UV-induced transformations in matrix-isolated 6-methoxyindole

A.J. Lopes Jesus, I. Reva, R. Fausto

Abstract

The UV-induced transformations of 6-methoxyindole isolated in both xenon and argon matrices 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-indoly 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 photoduced 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 photolysis involves electronic transitions to the first excited 1ππ* states [17,18], commonly labeled as 1Lo and 1La [19], followed by transfer of their populations to the lowest ππ* excited state by means of conical intersections [3]. Owing to the dissociative character of the ππ* 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-indoly 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-indoly 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 30 K induced by monochromatic UV-light at \( \lambda \leq 305 \text{ nm} \) (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 photoproduc ts.

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 cryomattres 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 \( \text{N}_2 \). The spectra were acquired with 0.5 cm\(^{-1}\) resolution. In order to avoid interference of atmospheric \( \text{H}_2\text{O} \) and \( \text{CO} \) 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 > \( \lambda \) > 293 nm interval will be discussed. Despite these experiments have been conducted both in xenon and argon matrices, 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
3.1. UV-induced conformational isomerization in 1H-6MOI

1H-6MOI is known to adopt two conformers bearing a planar heavy atom skeleton [28,29]. In one of them the OCH₃ and NH groups point to the same direction, 1H-s (s = synperiplanar), while in the other the two groups point to opposite directions, 1H-a (a = antiperiplanar), see Fig. 1. Theoretical calculations carried out at different levels of theory predicted 1H-s to be more stable than 1H-a by 1.7–3.1 kJmol⁻¹ [22,27–29]. Spectral signatures of both conformers were experimentally identified in low-temperature xenon and argon matrices, which allowed estimating their relative abundances [27,29]. Additionally, after the deposition, matrices enriched in any of the two conformers could be prepared, either by thermal annealing, or by applying narrowband near-infrared light excitation [27,29].

The excitation energies of 1H-s and 1H-a determined by Brand et al. using rotationally resolved electronic spectroscopy were found to be 294.6 nm and 296.5 nm, respectively [28]. Nearly identical values (294.5 and 296.5 nm) have been reported by Sulkes and Borthwick [37]. With this information in mind, a series of narrowband UV-irradiations was performed on the compound isolated in a xenon matrix at 30 K and the structural modifications after each irradiation were followed by recording mid-infrared spectra.

Before starting the UV-irradiations, the matrix was enriched with the higher energy form [(1H-s)/[1H-a] ~ 0.5] by using selective near-infrared excitation as described in ref. [29]. The experiments initiated by tuning the laser at λ = 310 nm, followed by gradual application of more energetic (shorter wavelength) excitations. Following irradiations between 310 and 306 nm no appreciable spectral changes were observed. The first spectral indication of occurrence of phototransformations was observed upon irradiation at λ = 305 nm. As illustrated in the spectral fragments shown in Fig. 2 [traces (a) and (b)], exciting the sample at this wavelength led to a decrease of the absorptions at 896, 826 and 791 cm⁻¹, which are characteristic of 1H-a (marked with an open circle), and to an increase of those at 899 and 806 cm⁻¹, ascribed to 1H-s (marked with a closed circle), thus revealing the decrease of population of the anti form and increase of the population of the syn form. After approximately 20 min of successive irradiations at this wavelength, the [1H-s]/[1H-a] ratio increased from 0.5 to 1.2 [Fig. 2 (c)]. It is worth to be noted that during the successive UV-irradiations at λ = 305 nm, besides of the changes in the intensities of the bands assigned to the reactant conformers, new bands emerged in the IR-spectra as it will be discussed below. This confirms that the conformational isomerization is in fact triggered by the UV-light. Irradiations at λ = 305 nm were also carried out for a sample enriched with the most stable form [(1H-s)/[1H-a] ~ 2.6], which was prepared by annealing of a freshly deposited matrix from 30 to 40 K, followed by cooling it back to the initial temperature. However, after the UV-activation, the conformational composition remained practically unaltered, which indicates that at this wavelength only the less stable form is photoreactive.

Much more pronounced conformational variations were observed for the matrix-isolated compound by applying monochromatic UV-light of shorter wavelengths. Indeed, as depicted in Fig. 3, a very short period (2 min) of irradiation at λ = 303 nm practically induced a depopulation of 1H-a in favor of 1H-s [trace (b)], whereas subsequent irradiations at λ = 302 and 301 nm (one minute each) led to the regeneration of the first form at the cost of the second one [trace (c)], thus pointing out the wavelength-dependence and reversibility of the conformational isomerizations.

The fact that excitations at longer wavelengths (λ = 305-303 nm) trigger a population shift from the less stable form in favor of the most stable one, while excitations at shorter wavelengths (λ = 302–301 nm) cause the opposite effect, is consistent with the higher electronic excitation energy determined experimentally for 1H-a relative to 1H-s (see values above) [28,37], and is also in agreement with the relative position and intensity of the low-energy UV-absorptions (260–310 nm) calculated for the two conformers [TD-DFT(B3LYP)/6–311+G(d,p)], as illustrated in Fig. 4 (the vertical excitation energies and oscillator strengths of the lowest twenty four excited states calculated for the two conformers are given in Table S1). Wavelength selective UV-induced conformational isomerizations have been observed for other similar matrix-isolated compounds [38–41].

Identical UV-irradiation experiments have been conducted for the compound trapped in solid argon at 15 K. However, after exposing the argon matrix to narrowband UV-radiation with wavelengths ranging from 305 nm down to 301 nm, no spectral changes were observed that could be related with the occurrence of conformational isomerization. A small 1H-a → 1H-s interconversion was only detected upon excitations at λ = 300 nm but the
reverse transformation could not be observed by applying shorter wavelengths, because the intensity of the bands assigned to both conformers were found to decrease (see Supplementary material, Fig. S1), thereby indicating that both of them react to originate new species. These results point to a less effective conformational isomerization in the argon matrix, as compared to xenon, which may be ascribed to the different sizes and stiffness of the matrix cages in these two environments. Nevertheless, this explanation shall be taken as tentative, since the conformational isomerizations might just be less competitive in argon as compared to the other photoinduced processes, which will be discussed in the next sections in details.

3.2. UV-induced transformations involving the N–H bond rupture

Besides of the photorotamerization about the C–O bond, other transformations were observed upon exciting 1H-6MOI isolated in solid xenon (30 K) with monochromatic UV-light with wavelengths ranging from 305 to 301 nm. This is well evidenced by the new bands appearing in the IR spectra recorded upon consecutive UV-irradiations at \( \lambda = 305 \) nm, as shown in Fig. 5 (a) (1490–1415 cm\(^{-1}\) and 1315–1230 cm\(^{-1}\) fragments) and in Figs. S2 and S3 of the Supplementary material (wider spectral region), which indicate the photogeneration of new species. For the irradiations performed at shorter wavelengths (\( \lambda < 305 \) nm) no additional new bands were found to emerge in the IR spectra but only an intensification of those already observed after the irradiations at \( \lambda = 305 \) nm.

As referred before, the N–H bond cleavage, which results in the formation of the 6-methoxy-indolyl radical, henceforward abbreviated as Nrad (“N” in the acronym indicates that the radical is formed by abstraction of the H atom from the NH group, as opposite to a radical that might be formed by abstraction of the CH\(_3\) fragment from the methoxy group) and a hydrogen atom, is a very likely process to take place upon the UV-excitation of matrix-isolated 1H-6MOI. Since the photodetached H-atoms are very fast, they may leave the initial cage and travel across the matrix, thus allowing the stabilization of Nrad [42,43]. The recombination of the radical pair would either regenerate the precursor, or result in the formation of a new prototropic nH-6MOI tautomer. We have calculated the energies of the optimized structures of all possible new tautomers and the results of these calculations, carried out at the B3LYP/6-311++G(d,p) level of theory, are provided as Supplementary material (Table S2).

As in the parent indole molecule [23], the most stable new tautomer is 3H-6MOI and the energy increase for the second most stable new tautomer (2H-6MOI) is large (65 kJ mol\(^{-1}\), see Table S2). The stronger stabilization of 3H-6MOI relative to the other new nH-tautomers suggests that 1H-6MOI \( \rightarrow \) Nrad \( \rightarrow \) 3H-6MOI is a likely sequence of reactions that occur upon exciting the reactant with monochromatic UV-light. As such, 3H-6MOI and/or Nrad are very good candidates to explain some of the new bands emerging in the IR-spectra recorded after the UV-irradiations. The potential energy scans around the O–C–C\(_6\)–C\(_7\) dihedral calculated for both species (Fig. S4) reveal that they adopt two conformers exhibiting a planar skeleton, just as in the precursor (see Fig. 1). For Nrad these conformers are called Nrad-s and Nrad-a, while for 3H-6MOI they are here designated as 3H-s and 3H-a. The energies and optimized Cartesian coordinates for these four structures are provided in Tables S2–S5.

The vibrational spectra calculated for the two Nrad conformers (calculated harmonic wavenumbers and intensities are listed in Table S6) reveal the existence of various strong absorptions, with some of them predicted to appear in regions free from bands assigned to the reactant conformers (see Fig. 5 and Figs. S3 and S4). Thus, if stabilized in the xenon matrix, the IR-spectroscopic identification of this species should be possible. Indeed, the comparison of the IR-spectra of the reactant molecule isolated in a xenon matrix at 30 K recorded before any UV-irradiation and after 20 min of successive irradiations at \( \lambda = 305 \) nm [see traces (1) and (2) in Fig. 5(a)] with the IR spectra simulated for Nrad-s and Nrad-a [Fig. 5(b)] reveals that most of the new features emerging in these spectral regions after the UV-irradiations (1471, 1427, 1420, 1314, 1301, 1260 and 1244 cm\(^{-1}\), all marked with closed circles) are nicely reproduced by the absorptions predicted for the two Nrad conformers. Signatures of Nrad are also found in other spectral regions, as illustrated in Figs. S3 and S4. Besides of this spectral concordance, the similar pattern of intensity changes exhibited by this set of bands during the consecutive irradiations at \( \lambda = 305 \) nm reinforces their assignment to both Nrad conformers. The fact that a unique UV-excited conformer of the precursor (1H-a, see discussion above) originates two radical conformers is easily understood by the occurrence of excited state conformational isomerisation, as demonstrated above for the precursor, concomitantly with the N–H bond rupture. The formation of methoxy-indolyl radicals was also observed in 4- and 5-methoxyindole from...
the TKER (total kinetic energy release) spectra arising from the photolysis of the jet-cooled molecules [14].

Regarding 3H-6MOI, its spectral identification is much more difficult since most of the intense vibrations predicted for 3H-a and 3H-s overlap with bands already assigned to the radical and to the precursor (see Fig. 5(c); the harmonic frequencies and infrared intensities calculated for 3H-a and 3H-s are listed in Table S7). In spite of that, spectral signatures of this tautomer could be identified at 1282, 1276, 1266 and 1237 cm⁻¹ [bands marked with open circles in Fig. 5(a)]. Due to the very low intensity of these four bands in the IR spectrum recorded after the irradiations at \( \lambda = 305 \) nm, a new spectrum, recorded after irradiation at a shorter wavelength (\( \lambda = 301 \) nm), was added to Fig. 5(a) for better visualization of these new features [trace (3)]. For the absorption appearing at 1482 cm⁻¹, which can be ascribable either to the radical or tautomer based on the comparison of the experimental with the calculated spectra (Fig. 5), it will be demonstrated below that its major contribution comes from 3H-6MOI.

The photoproduction of Nrad and 3H-6MOI was also spectroscopically observed upon UV-irradiations carried out for the reactant trapped in an argon matrix (16 K) at wavelengths ranging between 300 and 296 nm, as shown in Figs. 55 and 56.

In an attempt to give additional support to the photo-generation of Nrad and 3H-6MOI, at the end of the sequence of the UV-irradiations at \( \lambda = 305 \) nm performed for the compound isolated in the xenon matrix, the sample was annealed from 30 to 40 K and the spectral variations observed during this process are represented in Fig. 6 as a difference spectrum [‘after annealing’ minus ‘before annealing’ traces (a)]. In a separate experiment, a freshly deposited xenon matrix was annealed between the same temperatures and the difference spectrum was included in the same figure [trace (b)] to be used as reference. In the difference spectrum recorded for the freshly deposited matrix, the spectral variations observed upon annealing indicate the occurrence of conformational relaxation in the reactant, i.e., the less stable conformer (1H-a) is converted into the most stable (1H-s) one [27]. Since a significant amount of the reactant still persists in the matrix after the consecutive UV-irradiations at \( \lambda = 305 \) nm, the same conformational variation is observed upon annealing of the UV-irradiated sample, as clearly evidenced from the comparison of the two difference spectra. However, in addition to this transformation, the difference spectrum (‘after annealing’ minus ‘before annealing’) recorded after the sequence of UV-irradiations at \( \lambda = 305 \) nm also shows a decrease in the intensity of the bands previously assigned to both Nrad conformers. This experimental result indicates that the radical is consumed upon annealing. Since none of the bands assigned to the radical grow up, the occurrence of conformational relaxation in this species can be ruled out, which is consistent with the relatively high energy barrier for the conformational interconversion (20 kJ mol⁻¹, value calculated at the B3LYP/6-311+G(d,p) level, Fig. S2) and with the vanishingly small energy difference between the two radical conformers, which is within the computational error (the B3LYP zero-point energy difference amounts to only 0.005 kJ mol⁻¹, see Table S3) [44,45]. Therefore, the consumption of Nrad during annealing can only be explained by the enhancement of diffusion of the hydrogen atom in the less rigid annealed matrix, which facilitates its reattachment to Nrad. This process may lead to a partial recovery of the precursor and/or formation of 3H-6MOI. The first possibility was checked by choosing pairs

![Fig. 5](image_url)
of bands assigned to the precursor conformers (1H-a and 1H-s), with both band components exhibiting identical intrinsic calculated intensities, and find out if the total integrated area of these bands increased after annealing. For the pairs of bands satisfying this criterion we didn’t find any significant changes of their integrated areas, which should mean that the recombination of the hydrogen atom at the original site (N1) is unlikely. To verify the second possibility, we tried to identify in the difference spectrum obtained for the UV-irradiated sample [trace (a) in Fig. 6] the presence of new positive bands that could be explained by 3H-6MOI. The positive bands identified at 1266 and 1236 cm⁻¹, the positions of the most intense absorptions predicted for this tautomer, is a quite consistent spectral indication of the formation of this species during annealing.

Besides allowing confirming the presence of the radical and 3H-6MOI in the matrix, the spectral variations observed upon annealing of the UV-irradiated xenon matrix also enabled a more accurate assignment of the bands attributed to the photoproducts. The most elucidative example concerns the feature emerging at 1481 cm⁻¹, whose assignment to any of the two photoproducts based on spectral comparison is rather difficult as both of them are predicted to absorb close to this wavenumber (see Fig. 5). However, the fact that this band grows up during annealing indicates that its major contribution comes from 3H-6MOI and not from Nrad.

3.3. Additional UV-induced reactions

From the early stages of the UV-irradiations, a new prominent band was found at 2150–2110 cm⁻¹ in the IR spectra recorded in both xenon and argon matrices (see Fig. 7 (a) and Fig. S7). Since this new broad feature cannot be explained neither by Nrad nor by 3H-6MOI (none of these species is predicted to absorb in this region), it can be inferred that other transformations take place in the UV-excited 1H-6MOI. A very plausible reaction may be the rupture of the O-CH₃ bond, followed by the migration of the methyl group from C6 to C5 or C7, thus originating 5- or 7-methyl-6-indolone, respectively (see Fig. 8). The O-CH₃ dissociation channel has previously shown to play a role in the laser-induced photolysis of matrix-isolated anisole [46,47], but its role in the photolysis of methoxyindoles has never been investigated before, though it has been suggested that it might explain the shorter excited state lifetimes of methoxyindoles as compared to indole [28].

These two methyl-6-indolone isomers may in turn undergo ring opening, leading to the formation of ketene species (their geometries are displayed in Fig. S8 and the calculated harmonic wavenumbers and intensities are listed in Tables S10–S11), which are predicted to exhibit strong absorptions at wavenumbers close to the position where the new prominent band is found to appear [43,48]. These absorptions correspond to the antisymmetric stretching vibration of the ketene group (νC=O) and are predicted to appear at ν = 2150 cm⁻¹ (I = 1108 km mol⁻¹) and at ν = 2144 cm⁻¹ (I = 1867 km mol⁻¹) for the open ring-ketenes obtained from 5- and 7-methyl-6-indolone, respectively. Another contribution to the strong feature emerging within the 2150–2110 cm⁻¹ interval may come from the decomposition of opening ketenes giving rise to the formation of carbon monoxide, which is known to absorb at 2134–2133 cm⁻¹ [xenon] [49] and at 2140–2137 cm⁻¹ (argon) [50,51]. The occurrence of O-CH₃ bond fission during the UV-irradiations is also supported by the appearance of a very weak band at ~1663 cm⁻¹ [Fig. 7(b)], which might be ascribable to the stretching vibration of the carbonyl group (νC=O) of the two methyl-6-indolone isomers. In fact, the wavenumbers corresponding to this stretching vibration were calculated to be 1650 cm⁻¹ and 1675 cm⁻¹ for 5-methyl-6-indolone and 7-methyl-6-indolone, respectively (see Tables S8–S9).
As schematized in Fig. 8, the first species generated from the O–CH₃ bond rupture are the 6-indoxyl and methyl radicals. However, it was not possible to identify in the experimental spectra recorded after the UV-irradiations bands that could be firmly assigned to any of these two intermediate species. This may be explained by the large volume of the methyl radical which is not expected to easily leave the original matrix cage and instead should promptly recombine with the 6-indoxyl radical.

4. Conclusions

In the present work, the photochemical behaviour of 1H-6MOI trapped in low-temperature matrices has been thoroughly investigated. For the compound isolated in xenon it was demonstrated that the relative proportion of the 1H-s and 1H-a conformers can be selectively controlled by irradiating the molecule with monochromatic UV-light. Excitations at λ = 305–303 nm were found to induce a 1H-a → 1H-s conversion, while the reverse transformation could be observed by using slightly shorter wavelengths (λ = 302–301 nm), in accordance with the relative excitation energies of the two conformers.

UV-excitations at λ ≤ 305 nm also induced the N–H bond breakage, leading to the photogeneration of the 6-methoxy-indolyl radical and 3H-6MOI tautomer. The annealing experiments carried out in a xenon matrix previously subjected to UV-irradiation confirmed the stabilization of both photoproducts.

A few new IR-absorptions emerging upon the UV-irradiations which could not be explained neither by the radical nor by the new tautomer, were attributed to species generated from the ring opening of the indolones, were identified as the main photoproducts. Unlike to the N–H dissociation channel, no spectral indication has been found for the stabilization of the 6-indoxyl radical in the matrix. This may be attributed to the large volume of the abstracted methyl radical, which leads to a very quick recombination of the radical pair.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2016.12.024.

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