

On the tautomerism of 2-mercaptobenzimidazol: A photoinduced reaction in solid argon

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Contrarily to what happens for the oxo-hydroxo tautomerism, the thione-thiol tautomerism has been only scarcely investigated in spite of its relevance in both chemical and biochemical terms [1,2]. In the present study, the thione-thiol phototautomerization of 2-mercaptobenzimidazole (**2-MBI**; Fig. 1) isolated in a cryogenic (15 K) argon matrix has been addressed using *in situ* narrowband UV irradiation of the matrix-isolated compound and infrared spectroscopy probing. The initially deposited matrix was found to contain exclusively the thione tautomer of **2-MBI**, which corresponds to its thermodynamically most stable form. Upon irradiation at $\lambda = 307$ nm, this tautomer converts into the thiol tautomer *via* intramolecular hydrogen atom transfer. Subsequent irradiation at $\lambda = 246$ nm selectively converts-back the thiol form into the thione tautomer, demonstrating the photoreversibility of the investigated photoprocess. The possibility of selectively convert each one of the tautomers of **2-MBI** into the other one in an efficient way using optical excitation at different wavelengths makes this molecule a good candidate for investigation as a molecular switch.

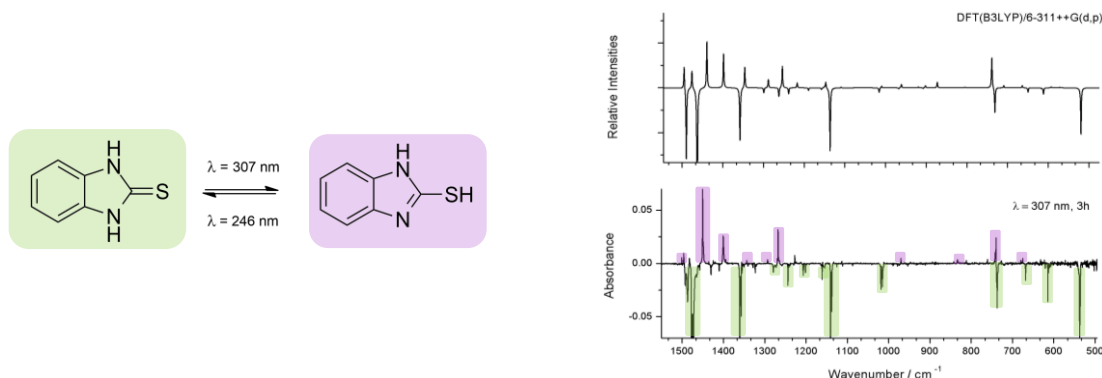


Figure 1. Observed phototautomerism in **2-MBI**. *Left*: observed photoprocesses and structures of the two tautomers. *Right*: infrared difference spectrum ($\lambda = 307$ nm irradiated *minus* as-deposited matrix) showing the thione→thiol transformation (*bottom*); calculated infrared difference spectrum (thiol *minus* thione) (*top*).

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