

*Halogen bonding in 4-cyanopyridine co-crystals with halogenated benzoic acid*Sowmya A<sup>1</sup>, GN Anil Kumar<sup>1</sup><sup>1</sup>Dept Of Physics, Ramaiah Institute Of Technology, Bengaluru, India

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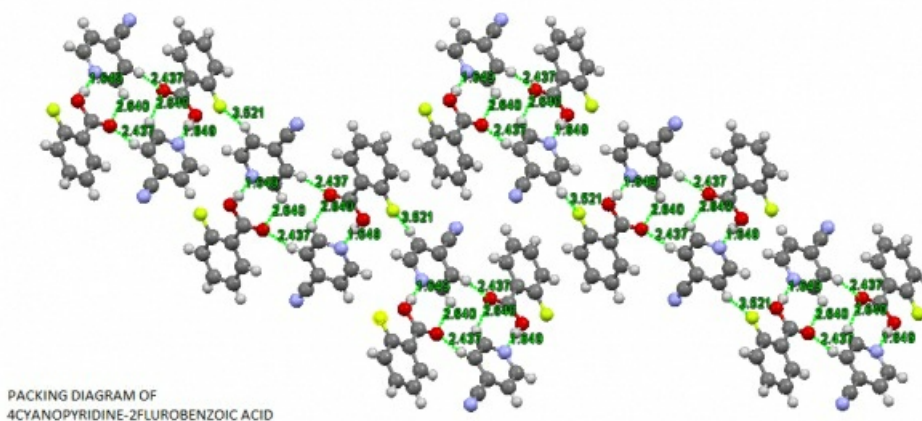
The halogen bond is an attractive interaction formed between positively charged region ( $\sigma$ -hole) of a covalently bound halogen and an electron donor (nucleophile) [1]. In past few decades, halogen bonding emerged as significant tool in crystal engineering and supramolecular chemistry because of its strength and directionality. Recently halogens-analogous interactions have also been observed with other elements giving rise to a family of interactions such as chalcogen, pnictogen, tetrel triel etc., generally referred as  $\sigma$ -hole interactions [2]. The competition of halogen and hydrogen bonding has been extensively studied in solid state by crystallizing the molecules. In view of this we planned to perform a combined crystallographic and computational study on a series of structurally equivalent halogen donors which will form halogen bonded complexes with a series of structurally similar bases with tuneable basicities. This should enable us to observe the effect of the halogen acceptor Lewis basicity on the halogen bond formation with different halogens thus providing a detailed insight into halogen bonding. For this purpose, we have chosen co-crystals of 4-cyanopyridine with halogenated benzoic acid derivatives as a platform for a comparative study of halogen bonding. The pyridine derivatives [3] were chosen so that they cover as wide range of basicities as possible (pKa value range from 0.9 to 8.8,) while avoiding hydrogen bond donor substituents, which could significantly perturb the halogen bonding.

Co-crystals of series of substituted benzoic acid with 4-cyanopyridine have been successfully prepared by slow evaporation using Ethanol. Single crystal diffraction experiments were performed at 293 K on an Oxford Diffraction Xcalibur diffractometer. All structures were solved by direct methods and refined using the SHELXS and SHELXL programs respectively. Geometry optimizations for all investigated compounds were performed using the B3LYP basis set starting from crystallographically determined structures. Hirshfeld surfaces were calculated and plotted using Crystal Explorer. PIXEL energy calculations were also carried out to calculate the interaction energies. The conformation of molecules revealed that molecules are primarily stabilized by O-H...N and C-H...O hydrogen bonds. Also halogen bonding such as X...X, X...Cg, Cg...Cg other weak interactions between the molecules and their role in the crystal packing will be presented.

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3) Madhukar Hemamalini et al.; Acta Cryst.(2010).E66.0578.



**Keywords:** [Co-Crystals](#), [Halogen bonding](#), [Hirshfeld analysis](#)