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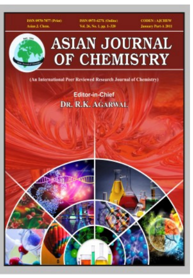

Hydrogen-Atom Addition to Adenine-Thymine Base Pair: Structural Perturbation and Electronic Properties

Yuexia Lin, Hongyan Wang*, Feng Zhang, Simin Gao and Yingxi Wu

School of Physical Science and Technology, Southwest Jiaotong University, Chengdu 610031, P.R. China

*Corresponding author: E-mail: hongyanw@home.swjtu.edu.cn

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Geometry structures, relative energies and electron affinities of the 14 isomers generated by hydrogen-atom addition to the Watson-Crick adenine-thymine base pair were studied theoretically using B3LYP/DZP++ method. When a hydrogen-atom adds to atoms adjacent to two hydrogen-bonds and atoms within the C4=C5 bond shared by the five-membered and six-membered rings of adenine, the planarity for adenine-thymine (AT) base pair is destroyed. Generally, structures which a hydrogen-atom adds to atoms remote from hydrogen-bonds lie lower energy. The lowest energy radical is $H^\bullet A_{C8}T$ that with the hydrogen-atom attached to the C8 position of adenine. Structures $(AT+H)^\bullet$ which hydrogen-atom addition to C atom are more likely to adsorb electron to form anions, because of the larger adiabatic electron affinity and positive vertical detachment energy, than those tautomers which hydrogen-atom addition to N or O atom.

Keywords: Density functional theory, DNA damage, Base pair, Electron affinity, Hydrogen bond.

INTRODUCTION

Biomolecule radicals generated by ionizing radiation has recently received considerable attentions due to the connection with DNA lesions[1-22]. Removing[3-9] or adding a hydrogen-atom[10-12] is a method commonly used in producing radicals. Bera and Schaefer[4] studied the dehydrogenated guanine-cytosine base pair radicals using B3LYP/DZP++ functional method. Turecek and Yao[10] explored the structures and energies of radicals produced by hydrogen-atom addition to cytosine tautomers, 1-methylcytosine and cytosine-water complexes. These studies about radicals contributed to understanding of DNA lesions.

The electron affinities and dissociation energies of a number of DNA subunits have been experimentally determined accurately *via* photoelectron techniques[13-16], and theoretical predictions become more and more accurate with the development of computers and cost effective[12,16-24]. The DNA radical tautomers, which differ only in the position of one atom remain challenges for experiment. Thus the study of radical tautomers may look to explanations *via* reliable theoretical approaches. Zhang and Schaefer[12] reported the properties of GC base pair after hydrogen-atom addition utilizing the density functional theory method, whose results showed that the geometry structure of GC base pair was significantly changed by the addition of hydrogen-atom, especially the hydrogen bonds, which may cause DNA damage.

In this paper we study the 14 $(AT+H)^\bullet$ radicals resulting from hydrogen-atom addition to adenine-thymine (AT) base pair. The geometrical structures, relative energies, as well as electronic properties are discussed to analyze the effect of hydrogen-atom addition for further clarification of the mechanism of DNA damage and repair.

THEORETICAL METHODS

The geometries of 14 AT base pairs after hydrogen-atom addition and the corresponding anions were fully optimized using the B3LYP/DZP++ and BP86/DZP++ density function. The B3LYP method is a combination of the Becke three-parameter exchange functional (B3)[25] and the dynamic correlation functional of Lee, Yang and Parr (LYP)[26]. Such DFT methods have been used in many studies[27,28] of related hydrogen-bonded systems. The BP86 functional combines the Beck's 1988 pure DFT exchange functional (B)[29] with Predew's correlation functional (P86)[30,31]. The investigations seem to show that non-local methods including gradient corrections, particularly B3LYP, provide reliable results. Vibrational frequency analyses were also performed at the same level of theory to ensure the structures $(AT+H)^\bullet$ are local minima. The Gaussian 03[32] suite of DFT program was used for the computations.

Double-ζ quality basis sets with polarization and diffuse functions (DZP++) are used in this research. The DZP++ basis sets were constructed by augmenting the Huzinaga-

Dunning[33,34] set of contracted double-ζ Gaussian functions with one set of p-type polarization functions for each H atom and one set of five d-type polarization functions for each C, N and O atom [$\alpha_p(H) = 0.75$, $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$, $\alpha_d(O) = 0.85$]. To complete the DZP++ basis, one even-tempered diffuse s function was added to each H atom, while one set of even-tempered diffuse s and p functions were centered on each heavy atom. The even-tempered orbital exponents were determined according to the prescription of Lee and Schaefer:[35]

$$\alpha_{\text{diffuse}} = \frac{1}{2}\left(\frac{\alpha_1}{\alpha_2} + \frac{\alpha_2}{\alpha_3}\right)\alpha_1$$

where α_1, α_2 and α_3 are the three smallest Gaussian orbital exponents of the s- or p- type function for a given atom ($\alpha_1 < \alpha_2 < \alpha_3$). The final DZP++ set includes six functions per H atom (5s1p/3s1p) and nineteen functions per C, N, or O atom (10s6p1d/5s3p1d), yielding a total of 433 contracted Gaussian functions for each $(AT+H)^{\bullet}$ base pair structure. This basis has the tactical advantage that it has previously been used in many previous studies[36] of electron affinities.

The electron affinities were determined as follows. The adiabatic electron affinity (AEA) is defined as the energy difference between the neutral and corresponding anion species at their respective optimized geometries:

AEA = E (optimized neutral)-E (optimized anion)

The vertical electron affinity (VEA) of the radical is determined as VEA = E (optimized neutral)-E (anion at optimized neutral geometry). The anion vertical detachment energy (VDE) is defined *via* VDE = E (neutral at optimized anion geometry)-E (optimized anion).

RESULTS AND DISCUSSION

Standard atom numbering for the AT base pair is used in Fig. 1, in which the bond lengths of the optimized neutral AT base pair have been marked in order to compare with the $(AT+H)^{\bullet}$ isomers. Fourteen $(AT+H)^{\bullet}$ tautomers are obtained when the hydrogen atom has been added to the seven C=C, C=N and C=O double bonds. A generic label is used to represent the radicals resulting from hydrogen-atom addition to the AT base pair (Fig. 1). The label $H^{\bullet}A_{N7}T$ means that a hydrogen-atom has been attached to the N7 site of the adenine moiety. The present discussions of the structural and energetic features are made primarily from the B3LYP results. The structural and energetic information, which are predicted by BP86 method, are accessible in the supporting information.

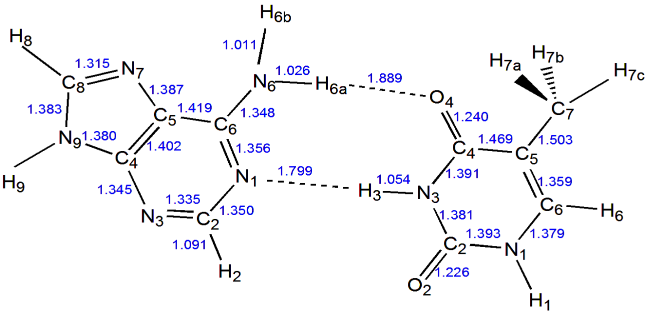

Fig. 1. Optimized geometry of the AT base pair

$H^{\bullet}A_{N1}T$ and $H^{\bullet}A_{C6}T$: When a hydrogen-atom adds to the adenine N1 or C6 site, the N1 = C6 double bond is weakened to form the $H^{\bullet}A_{N1}T$ and $H^{\bullet}A_{C6}T$ radicals (Fig. 2). The structure $H^{\bullet}A_{N1}T$ presents a propeller like twist (Fig. 2b). The interplanar angle between the two bases is 133.0° (C4(A)-C6(A)-C2(A)-N3(T) dihedral angle is 133.0°). Due to the addition hydrogen-atom site N1 is located at the junction of the two bases, two moieties keep away from each other after hydrogen-atom addition. The H6a…O4 and N1…H3 lengths are elongated by 0.131 and 0.242 Å, respectively. The bonds of the adenine six-membered ring are significantly changed. The C6-N1(A), N1-C2(A) and C6-N6(A) are weakened by 0.089, 0.086 and 0.040 Å, respectively. Whereas, the C5-C6(A) and C2=N3(A) bonds are strengthened by 0.035 and 0.031 Å, respectively. A smaller structure perturbation takes place in cytosine compared with adenine base. The N3-H3(T) bond length decreases 0.020 Å.

For the structure $H^{\bullet}A_{C6}T$, the addition hydrogen-atom site C6 contacts with a amino group. Thus the amino group moves out of the adenine plane by 34.7° (dihedral angle N1(A)-C4(A)-C5(A)-N6(A) is 34.7°) after hydrogen-atom addition.

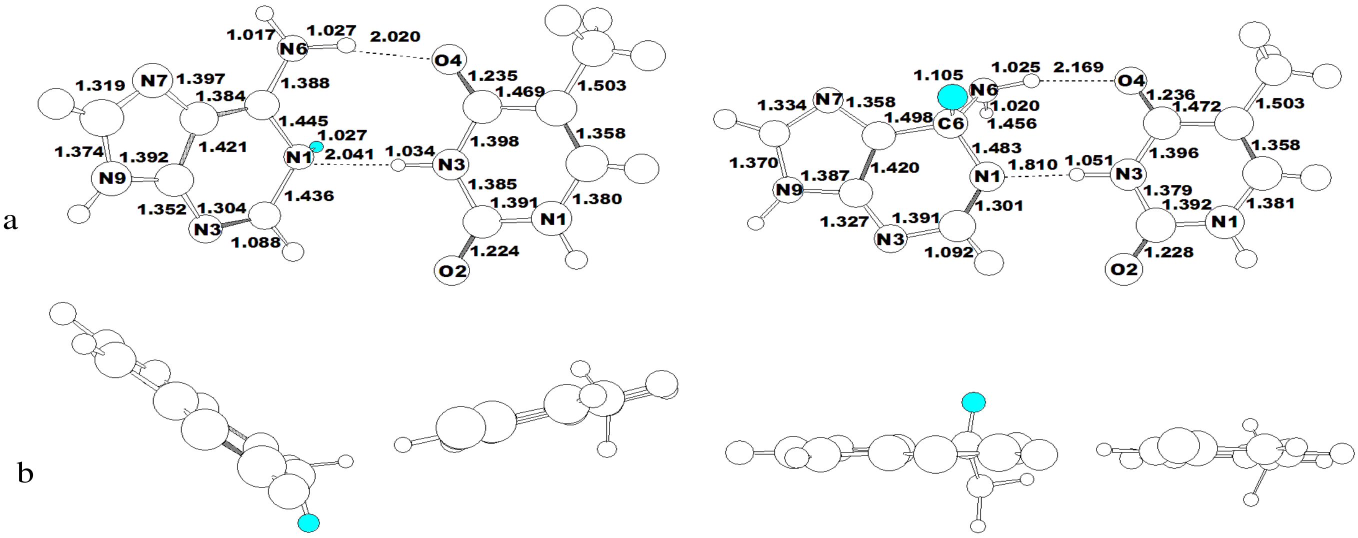

Fig. 2a. Optimized geometry of the $H^{\bullet}A_{N1}T$ and $H^{\bullet}A_{C6}T$ radicals; 2b. Side view of the $H^{\bullet}A_{N1}T$ and $H^{\bullet}A_{C6}T$ radicals

The addition hydrogen-atom also lies out of the adenine plane (Fig. 2b). The C6-N1(A), C6-N6(A) and C6-C5(A) bonds are elongated by 0.127, 0.108 and 0.079 Å and the C2-N3(A) bond length increases 0.056 Å. Simultaneously, the N1-C2(A) and C5-N7(A) are shortened by 0.049 and 0.029 Å, respectively. The H6a…O4 length is weakened by 0.280 Å due to the H6a moves out the adenine plane, while the other hydrogen bond N1…H3-N3 changes almost nothing.

$\mathrm{H^{\bullet}A_{C2}T}$ and $\mathrm{H^{\bullet}A_{N3}T}$: The structure $\mathrm{H^{\bullet}A_{C2}T}$ is generated by a hydrogen-atom addition to the C2 site of the adenine (Fig. 3). The planarity of the base pair is not destroyed, nevertheless, the structure bond lengths significantly change, especially the six-membered ring of the adenine. The N1-C2(A) and C2-N3(A) bonds elongate to 1.465 and 1.448 Å, respectively. Simultaneously, the C5-C6(A) and C5-C4(A) bonds are weakened, while the N3-C4(A) and N1-C6(A) bonds are strengthened and the adjacent C5-N7(A) bond is also shortened by 0.025 Å. The H6a and H3 in the hydrogen bonds N6-H6a…O4 and N1…H3-N3 are likely to transfer to the opposite base, especially the H3. As a result, the N1…H3 length decreases 0.664 Å and the H3-N3(T) bond length increases 0.445 Å. Only the N3-C4(T) and C4-O4(T) bonds significantly change in thymine moiety.

Structure $\mathrm{H^{\bullet}A_{N3}T}$, shown in Fig. 3, formed by adding a hydrogen-atom to the N3 site of adenine. The AT planarity is retained in this radical and the bond lengths change little. For the adenine base, the major bond length changes are distributed in the six-membered ring. The C2-N3(A) double bond change to single bond and increases 0.103 Å. The N3-C4(A), C5-C6(A) and C6-N6(A) are elongated by 0.044, 0.033 and 0.026 Å, respectively. While the N1-C6(A) bond is shortened by 0.020 Å. Only the H6a…O4 length increases 0.110 Å in the two hydrogen bonds. There is no apparent change in thymine base.

$\mathrm{H^{\bullet}A_{C4}T}$ and $\mathrm{H^{\bullet}A_{C5}T}$: When a hydrogen-atom adds to the C4=C5(A) double bond of adenine, the structures $\mathrm{H^{\bullet}A_{C4}T}$ and $\mathrm{H^{\bullet}A_{C5}T}$ are produced (Fig. 4a). The six-membered ring and five-membered ring share the C4=C5(A) bond, thus, the AT base pairs become such with a raised top and a concave bottom (Fig. 4b). For the structure $\mathrm{H^{\bullet}A_{C4}T}$, the three bonds connected to C4 site change dramatically. The N6-H6a…O4 hydrogen bond length is decreased, while H3 transfers from thymine to adenine following the hydrogen bond N1…H3-N3 which make the N1…H3 length and H3-N3 bond become to 1.132 and 1.500 Å (1.799 and 1.054 Å in AT base pair), respectively. For the structure $\mathrm{H^{\bullet}A_{C5}T}$, the three bonds connected to C5 site significantly change. There are no dramatical change in two hydrogen bonds and thymine. Thus the structure $\mathrm{H^{\bullet}A_{C4}T}$ changes more widely than the structure $\mathrm{H^{\bullet}A_{C5}T}$ compared with the AT base pair.

$\mathrm{H^{\bullet}A_{N7}T}$ and $\mathrm{H^{\bullet}A_{C8}T}$: When a hydrogen-atom adds to the N7 or C8 site of the N7=C8 double bond in adenine, the structure $\mathrm{H^{\bullet}A_{N7}T}$ or $\mathrm{H^{\bullet}A_{C8}T}$ is formed (Fig. 5). The geometrical structure of this two $\mathrm{(AT+H)^{\bullet}}$ radicals remain planarity due to the N7=C8 bond is far away from the two hydrogen bonds. For the structure $\mathrm{H^{\bullet}A_{N7}T}$, the N7-C8(A), C8-N9(A), C6-N6(A)

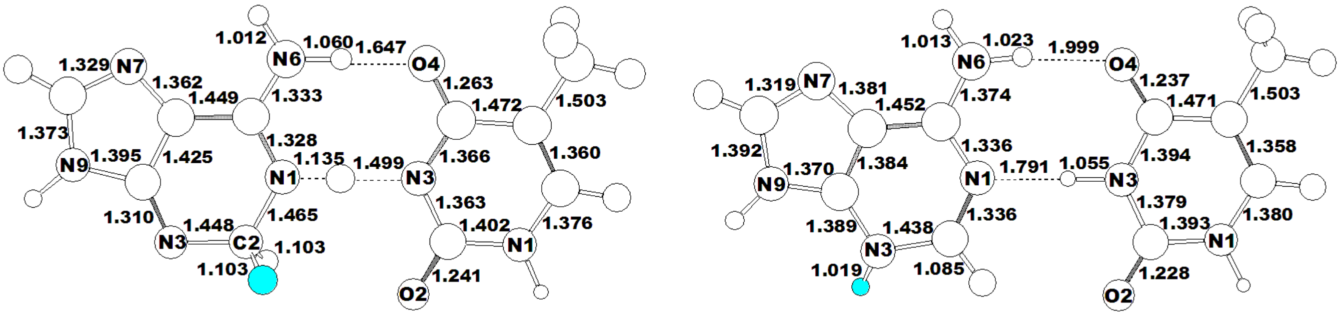

Fig. 3. Optimized geometry of the $\mathrm{H^{\bullet}A_{C2}T}$ and $\mathrm{H^{\bullet}A_{N3}T}$ radicals

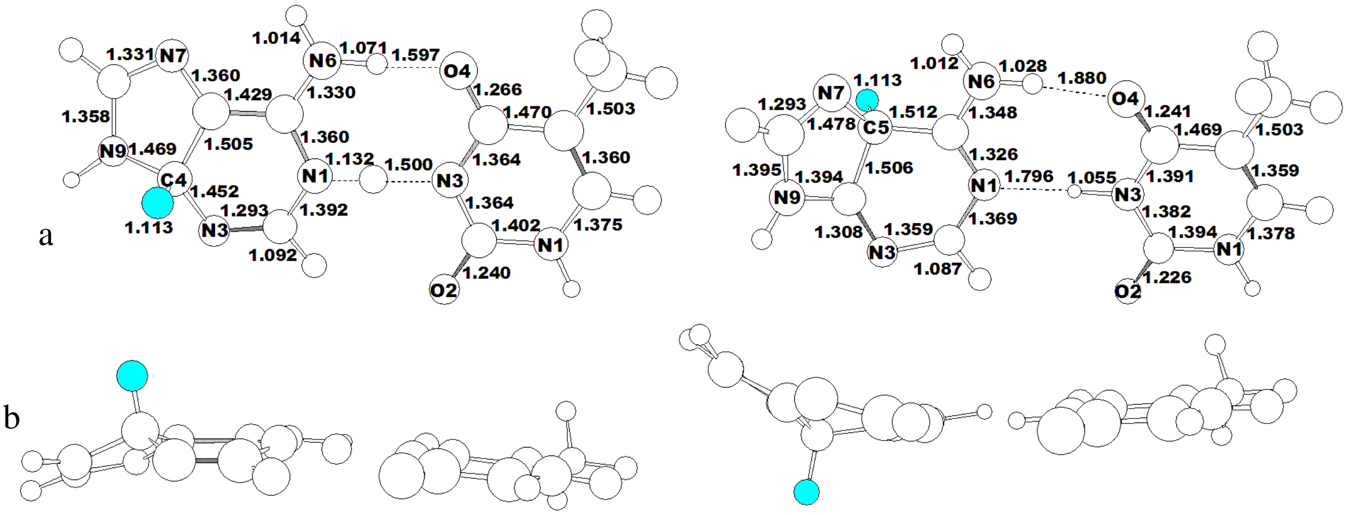

Fig. 4a. Optimized geometry of the $\mathrm{H^{\bullet}A_{C4}T}$ and $\mathrm{H^{\bullet}A_{C5}T}$ radicals; 4b Side view of the $\mathrm{H^{\bullet}A_{C4}T}$ and $\mathrm{H^{\bullet}A_{C5}T}$ radicals

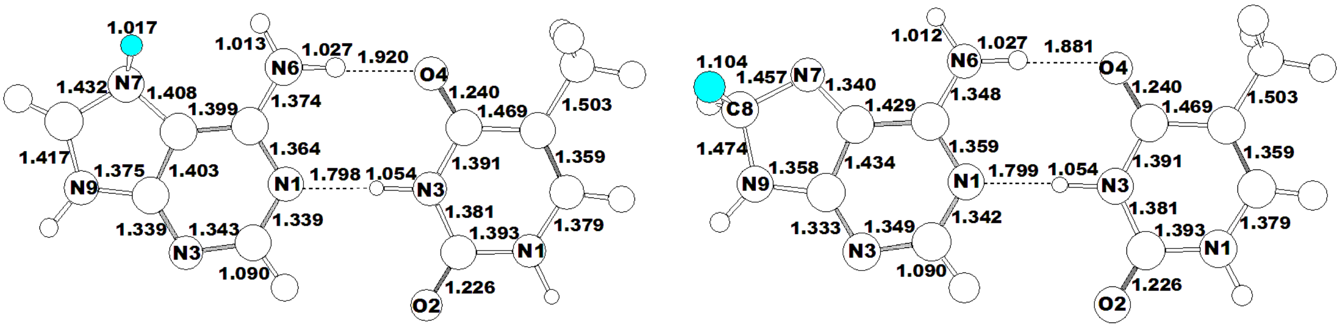

Fig. 5. Optimized geometry of the $H^{\bullet}A_{N7}T$ and $H^{\bullet}A_{C8}T$ radicals

and C5-N7(A) bond lengths increase 0.117, 0.034, 0.026 and 0.021 Å, respectively, while the C5-C6(A) bond length decreases 0.020 Å. The H6a…O4 length increases 0.031Å in view of the hydrogen bonds. For the structure $H^{\bullet}A_{C8}T$, the N7-C8(A), C8-N9(A) and C4-C5(A) bonds are weakened by 0.142, 0.091 and 0.032 Å, respectively. While, the C5-N7(A) and C4-N9(A) bonds are strengthened by 0.047 and 0.022 Å, respectively.

$AT_{C2}H^{\bullet}$ and $AT_{O2}H^{\bullet}$: As radical structures resulting from hydrogen-atom addition to the C2 or O2 site of thymine, $AT_{C2}H^{\bullet}$ and $AT_{O2}H^{\bullet}$ maintain the planarity of AT base pair (Fig. 6). For the structure $AT_{C2}H^{\bullet}$, O2 atom moves out of the AT plane by 2.3° (dihedral angle N3(T)-C5(T)-N1(T)-O2(T) is 2.3°) caused by the addition of hydrogen-atom. The C2-O2(T), C2-N3(T) and N1-C2(T) bond lengths elongate 0.097, 0.061 and 0.059 Å, while the N3-C4(T) bond shortens 0.013 Å. The addition hydrogen-atom site C2 is next to the junction of the two bases, which makes the H6a…O4 length decreases 0.033 Å and the N1…H3 length increases 0.061 Å. The bond (C2-H bond length is 1.155 Å in $AT_{C2}H^{\bullet}$) formed by the addition hydrogen-atom and the addition hydrogen-atom site is the longest one in the 14 considered $(AT+H)^{\bullet}$ radicals. For the structure $AT_{O2}H^{\bullet}$, O2 atom lies out of the AT plane by 7.6° (dihedral angle N3(T)-C5(T)-N1(T)-O2(T) is -7.6°) after the hydrogen-atom addition. The C2-O2(T) and C2-N3(T) bond are elongated by 0.152 and 0.023Å, respectively. The H6a…O4 length decreases 0.055 Å and the N1…H3 length increases 0.076 Å.

$AT_{C4}H^{\bullet}$ and $AT_{O4}H^{\bullet}$: Structures $AT_{C4}H^{\bullet}$ and $AT_{O4}H^{\bullet}$ (Fig. 7a) change dramatically compared with the AT base pair due

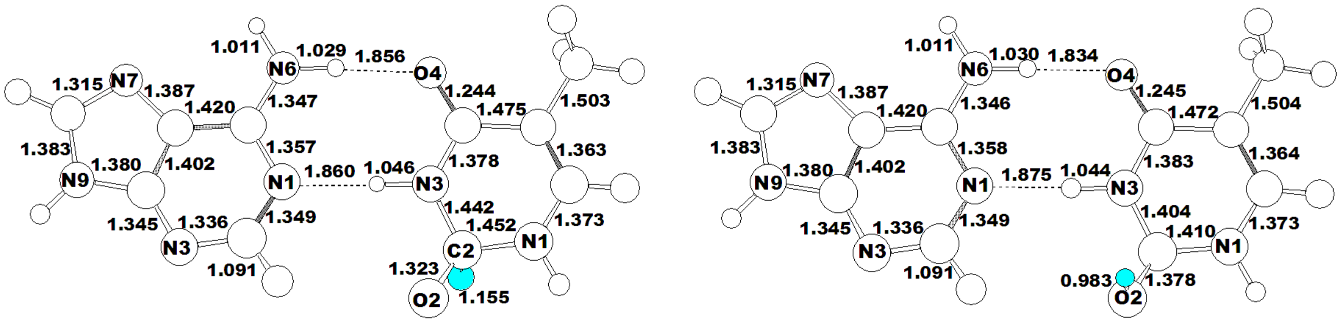

Fig. 6. Optimized geometry of the $AT_{C2}H^{\bullet}$ and $AT_{O2}H^{\bullet}$ radicals

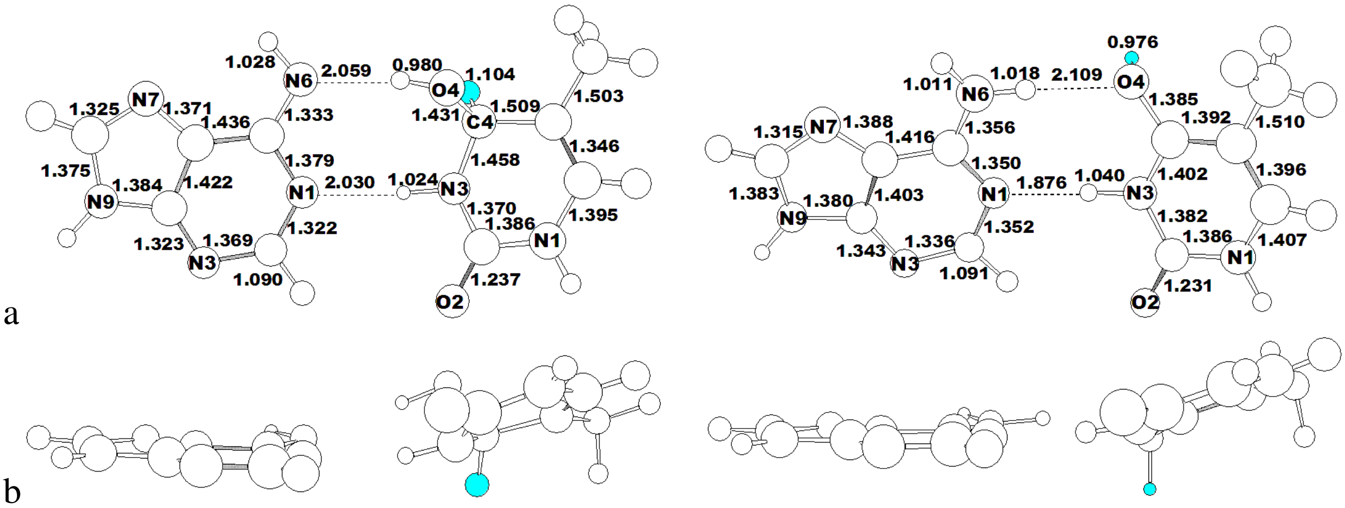

Fig. 7a. Optimized geometry of the $AT_{C4}H^{\bullet}$ and $AT_{O4}H^{\bullet}$ radicals; 7b Side view of the $AT_{C4}H^{\bullet}$ and $AT_{O4}H^{\bullet}$ radicals

to the addition hydrogen-atom sites connected to the hydrogen bonds. For the structure $AT_{C4}H^{\bullet}$, the AT planarity disappears when the hydrogen-atom attaches to the C4 site of thymine, with a resulting C2(A)-C4(A)-C6(A)-C6(T) torsion angle of 18.1° (Fig. 7b). The three bonds, connect to C4 site, C4-O4(T), N3-C4(T) and C4-C5(T) bonds increase 0.191, 0.067 and 0.040 Å, respectively. Simultaneously, the C2-N3(A) and N1-C6(A) bonds increase 0.034 and 0.023 Å, while the N1-C2(A) and N3-C4(A) bonds decrease 0.028 and 0.022 Å, respectively. The H6a transfers from N6 site to O4 site following the N6-H6a…O4 hydrogen bond. The N1…H3 length elongates 0.231 Å and the H3-N3 bond shortens 0.030 Å in the N1…H3-N3 hydrogen bond. For the structure $AT_{O4}H^{\bullet}$, the torsion angle of adenine and thymine bases is 13.6° (C2(A)-C4(A)-C6(A)-C6(T)=-13.6°). The O4-C4(T), C5-C6(T) and N1-C6(T) are weakened by 0.145, 0.037 and 0.028 Å, respectively. The C4-C5(T) bond is strengthened by 0.077 Å. The H6a…O4 length increases 0.220 Å in the N6-H6a…O4 hydrogen bond and the N1…H3 length elongates 0.077 Å in the N1…H3-N3 hydrogen bond.

$AT_{C5}H^{\bullet}$ and $AT_{C6}H^{\bullet}$: The structures $AT_{C5}H^{\bullet}$ and $AT_{C6}H^{\bullet}$ (Fig. 8) are formed by hydrogen-atom attaches to the C5 or C6 site of the C5=C6(T) double bond. For the structure $AT_{C5}H^{\bullet}$, the atom C5 connects with a methyl group, thus the addition of hydrogen-atom makes the methyl group move out of the AT plane by 3.7° (C6(T)-N1(T)-C4(T)-C7(T)=-3.7°). the three bonds linked to the C5 atom C5-C6(T), C4-C5(T), C5-C7(T) elongate 0.139, 0.064 and 0.033 Å, respectively and the H6a…O4 length increases 0.036 Å. For the structure $AT_{C6}H^{\bullet}$, the planarity of AT base pair maintains and the bonds of the structure change little, because of the addition hydrogen-atom site C6 aloof from the hydrogen bonds. The conjoint C5-C6(T) and C6-N1(T) bonds are weakened by 0.137 and 0.073 Å, respectively. While the N1-C2(T) bond is strengthened by 0.021 Å. The H6a…O4 and N1…H3 lengths both increase 0.020 Å.

Relative energies and electronic properties: Total and relative energies of $(AT+H)^{\bullet}$ base pair tautomers are presented in Table-1. The structure $H^{\bullet}A_{C8}T$ is defined as the zero of energy, which lies the lowest energy in this work, due to the C8 site being far away from the hydrogen bonds. The structures $AT_{C6}H^{\bullet}$ and $AT_{C5}H^{\bullet}$ are predicted to lie 0.9 and 3.5 kcal/mol above the global minimum $H^{\bullet}A_{C8}T$ (1.0 and 3.9 kcal/mol after ZPVE corrections). Thus, the structures resulting from the hydrogen-atom attached to the sites which are far away from the hydrogen bonds possess smaller geometry perturbations and lower relative energies. The structure $AT_{C2}H^{\bullet}$ has the highest energy in this series, lying higher 42.5 kcal/mol above the lowest energy radical $H^{\bullet}A_{C8}T$, in which the C2-H(T) length reaches 1.155 Å.

TABLE-1
TOTAL AND RELATIVE ENERGIES OF $(AT+H)^{\bullet}$
BASE PAIR TAUTOMERS

Radicals	Total Energy (Eh)	Relatively energy (kcal/mol)	Relatively energy (ZPVE corrected)
$H^{\bullet}A_{C8}T$	-922.22197	0.0	0.0
$AT_{C6}H^{\bullet}$	-922.22052	0.9	1.0
$AT_{C5}H^{\bullet}$	-922.21639	3.5	3.9
$H^{\bullet}A_{N7}T$	-922.19967	14.0	14.2
$H^{\bullet}A_{C2}T$	-922.19964	14.0	12.5
$AT_{O4}H^{\bullet}$	-922.19491	17.0	16.0
$H^{\bullet}A_{N3}T$	-922.19473	17.1	16.3
$H^{\bullet}A_{C5}T$	-922.19403	17.5	17.0
$H^{\bullet}A_{C6}T$	-922.18472	23.4	23.5
$H^{\bullet}A_{N1}T$	-922.18346	24.2	23.5
$H^{\bullet}A_{C4}T$	-922.18063	25.9	24.3
$AT_{O2}H^{\bullet}$	-922.18006	26.3	26.4
$AT_{C4}H^{\bullet}$	-922.16155	37.9	37.9
$AT_{C2}H^{\bullet}$	-922.15419	42.5	41.4

The ability for base pair radical to capture electron plays an important role in DNA damage and repair. The neutral radicals with larger electron affinity have more powerful ability to attach electron. The electron affinities (EA) and the corresponding anion vertical detachment energy (VDE) are reported in Table-2. Hydrogen-atom addition make AEA and VDE of the AT base pair significantly increase, which demonstrates that the base pairs after hydrogen-atom addition are more likely to attach electron to form anions induced by ionizing radiation. The radicals generated by a hydrogen-atom attaches to N or O atom lie small AEA values and negative VEA values. Instead, the radicals produced by a hydrogen-atom attaches to C atom lie large AEA values and positive VEA values. Thus, the structures produced by a hydrogen-atom attaches to C atom are more likely to attach electron to form anions and then lead to radiation damage, especially the structures $H^{\bullet}A_{C6}T$, $AT_{C2}H^{\bullet}$ and $AT_{C4}H^{\bullet}$. The AEA values of the three structures are 2.92, 2.93 and 3.39 eV (2.93, 2.95 and 3.40 eV after ZPVE corrections) and the VDE values of the corresponding anions reach 3.74, 3.38 and 3.58 eV, respectively.

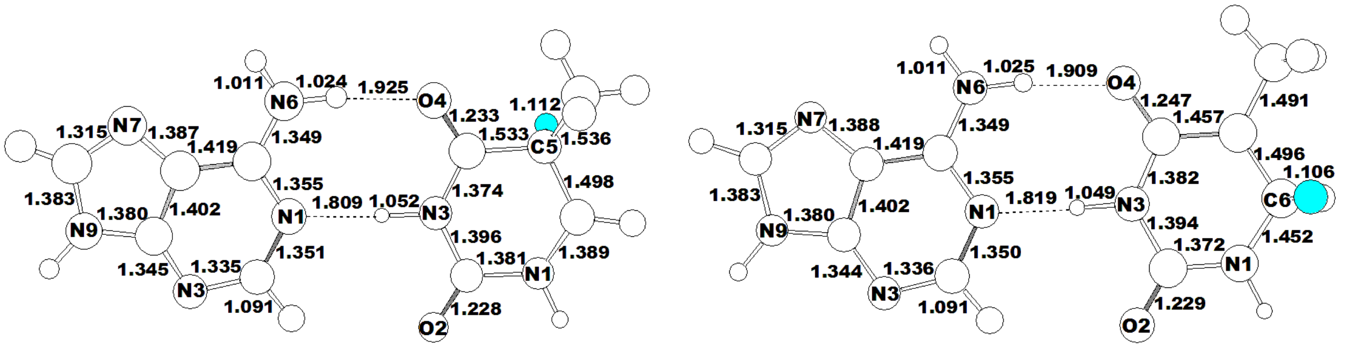

Fig. 8. Optimized geometry of the $AT_{C5}H^{\bullet}$ and $AT_{C6}H^{\bullet}$ radicals

TABLE-2
ELECTRON AFFINITY OF THE $(AT+H)^{\bullet}$ RADICALS

Radicals	AEA(eV) (ZPVE Corrected)	VEA(eV)	VDE(eV)
AT	0.19 (0.36)	-0.09	0.89
$H^{\bullet}A_{N1}T$	0.56 (0.61)	-0.30	1.96
$H^{\bullet}A_{C2}T$	2.44 (2.42)	1.94	2.98
$H^{\bullet}A_{N3}T$	0.53 (0.57)	-0.34	1.93
$H^{\bullet}A_{C4}T$	2.43 (2.40)	1.85	3.05
$H^{\bullet}A_{C5}T$	1.12 (1.18)	0.47	1.95
$H^{\bullet}A_{C6}T$	2.92 (2.93)	2.01	3.74
$H^{\bullet}A_{N7}T$	0.32 (0.45)	-0.07	1.09
$H^{\bullet}A_{C8}T$	1.49 (1.55)	0.95	2.26
$AT_{C2}H^{\bullet}$	2.93 (2.95)	2.28	3.38
$AT_{O2}H^{\bullet}$	0.54 (0.63)	-0.04	1.40
$AT_{C4}H^{\bullet}$	3.39 (3.40)	3.12	3.58
$AT_{O4}H^{\bullet}$	0.39 (0.43)	-0.18	1.25
$AT_{C5}H^{\bullet}$	0.78 (0.85)	0.30	1.39
$AT_{C6}H^{\bullet}$	2.04 (2.09)	1.56	2.56

Conclusions

By comparison of the 14 $(AT+H)^{\bullet}$ radical geometry structures, the main conclusion are as follows:

(i) When hydrogen-atom attaches to the C4=C5 double bond, the joint of the six-membered ring and five-membered ring of the adenine, the relevant structures $H^{\bullet}A_{C4}T$ and $H^{\bullet}A_{C5}T$ are more likely to produce distortion.

(ii) When hydrogen-atom attaches to an atom that is close to or directly related to the two interstrand hydrogen bonds of the base pair, the corresponding structures $H^{\bullet}A_{N1}T$, $AT_{C4}H^{\bullet}$ and $AT_{O4}H^{\bullet}$ are more likely to produce distortion.

(iii) When hydrogen-atom attaches to an atom that linked to functional groups (C6 site of adenine and C5 site of thymine), the connected functional groups are more likely to move out of the plane of the AT base pair.

(iv) For the structures $H^{\bullet}A_{C2}T$ and $H^{\bullet}A_{C4}T$, H3 transfers following the hydrogen N1…H3-N3. For the structure $AT_{C4}H^{\bullet}$, H6a transfers to form H6a-O4(T) bond following the hydrogen N6-H6a…O4. These significant geometry disturbances may cause DNA mutation.

The structures when hydrogen-atom adds to an atom away from the adenine-thymine hydrogen bonds lie lower in relative energy. The radical $H^{\bullet}A_{C8}T$ is the lowest energy AT base pair after hydrogen-atom addition in this work. The radicals which hydrogen-atom adds to C atom have larger AEA and VEA values than that of hydrogen-atom adds to N or O atom. Thus the structures which hydrogen-atom adds to C atom are more likely to attach an electron to form anion and then lead to ionization damage. The corresponding anions have larger VDE value, which show the ability of bound electron, thus it is not easy to ionize an electron to come back to neutral.

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