

Poster Presentations

[MS25-P25] Structural and energetic studies of FABT and FABTH⁺ solvates

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2-(4-fluorophenylamino)-5-(2,4-dihydroxybenzeno)-1,3,4-thiadiazole (FABT) is a biologically active compound. It forms planar molecules (FABT) and cations (FABTH⁺). Details of structural and computational studies of two polymorphs of FABT DMSO solvates [1] and three alcohol solvates of FABTH⁺ chloride [2] are presented. Structures of both polymorphs of FABT DMSO solvates (the triclinic P-1 abbreviated **FBDM I** and the monoclinic P21/n abbreviated **FBDM II**) are stabilized by hydrogen bonds between the FABT and DMSO moieties. The geometry of both polymorphic molecules is very much alike with almost no significant difference in the corresponding bond lengths and valence angles. The only exceptions are the valence angles associated with the terminal *para*-hydroxyl group which is differently H-bonded to the solvent molecules in both polymorphs. Additionally, the **FBDM II** molecule is slightly bent comparing to **FBDM I**. Both polymorphs have also a very similar packing with layers of FABT molecules separated by DMSO moieties. As can be seen from the Hirshfeld surface analysis [3], the most significant differences in the relative contributions of intermolecular interactions to the Hirshfeld surface area for **FBDM** polymorphs are found for the C...H, C...C and H...H interactions. It appears that the **FBDM I** polymorph crystallises first and is thermodynamically less stable, while **FBDM II** is thermodynamically more stable but occurs in the crystallization mixture after much longer time. The computational results allow to identify

the more stable polymorph (**FBDM II** *ca.* -9.93 kJ·mol⁻¹). Single crystals of the FABTH⁺ chloride grown from water solutions of different alcohols such as methanol, propan-2-ol and butanol show structural changes induced mostly by hydrogen bond interactions with chloride anions and solvent molecules. For structures with the alcohol molecules build in the crystal lattice, the FABTH⁺ moiety takes the conformation with the *o*-OH (*orto* position) group from the resorcin ring on the same side of the molecule as the sulphur atom in the thiadiazole ring, whereas in the alcohol free crystals grown from the butanol-water mixture, this group is situated on the other side of the thiadiazole ring. The incorporation of the alcohol molecules into the crystal structures formed by FABTH⁺ cations strongly depends on their size and it influences the **properties of crystal lattices**. In the case of the FABTH⁺Cl⁻ crystallized from butanol, the crystal structure consists of columns of FABTH⁺ cations forming intermolecular channels containing two water molecules and two chloride anions related by centers of symmetry. The crystal structure of FABTH⁺Cl⁻ crystallized from methanol is built of two separate layers consisting of FABTH⁺ cations and methanol and chloride anions repeating periodically. FABTH⁺Cl⁻ crystallised from propan-2-ol forms a 3D structure with separate water and propan-2-ol molecules glued by chloride anions and layers of the FABTH⁺ cations. The Hirshfeld surface analysis is a very useful tool in identifying subtle differences between the solvates. The DFT computations allow us to estimate the energy difference between the two conformers to be 3.2 kcal/mole and the rotational barrier to be 12.6 kcal/mole.

[1] Hoser A. A., Kamiński D.M., Matwijczuk A., Niewiadomy A., Gagoś M., Woźniak K. (2013) *CrystEngComm*. **15**(10), 1978-1988

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[3] Spackman M. A., Jayatilaka D., (2009)
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Keywords: thiadiazole, polymorphs, solvates