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Interactions studies in the crystal structures of Thiosemicarbazones and their Thiazol derivatives

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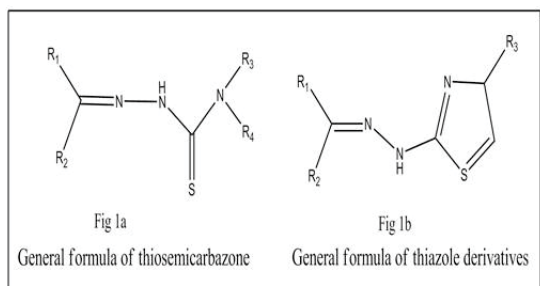
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Thiosemicarbazone compounds have been the subject of intense research for the last twenty years due to their biological and medicinal properties (1). Other interesting application is the possibility of obtaining thiazoles derivatives from thiosemicarbazones using the Hantzsch Reaction; these compounds also present pharmaceutical and biological activities (2). Structurally thiosemicarbazones are versatile building blocks in the synthesis of densely substituted blocks (3).

In this work we present the crystal structure of some thiosemicarbazones (figure-1a) and their thiazol derivatives (figure-1b), focusing in the study of the interactions that stabilize the crystal lattice.

In general, in the molecular crystals of thiosemicarbazones, hydrogen bonds interactions are established through -NH-C(S)-NH-N= fragment, forming in many cases *synthons*. Even though that $\text{C=S}\cdots\text{H-N}$ hydrogen bond is weaker than their $\text{C=O}\cdots\text{H-N}$ analogous, the effective electronegativity of S is increased by conjugative interactions between C=S and the lone pair of one or more N substituyents. This effect is called *resonance-induced hydrogen bonding at Sulfur Acceptor* (4). Due to the low solubility of thiosemicarbazones we use different mixtures of solvents in order to crystallize these compounds. For this reason is possible the inclusion of solvent molecules in the crystal lattice to form the corresponding solvates (5), in these cases we analyze the influence of the solvent in the *synthons* formation.

In thiazol compounds which contain halogen atoms (Cl) and phenyl groups, $\text{C-H}\cdots\text{Cl}$ and π - π stacking interactions have been also studied.



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Structural studies of cycloheptylamine and alcohols co-crystals

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Cycloheptylamine is a primary amine with aliphatic seven-member ring. The compound is liquid at room temperature and its melting point, according to Jean-Claude Bradley Melting Point Dataset yields 255K. The crystal structure of this amine is not known. Primary amines are capable to co-crystallize with alcohols due to the formation of hydrogen bonds between amino and hydroxyl groups. The common motifs in such systems are ribbons with two different symmetries (-1 and 2_1). The aim of the work was a systematic investigation of the feasibility of the amine cocrystallization with low molecular weight monohydric alcohols. A seven-membered carbon ring with or without a heteroatom is relatively labile, therefore an additional goal of the work was a conformational analysis of this molecular fragment.

The examined mixtures are liquid at room temperature, thus during experiments special approach was necessary. The sample placed in thin-wall glass capillary and cooled was irradiated with focused IR laser beam[1]. This *in situ* crystallization technique gave sample suitable for single crystal X-ray analysis. However, in most cases obtained phases were oligocrytalline. During experiments, the structures of the neat amine and 12 co-crystals with alcohols were obtained. Interestingly the melting point of the amine is equal to 204K. In all by one of the co-crystals, molecules are arranged in one-dimensional ribbons with hydrogen bonds presents between NH_2 and OH groups. In the co-crystal with methanol, molecules are organized in layers. It was not possible to obtain a co-crystal with *tert*-butanol, probably due to the large steric hindrance of the aliphatic group of the alcohol. In the majority of the structures the amine ring is disordered.

The seven-member aliphatic ring may exist in many conformations. Therefore the puckering analysis of the obtained structures and those retrieved from the Cambridge Structural Database[2] containing seven-membered rings was performed. Any seven-membered ring can be divided into four orthogonal modes, corresponding to two irreducible representations of incline from the XY plane for the D_{7h} group[3]. Presentation of the results, in form of a quaternary phase diagram, characteristic for mixtures containing four components, shows that the majority of points are located on the section plane of the tetrahedron, and the deviating ones correspond to structures where the disorder of the ring was probably overseen.

Relatively small variability of the structural motifs in obtained co-crystals can be used to design new systems with the appropriate arrangement of molecules, which, for example, will exhibit photochemical activity.