Photoreactive salt cocrystal: N+-H···N hydrogen bond and cation-π interactions support a cascade-like photodimerization of a 4-stilbazole

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COMMUNICATION

Photoreactive salt cocrystal: N^+-H···N hydrogen bond and cation-π interactions support a cascade-like photodimerization of a 4-stilbazole

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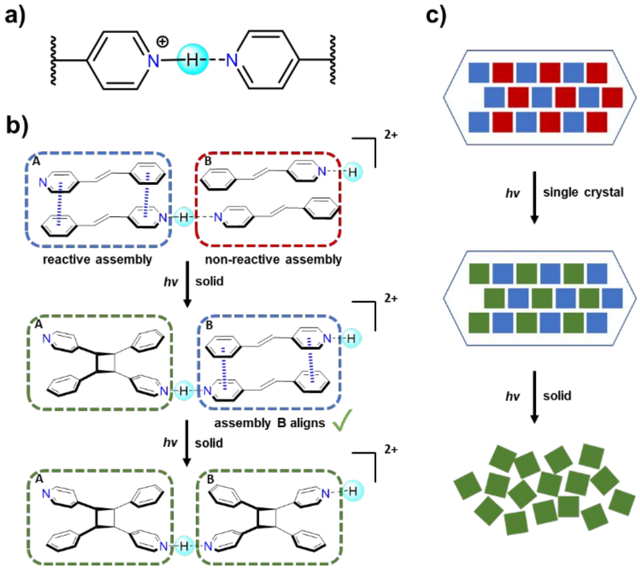
We describe hydrogen bonds (i.e., N^+-H···N) in combination with cation···π interactions to enable a cascade-like [2+2] photodimerization of 4-stilbazole in a salt cocrystal. A four-component crystal assembly is composed of photoactive pyridinium ion pair 4-stilbzH$^+$ (4-stilbz = *trans*-1-(4-pyridyl)-2-(phenyl)ethylene) and photostable molecule pair 4-stilbz. UV iradition gives *rctt*-1,2-bis(4-pyridyl)-3,4-bis(phenyl)cyclobutane (4-pyr-ph-cb) in quantitative yield. An intermediate structure 2(4-stilbz)·(4-pyr-ph-cb)2H$^+$ is isolated that undergoes a partial single-crystal-to-single-crystal transformation. The single-crystal X-ray data provides a snapshot of movements in the salt cocrystal in the course of the photodimerization.

The hydrogen bond is a "master-key" interaction in crystal engineering, providing manifold opportunities to generate supramolecular materials such as polymers and photoactive solids.[1] In the latter, there has in recent years been a great deal of interest to direct intermolecular [2+2] photodimerizations in the organic solid state using hydrogen bonds.[2] Hydrogen bonds of X-H···X type involve a nearly linear geometry where donor and acceptor are identical. The N^+-H···N hydrogen bond involving pyridines is, in particular, one of the most exploited X-H···X hydrogen bonds in crystal engineering (**Scheme 1a**).[3]

With exception to work of Peedikakkal,[4] all examples involving the use of hydrogen bonds to support a photodimerization in the solid state have involved hydrogen bonds with different donor and acceptor groups (i.e., X-H···Y). The interaction reported here involves a highly electron-deficient pyridinium moiety and neutral pyridyl group bridged by a proton (**Scheme 1a**). The N···N distance normally lies within a distance of 2.6-2.8 Å. Importantly, X^+-H···X type hydrogen bonds are unique from a synthetic standpoint since one of the two identical hydrogen bonding functional groups must either gain or lose a proton to support charge formation and assembly of the bridge; consequently, one of the two components is also typically charge neutral and the outcome is a salt cocrystal.



Scheme 1 (a) N^+-H···N hydrogen bond. (b) Regiocontrolled cascade-like [2+2] photodimerization of 4-stilbazole. (c) Cascade transformation process (blue: photoactive assemblies; red: photostable assemblies; green: cyclobutane products).

Recently, there have been reports of [2+2] photodimerizations that occur in the solid state to proceed as cascade-like reactions.[5] In the solids, C=C bonds that do not conform to the criteria of Schmidt undergo sufficient molecular movements to facilitate photodimerization processes. As part of our efforts to investigate photoactive solids,[6] herein we report use of the N^+-H···N hydrogen bond along with the cation-π interaction to support a cascade-like [2+2] photodimerization of a **4-stilbz** in the solid state.[7] We show the combined forces to support the formation of photoactive pyridinium **4-stilbzH$^+$** assemblies that react to give head-to-tail (*ht*) **4-pyr-ph-cb** that involves a SCSC transformation. In the process, the photodimerization making up the SCSC reaction serves to trigger rearrangement of a photostable stacked pair of

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molecules (i.e., **4-stilbz**) to become photoreactive. The result is the regiocontrolled formation of **4-pyr-ph-cb** in quantitative yield. To our knowledge, our work represents the first case of a N$^+$-H···N hydrogen bond that supports a SCSC [2+2] photodimerization.

Mixing of an ethanol (1 mL) solution of ammonium hexafluorophosphate (**NH_4PF_6**, 18 mg, 0.11 mmol) with **4-stilbz** (40 mg, 0.22 mmol) in THF (4 mL) afforded colorless single crystals of [**4-stilbz**·(**4-stilbzH$^+$**)(**PF_6^-**)] as irregular prisms by slow evaporation in a period of 3 days. Single-crystal X-ray diffraction and ^{1}H NMR spectroscopy confirmed the composition of the solid as [**4-stilbz**·(**4-stilbzH$^+$**)(**PF_6^-**)]. Individual datasets for [**4-stilbz**·(**4-stilbzH$^+$**)(**PF_6^-**)] were collected at room temperature (298K) and low temperature (125K). While refinement afforded better agreement of data (i.e. lower R-value) at the lower temperature, details of the room temperature structure are mostly described here to be consistent with the conditions at which the photodimerization was conducted.

The components of [**4-stilbz**·(**4-stilbzH$^+$**)(**PF_6^-**)] crystallize in the triclinic space group *P*-1. The asymmetric unit consists of a pyridinium ion **4-stilbzH$^+$**, **4-stilbz** molecule and hexafluorophosphate (**PF_6^-**) ion that form a salt cocrystal. Each **4-stilbzH$^+$** ion and **4-stilbz** molecule are disordered over two positions and interact by N$^+$-H···N hydrogen bond to form a linear two-component dimeric array (N$^+$···N 2.716(17) Å; N$^+$-H···N 170°) (**Fig. 1a**). The data at the lower temperature shows markedly less disorder and is consistent with pedal motion of the C=C bond. The components stack in a *ht* orientation through face-to-face cation···π interactions of the pyridinium and phenyl groups. The outcome is stacking of two pyridinium ions to generate a four-component assembly (**Fig. 1b**). The C=C bonds of each face-to-face stacked **4-stilbzH$^+$** assembly are parallel and separated by 3.89 Å, which falls within the criteria of Schmidt.[8] Adjacent stacked assemblies are arranged offset by face-to-face molecule-molecule contacts, with the molecules (dark and light gray) stacking *ht* and interacting via displaced π···π contacts. The C=C bonds of the stacked molecules of the salt cocrystal are separated by 4.56 Å (**Fig. 1c**).

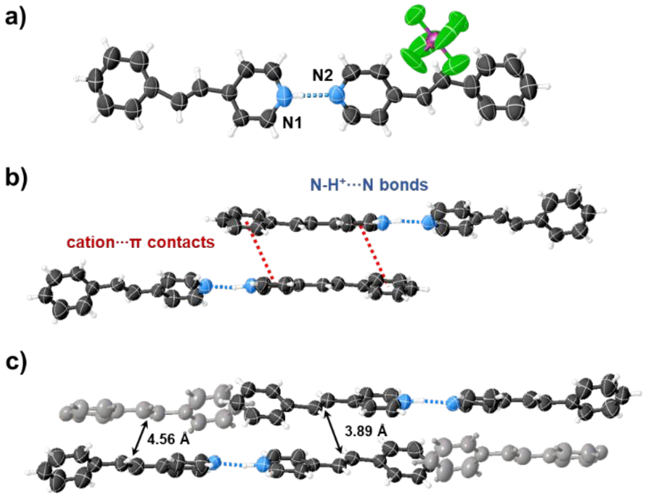

Fig. 1 Crystal structure [**4-stilbz**·(**4-stilbzH$^+$**)(**PF_6^-**)]. ORTEP views of (a) two-component dimeric array, (b) four-component assembly, (c) stacking of four-component assemblies.

It is only the stacked **4-stilbzH$^+$** ions that conform to the geometry criteria for a [2+2] photodimerization. However, when a powdered crystalline sample of [**4-stilbz**·(**4-stilbzH$^+$**)(**PF_6^-**)] was irradiated using UV light (450 W medium pressure Hg vapor lamp) for a period of 20 h, all C=C bonds reacted to form **4-pyr-ph-cb** in quantitative yield. The generation of the photoproduct was evidenced by the disappearance of the olefinic signal at 7.78 ppm and the appearance of the cyclobutane signal at 4.75 ppm (**Fig. S2**).

An explanation for the quantitative conversion of the stacked C=C bonds of [**4-stilbz**·(**4-stilbzH$^+$**)(**PF_6^-**)] can be rationalized on the basis of the solid undergoing a partial SCSC transformation. When [**4-stilbz**·(**4-stilbzH$^+$**)(**PF_6^-**)] was subjected to UV light for a period of 8 h using a Gel Nail Dryer as a source,[9] the stacked **4-stilbzH$^+$** ions reacted in a SCSC process to form [**2**(**4-stilbz**)·(**4-pyr-ph-cb2H$^+$**)(**$2PF_6^-$**)] (**Fig.2**). The presence of a single cyclobutane is consistent with pedal motion.[10] The generation of the photoproduct was accompanied by bending of the N$^+$-H···N hydrogen bond (i.e., N$^+$-H···N 170° to 145°) and tilting of the 4-pyridyl moieties (**Fig. 2a**).[11] The tilting resulted in an *ca.* 25 degree rotation of the **4-stilbz** molecule such that the stacked molecules are engaged exclusively in face-to-face π···π forces (**Fig. 2c**). We suggest that the molecular movements enable the remaining C=C bonds to react quantitatively to form **4-pyr-ph-cb**, although we note the stacking distance to increase slightly from 4.56 to 4.62 Å (**Fig. 2c**). Accumulations and releases of stress and strain may also contribute to the C=C bonds reacting.[12]

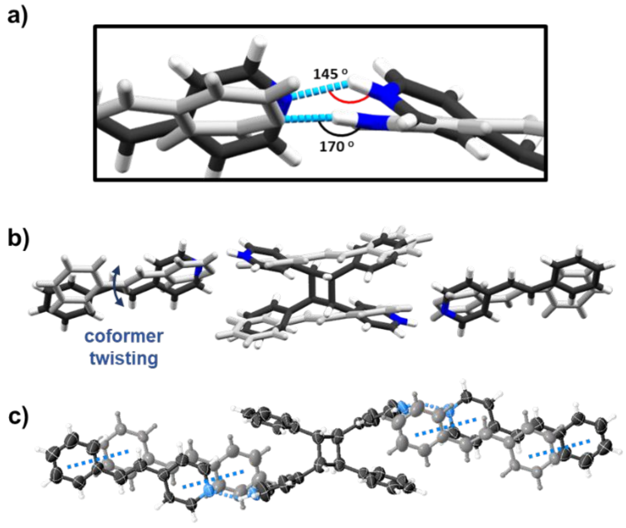

Fig. 2 Crystal structure of [**2**(**4-stilbz**)·(**4-pyr-ph-cb2H$^+$**)(**$2PF_6^-$**)]: (a) N$^+$-H···N hydrogen bond. (b) twisting of **4-stilbz** coformer. (c) extended stacking of **4-stilbz** and **4-pyr-ph-cb2H$^+$** after photodimerization.

B3LYP density functional molecular calculations using 3-21G basis set in the gas phase were performed to probe the driving force of the selective face-to-face stacking of [**4-stilbz**·(**4-stilbzH$^+$**)(**PF_6^-**)].[13] Electrostatic potential maps of **4-stilbz/4-stilbzH$^+$** monomer, the two-component dimeric array and the four-component assembly as derived from the X-ray data of [**4-stilbz**·(**4-stilbzH$^+$**)(**PF_6^-**)] and [**2**(**4-stilbz**)·(**4-pyr-ph-cb2H$^+$**)(**$2PF_6^-$**)] revealed the pyridinium and phenyl groups to be electron-deficient (blue) and electron-rich (red), respectively (**Fig. 3**). The opposite electrostatic potentials of the pyridinium and phenyl groups are complimentary and account for the face-to-face stacking of the photoactive pairs of **4-stilbzH$^+$** ions within the salt cocrystal.

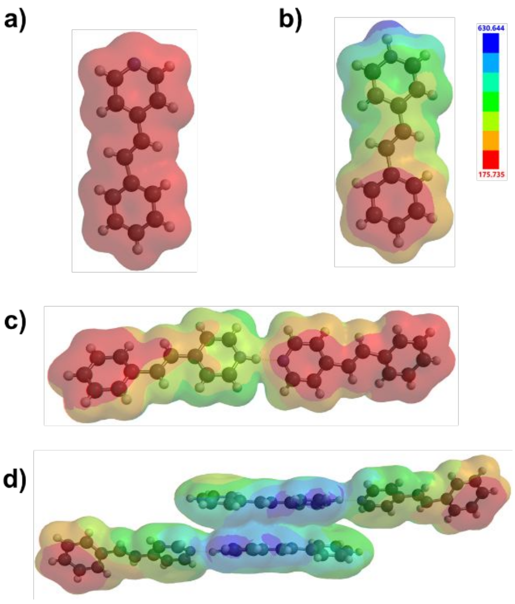

Fig. 3 Electrostatic potential maps (a) **4-stilbz,** (b) **4-stilbzH$^+$**, (c) **4-stilbz**·(**4-stilbzH$^+$**) pair and (d) *ht* face-to-face stacking of **4-stilbzH$^+$** pair calculated with B3LYP method using 3-21G basis set.

Conclusions

We have shown that the N$^+$-H···N type hydrogen bond can support a [2+2] photodimerization in the solid state. The photodimerization proceeded in a cascade-like process via a partial SCSC transformation. We expect uses of the less common type of hydrogen bond to extend a toolbox to enable the design and synthesis of photoactive solid-state materials. The observations of the cascade-like process can also extend our understanding of dynamic processes in organic solids.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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