

(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

Fiorenzo Zordan, Lee Brammer, Paul Sherwood, *Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK. Computational Science and Engineering Department, CCLRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK.* E-mail: lee.brammer@sheffield.ac.uk

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 AuX₄⁻ (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.

[1] Desiraju G. R., *Crystal Engineering – The design of organic solids*, Elsevier, 1989. [2] Zordan F., Brammer L., Sherwood P., *J. Am. Chem. Soc.*, 2005, **127**, in press. [3] Brammer L., Bruton E. A., Sherwood P., *Cryst. Growth Des.* 2001, **1**, 277.

Keywords: crystal engineering, halogen bonds, interaction energy

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Halogen Bonds in Inorganic Crystal Design

Guillermo Minguez, Lee Brammer, *Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK.* E-mail: lee.brammer@sheffield.ac.uk

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 (n-halopyridinium)₂MX₄ (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.

[1] Brammer L., Bruton E. A., Sherwood P., *Cryst. Growth Des.*, 2001, **1**, 277.

[2] Brammer L., Minguez Espallargas G., Adams H., *CrystEngComm*, 2003, **5**, 343. [3] Zordan F., Brammer L., Sherwood P., *J. Am. Chem. Soc.*, 2005, **127**,

in press.

Keywords: crystal engineering, halogen bonds, databases

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Control of Reactivity in the Solid State through Principles of Supramolecular Chemistry

Tomislav Friščić, Leonard R. Mac Gillivray, *Department of Chemistry, University of Iowa, 305 Chemistry Building, Iowa City, IA 52242-1294 USA.* E-mail: tomislav-friscic@uiowa.edu

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 lison 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

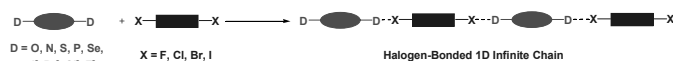
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Halogen Bonding in Crystal Engineering

Pierangelo Metrangolo^a, Tullio Pilati^b, Giuseppe Resnati^a, Maurizio Ursini^a, ^a*Department of Chemistry, Materials, and Chemical Engineering "G. Natta", Polytechnic of Milan.* ^b*ISTM-CNR, Milan, Italy.* E-mail: pierangelo.metrangolo@polimi.it

Halogen bonding is the non-covalent interaction between halogen atoms (Lewis acids) and neutral or anionic Lewis bases¹. 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.



[1] Metrangolo P., Neukirch H., Pilati T., Resnati G., *Acc. Chem. Res.*, 2005, in press.

Keywords: supramolecular chemistry, halogens, intermolecular interactions

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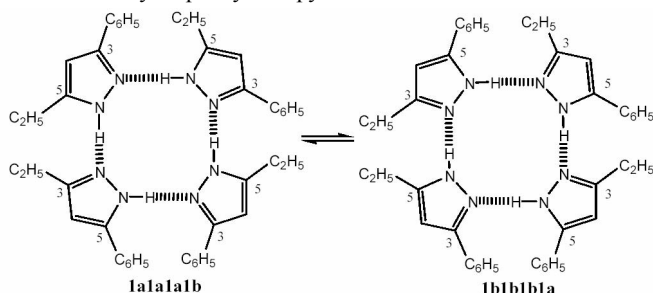
A Non-symmetric Disordered Tetramer: The Unusual Structure of 3(5)-ethyl-5(3)-phenyl-1H-pyrazole in the Solid State

Rosa M. Claramunt^a, Pilar Cornago^a, M. Dolores Santa María^a, Verónica Torres^a, Elena Pinilla^b, M. Rosario Torres^b, José Elguero^c, ^a*Departamento de Química Orgánica y Bio-Orgánica, Facultad de Ciencias, UNED, Madrid.* ^b*Química Inorgánica I, Facultad de Ciencias Químicas Universidad Complutense de Madrid.* ^c*Instituto de*

Química Médica (CSIC), Madrid, Spain. E-mail: rclaramunt@ccia.uned.es

Institut de Chimie, Université de Neuchâtel, Av.de Bellevaux 51, CH-2007 Neuchâtel, Switzerland. E-mail: antonia.neels@unine.ch

In a systematic exploration of 3,5-disubstituted pyrazoles for crystal engineering purposes, we prepared the still unknown 3(5)-ethyl-5(3)-phenyl-1*H*-pyrazole **1**.¹ Its X-ray structure has been determined: it is a hydrogen-bonded tetramer of a new type formed by three tautomers 5-ethyl-3-phenyl-1*H*-pyrazoles of class **a**, and one tautomer 3-ethyl-5-phenyl-1*H*-pyrazole of class **b**.



The 3(5)-ethyl-5(3)-phenyl-1*H*-pyrazole tetramer.

The NH protons are disordered even at low temperature, so there are two questions that could be asked: Is the disorder static or dynamic (SSPT)? What are the proportions of both tetramers **1a1a1a1b/1b1b1b1a** (either static mixture or dynamic equilibrium)? We have tried to answer these questions by a combination of DFT calculations, analysis of the X-ray geometries and ¹³C and ¹⁵N CPMAS NMR. For this last purpose, the [¹⁵N₂]-labelled derivative of **1** was prepared.

[1] Torres V., Cornago P., Claramunt R. M., Loshkin V., Samat A., Pinilla E., Torres M. R., in progress: 3(5)-ethyl-5(3)-phenyl-1*H*-pyrazole **1**, yellow-reddish solid of m.p. 80.1 °C.

Keywords: hydrogen bonding, pyrazoles, supramolecular architectures

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Topologic Features of Three Structures Based on I...Base Halogen Bonding

Tullio Pilati^a, Pierangelo Metrangolo^b, Davide M. Proserpio^c, Giuseppe Resnati^b, ^aISTM-CNR, Milan, Italy. ^bDCMIC "G. Natta", Polytechnic of Milan, Italy. ^cDCSSI, University of Milan, Italy. E-mail: Tullio.Pilati@istm.cnr.it

The halogen bonding, that is the n→σ* electron donation from Lewis bases to halogen atoms (Lewis acids) is an interaction that has attracted an increasing attention, especially in haloperfluorocarbons where the heavy halogen atom (I, Br) is highly polarized¹. We have recently studied the three component structure of the cryptate K.2.2.2 with KI and 1,8-diiodo-perfluorooctane showing a very unusual borromean assembly of the superanion². We present here other three halogen-bonded supra-molecular arrays showing unusual topologic features: the assembly of tetra(4-pyridyl)pentaerythritol . 1,4-diiodo-octafluorobutane **1**, tetra(4-pyridyl)pentaerythritol . 1,8-diiodo-hexafluorooctane **2**, and tetra(4-pyridyl)pentaerythritol . tetra(4-iodo-tetrafluorophenyl)pentaerythritol **3**. The three structures present macrocyclic interpenetrate assembly. **1**, **2**, **3** show 2D 5-fold 4⁴ layers, 8-fold diamondoid class Ia, 10-fold diamondoid class IIIa topologies, respectively.

[1] Metrangolo P., Resnati G., *Enciclopedia of Supramolecular Chemistry*, ed. Steed J. W. and Atwood J. J., Marcel Decker Inc., New York, 2004, pp.1484.

[2] Liantonio R., Metrangolo P., Pilati T., Resnati G. *Crystal Growth & Design*, 2003, **3**, 355. [3] Blatov V.A., Carlucci L., Ciani G., Proserpio D.M., *CrystEngComm*, 2004, **6**, 377.

Keywords: topology, crystal engineering, halogen bonding

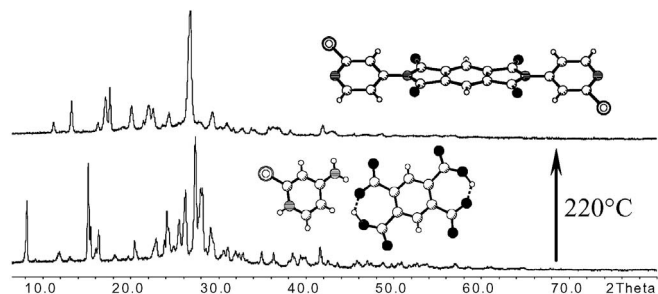
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Inter- and Intra-solid Reactions Studied by X-ray Powder Diffraction

Antonia Neels, Déborah Gonzalez Mantero, Helen Stoeckli-Evans,

In solid state chemistry when only microcrystalline materials are obtained, X-ray powder diffraction becomes the most important tool for analysing unknown phases. *Ab-initio* structure determinations have been carried out on metal organic compounds obtained in solid state transformation processes [1,2], and on new organic materials. The latter were synthesised by solvent free reactions applying green chemistry principles. The competition of inter- and intramolecular interactions in organic crystals and co-crystals will be discussed.



[1] Neels A., Wang Y., Stoeckli-Evans H., *Z. Kristallogr.*, 2004, **219**, 892. [2] Neels A., Alfonso M., González D., Stoeckli-Evans H., *Chimia*, 2003, **57**, 619.

Keywords: green chemistry, crystal engineering, X-ray powder diffraction

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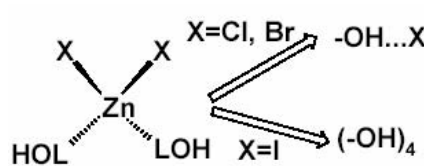
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Anion-Dependent Switch between Sheets and Diamondoid Assembly for Zn(LOH)₂X₂

Elsa Bosetti, Alessia Bacchi, Mauro Carcelli, Department of Chemistry GIAF, University of Parma, Italy. E-mail: elsabosetti@libero.it

We are currently studying the modes of solid state association of M(LOH)₂X₂ molecular building blocks built by complexation of transition metals with LOH (α-(4-pyridyl)benzhydrol), with the scope of designing organic-inorganic hybrid materials capable of uptaking/releasing small guests by solid-gas processes [1].

Here we show the abrupt change in crystal organization of Zn(LOH)₂X₂ on passing from X= Cl, Br to X=I. The smaller and more electronegative halides participate to -OH...X hydrogen bonds giving an overall arrangement of the structures in bidimensional sheets. Zinc behaves as a distorted square nodes in the network topology. The iodine atom switches the basic supramolecular synthon from -OH...X



to tetrahedral -(OH)₄ nests assembled by -OH...H hydrogen bonds, which give a non-covalent diamondoid network where the metal acts as a spacer between

tetraedra nodes.

[1] Bacchi A., Bosetti E., Carcelli M., Pelagatti P., Rogolino D., Pelizzi G., *Inorg. Chem.*, 2005, **44** (2), 431 - 442.

Keywords: crystal engineering, nonbonded interactions, diamondoid

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2-D and 3-D Metal-Organic Frameworks: A Crystal Engineering Approach

Déborah González Mantero, Antonia Neels, Fritz Stoeckli, Helen Stoeckli-Evans, Department of Physical Chemistry, University of Neuchâtel, Switzerland. E-mail: deborah.gonzalez@unine.ch

The synthesis of new metal-organic frameworks can be carried out