# Supplementary Materials: The Thermodynamic and Kinetic Properties of 2-Hydroxypyridine/ 2-Pyridone Tautomerization: A Theoretical and Computational Revisit

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**Table S1.** Standard orientation of 2-hydroxypyridine (2-HPY) calculated by using CAM-B3LYP/ aug-cc-pvdz level of theory.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | *X* | *Y* | *Z* |
| 1 | 6 | 0 | −1.003643 | −1.231244 | 0.000058 |
| 2 | 6 | 0 | 0.904003 | 0.030899 | −0.000008 |
| 3 | 6 | 0 | 0.186126 | 1.237950 | −0.000042 |
| 4 | 6 | 0 | −1.201170 | 1.156316 | −0.000007 |
| 5 | 6 | 0 | −1.819476 | −0.102518 | 0.000050 |
| 6 | 1 | 0 | −1.437416 | −2.233442 | 0.000105 |
| 7 | 1 | 0 | 0.716025 | 2.188796 | −0.000091 |
| 8 | 1 | 0 | −1.800651 | 2.067596 | −0.000023 |
| 9 | 1 | 0 | −2.903707 | −0.203699 | 0.000081 |
| 10 | 7 | 0 | 0.338955 | −1.173142 | 0.000033 |
| 11 | 8 | 0 | 2.260559 | 0.084668 | −0.000070 |
| 12 | 1 | 0 | 2.573552 | −0.833016 | −0.000054 |

**Table S2.** Standard orientation of 2-pyridone (2-PY) calculated by using CAM-B3LYP/aug-cc-pvdz level of theory.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | *X* | *Y* | *Z* |
| 1 | 6 | 0 | −1.059541 | −1.191802 | 0.000000 |
| 2 | 6 | 0 | 1.064458 | 0.063913 | −0.000001 |
| 3 | 6 | 0 | 0.249231 | 1.266037 | 0.000000 |
| 4 | 6 | 0 | −1.118464 | 1.203656 | 0.000000 |
| 5 | 6 | 0 | −1.807288 | −0.048084 | 0.000000 |
| 6 | 1 | 0 | −1.493091 | −2.190520 | 0.000001 |
| 7 | 1 | 0 | 0.784351 | 2.213949 | 0.000000 |
| 8 | 1 | 0 | −1.699035 | 2.128112 | 0.000001 |
| 9 | 1 | 0 | −2.892873 | −0.101857 | 0.000001 |
| 10 | 7 | 0 | 0.303930 | −1.124328 | 0.000000 |
| 11 | 8 | 0 | 2.293296 | 0.004077 | 0.000000 |
| 12 | 1 | 0 | 0.856392 | −1.974323 | 0.000000 |

**Table S3.** Standard orientation of pyridine (PY) calculated by using CAM-B3LYP/aug-cc-pvdz level of theory.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | *X* | *Y* | *Z* |
| 1 | 6 | 0 | 1.231090 | −0.557746 | −0.000046 |
| 2 | 6 | 0 | −1.025456 | −0.867754 | 0.000023 |
| 3 | 6 | 0 | −1.282063 | 0.507596 | 0.000055 |
| 4 | 6 | 0 | −0.190954 | 1.357671 | 0.000019 |
| 5 | 6 | 0 | 1.100074 | 0.821991 | −0.000037 |
| 6 | 1 | 0 | 2.217440 | −1.024352 | −0.000092 |
| 7 | 1 | 0 | −2.307722 | 0.869475 | 0.000103 |
| 8 | 1 | 0 | −0.341407 | 2.437261 | 0.000035 |
| 9 | 1 | 0 | 1.980886 | 1.460596 | −0.000069 |
| 10 | 7 | 0 | 0.187293 | −1.395952 | −0.000019 |
| 11 | 1 | 0 | −1.856403 | −1.541865 | 0.000069 |

**Table S4.** Some selected bond lengths (Å), bond angles and dihedral angles (degrees) of the optimized structures of 2-pyridone (2-PY) (top 11 lines) and 2-Hydroxypyridine (2-HPY) (bottom 11 lines) which have estimated by using different methods with 6-311++G** and aug-cc-pvdz basis sets. The crystal structure of 2-Pyridone and the microwave-normalized structure of 2-HPY are listed for comparison purposes.

| Parameter | | C2O11 | N10C2 | C2C3 | N10C1 | O11C2C3 | N10C2C3 | C2C3C4 | O11C2C3C4 | O11C2N10C1 | N10C2C3C4 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| B3LYP | 6-311++G** | 1.223 | 1.411 | 1.451 | 1.364 | 127.0 | 113.0 | 121.6 | −180.0 | 180.0 | 0.0 |
| | Aug-cc-pvdz | 1.230 | 1.411 | 1.452 | 1.365 | 126.9 | 113.2 | 121.5 | −180.0 | 180.0 | 0.00 |
| CAM-B3LYP | 6-311++G** | 1.220 | 1.399 | 1.449 | 1.362 | 126.6 | 113.3 | 121.5 | −180.0 | 180.0 | 0.00 |
| | Aug-cc-pvdz | 1.225 | 1.399 | 1.450 | 1.363 | 126.6 | 113.5 | 121.4 | −180.0 | 180.0 | 0.00 |
| WB97XD | 6-311++G** | 1.220 | 1.401 | 1.451 | 1.361 | 126.7 | 113.2 | 121.5 | −180.0 | 180.0 | 0.00 |
| | Aug-cc-pvdz | 1.220 | 1.397 | 1.448 | 1.357 | 126.7 | 113.2 | 121.5 | −180.0 | 180.0 | 0.00 |
| M062X | 6-311++G** | 1.220 | 1.402 | 1.453 | 1.362 | 126.7 | 113.1 | 121.5 | −180.0 | 180.0 | 0.00 |
| | Aug-cc-pvdz | 1.220 | 1.398 | 1.449 | 1.358 | 126.7 | 113.2 | 121.4 | −180.0 | 180.0 | 0.00 |
| CCSD | 6-311++G** | 1.221 | 1.399 | 1.465 | 1.375 | 126.0 | 113.4 | 121.5 | −180.0 | 180.0 | 0.00 |
| | Aug-cc-pvdz | 1.232 | 1.403 | 1.463 | 1.379 | 126.0 | 113.6 | 121.4 | −180.0 | 180.0 | 0.00 |
| Experimental [a] | | 1.252 | 1.379 | 1.437 | 1.362 | 124.8 | 115.0 | 121.1 | −177.6 | 177.7 | 2.1 |
| B3LYP | 6-311++G** | 1.354 | 1.326 | 1.401 | 1.341 | 118.5 | 124.0 | 117.4 | −180.0 | 180.0 | 0.0 |
| | Aug-cc-pvdz | 1.353 | 1.323 | 1.397 | 1.338 | 118.6 | 123.9 | 117.5 | −180.0 | 180.0 | 0.00 |
| CAM-B3LYP | 6-311++G** | 1.348 | 1.319 | 1.395 | 1.336 | 118.5 | 124.0 | 117.4 | −180.0 | 180.0 | 0.00 |
| | Aug-cc-pvdz | 1.351 | 1.323 | 1.399 | 1.339 | 118.5 | 124.1 | 117.4 | −180.0 | 180.0 | 0.00 |
| WB97XD | 6-311++G** | 1.346 | 1.322 | 1.398 | 1.337 | 118.5 | 124.1 | 117.4 | −180.0 | 180.0 | 0.00 |
| | Aug-cc-pvdz | 1.350 | 1.326 | 1.401 | 1.340 | 118.4 | 124.2 | 117.3 | −180.0 | 180.0 | 0.00 |
| M062X | 6-311++G** | 1.348 | 1.321 | 1.399 | 1.338 | 118.3 | 124.2 | 117.4 | −180.0 | 180.0 | 0.00 |
| | Aug-cc-pvdz | 1.351 | 1.324 | 1.402 | 1.340 | 118.2 | 124.3 | 117.3 | −180.0 | 180.0 | 0.00 |
| CCSD | 6-311++G** | 1.354 | 1.325 | 1.407 | 1.348 | 118.0 | 124.5 | 117.3 | −180.0 | 180.0 | 0.00 |
| | Aug-cc-pvdz | 1.364 | 1.333 | 1.413 | 1.355 | 118.0 | 124.6 | 117.3 | −180.0 | 180.0 | 0.00 |
| Normalized [b] | | 1.336 | 1.320 | 1.41 | 1.34 | 118 | 124.1 | 117.5 | - | - | - |

[a] Taken from Reference [2]; [b] Taken from Reference [7].

**Table S5.** Standard orientation of the transition state (T.S.) calculated by using B3LYP/6-311++G** level of theory.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | *X* | *Y* | *Z* |
| 1 | 6 | 0 | 0.894017 | −1.288327 | 0.000014 |
| 2 | 6 | 0 | −0.959359 | 0.205596 | −0.000009 |
| 3 | 6 | 0 | −0.112054 | 1.335076 | −0.000007 |
| 4 | 6 | 0 | 1.252633 | 1.090093 | 0.000005 |
| 5 | 6 | 0 | 1.778009 | −0.219808 | 0.000016 |
| 6 | 1 | 0 | 1.214283 | −2.325567 | 0.000022 |
| 7 | 1 | 0 | −0.525865 | 2.336249 | −0.000016 |
| 8 | 1 | 0 | 1.939885 | 1.932583 | 0.000007 |
| 9 | 1 | 0 | 2.847723 | −0.393839 | 0.000026 |
| 10 | 8 | 0 | −2.238063 | 0.037676 | −0.000020 |
| 11 | 1 | 0 | −1.714105 | −1.235007 | −0.000009 |
| 12 | 7 | 0 | −0.425270 | −1.050229 | 0.000002 |

**Table S6.** Imaginary frequencies (negative Signs) Harmonic frequencies ($cm^{-1}$), IR intensities (km/Mole), Reduced masses (amu), force constants (mDyne/Å), and normal coordinates calculated for the transition state (T.S.) by using B3LYP/6-311++G** level of theory.

| **Imaginary Freq.** | −1889.5981 | | | |
|---|---|---|---|---|
| **Reduced Masses** | 1.0705 | | | |
| **Force Constants** | 2.2521 | | | |
| **IR Intensities** | 580.9988 | | | |
| **Atom Number** | **Mass Number** | *X* | *Y* | *Z* |
| 1 | 6 | 0.00 | −0.01 | 0.00 |
| 2 | 6 | −0.05 | 0.01 | 0.00 |
| 3 | 6 | 0.01 | 0.00 | 0.00 |
| 4 | 6 | −0.01 | 0.00 | 0.00 |
| 5 | 6 | −0.01 | −0.01 | 0.00 |
| 6 | 1 | 0.00 | −0.01 | 0.00 |
| 7 | 1 | 0.00 | 0.00 | 0.00 |
| 8 | 1 | 0.00 | 0.00 | 0.00 |
| 9 | 1 | −0.01 | −0.01 | 0.00 |
| 10 | 8 | 0.01 | 0.04 | 0.00 |
| 11 | 1 | 0.80 | −0.59 | 0.00 |
| 12 | 7 | −0.02 | 0.00 | 0.00 |

**Table S7.** Standard orientation of the transition state (T.S.) of the double proton shifts between a mixed dimer tautomerization of 2-HPY↔2-PY using B3LYP/6-311++G** level of theory.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | *X* | *Y* | *Z* |
| 1 | 6 | 0 | 2.016618 | −1.540155 | −0.000186 |
| 2 | 6 | 0 | 3.392801 | −1.551071 | 0.000391 |
| 3 | 6 | 0 | 4.058686 | −0.303647 | 0.000714 |
| 4 | 6 | 0 | 3.337370 | 0.866023 | 0.000434 |
| 5 | 6 | 0 | 1.910516 | 0.837407 | −0.000207 |
| 6 | 1 | 0 | 1.443911 | −2.460302 | −0.000423 |
| 7 | 1 | 0 | 3.938541 | −2.483769 | 0.000607 |
| 8 | 1 | 0 | 5.142238 | −0.271514 | 0.001186 |
| 9 | 1 | 0 | 3.807521 | 1.838608 | 0.000673 |
| 10 | 7 | 0 | 1.293419 | −0.389741 | −0.000491 |
| 11 | 8 | 0 | 1.221139 | 1.938550 | −0.000529 |
| 12 | 1 | 0 | −0.000043 | −0.416342 | −0.000651 |
| 13 | 6 | 0 | −4.058719 | −0.303515 | 0.000683 |
| 14 | 6 | 0 | −3.337346 | 0.866106 | 0.000410 |
| 15 | 6 | 0 | −1.910460 | 0.837458 | −0.000216 |
| 16 | 6 | 0 | −2.016735 | −1.540155 | −0.000202 |
| 17 | 1 | 0 | −5.142272 | −0.271322 | 0.001144 |
| 18 | 1 | 0 | −3.807455 | 1.838713 | 0.000643 |
| 19 | 1 | 0 | 0.000431 | 1.905944 | −0.001177 |
| 20 | 8 | 0 | −1.220960 | 1.938448 | −0.000518 |
| 21 | 7 | 0 | −1.293476 | −0.389794 | −0.000489 |
| 22 | 6 | 0 | −3.392914 | −1.550992 | 0.000364 |
| 23 | 1 | 0 | −3.938712 | −2.483656 | 0.000567 |
| 24 | 1 | 0 | −1.444093 | −2.460346 | −0.000441 |

**Table S8.** Imaginary frequencies (negative Signs) Harmonic frequencies ($cm^{-1}$), IR intensities (km/Mole), Reduced masses (amu), force constants (mDyne/Å), and normal coordinates calculated for the transition state (T.S.) of the double proton shifts between a mixed dimer tautomerization of 2-HPY↔2-PY using B3LYP/6-311++G** level of theory.

| **Imaginary Frequency** | −1310.7244 | | | |
|---|---|---|---|---|
| **Reduced Masses** | 1.0771 | | | |
| **Force Constants** | 1.0903 | | | |
| **IR Intensity** | 500.4067 | | | |
| **Atom Number** | **Mass Number** | ***X*** | ***Y*** | ***Z*** |
| 1 | 6 | 0.00 | −0.02 | 0.00 |
| 2 | 6 | −0.01 | 0.00 | 0.00 |
| 3 | 6 | 0.00 | 0.01 | 0.00 |
| 4 | 6 | 0.01 | −0.01 | 0.00 |
| 5 | 6 | −0.01 | 0.04 | 0.00 |
| 6 | 1 | −0.01 | 0.00 | 0.00 |
| 7 | 1 | −0.01 | 0.00 | 0.00 |
| 8 | 1 | 0.00 | 0.00 | 0.00 |
| 9 | 1 | −0.01 | 0.00 | 0.00 |
| 10 | 7 | −0.01 | 0.00 | 0.00 |
| 11 | 8 | 0.01 | −0.02 | 0.00 |
| 12 | 1 | 0.83 | 0.00 | 0.00 |
| 13 | 6 | 0.00 | −0.01 | 0.00 |
| 14 | 6 | 0.01 | 0.01 | 0.00 |
| 15 | 6 | −0.01 | −0.04 | 0.00 |
| 16 | 6 | 0.00 | 0.02 | 0.00 |
| 17 | 1 | 0.00 | 0.00 | 0.00 |
| 18 | 1 | −0.01 | 0.00 | 0.00 |
| 19 | 1 | −0.55 | 0.00 | 0.00 |
| 20 | 8 | 0.01 | 0.02 | 0.00 |
| 21 | 7 | −0.01 | 0.00 | 0.00 |
| 22 | 6 | −0.01 | 0.00 | 0.00 |
| 23 | 1 | −0.01 | 0.00 | 0.00 |
| 24 | 1 | −0.01 | 0.00 | 0.00 |

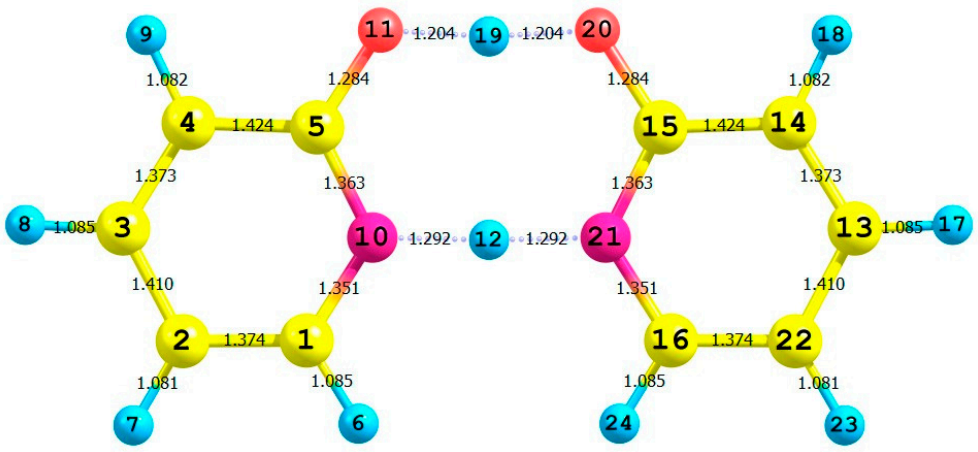


**Figure S1.** The structure of the Transition State for the double proton shifts between a mixed dimer tautomerization of 2-HPY↔2-PY using B3LYP/6-311++G** level of theory. The color scheme is pink: nitrogen; yellow: carbon; blue: hydrogen; and red: oxygen.