Exploring the role of neutral/ionized TPI hydrogen bonds and OPI halogen bonds for multifacial recognition in 5-halouracils/aminoazine cocrystals

Gustavo Portalone[a] *and Kari Rissanen*[b]

[a]Department of Chemistry, Sapienza University of Rome, P.le A. Moro, 5. 00141 Rome. Italy. E-mail: gustavo.portalone@uniroma1.it. [B]Department of Chemistry, University of Jyväskylä, Nanoscience Center, PO Box. 35, Finland.

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Ten new heterodimers were synthesized in different stoichiometry to explore the role exerted by potential proton-transfer reactions in the supramolecular structures of A-B cocrystals formed by 5-haloderivatives of uracil (halogen = F, Cl, Br, I; coformer A) coupled with aminoazines as 2-aminoadenine simulants (melamine, 2,4,6-triaminopyrimidine, 2,6-diaminopyridine; coformer B) for pyrimidine nucleobase recognition. The crystallographic analysis showed that in all binary cocrystals the expected three-point hydrogen bonds (TPI), charged or uncharged depending on the acid/base properties of the components, were used for *WC* interfacial recognition. Moreover, the general ability of pyrimidine nucleobases to provide electron donating groups to halogen bonding has been confirmed in six of eight cocrystals containing the 5-bromo or 5-Iododerivatives coupled with 2,4,6-triaminopyrimidine or 2,6-diaminopyridine. “Lateral” one-point halogen bonds cooperate with hydrogen bonds in directing the overall crystal structures. Considerations of the relative acidities of coformers A and of the relative basicities of coformers B allowed us to design and characterize by single-crystal X-ray diffraction the first ternary pyrimidine nucleobase-containing cocrystal based on the *JANUS-WEDGE* concept [1]: the (1:1:1) triad showing a 2,4,6-triaminopyrimidine molecule wedged *via* neutral and ionized TPI between the 5-fluorouracil/1-methyluracil pair in reverse *WC* fashion (Fig. 1).

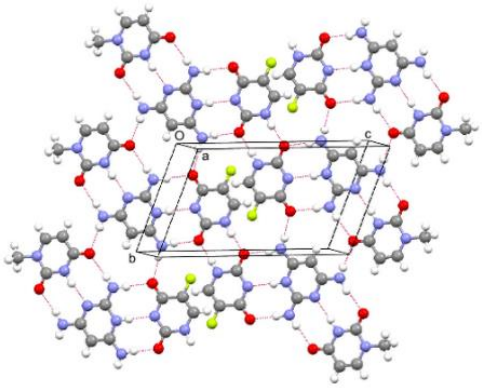

Fig. 1. A partial packing diagram of the (1:1:1) triad.

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[1] Branda, N., Kurz, G. & Lehn, J.-M. (1996). Chem Commun. 2443-2444.

Résumé of presenting author

Name and surname	**Gustavo Portalone**
Department	**Chemistry**
Institution	**“Sapienza” University of Rome**
Country	**Italy**

Dr Gustavo Portalone authored more than 130 scientific papers in the field of X-ray crystallography, gas electron diffraction, quantum chemical calculations of molecular interactions and a book of Chemistry. As chair of the teaching commitee of the Italian Crystallographic Association, he has organized the annual school of crystallography (1994-6) and edited the proceedings in three volumes. He has been elected secretary of the Italian Crystallographic Association (2003-5). Since 2007 he is responsible for the RX diffraction laboratory of the Chemistry Department of “Sapienza” University. Member of the editorial board of the Journal of Chemistry, the Dataset Papers in Chemistry, the Journal of Crystallography and AIMS Material Science. The research of his group focuses on the design, synthesis and structures of supramolecular inorganic and bioinorganic systems assembled via hydrogen and halogen bonds. Results come from the combined approach of XRD, ab initio and molecular dynamics calculations, AFM and thermodynamic measurements.

(Maximum 150 words)