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Formation of different photodimers of isoquinolinone by irradiation of solid molecular compounds[†]‡

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[4 + 4] Photodimerization of isoquinolin-3(2*H*)-one (isoquinolinone) (1) may yield 12 different isomers depending on the relative geometry of the two monomers prior to the reaction. Irradiation of the solid neat compound shows that of all possible dimers only the dimer between the two hetero-rings having an inversion center is produced. On the other hand, exposure to UV light of solid molecular compounds composed of isoquinolinone as the guest molecule and different host molecules shows to produce few other isomers of the dimer. The use of different host molecules affects the packing of the molecules in the crystal. As a result, the relative geometries between two monomer molecules are varied enabling photochemical dimerization to yield different isomers. When 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6diol (I) is used as the host molecule, two polymorphic forms of the molecular compound are obtained. Irradiation of single-crystal of the two polymorphs yields a mixture of isomers of the dimer. When the host molecule is cyclohexanol-1,2,4,5-tetracarboxylic acid (II) three isomers are expected, and when the host molecule is 1,3-benzenediol (III) a single isomer is formed which is identical to that obtained from the neat isoquinolinone.

Introduction

Traditionally most synthetic chemistry, especially when photochemical reactions are involved, is carried out in solution; however, there are enormous examples where synthetic chemistry in the solid state has advantages that do not exist in solution. Those examples are described in many publications starting from the work of Schmidt and his co-workers¹ followed by many review articles and books.² This is especially due to the fact that in the crystal, the molecules are fixed and if it provides the geometrical requirements needed for a photoreaction to take place, the resulted product will be specific and determined by the relative geometry of the reacting molecules. This advantage provides the ability to control asymmetric syntheses as pointed out already in 1975.3 For example, enantioselective reactions can be performed by the use of inclusion compounds with a chiral host molecule,⁴ or by using ionic chiral auxiliaries⁵ and zeolites.⁶ One of the best ways to follow and understand the

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photochemical reaction is by monitoring the crystal structure along its progress. Therefore a reaction that undergoes singlecrystal to single-crystal transformation is preferred. A general method describes the induction of such a homogeneous photochemical reaction by irradiating the crystal with wavelength corresponding to the chromophore's absorption tail was published.⁷ However, in most cases if the photochemical reaction is executed on the neat light sensitive compound, the reaction does not proceed to full conversion before the crystal disintegrates. Therefore, monitoring of the reaction process is very limited.

Although, photochemical reactions that are carried out on solid neat compounds may yield unique product it is limited to a single one unless the compound crystallizes in different forms. The advantage of carrying out photochemical reactions on solid molecular compounds composed of light stable host molecule and light sensitive guest molecule is that it may yield different products depending on the structures enforced by the host molecule. Using such molecular compound provides a method to alter the reactive molecular environment expressed by different molecular packing by using different host molecules. The change of the environment or the molecular packing allows, in some cases, the synthesis of different products⁸ or allows specific reactions. Early work on such systems shows also an example of photochemical reaction between the guest and the host molecules.9 In a recently reported work the effect of the environment on molecular properties was studied.¹⁰ The guest molecules undergo photoreaction which takes place in cavities formed by the host molecules, therefore, in the cases where the volume of the cavity is sufficiently big to

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[†] The paper is dedicated to the memory of Professor Fumio Toda, who contributed significantly to the field of solid-state chemistry.

accommodate the product, single-crystal to single-crystal transformations can take place.^{2,11} If the volume of the product is significantly larger than that of the reactant, the crystal is likely to undergo disintegration. In cases where the photochemical reaction takes place in a single-crystal to single-crystal transformation, monitoring of the structural changes is possible.

In the following example the effect of replacing the host molecule on the molecular packing will be revealed. The aim of this example is to demonstrate a method for synthesizing different isomers in photochemical reactions by varying the host molecules. It is not claimed that this is a mature method for preplanned synthesis that can be used regularly because the molecular packing cannot envisage when one uses different host molecules. Nevertheless, it is helpful to know that in those cases when "nothing helps" one could try this method.

Isoquinolinone can undergo [4 + 4] photodimerization to many products depending on the relative geometry of the two monomers. The two monomers may be related to each other either by a crystallographic symmetry or by a non-crystallographic symmetry (pseudo symmetry). Scheme 1 shows four ways to align the two monomers with respect to each other (1, 2, 3, or 4). In 1 the two monomers are related by inversion center (real or pseudo) and dimerization may lead to one of the three products 5, 6, or 7. The two monomers in 2 are related by mirror plane (real or pseudo) and dimerization may lead to one of the dimers 8, 9, or 10. The monomers are related by two fold symmetry in cases 3, and 4 and dimerization will yield one of the three products 11, 12, or 13 from 3, and 14, 15, or 16, from dimerization of 4. Out of the twelve possible dimers it is expected that only one will be obtained by illumination of a crystal of the neat isoquinolinone, unless it crystallized in different crystallographic forms (polymorphs).

The crystal structure of isoquinolinone was not published before and will be described later in this paper.

There are some geometrical prerequisite for photodimerization to take place. The distances between the atoms to be bonded should be less than 4.2 Å,¹ and the lateral shift of the p-orbitals of the reacting atoms should be small to allow an effective overlap between them.¹² There are two sites for possible bond formation to form a dimer of isoquinolinone: the benzene ring and the hetero ring. The product will be dependent on the relative translation of the two molecular planes and on the symmetry between the two monomers. As pointed out above, in principle, the crystal structure of the neat compound provides a single orientation with a fixed relative translation of the two monomers and therefore if the geometrical prerequisite for photodimerization is fulfilled, a single product will be expected. However, in molecular compounds the use of different host molecules, two monomers may adopt different relative geometries leading to different isomers of the dimers. This will be described by the use of molecular compounds with isoquinolinone as the guest molecule and three different host molecules, I, II, and III.





Scheme 1

Molecular compounds

Isoquinolin-3(2*H***)-one (1).** A solution of 1 (0.25 mmol, 0.0365 g) in 4 mL of methanol was slowly evaporated at room temperature to yield yellow prism crystals.

1,1,6,6-Tetraphenyl-2,4-hexadiyne-1,6-diol (I) : 2(isoquinolin-3(2H)-one (1)). A mixture of 1 (0.5 mmol, 0.0726 g) and I (0.25 mmol, 0.1034 g) in methanol (10 mL) was refluxed for 30 min in an oil bath (80 $^{\circ}$ C). The mixture was cooled for one night. The molecular compound crystallized in two modifications: mostly as yellow prism and the rest as yellow cubes.

Cyclohexane-1,2,4,5-tetracarboxylic acid (II): 2(isoquinolin-3(2*H*)-one (1)), H₂O. A mixture of 1 (0.25 mmol, 0.0365 g) and II (0.125 mmol, 0.0325 g) in 6 mL of methanol was refluxed for 30 min in an oil bath (80 °C). The filtrate was allowed to evaporate for a few days and resulted in red-yellow plate crystals.

1,3-Benzenediol (III) : isoquinolin-3(2H)-one (1). A mixture of **1** (0.25 mmol, 0.0365 g) and **III** (0.25 mmol, 0.0275 g) in 10 mL of methanol was refluxed for 30 min. The filtrate stood at room temperature for about two weeks, forming red-yellow prism crystals.

Irradiation

Single crystal was irradiated either with UV LED in the range 350-390 nm with the maximum of 365 nm set to 95 mW or with the third (355 nm) harmonics of a circularly polarized pulsed Nd:VO₄ laser. The laser was set to pulse width of 35 ns and 10 kHz. The average power was less than 1 mW for a spot with a diameter of \sim 1 mm. The crystal revolved while it was exposed to the light. Irradiation of powder sample of **I**–1 was carried out by sunlight for 8 h. Recrystallization from methanol yielded pale yellow prism crystals of the molecular compound composed of **I** as the host and a dimer of 1. Irradiation of a single crystal of **III–1** shows that the crystal disintegrated after a few percent of conversion. Irradiation of powder sample of the same molecular compound yielded insoluble product in most common organic solvents. Insoluble product was also obtained when pure isoquinolinone was irradiated. The product from the last two



Fig. 1 Hydrogen bonding and intermolecular geometry in 1.

experiments was recrystallized from acetic acid and found to be dimer 6 (Scheme 1).

X-Ray crystal structure

X-Ray diffraction intensities were measured either by KappaCCD Nonius Diffractometer or by a Bruker Smart APEX2 CCD diffractometer installed at a rotating anode source (Mo K α , $\lambda = 0.71073$ Å). The crystal structures were solved by direct methods (SHELX97).¹³ All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were located in difference Fourier maps and refined by riding on their parent atoms.§

Results and discussion

Crystal structures before irradiation

The neat guest compound isoquinolin-3(2*H*)-one (1) crystallized in a monoclinic P_{21}/c space group as a disordered molecule consists of a 50 : 50% mixture of pyridone and hydroxypyridine (Fig. 1). As a result of the disorder the CO distance of 1.309(3) Å is longer than that of a C=O bond length observed in the other

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[§] Crystal data. Compound 1: C₉H₇NO, M = 145.16, monoclinic, a =9.868(2), b = 6.0890(10), c = 12.466(2) Å, $\beta = 108.14(3)^{\circ}$, U = 711.8(2)Å³, T = 293 K, space group $P2_1/c$ (no. 14), Z = 4, 4352 reflections measured, 1258 unique ($R_{int} = 0.0671$), 950 reflections with $I > 2\sigma(I)$ which were used in all calculations. $R[F^2 > 2\sigma(F^2)] = 0.0661$. Compound 1d: $C_{18}H_{14}N_2O_2 \cdot 2(C_2H_4O_2), M = 410.42$, triclinic, a = 7.102(6), b =7.909(6), c = 9.350(5) Å, $\alpha = 97.37(3)^{\circ}$, $\beta = 95.76(3)^{\circ}$, $\gamma = 101.14(3)^{\circ}$, U = 506.8(6) Å³, T = 293 K, space group $P\bar{1}$ (no. 2), Z = 1, 5330 reflections measured, 1905 unique ($R_{int} = 0.053$), 1032 reflections with I > $2\sigma(I)$ which were used in all calculations. $R[F^2 > 2\sigma(F^2)] = 0.0482$. Compound I-1m: $C_{30}H_{22}O_2 \cdot 2(C_9H_7NO)$, M = 704.79, monoclinic, a =27.1065(2), b = 9.2347(4), c = 16.4901(8) Å, $\beta = 115.402(1)^{\circ}$, U =3728.7(3) Å³, T = 286 K, space group C2/c (no. 15), Z = 4, 12 369 reflections measured, 3828 unique ($R_{int} = 0.0313$), 2565 reflections with $I > 2\sigma(I)$ which were used in all calculations. $R[F^2 > 2\sigma(F^2)] = 0.0416.Compound$ I-10: $C_{30}H_{22}O_2 \cdot 2(C_9H_7NO)$, M = 704.79, orthorhombic, a = 25.4736(9), b = 8.5626(3), c = 16.9318(6) Å, U =3693.2(2) Å³, T = 260 K, space group *Pbcn* (no. 60), Z = 4, 27 377 reflections measured, 4601 unique ($R_{int} = 0.0391$), 3130 reflections with $I > 2\sigma(I)$ which were used in all calculations. $R[F^2 > 2\sigma(F^2)] = 0.0420$. Compound II-1: $C_{10}H_{12}O_8 \cdot 2(C_9H_7NO) \cdot H_2O$, M = 568.52, monoclinic, a = 13.372(3), b = 7.1670(10), c = 28.248(6) Å, $\beta = 108.79(3)^{\circ}, U =$ 2562.9(10) Å³, T = 293 K, space group $P2_1/c$ (no. 14), Z = 4, 15 706 reflections measured, 4683 unique ($R_{int} = 0.059$), 2689 reflections with I > $2\sigma(I)$ which were used in all calculations. $R[F^2 > 2\sigma(F^2)] = 0.0501$. Compound III-1: $C_6H_6O_2 \cdot C_9H_7NO$, M = 255.26, monoclinic, a =5.728(1), b = 22.789(4), c = 11.111(2) Å, $\beta = 116.90(3)^{\circ}$, U = 1293.4(5)Å³, T = 293 K, space group $P2_1/c$ (no. 14), Z = 4, 8147 reflections measured, 2256 unique ($R_{int} = 0.0630$), 1341 reflections with $I > 2\sigma(I)$ which were used in all calculations. $R[F^2 > 2\sigma(F^2)] = 0.0511$. Compound *I-1dp*: $C_{30}H_{22}O_2 \cdot 2(C_{18}H_{14}N_2O_2) \cdot C_2H_4O_2$, M = 557.60, monoclinic, $a = 14.166(3), \ \bar{b} = 9.432(2), \ \bar{c} = 20.139(4) \ \text{Å}, \ \beta = 91.88(2)^{\circ}, \ U =$ 2689.4(10) Å³, T = 293 K, space group $P2_1/c$ (no. 14), Z = 2, 17 677 reflections measured, 4896 unique ($R_{int} = 0.089$), 3162 reflections with I > $2\sigma(I)$ which were used in all calculations. $R[F^2 > 2\sigma(F^2)] = 0.0593$. Compound I-1md: $C_{30}H_{22}O_2 \cdot C_{18}H_{14}N_2O_2$, M = 704.49, monoclinic, a = 26.761(8), b = 9.111(3), c = 16.998(6) Å, $\beta = 114.443(9)^{\circ}, U = 16.998(6)$ 3773(2) Å³, T = 286 K, space group C2/c (no. 15), Z = 4, 12 247 reflections measured, 3873 unique ($R_{int} = 0.0971$), 1294 reflections with $I > 2\sigma(I)$ which were used in all calculations. $R[F^2 > 2\sigma(F^2)] = 0.0879$. *Compound I*-1*od*: $C_{30}H_{22}O_2 \cdot C_{18}H_{14}N_2O_2$, M = 704.49, orthorhombic, a = 25.479(3), b = 8.1154(8), c = 17.987(2) Å, U = 3719.3(7) Å³, T = 1000286 K, space group Pbcn (no. 60), Z = 4, 11 003 reflections measured, 3524 unique ($R_{int} = 0.045$), 1655 reflections with $I > 2\sigma(I)$ which were used in all calculations. $R[F^2 > 2\sigma(F^2)] = 0.0901$.

compounds presented here (1.274-1.285 Å). The OC–N bond length of 1.357(3) Å is shorter in 1 than in the other crystal structures with isoquinolinone (1.375-1.382 Å). The molecules



Fig. 2 Hydrogen bonding in I-1m.



Fig. 3 Hydrogen bonds in I-10.

Table 1	Undro gon	handing	a a a ma a t m
I able I	riyurogen	bonuing	geometry

formed hydrogen bonded dimers, typically to molecules consisting of H–N–C=O groups (Fig. 1). The distance between the potentially reactive atoms (C2 and C9) is 3.713(3) Å, and the lateral shift of the p-orbitals of the atoms C2 and C9 (of a molecule that is related by inversion center) is 1.476 Å.

The molecular compound I-1 crystallized in two polymorphic forms: monoclinic C2/c space group (I-1m) (Fig. 2) and orthorhombic *Pbcn* space group (I-1o) (Fig. 3). In both host molecule (I) is occupying an inversion center and is hydrogen bonded to two guest molecules (1) via their carbonyl groups (hydrogen bonding geometry is given in Table 1). The guest molecules are hydrogen bonded to each other (see Table 1) and each two are

 Table 2
 Relevant geometry for possible photodimerization in the solid state

Compound	Atoms	ď/Å	p/Å	l/Å	Possible dimer (Scheme 1)
1	C2–C9	3.713	3.407	1.476	6
I–1m	C17-C22	3.699	3.504	1.185	5
	C19-C24	3.711	3.504	1.222	5
	C19-C22	4.228	3.504	2.366	7
I–10	C17–C22	3.685	3.487	1.192	5
	C19–C24	3.749	3.487	1.377	5
	C17–C24	4.110	3.487	2.176	6
II-1	C4–C4A	3.725	3.329	1.671	10
	C7–C7A	3.839	3.329	1.912	10
	C2–C4A	3.616	3.329	1.412	9
	C9–C7A	3.703	3.329	1.622	9
	C2–C2A	3.732	3.329	1.687	8
	C9–C9A	3.803	3.329	1.839	8
III–1	C2–C9	3.813	3.495	1.524	6
	C2–C4	4.072	3.492	2.095	9
	С7–С9	4.082	3.488	2.121	9

D–H···A	D–H	Н…А	D····A	D–H···A	Symop-for-A
1					
O11 H1O1 N1	0.82	1.88	2.684(3)	166	-x, -y + 2, -z
N1 H1N1 O11	0.86	1.83	2.684(3)	172	-x, -y + 2, -z
1d					· •
O3 H3 O1	1.03(3)	1.62(3)	2.641(3)	169(3)	-x, -y + 1, -z
N1 H1 O1	1.08(3)	1.90(3)	2.930(3)	159(2)	-x - 1, -y + 1, -z + 1
I–1m					
O1 H1 O2	0.82	1.853	2.672(2)	176	x, -y + 1, z + 1/2
N1 H1N O2	0.86	1.88	2.731(2)	170	-x, -y + 1, -z
I-10					
O1 H1O1 O2	0.82	1.87	2.687(2)	173	x, -y + 1, z + 1/2
N1 H1N1 O2	0.86	1.844	2.703(2)	175	-x + 1, -y + 1, -z
II–1					
N1A H1A O1	0.86	1.88	2.743(3)	177	-x, -y + 1, -z
N1 H1 O1A	0.86	1.89	2.754(3)	178	-x, -y + 1, -z
O2 H2O O5	0.75(3)	2.03(3)	2.734(3)	155(3)	-x, y + 1/2, -z + 1/2
O4 H4O O1	0.82	1.74	2.492(3)	151	-x, y + 1/2, -z + 1/2
O7 H7O O1A	0.82	1.76	2.565(3)	168	-x, y-1/2, -z + 1/2
O9 H9O O8	0.87(3)	1.81(3)	2.680(3)	173(3)	-x + 1, -y, -z + 1
O30 H30A O5	0.98(2)	1.95(2)	2.858(2)	152(2)	-x, y + 1/2, -z + 1/2
O30 H30B O3	0.95(2)	1.98(2)	2.926(2)	172(2)	x, y, z
III–1					
N1 H1 O1	0.86	1.88	2.737(3)	178	-x - 1, -y, -z + 1
O2 H2 O3	0.82	1.90	2.705(3)	168	x, -y + 1/2, z - 1/2
O3 H3 O1	0.82	1.81	2.616(3)	165	-x, -y, -z + 2



Fig. 4 Hydrogen bonding in II–1.

related by inversion center. The result is that the carbonyl oxygen of the guest molecule involved in a bifurcated hydrogen bond. The relevant geometry with relation to the potential photodimerization is given in Table 2.

The molecular compound II–1 crystallized in monoclinic $P2_1/c$ space group with a molecule of water. The host molecule has two carboxyl groups in equatorial and two in axial positions. The

conformation is different from the one observed in its neat crystal.¹⁴ In the latter the molecule adopts mirror symmetry while in the present structure, the carboxyl groups orient themselves in accordance with the hydrogen bonds (Fig. 4). The presence of four carboxyl groups of the host molecule provides four acceptor and four donor groups for hydrogen bonding. The two guest molecules add additional two hydrogen acceptor and two



Fig. 5 Hydrogen bonding in III-1.



Fig. 7 Relevant distances in I-10.



Fig. 6 Relevant distances in I-1m.



Fig. 8 Relevant distances in II-1.



Fig. 9 Relevant distances in III-1.



Fig. 10 Hydrogen bonding in 1d : acetic acid.

hydrogen donor groups. The presence of the water molecule balances the need for a complete use of hydrogen bonding. One of the carboxyl groups is used to form a dimer to a second host molecule. Two carboxyl groups are hydrogen bonded to two other host molecules through water molecule. The remaining unused carboxylic acid group is hydrogen bonded to the guest molecule through its hydroxyl group, while the carbonyl oxygen of the host molecule is left idle. Each two guest molecules are hydrogen bonded to each other *via* a dimer-like arrangement. As a result of this complex hydrogen bonding scheme (Table 1), two molecules of isoquinolinone are almost parallel (the angle between the two mean planes is 2.11°) and related to each other by a non-crystallographic translation (see **2** in Scheme 1) with an average interplanar distance of 3.329(4) Å.

The molecular compound **III–1** crystallized in a monoclinic $P2_1/c$ space group. The guest molecules are related by inversion centers. The carbonyl group in each isoquinolinone involved in a bifurcated hydrogen bond: with a second isoquinolinone molecule and with a hydroxyl group of the host molecule. The hydroxyl group of the host molecule is also hydrogen bonded to a second host molecule (Fig. 5). The guest molecules in different planes are related by inversion centers with an intermolecular distance of 3.495(4) Å.

Photodimerization will take place if the relative geometry between the reacting centers fulfills the geometric requirements set up for similar solid state photochemical reactions.^{1,12} The three most relevant geometric parameters are: the intermolecular distances between the reacting atoms (Fig. 1 and 6–9, and *d* in Table 2), the interplanar distance (*p* in Table 2), and the lateral shift between the p-orbitals of the reacting atoms (I in Table 2).

According to Table 2, irradiation of the 4 molecular compounds might yield six different dimers out of the 12 theoretical dimers shown in Scheme 1, while irradiation of 1 will yield a single dimer (6 in Scheme 1). However, a few of the possible dimers such as 7 (from I–1m) and 9 (from III–1) might be failed to be produced due to the large lateral shift of the two p-orbitals and therefore a poor overlap that is needed for the photo-dimerization. Also one should consider the competition between the productions of different isomers that might affect the relative yield of some of them when more than a single isomer is expected.

Crystal structure after irradiation

Compound 1d crystallizes in a triclinic $P\bar{1}$ space group with a molecule of acetic acid (Fig. 10). As expected from the crystal



Fig. 11 Hydrogen bonding in I-1dp.



Fig. 12 Hydrogen bonding and the disorder in I–1md. The two isomers are shown in green and yellow (hydrogen atoms are absent).



Fig. 13 Hydrogen bonds and disordered isomers in **I–10d**. Isomers **5** are shown in yellow and isomer **6** is shown in green.

structure of the molecular compound with resorcinol (III-1), irradiation leads to isomer 6 (Scheme 1 and Table 2).

Irradiation of powder sample of **I–1m** and recrystallization yielded the molecular compound with dimer **5** (Scheme 1). The molecular compound crystallized in a monoclinic $P2_1/c$ space group with a disordered molecule of acetic acid. The dimer is hydrogen bonded to both a molecule of host and to another guest molecule forming an infinite chain (Fig. 11).

Irradiation of a single crystal of **I–1m** proceeded to full conversion in a single-crystal to single-crystal transformation. Unfortunately, the guest molecules are disordered and it is impossible to get information regarding the relative amount of the different species formed as a result of the irradiation at different stages of the reaction. Upon full conversion it was found that the species resulted are two identical isomers (**5** in Scheme 1) related by inversion center (Fig. 12).

Irradiation of a single crystal of the orthorhombic polymorph of **I–1** (**I–10**) also showed single-crystal to single-crystal transformation. The disorder of the formed dimers is more complicated than in the photodimerization of the monoclinic polymorph (Fig. 13). In this sample isomer **5** is obtained (similar to that obtained with the monoclinic form) with an additional isomer **6** (Scheme 1). This can be explained by the shorter intermolecular distances between the active atoms 4.110 Å compared with 4.228 Å in the monoclinic polymorph (Fig. 6 and 7, and Table 2). Also the lateral shift between the p-orbitals of these atoms is smaller (2.176 Å) in the orthorhombic polymorph, compared with 2.366 Å in the monoclinic polymorph.

Conclusions

It was demonstrated that molecular compounds composed of light-stable host molecules and light-sensitive guest molecules are chemical systems that can be manipulated to achieve relative geometry of the guest molecules to enable photochemical reactions leading to different isomers. In photodimerization the use of different host molecules imposes different molecular packing which naturally determine the relative lateral shift and the distances between the two potentially reactive guest molecules. As a result it determines whether the photodimerization will take place and what would be the product.

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