Photodimerization Mechanism of Bis(3,4,5-trifluorobenzyl) (*E*,*E*)-Muconate in a Columnar Assembly in the Crystalline State

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We have revealed the photoreaction mechanism for the single-crystal-to-single-crystal transformation of bis(3,4,5-trifluorobenzyl) (*E*,*E*)-muconate (**1**) to the corresponding dimer. The [2 + 2] photodimerization randomly occurred in the columnar assembly of monomer molecules in the crystals of **1**, followed by the formation of a trimer. The photoreaction was directly monitored by an X-ray single crystal structure analysis as well as the product analysis by NMR and MS spectroscopies.

Solid-state organic syntheses have attracted much interest due to the high regio- and stereoselectivity of these reactions.[1] The solid-state [2 + 2] photodimerizations of unsaturated compounds have been intensively studied since the 1960s.[1a,2] The synthesis of ladder-shaped molecules from dienes and trienes was also reported via photodimerization using a linear template under the supramolecular control of the structure and reactivity of the substrates in the crystals.[3] In our previous paper,[4] we revealed the solid-state photoreactions of a series of fluorine-substituted benzyl muconates. Muconic derivatives as one of the 1,3-diene compounds produce [2 + 2] dimers,[2c,2d,4] EE-isomers,[5] and stereoregular polymers,[6] depending on the monomer structure and molecular packing in the crystals. Monitoring the process of a solid-state reaction using X-ray crystal structure analysis provides us with important information regarding the reaction mechanism in the solid state. Recently, we observed a change in the crystal structure during the photodimerization of bis(3,4,5-trifluorobenzyl) (*E*,*E*)-muconate (**1**) (Chart 1) in the crystalline state. In this communication, we report the reaction mechanism for the photodimerization of **1** in the crystalline state, investigated by a X-ray single crystal structure analysis as well as product analyses.

We carefully carried out the photoreaction of **1** using an ultra-high-pressure UV-lamp (250 W, a distance of 5 cm) with some optical filters (IRA-25S, UV-31, and UV-D36A) under atmospheric conditions at room temperature for 20 h and observed the change in the single-crystal structure. Table 1 summarizes the results of the single crystal structure analysis[7] before and after UV irradiation. The crystal maintains the same space group and similar lattice parameters during the reaction.

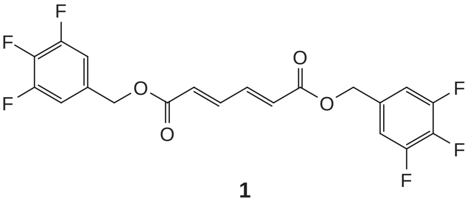

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Chart 1.

For the crystals after photoirradiation, a disordered structure was observed and the structure had separated into the monomer and a product with an occupancy factor of 27.9% for the latter (Figure 1). The product apparently seems to have a ladder structure, but in an actual case, the dimer including a cyclobutane ring is randomly formed at a specific position in the lattice. The molecule **1** has double bonds at four crystallographically equivalent positions for the cyclobutane ring formation. A cyclobutane ring can be randomly formed in the columnar structure consisting of the translational arrangement of the **1** molecules, which have a centro-symmetrical structure, because no pair is observed in a columnar assembly in the monomer crystals. The predominant formation of the [2 + 2] photodimer during the initial stage of the reaction of **1** in the crystalline state has already been reported in our previous paper.[4]

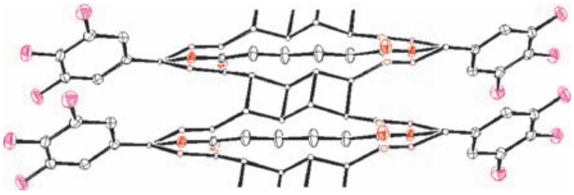


Figure 1. ORTEP drawing of **1** after UV irradiation. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are plotted at the 10% probability level. Photoproduct is superimposed on monomer molecules.

Table 1. Crystallographic data of **1** before and after UV irradiation

Conversion	0%	27.9%
Chemical formula	$C_{20}H_{12}O_4F_6$	$C_{20}H_{12}O_4F_6$
Formula weight	430.30	430.30
Crystal habit	block	block
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
T/K	296	296
a/Å	3.966(2)	3.979(3)
b/Å	20.041(10)	20.55(2)
c/Å	11.556(6)	11.537(8)
β/deg	96.784(15)	95.15(4)
V/Å^3	912.0(8)	939.7(13)
Z	2	2
ρ_{calcd}/g cm^{-3}	1.567	1.521
Reflns measured	8431	6897
Unique reflns	2079	2109
No obsd ($I > 2\sigma(I)$)	1333	737
R_1 ($I > 2\sigma(I)$), wR_2 (all)	0.0697, 0.2075	0.0657, 0.2159
GOF	1.082	0.876

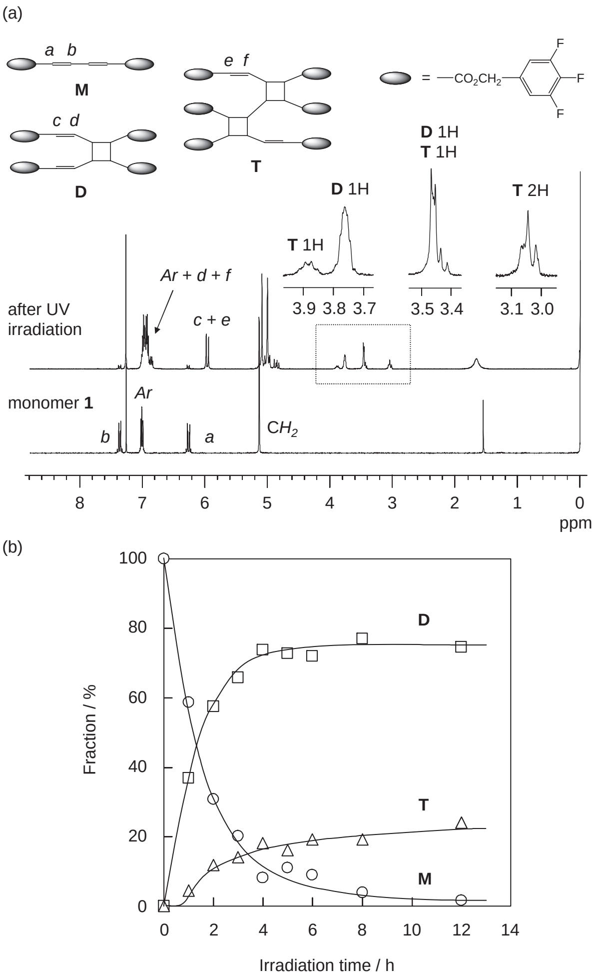
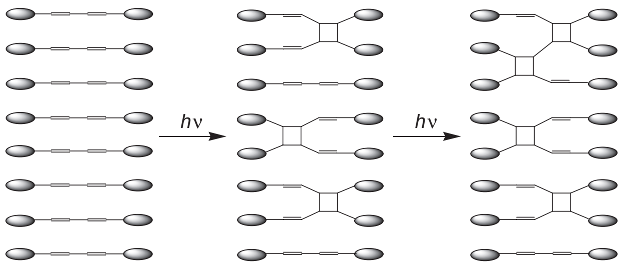


Figure 2. (a) ^{1}H NMR spectra of the starting **1** and photoproducts after UV irradiation (92% conversion). (b) Change in the fraction of products during the photoreaction. (○) Monomer, (□) dimer, and (△) trimer.



Scheme 1.

In the present study, we investigated the photoreactions up to the high conversion of **1**. In the NMR spectrum (Figure 2a) of the photoproducts, a trimer was also confirmed in addition to the formation of a dimer.[8] In the NMR spectra of the products, peaks due to the two methine protons of a cyclobutane group for the dimer were observed at 3.48 and 3.77 ppm during the initial stage of reaction, and then the other peaks were also additionally observed at 3.05, 3.43, and 3.89 ppm. The latter peaks are assigned to the trimer. The trimer was isolated as a white powder by the concentration of the chloroform solution containing a mixture of the products after photoirradiation.

Figure 2b shows the fractions of the unreacted **1**, and the resulting dimer and trimer as a function of the photoirradiation time. This result supports the dimer formation during the initial period of the reaction and the production of a trimer by a further reaction between the resulting dimer and the remaining monomer, as shown in Scheme 1. It is due to the random formation of the dimer in the columnar assembly of the monomer molecules, as was already shown in the X-ray single crystal structure analysis. A trace of a higher oligomer was also detected in the NMR spectra at the higher conversion, but it could not be isolated.

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8 Dimer of **1**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.00–6.91 (m, *o*-Ph, C*H*=CHCO$_2$R, 10H), 5.98–5.94 (d, $J = 15.6$ Hz, CH=C*H*CO$_2$R, 2H), 5.12–4.96 (m, CH$_2$, 8H), 3.78–3.75 (m, 2H), 3.47–3.45 (m, 2H); MS (FAB): calcd for $C_{40}H_{24}O_8F_{12}$ 860.1; found 861.1 $[M + H]^+$. Trimer of **1**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.00–6.83 (m, *o*-Ph, C*H*=CHCO$_2$R, 14H), 5.98–5.94 (d, $J = 15.6$ Hz, CH=C*H*CO$_2$R, 2H), 5.09–4.76 (m, CH$_2$, 12H), 3.91–3.85 (m, 2H), 3.49–3.41 (m, 2H), 3.06–3.02 (m, 4H); MS (FAB): calcd for $C_{60}H_{36}O_{12}F_{18}$ 1290.2; found 1291.3 $[M + H]^+$.

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