The lowest-energy D–A transition state **TS-1** (*endo*) is favored over **TS-2** (*exo*) by 2.33 kcal/mol.



**Figure 1.** DFT-calculated Gibbs free energies at the ωB97X-D/6-311++G(d,p), CPCM(H2O)//ωB97X-D/6-31G(d), CPCM(H2O) level of theory for transition states *endo* **TS-1** and *exo* **TS-2**.

# **Table S1.** Calculated energies (Hartree) for optimized **TS-1** structures

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | ***E****a* | **Δ*G****b* | ***G*** ( = ***E****+* **Δ*G***) | Relative ***G*** |
| **2** | -1150.241014 | 0.304394 | -1149.936620 | - |
| **4** | -1034.464154 | 0.256370 | -1034.207784 | - |
| **2**, **4** | -2184.705168 | 0.560764 | -2184.144404 | 0.000000 |
| **TS-1** | -2184.700617 | 0.591673 | -2184.108944 | 0.035460 |
| **1** | -2184.778822 | 0.599133 | -2184.179689 | -0.035285 |

*a* single point energies calculated at ωB97X-D/6-311++G(d,p), CPCM(H2O)

*b* thermal corrections to ***G*** calculated at ωB97X-D/6-31G(d), CPCM(H2O)

# **Table S2.** Calculated energies (kcal/mol) for optimized **TS-1** structures

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | ***E****a* | **Δ*G****b* | ***G*** ( = ***E****+* **Δ*G***) | Relative ***G*** |
| **2** | -721787.738865 | 191.010279 | -721596.728586 | - |
| **4** | -649136.601264 | 160.874739 | -648975.726525 | - |
| **2**, **4** | -1370924.340129 | 351.885018 | -1370572.455111 | 0.000000 |
| **TS-1** | -1370921.484274 | 371.280724 | -1370550.203550 | 22.251561 |
| **1** | -1370970.558744 | 375.961949 | -1370594.596795 | -22.141684 |

*a* single point energies calculated at ωB97X-D/6-311++G(d,p), CPCM(H2O)

*b* thermal corrections to ***G*** calculated at ωB97X-D/6-31G(d), CPCM(H2O)

# **Table S3.** Calculated energies (Hartree) for optimized **TS-2** structures

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | ***E****a* | **Δ*G****b* | ***G*** ( = ***E****+* **Δ*G***) | Relative ***G*** |
| **2** | -1150.241014 | 0.304394 | -1149.936620 | - |
| **4** | -1034.464154 | 0.256370 | -1034.207784 | - |
| **2**, **4** | -2184.705168 | 0.560764 | -2184.144404 | 0.000000 |
| **TS-2** | -2184.697305 | 0.592078 | -2184.105227 | 0.039177 |
| **exo-1** | -2184.774135 | 0.597953 | -2184.176182 | -0.031777 |

*a* single point energies calculated at ωB97X-D/6-311++G(d,p), CPCM(H2O)

*b* thermal corrections to ***G*** calculated at ωB97X-D/6-31G(d), CPCM(H2O)

# **Table S4.** Calculated energies (kcal/mol) for optimized **TS-2** structures

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | ***E****a* | **Δ*G****b* | ***G*** ( = ***E****+* **Δ*G***) | Relative ***G*** |
| **2** | -721787.738865 | 191.010279 | -721596.728586 | - |
| **4** | -649136.601264 | 160.874739 | -648975.726525 | - |
| **2**, **4** | -1370924.340129 | 351.885018 | -1370572.455111 | 0.000000 |
| **TS-2** | -1370919.406068 | 371.534866 | -1370547.871202 | 24.583909 |
| **exo-1** | -1370967.617266 | 375.221487 | -1370592.395779 | -19.940668 |

*a* single point energies calculated at ωB97X-D/6-311++G(d,p), CPCM(H2O)

*b* thermal corrections to ***G*** calculated at ωB97X-D/6-31G(d), CPCM(H2O)