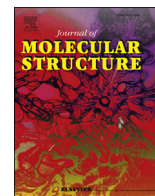




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An insight into methimazole phototautomerism: Central role of the thiyl radical and effect of benzo substitution

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ABSTRACT

The thione/thiol tautomerism in methimazole (1-methyl-2-thioimidazole; **MTI**) and 1-methyl-2-thiobenzimidazole (**MTBI**) has been investigated by matrix isolation infrared spectroscopy and quantum chemical calculations performed at the DFT(B3LYP)/6-311++G(d,p) level. The two compounds were shown to pass to the gas phase from the crystalline state, where they exist in the thione form, upon sublimation, without tautomerizing. The thione form of the compounds could then be isolated in the cryogenic matrices and vibrationally characterized. Narrowband UV-irradiation of the thione forms at 261 or 307 nm, for **MTI** and **MTBI**, respectively, allowed their conversion into the corresponding thiol forms, which were observed experimentally for the first time and could then be also characterized vibrationally in details. **MTBI** thiol could subsequently be converted back to the thione form upon irradiation at 246 nm, while the thiol→thione tautomerization could not be induced for **MTI**. The experimental results were rationalized in terms of the PhotoInduced Detachment Association (PIDA) mechanism and taking into account both the structures of the thiyl radicals resulting from the photo-detachment process and the effects due to the benzo-substituent. In the case of **MTI**, besides the photoinduced thione→thiol tautomerization, photofragmentation was observed, through imidazole ring disassembling, yielding *N*-vinylidenemethanamine (**NVM**). On the whole, this study aims to further understanding on thione/thiol tautomerism and photochemistry of thiones and thiols.

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1. Introduction

Intramolecular UV-induced hydrogen-atom-transfer processes from a nitrogen atom of a heterocyclic ring to an exocyclic oxygen atom have been the subject of some recent studies, starting with the prototype 4(3*H*)-pyrimidinone system [1–3]. A considerable number of processes of this type, taking place in molecules bearing one or more heteroatoms, such as cytosine [4,5], isocytosine [6], 3(2*H*)-pyridazinone [7], 2(1*H*)-pyridinone [8], 7-azaindole [9], 4(3*H*)-pyrimidinethione [10] and 3(2*H*)-pyridazinethione [10], have been observed. When one of the heteroatoms involved in the H-atom transfer is a sulfur, the process leads to thione/thiol tautomerism.

Recently, we investigated the UV-induced thione/thiol tautomerism in 2-thiobenzimidazole isolated in solid argon [11], showing that this chemical system has good properties regarding selective reversible phototautomerization, which makes it a promising

candidate for future potential applications as a molecular photo-switch. In the present article, we report on our investigations on the phototautomerization in methimazole (1-methyl-2-thioimidazole; **MTI**) and its benzo-substituted analogue, 1-methyl-2-thiobenzimidazole (**MTBI**) (Fig. 1). This investigation aims to contribute to the advancing of the present understanding on thione/thiol photoinduced tautomerism, shed light on the role of involved intermediates, and evaluate the effect of presence of the benzo-substituent fused to the active thioimidazole moiety.

Matrix isolation was selected as main experimental technique, since the physical-chemical conditions that are achieved under matrix isolation conditions are particularly suitable for the desired type of studies [12–14]. Together, the cage confinement of the molecules to be investigated in solid inert materials (e.g., argon) and the low work-temperature (a few Kelvin) constitute an ideal environment for single-molecule photochemical investigations, in particular when appropriate narrowband light sources are used for the photochemical excitation of the trapped molecules [15–19]. The matrix isolation studies reported in this article were complemented by the theoretical investigation of the systems under

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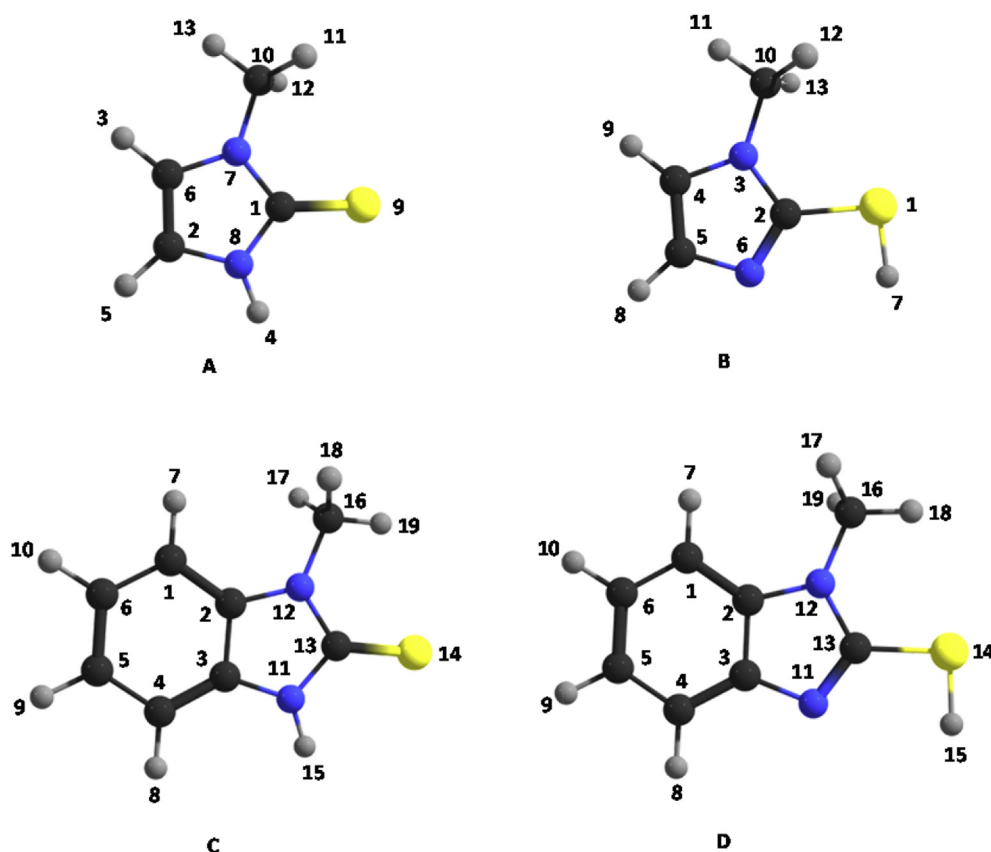


Fig. 1. Equilibrium structures of **MTI** thione (A) and thiol (B) tautomers and of **MTBI** thione (C) and thiol (D) tautomers, optimized at the B3LYP/6-311++G(d,p) level, with adopted atom numbering.

analysis, carried out at the Density Functional Theory (DFT) level.

As described in details below, the two studied molecules, while exhibiting the same general pattern of reactivity, which could be understood at light of the PhotoInduced Detachment Association (PIDA) mechanism [20–22], show also some differential structural features and chemical behavior that are here successfully explained taking into account the structures of the corresponding thiyl radical intermediates and the effect of the benzo-substituent in **MTI**. Besides the detailed study of the thione/thiol tautomerism in **MTI** and **MTBI**, and the first experimental observation and vibrational characterization of the thiol tautomers of these two compounds, the dominant photofragmentation reaction taking place for matrix-isolated **MTI** is also described.

2. Materials and methods

2.1. Computational details

Quantum chemical calculations were performed with the Gaussian 09 [23] software package. Equilibrium geometries, energies and vibrational frequencies were calculated using the Density Functional Theory (DFT) method with the Becke's three-parameter Lee, Yang and Parr exchange functional (B3LYP) [24–26], and the 6-311++G(d,p) basis set [27]. Ultraviolet absorption spectra were computed at the TD-DFT level, using the same functional and basis set.

The obtained harmonic vibrational frequencies were scaled down by a factor of 0.954, above 2700 cm^{-1} , and by 0.985 below this frequency, in order to correct mainly for the shortcomings associated with the effects of anharmonicity and basis set

limitations. Graphical representation of the calculated spectra was done by simulating each band by a Lorentzian function centered at the scaled wavenumbers, and using a full-width-at-half-height of 2 cm^{-1} . The calculated intensities of the simulated bands correspond to the areas below the Lorentzian functions. Normal mode analyses were performed in the internal coordinates space as implemented first by Schachtschneider and Mortimer [28], by calculation of the potential energy distribution (PED), using a modified version of the program BALGA.

2.2. Experimental methods

Commercial methimazole (1-methyl-2-thioimidazole; **MTI**) and 1-methyl-2-thiobenzimidazole (**MTBI**) were purchased from Sigma-Aldrich (powder; 97% and 95% purity, respectively). Since the compounds are hygroscopic, they were first dried for some hours *in vacuo* (at $\sim 10^{-6}$ mbar). After this procedure, the samples, placed in a mini-glass oven attached to the vacuum chamber, were sublimated ($\sim 380\text{--}390\text{ K}$) and the vapors were co-condensed onto an optical cold ($10\text{--}15\text{ K}$) CsI window, together with a large excess of argon (N60, supplied by Air Liquide), in a $\sim 1:1000$ solute to matrix ratio. The CsI window was cooled by a closed-cycle helium refrigerator whose principal component is an APD Cryogenics DE-201A expander, and its temperature was measured by a Scientific Instruments, Model 9650-1, temperature.

The matrix isolation infrared spectra were recorded in the $4000\text{--}400\text{ cm}^{-1}$ range, with 0.5 cm^{-1} resolution, in a Thermo Nicolet 6700 Fourier-transform infrared (FTIR) spectrometer, equipped with a Ge/KBr beam splitter and a deuterated triglycine sulfate (DTGS) detector.

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