

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

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Received 15 April 2003; revised 20 June 2003; accepted 24 June 2003

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 a guest or in the presence of other guests. Internal rotation around the double bond bearing the very large triphenylhydroxymethyl substituent 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 atomic force microscopy (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 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. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: *cis*–*trans* isomerization; inclusion crystal; x-ray structure; atomic force microscopy; hula-twist; amorphous phase

INTRODUCTION

Photochemical *cis*–*trans* isomerizations in constrained media have attracted special interest in recent years in relation to the photoisomerization of chromophores in biological systems (e.g. photoactive yellow protein and retinoid-binding proteins).¹ Recently, various *cis*–*trans* isomerizations of C=C double bonds, e.g. of 2-benzylidenebutyrolactone and 1,2-dibenzoyl ethene, in the crystalline state have been reported.^{2,3} 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).

RESULTS AND DISCUSSION

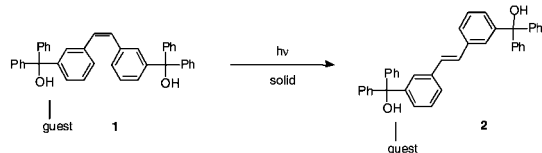
Preparations and solid-state photolyses

The host compound (**1**) was prepared according to the method shown in Scheme 2. Treatment of ethyl 3-bromo-

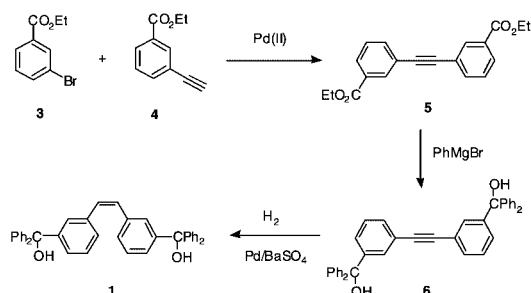
benzoate (**3**) with ethyl 3-ethynylbenzoate (**4**) in the presence of a Pd(II) catalyst gave 3,3'-bis(carboethoxy) diphenylacetylene (**5**), which upon treatment with PhMgBr in dry THF followed by hydrogenation on Pd–BaSO₄ gave *cis*-3,3'-bis(diphenylhydroxymethyl)stilbene (**1**). The host compound (**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.

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 × 1.0 × 0.5 mm) 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 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

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



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

thermogravimetric 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, γ -butyrolactone, dioxane, DMSO, DMF and pyridine occurred efficiently (although 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 ^1H 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.

X-ray analysis

The molecular structure in the crystals of **1**·acetone is shown in Fig. 1. The acetone molecule is connected to the

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

Guest	Host:guest ratio	Z: m.p. (°C)	Conversion (%)	Host:guest 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
γ -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

^a The photolyses of powdered crystals were carried out for 6 h.

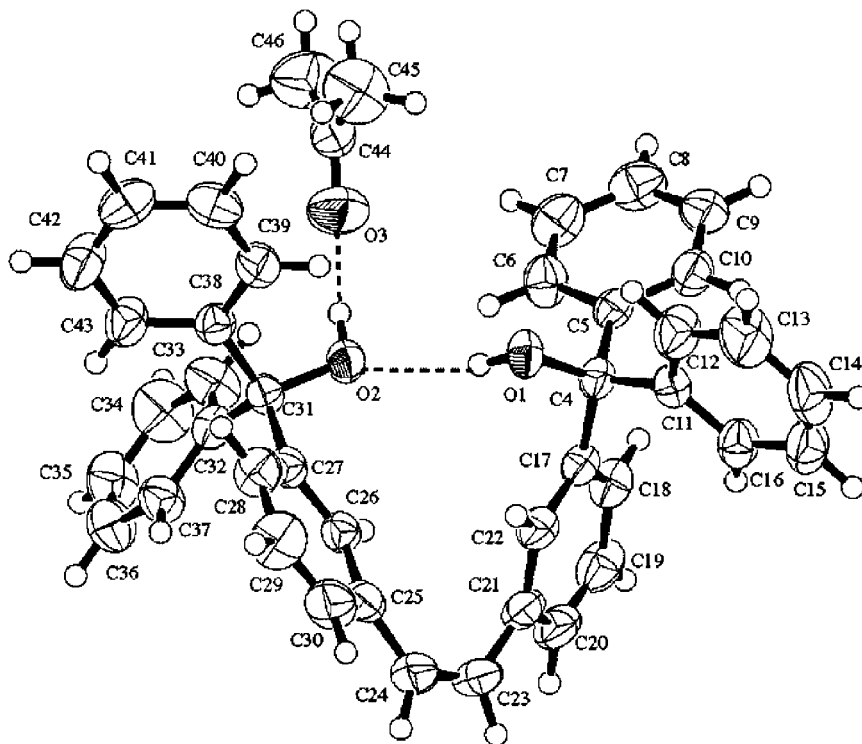


Figure 1. The molecular structure of **1**·acetone with displacement ellipsoids at the 50% probability level

host **1** by the O2—H2···O3 hydrogen bond with an O2···O3 distance of 2.829(4) Å and it is not disordered. There is also an intramolecular O1—H1···O2 hydrogen bond of the host molecule [O1···O2 distance 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)°.

Supermicroscopic analysis with AFM

The crystals of **1**·*acetone* keep their guest upon photoisomerization. However, at the molecular resolution (in the 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 °C (Fig. 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 °C) is performed at room temperature: initially sharp crystal edges become smoother and AFM [Fig. 3(d)] detects softened surface regions, but not in irradiations at <-15 °C. Both almost acetone-free (<6%) crystals of **1** and the crystals of **1**·*acetone* undergo *cis*–*trans* photoisomerization also at -17 to -15 °C and (more slowly) at -70 °C, as checked by ^1H NMR analysis. If a prismatic crystal of **1**·*acetone* was irradiated for 6 h at -17 to -15 °C through a Pyrex filter, no microscopic change was observed even though the crystal was 30% converted to **2**·*acetone*.

Long irradiation (20 h; the irradiation times for high conversion are rather long owing to internal filtering by the strong light absorption of the product **2**) up to nearly complete conversion also did not disintegrate the single

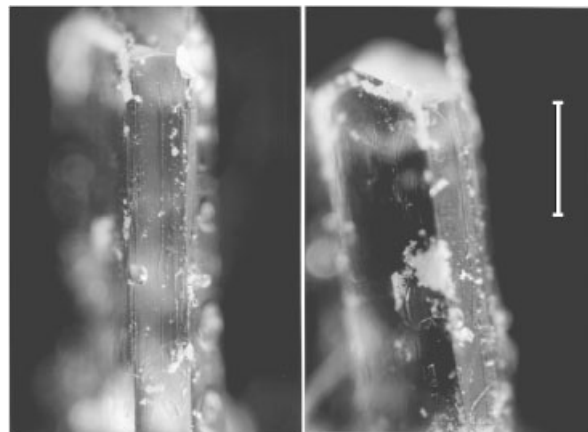


Figure 2. Micrographs of a crystal of **1**·*acetone*: the white bar corresponds to 0.1 mm. Left image, (010) face before irradiation; right image, after 6 h of irradiation with a 700 W Hg high-pressure lamp through Pyrex at a 15 cm distance and -17 to -15 °C. The irradiated crystal was tilted in order 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 on tilting it with tweezers

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 used successfully to prove and disprove several claims of topotaxy in various molecular crystals very sensitively.⁴

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 was measured at various times. Figure 3 shows that the initial surface has some

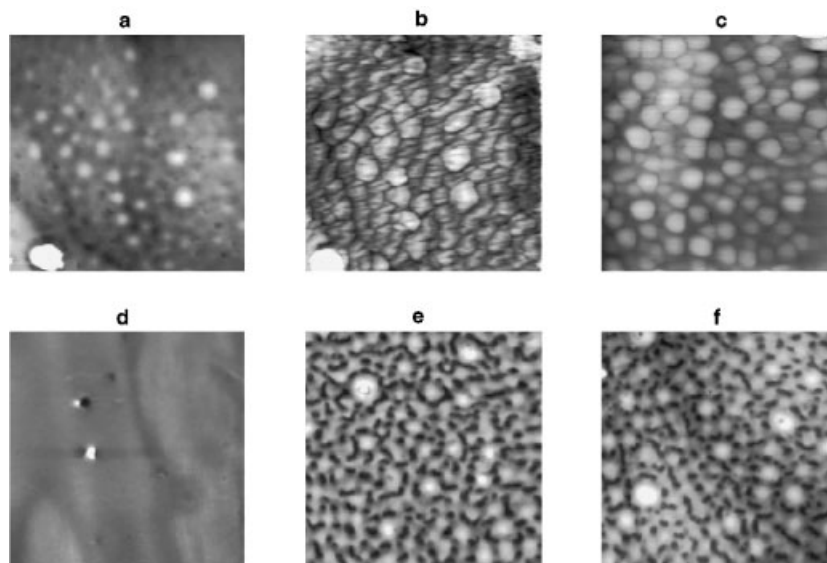


Figure 3. 10 μm AFM topographies of the (100) face of **1**·*acetone*: (a) fresh surface of a flat plate specimen; (b) after 4 h; (c) after 10 h of irradiation with an old 125 W Hg lamp through Pyrex at a 3 cm distance from the lamp and 20–25 °C; (d) after 3 h of irradiation with a 700 W Hg lamp at room 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 a 15 cm distance from the lamp; the Z-scale is 100 nm

roughness ($R_{ms} = 7$ nm, excluding the large feature) with a maximum height of 62 nm (excluding the large feature) obviously from some efflorescence on resting for 2 weeks in a bottle without an 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 Fig. 3(c). Clearly, a 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 from a fresh 700 W Hg lamp is applied, similar features form within minutes ($R_{ms} = 7$ nm, maximum height 55 nm), that keep their shape but collapse after 3 h of irradiation followed by apparent local melting [Fig. 3(d)].

A very flat surface part of **1-acetone** on (100) ($R_{ms} = 3.5$ nm, maximum 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, maximum height 116 nm) [Fig. 3(e/f)]. The surface did not change significantly further after 15 min of irradiation ($R_{ms} = 12$ nm, maximum height 125 nm). Therefore, these features are again interpreted as the formation of a cover that is the result of initial efflorescence but not of 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 Fig. 3(e) upon irradiation. The (010) surface (Fig. 2) had humps parallel to the long crystal *c*-axis and was scanned with the AFM tip at sites where these were least pronounced. No change was detectable. Even very long irradiation did not change the shape of the side-face, as shown in Fig. 4. The conversion of the crystal in Fig. 4(d) was detected with ^1H NMR to be 56%. Similarly, no change of the surface was detected on the (110) face on irradiation under the same conditions. Clearly, no long-range movements of molecules [except for the initial efflorescence on (100)] can be detected with AFM and this observation points to either a topotactic reaction or the formation of an amorphous phase in the crystal of **1-acetone** to give **2-acetone**. In both cases no new crystalline phase has to be formed.

Mechanistic interpretation

The crystal structure of **1-acetone** ($P2_1/n$) exhibits a layered structure on (010) and (001). The monolayers are in the (100) and (010) planes. All hydrogen bonds are within the host-guest pairs (see also Fig. 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.² This is shown in Fig. 5, which represents a rather large crystal section.

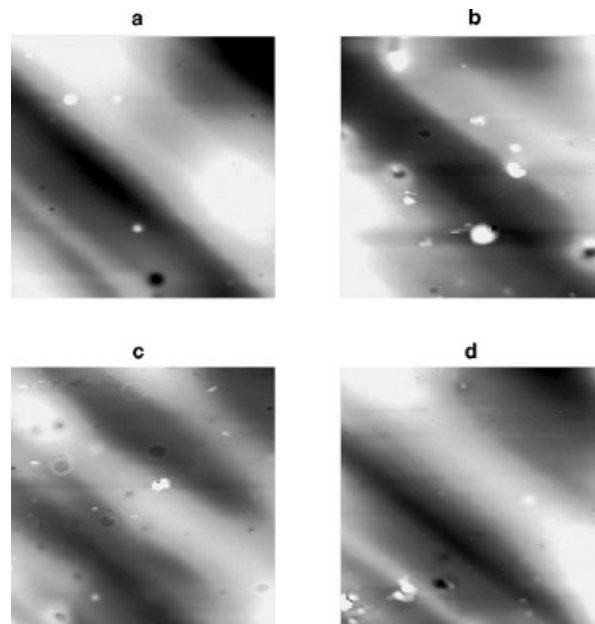


Figure 4. 7.5 μm AFM topographies of **1-acetone** on its (010) face [frequently larger than (100) in its well-formed six-sided prisms]: (a) fresh; (b) after 4 h, (c) after 6 h and (d) after 9 h of irradiation under argon at -15 to -17 °C with a 700 W Hg lamp through Pyrex at a 15 cm distance. We do 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. The Z scale is 140 nm

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 Fig. 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 (Fig. 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 shown in Fig. 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 the molecular shapes of **1** (in **1-acetone**) and **2** (in **2-0.75 benzene**)⁵ in Fig. 6. The vinylic substituents are very large. The huge geometric change is clearly seen in addition to 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 therefore not modeled and depicted. A closer inspection of the

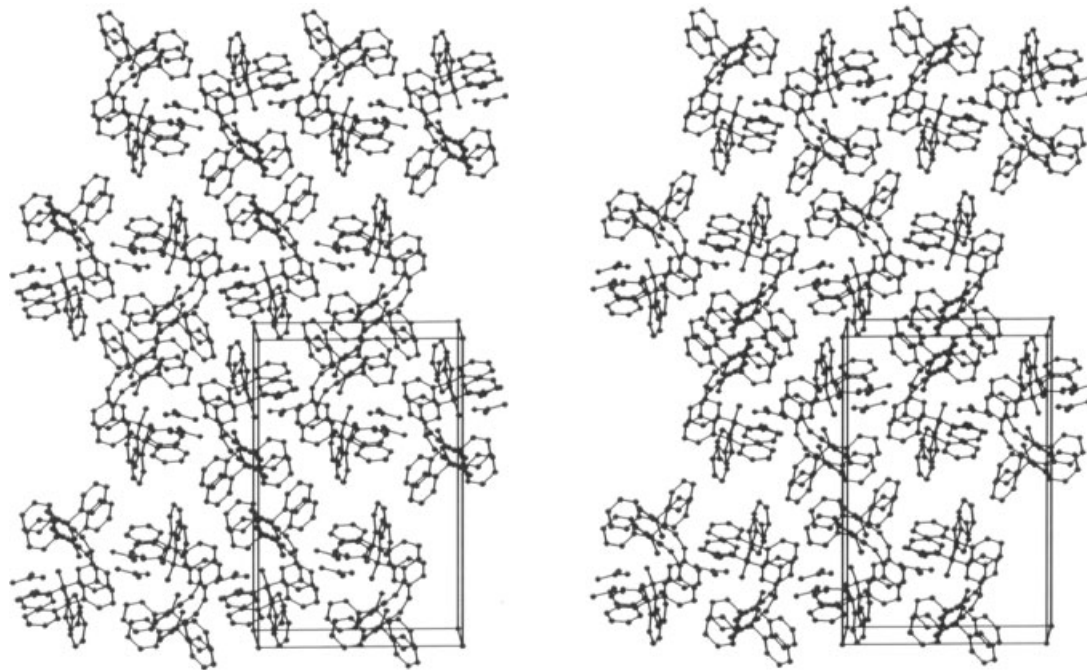


Figure 5. Stereoscopic representation of the crystal packing in **1-acetone** on (001) with the (100) face on top and (010) to the right; acetone can escape from the monolayers on (100) but not through the monolayers on (010); hydrogen atoms are omitted for clarity

lattice in Fig. 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.² 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.⁶ 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

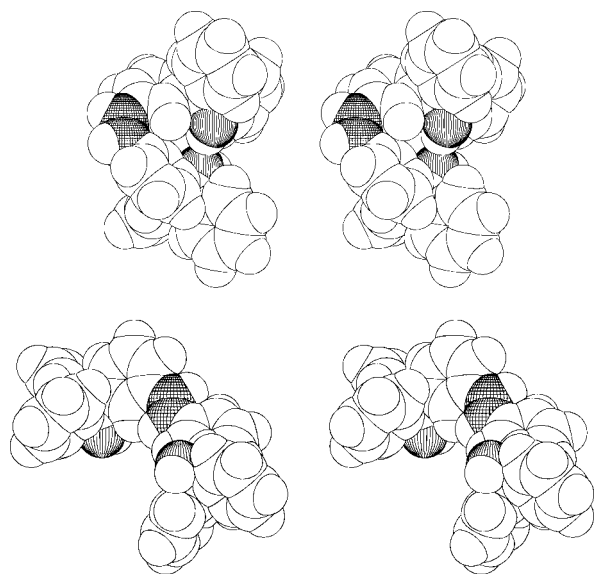
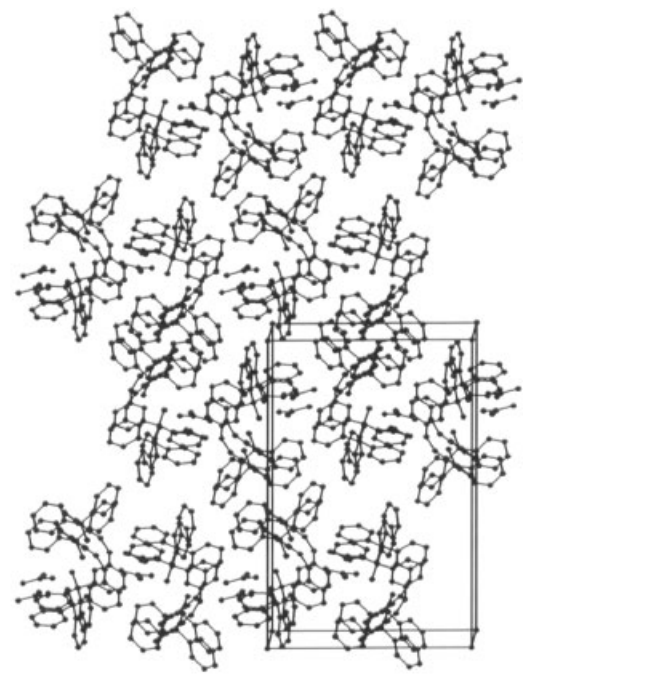
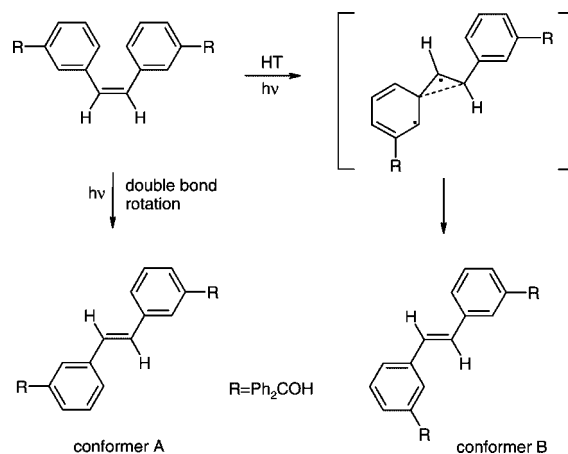


Figure 6. Stereoscopic representation of the space-filling molecules from x-ray data in their crystals:⁵ top, **1-acetone**; bottom, **2.0.75 benzene**. O, meridian; double bond C, grid



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 spheres 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 far too large for such a process with **1**. The 'hula-twist' (HT) mechanism of Liu and co-workers^{1,7} 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



Scheme 3. Comparison of the rotational and HT mechanisms of the *cis-trans* photoisomerization of **1** showing the difference in the conformational result

two mechanisms giving conformers A and 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 similarly 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.³ 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.

Figure 5 indicates that HT might occur much more easily along the vertical layers inasmuch as there is also some movement possible along the horizontal layer direction. This mechanism appears much more likely for geometric reasons, because the doubly layered anisotropic crystal packing is largely in favor (Fig. 5). However, both mechanisms can still not be quantitatively modeled. We note that *cis*–*trans* photoisomerizations of stilbenes with even larger dendrimeric substituents have been interpreted as HT isomerizations on the basis of quantum yields and fluorescence arguments, although in solution.⁸ In that case the ‘confinement’ is the solvent that would have to be pushed away by the huge substituent if it were to rotate by ca 90° during the 10 ns lifetime of the electronically excited dendrimer.

Most rewarding are the following questions: can the HT mechanism be proven by x-ray diffraction in the present case by means of a conformational analysis of the product **2** (rotation and HT lead to different conformers, Scheme 3)³ if the isomerization of **1** were a topotactic conversion, or is it a Kohlschütter-type topochemical reaction⁹ leading to colloidal particles within the shape of the original crystal (not to be confused with the Schmidt-type topochemical reaction¹⁰ 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 on 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% after 1 h and to 20% after 3 h of 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 (Figs 2 and 4). Hence, the present example failed to provide 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,^{1,3} appear most likely, owing to the presence of the layers and of the cages that serve also for the accommodation of the final product **2** (Fig. 5) (the so-called ‘bicycle pedal’ mechanism for 1,3-dienes¹¹ is also volume conserving, but does not apply here).

CONCLUSIONS

Solid-state reactions without molecular migrations beyond geometric relaxation are considered topotactic processes irrespective of the chemical mechanism, but they must always be secured at the molecular precision of the AFM^{2,4,12} and essentially keep the crystal structure. A previous claim of a topotactic *trans*–*cis* photoisomerization of 1,2-dibenzoylene¹³ was excluded by AFM as it exhibited long-range molecular movements along cleavage planes.^{4,14} 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 short-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 results further challenge conclusions about 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 that further crystal reactions have been found previously where the macroscopic shape of single crystals did not change but which were nevertheless not topotactic when the (thermal) reaction occurred exclusively at outer and inner surfaces¹⁵ or after creation of submicroscopic cracks in the bulk¹⁶ or by using the voids of empty space in the lattice.¹⁶

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

EXPERIMENTAL

¹H NMR spectra were recorded in CDCl₃ on JEOL Lambda 300 and Bruker WP 500 instruments. 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 have been described elsewhere.² A NanoScope II instrument (Digital Instruments) was used in contact

mode at 10–30 nN force with non-scraping (symmetric) standard Si₃N₄ tips (spring constant 0.12 N m⁻¹).² 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 with the cold bottom (circulating bath at -17 to -15 °C or -70 °C) at a 10 cm distance from the quartz window and an additional 5 cm from the 700 W Hg lamp that was cooled by tap water (14 °C) running through a double-walled Pyrex tube. Fixed-lattice modeling was performed with the program Schakal (E. Keller, Freiburg).

3,3'-Bis(carbethoxy)diphenylacetylene (5). A mixture of ethyl 3-bromobenzoate (**3**) (4.5 g, 26 mmol), ethyl 3-ethynylbenzoate (**4**) (5.9 g, 26 mmol), PdCl₂(PPh₃)₂ (0.05 g), PPh₃ (0.26 g) and CuI (0.05 g) in Et₃N (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), ν 1739 (C=O) cm⁻¹, ¹H NMR (300 MHz, CDCl₃), δ 1.42 (t, J = 7 Hz, 3H, CH₃), 4.41 (q, J = 7 Hz, 2H, CH₂), 7.45–8.22 (m, 8H, Ar).

3,3'-Bis(hydroxydiphenylmethyl)diphenylacetylene (6). A solution of **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), ν 3407 (OH) cm⁻¹; ¹H NMR (300 MHz, CDCl₃), δ 2.77 (s, 2H, OH), 7.25–7.33 (m, 28H, Ar). Anal. Calcd for C₄₀H₃₀O₂ (**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 **6** (1.00 g, 1.84 mmol) and Pd–BaSO₄ (0.2 g) in THF (100 ml) was stirred under an H₂ 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 × 0.05 × 0.3–0.4 mm and had very rough surfaces, unsuitable for x-ray diffraction or even AFM studies. IR (Nujol), ν 3559, 3459 (OH) cm⁻¹; UV (CHCl₃), λ_{\max} (ϵ) 243 (25 000), 285 nm (15 000); ¹H NMR (300 MHz, CDCl₃), δ 2.86 (s, 2H, OH), 6.52 (s, 2H, =CH), 7.14–7.27 (m, 28H, Ar). Anal. Calcd for C₄₀H₃₂O₂ (**1**; 542.66): C, 87.92; H 6.05. Found C, 88.20; H, 5.92%.

Recrystallization of **1** from acetone gave the complex **1**-acetone; m.p. 80–85 °C. IR (Nujol), ν 3475, 3377 (OH), 1695 (C=O) cm⁻¹. Anal. Calcd for C₄₃H₃₈O₃ (**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 of **1** (30 mg with <6% acetone) were spread on a cooled glass surface under 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 ¹H 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** with 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), ν 3550, 3445 (OH) cm⁻¹; UV(CHCl₃), λ_{\max} (ϵ) 242 (12 500), 304 (12 900), 316 nm (9200); ¹H NMR (300 MHz, CDCl₃), δ 3.05 (s, 2H, OH), 6.98 (s, 2H, =CH), 7.24–7.44 (m, 28H, Ar). Anal. Calcd for C₄₀H₃₂O₂ (**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), ν 3411 (OH), 1698 and 1685 (C=O) cm⁻¹. Anal. Calcd for C₄₃H₃₈O₃ (**2**-acetone; 542.66): C, 85.68; H, 6.35. Found: C, 85.26; H, 6.50%.

Irradiation of 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 crystals of **2** or **2**-acetone unchanged (determined by ¹H NMR).

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

Synthesis of the other inclusion complexes 1-guest in Table 1. The other inclusion complexes of **1**-guest were synthesized by recrystallization of **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 in Table 1. Amounts of 50 mg of the powdered crystals of the **1-guest** inclusion complexes were irradiated as described above and the data are summarized in Table 1. The conversion was determined by ^1H 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: $\text{C}_{40}\text{H}_{32}\text{O}_2 \cdot \text{C}_3\text{H}_6\text{O}$, $M_r = 602.77$, crystal dimensions $0.4 \times 0.3 \times 0.2$ mm, colorless prism. X-ray intensities were measured on a Rigaku AFC-7R diffractometer with $\text{Mo K}\alpha$ radiation at 297 K, monoclinic $P2_1/n$: a , 24.413(3); b , 16.229(3); c , 8.634(1) Å; β , 99.07(1)°; V , 3378.0(9) Å³; Z , 4; D_x , 1.185 g cm⁻³; μ , 0.073 mm⁻¹. A crystal specimen was sealed in a capillary, and there was no intensity decay of standard reflections. Data collection of 9071 reflections (θ_{max} : 27.5°), 7764 independent reflections (R_{int} : 0.022), 3144 observed reflections with $I > 2\sigma(I)$, 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 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 (or from the Cambridge Crystallographic Data Centre).

In the low-temperature irradiation in the x-ray diffractometer a single crystal of $0.6 \times 0.5 \times 0.2$ mm was coated with adhesive, mounted and kept constant at 250 K using cold nitrogen gas. Lattice constants before photolysis (monoclinic $P2_1/n$), a , 24.383(5); b , 16.233(5); c , 8.6096(16) Å; β , 99.241(15)°; V , 3363.3(14) Å³ changed to a , 24.416(8); b , 16.246(7); c , 8.625(2) Å; β , 99.18(3)°, V , 3378(2) Å³ 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 average, the peak intensity decreased to 60% after 1 h and to 20% after 3 h of 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 was measured as 36% by 500 MHz ^1H NMR in CDCl_3 .

Acknowledgement

K. T. acknowledges financial support from the Asahi Glass Foundation.

REFERENCES

- Liu RSH, Hammond GS. *Chem. Eur. J.* 2001; **7**: 4537–4544.
- Kaupp G, Haak M. *Angew. Chem., Int. Ed. Engl.* 1996; **35**: 2774–2777; Kaupp G. In *Comprehensive Supramolecular Chemistry*, vol. 8, Davies JED (ed.). Elsevier: Oxford, 1996; 381–423.
- Kaupp G. *Photochem. Photobiol.* 2002; **76**: 590–595.
- Kaupp G. *Curr. Opin. Solid State Mater. Sci.* 2002; **6**: 131–138.
- Ohba S, Hiratsuka T, Tanaka K. *Acta Crystallogr., Sect. E* 2002; **58**: o1013–o1015.
- Gavezotti A. *J. Am. Chem. Soc.* 1983; **105**: 5220–5225; Zimmerman HE, Nesterov EE. *J. Am. Chem. Soc.* 2002; **124**: 1169–1171.
- Liu RSH, Asato AE. *Proc. Natl. Acad. Sci. USA* 1985; **82**: 259–263.
- Uda M, Mizutani T, Hayakawa J, Momatake A, Ikegami M, Nagahata R, Arai T. *Photochem. Photobiol.* 2002; **76**: 596–605.
- Kohlschütter V. *Z. Anorg. Allg. Chem.* 1919; **105**: 1–25.
- Schmidt GMJ. *J. Chem. Soc.* 1964; 2014–2021.
- Liu RSH, Hammond GS. *Proc. Natl. Acad. Sci. USA* 2000; **97**: 11153–11158; Müller AM, Lochbrenner S, Schmid WE, Fuss W. *Angew. Chem., Int. Ed. Engl.* 1998; **37**: 505–507.
- Kaupp G. *Adv. Photochem.* 1995; **19**: 119–177.
- Bart JJC, Schmidt GMJ. *Recl. Trav. Chim. Pays-Bas* 1978; **97**: 231–238.
- Kaupp G, Schmeyerers J. *J. Photochem. Photobiol. B: Biol.* 2000; **59**: 15–19.
- Kaupp G, Schmeyerers J, Kato M, Tanaka K, Harata N, Toda F. *J. Phys. Org. Chem.* 2001; **14**: 444–452.
- Kaupp G, Schmeyerers J, Kato M, Tanaka K, Toda F. *J. Phys. Org. Chem.* 2002; **15**: 148–153.
- Nakanishi H, Jones W, Thomas JM, Hursthouse MB, Motvalli M. *J. Phys. Chem.* 1981; **85**: 3636–3642.