# Conformational behavior and tautomer selective photochemistry in low temperature matrices: the case of 5-(1*H*-tetrazol-1-yl)-1,2,4-triazole.

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The conformational properties and the photolysis behavior of one of the simplest N–C bonded bicyclic azoles, 5-(1*H*-tetrazol-1-yl)-1,2,4-triazole (**T**), were studied in argon and xenon matrices by infrared spectroscopy. Analysis of the experimental results was supported by extensive theoretical calculations carried out at the B3LYP/6-311++G(2d,2p) level of approximation. Out of the eight **T** minima located on the potential energy surface, the three most stable species were detected in low temperature matrices, namely, 5-(1*H*-tetrazol-1-yl)-1*H*-1,2,4-triazole (**T1**) and two conformers of 5-(1*H*-tetrazol-1-yl)-2*H*-1,2,4-triazole (**T2a** and **T2b**). With increase of the substrate temperature either during deposition of the matrices or during annealing the **T2b** → **T2a** conversion took place, in agreement with the predicted low energy barrier for this transformation (5.38 kJ $mol^{-1}$). Both broad band and narrow band laser UV irradiations of **T** isolated in Xe and Ar matrices induce unimolecular decomposition involving cleavage of the tetrazole ring of **T1** and **T2a** (**T2b**) that leads to the production of 1*H*-1,2,4-triazol-5-yl carbodiimide (**P1**) and 1*H*-1,2,4-triazol-3-yl carbodiimide (**P2**), respectively. When the laser is used, in addition to the main **P1** and **P2** photoproducts, several minor products could be successfully identified in the matrices: *N*-cyanocarbodiimide HNCNCN (detected for the first time) associated with nitrilimine HNNCH and HCN. An interesting phenomenon of tautomer-selective photochemistry was observed for the matrix-isolated compound. It could be explained by the different LUMO–HOMO energy gaps estimated for **T1**, **T2a**, and **T2b**, connected with different threshold energies necessary to start the photolysis of **T1** and **T2a** (**T2b**).

Adres publiczny

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