Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Ab Initio Molecular Dynamics Relaxation and Intersystem Crossing Mechanisms of 5-Azacytosine

Antonio Carlos Borin*[1], Sebastian Mai†[2], Philipp Marquetand‡[2] and Leticia González§[2]

[1]Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo, NAP-PhotoTech the USP Consortium for Photochemical Technology, Av. Prof. Lineu Prestes 748, 05508-000, São Paulo, SP, Brazil.
[2]Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Währinger Straße 17, 1090 Vienna, Austria.

Cartesian coordinates of the optimized points

Optimized with MRCIS

Stationary points, conical intersections, and intersystem crossing were optimized at the MRCIS level of theory and the def2-SVP basis sets, with a CAS(6,5) reference space (MRCIS(6,5)) based on a SA($3S+2T$)-CASSCF(12,9) orbitals (averaging over 3 singlet and 2 triplet states in a single CASSCF (complete-active-space self-consisent-field) calculation). All geometries are given in `.xyz` format in Å.

```
12
S0 minimum
C +0.935445 +0.841721 -0.001999
C -0.259672 -1.102571 +0.004465
C -1.447353 +0.785618 +0.004022
N -0.308212 +1.490692 +0.000655
N +0.882127 -0.506338 +0.000772
N -0.294771 -2.443873 +0.006775
N -1.464034 -0.502014 +0.006118
O +1.967265 +1.522002 -0.006279
H -2.378925 +1.340745 +0.005207
H -0.310211 +2.491343 -0.001789
H -1.174328 -2.910534 +0.011478
H +0.559062 -2.957426 +0.007013
```

```
12
S1 minimum (1pipi*)
C +0.888321 +0.806950 -0.002767
C -0.382071 -1.127271 +0.038820
C -1.480746 +0.839174 +0.146849
N -0.283220 +1.508776 -0.059506
N +0.900226 -0.499149 +0.097660
N -0.272204 -2.469598 -0.099260
N -1.480895 -0.527572 +0.105429
O +1.971923 +1.509660 -0.033796
H -2.398527 +1.390555 +0.023599
H -0.236615 +2.504992 -0.119700
H -1.106896 -3.006082 +0.010234
H +0.591971 -2.889991 +0.167944
```

*ancborin@iq.usp.br
†sebastian.mai@univie.ac.at
‡philipp.marquetand@univie.ac.at
§leticia.gonzalez@univie.ac.at

```
12
S1 minimum (1nNpi*)
C +0.985426 +0.975323 +0.010694
C -0.359534 -1.186024 -0.032026
C -1.476407 +0.818969 -0.041707
N -0.252591 +1.535524 +0.129648
N +0.795914 -0.437992 -0.083996
N -0.261498 -2.549538 -0.109657
N -1.508079 -0.540602 +0.015567
O +2.012486 +1.500370 -0.002114
H -2.380871 +1.376642 +0.137375
H -0.263362 +2.535056 +0.105821
H -1.129373 -3.013292 +0.075326
H +0.518963 -2.959317 +0.365695
12
T1 minimum (3pipi*)
C +0.908597 +0.847181 -0.126423
C -0.382193 -1.116004 +0.084433
C -1.467825 +0.824700 +0.188750
N -0.281332 +1.513514 -0.020862
N +0.827873 -0.432704 +0.422884
N -0.209206 -2.437500 -0.195006
N -1.470303 -0.513210 +0.111145
O +1.947708 +1.347450 -0.560532
H -2.384171 +1.390094 +0.183783
H -0.293056 +2.473580 -0.304696
H -1.062628 -2.950737 -0.291242
H +0.510919 -2.906703 +0.317099
12
S1/S2 CoIn (1nNpi*/1pipi*)
C +0.920616 +0.847720 +0.007961
C -0.375374 -1.146254 -0.002914
C -1.476037 +0.833959 +0.003368
N -0.276428 +1.530804 +0.001358
N +0.874679 -0.481430 -0.010991
N -0.263682 -2.494591 -0.049014
N -1.458741 -0.525862 +0.011950
O +1.993424 +1.511635 +0.026444
H -2.401093 +1.382326 +0.041282
H -0.242587 +2.528570 +0.037237
H -1.093772 -3.018975 +0.132242
H +0.606153 -2.894623 +0.232122
12
S0/S1 CoIn (S1/S0 alpha, constrained)
C +0.819814 +0.748009 +0.028823
C -0.469709 -1.117660 +0.158940
C -1.418858 +0.845663 +0.411795
N -0.282422 +1.463784 -0.201019
N +0.826739 -0.448870 +0.499174
N -0.184049 -2.394045 -0.196014
N -1.547468 -0.548136 +0.054648
O +2.041383 +1.482926 -0.143426
H -2.323006 +1.434335 +0.361833
H -0.289012 +2.268915 -0.794959
H -0.966316 -2.974406 -0.417493
H +0.596883 -2.830119 +0.245081
12
S0/S1 CoIn (S1/S0 beta)
C +0.900545 +0.915413 +0.064447
C -0.282804 -1.155864 -0.021627
C -1.454827 +0.837135 -0.236618
N -0.326306 +1.543304 +0.220173
N +0.860289 -0.507045 +0.076258
N -0.310431 -2.512833 -0.165470
N -1.407775 -0.473385 +0.297333
O +1.913163 +1.497934 -0.039179
H -1.716688 +0.906247 -1.292806
H -0.289273 +2.535709 +0.087884
H -1.145381 -2.954873 +0.163311
H +0.534344 -2.976129 +0.105852
12
S0/S1 CoIn (S1/S0 gamma)
C +0.919362 +0.786405 -0.092269
C -0.444676 -1.126179 +0.124366
C -1.364245 +0.793618 +0.390769
N -0.244595 +1.478185 -0.160461
N +0.592324 -0.360209 +0.698127
N -0.159891 -2.385431 -0.305237
N -1.603878 -0.539399 +0.073620
O +1.965776 +1.028270 -0.555680
H -2.193153 +1.410465 +0.707782
H -0.349093 +2.216735 -0.829783
H -0.958661 -2.937492 -0.546899
H +0.557719 -2.878071 +0.186313
12
S1/T2 MECP (1nNpi*/3pipi)
C +0.979224 +0.968209 +0.009833
C -0.357074 -1.180962 -0.029498
C -1.478427 +0.822270 -0.040564
N -0.256088 +1.534497 +0.125427
N +0.820913 -0.453424 -0.074748
N -0.263983 -2.543850 -0.117765
N -1.508411 -0.541871 +0.019100
O +2.003727 +1.499552 -0.007853
H -2.383365 +1.378790 +0.139615
H -0.266534 +2.533528 +0.095107
H -1.130889 -3.009869 +0.066076
H +0.521595 -2.957183 +0.345752
```

Optimized with MS-CASPT2

These CoIns were optimized at the MS-CASPT2[1] level of theory with numerical gradients, the algo-rithm of Levine et al.,[2] and the ORCA optimizer.[3] The calculations employed orbitals from an SA(4S)-CASSCF(14,10)/ANO-L-VDZP calculation with Cholesky decomposition and a non-relativistic Hamiltonian; in the MS-CASPT2 step, all four roots were included, the IPEA shift[4] was set to zero, and an imaginary shift[5] of 0.2 a.u. was applied. For S_1/S_0 (α), the C_2=O bond length was constrained to 1.44Å in order to avoid convergence to the S_1/S_0 (γ) CoIn. All geometries are given in `.xyz` format in Å.

```
12
S0/S1 CoIn (S1/S0 alpha, constrained)
C +0.766409 +0.747264 +0.074537
C -0.410056 -1.116020 +0.143600
C -1.439537 +0.875230 +0.467270
N -0.291310 +1.449070 -0.307190
N +0.882807 -0.452253 +0.462587
N -0.176420 -2.429092 -0.233676
N -1.546309 -0.543555 +0.088506
O +1.983034 +1.505158 -0.011629
H -2.345421 +1.454896 +0.254642
H -0.231722 +2.428132 -0.579970
H -1.049881 -2.961368 -0.269825
H +0.546666 -2.875023 +0.334437
```

```
12
S0/S1 CoIn (S0/S1 beta)
C +0.913226 +0.921870 +0.139561
C -0.298461 -1.121526 +0.134020
C -1.468952 +0.807904 -0.185833
N -0.319441 +1.578493 +0.125768
N +0.880603 -0.502382 +0.257864
N -0.343936 -2.430941 -0.186336
N -1.421387 -0.456619 +0.549557
O +1.985092 +1.507978 +0.078956
H -1.726468 +0.690351 -1.251133
H -0.274255 +2.537666 -0.229991
H -1.197720 -2.945277 +0.027399
H +0.546552 -2.931905 -0.200272
```

```
12
S0/S1 CoIn (S0/S1 gamma)
C +0.903770 +0.744051 -0.122225
C -0.461030 -1.140762 +0.197079
C -1.359583 +0.837783 +0.514785
N -0.250975 +1.485721 -0.099121
N +0.625469 -0.349042 +0.793614
N -0.121901 -2.359588 -0.334138
N -1.611289 -0.569215 +0.158352
O +1.960637 +0.910303 -0.701197
H -2.255417 +1.460284 +0.475035
H -0.372098 +2.269522 -0.741247
H -0.924150 -2.917867 -0.634027
H +0.583556 -2.884294 +0.183738
```

Conical intersections

In Figure S1 we show the structures of the S_1/S_0 conical intersections (CoIns) of 5AC. The CoIns in (a) – (c) were optimized with the MS-CASPT2 method in order to improve upon the results from Giussani et al.,[6] which were optimized with the SS-CASPT2//CASSCF method. The reoptimizations at the MS-CASPT2 level was necessary, because SS-CASPT2 does not predict the correct topology of conical intersections.[7] The CoIns in (d) – (f) were optimized with the MRCIS method specified in the main manuscript.

The MS-CASPT2 optimizations showed that S_1/S_0 (α) is actually not a minimum on the S_1/S_0 intersection seam, as previously reported by Giussani et al.[6] Instead, on both MS-CASPT2 and MRCIS levels the optimization of S_1/S_0 (α)—characterized by a very long C_2=O bond—leads to S_1/S_0 (γ). Hence, the structures of S_1/S_0 (α) shown in Figure S1 (a) and (d) could only be obtained with optimizations under a constrained C_2=O bond length.

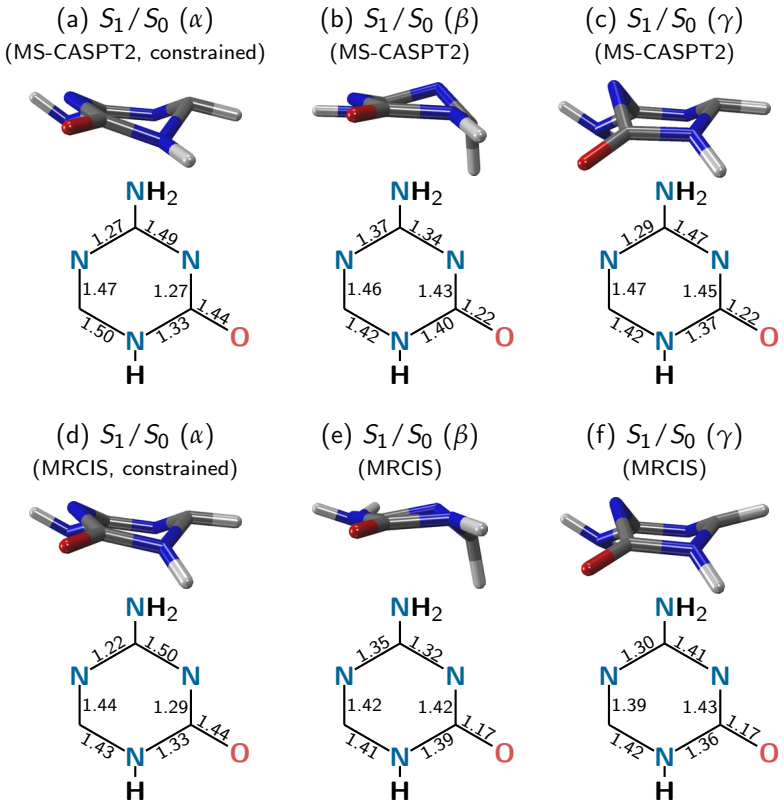

Figure S1: Depictions of the conical intersection geometries of 5AC. The CoIns α, β, and γ in the top row were obtained with MS-CASPT2 optimizations, whereas the bottom row was optimized with MRCIS. Note that the α CoIns (panels (a) and (d)) are not real minima on the intersection seam, but were obtained by constraining the C=O bond length.

Supplementary References

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