Electronic Supplementary File

Excited State Deactivation Mechanisms of Protonated Adenine: a Theoretical Study

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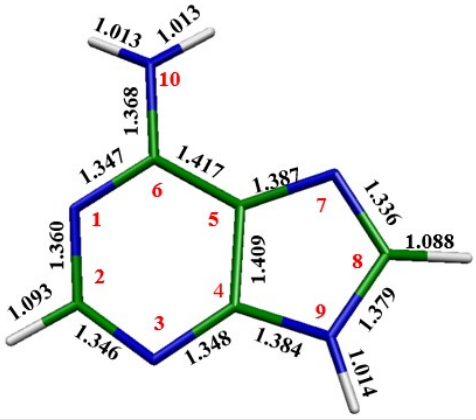
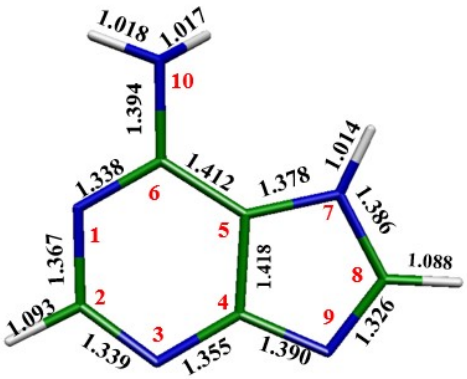
Optimized Structures of lowest lying isomers (1^+, 2^+ and 3^+):

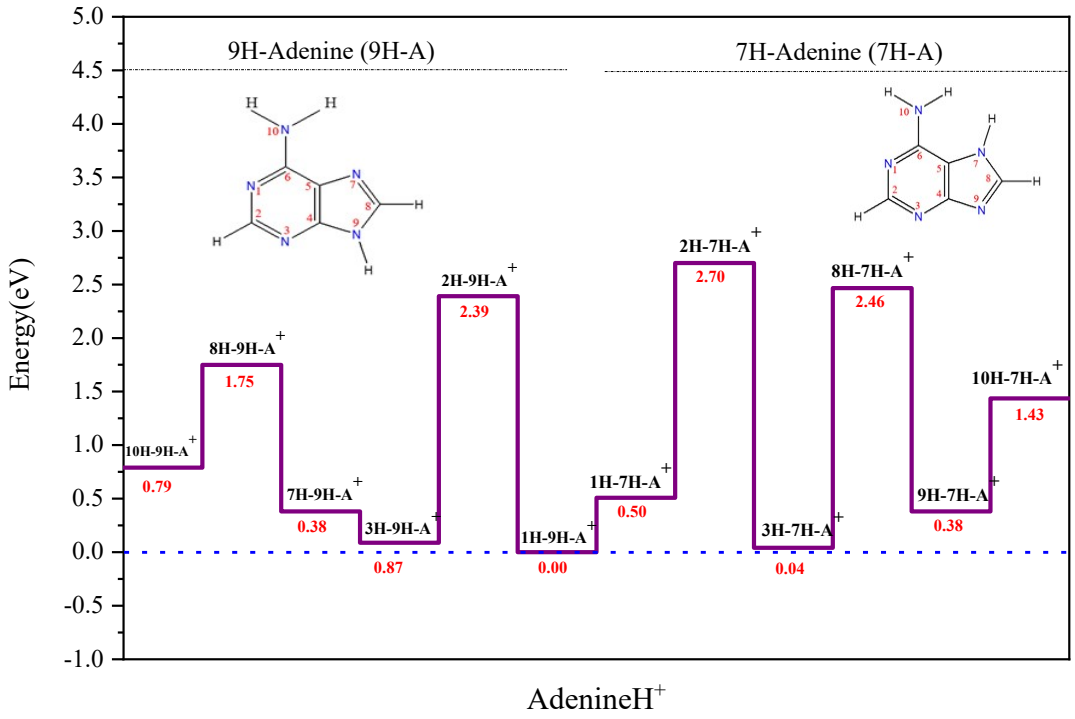
The optimized ground state geometry of the three most stable protonated isomers of adenine (**1**$^+$, **2**$^+$ and **3**$^+$) has been determined at the MP2/aug-cc-pVDZ level of theory. The optimized structures possess the *Cs* symmetry point group and planar form. In fact, our results showed that three protonated isomers are very similar in bond lengths and only slight differences have been determined. The N_1-C_2 bond length has been predicted to be 1.391 Å in the isomer **1**$^+$, while that has been predicted to be 1.325 and 1.318 Å respectively in **2**$^+$ and **3**$^+$ isomers. Also, the bond length of C_2=N_3 in **1**$^+$ (1.313 Å) is shorter than that of **2**$^+$ (1.355 Å) and **3**$^+$ (1.369 Å). The C_8–N_9 bond in **1**$^+$ and **2**$^+$ is predicted to be longer (1.381, 1.392 Å) than that of the **3**$^+$ (1.335 Å). The C_5–C_6 bond length is similar in isomer **2**$^+$ and **3**$^+$ (1.422 Å), in the event that the C_5–C_6 bond length has been predicted to be 1.413 Å in the isomer **1**$^+$. The C_6-N_{10} bond is the most elongated in isomer **2**$^+$ (1.341 Å) and the shortest in isomer **1**$^+$ (1.318 Å) among the three isomers. The C_5–N_7 bond length has been predicted to lie within 1.373 Å to 1.380 Å for three most stable protonated isomers. The N_7–C_8 bond length in **1**$^+$ and **3**$^+$ are quite similar (1.337, 1.329 Å), while it is elongated in isomer **2**$^+$ (1.378 Å). The C_4–N_9 bond lengths are between 1.361 Å and 1.369 Å. Our results showed that the bond length of N_3=C_4 in **1**$^+$ (1.359Å) is shorter than that of **2**$^+$ (1.368 Å) and **3**$^+$ (1.367 Å). The C_4–C_5 bond lengths are gained 1.412 Å, 1.409 Å and 1.404 Å in isomers **1**$^+$, **2**$^+$ and **3**$^+$ respectively.

Optimized Ground State Geometry of 9HA and 7HA

The optimized ground state geometry of the 9HA and 7HA has been determined at the MP2/aug-cc-pVDZ level of theory. Comparison the optimized geometries of neutral and protonated 9HA (1H-9H-A^+, $\mathbf{1}^+$) exhibits that the C_6-N_{10} bond length decrease from 1.368 Å (in the 9HA) to 1.337 Å (in the $\mathbf{1}^+$). The N_1=C_6 bond length has been predicted to be 1.347 Å in the 9HA, while The N_1-C_6 bond in isomer $\mathbf{1}^+$ is 1.369 Å. The N_1-C_2 bond length in $\mathbf{1}^+$ (1.391 Å) is longer thane one of the 9HA (1.360 Å). The C_2=N_3 bond in 9HA (1.346 Å) is longer than the isomer $\mathbf{1}^+$ (1.313 Å). The C_6–N_1–C_2 angle increases from 118.48 º in 9HA to 124.18 º in isomer $\mathbf{1}^+$. The N_1–C_2–N_3 angle decreases from 128.84 º in 9HA to 124.40 º in isomer $\mathbf{1}^+$.

Comparison the optimized ground state geometries of neutral and protonated 7HA (and 3H-7H-A^+ named as $\mathbf{2}^+$) exhibits that the C_6-N_{10} bond length decrease from 1.394 Å (in the 7HA) to 1.341 Å (in the $\mathbf{2}^+$). The N_1=C_6 bond length has been predicted to be 1.338 Å in the 7HA, while The N_1-C_6 bond in isomer $\mathbf{2}^+$ is 1.364 Å. The N_1-C_2 bond length in $\mathbf{2}^+$ (1.325 Å) is shorter than that of the 7HA (1.367 Å). The C_2=N_3 bond in 7HA (1.339 Å) is shorter than the isomer $\mathbf{2}^+$ (1.355 Å). The N_3-C_4 bond length in $\mathbf{2}^+$ (1.368 Å) is elongated than in the 7HA (1.355 Å). The C_2–N_3–C_4 angle increases from 113.01 º in 7HA to 118.32 º in isomer $\mathbf{2}^+$. The N_1–C_2–N_3 angle decreases from 128.57 º in 7HA to 124.43 º in isomer $\mathbf{2}^+$.

	
9HA	7HA



10H-9H-A$^+$	*8H-9H-A*$^+$	*7H-9H-A*$^+$	*3H-9H-A*$^+$
2H-9H-A$^+$	*1H-9H-A*$^+$	*1H-7H-A*$^+$	*2H-7H-A*$^+$
3H-7H-A$^+$	*8H-7H-A*$^+$	*9H-7H-A*$^+$	*10H-7H-A*$^+$

Figure S1. *Relative stability (upper panel) and the optimized geometry (lower panel) for selected protonated isomers of Adenine determined at the MP2/aug-cc-pVDZ level.*

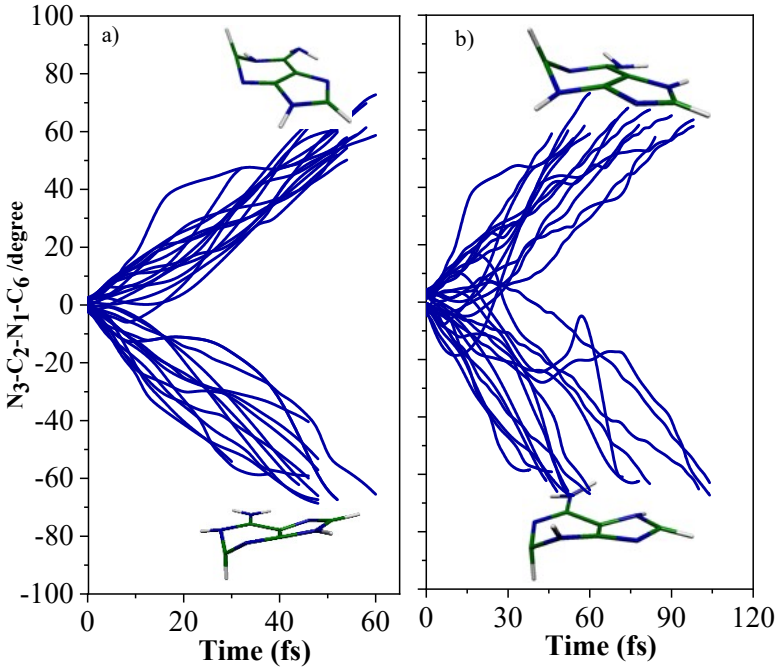


Figure S2. *Time evolution of the dihedral angles of N_3–C_2–N_1–C_6 for the* **1**$^+$ and **2**$^+$, *(a and be respectively), for trajectories with relaxation pathway ending at $^1\pi\pi^*/S_0$ intersection by out-of-plane distortion of C_2-pukering. Insets show the end points for a typical selected trajectory.*

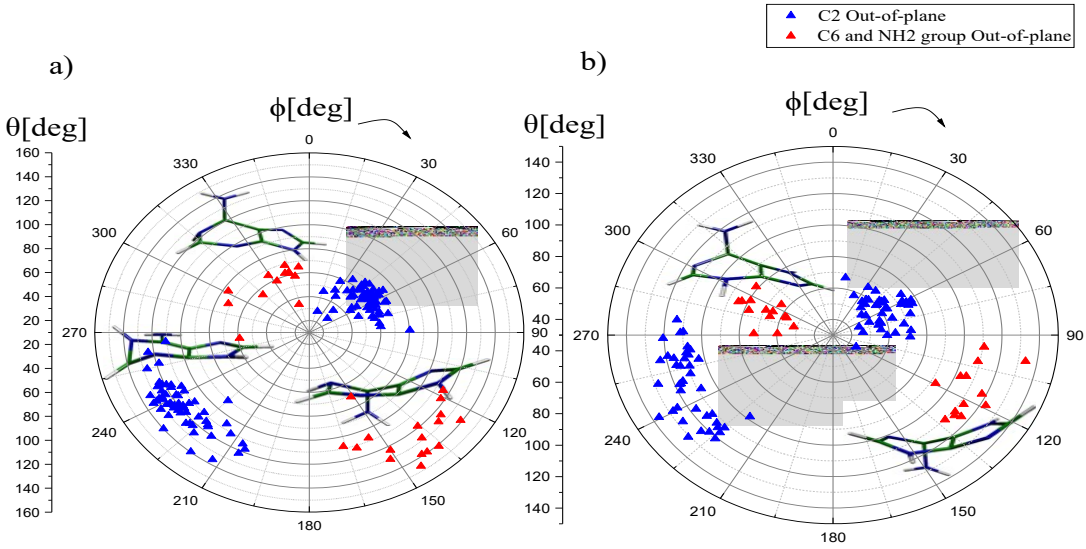
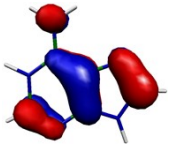
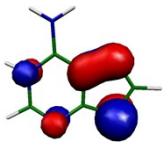
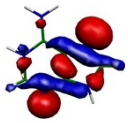
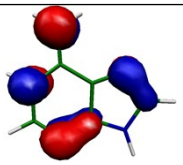
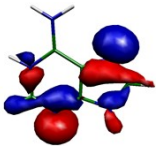
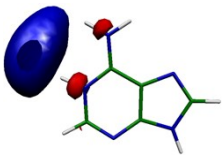
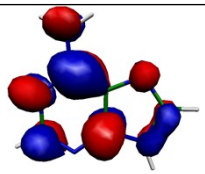
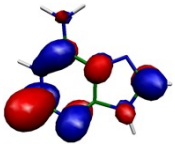
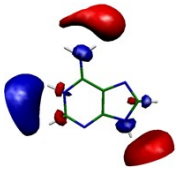
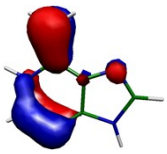


Figure S3. The distribution of Cremer – Pople parameters with polar plot (ɵ, ϕ) at ππ*/S_0 crossing for 1H-9H-A^+ (a) and 3H-7H-A^+ (b).

Table S1: Schemes of valence molecular orbitals of 1H-9H-A$^+$ (**1**$^+$) and 3H-7H-A$^+$(**2**$^+$) involved four occupied and four virtual orbitals in CASSCF (8,8) geometry optimization of conical intersections and six occupied and four virtual orbitals in the PEs curve at the CASPT2 (12, 10) level.

The most stable protonated isomers (1$^+$)				
HOMO (π)	*HOMO-1 (π)*	*HOMO-2 (n)*	*HOMO-3 (π)*	*HOMO-4 (n)*
				
LUMO (σ)*	*LUMO+1 (π*)*	*LUMO+2 (π*)*	*LUMO+3 (σ*)*	*HOMO-5 (π)*
				

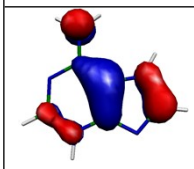
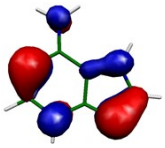
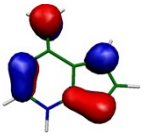
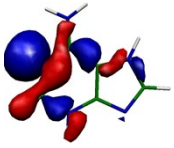
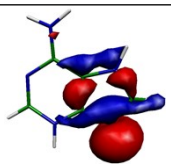
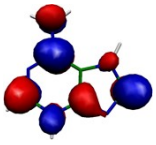
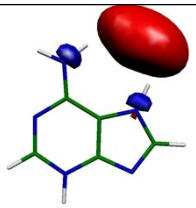
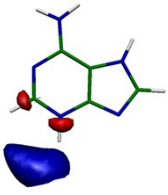
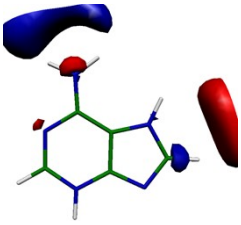
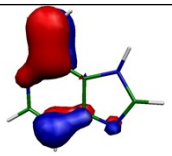
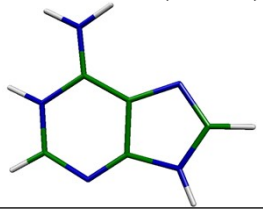
The second most stable protonated isomer (2$^+$)				
HOMO (π)	*HOMO-1 (π)*	*HOMO-2 (π)*	*HOMO-3 (n)*	*HOMO-4 (n)*
				
LUMO (π)*	*LUMO+1 (σ*)*	*LUMO+2 (σ*)*	*LUMO+3 (σ*)*	*HOMO-5 (π)*
				

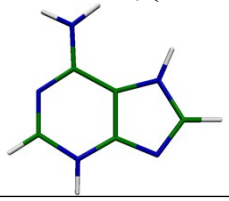
Table S2: The xyz coordinates of the ground state optimized geometry of the most stable isomer of AH^+. The energetic values (in eV) represent the relative stabilities at the MP2/aug-cc-pVDZ level of theory.

1H-9H-A^+- (0.0 eV)



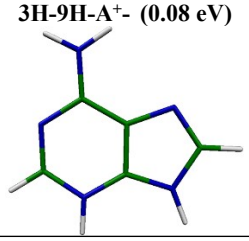
N	3.61313	-0.63913	0.25996
N	3.18660	1.70033	0.00634
C	4.01212	0.68743	0.13312
C	1.88228	1.31747	0.01152
C	1.37857	0.00462	0.13424
C	2.30820	-1.05139	0.26820
N	0.00688	-0.03172	0.10164
N	0.76263	2.09819	-0.09912
N	1.96373	-2.33725	0.39233
C	-0.32918	1.25502	-0.04066
H	5.09101	0.84937	0.14497
H	-1.34941	1.62813	-0.10638
H	0.74686	3.11095	-0.20454
H	2.63746	-3.08824	0.48786
H	0.97379	-2.56767	0.39002
H	4.35434	-1.33412	0.35151

3H-7H-A^+- S_0 (0.04 eV)



N	3.63291	-0.64835	0.29478
N	3.06189	1.64598	0.10899
C	3.95719	0.63473	0.22116
C	1.73093	1.33305	0.06787
C	1.33599	-0.01777	0.14278
C	2.32475	-1.03259	0.25981
N	-0.03932	0.04121	0.07352
N	0.67678	2.18634	-0.04123
N	2.08185	-2.34895	0.33955
C	-0.38117	1.37183	-0.03492
H	5.01205	0.91327	0.25146
H	-1.41811	1.69419	-0.10647
H	2.87521	-2.97828	0.42089
H	1.14915	-2.74044	0.32341
H	-0.70117	-0.72968	0.09554
H	3.36507	2.61947	0.05584

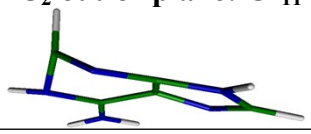
3H-9H-A^{+}- (0.08 eV)



N	1.79668	-0.95985	0.13289
N	1.27623	1.35284	-0.12696
C	2.14701	0.30426	0.00093
C	-0.05728	1.05394	-0.11559
C	-0.50592	-0.26888	0.02120
C	0.46696	-1.29793	0.14859
N	-1.88447	-0.32435	0.00542
N	-1.18229	1.82231	-0.21698
N	0.14536	-2.58195	0.28323
C	-2.25825	0.94282	-0.13832
H	3.20747	0.56423	-0.01054
H	-3.28500	1.29928	-0.19334
H	-1.24473	2.83139	-0.32771
H	0.88175	-3.27577	0.37043
H	-0.82933	-2.86668	0.29878
H	1.63674	2.30078	-0.22439

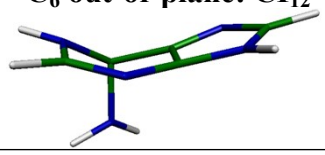
The xyz coordinates of the CASSCF (8,8)/cc-pVDZ optimized geometry of the S_1/S_0 conical intersections ($CI_{1\text{-}3}$) resulting from out-of-plane deformation of 1H-9H-A^+.

1^+
C_2 out-of-plane: CI_{11}



N	3.67400	-0.64300	0.40800
N	3.18700	1.58700	0.17500
C	3.89900	0.55100	-0.31700
C	1.90900	1.36700	-0.07400
C	1.47100	0.02700	-0.17500
C	2.36900	-1.01600	0.20400
N	0.09100	-0.02400	-0.15000
N	0.78500	2.10700	-0.00500
N	1.97100	-2.24700	0.36600
C	-0.27900	1.21400	-0.07500
H	4.15100	0.49200	-1.37300
H	-1.29900	1.55800	-0.06400
H	0.72500	3.10200	0.07400
H	2.58100	-2.97300	0.68400
H	0.99900	-2.46100	0.23600
H	4.37500	-1.36100	0.42100

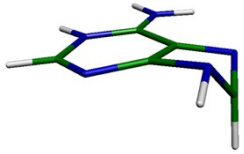
1^+
$-C_6$ out-of-plane: CI_{12}



N	1.90531	-0.07319	-0.35089
N	0.56385	-0.32700	1.57420
C	1.72206	-0.26664	0.97635
C	-0.48184	-0.24687	0.74436
C	-0.42637	0.06713	-0.66926
C	0.88962	0.65977	-1.05454
N	-1.56623	-0.25273	-1.26395
N	-1.70349	-0.73642	0.93070
N	0.79013	1.98542	-0.67364
C	-2.34495	-0.71555	-0.29508
H	2.60883	-0.41762	1.57976
H	-3.35841	-1.05349	-0.42180
H	-2.04986	-1.14016	1.78100
H	1.63430	2.46927	-0.42965
H	0.17376	2.54107	-1.23716
H	2.83155	-0.13005	-0.72652

1^+

C_8 out-of-plane: CI_{13}

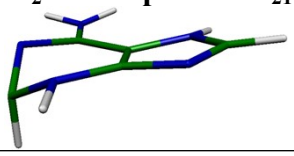


N	3.54800	-0.63300	0.19000
N	3.03200	1.68400	-0.03300
C	3.89600	0.73000	-0.01500
C	1.76100	1.30000	0.18200
C	1.29400	-0.03600	0.19000
C	2.30600	-1.08000	0.28900
N	-0.04100	-0.10200	0.04700
N	0.56400	2.12600	0.34500
N	1.97600	-2.33100	0.45700
C	-0.00800	1.20700	-0.52300
H	4.95100	0.91000	-0.13400
H	-0.06900	1.33600	-1.60100
H	0.68400	3.04200	-0.05800
H	2.64700	-3.06800	0.54900
H	1.00200	-2.56600	0.50100
H	4.30800	-1.28700	0.22800

The xyz coordinates of the CASSCF (8,8)/cc-pVDZ optimized geometry of the S_1/S_0 conical intersections ($CI_{1\text{-}3}$) resulting from out-of-plane deformation of 3H-7H-A^+.

2^+

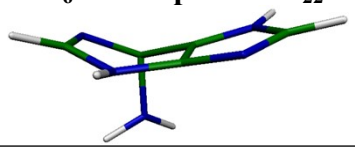
C_2 out-of-plane: CI_{21}



N	3.57200	-0.53700	0.61300
N	3.07700	1.70700	0.32100
C	3.96300	0.64900	-0.06900
C	1.80200	1.35500	0.14100
C	1.42700	-0.01900	0.00700
C	2.34800	-1.03400	0.25000
N	0.03900	0.03200	-0.05300
N	0.73000	2.15500	0.09900
N	2.12400	-2.34500	0.31000
C	-0.29100	1.33100	-0.02500
H	4.13800	0.53400	-1.13800
H	-1.31500	1.66100	-0.10300
H	2.86400	-2.93900	0.62900
H	1.19800	-2.71300	0.35900
H	-0.59600	-0.71500	-0.24700
H	3.34300	2.66800	0.22300

2^+

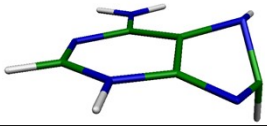
C_6 out-of-plane: CI_{22}



N	3.51500	-0.75300	0.57200
N	3.06800	1.43700	-0.27100
C	3.87800	0.44500	0.34300
C	1.74200	1.22200	-0.28800
C	1.25600	-0.08000	0.03300
C	2.28700	-1.17700	-0.01700
N	-0.04200	0.07000	0.22100
N	0.73400	2.12000	-0.28800
N	2.37200	-1.37900	-1.38700
C	-0.32900	1.41900	-0.00100
H	4.84500	0.79800	0.67500
H	-1.33000	1.80700	0.08700
H	3.28900	-1.50100	-1.77900
H	1.69500	-2.01000	-1.77400
H	-0.69400	-0.63300	0.51200
H	3.39500	2.38500	-0.27800

2^+

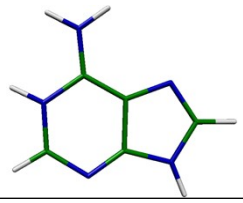
C_8 out-of-plane:CI_{23}



N	3.55500	-0.61000	0.17900
N	3.06100	1.70300	0.21200
C	3.89500	0.64500	0.23400
C	1.72000	1.45000	0.08500
C	1.28300	0.07100	0.28500
C	2.24100	-0.96500	0.16700
N	-0.11300	0.17100	0.56800
N	0.73100	2.18900	-0.26800
N	1.97500	-2.25100	0.13800
C	-0.17000	1.09000	-0.52800
H	4.94900	0.87700	0.29100
H	-0.29900	0.77600	-1.56100
H	2.74000	-2.89800	0.13000
H	1.04500	-2.61200	0.15500
H	-0.64000	-0.67200	0.40500
H	3.42000	2.63900	0.15000

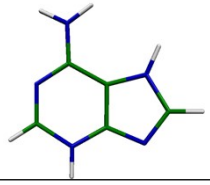
The xyz coordinates of the first excited state (S1) optimized geometry of $\mathbf{1}^+$ and $\mathbf{2}^+$ at the ADC(2)/aug-cc-pVDZ level of theory and in the Cs symmetry point group.

$\mathbf{1}^+$



N	1.79286	0.56053	0.00000
N	-0.23170	2.01432	0.00000
C	1.17203	1.82014	0.00000
C	-0.90025	0.91526	0.00000
C	-0.35516	-0.47748	0.00000
C	1.02611	-0.62618	0.00000
N	-1.35944	-1.41010	0.00000
N	-2.28880	0.69086	0.00000
N	1.67498	-1.80313	0.00000
C	-2.48691	-0.66600	0.00000
H	1.82491	2.69256	0.00000
H	-3.48736	-1.09933	0.00000
H	-3.01001	1.40897	0.00000
H	2.69033	-1.86972	0.00000
H	1.12888	-2.66490	0.00000
H	2.80952	0.51419	0.00000

$\mathbf{2}^+$



N	1.95223	0.58264	0.00000
N	-0.05477	2.00040	0.00000
C	1.39599	1.80698	0.00000
C	-0.85086	0.91289	0.00000
C	-0.27132	-0.39926	0.00000
C	1.21208	-0.51683	0.00000
N	-1.33892	-1.22982	0.00000
N	-2.22011	0.86667	0.00000
N	1.82256	-1.73724	0.00000
C	-2.50978	-0.43011	0.00000
H	2.00469	2.70922	0.00000
H	-3.50273	-0.87539	0.00000
H	2.84291	-1.76291	0.00000
H	1.31235	-2.61492	0.00000
H	-1.33699	-2.24927	0.00000
H	-0.45733	2.93695	0.00000

Table S3. *Vertical transition energies, oscillator strength, S_1-S_0 adiabatic and the S_2-S_0 adiabatic transition energy for 9HA and 7HA, determined at the ADC (2)/aug-cc-pVDZ level of theory.*

9H-A			**7H-A**		
Excited state	Transition energy/eV	Oscillator strengths	Excited state	Transition energy/eV	Oscillator strengths
$S_1(n\pi^*_1)$	4.98	0.014	$S_1(n\pi^*_1)$	4.75	0.014
S_1-S_0 adiabatic transition energy	**4.30**			**4.09**	
$S_2(\pi\pi^*_1)$	5.09	0.255	$S_2(\pi\pi^*_1)$	4.87	0.117
$S_3(\pi\pi^*_2)$	5.11	0.030	$S_3(\pi\pi^*_2)$	5.08	0.010
$S_4(\pi\pi^*_3)$	5.39	0.010	$S_4(n\pi^*_2)$	5.38	0.001
$S_5(n\pi^*_2)$	5.62	0.002	$S_5(\pi\pi^*_3)$	5.50	0.054