

The shape of the conical intersections of monohydrated pyrimidine bases cytosine, uracil, and thymine: a theoretical study

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Abstract Three conical intersections of monohydrated cytosine, uracil, and thymine were found between the S_0 and S_1 states. The pyrimidine bases in these conical intersections have unusual shape with rather distorted aromatic rings caused by the strong interactions between the pyrimidines and the water molecule. The conical intersections of uracil and thymine monohydrates have structures with considerable out-of-plane deviation of one of the carbonyl groups. The conical intersection of cytosine monohydrate showed a ring cleavage of the N^1-C^2 bond, while the NH_2 group is almost perpendicular to the aromatic ring. The three conical intersections show a tendency to form Dewar forms. Thus, in the theoretical study we included the possible Dewar forms of the monohydrated pyrimidine bases closely related to the structures of the conical intersections.

Keywords Branching space · Conical intersections · CASSCF calculations · Cytosine · Thymine · Uracil

Introduction

Cytosine, uracil, and thymine are the major chromophores of nucleic acids. Absorbing UV light (near 260 nm) they lead to $^1\pi\pi^*$ excited states which can be observed as major absorption maxima in the UV spectra. Canuel et al. [1] and Kang et al. [2] demonstrated experimentally that pyrimidine bases undergo ultrafast relaxation of the excited states to the ground electronic state S_0 . These relaxations occur in

the picosecond timescale. For cytosine, uracil, and thymine the relaxation times are 1.86, 1.05, and 5.12 ps [1]. Such favorable internal conversion processes in pyrimidine bases provide a self-protection mechanism preventing photochemical reactions induced by UV radiation.

Computational results for isolated cytosine [3–6], uracil [7], and thymine [8, 9] showed that the ultrafast decay is due to the energetically accessible conical intersection S_0/S_1 . For uracil it has been discussed that the most common internal conversion of the $^1\pi\pi^*$ excited state passes through an ethylene-like conical intersection S_0/S_1 , i.e., a conical intersection with one hydrogen atom from the $C=C$ double bond which is almost perpendicular to the aromatic ring [10–12]. The same structure of the ethylene-like conical intersection S_0/S_1 was also described for thymine [9, 11, 12] and cytosine [11]. Some authors found a low-lying conical intersection S_0/S_1 for thymine in which the methyl group is perpendicularly situated with respect to the aromatic ring [11]. No low-lying conical intersections S_0/S_1 associated with out-of-plane deformations of the carbonyl oxygen atoms have been reported so far.

Shukla and Leszczynski [13] performed a comparison between uracil and trihydrated uracil based on the configuration interaction technique (CIS)-calculated vertical excitation energies of the systems. They predicted vertical excitation energies of the bright $^1\pi\pi^*$ excited states of the system at 6.83 and 6.74 eV. The absorption maximum of uracil is at 5.1 eV in the gas phase [14] and 4.8 eV in aqueous solution [15]. As Neiss et al. [16] reported, the CIS method always gives higher energies for vertical excitation energies of the bases than, for example, density functional theory (DFT) or multi-reference configuration interaction (MRCI) methods. The absorption maxima of thymine in the gas phase and aqueous solution are at 4.8 eV [14] and 4.7 eV [17]. These data show that the hydration of uracil

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and thymine leads to the reduction of vertical excitation energies. In other words, the hydration of these bases provokes a red shift of the UV absorption maximum. The gas phase absorption maximum of cytosine is at 4.5 eV [18]. In aqueous solution this maximum is blue-shifted (at 4.7 eV) [19, 20].

Blancafort and Migani [21] and Yoshikawa and Matsika [22] discussed the influence of the water molecule on the energy and structures of monohydrated cytosine and uracil. However, they examined water molecules as a small perturbation to the pyrimidine ring. The hydration of the pyrimidine nucleobases is the subject of a lot of theoretical papers. For example, Aleman [23, 24] explored the solvation of cytosine and thymine bases by using discrete/self-consistent reaction field (SCRf) models. The analysis of the free energies of solvation showed that the most stable monohydrated cytosine is formed between the amino group of the compound and the water molecule [23, 24]. Thymine forms a stable complex with the carbonyl oxygen which is closest to the CH₃ group [23]. The theoretical investigation by van Mourik et al. [25, 26] showed that the most stable monohydrated uracil complex is formed between the water molecule and the oxygen atom of uracil from the carbonyl group which is situated between the two nitrogen atoms from the ring.

The purpose of the current study was to find low-lying conical intersections S_0/S_1 in monohydrates of cytosine, uracil, and thymine which mediate the relaxations of the excited states of these supersystems to the ground state. These conical intersections are important because they would be directly involved in the intermolecular proton transfer processes occurring in the ground or excited state.

Results and discussion

Geometry optimization of the conical intersections

The structures of the hydrated and anhydrous conical intersections are illustrated in Fig. 1. Selected structural parameters of the optimized conical intersections are listed in Table 1. The anhydrous conical intersections have the same structural parameters because they were studied by single-point calculations. The water molecule plays a crucial role in the monohydrated conical intersections. It binds the two oxygen atoms in uracil and thymine and predisposes a direct intermolecular proton transfer between these atoms. In the conical intersection CI_C such a proton transfer is expected between the amino group and the oxygen atom.

This structure of the conical intersection is closely related (by the mutual orientation of the water and cytosine molecules) to the most stable cytosine–water complex

found by Aleman [23]. Such structures of the conical intersections with respect to the pyrimidine rings have never been found. The conical intersections of monohydrated and anhydrous cytosine (CI_C) show a ring cleavage at the N^1-C^2 bond which is associated with a disruption of the aromaticity of the pyrimidine ring. Because the N^1-C^2 bond is extremely long (2.095 Å), it shows fragmentation of the cytosine molecule. The conical intersection CI_C (Fig. 1a) forms weak H-bonds (over 2 Å) with water and shows a trend for disruption of the H-bonded complex. Nevertheless, such conical intersections can not be found (by optimizations) without the water molecule (e.g., CI_C). The weak H-bonds reflect the bonding parameters of CI_C which will be discussed below. The data in Table 1 show the largest distortion of the aromatic ring for the conical intersection CI_C . The bond N^1-C^2 bond is long, but the bond N^1-C^6 is quite short, resembling a double bond.

The conical intersections of monohydrated uracil (CI_U) and thymine (CI_T) are almost identical in structure. They have one short H-bond between the water oxygen atom and the hydrogen atom from the OH group of uracil and thymine. In these conical intersections H-bonds between the carbonyl oxygen atom and the water hydrogens are also formed. The structures of the conical intersections indicate a direct proton transfer between the OH and O=C groups of uracil and thymine, assisted by a water molecule. Such proton migration in anhydrous uracil and thymine is not possible in the ground state. Miles et al. [27] reported a UV maximum of uridine at 4.77 eV in aqueous solution. Our investigation of possible tautomers of (deoxy)uridine unambiguously showed that this maximum corresponds to the hydroxo form of uracil in uridine [28]. In other words, the hydroxo form of uracil (or thymine) is also important and the photochemical water-assisted proton transfer between oxo and hydroxo tautomers of uracil (and thymine) can be mediated by the conical intersection CI_U (and CI_T). The deviation of the N^1 atom from the aromatic ring plane (see Table 1) for CI_U and CI_T is smaller than for the conical intersection CI_C . In the conical intersection CI_U the water molecule forms a hydrogen bridge with the same oxygen atom for uracil as in the most stable monohydrated uracil [25].

Uracil and thymine have rather unusual shape in the conical intersections CI_U/CI_U' and CI_T/CI_T' . As is known [10–12], the $^1\pi\pi^*$ excited states of these nucleic acid bases relax through an ethylene-like conical intersection associated with a twisting around the C=C double bond. Obviously, H-bonded water drastically changes the photochemistry of the bases and allows new conical intersections to mediate the photoprocesses, in particular photo-induced proton transfers. The mechanisms of these processes will be the subject of our future research. In this regard, the anhydrous conical intersections do not

Fig. 1 Conical intersections of monohydrated and anhydrous **a** cytosine, **b** uracil, and **c** thymine. The monohydrated forms were optimized at the complete active space self-consistent field (CASSCF)(6,6)/6-31G* level, whereas the anhydrous forms originate from the monohydrated systems (single-point calculations)

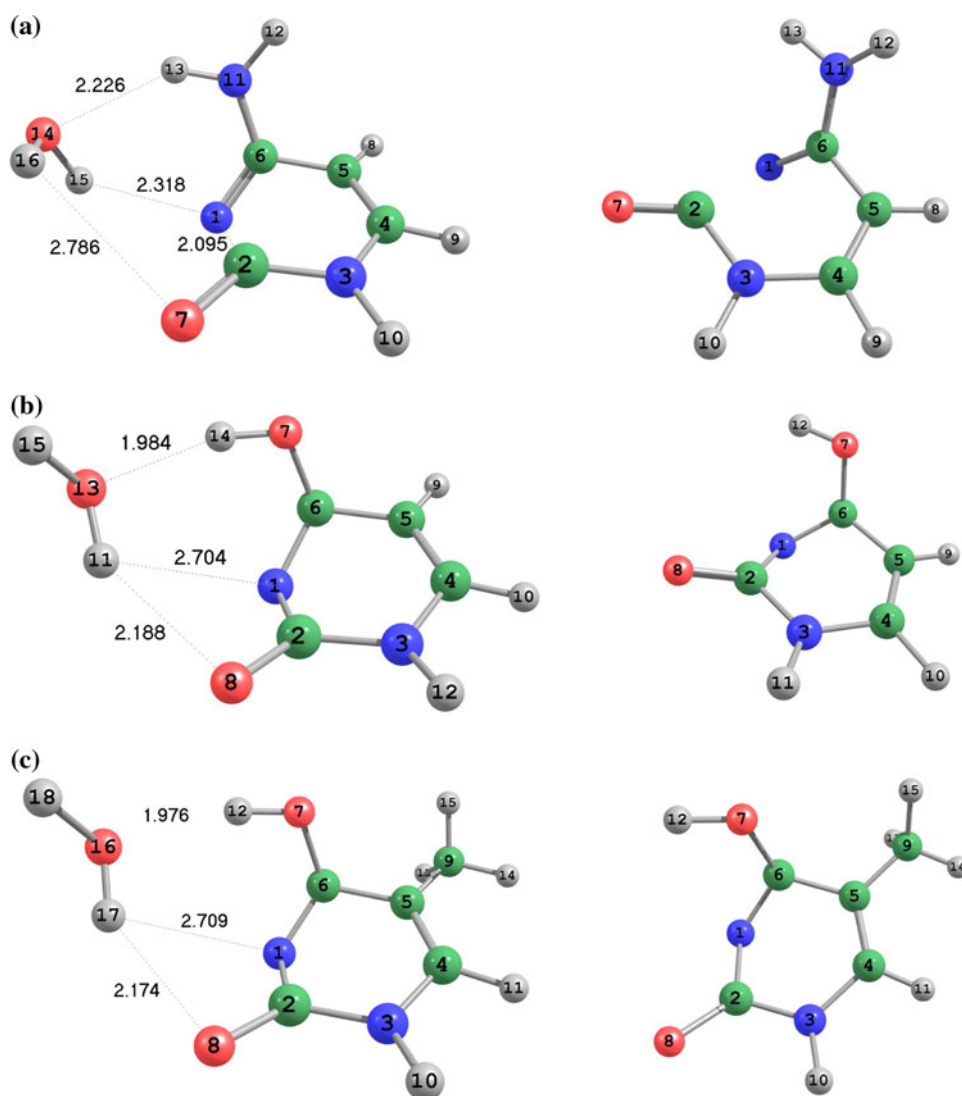


Table 1 Selected structural parameters of the conical intersections

Parameter	CI _C	CI _U	CI _T
$r(N^1C^2)$	2.095	1.401	1.401
$r(C^2N^3)$	1.362	1.360	1.356
$r(N^3C^4)$	1.402	1.414	1.418
$r(C^4C^5)$	1.345	1.341	1.343
$r(C^5C^6)$	1.483	1.484	1.490
$r(N^1C^6)$	1.303	1.420	1.419
$d(N^1C^2N^3C^4)$	27.9	18.4	18.2
$d(C^2N^3C^4C^5)$	-1.0	6.4	6.8
$d(N^3C^4C^5C^6)$	0.6	0.1	-0.4
$d(N^3C^2N^1C^6)$	-61.3	-51.5	-51.3
$d(N^1C^6N^1C^2)$	-96.6	-	-
$d(O^7C^6N^1C^2)$	-	-75.3	-75.4

r in Å; d in degree

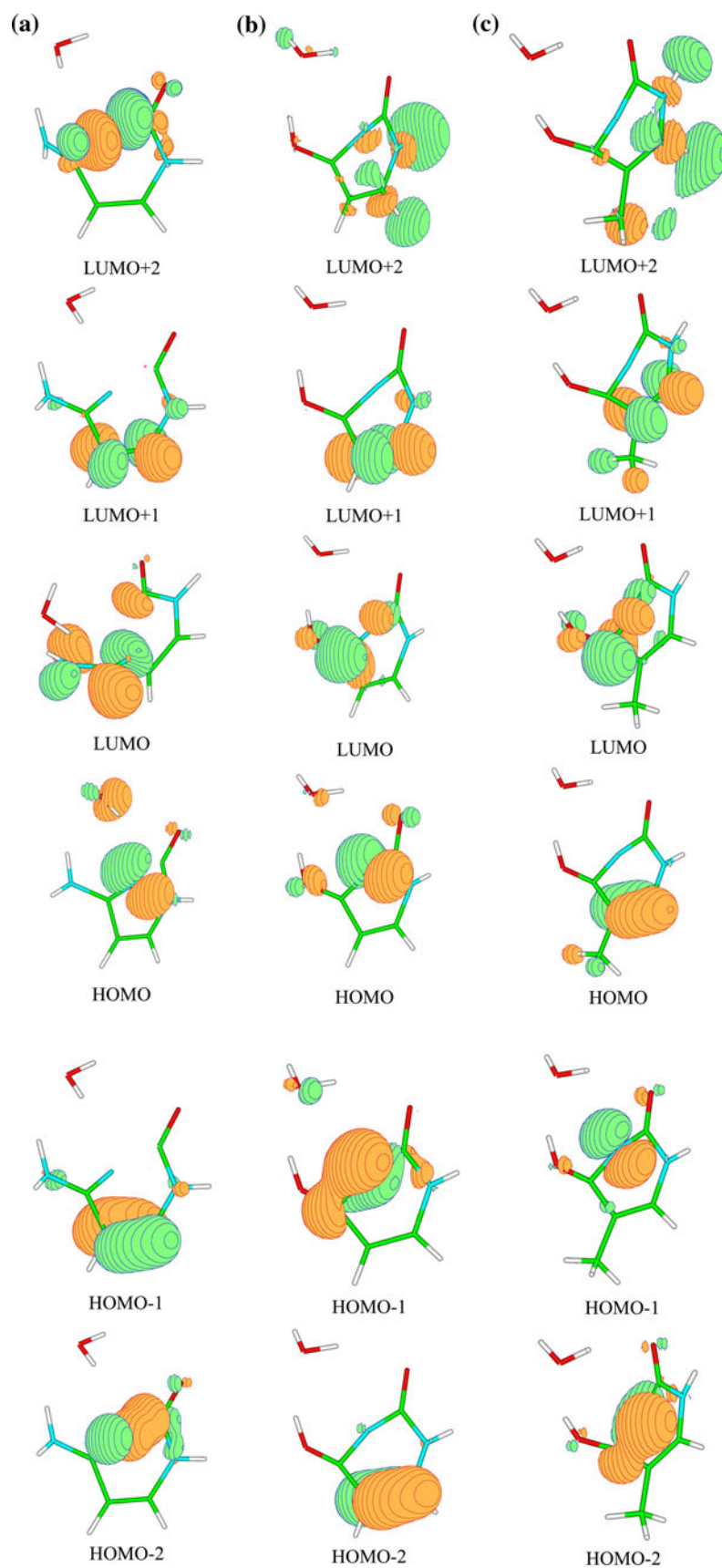
contribute to the relaxation proton transfer mechanisms of the excited pyrimidines and they are only involved in the current study to understand the role of the water molecule.

Analysis of active molecular orbitals of the conical intersections

Because of the importance of the monohydrated conical intersections we performed an orbital analysis to understand the origin of the crossing of the two states S_0 and S_1 . Figure 2 shows the active orbitals of the monohydrated conical intersections.

As can be seen, the strong distortion of the aromatic structures leads to the inclusion of σ -orbitals in the active space of each CI (the active space is not manipulated). The lowest unoccupied molecular orbital (LUMO) of the

Fig. 2 Molecular orbitals from the active space of monohydrated **a** cytosine, **b** uracil, and **c** thymine



conical intersection CI_C is of σ -type and it is situated along the N^1-C^2 bond; the orbital LUMO+2 behaves similarly. All other orbitals are of π -type. The highest occupied molecular orbital (HOMO) of this conical intersection can be assigned as a π -orbital with a contribution from one of the sp^3 -hybridized orbitals of the water oxygen atom.

The active space of the conical intersections CI_U and CI_T has one σ -orbital less than the active space of CI_C . This σ -orbital has the highest energy and involves the atoms N^3 and C^4 and the hydrogen atoms which are bound to these atoms. It is interesting to note that in the active orbitals HOMO, LUMO+1, and LUMO+2 of CI_T the $1s$ atomic orbital (AO) of the methyl hydrogen atoms contributes to the electron density distribution; this can be explained by the hyperconjugation which exists between the methyl hydrogen atoms and the aromatic ring.

Gradient difference ($|GD|$) and derivative coupling ($|DC|$) vectors

The magnitudes of the branching space vectors $|GD|$ and $|DC|$ of the monohydrated and anhydrous conical intersections are listed in Table 2.

The lowest values for these vectors were calculated for the conical intersections of cytosine. The data show that the anhydrous conical intersections have slightly higher values for $|GD|$ and slightly lower values for $|DC|$ than those of monohydrated conical intersections. To understand the nature of the conical intersections we visualized the vectors $|GD|$ and $|DC|$ as normal modes. They are illustrated in Fig. 3.

For the conical intersection CI_C the vectors show a trend to close the aromatic ring or to form the Dewar structure. The latter is also valid for the conical intersections CI_U and CI_T . One can suppose that the Dewar forms of the examined monohydrates could be formed photochemically through the monohydrated conical intersections (Fig. 1). This fact explains the inclusion of the Dewar structures in the current study.

The vectors of anhydrous conical intersections show atom displacements quite different from these of monohydrated conical intersections. The $|GD|$ vector indicates

the possibility of these structures forming the usual conical intersections known for pyrimidine bases [3–12], i.e., conical intersections related to the C=C out-of-plane deformations. The $|DC|$ vector of the conical intersection CI_C clearly shows a tendency toward a ring restoration. A considerable stabilization of the monohydrated conical intersections is observed due to the intermolecular hydrogen bonds (see Table 2). The bonding energies are rather high which means that the monohydrated conical intersections are stable dimers. The large affinity of the amino group and the oxygen atom(s) of pyrimidine bases to form H-bonded systems with water is the only reason for the formation (optimization) of such conical intersections.

The multi-configurational self-consistent field (MCSCF)(10,9) energy gaps between the states S_0 and S_1 of the conical intersections CI_C , CI_U , CI_T , $CI_{C'}$, $CI_{U'}$, and $CI_{T'}$ are 0.06, 0.23, 0.21, 0.17, 0.23, and 0.23 eV.

H-bonded complexes

We optimized (MP2/6-31G*) the structures of the H-bonded complexes (as stable minima) of cytosine, thymine, and uracil with one water molecule, which potentially can be formed by the conical intersections through an ultrafast deactivation of the excited electronic states. In all cases the pyrimidine ring has almost planar structure. Discussion of the planarity and non-planarity of the monohydrated pyrimidine bases can be found in work by Isayev et al. [29, 30] based on Car–Parrinello molecular dynamics simulations. They found that each pyrimidine base has a non-planar effective conformation despite the fact that the ground state equilibrium geometry is planar [30]. More frequently the population of the planar geometry of the pyrimidine ring is not more than 30% [29]. From this point of view when we mention below “planar bases” we have in mind all these findings.

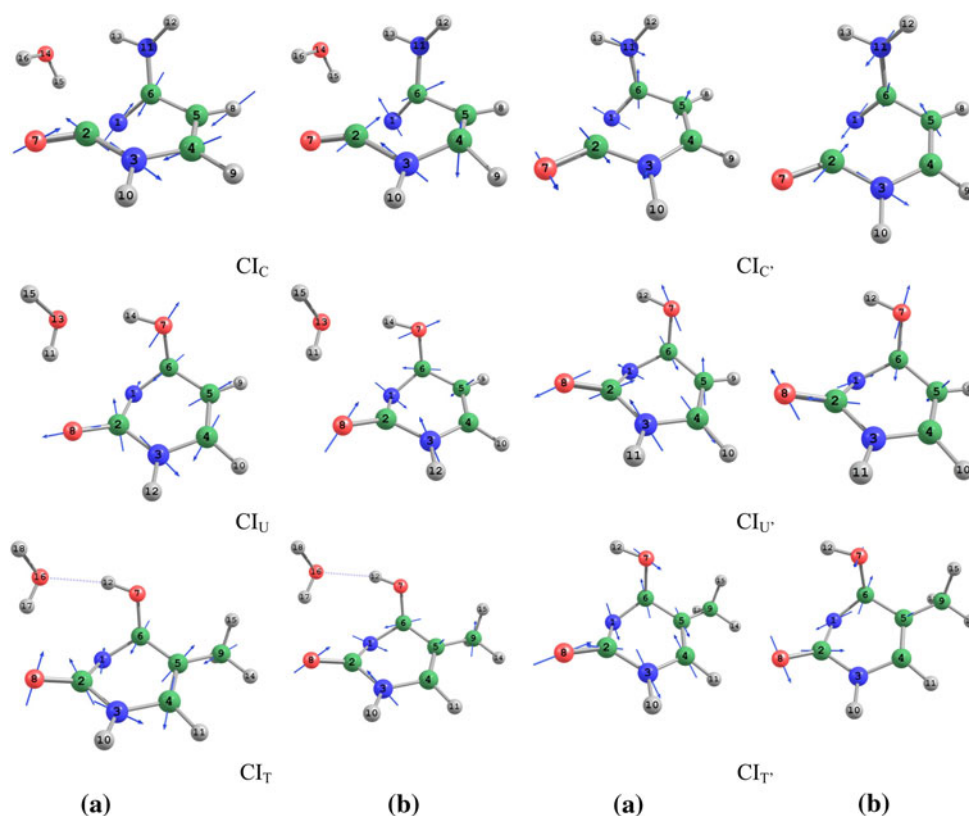
The Dewar structures of the complexes which could be also formed from the excited states via the conical intersections CI_U , CI_T , and CI_C could be potential photo-products. All stable H-bonded complexes are presented in Fig. 4.

Table 2 Branching space vectors ($|GD|$, $|DC|$) and bonding parameters (in kJ mol^{-1}) of the conical intersections

	CI_C	CI_U	CI_T	$CI_{C'}$	$CI_{U'}$	$CI_{T'}$
$ GD $, a.u.	0.163409	0.248860	0.250769	0.171836	0.250317	0.251918
$ DC $, a.u.	0.068123	0.111008	0.110081	0.062380	0.107700	0.106820
ΔE_b	−51.3	−38.5	−52.3	–	–	–
ΔE	−70.5	−64.4	−71.7	–	–	–
BSSE	19.2	25.9	19.4	–	–	–

BSSE basis set superposition error

Fig. 3 Vectors **a** $|GD|$ and **b** $|DC|$ of conical intersections visualized as normal modes



As can be seen, the shortest intermolecular H-bonds are formed in the hydroxo uracil/thymine complexes. These tautomers are also included in the conical intersections CI_U and CI_T . In the most stable tautomers—amino for cytosine, and oxo for uracil and thymine—the two intermolecular H-bonds are almost equivalent. The Dewar structures of the complexes resemble a half-open book with respect to the aromatic ring. This structure of the ring is predisposed for strong H-bridges. As a result shorter H-bonds are formed as compared with the complexes with the planar bases. We assume that all these structures can lead to the conical intersections CI_U , CI_T , and CI_C after excitation with UV light. Conversely, they can be produced photochemically via these conical intersections.

We calculated the vertical excitation energies of the minima which are listed in Table 3.

The data show that the deformation of the aromatic ring leads to the stabilization of the $^1\pi\pi^*$ state and destabilization of the $^1n\pi^*$ electronic excited state. Comparing the monohydrates U_D and T_D one can see that the substitution (with methyl group in thymine) of the aromatic ring at the C^5 position provokes stabilization of the $^1\pi\pi^*$ state. However, this substitution provokes a destabilization of the dark $^1n\pi^*$ excited state. The same effect for the $^1\pi\pi^*$ state is observed in the monohydrates $U1_P$ and $T1_P$ as well as $U2_P$ and $T2_P$.

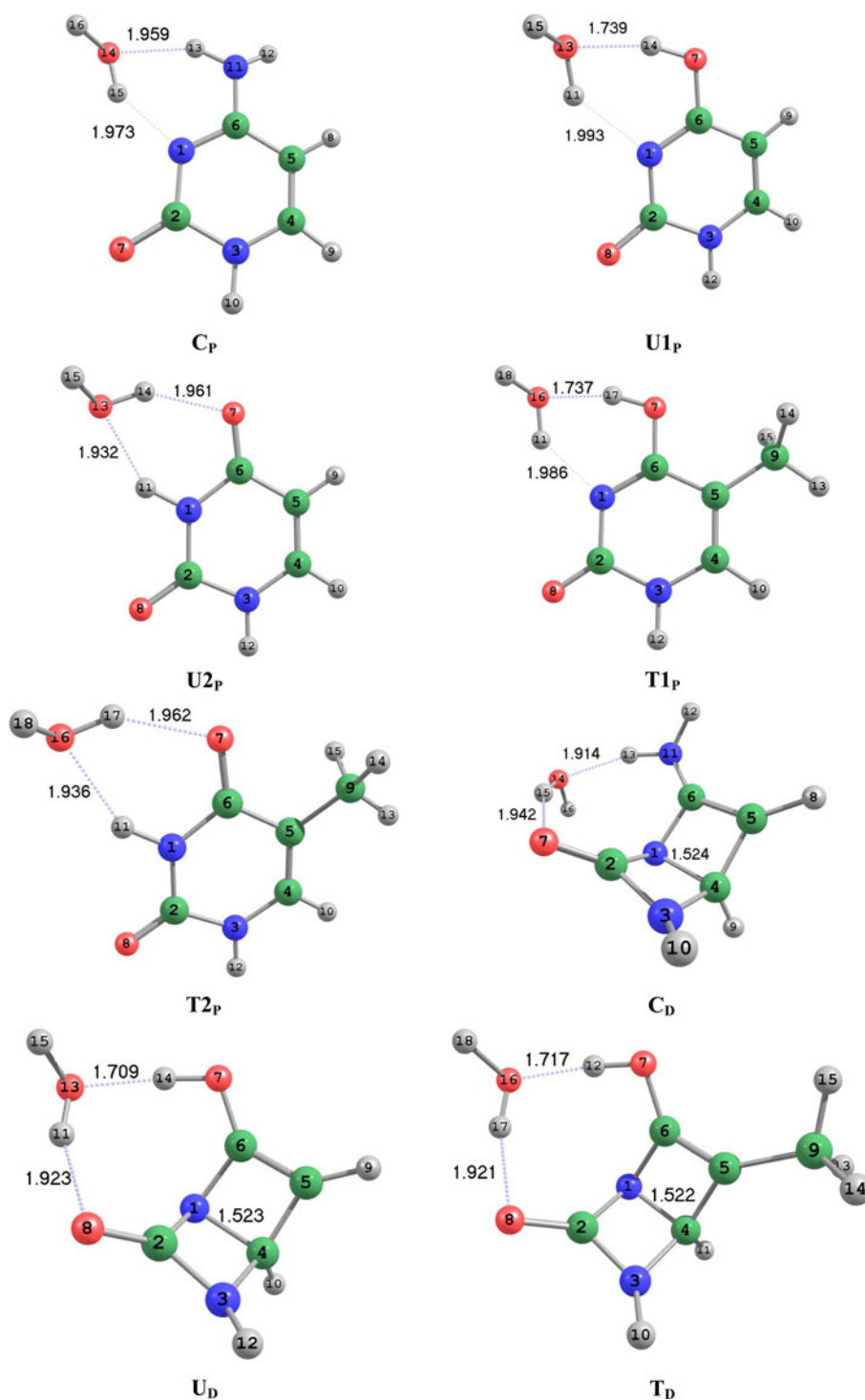
Table 3 also lists the calculated bonding energies of the monohydrated cytosine, uracil and thymine, their planar structures, and the Dewar structures. As can be seen, the hydroxo tautomers of planar uracil and thymine form the most stable H-bonded complexes. The Dewar form of these compounds additionally stabilizes the supersystems. The cytosine complexes have moderate stability, whereas the lowest stability was estimated for the complexes with the oxo forms of uracil and thymine. It can be deduced that the Dewar form of the pyrimidine bases is stabilized by H-bonding with water (in this case) or other small protic molecules. The BSSE varies in the interval 19.1–25.9 kJ mol^{-1} .

The monohydrates of planar pyrimidine bases have higher $^1\pi\pi^*$ vertical excitation energies than the Dewar bases. The $^1\pi\pi^*$ vertical excitation energies of the latter are rather close to the experimental positions of the UV bands, in aqueous solutions, of cytosine, uracil, and thymine. Therefore, the experimental UV spectra of irradiated aqueous solutions of cytosine, uracil, and thymine should be interpreted carefully because of the high probability for signals from the Dewar forms.

Energy-level diagrams

In order to clarify the role of the monohydrated conical intersections in the photochemistry of the intermolecular

Fig. 4 Optimized geometries of the H-bonded complexes' minima. The subscripts 'P' and 'D' indicate the planar and Dewar structures



proton transfer processes we constructed energy-level diagrams with the exact positions of the concrete electronic states and the conical intersections (the recalculated energies at the MCSCF(10,9) level are listed in Table 4) as obtained by MCSCF calculations.

The energy-level diagram for cytosine (Fig. 5a) shows a possible deactivation channel (radiationless) of the $^1\pi\pi^*$

state of C_P through the conical intersection CI_C . The photoproduction of the Dewar form C_D is also possible, mediated by the same conical intersection.

These findings for monohydrated cytosine are also true for monohydrated uracil and thymine (Fig. 5b,c). However, monohydrated uracil and thymine can participate in photo-induced intermolecular proton transfer processes in excited

Table 3 Vertical excitation energies of the complexes' minima (eV) and bonding energies (kJ mol⁻¹)

	C _P	U _{1P}	U _{2P}	T _{1P}	T _{2P}	C _D	U _D	T _D
Vertical excitation energies, MCQDPT2(10,9)								
¹ n ₀ π*	5.983	5.947	5.462	5.514	6.533	7.125	6.784	7.501
¹ ππ*	5.360	6.072	5.593	4.602	5.085	4.847	4.954	4.616
Vertical excitation energies, MCSCF(10,9)								
¹ n ₀ π*	5.904	4.694	5.608	5.557	7.059	7.826	8.331	8.246
¹ ππ*	5.415	4.895	6.949	5.073	6.530	6.435	6.847	6.833
Bonding energies								
ΔE _b	-45.0	-51.7	-35.9	-52.4	-35.5	-45.2	-63.2	-62.0
ΔE	-64.1	-72.7	-55.6	-73.6	-55.3	-68.2	-85.5	-84.4
BSSE	19.1	21.0	19.8	21.2	19.8	23.0	22.3	22.4

Table 4 MCSCF(10,9) energies of the conical intersections and vertical excitation energies of the single bases (monomers) with geometries as determined in the conical intersections

CI	Energy	CI	Energy
CI _C	-468.539168	CI _{C'}	-392.514208
CI _U	-488.398105	CI _{U'}	-412.364194
CI _T	-527.430791	CI _{T'}	-451.402635

states, mediated by the conical intersections CI_U and CI_T. All these mechanisms will be the subject of our future research.

Conclusion

In this study we report about several (monohydrated and anhydrous) new conical intersections of cytosine, uracil, and thymine. The pyrimidine bases in these conical intersections have unusual shape: the NH₂ group of cytosine and one of the C=O bonds of uracil and thymine are almost perpendicular to the aromatic ring.

The comparison of the monohydrates of the almost planar pyrimidine bases and their Dewar structures showed that the deformation of the aromatic ring leads to the stabilization of the ¹ππ* state and a destabilization of the ¹nπ* electronic excited state. Furthermore, the substitution of C⁵ of uracil with a methyl group (as in thymine) leads to the stabilization of the ¹ππ* state of the complex.

The stability analysis of the planar and Dewar monohydrates of pyrimidine bases shows that the Dewar form of pyrimidines is stabilized by H-bonding with water. In other words, this form could be observed in irradiated aqueous solutions of cytosine, uracil, and thymine.

The constructed energy-level diagrams showed that the photo-induced intermolecular proton transfer (assisted by water) in uracil/thymine could be mediated by the conical intersections CI_U and CI_T. Furthermore, the three conical

intersections CI_C, CI_U, and CI_T would mediate the photo-production of the Dewar forms of monohydrated cytosine, uracil, and thymine.

Methods

The structures of conical intersections were optimized at the CASSCF(6,6)/6-31G* level. The initial structures of the conical intersection correspond to the thermal transition state geometries of the oxo-hydroxo tautomer transformations which we studied earlier [31–33]. We supposed that the eventual conical intersections should lie near and/or above these transition states. We also found the conical intersections originating from the corresponding monohydrated complexes without the water molecule (so-called anhydrous conical intersections). They were studied by single-point calculations. The optimization (fully relaxed internal coordinates) of the anhydrous conical intersection is not possible because it leads to the well-known conical intersections of pyrimidine bases described in numerous papers [9–12]. In fact many conical intersections can be found on the degenerated coordinate hypersurfaces S₀/S₁ of each pyrimidine base. Some of them are not involved in the relaxation mechanisms of pyrimidine bases known so far. This is the case with the anhydrous conical intersections studied here. The most important fact is that the monohydrated conical intersections would mediate the relaxation processes of intermolecular H-transfer in pyrimidine bases which will be the subject of our future investigation.

Branching space vectors |**GD**| (gradient difference) and |**DC**| (derivative coupling) of all conical intersections were calculated at the same theoretical level. The *x*, *y*, *z* components (for each atom) of the vectors were used for a visualization as “normal modes” with the program ChemCraft [34].

The MP2 optimized structures of H-bonded complexes (planar and Dewar) which correspond to energy minima

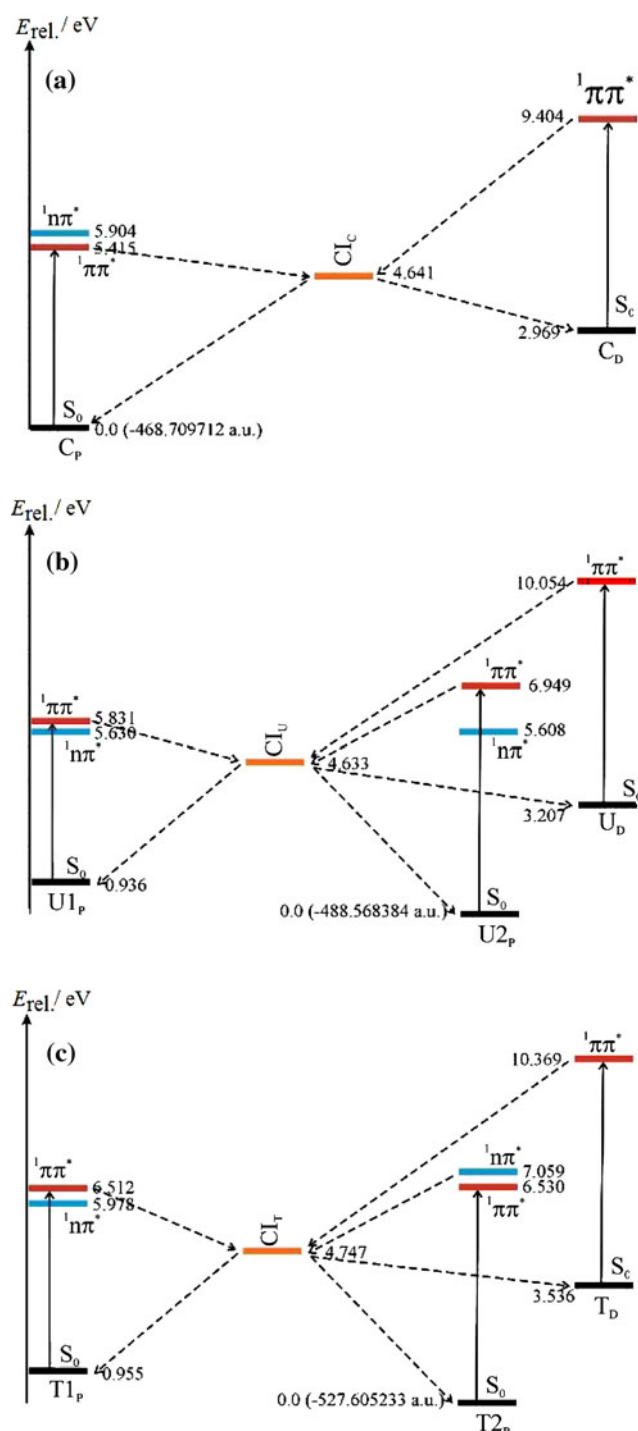


Fig. 5 Energy-level diagrams of the electronic states of the stable minima and conical intersections. The diagrams are constructed according to the MCSCF(10,9) calculations. The dark ${}^1n\pi^*$ states of the Dewar forms are not included in the diagrams because they have very high energies (over 11 eV)

(no imaginary frequencies in the vibration spectrum) were used to calculate their vertical excitation energies at the MCQDPT2(10,9)/6-31G* and MCSCF(10,9)/6-31G* levels. The active space for the complexes with planar

pyrimidines was constructed from ten electrons on nine orbitals: seven π -, one n_0 -, and one σ^* -orbital. Four π -orbitals are doubly occupied while three are unoccupied. For the complexes of pyrimidines with the Dewar form one of the π^* -orbitals is replaced by a σ^* -orbital. This comes from the fact that the Dewar form of pyrimidines is strongly distorted. Therefore, the π^* -orbitals have much higher energy than the σ^* -orbitals.

We used the recomputed MCSCF(10,9)/6-31G* energies of the conical intersections and those of the planar and Dewar structures to construct the energy-level diagrams of the possible excited-state reaction paths. The reaction mechanisms studied by minimum-energy-path (MEP), relaxed-scan (coordinate-driven reaction paths), or linear interpolation in internal coordinates (LIIC) approaches will be the subject of our future research. The method MCQDPT2 predicts a rather large gap between the states S_0 and S_1 . Unfortunately, it is not possible to optimize the conical intersections using this method.

Bonding energies (ΔE_b) and BSSE for each H-bonded complex were estimated according to the equations [35–37]:

$$\Delta E_b = E_{SS} - \sum_{i=1}^n E'_{m_i}$$

$$BSSE = \sum_{i=1}^n (E_{m_i}^{SP} - E'_{m_i})$$

where E_{SS} is the energy of the complex (supersystem), E'_{m_i} is the energy of i th monomer in the supersystem calculated with “ghost” orbitals of the other monomer, $E_{m_i}^{SP}$ are the energies of the individual monomers frozen in their aggregate geometries, found by single-point calculations.

The energy ΔE of the H-bonded complexes was calculated using the equation:

$$\Delta E = E_{SS} - \sum_{i=1}^n E_{m_i}^{SP}$$

The optimizations and MP2/CASSCF(6,6) calculations were performed with the Gaussian 03 software package [38]. The MCQDPT2 and MCSCF calculations were performed with the GAMESS-US ab initio package [39].

References

1. Canuel C, Mons M, Piuze F, Tardivel B, Dimicoli I, Elhanine M (2005) *J Chem Phys* 122:074316
2. Kang HK, Lee KT, Jung B, Ko YJ, Kim SK (2002) *J Am Chem Soc* 124:12958
3. Merchan M, Serrano-Andres L, Robb MA, Blancafort L (2005) *J Am Chem Soc* 127:1820
4. Kistler KA, Matsika S (2007) *J Phys Chem A* 111:2650
5. Kistler KA, Matsika S (2008) *J Chem Phys* 128:215102

6. Blancafort L (2007) *Photochem Photobiol* 83:603
7. Matsika S (2004) *J Phys Chem A* 108:7584
8. Zechmann G, Berbatti M (2008) *J Phys Chem A* 112:8273
9. Perun S, Sobolewski AL, Domcke W (2006) *J Phys Chem A* 110:13238
10. Zgierski MZ, Patchkovskii S, Fujiwara T, Lim EC (2005) *J Phys Chem A* 109:9384
11. Merchan M, Gonzalez-Luque R, Climent T, Serrano-Andres L, Rodriguez E, Reguero M, Pelaez D (2006) *J Phys Chem B* 110:26471
12. Gustavsson T, Banyasz A, Lazzarotto E, Markovitsi D, Scalmani G, Frisch MJ, Barone V, Improta R (2006) *J Am Chem Soc* 128:607
13. Shukla MK, Leszczynski J (2002) *J Phys Chem A* 106:8642
14. Clark LB, Peschel GG, Tinoco I Jr (1965) *J Phys Chem* 69:3615
15. Clark LB, Tinoco I Jr (1965) *J Am Chem Soc* 87:11
16. Neiss C, Saalfrank P, Parac M, Grimme S (2003) *J Phys Chem A* 107:140
17. Voet D, Gratzer WB, Cox RA, Doty P (1963) *Biopolymers* 1:193
18. Vigny P, Ballini JP (1997) In: Pullman B, Goldblum N (eds) *Excited states in organic chemistry and biochemistry*. Reidel, Dordrecht, p 1
19. Callis PR (1983) *Ann Rev Phys Chem* 34:329
20. Zaloudek F, Novros JS, Clark LB (1985) *J Am Chem Soc* 107:7344
21. Blancafort L, Migani A (2007) *J Photochem Photobiol A* 190:283
22. Yoshikawa A, Matsika S (2008) *Chem Phys* 347:393
23. Aleman C (1999) *Chem Phys Lett* 302:461
24. Aleman C (1999) *Chem Phys* 244:151
25. van Mourik T, Price SL, Clary DC (1999) *J Phys Chem A* 103:1611
26. Danilov VI, van Mourik T, Poltev VI (2006) *Chem Phys Lett* 429:255
27. Miles DW, Robins RK, Eyring H (1967) *Proc Natl Acad Sci U S A* 57:1138
28. Delchev VD (2010) *J Mol Mod* 16:749
29. Isayev O, Furmanchuk A, Shishkin OV, Gorb L, Leszczynski J (2007) *J Phys Chem B* 111:3476
30. Furmanchuk A, Shishkin OV, Isayev O, Gorb L, Leszczynski J (2010) *Phys Chem Chem Phys* 12:9945
31. Delchev VB, Shterev IG, Mikosch H (2008) *Monatsh Chem* 139:349
32. Delchev VB, Shterev IG (2009) *J Mol Mod* 15:411
33. Shterev IG, Delchev VB (2009) *Monatsh Chem* 140:1381
34. Zhurko GA, Zhurko DA (2007) *ChemCraft 1.5* (build 282)
35. Boys SF, Bernadi F (1970) *Mol Phys* 19:553
36. Hobza P, Zahradnik R (1989) *Intermolecular complexes*. Mir, Moscow (in Russian)
37. Simon S, Duran M, Dannenberg JJ (1999) *J Phys Chem A* 103:1640
38. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) *Gaussian 03*, revision D.01. Gaussian Inc, Wallingford
39. Schmidt MW, Baldrige KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su SJ, Windus TL, Dupuis M, Montgomery JM (1993) *J Comput Chem* 14:1347