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Volume-Demanding Cis−Trans Isomerization of 1,2-Diaryl Olefins in the Solid State

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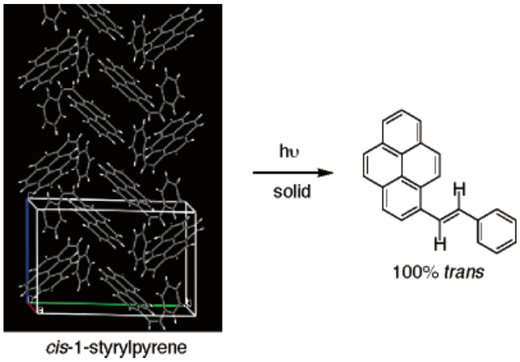

Volume-demanding cis−trans photoisomerization of the aromatic substituted alkenes **1**−**3** in the solid state at room temperature and at 50 °C is presented. Alkene **3** did not undergo the cis−trans isomerization in the solid state either at room temperature or at 50 °C. The importance of the presence of void space near the reaction center to facilitate the large volume change during cis−trans photoisomerization is discussed.

Introduction

The concept of a reaction cavity was formulated by Cohen to describe photodimerization reactions in crystals.[1] According to this concept, large distortion of the reaction cavity will not be tolerated by surrounding molecules and, therefore, molecules in the crystalline state would not undergo a reaction that requires large motions. However, a few years ago, we and others presented examples wherein molecules upon excitation undergo large motions in the crystalline state prior to dimerization.[2] Ogawa and co-workers have reported the presence of orientational disorder in stilbenes and azobenzenes,[3a,b] and Garcia-Garibay and co-workers have demonstrated a large crankshaft-type motion in crystals of the highly congested bis(triarylmethyl)peroxide.[3c] Recently, we reported examples of a [2+2] photodimerization reaction of a diamine double salt of substituted cinnamic acids with *trans*-1,2-diaminocyclohexane in the solid state that required a large pedal-like rotation of the alkene chromophore prior to dimerization.[4] These examples clearly suggest that certain amounts of molecular motions are tolerated within a crystal. We now report that one-way cis−trans isomerization of aromatic substituted alkenes requires much larger molecular motions in the solid state compared to the examples discussed above. These examples emphasize the need

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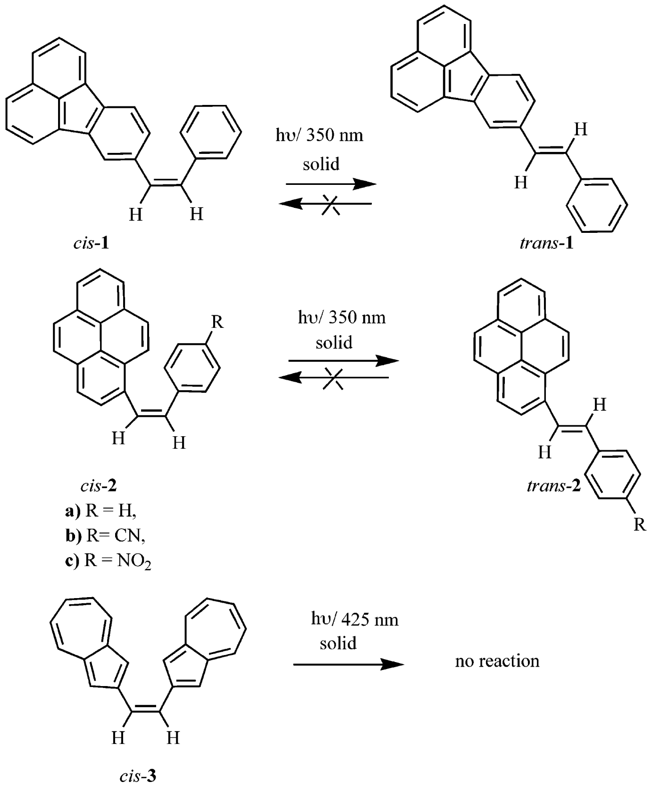
SCHEME 1



for void space near the reacting molecules. Crystalline *cis*-olefins, *cis*-**1** and *cis*-**2a**−**c**, upon irradiation undergo one-way geometric isomerization to yield the corresponding trans isomers (Scheme 1). However, olefin *cis*-**3** was photostable even after several hours of photoreaction in the crystalline state. To understand the factors that control the geometric isomerization of *cis*-**1** and *cis*-**2a**−**c** and the absence of such a process in *cis*-**3**, we have obtained crystal structures of these olefins. Results of photochemical and X-ray structural studies are presented in this report.

Results

Crushed crystals (5 mg) of *cis*- or *trans*-**1**−**3** were sandwiched between Pyrex plates, sealed with Parafilm, and irradiated using a 450 W medium-pressure mercury lamp. The wavelengths of irradiation were selected using appropriate filters (>350 nm, Corning-0-52 cutoff filter for *cis*-**1** and *cis*-**2a**−**c**; and >425 nm, Corning-3-73 cutoff filter for *cis*-**3**). For high-temperature irradiations, the above setup was placed directly on a thermostatically controlled hot plate and the temperature was monitored using a thermocouple. The crystals neither melted nor decomposed during irradiation at these temperatures. Solid-state irradiation of substrate *cis*-**1** for 18 h at room temperature led to 25% geometric photoisomerization yielding *trans*-**1**. Photoreaction of this substrate at an elevated temperature (50 °C) for 18 h of irradiation increased the rate of the isomerization process, giving 60% *trans*-**1**. Solution photobehavior of **1**−**3**, investigated previously, has shown that *cis*-**1** and *cis*-**2a** isomerize from both cis and trans isomers, whereas *cis*-**2b**, *cis*-**2c**, and *cis*-**3** proceed only from cis to trans.[5] Photolysis of *cis*-**2a**−**c** in the solid state also led to one-way cis−trans isomerization with an increased rate of geometric isomerization when irradiated at 50 °C. On the other hand, photolysis of *cis*-**3** as a solid did not result in cis−trans isomerization even after several hours of irradiation both at room temperature and at 50 °C (Scheme 1 and Table 1). In contrast to the cis isomers, photolysis of *trans*-**1**, -**2a**−**c**, and -**3** as crystals did not result in the corresponding cis isomers either at room temperature or at 50 °C.

TABLE 1. Results of Photochemical Studies of Substrates 1−3 in the Solid State

reactant[a]	product[a]	medium	temp (°C)	duration of hυ* (hrs)	% conversion
cis-**1**	*trans*-**1**	benzene	rt	2	c:t = 15:85[b]
cis-**1**	*trans*-**1**	solid	rt	18	25
cis-**1**	*trans*-**1**	solid	50	18	60
trans-**1**	*cis*-**1**	solid	rt	12	[c]
cis-**2a**	*trans*-**2a**	benzene	rt	2	c:t = 2:98[b]
cis-**2a**	*trans*-**2a**	solid	rt	18	55
cis-**2a**	*trans*-**2a**	solid	50	18	100
trans-**2a**	*cis*-**2a**	solid	rt	12	[c]
cis-**2b**	*trans*-**2b**	benzene	rt	2	c:t = 0:100[b]
cis-**2b**	*trans*-**2b**	solid	rt	18	75
cis-**2b**	*trans*-**2b**	solid	50	18	90
cis-**2c**	*trans*-**2c**	benzene	rt	2	c:t = 0:100[b]
cis-**2c**	*trans*-**2c**	solid	rt	18	45
cis-**2c**	*trans*-**2c**	solid	50	18	70
cis-**3**	*trans*-**3**	benzene	rt	2	c:t = 0:100[b]
cis-**3**	*trans*-**3**	solid	rt	18	[c]
cis-**3**	*trans*-**3**	solid	50	18	[c]

[a] Melting points: *cis*-**1** = 100−101 °C, *trans*-**1** = 131−133 °C; *cis*-**2a** = 102−103 °C, *trans*-**2a** = 156 °C; *cis*-**2b** = 130−131 °C, *trans*-**2b** = 193−194 °C; *cis*-**2c** = 141−142 °C, *trans*-**2c** = 219−220 °C; *cis*-**3** = 133−135 °C, *trans*-**3** = 305−306 °C. [b] Represents ratio at the photostationary state. [c] No reaction.

Discussion

In 1964, Schmidt et al. reported that several crystalline *cis*-cinnamic acids upon irradiation yielded the corresponding trans isomers.[6] The authors suggested that the isomerization occurred through a mechanism involving a metastable cyclobutane intermediate. On the basis of the photobehavior of *trans*-2,4-dichlorocinnamic acid salt with *trans*-1,2-diaminocyclohexane, we suggested that the above mechanism might not be general.[4] In the present study, except for *cis*-**3**, all other substrates (*cis*-**1** and *cis*-**2a**−**c**) were photoreactive in the solid state and gave the corresponding trans isomers (Scheme 1, Table 1). Irradiation of *cis*-**2a** as crystals for 18 h at 50 °C was remarkable in leading conversion to 100% *trans*-**2a**. Perusal of Table 1 reveals that the yield of the trans isomer for the same duration of irradiation increased upon increasing the temperature to 50 °C. The greater percentage of conversion at 50 °C as compared to that over the same time period at room temperature suggests that the molecules have more rotational freedom at the higher temperature. This could be due to an expansion of the crystal lattice that increases the intermolecular distance enough to permit a more facile rotation of the phenyl moiety. Alternatively, the elevated temperature could cause a phase change or destruction

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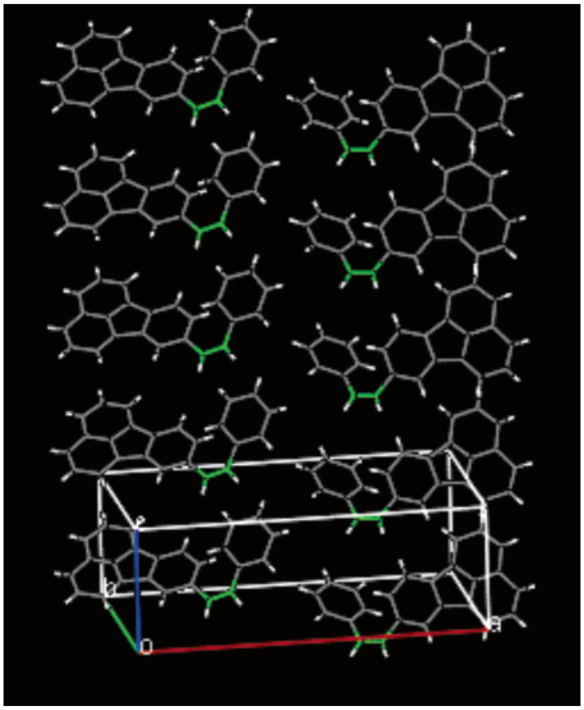

FIGURE 1. Packing diagram of *cis*-**1** showing the cavity along the *c*-axis.

TABLE 2. End-to-End Alkene−Alkene Distances Obtained from Crystal Structures

compound	adjacent C=C distances (Å)	short contacts for R_1, R_2[a,b] top face	bottom face
cis-**1**	6.77	no, yes	yes, yes
cis-**2a**	5.3, 5.2[c]	no, yes	yes, yes
cis-**2b**	8.1	no, yes	no, yes
cis-**2c**	7.57	no, yes	yes, yes
cis-**3**	4.25, 4.27, and 4.9, 5.2[d]	yes, yes	yes, yes

[a] *cis*-**1**: R_1 = phenyl, R_2 = 8-fluoranthyl. *cis*-**2a**−**c**: R_1 = phenyl, *p*-cyanophenyl, and *p*-nitrophenyl, R_2 = pyrene. *cis*-**3**: R_1=R_2 = diazulene. [b] Short contact is defined as the intermolecular distance by which two atoms are separated by less than the sum of van der Waals radii (C−C, C−H, and H−H are 3.4, 2.9, and 2.4 Å, respectively). [c] Two alkene ends are nonequivalent. [d] Two independent pairs with nonequivalent ends.

of crystallinity which would lead to a relaxation of the intermolecular contacts to the phenyl group.

Drawings generated through the MERCURY[7] and PLATON[8] programs, packing diagrams, short contacts, and the cavity plots of the molecules (*cis*-**1**, *cis*-**2a**−**c**, and *cis*-**3**) are shown in Figures 1−5. Torsion angles between the aromatic rings and the double bonds for all substrates are presented in the Supporting Information. The crystal structure of *cis*-**1** shows neighboring molecules stacked along the *c*-axis (Figure 1) with the alkene chromophores separated by 6.77 Å (Table 2). As this distance is significantly greater than that of 4.2 Å postulated by Schmidt as appropriate for the [2+2] formation of the metastable dimer, it appears that isomerization of *cis*-**1** to *trans*-**1** is very unlikely to proceed via a dimer pathway. A similar situation exists for the other reactive olefins, *cis*-**2a**−**c**, where the distances between neighboring olefinic double bonds are also larger (>5 Å) than the proposed maximum distance for formation of dimer intermediates.

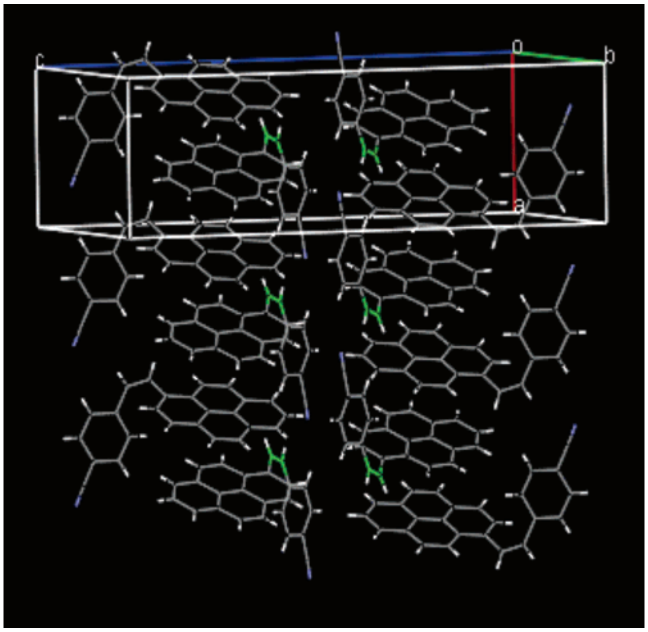

FIGURE 2. Packing diagram of *cis*-**2b** showing the empty channel along the *a*-axis.

Having ruled out a metastable dimer as an intermediate during geometric isomerization, we examined the crystal structures of *cis*-**1** and **-2** for clues to other possible mechanisms for isomerization in the crystalline state. The presence of void space in the crystal lattice was scrutinized by examining the molecular packing along the *a*-, *b*-, and *c*-axes and parallel to the ab, ac, and bc faces. As shown in Figure 1, an empty channel along the *c*-axis is evident in the case of *cis*-**1**. Because the presence of an empty channel is adjacent to the phenyl side of the molecule, we believe that the rotation of this side of the alkene is more likely than rotation of the side with the bulkier fluoroanthenyl moiety. Our reasoning is supported by the absence of short-contact atoms with the phenyl moiety along the top face of the molecule (Table 2). The few short contacts near the phenyl moiety are not on the plane in which the rotation of the double bond is expected to occur (see Supporting Information).

The reactivity during photoreaction of *cis*-1-styryl pyrenes *cis*-**2a**−**c** differed, as shown in Table 1. Although solid-state irradiation of *cis*-**2b** for 18 h at room temperature led to 75% conversion to *trans*-**2b**, irradiation of *cis*-**2a** and **-2c** gave only 55 and 45% conversion to corresponding trans isomers, respectively. On the basis of the presence of a void space adjacent to the phenyl moiety along the *a*-axis on examining the crystal structure of *cis*-**2b** (Figure 2), we anticipate that the phenyl side of the C=C bond of *cis*-**2b** will undergo rotation upon excitation. Analysis of crystal structures of *cis*-**2a** and **-2c** reveals the presence of void space near the phenyl moiety (Figure 3, Table 2). In the case of substrate *cis*-**2a**, the adjacent alkene molecules are aligned in a criss-cross fashion. In such an arrangement, rotation of the alkene along with the phenyl moiety can occur in the direction represented by the arrows in Figure 3a. Analysis of packing diagrams generated using the PLATON program[8] showed the presence of cavities in the crystal lattices of *cis*-**2a** and *cis*-**2c**. The presence of a cavity

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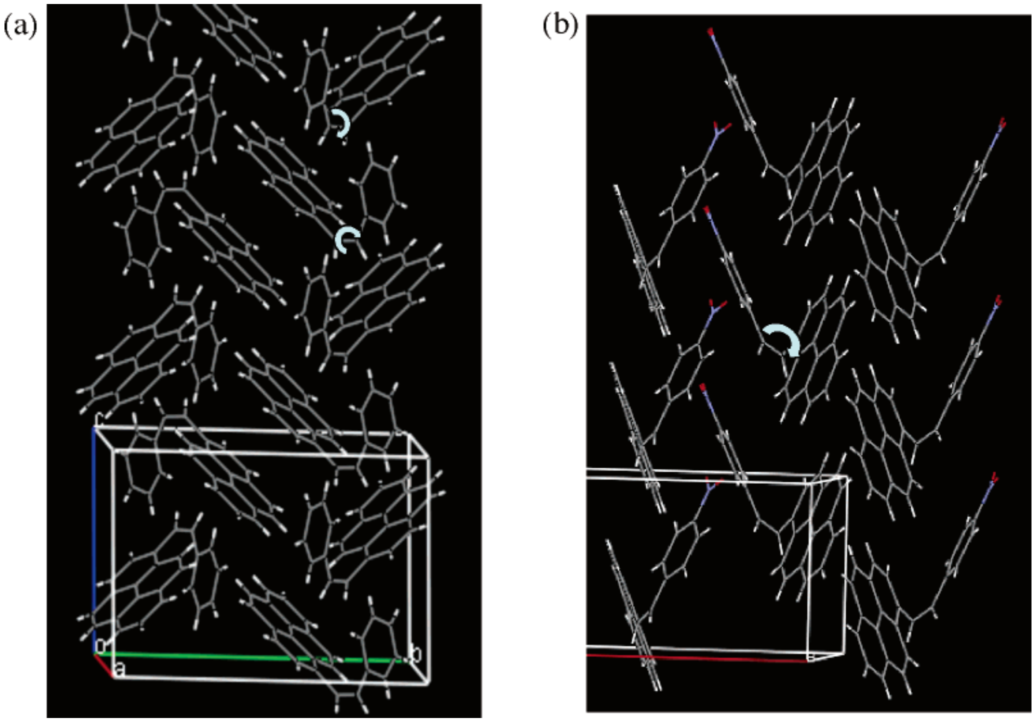

FIGURE 3. (a) Packing diagram of *cis*-**2a** along the *c*-axis. (b) Packing diagram of *cis*-**2c** along the *c*-axis.

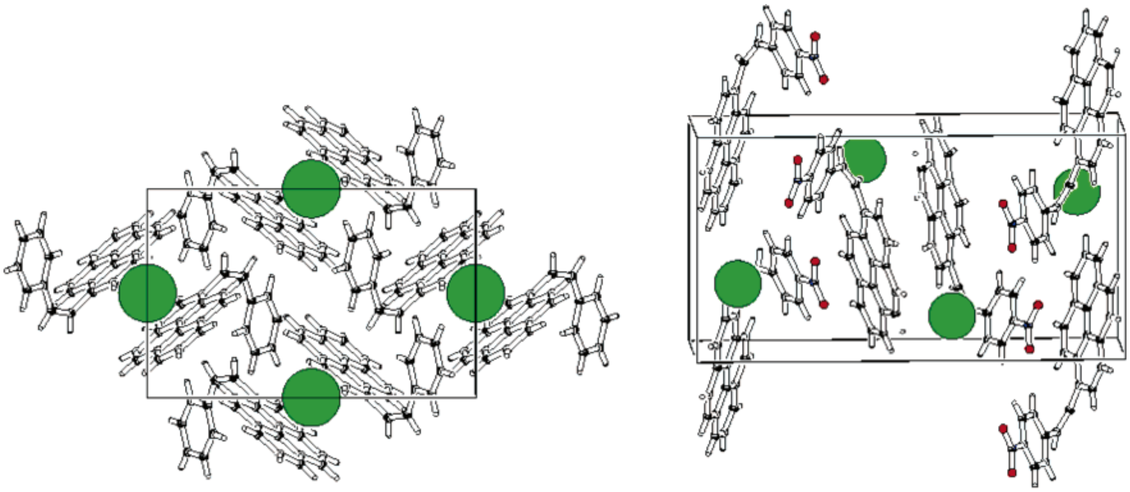
(a) (b)

FIGURE 4. Cavity plot generated using the PLATON program for (a) *cis*-**2a** and (b) *cis*-**2c** molecules.

with a volume of 10.08 Å^3, between two adjacent pyrene moieties in *cis*-**2a**, increases the packing distance between two adjacent cis molecules (Figure 4a). Similarly, in the case of *cis*-**2c**, the reaction cavity (each cavity volume is 5.9 Å^3) is located adjacent to the alkene and phenyl moieties, thereby creating void space near the reaction center (Figure 4b). Stereoscopic views of *cis*-**1**, -**2a**–**c** (see Supporting Information) are useful in visualizing the presence of void space around the reaction center.

During our investigation of the one-way geometric isomerization process in the solid state, we noted that *cis*-**3** (Scheme 1) did not undergo cis–trans isomerization in the solid state. The crystal structure of *cis*-**3** clearly supports the model that free volume is required for the occurrence of geometric isomerization in the crystalline state (Figure 5). The crystal structure of *cis*-**3** reveals that there are eight molecules in the unit cell ($Z = 8$). It also reveals the presence of many atoms within the short contacts on both the top and the bottom faces of the azulene moieties of the alkene (Table 2). Analysis of the crystal lattice along all directions showed no void space near the reaction site. We suggest that the absence of free space and the presence of too many short contacts with nearby atoms near the aryl group endow photostability to **3c**.

The conventional model of photochemical geometric isomerization is torsional relaxation of the double bond which involves a one-bond flip process (OBF), i.e., turning over one-half of the molecule. This is a three-dimensional process requiring the presence of a large free volume within a reaction cavity. In the

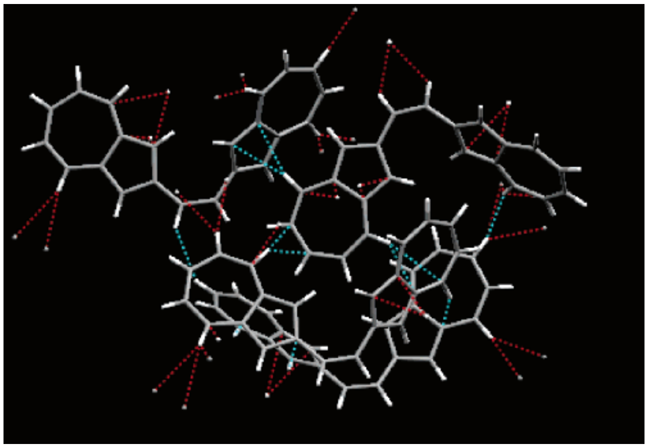

FIGURE 5. Crystal structure of *cis*-**3** showing short contacts.

absence of a large globular (three-dimensional) free volume, this process would be prevented in a crystal by the walls of the reaction cavity. An alternative mechanism known as the "hula-twist" is being currently considered as a possibility in a constrained medium.[9] The hula-twist process (HT), unlike conventional one-bond processes, requires less volume change during cis−trans conversion. The hula-twist is more of a two-dimensional rather than a three-dimensional process. During the cis−trans conversion via a one-bond flip mechanism, one-half of the molecule undergoes a 180° flip; i.e., half of the molecule rises from the molecular plane and sweeps a 180° motion before it rests on the same plane in a different geometry. On the other hand, a hula-twist process which involves a simultaneous rotation of two adjacent bonds (a single and a double bond) or a 180° translocation of one C−H unit results in cis−trans isomerization. In the hula-twist process, only one C−H unit of the molecule rises above the molecular plane during cis−trans conversion. Therefore, the volume demand on this process is much less than that during the one-bond flip. The point to be noted is that, between the one-bond flip and the hula-twist, the latter would be preferred under conditions where the reaction cavity has only a limited free volume. Although the suggestion has been made that the geometric isomerization within a crystal may occur via a hula-twist process, concrete evidence in favor of this is still lacking.[10] The occurrence of geometric isomerization in crystalline *cis*-**1** and -**2a**−**c** in this study can be understood on the basis of the conventional one-bond flip on the phenyl side of the alkenes. However, the possibility of the hula-twist mechanism could not be fully ruled out. Molecules in crystalline *cis*-**3** must be so tightly packed so that neither the one-bond flip nor the hula-twist is able to generate the trans isomer.

Conclusion

There is a general belief that reactions that require large motions would not occur in the solid state. This is based on the assumption that molecules are densely packed in the crystalline state. If for any reason the packing is such that it leaves void space near the reacting molecules, this space could be utilized during the transformation of a reactant to a product. In the examples provided above, this is exactly what happens. Cohen defines a reaction cavity as the space occupied by the reactant molecules plus the empty space surrounding it. In the crystalline state, unlike in biological media, the reaction cavity is rigid and the space needed for a given reaction must be built in.[11] Therefore, in loosely packed crystals, the occurrence of geometric isomerization requiring large motions should not be a surprise.[12]

Experimental Section

The synthesis and characterization of **1**−**3** have been reported previously.[5]

Photoreaction and Analysis Procedure. Crystals **1**−**3** (∼5 mg), either as ground single crystals or in polycrystalline form (powder), were sandwiched between two Pyrex plates and spread to cover a surface area of 2−3 cm^2. The plates were sealed with Parafilm on all the sides before the irradiation process. After the irradiation, the solid was dissolved in 2 mL of $CDCl_3$ and analyzed using ^{1}H NMR. The melting points of the substrates were determined and are uncorrected. Irradiations were performed using a 450 W medium-pressure mercury arc lamp in a water-cooled immersion well. Photoreactions were conducted using appropriate filters (350 nm, Corning-0-52 cutoff filter for *cis*-**1** and *cis*-**2a**−**c**; and 425 nm, Corning-3-73 cutoff filter for *cis*-**3**).

Crystal Structure Determination. Full spheres of data were collected using 606 scans in ω (0.3° per scan) at $\varphi = 0$, 120, and 240°.[13a,b] The raw data were reduced to F^2 values using the SAINT+ software,[13c] and global refinements of unit-cell parameters employing approximately 2000−5000 reflections chosen from the full data sets were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as for corrections for any crystal deterioration during the data collection (SADABS[13d]). All structures were completed by successive cycles of full-matrix, least-squares refinement followed by the calculation of difference maps. All hydrogen atoms attached to carbon were placed in calculated positions with isotropic displacement parameters 20% larger than those of the attached atoms and allowed to ride. All computations associated with structure solution, refinement, and presentation were performed with the SHELXTL[13b] package. The cavity plots were obtained using the PLATON[8] program. For crystal structure visualization, MERCURY (CSD software)[7] was used.

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Supporting Information Available: Dihedral angles, packing diagrams generated through the Mercury program showing the short contacts for **1**−**3**, and the stereoscopic view of the packing diagrams of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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