Supporting Information

Proton Transfer Induced SOMO-to-HOMO Level Switching in One-electron Oxidized A-T and G-C Base Pairs: A Density Functional Theory Study

Anil Kumar and M. D. Sevilla
Department of Chemistry, Oakland University, Rochester, Michigan 48309

Full reference 26.

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09; Gaussian, Inc.: Wallingford CT, 2009.

Figure Captions

Scheme 1- Schematic diagram showing the molecular orbital configurations of (a) A-T and (b) G-C base pairs in their neutral, one- and two-electron oxidized states. PT designates the proton transfer and its location in the base pair is highlighted by solid pink circle. Location of SOMO (singly occupied molecular orbital) is highlighted by green color in the MO configuration. For closed shell systems (neutral or singlet state) HOMO distributions are shown and for open shell systems (doublet and triplet state) spin density distributions are shown. HOMO = Highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital; HDMO = highest doubly occupied molecular orbital and SOMO = singly occupied molecular orbital. Up and down arrows show α and β spins of electrons.

Figure S1- Molecular orbital (MO) plots of A-T base pair in their neutral, radical cation ($A^{\bullet+}$-T) and proton transferred radical cation $A(-H)^{\bullet}$-$T(H^{+})$ states. Spin density distributions of $A^{\bullet+}$-T and

$A(-H)^{\bullet}$-$T(H^{+})$ are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the ωb97x/6-31++G(d) method.

Figure S2- Molecular orbital (MO) plots of A-T base pair in their neutral, radical cation ($A^{\bullet+}$-T) and proton transferred radical cation $A(-H)^{\bullet}$-$T(H^{+})$ states. Spin density distributions of $A^{\bullet+}$-T and $A(-H)^{\bullet}$-$T(H^{+})$ are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the B3LYP/6-31++G(d) method.

Figure S3- Molecular orbital (MO) plots of A-T base pair in their neutral, radical cation ($A^{\bullet+}$-T) and proton transferred radical cation $A(-H)^{\bullet}$-$T(H^{+})$ states. Spin density distributions of $A^{\bullet+}$-T and $A(-H)^{\bullet}$-$T(H^{+})$ are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the M06-2x/6-31++G(d) method.

Figure S4- Molecular orbital (MO) plots of G-C base pair in their neutral, radical cation ($G^{\bullet+}$-C) and proton transferred radical cation $G(-H)^{\bullet}$-$C(H^{+})$ states. Spin density distributions of $G^{\bullet+}$-C and $G(-H)^{\bullet}$-$C(H^{+})$ are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the ωb97x/6-31++G(d) method.

Figure S5- Molecular orbital (MO) plots of G-C base pair in their neutral, radical cation ($G^{\bullet+}$-C) and proton transferred radical cation $G(-H)^{\bullet}$-$C(H^{+})$ states. Spin density distributions of $G^{\bullet+}$-C and $G(-H)^{\bullet}$-$C(H^{+})$ are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the B3LYP/6-31++G(d) method.

Figure S6- Molecular orbital (MO) plots of G-C base pair in their neutral, radical cation ($G^{\bullet+}$-C) and proton transferred radical cation $G(-H)^{\bullet}$-$C(H^{+})$ states. Spin density distributions of $G^{\bullet+}$-C and $G(-H)^{\bullet}$-$C(H^{+})$ are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the M06-2x/6-31++G(d) method.

Figure S7- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of A-T base pair using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. Relative stability between $A^{\bullet+}$-T and $A(-H)^{\bullet}$-$T(H^{+})$ are given in kcal/mol. TE = Total energy in A.U.

Figure S8- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of $A^{\bullet+}$-T in their singlet and triplet states using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. Relative stability between singlet and triplet are given in kcal/mol. TE = Total energy in A.U.

Figure S9- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of adenine (A) using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Figure S10- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of $A(N6\text{-}H)^{\bullet}$ using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Figure S11- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of $A^{\bullet+}$ (adenine radical cation) in singlet and triplet states using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Figure S12- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of thymine (T) using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Figure S13- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of O4-protonated thymine ($T(O4\text{-}H^+)$) using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Figure S14- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of G-C base pair using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. Relative stability between $G^{\bullet+}$-C and $G(-H)^{\bullet}$-$C(H^+)$ are given in kcal/mol. TE = Total energy in A.U.

Figure S15- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of $G^{\bullet+}$-C in their singlet and triplet states using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. Relative stability between singlet and triplet are given in kcal/mol. TE = Total energy in A.U.

Figure S16- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of guanine (G) using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Figure S17- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of $G(N1\text{-}H)^{\bullet}$ using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Figure S18- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of $G^{\bullet+}$ (guanine radical cation) in singlet and triplet states using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Figure S19- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of cytosine (C) using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Figure S20- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of N3-protonated cytosine ($C(N3\text{-}H^+)$) using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Figure S21- Molecular orbital (MO) plots of G-C base pair in their neutral, radical cation ($G^{\bullet+}$-C) and proton transferred radical cation $G(-H)^{\bullet}$-$C(H^+)$) states in **solution using polarized continuum model (PCM)**. Spin density distributions of $G^{\bullet+}$-C and $G(-H)^{\bullet}$-$C(H^+)$ are also shown.

Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the ωb97x-PCM/6-31++G(d) method.

Figure S22- Molecular orbital (MO) plots of A-T base pair in their neutral, radical cation ($A^{\bullet+}$-T) and proton transferred radical cation $A(-H)^{\bullet}$-$A(H^{+})$ states in **solution using polarized continuum model (PCM)**. Spin density distributions of $A^{\bullet+}$-T and $A(-H)^{\bullet}$-$T(H^{+})$ are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the ωb97x-PCM/6-31++G(d) method.

Figure S23- Molecular orbital (MO) plots of (5'-G-3')•(3'-C-5') in their neutral, radical cation (5'-$G^{\bullet+}$-3')•(3'-C-5') and proton transferred radical cation (5'-$G(-H)^{\bullet}$-3')•(3'-(H^{+})C-5') states. Spin density distributions of (5'-$G^{\bullet+}$-3')•(3'-C-5') and (5'-$G(-H)^{\bullet}$-3')•(3'-(H^{+})C-5') are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the ωb97x/6-31G(d) method to save computational time.

Figure S24- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of (5'-G-3')•(3'-C-5') using the ωb97x/6-31G(d) method. Relative stability between (5'-$G^{\bullet+}$-3')•(3'-C-5') and proton transferred (5'-$G(-H)^{\bullet}$-3')•(3'-(H^{+})C-5') in kcal/mol. TE = Total energy in A.U.

Figure S25- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of (5'-$G^{\bullet+}$-3')•(3'-C-5') and (5'-$G(-H)^{\bullet}$-3')•(3'-(H^{+})C-5') in triplet and singlet states using the ωb97x/6-31G(d) method. Relative stability between triplet and singlet states in kcal/mol. TE = Total energy in A.U.

Figure S26- Molecular orbital (MO) plots of (5'-A-3')•(3'-T-5') in their neutral, radical cation (5'-$A^{\bullet+}$-3')•(3'-T-5') and proton transferred radical cation (5'-$A(-H)^{\bullet}$-3')•(3'-(H^{+})T-5') states. Spin density distributions of (5'-$A^{\bullet+}$-3')•(3'-T-5') and (5'-$A(-H)^{\bullet}$-3')•(3'-(H^{+})T-5') are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the ωb97x/6-31G(d) method to save computational time.

Figure S27- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of (5'-A-3')•(3'-T-5') using the ωb97x/6-31G(d) method. Relative stability between (5'-$A^{\bullet+}$-3')•(3'-T-5') and proton transferred (5'-$A(-H)^{\bullet}$-3')•(3'-(H^{+})T-5') in kcal/mol. TE = Total energy in A.U.

Figure S28- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of (5'-$A^{\bullet+}$-3')•(3'-T-5') and (5'-$A(-H)^{\bullet}$-3')•(3'-(H^{+})A-5') in triplet and singlet states using the ωb97x/6-31G(d) method. Relative stability between triplet and singlet states in kcal/mol. TE = Total energy in A.U.

Figure S29- Molecular orbital (MO) plots of $A^{\bullet+}$-T and $G^{\bullet+}$-C base pair radical cations. Spin density distributions of $A^{\bullet+}$-T and $G^{\bullet+}$-C are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the *ab initio* **MP2/6-31++G(D)** method using the ωb97x/6-31++G(d) optimized geometries

Figure S30- Calculated hydrogen-bond lengths in Å in neutral G-C and A-T base pairs. Experimental X-ray crystallographic[a,b] values are given in parentheses.

Figure S31- ωb97x/6-31++G(d) calculated hydrogen-bond lengths in Å in radical cation of G-C base pair. (i) $G^{\bullet+}$-C (top figure), (ii) PT in between G and C in $(G^{\bullet}\text{-}C)^{+}$ (middle figure) and (iii) PT transferred $G(-H)^{\bullet}$-$C(H^{+})$. Mulliken charges of two nitrogens are given in blue color and H^{+} in pink color. Pink circle shows the location of the H^{+} between the two bases.

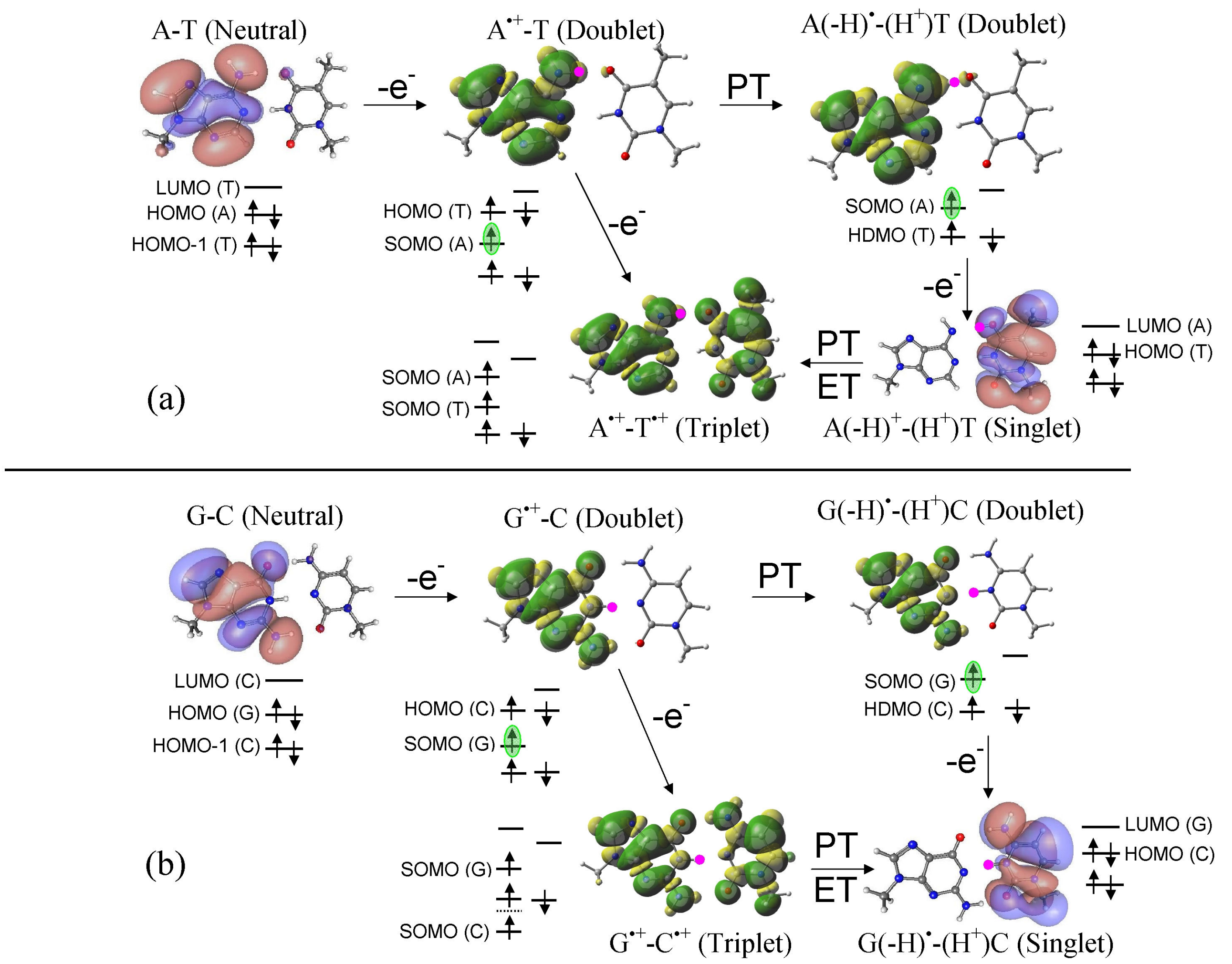
CASSCF(11,11)/def2-SV(P) and CASSCF(11,11)/6-31G calculation of one-electron oxidized A-T base pair ($A^{\bullet+}$-T). ωb97x/6-31++G(d) calculated optimized geometry is used for the calculation.**

Optimized geometries by of structures calculated by the ωb97x/6-31++G(d) method

---

Spin density, molecular orbitals and molecular structures were plotted using GaussView,[1] IQmol[2] and Jmol[3].

1. GaussView; Gaussian, Inc.: Pittsburgh, PA, 2003.
2. Free open-source molecular editor and visualization package; available at http://www.iqmol.org.
3. Jmol: An open-source Java Viewer for chemical structures in 3D; Jmol Development Team, An Open-Science Project, 2004; available at http://jmol.sourceforge.net.



Scheme 1- Schematic diagram showing the molecular orbital configurations of (a) A-T and (b) G-C base pairs in their neutral, one- and two-electron oxidized states. PT designates the proton transfer and its location in the base pair is highlighted by solid pink circle. Location of SOMO (singly occupied molecular orbital) is highlighted by green color in the MO configuration. For closed shell systems (neutral or singlet state) HOMO distributions are shown and for open shell systems (doublet and triplet state) spin density distributions are shown. HOMO = Highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital; HDMO = highest doubly occupied molecular orbital and SOMO = singly occupied molecular orbital. Up and down arrows show α and β spins of electrons. ET = electron transfer; PT = proton transfer.

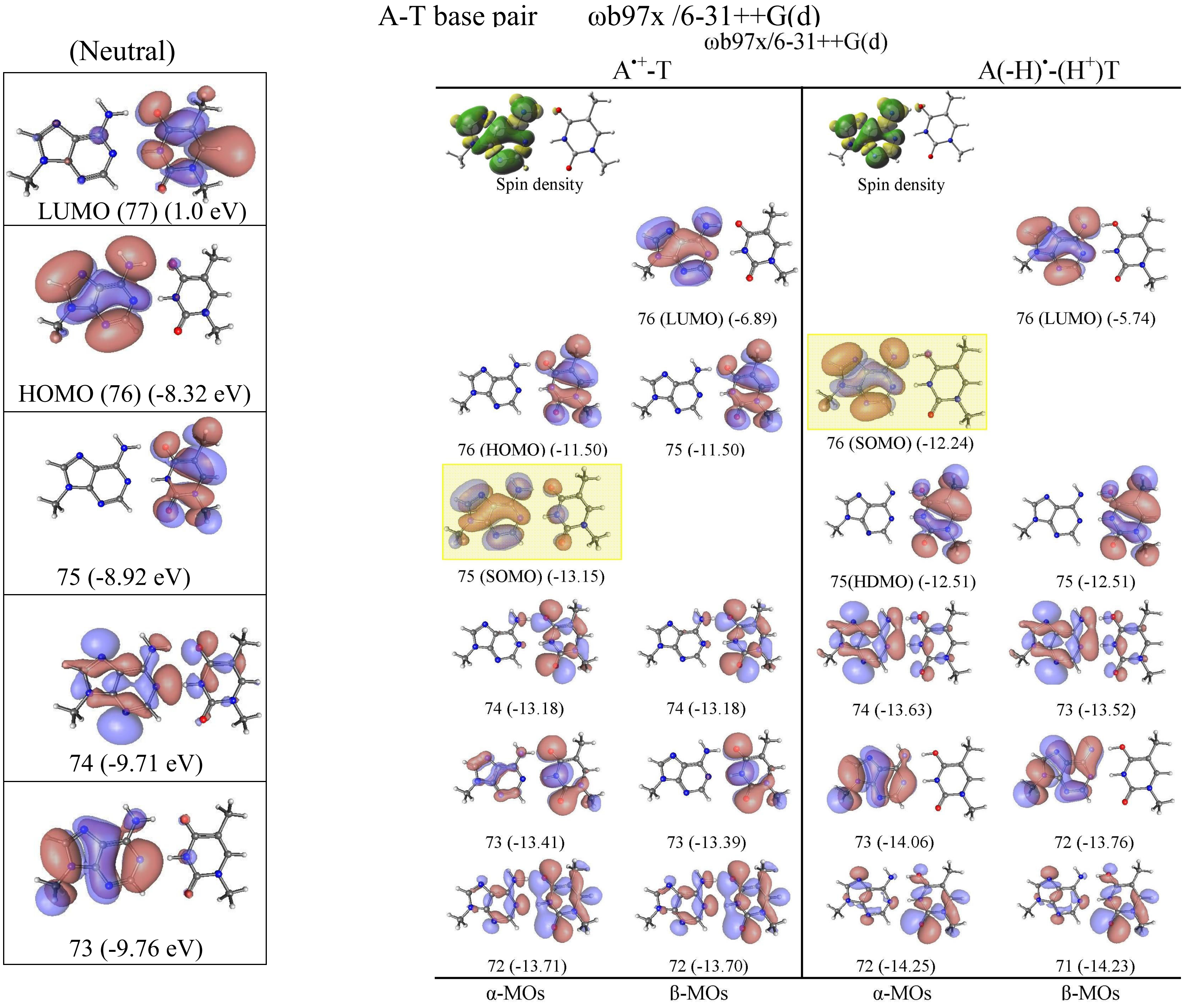


Figure S1- Molecular orbital (MO) plots of A-T base pair in their neutral, radical cation ($A^{\bullet+}$-T) and proton transferred radical cation $A(-H)^{\bullet}$-$T(H^{+})$ states. Spin density distributions of $A^{\bullet+}$-T and $A(-H)^{\bullet}$-$T(H^{+})$ are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the ωb97x/6-31++G(d) method.

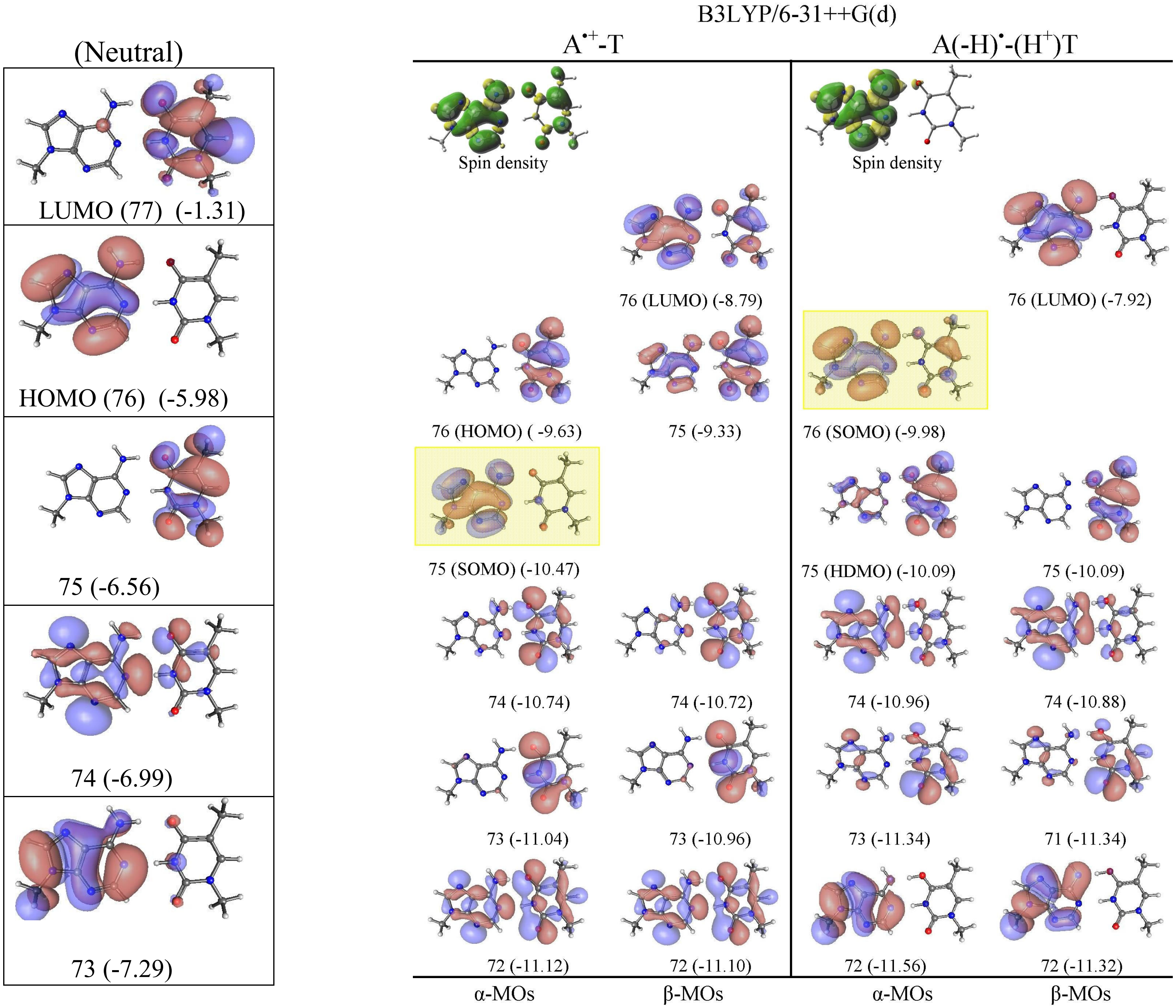


Figure S2- Molecular orbital (MO) plots of A-T base pair in their neutral, radical cation ($A^{\bullet+}$-T) and proton transferred radical cation $A(-H)^{\bullet}$-$T(H^{+})$ states. Spin density distributions of $A^{\bullet+}$-T and $A(-H)^{\bullet}$-$T(H^{+})$ are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the B3LYP/6-31++G(d) method.

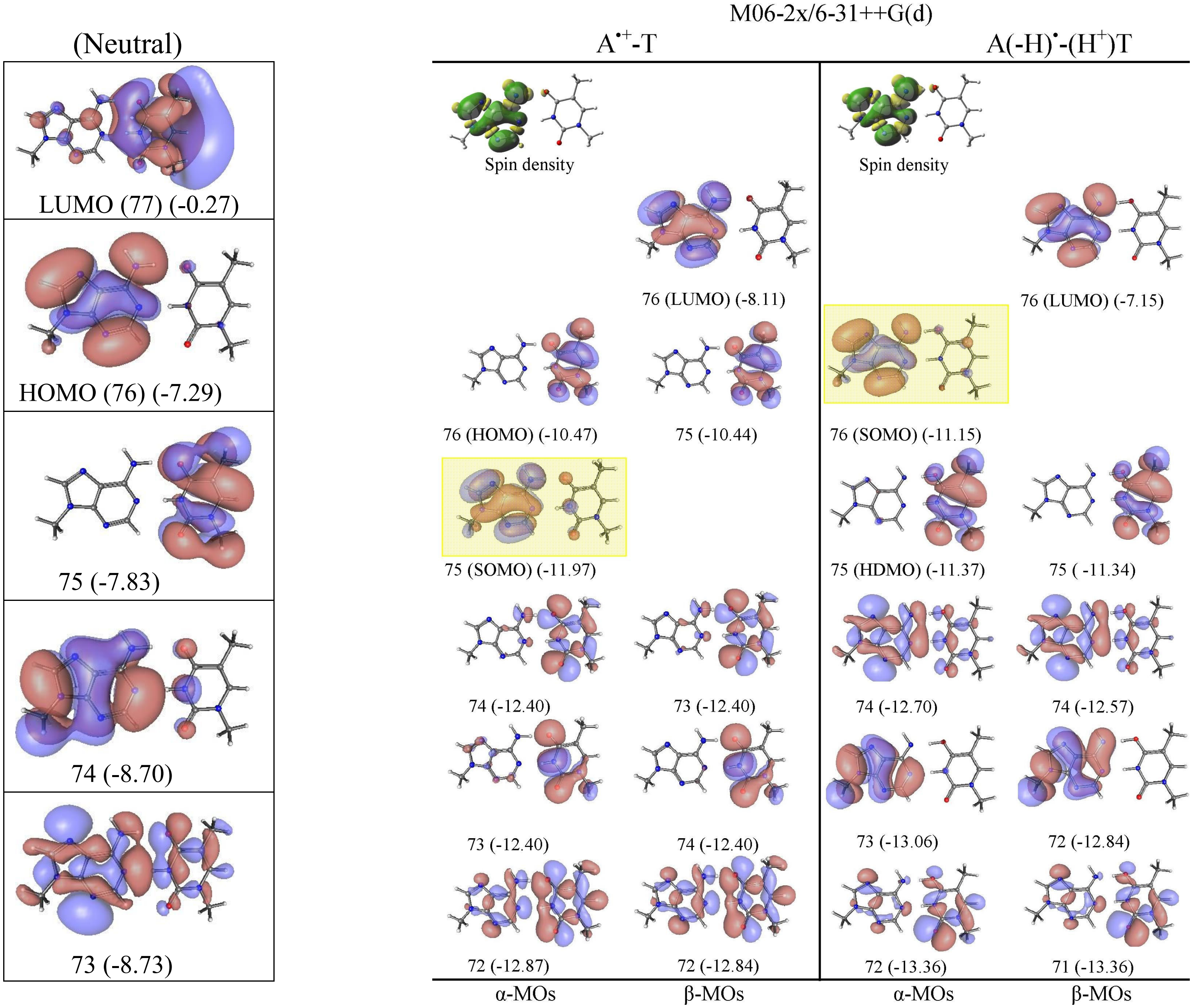


Figure S3- Molecular orbital (MO) plots of A-T base pair in their neutral, radical cation (A$^{\bullet+}$-T) and proton transferred radical cation A(-H)$^{\bullet}$-T(H^{+}) states. Spin density distributions of A$^{\bullet+}$-T and A(-H)$^{\bullet}$-T(H^{+}) are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the M06-2x/6-31++G(d) method.

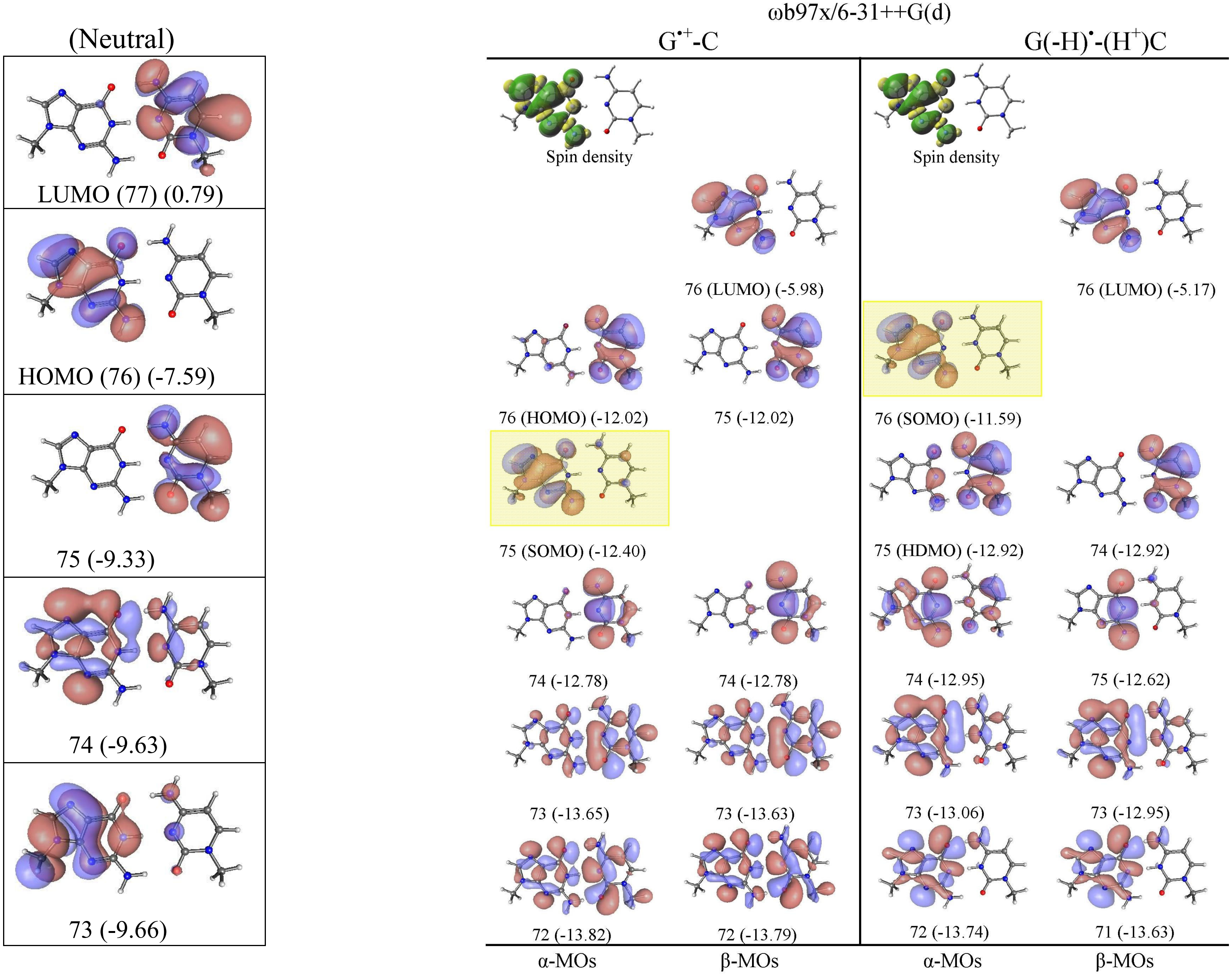


Figure S4- Molecular orbital (MO) plots of G-C base pair in their neutral, radical cation ($G^{\bullet+}$-C) and proton transferred radical cation $G(-H)^{\bullet}$-$C(H^{+})$ states. Spin density distributions of $G^{\bullet+}$-C and $G(-H)^{\bullet}$-$C(H^{+})$ are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the ωb97x/6-31++G(d) method.

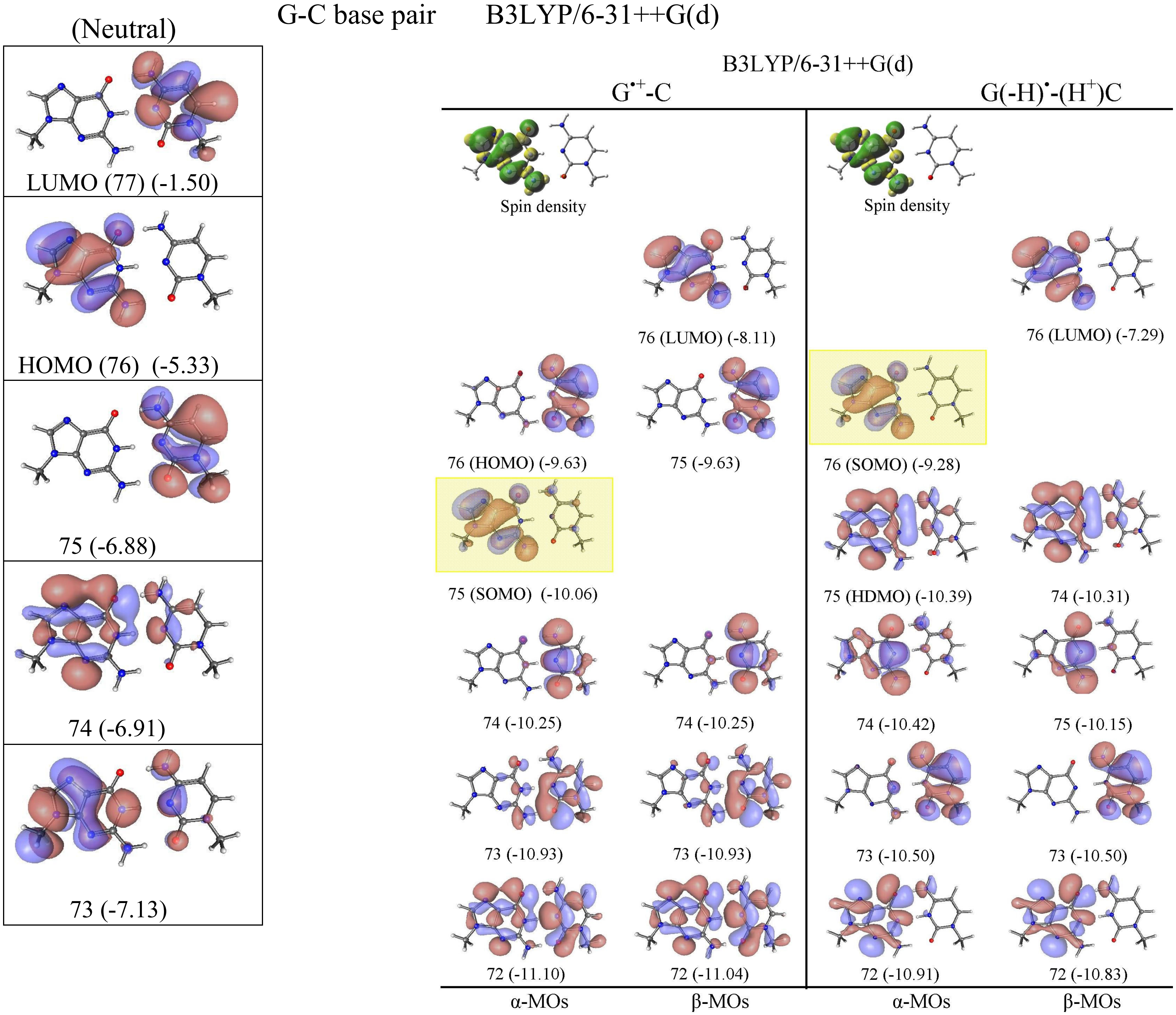


Figure S5- Molecular orbital (MO) plots of G-C base pair in their neutral, radical cation ($G^{\bullet+}$-C) and proton transferred radical cation $G(-H)^{\bullet}$-$C(H^{+})$ states. Spin density distributions of $G^{\bullet+}$-C and $G(-H)^{\bullet}$-$C(H^{+})$ are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the B3LYP/6-31++G(d) method.

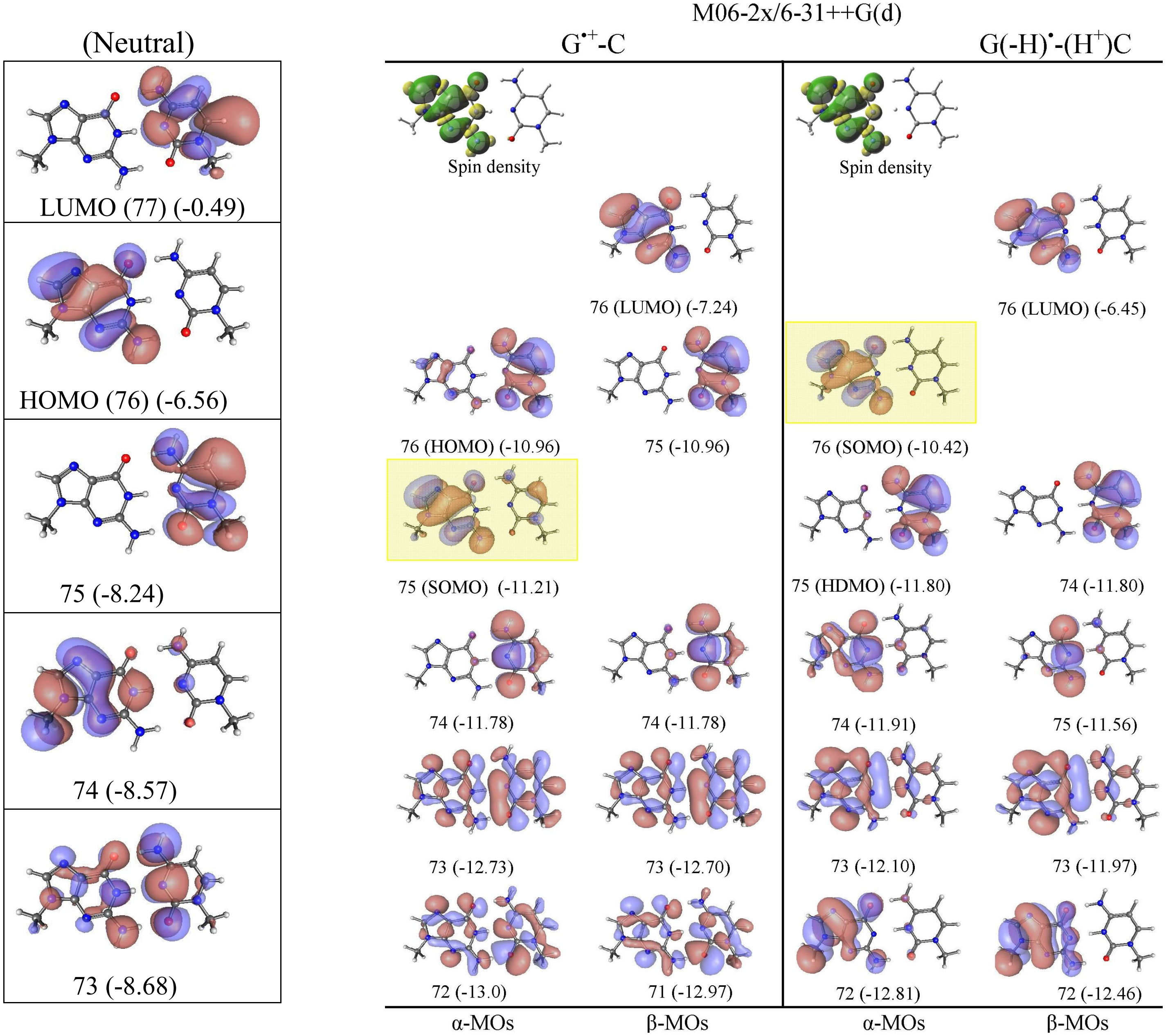
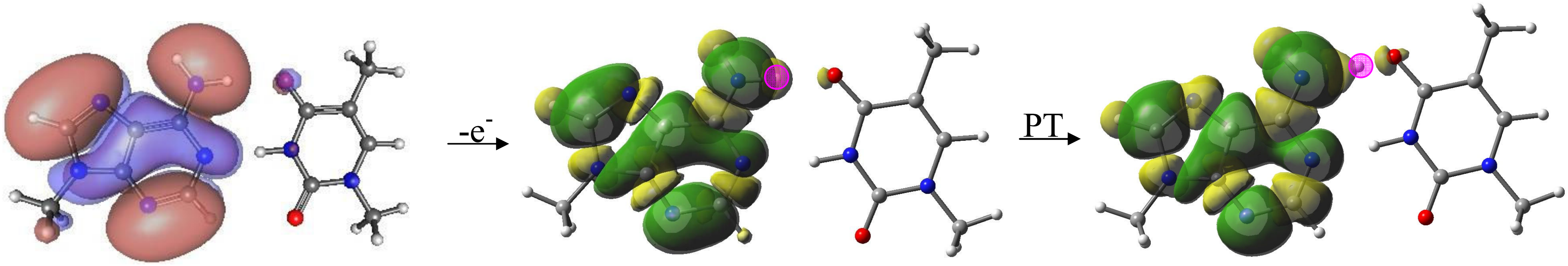


Figure S6- Molecular orbital (MO) plots of G-C base pair in their neutral, radical cation ($G^{\bullet+}$-C) and proton transferred radical cation G(-H)$^{\bullet}$-C(H^{+}) states. Spin density distributions of $G^{\bullet+}$-C and G(-H)$^{\bullet}$-C(H^{+}) are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the M06-2x/6-31++G(d) method.

A-T base pair



Neutral (singlet)
MO = HOMO
TE = -999.896937614 A.U. (ωb97x)
TE = -1000.14318621 A.U. (B3LYP)
TE = -999.731661395 A.U. (M06-2x)

Radical cation (A$^{\bullet+}$-T)
Spin density plot
TE (vert) = -999.603318675 A.U. (ωb97x)
TE (opt) = -999.616674723 A.U. (ωb97x)
TE (vert) = -999.864700709 A.U. (B3LYP)
TE (opt) = -999.869874139 A.U. (B3LYP)
TE (vert) = -999.434592300 A.U. (M06-2x)
TE (opt) = -999.447980392 A.U. (M06-2x)

IP = TE (A$^{\bullet+}$-T) – TE (Neutral)
IP (vert) = 7.99 eV (ωb97x)
IP (adia) = 7.62 eV (ωb97x)
IP (vert) = 7.58 eV (B3LYP)
IP (adia) = 7.43 eV (B3LYP)
IP (vert) = 8.08 eV (M06-2x)
IP (adia) = 7.72 eV (M06-2x)

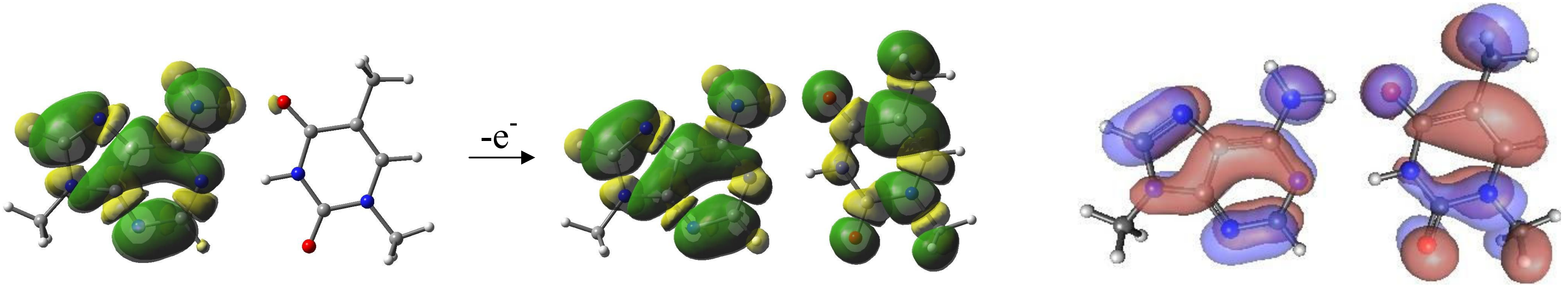
Radical cation PT (A(N6-H)$^{\bullet}$-(O4-H^{+})T)
Spin density plot
TE (opt) = -999.610066607 A.U. (ωb97x)
TE (opt) = -999.862802704 A.U. (B3LYP)
TE (opt) = -999.444830192 A.U. (M06-2x)

Relative stability (ΔE) with respect to A$^{\bullet+}$-T
ΔE = TE ((A(N6-H)$^{\bullet}$-(O4-H^{+})T) -TE (A$^{\bullet+}$-T)
ΔE = 4.15 kcal/mol (ωb97x)
ΔE = 4.44 kcal/mol (B3LYP)
ΔE = 1.98 kcal/mol (M06-2x)

IP = TE (A(N6-H)$^{\bullet}$-(N3-H^{+})T) – TE (Neutral)
IP (adia) = 7.80 eV (ωb97x)
IP (adia) = 7.63 eV (B3LYP)
IP (adia) = 7.80 eV (M06-2x)

Figure S7- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of A-T base pair using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. Relative stability between A$^{\bullet+}$-T and A(-H)$^{\bullet}$-T(H^{+}) are given in kcal/mol. TE = Total energy in A.U.

$A^{\bullet +}$-T (radical cation)



Radical cation ($A^{\bullet +}$-T) (doublet)
Spin density plot
TE = -999.616674723 A.U. (ωb97x)
TE = -999.869874139 A.U. (B3LYP)
TE = -999.447980392 A.U. (M06-2x)

(a) Second oxidation (A-T)$^{+2}$ (Triplet)
Spin density plot for triplet state
TE (vert) = -999.207996805 A.U. (ωb97x)
TE (opt) = -999.222672458 A.U. (ωb97x)
TE (vert) = -999.468720628 A.U. (B3LYP)
TE (opt) = -999.476799602 A.U. (B3LYP)
TE (vert) = -999.035280356 A.U. (M06-2x)
TE (opt) = -999.050530415 A.U. (M06-2x)

IP = TE (A-T)$^{+2}$ – TE ($A^{\bullet +}$-T)
IP (vert) = 11.12 eV (ωb97x)
IP (adia) = 10.72 eV (ωb97x)
IP (vert) = 10.91 eV (B3LYP)
IP (adia) = 10.69 eV (B3LYP)
IP (vert) = 11.23 eV (M06-2x)
IP (adia) = 10.81 eV (M06-2x)

Stability with respect to singlet state
ΔE = TE (Triplet) – TE (Singlet)
ΔE = -18.11 kcal/mol (ωb97x)
ΔE = -15.40 kcal/mol (B3LYP)
ΔE = -13.74 kcal/mol (M06-2x)

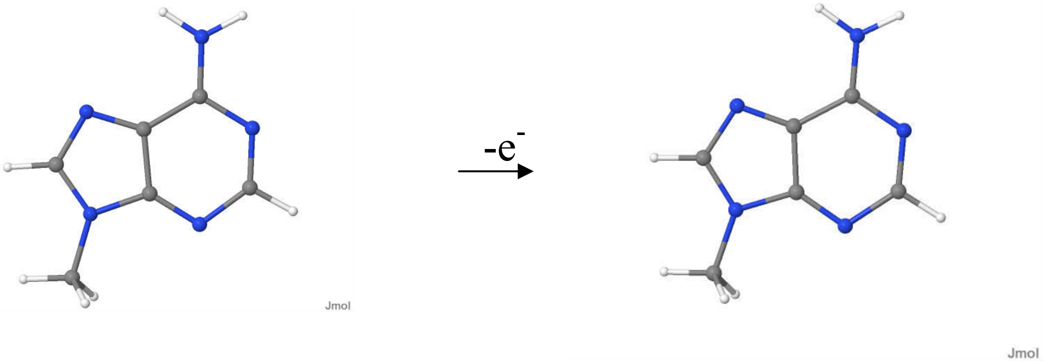
(b) Second oxidation (A-T)$^{+2}$ (Singlet)
MO= HOMO plot (B3LYP calculation)
TE (vert) = -999.150894408 A.U. (ωb97x)
[a]TE (opt) = -999.193808642 A.U. (ωb97x)
TE (vert) = -999.447491210 A.U. (B3LYP)
[b]TE (opt) = -999.452266069 A.U. B3LYP)
TE (vert) = -998.998413811 A.U. (M06-2x)
[a]TE (opt) = -999.028623036 A.U. (M06-2x)

IP = TE (A-T)$^{+2}$ – TE ($A^{\bullet +}$-T)
IP (vert) = 12.67 eV (ωb97x)
IP (adia) = 11.50 eV (ωb97x)
IP (vert) = 11.49 eV (B3LYP)
IP (adia) = 11.36 eV (B3LYP)
IP (vert) = 12.23 eV (M06-2x)
IP (adia) = 11.41 eV (M06-2x)

[a]N6 proton of A transfers to O4 of T.
[b]No proton transfer.

Figure S8- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of $A^{\bullet +}$-T in their singlet and triplet states using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. Relative stability between singlet and triplet are given in kcal/mol. TE = Total energy in A.U.

Adenine (A)



Neutral (singlet)

TE = -506.526211220 A.U. (ωb97x)
TE = -506.653966407 A.U. (B3LYP)
TE = -506.448696166 A.U. (M06-2x)

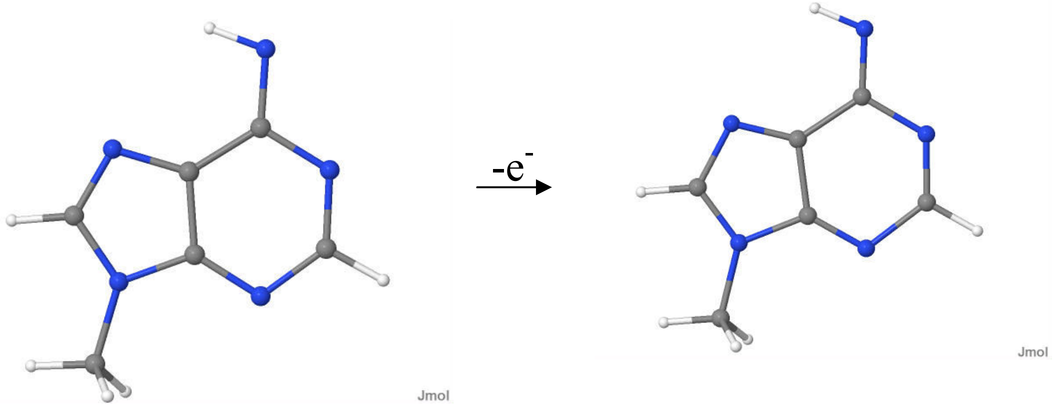
Radical cation ($A^{\bullet+}$)

TE (vert) = -506.222231158 A.U. (ωb97x)
TE (opt) = -506.232589378 A.U. (ωb97x)
TE (vert) = -506.356979434 A.U. (B3LYP)
TE (opt) = -506.364503844 A.U. (B3LYP)
TE (vert) = -506.142046712 A.U. (M06-2x)
TE (opt) = -506.151931945 A.U. (M06-2x)

IP = TE ($A^{\bullet+}$) – TE (Neutral)
IP (vert) = 8.27 eV (ωb97x)
IP (adia) = 7.99 eV (ωb97x)
IP (vert) = 8.08 eV (B3LYP)
IP (adia) = 7.87 eV (B3LYP)
IP (vert) = 8.34 eV (M06-2x)
IP (adia) = 8.07 eV (M06-2x)

Figure S9- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of adenine (A) using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Adenine(N6-H)$^\bullet$ (A(N6-H)$^\bullet$)



A(N6-H)$^\bullet$ (radical) (doublet)

TE = -505.852465614 A.U. (ωb97x)
TE = -505.984536915 A.U. (B3LYP)
TE = -505.775031411 A.U. (M06-2x)

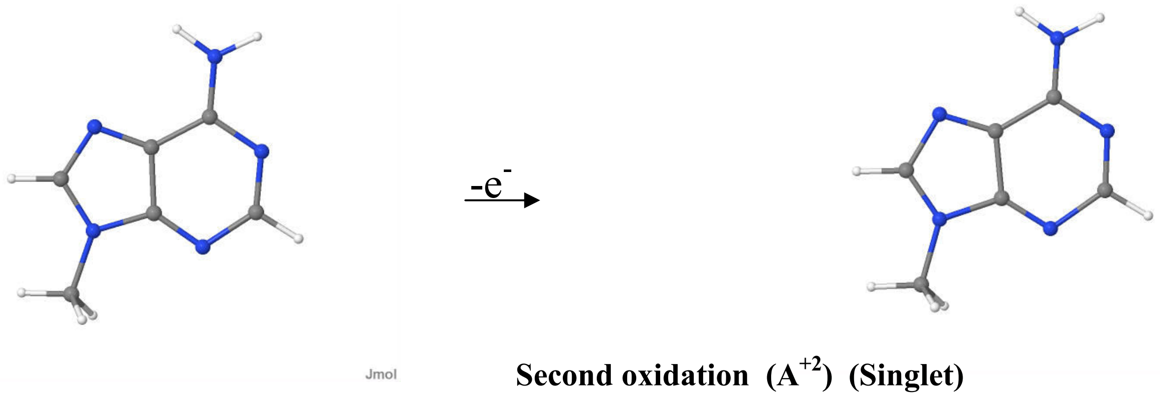
A(N6-H)$^+$ (cation)

TE (vert) = -505.528478118 A.U. (ωb97x)
TE (opt) = -505.544056952 A.U. (ωb97x)
TE (vert) = -505.670410554 A.U. (B3LYP)
TE (opt) = -505.680585365 A.U. (B3LYP)
TE (vert) = -505.454274067 A.U. (M06-2x)
TE (opt) = -505.469014238 A.U. (M06-2x)

IP = TE (A(N6-H)$^+$) – TE (A(N6-H)$^\bullet$)
IP (vert) = 8.81 eV (ωb97x)
IP (adia) = 8.39 eV (ωb97x)
IP (vert) = 8.54 eV (B3LYP)
IP (adia) = 8.27 eV (B3LYP)
IP (vert) = 8.73 eV (M06-2x)
IP (adia) = 8.32 eV (M06-2x)

Figure S10- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of A(N6-H)$^\bullet$ using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Adenine radical cation ($A^{\bullet+}$)



$A^{\bullet+}$ (radical cation) (doublet)

TE = -506.232589378 A.U. (ωb97x)
TE = -506.364503844 A.U. (B3LYP)
TE = -506.151931945 A.U. (M06-2x)

Second oxidation (A^{+2}) (Singlet)

TE (vert) = -505.735968816 A.U. (ωb97x)
TE (opt) = -505.751806372 A.U. (ωb97x)
TE (vert) = -505.872314028 A.U. (B3LYP)
TE (opt) = -505.884286777 A.U. (B3LYP)
TE (vert) = -505.655548234 A.U. (M06-2x)
TE (opt) = -505.670477372 A.U. (M06-2x)

IP = TE (A^{+2}) – TE ($A^{\bullet+}$)
IP (vert) = 13.51 eV (ωb97x)
IP (adia) = 13.08 eV (ωb97x)
IP (vert) = 13.39 eV (B3LYP)
IP (adia) = 13.06 eV (B3LYP)
IP (vert) = 13.50 eV (M06-2x)
IP (adia) = 13.10 eV (M06-2x)

Stability with respect to triplet state
ΔE = TE (Singlet) – TE (Triplet)
ΔE = -23.41 kcal/mol (ωb97x)
ΔE = -14.57 kcal/mol (B3LYP)
ΔE = -24.00 kcal/mol (M06-2x)

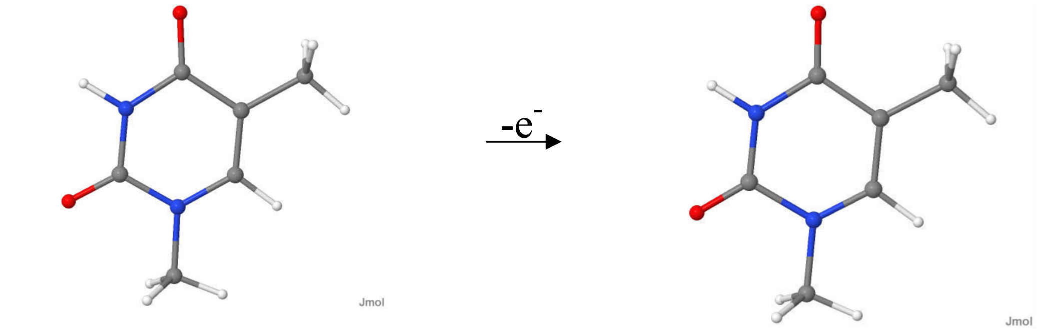
Second oxidation (A^{+2}) (Triplet)

TE (vert) = -505.697741138 A.U. (ωb97x)
TE (opt) = -505.714495298 A.U. (ωb97x)
TE (vert) = -505.847570408 A.U. (B3LYP)
TE (opt) = -505.861069514 A.U. (B3LYP)
TE (vert) = -505.616142722 A.U. (M06-2x)
TE (opt) = -505.632224684 A.U. (M06-2x)

IP = TE (A^{+2}) – TE ($A^{\bullet+}$)
IP (vert) = 14.55 eV (ωb97x)
IP (adia) = 14.09 eV (ωb97x)
IP (vert) = 14.06 eV (B3LYP)
IP (adia) = 13.69 eV (B3LYP)
IP (vert) = 14.57 eV (M06-2x)
IP (adia) = 14.14 eV (M06-2x)

Figure S11- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of $A^{\bullet+}$ (adenine radical cation) in singlet and triplet states using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Thymine (T)



Thymine Neutral (singlet)

TE = -493.346405283 A.U. (ωb97x)
TE = -493.469141148 A.U. (B3LYP)
TE = -493.259222838 A.U. (M06-2x)

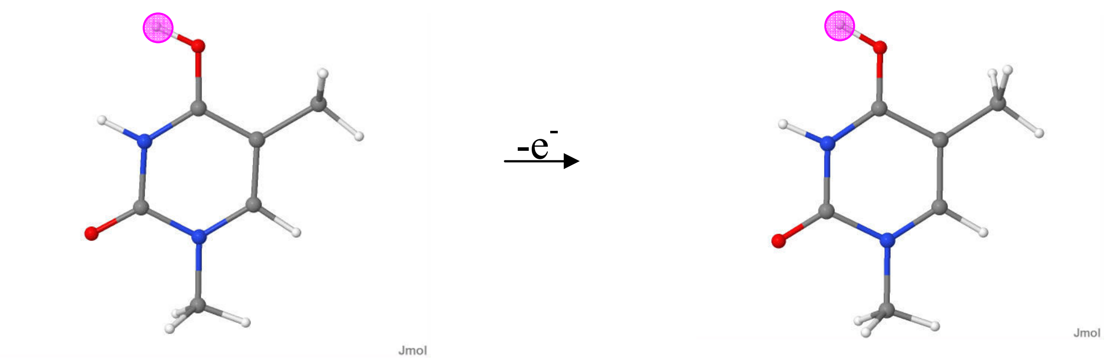
Radical cation ($T^{\bullet +}$)

TE (vert) = -493.022638292 A.U. (ωb97x)
TE (opt) = -493.033132165 A.U. (ωb97x)
TE (vert) = -493.151107842 A.U. (B3LYP)
TE (opt) = -493.158790904 A.U. (B3LYP)
TE (vert) = -492.932799589 A.U. (M06-2x)
TE (opt) = -492.942726101 A.U. (M06-2x)

IP = TE ($T^{\bullet +}$) – TE (Neutral)
IP (vert) = 8.81 eV (ωb97x)
IP (adia) = 8.52 eV (ωb97x)
IP (vert) = 8.65 eV (B3LYP)
IP (adia) = 8.44 eV (B3LYP)
IP (vert) = 8.88 eV (M06-2x)
IP (adia) = 8.61 eV (M06-2x)

Figure S12- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of thymine (T) using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

O4-protonated Thymine (T(O4-H$^+$))



T(O4-H$^+$) (Neutral) (singlet)

TE = -493.682671986 A.U. (ωb97x)
TE = -493.806785396 A.U. (B3LYP)
TE = -493.594239002 A.U. (M06-2x)

Radical cation (T(O4-H$^+$)$^{\bullet+}$

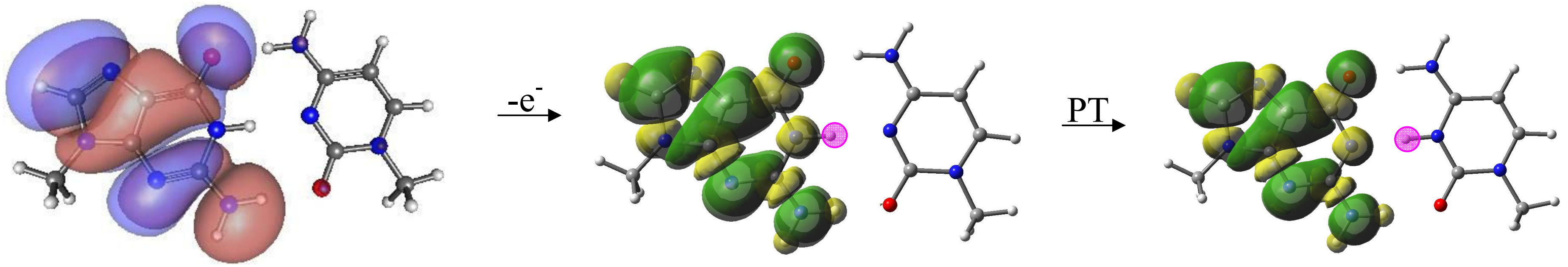
TE (vert) = -493.181791526 A.U. (ωb97x)
TE (opt) = -493.191529860 A.U. (ωb97x)
TE (vert) = -493.311178335 A.U. (B3LYP)
TE (opt) = -493.318507459 A.U. (B3LYP)
TE (vert) = -493.090241000 A.U. (M06-2x)
TE (opt) = -493.099572174 A.U. (M06-2x)

IP = TE (T$^{\bullet+}$) – TE (Neutral)

IP (vert) = 13.62 eV (ωb97x)
IP (adia) = 13.36 eV (ωb97x)
IP (vert) = 13.48 eV (B3LYP)
IP (adia) = 13.28 eV (B3LYP)
IP (vert) = 13.71 eV (M06-2x)
IP (adia) = 13.46 eV (M06-2x)

Figure S13- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of O4-protonated thymine (T(O4-H$^+$) using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

G-C base pair



Neutral (singlet)
MO = HOMO
TE = -1015.94611414 A.U. (ωb97x)
TE = -1016.19297948 A.U. (B3LYP)
TE = -1015.78110991 A.U. (M06-2x)

Radical cation ($G^{\bullet+}$-C)
Spin density plot
TE (vert) = -1015.68008855 A.U. (ωb97x)
TE (opt) = -1015.69568698 A.U. (ωb97x)
TE (vert) = -1015.93337387 A.U. (B3LYP)
TE (opt) = -1015.94596270 A.U. (B3LYP)
TE (vert) = -1015.51156628 A.U. (M06-2x)
TE (opt) = -1015.52696491 A.U. (M06-2x)

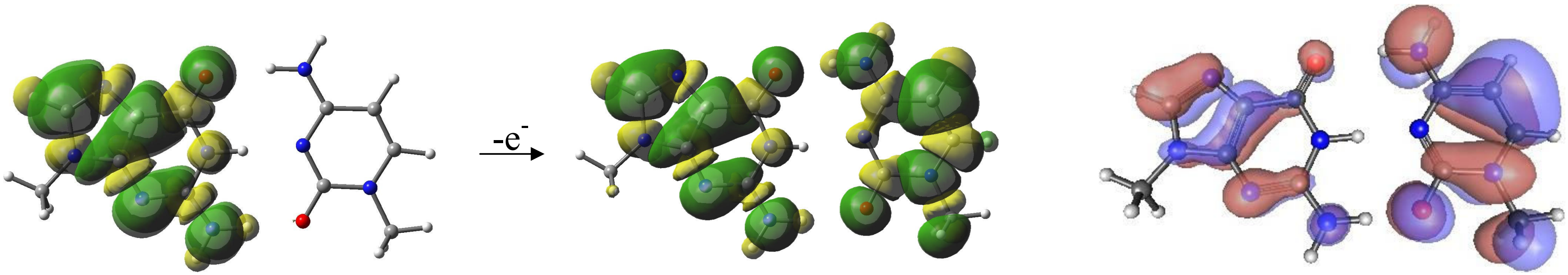
IP = TE ($G^{\bullet+}$-C) – TE (Neutral)
IP (vert) = 7.24 eV (ωb97x)
IP (adia) = 6.81 eV (ωb97x)
IP (vert) = 7.06 eV (B3LYP)
IP (adia) = 6.72 eV (B3LYP)
IP (vert) = 7.33 eV (M06-2x)
IP (adia) = 6.91 eV (M06-2x)

Radical cation PT (G(N1-H)$^{\bullet}$-(N3-H^{+})C)
Spin density plot
TE (opt) = -1015.69399298 A.U. (ωb97x)
TE (opt) = -1015.94451492 A.U. (B3LYP)
TE (opt) = -1015.52500566 A.U. (M06-2x)
Stability (ΔE) with respect to $G^{\bullet+}$-C
ΔE = TE ($G^{\bullet+}$-C) – TE ((G(N1-H)$^{\bullet}$-(N3-H^{+})C)
ΔE = 1.06 kcal/mol (ωb97x)
ΔE = 0.91 kcal/mol (B3LYP)
ΔE = 1.23 kcal/mol (M06-2x)

IP = TE (G(N1-H)$^{\bullet}$-(N3-H^{+})C) – TE (Neutral)
IP (adia) = 6.86 eV (ωb97x)
IP (adia) = 6.76 eV (B3LYP)
IP (adia) = 6.97 eV (M06-2x)

Figure S14- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of G-C base pair using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. Relative stability between $G^{\bullet+}$-C and G(-H)$^{\bullet}$-C(H^{+}) are given in kcal/mol. TE = Total energy in A.U.

$G^{\bullet+}$-C (radical cation)



Radical cation ($G^{\bullet+}$-C) (doublet)
Spin density plot

TE = -1015.69568698 A.U. (ωb97x)
TE = -1015.94596270 A.U. (B3LYP)
TE = -1015.52696491 A.U. (M06-2x)

Stability between triplet (**$G^{\bullet+}$-$C^{\bullet+}$**) **and proton transferred singlet G(-H)$^{+}$-(H^{+})C.**
ΔE = TE (Triplet) – TE (Singlet)

ΔE = -1015.28161379 – (-1015.29846906)
= 10.58 kcal/mol (ωb97x)
Singlet PT **G(-H)$^{+}$-(H^{+})C is more stable than triplet** (**$G^{\bullet+}$-$C^{\bullet+}$**) **by 10.58 kcal/mol**

(a) Second oxidation (G-C)$^{+2}$ (Triplet)
Spin density plot for triplet state
TE (vert) = -1015.26666609 A.U. (ωb97x)
TE (opt) = -1015.28161379 A.U. (ωb97x)
TE (vert) = -1015.52395015 A.U. (B3LYP)
TE (opt) = -1015.53679652 A.U. (B3LYP)
TE (vert) = -1015.09437387 A.U. (M06-2x)
TE (opt) = -1015.10996435 A.U. (M06-2x)

IP = TE (A-T)$^{+2}$ – TE ($A^{\bullet+}$-T)
IP (vert) = 11.67 eV (ωb97x)
IP (adia) = 11.26 eV (ωb97x)
IP (vert) = 11.48 eV (B3LYP)
IP (adia) = 11.13 eV (B3LYP)
IP (vert) = 11.77 eV (M06-2x)
IP (adia) = 11.34 eV (M06-2x)

Stability with respect to singlet state
ΔE = TE (a) – TE (b)
ΔE = 1.98 kcal/mol (ωb97x)
ΔE = -7.40 kcal/mol (ωb97x) (N2-H contrained)
ΔE = -2.95 kcal/mol (B3LYP)
ΔE = 6.42 kcal/mol (M06-2x)

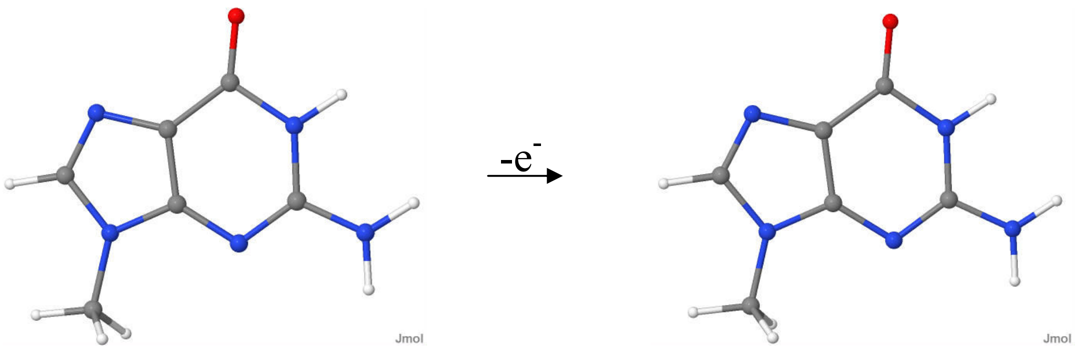
(b) Second oxidation (G-C)$^{+2}$ (Singlet)
MO= HOMO plot (B3LYP calculation)
TE (vert) = -1015.25134796 A.U. (ωb97x)
[a]TE (opt) = -1015.28477708 A.U. (ωb97x)
[b]TE (opt) = -1015.26982257 A.U. (ωb97x)
TE (vert) = -1015.52711892 A.U. (B3LYP)
[c]TE (opt) = -1015.53209904 A.U. B3LYP)
TE (vert) = -1015.08866281 A.U. (M06-2x)
[a]TE (opt) = -1015.12019052 A.U. (M06-2x)
[d]TE (vert) = -1015.27998771 A.U. (ωb97x)
[d] TE (adia) = -1015.29846906 A.U. (ωb97x)

IP = TE (G-C)$^{+2}$ – TE ($G^{\bullet+}$-C)
IP (vert) = 12.09 eV (ωb97x)
IP (adia) = 11.18 eV (ωb97x)
IP (vert) = 11.39 eV (B3LYP)
IP (adia) = 11.26 eV (B3LYP)
IP (vert) = 11.92 eV (M06-2x)
IP (adia) = 11.06 eV (M06-2x)
----

[a]N2 proton of G transfers to O2 of C.
[b]N2-H bond constrained.
[c]No proton transfer.
[d]N1 proton of G transferred to N3 of C.

Figure S15- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of $G^{\bullet+}$-C in their singlet and triplet states using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. Relative stability between singlet and triplet are given in kcal/mol. TE = Total energy in A.U.

Guanine (G)



Neutral (singlet)

TE = -581.747913109 A.U. (ωb97x)
TE = -581.889089657 A.U. (B3LYP)
TE = -581.657966434 A.U. (M06-2x)

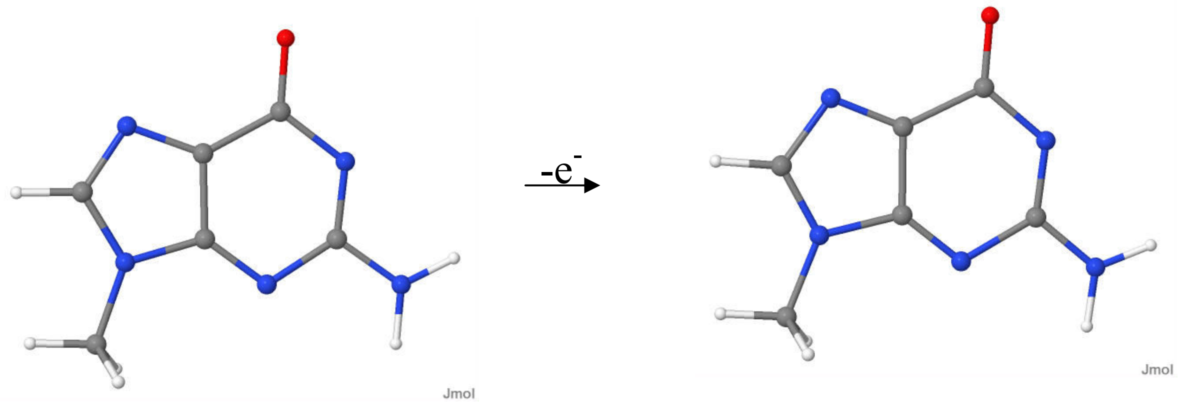
Radical cation ($G^{\bullet +}$)

TE (vert) = -581.459093506 A.U. (ωb97x)
TE (opt) = -581.471021197 A.U. (ωb97x)
TE (vert) = -581.605962036 A.U. (B3LYP)
TE (opt) = -581.614942395 A.U. (B3LYP)
TE (vert) = -581.365594326 A.U. (M06-2x)
TE (opt) = -581.377091553 A.U. (M06-2x)

IP = TE ($G^{\bullet +}$) – TE (Neutral)
IP (vert) = 7.86 eV (ωb97x)
IP (adia) = 7.53 eV (ωb97x)
IP (vert) = 7.70 eV (B3LYP)
IP (adia) = 7.46 eV (B3LYP
IP (vert) = 7.95 eV (M06-2x)
IP (adia) = 7.64 eV (M06-2x)

Figure S16- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of guanine (G) using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Guanine(N1-H)$^\bullet$ (G(N1-H)$^\bullet$)



G(N1-H)$^\bullet$ (radical) (Doublet)

TE = -581.090313917 A.U. (ωb97x)
TE = -581.235723535 A.U. (B3LYP)
TE = -581.000771446 A.U. (M06-2x)

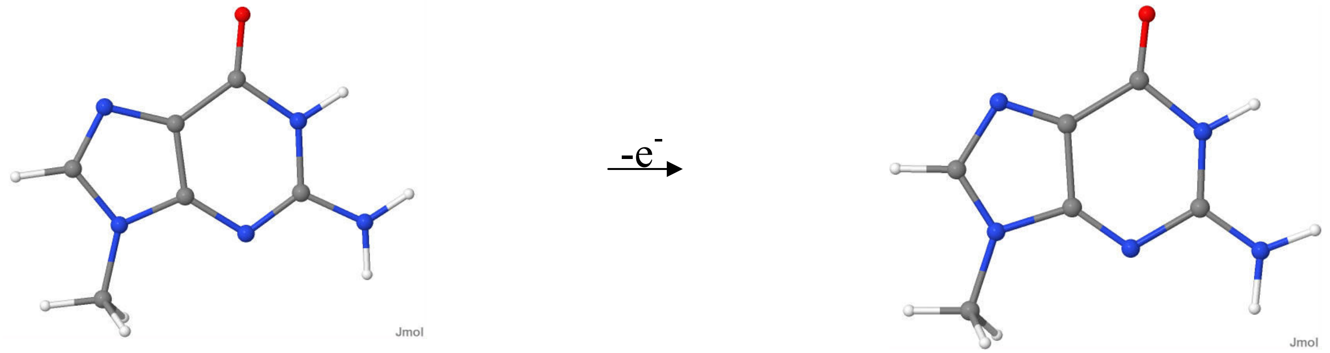
G(N1-H)$^+$ (cation) (singlet)

TE (vert) = -580.774676731 A.U. (ωb97x)
TE (opt) = -580.788417533 A.U. (ωb97x)
TE (vert) = -580.927782189 A.U. (B3LYP)
TE (opt) = -580.937748191 A.U. (B3LYP)
TE (vert) = -580.687273366 A.U. (M06-2x)
TE (opt) = -580.700404873 A.U. (M06-2x)

IP = TE (A(N6-H)$^+$) – TE (A(N6-H)$^\bullet$)
IP (vert) = 8.56 eV (ωb97x)
IP (adia) = 8.21 eV (ωb97x)
IP (vert) = 8.38 eV (B3LYP)
IP (adia) = 8.11 eV (B3LYP)
IP (vert) = 8.53 eV (M06-2x)
IP (adia) = 8.17 eV (M06-2x)

Figure S17- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of G(N1-H)$^\bullet$ using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Guanine radical cation ($G^{\bullet+}$)



$G^{\bullet+}$ (Radical cation) (doublet)

TE (opt) = -581.471021197 A.U. (ωb97x)
TE (opt) = -581.614942395 A.U. (B3LYP)
TE (opt) = -581.377091553 A.U. (M06-2x)

Second oxidation (G^{+2}) (Singlet)

TE (vert) = -580.989113814 A.U. (ωb97x)
TE (opt) = -581.005429558 A.U. (ωb97x)
TE (vert) = -581.138688404 A.U. (B3LYP)
TE (opt) = -581.150880209 A.U. (B3LYP)
TE (vert) = -580.896431642 A.U. (M06-2x)
TE (opt) = -580.911763880 A.U. (M06-2x)

IP = TE (G^{+2}) – TE ($G^{\bullet+}$)
IP (vert) = 13.11 eV (ωb97x)
IP (adia) = 12.66 eV (ωb97x)
IP (vert) = 12.95 eV (B3LYP)
IP (adia) = 12.62 eV (B3LYP)
IP (vert) = 13.07 eV (M06-2x)
IP (adia) = 12.66 eV (M06-2x)

Stability with respect to triplet state
ΔE = TE (Singlet) – TE (Triplet)
ΔE = -55.31 kcal/mol (ωb97x)
ΔE = -28.77 kcal/mol (B3LYP)
ΔE = -41.67 kcal/mol

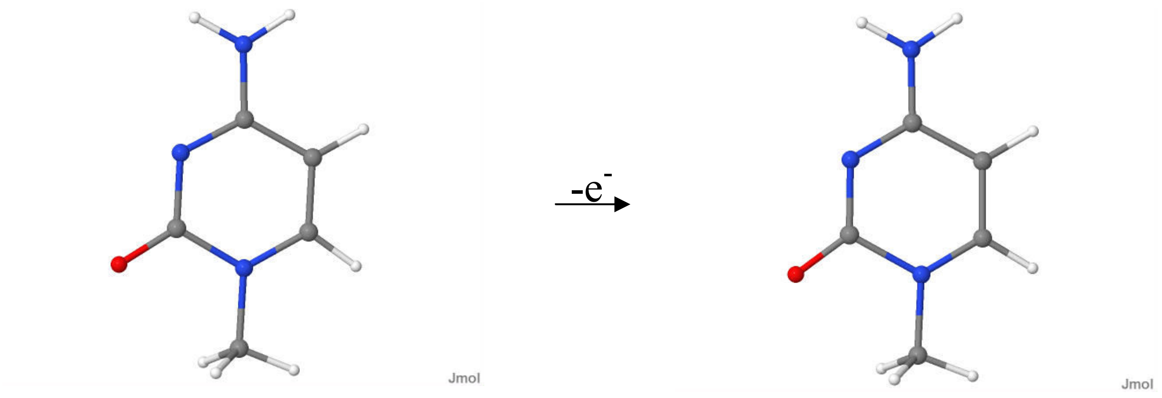
Second oxidation (G^{+2}) (Triplet)

TE (vert) = -580.909918324 A.U. (ωb97x)
TE (opt) = -580.917287955 A.U. (ωb97x)
TE (vert) = -581.096757380 A.U. (B3LYP)
TE (opt) = -581.105036675 A.U. (B3LYP)
TE (vert) = -580.832057805 A.U. (M06-2x)
TE (opt) = -580.845329132 A.U. (M06-2x)

IP = TE (G^{+2}) – TE ($G^{\bullet+}$)
IP (vert) = 15.26 eV (ωb97x)
IP (adia) = 15.06 eV (ωb97x)
IP (vert) = 14.10 eV (B3LYP)
IP (adia) = 13.87 eV (B3LYP)
IP (vert) = 14.83 eV (M06-2x)
IP (adia) = 14.46 eV (M06-2x)

Figure S18- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of $G^{\bullet+}$ (guanine radical cation) in singlet and triplet states using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

Cytosine (C)



Neutral (singlet)

TE = -434.150198337 A.U. (ωb97x)
TE = -434.261420915 A.U. (B3LYP)
TE = -434.076423881 A.U. (M06-2x)

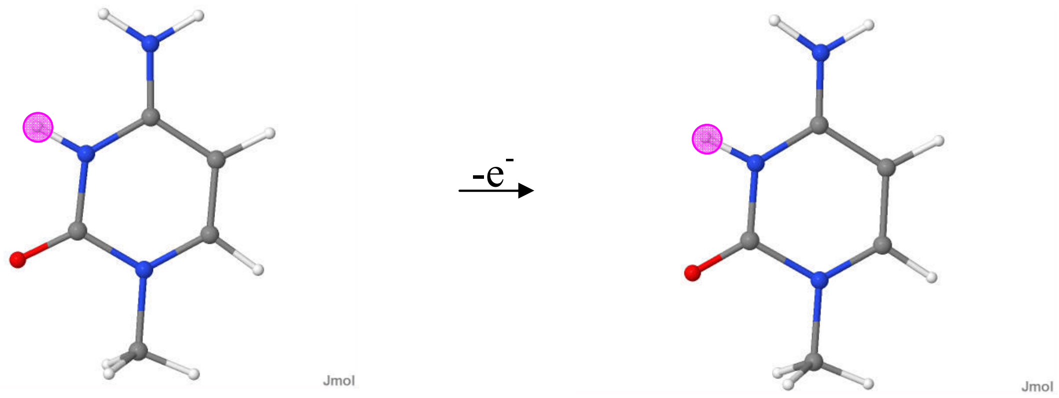
Radical cation ($C^{\bullet+}$)

TE (vert) = -433.834382543 A.U. (ωb97x)
TE (opt) = -433.839767490 A.U. (ωb97x)
TE (vert) = -433.952581050 A.U. (B3LYP)
TE (opt) = -433.956446932 A.U. (B3LYP)
TE (vert) = -433.757561488 A.U. (M06-2x)
TE (opt) = -433.762942696 A.U. (M06-2x)

IP = TE ($G^{\bullet+}$) – TE (Neutral)
IP (vert) = 8.59 eV (ωb97x)
IP (adia) = 8.44 eV (ωb97x)
IP (vert) = 8.40 eV (B3LYP)
IP (adia) = 8.30 eV (B3LYP
IP (vert) = 8.67 eV (M06-2x)
IP (adia) = 8.53 eV (M06-2x)

Figure S19- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of cytosine (C) using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

N3-protonated Cytosine (C(N3-H$^+$))



C(N3-H$^+$) (Neutral) (singlet)

TE = -434.529441519 A.U. (ωb97x)
TE = -434.639761425 A.U. (B3LYP)
TE = -434.450664107 A.U. (M06-2x)

Radical cation (C(N3-H$^+$)$^{\bullet+}$
TE (vert) = -434.027724467 A.U. (ωb97x)
TE (opt) = -434.035094549 A.U. (ωb97x)
TE (vert) = -434.143389228 A.U. (B3LYP)
TE (opt) = -434.148497719 A.U. (B3LYP)
TE (vert) = -433.945572625 A.U. (M06-2x)
TE (opt) = -433.952763917 A.U. (M06-2x)

IP = TE (T$^{\bullet+}$) – TE (Neutral)
IP (vert) = 13.65 eV (ωb97x)
IP (adia) = 13.45 eV (ωb97x)
IP (vert) = 13.50 eV (B3LYP)
IP (adia) = 13.36 eV (B3LYP)
IP (vert) = 13.74 eV (M06-2x)
IP (adia) = 13.54 eV (M06-2x)

Figure S20- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of N3-protonated cytosine (C(N3-H$^+$) using ωb97x/6-31++G(d), B3LYP/6-31++G(d) and M06-2x/6-31++G(d) methods. TE = Total energy in A.U.

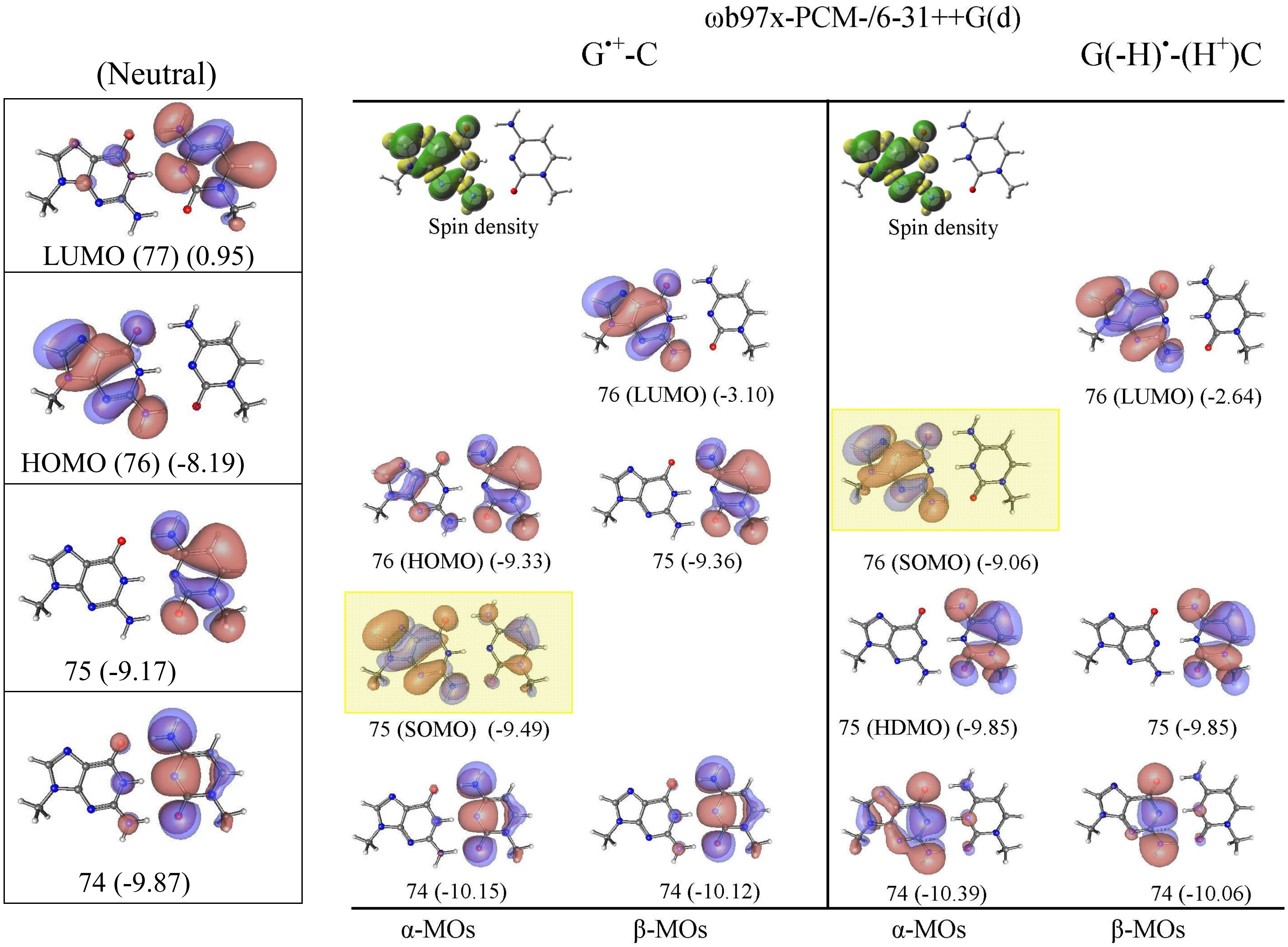


Figure S21- Molecular orbital (MO) plots of G-C base pair in their neutral, radical cation ($G^{\bullet +}$-C) and proton transferred radical cation G(-H)$^{\bullet}$-C(H^{+}) states **in solution using polarized continuum model (PCM).** Spin density distributions of $G^{\bullet +}$-C and G(-H)$^{\bullet}$-C(H^{+}) are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the ωb97x-PCM/6-31++G(d) method.

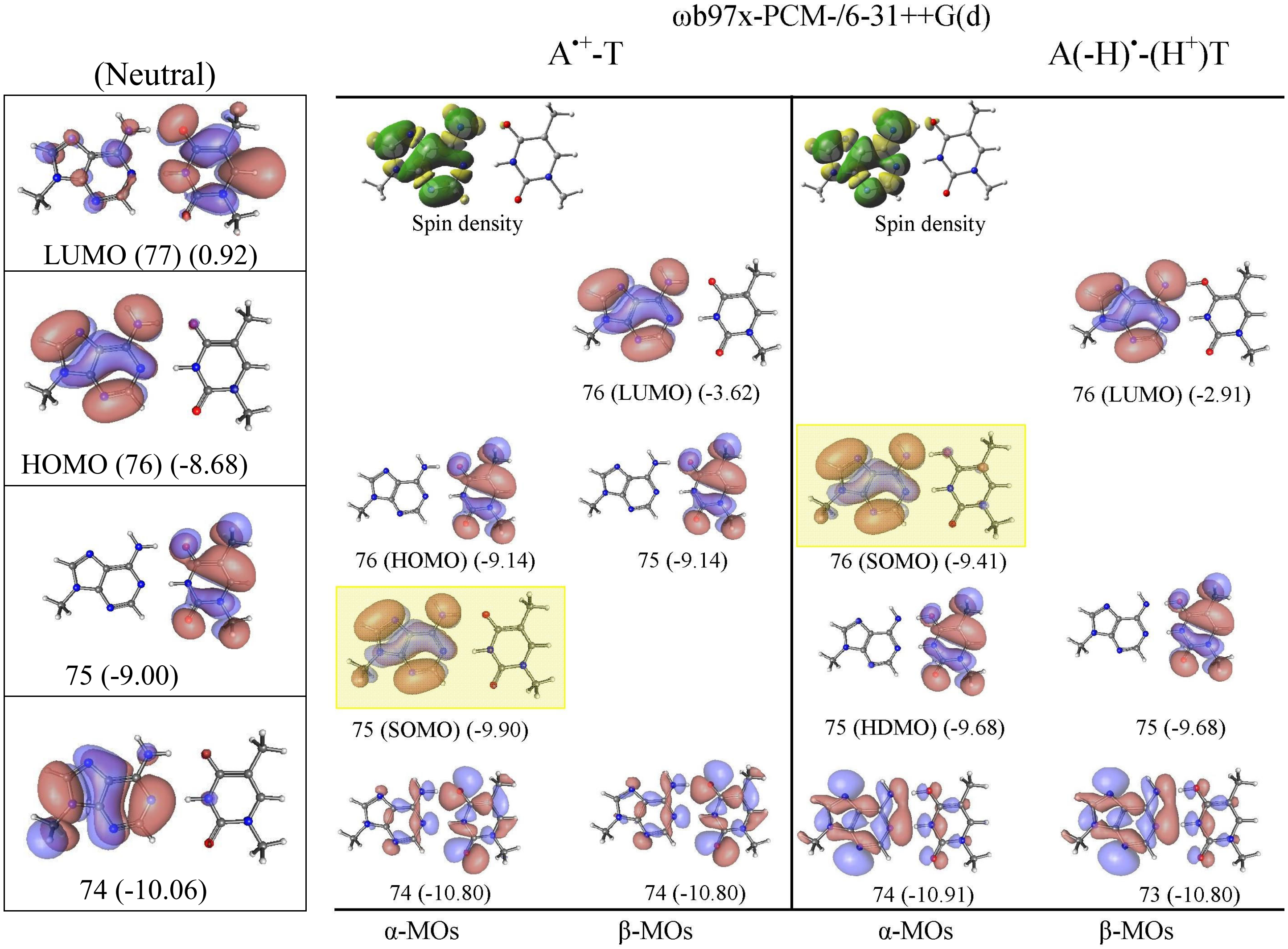


Figure S22- Molecular orbital (MO) plots of A-T base pair in their neutral, radical cation (A$^{\bullet+}$-T) and proton transferred radical cation A(-H)$^{\bullet}$-A(H^{+}) **states in solution using polarized continuum model (PCM).** Spin density distributions of A$^{\bullet+}$-T and A(-H)$^{\bullet}$-T(H^{+}) are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the ωb97x-PCM/6-31++G(d) method.

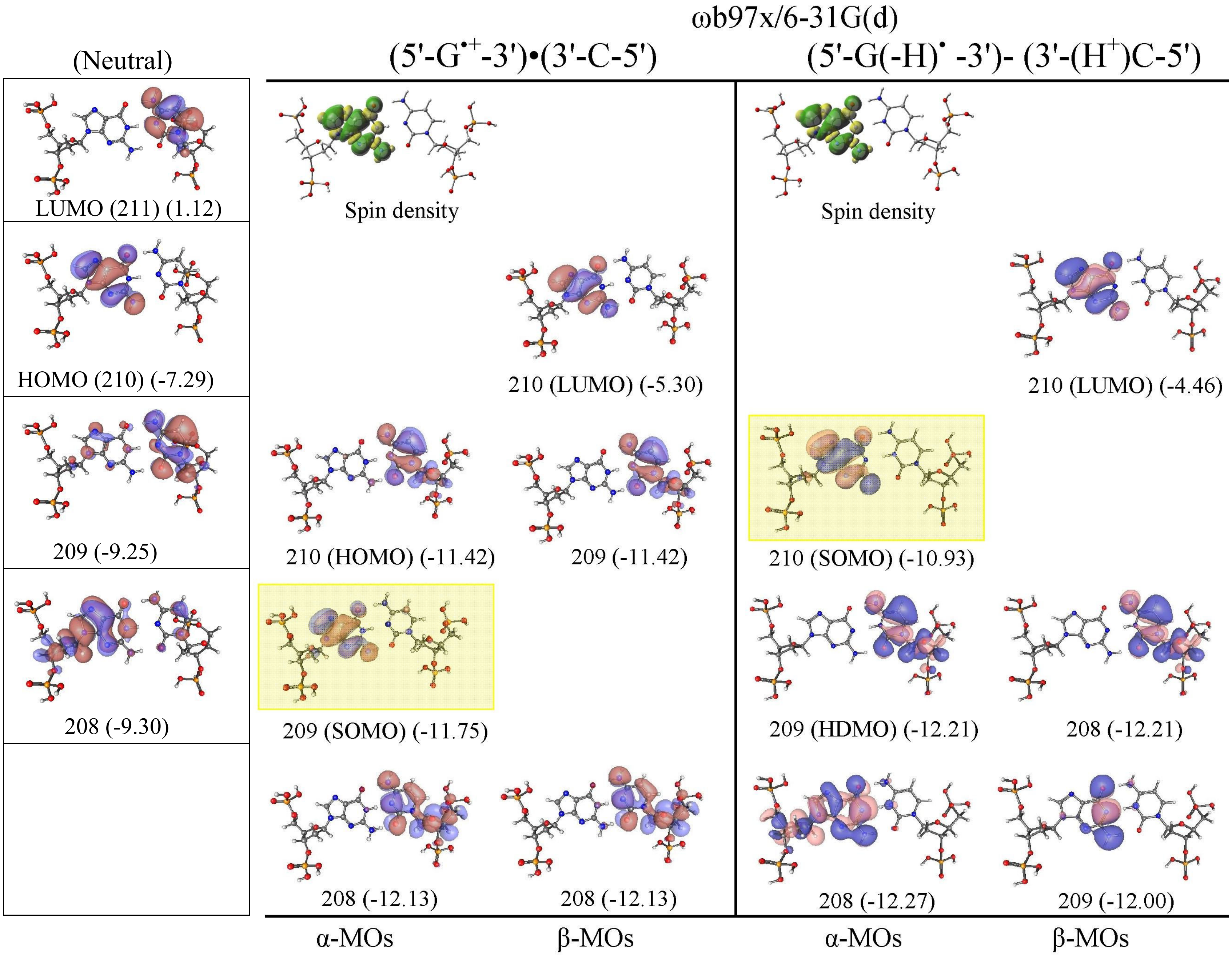
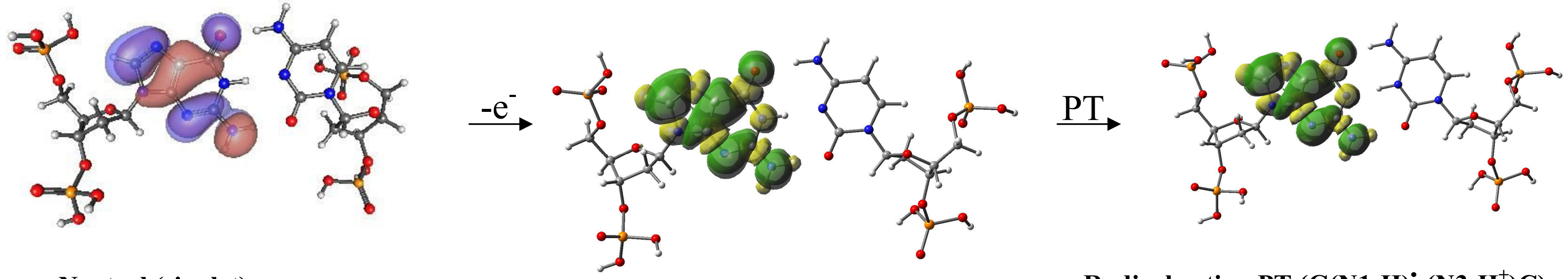


Figure S23- Molecular orbital (MO) plots of (5'-G-3')•(3'-C-5') in their neutral, radical cation (5'-G$^{•+}$-3')•(3'-C-5') and proton transferred radical cation (5'-G(-H)$^{•}$-3')•(3'-(H^{+})C-5') states. Spin density distributions of (5'-G$^{•+}$-3')•(3'-C-5') and (5'-G(-H)$^{•}$-3')•(3'-(H^{+})C-5') are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the ωb97x/6-31G(d) method to save computational time.

(5'-G-3')•(3'-C-5')   ωb97x/6-31G(d)



Neutral (singlet)
MO = HOMO
TE = -4049.73526111 A.U.

Radical cation ($G^{\bullet+}$-C)
Spin density plot
TE (Vert) = -4049.48174210 A.U.
TE (adia) = -4049.50359926 A.U.

IP = TE ($G^{\bullet+}$-C) – TE (Neutral)
IP (vert) = 6.90 eV
IP (adia) = 6.30 eV

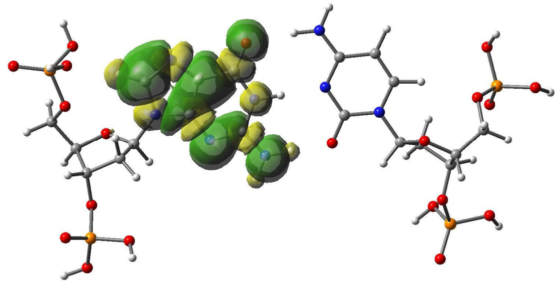
Radical cation PT (G(N1-H)$^{\bullet}$-(N3-H^+)C)
Spin density plot
TE (opt) = -4049.50198471 A.U.

Stability (ΔE) with respect to $G^{\bullet+}$-C
ΔE = TE ($G^{\bullet+}$-C) – TE ((G(N1-H)$^{\bullet}$-(N3-H^+)C)
ΔE = 1.01 kcal/mol

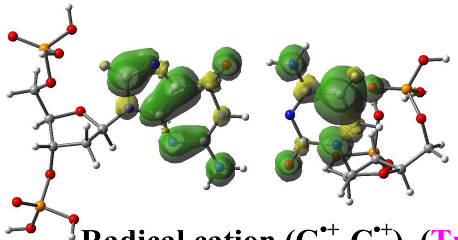
IP = TE (G(N1-H)$^{\bullet}$-(N3-H^+)C) – TE (Neutral)
IP (adia) = 6.35 eV

Figure S24- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of (5'-G-3')•(3'-C-5') using the ωb97x/6-31G(d) method. Relative stability between (5'-$G^{\bullet+}$-3')•(3'-C-5') and proton transferred (5'-G(-H)$^{\bullet}$-3')•(3'-(H^+)C-5') in kcal/mol. TE = Total energy in A.U.

(5'-G$^{\bullet+}$-3')•d(3'-C-5') (radical cation) ωb97x/6-31G(d)



$\xrightarrow{-e^-}$



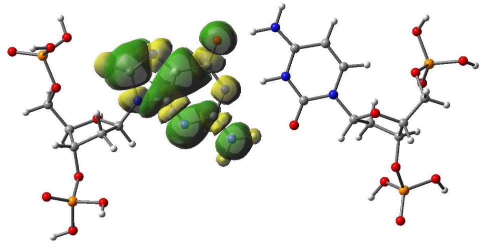
Radical cation (G$^{\bullet+}$-C)
Spin density plot
TE = -4049.50359926 A.U.

Radical cation (G$^{\bullet+}$-C$^{\bullet+}$) (Triplet state)
Spin density plot
TE (Vert) = -4049.10014032 A.U.
TE (adia) = -4049.13879653 A.U.

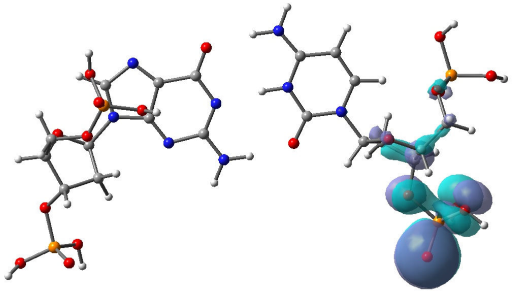
IP = TE (G$^{\bullet+}$-C$^{\bullet+}$) – TE (G$^{\bullet+}$-C)
IP (vert) = 10.97 eV
IP (adia) = 9.92 eV

Relative stability between triplet and singlet states

ΔE = TE (G$^{\bullet+}$-C$^{\bullet+}$) (triplet) – TE (G(N1-H)$^{\bullet}$-(N3-H^{+})C) (singlet)
ΔE = -4049.13879653 - -4049.14517879
= 4.0 kcal/mol



$\xrightarrow{-e^-}$



Radical cation PT (G(-H)$^{\bullet}$-(H^{+})C)
Spin density plot
TE = -4049.50198471 A.U.

Radical cation PT (G(-H)$^{+}$-(H^{+})C) (Singlet state)
HOMO plot
TE (vert) = -4049.11436183 A.U.
TE (adia) = -4049.14517879 A.U.

IP = TE (G(N1-H)$^{\bullet}$-(N3-H^{+})C) – TE (G(-H)$^{+}$-(H^{+})C)
IP (vert) = 10.54 eV
IP (adia) = 9.71 eV

Figure S25- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of (5'-G$^{\bullet+}$-3')•(3'-C-5') and (5'-G(-H)$^{\bullet}$-3')•(3'-(H^{+})C-5') in triplet and singlet states using the ωb97x/6-31G(d) method. Relative stability between triplet and singlet states in kcal/mol. TE = Total energy in A.U.

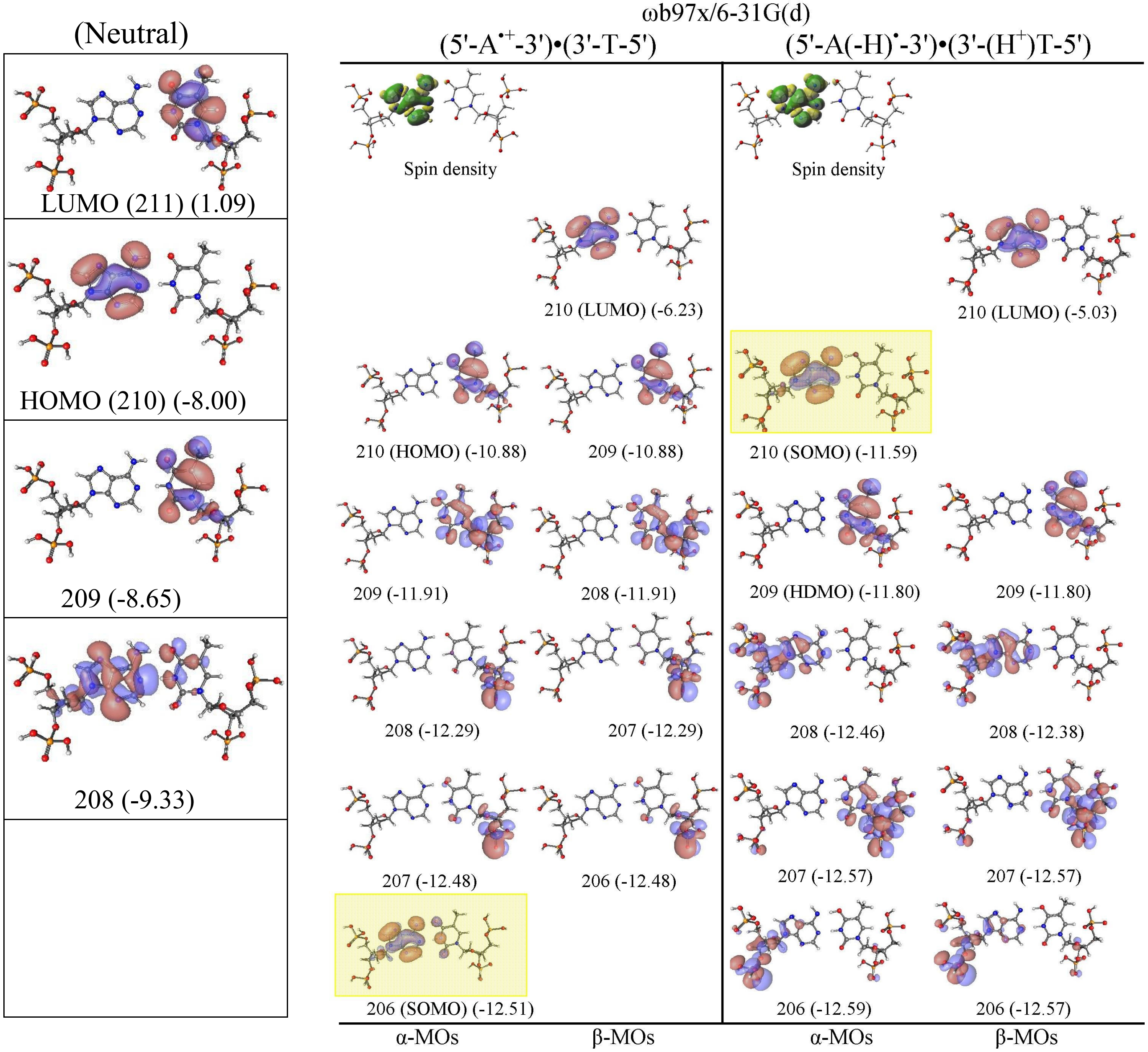
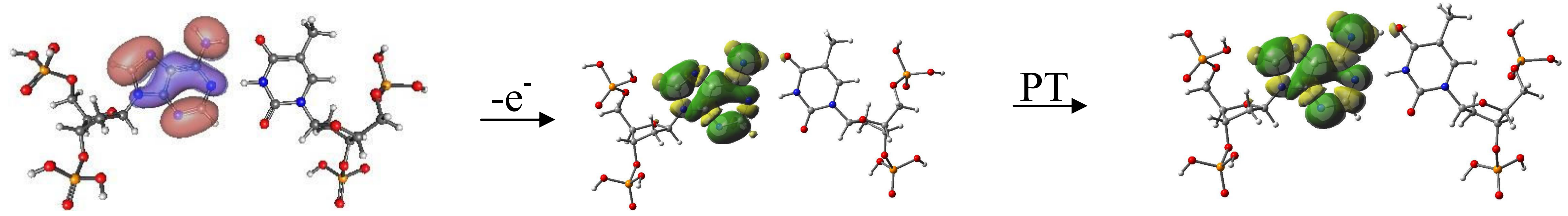


Figure S26- Molecular orbital (MO) plots of (5'-A-3')•(3'-T-5') in their neutral, radical cation (5'-A$^{\bullet+}$-3')•(3'-T-5') and proton transferred radical cation (5'-A(-H)$^{\bullet}$-3')•(3'-(H^{+})T-5') states. Spin density distributions of (5'-A$^{\bullet+}$-3')•(3'-T-5') and (5'-A(-H)$^{\bullet}$-3')•(3'-(H^{+})T-5') are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the ωb97x/6-31G(d) method to save computational time.

(5'-A-3')•(3'-T-5') ωb97x/6-31G(d)



Neutral (singlet)
MO = HOMO
TE = -4033.68803586 A.U.

Radical cation (A$^{\bullet+}$-T)
Spin density plot
TE (Vert) = -4033.40707046 A.U.
TE (adia) = -4033.42640196 A.U.

IP = TE (A$^{\bullet+}$-T) – TE (Neutral)
IP (vert) = 7.64 eV
IP (adia) = 7.12 eV

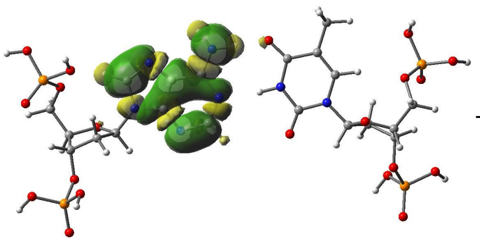
Radical cation PT (A(N6-H)$^{\bullet}$-(O4-H^{+})T)
Spin density plot
TE (opt) = -4033.42117433 A.U.

Stability (ΔE) with respect to G$^{\bullet+}$-C
ΔE = TE (A$^{\bullet+}$-T) – TE ((A(N6-H)$^{\bullet}$-(O4-H^{+})T)
ΔE = 3.28 kcal/mol

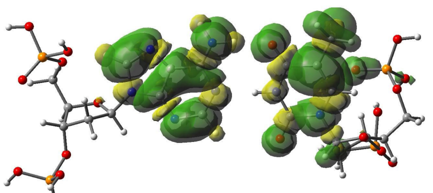
IP = TE (A(N6-H)$^{\bullet}$-(O4-H^{+})C) – TE (Neutral)
IP (adia) = 7.26 eV

Figure S27- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of (5'-A-3')•(3'-T-5') using the ωb97x/6-31G(d) method. Relative stability between (5'-A$^{\bullet+}$-3')•(3'-T-5') and proton transferred (5'-A(-H)$^{\bullet}$-3')•(3'-(H^{+})T-5') in kcal/mol. TE = Total energy in A.U.

$(5'\text{-}A^{\bullet+}\text{-}3')\bullet(3'\text{-}T\text{-}5')$ (radical cation) ωb97x/6-31G(d)



$\xrightarrow{-e^{-}}$



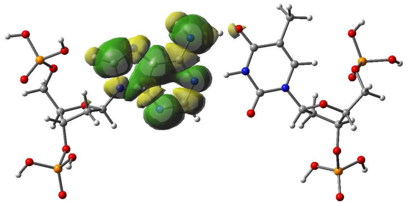
Radical cation ($A^{\bullet+}$-T)
Spin density plot
TE = -4033.42640196 A.U.

Radical cation ($A^{\bullet+}$-$T^{\bullet+}$) (Triplet state)
Spin density plot
TE (Vert) = -4033.04368994 A.U.
TE (adia) = -4033.08318223 A.U.

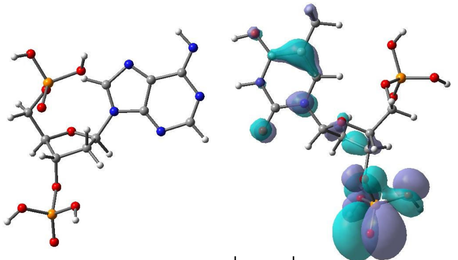
IP = TE ($A^{\bullet+}$-$T^{\bullet+}$) – TE ($A^{\bullet+}$-T)
IP (vert) = 10.41 eV
IP (adia) = 9.34 eV

Relative stability between triplet and singlet states

ΔE = TE ($A^{\bullet+}$-$T^{\bullet+}$) (triplet) – TE (A(N6-H)$^{\bullet}$-(O4-H^{+})C) (singlet)
ΔE = -4033.08318223 - -4033.03666374
= -29.19 kcal/mol



$\xrightarrow{-e^{-}}$



Radical cation PT (A(-H)$^{\bullet}$-(H^{+})T)
Spin density plot
TE (opt) = -4033.42117433 A.U.

Radical cation PT (A(-H)$^{+}$-(H^{+})T) (Singlet state)
HOMO plot
TE (vert) = -4033.00885614 A.U.
TE (adia) = -4033.03666374 A.U.

IP = TE (A(-H)$^{\bullet}$-(H^{+})T) – TE (A(-H)$^{+}$-(H^{+})T)
IP (vert) = 11.22 eV
IP (adia) = 10.46 eV

Figure S28- Calculated vertical and adiabatic ionization potentials (IP(vert) and IP(adia)) in eV of $(5'\text{-}A^{\bullet+}\text{-}3')\bullet(3'\text{-}T\text{-}5')$ and (5'-A(-H)$^{\bullet}$-3')•(3'-(H^{+})A-5') in triplet and singlet states using the ωb97x/6-31G(d) method. Relative stability between triplet and singlet states in kcal/mol. TE = Total energy in A.U.

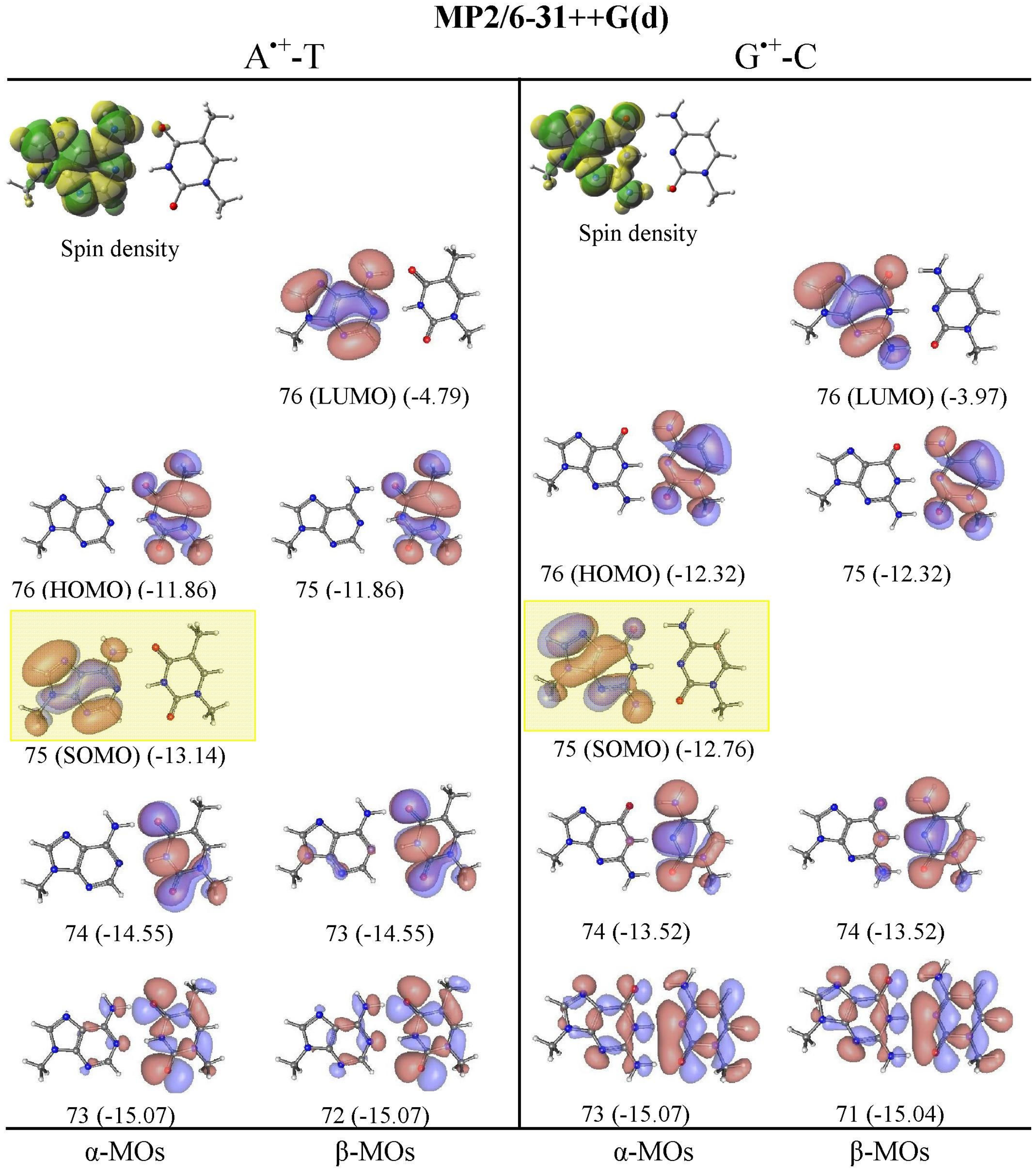
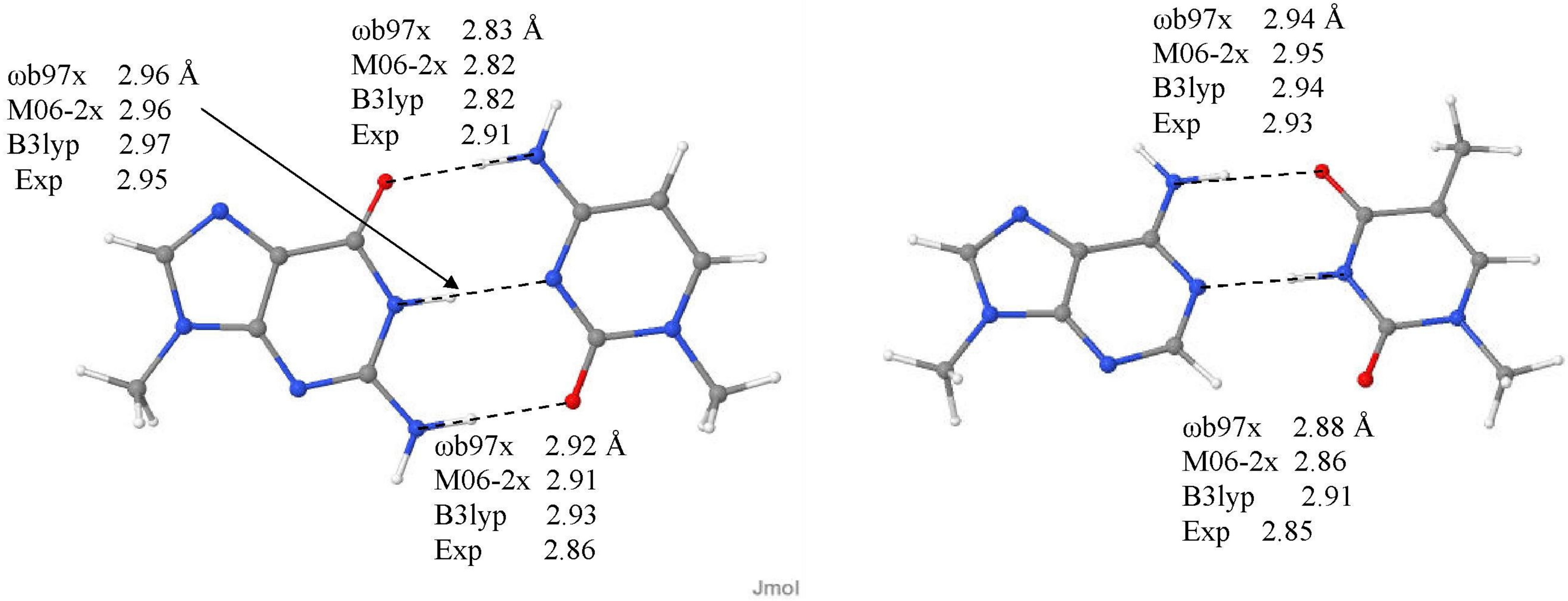


Figure S29- Molecular orbital (MO) plots of $A^{\bullet+}$-T and $G^{\bullet+}$-C base pair radical cations. Spin density distributions of $A^{\bullet+}$-T and $G^{\bullet+}$-C are also shown. Below each figure MO number and its energy in eV in parentheses are given. Calculations were done using the *ab initio* **MP2/6-31++G(D)** method using the ωb97x/6-31++G(d) optimized geometries.



(a) G-C

(b) A-T

Figure S30- Calculated hydrogen-bond lengths in Å in neutral G-C and A-T base pairs. Experimental X-ray crystallographic[a,b] values are given in parentheses.

[a] Rosenberg, J. M.; Seeman, N. C.; Day, R. O.; Rich, A. *J. Mol. Biol.* **1976**, 104, 145. (For G-C)
[b] Seeman, N. C.; Rosenberg, J. M.; Suddath, F. L.; Kim, J. J. P.; Rich, A. *J Mol Biol* **1976**, 104, 109. (For A-T)

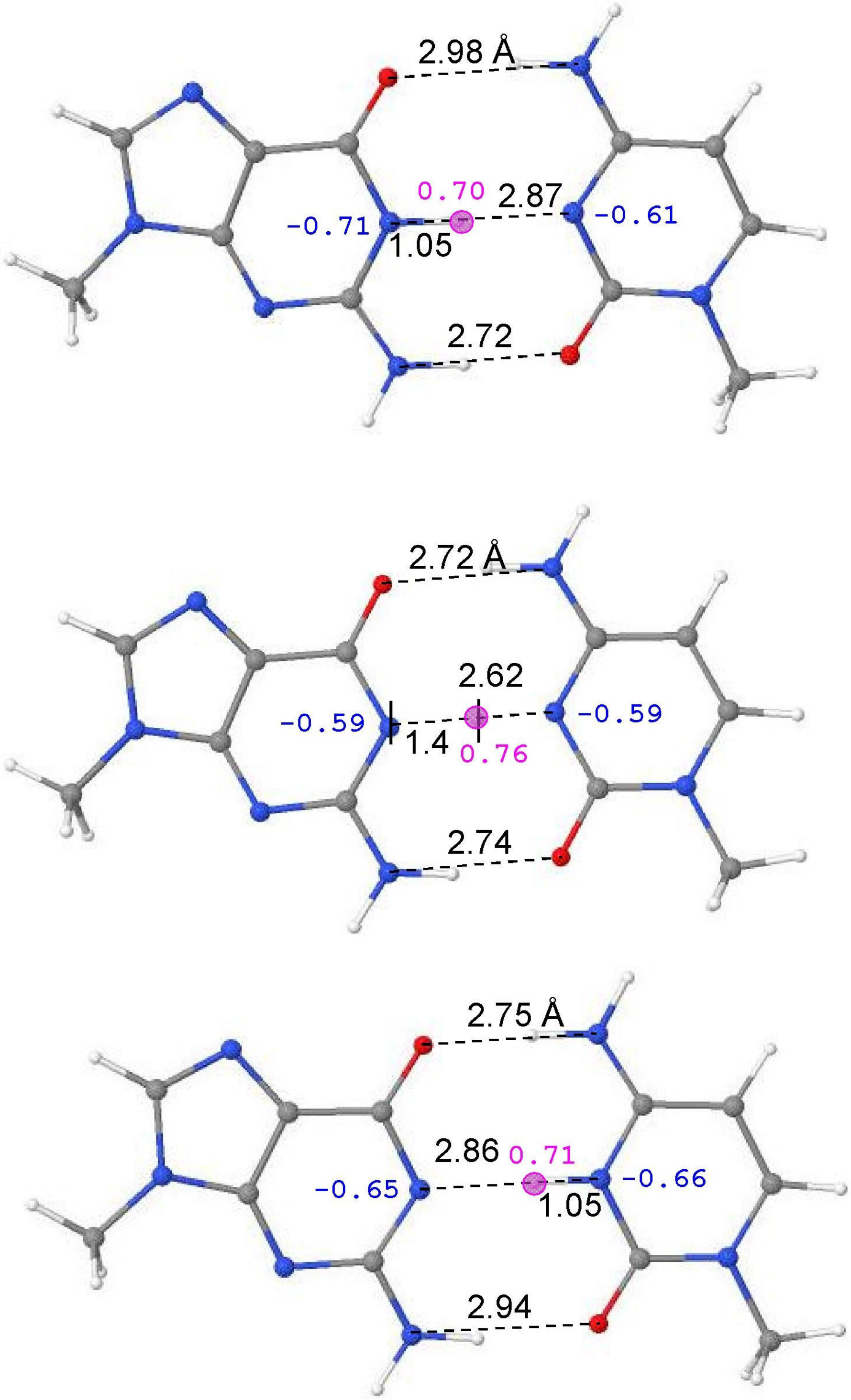


Figure S31- ωb97x/6-31++G(d) calculated hydrogen-bond lengths in Å in radical cation of G-C base pair. (i) $G^{\bullet+}$-C (top figure), (ii) PT in between G and C in $(G^{\bullet}\text{-}C)^{+}$ (middle figure) and (iii) PT transferred $G(-H)^{\bullet}\text{-}C(H^{+})$. Mulliken charges of two nitrogens are given in blue color and H^{+} in pink color. Pink circle shows the location of the H^{+} between the two bases.

```
#CASSCF(11,11)/def2-SV(P) pop=full  guess=alter
```

Charge = 1 Multiplicity = 2

TE = -993.1487521768 A.U.

Orbital	Occupancy	
71	1.94601	
72	1.95764	
73	1.94978	
74	1.99988	
75	0.99893	(SOMO)
76	1.93064	(HOMO)
77	0.07058	
78	0.05490	
79	0.01000	
80	0.04114	
81	0.04051	

```
#CASSCF(11,11)/def2-SV(P) pop=full
```

Charge = 1 Multiplicity = 2

TE = -993.1487516700 A.U. (Less stable than above)

Orbital	Occupancy	
71	1.94601	
72	1.95764	
73	1.94973	
74	1.99988	
75	1.93064	(HOMO)
76	0.99893	(SOMO)
77	0.07058	
78	0.05490	
79	0.01001	
80	0.04114	
81	0.04052	

#CASSCF(11,11)/6-31g pop=full guess=alter**

Charge = 1 Multiplicity = 2

TE= -993.9796768451 A.U.

Orbital	Occupancy	
71	1.94636	
72	1.95860	
73	1.94955	
74	1.99988	
75	0.99879	(SOMO)
76	1.92954	(HOMO)
77	0.07155	
78	0.05469	
79	0.01004	
80	0.04031	
81	0.04070	

#CASSCF(11,11)/6-31g pop=full**

Charge = 1 Multiplicity = 2

TE= -993.9796737162 A.U. **(Less stable than above)**

Orbital	Occupancy	
71	1.94631	
72	1.95860	
73	1.94955	
74	1.99988	
75	1.92954	(HOMO)
76	0.99879	(SOMO)
77	0.07155	
78	0.05466	
79	0.01008	
80	0.04031	
81	0.04073	

Optimized geometries

1. wb97x/6-31++G(d) optimized geometry of **neutral** A-T base pair.
TE = -999.896937614 A.U.

Charge = 0 Multiplicity = 1

1	0.927475	-0.138806	-0.000096
7	-0.912519	-0.160623	-0.000069
7	-1.066199	2.157012	-0.000018
6	-1.663311	0.957302	-0.000032
6	-1.514085	-1.364938	-0.000079
7	-2.811465	-1.631755	-0.000060
6	-3.541376	-0.503681	-0.000024
6	-3.066084	0.799725	-0.000006
7	-4.104793	1.710304	0.000040
6	-5.172782	0.958198	0.000049
7	-4.907863	-0.390550	0.000009
8	1.878564	2.163674	-0.000064
6	2.562844	1.139473	-0.000064
7	1.968288	-0.106378	-0.000142
6	2.602534	-1.328105	-0.000061
7	3.987643	-1.265997	-0.000066
6	4.647314	-0.056627	0.000031
6	4.024337	1.139129	0.000015
8	2.000242	-2.390691	0.000071
6	4.740057	2.456554	0.000083
1	-0.047693	2.233330	-0.000013
1	-1.636729	2.988512	0.000020
1	-0.832725	-2.214670	-0.000105
1	-6.192869	1.326041	0.000083
1	5.731958	-0.131213	0.000104
1	4.466040	3.048427	-0.879691
1	4.465904	3.048408	0.879828
1	5.825488	2.313009	0.000167
6	-5.852000	-1.489831	0.000001
1	-5.708714	-2.108715	-0.889448
1	-5.708613	-2.108810	0.889367
1	-6.865094	-1.081298	0.000080
6	4.702701	-2.536089	0.000239
1	4.439360	-3.117612	0.887271
1	4.437899	-3.118753	-0.885591
1	5.775318	-2.332476	-0.000790

2. wb97x/6-31++G(d) optimized geometry of **radical cation** A$^{\bullet+}$-T base pair.
TE = -999.616674723 A.U.

Charge = 1 Multiplicity = 2

1	-1.040934	-0.358819	0.000564
7	0.968214	-0.332481	0.000306
7	0.999322	1.976945	0.000446
6	1.659909	0.848177	0.000271
6	1.626006	-1.466621	0.000171
7	2.988884	-1.657846	-0.000010
6	3.648658	-0.536642	-0.000059
6	3.094415	0.778786	0.000060
7	4.045281	1.715343	-0.000031
6	5.185083	1.007316	-0.000211
7	5.015980	-0.330902	-0.000230
8	-1.696448	2.026790	0.000270
6	-2.506975	1.084119	0.000116
7	-2.052593	-0.212735	0.000315
6	-2.810525	-1.371374	0.000111
7	-4.173796	-1.156725	-0.000082
6	-4.692610	0.116648	-0.000316
6	-3.946376	1.246212	-0.000247
8	-2.298783	-2.476944	0.000388
6	-4.523453	2.631141	-0.000471
1	-0.060202	1.987002	0.000698
1	1.512665	2.854104	0.000437
1	1.027476	-2.375117	0.000198
1	6.170779	1.459481	-0.000323
1	-5.778292	0.163105	-0.000543
1	-4.195315	3.191434	0.880949
1	-4.194898	3.191321	-0.881807
1	-5.616745	2.597521	-0.000727
6	6.036655	-1.377306	-0.000375
1	5.922982	-1.994835	0.892364
1	5.922644	-1.994915	-0.893015
1	7.019032	-0.903511	-0.000583
6	-5.027908	-2.344863	-0.000294
1	-4.827101	-2.947471	-0.888635
1	-4.826014	-2.948489	0.887097
1	-6.070550	-2.024345	0.000539

3. wb97x/6-31++G(d) optimized geometry of **proton transferred radical cation** A(-H)$^{\bullet}$-(H^{+})T base pair. **(TE = -999.610066607 A.U.)**

Charge = 1 Multiplicity = 2

1	0.883244	-0.226704	-0.000052
7	-0.895348	-0.357315	-0.000031
7	-0.846501	1.948734	-0.000002
6	-1.561919	0.855908	-0.000006
6	-1.566860	-1.483119	-0.000039
7	-2.924903	-1.647257	-0.000026
6	-3.569086	-0.507326	-0.000002
6	-2.992716	0.793418	0.000010
7	-3.941133	1.750125	0.000034
6	-5.078535	1.064676	0.000047
7	-4.927012	-0.286010	0.000017
8	1.791216	2.160806	-0.000017
6	2.505791	1.086441	-0.000024
7	1.926799	-0.126668	-0.000042
6	2.607382	-1.343147	-0.000052
7	3.989101	-1.223393	-0.000001
6	4.595322	-0.004605	0.000016
6	3.925375	1.182314	-0.000006
8	2.023560	-2.404624	0.000015
6	4.597150	2.525795	0.000008
1	-1.430877	2.787104	0.000019
1	-0.980430	-2.399464	-0.000063
1	-6.061358	1.522741	0.000067
1	5.681731	-0.030382	0.000048
1	4.314068	3.107218	-0.882863
1	4.314030	3.107218	0.882868
1	5.684318	2.410263	0.000032
6	-5.962718	-1.312783	-0.000001
1	-5.863585	-1.934388	-0.892006
1	-5.863454	-1.934543	0.891881
1	-6.937577	-0.823004	0.000114
6	4.750797	-2.477354	0.000066
1	4.498542	-3.059235	0.888595
1	4.498414	-3.059395	-0.888319
1	5.814790	-2.238744	-0.000035
1	0.763018	2.033047	-0.000012

4. wb97x/6-31++G(d) optimized geometry of **$\mathbf{A}^{\bullet+}$-$\mathbf{T}^{\bullet+}$** base pair (double oxidation) in triplet state, see **Figure 3** in the text. (**TE = -999.222672458 A.U.**)

Charge = 2 Multiplicity = 3

1	0.986367	-0.244859	0.000036
7	-0.957385	-0.193478	-0.000012
7	-1.132543	2.123581	-0.000002
6	-1.709789	0.944288	-0.000013
6	-1.572345	-1.365674	-0.000024
7	-2.912747	-1.625841	-0.000039
6	-3.632494	-0.542534	-0.000037
6	-3.139996	0.800303	-0.000022
7	-4.125009	1.687273	-0.000012
6	-5.240952	0.921640	-0.000031
7	-5.008969	-0.402107	-0.000038
8	1.825692	2.099142	-0.000050
6	2.540428	1.113310	-0.000023
7	2.020377	-0.162278	0.000022
6	2.723137	-1.339531	0.000074
7	4.170237	-1.190562	0.000074
6	4.752469	-0.005631	0.000023
6	4.023204	1.202091	-0.000032
8	2.234709	-2.432983	0.000137
6	4.668427	2.528119	-0.000095
1	-0.110495	2.210020	0.000007
1	-1.699842	2.967037	-0.000001
1	-0.932729	-2.245890	-0.000022
1	-6.244981	1.333131	-0.000026
1	5.840630	0.009028	0.000026
1	4.334993	3.106256	-0.873349
1	4.334929	3.106374	0.873055
1	5.758022	2.463731	-0.000054
6	-5.984501	-1.498356	-0.000067
1	-5.840522	-2.106637	-0.894462
1	-5.840266	-2.106901	0.894106
1	-6.986446	-1.068131	0.000143
6	4.938138	-2.449693	0.000148
1	4.672010	-3.024040	0.889783
1	4.671886	-3.024222	-0.889330
1	6.001146	-2.210273	0.000050

5. wb97x/6-31G(d) optimized geometry of **(5'-A-3')•(3'-T-5')** base pair.

TE = -4033.68803586 A.U.

Charge = 0 Multiplicity = 1

8	10.427552	-2.582873	-1.189927
15	9.506407	-1.796862	-0.140187
8	8.803327	-2.946355	0.725053
8	10.188798	-0.750686	0.646179
8	8.294127	-1.334609	-1.064309
6	8.468582	-0.203255	-1.937928
6	7.503850	0.902540	-1.549263
8	6.172899	0.458752	-1.766392
6	5.416575	0.496179	-0.566490
6	7.599266	1.328686	-0.076357
6	6.439477	0.584788	0.567368
8	7.401843	2.755169	-0.061474
1	8.248819	-0.548698	-2.950411
1	9.499464	0.165642	-1.895556
1	7.705174	1.771142	-2.188626
1	4.734593	1.353689	-0.570718
1	8.566492	1.092602	0.376336
1	6.768714	-0.421964	0.842511
1	6.041028	1.081572	1.454105
7	4.579262	-0.676442	-0.504247
6	4.970613	-1.998722	-0.581281
7	3.979186	-2.842144	-0.515866
6	2.863512	-2.033385	-0.394729
6	1.488172	-2.324374	-0.273331
7	1.004121	-3.572742	-0.254781
7	0.640189	-1.284650	-0.170947
6	1.122134	-0.029915	-0.185025
7	2.382442	0.360608	-0.287920
6	3.209219	-0.690957	-0.392541
1	6.015708	-2.262896	-0.699118
1	0.001906	-3.739014	-0.156608
1	1.645633	-4.345026	-0.335128
1	0.363247	0.746662	-0.097692
15	7.553024	3.653520	1.247215
8	8.543767	2.823730	2.214090
8	7.957943	5.042533	0.999288
8	6.127870	3.436756	1.956245
8	-10.472094	-1.683761	1.022575
15	-9.088443	-1.653288	0.193373
8	-8.636241	-3.174547	-0.005024
8	-9.148898	-0.887656	-1.059934
8	-8.053643	-1.201047	1.321119
6	-8.170192	0.057362	2.007593
6	-7.134790	1.059110	1.523621
8	-5.843610	0.493901	1.686761
6	-5.098242	0.584137	0.478815
6	-7.254641	1.497853	0.052455
6	-6.139007	0.727502	-0.630897
8	-6.994440	2.917285	0.046623
1	-7.987318	-0.165678	3.060987

1	-9.183227	0.461952	1.904157
1	-7.229957	1.953397	2.153814
1	-4.415393	1.436043	0.513767
1	-8.237897	1.304877	-0.383483
1	-6.525174	-0.250067	-0.937643
1	-5.753840	1.239282	-1.514597
7	-4.258859	-0.593369	0.363382
6	-2.883434	-0.423953	0.214373
8	-2.349329	0.669902	0.155634
7	-2.176755	-1.600116	0.123059
6	-2.673880	-2.887687	0.162346
8	-1.927122	-3.858611	0.062824
6	-4.122399	-2.992153	0.331393
6	-4.737182	-4.357433	0.393008
6	-4.826137	-1.851117	0.432828
1	-1.147367	-1.488135	0.008751
1	-4.457685	-4.945440	-0.486890
1	-5.829198	-4.287724	0.430445
1	-4.385478	-4.909965	1.270907
1	-5.899846	-1.853538	0.594745
15	-7.389206	3.879046	-1.159639
8	-8.867922	3.348866	-1.492823
8	-7.189351	5.301074	-0.861396
8	-6.575847	3.376161	-2.464951
1	5.916532	4.174784	2.545481
1	9.427075	3.219183	2.207173
1	8.742777	-2.678955	1.653196
1	11.332235	-2.678467	-0.859431
1	-8.591377	-3.661339	0.830631
1	-11.221304	-1.504396	0.435901
1	-5.857678	3.997417	-2.655186
1	-9.186497	3.665712	-2.349052

6. wb97x/6-31G(d) optimized geometry of **(5'-$A^{\bullet +}$-3')•(3'-T-5')** base pair.

TE = -4033.42640196 A.U.

Charge = 1 Multiplicity = 2

8	9.696112	-3.568315	-0.197881
15	9.017021	-2.180080	0.224930
8	7.762262	-2.673083	1.094600
8	9.950812	-1.188742	0.784137
8	8.162004	-1.664305	-1.028579
6	8.632231	-0.564734	-1.830034
6	7.820506	0.690146	-1.559217
8	6.437826	0.420504	-1.824596
6	5.661919	0.607685	-0.673206
6	7.877513	1.238475	-0.125777
6	6.621237	0.662170	0.515415
8	7.745427	2.661785	-0.240478

1	8.496516	-0.869104	-2.869966
1	9.692512	-0.371774	-1.640656
1	8.158176	1.468038	-2.252518
1	5.041283	1.506695	-0.757425
1	8.801475	0.970192	0.397015
1	6.813924	-0.345379	0.897084
1	6.257729	1.286915	1.332508
7	4.708737	-0.512497	-0.595055
6	4.985409	-1.828753	-0.729144
7	3.905216	-2.626597	-0.667094
6	2.893289	-1.776169	-0.496708
6	1.477738	-1.968151	-0.357023
7	0.910784	-3.147542	-0.374465
7	0.701744	-0.856235	-0.201475
6	1.262714	0.329219	-0.182322
7	2.595259	0.638033	-0.296343
6	3.339188	-0.418196	-0.449538
1	6.001680	-2.179876	-0.877605
1	-0.138267	-3.249482	-0.265503
1	1.492109	-3.971042	-0.494439
1	0.589105	1.174732	-0.058549
15	8.340254	3.665486	0.858811
8	9.870678	3.210791	1.066431
8	8.151663	5.078392	0.525070
8	7.641888	3.084039	2.184783
8	-10.411032	-2.078899	0.679869
15	-8.975839	-1.910757	-0.028831
8	-8.413282	-3.389936	-0.265569
8	-8.966435	-1.073101	-1.236508
8	-8.060089	-1.455163	1.201316
6	-8.336102	-0.267809	1.964214
6	-7.403131	0.876321	1.602032
8	-6.055567	0.441432	1.763608
6	-5.304018	0.697823	0.593451
6	-7.520156	1.436633	0.173279
6	-6.321438	0.832755	-0.537250
8	-7.373344	2.863084	0.297824
1	-8.169301	-0.546587	3.006925
1	-9.382949	0.032382	1.846046
1	-7.606313	1.693352	2.305604
1	-4.694556	1.597005	0.712938
1	-8.469105	1.197928	-0.313159
1	-6.605158	-0.146665	-0.935845
1	-5.970199	1.456051	-1.361433
7	-4.358300	-0.403080	0.410896
6	-3.013922	-0.111230	0.260308
8	-2.539469	1.008894	0.252191
7	-2.218539	-1.232830	0.101236
6	-2.606044	-2.551073	0.072650
8	-1.764201	-3.448536	-0.084455
6	-4.026732	-2.784805	0.239583
6	-4.542064	-4.193173	0.223133
6	-4.815951	-1.702889	0.410758
1	-1.223594	-1.028096	-0.009372
1	-4.208549	-4.715353	-0.678809
1	-5.635868	-4.199362	0.238764

1	-4.172332	-4.761898	1.082842
1	-5.884325	-1.801935	0.579886
15	-7.932982	3.892163	-0.785550
8	-9.416322	3.312983	-0.986333
8	-7.759826	5.298524	-0.411251
8	-7.225453	3.507296	-2.188202
1	7.890448	3.582478	2.977123
1	10.471819	3.862813	0.676959
1	8.017944	-3.276050	1.808532
1	10.662463	-3.497377	-0.213804
1	-8.571353	-3.974741	0.489899
1	-11.131289	-1.910126	0.054160
1	-6.626851	4.222589	-2.448819
1	-9.900631	3.770106	-1.688109

7. wb97x/6-31G(d) optimized geometry of proton transferred **(5'-A(-H)$^{\bullet}$-3')•(3'-(H^{+})T-5')** base pair. **TE = -4033.42117433 A.U.**

Charge = 1 Multiplicity = 2

8	9.665764	-3.507808	-0.501423
15	9.002144	-2.136943	0.003445
8	7.875838	-2.665312	1.014425
8	9.975115	-1.127191	0.453934
8	7.996543	-1.642126	-1.138219
6	8.341563	-0.529402	-1.983279
6	7.518787	0.697247	-1.627902
8	6.129882	0.388355	-1.766176
6	5.455154	0.551578	-0.542603
6	7.697417	1.230634	-0.199038
6	6.524369	0.611587	0.548110
8	7.515221	2.653465	-0.276809
1	8.109030	-0.840609	-3.003942
1	9.408531	-0.299402	-1.903513
1	7.772474	1.490798	-2.339874
1	4.827923	1.449888	-0.561324
1	8.675209	0.984782	0.228054
1	6.778724	-0.396843	0.889127
1	6.225719	1.211258	1.409303
7	4.525213	-0.567295	-0.390201
6	4.810963	-1.896927	-0.492502
7	3.751893	-2.690738	-0.386555
6	2.723539	-1.836854	-0.218222
6	1.317796	-2.048903	-0.054628
7	0.719826	-3.209804	-0.035695
7	0.540351	-0.914142	0.086935
6	1.090624	0.274141	0.064617
7	2.413127	0.581080	-0.085045

6	3.162997	-0.482684	-0.221529
1	5.827489	-2.239355	-0.654031
1	-0.882336	-3.453779	0.110381
1	1.388154	-3.973532	-0.150605
1	0.415663	1.119563	0.179787
15	8.211503	3.654258	0.759601
8	9.778499	3.279191	0.738386
8	7.913046	5.065357	0.504080
8	7.742989	3.002241	2.151971
8	-10.348690	-1.916595	-0.019368
15	-8.802189	-1.814576	-0.443715
8	-8.288800	-3.319004	-0.627524
8	-8.512365	-0.942026	-1.590135
8	-8.102757	-1.448954	0.950463
6	-8.451577	-0.275193	1.704272
6	-7.440564	0.847421	1.531543
8	-6.136416	0.346611	1.834360
6	-5.232792	0.652564	0.800380
6	-7.348150	1.506598	0.143558
6	-6.075301	0.918877	-0.444288
8	-7.200233	2.913354	0.392598
1	-8.454332	-0.594509	2.748671
1	-9.458592	0.067299	1.442786
1	-7.699320	1.627350	2.257648
1	-4.594471	1.497630	1.070181
1	-8.224186	1.326252	-0.484166
1	-6.326692	-0.016025	-0.956171
1	-5.595593	1.593178	-1.156030
7	-4.324341	-0.501008	0.647943
6	-2.965700	-0.257111	0.511127
8	-2.457166	0.841489	0.500358
7	-2.201143	-1.416008	0.374577
6	-2.680831	-2.669960	0.332472
8	-1.887055	-3.677229	0.189839
6	-4.081625	-2.882653	0.447073
6	-4.656749	-4.268585	0.386540
6	-4.836471	-1.762703	0.613392
1	-1.173859	-1.225824	0.275949
1	-4.273068	-4.809576	-0.483116
1	-5.745610	-4.215942	0.301534
1	-4.398368	-4.848959	1.278094
1	-5.914284	-1.817839	0.744746
15	-7.521955	4.039726	-0.694906
8	-8.904992	3.475964	-1.280676
8	-7.474087	5.404346	-0.164531
8	-6.496350	3.783774	-1.918169

1	8.114767	3.466434	2.916078
1	10.281228	3.967221	0.278256
1	8.230447	-3.265024	1.687130
1	10.620413	-3.404362	-0.630026
1	-8.691463	-3.932411	0.004688
1	-10.934973	-1.675306	-0.752418
1	-5.878096	4.526999	-1.979027
1	-9.260143	4.027816	-1.991897

8. wb97x/6-31G(d) optimized geometry of **(5'-A$^{\bullet+}$-3')•(3'-T$^{\bullet+}$-5')** base pair in triplet state**. TE = -4033.08318223 A.U.**

Charge = 2 Multiplicity = 3

8	9.251640	-3.573738	-1.153360
15	8.616706	-2.290380	-0.442162
8	7.454072	-2.939683	0.456526
8	9.589336	-1.376170	0.176315
8	7.627242	-1.595427	-1.499620
6	8.034759	-0.400162	-2.191971
6	7.315670	0.819569	-1.642638
8	5.894865	0.612834	-1.737293
6	5.305917	0.637658	-0.471858
6	7.584637	1.170829	-0.172791
6	6.424379	0.507561	0.561055
8	7.440661	2.591571	-0.074595
1	7.759870	-0.548512	-3.238250
1	9.116900	-0.256111	-2.118149
1	7.574863	1.679171	-2.269156
1	4.698922	1.539171	-0.332266
1	8.568429	0.838768	0.174257
1	6.643219	-0.545648	0.761685
1	6.203739	1.010811	1.503555
7	4.337599	-0.484779	-0.421296
6	4.563464	-1.762331	-0.784830
7	3.468288	-2.557692	-0.710734
6	2.513423	-1.737560	-0.297242
6	1.116567	-1.940268	-0.030916
7	0.545945	-3.114439	-0.172132
7	0.385721	-0.865795	0.373348
6	0.988504	0.304937	0.505306
7	2.296069	0.619336	0.290672
6	2.999071	-0.404319	-0.101442
1	5.544827	-2.095946	-1.112066
1	-0.455841	-3.237225	0.022944
1	1.099112	-3.908399	-0.478505

1	0.358295	1.130600	0.829326
15	8.224669	3.452899	1.032643
8	9.775408	3.069761	0.852999
8	7.915166	4.881645	0.972274
8	7.835697	2.620829	2.352774
8	-8.734801	-0.713105	-1.441242
15	-7.805912	-1.582094	-0.501654
8	-8.297929	-3.081579	-0.627741
8	-6.338166	-1.468820	-0.706579
8	-8.240085	-1.182304	0.997713
6	-8.717240	0.114785	1.381295
6	-7.619851	1.149785	1.552511
8	-6.614274	0.671672	2.470255
6	-5.352911	1.095585	2.083867
6	-6.831287	1.589651	0.316753
6	-5.533337	2.093820	0.941233
8	-7.600480	2.571127	-0.358874
1	-9.224388	-0.039926	2.335134
1	-9.442777	0.485697	0.649635
1	-8.089209	2.045005	1.981846
1	-4.793253	1.482748	2.937686
1	-6.609361	0.754045	-0.352336
1	-4.690956	2.144806	0.251702
1	-5.690737	3.087921	1.372858
7	-4.566774	-0.135835	1.631788
6	-3.175964	0.073576	1.341698
8	-2.679041	1.162169	1.464639
7	-2.493498	-1.046886	0.943261
6	-2.995403	-2.324981	0.817175
8	-2.294168	-3.258233	0.460903
6	-4.422006	-2.480678	1.155874
6	-5.073574	-3.794547	1.004358
6	-5.132847	-1.320412	1.560803
1	-1.486448	-0.917315	0.742425
1	-4.396077	-4.602253	1.294409
1	-5.313488	-3.935829	-0.060594
1	-6.010522	-3.854153	1.562808
1	-6.170347	-1.375257	1.877442
15	-7.358281	2.959901	-1.893663
8	-7.489568	1.480875	-2.571915
8	-8.228965	4.011385	-2.406369
8	-5.777562	3.225131	-2.009653
1	8.303597	2.938170	3.139609
1	10.272754	3.812472	0.478589
1	7.783193	-3.646462	1.032468
1	10.214500	-3.499179	-1.240565

1	-9.257977	-3.212611	-0.589214
1	-8.292868	0.016783	-1.932118
1	-5.603880	4.145881	-2.262486
1	-7.449466	1.526026	-3.541184

9. wb97x/6-31++G(d) optimized geometry of **neutral** G-C base pair.
TE = -1015.94611414 A.U.

Charge = 0 Multiplicity = 1

1	0.314042	0.037650	-0.000082
7	2.225592	0.328775	-0.000036
7	-4.642805	-0.325284	0.000072
6	-4.950418	1.021060	-0.000102
7	-3.903791	1.794768	0.000173
6	-2.836812	0.917512	0.000003
6	-1.425045	1.147820	-0.000046
8	-0.812859	2.220299	-0.000018
7	-0.711976	-0.058700	-0.000078
6	-1.260378	-1.316951	-0.000081
7	-0.391365	-2.347227	-0.000099
7	-2.558797	-1.544194	-0.000047
6	-3.279724	-0.398971	-0.000010
7	4.378908	-0.674249	0.000042
6	2.979169	-0.798882	-0.000004
8	2.496346	-1.935663	-0.000011
6	2.790770	1.533977	-0.000022
7	1.989393	2.601286	-0.000043
6	4.222119	1.689610	0.000020
6	4.958983	0.555577	0.000051
1	-5.981230	1.357167	-0.000121
1	2.375769	3.531822	-0.000023
1	4.691175	2.666640	0.000029
1	6.045267	0.568411	0.000087
1	0.622842	-2.219980	-0.000081
1	-0.781217	-3.275877	-0.000076
1	0.964268	2.484363	-0.000048
6	-5.552697	-1.451027	0.000108
1	-5.393867	-2.066576	-0.889509
1	-5.393260	-2.067003	0.889319
1	-6.577329	-1.071748	0.000546
6	5.164823	-1.902151	0.000085
1	4.929720	-2.496601	0.885908
1	4.929747	-2.496643	-0.885716
1	6.225325	-1.640379	0.000096

10. wb97x/6-31++G(d) optimized geometry of **radical cation** G$^{\bullet+}$-C base pair.
TE = -1015.69568698 A.U.

Charge = 1 Multiplicity = 2

1	-0.399834	0.112341	0.000075
7	-2.199477	0.387874	0.000045
7	4.629485	-0.341856	-0.000060
6	4.920013	0.984487	-0.000098
7	3.847839	1.782587	-0.000077
6	2.816580	0.939920	-0.000010
6	1.373991	1.188948	0.000037
8	0.825289	2.271426	0.000058
7	0.644515	-0.005152	0.000058
6	1.181501	-1.258408	0.000048
7	0.372601	-2.289701	0.000060
7	2.529366	-1.507669	0.000033
6	3.257195	-0.423194	-0.000001
7	-4.277189	-0.758507	-0.000066
6	-2.886153	-0.782797	-0.000018
8	-2.318353	-1.887934	-0.000028
6	-2.849201	1.555630	0.000064
7	-2.125463	2.678861	0.000117
6	-4.280634	1.611465	0.000026
6	-4.939781	0.429571	-0.000040
1	5.942627	1.344761	-0.000153
1	-2.572683	3.582599	0.000126
1	-4.815089	2.553964	0.000046
1	-6.023791	0.368909	-0.000078
1	-0.666638	-2.177266	0.000051
1	0.788877	-3.212363	0.000058
1	-1.108242	2.639020	0.000119
6	5.553559	-1.471305	0.000005
1	5.391280	-2.077371	0.893417
1	5.390173	-2.078320	-0.892557
1	6.573368	-1.084017	-0.000844
6	-4.984365	-2.039729	-0.000144
1	-4.712759	-2.614080	-0.887934
1	-4.712811	-2.614160	0.887610
1	-6.057931	-1.844544	-0.000168

11. wb97x/6-31++G(d) optimized geometry of proton transferred **radical cation** G(-H)$^{\bullet}$-(H^{+})C base pair. **TE = -1015.69399298 A.U.**

Charge = 1 Multiplicity = 2

7	-2.220612	0.338954	0.001514
7	4.651551	-0.279519	-0.004380
6	4.874049	1.060509	-0.008380
7	3.766078	1.804113	-0.008400
6	2.772759	0.909252	-0.003143
6	1.314098	1.063564	-0.000852
8	0.764028	2.168091	-0.001064
7	0.600650	-0.107061	0.001862
6	1.224023	-1.292132	0.003309
7	0.485849	-2.397511	0.004565
7	2.592698	-1.530699	0.003737
6	3.281484	-0.425924	-0.000042
7	-4.328449	-0.692371	-0.002785
6	-2.950217	-0.835977	-0.001738
8	-2.414208	-1.930898	-0.003624
6	-2.755748	1.584893	0.004308
7	-1.946888	2.621779	0.006767
6	-4.179803	1.689611	0.004278
6	-4.901557	0.542732	0.000487
1	5.878095	1.469685	-0.012482
1	-2.329792	3.556966	0.008821
1	-4.664460	2.657876	0.006789
1	-5.987193	0.555134	-0.000213
1	-0.532391	-2.345504	0.002568
1	0.951817	-3.293429	0.005562
1	-0.913706	2.503395	0.004767
6	5.627984	-1.359920	0.008491
1	5.560165	-1.911158	0.948975
1	5.434603	-2.036683	-0.826206
1	6.625297	-0.929216	-0.093794
6	-5.122717	-1.926340	-0.007352
1	-4.889302	-2.511170	-0.898926
1	-4.888711	-2.518110	0.879446
1	-6.179573	-1.657499	-0.005982
1	-1.175690	0.196778	0.001825

12. wb97x/6-31++G(d) optimized geometry of **G(-H)$^+$-(H$^+$)C** base pair (double oxidation) in singlet state, see **Figure 3** in the text. (**TE = -1015.29846906 A.U.)**

Charge = 2 Multiplicity = 1

7	-2.296279	0.403648	0.001440
7	4.733271	-0.265298	-0.001884
6	4.932409	1.026401	-0.005505
7	3.766840	1.811901	-0.005142
6	2.805816	0.958083	-0.001110
6	1.309178	1.105766	0.000950
8	0.775372	2.197424	0.001237
7	0.623516	-0.077103	0.002560
6	1.222958	-1.253180	0.002739
7	0.531212	-2.365655	0.003066
7	2.652400	-1.494433	0.002310
6	3.318232	-0.427001	0.000886
7	-4.308935	-0.788876	-0.002092
6	-2.931480	-0.828177	-0.000373
8	-2.294939	-1.871150	-0.000450
6	-2.917901	1.609599	0.001834
7	-2.178549	2.704107	0.003412
6	-4.338382	1.605079	0.000456
6	-4.970261	0.401900	-0.001552
1	5.922631	1.475568	-0.008728
1	-2.618137	3.615374	0.003789
1	-4.899820	2.531312	0.000799
1	-6.054027	0.334112	-0.002896
1	-0.498784	-2.317210	0.002498
1	1.000971	-3.264002	0.003408
1	-1.157546	2.666294	0.003660
6	5.718074	-1.359618	0.001616
1	5.587451	-1.944805	0.913650
1	5.549859	-1.983359	-0.878000
1	6.717353	-0.924406	-0.029153
6	-5.017523	-2.080391	-0.004582
1	-4.743242	-2.646005	-0.896554
1	-4.744526	-2.648728	0.886042
1	-6.089823	-1.884756	-0.005073
1	-1.266871	0.331619	0.002413

13. wb97x/6-31G(d) optimized geometry of **(5'-G-3')•(3'-C-5')** base pair.

TE = -4049.73526111 A.U.

Charge = 0 Multiplicity = 1

8	-7.624823	-3.363943	1.098969
15	-8.819520	-2.454196	0.539380
8	-8.876895	-2.844094	-1.013463
8	-10.100657	-2.522683	1.260286
8	-8.095874	-1.029484	0.492333
6	-8.069619	-0.244688	1.696248
6	-7.018957	0.838499	1.541967
8	-5.726008	0.263054	1.647535
6	-4.954097	0.524861	0.484671
6	-7.072861	1.562993	0.189299
6	-5.967553	0.884750	-0.603386
8	-6.749176	2.948124	0.443412
1	-7.805267	-0.874479	2.552162
1	-9.061600	0.190458	1.856411
1	-7.157032	1.567756	2.350083
1	-4.248594	1.343412	0.666412
1	-8.056966	1.508110	-0.284770
1	-6.358337	-0.029696	-1.059047
1	-5.543058	1.527659	-1.377311
7	-4.155757	-0.637352	0.192892
6	-4.569793	-1.959367	0.136950
7	-3.606835	-2.784598	-0.145580
6	-2.492302	-1.977085	-0.286449
6	-1.132848	-2.297092	-0.596736
8	-0.630881	-3.400988	-0.820208
7	-0.336059	-1.144065	-0.631266
6	-0.768263	0.137824	-0.403918
7	0.163618	1.106180	-0.497146
7	-2.016515	0.446441	-0.118931
6	-2.812767	-0.645118	-0.073391
1	-5.597169	-2.232762	0.345751
1	0.659443	-1.297307	-0.843809
1	1.150879	0.913698	-0.669234
1	-0.137829	2.044114	-0.293270
15	-7.212645	4.049274	-0.615431
8	-8.566804	3.889743	-1.174286
8	-6.948310	5.411988	0.185221
8	-6.006705	4.031402	-1.674483
8	7.727710	-3.471267	1.917017
15	6.980116	-2.084085	1.588674
8	5.423458	-2.421783	1.467621
8	7.297969	-0.982562	2.509254
8	7.353102	-1.877112	0.046383
6	8.419935	-1.016641	-0.370174
6	7.869394	0.285441	-0.937572
8	6.885015	0.012610	-1.936890
6	5.593427	0.367162	-1.504817
6	7.197228	1.216665	0.074439
6	5.717261	0.903040	-0.072235
8	7.477539	2.558620	-0.374293

1	8.956997	-1.559380	-1.152027
1	9.106459	-0.809314	0.457598
1	8.697396	0.817302	-1.418793
1	5.175779	1.108117	-2.191029
1	7.568248	1.074644	1.093284
1	5.418829	0.135756	0.647752
1	5.091093	1.777352	0.098964
7	4.705606	-0.817382	-1.567545
6	3.348595	-0.592676	-1.263338
8	2.995046	0.566474	-1.034811
7	2.508192	-1.654172	-1.231444
6	2.949443	-2.886885	-1.476002
7	2.072062	-3.887361	-1.419623
6	4.331502	-3.137140	-1.795410
6	5.155652	-2.060299	-1.857657
1	1.078591	-3.705039	-1.200337
1	2.363062	-4.830486	-1.618944
1	4.684238	-4.127874	-2.058284
1	6.200620	-2.125296	-2.129100
15	7.506524	3.798566	0.625405
8	8.496694	3.238635	1.758931
8	7.816113	5.072069	-0.032702
8	6.097706	3.801013	1.419420
1	5.189948	-2.898130	0.651428
1	7.915536	-3.539415	2.864383
1	8.447018	3.751790	2.577111
1	5.543903	4.526610	1.096708
1	-6.274382	4.444346	-2.507973
1	-7.764139	5.721320	0.603545
1	-7.929947	-4.234643	1.390887
1	-9.765031	-2.689832	-1.365336

14. wb97x/6-31G(d) optimized geometry of **(5'-$G^{\bullet+}$-3')•(3'-C-5')** base pair.

TE = -4049.50359926 A.U.

Charge = 1 Multiplicity = 2

8	-7.936760	-3.380367	0.784074
15	-8.937367	-2.571630	-0.184596
8	-8.444461	-2.989823	-1.645848
8	-10.372623	-2.702360	0.092284
8	-8.296958	-1.106287	-0.045905
6	-8.697282	-0.307772	1.079149
6	-7.695555	0.816481	1.240824
8	-6.439717	0.277242	1.675704
6	-5.431023	0.550699	0.742573
6	-7.397695	1.594464	-0.046193

6	-6.126716	0.932133	-0.563206
8	-7.130352	2.950718	0.343692
1	-8.705821	-0.913934	1.991636
1	-9.702016	0.088774	0.902261
1	-8.059279	1.504242	2.011137
1	-4.762227	1.341836	1.101097
1	-8.224093	1.572568	-0.762548
1	-6.388092	0.031150	-1.124985
1	-5.526402	1.599570	-1.185012
7	-4.596695	-0.652377	0.634924
6	-4.996119	-1.951333	0.704251
7	-3.991306	-2.829391	0.593328
6	-2.905669	-2.072101	0.452294
6	-1.498435	-2.437256	0.285982
8	-1.046229	-3.562388	0.236384
7	-0.680958	-1.306347	0.184118
6	-1.114988	-0.014861	0.228762
7	-0.230040	0.946766	0.126495
7	-2.427036	0.344285	0.371814
6	-3.233924	-0.677307	0.477190
1	-6.034420	-2.229890	0.849317
1	0.346247	-1.497809	0.060110
1	0.791445	0.754781	0.014459
1	-0.573767	1.897125	0.160005
15	-7.279789	4.102539	-0.766283
8	-8.394147	3.928348	-1.710510
8	-7.297841	5.429197	0.121379
8	-5.798651	4.113907	-1.387769
8	10.495057	-1.844239	-0.381893
15	9.028626	-1.805324	0.279818
8	8.646222	-3.318360	0.618215
8	8.874763	-0.884651	1.414500
8	8.105912	-1.551477	-1.006648
6	8.278251	-0.385882	-1.832020
6	7.205322	0.659677	-1.579256
8	5.924621	0.067415	-1.796032
6	5.082128	0.289629	-0.684763
6	7.166038	1.285098	-0.173894
6	6.009802	0.562700	0.495636
8	6.837608	2.673439	-0.365861
1	8.194030	-0.741079	-2.861536
1	9.276115	0.043799	-1.692439
1	7.356504	1.464173	-2.309444
1	4.397449	1.118545	-0.873081
1	8.107018	1.187027	0.372831
1	6.377763	-0.371539	0.932278

1	5.546819	1.160544	1.282502
7	4.239665	-0.901411	-0.518994
6	2.874763	-0.747702	-0.283279
8	2.410757	0.396336	-0.171854
7	2.100769	-1.859332	-0.177527
6	2.643281	-3.076372	-0.269380
7	1.835393	-4.133258	-0.158231
6	4.047637	-3.257133	-0.482062
6	4.798251	-2.140921	-0.608329
1	0.835985	-4.009271	-0.010995
1	2.203141	-5.068866	-0.220645
1	4.488198	-4.243932	-0.552723
1	5.868001	-2.159122	-0.796537
15	7.288804	3.806818	0.663490
8	8.858740	3.488373	0.758044
8	6.852760	5.155386	0.289662
8	6.754897	3.333502	2.114445
1	8.920368	-3.940357	-0.071131
1	11.169967	-1.544944	0.245619
1	9.307607	4.025222	1.426323
1	6.085349	3.958810	2.427664
1	-5.753861	4.667857	-2.181408
1	-8.199053	5.767283	0.228923
1	-8.290469	-4.246159	1.037699
1	-9.182330	-2.989718	-2.273501

15. wb97x/6-31G(d) optimized geometry of proton transferred **(5'-G(-H)$^{\bullet}$-3')•(3'-(H^{+})C-5')** base pair. **TE = -4049.50198471 A.U.**

Charge = 1 Multiplicity = 2

8	-7.757977	-3.505705	0.887940
15	-8.943917	-2.724003	0.132656
8	-8.710370	-3.115216	-1.400000
8	-10.302367	-2.909468	0.658640
8	-8.347322	-1.235998	0.181262
6	-8.630649	-0.441141	1.344681
6	-7.674880	0.733947	1.360767
8	-6.354803	0.268901	1.657152
6	-5.467711	0.579132	0.611974
6	-7.573973	1.485272	0.027631
6	-6.329297	0.884758	-0.612939
8	-7.352972	2.870183	0.345699
1	-8.484950	-1.032925	2.254622
1	-9.669315	-0.098574	1.301476

1	-7.985448	1.426643	2.150281
1	-4.821920	1.423529	0.880218
1	-8.474435	1.389006	-0.585922
1	-6.594872	-0.044582	-1.124559
1	-5.845157	1.569067	-1.312731
7	-4.573015	-0.562159	0.440315
6	-4.893942	-1.885812	0.489321
7	-3.846964	-2.700787	0.342955
6	-2.802732	-1.877566	0.201439
6	-1.372435	-2.138448	0.009303
8	-0.918724	-3.282083	-0.065039
7	-0.579243	-1.021987	-0.078888
6	-1.111956	0.203091	0.004562
7	-0.301961	1.253302	-0.079424
7	-2.447264	0.541873	0.170978
6	-3.208649	-0.509214	0.263957
1	-5.911336	-2.224744	0.652032
1	1.159894	-1.383748	-0.294478
1	0.702811	1.132539	-0.197996
1	-0.704744	2.175906	-0.016674
15	-7.740914	3.971823	-0.754059
8	-8.987149	3.721786	-1.495035
8	-7.677971	5.325975	0.091043
8	-6.389522	4.032241	-1.620141
8	10.396188	-2.152367	-0.008491
15	8.865190	-2.026920	0.464429
8	8.343817	-3.517972	0.699065
8	8.620863	-1.123219	1.596931
8	8.127697	-1.677157	-0.917918
6	8.479261	-0.513366	-1.686583
6	7.480618	0.618504	-1.510277
8	6.172297	0.135600	-1.831375
6	5.269554	0.423108	-0.792329
6	7.379185	1.254478	-0.112753
6	6.110909	0.644295	0.460998
8	7.200455	2.662882	-0.332950
1	8.468651	-0.839116	-2.729100
1	9.491575	-0.176813	-1.438594
1	7.751941	1.405184	-2.224051
1	4.646518	1.286056	-1.038801
1	8.256555	1.072325	0.512518
1	6.361153	-0.307064	0.941625
1	5.634277	1.296213	1.195075
7	4.344451	-0.723919	-0.683345
6	2.995045	-0.470136	-0.498870
8	2.541228	0.656461	-0.401248

7	2.186942	-1.590875	-0.424736
6	2.624986	-2.871297	-0.496081
7	1.744731	-3.843544	-0.403616
6	4.024758	-3.083161	-0.668471
6	4.826709	-1.996474	-0.759747
1	0.729057	-3.652880	-0.276840
1	2.057210	-4.802233	-0.452072
1	4.427991	-4.085599	-0.730081
1	5.900625	-2.072599	-0.909212
15	7.642209	3.763459	0.739265
8	9.138416	3.268437	1.039287
8	7.421684	5.143709	0.301016
8	6.864062	3.381491	2.103447
1	8.718128	-4.152842	0.071072
1	11.008102	-1.906622	0.701819
1	9.582272	3.808229	1.708801
1	6.248798	4.093633	2.332230
1	-6.523075	4.524995	-2.443411
1	-8.565376	5.620269	0.343246
1	-8.020398	-4.397193	1.161555
1	-9.545822	-3.102472	-1.889862

16. wb97x/6-31G(d) optimized geometry of **(5'-G(-H)$^+$-3')•(3'-(H$^+$)C-5')** base pair in singlet state**.** **TE** = **-4049.14517879 A.U.**

Charge = 2 Multiplicity = 1

8	6.176725	-3.357663	0.670862
15	5.844330	-2.401839	1.933679
8	4.292463	-2.002550	1.694496
8	6.154663	-2.950260	3.252383
8	6.505347	-1.045839	1.423113
6	7.908816	-0.942965	1.113696
6	8.058532	0.062356	-0.011678
8	7.408487	-0.421483	-1.210414
6	6.177103	0.184226	-1.374859
6	7.412633	1.423374	0.241920
6	5.983835	1.240831	-0.282599
8	8.127831	2.360844	-0.556745
1	8.298484	-1.914629	0.794924
1	8.445165	-0.610430	2.006909
1	9.117690	0.179827	-0.253620
1	6.086180	0.574942	-2.392518
1	7.433176	1.727777	1.292607
1	5.341079	0.875537	0.519207

1	5.572727	2.169289	-0.683639
7	5.136450	-0.923244	-1.293540
6	5.364470	-2.189216	-1.525381
7	4.231084	-3.024109	-1.445249
6	3.280922	-2.228881	-1.116874
6	1.820231	-2.458350	-0.866302
8	1.339513	-3.575091	-0.893467
7	1.101694	-1.323707	-0.608725
6	1.657955	-0.124473	-0.587229
7	0.934442	0.942126	-0.348499
7	3.047051	0.194221	-0.803839
6	3.749488	-0.829506	-1.015548
1	6.348388	-2.561253	-1.784942
1	-0.735914	-1.741891	-0.357236
1	-0.078162	0.842417	-0.184900
1	1.369333	1.855980	-0.335661
15	7.878241	3.933403	-0.267419
8	7.468313	4.213882	1.116327
8	9.208013	4.629238	-0.793349
8	6.834670	4.249700	-1.443230
8	-9.890882	-1.555004	-0.409956
15	-8.350541	-1.592884	-0.851772
8	-8.014903	-3.115888	-1.195122
8	-7.951867	-0.644085	-1.901671
8	-7.596426	-1.445859	0.560740
6	-7.835254	-0.334863	1.443951
6	-6.743620	0.717641	1.357996
8	-5.468143	0.088764	1.574264
6	-4.579980	0.410299	0.544370
6	-6.617398	1.497937	0.033870
6	-5.424768	0.849128	-0.647266
8	-6.260977	2.854555	0.322999
1	-7.846856	-0.762123	2.448861
1	-8.812891	0.117704	1.247747
1	-6.919023	1.431885	2.168305
1	-3.858263	1.168170	0.858960
1	-7.514732	1.457399	-0.590028
1	-5.775162	-0.011237	-1.226063
1	-4.905677	1.543779	-1.309824
7	-3.777098	-0.812887	0.262813
6	-2.425008	-0.680545	0.040451
8	-1.836428	0.389411	0.045240
7	-1.750036	-1.867484	-0.201212
6	-2.316842	-3.097847	-0.253987
7	-1.539655	-4.136720	-0.505046
6	-3.714822	-3.181180	-0.031341

6	-4.388080	-2.029083	0.225414
1	-0.533663	-4.034105	-0.656522
1	-1.938317	-5.063603	-0.555852
1	-4.227505	-4.133956	-0.060720
1	-5.457971	-2.010234	0.425459
15	-7.378656	3.996965	0.474312
8	-8.348908	3.295418	1.550371
8	-6.827333	5.318591	0.775188
8	-8.263015	3.899576	-0.865608
1	-8.545412	-3.746827	-0.686272
1	-10.459833	-1.176958	-1.098285
1	-9.050774	3.890871	1.853854
1	-8.087663	4.650609	-1.451945
1	6.673466	5.199394	-1.553528
1	9.796930	4.895859	-0.070887
1	6.207811	-4.296417	0.918312
1	3.802795	-2.113150	2.525370