

# Unidirectional *cis-trans*-photoisomerization of *cis*-3,3'-bis(diphenylhydroxymethyl) stilbene in inclusion complex crystals

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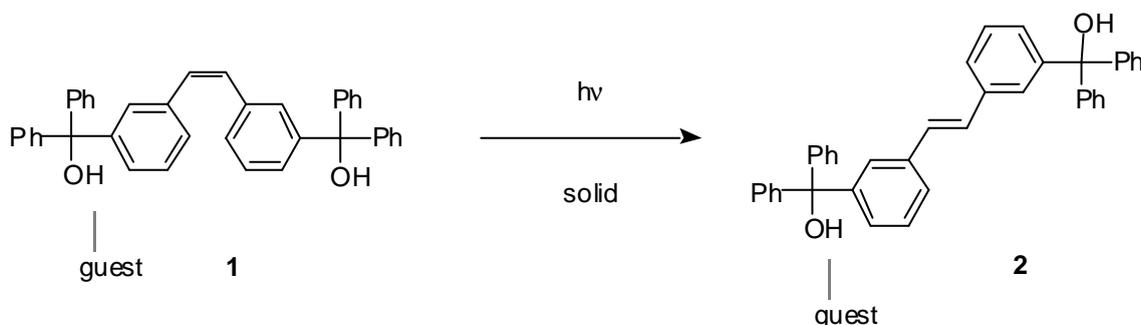
ABSTRACT: When a 1:1 complex of *cis*-3,3'-bis(diphenylhydroxymethyl) stilbene (**1**) with acetone was irradiated in the solid state at room temperature using a high-pressure mercury lamp with a Pyrex filter for 6 h, a 1:1 complex of the *trans*-isomer (**2**) with acetone was obtained without losing the guest acetone molecules. Similar results were obtained without guest or in the presence of other guests. Internal rotation around the double bond bearing the very large triphenylhydroxymethyl substituents is hardly imaginable in the confinement of the crystal. Therefore, the geometrically easier "hula-twist" (HT) mechanism with its movements primarily in the molecular plane provides a viable mechanistic alternative for the *cis-trans*-isomerization. The solid-state mechanism of the reaction was studied by X-ray and AFM analyses. Face selective efflorescence formed a protective cover on (100) and can be related to the crystal structure. Further molecular migration was not detected with the sensitivity of the AFM

and the crystal of **1**·acetone did not lose its clarity and microscopic shape. The *cis-trans*-conversion profits from cages that are present in the crystal lattice. X-ray structural analysis confirmed a strong loss of crystallinity upon the photochemical conversion of **1**·acetone which precludes a definitive conformational proof of HT by X-ray diffraction. The formation of the amorphous phase excludes a topotactic reaction.

**KEYWORDS:** *cis-trans* isomerization; inclusion crystal; X-ray structure; atomic force microscopy (AFM); hula-twist (HT); amorphous phase

## INTRODUCTION

Photochemical *cis-trans* isomerizations in constrained media are of special interest in recent years in relation to the photoisomerization of chromophores in biological systems (e.g., photoactive yellow protein and retinoid-binding proteins).<sup>1</sup> Recently, various *cis-trans* isomerizations of C=C double bonds, e.g. of 2-benzylidene-butyrolactone and 1,2-dibenzoyl-ethene in the crystalline state have been reported.<sup>2,3</sup> We now report the unidirectional photoisomerization of *cis*-3,3'-bis(diphenylhydroxymethyl) stilbene (**1**) to its *trans*-isomer (**2**), neat and in inclusion crystals with guest molecules (Scheme 1).



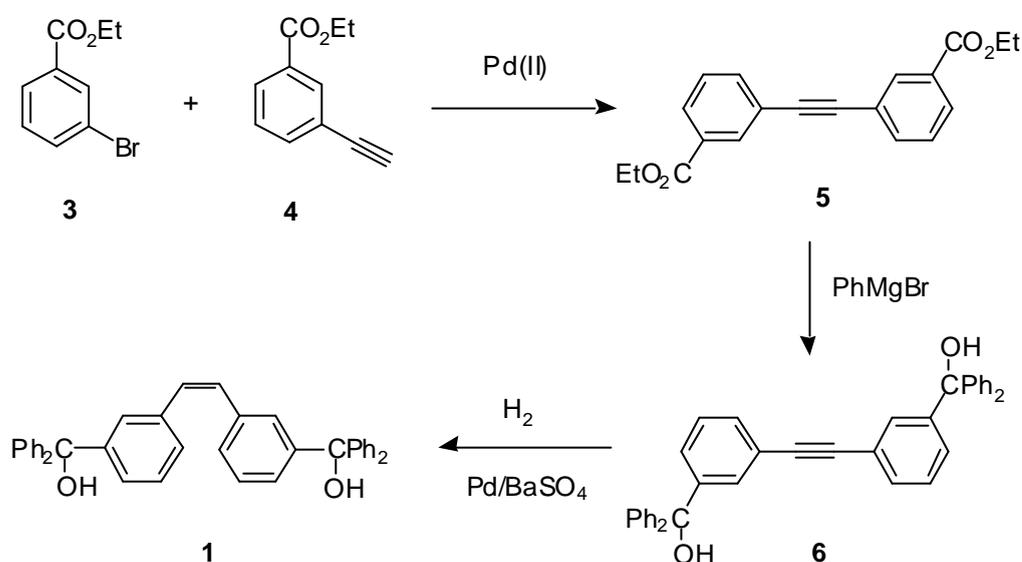
**Scheme 1.** Solid state photoisomerization of **1** to give **2**.

## RESULTS AND DISCUSSION

### Preparations and solid-state photolyses

The host compound (**1**) was prepared according to the method shown in Scheme 2.

Treatment of 3-bromo-benzoic acid ethyl ester (**3**) with 3-ethynyl-benzoic acid ethyl ester (**4**) in the presence of a Pd(II) catalyst gave 3,3'-bis(carboethoxy) diphenylacetylene (**5**), which upon treatment with PhMgBr in dry THF followed by hydrogenation on Pd/BaSO<sub>4</sub> gave *cis*-3,3'-bis(diphenylhydroxymethyl) stilbene (**1**). The host compound (**1**) formed stable inclusion complex crystals with various kinds of guest compounds (Table 1). For example, when **1** was recrystallized from acetone, a 1:1 inclusion crystal was obtained as colorless prisms.



**Scheme 2.** Synthesis of the host compound **1**.

The various host-guest compounds of *cis*-**1** and also guest-free **1** (see Experimental) underwent solid-state geometric isomerization to give the *trans*-isomer **2**. Very interestingly, when a single crystal (3.0 x 1.0 x 0.5 mm<sup>3</sup>) or powder of the 1:1 inclusion complex of **1** with acetone (**1**·acetone) was irradiated with a 400 W high-pressure mercury lamp using a Pyrex filter from a distance of 10 cm at room temperature for 12 h or 6 h, respectively, a pale yellow crystal (or powder) of the 1:1 acetone complex of **2** with acetone (**2**·acetone) was formed. A 92% conversion of the powder was obtained. After photolysis, the single crystal was still clear and the microscopic crystal shape had not changed. It is also surprising that the guest acetone molecules were mostly held in the crystal (about 94% retained as detected by thermo gravimetric analysis) despite the

drastic change in the shape of the host molecule during isomerization. Similarly, the *cis-trans* isomerization of **1** and of its inclusion crystals with cyclopentanone,  $\gamma$ -butyrolactone, dioxane, DMSO, DMF and pyridine occurred efficiently (though slowly) in the solid state without loss of the guests (Table 1). On the other hand, prolonged irradiation of **2** or of its acetone inclusion complex **2**·acetone did not change the material: no trace of **1** could be detected by  $^1\text{H}$  NMR analysis. The unidirectional photoisomerization of **1** to **2** in the inclusion complex with acetone was investigated by X-ray diffraction and atomic force microscopy (AFM) analysis.

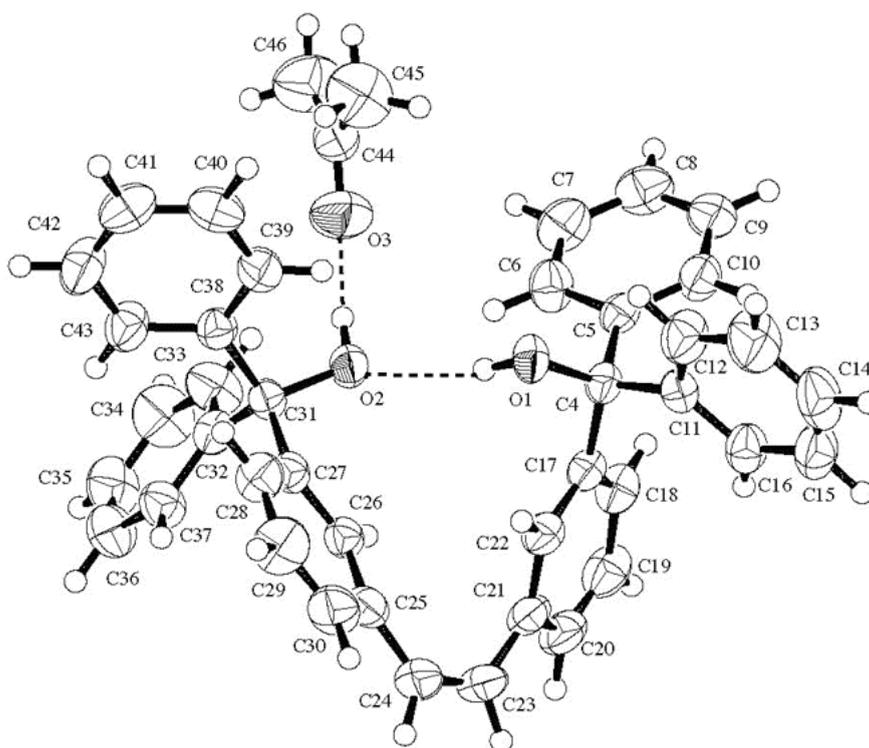
**Table 1.** Host-guest complexes of *cis*-3,3'-bis(diphenylhydroxymethyl) stilbene (**1**) and their photoisomerization in the solid-state.<sup>a</sup>

guest	h:g ratio	Z: m.p. (°C)	conversion (%)	h:g ratio	E: m.p. (°C)
acetone	1:1	77-82	92	1:1	70-75
cyclopentanone	1:1	75-83	93	1:1	65-70
$\gamma$ -butyrolactone	1:1	85-90	95	1:1	55-60
dioxane	1:1	110-115	71	1:1	85-90
DMSO	1:2	130-135	68	1:2	120-130
DMF	1:2	78-83	72	1:2	90-95
pyridine	1:1	93-95	92	1:1	75-78
–	–	170-175	93	–	68-73

<sup>a</sup> The photolyses of powdered crystals were carried out for 6 h.

### X-ray analysis

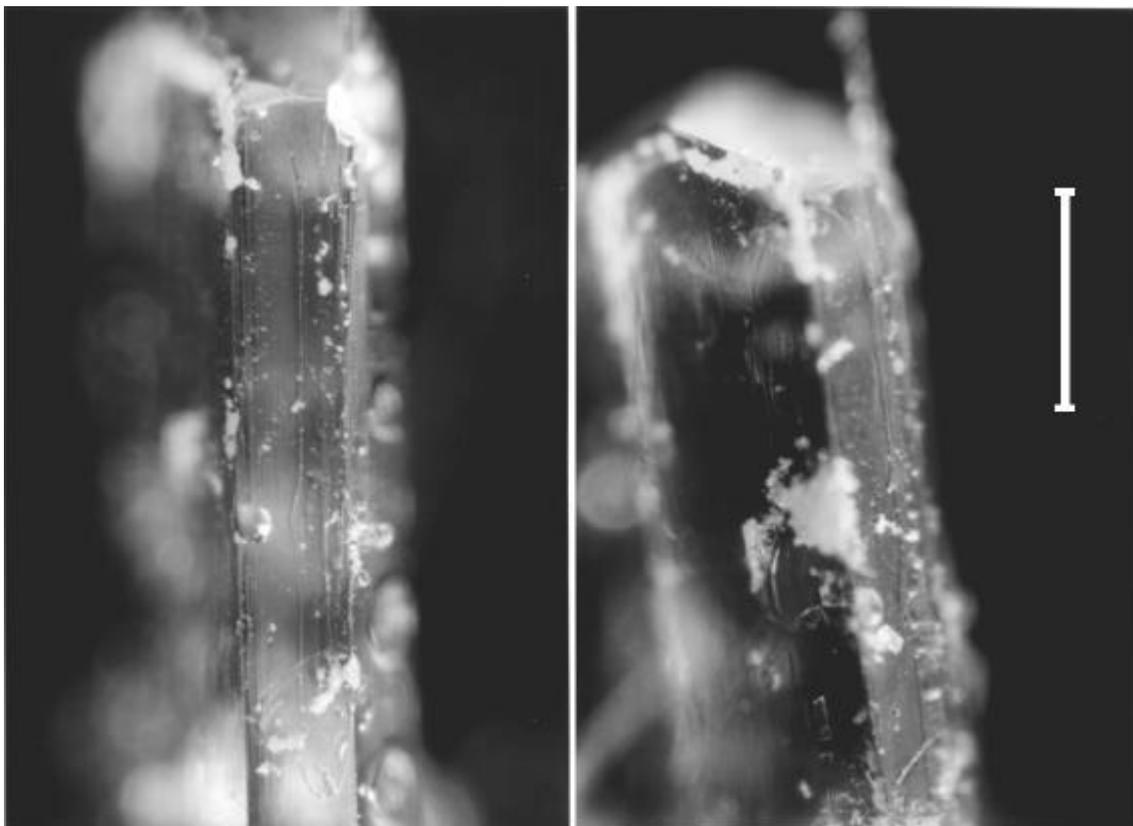
The molecular structure in the crystals of **1**·acetone is shown in Figure 1. The acetone molecule is connected to the host **1** by the O2-H2 $\cdots$ O3 hydrogen bond with the O2 $\cdots$ O3 distance of 2.829(4) Å and it is not disordered. There is also an intramolecular O1-H1 $\cdots$ O2 hydrogen bond of the host molecule (O1 $\cdots$ O2 distance of 2.993(3) Å). The dihedral angle between the two phenyl rings of the *cis*-stilbene moiety is 47.8(1)°, and the central C21-C23=C24-C25 torsion angle is 7.5(8)°.



**Figure 1.** The molecular structure of **1·acetone** with displacement ellipsoids at the 50% probability level.

### Supermicroscopic Analysis with AFM

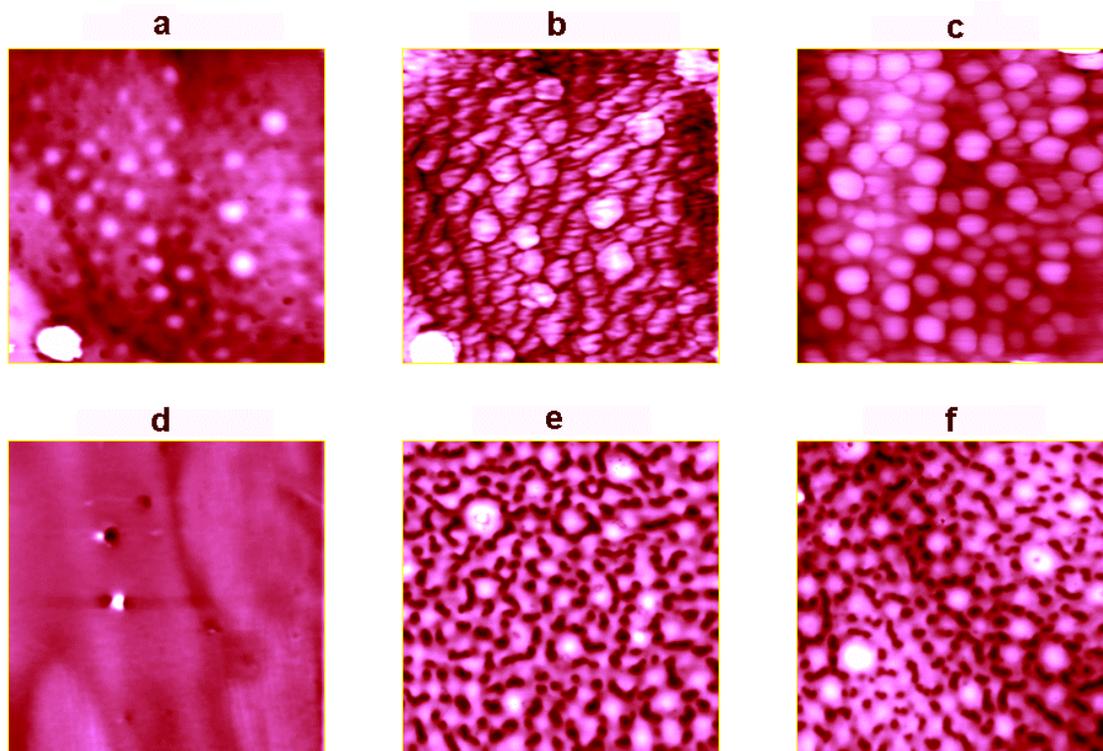
The crystals of **1·acetone** keep their guest upon the photoisomerization. However, at the molecular resolution (in Z-direction) of AFM, surface reconstruction or efflorescence may occur with loss of some acetone in the surface region. This seems to be a problem at room temperature, but less so at  $-17$  to  $-15^{\circ}\text{C}$  (Figure 2). Low-temperature irradiation is also required because there are signs of local melting if high intensity irradiation (700 W Hg lamp through Pyrex cooled to  $14^{\circ}\text{C}$ ) is performed at room temperature: initially sharp crystal edges become smoother and AFM (Figure 3d) detects softened surface regions, but not in irradiations at  $< -15^{\circ}\text{C}$ . Both, almost acetone-free ( $< 6\%$ ) crystals of **1** and the crystals of **1·acetone** undergo the *cis-trans*-photoisomerization also at  $-17$  to  $-15^{\circ}\text{C}$  and (more slowly) at  $-70^{\circ}\text{C}$ , as was checked by  $^1\text{H-NMR}$  analysis. If a prismatic crystal of **1·acetone** was irradiated for 6 h at  $-17$  to  $-15^{\circ}\text{C}$  through a Pyrex filter, no microscopic change was observed even though the crystal was 30% converted to **2·acetone**.



**Figure 2.** Micrographs of a crystal of **1·acetone**; the white bar corresponds to 0.1 mm; left image: (010)-face before irradiation; right image: after 6 h irradiation with a 700 W Hg high-pressure lamp through Pyrex at 15 cm distance and -17 to -15°C. The irradiated crystal was tilted in order to visualize both the (110)-face and the (010)-face. Two small crystallites on (010) are the result of some remote crystal breakage that happened upon its tilt with a tweezers.

Also long irradiation (20 h; the irradiation times for high conversion are rather long due to internal filtering by the strong light absorption of the product **2**) up to nearly complete conversion did not disintegrate the single crystals. There was the expectation that this highly space demanding *cis-trans*-isomerization had occurred in a topotactic manner. Therefore the AFM results in combination with X-ray diffraction are of particular interest for the substantiation or exclusion of that assumption. AFM has been successfully used to prove and disprove several claims of topotaxy in various molecular crystals very sensibly.<sup>4</sup>

The main surface (100) of a flat plate-like crystal of **1•acetone** was irradiated at a low light intensity at 20-25°C and the surface change measured at various times. Figure 3



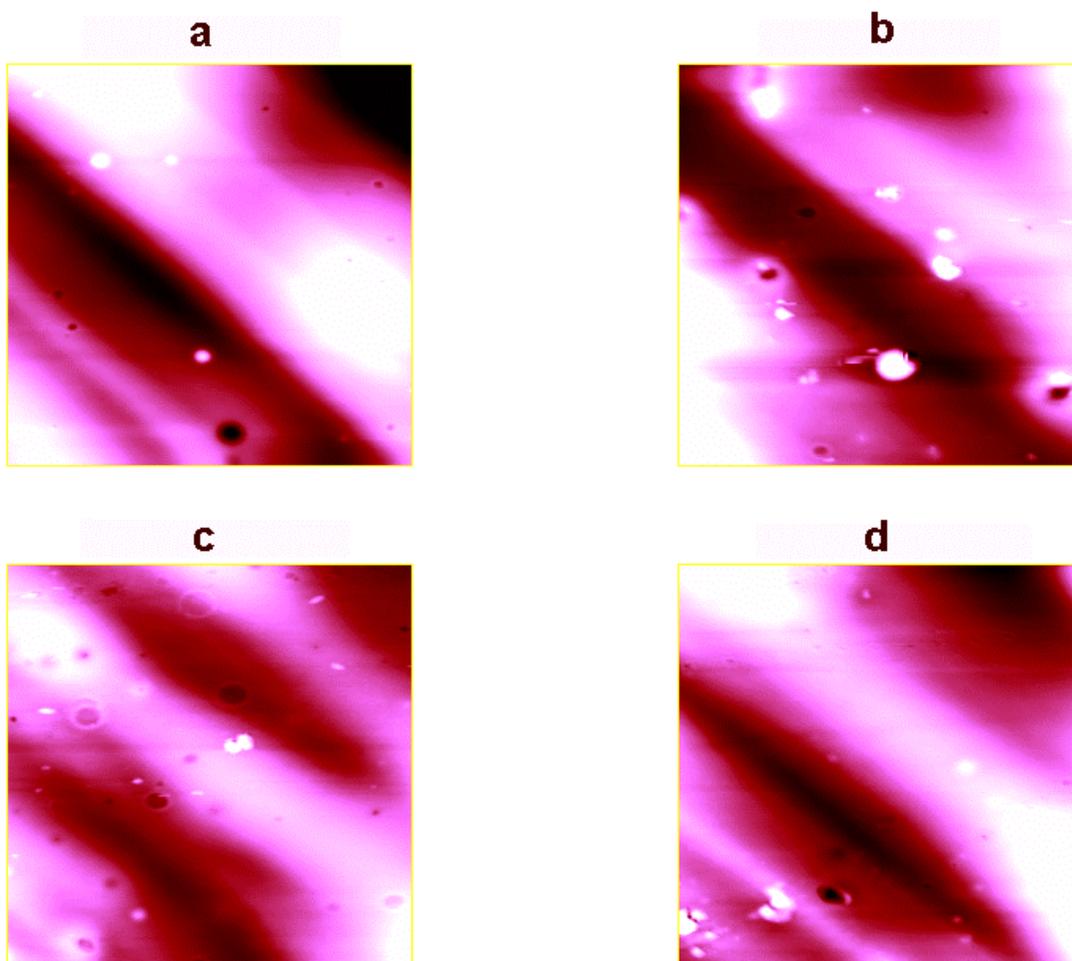
**Figure 3.** 10  $\mu\text{m}$  AFM topographies of the (100)-face of **1•acetone**; a: fresh surface of a flat plate specimen; b: after 4 h; c: after 10 h irradiation with an old 125 W Hg lamp through Pyrex at 3 cm distance from the lamp and 20-25°C; d: after 3 h irradiation with a 700 W Hg lamp at room temperature; e: a fresh surface after 5 and f: after 15 min irradiation with a 700 W Hg lamp at -17 to -15°C and 15 cm distance from the lamp; the Z-scale is 100 nm

shows that the initial surface has some roughness ( $R_{ms} = 7$  nm, excluding the large feature) with a maximal height of 62 nm (excluding the large feature) obviously from some efflorescence upon 2 weeks rest in a bottle without acetone atmosphere. These values increase to 12 and 88 nm in b and 9 and 85 nm in c. It is clearly seen (a and b) how the original positive features increase while the craters disappear. That change comes to a stop in Figure 3c. Clearly, a rather thin cover is formed on (100) which prevents further efflorescence, while the conversion to **2•acetone** in the bulk exceeds 50%. If a much higher light intensity of a fresh 700 W Hg lamp is applied, similar features form within

minutes ( $R_{ms} = 7$  nm, max. height 55 nm), that keep their shape but collapse after 3 h irradiation followed by apparent local melting (Figure 3d).

A very flat surface part of **1·acetone** on (100) ( $R_{ms} = 3.5$  nm, max. height 48 nm) was irradiated under argon at -17 to -15°C with the 700 W Hg lamp. It gave comparable signs of efflorescence with fewer hills and formation of craters around them on (100) ( $R_{ms} = 12$  nm, max. height 116 nm) (Figure 3e/f). The surface did not change significantly further after 15 min irradiation ( $R_{ms} = 12$  nm, max. height 125 nm). Therefore, these features are interpreted as the formation of a cover that is the result of initial efflorescence but not of the bulk photoisomerization.

Well formed six-sided prismatic crystals of **1·acetone** were probed on all of the paired faces along the *c*-axis. The now smaller developed (100) face was securely identified by the features similar to those in Figure 3e upon irradiation. The (010)-surface (Fig. 2) has the humps parallel to the long crystal *c*-axis and is scanned with the AFM tip at sites where these are least pronounced. It turns out that no change is detectable. Even very long irradiation does not change the shape of the side-face as is shown in Figure 4. The conversion of the crystal in Figure 4d was detected with <sup>1</sup>H-NMR to be 56%. Similarly, no change of the surface was detected on the (110)-face upon irradiation under the same conditions. Clearly, no long-range movements of molecules [except for the initial efflorescence on (100)] can be detected with the AFM and this observation points to either a topotactic reaction or to the formation of an amorphous phase in the crystal of **1·acetone** to give **2·acetone**. In both of these cases no new crystalline phase has to be formed.

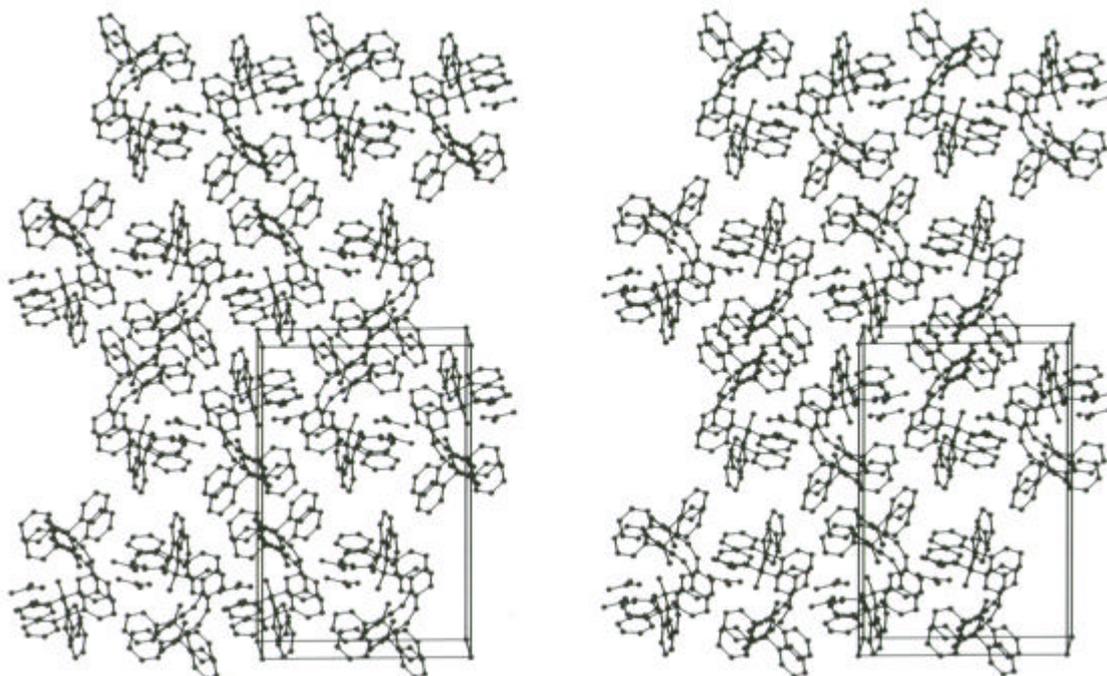


**Figure 4.** 7.5  $\mu\text{m}$  AFM topographies of **1·acetone** on its (010)-face [frequently larger than (100) in its well formed six-sided prisms]; a: fresh; b: after 4 h, c: after 6 h and d: after 9 h irradiation under argon at  $-15$  to  $-17^\circ\text{C}$  with a 700 W Hg lamp through Pyrex at 15 cm distance. We do not see precisely the same site on the (010)-face in a-d, as the sample holder had to be removed from the AFM stage for the irradiations.

### Mechanistic Interpretation

The crystal structure of **1·acetone** ( $P2_1/n$ ) exhibits a layered structure on (010) and (001). The mono-layers are in the (100)- and in the (010)-plane. All hydrogen bonds are within the host-guest pairs (see also Figure 1). Thus, the layers are not interlinked by hydrogen bonds, but they interlock considerably and do not leave good cleavage planes for easy

molecular migrations.<sup>2</sup> This is shown in Figure 5 which represents a rather large crystal section.

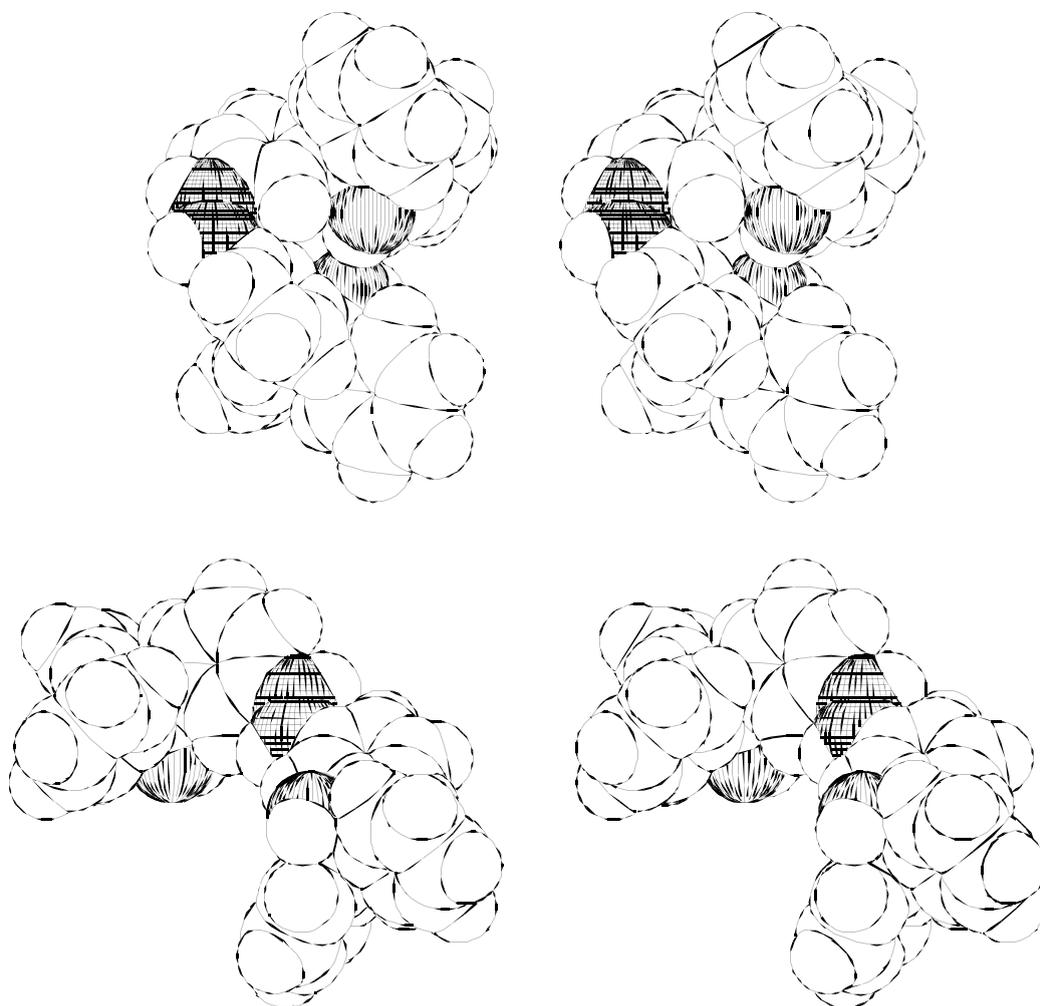


**Figure 5.** Stereoscopic representation of the crystal packing in **1·acetone** on (001) with the (100)-face on top and (010) to the right; acetone can escape from the monolayers on (100) but not through the monolayers on (010); hydrogen atoms are omitted for clarity.

The AFM results on (100) are in agreement with the molecular packing: acetone molecules may escape from the uppermost monolayer and thus start the nucleation for the efflorescence also from lower layers which finally creates a thin tight cover with the hills that are seen in Figure 3. At lower temperature, the nucleation is more selective and fewer hills can grow to a limiting height. After buildup of the stable layer no further distortion due to efflorescence occurs. The (010)-face can only lose the acetone molecules that are directly at the outer surface. The next layer acetone molecules are shielded by host molecules and cannot escape (Figure 5). The (110) face exhibits a similar situation. Thus, protecting efflorescence is only observed on (100). Furthermore, as all molecular layers interlock no molecular migrations apart from the formation of the protecting efflorescence cover can occur and no photoproduct molecules exit, as is shown in Figure 4.

How then might the extremely space-demanding *cis-trans*-isomerization of **1** to give **2**

occur without destruction of the crystal? The difficulties are evident from a comparison of



**Figure 6.** Stereoscopic representation of the space filling molecules from X-ray data in their crystals<sup>5</sup>; top: of **1**·acetone; bottom: **2**·3/4 benzene; O: meridian; double bond C: grid.

the molecular shapes of **1** (in **1**·acetone) and **2** (in **2**·3/4 benzene)<sup>5</sup> in Figure 6. The vinylic substituents are very large. The huge geometric change is clearly seen as well as the conformational difference in the two experimental shapes of these molecules in the crystals. The geometry of the “90° rotated transition state” for a hardly imaginable double bond rotational isomerization cannot be assessed and is thus not modeled and depicted. A closer inspection of the lattice in Figure 5 reveals the presence of cages that apparently can help to accommodate the more extended molecules **2** which avoids the necessity of

leaving the lattice by far-reaching migration.<sup>2</sup> Semiempirical PM3 calculations indicate only minor changes of the space filling CPK-volumes (0.3%) and -surfaces (2.3%) between **1** and **2**. This is not enough to invoke static “cavity” models.<sup>6</sup> Dynamic approaches are still qualitative but can be used in the fixed lattice for judgments in extreme situations. A rotational mechanism would meet with the situation that it does not initially profit from the packing as the modeling arrives at unsurmountable van der Waals interactions (down to 45% of the standard distance) already at  $\pm 10^\circ$  rotation. If that should proceed to a “90° rotated transition state” it would require that numerous neighboring molecules in the first, second and third sphere must be pushed away from their lattice sites during the lifetime of the electronic excitation while the reacting molecule also translocates. The vinylic substituents are by far too large for such a process with **1**. The “hula-twist” (HT) mechanism of Liu<sup>1,7</sup> appears more likely, as it requires only the out-of-plane translocation of one of the C-H units and movement of one of the huge substituents within its molecular plane. Scheme 3 summarizes the two mechanisms giving conformer A and conformer B, respectively. In the HT-mechanism only one of the double bond C-H undergoes a space saving out-of-plane translocation, while the *m*-triphenylhydroxymethyl substituent at the same C moves essentially within its original plane and passes a structure that may be drawn similar to a triangle. Continuation of the in-plane movement of the aryl moiety leads to conformer B which might survive in the confinement of a crystal lattice.<sup>3</sup> In the rotational mechanism either one end (180°) or both ends (90°, each) of the double bond with their huge substituents would have to undergo a space consuming out-of-plane translocation to form conformer A.



diffraction in the present case by means of a conformational analysis of the product **2** (rotation and HT lead to different conformers)<sup>3</sup> if the isomerization of **1** were a topotactic conversion, or is it a Kohlschütter-type topochemical reaction<sup>9</sup> leading to colloidal particles within the shape of the original crystal (not to be confused with the Schmidt-type topochemical reaction<sup>10</sup> which assumes formation of a crystalline phase with a provision of minimal atomic and molecular movements)? It turned out that an amorphous phase was occurring in the irradiation of **1** and therefore a conformational proof of HT was not possible with X-ray diffraction upon low-temperature (250 K) irradiation. The observed lattice changes were very small when the single crystal was irradiated up to 36% conversion after 3 h. Importantly, the peak half-width of the X-ray diffraction signals did not increase, but the peak intensity decreased gradually to 60% in 1 h and to 20% after 3 h irradiation, while the crystal remained transparent. The difference electron-density maps did not show any contribution of the *trans*-isomer **2**. Clearly, an X-ray amorphous phase was produced without (sub)microscopic change of the crystal (Figures 2 and 4). Thus, the present example failed to provide the definitive experimental proof of HT by exclusion of rotation. However, volume-conserving HT motions - where the bulky substituents do not leave the planes occupied by the vinylic benzene rings and only one of the olefinic C-H units undergoes out-of-plane translocation<sup>1,3</sup> - appear most likely, due to the presence of the layers and of the cages that serve also for the accommodation of the final product **2** (Figure 5).<sup>11</sup>

## CONCLUSIONS

Solid-state reactions without molecular migrations beyond geometric relaxation are considered topotactic processes irrespective of the chemical mechanism, but they must be always secured at the molecular precision of the AFM<sup>2,4,12</sup> and essentially keep the crystal structure. A previous claim of a topotactic *trans-cis*-photoisomerization of 1,2-dibenzoylene<sup>13</sup> was excluded by AFM as it exhibited long-range molecular movements along cleavage planes.<sup>4,14</sup> The initial hopes to realize the first topotactic *cis-trans*-photoisomerization with **1**-acetone crystals that did not (sub)microscopically change were not fulfilled, as an amorphous phase occurred by necessarily low-distance molecular movements that could not be traced by AFM on the rough surfaces. This shows

that AFM is a necessary but not a sufficient condition for the proof of topotaxy, as an amorphous phase may form without detectable molecular migrations at the molecular Z-scale. The unusual present result further challenges conclusions of topotaxy that are only derived from dynamic X-ray investigations (without invoking AFM evidence), if there was a considerable drop in peak intensity which is frequently not documented or excluded. It should be noted here, that further crystal reactions have been previously found where the macroscopic shape did not change but which were nevertheless not topotactic when the (thermal) reaction occurred exclusively at outer and inner surfaces<sup>15</sup> or after creation of submicroscopic cracks in the bulk<sup>16</sup> or by using the voids of empty space in the lattice.<sup>16</sup>

It is to be expected that the search for void space in suitable positions of crystal lattices will reveal topotactic crystal reactions<sup>4,17</sup> without the requirement for absence of geometric change (< 4%) from reactant to product<sup>4,17</sup> even if there is always the possibility for the creation of an amorphous phase.

## EXPERIMENTAL

<sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> on an JEOL Lambda 300 and on a Bruker WP 500 instrument. IR spectra were recorded with a JASCO FT-IR 200 spectrometer. UV spectra were measured on a Shimadzu MPS-2000 spectrometer. All melting points were determined using a Yanaco micro melting-point apparatus and were uncorrected. The details of AFM measurements on organic crystals were described elsewhere.<sup>2</sup> A NanoScope II instrument of Digital Instruments was used in contact mode at 10-30 nN force with non-scraping (symmetric) standard Si<sub>3</sub>N<sub>4</sub> tips (spring constant 0.12 N m<sup>-1</sup>).<sup>2</sup> The crystals were glued to a conducting tab (Plano) on a magnetic plate. Low temperature irradiations used a double walled cooled beaker with the sample plate in direct contact to the cold bottom (circulating bath at -17 to -15°C or -70°C) at 10 cm distance to the quartz window and 5 additional cm to the 700 W Hg lamp that was cooled by tape water (14°C) running through a double walled Pyrex tube. Fixed-lattice modeling was performed with the program Schakal of E. Keller, Freiburg.

*3,3'-Bis(carbethoxy)diphenylacetylene (5)*. A mixture of 3-bromo-benzoic acid ethyl ester (**3**) (4.5 g, 26 mmol), 3-ethynyl-benzoic acid ethyl ester (**4**) (5.9 g, 26 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.05 g), PPh<sub>3</sub> (0.26 g) and CuI (0.05 g) in Et<sub>3</sub>N (200 ml) was heated under reflux for 5 h. After filtration, the organic layer was evaporated to give, after recrystallization from acetone, 3,3'-bis(carbethoxy)diphenylacetylene (**5**) as colorless prisms (5.6 g, yield 67%, m.p. 60-68°C). IR (nujol),  $\nu$ : 1739 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$ : 1.42 (t,  $J$  = 7 Hz, 3H, CH<sub>3</sub>), 4.41 (q,  $J$  = 7 Hz, 2H, CH<sub>2</sub>), 7.45-8.22 (m, 8H, Ar).

*3,3'-Bis(hydroxydiphenylmethyl)diphenylacetylene (6)*. A solution of compound **5** (4.30 g, 13.3 mmol) in dry THF (30 ml) was added with stirring to a solution of PhMgBr in THF (200 ml), prepared from Mg (3.30 g, 133.9 mmol) and bromobenzene (21.0 g, 133.9 mmol), and the mixture was stirred for 6 h. Conventional workup gave crude crystals of 3,3'-bis(hydroxydiphenylmethyl)diphenylacetylene (**6**). Recrystallization of the crude crystals from acetone gave the 1:1 inclusion complex of **6** with acetone as colorless prisms, which upon heating, gave pure **6** as a white powder (5.9 g, yield 81%, m.p. 85-90°C). IR (nujol),  $\nu$ : 3407 (OH) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.77 (s, 2H, OH), 7.25-7.33 (m, 28H, Ar). Anal. Calcd for C<sub>40</sub>H<sub>30</sub>O<sub>2</sub> (**6**; 542.66): C, 88.53; H, 5.57. Found C, 88.30; H 5.74%.

*cis-3,3'-Bis(diphenylhydroxymethyl) stilbene (1)*. A mixture of compound **6** (1.00 g, 1.84 mmol) and Pd-BaSO<sub>4</sub> (0.2 g) in THF (100 ml) was stirred under H<sub>2</sub> atmosphere for 6 h. After filtration, the organic layer was evaporated to give, after recrystallization from toluene, *cis*-3,3'-bis(diphenylhydroxymethyl) stilbene (**1**) as colorless prisms (0.85 g, yield 85%, m.p. 170-175°C). These could not be grown larger than 0.05 x 0.05 x 0.3-0.4 mm<sup>3</sup> and had very rough surfaces, unsuitable for X-ray diffraction or even AFM studies. IR (nujol),  $\nu$ : 3559, 3459 (OH) cm<sup>-1</sup>. UV(CHCl<sub>3</sub>),  $I_{max}$  ( $\epsilon$ ): 243 (25000), 285 (15000) nm. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.86 (s, 2H, OH), 6.52 (s, 2H, =CH), 7.14-7.27 (m, 28H, Ar). Anal. Calcd for C<sub>40</sub>H<sub>32</sub>O<sub>2</sub> (**1**; 542.66): C, 87.92; H 6.05. Found C, 88.20; H, 5.92.

Recrystallization of compound **1** from acetone gave the complex **1**·acetone; m.p. 80-85°C. IR (nujol),  $\nu$  = 3475, 3377 (OH), 1695 (C=O) cm<sup>-1</sup>. Anal. Calcd for C<sub>43</sub>H<sub>38</sub>O<sub>3</sub> (**1**·acetone; 542.66): C, 85.68; H, 6.35. Found C 85.92, H 6.45.

*Low temperature photolysis of solid 1.* Powdered crystals **1** (30 mg with < 6% acetone) were spread on a cooled glass surface in a vacuum and irradiated with a 700 W Hg high pressure lamp through a Pyrex filter from a distance of 15 cm for 12 h. The conversion was detected by <sup>1</sup>H NMR. It was >93% (measured after 8 h) at -15 to -17°C and 42% at -70°C. The corresponding experiments with **1·acetone** gave conversions of 56% and 10%, respectively.

*trans-3,3'-Bis(diphenylhydroxymethyl) stilbene (2).* Solid-state photolysis of the powdered 1:1 acetone complex of **1** (0.20 g, 0.38 mmol) for 6 h using a 400 W high-pressure Hg lamp gave crude crystals of the 1:1 acetone complex of **2** at 92% conversion. Recrystallization of the crude crystals from acetone gave the pure 1:1 inclusion complex **2** with acetone as colorless needles of **2·acetone** which, upon heating, gave pure **2** as a white powder (0.19 g, 92% yield, m.p. 68-73°C). Irradiation of well developed crystals of **1·acetone** gave similar conversions at 12 h irradiation without destruction of the still clear crystals.

**2.** IR (nujol),  $\tilde{\nu}$ : 3550, 3445 (OH) cm<sup>-1</sup>. UV(CHCl<sub>3</sub>),  $I_{max}$  ( $\epsilon$ ): 242 (12500), 304 (12900), 316 (9200) nm. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$ : 3.05 (s, 2H, OH), 6.98 (s, 2H, =CH), 7.24-7.44 (m, 28H, Ar). Anal. Calcd for C<sub>40</sub>H<sub>32</sub>O<sub>2</sub> (**2**; 544.68): C, 88.20; H, 5.92. Found: C, 88.07; H, 6.20.

**2·acetone.** m.p. 70-75°C. IR (nujol),  $\tilde{\nu}$ : 3411 (OH), 1698 and 1685 (C=O) cm<sup>-1</sup>. Anal. Calcd for C<sub>43</sub>H<sub>38</sub>O<sub>3</sub> (**2·acetone**; 542.66): C, 85.68; H, 6.35. Found: C, 85.26; H, 6.50.

*Irradiation of compounds 2 and 2·acetone.* The powdered crystals of **2** or **2·acetone** were irradiated for 12 h using a 400 W high-pressure Hg lamp to give the crystals of **2** or **2·acetone** unchanged (determined by <sup>1</sup>H-NMR).

*Preparation of the single crystals of 1·acetone.* The single crystals of **1·acetone** were prepared by slow evaporation of the acetone solution of **1** at room temperature. Both prismatic (Figure 2) and plate-like crystals [the latter with (100) as the main face] could be obtained. For AFM investigation, the prismatic crystals were directly taken from a saturated solution and dried on a filter paper in air and all of the paired faces along the *c*-axis that could be mounted horizontally.

*Synthesis of the other inclusion complexes 1·guest of Table 1.* The other inclusion complexes of **1·guest** were synthesized by recrystallization of compound **1** from the neat guest compounds. Guest-free crystals of **1** that were suitable for X-ray diffraction or AFM could not be obtained from toluene.

*General procedure for the photoisomerization of the other inclusion complexes of Table 1.* 50 mg quantities of the powdered crystals of the inclusion complexes **1·guest** were irradiated as described above and the data are summarized in Table 1. The conversion was determined by <sup>1</sup>H-NMR analysis. The guest molecules were still present in all cases.

#### *X-ray structure analysis of*

*cis-3,3'-bis(diphenylhydroxymethyl)stilbene·acetone (1·acetone).* Crystal data: C<sub>40</sub>H<sub>32</sub>O<sub>2</sub>·C<sub>3</sub>H<sub>6</sub>O, Mw = 602.77, crystal dimensions 0.4 × 0.3 × 0.2 mm<sup>3</sup>, colorless prism. X-ray intensities were measured on a Rigaku AFC-7R diffractometer with Mo K<sub>α</sub> radiation at 297 K, monoclinic *P*2<sub>1</sub>/*n*, *a*: 24.413(3), *b*: 16.229(3), *c*: 8.634(1) Å, β: 99.07(1)°, *V*: 3378.0(9) Å<sup>3</sup>, *Z*: 4, *D*<sub>x</sub>: 1.185 Mg m<sup>-3</sup>, μ: 0.073 mm<sup>-1</sup>. A crystal specimen was sealed in a capillary, and there was no intensity decay of standard reflections. Data collection of 9071 reflections (θ<sub>max</sub>: 27.5°), 7764 independent reflections (*R*<sub>int</sub>: 0.022), 3144 observed reflections with *I* > 2*s* (*I*), 423 parameters. The hydroxyl H atoms were located from difference syntheses and refined isotropically. The other H-atom positional parameters were calculated geometrically and constrained. *R*(*F*)=0.054 for 3144 observed reflections, *wR*(*F*)=0.0911 for all the 5994 reflections. CCDC 187574 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

In the low-temperature irradiation at the X-ray diffractometer a single crystal of 0.6 × 0.5 × 0.2 mm<sup>3</sup> was coated by adhesive, mounted and constantly kept at 250 K using cold nitrogen gas. The lattice constants before photolysis (monoclinic *P*2<sub>1</sub>/*n*) *a*: 24.383(5), *b*: 16.233(5), *c*: 8.6096(16) Å, β: 99.241(15) deg, *V*: 3363.3(14) Å<sup>3</sup> changed to *a*: 24.416(8), *b*: 16.246(7), *c*: 8.625(2) Å, β: 99.18(3) deg, *V*: 3378(2) Å<sup>3</sup> after photolysis for 3 h with a 250 W ultra-high-pressure Hg lamp through a Pyrex filter. The peak half-widths of the

X-ray diffraction signals did not increase, but the peak intensity decreased gradually. On an average, the peak intensity decreased to 60% in 1 h and to 20% after 3 h irradiation. The crystal structure analyses before and after photolysis did not show any change. The transparent crystal was sent from Yokohama, Japan, to Oldenburg, Germany, and its chemical conversion detected to be 36% by 500 Mc  $^1\text{H}$  NMR in  $\text{CDCl}_3$ .

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