[2+2] solid-state photodimerisation is a challenging task in some organic compounds like olefins. However, there are some reports to address such problems through co-crystallisation approach. For instance, co-crystallization of 1,2-bis(4-pyridyl)ethylene with resorcinol [1] (O-H•••N), thiourea[2] (Type I, Type II N-H•••N) and utilization of Ag•••Ag weak interactions in such a reaction of N,N'-bis(3-(4-pyridyl)acryloyl)-hydrazine (4-PAH)[3]. Here, we describe a ternary co-crystal approach to performing the [2+2] solid-state photodimerisation reaction. For the strategy, we chose a ditopic hydrogen-bond donor and two different hydrogen bond acceptors. Among the hydrogen bond acceptors one acceptor is useful to make acid-base synthon (result in dimer) and another acceptor is helpful to assemble this further through phenol-pyridine synthon, giving rise to the ternary co-crystal. As we anticipated the crystallization of 4-hydroxycinnamic acid (ditopic hydrogen bond donor) with 2-amino pyridine (first acceptor) and 1,2-bis(4-pyridyl)ethylene (second acceptor) yielded a ternary co-crystal. The crystal structure reveals that acid-amide dimer is formed between 4-hydroxycinnamic acid and 2-amino pyridine by the proton transfer from acid to base with carboxylic acid-aminopyridine synthon. The free O-H and N-H groups of acid and pyridine, respectively are connected to 1,2-bis(4-pyridyl)ethylen by O-H•••N and N-H•••N hydrogen bonds with phenol-pyridine and amine-pyridine synthons. From the crystal packing of ternary co-crystal (Figure 1), the olefin satisfies the criteria of Schmidt condition for photodimerisation reaction and a powdered crystalline sample was exposed to UV irradiation for 20 h, which yielded the photodimerised product in a quantitative yield.


Keywords: Synthon approach, Photodimerisation and ternary co-crystal