

## Supporting Information

### **Rearrangement and Hydrogen Scrambling Pathways of the Toluene Radical Cation: A Computational Study**

by

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| Pages S3–S12 | xyz-matrices for the BHandHLYP optimized stationary points.                                               |

Note that the 6-311+G(d,p) basis set has been used throughout.

**Table S1.** Absolute BHandHLYP SCF and CCSD(T) energies, in Hartree, of the BHandHLYP optimized stationary points. BHandHLYP thermal corrections to Gibbs energy at 298.15 K and 1.0 atm. The 6-311+G(d,p) basis set was used throughout.

| <b><i>Stationary point</i></b> | <b><i>BHandHLYP SCF</i></b> | <b><i>CCSD(T)</i></b> | <b><i>Gibbs correction</i></b> |
|--------------------------------|-----------------------------|-----------------------|--------------------------------|
| <b>1</b>                       | -271.146833474              | -270.5553030          | 0.098290                       |
| <b>2</b>                       | -271.087391002              | -270.4997225          | 0.096499                       |
| <b>3</b>                       | -271.112638569              | -270.5276239          | 0.102154                       |
| <b>4</b>                       | -271.121594519              | -270.5278075          | 0.101102                       |
| <b>5</b>                       | -271.134169009              | -270.5412309          | 0.100085                       |
| <b>6</b>                       | -271.058559235              | -270.4762396          | 0.099669                       |
| <b>5m</b>                      | -271.110704901              | -270.5177450          | 0.097968                       |
| <b>5p</b>                      | -271.129374693              | -270.5373726          | 0.099573                       |
| <b>TS12</b>                    | -271.079744712              | -270.4912970          | 0.095900                       |
| <b>TS23</b>                    | -271.086100433              | -270.4985521          | 0.098300                       |
| <b>TS34</b>                    | -271.095962509              | -270.5127949          | 0.100460                       |
| <b>TS22</b>                    | -271.086241027              | -270.4984898          | 0.097051                       |
| <b>TS33</b>                    | -271.061592274              | -270.4825891          | 0.100014                       |
| <b>TS4[1,2]</b>                | -271.076298167              | -270.4848364          | 0.096596                       |
| <b>TS4[1,5]</b>                | -271.037060334              | -270.4612942          | 0.095941                       |
| <b>TS15</b>                    | -271.025413838              | -270.4428624          | 0.095384                       |
| <b>TS25</b>                    | -271.082510881              | -270.4951368          | 0.095772                       |
| <b>TS53</b>                    | -271.016388695              | -270.4344656          | 0.095141                       |
| <b>TS56</b>                    | -271.058447965              | -270.4761508          | 0.099274                       |
| <b>TS64</b>                    | -271.020072101              | -270.4387671          | 0.097006                       |
| <b>TS55m</b>                   | -271.096764272              | -270.5070599          | 0.096558                       |
| <b>TS5m5p</b>                  | -271.095014663              | -270.5056957          | 0.096535                       |

# xyz-matrices for the BHandHLYP/6-311+G(d,p) optimized stationary points

1

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.009522  | -0.012865 | 0.001937  |
| c | 0.014989  | 0.011100  | 1.417190  |
| c | 1.187469  | -0.030061 | -0.670526 |
| c | 2.426034  | -0.026725 | 0.042999  |
| c | 2.408339  | -0.000016 | 1.472719  |
| c | 1.229423  | 0.017214  | 2.143416  |
| c | 3.705677  | -0.016326 | -0.684539 |
| h | 4.501782  | -0.482919 | -0.115999 |
| h | 3.623250  | -0.468513 | -1.665631 |
| h | 3.997224  | 1.028791  | -0.837815 |
| h | 3.345541  | 0.003107  | 2.001360  |
| h | 1.204098  | 0.034287  | 3.218329  |
| h | -0.920794 | 0.025698  | 1.949979  |
| h | -0.928394 | -0.018272 | -0.524089 |
| h | 1.210248  | -0.049463 | -1.746066 |

2

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.008516  | 0.030639  | 0.028326  |
| c | -0.013671 | -0.048708 | 1.514784  |
| c | 1.279543  | -0.026728 | 2.204527  |
| c | -1.112097 | 0.634241  | 2.204685  |
| c | -0.959027 | 1.142126  | 3.455756  |
| c | 0.297181  | 1.075559  | 4.069381  |
| c | 1.409188  | 0.487456  | 3.455630  |
| h | 0.887249  | -0.274710 | -0.507653 |
| h | -0.902826 | 0.215136  | -0.508418 |
| h | -0.307496 | -1.111704 | 1.759827  |
| h | 2.119810  | -0.480468 | 1.705114  |
| h | -2.066216 | 0.676043  | 1.705433  |
| h | -1.781905 | 1.608115  | 3.966965  |
| h | 0.411946  | 1.490725  | 5.057753  |
| h | 2.354610  | 0.464881  | 3.966769  |

3

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.006259  | 0.008475  | 0.011024  |
| c | 0.000234  | 0.003791  | 1.533501  |
| c | 1.317546  | 0.003773  | 0.784658  |
| c | -0.379225 | 1.234306  | 2.177415  |
| c | 0.330977  | 2.406202  | 1.994005  |
| c | 1.544226  | 2.406134  | 1.304446  |
| c | 2.065104  | 1.234263  | 0.787932  |
| h | -0.266616 | -0.912862 | -0.469097 |
| h | -0.281328 | 0.911894  | -0.494453 |
| h | -0.328300 | -0.916410 | 1.983380  |
| h | 1.872062  | -0.916465 | 0.732297  |
| h | -1.247481 | 1.234543  | 2.815871  |
| h | -0.024752 | 3.316929  | 2.442896  |
| h | 2.111883  | 3.316889  | 1.228480  |
| h | 3.057805  | 1.234544  | 0.368399  |

4

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | -1.464286 | 0.000000  | -0.635106 |
| c | -1.465334 | 0.000000  | 0.723628  |
| c | -0.361670 | 0.000000  | 1.597122  |
| c | 0.990351  | 0.000000  | 1.304154  |
| c | 1.633461  | 0.000000  | 0.052171  |
| c | 1.070015  | 0.000000  | -1.184209 |
| c | -0.347478 | 0.000000  | -1.603375 |
| h | -2.434970 | 0.000000  | -1.106730 |
| h | -2.431633 | 0.000000  | 1.199178  |
| h | -0.605772 | 0.000000  | 2.646911  |
| h | 1.647189  | 0.000000  | 2.158675  |
| h | 2.709941  | 0.000000  | 0.084933  |
| h | 1.758291  | 0.000000  | -2.015436 |
| h | -0.494578 | 0.848820  | -2.282628 |
| h | -0.494578 | -0.848820 | -2.282628 |

**5**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.074835  | -0.000954 | 0.047931  |
| c | 0.060706  | -0.000822 | 1.520789  |
| c | 1.201382  | -0.000424 | 2.259907  |
| c | 2.452598  | -0.000094 | 1.616708  |
| c | 2.565182  | -0.000145 | 0.238360  |
| c | 1.428506  | -0.000538 | -0.587363 |
| c | 1.578043  | -0.000544 | -1.948881 |
| h | -0.503465 | -0.860631 | -0.301731 |
| h | -0.504118 | 0.858196  | -0.301931 |
| h | -0.899866 | -0.001077 | 2.008454  |
| h | 1.156868  | -0.000356 | 3.334326  |
| h | 3.348727  | 0.000213  | 2.213763  |
| h | 3.542486  | 0.000131  | -0.213008 |
| h | 0.729675  | -0.000846 | -2.611947 |
| h | 2.556818  | -0.000272 | -2.396059 |

**6**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.049069  | 0.046940  | -0.087455 |
| c | 0.010973  | 0.028079  | 1.556149  |
| c | 1.223814  | 0.143763  | 0.676774  |
| c | -0.329740 | 1.204694  | 2.234670  |
| c | 0.283085  | 2.445364  | 1.964819  |
| c | 1.470784  | 2.490164  | 1.315859  |
| c | 2.167247  | 1.274068  | 0.798828  |
| h | -0.320354 | -0.914779 | -0.402643 |
| h | -0.348085 | 0.906612  | -0.608686 |
| h | -0.348328 | -0.919032 | 1.914347  |
| h | -1.051962 | 1.149707  | 3.034930  |
| h | -0.140301 | 3.341217  | 2.382869  |
| h | 1.977364  | 3.434727  | 1.195807  |
| h | 2.621854  | 1.490449  | -0.165186 |
| h | 2.992962  | 1.041093  | 1.474933  |

**TS12**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.038589  | 0.013501  | -0.008337 |
| c | 0.046491  | -0.003439 | 1.390954  |
| c | 1.213069  | 0.020926  | -0.696722 |
| c | 2.478218  | 0.034398  | 0.010793  |
| c | 2.437076  | 0.011898  | 1.459671  |
| c | 1.243886  | 0.004888  | 2.115156  |
| c | 3.724722  | -0.263678 | -0.698087 |
| h | 4.653777  | -0.277699 | -0.157565 |
| h | 3.736565  | -0.271075 | -1.772949 |
| h | 2.904791  | 1.091254  | -0.226475 |
| h | 3.366856  | 0.023180  | 2.002540  |
| h | 1.219474  | -0.003069 | 3.190042  |
| h | -0.889676 | -0.011489 | 1.922281  |
| h | -0.896844 | 0.011875  | -0.538435 |
| h | 1.223751  | 0.038767  | -1.773231 |

**TS23**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.021561  | 0.012597  | 0.012104  |
| c | -0.013606 | -0.006811 | 1.535884  |
| c | 1.412692  | -0.010292 | 1.899330  |
| c | -0.792745 | 1.125287  | 2.064157  |
| c | -0.209543 | 2.130171  | 2.756138  |
| c | 1.179876  | 2.086958  | 2.985865  |
| c | 1.990112  | 1.034355  | 2.558765  |
| h | 0.175823  | -0.912444 | -0.511274 |
| h | 0.119511  | 0.949414  | -0.504108 |
| h | -0.483041 | -0.946162 | 1.839214  |
| h | 2.002628  | -0.853613 | 1.581080  |
| h | -1.849770 | 1.138747  | 1.855235  |
| h | -0.783981 | 2.960230  | 3.125569  |
| h | 1.636599  | 2.904996  | 3.520115  |
| h | 3.043973  | 1.044698  | 2.770023  |

**TS34**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.028918  | -0.011979 | 0.020149  |
| c | -0.080611 | 0.018007  | 1.536738  |
| c | 1.464524  | 0.022715  | 0.208687  |
| c | 0.104073  | 1.136160  | 2.271437  |
| c | 0.695618  | 2.352562  | 1.796055  |
| c | 1.693853  | 2.403417  | 0.838576  |
| c | 2.177835  | 1.257619  | 0.241665  |
| h | -0.360122 | -0.932897 | -0.383864 |
| h | -0.393120 | 0.863145  | -0.452747 |
| h | -0.370980 | -0.900204 | 2.017003  |
| h | 2.013626  | -0.904070 | 0.280443  |
| h | -0.190923 | 1.117431  | 3.308720  |
| h | 0.446147  | 3.259829  | 2.321477  |
| h | 2.205485  | 3.334535  | 0.670875  |
| h | 3.144171  | 1.269463  | -0.240144 |

**TS22**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | -0.429747 | -0.234385 | -0.095553 |
| c | 0.206031  | 0.131427  | 1.226552  |
| c | 1.677690  | 0.172115  | 1.156620  |
| c | -0.421224 | 1.309787  | 1.851379  |
| c | 0.311909  | 2.341155  | 2.340659  |
| c | 1.708906  | 2.290091  | 2.231967  |
| c | 2.393540  | 1.212954  | 1.651421  |
| h | -0.965136 | -1.157088 | -0.206881 |
| h | -0.337143 | 0.443460  | -0.923539 |
| h | -0.013495 | -0.698090 | 1.921571  |
| h | 2.171792  | -0.669369 | 0.699602  |
| h | -1.496921 | 1.319281  | 1.913752  |
| h | -0.158892 | 3.192498  | 2.797926  |
| h | 2.284445  | 3.118076  | 2.614910  |
| h | 3.467048  | 1.227247  | 1.597471  |

**TS33**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | -0.003888 | -0.003163 | -0.037517 |
| c | 0.001178  | 0.021332  | 1.727618  |
| c | 1.386809  | 0.006321  | 2.192291  |
| c | -0.462015 | 1.144171  | 1.003698  |
| c | 0.515813  | 1.675701  | 0.131546  |
| c | 1.911367  | 1.692694  | 0.565312  |
| c | 2.289067  | 0.886536  | 1.623516  |
| h | 0.944645  | -0.465769 | -0.211523 |
| h | -0.837858 | -0.321200 | -0.635829 |
| h | -0.726817 | -0.618796 | 2.193309  |
| h | 1.663739  | -0.686983 | 2.963754  |
| h | -1.509653 | 1.358742  | 0.888188  |
| h | 0.191574  | 2.333255  | -0.655294 |
| h | 2.602969  | 2.332269  | 0.050396  |
| h | 3.303060  | 0.916422  | 1.981460  |

**TS4[1,2]**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.011155  | 0.003270  | 0.000763  |
| c | 0.008614  | -0.006802 | 1.438480  |
| c | 1.105592  | -0.000681 | 2.258771  |
| c | 2.476008  | -0.024842 | 1.942099  |
| c | 3.076548  | -0.051168 | 0.670252  |
| c | 2.507565  | -0.070842 | -0.575611 |
| c | 1.102993  | -0.024621 | -0.879283 |
| h | -0.950246 | 0.121800  | -0.476193 |
| h | -0.965068 | 0.001949  | 1.893239  |
| h | 0.885315  | 0.027721  | 3.313989  |
| h | 3.151024  | -0.011094 | 2.779134  |
| h | 4.154838  | -0.056146 | 0.678851  |
| h | 3.158406  | -0.103903 | -1.430164 |
| h | 0.844478  | 0.075871  | -1.922779 |
| h | 0.428004  | -1.131273 | -0.563780 |

**TS4[1,5]**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.005915  | 0.003663  | 0.005365  |
| c | 0.005961  | 0.003621  | 1.318748  |
| c | 1.430438  | 0.004588  | 1.811667  |
| c | 2.110462  | 1.284112  | 1.844451  |
| c | 2.360050  | 1.953560  | 0.662033  |
| c | 2.110381  | 1.284184  | -0.520408 |
| c | 1.430357  | 0.004660  | -0.487656 |
| h | -0.830318 | 0.039254  | -0.668291 |
| h | -0.830224 | 0.039171  | 1.992465  |
| h | 1.711406  | -0.724165 | 2.564142  |
| h | 2.469432  | 1.671729  | 2.784917  |
| h | 2.852865  | 2.908509  | 0.662045  |
| h | 2.469290  | 1.671856  | -1.460875 |
| h | 1.711270  | -0.724047 | -1.240196 |
| h | 1.925647  | -0.482263 | 0.661973  |

**TS15**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.148920  | -0.256108 | -0.037574 |
| c | 0.086081  | -0.118055 | 1.312395  |
| c | 1.442141  | 0.023023  | -0.677766 |
| c | 2.605234  | -0.095966 | 0.226200  |
| c | 2.514266  | -0.074586 | 1.582047  |
| c | 1.233486  | 0.067861  | 2.133173  |
| c | 3.057485  | -0.920312 | -0.858690 |
| h | 3.629295  | -0.511428 | -1.681665 |
| h | 3.028560  | -1.996562 | -0.754212 |
| h | 1.754279  | -0.852713 | -1.501940 |
| h | 3.376822  | -0.223838 | 2.207709  |
| h | 1.109994  | 0.181122  | 3.194480  |
| h | -0.878239 | -0.160233 | 1.789303  |
| h | -0.724715 | -0.408351 | -0.643713 |
| h | 1.496429  | 0.864492  | -1.364484 |

**TS25**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.014223  | -0.000363 | -0.001899 |
| c | 0.007203  | -0.001280 | 1.385885  |
| c | 1.200095  | 0.000524  | 2.073208  |
| c | 2.433148  | -0.037745 | 1.397600  |
| c | 2.476541  | -0.054848 | 0.038874  |
| c | 1.261366  | -0.064282 | -0.741525 |
| c | 1.296456  | 0.147854  | -2.175168 |
| h | 0.829360  | -1.168179 | -0.528137 |
| h | -0.903713 | -0.010338 | -0.565322 |
| h | -0.931876 | 0.017823  | 1.908734  |
| h | 1.191336  | 0.015229  | 3.149562  |
| h | 3.347591  | -0.039143 | 1.963795  |
| h | 3.416963  | -0.067482 | -0.484068 |
| h | 0.386954  | 0.199993  | -2.744213 |
| h | 2.239778  | 0.207072  | -2.683902 |

**TS53**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | -0.044963 | -0.005160 | 0.019922  |
| c | 0.001877  | 0.001668  | 1.692713  |
| c | 1.121623  | 0.074991  | 0.833642  |
| c | -0.027516 | 1.082867  | 2.691368  |
| c | 1.165221  | 1.694735  | 3.025336  |
| c | 2.357251  | 1.482231  | 2.330664  |
| c | 2.272659  | 0.815051  | 1.048433  |
| h | -0.460258 | -0.952242 | -0.271864 |
| h | -0.278487 | 0.842578  | -0.603992 |
| h | -0.446949 | -0.942938 | 1.953723  |
| h | -0.935428 | 1.303252  | 3.222729  |
| h | 1.179931  | 2.377647  | 3.858006  |
| h | 3.283467  | 1.922630  | 2.646762  |
| h | 2.907900  | 1.095187  | 0.220713  |
| h | 2.385114  | -0.475466 | 1.063047  |

**TS56**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.016104  | -0.008930 | -0.008047 |
| c | 0.021123  | 0.006809  | 1.691428  |
| c | 1.177970  | 0.014538  | 0.767097  |
| c | -0.210343 | 1.205651  | 2.377049  |
| c | 0.511618  | 2.383905  | 2.093433  |
| c | 1.665135  | 2.329390  | 1.386802  |
| c | 2.227047  | 1.054582  | 0.837494  |
| h | -0.487636 | -0.934314 | -0.230894 |
| h | -0.297010 | 0.858569  | -0.573062 |
| h | -0.450399 | -0.901147 | 2.018990  |
| h | -0.929642 | 1.212479  | 3.180466  |
| h | 0.183020  | 3.314337  | 2.521152  |
| h | 2.242019  | 3.226650  | 1.230842  |
| h | 2.658023  | 1.227352  | -0.144908 |
| h | 3.051417  | 0.738869  | 1.480869  |

**TS64**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.004104  | -0.002330 | 0.001938  |
| c | 0.000082  | 0.001438  | 1.508803  |
| c | 1.430689  | 0.003061  | -0.335033 |
| c | 0.560624  | 0.972097  | 2.234712  |
| c | 1.331983  | 2.096933  | 1.748244  |
| c | 2.152665  | 2.130591  | 0.687082  |
| c | 2.407502  | 0.948556  | -0.138325 |
| h | -0.505144 | -0.863391 | -0.411754 |
| h | -0.460197 | 0.898273  | -0.404072 |
| h | -0.483355 | -0.824891 | 2.000377  |
| h | 0.416445  | 0.942482  | 3.302800  |
| h | 1.319321  | 2.974792  | 2.374723  |
| h | 2.737325  | 3.007709  | 0.472604  |
| h | 1.833819  | 0.978967  | -1.248882 |
| h | 3.422518  | 0.720219  | -0.438809 |

**TS55m**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.172951  | 0.192140  | -0.028474 |
| c | 0.026993  | 0.091790  | 1.384263  |
| c | 1.182964  | -0.026512 | 2.209916  |
| c | 2.419665  | -0.104168 | 1.614006  |
| c | 2.559874  | -0.051138 | 0.232442  |
| c | 1.454487  | 0.085181  | -0.638775 |
| c | 1.574724  | 0.159203  | -2.023955 |
| h | -0.109167 | -0.965933 | 0.785240  |
| h | -0.712857 | 0.316262  | -0.629392 |
| h | -0.939967 | 0.287167  | 1.818460  |
| h | 1.065370  | -0.060746 | 3.277154  |
| h | 3.299226  | -0.201766 | 2.225593  |
| h | 3.543972  | -0.119845 | -0.198236 |
| h | 0.709730  | 0.260566  | -2.654079 |
| h | 2.540405  | 0.129635  | -2.494844 |

**TS5m5p**

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| c | 0.140280  | 0.213222  | -0.120974 |
| c | -0.040387 | 0.106114  | 1.276477  |
| c | 1.095243  | -0.053230 | 2.129792  |
| c | 2.379534  | -0.157195 | 1.558798  |
| c | 2.527350  | -0.057468 | 0.209412  |
| c | 1.418713  | 0.124608  | -0.680021 |
| c | 1.626519  | 0.217431  | -2.062390 |
| h | 0.261150  | -1.051262 | 1.631683  |
| h | -0.720589 | 0.366086  | -0.746650 |
| h | -1.005882 | 0.284767  | 1.719505  |
| h | 0.945252  | -0.091550 | 3.195083  |
| h | 3.230254  | -0.295357 | 2.200814  |
| h | 3.513830  | -0.125561 | -0.217262 |
| h | 0.801551  | 0.357465  | -2.736937 |
| h | 2.615558  | 0.153765  | -2.478010 |