GI-MS48-P12 | OVERCOMING AMBIGUOUS TAUTOMER ASSIGNMENT IN 1,2,4-TRIAZOLE CRYSTAL STRUCTURES

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Formerly we located hydrogen atoms in difference maps. Modern software conveniently calculates positions, but 1,2,4-triazole tautomers should provide warning. A hydrogen atom on one of two adjacent N atoms gives 1*H* with C-NH and C=N bonds. Placing that H atom on the isolated N atom; 4*H,* leaves C=N bonds and approximate C_{2v} symmetry. The parent 1*H* tautomer, TRAZOL02 (neutron data, 15 K, R = 2.9 %) has misleadingly similar C-NH and C=N distances of 1.334 and 1.325 Å but distinctive annular bond angles: 110.20° at NH, 102.67° and 102.89° at "bare" N. Chatar Singh (1965) guided the placement of H atoms by such angles.

High-level *ab initio* calculations (Balabin, 2009) show greater stability of the t*H* tautomer by 6.25 kcal mol^{-1}. Searching the November 2018 CSD for neutral 1,2,4-triazoles yielded 198 hits in the 1*H* form, just 7 in 4*H*. Are these 7 legitimate? CLTRZL and JUGYOB were redetermined as 1*H*. DAMTRZ21 with similar cell dimensions to earlier 1*H* structures should be 1*H.* Endocyclic angles in MAJSOH and both independent triazole moieties of FALDAZ imply 1*H*. FUZPOH lacks possible N-H…N interactions, but changing tautomer to 1*H* facilitates C-H…N . DEGNIM is credible as 4*H*: its triazole ring, incorporated in a crown ether, donates N4-H…O to an enveloped water molecule.

Keywords: 1,2,4-triazoles, tautomers, geometrical criteria

[1] Balabin, R. M. (2009) J. Chem. Phys., 131, 154307.
[2] Chatar Singh (1965) Acta Cryst., 19, 861.