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Cation−π Controlled Solid-State Photodimerization of 4-Azachalcones

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The solid-state photodimerization of alkenes has received considerable attention in synthetic organic photochemistry because it can afford products not obtainable in solution.[1] Despite its significant synthetic potential, controlling the crystal packing modes is generally a difficult issue; therefore, much effort has been made to align olefinic molecules in an arrangement suitable for photodimerization with the help of hosts,[2] self-assembled hosts,[3] and templates.[4] Nevertheless, one-component crystals are still attractive media because their photolysis leads to waste-free reactions. To achieve the direct photodimerization of homocrystals, attractive noncovalent interactions including hydrogen bond,[5] halogen bond,[6] donor−acceptor,[7] and π−π[8] and perfluorophenyl−π[9] stackings have proven to be effective tools to assemble crystals.

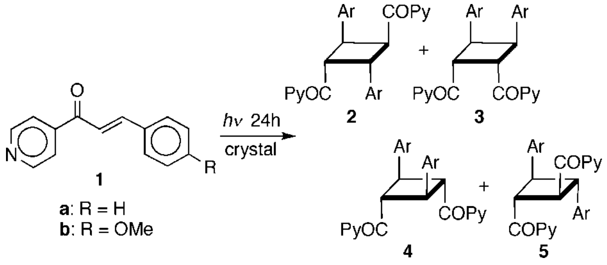
Recently, we reported that a cation−π interaction[10] between a pyridinium ring and an aromatic ring plays a key role in the stereoselective photodimerization of *trans*-styrylpyridines in a HCl−methanol solution.[11] This observation prompted us to investigate the utility of the cation−π interaction in the solid-state [2 + 2] photodimerization. We now report that the cation−π interaction serves as a powerful tool to arrange 4-azachalcone hydrochlorides in a head-to-tail fashion, the photolysis of which resulted in a *syn* head-to-tail dimer with excellent stereoselectivities and quantitative yields.

4-Azachalcone (**1a**) and 4′-methoxy-4-azachalcone (**1b**) and their HCl salts were employed as substrates for the photodimerization. When the powdered crystals of **1a**, placed between two Pyrex plates, were irradiated with a 250 W high-pressure mercury lamp for 24 h, a mixture of dimers **2a**−**5a** was produced along with recovery of 6% of **1a** (Table 1, entry 1). The X-ray structural analysis of **2a** determined the major product to be the *syn*HT dimer. The structures of the minor products **3a**−**5a** were assigned by comparison of the ^{1}H NMR data with those for the reported structurally related chalcone dimers.[12] On the other hand, irradiation of the HCl salt of **1a** resulted in the quantitative conversion into **2a** (entry 2).

In order to gain insight into the significant differences in the product selectivities depending on whether or not the pyridine unit has a cationic charge, comparison of the packing structures of **1a** and **1a**·HCl were carried out. Figure 1a and 1b show the two reactive molecules extracted from the X-ray packing diagrams of **1a** and **1a**·HCl, respectively. The molecules of **1a** orient themselves in a nonparallel manner with a 4.893 Å separation between the pyridine and the phenyl rings, suggesting no attractive interaction between them. The separation of 4.246(2) Å for the two neighboring double bonds is close to the limit of Schmidt's requirement.[13]

On the other hand, the molecules of **1a**·HCl are arranged parallel to each other in a head-to-tail orientation. The distances between the centroids of the neighboring two rings and the two double bonds are 3.954 and 3.980 Å, respectively, which are much shorter than those of **1a**. The close contact of the two molecules in **1a**·HCl could be a result of the cation−π interactions of the pyridinium ring and the phenyl ring, which would be responsible for the excellent selectivity.

Table 1. Photodimerization of **1a** and **1b** and Their HCl Salts in the Solid State



entry	compd	conv	products (%)[a,b] 2	3	4	5
1	**1a**	94	49	17	12	21
2	**1a**-HCl	99	>99	0	0	0
3	**1b**	90	20	67	1	12
4	**1b**-HCl	99	>99	0	0	0

[a] Determined by ^{1}H NMR. [b] The structures of **2a** and **2b** were determined by X-ray crystallographic analyses.

In contrast to **1a**, molecules **1b**, having a methoxy group on the aromatic ring, are arranged in a head-to-head orientation as shown in Figure 1c, suggesting the difficulty in predicting the packing modes regardless of their structural similarity. Irradiation of the crystals of **1b** produced the *syn*HH dimer **3a** in 67% yield as expected from the preorganized head-to-head orientation (Table 1, entry 3). The structures of **3a** and the three minor isomers were assigned by comparison of the ^{1}H NMR spectra with those for the reported dimers of the 4-methoxychalcones.[12b,14]

The effectiveness of the cation−π interaction as a tool to control the orientation of the molecules was demonstrated by changing the packing mode of **1b**. While **1b** prefers a head-to-head arrangement in the crystal as described above, the conversion of **1b** into the HCl salt caused a change in the packing mode to a head-to-tail orientation, in which the separations of the two neighboring rings and two double bonds were 3.654 and 3.789 Å, respectively (Figure 1d). The remarkable changes in the packing modes, whether or not having a cationic charge, suggested the critical role of the cation−π interaction in the crystal packing modes. The photodimerization of **1b**·HCl leads to the quantitative conversion to the *syn*HT dimer **2b**, the structure of which was elucidated by an X-ray crystallographic analysis.

The preference for the head-to-tail orientation of the pyridinium compounds has also been observed in a *N*-methylnicotinium salt[15] and a 4-styrylpyridinium salt.[11] These characteristic

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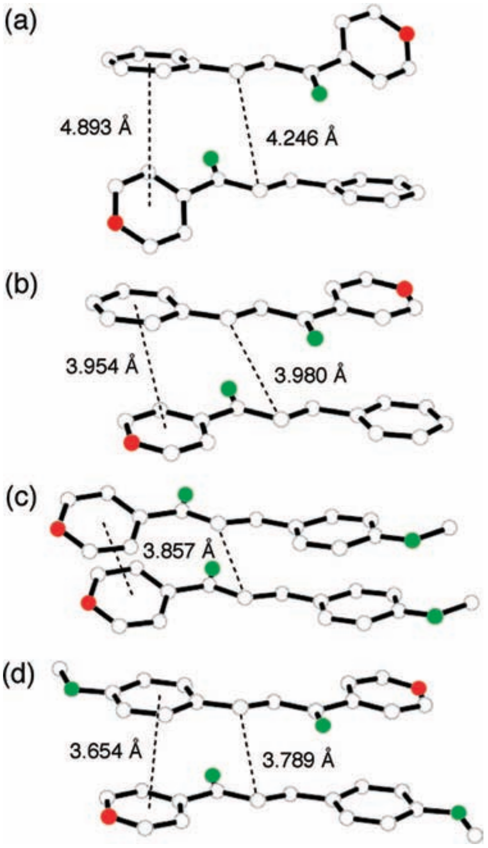
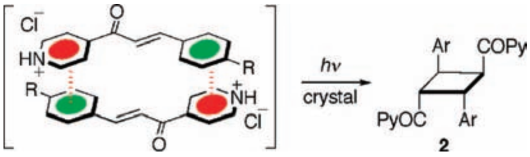


Figure 1. X-ray structures of two neighboring molecules for (a) **1a**, (b) **1a**·HCl, (c) **1b**, and (d) **1b**·HCl. The hydrogen atoms are omitted for clarity. The nitrogen and oxygen atoms are indicated by the red and green colors, respectively.

features would be a result of maximum stabilization in the crystal by forming cation−π complexes as shown in Scheme 1, which are supported by the significantly larger $\mathrm{Py^+\cdots Ar}$ interaction energy (−8.34 kcal/mol) than that for the $\mathrm{Py\cdots Ar}$ interaction (−3.04 kcal/mol).[16]

Scheme 1. Head-to-Tail Arrangement of Azachalcone through Cation−π Interactions and the Formation of *syn*HT Dimer **2**



In summary, we demonstrated that a cation−π interaction serves as a powerful tool to control the crystal packing modes. The cation−π controlled photodimerization reactions of the 4-azachalcones exclusively provided the *syn*HT dimers, in which only the protonation of the pyridine part is critical to the attainment of the excellent selectivity. These observations provide a valuable insight into the field of organic photochemistry as well as in the field of crystal engineering.

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Supporting Information Available: Experimental details and characterization of new compounds. ^{1}H NMR spectra for **1a**·HCl, **1b**·HCl, **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **5a**, and **5b**. X-Ray crystallographic data and CIF files for **1a**, **1a**·HCl, **1b**, **1b**·HCl, **2a**, and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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