Electronic Supplementary File

Theoretical insights on the excited state deactivation mechanisms of protonated Thymine and Cytosine

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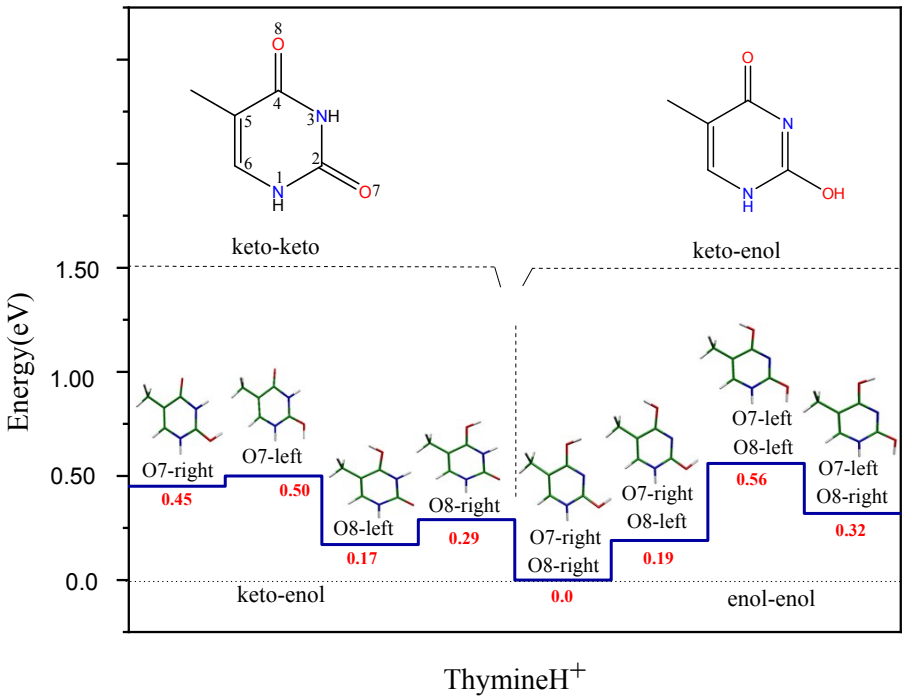


Figure S1. *Relative stability for selected protonated isomers of Thymine determined at the MP2/aug-cc-pVDZ level.*

Table S1: *The xyz coordinates of the ground state optimized geometry of the most stable isomer of* TH^+. *The energetic values (in eV) represent the relative stabilities at the MP2/aug-cc-pVDZ level of theory*.

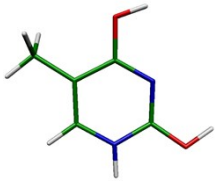
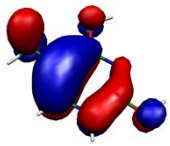
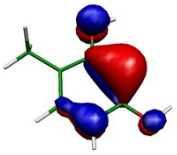
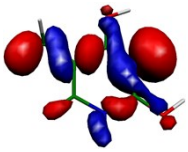
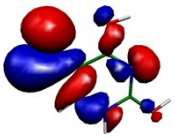
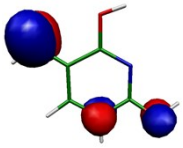
TH^+- minima S_0 (0.0 eV)			
			
C	-6.38400	3.33200	0.01500
C	-5.11100	2.67900	0.00500
C	-5.16800	1.29900	0.00100
C	-7.53600	1.36600	0.01600
C	-3.82700	3.46200	0.00000
N	-6.38400	0.65900	0.00600
N	-7.56500	2.69200	0.02000
O	-8.63900	0.63000	0.02000
O	-6.37900	4.65700	0.01900
H	-6.44200	-0.36000	0.00400
H	-2.96100	2.78800	-0.00600
H	-3.77600	4.10700	0.89000
H	-3.78500	4.11100	-0.88800
H	-4.28400	0.65900	-0.00600
H	-7.30000	4.98400	0.02500
H	-9.41600	1.22100	0.02700

Table S2: *Schemes of valence molecular orbitals of TH^+ 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.*

***TH*$^+$**	*HOMO (π)*	*HOMO-1 (π)*	*HOMO-2 (n)*	*HOMO-3 (n)*	*HOMO-4 (π)*
					
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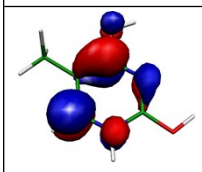
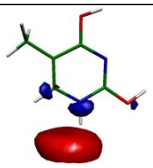
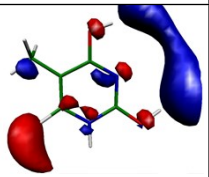
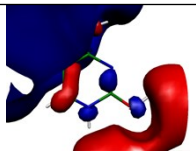
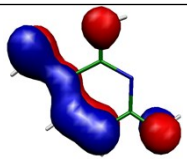
					

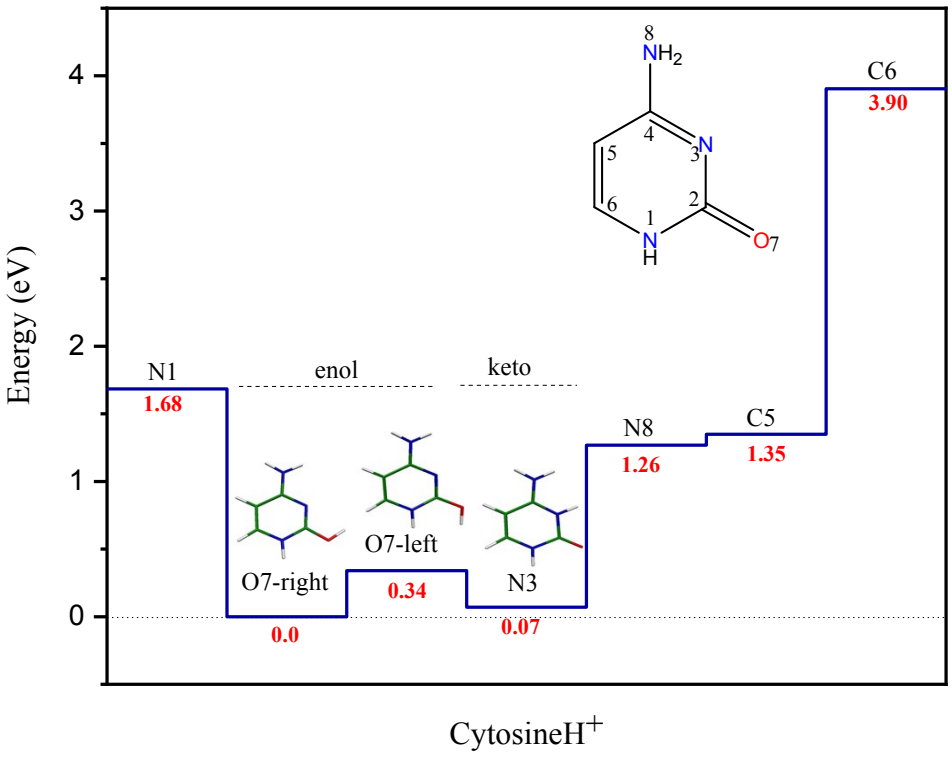
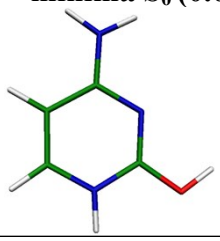


Figure S2. *Relative stability for selected protonated isomers of Cytosine determined at the MP2/aug-cc-pVDZ level*

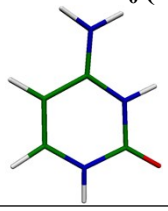
Table S3: *The xyz coordinates of the ground state optimized geometry of the most stable isomer of CH^+ (CHE^+) and the second most stable isomer of CH^+ (CHK^+). The energetic values (in eV) represent the relative stabilities at the MP2/aug-cc-pVDZ level of theory.*

CHE^+- minima S_0 (0.0 eV)



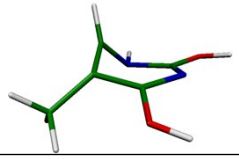
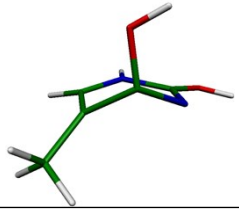
C	-1.27700	-0.82800	0.00300
N	-1.34400	0.53100	0.00900
C	-0.01800	-1.51900	-0.00300
C	1.12200	-0.75600	-0.00100
C	-0.20800	1.19900	0.01000
N	1.01800	0.61300	0.00500
N	-2.44200	-1.48200	0.00200
O	-0.16800	2.52600	0.01600
H	0.04400	-2.60800	-0.00800
H	2.13000	-1.17100	-0.00500
H	1.84500	1.21000	0.00700
H	-3.30800	-0.95300	0.00600
H	-2.48400	-2.49500	-0.00300
H	-1.08300	2.86500	0.02000

CHK^+- minima S_0 (0.07 eV)

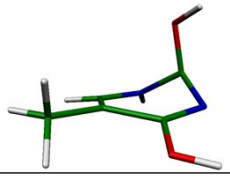


C	-1.29800	-0.85900	0.00200
N	-1.30000	0.50000	0.00800
C	-0.03800	-1.52600	-0.00300
C	1.09800	-0.75100	-0.00100
C	-0.15700	1.33800	0.01000
N	1.03500	0.61000	0.00500
N	-2.46100	-1.51500	0.00100
O	-0.23700	2.54800	0.01500
H	0.02300	-2.61300	-0.00700
H	2.09800	-1.18800	-0.00400
H	1.88500	1.17300	0.00600
H	-3.35600	-1.03700	0.00400
H	-2.47100	-2.52900	-0.00300
H	-2.17700	1.02400	0.01100

Table S4: *The xyz coordinates of the CASSCF (8,8)/cc-pVDZ optimized geometry of the S_1/S_0 conical intersections (CI_{1-3}) resulting from out-of-plane deformation of TH^+.*

TH^+- C_6 out-of-plane: CI_1			
			
C	-6.44700	3.53000	0.34300
C	-5.23700	2.89300	0.61400
C	-5.44400	1.48200	0.95300
C	-7.36700	1.49200	-0.06400
C	-3.96300	3.28900	-0.11000
N	-6.07500	0.86500	-0.07800
N	-7.58000	2.74400	0.16600
O	-8.30800	0.63100	-0.24300
O	-6.51600	4.78900	0.02200
H	-6.14600	-0.14100	-0.07900
H	-3.62300	2.48000	-0.75800
H	-3.17900	3.48700	0.62100
H	-4.12600	4.18300	-0.70700
H	-5.39400	1.04000	1.94500
H	-7.35100	5.00300	-0.38200
H	-9.17100	1.03500	-0.16700
TH^+- C_4 out-of-plane: CI_2			
			
C	-6.34000	3.27900	0.78000
C	-5.05500	2.69600	0.37300
C	-5.14000	1.28000	0.47600
C	-7.47600	1.57700	-0.01000
C	-3.92800	3.42700	-0.27300
N	-6.35300	0.77700	0.39100
N	-7.43900	2.86400	-0.03300
O	-8.43200	0.79800	-0.45200
O	-6.49900	3.09700	2.10200
H	-6.48400	-0.22300	0.34500
H	-3.18100	2.75100	-0.68500
H	-3.44900	4.07500	0.46500
H	-4.31400	4.07100	-1.06700
H	-4.30900	0.58900	0.41600
H	-7.37500	3.33700	2.38400
H	-9.17300	1.31200	-0.76000

TH^{+}- C_2 out-of-plane: CI_3



C	-6.50400	3.29900	-0.02700
C	-5.17400	2.63600	0.14100
C	-5.17800	1.22300	-0.01800
C	-7.36700	1.40500	0.62200
C	-3.91900	3.43900	0.25100
N	-6.36500	0.66300	-0.07700
N	-7.64200	2.65600	0.03500
O	-7.19200	1.33500	1.93300
O	-6.43200	4.56600	-0.35500
H	-6.56300	-0.19300	-0.56800
H	-3.04000	2.79700	0.25700
H	-3.93300	4.02300	1.17300
H	-3.84800	4.14300	-0.57800
H	-4.27700	0.64500	-0.17800
H	-7.30200	4.92500	-0.50800
H	-7.65100	2.03900	2.38000

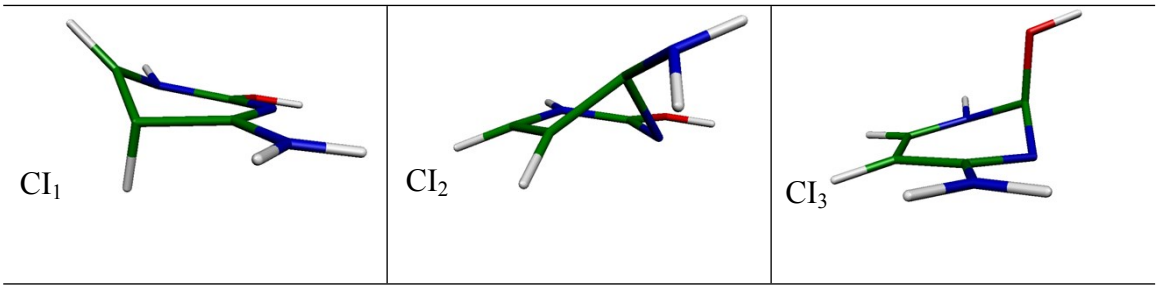
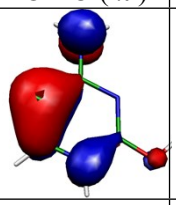
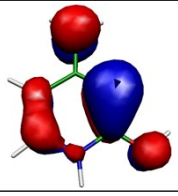
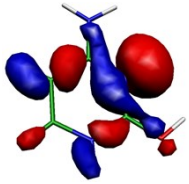
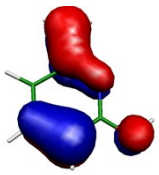
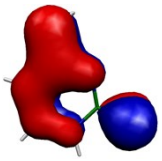
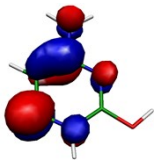
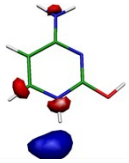
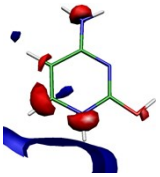
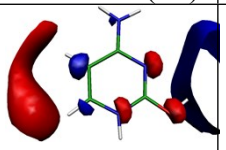
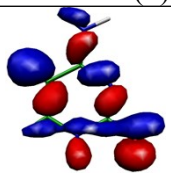


Figure S3. *Optimized geometries of the conical intersections located for* CHE^+ *determined at CASSCF (8,8)/cc-pVDZ level.*

Table S5: *Schemes of valence molecular orbitals of CHE^+ and CHK^+ 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.*

CHE^+	HOMO (π)	HOMO-1 (π)	HOMO-2 (n)	HOMO-3 (π)	HOMO-4 (π)
					
	LUMO (π*)	LUMO+1 (σ*)	LUMO+2 (σ*)	LUMO+3 (σ*)	HOMO-5 (n)
					

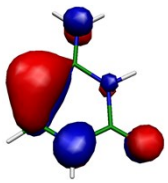
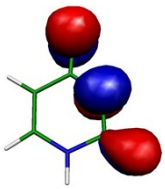
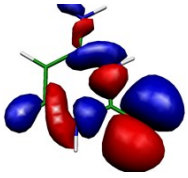
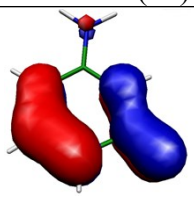
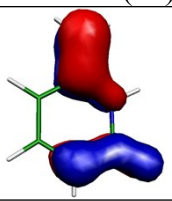
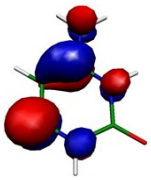
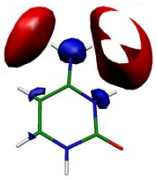
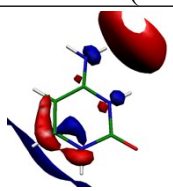
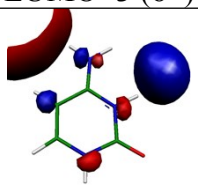
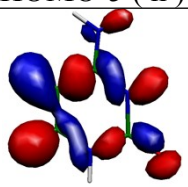
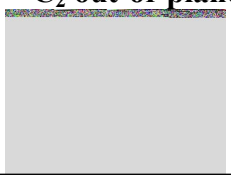
CHK^+	HOMO (π)	HOMO-1 (π)	HOMO-2 (n)	HOMO-3 (π)	HOMO-4 (π)
					
	LUMO (π*)	LUMO+1 (σ*)	LUMO+2 (σ*)	LUMO+3 (σ*)	HOMO-5 (n)
					

Table S6: *The xyz coordinates of the CASSCF (8,8)/cc-pVDZ optimized geometry of the S_1/S_0 conical intersections (CI_{1-3}) and ($CI_{1,2}$) resulting from out-of-plane deformation of CHE^+ and CHK^+ respectively.*

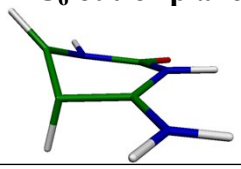
CHE^+- C_6 out-of-plane: CI_1			
C	-1.08000	-0.78400	0.76600
N	-1.14300	0.57900	0.53100
C	0.21900	-1.45000	0.73100
C	1.09900	-0.80100	-0.22500
C	-0.03600	1.16500	0.25400
N	1.17000	0.52600	-0.07500
N	-2.17300	-1.34800	1.15600
O	0.07500	2.45300	0.13600
H	0.62200	-1.20600	1.72800
H	1.66400	-1.27100	-1.02100
H	1.85300	1.10000	-0.54500
H	-3.00200	-0.80100	1.31200
H	-2.18800	-2.33600	1.33600
H	-0.75400	2.88500	0.32400
CHE^+- C_4 out-of-plane: CI_2			
C	-1.19100	-0.97200	-0.36300
N	-1.05500	0.21200	0.56000
C	0.02000	-1.40400	0.30900
C	1.24700	-0.75500	0.00000
C	-0.10800	1.06000	0.08100
N	1.06200	0.58500	-0.30100
N	-2.33300	-1.72100	-0.40700
O	-0.30300	2.33000	0.01700
H	0.00200	-2.20300	1.04100
H	2.23800	-1.11500	0.22000
H	1.79300	1.19800	-0.62000
H	-2.51600	-2.30100	0.39400
H	-3.15100	-1.21200	-0.68300
H	-1.17800	2.57400	0.31200

CHE$^+$- C_2 out-of-plane:CI_3



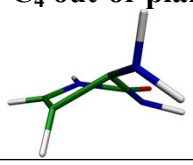
C	-1.27200	-0.88000	-0.04900
N	-1.25300	0.47400	-0.35300
C	-0.00900	-1.52600	-0.03900
C	1.09700	-0.71700	-0.01900
C	-0.21800	1.23000	0.32400
N	1.02700	0.63000	-0.01300
N	-2.42700	-1.45500	0.09400
O	-0.44900	1.36500	1.64200
H	0.07300	-2.59900	-0.08200
H	2.08800	-1.14700	-0.02800
H	1.85200	1.14900	0.21300
H	-3.27500	-0.92700	0.00800
H	-2.49500	-2.43900	0.26900
H	-0.84400	2.20700	1.83900

CHK$^+$- C_6 out-of-plane: CI_1



C	-1.27700	-1.03300	0.16900
N	-1.34000	0.30200	0.14800
C	0.07800	-1.57000	0.23500
C	1.02100	-0.64100	0.85300
C	-0.20700	1.13900	-0.08600
N	1.02100	0.57000	0.22700
N	-2.34200	-1.77200	0.03700
O	-0.36000	2.26500	-0.47100
H	0.37600	-1.90500	-0.76100
H	1.61100	-0.80600	1.74200
H	1.77800	1.22900	0.30500
H	-3.24900	-1.38700	-0.14900
H	-2.26600	-2.76700	0.13000
H	-2.21500	0.78300	0.03400

CHK^{+}- C_4 out-of-plane: CI_2



C	-1.20400	-0.96700	-0.19100
N	-1.12100	0.17700	0.65100
C	0.17600	-1.60700	0.18800
C	1.26900	-0.74800	-0.11100
C	-0.17900	1.11200	0.29800
N	1.01600	0.51700	-0.25900
N	-2.35600	-1.72300	-0.17600
O	-0.20900	2.29700	0.47200
H	0.25000	-2.21800	1.08200
H	2.28400	-1.10100	-0.25800
H	1.73600	1.17300	-0.51400
H	-2.98500	-1.57900	0.59200
H	-2.84000	-1.76900	-1.05300
H	-1.92200	0.53600	1.14100

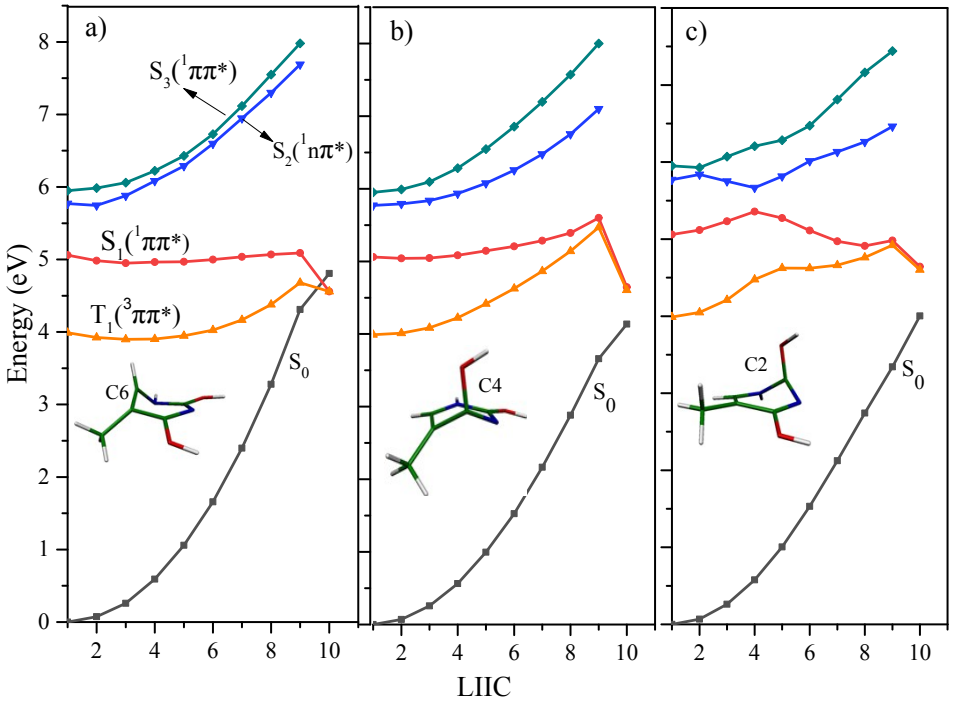


Figure S4. *Potential energy curves along the LIIC reaction paths connecting the $^1\pi\pi^*$ minima of TH^+. The curves were calculated at the ADC (2) /aug-cc-pVDZ level of theory for ground state, three singlet exsited state and the first triplet excited state. The insets, exhibit the CASSCF (8,8)/aug-cc-pVDZ optimized geometries of three different conical intersections ($CI_{1\text{-}3}$) arisen from out-of-plane deformation of TH^+.*

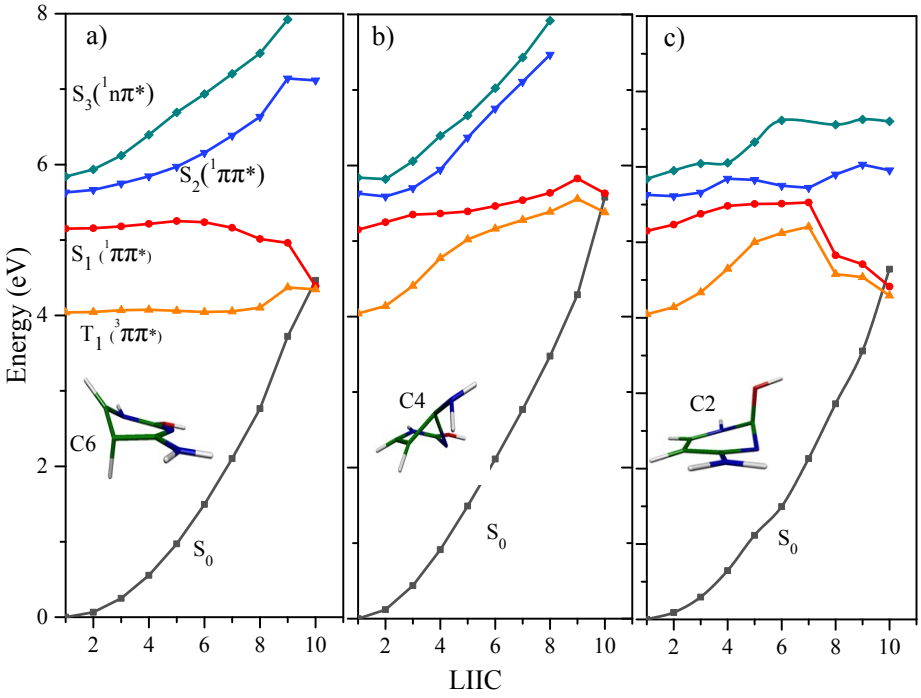


Figure S5. *Potential energy curves along the LIIC reaction paths connecting the $^1\pi\pi^*$ minima of CHE$^+$. The curves were calculated at the ADC (2) /aug-cc-pVDZ level of theory for ground state, three singlet excited state and the first triplet excited state. The insets, exhibit the CASSCF (8,8)/aug-cc-pVDZ optimized geometries of three different conical intersections (CI_{1-3}) arisen from out-of-plane deformation of CHE$^+$.*

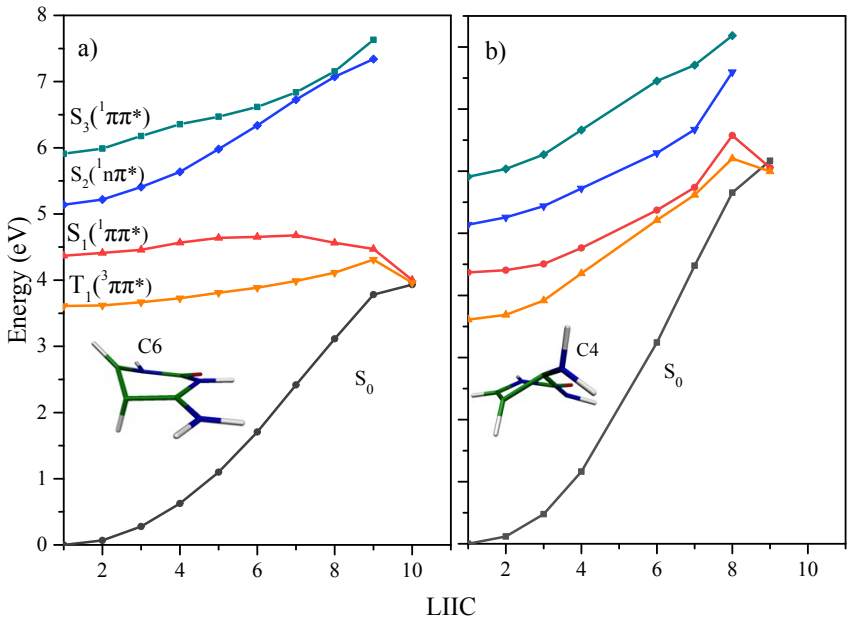


Figure S6. *Potential energy curves along the LIIC reaction paths connecting the $^1\pi\pi^*$ minima of CHK^+. The curves were calculated at the ADC (2) /aug-cc-pVDZ level of theory for ground state, three singlet exsited state and the first triplet excited state. The insets, exhibit the CASSCF (8,8)/aug-cc-pVDZ optimized geometries of three different conical intersections ($CI_{1,2}$) arisen from out-of-plane deformation of CHK^+.*