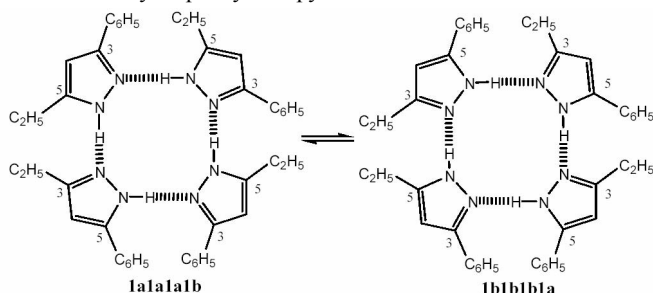


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In a systematic exploration of 3,5-disubstituted pyrazoles for crystal engineering purposes, we prepared the still unknown 3(5)-ethyl-5(3)-phenyl-1*H*-pyrazole **1**.¹ Its X-ray structure has been determined: it is a hydrogen-bonded tetramer of a new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

P.09.05.12

Acta Cryst. (2005). A61, C363

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

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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

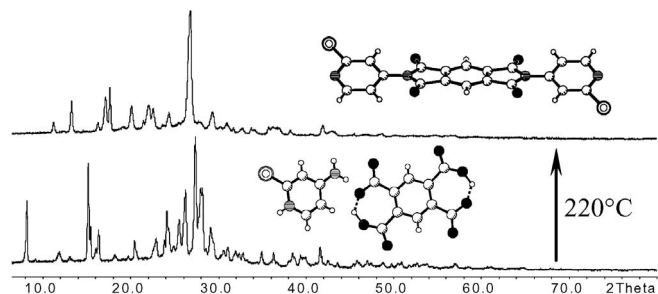
P.09.05.13

Acta Cryst. (2005). A61, C363

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

P.09.05.14

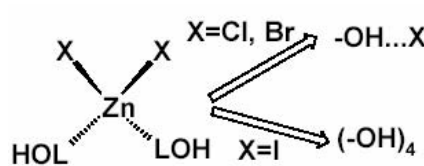
Acta Cryst. (2005). A61, C363

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

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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.

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Keywords: crystal engineering, nonbonded interactions, diamondoid

P.09.05.15

Acta Cryst. (2005). A61, C363-C364

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

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