DOI: 10.1002/ejoc.200600193

Solid-State Photodimerization of Guest Molecules in Inclusion Compounds

Irena Zouev,[a] Tali Lavy,[a] and Menahem Kaftory*[a]

Keywords: Photochemistry / Solid state / Structure elucidation / Host–guest systems

Photochemical dimerization reactions of 1,3-diphenyl-1-propen-3-one (chalcone), 9-acetylanthracene, and 9-(methoxycarbonyl)anthracene as guest molecules in inclusion compounds with 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol were studied. The irradiation of a single crystal containing chalcone was carried out in a single step and resulted in a single crystal containing the photodimer in full occupancy. In the case of the crystal containing 9-acetylanthracene, X-ray diffraction data were collected after irradiation for different periods of time. Only one of the two crystallographically independent pairs of 9-acetylanthracene underwent solid-state photodimerization at ca. 11% conversion to the head-to-tail dimer. Photodimerization of the 9-(methoxycarbonyl)anthracene inclusion compound led, after irradiation for 2.5 h, to ca. 37% conversion. It was found that the molecules that were arranged in stacks had undergone photodimerization in two different ways, so that on the average it looked as if all the guest molecules had polymerized.
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

Inducing photochemical reactions in inclusion compounds has proved to be a unique method for synthesizing a large variety of compounds.[1] The volume of space available for the guest molecules determines whether the reaction will be heterogeneous or homogeneous. In cases where the size of the reaction core is large enough to accommodate the substrate and the product (not simultaneously), the reaction is expected to be homogeneous. In a neat, solid, photoreactive compound, the molecular structural changes induced by the reaction affect and interfere with the neighboring molecules. However, the same molecule in inclusion compounds is surrounded by host molecules that are not involved in the reaction, and are thus not expected to undergo structural changes. Therefore, the volume available for the guest molecule to accommodate its structural change determines the homogeneity of the reaction. This volume is also called "reaction cavity", originally introduced and developed by Cohen to describe reactions in crystals.[2] This model was further developed by Weiss, Ramamurthy and Hammond[3] and also by Garcia-Garibay.[4]

The $(4\pi_s + 4\pi_s)$ photocycloadditions are among the oldest known, and with the $(2\pi_s + 2\pi_s)$ cycloadditions, constitute an important group of photochemical reactions. In these reactions, 8π electrons are involved, and "s" denotes "suprafacial", which means that bonds are formed or broken on the same face of the reaction system. Molecules known to date as being involved in such processes are mainly of the anthracene type.[5] The most reactive positions are 9 and 10.

The photochemical behavior of 9-benzoylanthracene and 9-acetylanthracene was investigated by Becker et al. in 1993.[6] It was found that irradiation of crystalline 9-benzoylanthracene led to the formation of a head-to-tail dimer in 50% yield. The photochemical reaction of 9-acetylanthracene resulted in complete consumption of the starting material to form diacetyl-substituted dianthracene, together with anthraquinone (10%). However, in both cases it was impossible to determine the crystal structure of the product, because the crystals disintegrated during the irradiation.

The monitoring of 9-methylanthracene photodimerization (as a pure compound) applied to a single crystal was published.[7] It was shown that the [4+4] photodimerization reaction took place to yield head-to-tail isomers. The reaction was homogeneous up to 28% conversion, and then the crystal underwent disintegration. We wanted to determine if there was sufficient volume in the anthracene derivative inclusion compound for a homogeneous [4+4] photodimerization reaction. For the host molecule, tetraphenylhexa-2,4-diyne-1,6-diol (**1**) was chosen. Two cases of [4+4] photochemical reactions, occurring in the single crystal of inclusion compounds **1–a** and **1–c**, are described in this paper, as well as the homogeneous [2+2] photodimerization of 1,3-diphenyl-1-propen-3-one (chalcone) in a single crystal.

The structure of the inclusion compound **1–e** was investigated previously.[8] It crystallizes in the triclinic space group $P\bar{1}$. The guest molecules are linked to the host molecules by hydrogen bonding between the hydroxy groups of the host molecules and the carboxyl oxygen atoms of the guest molecules. The host molecule occupies a crystallographic inversion center (1/2, 1/2, 0). The guest molecules are

[a] Department of Chemistry, Technion – Israel Institue of Technology,
Haifa 32000, Israel
Fax: +972-4829-5705
E-mail: kraftory@tx.technion.ac.il

 InterScience © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

packed in parallel pairs related by another inversion center (1/2, 1/2, 1/2). As a result, the planes of the double bonds are parallel, and the distance between the potentially reacting atoms is 3.87 Å. This distance is within the range proposed for photodimerization.[9] This arrangement enables the photodimerization to yield the *syn*-head-to-tail product. This photodimerization was carried out in the molten state, and the photoproduct alone was crystallized after the reaction.[10] We report here on the homogeneous photodimerization of the chalcone molecules in this inclusion compound.

Results and Discussion

[4+4] Photochemical Reaction

The inclusion compound **1–a** is composed of 9-acetylanthracene (**a**) as a guest molecule and tetraphenylhexa-2,4-diyne-1,6-diol (**1**) as a host (see Scheme 1). **1–a** crystallizes in the monoclinic space group $P2_1/c$. The crystal structure shows hydrogen bonds of the type OH···O=C. The OH hydrogen atom of the host molecule is hydrogen-bonded to the acetyl oxygen atom of the guest molecule. There are two crystallographically independent guest molecules, and each of them forms a pair with a molecule related by an inversion center (see for example Figure 1).

The distance between the potential reactive centers of the two anthracene derivative molecules (to yield a head-to-tail dimer) is less than 4.2 Å, the limit proposed for photodimerization.[9] Guest molecule pairs of two types are present in the unit cell (see Figures 2 and 3). The distance between the potential reactive centers in the first type (A) is 3.805(1) Å, and 3.714(1) Å in the second type (B).

In order to induce homogeneous photochemical reactions in neat solid compounds, one may use the method of Enkelman.[10] However, when irradiating inclusion compounds where the host is light-stable and the guest is light-sensitive, we have found that the homogeneous/heterogeneous photochemical reaction is dependent on the space provided for the reaction.[11] The main absorption bands

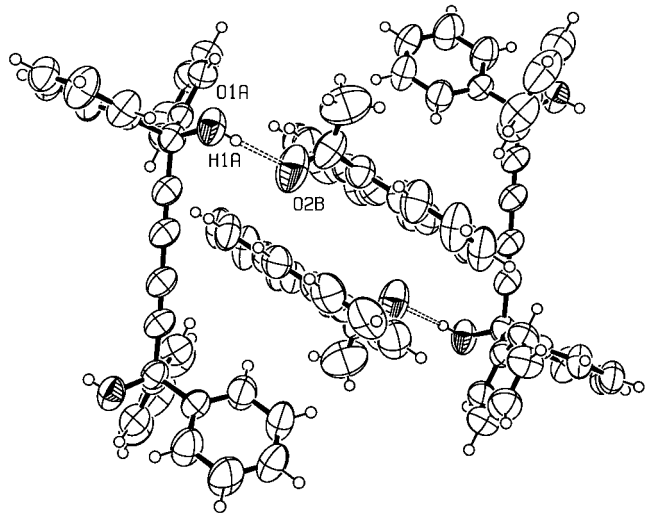


Figure 1. View of the guest molecules surrounded by the host molecules. Hydrogen bonds are shown by dashed lines.

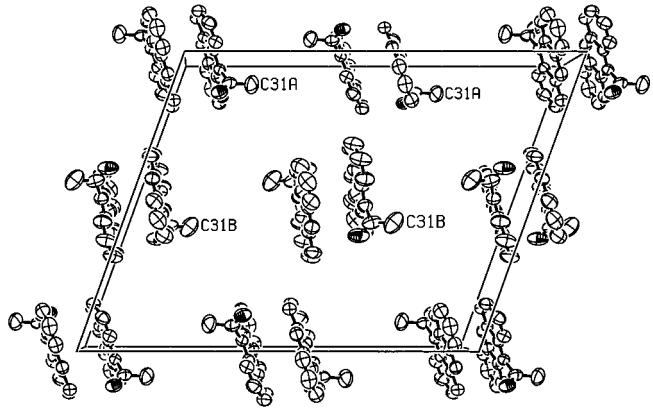
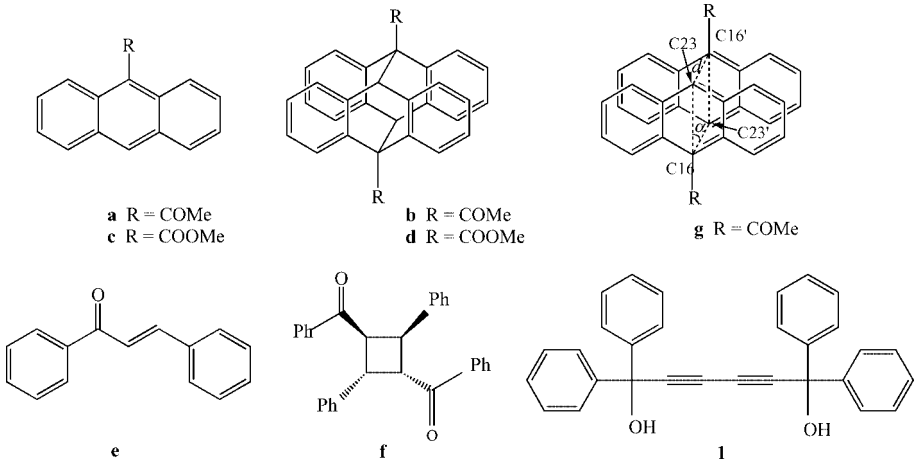


Figure 2. Molecular packing of **1–a**, showing the two types of guest molecules (A and B). The host molecules are not shown for clarity.

are at λ = 345–387 nm (for **1–a**) and λ = 344–381 nm (for **1–c**). The two crystals were irradiated at the chromophore absorption tail. It was very surprising to see that only the



Scheme 1.

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

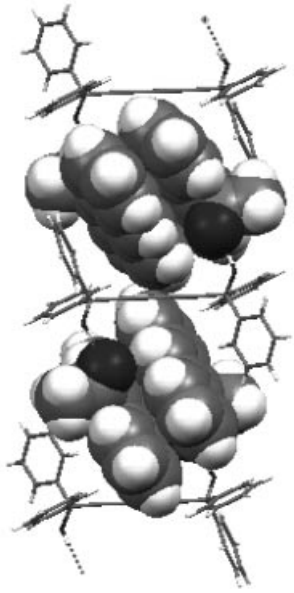


Figure 3. View of the guest molecules of A and B types (drawn in space-filling style) embedded within the host molecules (drawn in stick style).

guest molecules B underwent approximately 11% conversion to dimer after 3 h of irradiation, while the A molecules did not dimerize, as far as one can tell from the X-ray crystal structure determination (see Figure 4).

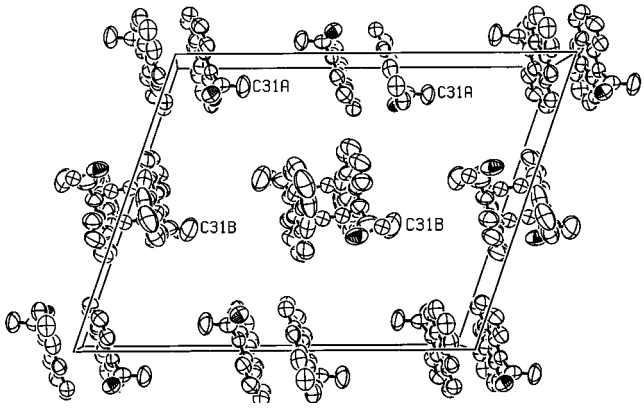


Figure 4. Packing of molecules in the unit cell after 3 h of irradiation. The host molecules and hydrogen atoms are not shown for clarity.

Why do molecules of type B undergo photodimerization, while those of type A do not? The answer can be found by comparing the mutual geometry of the molecules in each pair. Such a comparison for the two pairs (in A and B) is given in Table 1. The torsion angles C16···C23···C16′···C23′, and C23···C16···C23′···C16′ are 0° because of the presence of an inversion center between the two monomers. *K* is the angle between the plane formed by the atoms C16···C23···C16′···C23′ and the plane of the central ring of the anthracene fragment.

Table 1. The mutual orientation of the guest molecules (for notation see Scheme 1, **g**).

Guest molecule	*d* [Å]	*α* [°]	*K* [°]
Type A	3.805	91.9 88.1	69.1
Type B	3.714	82.1 97.9	68.6
Ideal values	<4.2	90	90

The geometric parameters given in Table 1 for the pairs of molecules of type A and type B are very similar and cannot provide the answer to the question. The other parameter that might affect the dimerization of the guest molecules within the inclusion compound is the space available for the reaction. One may calculate this parameter by deleting the guest molecules and computing the voids that remain in the unit cell of the crystal before irradiation.[12] The calculated volume provided by host molecules surrounding the B guest molecules is 1391 Å^3. In the case of molecules of A, this parameter is smaller, 1368 Å^3. This difference can explain the different behavior of the guest pairs. As a result, guest molecules of type B undergo photodimerization (see Figure 5), while those of type A do not. Eventually, the unreacted pairs do react, but at this stage, due to the lack of space, the crystal disintegrates.

The hydrogen bonds between the host molecules and the guest molecules of type B do not significantly vary as a result of the dimerization [2.798(3) to 2.803(7) Å] (see Table 2). The host molecules approach each other, and as a result, the distances between the nearest host molecules B decrease from 11.806(3) to 11.634(7) Å. The anisotropic displacement parameters (ADPs, they are the mean-square displacements of the atoms from their positions) of the phenyl rings of these host molecules increase, meaning that the rotation of the rings is slightly different in each unit cell.

As for the host molecules embedding guest molecules of type A, their positions are almost unaffected by the above change, and the distances between them increase from 11.322(3) Å to 11.345(6) Å. The hydrogen bonds between the host and guest molecules of type A are not significantly different [2.777(3) Å to 2.815(6) Å].

The inclusion compound with 9-(methoxycarbonyl)anthracene (**1–c**) was prepared. It crystallizes in the orthorhombic space group *Pbca*. The crystal structure shows hydrogen bonds of the type OH···O=C. The OH group of the host molecule is hydrogen-bonded to the acetyl oxygen atom of the guest molecule. Adjacent guest molecules are situated head-to-tail in the unit cell. Unlike the previous structure, the guest molecules are related by a non-crystallographic pseudo-inversion center, and therefore are not parallel to each other. The distances between the reactive centers are 4.401(1) Å and 3.946(1) Å. The angle between the planes of the two middle rings of the adjacent guest molecules is 8.95°. These parameters are not ideal for successful photodimerization. The guest molecules are packed in infinite stacks along the *a*-axis; parallel stacks are packed in

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

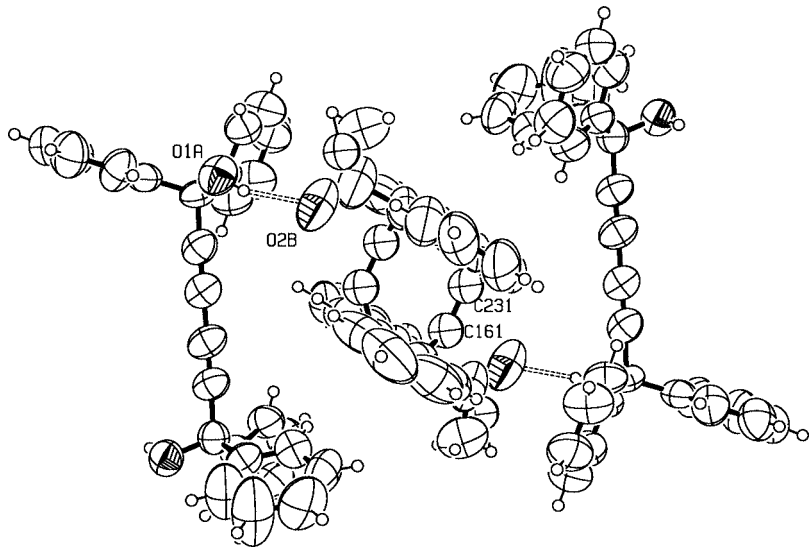


Figure 5. View of the dimer molecule surrounded by host molecules. Hydrogen bonds are shown by dashed lines.

Table 2. Comparison of hydrogen-bond geometries.

		D–H···A	*d*(D–H)	*d*(D···A)	∠(DHA)
1–a	O1A–H1A–O2B[a]	1.982	0.820	2.798(3)	173.9
	O1B–H1B–O2A[b]	1.962	0.820	2.777(3)	173.0
1–b	O1A–H1A–O2B[a]	2.038	0.820	2.803(7)	155.0
	O1B–H1B–O2A[b]	2.002	0.820	2.815(6)	171.5
1–c	O1–H1–O2[c]	2.023	0.820	2.825(2)	165.6
1–d	O1–H1–O2[c]	2.006	0.820	2.811(5)	166.6
1–e	O1–H1–O2[d]	1.697	1.067	2.754(3)	169.9
1–f	O1–H1–O2[d]	2.083	0.820	2.847(5)	154.9

[a] $-x+1$, $y-1/2$, $-z+1/2$. [b] $-x+2$, $y+1/2$, $-z+1/2$. [c] $-x+1/2$, $y+1/2$, z. [d] $-x+1$, $-y+1$, $-z+1$.

herringbone fashion and are embedded between the host molecules. Within a stack of guest molecules, each neighboring pair may photochemically dimerize (Figure 6).

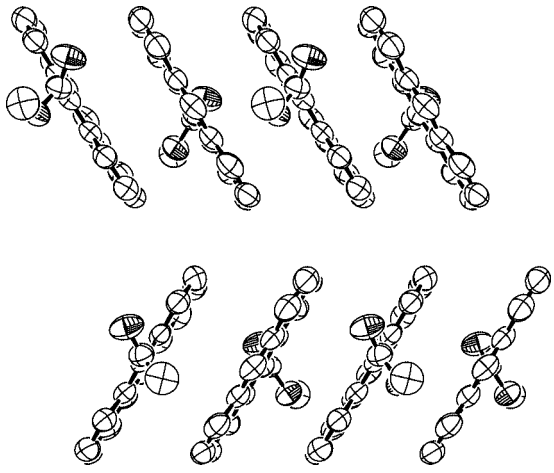


Figure 6. Stacking of guest molecules of **1–c**.

After irradiation for 2.5 h, to about 37% conversion, it was found that the molecules in the stacks had undergone photodimerization to form a polymeric molecule (Figure 7).

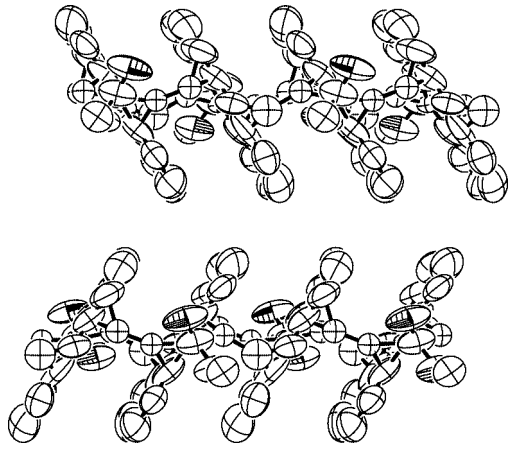


Figure 7. Stacking of guest molecules of **1–d**.

The picture (Figure 7) appears as if a polymer chain is formed; however, this is misleading: the crystal structure is a reflection of the average structure of different unit cells. Therefore, in one unit cell the first and the second molecule undergo dimerization and the rest is dimerized accordingly; in another unit cell the second and third molecule undergo dimerization and the rest are dimerized accordingly.[13] On average, it looks as if all the guest molecules are dimerized to form a polymer.

[2+2] Photochemical Reaction

The crystal structure of **1–e** is known;[8] however, we have repeated the data collection and refinement in a different unit cell setting so that it will resemble the unit cell of the irradiated crystal (see Table 3). Irradiation of a single crystal of inclusion compound **1–e** resulted in photodimerization of the diphenyl-1-propen-3-one (chalcone) molecules to yield 1,3-dibenzoyl-2,4-diphenylcyclobutane (**f**) without

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 3. Crystallographic data for **1–a**, **1–b**, **1–c**, **1–d**, **1–e** and **1–f**.

	1–a	**1–b**	**1–c**	**1–d**	**1–e**	**1–f**
Empirical formula	$C_{62}H_{46}O_4$	$C_{62}H_{46}O_4$	$C_{31}H_{23}O_3$	$C_{31}H_{23}O_3$	$C_{30}H_{22}O_2{\cdot}2C_{15}H_{12}O$	$C_{30}H_{22}O_2{\cdot}C_{30}H_{24}O_2$
M_r	854.99	854.99	443.49	443.49	830.97	830.97
Crystal form, color	prism, yellow	prism, yellow	plate, yellow	plate, yellow	prism, colorless	prism, pale yellow
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$Pbca$	$Pbca$	$P\bar{1}$	$P\bar{1}$
a [Å]	20.436(4)	20.410(4)	8.310(2)	8.343(2)	8.5360 (6)	8.390(1)
b [Å]	9.305(2)	9.269(2)	18.688(4)	18.740(4)	12.2918(9)	11.913(1)
c [Å]	25.843(5)	26.045(5)	30.006(6)	29.943(6)	12.6197(9)	12.981(1)
α [°]	90	90	90	90	82.021(6)	84.472(10)
β [°]	109.86(2)	109.24(2)	90	90	70.007(5)	76.555(10)
γ [°]	90	90	90	90	68.763(9)	70.366(10)
V [Å^3]	4622.0(16)	4652.0(16)	4659.9(18)	4681.5(18)	1159.63(14)	1188.3(2)
Z	4	4	8	8	1	1
D_x [Mg m^{-3}]	1.229	1.221	1.264	1.258	1.190	1.161
No. of parameters	630	608	327	333	290	289
μ [mm^{-1}]	0.075	0.075	0.080	0.080	0.073	0.071
$2\theta_{max}$ [°]	50.1	50.1	50.1	50.1	50.1	39.3
Reflections collected	10363	7260	4382	3814	4801	2032
Independent reflections	7982	6763	4024	3758	4086	2032
Observed reflections	4414	2749	1890	1927	2008	1318
Largest difference peak[e·Å^{-3}]	0.286	0.200	0.233	0.376	0.306	0.127
Largest difference hole[e·Å^{-3}]	–0.149	–0.196	–0.249	–0.253	–0.307	–0.139
R[a]	0.0672	0.11	0.0576	0.1194	0.0652	0.0720
wR[a]	0.1761	0.2937	0.1228	0.3002	0.2011	0.2212
GOF[b]	1.032	1.033	0.892	2.036	0.905	1.085

[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] $GOF = [\Sigma w(|F_o|-|F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observations and N_v is the number of variables.

destruction of the crystalline nature of the single crystal. However, the crystal quality was decreased due to the reaction, as indicated by the crystal data. The crystal structure of the inclusion compound with the photoproduct was solved and is discussed below. The host in inclusion compound **1–f** still occupies a crystallographic inversion center, as does the photoproduct. The photoproduct with the host is shown in Figure 8, and the photoproduct itself is shown in Figure 9 in a view perpendicular to the four-membered ring.

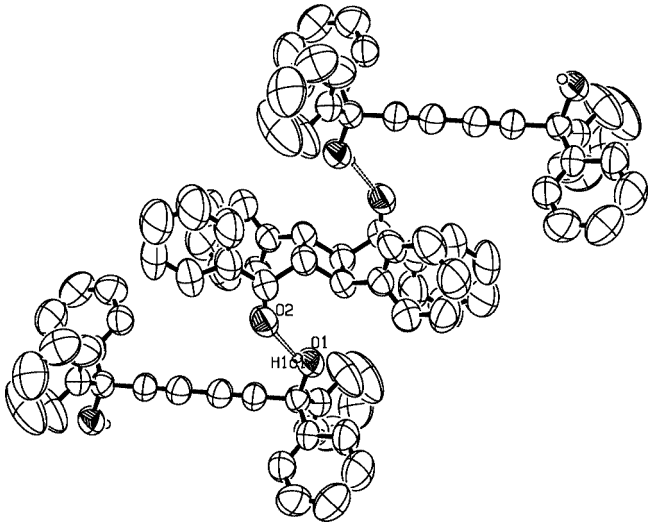


Figure 8. Hydrogen bonding between the host and guest molecules in **1–f** (hydrogen atoms are omitted for clarity).

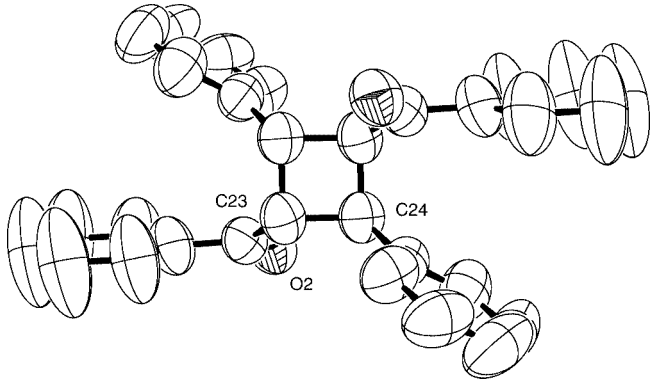


Figure 9. 1,3-Dibenzoyl-2,4-diphenylcyclobutane (hydrogen atoms are omitted for clarity reasons).

The distance between the reactive centers prior to irradiation is 3.856(4) Å, and as a result of the photodimerization, two new bonds have been formed with bond lengths of 1.565(7) Å. It is therefore expected that, as a result of the decrease in the proximity of the two monomers, the volume of the dimer will be less than the sum of the volumes of two monomers. However, this is evidently not the case. The volume of the unit cell of the inclusion compound with the product is larger by 2.5% than that of the inclusion compound with the monomers. The effective volume of the dimer increases due to the change in geometry compared with the two parallel planar chalcone molecules. The changes of the hybridization from sp^2 to sp^3 of the connecting atoms, as well as the rotation of the phenyl substituents, cause an increase of the effective volume. The ADPs of the phenyl

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

substituents reflect the direction of the movement of the chalcone molecules toward each other. The hydrogen-bond length between the host and the guest is longer in inclusion compound **1–f** than in the inclusion compound **1–e** prior to the irradiation (see Table 2 and Figure 9).

Experimental Section

Synthesis: The host compound **1** was obtained from Prof. Toda. The guest compounds **a** and **e** are commercially available. Inclusion compound **1–a** was obtained by dissolving a 2:1 mixture of the host compound **1** and the guest compound **a** in a 1:1 ethyl acetate/heptane solution. The solution was kept at room temperature, and yellow crystals were obtained within 2 d. 9-(Methoxycarbonyl)anthracene (**c**) was prepared according to the procedure of Parish.[14] Inclusion compound **1–c** was obtained by dissolving a 2:1 mixture of the host compound **1** and the guest compound **c** in a 1:1 ethyl acetate/heptane solution. The solution was kept in a refrigerator, and yellow crystals were obtained within several days. Crystals of inclusion compounds **1–e** were prepared by dissolving a 1:2 mixture of host compound **1** and guest compound **e** in ethyl acetate. The solution was kept at room temperature and after a week pale yellow prism crystals were obtained.

Irradiation Experiment: The irradiation system consisted of an Osram Xe short arc lamp (150 W). A single crystal was attached with grease to a thin piece of glass and mounted ca. 2 cm in front of the focused beam on a device that revolved at 1 rpm. The irradiation of **1–a** was carried out using a KV-400 filter, therefore the wavelength of the irradiation was above 400 nm. X-ray diffraction data was collected after 1, 2, and 3 h of irradiation. After 4 h of irradiation, the crystal had disintegrated. The irradiation of **1–c** was carried out using two Perspex glass filters, therefore the wavelength of the irradiation was above 400 nm. The irradiation was done in four intervals (60/60/45/30 min), until the crystal had disintegrated. A single crystal of **1–e** was irradiated for 10 min without filter.

Crystal Structure Determination: The X-ray diffraction data was collected at room temperature with Mo-K_α radiation (λ = 0.71073 Å). The crystal structures were determined by using the maXus direct method,[15] and refined anisotropically with respect to the non-hydrogen atoms by using the SHELX97 program package.[16] 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. For crystal structures containing the reactant and the product molecules, the atomic coordinates for the monomer were taken from the parent crystal as a starting model for refinement. The conversions of the reactions were estimated by the use of the occupation factor resulting from the crystal structure refinement procedure. For the inclusion compound **1–a**, restriction on the geometry was used. The crystallographic data for the inclusion compounds before irradiation (**1–a**, **1–c**, **1–e**) and after irradiation (**1–b**, **1–d**, **1–f**) are given in Table 3. CCDC-600248 to -600253 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

[1] K. Tanaka, F. Toda, in: *Organic Solid-State Reactions* (Ed.: F. Toda), Kluwer Academic Publishers, Dodrecht, **2002**, pp.109–158.
[2] M. D. Cohen, *Angew. Chem.* **1975**, *87*, 439–447.
[3] R. G. Weiss, V. Ramamurthy, G. Hammond, *Acc. Chem. Res.* **1993**, *26*, 530–536.
[4] A. E. Keating, M. A. Garcia-Garibay, *Mol. Supramol. Photochem. – Org. Inorg. Photochem.* **1998**, *2*, 195–248.
[5] H. Bouas-Laurent, J.-P. Desvergne, A. Castellan, R. Lapouyade, *Chem. Soc. Rev.* **2000**, *29*, 43–55.
[6] H.-D. Becker, V. Langer, H.-C. Becker, *J. Org. Chem.* **1993**, *58*, 6394–6396.
[7] I. Turowska-Tyrk, E. Trzop, *Acta Crystallogr., Sect. B* **2003**, *59*, 779–786.
[8] M. Kaftory, K. Tanaka, F. J. Toda, *Org. Chem.* **1985**, *50*, 2154–2158.
[9] a) G. M. J. Schmidt, *Pure Appl. Chem.* **1971**, *27*, 647–678; b) V. Ramamurthy, K. Venkatesan, *Chem. Rev.* **1987**, *87*, 433–481.
[10] V. Enkelman, G. Wegner, *J. Am. Chem. Soc.* **1993**, *115*, 10390–10391.
[11] T. Lavy, Y. Sheinin, M. Kaftory, *Eur. J. Org. Chem.* **2004**, 4802–4808.
[12] The voids have been calculated using the *PLATON* software: A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
[13] M. Kaftory, V. Shteiman, T. Lavy, J. R. Scheffer, J. Yang, V. Enkelman, *Eur. J. Org. Chem.* **2005**, *5*, 847–853.
[14] R. Parish, L. Stock, *Tetrahedron Lett.* **1964**, *20*, 1285–1288.
[15] S. Mackay, C. J. Gilmore, C. Edwards, M. Tremayne, N. Stuart, K. Shankland, *maXus, A computer program for the solution and refinement of crystal structures from different data*, University of Glasgow, Scotland.
[16] G. M. Sheldrick, *SHELXL-97, Program for the refinement of crystal structures*, University of Göttingen, Germany, **1997**.

Received: March 5, 2006
Published Online: July 19, 2006

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim