Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information: Mechanistic insights into photoinduced damage of DNA and RNA nucleobases in the gas phase and in bulk solution

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Potential Energy (PE) profiles (derived from linear interpolation in internal coordinates LIIC) calculated using the TDDFT method for both photochemical formation of uracil and thymine hydrate in the gas phase are provided in Section 1. The PE profile associated with photohydrate formation of thymine in the gas phase using the CASPT2 method is also provided in the same section along with the CASPT2 calculation of LIIC between uracil-water Franck Condon (FC) geometry and the optimised barrier top. The (20,14) active space at the conical intersection (CI) for 6-HU formation and the transition states located for both U/T photohydrate formation is also provided in this section.

Vertical excitation energies (VEEs) and oscillator strengths at FC geometry of both uracil-water and thymine-water at CASPT2, TDDFT and EOM-EE-CCSD methods are provided in tables in Section 2.

Cartesian coordinates associated with U/T+H_2O optimised geometries and dispersively bound geometries, 6-HU/T optimised geometries and the final geometries in our PE profile calculation and minimum energy CI for those paths are provided in Section 3.

Section 1:

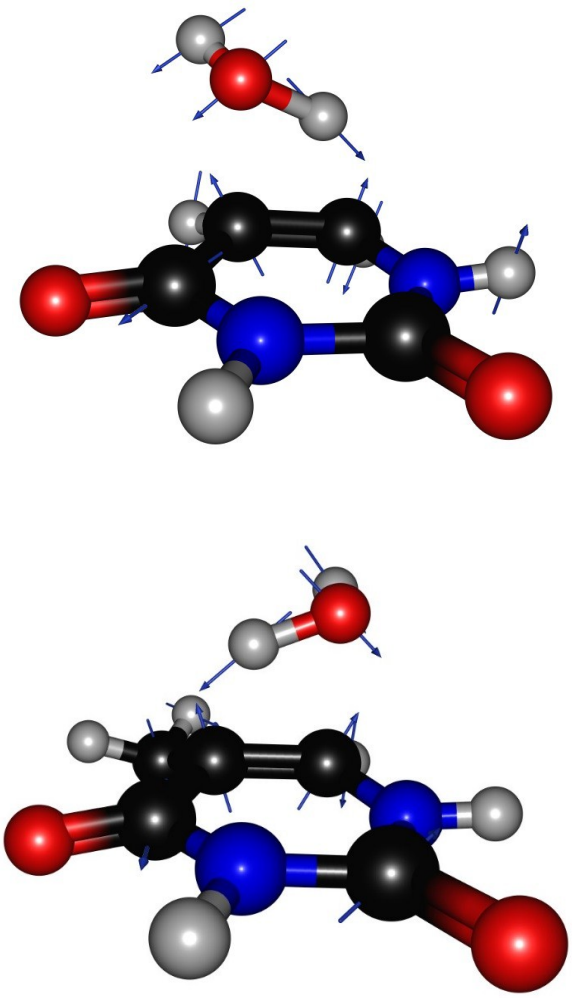

Fig S1: Eigenvectors associated with the imaginary normal mode wavenumber of the TS geometry associated with the T/U + water reaction.

Uracil Photohydrate: TDDFT/B3LYP/6-31G(d) Reaction Path

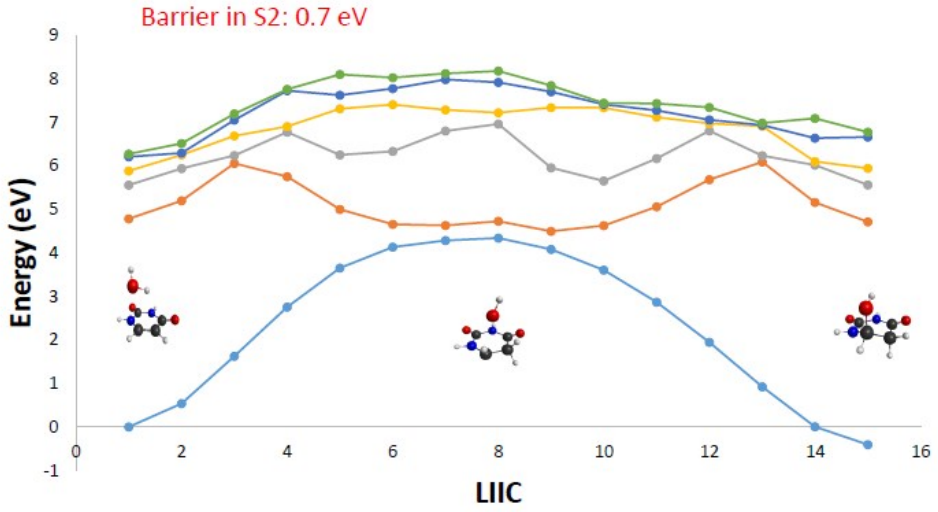

Fig. S2.1 : PE profile of photohydrate formation of U in gas phase at TDDFT/B3LYP/6-31G(d) level. The PE profile is obtained from LIIC between reactant-CI and CI-product.

Thymine Photohydrate: TDDFT/B3LYP/6-31G(d) Reaction Path

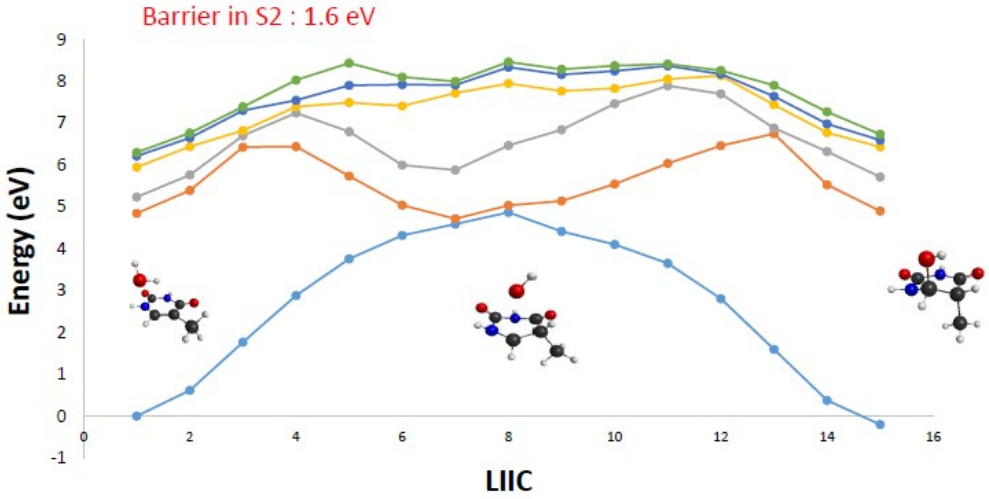

Fig. S2.2 : PE profile of photohydrate formation of T in gas phase at TDDFT/B3LYP/6-31G(d) level. The PE profile is obtained from LIIC between reactant-CI and CI-product.

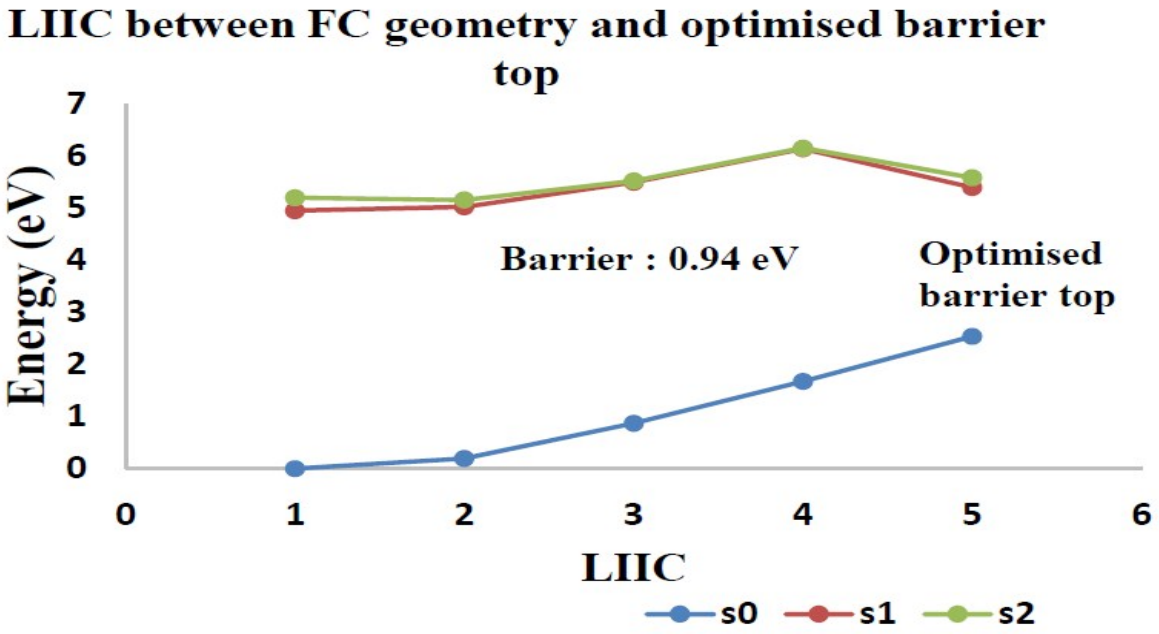

Fig. S3 : PE profile between U+H_2O at FC geometry and the optimised barrier top in gas phase at CASPT2/CASSCF(20,14)/6-31G(d) level

Thymine Photohydrate: CASPT2/CASSCF(20,14)/6-31G(d) Reaction Path

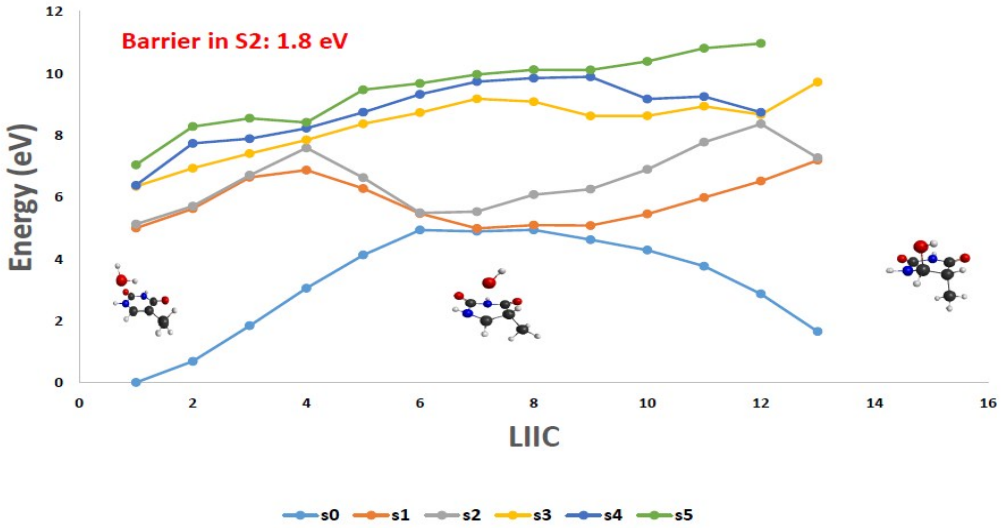

Fig. S4 : PE profile of photohydrate formation of T in gas phase at CASPT2/CASSCF(20,14)/6-31G(d) level. The PE profile is obtained from LIIC between reactant-CI and CI-product.

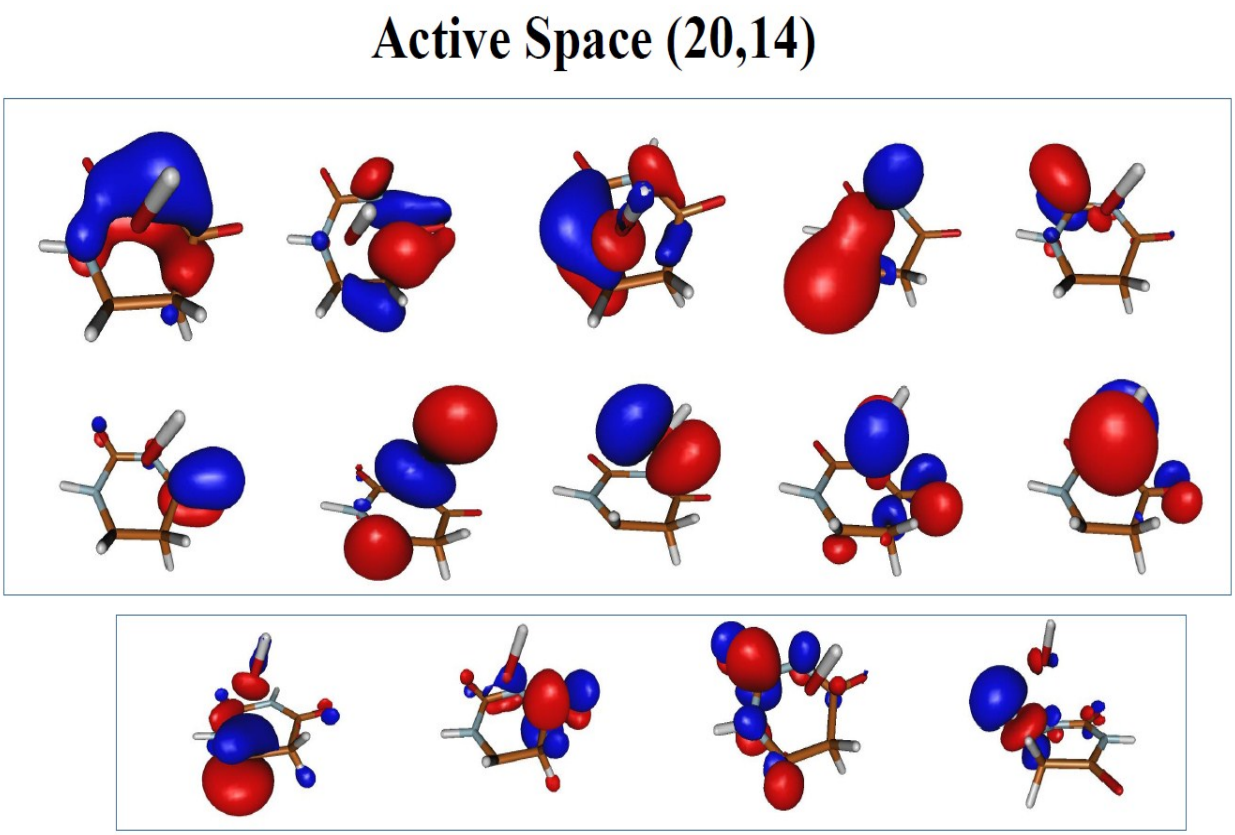

Fig. S5: Active space at CI for 6-HU photoreaction

Section 2:

<u>VEEs and Oscillator strengths for U-H_2O dispersively bound:</u>

Method: CASPT2/CASSCF(20,14)/6-31G(d)

State	E (eV)	Character	f
s0	0.000		
s1	4.956	nπ*	0.000731
s2	5.202	ππ*	0.230922
s3	6.241	ππ*	0.004383
s4	6.519	nπ*	0.000522
s5	6.920	ππ*	0.196573

Method: TDDFT/B3LYP/6-31G(d)

State	E (eV)	Character	f
s0	0.000		
s1	4.787	nπ*	0.00008
s2	5.561	ππ*	0.11539
s3	5.885	nπ*	0.00012
s4	6.211	ππ*	0.03565
s5	6.275	nπ*	0.00007

Method: EOM-EE-CCSD/6-311G(d)

State	E (eV)	Character	f
s0	0.000		
s1	5.322	nπ*	0.00013
s2	5.755	ππ*	0.210818
s3	6.658	nπ*	0.000008
s4	7.014	ππ*	0.051292
		π	
s5	7.164	π*/diffuseσ*	0.003752

<u>VEEs and oscillator strengths for T-H_2O dispersively bound:</u>

Method: CASPT2/CASSCF(20,14)/6-31G(d)

State	E (eV)	Character	f
s0	0.000		
s1	4.997	nπ*	0.000729
s2	5.122	ππ*	0.224125
s3	6.341	ππ*	0.026076
s4	6.379	nπ*	0.000608
s5	7.041	ππ*	0.198453

Method: TDDFT/B3LYP/6-31G(d)

State	E (eV)	Character	f
s0	0.000		
s1	4.848	nπ*	3.83E-05
s2	5.236	ππ*	0.121634
s3	5.952	nπ*	0.000106
s4	6.219	ππ*	0.0755
s5	6.302	nπ*	0.001342

Method: EOM-EE-CCSD/6-311G(d)

State	E (eV)	Character	f
s0	0.000		
s1	5.344	nπ*	0.000106
s2	5.730	ππ*	0.218559
s3	6.737	nπ*	0.000123
s4	7.045	ππ*	0.06696
s5	7.092	π diffuseσ*	0.003153

VEEs and oscillator strengths for U-H_2O optimised structure:

Method: TDDFT/B3LYP/6-31G(d)

State	Energy (eV)	Character	f
s0	0.000		
s1	4.735	nπ*	0.00013
s2	5.309	ππ*	0.14279
s3	5.946	nπ*	0.00031
s4	6.083	ππ*	0.02540
s5	6.246	nπ*	0.00036

Method: EOM-EE-CCSD/6-311G(d)

State	Energy (eV)	Character	f
s0	0.000		
s1	5.252	nπ*	0.000115
s2	5.709	ππ*	0.237651
s3	6.768	nπ*	0.000059
s4	6.999	ππ*	0.041158
s5	7.200	ππ*	0.181795

VEEs and oscillator strengths for T-H_2O optimised structure:

Method: TDDFT/B3LYP/6-31G(d)

State	Energy (eV)	Character	f
s0	0.000		
s1	4.821	nπ*	7.16E-05
s2	5.184	ππ*	0.148501
s3	6.029	nπ*	0.00043
s4	6.164	ππ*	0.088209
s5	6.306	nπ*	0.002124

Method: EOM-EE-CCSD/6-311G(d)

State	Energy (eV)	Character	f
s0	0.000		
s1	5.283	nπ*	0.000064
s2	5.647	ππ*	0.250275
s3	6.848	nπ*	0.000262
s4	6.957	ππ*	0.134025
s5	7.097	ππ*	0.163222

Section 4:

Cartesian Coordinates in Angstroms:

Optimised ground state geometry of U-H_2O at B3LYP/6-31G(d) level:

N	1.244934	1.111477	-3.677669
N	2.328981	3.087266	-4.211644
C	0.054972	1.653031	-4.095966
C	-0.034255	2.910284	-4.585386
C	1.160345	3.740303	-4.677041
C	2.438384	1.811643	-3.702975
O	1.224257	4.883456	-5.096107
O	3.501275	1.333764	-3.306617
O	2.427454	-1.107659	-2.464379
H	3.097694	-0.395065	-2.561636
H	2.735993	-1.807911	-3.059657
H	-0.804662	0.997356	-4.005074
H	-0.973915	3.331842	-4.915477
H	3.186590	3.627331	-4.244581
H	1.321154	0.165181	-3.281191

Optimised ground state geometry of 6-HU at B3LYP/6-31G(d) level:

N	2.407648	2.299900	-2.535985
N	2.907108	3.174018	-4.648930
C	1.465634	1.358414	-3.120990
C	0.776813	2.031236	-4.312716
C	1.743703	2.722563	-5.260427
C	3.274711	3.055504	-3.295614
O	1.530899	2.903835	-6.442803

O	4.275745	3.595023	-2.863437
O	2.047286	0.108260	-3.447432
H	2.703855	0.243788	-4.151205
H	0.195129	1.300973	-4.878302
H	0.724914	1.114549	-2.356645
H	0.084542	2.799404	-3.943772
H	3.544608	3.720265	-5.218173
H	2.792406	2.065269	-1.628768

Optimised ground state geometry of T-H_2O at B3LYP/6-31G(d) level:

N	-0.133626	-1.032928	0.751870
N	0.805233	0.798881	-0.294215
C	-1.340717	-0.755965	0.149893
C	-1.524579	0.290357	-0.689765
C	-0.382038	1.166205	-0.963428
C	-2.829334	0.612368	-1.358480
C	0.995094	-0.263566	0.564335
O	2.073575	-0.501716	1.110293
O	-0.397015	2.143223	-1.696478
O	1.181646	-2.738146	2.534333
H	-2.723108	0.601775	-2.449308
H	-3.606798	-0.104621	-1.077018
H	-3.168795	1.618896	-1.088614
H	1.581024	-3.526449	2.135610
H	1.782473	-2.005584	2.270798
H	-2.141598	-1.444629	0.399846
H	1.612305	1.390755	-0.456889

H	-0.000523	-1.825984	1.392524

Optimised ground state geometry of 6-HT at B3LYP/6-31G(d) level:

N	0.232720	0.035679	1.478997
N	0.928820	0.690781	-0.658508
C	-0.669435	-0.927739	0.902621
C	-1.268848	-0.361233	-0.393664
C	-2.306691	0.747433	-0.132545
C	-0.174689	0.167782	-1.315179
C	1.209714	0.648974	0.714017
O	2.213464	1.156539	1.175655
O	-0.272066	0.196980	-2.527110
O	0.065076	-2.128724	0.670880
H	0.559509	-0.155784	2.418651
H	-2.701101	1.122670	-1.080957
H	-3.143279	0.356922	0.457536
H	-1.862759	1.583069	0.416950
H	-1.756355	-1.176434	-0.939390
H	-0.542476	-2.795303	0.310365
H	1.653859	1.106001	-1.232860
H	-1.471508	-1.108235	1.632086

S_0/S_1 conical intersection for formation 6-HU at SA3-CASSCF(6,6)/6-31G(d) level:

N 1.8805 2.0262 -2.4085

N 2.4403 2.6342 -4.5910

C 0.6476 1.4855 -2.7508

C 0.1788 1.7807 -4.1350

C 1.1678 2.4044 -5.0910

C 2.8186 2.5462 -3.2683

O 0.9266 2.6130 -6.2482

O 3.9037 2.8910 -2.9112

O 1.7033 -0.3381 -4.0095

H 1.9451 -1.0547 -4.5908

H -0.0038 0.7874 -4.5352

H 0.5075 0.3132 -2.5982

H -0.7402 2.3468 -4.1559

H 3.1031 3.0708 -5.1987

H 2.2831 1.7967 -1.5268

S_0/S_1 conical intersection (1) for 6-HT formation at SA3-CASSCF(6,6)/6-31G(d) level:

N 0.4065 1.9517 -2.3527

N 0.7503 2.9379 -4.4393

C -0.8905 1.7773 -2.7301

C -1.3987 1.7613 -4.1434

C -0.3576 2.4230 -5.0702

C 1.3207 2.3904 -3.2931

C -2.6876 2.6478 -4.2806

O -0.6127 2.6886 -6.2037

O 2.5020 2.3427 -3.1388

O 0.3570 -0.2763 -3.9510

H 1.4152 3.3185 -5.0774

H 0.6952 1.1570 -1.7979

H -2.6678 3.3275 -3.4246

H -3.6470 2.1466 -4.2684

H -2.6596 3.2807 -5.1602

H 0.1464 -1.0224 -4.5497

H -1.7337 0.6196 -4.1851

H -1.6160 1.6414 -1.9502

S_0/S_1 conical Intersection (2) for 6-HT formation at SA3-CASSCF(6,6)/6-31G(d) level (gradient did not converge):

N -0.7591 1.8916 -2.4127

N -0.2119 2.3467 -4.6353

C -2.0457 1.4519 -2.6972

C -2.5269 1.7266 -4.0812

C -1.5144 2.2130 -5.0909

C 0.1963 2.2836 -3.3201

C -3.7594 2.6495 -4.1158

O -1.7702 2.3906 -6.2501

O 1.3184 2.5427 -3.0077

O -1.1983 -0.5158 -3.8945

H 0.4693 2.6926 -5.2798

H -0.3527 1.6657 -1.5318

H -4.0974 2.8719 -3.0500

H -4.6038 2.1345 -4.6827

H -3.4891 3.6249 -4.6402

H -1.0402 -1.2771 -4.4472

H -2.8111 0.7374 -4.4291

H -2.2871 0.3057 -2.4855

U-H_2O dispersively bound complex - initial geometry for excited state path:

N 1.9505 1.9062 -2.5785

N 2.3935 3.0054 -4.5583

C 0.6702 1.6605 -2.9950

C 0.2098 2.0997 -4.1829

C 1.0971 2.8324 -5.0772

C 2.8874 2.5956 -3.3349

O 0.8136 3.2653 -6.1760

O 4.0185 2.8057 -2.9531

O 1.2377 -1.0049 -3.7800

H 2.0597 -1.4223 -4.0613

H 0.9796 -0.4513 -4.5265

H 0.0637 1.0821 -2.3099

H -0.8083 1.9234 -4.5008

H 3.0411 3.5233 -5.1388

H 2.2951 1.5212 -1.7122

T-H_2O dispersively bound complex - initial geometry for excited state path:

N 0.4865 1.8417 -2.5927

N 0.9925 3.1234 -4.4362

C -0.8457 1.8754 -2.9297

C -1.3058 2.5331 -4.0124

C -0.3367 3.2246 -4.8674

C 1.4844 2.4440 -3.3361

C -2.7527 2.6025 -4.3988

O -0.6119 3.8397 -5.8803

O 2.6619 2.3776 -3.0527

O -0.8521 -0.9508 -3.6864

H 1.6851 3.5891 -5.0088

H 0.8039 1.2631 -1.8299

H -3.0984 3.6410 -4.4204

H -3.3760 2.0409 -3.6972

H -2.9079 2.1994 -5.4050

H -0.2351 -1.6015 -4.0394

H -0.9761 -0.3209 -4.4062

H -1.4989 1.3205 -2.2668

6-HU final geometry for excited state path:

N 2.3995 2.3039 -2.5385

N 2.9148 3.1468 -4.6519

C 1.4697 1.3592 -3.1242

C 0.7785 2.0304 -4.3103

C 1.7407 2.7228 -5.2534

C 3.2707 3.0445 -3.2992

O 1.5190 2.9242 -6.4258

O 4.2671 3.5837 -2.8697

O 2.0612 0.1266 -3.4531

H 2.7141 0.2693 -4.1519

H 0.2003 1.2994 -4.8772

H 0.7286 1.1107 -2.3632

H 0.0872 2.7970 -3.9404

H 3.5495 3.6944 -5.2198

H 2.7741 2.0801 -1.6266

6-HT final geometry for excited state path:

N 1.1051 1.9066 -2.5527

N 1.7082 2.7584 -4.6406

C 0.2174 0.9705 -3.1820

C -0.4469 1.6330 -4.3924

C 0.5896 2.2793 -5.2963

C 2.0368 2.6050 -3.2917

C -1.4917 2.6814 -3.9869

O 0.4358 2.4325 -6.4881

O 3.0420 3.0924 -2.8240

O 0.9741 -0.1676 -3.5484

H 2.3969 3.2463 -5.1988

H 1.4661 1.6469 -1.6447

H -1.0377 3.4733 -3.3840

H -2.2892 2.2169 -3.3982

H -1.9373 3.1306 -4.8779

H 0.3838 -0.8122 -3.9590

H -0.9370 0.8602 -4.9934

H -0.5513 0.6996 -2.4451

Transition State geometry for 6-HU formation:

N	2.87505	2.70814	-2.57718
C	1.69966	2.189	-3.04985
H	0.98691	1.91333	-2.28176
C	1.22905	2.60941	-4.36355
H	0.15706	2.68476	-4.50793
C	2.03715	3.5466	-5.12539
O	1.73	4.09056	-6.16573
N	3.33501	3.76529	-4.59445

H	3.93442	4.37702	-5.13353
C	3.78964	3.44529	-3.34088
O	4.8706	3.75961	-2.89443
H	3.21164	2.46382	-1.6566
O	1.95761	0.49424	-3.6401
H	2.90895	0.30435	-3.70812
H	1.61332	1.24437	-4.54787

Transition State geometry for 6-HT formation:

N	3.52772	2.75763	-2.07364
C	2.35245	2.21188	-2.49199
H	1.59671	2.12461	-1.71694
C	1.9522	2.34874	-3.88661
C	2.85279	3.07953	-4.7712
O	2.60724	3.4183	-5.91293
N	4.13469	3.33608	-4.23883
H	4.79979	3.76734	-4.8674
C	4.53159	3.2282	-2.93063
O	5.62568	3.53272	-2.51265
H	3.84742	2.60332	-1.12765
C	0.47221	2.41613	-4.20584
H	0.32749	2.27422	-5.27846
H	-0.08123	1.62798	-3.68189
H	0.0269	3.38146	-3.93605
H	2.35308	1.00009	-3.77442
O	2.67747	0.40609	-2.73106
H	1.9316	-0.13901	-2.43166