Scalable Synthesis of a Cyclobutane-1, 2-diacid Building Block from *trans*-Cinnamic Acid *via* Photoreaction

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Dicarboxylic acids and their derivatives have a variety of applications in many fields such as polymers, pharmaceuticals, and metal-organic materials. Cyclobutanedicarboxylic acids (CBDAs) represent a family of promising diacids that can be synthesized by using photoreaction.

It has been known for about a century that both CBDA-1 (*α*-truxillic acid) and CBDA-4 (*β*-truxinic acid) could be synthesized from two polymorphs: *α*- and *β*-*trans*-cinnamic acid, respectively. However, researchers had to take a detour to make CBDA-4 by turning *trans*-cinnamic acid into its *p*-nitrophenyl ester or 1,3-trimethylene diester for photodimerization, and then hydrolyzed the ester dimer back to CBDA-4. This is because that the metastable crystalline *β*-form (head-to-head packing) of *trans*-cinnamic acid is readily to transfer to the stable *α*- form (head-to-tail packing). The low energy barrier from the *β*-form to the *α*-form renders reliable synthesis of CBDA-4 challenging because the *β*-form gives CBDA-4 after photodimerization and *α*-form leads to CBDA-1, which also explained the conflicting experimental results about CBDA-4 synthesis in the literature.

In this presentation, we will show a facile and scalable preparation method of CBDA-4 accomplished by capturing and photodimerizing the metastable crystalline solid of *trans*-cinnamic acid. This synthetic approach builds a foundation for investigating the properties and applications of the useful diacid and its derivatives. The X-ray crystal structure of CBDA-4 was determined for the first time. The synthesis of a series of mono- and di-esters derived from CBDA-4, which have similar structure to the widely used phthalates, will also be discussed.

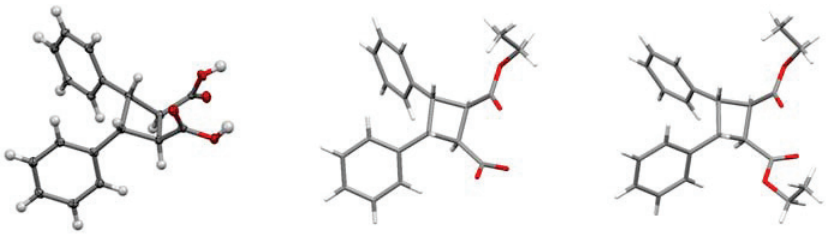

Fig. 1. Crystal structures of CBDA-4 (ellipsoid), its mono- and diethyl esters (capped sticks).

References
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