Supplementary Materials

Radiation induced one-electron oxidation of 2-thiouracil in aqueous solutions

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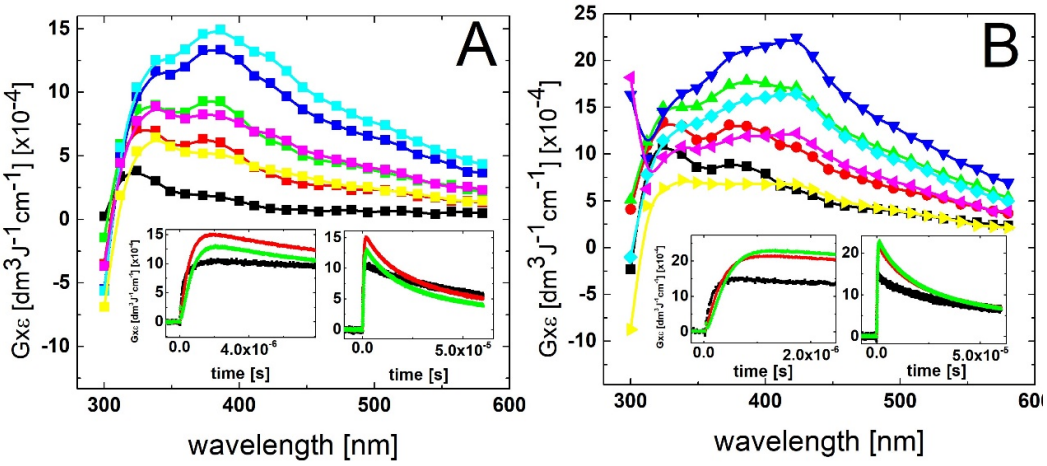

Figure S1. Transient absorption spectra recorded in N_2O-saturated unbuffered aqueous solution at pH = 4 containing (**A**) 0.2 mM of 2-TU 100 ns (■), 300 ns (■), 500 ns (■), 1 μs (■), 2 μs (■), 25 μs (■) and 60 μs (■) after electron pulse. Inserts: time profiles representing growth (left) and decay (right) of transient absorptions at λ = 338 nm (■), 386 nm (■) and 426 nm (■); (**B**) 0.5 mM of 2-TU 200 ns (■), 300 ns (■), 500 ns (■), 1 μs (■), 10 μs (■), 25 μs (■) and 60 μs (■) after electron pulse. Inserts: time profiles representing growth (left) and decay (right) of transient absorptions at λ = 338 nm (■), 386 nm (■) and 426 nm (■).

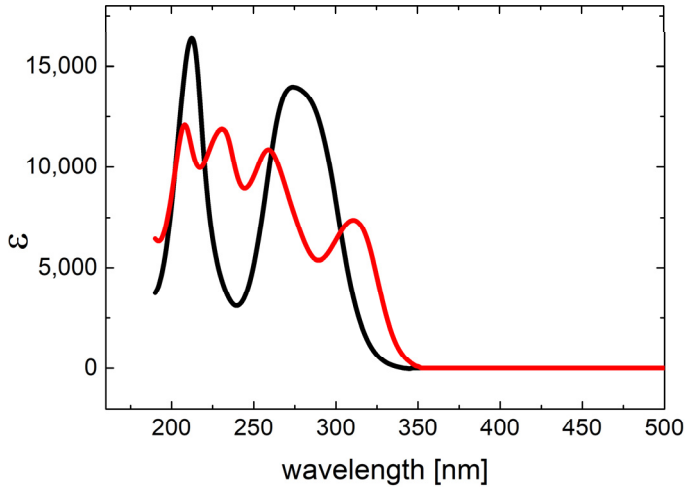

Figure S2. Absorption spectra recorded in aqueous solutions containing 2-thiouracil at pH = 4 (black line) and pH = 10 (red line).

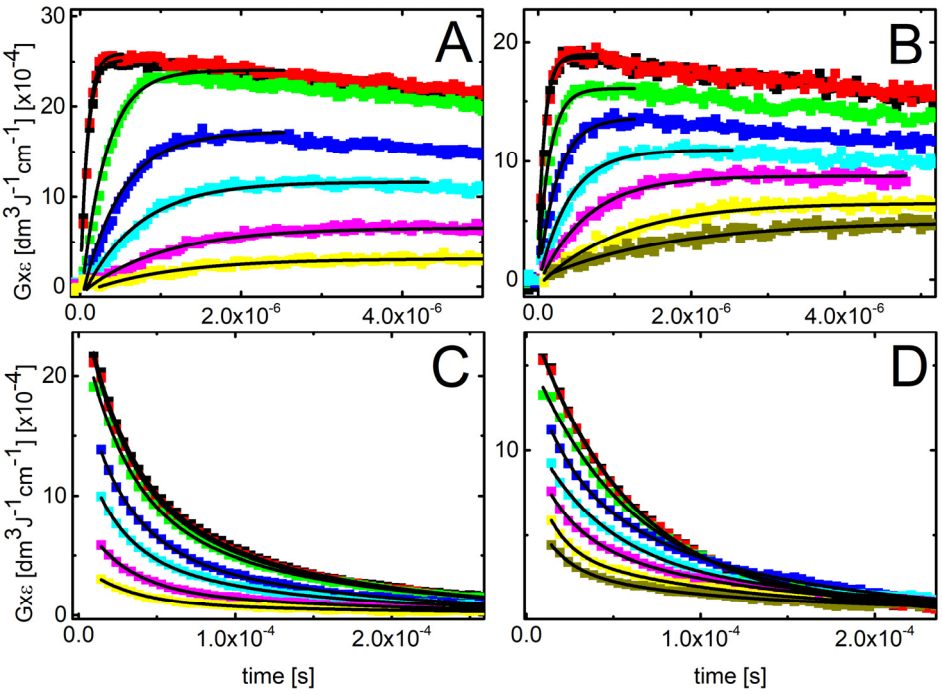

Figure S3. Time profiles representing growth (top panels) and decay (bottom panels) of transient absorptions at λ = 420 nm at pH = 4 (**A** and **C** panels) and at pH = 10 (**B** and **D** panels) at various concentration of 2-TU: A and C panels: 0, 047 mM (■), 0.094 mM (■), 0.188 mM (■), 0.375 mM (■), 0.75 mM (■), and 3 mM (■, ■); B and D panels: 0.047 mM (■), 0.094 mM (■), 0.188 mM (■), 0.375 mM (■), 0.75 mM (■), 1.5 mM (■), and 3 mM (■, ■). .

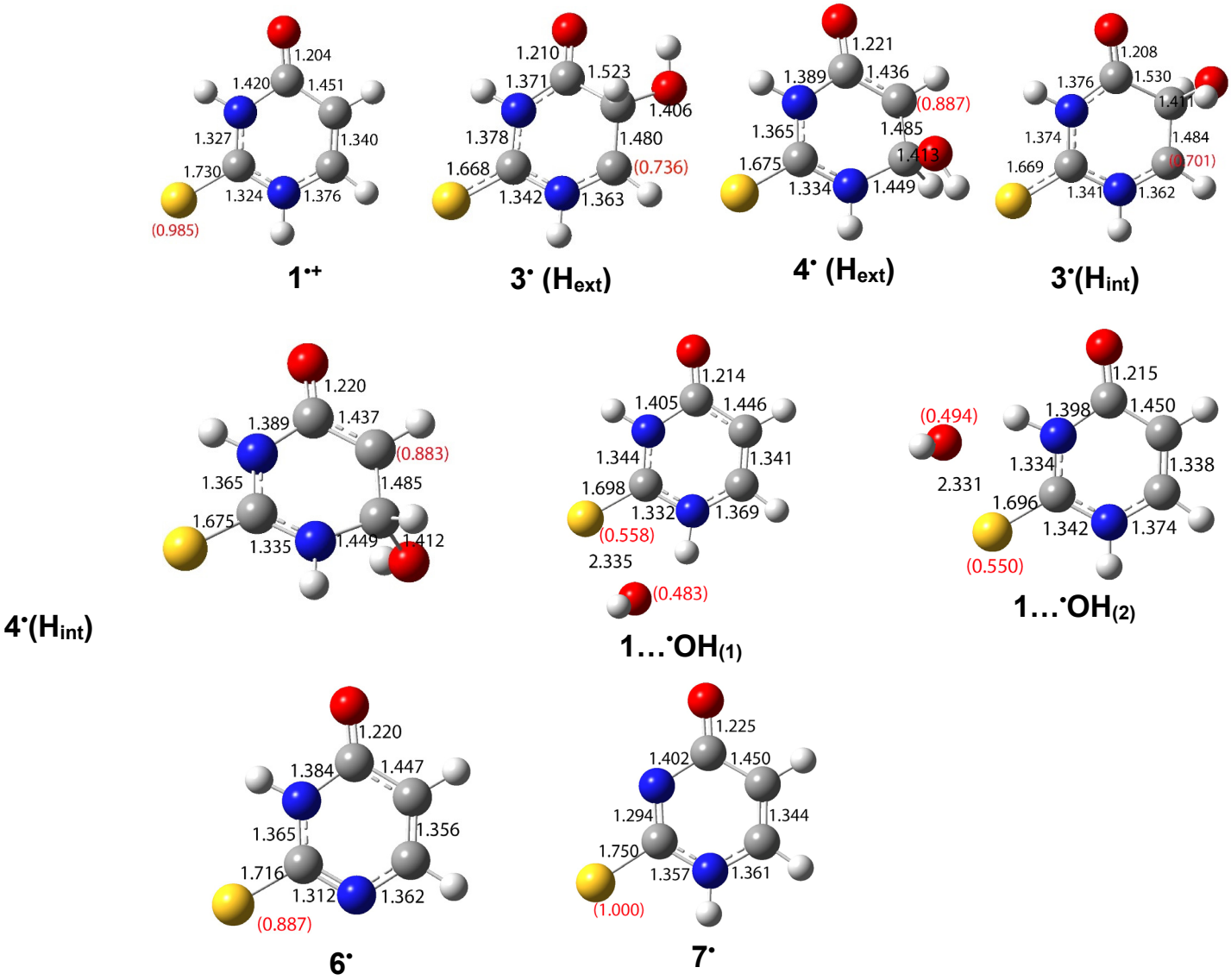

Figure S4. Solution phase (PCM) optimized geometries (ωB97x/aug-cc-pvtz) of monomer type transients expected to be formed in solutions at pH = 4 (lower than the first pK_a of 2-thiouracil). Selected bond lengths are in Å units. Maximum spin population is given in red color in parentheses.

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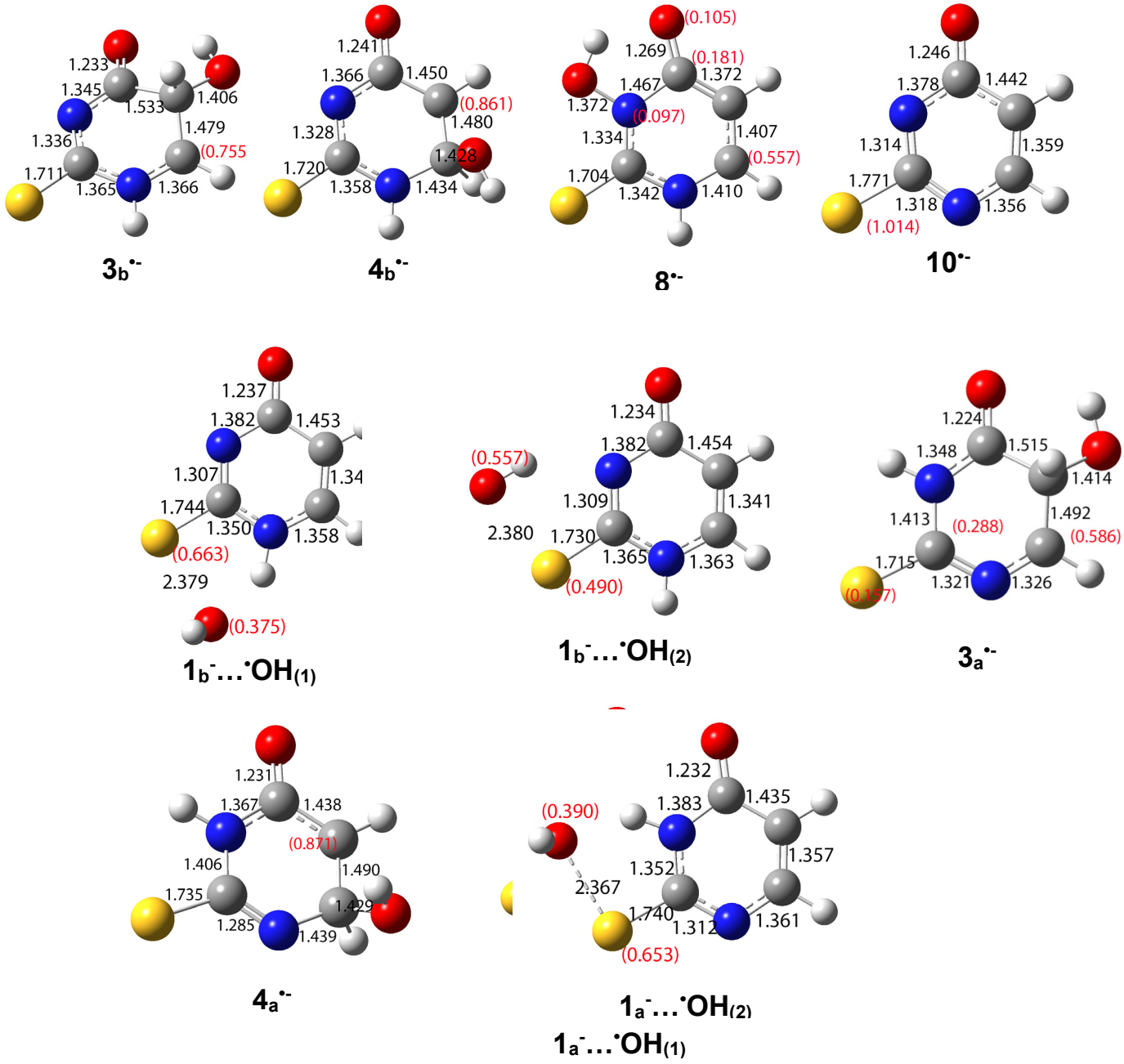


Figure S5. Solution phase (PCM) optimized geometries (ωB97x/aug-cc-pvtz) of monomer type transients expected to be formed in solutions at pH = 10 (higher than the first pK_a of 2-thiouracil). Selected bond lengths are in Å units. Maximum spin population is given in red color in parentheses.

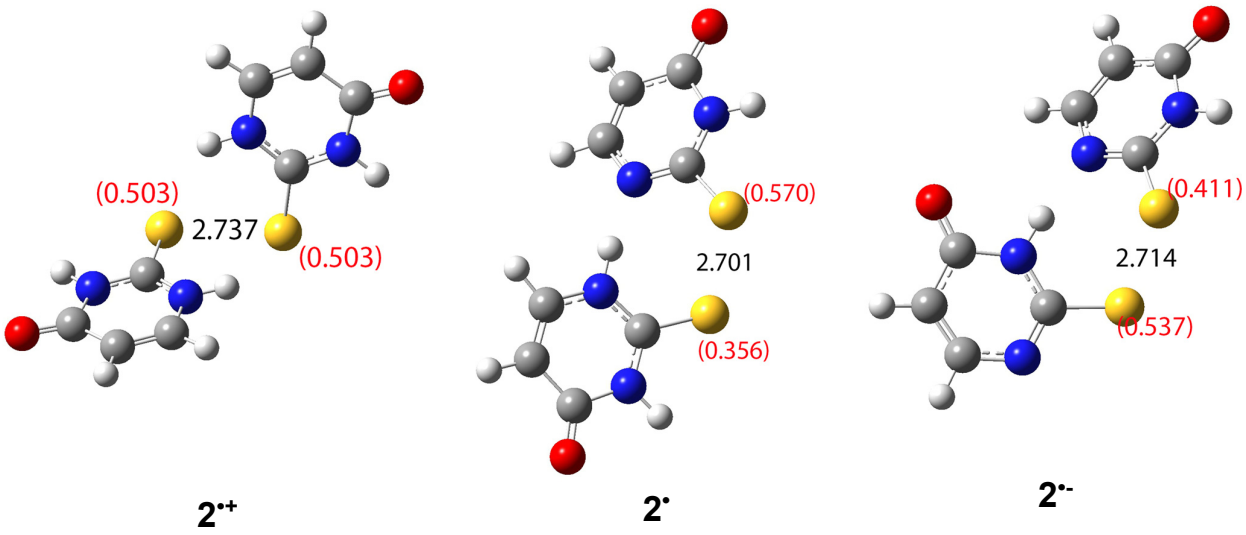
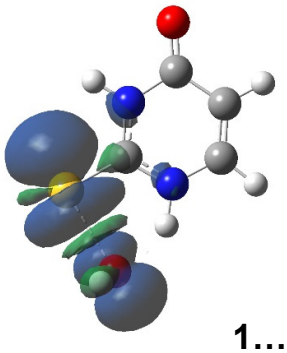
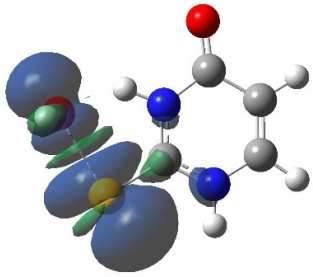


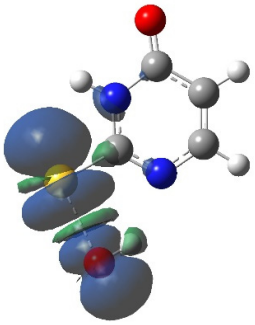
Figure S6. Solution phase (PCM) optimized geometries (ωB97x/aug-cc-pvtz) of 2c-3e SS dimers; SS bond lengths are in Å units. Maximum spin population is given in red color in parentheses.



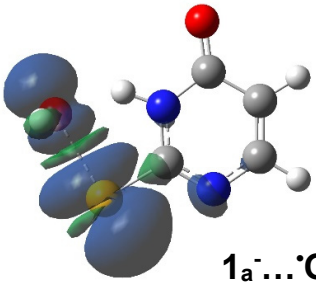
1…˙OH$_{(1)}$



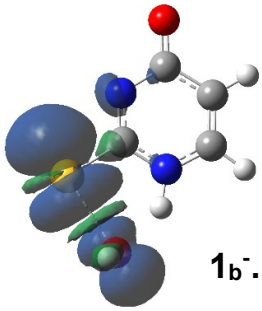
1…˙OH$_{(2)}$



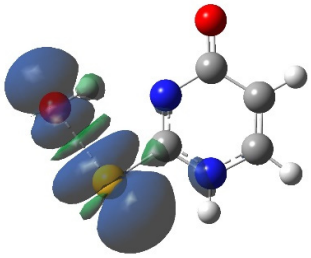
1$_a^-$…˙OH$_{(1)}$



1$_a^-$…˙OH$_{(2)}$



1$_b^-$…˙OH$_{(1)}$



1$_b^-$…˙OH$_{(2)}$

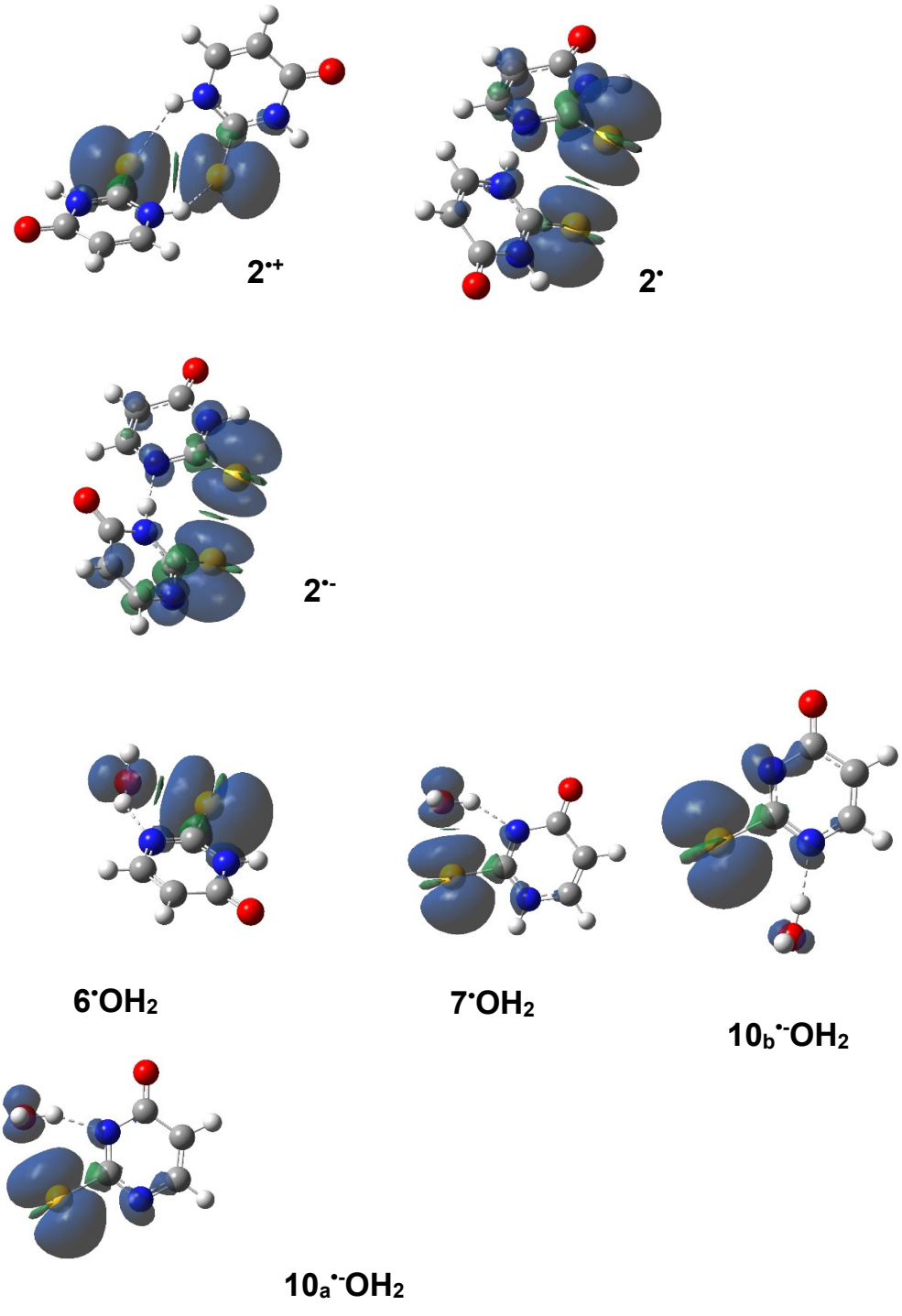


Figure S7. Computed SCF spin density = 0.001 bohr^{-3} isosurfaces of various 2c-3e intermediates produced in •OH induced oxidation of 2-TU at pH = 4 and 10.

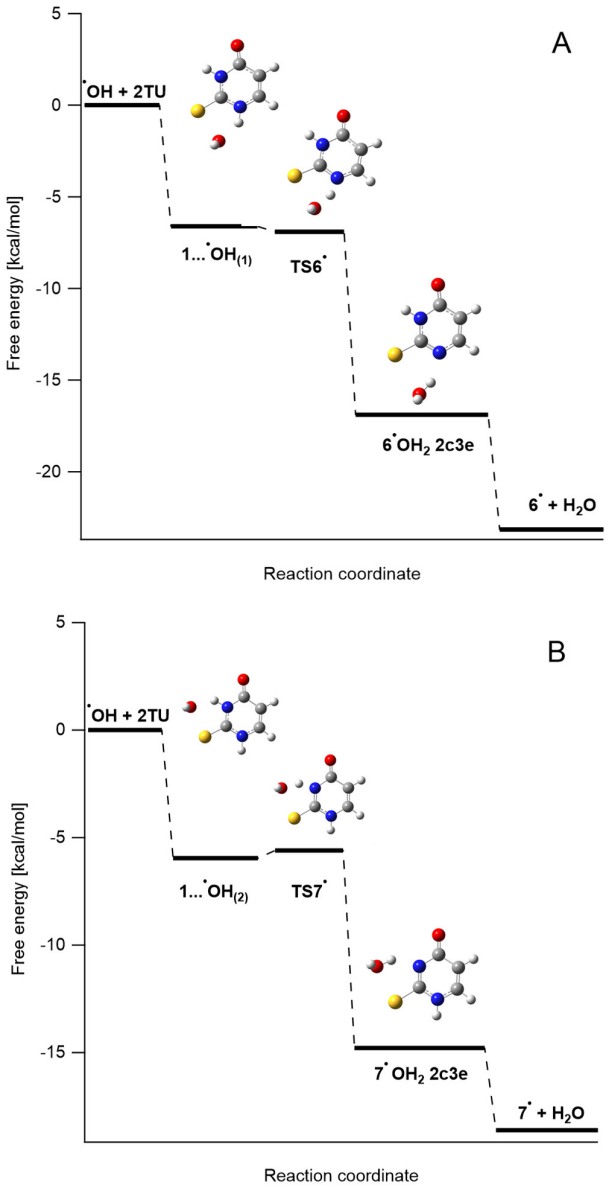


Figure S8. Relative energy profiles in aqueous phase (PCM) for the H abstraction from neutral 2-TU at N1 (**A**) and N3(**B**) positions via 2c-3e OH adducts at ωB97x/aug-cc-pvtz level of theory.

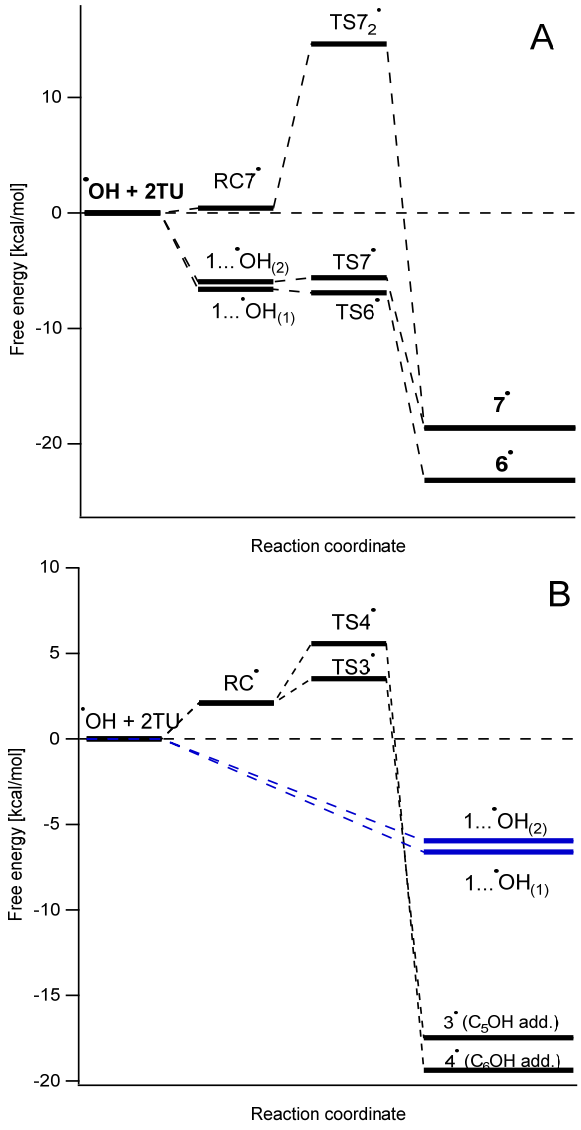


Figure S9. Relative energy profiles in aqueous phase (PCM) for H abstraction (A) and •OH addition (**B**) reactions from/to neutral 2-TU at ωB97x/aug-cc-pvtz level of theory.

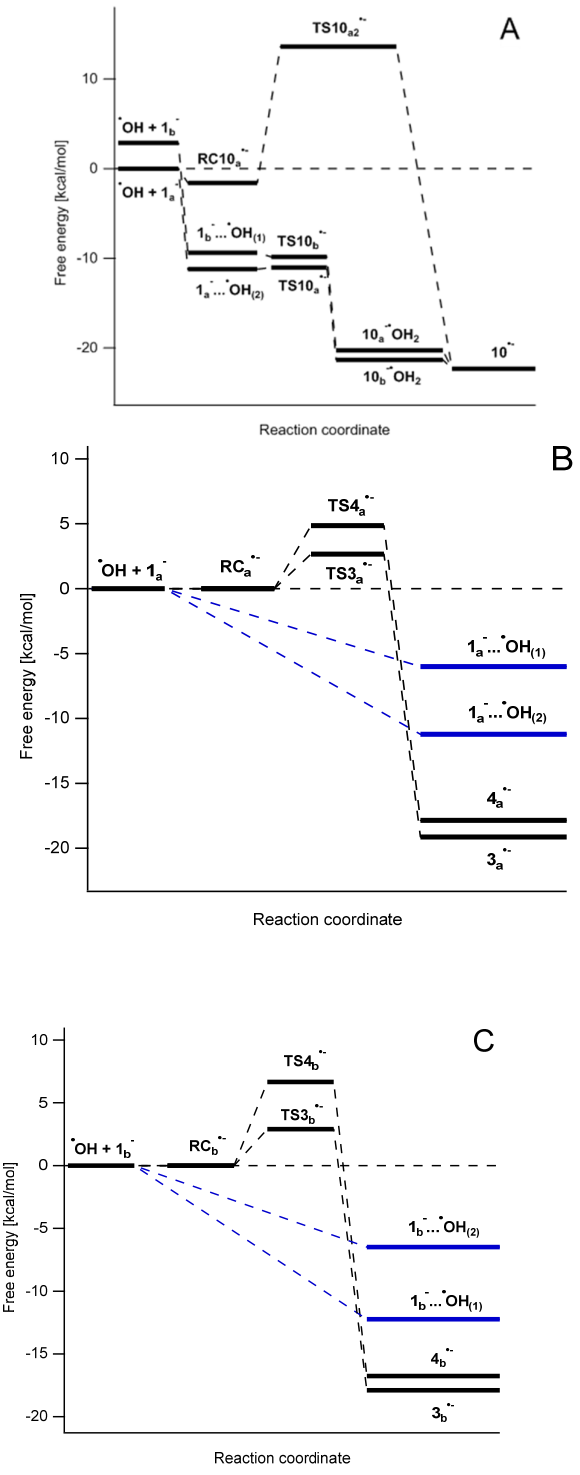


Figure S10. Relative energy profiles in aqueous phase (PCM) for H abstraction (A) and the •OH addition reactions (B and C) to/from 2-TU^{-} monoanions (subscripts a or b indicate the site of deprotonation of neutral 2-TU as N1 or N3, respectively) at ωB97x/aug-cc-pvtz level of theory.

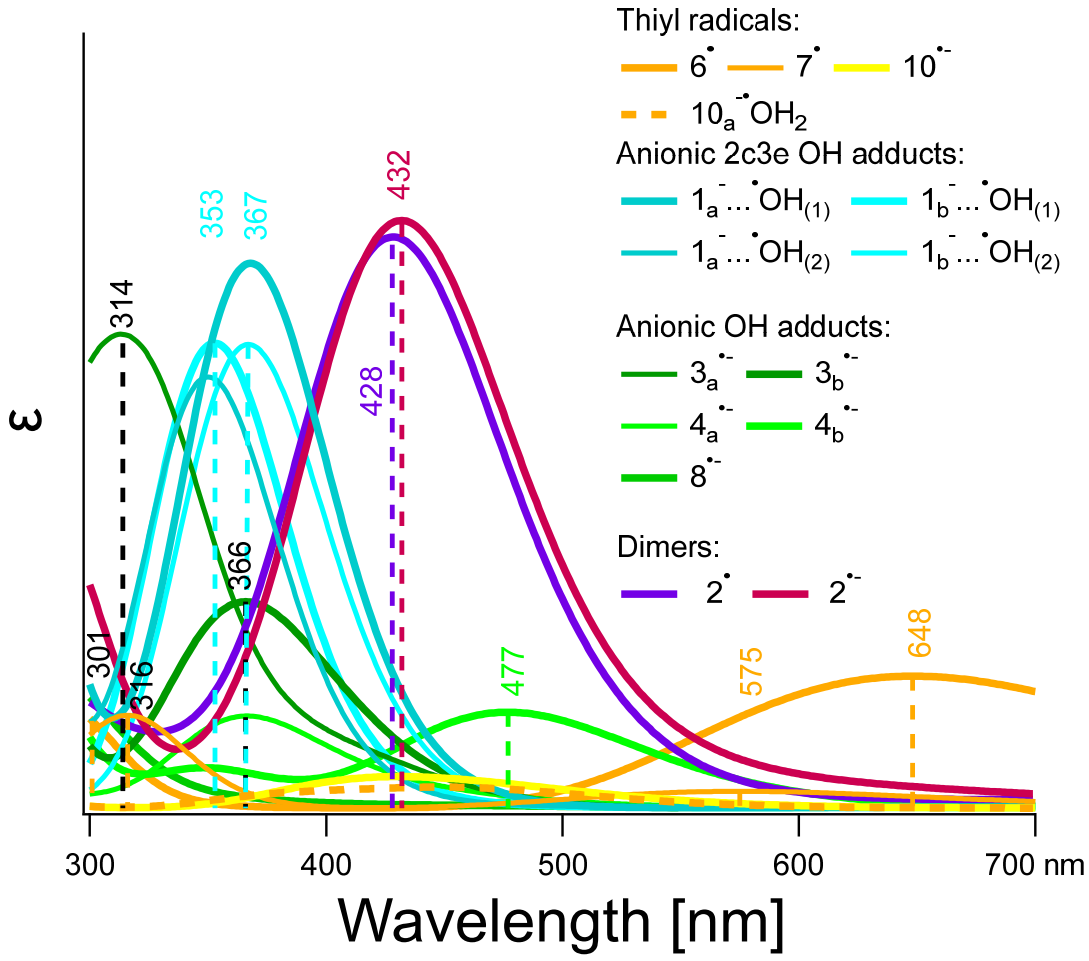


Figure S11. TD-DFT calculated absorption spectra of potential transients (see legend for symbols and Figures S4 and S5 for geometries) produced in •OH–induced oxidation of 2-thiouracil (2-TU) in water at pH = 10 (higher than its first pKa = 7.75).

Table S1. Thermochemistry values for the reactants, products, prereactive complexes, and transition states optimized structures (tight convergence with ultrafine grid) at the ωB97x/aug-cc-pvtz level of theory with water solvation modeled by IEFPCM. ε_0 - electronic energy, ε_{ZPE} - zero-point energy correction, E_{tot} - thermal correction to energy, H_{corr} – themal correction to enthalpy, G_{corr} - thermal correction to free energy.

Molecule	ε_0	ε_{ZPE}	E_{tot}	H_{corr}	G_{corr}	$\varepsilon_0 + \varepsilon_{ZPE}$	$\varepsilon_0 + E_{tot}$	$\varepsilon_0 + H_{corr}$	$\varepsilon_0 + G_{corr}$
				[Hartree]					
$^{\bullet}$OH	-75.744596	0.008589	0.010949	0.0119	-0.00833	-75.736007	-75.73365	-75.7327	-75.752927
H_2O	-76.448102	0.02147	0.024305	0.02525	0.00383	-76.426632	-76.423796	-76.422852	-76.444269
1	-737.8424036	0.086445	0.092753	0.093697	0.055325	-737.755958	-737.749651	-737.748707	-737.787078
1^-_a	-737.375525	0.072888	0.078988	0.079932	0.041939	-737.302637	-737.296537	-737.295593	-737.333586
1^-_b	-737.370885	0.07294	0.07912	0.080064	0.04185	-737.297945	-737.291765	-737.290821	-737.329035
$1^{\bullet+}$	-737.602067	0.085354	0.09143	0.092374	0.053749	-737.516713	-737.510637	-737.509693	-737.548319
$2^{\bullet+}$	-1475.476283	0.17454	0.188957	0.189902	0.12893	-1475.301743	-1475.28733	-1475.28638	-1475.347353
$2^{\bullet}$	-1475.0371	0.160706	0.174726	0.175671	0.11651	-1474.87639	-1474.8624	-1474.86143	-1474.920591
$2^{\bullet-}$	-1474.576029	0.147219	0.161258	0.162203	0.102184	-1474.42881	-1474.41477	-1474.41383	-1474.473845
$3^{\bullet}$ (H_{ext})	-813.633392	0.100136	0.108471	0.109415	0.065544	-813.533256	-813.524921	-813.523977	-813.567848
$3^{\bullet}$ (H_{int})	-813.63221	0.100552	0.108752	0.109696	0.06606	-813.531656	-813.52346	-813.522512	-813.56615
$4^{\bullet}$ (H_{ext})	-813.636492	0.100398	0.108639	0.109584	0.065835	-813.536093	-813.527852	-813.526908	-813.570657
$4^{\bullet}$ (H_{int})	-813.63739	0.100649	0.108713	0.109657	0.06652	-813.536743	-813.52868	-813.527735	-813.57087
1…$^{\bullet}$OH$_{(1)}$	-813.614772	0.098528	0.106944	0.107889	0.06424	-813.516243	-813.507827	-813.506883	-813.550531
1…$^{\bullet}$OH$_{(2)}$	-813.613767	0.09861	0.107086	0.108031	0.064273	-813.515156	-813.50668	-813.505736	-813.549494
1_a^-…$^{\bullet}$OH$_{(1)}$	-813.14618	0.085351	0.093841	0.094785	0.05012	-813.060823	-813.05233	-813.051389	-813.09606
1_a^-…$^{\bullet}$OH$_{(2)}$	-813.15511	0.084989	0.093315	0.094259	0.05074	-813.070125	-813.0618	-813.060854	-813.10437
1_b^-…$^{\bullet}$OH$_{(1)}$	-813.151981	0.084918	0.093285	0.094229	0.050529	-813.067063	-813.058696	-813.057752	-813.101452
1_b^-…$^{\bullet}$OH$_{(2)}$	-813.142041	0.085453	0.094006	0.09495	0.049729	-813.056588	-813.048035	-813.047091	-813.092312
$3_a^{\bullet-}$	-813.16927	0.086575	0.09457	0.095514	0.05229	-813.082696	-813.0747	-813.073757	-813.11698
$3_b^{\bullet-}$	-813.163469	0.086657	0.094506	0.09545	0.053	-813.076812	-813.068964	-813.068019	-813.110469
$4_a^{\bullet-}$	-813.16061	0.086611	0.09472	0.095664	0.05197	-813.074	-813.06589	-813.064948	-813.10865
$4_b^{\bullet-}$	-813.160776	0.086666	0.094799	0.095743	0.052095	-813.07411	-813.065977	-813.065032	-813.108681
$6^{\bullet}$	-737.1732	0.072322	0.078585	0.079529	0.040563	-737.100878	-737.094615	-737.093671	-737.132637
$7^{\bullet}$	-737.165978	0.071974	0.077841	0.078785	0.04059	-737.094004	-737.088137	-737.087193	-737.125387
$8^{\bullet-}$	-813.099416	0.084452	0.092111	0.093055	0.051217	-813.014964	-813.007306	-813.006362	-813.048199
$10^{\bullet-}$	-736.70548	0.05948	0.065641	0.066585	0.027672	-736.645999	-736.639838	-736.638894	-736.677807
RC$^{\bullet}$	-813.59673	0.096897	0.10647	0.107415	0.06005	-813.499828	-813.49026	-813.48931	-813.53667
TS3$^{\bullet}$	-813.59636	0.097169	0.105805	0.10675	0.06197	-813.499195	-813.49056	-813.489615	-813.5344
TS4$^{\bullet}$	-813.5944	0.09756	0.105799	0.106744	0.06326	-813.496841	-813.4886	-813.487657	-813.53114
RC7$^{\bullet}$	-813.60134	0.097785	0.106581	0.107525	0.062	-813.503555	-813.4948	-813.493814	-813.53934
TS3a$^{\bullet-}$	-813.13174	0.083868	0.091918	0.092863	0.04948	-813.047867	-813.03982	-813.038872	-813.08226
TS4a$^{\bullet-}$	-813.12891	0.08412	0.092098	0.093042	0.05015	-813.044791	-813.03681	-813.035869	-813.07876
TS3b$^{\bullet-}$	-813.1266	0.083889	0.09212	0.0931	0.0492	-813.0427	-813.034	-813.033489	-813.0773
TS4b$^{\bullet-}$	-813.12573	0.084081	0.092196	0.09314	0.04983	-813.04165	-813.03354	-813.032592	-813.07591
TS6$^{\bullet}$	-813.61188	0.094589	0.102506	0.10345	0.06086	-813.517286	-813.50937	-813.508426	-813.55102
TS7$^{\bullet}$	-813.6098	0.09465	0.102607	0.10355	0.06086	-813.515152	-813.5072	-813.506249	-813.548938
$TS7_2^{\bullet}$	-813.57713	0.094145	0.101977	0.102921	0.06042	-813.482985	-813.47515	-813.474209	-813.51671
$TS10a_2^{\bullet-}$	-813.11129	0.080194	0.087976	0.08892	0.04647	-813.031091	-813.02331	-813.022365	-813.06482
TS10b$^{\bullet-}$	-813.14897	0.08067	0.08864	0.089584	0.04676	-813.068297	-813.06033	-813.059383	-813.10221
$6^{\bullet}OH_2$	-813.628421	0.097692	0.107007	0.107951	0.06149	-813.530729	-813.52141	-813.52047	-813.566927

Table S2. Determination of free energies of reactions* of ˙OH addition (or H abstraction) to (from) 2TU at pH = 4 and 10.

Reaction	Σ(ε_0 + G_{corr}) [Hartree]		$\Delta_r G^0$(298K) [kcal/mol]
	Reactants	Products	
˙OH + 1 → 1…˙OH(1)	-813.540005	-813.5505	-6.60
˙OH + 1 → 1…˙OH(2)	-813.540005	-813.5495	-5.95
˙OH + 1 → 6˙ + H_2O	-813.540005	-813.57691	-23.16
˙OH + 1 → 6˙OH_2	-813.540005	-813.566927	-16.89
˙OH + 1 → 7˙ + H_2O	-813.540005	-813.56966	-18.61
˙OH + 1 → 7˙OH_2	-813.540005	-813.563564	-14.78
˙OH + 1 →TS6˙	-813.540005	-813.55102	-6.91
˙OH + 1 →TS7˙	-813.540005	-813.548938	-5.61
˙OH + 1 →$TS7_2$˙	-813.540005	-813.51671	14.62
˙OH + 1 →RC7˙	-813.540005	-813.53934	0.42
˙OH + 1 → 3˙ (H_{int})	-813.540005	-813.566148	-16.40
˙OH + 1 → 4˙ (H_{ext})	-813.540005	-813.570657	-19.23
˙OH + 1 → 4˙ (H_{int})	-813.540005	-813.570871	-19.37
˙OH + 1 → RC˙	-813.540005	-813.536672	2.09
˙OH + 1 →TS3˙	-813.540005	-813.538077	3.52
˙OH + 1 →TS4˙	-813.540005	-813.534398	5.56
˙OH + 1^-_a → $1a^-$…˙OH(1)	-813.08651	-813.09606	-5.99
˙OH + 1^-_a → $1a^-$…˙OH(2)	-813.08651	-813.10437	-11.20
˙OH + 1^-_b → $1b^-$…˙OH(1)	-813.081962	-813.10145	-12.23
˙OH + 1^-_b → $1b^-$…˙OH(2)	-813.081962	-813.09231	-6.49
˙OH + 1^-_a → $10^{\bullet-}$ + H_2O	-813.08651	-813.12208	-22.32
˙OH + 1^-_b → $10^{\bullet-}$ + H_2O	-813.081962	-813.12208	-25.17
˙OH + 1^-_a → $TS10_{a2}^{\bullet-}$	-813.08651	-813.06482	13.61
˙OH + 1^-_b → $TS10_b^{\bullet-}$	-813.081962	-813.10221	-12.7
˙OH + 1^-_a → $3_a^{\bullet-}$	-813.08651	-813.117	-19.12
˙OH + 1^-_a → $4_a^{\bullet-}$	-813.08651	-813.1086	-13.89
˙OH + 1^-_b → $3_b^{\bullet-}$	-813.081962	-813.1105	-17.89
˙OH + 1^-_b → $4_b^{\bullet-}$	-813.081962	-813.1087	-16.77
˙OH + 1^-_a → $TS3_a^{\bullet-}$	-813.08651	-813.08226	2.69
˙OH + 1^-_a → $TS4_a^{\bullet-}$	-813.08651	-813.0788	4.86
˙OH + 1^-_b → $TS3_b^{\bullet-}$	-813.081962	-813.07732	2.91
˙OH + 1^-_b → $TS4_b^{\bullet-}$	-813.081962	-813.0759	6.65
1 + $1^{\bullet+}$ → $2^{\bullet+}$	-1475.3354	-1475.3474	-7.50
1 + 6˙ → 2˙	-1474.9197	-1474.9206	-0.55
$1a^-$ + 6˙→ $2^{\bullet-}$	-1474.4662	-1474.4758	-6.040

CARTESIAN COORDINATES OF THE STUDIED STRUCTURES

Table S3. Cartesian x, y, and z coordinates (in Å) of the optimized structures (tight with ultrafine grid) at the ωB97x/aug-cc-pvtz level of theory with water solvation modeled by IEFPCM.

1 (2TU)			
C	0.84182900	1.71442500	-0.00000100
C	1.84393200	0.82615200	-0.00001800
H	0.99907800	2.78268500	-0.00000300
H	2.87643400	1.13463100	-0.00004200
C	1.53526600	-0.58714300	-0.00000200
O	2.33715000	-1.50148300	0.00002500
C	-0.85482300	0.02165100	-0.00000100
S	-2.45886400	-0.44068600	0.00000000
N	0.16473200	-0.87015000	-0.00002200
H	-0.08957600	-1.84725300	-0.00003600
N	-0.46978500	1.31789900	0.00001900
H	-1.20316500	2.00802600	0.00003800

1^{-}_{a} ($2TU^{-}_{a}$, 2TU deprotonated at N_1)			
C	0.81492800	1.71389600	-0.00000100
C	1.83212400	0.81225500	-0.00000100
H	1.04515700	2.77458100	-0.00000200
H	2.86864800	1.11358000	0.00000000
C	1.50875100	-0.58103600	-0.00000400
O	2.29566900	-1.53015800	0.00000000
C	-0.83982300	0.13969300	0.00000700
S	-2.46687200	-0.41220700	-0.00000200
N	0.14355500	-0.81619700	0.00000200
H	-0.14925400	-1.78138200	0.00000200
N	-0.50867400	1.41919000	0.00000000

1^{-}_{b} ($2TU^{-}_{b}$, 2TU deprotonated at N_3)			
C	-0.81887700	1.70252700	-0.00000600
C	-1.81944400	0.80957600	-0.00000300
H	-0.96432800	2.77343900	-0.00002000
H	-2.85291300	1.12031300	-0.00001500
C	-1.49174500	-0.60722700	0.00000100
O	-2.37561300	-1.47528400	-0.00000800
C	0.78914300	-0.06045900	0.00003300
S	2.46673700	-0.45120300	-0.00001100
N	-0.16267100	-0.96934300	0.00001000
N	0.47247200	1.27341400	0.00000700
H	1.23128600	1.93276400	-0.00000200

$1^{\bullet+}$			
C	-0.83479500	1.72469500	-0.00000200
C	-1.83385000	0.83172500	-0.00000200
H	-0.98365900	2.79296400	-0.00000500
H	-2.86467200	1.14822300	-0.00000700
C	-1.55305200	-0.59139300	0.00000500
O	-2.34775900	-1.49533400	-0.00000100
C	0.80845300	0.02664500	0.00000100
S	2.47403700	-0.44273900	-0.00000100
N	-0.16244500	-0.87752200	0.00000100
H	0.09775500	-1.85658000	-0.00000400
N	0.47734400	1.30888900	0.00000300
H	1.22323700	1.99228600	0.00000700

3·			
C	-0.66820500	-1.55769500	-0.00479500
C	-1.61365700	-0.47754900	-0.36706300
H	-0.97118800	-2.58966000	0.04580900
C	-1.02833900	0.89784000	-0.07629400
O	-1.73819000	1.86769700	0.06096300
C	1.22773700	-0.07024600	0.00309300
S	2.87682500	0.17865600	0.04067400
N	0.33940700	0.98233300	-0.02715100
N	0.66800200	-1.28983600	0.02957500
H	1.31527600	-2.05927900	0.10783700
H	0.73913100	1.90635900	0.04297700
H	-1.80216700	-0.48797500	-1.45387800
O	-2.82340100	-0.66028900	0.32674400
H	-3.37460900	0.11122800	0.15820700

4·			
C	-1.10973100	-1.25475700	0.38818500
C	-1.08715800	1.27276700	0.01991700
O	-1.62548600	2.35956700	-0.11921200
C	1.01039800	0.00368500	0.06082600
S	2.68029700	0.02787100	-0.06814100
N	0.28161400	1.13328200	-0.17403100
N	0.32999200	-1.08905500	0.41387600
H	0.88752000	-1.90717700	0.59723100
H	0.79806300	1.96372700	-0.41872700
H	-1.39518000	-1.81179300	1.28251900
O	-1.53203100	-1.95484600	-0.76442700
H	-1.52083700	-2.89894400	-0.58521900
C	-1.78465300	0.06841700	0.37438200
H	-2.84857000	0.12022500	0.54478500

1... ·OH(1)			
C	0.79292200	1.74530400	-0.00847500
C	1.98598100	1.13341000	-0.00445300
H	0.67926200	2.81917400	-0.01222100
H	2.90930300	1.68949000	-0.00462400
C	2.04806700	-0.31175800	0.00108500
O	3.05133400	-0.99584800	0.00550600
C	-0.39734800	-0.29952400	-0.00416900
S	-1.86563800	-1.14992300	-0.00238700
N	0.78806100	-0.93371200	0.00059600
H	0.78767700	-1.94416900	0.00317200
N	-0.37544700	1.03205200	-0.00751500
H	-1.32995200	1.43752900	-0.00714900
O	-2.95945700	0.90958100	0.11220400
H	-3.39713000	0.79391800	-0.73817500

1... ·OH(2)			
C	-1.72564700	-1.52051300	0.00159700
C	-2.32906700	-0.32568600	-0.00053800
H	-2.26048200	-2.45833900	0.00386300
H	-3.40327500	-0.23655400	0.00050600
C	-1.52722500	0.88198800	-0.00375000
O	-1.94762900	2.02202000	-0.00620800
C	0.44258200	-0.54962000	-0.00252000
S	2.13251900	-0.69607100	-0.00165500
N	-0.14855900	0.64684500	-0.00339800
H	0.53824700	1.42181700	-0.00397000
N	-0.35569200	-1.62852100	0.00075000

H	0.07686900	-2.53824600	0.00092700
O	2.26995900	1.62820900	0.10840900
H	2.71560500	1.70135400	-0.74264900

6•			
C	-0.77346900	1.73326400	0.00000000
C	-1.79471300	0.84176300	0.00000000
H	-0.97191300	2.79733500	0.00000200
H	-2.82709300	1.15785400	0.00000200
C	-1.51507800	-0.57811800	-0.00000200
O	-2.33888700	-1.47862900	0.00000100
C	0.81921300	0.10310500	-0.00000100
S	2.45463800	-0.41581800	0.00000000
N	-0.15766100	-0.85044500	0.00000000
N	0.54384900	1.38604000	0.00000000
H	0.11685300	-1.82232300	0.00000000

7•			
C	0.81895500	1.70816400	0.00000000
C	1.81272500	0.80275300	-0.00000900
H	0.97609100	2.77638300	0.00000800
H	2.84594300	1.11395200	-0.00000900
C	1.50042800	-0.61316000	-0.00001600
O	2.35448300	-1.49113400	0.00002300
C	-0.75983000	-0.03651200	-0.00000500
S	-2.45782400	-0.46072200	0.00000300
N	0.14313500	-0.96403500	-0.00001800
N	-0.47645100	1.29080400	0.00000800
H	-1.23318300	1.95542800	0.00002900

2$^{•+}$			
C	-2.66412700	-0.50294100	1.79143000
C	-3.81961100	0.12863600	1.56208000
H	-2.38795300	-0.91401000	2.75053500
H	-4.55359000	0.26563000	2.33933100
C	-4.10428200	0.64332500	0.23969700
O	-5.09916100	1.23086600	-0.11696200
C	-1.91860700	-0.22760900	-0.44717500
S	-0.77901900	-0.42591700	-1.70660900
N	-3.07232200	0.40266900	-0.69382800
H	-3.23614800	0.74818900	-1.63011200
N	-1.72961100	-0.67416000	0.79344200
H	-0.86417500	-1.16133300	0.98905700
C	4.33961600	-0.12116700	0.87606200
C	4.16335500	1.17797600	0.61495300
H	5.22600300	-0.52309100	1.34276400
H	4.91402100	1.91115900	0.86091600
C	2.93847500	1.62185600	-0.01479400
O	2.63960500	2.75543600	-0.31185200
C	2.21906400	-0.71803600	-0.02119700
S	1.07477400	-1.93685700	-0.38306000
N	2.03053900	0.57509500	-0.28914400
H	1.16080300	0.83927900	-0.74001000
N	3.37516100	-1.05203400	0.55775800
H	3.53574100	-2.02509100	0.76880100

	2·		
C	-2.56874700	-0.50671300	1.78182700
C	-3.71565000	0.15375300	1.58620200
H	-2.27690500	-0.92318800	2.73418700
H	-4.42309300	0.31009600	2.38409000
C	-4.02361200	0.67334900	0.27139700
O	-5.01692100	1.28612300	-0.05481600
C	-1.87884400	-0.25243600	-0.48125900
S	-0.77599100	-0.48983500	-1.75128500
N	-3.02854700	0.40928400	-0.68851300
H	-3.20633900	0.75940700	-1.61987800
N	-1.67041000	-0.70258600	0.76001400
H	-0.80829800	-1.21361100	0.92066500
C	4.26753700	-0.09596000	0.95206900
C	4.09425200	1.20709300	0.63049400
H	5.16237500	-0.41354300	1.47414300
H	4.82699100	1.96017000	0.87739100
C	2.90116700	1.60524300	-0.06256500
O	2.59443800	2.73471400	-0.42551600
C	2.29613700	-0.74245400	0.04305500
S	1.12702500	-1.99092200	-0.33588900
N	2.04262900	0.53845900	-0.31720600
H	1.18219000	0.74737500	-0.80895400
N	3.38103700	-1.09551900	0.66691600

	2·-		
C	-2.20227800	1.72397900	0.53639800
C	-3.54064000	1.65275200	0.52861300
H	-1.66056000	2.59420500	0.87770600
H	-4.15542400	2.46987300	0.86951800
C	-4.18486700	0.44939800	0.05294100
O	-5.37885400	0.24008900	-0.01656700
C	-1.94036800	-0.45631600	-0.34158800
S	-0.97836000	-1.74717200	-0.88952600
N	-3.28282000	-0.54957300	-0.34901300
H	-3.69083700	-1.41715600	-0.66839100
N	-1.41771800	0.68727200	0.10060800
H	-0.37823200	0.78433900	0.07891900
C	2.20711500	1.74750500	-0.47966400
C	3.55319700	1.65351600	-0.54032300
H	1.70423500	2.65382400	-0.79390200
H	4.16759600	2.46528100	-0.89806300
C	4.19261300	0.43427800	-0.12481900
O	5.39122100	0.19101200	-0.11891800
C	1.93841400	-0.36476700	0.34631000
S	1.00068800	-1.69800400	0.95511100
N	3.28323800	-0.53669800	0.29224100
H	3.66994500	-1.42813500	0.56746900

1_a^-... $^{\cdot}OH_{(1)}$			
C	-0.81553000	1.74569500	-0.01739700
C	-2.01610100	1.11595100	-0.00288500
H	-0.77611300	2.82938400	-0.02647400
H	-2.94914100	1.65838900	0.00016300
C	-2.04472400	-0.31732700	0.00988700
O	-3.03784700	-1.04140500	0.02556000
C	0.39755300	-0.18476600	-0.01295600
S	1.85218300	-1.11354700	-0.02091600
N	-0.77654300	-0.88246400	0.00350800
H	-0.73242500	-1.89076100	0.01306100
N	0.39674500	1.12878500	-0.02262100
O	3.27610400	0.79624100	0.04875100
H	2.44808600	1.29949000	0.02731600

1_a^-... $^{\cdot}OH_{(2)}$			
C	1.67982900	-1.54899000	0.00357100
C	2.30834400	-0.34586200	0.00428000
H	2.26497000	-2.46227100	0.00534400
H	3.38490500	-0.26404700	0.00642900
C	1.51849800	0.85225200	0.00148100
O	1.93799000	2.01094300	0.00194500
C	-0.38952900	-0.63402500	-0.00067500
S	-2.12734100	-0.72321300	-0.00264200
N	0.15851800	0.60196000	-0.00214700
H	-0.54365600	1.36227600	-0.00250200
N	0.33138100	-1.73007800	0.00077200
O	-2.25383600	1.63803900	-0.09861700
H	-2.67414300	1.70016800	0.76405800

1_b^-... $^{\cdot}OH_{(1)}$			
C	0.78616100	-1.72708500	-0.00074300
C	1.97491500	-1.09959000	0.00297200
H	0.67413200	-2.80226900	-0.00151300
H	2.90240300	-1.65173100	0.00527300
C	2.00975200	0.35329000	0.00350400
O	3.07412700	0.98331800	0.00713300
C	-0.31439500	0.34577400	-0.00260300
S	-1.84892400	1.17448900	-0.00623900
N	0.80219800	1.02619200	-0.00012800
N	-0.36351300	-1.00369400	-0.00417800
H	-1.32832600	-1.38285800	-0.00298800
O	-2.96335400	-0.92579500	-0.09043900
H	-3.36101100	-0.80697900	0.77686300

1_b^-... $^{\cdot}OH_{(2)}$			
C	1.74016200	1.50047000	-0.00000200
C	2.33511400	0.29892100	-0.00001200
H	2.27404000	2.43985800	-0.00000400
H	3.40987900	0.20325700	-0.00002400
C	1.50836400	-0.89702600	-0.00000100
O	1.99712100	-2.03044600	0.00001100
C	-0.39695200	0.46463300	0.00000200
S	-2.10824300	0.71840500	0.00000000
N	0.13600800	-0.73129400	-0.00000400
N	0.37963800	1.58687000	0.00001000
O	-2.61643800	-1.60644200	-0.00000300
H	-1.65313900	-1.71814100	-0.00000600
H	-0.07400700	2.48463900	0.00001600

$3_a^{\bullet-}$ H_{ext}			
C	0.62541600	-1.55865500	-0.03139100
C	1.57240800	-0.48431200	0.38852600
H	1.02326700	-2.55604400	-0.17518000
C	0.99728900	0.88090000	0.06988600
O	1.72828900	1.84922100	-0.09550200
C	-1.21304100	-0.17736700	-0.01508600
S	-2.89460400	0.15755300	-0.01031300
N	-0.34873900	0.93980200	0.02039500
N	-0.68743600	-1.38614800	-0.10904800
H	-0.77221500	1.84743600	-0.09479200
H	1.71159600	-0.50562200	1.48329600
O	2.82972500	-0.64540300	-0.23754700
H	3.24770300	0.22387500	-0.23496000

$4_a^{\bullet-}$ H_{int}			
C	-1.13872800	-1.17671200	0.41042200
C	-0.98287000	1.34181100	0.00228800
O	-1.45732000	2.46737400	-0.15040000
C	0.97244500	-0.14567500	0.08496300
S	2.69919800	-0.11144100	-0.07787100
N	0.36585300	1.11808600	-0.02233500
N	0.29443400	-1.21847000	0.28807100
H	0.97103700	1.90609700	-0.18305000
H	-1.41454600	-1.54580600	1.40595700
O	-1.73812700	-2.12589800	-0.47343000
H	-1.43059000	-1.92413000	-1.36220000
C	-1.77152100	0.15794800	0.21459900
H	-2.84746900	0.25354500	0.24207700

$3_b^{\bullet-}$			
C	0.64745400	-1.51797100	-0.19489300
C	1.52153800	-0.49244200	0.41536400
H	0.95061000	-2.53956800	-0.35629400
C	0.97747300	0.88541300	0.02177700
O	1.80776100	1.76423700	-0.22233500
C	-1.18062500	0.03566500	-0.02985900
S	-2.88041000	0.20023400	0.07140000
N	-0.35264500	1.08406800	-0.00533100
N	-0.68682200	-1.22631800	-0.19520000
H	-1.36319000	-1.95503800	-0.35123600
H	1.46205600	-0.54990800	1.51717300
O	2.86392900	-0.62739700	0.01767600
H	3.14479400	0.27782100	-0.18537800

$4_b^{\bullet-}$			
C	1.05678400	-1.25476000	-0.40203800
C	1.05954600	1.26918800	-0.00274200
O	1.71431800	2.31403600	0.14069000
C	-0.96780000	0.12864500	-0.04646200
S	-2.68306400	0.08269200	0.07928500
N	-0.29381900	1.24980100	0.18066800
N	-0.35978000	-1.02943400	-0.41360600
H	-0.96346400	-1.81747000	-0.57057900
H	1.33282400	-1.81333400	-1.30072900
O	1.47748800	-2.00425300	0.73871200
H	1.34130900	-2.93856300	0.56129400
C	1.75675600	0.04888000	-0.35947800
H	2.82738000	0.07374200	-0.49886200

$8^{\bullet-}$

C	-0.81106900	2.02834200	0.00024300
C	-1.85616000	1.08611000	-0.00005900
H	-0.92913800	3.09714800	-0.00046900
H	-2.88494000	1.41570300	-0.00022400
C	-1.59777500	-0.26129600	-0.00003300
O	-2.34757300	-1.28458900	-0.00015500
C	0.85488900	0.24762900	0.00003400
S	2.49035800	-0.23129400	-0.00009100
N	-0.17107500	-0.60437500	0.00023600
N	0.51250800	1.54539300	-0.00002100
H	1.28079300	2.19199400	-0.00001600
O	0.05367600	-1.95786200	0.00010300
H	-0.89060300	-2.25636800	-0.00001900
$10^{\cdot-}$			
C	1.78330800	-0.59623800	0.00000000
C	0.97681700	-1.69043300	0.00000000
H	2.86311200	-0.70442500	0.00000000
H	1.38512000	-2.69170000	0.00000000
C	-0.45413200	-1.51132900	0.00000000
O	-1.26079200	-2.46168500	0.00000000
C	0.00000000	0.74753300	0.00000000
S	-0.68148800	2.38184900	0.00000000
N	-0.90120100	-0.20825300	0.00000000
N	1.31633700	0.67722700	0.00000000
TS6$^{\cdot}$			
C	-0.72507900	1.73228200	-0.00338500
C	-1.93863500	1.15238500	0.00145300
H	-0.59564200	2.80532900	-0.00591400
H	-2.84698000	1.73341600	0.00292300
C	-2.04443100	-0.28807500	0.00425700
O	-3.06707100	-0.94646000	0.00899300
N	-0.80135400	-0.94235300	0.00123700
H	-0.82484300	-1.95254900	0.00344200
N	0.42916000	1.00163800	-0.00590900
H	1.57084800	1.28864000	-0.00964900
O	2.84375800	0.97409400	-0.08973300
H	3.23307500	0.95618400	0.79042800
C	0.38615000	-0.31520700	-0.00287400
S	1.86171100	-1.19721300	-0.00620700
TS7$^{\cdot}$			
C	1.70206000	-1.54409000	0.00614400
C	2.29504400	-0.34380200	0.00466200
H	2.24054000	-2.47981500	0.00967100
H	3.36935800	-0.25022300	0.00664500
C	1.48502900	0.86289000	-0.00030000
O	1.92548200	1.99942700	-0.00098800
C	-0.43990700	-0.55621700	-0.00107100
N	0.10946800	0.64123800	-0.00452400
H	-0.80292100	1.40856500	-0.01197000
N	0.33175800	-1.65243100	0.00332400
H	-0.10354500	-2.56065700	0.00498000
O	-2.06478200	1.69462200	-0.09632200
H	-2.41906600	1.86101100	0.78318500
S	-2.15699400	-0.68535100	-0.00389000
TS7$_2^{\cdot}$			
C	0.23739400	2.20954900	0.00545900
C	-1.05452100	1.82635900	-0.00025800
H	0.54491000	3.24489800	0.00983600
H	-1.86827000	2.53161100	-0.00039200
C	-1.29523300	0.41946300	-0.00618600
O	-2.46226000	-0.07357400	-0.00663400
C	1.02645100	-0.05232800	-0.00030400
N	-0.25861600	-0.44143600	-0.00799900
H	-0.89465800	-1.56352800	-0.01362800
N	1.24071500	1.29470700	0.00584100

H	2.20074100	1.60120500	0.01009000
O	-1.91656900	-2.15998800	-0.09435600
H	-2.28100300	-2.26690500	0.79375400
S	2.31060500	-1.12937100	0.00194400

$TS10_a^{\bullet-}$

C	1.64514200	-1.58097300	0.01107800
C	2.26637300	-0.37420000	0.00830700
H	2.22951900	-2.49478300	0.01866700
H	3.34344800	-0.29075200	0.01350400
C	1.47197900	0.82558000	-0.00257700
O	1.91979900	1.97935100	-0.00570300
C	-0.39357700	-0.63772800	-0.00396400
N	0.11327100	0.59899100	-0.00953200
H	-0.80099200	1.37539400	-0.01564700
N	0.29511200	-1.75405800	0.00466200
O	-2.02072800	1.76929000	-0.08768500
H	-2.35188400	1.91728400	0.80197000
S	-2.15067800	-0.73792900	-0.00714700

$TS10_{a2}^{\bullet-}$

C	-0.70092300	1.71504500	-0.00901100
C	-1.91635300	1.12863900	0.00046100
H	-0.56754900	2.78918300	-0.01428900
H	-2.82412200	1.71370300	0.00309700
C	-2.00692400	-0.31830000	0.00672600
O	-3.09288700	-0.91567600	0.01603100
N	-0.82049500	-1.02802900	0.00168200
N	0.43194100	0.97110900	-0.01289100
H	1.58004100	1.24339400	-0.01248000
O	2.86453300	1.02256700	-0.07883600
H	3.22429600	0.99040600	0.81132700
C	0.30378000	-0.36056300	-0.00664500
S	1.81603500	-1.26139400	-0.00974600

$TS10_b^{\bullet-}$

C	0.17937800	2.21437200	0.00791800
C	-1.12493500	1.78422900	-0.00031300
H	0.38399100	3.28040200	0.01392500
H	-1.96665400	2.45787700	0.00020400
C	-1.29245300	0.39025600	-0.00857500
O	-2.44985500	-0.18278800	-0.00878900
C	1.04528300	0.09827100	-0.00036600
N	-0.21311800	-0.40299000	-0.01103700
H	-0.76738200	-1.55993900	-0.01583800
N	1.25660900	1.42087300	0.00855800
O	-1.72424300	-2.26148200	-0.09037400
H	-2.08173100	-2.37543700	0.79665500
S	2.35478000	-1.01854300	0.00148300
C	0.17937800	2.21437200	0.00791800

$RC^{\bullet}$

N	0.17881400	1.01142000	0.03520600
C	-1.19006700	0.95776300	-0.24361600
C	-1.64385500	-0.33575800	-0.71628800
C	-0.74681100	-1.32807300	-0.87916300
N	0.57108300	-1.15130300	-0.58232200
C	1.08169400	0.01163100	-0.10447700
O	-1.87847000	1.94500200	-0.08284900
O	-1.72614600	-1.13459700	1.61355700
H	1.21962200	-1.91278200	-0.69868100
H	0.53023200	1.89282100	0.38032000
H	-2.68120100	-0.45921800	-0.98141600
H	-1.01299100	-2.30697300	-1.24963000
H	-2.57807000	-1.56609200	1.44215100

$TS4^{\bullet}$

C	0.89742700	-1.20905700	-0.75241100
C	1.16340300	1.11241000	-0.09086100

O	1.78577800	2.13234200	0.12922800
C	-1.04967500	0.02927900	-0.09982400
S	-2.68715900	0.10883600	0.17530900
N	-0.21563800	1.07322500	0.12943300
N	-0.44889900	-1.09001000	-0.58033700
H	-1.04440500	-1.88658300	-0.73743700
H	-0.63821000	1.92096300	0.47876500
H	1.23245100	-2.13342600	-1.19494600
O	1.52285900	-1.67077600	1.20633100
H	2.46526500	-1.86946800	1.10944600
C	1.72038500	-0.12763200	-0.58650900
H	2.77287100	-0.17790800	-0.81127800

TS3$^{\cdot}$

C	-1.17108900	0.91243800	-0.28153500
C	-1.62815300	-0.43413300	-0.60002600
C	-0.70699900	-1.42058900	-0.75548100
N	0.60395900	-1.20628200	-0.47810600
C	1.10612700	-0.00590900	-0.08017100
N	0.19518400	0.99598400	-0.01058500
O	-1.86312300	1.90611400	-0.23644100
H	1.26472900	-1.96277600	-0.55536600
H	0.54460400	1.90600700	0.25276700
H	-2.65226600	-0.56871000	-0.90588800
H	-0.96392800	-2.41905400	-1.07631200
O	-1.92193100	-0.84521200	1.51628100
H	-2.54231000	-1.57428400	1.37480900
S	2.71476700	0.20580300	0.27471100

TS3$_a$$^{\cdot-}$

C	-1.06246900	0.68644000	-0.48519600
C	-1.42726100	-0.68377900	-0.66326000
C	-0.45670700	-1.63724600	-0.50043200
N	0.82791800	-1.40445000	-0.18210200
C	1.20059300	-0.13626500	-0.02798300
N	0.27477800	0.86193900	-0.18395500
O	-1.81774800	1.66277300	-0.54328000
H	0.58784000	1.81086900	-0.04437900
H	-2.42779200	-0.93272600	-0.97928800
H	-0.71560600	-2.68262100	-0.63509400
O	-2.75762000	-0.33902200	1.47909200
H	-2.85892000	0.49945400	0.99461300
S	2.79835100	0.32110600	0.36258000

TS3$_b$$^{\cdot-}$

C	1.06255800	0.83155900	-0.39761500
C	1.48016000	-0.52584100	-0.72270700
C	0.56087700	-1.51425200	-0.65447000
N	-0.70699800	-1.22506600	-0.29180400
C	-1.12019800	0.06681100	-0.04084500
N	-0.25828500	1.05906400	-0.09925000
O	1.88647700	1.75681200	-0.36192500
H	-1.40142800	-1.95073800	-0.23258500
H	2.48296000	-0.71419100	-1.07100200
H	0.77449300	-2.55047600	-0.87495600
O	2.45695100	-0.67401800	1.50326500
H	2.72262500	0.21877700	1.22617900
S	-2.77934200	0.27166400	0.34080300

TS4$_a$$^{\cdot-}$

C	0.87648800	-1.21937500	-0.71452700
C	1.10632500	1.12260900	-0.08662200
O	1.69812200	2.17789900	0.12343800
C	-1.02457600	-0.09511900	-0.12091900
S	-2.70228200	0.05482000	0.15729600

N	-0.25130900	1.01457800	0.14220500
N	-0.46659800	-1.20723900	-0.57354800
H	-0.72516200	1.83819500	0.47919200
H	1.28755000	-2.10794200	-1.17500400
O	1.61439000	-1.62823000	1.13708600
H	2.53798700	-1.85695500	0.97412800
C	1.69470700	-0.09018100	-0.58243500
H	2.74371900	-0.10675900	-0.83283200

$TS4_b^{\bullet-}$

C	0.86540800	-1.18259700	-0.76680900
C	1.09966700	1.13643500	-0.06366100
O	1.80586900	2.12914700	0.14215500
C	-1.01118500	0.12562700	-0.07203600
S	-2.70304200	0.10516900	0.18874600
N	-0.25300300	1.17088400	0.17739400
N	-0.46191400	-1.03715500	-0.58075600
H	1.19426900	-2.10007100	-1.22860700
O	1.57636600	-1.70492800	1.15897000
H	2.51931600	-1.86318900	1.02117900
C	1.68418400	-0.09580500	-0.57480900
H	2.73754300	-0.13909100	-0.80216300
H	-1.08436400	-1.81216900	-0.73191500

$RC10_b^{\bullet-}$

C	0.87720700	2.10188100	-0.00003000
C	-0.48466700	2.06061500	-0.00000700
H	1.37909100	3.06406400	-0.00005400
H	-1.09019300	2.95364800	-0.00001100
C	-1.11581500	0.78716100	0.00002300
O	-2.34249200	0.57097100	0.00004800
C	1.13709700	-0.16723400	0.00000100
N	-0.23217100	-0.26962100	0.00002600
H	-0.62539500	-1.20134000	0.00005000
N	1.70056200	1.03014500	-0.00002700
O	-2.92204700	-2.03626200	-0.00005400
H	-2.80333000	-1.04350600	-0.00001500

$RC7^{\bullet}$

C	0.79874600	2.13700700	-0.00006100
C	-0.54062800	2.07188200	-0.00001000
H	1.34508100	3.06849900	-0.00011000
H	-1.15509600	2.95683100	-0.00001700
C	-1.17489900	0.77861400	0.00004900
O	-2.38496500	0.57878600	0.00008900
C	1.05841600	-0.24482700	0.00000800
N	-0.29743300	-0.30079100	0.00005700
H	-0.71561500	-1.22513800	0.00011300
N	1.56988800	1.00787000	-0.00005300
H	2.57417900	1.08500800	-0.00009300
O	-2.76557000	-2.12939500	-0.00012200
H	-2.83976800	-1.14175600	0.00003500
S	2.01490700	-1.60901100	0.00002500

$6^{\bullet}OH_2$

C	-0.68348700	1.73946400	-0.00651000
C	-1.93181600	1.22555500	0.00007800
H	-0.52752100	2.81072900	-0.01119800
H	-2.80869000	1.85440900	0.00090000
C	-2.11091900	-0.20218100	0.00546500
O	-3.16483200	-0.81788200	0.01185300
N	-0.89924000	-0.90100600	0.00167000
H	-0.96732400	-1.90914700	0.00250700
N	0.46222900	0.98904000	-0.00710700
H	2.31180500	1.27568000	-0.01905100
O	3.23622800	0.96664500	-0.08833500
H	3.58998600	1.01006400	0.80361100
C	0.31236000	-0.29999900	-0.00349000

S	1.71080200	-1.35156900	-0.00625700
7·OH₂			
C	1.91922900	-1.37148900	0.00931500
C	2.35582500	-0.10532400	0.00681600
H	2.56655400	-2.23554100	0.01516300
H	3.41058800	0.12119500	0.01086500
C	1.39577700	0.98671900	-0.00209100
O	1.72251700	2.16699300	-0.00656500
C	-0.30518200	-0.60952200	-0.00157600
N	0.04562400	0.63704400	-0.00425300
H	-1.53897700	1.63008600	-0.02247500
N	0.57420500	-1.63434900	0.00368000
H	0.24803200	-2.58710100	0.00285300
O	-2.50899200	1.73081700	-0.09245600
H	-2.81300600	1.91843900	0.79901500
S	-2.00713000	-1.02817000	-0.00525200
10_a·OH₂			
C	1.81023600	-1.46688800	0.03638400
C	2.32292900	-0.20391800	0.02124000
H	2.47004000	-2.33419800	0.06303700
H	3.39344300	-0.02436000	0.03535900
C	1.42009800	0.92857100	-0.01438100
O	1.79485900	2.11247500	-0.03052600
C	-0.27860800	-0.66101600	-0.01135000
N	0.06768100	0.61413800	-0.02971200
H	-1.43185100	1.61557900	-0.05915700
N	0.47788000	-1.74598500	0.01966900
O	-2.39990000	1.82349500	-0.04330500
H	-2.60568200	1.84677500	0.90055500
S	-2.02828000	-1.01557000	-0.02938700
C	1.81023600	-1.46688800	0.03638400