

TRANSFORMATIONS AND CRYSTAL STRUCTURES OF A SUBSTITUED TRIAZINE AND ITS SALT FORMS: A VT-XRPD, SDPD AND CASTEP STUDY

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Structure determination from powder diffraction data (SDPD) using simulated annealing (SA) has become a widely used tool for structural analysis in the absence of single crystals. Once the global minimum has been located and the structure solved, Rietveld refinement^[1] is typically carried out to obtain a final structure that is both chemically reasonable and gives the best possible fit to the data. It is often necessary to confirm that weakly-scattering hydrogen atoms are correctly located in the SA structure prior to refinement. Although manual location of hydrogen atom positions between nearby donor and acceptor atoms is often facile for rigid groups, this process can be non-trivial when studying multi-component crystals such as those formed by 2,4-diamino-6-methyl-1,3,5-triazine (DMT) and difluoroacetic acid (DFAA), where salt formation due to proton transfer cannot be excluded. A sample of (DMT⁺.DFA⁻)DFAA (1/1) solvate was prepared by recrystallization from DFAA solution and lab capillary data were collected in the range 3 – 70° 2θ. Data were also collected for a sample of (DMT⁺.DFA⁻) after desolvating the sample *in situ* by heating. Crystal structure determination of DMT, (DMT⁺.DFA⁻) DFAA (1/1) solvate and the desolvated (DMT⁺.DFA⁻) salt was then carried out using global optimisation as implemented in DASH^[2]. The best solution for each structure was geometry optimised using CASTEP^[3] which predicted proton transfer between DMT and DFAA. The optimised structures were used as the basis of a rigid-body Rietveld refinement in TOPAS^[4]. The application of DFT geometry optimisation has added value to the structure determination process, providing a reliable basis for the accurate assignment of hydrogen atom positions in the crystal structures of DMT and its salts and solvates.

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