UV-induced transformations of matrix-isolated 6-azacytosine

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UV-induced transformations were studied for monomers of 6-azacytosine isolated in low-temperature Ar matrices. In contrast to cytosine, where the amino-hydroxy (AH) tautomer is the lowest-energy form, the amino-oxo (AO) and imino-oxo (IO) isomers of 6-azacytosine were found to be the most stable and most populated. Due to the high relative energy of the AH tautomer of 6-azacytosine, this form is not populated in low-temperature matrices after their formation and prior to any irradiation. Excitation of 6-azacytosine monomers with UV light from the 328–300 nm range led to structural transformations of AO and IO forms. The initially most populated AO tautomer was observed either to convert, in a phototautomerization reaction, into the AH product or to undergo photodecarbonylation to yield 4-amino-1,2,3-(2H)-triazole. The relative efficiencies of the two processes depend on the wavelength and on the pulsed or continuous-wave character of the UV light used for excitation. For the IO tautomer of 6-azacytosine, the excitation with UV 328–300 nm light induced the photoconversion of the initially more populated anti IO1 isomer into the syn IO2 form. This transformation was found to be partially photoreversible. Published by AIP Publishing. https://doi.org/10.1063/1.5045735

I. INTRODUCTION

6-Azacytosine is an analog of the canonic nucleic acid base cytosine. As such, 6-azacytosine was investigated in the past using different methods.1–6 None of these studies concerned 6-azacytosine monomers in the gas phase or trapped in low-temperature inert matrices.

Theoretical investigations on isolated molecules of cytosine predict that the lowest-energy form of this compound is the amino-hydroxy (AH) tautomer.7–12 This tautomer was experimentally found to be the most populated form of cytosine in the gas phase,13 helium nanodroplets,14 and in low-temperature inert-gas matrices.15 In these experiments, the amino-oxo (AO) and imino-oxo (IO) isomers of cytosine were also observed, though in lower amount. Similar relative populations of tautomers were observed for cytosine derivatives such as 5-methylcytosine and 5-fluorocytosine isolated in argon matrices.12 Studies on these compounds revealed that substitution with the methyl group or fluorine atom at position 5 does not substantially affect the relative energies of cytosine tautomeric forms.

The structure of 6-azacytosine differs from that of cytosine in substitution of the C→H group at position 6 of the ring by a nitrogen atom. In the current work, we demonstrate that this seemingly slight structural modification has a profound effect on the relative energies of the tautomeric forms of the compound. As a consequence, the relative populations of 6-azacytosine isomers were found, in the present study, to dramatically differ from those previously observed for cytosine.

UV-induced transformations of matrix-isolated cytosine, 5-methylcytosine, and 5-fluorocytosine have been investigated in detail.12,15 Unimolecular photochemical transformations (such as oxo-hydroxy phototautomerism, syn-anti-isomerization within the imino-oxo forms, and photogeneration of open-ring conjugated isocyanate) were observed for these compounds. The main objective of the current study is the investigation of the unimolecular photochemistry of 6-azacytosine. In several aspects, the photochemical behavior of 6-azacytosine was found to be substantially different from that of cytosine.

II. EXPERIMENTAL SECTION

The sample of 6-azacytosine (98%) used in the present study was a commercial product supplied by Sigma. In order to prepare argon matrices containing isolated monomers of 6-azacytosine, a solid sample of the compound was heated (to ∼495 K) in a miniature glass oven placed in the vacuum chamber of a helium-cooled cryostat. Vapors of cytosine were deposited together with a large excess of argon (purity N60, supplied by Air Liquide) onto a CsI window cooled to 12 K. An APD Cryogenics closed-cycle helium refrigeration system with a DE-202A expander was used in the matrix-isolation experiments. The IR absorption spectra were recorded in the 4000–400 cm−1 range, with 0.5 cm−1 resolution, using a Thermo Nicolet 670 FTIR spectrometer equipped with a KBr beam splitter and a deuterated triglycine sulfate (DTGS) detector. Matrix-isolated monomers of 6-azacytosine

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were irradiated with UV light emitted by a continuous-wave HBO-200 high-pressure mercury lamp (fitted with cutoff filters) or by the frequency-doubled signal beam of the Quanta-Ray MOP-SL pulsed optical parametric oscillator (FWHM \( \sim 0.2 \text{ cm}^{-1} \), pulse energy \( \sim 1.0 \text{ mJ} \)) pumped with a pulsed (pulse duration 10 ns, repetition rate 10 Hz) Nd:YAG laser.

III. COMPUTATIONAL SECTION

The geometries of the five lowest-energy isomeric forms of 6-azacytosine (see the structures presented in Table I) were fully optimized at the Density Functional Theory (DFT) with Becke Three-Parameter functional,\(^\text{16}\) the Lee-Yang-Parr functional for the non-local correlation,\(^\text{17}\) and the Vosko-Wilk-Nusair functional III for the local correlation,\(^\text{18}\) commonly abbreviated as B3LYP,\(^\text{16-18}\) and Quadratic Configuration Interaction theory used in the truncated configuration space of Single and Double substitutions (QCISD),\(^\text{19}\) using the tight convergence criteria. The relative energies of the isomers were calculated using the QCISD method, at geometries optimized at this level. The harmonic vibrational frequencies and IR intensities were calculated using the DFT(B3LYP) method, using the superfine grid for the integral accuracy and the fine grid for the coupled-perturbed Hartree-Fock (CPHF) equations. To approximately correct for the neglected anharmonicity, the harmonic DFT frequencies were scaled by factors of 0.955 (for wavenumbers higher than 2000 cm\(^{-1}\)) and 0.970 (for wavenumbers lower than 2000 cm\(^{-1}\)).

IV. RESULTS AND DISCUSSION

A. Relative energies of 6-azacytosine isomers

The relative energies of the isomers of 6-azacytosine, calculated at the QCISD/6-31++G(d,p) level, are presented in Table I. For comparison, the relative energies of the isomeric forms of cytosine are also shown in this table. The amino-hydroxy (AH) tautomer has been theoretically predicted to be the lowest-energy form of cytosine.\(^\text{7-12}\) This AH tautomer was also experimentally observed as the most populated form of cytosine in the gas phase,\(^\text{13}\) helium nanodroplets,\(^\text{14}\) and in low-temperature inert gas matrices.\(^\text{15}\)

In a drastic contrast to the tautomerism of cytosine, the energies of the amino-hydroxy (AH) forms of 6-azacytosine

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<tr>
<th>Cytosine</th>
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<tr>
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<tr>
<td>AH2</td>
<td>1.06</td>
</tr>
<tr>
<td>AO</td>
<td>0.00</td>
</tr>
<tr>
<td>IO1</td>
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<tr>
<td>IO2</td>
<td>8.94</td>
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<td>AH2</td>
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<tr>
<td>AO</td>
<td>0.00</td>
</tr>
<tr>
<td>IO1</td>
<td>2.50</td>
</tr>
<tr>
<td>IO2</td>
<td>2.00</td>
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<td>10.94</td>
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<tr>
<td>IO2</td>
<td>5.66</td>
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\(\Delta E_{\text{el}}\) — calculated using the QCISD/6-31++G(d,p) method at geometries optimized at the same QCISD/6-31++G(d,p) level.

\(\Delta \text{ZPE} \) — vibrational zero-point energy (ZPE) calculated at the DFT(B3LYP)/6-31++G(d,p) level.

\(\Delta E_{\text{el}} \) — total internal energy at zero Kelvin.

\(\Delta \text{G}_{\text{corr}} \) — thermal contribution to the Gibbs free energy calculated at the DFT(B3LYP)/6-31++G(d,p) level for the temperature of 495 Kelvin.
are theoretically predicted to be much higher (by more than 20 kJ mol\(^{-1}\), Table I) than the energies of the amino-oxo (AO) or imino-oxo (IO1) forms. According to the relative Gibbs free energies, calculated for 6-azacytosine isomers and presented in Table I, the relative populations of AO, IO1, and IO2 in the gas phase, at 495 K, should constitute 75.2%, 16.9%, and 7.5% of the total. The populations of the amino-hydroxy forms should be negligibly small. Such relative populations of 6-azacytosine isomers are expected to be trapped in low-temperature matrices.

**B. Monomers of 6-azacytosine isolated in low-temperature Ar matrices**

The infrared spectrum of monomers of 6-azacytosine isolated in a low-temperature Ar matrix is presented in Fig. 1. This experimental spectrum is well reproduced by the superposition of the theoretical spectra predicted for the amino-oxo (AO) and imino-oxo (IO1) forms of the compound (Fig. 1). The infrared bands characteristic of the AO tautomer appear in the experimental spectrum at 3560 (\(\nu_{\text{as NH}}\)), 3458 (\(\nu_{\text{N1H}}\)), 3436 (\(\nu_{s NH}\)), and 1730/1737 cm\(^{-1}\) (\(\nu_{C=O}\)), whereas the characteristic bands due to the IO1 form were observed at 3490 (\(\nu_{N1H}\)) and 1756 cm\(^{-1}\) (\(\nu_{C=O}\)). The higher relative intensities of the bands due to AO, with respect to those assigned to IO1, indicate a higher relative population of AO in Ar matrices. From the ratio of the experimental intensities of the \(\nu_{C=O}\) bands due to AO and IO1 (scaled by the theoretical infrared intensities of these bands), the ratio of AO and IO1 isomers in a matrix can be estimated as [AO]:[IO1] = 3.1:1.

Alongside the bands assigned to AO and IO1, a small population of IO2 is indicated by the \(\nu_{C=O}\) band observed at 1754 cm\(^{-1}\), which was assigned to form IO2. The assignment of the band at 1754 cm\(^{-1}\) to IO2, based on the effects of the photochemical IO1 \(\leftrightarrow\) IO2 transformation, is described in Sec. IV C 2.

**C. Photochemical transformations of matrix-isolated molecules of 6-azacytosine**

Monomers of 6-azacytosine isolated in Ar matrices were irradiated with continuous-wave, broadband, filtered UV light from a high-pressure mercury lamp or with monochromatic,
tunable, pulsed UV light generated in an optical parametric oscillator. Broadband irradiations with UV $\lambda > 350$ nm light and monochromatic irradiations with UV $\lambda \geq 332$ nm light did not induce any photochemical transformations of matrix-isolated isomers of 6-azacytosine. First indications of photo-processes transforming the AO isomer of 6-azacytosine were observed when Ar matrices were irradiated with monochromatic light at 328 nm or with broadband $\lambda > 320$ nm UV light. Upon such irradiation, the processes consuming the AO form revealed themselves as a very slow decrease of the IR bands due to the AO tautomer. Significantly more efficient phototransformation of AO into photoproducts was observed when Ar matrices were irradiated at shorter wavelengths: with monochromatic $\lambda = 324$ nm or with broadband $\lambda > 300$ nm UV light. The onset of the photoreactivity of 6-azacytosine, observed in the current work, is in agreement with the UV-spectra of this compound in solutions, showing the lowest-energy UV-absorption band extending to wavelengths longer than 310 nm.

1. **UV-induced amino-oxo $\rightarrow$ amino-hydroxy phototautomerism**

The effects of exposure of isolated 6-azacytosine monomers to $\lambda = 324$ nm or $\lambda > 300$ nm UV light are presented in Fig. 2. In this figure, the spectrum recorded after irradiation with monochromatic, pulsed $\lambda = 324$ nm light [trace (b)] is juxtaposed with the spectrum recorded after irradiation with broadband, continuous-wave $\lambda > 300$ nm UV light [trace (c)]. From this comparison, it is easy to notice that the effects of both types of irradiation are not exactly the same. For instance, there are new IR bands (e.g., these at 1396, 1266, and 1073 cm$^{-1}$) due to one of the photogenerated products, which are substantially more intense in spectrum (c) recorded after broadband UV ($\lambda > 300$ nm) irradiation than in spectrum (b) recorded after irradiation with pulsed UV ($\lambda = 324$ nm) light. The spectral positions and relative intensities of these bands are in a good agreement (Fig. 3) with the theoretically predicted spectrum of the amino-hydroxy AH1 form. Moreover, in the high-wavenumber range of the spectrum (Fig. 2), a new band ascribable to the $\nu_{OH}$ vibration appears at 3573 cm$^{-1}$ in the spectrum recorded after UV ($\lambda > 300$ nm) irradiation. These observations provide evidence of the oxo $\rightarrow$ hydroxy phototautomeric transformation converting the AO form of 6-azacytosine into the amino-hydroxy AH tautomer. Of the two AH1 and AH2 conformers of the amino-hydroxy tautomer, only the spectrum predicted for AH1 reproduces well the experimental bands of the photoproduct presented in Fig. 3. Hence, AH1 must be one of the major products generated upon excitation of AO with UV light with wavelengths from the 300–328 nm range. However, the generation of the AH1 product was significantly less pronounced when matrix-isolated 6-azacytosine was excited with pulsed UV ($\lambda = 324$ nm) light. The latter type of irradiation must lead to an effective transformation of the AO form of 6-azacytosine into a photoproduct other than AH1 (see Sec. IV C 3).

2. **UV-induced anti $\leftrightarrow$ syn (IO1 $\leftrightarrow$ IO2) transformation within the imino-oxo tautomer**

The anti $\leftrightarrow$ syn isomerization, transforming the IO1 and IO2 forms of 6-azacytosine into each other, occurred upon monochromatic or broadband UV irradiations at wavelengths shorter than 328 nm. For irradiations at wavelengths from the 328–300 nm range, this photoisomerization revealed itself (Fig. 4) as a decrease of the population of the IO1 form, accompanied by an increase of the population of IO2. The final stage of the phototransformation was always a photostationary state, corresponding to the photoequilibrium between the IO1 $\rightarrow$ IO2 and IO2 $\rightarrow$ IO1 conversions. The bands due to IO2, present already in the spectrum recorded before any irradiation and growing several times upon UV excitation at 328–300 nm, were observed (Figs. 4 and 5) at 1754, 1665, 1062/1057, 827, 702, and 590/588 cm$^{-1}$. The IO1 $\leftrightarrow$ IO2...
phototransformation can be most conveniently followed (Fig. 4) by the observation of intensity changes of the νC=O bands at 1756 cm\(^{-1}\) (due to IO1) and at 1754 cm\(^{-1}\) (due to IO2). The theoretically predicted absolute intensities of the νC=O bands of IO1 and IO2 are nearly exactly the same (Fig. 4). The comparison of the relative intensities of the νC=O bands due to IO1 and IO2, in the spectra recorded before any irradiation and after irradiation at 316 nm, shows that the photoprocess involves only the IO1 and IO2 forms converting into each other and that the total population of the imino-oxo tautomer (IO1 + IO2) neither increases nor decreases by excitations with UV light with wavelengths from the 328–290 nm range. Photoreversibility of the IO1 ↔ IO2 transformation was directly demonstrated when a matrix, previously irradiated at λ = 300 nm, was subsequently excited at λ = 290 nm. The latter irradiation led to a net IO2 → IO1 population shift, which is a shift in the opposite direction with respect to the net IO1 → IO2 transformation, observed when the matrix was irradiated at longer (328–300 nm) UV wavelengths.

Shorter-wavelength UV irradiation (280–270 nm) led to a destructive depopulation of both IO1 and IO2 imino-oxo forms. Prolonged UV irradiation at 280–270 nm resulted in total disappearance of the 6-azacytosine molecules adopting the imino-oxo tautomeric form.

3. UV-induced decarbonylation of 6-azacytosine and generation of 4-amino-1,2,3-(2H)-triazole

Phototransformations of 6-azacytosine, induced by irradiation of the compound with UV light from the 328–300 nm range, are reflected by the changes in the 3600–3400 cm\(^{-1}\) region of the IR spectrum (Fig. 2). Because the excitation at 328–300 nm led to the conversion of the AO form of the compound into photoproducts, the IR bands due to this form (observed at 3560, 3458, and 3436 cm\(^{-1}\)) substantially decreased in intensity [Figs. 2(b) and 2(c)]. A new band due
FIG. 7. Fragments of the infrared spectra of 6-azacytosine monomers isolated in an Ar matrix: (a, black) recorded after irradiation with monochromatic $\lambda = 270$ nm light; (b, red) recorded after subsequent irradiation with monochromatic $\lambda = 250$ nm light. The IR bands disappearing upon the latter irradiation were assigned to 4-amino-1,2,3-(2H)-triazole (see Fig. 8).

to the $\nu$OH vibration of the AH1 photoproduct appeared at 3573 cm$^{-1}$. Quite unexpectedly, upon irradiations at 328–300 nm, an IR band grew also at 3489 cm$^{-1}$, nearly exactly at the spectral position (3490 cm$^{-1}$) of the $\nu$N1H band owing to the IO1 form. This growing band cannot be due to the IO1 or IO2 imino-oxo forms. Upon irradiations at 328–300 nm, the sum of populations of IO1 and IO2 did not increase (as described above), but the band at 3489 cm$^{-1}$ grew several times, with respect to the initial intensity of the band at 3490 cm$^{-1}$. Hence, the band at 3489 cm$^{-1}$, growing upon excitations at 328–300 nm, must be the spectral indication of some photoproduct (other than the amino-hydroxy or imino-oxo forms of 6-azacytosine) that is photogenerated at the cost of decreasing population of AO. Moreover, the band at 3489 cm$^{-1}$ stays present in the spectra recorded after shorter-wavelength irradiations (at 280–270 nm), when the AO, IO1, and IO2 forms are already totally depopulated.

In search of the structure of the photoproduct being the carrier of the band at 3489 cm$^{-1}$, photodecarbonylation of 6-azacytosine has to be taken into account. This process, indicated by the appearance of the bands at 2153/2151/2149/2145/2139 cm$^{-1}$ (Fig. 6), occurred already upon irradiations at 328–320 nm. Structured bands appearing at 2155–2135 cm$^{-1}$ are characteristic of CO molecules trapped in the same matrix cage with other fragment(s) created from a molecule undergoing decarbonylation.\textsuperscript{23–25}

The infrared spectrum of the species photogenerated from AO and being the carrier of the band at 3489 cm$^{-1}$ was obtained, thanks to selective bleaching of this product that occurs upon excitation at 250 nm (Fig. 7). The spectrum consisting of the bands which disappeared upon irradiation at 250 nm is very well reproduced (Fig. 8) by the spectrum theoretically predicted for 4-amino-1,2,3-(2H)-triazole (TZ). This compound (consisting of the triazole ring with the amino group attached at position 4) is built of the atoms remaining (as one molecular fragment) after decarbonylation of 6-azacytosine (Fig. 9). The intense band at 3489 cm$^{-1}$ should be assigned to the stretching $\nu$N2H vibration in 4-amino-1,2,3-(2H)-triazole, whereas the weaker bands at 3503 and 3400 cm$^{-1}$ should be assigned to the antisymmetric and symmetric stretching vibrations of the NH$_2$ group attached at position 4 to the triazole ring.

FIG. 9. UV-induced transformations observed for 6-azacytosine monomers isolated in Ar matrices.
On the basis of the reasons described above, TZ has been identified as the second (alongside the AH1 form) product of the UV-induced conversions of the AO tautomer of 6-azacytosine. As it is illustrated in Fig. 2, the relative efficiency of the phototautomerization reaction converting AO into AH1 and the photodecarbonylation leading to the 4-amino-1,2,3-(2H)-triazole product is a sensitive function of the wavelength and continuous-wave or pulsed character of UV light used for excitation.

V. CONCLUDING DISCUSSION

The theoretical and experimental studies on tautomerism of 6-azacytosine revealed that it is drastically different from that of cytosine. Whereas the amino-hydroxy (AH) form of cytosine is the lowest-energy form of the compound, the analogous AH tautomer of 6-azacytosine has high relative energy (with respect to the amino-oxo or imino-oxo forms), and its population in the gas phase and in low-temperature matrices is negligible.

In the structure of the AH tautomer of 6-azacytosine, no hydrogen atoms are attached to any of the vicinal (N1 and N6) nitrogen atoms of the ring. The repulsion of the lone-electron pairs of N1 and N6 atoms is the most apparent factor that makes the energies of the AH1 and AH2 forms significantly higher than the energies of the AO and IO1 isomers. In these latter structures, instead of the destabilizing repulsion of the lone-pairs of N1 and N6 in AH, there is an energy-saving interaction between the lone-electron pair of N6 and the positively loaded hydrogen atom of the N1–H fragment.

The currently considered case of prototropic tautomerism of 6-azacytosine follows the rule that stems from our previous studies of heterocyclic compounds with two adjacent nitrogen atoms in the ring. For a number of such compounds, we have demonstrated that the tautomers with no hydrogen atoms attached to any of the two vicinal N-atoms of the ring have substantially higher energies than the forms with a hydrogen atom attached to one of these N-atoms. The tautomers of the latter type have been theoretically predicted as the most stable forms of 3(2H)-pyridazinone, 26,27 3(2H)-pyridazinethione, 28 3,6-dithiopyridazine, 29 1,3,4-thiadiazole-2-thione, 29 and maleic hydrazide. 20 For these compounds, the relative energies of the tautomers with no hydrogen atom attached to any of the adjacent nitrogen atoms were such high that the most stable forms with a hydrogen atom attached to only one of these vicinal nitrogen atoms were exclusively populated in low-temperature matrices obtained by freezing the gas phase equilibrium of the isomers. 27–32

The molecules of 6-azacytosine, adopting in freshly deposited Ar matrices the amino-oxo (AO) or imino-oxo (IO) tautomer, were excited with UV 328–300 nm light. Photochemical transformations of two types have been observed for molecules adopting the AO form. The first type of these phototransformations concerns the UV-induced phototautomerization transforming the AO form into the amino-hydroxy (AH) tautomer. Analogous oxo → hydroxy phototautomer transformations were previously observed for a number of matrix-isolated heterocyclic compounds such as 4(3H)-pyrimidinone, 33–35 2(1H)-pyridinone, 36,37 3(2H)-pyridazinone, 31 or cytosine. 15,35 Most probably, this phototautomerization transformation is governed by a Photo-Induced Dissociation Association (PIDA) mechanism, 39 where the hydrogen atom detaches from the N–H group of the UV-excited molecule (on the surface of the repulsive πσ* state) and then attaches back, but to the oxygen heteroatom.

Upon UV excitation, molecules of 6-azacytosine initially adopting the AO form underwent also photodecarbonylation. Both fragments generated in this photoprocess [carbon monoxide and 4-amino-1,2,3-(2H)-triazole] were identified on the basis of their IR spectral signatures. The relative efficiency of the photodecarbonylation process, in comparison to the efficiency of the competing oxo → hydroxy phototautomer reaction, was higher when pulsed UV light was used for irradiation.

UV 328–300 nm excitation of the imino-oxo (IO) form of 6-azacytosine induced bidirectional anti ↔ syn transformation, interconverting the two imino-oxo isomers (IO1 and IO2) into each other. Such phototransformation, converting the isomers by a flip of the H-atom (or a group of atoms) around a double C=N bond, is a classic photochemical process, observed for a number of matrix-isolated compounds. 40–42 including cytosine 15 and 1-methylcytosine. 43

Whereas tautomerism of 6-azacytosine is drastically different from that of cytosine, similarities as well as dissimilarities were found in the photochemical behavior of these two compounds. The oxo → hydroxy (AO → AH) phototautomer reaction and the IO1 ↔ IO2 photoisomerization are the patterns of photochemical behavior common for cytosine and 6-azacytosine. Extensive photodecarbonylation and generation of the product with a five-membered ring [4-amino-1,2,3-(2H)-triazole] was found only for the title compound of the current work.

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