

# High Resolution X-ray and Neutron Diffraction Studies on Co-crystals of Chloranilic Acid and Lutidines

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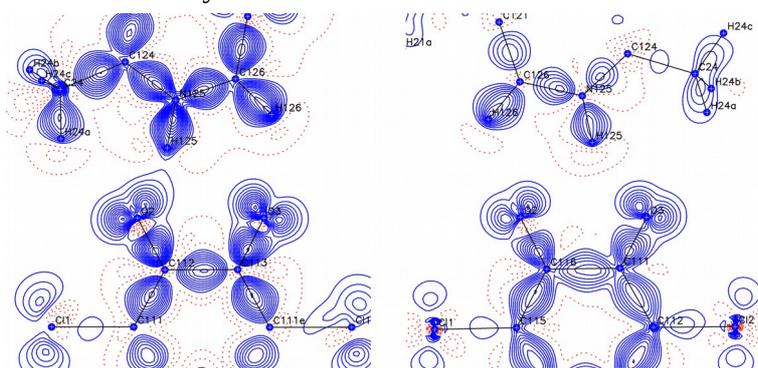
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Prediction of the intermolecular interaction patterns that a system will adopt represent a major tool used in the crystal engineering field to build materials with specific properties. The most prevalent design strategy utilises hydrogen bonding, but other types of intermolecular interactions such as  $\pi \cdots \pi$ <sup>1</sup> and halogen $\cdots$ halogen<sup>2</sup> have also been explored. The use of charge assisted hydrogen bonds for controlling the formation of a specific supramolecular synthon is much less studied<sup>3</sup> but studies have shown that predictable synthons can be formed, which represents a useful method for synthesis of materials with well-defined physical or chemical properties.

Chloranilic acid (CA) has a strong propensity for proton transfer, able to donate one or two hydrogen atoms to a base co-molecule forming charge assisted hydrogen bonds. Therefore, a number of co-crystals of chloranilic acid and various lutidine bases in a 1:1 and 1:2 ratio have been



*Lone pair of the O atoms pointing in the H(nitrogen) direction in both 2,4-left and 2,5-right lutidine-CA*

investigated using high resolution X-ray diffraction. Proton transfer from a chloranilic acid molecule to the lutidine molecules occurs in all the molecular complexes studied. The influence of the lutidine isomer (in particular the methyl substitution position) on the symmetry of the bifurcated hydrogen bonds was examined.

The deprotonation of chloranilic acid results in a delocalisation of the electronic distribution depending on the protonation state; this delocalization was confirmed by deformation density plots, atomic net charge calculations and the density at the bond critical points. A high dependency on the refinement model was found to significantly affect the characterization. Lattice energy calculations were also inconsistent in the ranking of the stability of molecular complexes depending on the method. Therefore, estimating the lattice energy even from theoretical approaches is currently insufficiently accurate to allow a definitive stability order for lutidine - chloranilic acid molecular complexes.

## References:

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3. D. M. Ward, *Chem. Comm.*, 2005, 5838–5842.