

**MS23-03 Fluorine substituents disturb the aggregation of molecules.** Vera Vasylyeva,<sup>a</sup> Klaus Merz,<sup>a</sup> <sup>a</sup>Ruhr-University Bochum, Germany  
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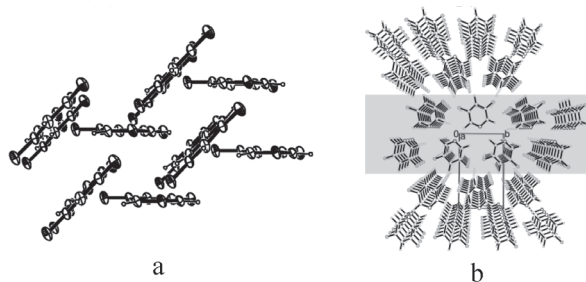
How well do we currently understand the aggregation of small molecules in the solid state [1]? Most of intermolecular interactions are not very strong and their formation is related to and affected by small changes in the molecular structure and the crystallisation conditions. Continuing our investigations on aggregation of substituted aromatic molecules in the solid state [2], we studied the influence and boundaries of weak directing substituents like fluorine on the aggregation of small molecules [3-5].

Organic C-F group forms only weak interactions compared to typical H bond acceptors such as oxygen and nitrogen. The question is whether fluorine substituents influence the aggregation of low melting compounds. Is there a relation between the substitution pattern of fluorine atoms and the crystal packing of the substituted compounds?

A comparison of fluorine-substituted benzonitriles shows, in opposite to Cl-, Br- and I-substituted benzenes, no supra-molecular synthons with weak intermolecular interactions on participation of fluorine or nitrogen. In contrast, several F-substituted pyridines show different intermolecular interactions depending on the substitution pattern of the fluorine atoms at the pyridine backbone.

Low temperature *in situ* crystallisation on the diffraktometer was used to investigate crystal structures of low melting fluorinated pyridines followed by analysis of the crystallisation behavior.

Theoretical study of the energies of weak intermolecular interactions via MP2 / 6-311 G\*\* theory level was used for the research of the basic motives in the solid state. The comparison of our experimental and theoretical findings shows how fluorine atoms influence the aggregation of substituted pyridines. The picture below shows the difference between basic structural motives in the experimental (a) and theoretical (b) crystal packing of 3,5-difluoropyridine.



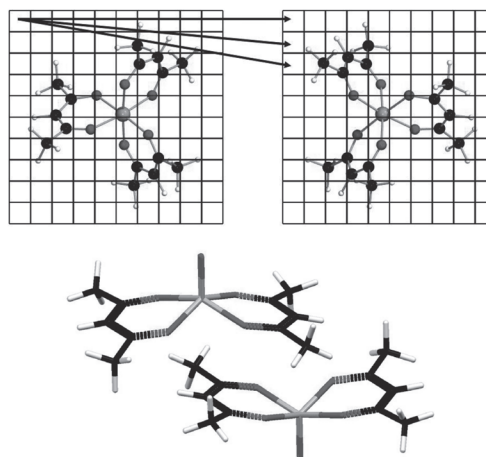
Crystal packing of 3,5-difluoropyridine from the geometrical and energetical perspective

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**Keywords: crystal engineering; halogen bonding; crystal packing analysis**

**MS23-04 Application of the PIXEL Method to Transition Metal Complexes** Andrew G. P. Maloney,<sup>a</sup> Simon Parsons,<sup>a</sup> and Peter A. Wood,<sup>b</sup> <sup>a</sup>Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3J, United Kingdom, <sup>b</sup>Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, United Kingdom  
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Solid state chemistry is governed by intermolecular interactions. By analysing the nature of these interactions we are able to rationalise observed crystal packing effects. Geometric analysis of crystal packing can sometimes miss important interactions, and so an approach which allows for an understanding of the energies between molecules is desirable. We have expanded the PIXEL [1] method to incorporate transition metal species and have taken into account the effects on the atomic parameters this method requires for different species upon ligation, allowing for facile analysis of the intermolecular interactions between inorganic compounds in the solid state. This method is subsequently validated by a thorough study which compares the results of the modified PIXEL method with a large set of experimentally determined sublimation enthalpies [2] for first row, second row and even some third row transition metal complexes. Specific interaction energies between molecules in the solid state have been compared with single point dimer energies using high level DFT-D calculations. Additionally, we apply the method to investigate to investigate supramolecular motifs in metal systems such as stacking interactions in porphyrins and acetylacetonate complexes.



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**Keywords: intermolecular interactions and packing in small-molecule crystals; PIXEL; high pressure**