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Photo-induced Dissociation of the N1–H Bond in the Imino Tautomers of Isocytosine in Water Medium

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Abstract: The imino tautomers of isocytosine were objects of investigation at the TD-DFT level of theory - TD BLYP/6-311++G(d,p). We studied the mechanisms of the H1-N detachment in these tautomers through excited-state reaction paths. It was proposed that these transformations occur through the $^1\pi\sigma^*$ excited-state reaction paths of the imino tautomers. The mechanisms involve dissociations of the N1–H bonds in the tautomers and lead to crossings between the reaction paths of $^1\pi\sigma^*$ and S_0 electronic states. One can suppose that such processes would facilitate the tautomerizations of the imino tautomers if further mechanisms have been found.

Keywords: conical intersections, TD-DFT calculations, excited states, H-detachments mechanisms, isocytosine.

INTRODUCTION

THE aromatic bioorganic compounds are major objects in a lot of theoretical and experimental studies due to their specific biology functions in living organisms. Among these compounds are the pyrimidine nucleic acid bases which are involved in the processes of encoding and transmission of genetic information.[1] It is well know that the pyrimidine bases are photostable molecules. That is way they are "selected" by the nature to prevent in a maximum degree the genetic code from the damaging impact of the UV light.[2–5] One interesting pyrimidine nucleobase is cytosine which is H-bounded complementary to guanine according to the Watson – Crick model.[1] Its rare analogue isocytosine is involved in a Watson – Crick base pair with the rare analogue of guanine – isoguanine. Isocytosine is tested and successfully used for the synthesis of new drugs,[6–10] new bioorganic compounds[13–18] and metalorganic compounds.[19] However as a rare analogue of cytosine it attracts much less attention than cytosine.

The crystal structure study of isocytosine has shown that two tautomeric forms of the compound are included in the unit cell: amino oxo 1H and 3H.[20] The space group is $P2_{1/n}$, while the unit cell parameters are a = 8.745, b = 11.412, β = 94,79°.[20,21] However the analysis of the IR spectra of UV irradiated isocytosine in an argon matrix has given evidence for more tautomeric form.[21–24] Those are the amino oxo and amino hydroxy forms of the compound. No information for the presence of the imino tautomers has been reported. Obviously these forms exhibit limited photostability and could be rapidly transformed into the stable amino oxo / hydroxy tautomers. Unfortunately this assumption does not have any reasonable explanation so far. Recently we proposed a mechanism explaining the oxo – hydroxy phototautomerism of isocytosine in water surroundings.[25] Our experiment gave information for the presence of these tautomers in water surroundings which is in accord with other observations.[26–29]

To explain the phototransformations of some pyrimidine derivatives Sobolewski has proposed so-called PIDA (photo-induced dissociation-association) mechanism.[30,31] The first step of the mechanism includes a dissociation of the N–H or O–H bond in the nucleic acid bases and their analogues along excited-state reaction paths. The second step is an association of the proton to another H-accepting centrum of the molecule. It has been shown that the active state involved in the PIDA mechanism is the repulsive $^1\pi\sigma^*$ excited state.[30–34] Such mechanisms for the imino forms of isocytosine have never been proposed so far.

Another channel for the non-radiative decay of the excited states of pyrimidines and purines to the ground state is connected with the deformations of the aromatic rings.[35–37] These mechanisms occur along the reaction paths of the $^1\pi\pi^*$ excited states of the compounds.[33,38–40]

The aim of the current research is to throw light upon the first step of the PIDA mechanism for some N1H imino tautomers of isocytosine in order to explain their limited photostability when irradiated with UV light. The study includes the mechanisms of photodissociation of the N_1–H bonds in the tautomers.

THEORETICAL METHODS

The ground-state equilibrium geometries of the tautomers under study were optimized at the TD-DFT level of computation - BLYP/6-311++G(d,p). Subsequent frequency calculations were performed in order to prove that the found structures are located in minima on the PESs. We used the relaxed-scan approach to follow the H-detachment mechanisms of the N1–H bonds in the tautomers of isocytosine in the ground state. This bond was elongated by a step of 0.08 Å. With the generated geometries we calculated their vertical excitation energies in order to follow the H-detachment mechanisms. The vertical excitation energies of the excited states along the reaction coordinates were computed with the same TD-DFT method and base set in the gas phase and in water surroundings. These energies are comparable with the experimental UV absorption spectra of organic compounds in water solution.[41,42] For example the calculated excitation energy of cytosine in water solution (PCM) is 4.88 eV while the UV absorption maximum is at 4.65 eV.[32,42]

The quantum chemical computations were carried out with the GAUSSIAN[43,44] and GAMESS-US[45] program packages. The first program was applied for the gas phase calculations while the second one for the computations in water medium (PCM). The TD-BLYP functional applied has shown high accuracy for the prediction of UV spectra of organic molecules in solvents.[46] TD-BLYP gives vertical excitation energies closest to the experimental UV absorption maxima of organic compounds among a great number of tested functionals and other *ab initio* methods applied together with solvent models.[46]

RESULTS AND DISCUSSIONS

Ground-state Equilibrium Geometries of the Tautomers

The ground-state equilibrium geometries of the tautomers under study are given in Figure 1. They are optimized in water surroundings. In the study was included also one amino oxo tautomer **D** in order to compare the results with the imino forms. Tautomer **D** has been proven to be available in water solution of isocytosine.[25]

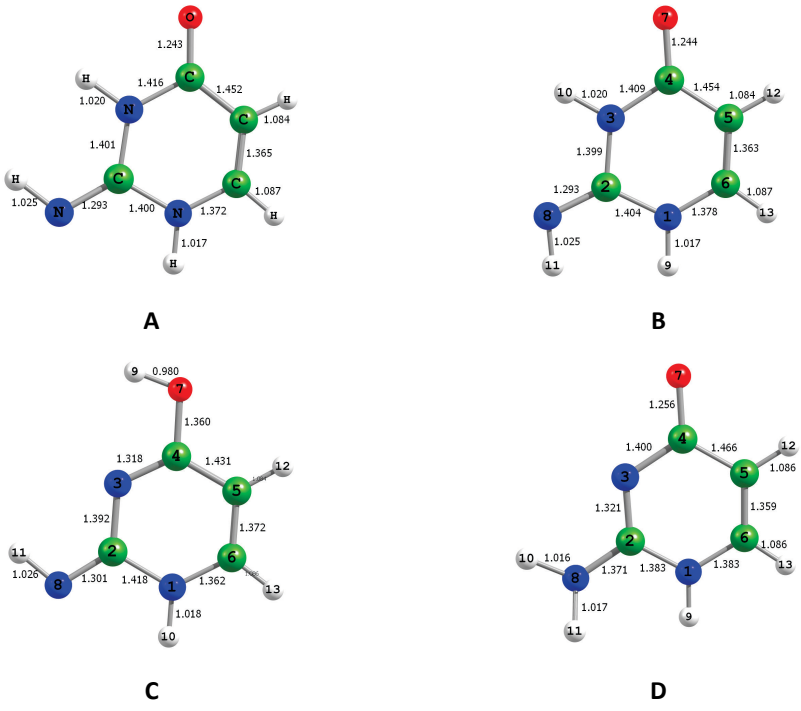

Figure 1. Optimized ground-state equilibrium geometries of the tautomers of isocytosine in water surroundings.

Table 1. Structural parameters of the ground-state equilibrium geometries of the tautomers optimized in water surroundings according to PCM

Parameter	Tautomer A	Tautomer B	Tautomer C	Tautomer D
< $N_1C_2N_3$	112.9	112.9	116.5	123.0
< $N_3C_4O_7$	119.5	119.8	118.1	120.0
< $C_4C_5C_6$	119.6	119.6	115.3	119.6
< $C_2N_1C_6$	123.7	123.5	123.1	119.8
< $H_{10}N_8C_2N_3$	–179.6	–0.3	–179.7	167.6
< $H_{11}N_8C_2N_3$	–0.1	179.9	179.7	–157.7
< $N_1C_2N_3C_4$	0.3	0.5	0.9	0.7
< $O_7C_4N_3C_2$	–179.9	179.9	–179.9	178.4
< $H_{12}C_5C_6N_1$	179.9	–179.9	179.9	179.7
< $H_{13}C_6N_1C_2$	179.5	179.6	–179.9	178.3

All angles are given in degrees.

The analysis of the free energies of tautomers in solvent shows that in water medium tautomer **D** is the most stable form (E = –394.967808 a.u.). The remaining tautomers have the following relative energies referred to the free energy of tautomer **D**: tautomer **A** (9.4 kJ mol^{-1}), tautomer **B** (10.7 kJ mol^{-1}), and tautomer **C** (54.3 kJ mol^{-1}).

According to the structural data listed in Table 1 all tautomers exhibit almost planar geometries because of the strong conjugation in their molecules. Only the amino group in tautomer **D** shows a slight pyramidal character which can be seen from the calculated values of the bond angles <$H_{11}N_8H_{10}$ = 115.4°, <$H_{11}N_8C_2$ = 118.6°, and <$C_2N_8H_{10}$ = 118.6°. The sum of these angles is Σδ = 352.6° which shows a deviation from the planar structure of the amino group: Δδ = 360 – Σδ = 360° – 352.6° = 7.4°.

Vertical Excitation Energies

The calculated vertical excitation energies of the tautomers under study are listed in Table 2. In Figure 2 are illustrated the gas phase molecular orbitals of tautomer **D** which are involved in the electron transitions. One can see that the lowest-lying excited state of tautomers **A**, **B**, and **C** in both

Table 2. Vertical excitation energies (eV) of the tautomers found at the TD-BLYP/6-311++G(d,p) level of theory

Gas phase							
A		**B**		**C**		**D**	
	eV		eV		eV		eV
$^1\pi\pi^*$	3.934	$^1\pi\pi^*$	3.931	$^1\pi\pi^*$	3.392	$^1n\pi^*$	3.594
$^1n\pi^*$	4.015	$^1n\pi^*$	4.016	$^1n\pi^*$	4.046	$^1n\sigma^*$	3.774
$^1\pi\sigma$*	4.690	$^1\pi\sigma^*$	4.415	$^1\pi\sigma^*$	4.341	$^1n\pi^*$	4.005
$^1n\sigma^*$	4.878	$^1n\pi^*$	4.682	$^1n\sigma$*	4.701	$^1\pi\sigma$*	4.349
$^1n\sigma$*	5.020	$^1n\sigma$*	4.752	$^1n\pi^*$	4.764	$^1n\sigma$*	4.563
$^1\pi\sigma$*	5.095	$^1\pi\pi$*	5.056	$^1\pi\sigma$*	5.139	$^1\pi\pi^*$	4.680
Water surroundings (PCM)[25]							
$^1\pi\pi^*$	3.919	$^1\pi\pi^*$	3.924	$^1\pi\pi^*$	3.534	$^1n\pi^*$	4.066
$^1n\pi^*$	4.268	$^1n\pi^*$	4.337	$^1n\pi^*$	4.467	$^1n\pi^*$	4.557
$^1\pi\sigma^*$	5.017	$^1n\pi^*$	4.898	$^1\pi\sigma^*$	4.765	$^1\pi\pi^*$	4.722
$^1n\pi^*$	5.061	$^1\pi\sigma^*$	4.999	$^1n\pi^*$	4.949	$^1\pi\pi^*$	4.839
$^1\pi\pi^*$	5.141	$^1\pi\pi^*$	5.119	$^1\pi\sigma^*$	5.086	$^1n\sigma^*$	5.085
$^1\pi\sigma^*$	5.454	$^1n\pi^*$	5.530	$^1\pi\pi^*$	5.223	$^1\pi\sigma^*$	5.217

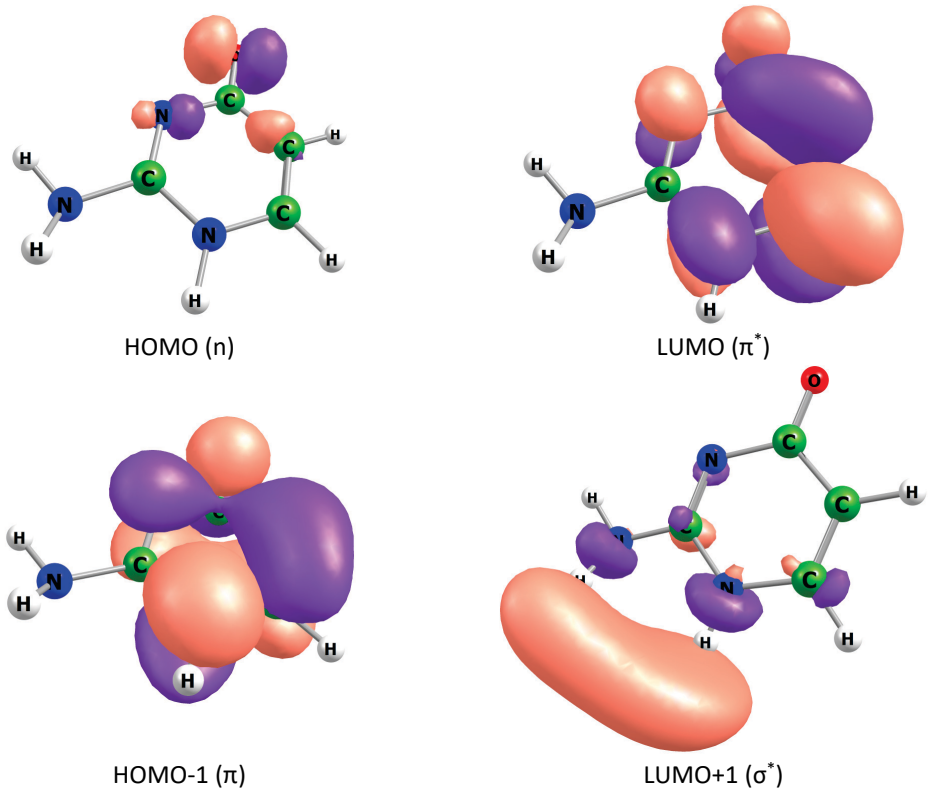

Figure 2. Gas phase molecular orbitals of oxo amino tautomer **D** involved in the electron transitions.

phases (gas and liquid – water) is the spectroscopically active $^1\pi\pi^*$ excited state. For tautomer **D** (oxo amino) the $^1\pi\pi^*$ excited state has energy of 4.68 eV in the gas phase which is in accord with other investigations.[25,32] In water surroundings it increases slightly the energy as for cytosine according to the investigations of Improta et al.[42] The $^1\pi\pi^*$ excited states can be directly populated by excitation of the ground states of tautomers. The dark $^1n\pi^*$ excited states of the tautomers **A**, **B**, and **C** have higher energies than the $^1\pi\pi^*$ excited states. Only for oxo amino tautomer **D** it is the lowest –lying excited state. However in water medium it increases drastically its energy, about 0.5 eV. For tautomer **D** we found two bright $^1n\sigma^*$ excited states which are located down the first $^1\pi\pi^*$ excited state. It is interesting to mention that these bright states increase drastically their energies in water surroundings. In water medium the $^1\pi\pi^*$ excited state of tautomer **D** is the lowest bright excited state. The interesting repulsive $^1\pi\sigma^*$ excited state has energy about 4.5 eV for tautomers in the gas phase. As became clear above this state is directly engaged in the PIDA mechanism.[30,31,33,34] In water surroundings it increases the energy to about 5 eV. This fact can leads to the conclusion that the H-detachment process of the tautomers in water medium requires more energy to occur than in the gas phase.

According to the theoretical study of Schreiber on the electronically excited states of 1H oxo amino cytosine in the gas phase the CAPT2 method predicts the best estimate of the energy of the $^1\pi\pi^*$ excited state followed by the TD-DFT methods.[47] The best estimate of the $^1\pi\pi^*$ vertical excitation energy of 1H oxo cytosine is 4.66 eV,[47] while the found here value for the 1H oxo isocytosine tautomer is 4.68 eV (see Table 2). The last value exactly matches the one found for cytosine by Improta at the MS-CASPT2 theoretical level.[42] The review paper of Improta has reported about a comparative analysis of excitation energies of DNA / RNA bases found at different levels.[42] In this paper the accuracy and the reliability of the TD-DFT methods has been commented in positive light.[42]

Excited-state Reaction Paths of the H-Detachments

Tautomer A

In tautomer **A** there are two N_{ring}–H bonds which can be dissociated through excited states. These two bonds are included in the current study. The excited-state reaction paths of the H-detachments are illustrated in Figures 3 and 4.

The presented reaction profiles of the mechanisms of H-detachment of the bonds N1–H and N3–H occur along the excited-state reaction paths of the repulsive $^1\pi\sigma^*$

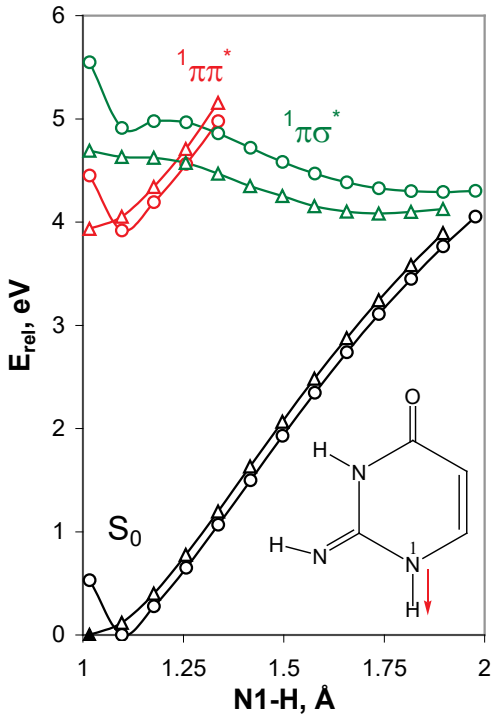

Figure 3. Excited-state reaction paths of the N1–H detachment in tautomer **A** (o - water surroundings, Δ - gas phase, ▲ - optimized geometry taken for the relaxed-scan)

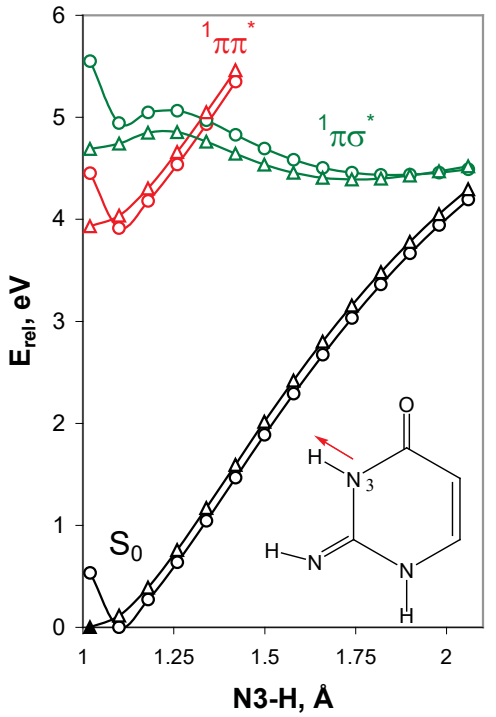

Figure 4. Excited-state reaction paths of the N3–H detachment in tautomer **A** (o - water surroundings, Δ - gas phase, ▲ - optimized geometry taken for the relaxed-scan).

excited states. The two mechanisms lead to crossings between the reaction paths of the S_0 and $^1\pi\sigma^*$ electronic states and imply conical intersections S_0/S_1. From such crossing point each mechanism could proceed, by internal conversion, in two directions: to the ground state of the same tautomer or to the ground state of another tautomer of isocytosine.

As seen the reaction paths of the ground state and the $^1\pi\pi^*$ excited state in the gas phase and in water medium are close in energy. Larger energy difference in both media show the reaction curves of the $^1\pi\sigma^*$ excited state. The energy of this state is lower in the gas phase than in water surroundings. This energy gap is more pronounced for the N1–H detachment mechanism.

For the two mechanisms discussed the $^1\pi\pi^*$ excited state shows an increase of the energy along the reaction coordinate. However this spectroscopically bright excited state can be directly populated through an optical transition from the ground state. In this way it can play a significant role for the further population of the repulsive $^1\pi\sigma^*$ excited state. It can occur along the $^1\pi\pi^*$ excited-state reaction path through a crossing point $^1\pi\pi^*/^1\pi\sigma^*$. For the N1–H photodissociation mechanism such a switch between the excited states requires an energy of 0.8 eV.

For the N3–H detachment mechanism (Figure 4) the $^1\pi\sigma^*$ excited-state reaction path in water surroundings shows a low energy barrier of 0.12 eV. Furthermore the population of the $^1\pi\sigma^*$ excited state from the $^1\pi\pi^*$ excited state through a conical intersection $^1\pi\pi^*/^1\pi\sigma^*$ occurs with an energy barrier of 1.02 eV. It is higher than for the N1–H dissociation mechanism.

Tautomer B

In Figure 5 are illustrated the excited-state reaction paths of the N1–H detachment mechanism of tautomer **B** of isocytosine. Again the process occurs along the $^1\pi\sigma^*$ excited-state reaction path in both media. We estimated a larger negative energy gradient of the excited-state reaction curve in the gas phase than in water surroundings. Along the $^1\pi\sigma^*$ excited-state reaction path there is no any energy hindrance for the H-detachment of tautomer **B**. The only energy barrier that should be overcame is for the excited-state "jump" $^1\pi\pi^* \rightarrow {}^1\pi\sigma$ (0.9 eV in water surroundings and only 0.6 eV in the gas phase) if the $^1\pi\sigma^*$ excited state is populated from the bright $^1\pi\pi^*$ excited state.

Tautomer C

The energy curves illustrated in Figure 6 show that the H-detachment of the N1–H bond of tautomer **C** occurs easy along the $^1\pi\sigma^*$ excited-state reaction path in the gas phase and in water surroundings. In water medium the energy decrease along the $^1\pi\sigma^*$ excited-state reaction path is 0.48 eV while in the gas phase it is 0.29 eV. In water medium

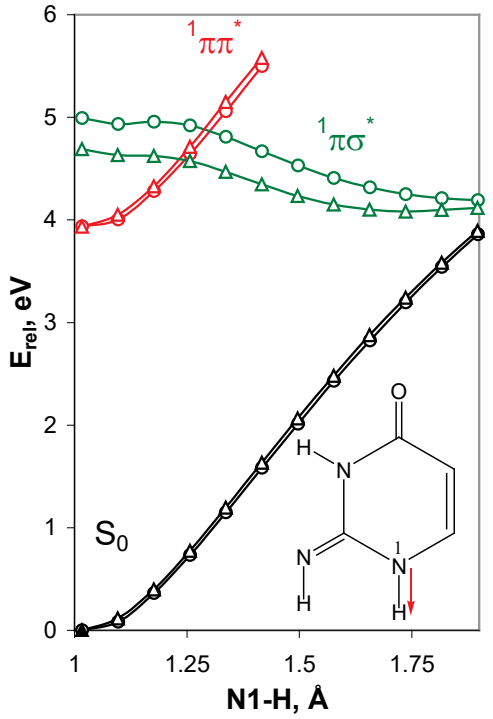

Figure 5. Excited-state reaction paths of the N1–H detachment in tautomer **B** (○ - water surroundings, Δ - gas phase, ▲ - optimized geometry taken for the relaxed-scan).

there is a low energy barrier along the excited-state reaction path of the driven state (0.14 eV). The non-radiative transition $^1\pi\pi^* \rightarrow {}^1\pi\sigma$ trough the crossing point $^1\pi\pi^*/{}^1\pi\sigma^*$ requires an energy barrier of 1.16 eV in water surroundings.

To follow the solvent influence on the studied photochemical reactions we modelled the reaction curves of the same process including acetonitrile as a solvent. The results are illustrated in Figure 7. As seen the reaction curves show completely different behaviour. The H-detachment is accompanied with a drastic increase of the energy of the ground state and this of the $^1\pi\sigma^*$ excited state. The reaction curves of these states lead to a crossing point S_0/S_1 which has higher energy than the vertical excitation energy of the $^1\pi\sigma^*$ excited state. The increase in energy of the $^1\pi\sigma^*$ excited state is 2.8 eV. In other words the photoreaction in acetonitrile should be forbidden.

Tautomer D

Tautomer **D** is an amino oxo form of isocytosine which is included in the study only for comparison with the imino tautomers. The excited-state reaction paths of the N1–H detachment mechanism for this tautomer are illustrated in Figure 8. As seen in water surroundings the energy of the $^1\pi\sigma^*$ excited state decreases only 0.5 eV along the reaction path. However in the gas phase there is an increase of the reaction energy of the same state along the reaction

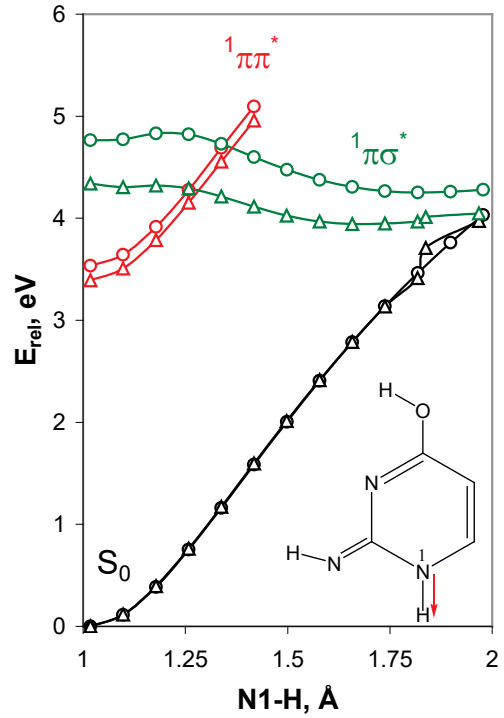

Figure 6. Excited-state reaction paths of the N1–H detachment in tautomer **C** (○ - water surroundings, Δ - gas phase, ▲ - optimized geometry taken for the relaxed-scan).

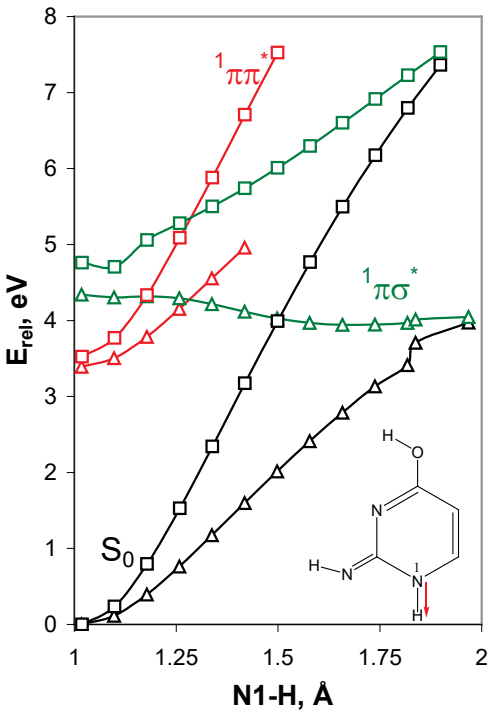

Figure 7. Excited-state reaction paths of the N1–H detachment in tautomer **C** (□ - acetonitrile surroundings, Δ - gas phase, ▲ - optimized geometry taken for the relaxed-scan).

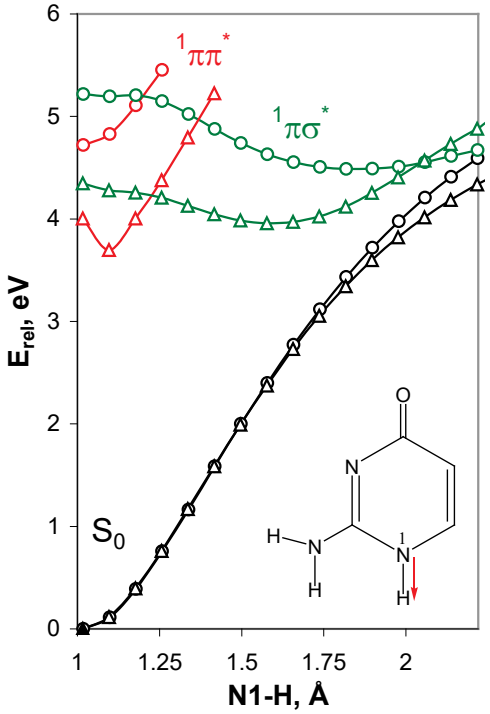

Figure 8. Excited-state reaction paths of the N1–H detachment in tautomer **D** (o - water surroundings, Δ - gas phase, ▲ - optimized geometry taken for the relaxed-scan).

coordinate. Moreover the $^1\pi\sigma^*$ excited-state reaction path shows a minimum which could be slowing down the H-detachment process through excited state by trapping of the excited system into it. Such shallow minimum is also available in water surroundings. All the findings support the conclusion that the H-detachment process of the amino oxo form is energetically hindered or with other words the probability to occur is very low. With respect to this mechanism tautomer **D** should be photostable.

CONCLUSIONS

We performed theoretical study of the N1–H bond dissociation mechanisms in the imino tautomers of isocytosine at the TD-BLYP/6-311++G(d,p) level of theory. The aim of the research was to explain the experimental fact why the imino tautomers of the compound are not observed in the irradiated water solution of isocytosine. The performed investigation of the N1–H detachment mechanisms of the imino tautomers showed that they can dissociate this bond along the $^1\pi\sigma^*$ excited-state reaction paths and crossing points S_0/S_1. We believe that the mechanisms (after the crossing points S_0/S_1) proceed further with H-attachments to form stable amino tautomers.

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