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UV-induced transformations in matrix-isolated 6-methoxyindole

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ABSTRACT

The UV-induced transformations of 6-methoxyindole isolated in both xenon and argon matrixes are discussed. Experimental evidence about the role played by the N–H dissociation channel in the photochemistry of the compound is provided, demonstrating easy formation of the 6-methoxy-indolyl radical plus H atom as primary photoproducts. The two radicals were found to recombine after annealing of the matrixes to a higher temperature, to yield a new prototropic tautomer of the original compound. Other two photoinduced processes were also observed: (1) isomerization between the two conformers of 6-methoxyindole, which was found to be selective in relation to the excitation wavelength and also sensitive to the matrix media; (2) formation of 5-methyl- and 7-methyl-6-indolones, which takes place via O–CH₃ dissociation and initial formation of 6-indoxyl and methyl radicals that promptly recombine, within the primarily occupied matrix cage, to produce the two observed indolones. The different observed photoprocesses are mechanistically interpreted with support from quantum chemical calculations. The wavelength selectivity for the isomerization/decomposition pathways was achieved by using narrowband (spectral width = 0.2 cm⁻¹) UV-light. Detection and characterization of the different photoproducts was accomplished by using infrared probing, complemented by theoretical calculations.

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1. Introduction

The photochemical behaviour of indole and respective derivatives has attracted considerable attention over the years [1–5]. This interest comes essentially from the fact that the heterocyclic indole ring is the chromophore of various molecules of biological interest, such as the neurotransmitter serotonin [6], the hormone melatonin [7], the anti-inflammatory drug indomethacin [8], and the essential amino acid tryptophan. The fluorescence of this last substituted indole is widely used as an indicator of structural changes in proteins [9,10].

This work is dedicated to the study of the main UV-induced transformations in 6-methoxyindole, a structural unit (as well as the other methoxyindole isomers) present in a wide range of biologically relevant molecules [11–13]. To the best of our knowledge, this is the first experimental study on the UV-induced transformations in a matrix-isolated indole derivative, thus complementing previous investigations of the photodissociation of hydroxy- and methoxy-substituted indoles in gas-phase [14].

As in the parent indole molecule [15], the N–H bond rupture (energy of dissociation ~382 kJ mol⁻¹ [16]) was found to constitute an important process upon near UV-excitation of methoxyindoles [14]. This photocleavage involves electronic transitions to the first excited ¹ππ* states [17,18], commonly labeled as ¹L_b and ¹L_a [19], followed by transfer of their populations to the lowest πσ* excited state by means of conical intersections [3]. Owing to the dissociative character of the πσ* excited state with respect to the N–H stretching coordinate, it has been theoretically predicted [3,20] and experimentally confirmed [16,21] that this state plays a role in the hydrogen atom release from the N–H group.

As a result of the dissociation of the N–H bond, a methoxy-indolyl radical is produced. If the released hydrogen recombines with the radical it may regenerate the starting molecule, or originate a new prototropic nH-tautomer [22–26], where n stands for the ring position at which the released hydrogen atom reconnects (n = 2–5 or 7; see atom numbering scheme in Fig. 1). Despite of the role that the methoxy-indolyl radical and nH-tautomers are expected to play in the photochemistry of methoxy-substituted indoles, to the best of our knowledge, the identification and characterization of these species by means of stationary spectroscopic techniques have never been reported so far.

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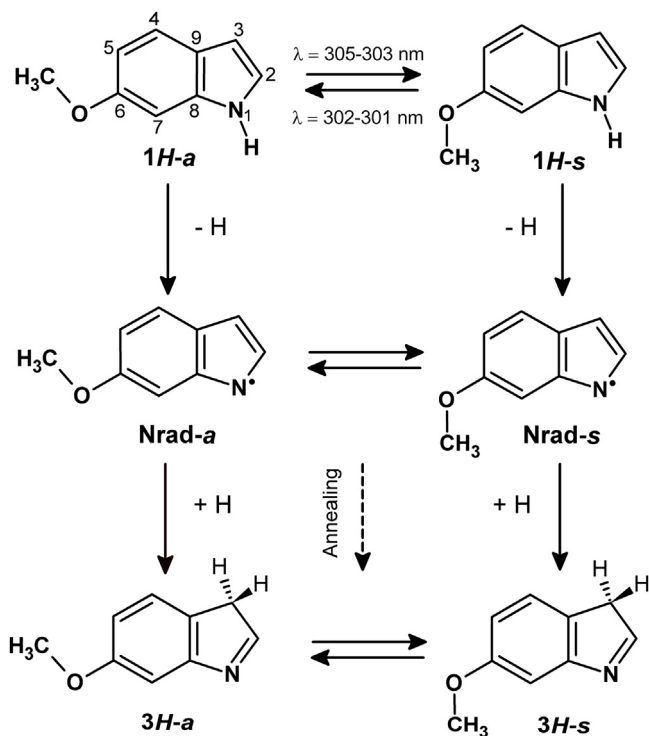


Fig. 1. Schematic illustration of the main transformations occurring in 1H-6MOI isolated in a xenon matrix at 30K induced by monochromatic UV-light at $\lambda \leq 305$ nm (solid arrows) and by annealing of the UV-irradiated matrix from 30 to 40 K (dashed arrow). The atom numbering scheme of the indole ring is provided in 1H-a.

Therefore, in the present study, we investigate the most relevant photoprocesses in 6-methoxyindole (hereafter abbreviated as 1H-6MOI to distinguish it from other tautomeric forms) isolated in low-temperature matrices of noble gases (xenon and argon) when it is excited with narrowband UV-light. One of the purposes of this study is to provide experimental evidence about the role played by the N–H dissociation channel in the photochemistry of 1H-6MOI and, simultaneously, trying to identify other possible isomerization/decomposition pathways. This will be accomplished through the infrared spectroscopic identification of the species generated upon subjecting the matrix-isolated reactant to tunable monochromatic UV-light, by means of comparison of the experimental data with the theoretical spectra calculated for the putative photoproducts.

Furthermore, since 1H-6MOI adopts two conformers bearing a planar heavy atom skeleton [27,28], differing from one another by the orientation of the OCH₃ fragment, another objective of this work is to examine the possibility of occurrence of UV-induced interconversions between the two conformers. These results will complement our previous studies on the thermally- and near-infrared light induced conformational isomerizations in matrix-isolated 1H-6MOI [27,29], and will provide additional information about the dynamics of conformational isomerization in substituted indoles [30].

2. Experimental and computational section

2.1. Matrix isolation experiments, UV-irradiations and IR-spectroscopy

Commercial 1H-6MOI was obtained from Apollo Scientific with a purity degree of 98% and was used without further purification. A few milligrams of the solid compound were introduced in a miniature glass oven which was then assembled inside the vacuum

chamber of a helium-cooled cryostat, constituted by an APD cryogenics closed-cycle helium refrigerator system with a DE-202A expander. The cryomatrices were prepared by co-deposition of vapours of the compound sublimated from the resistively heated oven (~ 323 K) and an excess of the host gas (argon N60 or xenon N48, both supplied by Air Liquide) onto a cooled CsI optical substrate (16 K for the argon depositions and 30 K for the xenon depositions). The temperature of the CsI window was measured directly at the sample holder with an accuracy of 0.1 K by using a silicon diode sensor connected to a digital controller (Scientific Instruments, Model 9650-1).

After the deposition, the monomers of the compound trapped in the host matrix were irradiated through the outer quartz window of the cryostat using monochromatic UV-radiation (spectral width = 0.2 cm⁻¹) with wavenumbers ranging from 310 to 301 nm (xenon matrix) or from 310 to 293 nm (argon matrix). The frequency-doubled signal beam of a Quanta-Ray MOPO-SL optical parametric oscillator, pumped with a pulsed Nd:YAG laser, was used as source of tunable light. The pulse energy, duration time, and repetition rate were ~ 2 mJ, 10 ns and 10 Hz, respectively. For each selected irradiation, the time of exposition of the sample to the UV-light varied from 1 to 10 min.

IR-spectroscopy was used for monitoring the photoprocesses taking place in the samples as a result of the UV-irradiations. Mid-infrared spectra were collected in a Thermo Nicolet 6700 Fourier-transform infrared (FTIR) spectrometer, equipped with a Ge/KBr beam splitter and a mercury cadmium telluride (MCT-B) detector, cooled by liquid N₂. The spectra were acquired with 0.5 cm⁻¹ resolution. In order to avoid interference of atmospheric H₂O and CO vapours, a continuous stream of dry air was used to purge the spectrometer.

2.2. Quantum-chemical calculations

The geometries of the reactants and products were fully optimized at the B3LYP/6-311++G(d,p) level of theory [31–33]. In order to simulate the IR-spectra of these species, harmonic vibrational calculations were conducted on the respective optimized geometries by using the same level of approximation. A multiplicative scale factor of 0.98 was used to correct the calculated wavenumbers. For graphical representation, simulated infrared spectra were constructed as follows: the scaled harmonic frequencies and calculated infrared intensities were used to convolute each peak by using Lorentzian functions with a full width at half-maximum (FWHM) of 1 cm⁻¹ so that the peak values would correspond to the calculated infrared absolute intensities. Time-dependent density functional theory calculations (TD-DFT) [34,35] were also performed at the B3LYP/6-311++G(d,p) level in order to obtain the vertical excitation energies of the low-energy electronic excited states for the reactant conformers. To obtain the theoretical absorption UV-spectra, each calculated transition was convoluted with a Lorentzian function having FWHM of 0.3 eV. All computations mentioned above were performed with the Gaussian 09 program package [36].

3. Results and discussion

In the following sections, the most important transformations in matrix-isolated 1H-6MOI upon excitation with narrowband UV-light within the $310 \geq \lambda \geq 293$ nm interval will be discussed. Despite these experiments have been conducted both in xenon and argon matrixes, the IR spectra recorded in xenon were found to be of much easier interpretation as compared to argon, mostly because of the less significant site-splitting effects in the first than in the second matrix. For this reason, the structural changes in the

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