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Exploiting the Hydrogen-Bonding Capacity of Organoboronic Acids to Direct Covalent Bond Formation in the Solid State: Templation and Catalysis of the [2 + 2] Photodimerization

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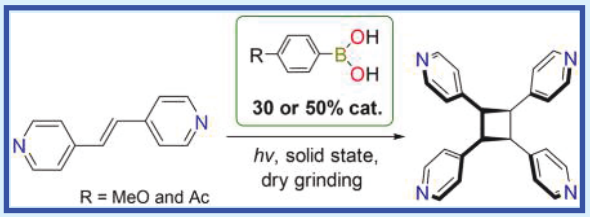
Supporting Information

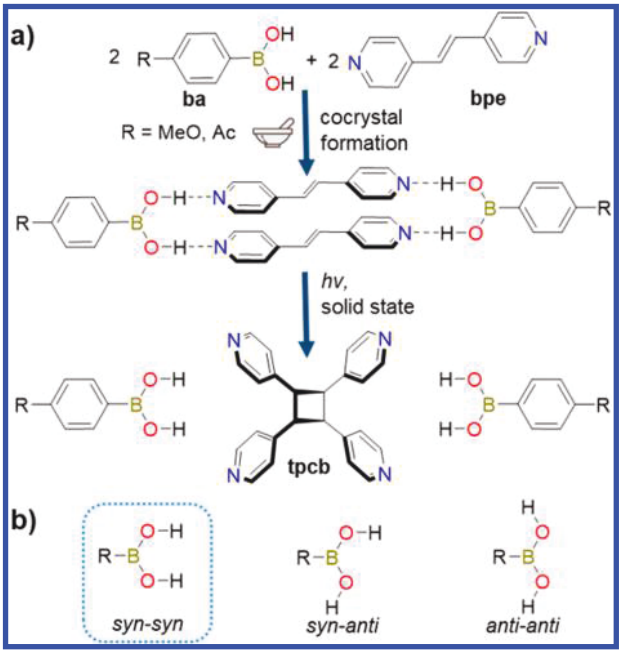
ABSTRACT: The ability of organoboronic acids to direct intermolecular [2 + 2] photodimerizations in the solid state is identified. The reactivity of 1,2-bis(4-pyridyl)ethylene (**bpe**) within cocrystals of discrete hydrogen-bonded molecular assemblies generates *rctt*-tetrakis(4-pyridyl)cyclobutane (**tpcb**) stereoselectively and in up to quantitative yield. Dry grinding of the boronic acids and excess **bpe** reveal the acids to function as supramolecular catalysts.



Organoboronic acids are among the most versatile and valuable reagents in organic synthetic chemistry.[1−5] The acids have also been utilized in supramolecular chemistry owing to the reversible nature of a coordinate bond to the B atom of the $B(OH)_2$ group.[6−8] While there has been considerable work on the construction of supramolecular frameworks and architectures based on organoboronic acids, there has been significantly less work on the ability of boronic acids to form hydrogen-bonded complexes.[9] Double hydrogen-bonded donor/acceptor complexes involving the $B(OH)_2$ group, for example, have just been shown to support the molecular recognition of diaza-type acceptors.[10] The ability of the $B(OH)_2$ group to enable organoboronic acids to function as hydrogen-bond-donor catalysts for conversion of CO_2 into organic carbonate in water has also recently been described.[11] To the best of our knowledge, there are no examples that demonstrate the hydrogen-bonding capacity of the $B(OH)_2$ group of an organoboronic acid to direct a chemical reaction in a solid.

Here, we reveal the hydrogen-bonding capacity of organoboronic acids to direct chemical reactivity[12−16] in the organic solid state (Scheme 1a). Specifically, we demonstrate 4-methoxyphenylboronic acid (**4-MeO-ba**) in the cocrystal (**4-MeO-ba**)·(**bpe**) (where **bpe** = *trans*-1,2-bis(4-pyridyl)-ethylene) to act as a bifunctional hydrogen-bond-donor template by assembling **bpe** by way of (B)O−H···N hydrogen bonds in a discrete four-component supramolecular assembly to undergo an intermolecular [2 + 2] photodimerization. The photocycloaddition reaction generates *rctt*-tetrakis(4-pyridyl)-cyclobutane (**tpcb**), which is photostable as a pure solid,[17] stereoselectively and in up to quantitative yield. We also reveal **4-MeO-ba** to act as a supramolecular catalyst[18] of the photoreaction. The generality of the approach is also demonstrated using 4-acetylphenylboronic acid (**4-Ac-ba**) to direct the photocycloaddition reaction in the cocrystal (**4-Ac-ba**)·(**bpe**).

Scheme 1. (a) [2 + 2] Photodimerization in Solid State Using Hydrogen-Bonded Assemblies of Boronic Acids and bpe and (b) Conformations of Boronic Acids in the Solid State



Our work involving organoboronic acids is inspired by Pedireddi[19−21] and Höpfl,[22] who demonstrated that organoboronic acids form cocrystals with pyridines. Specifically, studies of cocrystals and related hydrates of boronic acids with bipyridines showed the components to assemble by way of (B)O−H···N hydrogen bonds wherein the acids enforced the

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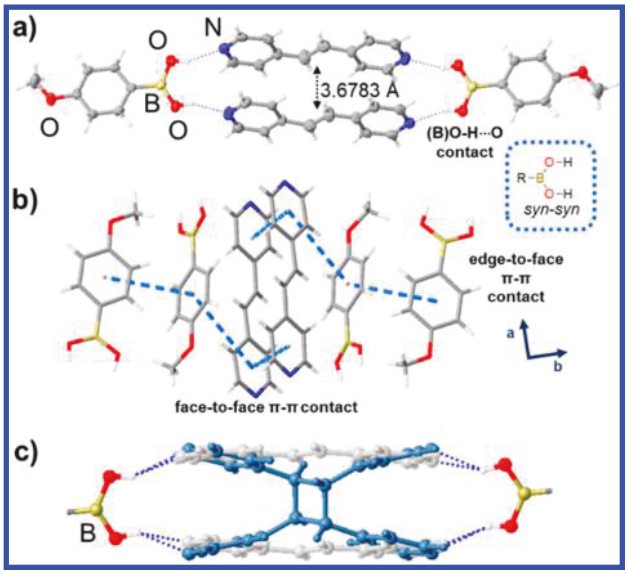

Figure 1. X-ray structure (**4-MeO-ba**)·(**bpe**): (a) discrete assemblies with stacked C═C bonds, (b) $\pi-\pi$ interactions, and (c) partial formation of **tpcb** (blue) from **bpe** (gray).

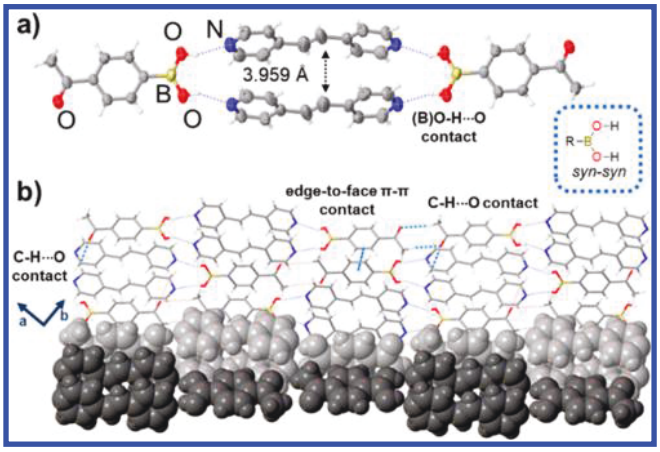

Figure 2. X-ray structure (**4-Ac-ba**)·(**bpe**): (a) assemblies and (b) tapes sustained by C−H···O forces.

pyridines to stack into face-to-face geometries. The observations prompted us to explore the use of organoboronic acids to direct the [2 + 2] photodimerization in the solid state.[12−16] In the design, a boronic acid, in a *syn*−*syn* conformation (Scheme 1b), would support the formation of discrete four-component hydrogen-bonded molecular assemblies wherein face-to-face stacking of a pyridyl-functionalized alkene would conform to the geometry of Schmidt to undergo the photodimerization.[23]

To test our hypothesis, dissolution of either **4-MeO-ba** or **4-Ac-ba** and **bpe** (1:1 ratio) in MeOH afforded single crystals as colorless plates of (**4-MeO-ba**)·(**bpe**) and (**4-Ac-ba**)·(**bpe**), respectively, upon cooling after 2 d. The formulations of (**4-MeO-ba**)·(**bpe**) and (**4-Ac-ba**)·(**bpe**) were confirmed by single-crystal X-ray diffraction, powder X-ray diffraction (PXRD), and ^{1}H NMR spectroscopy.

The components of (**4-MeO-ba**)·(**bpe**) crystallize in the triclinic space group $P\bar{1}$ as discrete four-component molecular assemblies sustained by four (B)O−H···N hydrogen bonds (Figure 1). Two unique assemblies (A and B) consisting of **4-MeO-ba** and **bpe** define the asymmetric unit [O···N (Å): 2.761(3)/2.808(2) (A) and 2.766(4)/2.825(7) (B)]. **4-MeO-ba** adopts the less stable *syn*−*syn* conformation,[24] with the 4-pyridyl groups and *p*-phenylene rings twisted approximately orthogonal [66.6°/69.1° (A) and 72.6°/77.0° (B)] (Figure 1a). The $B(OH)_2$ groups are coplanar [7.79° (A) and 4.89° (B)] with the *p*-phenylene rings. The stacked alkenes lie parallel with the carbon−carbon double (C═C) bonds separated by 3.722(3) (A) and 3.933(5) (B) Å. Importantly, the geometry conforms to the geometry criteria (C═C separation < 4.2 Å, parallel alignment) of Schmidt to undergo a [2 + 2] photodimerization.[23] The assemblies form edge-to-face and face-to-face π-stacks (Figure 1b), with C═C bonds of nearest-neighbor assemblies separated by 11.854(5) Å. The stacks pack to generate sheets. We note the X-ray data to suggest the hydrogen-bonded assemblies to be photoactive, as evidenced by the presence of electron density consistent with cyclobutane ring formation of **tpcb** (8% overall yield) (Figure 1c).

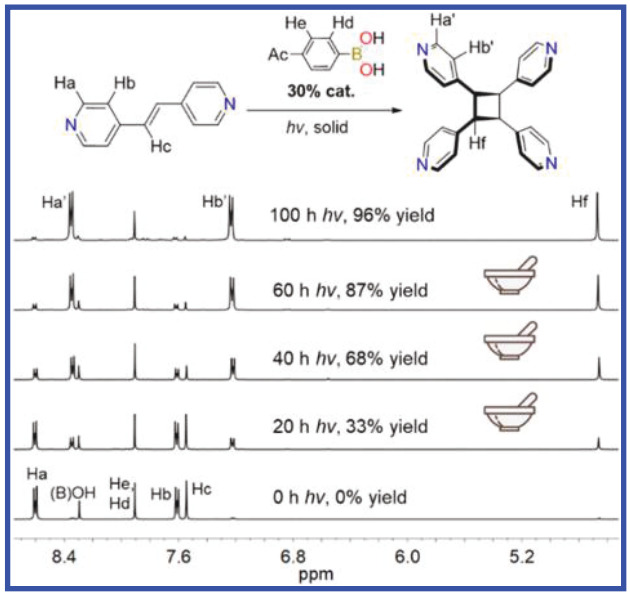

Figure 3. ^{1}H NMR spectra (300 MHz, DMSO-d_6) showing supramolecular photocatalysis using **4-Ac-ba** and **bpe** to afford **tpcb**.

The resilience of the hydrogen bonding is demonstrated in the cocrystal (**4-Ac-ba**)·(**bpe**) wherein the components, similar to (**4-MeO-ba**)·(**bpe**), form four-component hydrogen-bonded assemblies [O···N (Å): 2.777(4)/2.812(4) and 2.777(4)/2.817(5)] in the monoclinic space group $P2_1/n$. The alkenes stack face-to-face, with **4-Ac-ba** in the *syn*−*syn* conformation and the C═C bonds separated by 3.959(7) Å (Figure 2). The pyridyl groups and *p*-phenylene rings are approximately orthogonal (73.7° and 71.1°) and the $B(OH)_2$ groups are coplanar (3.62°) with the *p*-phenylene ring (Figure 2a). Adjacent assemblies interact by way of C−H···O forces involving the C═O group as tapes orthogonal to the *c*-axis (Figure 2b). The C═C bonds of nearest-neighbor tapes are separated by 7.352(7) Å.

Upon UV irradiation, both (**4-MeO-ba**)·(**bpe**) and (**4-Ac-ba**)·(**bpe**) react to form **tpcb** in near-quantitative yield. Thus, when powdered crystalline samples were irradiated for periods of *ca.* 100 h (Hg medium-pressure UV-lamp), **bpe** reacted to give **tpcb** in 96% yield in both solids. Subsequent applications of dry mortar-and-pestle grinding and exposure to UV-light afforded **tpcb** quantitatively.[25]

We have determined that both **4-MeO-ba** and **4-Ac-ba** act as supramolecular catalysts of the photodimerization.[18] Photo-

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catalysis was achieved using dry mortar-and-pestle grinding with 30% and 50% mol catalyst (Figure 3; see Supporting Information for additional NMR and PXRD data). The resulting PXRD data revealed mixtures of phases of reactive cocrystal and pure **bpe** following 20 h of exposure to UV light of each solid. Peaks attributed to crystallization of the photoproduct **tpcb** were also present.[18] The fact that the organoboronic acids support catalysis is significant given that the electron-deficient B atoms may form adducts with N-donors, which may thwart[26] catalytic turnover.

In summary, we have introduced the ability of organoboronic acids to direct the formation of covalent bonds in the solid state. The acids function as hydrogen-bond-donor templates in two-component cocrystals[27] and also function as supramolecular catalysts of the [2 + 2] photodimerization. Given the wide commercial availability of boronic acids,[28] we are now exploring uses of additional organoboronic acids to support the formation of photoactive solids and related multicomponent materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02439.

Experimental information, ^{1}H NMR spectra, powder and single-crystal (CCDC 1838793 and 1838794) X-ray diffraction data (PDF)

Accession Codes

CCDC 1838793−1838794 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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