Structure and Tautomerism of Mercapto-1,2,4-triazole Derivatives in the Solid State

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Molecular and crystal structures and tautomerism of new mercapto-1,2,4-triazole derivatives, which are structurally labile compounds capable to exist in different tautomeric forms, are discussed. X-Ray single crystal diffraction experiments show the existence of only 1*H*-triazole tautomer in crystal. As a result of our investigations it can be concluded, that for 3,5-substituted 1,2,4-triazoles usually crystallizes the tautomer, where hydrogen atom is bonded with the nitrogen (one of two neighbouring) situated near the electronodonor group, that is 3-R_A-5-R_D-1,2,4-(1*H*)-triazole. For 3-phenyl-5-mercapto-1,2,4-triazole two thion-thiolic tautomers were found in one crystal: two molecules of four symmetrically independent ones are 3-phenyl-4,5-dihydro-(1*H*)-1,2,4-triazole-5-tion tautomers, and the rest are 3-phenyl-5-mercapto-(1*H*)-1,2,4-triazole. The asymmetric part of the unit cell of 3(5)-(2-hydroxyethyl)thio-1,2,4-triazolinium oxalate consists of two cation-anion pairs. The two cations are the endocyclic tautomers: one of them is 3-(2-hydroxyethyl)thio-(1*H*),(4*H*)-1,2,4-triazolinium cation and the other is 5-(2-hydroxyethyl)thio-(1*H*),(4*H*)-1,2,4-triazolinium cation. The hydrogen bonds system (intra- and intermolecular ones) and crystal packing are also discussed. The crystal packing are stabilized by π-π-interactions between benzene rings and/or triazole heterocycles. The packing coefficient and solvent accessible potential area in crystal were also analyzed.

Keywords: triazoles, x-ray structure, tautomerism