Supporting Information for: Insights into the Deactivation of 5-Bromouracil after UV Excitation

Francesca Peccati,* Sebastian Mai,† Leticia González†

November 2, 2016

MS-CASPT2 Geometries

The following geometries of 5-bromouracil were optimized with MS-CASPT2(12,9)/ANO-RCC-VDZP. For state-averaging and multi-state treatment, four singlets or three triplets were used. The calculations were done with Molcas 8.0, using an IPEA shift of zero, an imaginary level shift of 0.3 a.u., and the Douglas-Kroll-Hess scalar-relativistic Hamiltonian.

```
12
S0 min -3017.895875
C +2.593512 -0.222280 +0.038020
N +1.817239 -1.374052 +0.106087
N +1.820018 +0.928609 +0.016124
C +0.420515 +1.060202 +0.036590
C -0.276129 -0.221097 +0.104128
C +0.445075 -1.374668 +0.137672
O +3.809942 -0.230391 +0.000890
O -0.095280 +2.172358 -0.005543
H +2.341064 +1.798650 -0.039884
H -0.025820 -2.348442 +0.187033
H +2.332546 -2.243385 +0.126974
Br -2.161345 -0.225354 +0.151685
```

```
12
T1 min -3017.786734
C +2.499331 -0.231593 -0.099666
N +1.732554 -1.384696 -0.033702
N +1.812776 +0.923500 +0.285298
C +0.421713 +1.095003 +0.189546
C -0.293909 -0.176691 +0.248591
C +0.490247 -1.379361 +0.580637
O +3.669919 -0.223411 -0.447543
O -0.075167 +2.200676 +0.072047
H +2.357644 +1.776040 +0.198077
H +0.041483 -2.325239 +0.845078
H +2.240934 -2.238646 -0.228181
Br -1.876188 -0.315430 -0.750410
```

```
12
S1 min -3017.744217
C +2.577804 -0.220493 +0.048783
N +1.822291 -1.366540 +0.125086
N +1.825424 +0.953874 +0.071580
C +0.432186 +0.959745 +0.047299
C -0.273703 -0.210910 +0.098812
C +0.423043 -1.426108 +0.144118
O +3.800354 -0.208315 -0.019216
O -0.093784 +2.211681 +0.007893
H +2.344346 +1.806094 -0.093610
H -0.040283 -2.398408 +0.190024
H +2.364984 -2.218696 +0.114489
Br -2.161324 -0.161773 +0.124516
```

```
12
S2S1 CoIn -3017.740644 & -3017.740562
C +2.602825 -0.130131 -0.010764
N +1.851709 -1.296877 +0.057084
N +1.874572 +1.013291 +0.323128
C +0.461426 +1.059319 +0.151578
C -0.230134 -0.139362 +0.238188
C +0.491333 -1.359579 +0.340157
O +3.794219 -0.138639 -0.287726
O -0.034278 +2.247471 -0.078423
H +2.364169 +1.880308 +0.128134
H +0.049789 -2.327331 +0.520621
H +2.384101 -2.143333 -0.118367
Br -2.104540 -0.178272 +0.099673
```

*Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain
†Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Währinger Straße 17, 1090 Vienna, Austria

```
12
S1S0 CoIn -3017.743518 & -3017.743082
C +1.958439 -0.237647 -0.312087
N +1.277050 -1.355149 +0.318549
N +1.567098 +0.977143 +0.166224
C +0.208320 +1.317503 +0.548945
C -0.580797 +0.130594 +0.975619
C +0.358292 -1.073708 +1.209022
O +2.867209 -0.470314 -1.077274
O -0.088772 +2.472018 +0.495973
H +2.084834 +1.758582 -0.221988
H +0.224230 -1.759596 +2.043254
H +1.715915 -2.261891 +0.157601
Br -1.400332 -0.298246 -0.731076
```

```
12
T2T1 CoIn -3017.744857 & -3017.744344
C +2.568862 -0.214887 -0.014905
N +1.815637 -1.362883 -0.028394
N +1.819151 +0.966966 +0.018139
C +0.423228 +0.988835 +0.107446
C -0.273986 -0.222422 +0.154128
C +0.423104 -1.398069 +0.160784
O +3.791323 -0.198527 -0.015069
O -0.050423 +2.138831 -0.464294
H +2.344595 +1.773021 +0.333976
H -0.024265 -2.371231 +0.303216
H +2.352454 -2.217412 -0.003093
Br -2.169208 -0.187459 +0.188062
```

```
12
S1T2 MXP -3017.739802 & -3017.740501
C +2.595622 -0.214758 +0.045562
N +1.803785 -1.362209 +0.106812
N +1.807845 +0.943051 +0.006083
C +0.437529 +0.926977 +0.041314
C -0.274910 -0.202139 +0.102601
C +0.437492 -1.429393 +0.130401
O +3.831481 -0.219290 +0.017289
O -0.071971 +2.236513 -0.004470
H +2.302539 +1.825280 -0.055395
H -0.029713 -2.401319 +0.186206
H +2.344053 -2.220627 +0.125332
Br -2.162415 -0.161934 +0.158037
```

```
12
S1 min (CBr=2.8A,CCBr=119deg) -3017.759514
C +2.575721 -0.227511 +0.048165
N +1.817604 -1.387343 +0.112008
N +1.817212 +0.929795 -0.019866
C +0.411261 +1.070983 -0.033571
C -0.238859 -0.222096 +0.039953
C +0.429163 -1.384103 +0.109457
O +3.797684 -0.232333 +0.052002
O -0.108231 +2.174423 -0.099108
H +2.353097 +1.791062 -0.068135
H -0.047182 -2.357597 +0.165717
H +2.344171 -2.248447 +0.164055
Br -3.035882 -0.333468 +0.105214
```

ADC(2) Geometries

The following geometries of 5-bromouracil were optimized with ADC(2)/def2-TZVP. The calculations were performed with Turbomole 7.0.

```
12
S0 min ADC E -2986.073995
C +2.580674 -0.222147 +0.036374
N +1.814023 -1.370339 +0.104824
N +1.817193 +0.927940 +0.005355
C +0.424728 +1.063791 +0.033616
C -0.265098 -0.223943 +0.106217
C +0.444288 -1.372420 +0.138493
O +3.794622 -0.231873 +0.007035
O -0.100238 +2.158813 -0.000869
H +2.342075 +1.794628 -0.044994
H -0.031291 -2.343330 +0.192140
H +2.332558 -2.236405 +0.129566
Br -2.132197 -0.224563 +0.152016
```

```
12
T1 boat min E -2985.966263
C +2.517907 -0.222616 -0.062806
N +1.743334 -1.374048 -0.037749
N +1.816972 +0.929301 +0.263594
C +0.424199 +1.088814 +0.135863
C -0.275374 -0.170740 +0.223166
C +0.494635 -1.396974 +0.559840
O +3.702076 -0.234652 -0.336554
O -0.076090 +2.191878 -0.030395
H +2.357507 +1.784186 +0.186052
H +0.006360 -2.354462 +0.668371
H +2.269612 -2.224523 -0.199176
Br -1.959803 -0.296013 -0.510433
```

```
12
S1 min -2985.947347
C +2.572216 -0.226718 +0.038338
N +1.821375 -1.366984 +0.116103
N +1.809927 +0.943550 +0.027503
C +0.432516 +0.923844 +0.043669
C -0.270760 -0.207235 +0.118585
C +0.432127 -1.444326 +0.203335
O +3.789193 -0.197498 -0.014156
O -0.083544 +2.232971 -0.010367
H +2.320046 +1.810850 -0.076092
H -0.032754 -2.414916 +0.111590
H +2.373857 -2.213003 +0.151728
Br -2.142862 -0.120382 +0.149536
```

```
12
S2S1 CoIn -2985.921551 & -2985.921540
C +2.534856 -0.128550 -0.115879
N +1.752915 -1.308688 -0.092509
N +1.856915 +0.963640 +0.379559
C +0.444098 +1.068760 +0.252863
C -0.245267 -0.074812 +0.302333
C +0.542989 -1.362028 +0.493095
O +3.692705 -0.143471 -0.482678
O +0.006374 +2.282223 +0.006815
H +2.364813 +1.840400 +0.328151
H +0.212766 -2.245928 +1.026727
H +2.292815 -2.147233 -0.295139
Br -1.950788 -0.257452 -0.440057
```

```
12
S0S1 CoIn -2985.945232 & -2985.945075
C +2.040450 -0.247992 -0.279204
N +1.307104 -1.332946 +0.260589
N +1.576135 +0.994624 +0.105791
C +0.257923 +1.308362 +0.525088
C -0.496458 +0.103825 +0.893587
C +0.324405 -1.102057 +1.148600
O +3.029407 -0.434097 -0.952770
O -0.142133 +2.450119 +0.472938
H +2.121877 +1.772710 -0.252260
H +0.160186 -1.794935 +1.968451
H +1.779902 -2.227570 +0.165520
Br -1.767312 -0.290752 -0.483568
```

```
12
T2T1 CoIn -2985.946820 & -2985.946713
C +2.571396 -0.222908 +0.046384
N +1.817983 -1.368897 +0.124005
N +1.815480 +0.938099 -0.042528
C +0.428195 +0.967882 +0.019720
C -0.269654 -0.192639 +0.089747
C +0.432034 -1.446513 +0.129387
O +3.789550 -0.211470 +0.047727
O -0.095210 +2.208029 -0.011072
H +2.329937 +1.807479 -0.092495
H -0.040664 -2.414863 +0.093375
H +2.371379 -2.213114 +0.185408
Br -2.129954 -0.156321 +0.150339
```

```
12
S1T2 MXP -2985.944987 & -2985.944989
C +2.570313 -0.223733 +0.041825
N +1.816065 -1.368019 +0.122823
N +1.814081 +0.942101 +0.025185
C +0.430302 +0.958256 +0.043548
C -0.268392 -0.189452 +0.134040
C +0.434873 -1.448717 +0.237373
O +3.787353 -0.212551 -0.011696
O -0.089620 +2.213654 -0.023108
H +2.323303 +1.808918 -0.087658
H -0.037603 -2.402791 +0.049902
H +2.371959 -2.212662 +0.157811
Br -2.131296 -0.144852 +0.169728
```

```
12
S1 min (CBr=2.8A,CCBr=119deg) -2985.923206
C +2.561966 -0.232482 +0.048026
N +1.800741 -1.390520 +0.110880
N +1.813216 +0.934712 -0.023850
C +0.411727 +1.109726 -0.035023
C -0.189757 -0.202767 +0.038700
C +0.423150 -1.384774 +0.110211
O +3.776457 -0.243798 +0.054817
O -0.104855 +2.203596 -0.097974
H +2.366988 +1.785882 -0.069443
H -0.089616 -2.338709 +0.166642
H +2.326591 -2.252538 +0.165033
Br -2.980848 -0.414961 +0.107873
```

MRCIS Geometries

The following geometries of 5-bromouracil were optimized with(10,8)/cc-pVDZ-DK. The calculations were performed with Columbus 7.0. The orbitals came from a SA-CASSCF(10,8)/cc-pVDZ-DK calculation, averaging over four singlets and three triplets simultaneously. For the MRCI, the CAS(10,8) reference space was restricted to have at most two electrons in the three antibonding orbitals. 22 inner core orbitals were kept frozen in the MRCI step.

```
12
S0 min -3016.549508
C +2.574450 -0.219017 +0.036389
N +1.825363 -1.365782 +0.104347
N +1.828072 +0.929069 +0.005037
C +0.432268 +1.060167 +0.033578
C -0.264690 -0.224419 +0.106225
C +0.445286 -1.374716 +0.138568
O +3.766419 -0.227452 +0.007540
O -0.086893 +2.144120 -0.000555
H +2.351888 +1.781537 -0.044666
H -0.025482 -2.345242 +0.192082
H +2.341601 -2.219713 +0.128623
Br -2.166946 -0.218400 +0.152605
```

```
12
T1 min -3016.434611
C +2.533945 -0.225142 +0.035106
N +1.778337 -1.381540 +0.093391
N +1.801300 +0.914151 -0.223077
C +0.431107 +1.047647 +0.096186
C -0.286127 -0.203179 -0.000197
C +0.493219 -1.399435 -0.425470
O +3.713832 -0.225649 +0.183786
O -0.039142 +2.122535 +0.402020
H +2.334410 +1.760420 -0.157414
H +0.023502 -2.354227 -0.594668
H +2.316022 -2.221258 +0.176555
Br -1.889308 -0.408809 +0.963251
```

```
12
S1 min -3016.395668
C +2.569456 -0.225511 +0.035906
N +1.838669 -1.368012 +0.092070
N +1.822056 +0.938395 +0.011582
C +0.429273 +0.959343 +0.036300
C -0.269690 -0.210921 +0.090434
C +0.431750 -1.431660 +0.118589
O +3.762330 -0.195535 +0.008868
O -0.072698 +2.186075 +0.002519
H +2.342432 +1.789828 -0.036626
H -0.032394 -2.399892 +0.166972
H +2.378557 -2.207030 +0.109257
Br -2.178674 -0.173655 +0.125850
```

```
12
S2S1 CoIn -3016.365491 & -3016.365381
C +2.418778 -0.150099 +0.175104
N +1.613358 -1.290422 +0.155870
N +1.805746 +0.955506 -0.359270
C +0.397626 +1.114095 -0.246975
C -0.345117 -0.045038 -0.438495
C +0.456572 -1.300023 -0.548679
O +3.535827 -0.184035 +0.578735
O -0.015384 +2.266854 +0.034734
H +2.347690 +1.795356 -0.284497
H +0.032114 -2.246732 -0.846848
H +2.068746 -2.128093 +0.468190
Br -2.002719 -0.263886 +0.539666
```

```
12
S1T2 MXP -3016.392558 & -3016.392484
C +2.542485 -0.235116 +0.010844
N +1.807318 -1.365588 +0.078632
N +1.802180 +0.950274 -0.064450
C +0.427783 +0.948053 +0.150295
C -0.271978 -0.203843 +0.335231
C +0.406145 -1.398965 +0.316927
O +3.734190 -0.194134 -0.000419
O -0.031678 +2.214691 +0.073622
H +2.339464 +1.760556 +0.178062
H -0.050863 -2.364610 +0.442677
H +2.344631 -2.199227 +0.188270
Br -2.179136 -0.087942 +0.565407
```

```
12
T2T1 CoIn -3016.401632 & -3016.401202
C +2.546912 -0.231906 +0.024953
N +1.805390 -1.366340 +0.096412
N +1.815148 +0.945626 -0.058553
C +0.434141 +0.974150 +0.161032
C -0.271373 -0.190532 +0.326630
C +0.405801 -1.398699 +0.302479
O +3.739788 -0.212503 +0.012938
O -0.072236 +2.205454 +0.119208
H +2.357057 +1.769495 +0.110923
H -0.060963 -2.360451 +0.419981
H +2.340130 -2.202139 +0.202113
Br -2.169255 -0.108008 +0.556983
```

1 Other Geometries

This geometry was reported by Kobylecka et al.[1] as the S_0 minimum of 5-bromouracil. It was computed at the CASSCF(12,10)/6-311G* level of theory, using a non-relativistic Hamiltonian.

```
12
Kobylecka CASSCF(12,10)/6-311G*
C +0.000000 +0.000000 +0.000000
N +0.000000 +0.000000 +1.393026
N +1.280253 +0.000000 -0.530377
C +2.520387 +0.000000 +0.139797
C +2.367687 +0.000000 +1.601476
C +1.140042 +0.000000 +2.158851
O -1.012793 +0.000000 -0.659778
O +3.558429 +0.000000 -0.477993
H +1.331866 +0.000000 -1.540858
H +0.988397 +0.000000 +3.230359
H -0.911372 +0.000000 +1.824706
Br +3.934298 +0.000000 +2.662710
```

This geometry was optimized at the MP2/ANO-RCC-VDZP level of theory, using Gaussian 09. The corresponding frequency calculation was employed for the generation of the initial conditions for the dynamics simulations.

```
12
Kobylecka CASSCF(12,10)/6-311G*
C +0.000000 +0.000000 +0.000000
N +0.000000 +0.000000 +1.393026
N +1.280253 +0.000000 -0.530377
C +2.520387 +0.000000 +0.139797
C +2.367687 +0.000000 +1.601476
C +1.140042 +0.000000 +2.158851
O -1.012793 +0.000000 -0.659778
O +3.558429 +0.000000 -0.477993
H +1.331866 +0.000000 -1.540858
H +0.988397 +0.000000 +3.230359
H -0.911372 +0.000000 +1.824706
Br +3.934298 +0.000000 +2.662710
```

Supplementary References

[1] Kobyłecka M, Migani A, Asturiol D, Rak J, Blancafort L, 2009. Benign decay vs. photolysis in the photophysics and photochemistry of 5-bromouracil. A computational study, *J. Phys. Chem. A* **113**, 5489–5495, doi:10.1021/jp811330v.