Effect of Crystal Structure on Photoreactivity of Unsaturated Carboxylic Acids in the Solid State

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Crystals provide an ideal environment for photoreactions of unsaturated molecules as reactants. The two commonly occurring reactions, isomerization and [2+2] photodimerization, can be initiated by light alone, and without a solvent, catalyst, or second reactant. The use of crystals as a reaction medium in synthetic methods complies with the principles of Green Chemistry [1], specifically those of organic synthesis without solvents [2] or in the solid state [3].

Another advantage of conducting reactions in crystals is the possibility to change the chemical reactivity of a molecule by providing a uniform and specific conformation and environment for the reactant molecule. This can alter the reaction pathway(s) and provide new opportunities for chemical synthesis. This altered reactivity was demonstrated in studies on trans-cinnamic acids, which showed significantly different photoreactivity from solution within each polymorph [4].

Our current studies attempt to explain recently made observations on altered reactivity of unsaturated carboxylic acids in the solid state [5,6]. The UV absorption spectra of the solid reactants display a significant bathochromic shift of the absorption bands as compared to the same molecules in solution. This shift can be explained based on the crystal structure of the reactants. In turn, the change in the absorption properties leads to a dramatic change in the reaction pathways, including their number and the products formed. We observed further changes in both absorption properties and photoreactivity of the molecules when they were incorporated in cocrystals with simple peptides [7,8]. It is worth to note that peptide themselves may act as reactants in the crystalline state [9]. A selection of new data from our ongoing research will be presented and discussed.

References