Singlet−Triplet Energy Gaps of Gas-Phase RNA and DNA Bases. A Quantum Chemical Study

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Electronic structure calculations using both ab initio MO and DFT methods, in conjunction with the 6-311++G-(d,p), 6-311++G(3df,2p), and aug-cc-pVTZ basis sets, have been applied to investigate the energies and structures of the lowest-lying triplet states of the series of five parent nucleotide RNA and DNA bases including uracil, thymine, cytosine, guanine, and adenine and the halogenated 5X and 6X-substituted uracils (X = F, Cl, and Br). The singlet−triplet gap ΔE_{ST} of uracil was evaluated using different functionals (B3LYP, B3P86, B3PW91, BP97-1, HCTH). MP2 and CCSD(T) methods were considered for uracil and thymine. For other bases, only B3LYP computations were performed. Computed results agree relatively well with those derived from recent electron impact study (Abouaf et al., *Chem. Phys. Lett.* **2003**, *381*, 486). For each base, the vertical triplet state is calculated at 3.5−3.8 eV above the corresponding singlet ground state but about 1 eV below the first excited singlet. Although geometrical relaxation of triplet structures involving out-of-plane distortions of hydrogen atoms leads to a stabilization of 0.7−0.8 eV, the triplet state is of ($\pi^* \leftarrow \pi$) character. The ΔE_{ST} values are evaluated as follows (values in eV and referred to S_0): uracil, 3.63 (vertical, exp, 3.65 ± 0.05)/3.00 (adiabatic); thymine, 3.50 (exp, 3.60 ± 0.05)/2.85; cytosine, 3.60/3.09; guanine, 3.84/3.06; adenine, 3.71/3.09. For uracil, halogen substitution at C(5) tends to reduce the ΔE_{ST} value by up to 0.3 eV whereas C(5) methylation and C(6) halogenation induce only small changes. A vibrational analysis pointed out that the frequencies associated with the main normal modes such as C=O and N−H stretching motions are only slightly shifted upon excitation.

1. Introduction

The generation of holes and hole transfers due to electron motion in different components of DNA continue to attract considerable research interests as they are the simplest models to the mutation and strand scission of DNA. The latter processes have been shown to play a certain role in carcinogenesis and aging phenomena.[1] Direct observations of hole transfers[2] and rate constants of some single-step hole transfers in DNA, for example, from GG to G or from G to GG, have been measured.[3] Earlier experimental evidence[4] demonstrated that the electronic spectra of double-stranded DNA closely resemble the sum of absorption spectra of the constituent purine and pyrimidine bases. In this respect, information on the electronic excitations upon absorption of radiation by the individual DNA bases is of crucial importance. In particular, the localization or delocalization character of the electronic excited states generated within the base chromophores, and the nature of the electronic interaction between the bases, constitute, among others, the basis of the DNA exciton models.[5]

Until recently, studies on the hole generation and transfer in RNA and DNA nucleobases have mainly been focused on the UV absorption and emission involving singlet electronic states, ionization, and electron-attachment processes.[6,7] Relatively little is known about their *triplet* electronic states, even though earlier kinetic studies[8] suggested that the formation of the photodimer between uracil, thymine, and orotic acid arises from the reaction of one molecule in a triplet state with a second one in its ground state. According to this simple model,[8] the triplet state T_1 formed by an intersystem crossing from the photoexcited S_1 state and underwent a self-quenching giving either a deactivation or a formation of photoproducts. Spectroscopic observation of the triplet state of uracil in solution has subsequently been reported.[9] Kinetic studies of flash photolysis of uracil and thymine, reported in the late 1960s, also provided additional evidence for a formation of a transient triplet state.[10] Weak fluorescence or phosphorescence of nucleobases has been observed,[10d] even though the appearance depends strongly on the solvent.

Theoretical studies on triplet nucleobases are rather scarce. Earlier empirical calculations[11] suggested singlet−triplet energy gaps of around 1.8 eV. Ab initio studies[12] using a multireference interaction configuration (MR-CI) and random phase approximation (RPA) methods using a double-ζ Cartesian Gaussian basis set, augmented with polarization and diffuse functions, led to the following results: (i) in adenine,[12a] the vertical lowest valence triplet state lies approximately at 24.930 cm^{-1} (3.09 eV) above the ground state, and four valence ($\pi \rightarrow \pi^*$) triplets are below the lowest excited singlet state; (ii) in guanine,[12a] while valence states T_1 and T_2 were found at approximately 28.280 cm^{-1} (3.50 eV) and 29.520 cm^{-1} (3.66 eV), both T_3 and T_4 states are essentially isoenergetic with the lowest excited singlet; (iii) the lowest triplet states of uracil and cytosine are valence ($\pi \rightarrow \pi^*$) states and are situated at about 25.400 cm^{-1} (3.15 eV) and 32.590 cm^{-1} (4.04 eV) above the ground states, respectively.[12b] Note that although these CI calculations represented a quite extensive investigation in the early 1990s, the expected errors in calculated transition energies were found to

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be within 12.000−15.000 cm^{-1}. Subsequent ab initio multiconfigurational CASSCF/CASPT2 studies[13,14] confirmed that, in each of the five parent nucleobases, the lowest-lying excited singlet state is vertically placed at around 4.4−5.0 eV above the corresponding ground state, implying that the triplet is actually the first excited state in DNA bases.

Marian et al.[15] carried out ab initio electronic structure calculations using a combination of multireference configuration interaction and density functional theory methods (DFT/MRCI) to investigate the electronic spectrum of uracil and its tautomers as well as their interaction with water oligomers (up to six water molecules). These authors also examined the singlet−triplet coupling in uracil and derived the phosphorescence lifetime due to a T−S transition. The direct spin−orbit interaction has been found to be negligibly small between T_1 and S_0, but it becomes important between T_2 and S_0. This indicated a much smaller radiative lifetime for T_2 ($\tau_P{}^0 \sim 1$ ms). The $^3(\pi^* \leftarrow \pi)$ T_1 state of uracil was calculated to be adiabatically located at 3.20 eV above the ground-state S_0, whereas the computed vertical deexcitation energy from the T_1 state of uracil amounts to only 2.73 eV.[15]

Abouaf, Pommier, and Dunet[16] recently studied the excitations of the lowest electronic states of thymine (T) and 5-bromouracil (5-BrU) using electron energy loss spectroscopy (EELS) under electron impact (0−100 eV) and with angular analysis. These authors observed that, under gaseous-phase conditions, the singlet absorptions have been blue shifted by about 0.3 eV with respect to the well-known UV−vis results in various media. In particular, new transitions, not observable in previous experiments, located at 3.6 eV for T and 3.35 eV for 5-BrU, with an estimated error of ± 0.08 eV, were also been identified. APD[16] actually assigned the latter bands to the excitation to the lowest-lying triplet states. The EELS excitation energies differ significantly from the available theoretical results mentioned above. Note that vibrational excitation in both molecules has also been recorded showing two distinct resonance regions at 1−2 and 4−5 eV.

In view of the scarcity of accurate quantitative information on triplet electronic states of nucleobases, we set out to calculate the singlet−triplet energy gaps in the five parent RNA and DNA bases, including uracil (U), thymine (T), cytosine (C), guanine (G), and adenine (A). For the sake of comparison with the available experimental results[16] and preliminary analysis of substituent effects, the halogenated uracils at both the 5th (5-XU) and 6th (6-XU) ring carbon positions, with X = F, Cl, and Br, have also been considered.

2. Methods of Calculation

Ab initio molecular orbital (MO) and density functional theory (DFT) calculations were carried out using the Gaussian 98 suite of programs.[17] Initial geometry optimizations and vibrational analyses were performed using the Hartree−Fock (HF) method in conjunction with the dp-polarized 6-31G(d,p) basis set. Geometrical parameters of the relevant equilibrium structures were reoptimized using the popular hybrid B3LYP functional[18,19] and the 6-311++G(d,p) basis set. Harmonic vibrational frequencies were also computed at the latter level of theory in order to determine the zero-point energies. The ZPE values were thereby evaluated without scaling the frequencies. The relative energies were subsequently derived from single-point electronic energy calculations using the B3LYP method with the larger 6-311++G(3df,2p) and correlation-consistent aug-cc-pVTZ basis sets. As for a useful test for the performance of DFT on this specific property, additional calculations using the BLYP, B3P86, B3PW91, BP97-1, and HCTH functionals (cf. refs 17, 20, and 21) have also been performed for uracil. While for uracil, thymine, and cytosine, coupled-cluster CCSD(T) calculations were carried out using the 6-311++G(2dp,2p) basis set,; only DFT calculations were performed for guanine, adenine, and halogeno-substituted uracils. For the purpose of calibration, ionization energies (IE) of the bases were also determined as corresponding experimental data are available. For open-shell systems, the unrestricted formalism (UHF, UCC, UB3LYP...) was employed, and in coupled-cluster theory computations, core orbitals were kept frozen.

Unless otherwise noted, relative energies quoted in the following discussion were evaluated at the B3LYP/6-311++G(3df,2p) + ZPE level. Throughout this paper, bond lengths are given in angstroms, bond angles in degrees, energy gaps, excitation energies, and ionization energies in eV, and relative energies in kcal/mol.

3. Results and Discussion

A. Uracil. Let us first examine in some details the structure and energy of the parent uracil molecule in its lowest-lying triplet state. The calculated results are summarized in Figures 1 and 2 and Tables 1 and 2. The letters **s** and **t** refer hereafter to the singlet ground and triplet states, respectively.

1. Molecular Geometry. In its singlet state, **U-s** possesses a planar form with a C_s point group and the orbital configuration is depicted as follows

$$\textbf{U-s}:\ {}^1A' \ ....(4a'')^2(24a')^2(5a'')^2(6a'')^0(25a')^0....$$

The shape of some frontier orbitals displayed in Figure 1 indicates that they essentially belong to the π system (π and π^* orbitals). The HOMO has thus a″ symmetry in which the atomic contributions arise mainly from the subunit containing both C═C and C═O bonds and N atom. The LUMO is another a″ orbital having larger atomic contributions from the same subunit. Accordingly, the vertical triplet state generated from a formal HOMO → LUMO transition in **U-s** corresponds to a valence ($\pi \rightarrow \pi^*$) triplet state, namely

$$\textbf{U-t}(\text{vertical}):\ {}^3A' \ ....(24a')^2(5a'')^1(6a'')^1....$$

Such an excitation is expected to lead to certain geometrical changes. Figure 2 displays a selection of geometrical parameters of **U-t** optimized at the B3LYP/6-311++G(d,p) level, along with those of **U-s** for the purpose of comparison. Geometry and vibrational frequencies of the latter have been analyzed in a previous work[22−25] and warrant thus no further comments. Following excitation, both C═O bonds remain almost unchanged as indicated by the fact that the relevant 2p lobes are small and mainly located at both O_2 and O_4 atoms. On the contrary, the bond distances around both N_1 and N_3 atoms are stretched (up to 0.04 Å). The C_5−C_6 bond, which is a typical double bond in **U-s** (1.346 Å), becomes almost a single bond in **U-t** (1.491 Å). Such an important change usually occurs in triplet alkenes due to a removal of an electron away from a C═C bond bearing bonding orbitals (Figure 1). In a similar way, the C_4−C_5 bond acquires more double-bond character in the exited state due to the occupation of the LUMO. As a consequence, most of the atoms, in particular the hydrogens H_5 and H_6, undergo significant out-of-plane distortions, up to 30° (Figure 2). Structural relaxation also results in modifications of the MO's shape. However, as seen in Figure 1, the singly

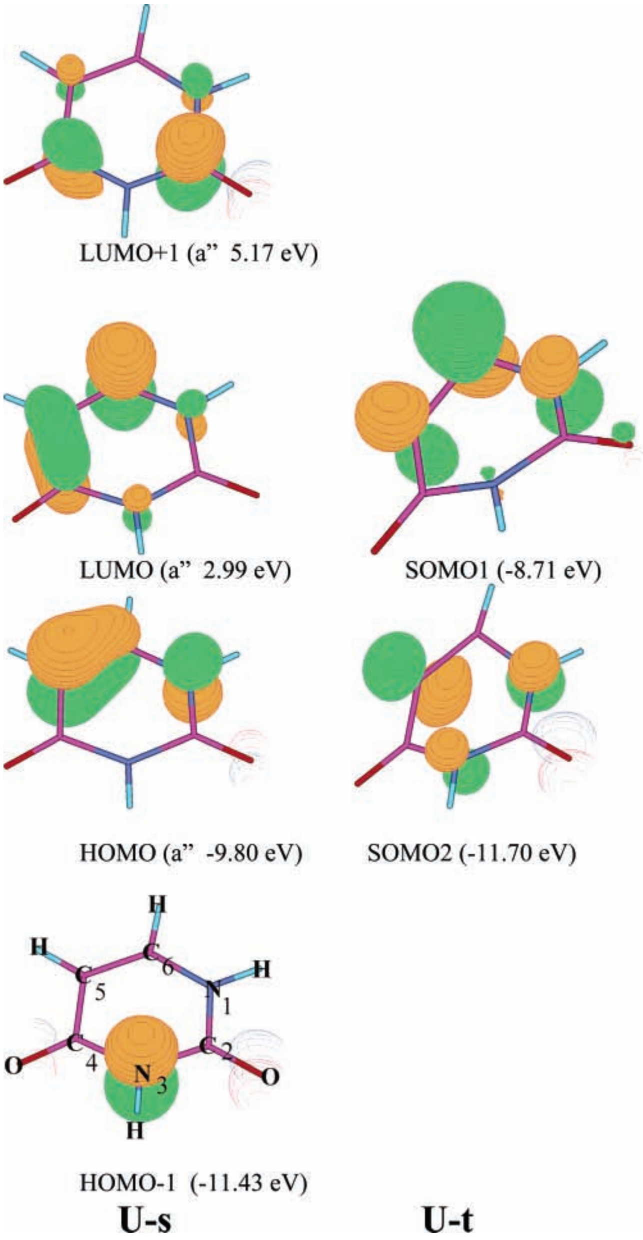


Figure 1. Shape of some frontier orbitals of uracil in its singlet ground state **U−s** and adiabatic triplet state **U−t** (α orbitals) obtained from (U)HF/6-31G(d,p) wave functions.

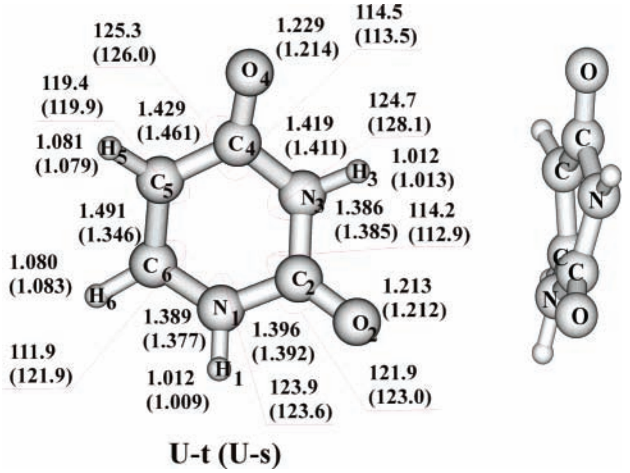


Figure 2. Selected UB3LYP/6-311++G(d,p) geometrical parameters of uracil in its lowest-lying triplet state **U−t**. Values given in parentheses are those of ground-state uracil **U−s**. Bond distances are given in angstroms and bond angles in degrees. A projection shows the out-of-plane distortion of triplet structure.

TABLE 1: Singlet−Triplet Energy Gap of Uracil (ΔE_{ST})

method	ΔE_{ST}, eV	
	adiabatic[a]	adiabatic[b]
Density Funtional		
B3LYP/6-311++G(d,p)	3.63	2.99
B3LYP/6-311++G(3df,2p)	3.63	3.02
B3LYP/aug-cc-pVTZ	3.62	3.00
BLYP/6-311++G(d,p)	3.55	2.95
BLYP/6-311++G(3df,2p)	3.55	2.96
B3P86/6-311++G(d,p)	3.64	3.12
B3P86/6-311++G(3df,2p)	3.62	3.12
B3PW91/6-311++G(d,p)	3.61	3.07
B3PW91/6-311++G(3df,2p)	3.59	3.08
B97−1/6-311++G(d,p)	3.97	3.03
B97−1/6-311++G(3df,2p)	3.91	3.05
HCTH/6-311++G(d,p)	3.52	2.97
HCTH/6-311++G(3df,2p)	3.50	2.98
Molecular Orbital		
MP2/6-311++G(d,p)	4.35	3.51
MP2/6-311++G(2df,2p)	4.31	3.46
CCSD(T)/6-31G(d,p)	3.98	3.15
CCSD(T)/6-311++G(d,p)	3.90	3.08
CCSD/6-311++G(2df,2p)	3.82	2.98
CCSD(T)/6-311++G(2df,2p)	3.91	3.07
experimental	3.65 ± 0.05[c]	

[a] On the basis of B3LYP/6-311++G(d,p)-optimized geometry of **U−s**. [b] On the basis of (U)B3LYP/6-311++G(d,p)-optimized geometries of both **U−s** and **U−t**. The values include the ZPE corrections 54.4 kcal/mol for **U−s** and 51.8 kcal/mol for **U−t**. Spin contamination in UHF wave functions for **U−t** is small, $\langle S^2\rangle \approx 2.08$. [c] Reference 26.

occupied orbitals (SOMO) in **U-t** retain the main features of their original orbitals.

2. Singlet−Triplet Energy Gap. Table 1 summarizes the singlet−triplet energy gaps ΔE_{ST} of uracil calculated using different quantum chemical methods. As for a convention, a positive ΔE_{ST} value corresponds to the position of the triplet state relative to the singlet ground state. It turns out that this quantity is less sensitive to the one-electron basis set employed. Both DFT and CCSD(T) methods yield similar values for the adiabatic energy gap (<0.1 eV). They result however in larger variations for the vertical counterpart (up to 0.3 eV). Comparatively, the second-order perturbation theory (U)MP2 consistently yields too large gaps and could thus not be used as a predictive method.

Of the different DFT methods employed, the calculated adiabatic energy gaps are comparable to each other, ranging from 2.95 eV by the pure BLYP functional to 3.07 eV by the hybrid B3PW91[20] functional. The present ab initio MO and DFT values are consistently smaller than that of 3.20 eV previously derived from the DFT/MRCI technique.[15]

Concerning the vertical gap, the HCTH functional provides the smallest value of 3.50 eV, whereas the B97-1 functional produces the largest gap of 3.97 eV. The latter belong to the most recent family of functionals including the gradient-corrected correlation.[21] For both quantities, results obtained by both pure and hybrid B3LYP functionals turn out to be quite similar.

Recently Abouaf and co-workers[26] obtained from EELS measurements a value of $\Delta E_{ST}(\text{vert}) = 3.65 \pm 0.05$ eV for uracil. The present results derived from hybrid functionals B3LYP, B3P86, and B3PW91 of around 3.59−3.64 eV agree well with the experimental estimate (cf. Table 1). It appears that, when using a basis set having at least a 6-311++G(d,p)

TABLE 2: B3LYP/6-311++G(d,p) Harmonic Vibrational Frequencies (cm^{-1}), Infrared Intensities ($km\ mol^{-1}$), Assignment, and PED for the normal Modes of Triplet Uracil U-t

no.	frequency	intensity	assignment,[a] PED (%, >10%)
1	119	2.9	γN3H3(38.0) − τ3rg(36.0)
2	172	1.1	τ2rg(67.0) + γN1H1(18.0)
3	214	0.6	τ1rg(55.0) + γN1H1(17.0)
4	379	25.8	βC4O4(27.0) -βC2O2(25.0) + β3rg(16.0) + β2rg(13.0)
5	469	41.6	γC6H6(38.0) − β2rg(19.0) − β3rg(10.0)
6	499	21.4	β3rg(27.0) − β2rg(18.0) − γC5H5(16.0) − γC4O4(15.0)
7	518	8.3	γC6H6(28.0) + β2rg(19.0) − γC4O4(15.0) -γC5H5(12.0)
8	535	20.9	γN1H1(29.0) + γC5H5(24.0) − γN3H3(16.0) + β3rg(15.0)
9	546	5.2	βC2O2(40.0) + βC4O4(35.0)
10	596	5.4	γN1H1(50.0) − γC6H6(22.0)
11	638	149.5	γN3H3(75.0)
12	714	11.9	γC4O4(44.0) − γC5H5(21.0) -τ1rg(17.0)
13	740	53.8	γC2O2(56.0) − τ1rg(15.0)
14	762	3.4	γC2O2(21.0) + νN1C2(15.0) + β1rg(12.0) + νC4C5(12.0)
15	933	9.1	νC5C6(30.0) − β1rg(21.0) + νC4C5(15.0)
16	959	19.5	β1rg(28.0)-νN1C2(23.0) − νC2N3(13.0)
17	1009	8.6	νN3C4(23.0) + βC5H5(18.0) − β1rg(17.0) − νC5C6(17.0)
18	1144	95.2	νC2N3(27.0)-νN1C6(16.0)+βC6H6(15.0)-βN1H1(13.0)-νN3C4(11.0)
19	1238	22.8	βC5H5(40.0) − νN3C4(15.0)
20	1357	124.9	βC5H5(21.0) − νC2N3(19.0) + νN1C2(18.0) + νC5C6(11.0)
21	1388	28.3	βN3H3(29.0) + βC6H6(21.0) + νC4O4(11.0) + νN1C6(11.0)
22	1398	5.5	βC6H6(33.0) − βN3H3(29.0)+ νN1C2(12.0)
23	1415	119.7	νC4C5(18.0) − νC5C6(12.0) − βN1H1(11.0) + νN1C6 (11.0)
24	1480	85.1	βN1H1(48.0) − νN1C6(15.0) + νN1C2(11.0)
25[b]	1612	149.2	νC4O4(65.0)
	(1767)	(791.6)	(νC4O4(69.0))
26[b]	1774	488.2	νC2O2(71.0)
	(1802)	(665.7)	(νC2O2(68.0))
27[b]	3216	4.2	νC5H5(70.0) − νC6H6(29.0)
	(3202)	(2.7)	(νC6H6(95.0))
28[b]	3226	1.0	νC6H6(70.0) + νC5H5(29.0)
	(3242)	(1.1)	νC5H5(96.0)
29[b]	3602	93.3	νN1H1(95.0)
	(3596)	(67.3)	(νN3H3(100.0))
30[b]	3608	63.1	νN3H3(95.0)
	(3638)	(107.2)	(νN1H1(100.0))

[a] ν, stretching; β, bending; γ, out of plane; δ1rg, δ2rg, and δ3rg, deformation of six-membered ring; τ1rg, τ2rg, and τ3rg, torsion of a six-membered ring. [b] From modes 25−30, the values given in parentheses in the second line of each row correspond to values of the singlet state **U−s**.

quality, the B3LYP functional seems to be able to reproduce reliable singlet−triplet energy separations for this type of compound. A similar performance of the functional has also been pointed out for evaluating ionization energies (IE) and electron affinities (EA) of nucleobases.[6b] Indeed, when using the B3LYP/6-311++G(3df,2p) level, we obtained for uracil the values of IE_{vert} = 9.46 eV and E_a = 9.22 eV. The latter almost coincides with the experimental value of 9.20 eV.[27]

In summary, in supplementing the experimental result ΔE_{ST}(vert) = 3.65 ± 0.05 eV for uracil, we would propose the adiabatic value, ΔE_{ST}(adi) = 3.00 ± 0.10 eV for uracil. An energy gain of 0.65 eV for the triplet structure corresponds well to the significant geometry relaxation mentioned above upon electronic transition. Regarding the computational methods, the hybrid B3LYP functional appears to reproduce best the experimental result. This lends a support for the choice of this functional to compute the gaps of remaining systems.

3. Harmonic Vibrational Analysis. In a different attempt to evaluate the structural changes upon excitation, we have performed an analysis of the fundamental vibrational modes of **U-t**. The UB3LYP/6-311++G(d,p) harmonic frequencies are kept unscaled. The nonredundant set of vibrations has been assigned using symmetrized internal coordinates together with the associated potential-energy distributions (PED) of calculated vibrational modes.[26] The PED matrix is classically defined as PED = Λ^{-1}**JF**, in which **F** stands for the harmonic force constants matrix in term of symmetrized internal coordinates, Λ is the corresponding eigenvalue matrix, and finally **J** is the Jacobian matrix of Λ with respect to **F**. Table 2 records the calculated results.

In comparison with **U-s**, only a few significant changes could be noted in the normal modes of **U-t**. The most intense absorption remains the C═O and N−H stretching motions, whose corresponding frequencies are reduced by at most 3−4% following triplet excitation.

B. Thymine. Thymine (T) is formally a 5-methyl substituted uracil. Therefore, its properties are expected to be close to those of uracil. Figure 3 shows the selected optimized geometrical parameters of both **T-t** and **T-s** structures. Again, the vertical triplet state is generated from a HOMO (π) → LUMO (π*) transition, having an orbital configuration of

$$\textbf{T-t}(\text{vertical}):\ {}^3A':....(27a')^2(6a'')^1(7a'')^1....$$

The most significant geometrical changes are equally observed for the $N_1C_6C_5C_4$ moiety with the largest stretching of the C_5C_6 bond in going from 1.348 Å in **T-s** to 1.497 Å in **T-t**. The CO bond distances remain almost intact (Figure 3).

The calculated energy gaps listed in Table 3 also show a good agreement, within 0.1 eV, with the experimental value of ΔE_{ST}(vert) = 3.60 ± 0.08 eV derived for thymine from EELS study.[16] All the results agree with each other, indicating that a methyl group at the 5th ring position induces a marginal reduction of 0.05−0.10 eV on the gap. A further test of confidence consists of calculating the ionization energy. In conjunction with the 6-311++G(d,p) and 6-311++G(3df,2p) basis sets, the B3LYP

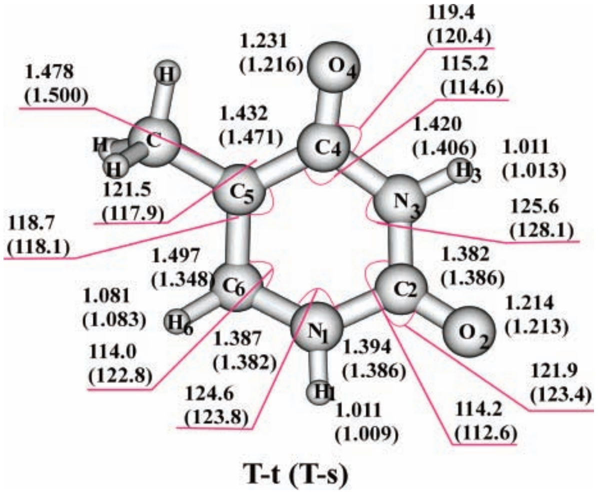


Figure 3. Selected (U)B3LYP/6-311++G(d,p) geometrical parameters of thymine **T−t** and **T−s** (values in parentheses).

TABLE 3: Singlet−Triplet Energy Gaps of Thymine (ΔE_{ST})

method	ΔE_{ST} vertical[a]	adiabatic[b]
B3LYP/6-311++G(d,p)	3.50	2.82
B3LYP/6-311++G(3df,2p)	3.50	2.84
B3LYP/aug-cc-pVTZ	3.49	2.85
CCSD(T)/6-31G(d,p)	3.91	3.07
CCSD(T)/6-311++G(d,p)	3.80	2.99
experimental[c]	3.60 ± 0.08	

[a] By use of the B3LYP/6-311++G(d,p) geometry of **T−s**. [b] By use of the B3LYP/6-311++G(d,p) geometries **T−s** and **T−t**. The values include zero-point corrections, 61.4 kcal/mol for **T−s** and 58.5 kcal/mol for **T−t**. [c] Experimental value taken from ref 16.

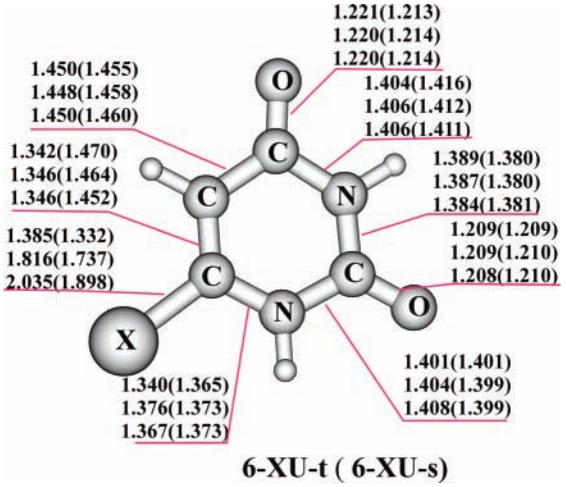
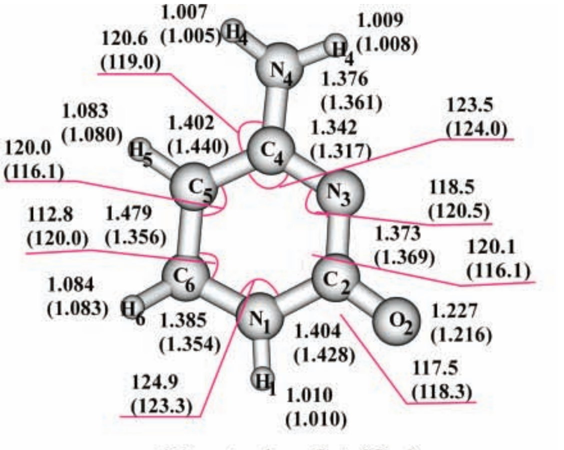


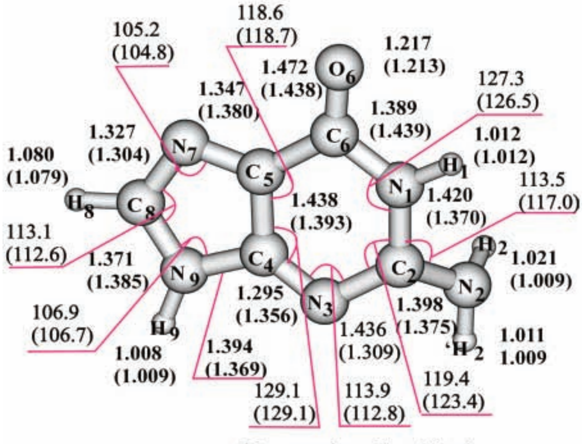
Figure 4. Selected (U)B3LYP/6-311++G(d,p) geometrical parameters of halogeno-uracils: **6-XU-t** and **6-XU-s** (parentheses), with X = F (upper), Cl (central), and Br (lower).

functional provides the IE_a(T) of 8.78 and 8.76 eV, respectively. The corresponding experimental value is 8.80−8.87 eV.[25] Thus it appears reasonable to predict that the adiabatic energy gap of thymine amounts to ΔE_{ST}(adi) = 2.85 ± 0.10 eV. A stabilization of 0.66 eV due to geometry relaxation of **T-t** is again similar to that of **U-t**.

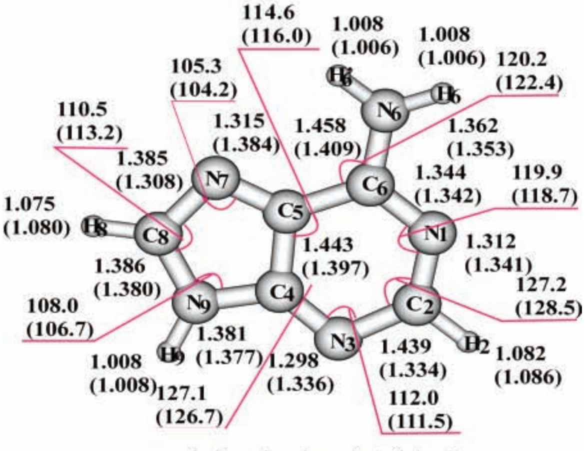
C. 5- and 6-Halogenated Uracils. It is of interest to examine this series of monosubstituted uracils as they allow a direct comparison with uracil and thymine (5-methyl uracil). As mentioned above, only the experimental EELS results for 5-BrU are available.[16] Figure 4 displays the optimized geometries of **6-XU-t** and **6-XU-s**, with X = F, Cl, and Br. On one hand, in going from F to Cl to Br, the parameters are only marginally modified, namely, by 0.02 Å for bond distances and 0.5° for bond angles, irrespective of the electronic state. On the other hand, comparison with the values given in both Figures 2 and 3 points out that the geometrical changes upon halogenation in both states are not really meaningful.



(a) cytosine C-t (C-s)



(b) guanine G-t (G-s)

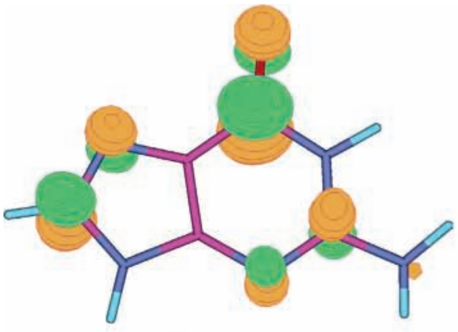


(c) adenine A-t (A-s)

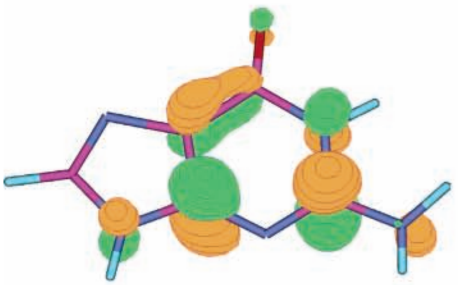
Figure 5. Selected (U)B3LYP/6-311++G(d,p) optimized parameters of (a) cytosine **C−t** and **C−s** (parentheses), (b) guanine **G−t** and **G−s** (parentheses), and (c) adenine **A−t** and **A−s** (parentheses).

By inspection of Table 4, a few points are worth noting:

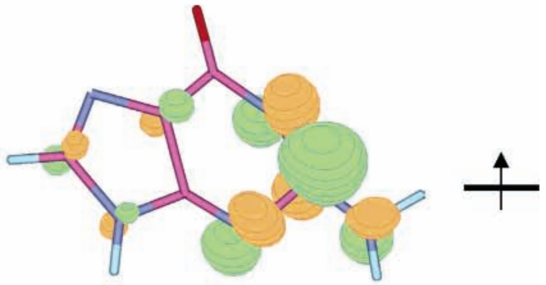
(i) Apart from **6-FU**, halogenation at both the 5th and 6th positions tends to reduce both vertical and adiabatic T−S energy gaps. While the reduction is appreciable and rather regular in



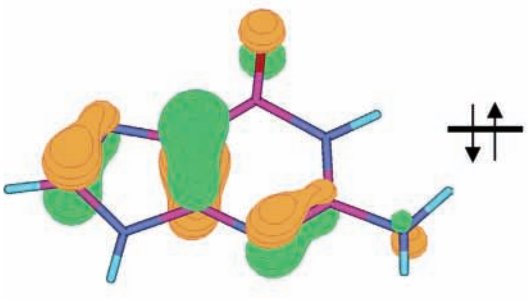
LUMO+1 (4.62 eV)



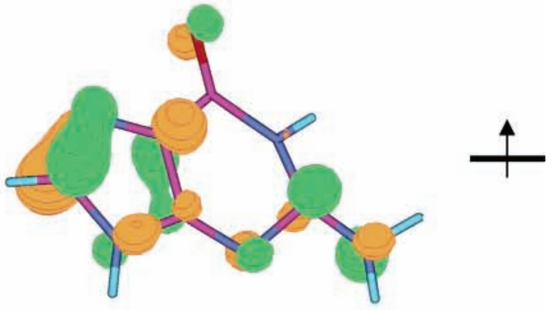
LUMO (4.08 eV)



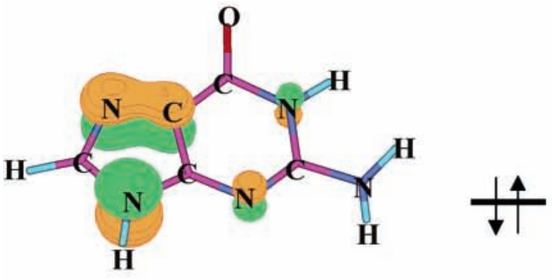
SOMO1 (-7.35 eV)



HOMO (-8.16 eV)



SOMO2 (-9.80 eV)



HOMO-1 (-10.88 eV)

Figure 6. Shape of some frontier orbitals of guanine in its singlet ground state **G−s** and adiabatic triplet state **G−t** (α orbitals) obtained from (U)HF/6-31G(d,p) wave functions.

the series **5-XU**, the vertical gaps remain almost unchanged in **6-XU** (X = Cl and Br).

(ii) With respect to the parent uracil, 5-bromination effectively reduces the vertical gap by about 0.3 eV. The calculated value for ΔE_{ST}(vert) = 3.30 eV, with a probable error of ±0.10, for **5-BrU** compares favorably with the experimental EELS result of 3.35 ± 0.08 eV obtained by APD.[16] This agreement lends further confidence on the reliability of other calculated results.

(iii) While geometry relaxation leads to an energy gain of 0.6−0.7 eV in triplet 5-X derivatives, which seems to be internally consistent, stabilization becomes markedly larger in the 6-X counterparts amounting up to 1.1 eV. Thus for each substituent X, the **6-XU** exhibits larger vertical and adiabatic gaps than its **5-XU** isomer. Note that in the ground state, of the two isomers, the **6-XU** shows a higher stability, ranging from 3 to 6 kcal/mol, than the **5-XU** counterpart.

TABLE 4: Singlet−Triplet Energy Gaps (ΔE_{ST}) and Ionization Energies IE of Halogeno-Uracils Calculated at the B3LYP/6-311++G(3df,2p) Level[a]

	ΔE_{ST}, eV		IE, eV	
uracil	vertical[a]	adiabatic[b]	vertical[a]	adiabatic[b]
H	3.62	3.01	9.70	9.36
5-F	3.40	2.70	9.35	9.15
5-Cl	3.36	2.68	9.13	8.93
5-Br	3.30 (3.35)[c]	2.64	9.07	8.84
6-F	3.96	2.88	9.78	9.45
6-Cl	3.59	2.73	9.59	9.27
6-Br	3.58	2.60	9.49	9.19

[a] On the basis of the B3LYP/6-311++G(d,p)-optimized geometries. [b] Including ZPE corrections. [c] Experimental value taken from ref 16.

TABLE 5: Calculated Singlet−Triplet Gaps ΔE_{ST} and Ionization Energies IE_a of Cytosine, Guanine, and Adenine

		ΔE_{ST},[a] eV		IE_a,[a] eV
method	molecule	vertical	adiabatic	adiabatic
	Cytosine			
B3LYP/6-311++G(d,p)		3.61	3.04	8.62
B3LYP/6-311++G(3df,2p)		3.60	3.09	8.60
B3LYP/aug-cc-pVTZ		3.63	3.07	8.60 (8.45; 8.68)[b]
CCSD(T)/6-31G(d,p)		3.97	3.23	
CCSD(T)/6-311++G(d,p)		3.94	3.17	
CCSD/6-311++G(2df,2p)		3.83	3.22	
CCSD(T)/6-311++G(2df,2p)		3.75	3.13	
	Guanine			
B3LYP/6-311++G(d,p)		3.87	3.02	7.68
B3LYP/6-311++G(3df,2p)		3.84	3.06	7.63 (7.77; 7.85)[b]
	Adenine			
B3LYP/6-311++G(d,p)		3.73	3.07	8.11
B3LYP/6-311++G(3df,2p)		3.71	3.09	8.07 (8.26; 7.80)[b])

[a] On the basis of the B3LYP/6-311++G(d,p)-optimized geometries. [b] Experimental values taken from refs 27 and 28.

(iv) The trends mentioned above are again manifested in ionization energies of the series (Table 4), even though the energy gains turn out to be much smaller upon electron removal (0.2−0.3 eV). In fact, all the ionized forms are characterized by a planar structure with a $^2A''$ ground state. In this regard, out-of-plane distortions appear to account for an energy gain of about 0.3−0.4 eV in the triplet equilibrium structure.

Overall, the energy separations ΔE_{ST} can be predicted to be 3.3−3.4 eV (vertical) and 2.6−2.7 eV (adiabatic) in **5-XU** and 3.6−3.9 eV (vertical) and 2.6−2.9 eV (adiabatic) in **6-XU**. These results thus emphasize a certain (nonlinear) correlation between the vertical and adiabatic ΔE_{ST} values. In contrast, no correlation could be found between the ΔE_{ST} and IEs.

D. Cytosine, Guanine, and Adenine. We now consider the last series of nucleobases investigated. The calculated results are presented in Figures 5 and 6 and Table 5. Again, the C=O bonds are not significantly affected, whereas the most important changes following triplet excitation are located at around the C_5C_6 bond in **C−t** and, in a lesser extent, to the bridged C_4C_5 bonds in both **G−t** and **A−t** (Figure 5). Indeed, in each case, this moiety is associated with the largest atomic contributions to the HOMO (Figure 6) from which a hole is being created.

Cytosine appears to have transition energies close to those of uracil (Table 5). Fusion of each of the latter bases with a five-membered ring gives rise to a rather marginal increase of the gaps, namely, by about 0.2 eV in guanine and 0.1 eV in adenine. In contrast, the IEs turn out to be substantially reduced, especially in guanine. The good agreement on IEs provides us with an additional support for the reliability of B3LYP values. Accordingly, we would predict the following values:

Cytosine (**C**): $\Delta E_{ST}(\text{vert}) = 3.60$ eV and $\Delta E_{ST}(\text{adi}) = 3.09$ eV;

Guanine (**G**): $\Delta E_{ST}(\text{vert}) = 3.84$ eV and $\Delta E_{ST}(\text{adi}) = 3.06$ eV;

Adenine (**A**): $\Delta E_{ST}(\text{vert}) = 3.71$ eV and $\Delta E_{ST}(\text{adi}) = 3.09$ eV.

4. Concluding Remarks

The present quantum chemical computations provide a strong theoretical support for the assignment of new absorption bands located at 3.65 eV for **U**, 3.60 eV for **T**, and 3.35 eV for **5-BrU**, recently detected by electron energy loss spectroscopy,[16,26] to transitions from ground singlet to lowest-lying triplet states. By the same way, both vertical and adiabatic energy gaps, as well as ionization energies, are also predicted for a series of parent nucleobases and 5- and 6-halo-uracils, in the gaseous phase, with an expected accuracy of ± 0.10 eV. The most remarkable fact is that while the adiabatic gaps of the parent bases are rather close to each other, the smallest gap being 2.85 eV in thymine and the largest of 3.09 eV in adenine, the vertical location of these transitions shows wider fluctuations. This clearly indicates the importance of structural relaxation upon excitation. Halogen substitution at C(5) leads to substantial alterations in triplet location.

The fact that a triplet state is confirmed to be by at least 1 eV below the first singlet excited state of nucleobases again emphasizes the utility of classical kinetic model for photoreactions involving intersystem crossing and quenching mechanisms.[8−10] Future studies of dimers and oligomers of different nucleobases, as well as their intermolecular interactions and reactivities in the lowest-lying triplet electronic state, in particular those related to the phosphorescence processes, are highly desirable.

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