

Towards a mechanistic understanding of the 2π - 2π photo-addition of cinnamic acid compounds

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Despite being referred to as "chemical graveyard" [1] crystals may play an important role in synthesis routes which require a stereo-specificity which is only present in a crystal lattice due to the fixed arrangement of the reacting molecules. The reaction yields of chemical reactions initiated by light absorption may also be higher than that in solution since the reacting molecules are very close to each other in the crystal lattice. But this density of absorbing molecules also poses challenges to a uniform absorption of photons in the respective crystal. To cure this, one can either use the high wavelength absorption edge of the optical transition of the molecules or one can make use of two or more photon absorption processes employing short laser pulses. The latter technique of course makes the chemical reaction more costly. But it allows to study the chemical reaction with femtosecond laser pump probe techniques.

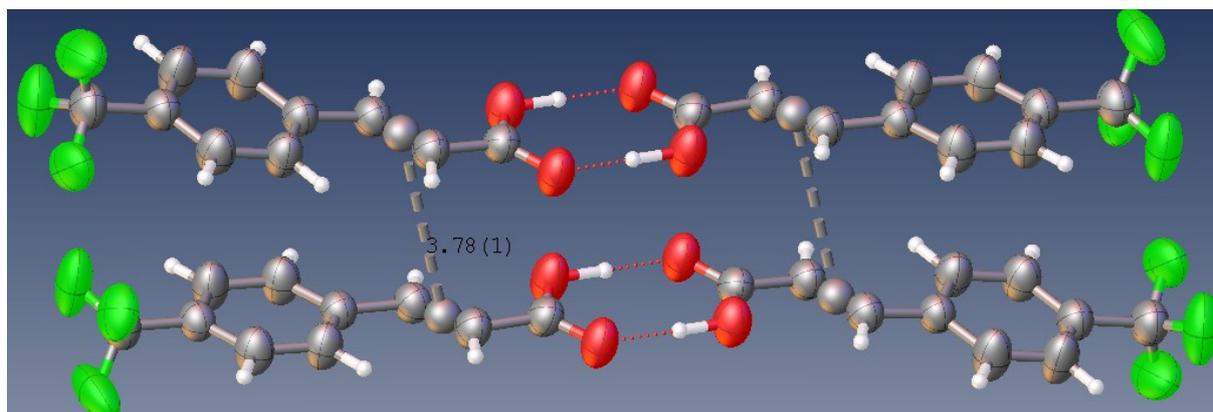


Figure 1 The arrangement of one of the disordered trans-4-trifluoromethyl cinnamic acid compounds in the crystal lattice. The distance between the C-C double bonds of the trans-4-trifluoromethyl compound involved in bond formation upon UV-irradiation is marked with a grey dashed line. Image made with the software Olex2.

Scattering methods such as visible pump single crystal x-ray probe techniques allow in principle to monitor electron density distribution versus time while performing the chemical reaction.

As a model system we considered two cinnamic acid derivatives trans-3-trifluoromethyl cinnamic acid and trans-4-trifluoromethyl cinnamic acid. Cinnamic acid compounds are known to form a four membered carbon atom ring out of two neighboring molecules exhibiting two carbon-carbon double bonds. In the trans-4-trifluoromethyl compound we confirmed the distance of the bonds between the involved carbon atoms to be 3.8 Å (see Figure 1). This is below the threshold for this type of reaction to occur [2].

[1] Klebe G. Wirkstoffdesign Entwurf und Wirkung von Arzneistoffen (2nd ed.). Springer. (2009).

- [2] Busse G, Tschentscher T, Plech A, Wulff M, Frederichs B, Techert S. First investigations of the kinetics of the topochemical reaction of p-formyl-trans-cinnamic acid by time-resolved X-ray diffraction. *Faraday Discussions*, 122 (2003)