MS34-P6 Co-crystals of 5,6-Dimethyl-2-thiouracil: further proof of the robustness of the *ADA−DAD* N—H···O/N—H···N/N—H···S-synthon

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One of the main goals in crystal engineering is the search for reliable non-covalent intermolecular interaction motifs ("synthons") for the design of new solids with desired properties.[1] The replacement of a strong hydrogen bond within a certain interaction with a weaker one, say N—H···O with N—H···S, may open up ways to new synthons.[2] Thereby, the robustness of the synthon still may be preserved due to the cooperativity of hydrogen bonding interactions.[3] Inspired by the cyanuric acid−melamine co-crystal, where an *ADA−DAD* N—H···O/N—H···N/N—H···O interaction is observed (*A* = acceptor, *D* = donor), the title compound 5,6-dimethyl-2-thiouracil (DMTU) was selected for co-crystallization. DMTU contains an ADA hydrogen-bonding site involving an S-atom as an acceptor and, therefore, should be capable of forming a mixed *ADA−DAD* N—H···O/N—H···N/N—H···S synthon with suitable coformers like 2,4-diaminopyrimidine (DAPY), 2,4,6-triaminopyrimidine (TAPY) or 2,4,6-triamino-1,3,5-triazine (melamine; MELA). Co-crystallization experiments yielded two solvates of DMTU, (I) and (II), one salt-hydrate and two co-crystal solvates with DAPY, (III) – (V), one co-crystal solvate and one co-crystal salt-solvate with TAPY, (VI) and (VII), and one co-crystal solvate with MELA, (VIII) (Fig. 1). The two solvates show the formation of dimers or tetramers in the crystal packing formed by either "pure" $R^2_2(8)$ N—H···O hydrogen bonds in (I) or by a combination of "pure" $R^2_2(8)$ N—H···O and "mixed" $R^2_2(8)$ N—H···O and N—H···S hydrogen bonds in (II). While DMTU showed an *AA−DD* motif with DAPY in (III) the synthesis of the desired *ADA−DAD* synthon was successful in co-crystals (IV) – (VIII). Moreover, due to a proton transfer along an N—H···N-hydrogen bond in (VII), one of the two observed *ADA−DAD* interactions was changed into an *AAA−DDD* motif. The results demonstrate, that the *ADA−DAD* N—H···O/N—H···N/N—H···S motif is a reliable synthon for the design of co-crystals of DMTU.

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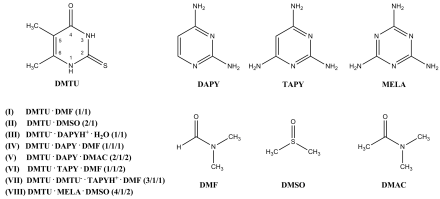

Figure 1. Structures of the compounds used and composition of the crystals.

Keywords: Co-crystals, crystal engineering, N—H···S hydrogen bonds