The Effects of Space Formed by Host Molecules in Inclusion Compounds on the Homogeneity/Heterogeneity of the Photoreaction in the Solid State

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Two inclusion compounds that contain a light-stable host molecule and a light-sensitive guest molecule have been crystallized, that is, 4,5-bis(hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxolane as the host molecule with tropolone methyl ether as the guest molecule and 2,3-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[4.5]decane as the host molecule with 4-(oxophenylacetyl)morpholine as the guest molecule. The two inclusion compounds undergo photochemical ring-closure reactions. However, while the first reacts by a heterogeneous process, the second undergoes a homogeneous photoreaction. The X-ray crystal structure of the two compounds clearly demonstrate that when the space required by the guest molecule to undergo the photoreaction fits the space provided by the host molecule, the reaction is homogeneous; when the space required by the guest is larger than that provided by the host molecule, the photoreaction is heterogeneous. Since the photochemical reaction of the inclusion compound with tropolone methyl ether as the guest is heterogeneous it could not be followed by single-crystal X-ray diffraction. The product of the photochemical reaction is 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one. The photochemical reaction of the second compound was followed by single-crystal X-ray diffraction and the crystal structure shows that the product is tetrahydro-2-phenyloxazolo[2,3-*c*][1,4]oxazine-3(2*H*)-one, and not the β-lactam system obtained in similar reactions.

Introduction

Photochemically and thermally activated solid-state reactions are highly dependent on the geometry of the reacting compound and its product. To understand the reaction mechanism, the course of the reaction and the factors that control the reaction, it is important to be able to follow the geometrical changes that occur during the reaction. Unfortunately most solid-state reactions occur with the destruction of the single-crystalline nature of the sample under study (heterogeneous reaction). In such heterogeneous solid-state reactions the structure of the reactant can be established and that of the product can be determined after recrystallization. Therefore, the events that take place during the reaction are a matter of speculation. Homogeneous solid-state reactions in which the single-crystal nature of the sample remains unchanged during the photoreaction and does not disintegrate during X-ray diffraction, which enables the determination of its crystal structure by X-ray diffraction methods, are quite rare.[1−10] In some cases the crystal structure of a solid solution that contains both the substrate and the product has been structurally analyzed.[4,5,10−13] In these rare cases the structures of the substrate and the product can be monitored. In other very exciting experiments, the structural changes that occur in photochromic salicylideneaniline crystals upon two-photon excitation were observed by X-ray diffraction of a single crystal[14] and the structure of the light-induced radical pair of hexaarylbiimidazolyl together with its ground-state substrate were determined by X-ray diffraction of a single crystal.[15]

Enkelmann and Wegner[16] utilized a general method in which a homogeneous photochemical reaction was imposed by irradiating the crystal with wavelengths of light that correspond to the chromophore's absorption tail. This method enables the structural changes that occur during photoreactions to be monitored. It may also provide another means by which new polymorphs of the product can be obtained.[17] In most single-crystal/single-crystal transformations that occur in photo or thermal reactions the reaction is topochemically assisted. Therefore the structures of the substrate and the product are quite similar.

In inclusion compounds molecules occupy the space formed by the host molecules. If the host molecules provide the topochemical conditions required for bimolecular reactions, and the guest molecules are photochemically active, regio- and stereoselective reactions can be anticipated.[18] If the host molecule is chiral, it induces chirality in the space where the guest molecules react and as a result enantioselective reactions take place.[19−22] Therefore, photochemical reactions of inclusion compounds have proved to be a unique method for the synthesis of a large variety of com-

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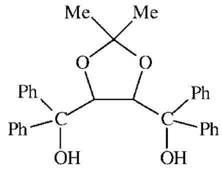
pounds.[23] The volume of the space available for the guest molecules determines whether the reaction will be heterogeneous or homogeneous. When the size of the reaction core is large enough to accommodate the substrate and the product (not at the same instant), the reaction is expected to be homogeneous. Whereas in a neat solid photoreactive compound the molecular structural changes are imposed by the reaction's affecting and interfering with the neighboring molecules, the same molecule in an inclusion compound is surrounded by host molecules that are inert to electromagnetic radiation and their structures therefore do not vary. Therefore the volume available to the guest molecule to accommodate its structural change determines the homogeneity of the reaction. This volume is also called the "reaction cavity", a term that was originally introduced and developed by Cohen to describe reactions in crystals.[24] The model was further developed by Weiss et al.[25] Examples of heterogeneous and homogeneous reactions in solid-state inclusion compounds determined by the size and shape of the space provided by the host molecules is demonstrated in this paper by the photoreaction of two inclusion compounds; 4,5-bis(hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxolane (**I**) as the host molecule with tropolone methyl ether (**1**) as the guest molecule and the other is the inclusion compound of 2,3-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[4.5]decane (**II**) as the host molecule with 4-(oxophenylacetyl)morpholine (**3**) as the guest molecule.



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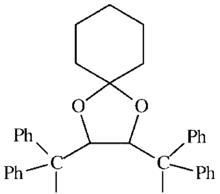

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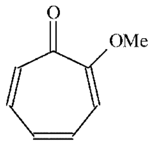

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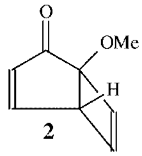

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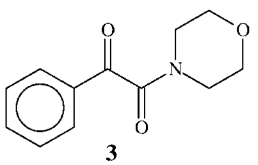

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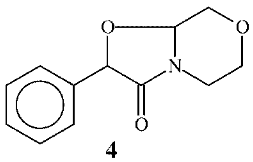

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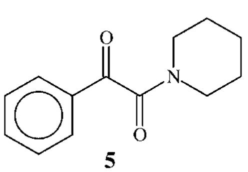

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Results and Discussion

Both inclusion compounds (**I**−**1** and **II**−**3**) undergo photoreactions to yield chiral products, although the absolute configurations of these products were not determined in the work described herein. It was found that while the former undergoes a heterogeneous photoreaction, the latter undergoes a homogeneous photoreaction. In the following discussion we will explain the reasons for the differences between the two types of photoreaction.

Crystal Structures of the Pre-Reacted Inclusion Compounds

The host−guest interactions of compounds **I**−**1** and **II**−**3** and the atomic labeling are shown in Figure 1 and Figure 2, respectively. Each compound (**I**−**1** and **II**−**3**) crystallizes in the monoclinic space group $P2_1$ with two crystallographically independent molecules in the asymmet-

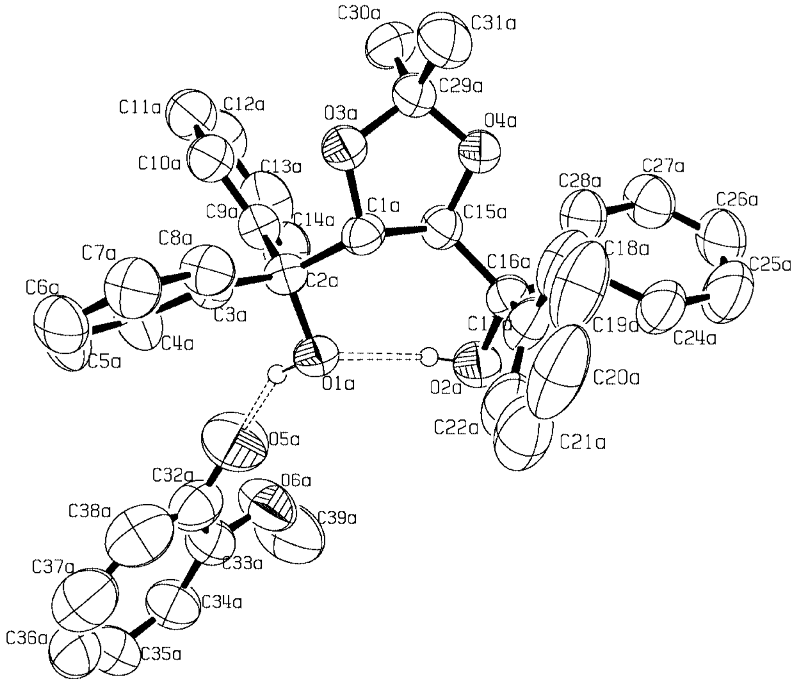


Figure 1. Host−guest interactions in **I**−**1**

Table 1. Comparison of the hydrogen-bond geometries in **I−1** and **II−3** before irradiation (atomic labels are shown in Figures 1 and 2)

D−H	d(D−H) [Å]	d(H···A) [Å]	<DHA [°]	d(D···A) [Å]	A	Symmetry
I−1						
O1a−H1Oa	0.993	1.756	155.50	2.691	O5a	
O2a−H2Oa	0.820	1.991	143.17	2.693	O1a	
O1b−H1Ob	0.820	1.948	157.37	2.723	O5b	
O2b−H2Ob	0.820	1.879	166.49	2.684	O1b	
II−3						
O1a−H1Oa	0.820	1.827	174.73	2.644	O2a	
O2a−H2Oa	0.820	2.019	138.56	2.689	O6a	$[-x, y - 1/2, -z - 1]$
O1b−H1Ob	0.820	2.002	138.63	2.673	O6b	$[x, y, z - 1]$
O2b−H2Ob	0.820	1.822	173.71	2.638	O1b	
II−4 (product)						
O1a−H1Oa	0.820	1.830	174.87	2.648	O2a	
O2a−H2Oa	0.820	1.959	150.87	2.705	O6a	$[-x, y - 1/2, -z - 1]$
O1b−H1Ob	0.820	1.962	151.96	2.714	O6b	$[x, y, z - 1]$
O2b−H2Ob	0.820	1.844	173.45	2.660	O1b	

ric unit (labeled as a and b). In each structure the guest molecules (**1** or **3**) are held by CO···HO hydrogen bonds formed between the carbonyl oxygen atom of the guest molecules and one of the hydroxy groups of the host molecules (**I** or **II**). The second hydroxy group of each host molecule is intramolecularly hydrogen bonded to the other hydroxy group through a HO···HO interaction. The hydrogen bond is similar to that observed in the crystal structure[5] of the pure host compounds (refcodes SEWVUL[26,27] and REPFOH[27] taken from the Cambridge Crystallographic Data Center[28]). Comparison of the hydrogen-bond geometries of **I−1** and **II−3** are compared in Table 1. In spite of the similarity between the two host molecules of the inclusion compounds, the conformations of the dioxolane rings are different. The symmetry of the five-membered ring in **I−1** is C_2 while that in **II−3** is C_m.

Because the host is chiral, there is no inversion center between the two independent host molecules. However the two guest molecules in **I−1** are related by a pseudo-inversion center and the dihedral angle between their mean planes is 5.9°. A mean plane calculation of the seven-membered tropolone ring shows that it is practically planar, the largest out-of-plane displacement of an atom from this plane being 0.031 Å in molecule a and 0.036 Å in molecule b. The out-of-plane displacements of the outer-ring atoms O5, O6, and C39 are 0.124, −0.530, and −0.124 Å for mol-

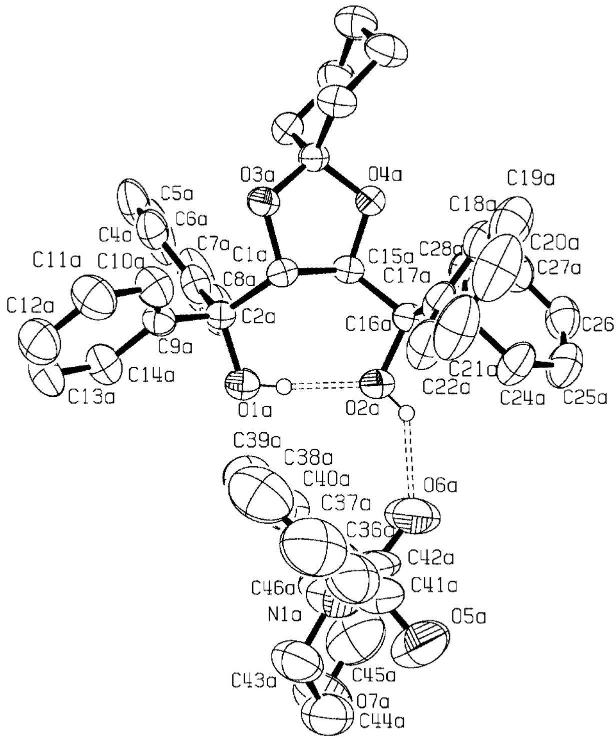


Figure 2. Host−guest interactions in **II−3**

Table 2. Comparison of selected torsion angles [°] in **3**, **4**, and **5**

Torsion angle	**II−3**(a)	**II−3**(b)	**II−4d**(a)	**II−4**(b)	GIKYUU (**5**)	GIKYOO (**5**)
N1−C43−C44−O7	−59.8	−55.7	−56.2	−54.0	−53.5	−54.9
C43−C44−O7−C45	60.7	57.8	63.7	62.2	55.6	51.9
C44−O7−C45−C46	−57.7	−57.8	−64.3	−61.9	−55.1	−51.0
O7−C45−C46−N1	53.6	55.4	53.3	51.7	53.2	51.4
C45−C46−N1−C43	−53.0	−53.0	−47.3	−46.2	−53.2	−52.6
C46−N1−C43−C44	56.7	53.1	50.0	47.8	53.3	55.9
C46−N1−C42−O6	3.9	6.5	5.1	5.7	−2.6	8.1
C43−N1−C42−C41	−4.9	−8.8	−5.8	−6.3	−5.6	0.7
O6−C42−C41−O5	−91.9	−90.2	−169.8	−167.9	−92.3	−85.4

ecule a and −0.097, 0.082, and 0.174 Å for molecule b. The dihedral angles between the phenyl rings are very similar in both host molecules: 77.7° compared with 78.4° between the phenyl rings formed by C3−C8 and C9−C14 in molecules a and b, respectively, and 80.0° compared with 83.6° between the phenyl rings formed by C17−C22 and C23−C28 in molecules a and b, respectively.

The crystal structure of pure 4-(oxophenylacetyl)morpholine (**3**) is not known; therefore selected torsion angles of the guest molecule **3** were compared with those of the irradiated product **4** as well as with those of 1-(benzoylcarbonyl)piperidine (**5**) (Table 2).[29] The comparison shows that the six-membered ring of each compound adopts the chair conformation. While the two carbonyl groups are almost perpendicular to each other before irradiation (the torsion angle O6−C42−C41−O5 is close to 90°), they adopt an anti-parallel orientation as a result of the ring closure caused by the irradiation (this torsion angle is close to 180°).

The solid-state photochemical reactions of the two inclusion compounds **I−1** and **II−3** involved ring-closure, but they exhibited different behavior. The first undergoes a heterogeneous reaction to produce 1-methoxybicyclo[3.2.0]-hepta-3,6-dien-2-one [(1*R*,5*R*)-**2**][30] and the second undergoes a homogeneous reaction to produce tetrahydro-2-phenyloxazolo[2,3-*c*][1,4]oxazin-3(2*H*)-one (**4**). The reason why two different types of photochemical reaction occur stems from the differences in space required for the reactions to take place, and the space provided by the host molecules.

The packing of tropolone methyl ether molecules in **I** is shown in Figure 3. The guest molecules are packed in pairs within the space provided by the host. The two guest molecules lie face-to-face with an inclination angle between the mean planes of the two molecules of 5.9°. The perpendicular separation between the mean planes is 3.66 Å. The best molecular fit between tropolone methyl ether (**1**) and its bicyclic photoproduct **2** as calculated by MM+[31] is shown in Figure 4. The atoms of the reactant tropolone are drawn in space-filling form and that of the product in stick-model style; the extra space is needed to accommodate two of the product's atoms, oxygen on one side and hydrogen on the other. The estimated additional width of the product compared with the reactant is given by the sum of the Van der Waals radii of oxygen and hydrogen (2.72 Å). The separation between the two molecules is not sufficient for the extra space needed by the product as shown above. Therefore as a result of the photoreaction the photoproduct is formed but the crystal is destroyed.

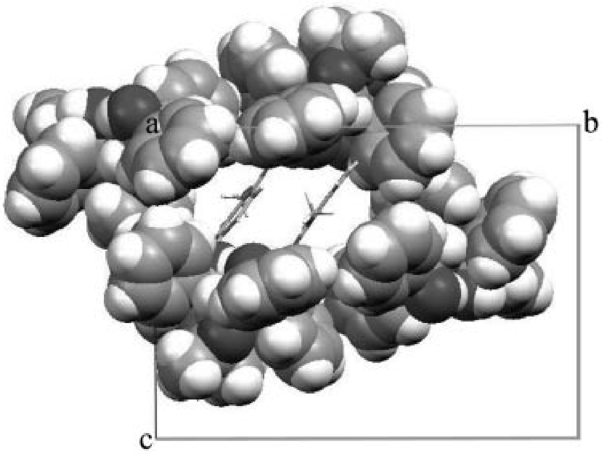


Figure 3. Packing of guest molecules of **1** (drawn in stick style) within the space provided by the host molecules of **I** (drawn in space-filling style)

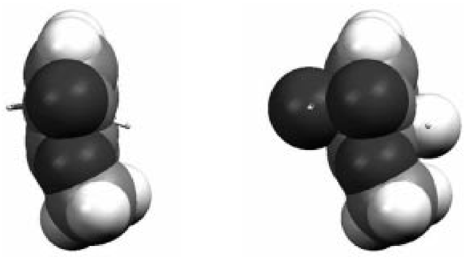


Figure 4. Best molecular fit of the reactant **1** and the product **2**; compound **1** is drawn in space-filling style, **2** is drawn in stick style (left); **1** and **2** are drawn in space-filling style, with the two atoms (oxygen and hydrogen) of **2** that are sticking out (right)

The best molecular fit between the guest molecule **3** and its photoproduct **4** is shown in Figure 5 and the core of the photoreaction is shown in Figure 6. Since the space required by **3** and by its irradiated product **4** are identical (Figure 5) a homogeneous reaction is anticipated. One may calculate the space available for the reaction by deleting the guest molecules and computing the voids that remain. It was found that the void before and after the reaction is practically the same (738.1 and 746.5 Å^3 for molecules a and b, respectively, before the reaction and 739.4 and 744.8 Å^3 for molecules a and b, respectively, after the reaction).

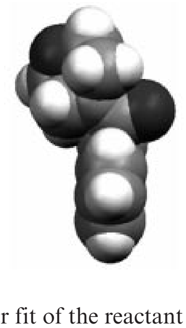


Figure 5. Best molecular fit of the reactant **3** (drawn in space-filling style) and the product **4** (drawn in stick style); **4** is buried within **3** and therefore it is not observed

The solid-state photochemistry of *N*,*N*-dialkyl-α-oxoamides **6**, where the alkyl substituents were H, Me, Ph, or $-(CH_2)_3-$, was investigated intensively by Aoyama and coworkers.[32−34] It was shown that the amides undergo type II cyclization to yield β-lactams **7** selectively (Scheme 1). The selectivity of the photoreaction may be explained in terms of the restraints of the crystal lattice on the molecular motion of the biradical intermediate formed by γ-hydrogen abstraction, but there is no firm evidence for this con-

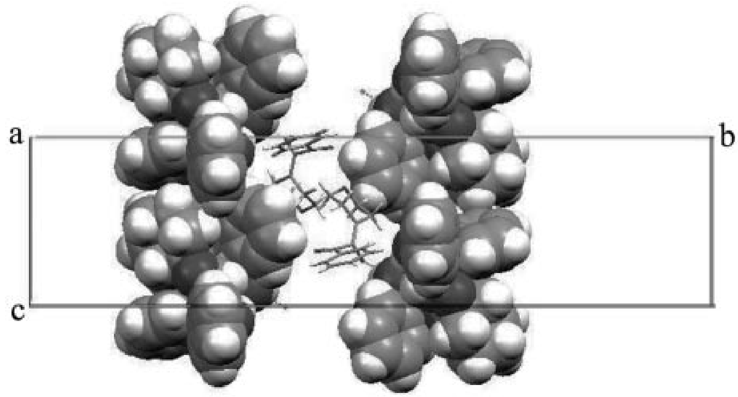
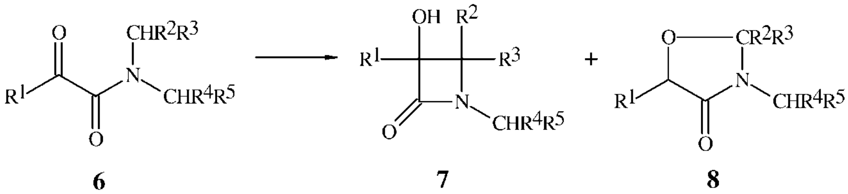


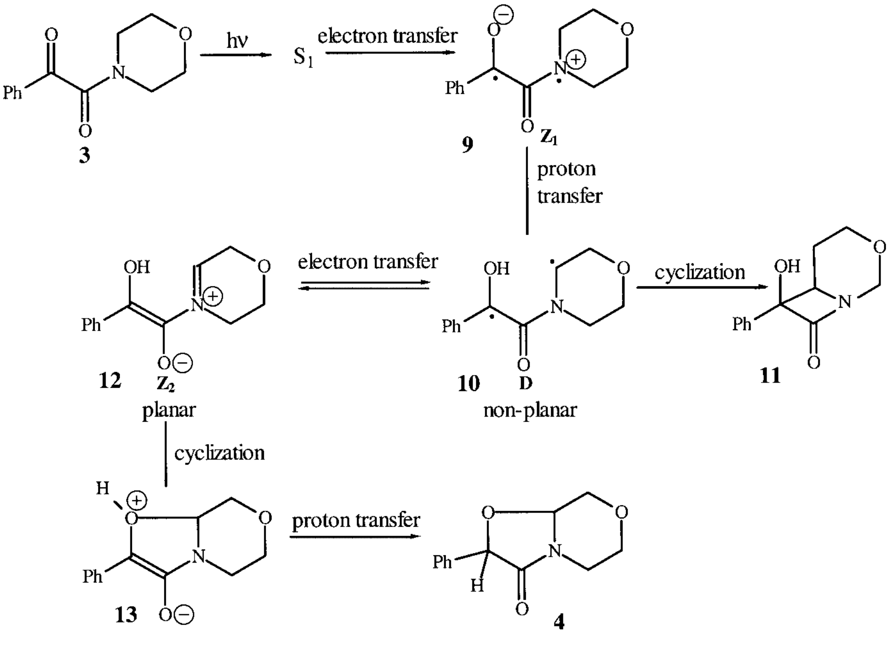
Figure 6. The guest molecules (drawn in stick style) embedded within the host molecules (drawn in space-filling style)



Scheme 1

clusion. Note that in the solid state the oxazolidin-4-one products **8** were obtained in low yields.

In light of the investigation by Aoyama and co-workers it was predicted that 4-(oxophenylacetyl)morpholine (**3**) should react photochemically to yield a β-lactam such as **7**, but instead, the oxazolidin-4-one **4** (similar to **8**) was obtained. From the mechanism proposed by Aoyama et al.,[34] the first step in the formation of the β-lactam involves the γ-hydrogen abstraction from C43 by O5 and the formation of a biradical. The shortest intramolecular O···H distances in the molecule are O5a···H43d 2.678 Å and O5b···H43e 2.654 Å. These distances are within the known range for γ-hydrogen abstraction suggested by Scheffer and co-workers.[35] This means that the formation of β-lactam **7** upon irradiation of the inclusion compound **II−3** cannot be ruled out. Nevertheless the formation of oxazolidin-4-one **4** is evident from the crystal structure determination of **II−4**. According to the mechanism proposed by Aoyama et al. for the production of the oxazolidin-4-one (such as **8**), the conformation around the OC−CO is *trans* in the hydrogen abstraction step; the next step involves a 1,4-hydrogen migration from O5 to O6 in which the conformation of the



Scheme 2

molecule is constrained to a planar or nearly planar *cisoid* transition state. Therefore the biradical must rotate about the OC−COH bond. This means that the O6−C42−C41−O5 torsion angle should vary from approximately 90° to approximately 180° (in the *transoid* conformation) then to about 0° (in the *cisoid* conformation) and back to about 180° in the product. These rotations cannot take place within the limited space provided by the host molecules. The mechanism proposed by Chesta and Whitten[36] (Scheme 2), which does not include the *transoid*-to-*cisoid* rotations required by the mechanism suggested by Aoyama et al., could, therefore, conceivably take place in a constrained media. Note that the space provided by the host molecules is large enough to accommodate the alternative product, azetidin-2-one (β-lactam **7**) and therefore the discrimination between the two products should be investigated. We are currently studying the effect of different host molecules on the solid-state photoproduct.

Conclusions

The results of the structural study of the photochemical reactions of two solid-state inclusion compounds show clearly the effect of the space provided by the host molecules on the homogeneity or heterogeneity of the reactions. When the space can accommodate the reactant before the reaction and is sufficient to accommodate the product at the end of the reaction, the reaction will be homogeneous. Since it is impossible to follow the structural changes that occur during the photoreaction we can only assume that in homogeneous photoreactions the photoreactive molecules do not undergo structural changes in the intermediate stages of the reactions that cannot be accommodated within the space provided by the host molecules.

Experimental Section

Inclusion compounds of **II** were obtained by dissolving a 1:1 mixture of the host and the guest in a 1:1 solution of petroleum ether and diethyl ether. The solution was shaken until it was clear. The solution was kept at room temperature and colorless crystals appeared after two weeks. The inclusion compound **I−1** was obtained as a gift from Professor F. Toda.[37]

The irradiation system consisted of an Osram Xe short arc lamp (150 W). A crystal of the inclusion compound **II−3** was irradiated for a total time of 8.5 hours. The irradiation was done in four intervals (20 minutes/50 minutes/3 hours/4 hours and 20 minutes) by mounting the crystal in front of the focused beam at a distance of approximately 2 cm from the light source. The crystal was attached with grease to a thin piece of glass attached to a solid piece of metal, and mounted on a device that revolved at 1 rpm. The irradiation of crystals of the inclusion compound **I−1** caused the formation of an amorphous material.

The crystal structures were determined by using the maXus direct method,[38] and refined anisotropically with respect to the non-hydrogen atoms by using the SHELXL97 program package.[39] Hydrogen atoms (except for hydroxy hydrogen atoms) were placed at calculated positions and refined isotropically by using the riding model. The hydroxy hydrogen atoms were placed at calculated positions and their geometries were idealized. The crystallographic data for **I−1**, **II−3**, and **II−4** are given in Table 3.

CCDC-236986, -236987, and -236988 contain the supplementary crystallographic data for this paper. These data can be obtained

Table 3. Crystallographic data and parameters for **I−1**, **II−3**, and **II−4**

	I−1	**II−3**	**II−4**
Formula	$C_{31}H_{30}O_4{\cdot}C_8H_8O_2$	$C_{34}H_{34}O_4{\cdot}C_{12}H_{13}NO_3$	$C_{34}H_{34}O_4{\cdot}C_{12}H_{13}NO_3$
M_r	602.69	725.85	725.85
Crystal color, habit	colorless, prism	colorless, prism	colorless, prism
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$
a [Å]	9.534(2)	9.443(1)	9.411(2)
b [Å]	21.640(4)	40.832(8)	40.817(8)
c [Å]	15.746(3)	10.073(2)	10.041(2)
β [°]	92.44(2)	91.20(2)	91.28(2)
V [Å^3]	3245.7(11)	3883.1(12)	3856.1(14)
Z	4	4	4
$D_{\text{calcd.}}$ [g·cm^{-3}]	1.233	1.242	1.250
μ (Mo$_{K\alpha}$) [cm^{-1}]	0.082	0.083	0.084
$2\theta_{\max}$ [°]	50.0	50.0	50.0
Reflections collected	8938	12743	12380
Independent reflections	5760	6951	6921
Observed reflections	3122	4305	4246
Largest difference peak [e·Å^{-3}]	0.191	0.230	0.400
Largest difference hole [e·Å^{-3}]	−0.201	−0.282	−0.269
No. of parameters	819	973	973
R[a]	0.0456	0.0434	0.0393
wR[a]	0.1133	0.1302	0.1225
GOF[b]	0.845	0.934	0.927

[a] $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$; $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [b] GOF $= [\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables.

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