

Electronic Supplementary Information for

3-methylation alters excited state decay in photoionised uracil

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Table S1. Vertical ionisation potentials (in eV) of the three lowest-lying cationic states of 1-methyl-uracil computed with different zeroth-order CASPT2 Hamiltonians, IPEA values being provided in a.u.

		${}^2\pi_{\text{H}}^+$	${}^2\text{nO}^+$	${}^2\pi_{\text{H-1}}^+$
CASSCF	-	7.917	9.214	9.339
CASPT2	IPEA = 0	9.060	9.667	10.158
	IPEA = 0.25	9.255	9.914	10.398
MS-CASPT2	IPEA = 0	9.199	9.793	10.241
	IPEA = 0.25	9.362	10.014	10.465
XMS-CASPT2	IPEA = 0	9.754	10.346	10.705
	IPEA = 0.25	9.869	10.545	10.877
Average	-	9.417	10.047	10.474
St Dev	-	0.323	0.336	0.274
Variance	-	0.569	0.580	0.524

Table S2. Vertical ionisation potentials (in eV) of the three lowest-lying cationic states of 3-methyl-uracil computed with different zeroth-order CASPT2 Hamiltonians, IPEA values being provided in a.u.

		${}^2\pi_{\text{H}}^+$	${}^2\text{nO}^+$	${}^2\pi_{\text{H-1}}^+$
CASSCF	-	8.313	8.976	9.226
CASPT2	IPEA = 0	9.123	9.507	9.754
	IPEA = 0.25	9.324	9.762	9.973
MS-CASPT2	IPEA = 0	9.166	9.533	9.779
	IPEA = 0.25	9.359	9.786	9.988
XMS-CASPT2	IPEA = 0	9.212	9.628	9.809
	IPEA = 0.25	9.395	9.894	10.009
Average	-	9.263	9.685	9.885
St Dev	-	0.111	0.154	0.116
Variance	-	0.333	0.392	0.341

Table S3. Conical intersection parameters for the different crossings found in Ura^+ , 1mUra^+ , 3mUra^+ and 5mUra^+ at the XMS-CASPT2 level of theory. Pitch (δ), asymmetry (Δ) and relative tilt (σ) are given in atomic units, whereas tilt headings (σ_s) are in degrees.

	δ	Δ	σ	σ_s (°)	P	B	Intersection Type
$({}^2\text{nO}^+ / {}^2\pi_{\text{H}}^+)_{\text{CI}}$							
Ura⁺	0.028	0.940	3.094	0.000	4.935	1.739	Sloped, single-path
1mUra⁺	0.028	0.944	3.893	0.139	7.797	2.033	Sloped, single-path
3mUra⁺	0.125	0.060	0.896	67.251	0.839	5.596	Peaked, single-path
5mUra⁺	0.030	0.961	3.308	0.047	5.582	1.802	Sloped, single-path

	$({}^2\pi_{H-1}^+ / {}^2n_{O^+})_{CI}$						
Ura⁺	0.037	0.845	1.667	0.012	1.506	1.217	Sloped, single-path
1mUra⁺	0.019	0.328	2.486	1.336	4.657	2.844	Sloped, single-path
3mUra⁺	0.090	0.974	0.140	0.017	0.010	0.217	Peaked, bifurcating
5mUra⁺	0.036	0.842	1.674	0.111	1.521	1.229	Sloped, single-path

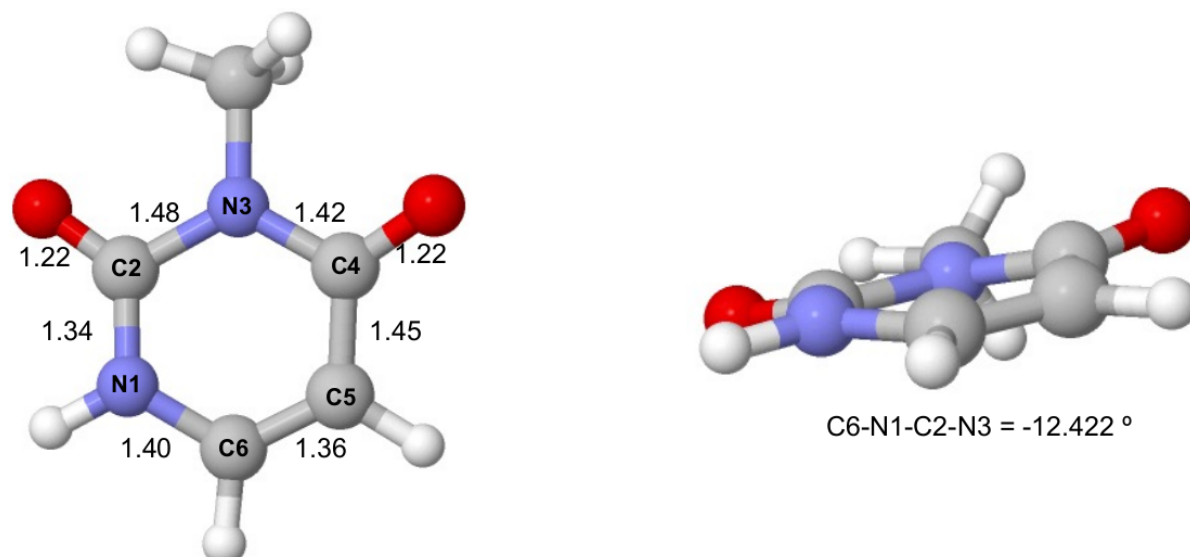


Figure S1. Structure of the effective 3-state conical intersection of 3mUra⁺.

Table S4. Cartesian coordinates (in Å) of the key structures optimised for uracil.

FC @ MP2

N	0.03469954	0.98940454	-0.00002904
N	-1.18206818	-0.98647191	0.00001387
C	-1.22813655	0.40796837	0.00000571
C	-0.00812071	-1.71531831	-0.00001675
C	1.21293151	-1.10717337	0.00000118
C	1.29727452	0.35404295	-0.00000397
O	2.33192137	1.01913064	0.00000447
O	-2.27685365	1.04332323	0.00002159
H	-0.12790040	-2.80102991	-0.00005690
H	0.04294107	2.01313969	-0.00001115
H	-2.09042036	-1.44813479	0.00004101
H	2.13547884	-1.68641014	0.00002999

$({}^2\pi_{H^+})_{min}$ @ XMS-CASPT2

N	0.03485001	1.031469163	-2.91047E-05
N	-1.153723866	-1.012897696	7.40848E-06
C	-1.214751733	0.437170583	0.00032121
C	-0.035063268	-1.747903382	0.000171453
C	1.208023777	-1.096335679	-0.000755136
C	1.289813374	0.391791009	-0.001141964

O	2.33678266	0.993771122	-3.75716E-05
O	-2.285848845	0.981522791	0.001010728
H	-0.142131121	-2.83708935	0.000983211
H	0.039265992	2.058472071	0.00072021
H	-2.079316353	-1.460297799	-0.000296339
H	2.146205914	-1.657718921	-0.000422812

$(^2\pi_H^+)_{\min}$ @ CASSCF

N	0.04023442	1.02863030	-0.00008058
N	-1.13735176	-1.00405969	-0.00000998
C	-1.18361997	0.44505864	0.00003377
C	-0.06604315	-1.72279567	-0.00000821
C	1.21062627	-1.07550505	0.00005671
C	1.26298914	0.36124335	-0.00001326
O	2.31947532	0.96465037	-0.00003232
O	-2.25790304	0.93939495	0.00016977
H	-0.17174387	-2.80011641	-0.00004968
H	0.05671088	2.03478172	-0.00011252
H	-2.05525496	-1.43976220	-0.00004978
H	2.12362673	-1.64904730	0.00009608

$(^2n_O^+)_{\min}$ @ XMS-CASPT2

N	0.05422745	1.01034833	-0.00019893
N	-1.17468090	-0.99257115	0.00085795
C	-1.23698555	0.40038213	-0.00012924
C	-0.01658089	-1.71558501	-0.00084773
C	1.22449332	-1.10837187	0.00053844
C	1.22961661	0.31959699	0.00007811
O	2.30940113	1.00742555	-0.00012210
O	-2.24540701	1.06135201	-0.00086594
H	-0.12943163	-2.80318162	-0.00377131
H	0.05567492	2.04026930	-0.00065421
H	-2.08555840	-1.46775018	0.00308602
H	2.15697697	-1.66944143	0.00202895

$(^2n_O^+)_{\min}$ @ CASSCF

N	0.05820673	0.99491641	-0.00011054
N	-1.16350625	-0.99130629	0.00006484
C	-1.21911555	0.39787616	0.00006689
C	-0.02554520	-1.69672861	-0.00014584
C	1.20627476	-1.09230285	0.00014002
C	1.18747697	0.30686815	-0.00002188
O	2.29637019	0.99710748	-0.00008484
O	-2.20849706	1.03573066	0.00022856
H	-0.12907665	-2.77218344	-0.00059434
H	0.06465102	2.00483202	-0.00026380
H	-2.05532077	-1.45808500	0.00021533
H	2.12982781	-1.64425165	0.00050561

$(^2n_O^+ / ^2\pi_H^+)_{CI}$ @ XMS-CASPT2

N	0.033704871	0.997066837	-2.80464E-05
N	-1.14205763	-1.028144343	8.46683E-06
C	-1.258453816	0.355053425	-3.22798E-05
C	0.043718487	-1.704958551	4.02175E-05
C	1.262808413	-1.078088069	4.70968E-05
C	1.203851216	0.342547385	2.16963E-05
O	2.283102945	1.071968666	3.81007E-05
O	-2.267097987	1.002421049	-6.72055E-05
H	-0.02876077	-2.795516147	8.04349E-05
H	-0.00740054	2.022011776	-5.50344E-05
H	-2.028112128	-1.535001716	1.00544E-05
H	2.210671314	-1.612353635	6.72055E-05

$(^2n_{O^+}/^2\pi_{H^+})_{CI}$ @ CASSCF

N	0.06589133	0.99184557	-0.00000550
N	-1.17890997	-0.98811089	-0.00000331
C	-1.23141304	0.37868993	-0.00000267
C	-0.01045436	-1.69395673	-0.00000320
C	1.20483080	-1.10237711	0.00000097
C	1.17443745	0.31196489	0.00000162
O	2.29276068	0.99454415	-0.00000511
O	-2.18536001	1.06742230	0.00000685
H	-0.11002607	-2.76869539	-0.00002160
H	0.05079858	2.00266876	0.00001373
H	-2.06220153	-1.46294931	0.00001310
H	2.13139214	-1.64857312	0.00000512

$(^2\pi_{H-1^+}/^2n_{O^+})_{CI}$ @ XMS-CASPT2

N	0.033269358	0.983985581	-2.75172E-05
N	-1.194783768	-0.992010021	5.82095E-06
C	-1.25365418	0.386701914	-1.42878E-05
C	-0.020502434	-1.722337253	-6.35012E-06
C	1.22119023	-1.14119613	-0.000106365
C	1.340922876	0.293410654	-1.69337E-05
O	2.310104731	1.040898567	4.76259E-05
O	-2.24830109	1.096005473	0.000104777
H	-0.154323889	-2.806745812	1.00544E-05
H	0.057395067	2.021047086	2.01087E-05
H	-2.099885463	-1.468832365	5.60928E-05
H	2.132755822	-1.739962022	-9.78977E-05

$(^2\pi_{H-1^+}/^2n_{O^+})_{CI}$ @ CASSCF

N	0.03837915	0.97536890	-0.00014048
N	-1.18503226	-0.98595132	0.00000905
C	-1.19828853	0.36197718	-0.00003203
C	-0.00342656	-1.72213732	-0.00004742
C	1.20161803	-1.12235587	0.00002364
C	1.25188898	0.32627324	0.00007855
O	2.24363613	1.06510559	0.00022535
O	-2.17205469	1.10001256	0.00017561

H	-0.12681702	-2.79305309	-0.00010456
H	0.03972860	1.99584056	-0.00023650
H	-2.07635160	-1.44757406	0.00005908
H	2.12846579	-1.67103335	-0.00001028

Table S5. Cartesian coordinates (in Å) of the key structures optimised for 1-methyl-uracil.

FC @ MP2			
N	0.040189	0.972754	0.076330
N	-1.195977	-0.994068	-0.002944
C	-1.217661	0.396493	0.080014
C	-0.014423	-1.695490	-0.079947
C	1.199693	-1.097621	-0.081051
C	1.298647	0.349460	0.001592
O	2.330068	1.015697	0.009992
O	-2.262399	1.035718	0.149245
H	-0.124014	-2.769627	-0.140213
H	0.047499	1.983026	0.135884
H	2.107272	-1.675147	-0.142499
C	-2.495777	-1.658322	-0.003179
H	-3.087227	-1.320098	-0.850272
H	-2.331136	-2.729315	-0.071470
H	-3.034283	-1.424303	0.911708

$(^2\pi_{\text{H}^+})_{\text{min}}$ @ XMS-CASPT2			
N	5.496603149594e-02	1.020844531920e+00	7.873272304683e-02
N	-1.188388011127e+00	-1.018926269083e+00	-4.643741492775e-03
C	-1.197643184131e+00	4.597137571593e-01	4.040530703639e-02
C	-5.975824651644e-02	-1.735838810638e+00	-3.069234310425e-02
C	1.193634245954e+00	-1.108901032109e+00	-2.997892999164e-03
C	1.297996296045e+00	3.584671053524e-01	3.485655146561e-02
O	2.354470789109e+00	9.584324414809e-01	2.491273318918e-02
O	-2.254142578850e+00	1.033453918020e+00	4.539693508717e-02
H	-1.606856108613e-01	-2.824496986402e+00	-8.228617378459e-02
H	7.838701606723e-02	2.046209817742e+00	1.055279275002e-01
H	2.118586772514e+00	-1.690178070902e+00	-2.552036673926e-02
C	-2.521223743441e+00	-1.646156322731e+00	-2.043156899483e-02
H	-3.079835193484e+00	-1.260411620338e+00	-8.868155007995e-01
H	-2.393401525349e+00	-2.733493935165e+00	-7.917988079669e-02
H	-3.057934491004e+00	-1.356078103011e+00	8.956434571081e-01

$(^2\pi_{\text{H}^+})_{\text{min}}$ @ CASSCF			
N	0.04455908	1.01895461	0.07892737
N	-1.17111596	-1.02611339	-0.00557138
C	-1.18018731	0.43683398	0.08127366
C	-0.06483609	-1.71355182	-0.07949781
C	1.20140892	-1.07497166	-0.07976734
C	1.27014312	0.36892591	0.00360680
O	2.31583720	0.97329184	0.00792598
O	-2.22998262	0.97452032	0.14463531

H	-0.14749996	-2.78855706	-0.14062770
H	0.05086684	2.02382679	0.13818712
H	2.11150743	-1.64976074	-0.14113897
C	-2.50749233	-1.68305337	-0.00428530
H	-3.06469982	-1.30704277	-0.85483283
H	-2.35654742	-2.75232424	-0.07207339
H	-3.01149008	-1.41182140	0.91642848

$({}^2n_o^+)_{\min}$ @ XMS-CASPT2

N	4.962483687879e-02	1.003462090102e+00	7.786425285322e-02
N	-1.182345528290e+00	-1.013020630929e+00	-4.475777033412e-03
C	-1.235516035344e+00	3.854062468208e-01	7.988102699744e-02
C	-4.379969133548e-03	-1.693337133707e+00	-8.017795181472e-02
C	1.232795615504e+00	-1.081627356049e+00	-8.110789475594e-02
C	1.228045162683e+00	3.441242963869e-01	3.435857235332e-03
O	2.308045704511e+00	1.034724136006e+00	1.186791283009e-02
O	-2.243839013951e+00	1.040471261444e+00	1.489243561836e-01
H	-8.663335382033e-02	-2.782111585786e+00	-1.422139828506e-01
H	3.114981410948e-02	2.027457199469e+00	1.390204605826e-01
H	2.169651514579e+00	-1.633830873054e+00	-1.419548570474e-01
C	-2.492348094356e+00	-1.698740816764e+00	-5.757142494372e-03
H	-3.080371889820e+00	-1.351339347018e+00	-8.659967715411e-01
H	-2.311833816269e+00	-2.778575287419e+00	-7.456400046454e-02
H	-3.026330029505e+00	-1.457426920132e+00	9.233182974666e-01

$({}^2n_o^+)_{\min}$ @ CASSCF

N	0.05363816	0.98853867	0.07684787
N	-1.17567658	-1.00950288	-0.00444855
C	-1.20288048	0.40315035	0.07996000
C	-0.04474706	-1.68252367	-0.07826718
C	1.20648741	-1.07967280	-0.08020007
C	1.20022678	0.28792248	0.00091775
O	2.30409857	1.01707133	0.01088427
O	-2.20262873	1.02522414	0.14680958
H	-0.13082808	-2.75678862	-0.13925272
H	0.06374896	1.99501259	0.13608735
H	2.11633276	-1.65034794	-0.14132126
C	-2.50061008	-1.67386486	-0.00394675
H	-3.06939161	-1.31408685	-0.85471715
H	-2.34109892	-2.74214860	-0.07193638
H	-3.01620010	-1.41882632	0.91577324

$({}^2n_o^+ / {}^2\pi_H^+)_{CI}$ @ XMS-CASPT2

N	4.916372212795e-02	1.001961433245e+00	7.778927628980e-02
N	-1.181731930687e+00	-1.015892688496e+00	-4.664247921521e-03
C	-1.248466760929e+00	3.644690557799e-01	7.901037804980e-02
C	1.262553156084e-02	-1.683957859055e+00	-8.011426585071e-02
C	1.244623817022e+00	-1.076118626776e+00	-8.104967179389e-02

C	1.213825115123e+00	3.454331516808e-01	4.012676972653e-03
O	2.290629453319e+00	1.068458495400e+00	1.440643746718e-02
O	-2.241751220287e+00	1.040992393702e+00	1.488615797898e-01
H	-6.201141380153e-02	-2.773048206868e+00	-1.424013689230e-01
H	1.092856678961e-02	2.025304885604e+00	1.394733764649e-01
H	2.183332685042e+00	-1.623567415350e+00	-1.415778115651e-01
C	-2.483264528576e+00	-1.721641545674e+00	-7.419873164029e-03
H	-3.074895209976e+00	-1.388950461857e+00	-8.699801734890e-01
H	-2.283420507484e+00	-2.798283500117e+00	-7.690212673242e-02
H	-3.021220570119e+00	-1.494870683204e+00	9.220433023282e-01

$(^2n_o+^2\pi_H^+)_{CI}$ @ CASSCF

N	0.08458307	0.98409868	0.07153698
N	-1.20342557	-0.98808468	-0.00439525
C	-1.22777352	0.36647588	0.07561308
C	-0.02335211	-1.67262732	-0.07737064
C	1.20789363	-1.09208223	-0.07795507
C	1.18322705	0.31374494	0.00368535
O	2.30446790	0.99863799	0.01164995
O	-2.15500704	1.08903672	0.14595280
H	-0.10769652	-2.74522480	-0.13744674
H	0.05896507	1.99332861	0.13160417
H	2.12573623	-1.64856077	-0.13605320
C	-2.51173310	-1.67316760	-0.00303843
H	-3.10272920	-1.34089229	-0.85050229
H	-2.33159649	-2.73830870	-0.07968431
H	-3.04108839	-1.45721744	0.91959358

$(^2\pi_{H-1}+^2n_o^+)_{CI}$ @ XMS-CASPT2

N	4.769231801515e-02	9.971728797064e-01	7.755002819901e-02
N	-1.286148006902e+00	-9.415633555119e-01	2.874961836958e-03
C	-1.160589086792e+00	3.718802143355e-01	-3.766576755831e-01
C	-2.039729614871e-01	-1.631893478343e+00	5.511605892498e-01
C	1.046416966172e+00	-1.101885196021e+00	7.537466191552e-01
C	1.329236225997e+00	2.785858288454e-01	4.314692693595e-01
O	2.336091754530e+00	9.457717908622e-01	3.966494089149e-01
O	-1.904979706791e+00	1.023433050725e+00	-1.097504255866e+00
H	-4.172670299880e-01	-2.676659602409e+00	7.915605499123e-01
H	1.088610273912e-01	2.019025546462e+00	-9.943568767544e-02
H	1.859386908720e+00	-1.724677910529e+00	1.133495057505e+00
C	-2.538065808931e+00	-1.630219457690e+00	-3.936323350133e-01
H	-2.586595476501e+00	-1.716990916981e+00	-1.490236390912e+00
H	-2.534658880193e+00	-2.623099252631e+00	7.366935399969e-02
H	-3.395764118878e+00	-1.045532732728e+00	-2.639784048114e-02

$(^2\pi_{H-1}+^2n_o^+)_{CI}$ @ CASSCF

N	0.04277151	0.95698669	0.07655721
N	-1.19914888	-0.99124857	-0.00214040
C	-1.18968138	0.34868953	0.07656951
C	-0.00490122	-1.70098110	-0.08028705
C	1.20269384	-1.11687177	-0.08223619

C	1.27191003	0.32365713	0.00072305
O	2.24942381	1.08016721	0.01419562
O	-2.15566644	1.11877344	0.14998091
H	-0.11418308	-2.77072494	-0.14036727
H	0.03730867	1.97886251	0.13779791
H	2.12054883	-1.67726953	-0.14339697
C	-2.51443015	-1.66350030	-0.00305514
H	-3.09821120	-1.33183576	-0.85631081
H	-2.34170067	-2.73000048	-0.07050678
H	-3.04626266	-1.43554705	0.91566639

Table S6. Cartesian coordinates (in Å) of the key structures optimised for 3-methyl-uracil.

FC @ MP2

N	0.011444	1.013000	-0.000739
N	-1.168998	-0.990487	-0.068791
C	-1.233830	0.396889	-0.073510
C	-0.004684	-1.714262	0.000103
C	1.192889	-1.095722	0.070070
C	1.260910	0.356892	0.073114
O	2.297556	1.017040	0.133598
O	-2.306050	0.990133	-0.136906
H	-0.118857	-2.788873	-0.005902
H	-2.066445	-1.446351	-0.121228
H	2.116929	-1.646961	0.124731
C	0.054159	2.474936	0.000814
H	0.533179	2.821424	0.912632
H	0.636710	2.820270	-0.849073
H	-0.965802	2.833785	-0.059362

(${}^2\pi_{\text{H}^+}$)_{min} @ XMS-CASPT2

N	1.313430556412e-02	1.060779550673e+00	-1.220269428673e-03
N	-1.152547668896e+00	-1.025076269035e+00	-7.030057894365e-02
C	-1.220257627592e+00	4.411508052094e-01	1.981573674101e-02
C	-4.373345679840e-02	-1.760181054055e+00	-1.134651866442e-01
C	1.193119817884e+00	-1.094446227631e+00	-1.083460177434e-01
C	1.255359771255e+00	3.817922995492e-01	-1.383955468767e-02
O	2.312510316792e+00	9.771537925131e-01	5.496512470675e-02
O	-2.310413699475e+00	9.435138131409e-01	9.649879939731e-02
H	-1.460591601372e-01	-2.849282871720e+00	-1.528077774523e-01
H	-2.083726337246e+00	-1.461789793625e+00	-6.773560108165e-02
H	2.140337091770e+00	-1.638686577013e+00	-1.436249337146e-01
C	5.720191844718e-02	2.542198056910e+00	8.803946586047e-02
H	4.781061778545e-01	2.829904765635e+00	1.061313425844e+00
H	6.996921350743e-01	2.916211844250e+00	-7.194576814656e-01
H	-9.683861416981e-01	2.911937145890e+00	-1.780116751292e-02

(${}^2\pi_{\text{H}^+}$)_{min} @ CASSCF

N	0.01575330	1.04381528	0.00018054
N	-1.13399951	-1.02833164	-0.06742853

C	-1.18932694	0.43163724	-0.07188169
C	-0.05744871	-1.75118416	-0.00311029
C	1.19400630	-1.08594814	0.07062853
C	1.22742645	0.36207447	0.07160876
O	2.28420542	0.95095432	0.13312893
O	-2.27386239	0.89257452	-0.13733784
H	-0.15862871	-2.82820511	-0.00844523
H	-2.05083669	-1.46086489	-0.12165633
H	2.12062330	-1.63431126	0.12568100
C	0.05857483	2.52707622	0.00174257
H	0.53318430	2.86611050	0.91618509
H	0.62771855	2.86585389	-0.85723732
H	-0.95828011	2.89046306	-0.05250708

$(^2\text{no}^+)_{\text{min}} @ \text{XMS-CASPT2}$

N	1.231359968220e-02	1.029003652306e+00	-1.230257286441e-03
N	-1.130800671999e+00	-1.033904712111e+00	-6.895093274368e-02
C	-1.251102786247e+00	3.559627725955e-01	-7.391777705755e-02
C	3.930610435673e-02	-1.720518326963e+00	1.517134820306e-03
C	1.250939886322e+00	-1.070333730952e+00	7.401528651464e-02
C	1.189885774148e+00	3.574761462997e-01	6.888895335339e-02
O	2.259118527739e+00	1.069165287110e+00	1.302524569599e-01
O	-2.296793375673e+00	9.513046339931e-01	-1.331014870453e-01
H	-3.546467783257e-02	-2.811056835219e+00	-2.599517966154e-03
H	-2.022145939341e+00	-1.532488543253e+00	-1.207524774865e-01
H	2.206902824199e+00	-1.589053770805e+00	1.312256629301e-01
C	2.544250564051e-02	2.513241740487e+00	-1.293474506921e-03
H	4.874075625036e-01	2.865478021239e+00	9.329769529132e-01
H	5.952367152927e-01	2.864391564191e+00	-8.743659258830e-01
H	-1.016971400457e+00	2.844947614853e+00	-6.350648235651e-02

$(^2\text{no}^+/^2\pi_{\text{H}}^+)_{\text{CI}} @ \text{XMS-CASPT2}$

N	1.229282025985e-02	1.028199119492e+00	-1.230510168648e-03
N	-1.130351188063e+00	-1.034665417400e+00	-6.892229982654e-02
C	-1.251581333391e+00	3.535485310833e-01	-7.979793304593e-02
C	4.140362596910e-02	-1.719797906908e+00	5.291594147896e-03
C	1.252097716178e+00	-1.069797188901e+00	7.979481638072e-02
C	1.188263881474e+00	3.572627679077e-01	7.354597530695e-02
O	2.256585399864e+00	1.072881901903e+00	1.394859192931e-01
O	-2.295521830709e+00	9.510643502614e-01	-1.472688173693e-01
H	-3.254106813776e-02	-2.810348811633e+00	2.964756063485e-03
H	-2.020378086926e+00	-1.534943149990e+00	-1.239319465044e-01
H	2.208019888926e+00	-1.588064109683e+00	1.404949815925e-01
C	2.486196811395e-02	2.512297730828e+00	-3.535575575894e-03
H	4.823685366983e-01	2.866552804139e+00	9.322311111241e-01
H	5.984866727227e-01	2.862391189181e+00	-8.747088133468e-01
H	-1.017345371966e+00	2.843664151970e+00	-7.133211763539e-02

$(^2\text{no}^+/^2\pi_{\text{H}}^+)_{\text{CI}} @ \text{CASSCF}$

N	0.01291062	1.02747960	-0.00128780
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N	-1.17372377	-0.99548550	-0.07129059
C	-1.22450307	0.35111103	-0.07259502
C	0.00145448	-1.72661466	-0.00008526
C	1.18654256	-1.11547370	0.06991005
C	1.23465590	0.32555398	0.07128136
O	2.24914154	1.02282067	0.13049565
O	-2.23084182	1.02369327	-0.12949564
H	-0.11441962	-2.79797863	-0.00615812
H	-2.05967165	-1.46210351	-0.11968517
H	2.12139985	-1.64759723	0.12601254
C	0.04235604	2.51826525	-0.00031636
H	0.53011892	2.82350795	0.91963161
H	0.63781434	2.82247225	-0.85483492
H	-0.97412497	2.87206353	-0.06203119

$(^2n\text{O}^+ / ^2\pi_{\text{H-1}}^+)_\text{CI}$ @ XMS-CASPT2

N	1.249876431047e-02	1.036172813072e+00	-1.228003862880e-03
N	-1.172262873489e+00	-1.019934721462e+00	-7.152047976810e-02
C	-1.271133723485e+00	3.514997369311e-01	-3.753854437246e-02
C	1.074042046935e-02	-1.719884861153e+00	-4.411437551518e-02
C	1.228075770396e+00	-1.096221656064e+00	1.111867429956e-02
C	1.289321605132e+00	3.454459636680e-01	4.486771583694e-02
O	2.285639037616e+00	1.061281999882e+00	1.019383045200e-01
O	-2.300200561562e+00	9.902786014029e-01	-3.050450422474e-02
H	-8.649894827152e-02	-2.807828076359e+00	-6.537578552152e-02
H	-2.066926176379e+00	-1.513602499338e+00	-9.865888967059e-02
H	2.164079809677e+00	-1.654778162367e+00	3.525629515753e-02
C	2.517203479016e-02	2.501770354585e+00	1.239865532153e-02
H	5.414693039967e-01	2.834785323863e+00	9.292788816264e-01
H	6.102949503760e-01	2.849878827167e+00	-8.557198778305e-01
H	-1.009648927403e+00	2.856377517688e+00	-2.322601412920e-02

$(^2n\text{O}^+ / ^2\pi_{\text{H-1}}^+)_\text{CI}$ @ CASSCF

N	0.01965622	1.02094120	-0.00056740
N	-1.17113919	-1.00027224	-0.07097703
C	-1.20998983	0.35463403	-0.07207286
C	-0.00771906	-1.72181697	-0.00047784
C	1.18443291	-1.10271972	0.06984773
C	1.20045848	0.32846625	0.06930602
O	2.24611860	1.01517762	0.12988912
O	-2.23013853	0.99984931	-0.13067323
H	-0.11429309	-2.79495715	-0.00588259
H	-2.06103006	-1.46253497	-0.11972670
H	2.11854028	-1.63554040	0.12581811
C	0.05464009	2.51218071	0.00070525
H	0.53236931	2.83026905	0.92183575
H	0.63909204	2.82926759	-0.85702620
H	-0.96188880	2.86877001	-0.06044700

Effective 3-state (${}^2\pi_{H-1}^+ / {}^2n_{O}^+ / {}^2\pi_{H^+}$) CI

N	1.265517205086e-02	1.042228571379e+00	-1.226100405991e-03
N	-1.148171422378e+00	-1.058821954800e+00	-6.998821584565e-02
C	-1.246492266722e+00	2.765862799873e-01	-1.617135878422e-01
C	8.922303526758e-02	-1.712078268991e+00	-9.183390055909e-02
C	1.270737592685e+00	-1.051110213658e+00	6.086278844183e-02
C	1.255342361348e+00	3.932186976985e-01	2.206948321904e-01
O	2.211599562237e+00	1.109208035025e+00	4.827804338228e-01
O	-2.259283232097e+00	9.367858469287e-01	-3.397636863067e-01
H	3.890625476156e-02	-2.800170771217e+00	-1.950732059745e-01
H	-2.014221570065e+00	-1.579118291918e+00	-2.125199876977e-01
H	2.230563718447e+00	-1.570204536848e+00	5.001969444840e-02
C	-5.486826417191e-02	2.512091822136e+00	-5.607833413265e-02
H	4.954963065404e-01	2.902445655577e+00	8.210385641979e-01
H	4.245438614215e-01	2.860797783417e+00	-9.936159956714e-01
H	-1.117874510380e+00	2.808844496272e+00	-4.289524426015e-02

Table S7. Cartesian coordinates (in Å) of the key structures optimised for 5-methyl-uracil.

FC @ MP2

N	-0.73042433	1.02831388	1.50040508
N	-1.11959596	-1.25083963	1.49936974
C	-1.68668649	0.01854766	1.49992376
C	0.24493500	-1.48786022	1.49935378
C	1.16162501	-0.47764858	1.49999124
C	2.64505357	-0.70274870	1.50024183
C	0.67237854	0.90503455	1.50047264
O	1.39115818	1.90590203	1.50090104
O	-2.89742344	0.22050628	1.49997039
H	0.53703822	-2.54049021	1.49893642
H	-1.10155397	1.98245134	1.50111563
H	-1.78550672	-2.02187217	1.49850342
H	2.87278305	-1.77793333	1.49850109
H	3.10290555	-0.23649919	2.38698362
H	3.10354633	-0.23347637	0.61544174

(${}^2\pi_{H^+}$)_{min} @ XMS-CASPT2

N	-0.750620641	1.062979007	1.503598236
N	-1.077481632	-1.274531801	1.499049431
C	-1.686256378	0.051152895	1.466711953
C	0.234336509	-1.527583713	1.52409379
C	1.164134366	-0.46941122	1.528604495
C	2.632846608	-0.675394426	1.549617585
C	0.651939185	0.93816044	1.510153152
O	1.387193055	1.899949692	1.502388008
O	-2.880862343	0.153530652	1.417884791
H	0.543411332	-2.577970424	1.540408847
H	-1.12631144	2.018014373	1.483718644
H	-1.765202707	-2.037519837	1.488979721

H	2.905000222	-1.738585104	1.567814923
H	3.061388959	-0.156465997	2.426555421
H	3.081990349	-0.182291951	0.667893342

$(^2\pi_{H^+})_{\min}$ @ CASSCF

N	-0.73848714	1.06613357	1.49769368
N	-1.06304621	-1.24982892	1.50172196
C	-1.65120095	0.06667795	1.50016018
C	0.20245897	-1.50522181	1.50115420
C	1.16085129	-0.44460487	1.49876514
C	2.63195349	-0.70736184	1.50003710
C	0.64791730	0.91465572	1.49738515
O	1.38481643	1.87521554	1.49615017
O	-2.83560131	0.12390878	1.50110505
H	0.50425488	-2.54405181	1.50240929
H	-1.10020657	2.00470736	1.49693174
H	-1.74346854	-2.00294266	1.50322075
H	2.84385044	-1.77239818	1.48385278
H	3.07941336	-0.26132329	2.38760243
H	3.08672709	-0.23217821	0.63192178

$(^2n_{O^+})_{\min}$ @ XMS-CASPT2

N	-0.719752688	1.049864413	1.499332011
N	-1.116870922	-1.249196922	1.50007868
C	-1.701968701	0.013050034	1.54116504
C	0.225905661	-1.4878875	1.47539416
C	1.173886569	-0.483716462	1.466588655
C	2.664667608	-0.693149902	1.444381742
C	0.622633362	0.845302577	1.485631619
O	1.3814028	1.875618663	1.489798887
O	-2.879547867	0.252975711	1.596971518
H	0.521197011	-2.541120654	1.466192831
H	-1.096551054	2.003522331	1.523800626
H	-1.77840144	-2.028507953	1.517683869
H	2.893412304	-1.769248794	1.429911397
H	3.137304163	-0.253271521	2.337508691
H	3.113527182	-0.235364171	0.548154875

$(^2n_{O^+})_{\min}$ @ CASSCF

N	-0.71274965	1.03961511	1.49933818
N	-1.10422813	-1.24680879	1.50008158
C	-1.67765138	0.01171759	1.50018827
C	0.22254807	-1.47339028	1.50017227
C	1.15465246	-0.46757678	1.50009465
C	2.64931769	-0.68628683	1.50055585
C	0.59000566	0.82082342	1.49942454
O	1.35592274	1.88116514	1.49835664
O	-2.83349734	0.24117275	1.50071347
H	0.51984145	-2.51142232	1.50072805
H	-1.08033639	1.97991686	1.49919072

H	-1.75093897	-2.01690995	1.49959852
H	2.86383832	-1.75057938	1.49224216
H	3.10546944	-0.25198293	2.38860146
H	3.10803855	-0.23806629	0.62082505

$(^2n_{O^+}/^2\pi_{H^+})_{CI}$ @ XMS-CASPT2

N	-0.708392845	1.050658708	1.50001412
N	-1.128839847	-1.247898851	1.499586016
C	-1.724103117	-0.004124406	1.453122688
C	0.222887236	-1.474668659	1.519365065
C	1.178068654	-0.48747309	1.544360211
C	2.676646059	-0.687799393	1.573810499
C	0.603034234	0.819625851	1.510968613
O	1.401432679	1.876137786	1.501612764
O	-2.882558884	0.269146302	1.401160152
H	0.519570321	-2.529775099	1.526894195
H	-1.094661892	2.00020545	1.460937045
H	-1.775786776	-2.038039489	1.471953451
H	2.913581357	-1.764259714	1.477829962
H	3.118587172	-0.334265765	2.513237789
H	3.161438338	-0.169341403	0.723995629

$(^2n_{O^+}/^2\pi_{H^+})_{CI}$ @ CASSCF

N	-0.70016013	1.03840403	1.50001500
N	-1.12859349	-1.25179607	1.49958629
C	-1.68486913	-0.01291148	1.50021800
C	0.23244258	-1.47358764	1.49922702
C	1.15359459	-0.48862115	1.49984919
C	2.65302096	-0.67769532	1.50046168
C	0.57469588	0.81275260	1.50022466
O	1.36391509	1.86465357	1.50027202
O	-2.82246459	0.29088368	1.50064392
H	0.52837767	-2.51074319	1.49899507
H	-1.08766105	1.97203444	1.49992063
H	-1.76674847	-2.02383003	1.49904169
H	2.88158475	-1.73864328	1.49685433
H	3.10572102	-0.23778385	2.38860719
H	3.10737683	-0.23172900	0.61619472

$(^2\pi_{H^{-1}}/^2n_{O^+})_{CI}$ @ XMS-CASPT2

N	-0.7509059590	1.0576904554	1.4987132250
N	-1.1988909091	-1.2159310167	1.5008882672
C	-1.6674748800	0.0131487768	1.8619540818
C	0.1378479247	-1.4552590671	1.1556460330
C	1.1154834321	-0.4958051157	1.1255304017
C	2.5653599299	-0.7854973061	0.8442838917
C	0.7461069224	0.8794327796	1.4223526114
O	1.4015924345	1.8765924116	1.6220560775
O	-2.6703570878	0.3192083227	2.4912714872
H	0.3556981919	-2.5031152871	0.9407418840

H	-1.1028851311	2.0266971409	1.6341435339
H	-1.8092460054	-2.0077511901	1.7202099208
H	2.7143286313	-1.8534265045	0.6319169021
H	3.1832723652	-0.5063440631	1.7119004253
H	2.9146296365	-0.1975709473	-0.0187847384

($^2\pi_{H-1}^+/^2n_{O^+}$)_{CI} @ CASSCF

N	-0.72083939	1.01541889	1.49875430
N	-1.12605354	-1.25149271	1.50092361
C	-1.64776604	-0.01188348	1.49999280
C	0.24929975	-1.49272791	1.50064241
C	1.16030276	-0.49803260	1.49957054
C	2.65308652	-0.69826728	1.50039418
C	0.64024968	0.85933625	1.49887539
O	1.28490807	1.92145244	1.49786404
O	-2.82257892	0.31372787	1.50027961
H	0.52475850	-2.53430222	1.50124698
H	-1.09333387	1.96483726	1.49803793
H	-1.77598050	-2.01596727	1.50168384
H	2.88523579	-1.75887395	1.48850597
H	3.09764520	-0.25111663	2.38782235
H	3.10129853	-0.23072131	0.62551745