(3AP)·(bpe) confirms the 1-D ladder-like structures. Future work will involve studying the photophysical properties of such solids.
Keywords: supramolecular chemistry, cocrystals, infinite arrays

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M–X···X'–C Halogen Bonds as Efficient and Reliable Supramolecular Synthons in Organic-inorganic Crystals
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The identification of non-covalent interactions in crystalline materials, the understanding of the role that these interactions play in directing supramolecular structures and the rationalisation within such structures of significant interactions with well defined geometry and reproducibility (synthons) is fundamental to crystal engineering, [1].

We have recently focused our attention in this area on the synthesis of molecular crystals in which the nucleophile-electrophile coupling between "inorganic" and "organic" halogens plays a vital role in the definition of the halogen bond synthon M–Cl···X–C (M = transition metal, X = Cl, Br, I), [2]. Theoretical calculations of the electrostatic potentials around the "organic" halogens rationalise the observed short directional interactions when integrated with previous studies of "inorganic" halogens as nucleophiles (in H-bond formation), [2,3].

Further studies have been made on halopyridinium salts of AuX_4^- (X = Cl, Br) where hydrogen bonds and halogen bonds cooperate in defining the crystalline structure. The nature of the halogen-halogen interactions is currently being studied via theoretical models, focusing on the evaluation of the interaction energies and of the individual components (electrostatic, charge transfer, etc.) of these interactions.

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Keywords: crystal engineering, halogen bonds, interaction energy

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Halogen Bonds in Inorganic Crystal Design
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The electronic properties of organic halogens (C-X) differ substantially from those of inorganic halogens (M-X). The latter are directional nucleophiles, [1], whereas the former can be tuned to serve as directional electrophiles, [2], [3]. Thus, similar to D-H··A hydrogen bonds, C-X··X'-M halogen bonds can serve as directional, non-covalent interactions that can be applied to molecular crystal design.

These non-covalent interactions have been investigated through synthesis of compounds of general formula $(\text{n-halopyridinium})_2MX_4$ (n = 3, 4; M = Co, Cu), which are propagated by N-H··X'-M hydrogen bonds and C-X··X'-M halogen bonds [X = Cl, Br, I, (≠ F);. X' = Cl, Br, I]. The geometry of the hydrogen bonds vary in this series (linear, symmetrically and asymmetrically bifurcated), but halogen bonds have well defined geometries (linear for the organic halogens, bent for the inorganic). Normalised halogen bond distances, $R_{XX'}$, decrease: (i) with increasing negative electrostatic potential at the inorganic halogen, suggesting that these interactions are predominantly electrostatic in nature; (ii) with heavier organic halogens, which have positive axial electrostatic potentials. Competition between hydrogen bonds and halogen bonds has also been explored in mixed halide systems. These studies are supported by a CSD study showing the preferred geometries of over 300 C-X··X'-M halogen bonds.

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Keywords: crystal engineering, halogen bonds, databases

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Control of Reactivity in the Solid State through Principles of Supramolecular Chemistry
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The crystalline solid state provides an environment that supports highly stereoselective reactions, wherein the stereochemistry of the product is largely controlled by the arrangement of molecules in the reactant crystal. However, the solid state has remained unexploited as a medium for synthetic chemistry, due to the difficulties related to achieving the crystal packing suitable for a reaction.

Our research group has approached the issue of controlling solid-state reactivity using principles of supramolecular chemistry, specifically template-controlled reactivity. Template-controlled solid-state synthesis uses linear templates, in the form of resorcinol, to direct solid-state [2+2] photodimerizations. The templates preorganize reactants within finite hydrogen-bonded molecular assemblies. Exposure of the assemblies in the solid state to ultraviolet radiation results in the stereospecific formation of a cyclobutane product.

The supramolecular nature of the liason between the reactant and the template provides the method with modularity that led us to explore the possibility to use the approach as a general way to conduct solid-state reactions. Specifically, we have addressed the construction of molecules with different sizes and shapes. In this contribution we report the construction of biologically relevant [3]- and [5]-ladderane frameworks, as well as the *ortho*-, *meta*- and *para*-[2.2]-cyclophane in quantitative yields and gram amounts.
Keywords: solid state reactivity, supramolecular assemblies, photochemistry

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Halogen Bonding in Crystal Engineering
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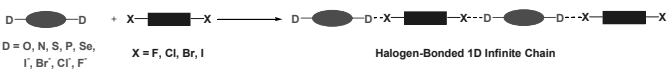
Halogen bonding is the non-covalent interaction between halogen atoms (Lewis acids) and neutral or anionic Lewis bases[1]. The main features of the interaction will be given and the close similarity with hydrogen bonding will become apparent. Some heuristic principles will be presented in order to develop a rational crystal engineering based on halogen bonding. The focus will be in particular on halogen bonded supramolecular architectures given by halocarbons and related structures. The potential of the interaction will be shown by useful applications in fields as diverse as synthetic chemistry, material science, and bioorganic chemistry.



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Keywords: supramolecular chemistry, **halogens**, **intermolecular interactions**

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A Non-symmetric Disordered Tetramer: The Unusual Structure of 3(5)-ethyl-5(3)-phenyl-1*H*-pyrazole in the Solid State
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