1.35331	1.340(10) [0.2]	1.343(3)	1.35098	1.38(3) [2.8]
C1-C1-C2 (deg)	126.36(19)	125.880	124.6(10) [1.4]	125.4(2)	123.809	131(2) [4.5]
C1-C2-C3 (deg)	126.83(15)	126.400	128.6(6) [1.4]	121.6(3)	120.817	121.1(17) [0.4]
C2-C3-O1 (deg)	127.17(15)	127.437	124.6(5) [2.0]	125.8(3)	125.633	132(2) [4.9]
C2-C3-O2 (deg)	110.32(12)	109.557	111.0(6) [0.6]	111.2(3)	110.507	100(2) [10]
C1-C1-C2-C3 (deg)	1.0(4)	0.03	1.9(12)	-178.5(2)	-179.93	179.4(17)
C1-C2-C3-O1 (deg)	8.1(3)	0.12	5.3(10)	-1.1(5)	0.42	6(4)
C1-C2-C3-O2 (deg)	-172.93(19)	-179.88	-176.5(7)	-177.8(3)	-179.57	-176.9(15)

^a The numbering of atoms for the determination of bond length and angle is shown in Fig. S2. ^b DFT calculation for single molecule at (R)B3LYP/6-311G(d) level of theory. The molecular conformation determined for the recrystallized **1** and **2** agreed well with the calculated one for each isomer.

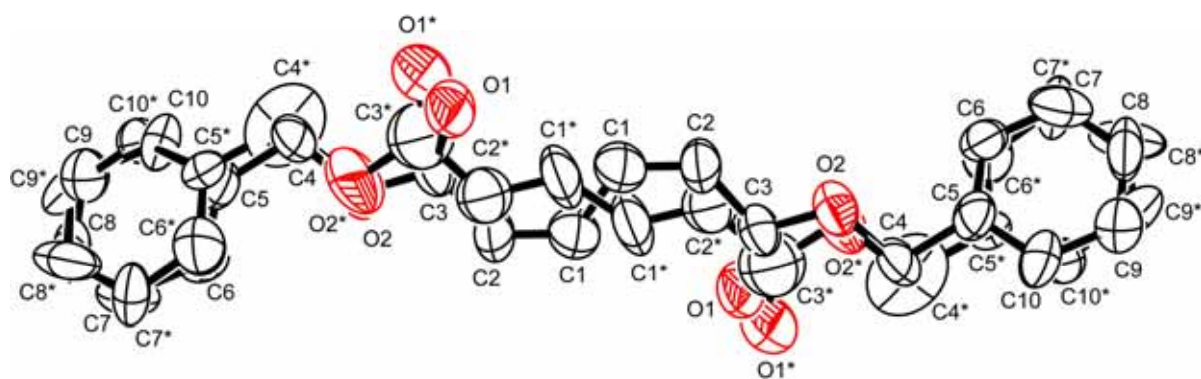


Fig. S2 ORTEP drawings and the numbering of the atoms for the crystal structure separated into **1** and **2** with a site occupancy factor of 35 % for **2**. The hydrogen atoms are omitted for clarity. The thermal ellipsoids are plotted at the 50 % probability level.

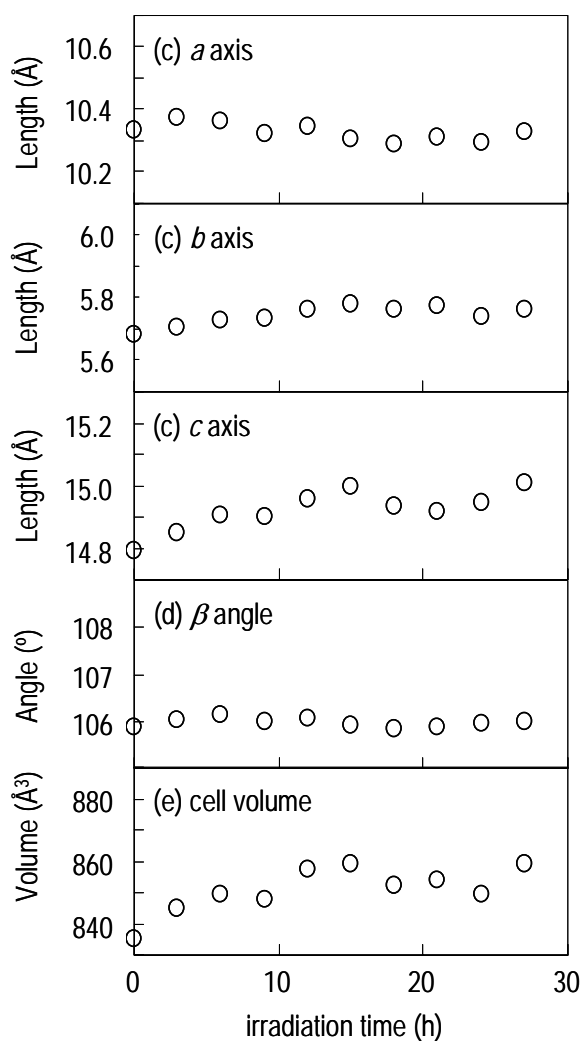


Fig. S3 Changes in (a) *a*-axis length, (b) *b*-axis length, (c) *c*-axis length, (d) β -angle, and (e) cell volume of **1** during the photoisomerization. The crystal lattice parameters were determined by single crystal structure analysis at each irradiation time. The conversion of **1** to **2** was 35% after a 27-h irradiation.

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