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Invited paper

UV-induced proton transfer in 3-amino-1,2,4-triazole

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ABSTRACT

UV-induced proton transfer between two tautomeric forms of 3-amino-1,2,4-triazole (1-AT, 2-AT) was followed by FTIR spectroscopy coupled with matrix isolation technique. The 1-AT → 2-AT photo-transformation was observed upon the 248 nm irradiation. State-averaged CASSCF(8,8)/6–311 ++G (2d,2p) approach was applied to study mechanism of the observed phototautomerization. The obtained results indicate that the S1/S0 conical intersection (CI) plays a crucial role in the mechanism under study. It was shown that the 1-AT(S1) → CI → 1-AT(S0)/2-AT(S0) path was responsible for the experimentally observed photo-induced tautomerization process.

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1. Introduction

UV-induced intramolecular proton transfer reactions have been observed and reported for numerous compounds. Those known as Excited-State Intramolecular Proton Transfer (ESIPT) involve proton movement along an intramolecular hydrogen bond existing in both ground and excited electronic state of the molecule [1]. However, another type of proton transfer is possible after electronic excitation of a molecule that does not contain intramolecular hydrogen bond. A characteristic feature of such tautomerization is that the proton involved in the reaction changes its position from an exocyclic group of the precursor to a ring heteroatom of the product. The proton transfer from the most common exocyclic groups C—OH, C—SH and C—NH_2 results in new exocyclic groups C=O, C=S and C=NH, respectively or reverse reactions take place. One of the first examples of such photo-tautomerism was reported by Nowak et al. for 4-oxopyrimidine isolated in low temperature matrices [2]. Since then a number of this type of photoreactions was observed and described, as for example: hydroxy-oxo [3–5], thiol-thione [6,7] and amino-imino [8–10]. ESIPT reaction in the molecular crystal of 7-(2-Pyridyl)-indole where the proton is transferred from the indolyl group nitrogen to the pyridyl group nitrogen has been studied using recently developed QM/QM theoretical approach [11].

Still different type of proton transfer is possible, where both reagent and product have a proton attached at different positions of the ring and no exocyclic group is involved. Iizumi et al. [12] reported UV-induced proton transfer between two adenine isomers through an adenine radical. A reversible phototautomerism between two thione forms of thiophenol with proton migrating between two carbon atoms of the ring was described as well. [13]

The latter type of proton transfer may be expected for azole derivatives possessing an endocyclic N—H group. Such tautomerism involves the hydrogen migration between different nitrogen atoms within the ring. Knowledge of the tautomeric preferences in organic molecules, especially in tetrazoles and triazoles, is of importance since their functionality or physicochemical activity may be tautomer sensitive [14–17]. A number of papers have been published concerning different triazole tautomers, solvent effects on the equilibria between them [18–21] as well as the proton transfer phenomena in azole-based coordination polymers [22]. However, to the best of our knowledge, UV-induced proton transfer between azole tautomers was not reported.

Photochemistry of organic flat heterocycle molecules has remained a subject of theoretical study which is motivated mainly by the importance of DNA bases, whereas the interest is focused mostly on the lowest $n\pi^*$ and $\pi\pi^*$ excited states. [23,24] According to Sobolewski and Domcke the electronic spectrum of such molecules can be quite complex due to the presence of a

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number of heteroatoms with lone pairs, which results in low-lying $^1n\pi^*$, $^1\pi\pi^*$ and N—H/O—H related $^1\pi\sigma^*$ states, while the later ones play an important role in the photochemistry of aromatic biomolecules [25–29]. The lowest $^1\pi\sigma^*$ state of molecules such as indole [26], pyrrole [27], phenol [28] or 9H-adenine [25] exhibits a repulsive potential energy surfaces with respect to NH/OH stretching coordinate, typically with a very shallow minimum at small values of NH/OH distance. Usually, $^1\pi\sigma^*$ is not the lowest excited state, but as for e.g. 9H-adenine it crosses $^1\pi\pi^*$,$^1n\pi^*$ and also S0 ground state, which forms the basis for the mechanism of radiationless deactivation of the excited molecules. In pyrrole, where $^1\pi\sigma^*$ is actually the lowest excited state, the $^1\pi\sigma^*$/S0 intersection is also present. The relatively high-energy character of $^1\pi\pi^*$ in organic molecules may be attributed to their reduced aromaticity due to the presence of several heteroatoms [25]. The intersection of $^1\pi\sigma^*$ with the ground state surface along a hydrogen-detachment coordinate is suggested to be a generic phenomenon in a class of aromatic molecules, such as those containing azine or enol group [25,29]. The case of 3-amino-1,2,4-triazole (AT) studied in this paper indicates that the class of molecules with the excited $^1\pi\sigma^*$ hydrogen-detachment surface is even larger.

The structure, isomerization pathways and vibrational spectra of AT in the ground electronic state isolated in low-temperature argon matrix have been studied by Pagacz-Kostrzewa et al. [30] The combination of FTIR spectroscopy and theoretical calculations led to the conclusion that AT existed in solid argon in two tautomeric forms: 1-AT and 2-AT and the results reported there form the background for the present experiment.

Here, we report the proton transfer reaction occurring upon UV radiation between two tautomers of AT isolated in low temperature matrices. Quantum chemical study of this reaction allowed us to rationalize the observed phenomenon and revealed that the proton transfer observed in S1 state of the 1-AT tautomer results from the repulsive character of underlying potential energy surface along the N—H coordinate.

2. Experimental and computational details

For low temperature matrices preparation, the AT sample (Fluka, 97%, purified by column chromatography) was allowed to sublimate at 333 K from a small electrically heated glass oven located in the vacuum vessel of the cryostat. The AT vapor was co-deposited with a large excess of the matrix gas (Ar or Xe) onto a cold CsI window held at a temperature equal to 15 K and 30 K for Ar and Xe, respectively.

Photochemical reactions were induced in AT/Ar and AT/Xe matrices by UV radiation of a pulsed optical parametric oscillator Vibrant (Opotek, Inc.) (repetition rate 10 Hz, pulse duration 7 ns, average pulse energy 3.3 mJ) pumped with a Nd:YAG laser (Quantel). FTIR spectra were collected at 11 K with a 0.5 cm^{-1} resolution by means of a Bruker IFS 66 spectrometer.

To support the interpretation of the experimental data, infrared spectra and thermochemical data of the species of interest in their ground electronic state were calculated at the MP2 and B3LYPD3 levels with the 6–311 + +G(3df,3pd) basis set using the Gaussian 09 program package [31]. To explain the mechanism of the proton transfer reaction we explored the topography of S1 potential energy surface using time dependent density functional theory approach (B3LYP coupled to 6–311 + +g(2d,2p) and aug-cc-pvtz basis sets: minima and transition states geometry optimization, IR spectra) and state averaged complete active space (CASSCF) approach with 8 electrons and 8 orbitals in active space (6–311 + +g(2d,2p): minima, transition states and S1/S0 conical intersection optimization, IR spectra), as implemented in Gaussian 09 [32–36]. More information on the orbitals included in the CASSCF active space is available in Supplementary data.

3. Results and discussion

3.1. FTIR detection of proton transfer reaction between 1-AT and 2-AT isolated in argon and xenon matrices

Among eleven minima located on the potential energy surface of 3-amino-1,2,4-triazole (AT) (cf. our earlier paper for details [30]) the two most stable are amino forms 1-AT and 2-AT differing in a position of the annular H-atom that is attached either to N1 or N2 atom of the triazole ring (see Fig. 1). According to the previously reported computations (MP2 and B3LYP with 6–311 + +G(2d,2p) basis set) [30], as well as those used here (MP2 and B3LYPD3 with 6–311 + +G(3df,3pd) basis set) the ZPE corrected energy difference between these two tautomers falls into the 0.83–1.19 kcal mol^{-1} range with 1-AT being a global minimum. On the basis of the calculated relative Gibbs free energies at different levels of theory, it was estimated that the equilibrium gaseous mixture (at evaporation temperature, 333 K) before matrix deposition contains 76–83% of 1-AT and 24–17% of 2-AT.

The key regions of the experimental infrared spectra obtained for freshly deposited AT/Ar and AT/Xe matrices are presented in Fig. 2 (black traces). The two most stable 1-AT and 2-AT tautomers are present in both matrices [30]. Positions of the bands observed for 1-AT and 2-AT in argon and xenon matrices together with the wavenumbers predicted by calculations are given in Table S1 in Supplementary data. The experimental populations, on the basis of the integrated absorbance of the 1-AT and 2-AT bands (at 1609 and 1623 cm^{-1}, respectively) divided by the absolute intensities calculated (B3LYPD3) for the corresponding vibrations, are estimated to be ca. 80% and 20%, respectively. These values are in a very good agreement with the theoretically predicted abundance (see Table S2 in Supplementary data).

Exposing both AT/Ar and AT/Xe matrices to the monochromatic radiation of the 248 nm wavelength promotes the 1-AT → 2-AT transformation as shown in Fig. 2 (red traces).

Upon subsequent irradiations at λ = 248 nm the bands assigned to the 2-AT species are gradually increasing at the expense of the 1-AT absorptions. The observed spectral changes are a clear evidence of the proton transfer between two tautomeric forms in the studied 3-amino-1,2,4-triazole molecule. According to the kinetic profiles presented in Fig. 3, after 40 min of irradiation at 248 nm more than 80% of the 1-AT tautomer was converted into the 2-AT form. Simultaneously, in addition to the tautomeric interconversion, other AT photoreactions leading to the sample decomposition take place in the studied matrices, with different rates depending on the wavelength applied. The best efficiency of the 1-AT → 2-AT phototransformation was observed at λ = 248 nm whereas the photodecomposition rate at this wavelength was still relatively low.

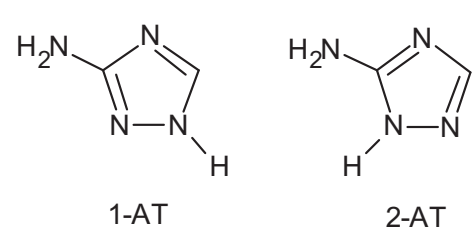

Fig. 1. The most stable AT tautomers.

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