# Supporting Information for:
# Mechanisms of Photostability in Kynurenines: A Joint Electronic-Structure and Dynamics Study

**Deniz Tuna,[1*] Nađa Došlić,[2] Momir Mališ,[2] Andrzej L. Sobolewski,[3] and Wolfgang Domcke[1]**

[1] *Department of Chemistry, Technische Universität München, 85747 Garching, Germany*

[2] *Division of Physical Chemistry, Ruđer Bošković Institute, 10002 Zagreb, Croatia*

[3] *Institute of Physics, Polish Academy of Sciences, 02668 Warsaw, Poland*

[*] *email: deniz.tuna@ch.tum.de*

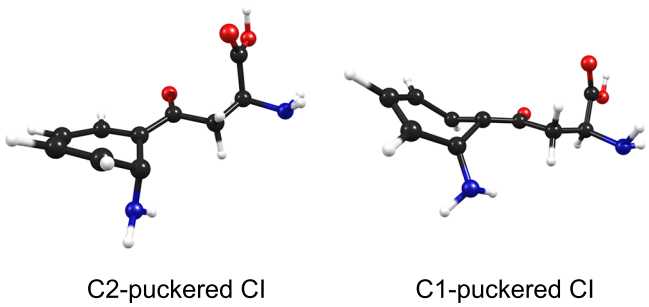


**Figure S1** Optimized geometries of two additional ring-puckered conical intersections of kynurenine: the C2-puckered conical intersection (in contrast to the C2-puckered conical intersection shown in Figure 6 in the article, here the C2 atom is displaced below the plane of the benzene moiety), and the C1-puckered conical intersection. For details consult the Computational Methods section in the article.

# Comparison of Vertical Excitation Energies at the ADC(2) and TDDFT Levels of Theory

Tables S1 and S2 show the vertical excitation energies and oscillator strengths of the *cis* and *trans* conformers of kynurenine computed at the ADC(2) and TDDFT levels of theory. While differences can be observed, both levels of theory are in agreement with regard to the physical nature, that is, the $n\pi^*$ or $\pi\pi^*$ character, of the $S_1$ and $S_2$ states for both conformers. The excitation energies for these two lowest excited states agree surprisingly well. From the $S_3$ state onwards, however, the excitation energies begin to deviate significantly. TDDFT yields a considerably larger density of excited states in the energy window up to about 6 eV.

**Table S1** Singlet vertical excitation energies (in eV) and oscillator strengths ($f$) of the *cis* conformer of kynurenine computed at the ADC(2) and TDDFT levels of theory. The states are listed in ascending order of energy. For details consult the Computational Methods section in the article.

| state | ADC(2) / eV | $f$ | TDDFT / eV | $f$ |
|---|---|---|---|---|
| $S_1$ | 3.79 ($\pi\pi^*$) | 0.1054 | 3.64 ($\pi\pi^*$) | 0.1006 |
| $S_2$ | 3.98 ($n\pi^*$) | 0.0205 | 3.98 ($n\pi^*$) | 0.0042 |
| $S_3$ | 5.28 ($\pi\pi^*$) | 0.0491 | 4.04 ($n\pi^*$) | 0.0024 |
| $S_4$ | 5.75 ($n\pi^*$) | 0.0015 | 5.03 ($\pi\pi^*$) | 0.1058 |
| $S_5$ | 5.90 ($n\pi^*$) | 0.0014 | 5.10 ($n\pi^*$) | 0.0016 |
| $S_6$ | 5.94 ($\pi\pi^*$) | 0.6437 | 5.49 ($\pi\pi^*$) | 0.1486 |

**Table S2** Singlet vertical excitation energies (in eV) and oscillator strengths ($f$) of the *trans* conformer of kynurenine computed at the ADC(2) and TDDFT levels of theory. The states are listed in ascending order of energy. For details consult the Computational Methods section in the article.

| state | ADC(2) / eV | $f$ | TDDFT / eV | $f$ |
|---|---|---|---|---|
| $S_1$ | 3.93 ($n\pi^*$) | 0.0001 | 3.92 ($n\pi^*$) | 0.0011 |
| $S_2$ | 4.22 ($\pi\pi^*$) | 0.0912 | 3.98 ($\pi\pi^*$) | 0.0766 |
| $S_3$ | 5.43 ($\pi\pi^*$) | 0.1490 | 4.39 ($n\pi^*$) | 0.0016 |
| $S_4$ | 5.78 ($n\pi^*$) | 0.0007 | 5.07 ($\pi\pi^*$) | 0.1481 |
| $S_5$ | 6.10 ($\pi\pi^*$) | 0.5991 | 5.45 ($n\pi^*$) | 0.0013 |

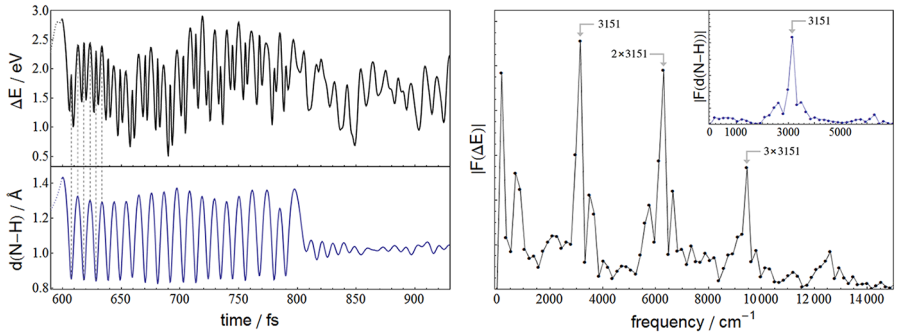


**Figure S2** Upper left panel: Time dependence of the ground-state potential energy, $\Delta E$, in the interval between 600 and 970 fs for the nonadiabatic trajectory shown in Figure 9 in the article. Lower left panel: Time dependence of the N–H bond distance ($d_{\mathrm{N-H}}$) in the same interval. Right panel: Discrete Fourier transform of the ground-state potential energy in the interval between 604.5 and 794.5 fs. Inset in right panel: Discrete Fourier transform of the N–H bond distance in the same time interval.

## Fourier Analysis

Figure S2 shows the time dependence of the ground-state potential energy, $\Delta E$, in the interval between 600 and 970 fs for the nonadiabatic trajectory shown in Figure 9 in the article (upper left panel). In the selected example shown in Figure 9 in the article, the relaxation to the ground state occurs by proton transfer from the ring-amino group to the keto group. Once the system has deactivated to the electronic ground state, the proton is back-transfered to the ring-amino group. The high-frequency large-amplitude oscillations of the potential energy are caused by vibrational excitation of the N–H bond of the ring-amino group. The time variation of the N–H distance ($d_{\mathrm{N-H}}$) is shown in the lower left panel. The vertical lines indicate a doubling of the oscillations of the potential energy with respect to the oscillations of the N–H distance. After 800 fs, the amplitude of both the potential energy and the bond length are reduced due to energy transfer from the N–H stretching-vibration to the hydrogen-bonded keto group. The discrete Fourier transform of the potential energy (right panel) and of the N–H bond length (inset in the right panel) in the interval between 604.5 and 794.5 fs (inset in the left panel) show the characteristic frequencies of the system. The N–H bond length oscillates with a frequency of 3151 $\mathrm{cm}^{-1}$, which is expectedly red-shifted with respect to the frequencies of the symmetric and antisymmetric normal modes of the amino group of aniline, which were computed at 3373 and 3465 $\mathrm{cm}^{-1}$ using the second-order perturbation treatment of Barone[1] in the Gaussian09 program package.[2] The energy difference between the two normal modes is below the employed frequency resolution (175 $\mathrm{cm}^{-1}$). The anharmonicity of the ground-state potential-energy sur-

face is apparent from the power spectrum ($|F(\Delta E)|$) where—apart from the expected peak at 2×3151 $cm^{-1}$—two maxima at 1×3151 $cm^{-1}$ and 3×3151 $cm^{-1}$ are clearly visible. The coupling between the high-frequency modes is visible as their energy difference superimposed on the low-frequency part of the spectrum.

# References


[1] V. Barone, *J. Chem. Phys.* **2004**, *120*, 3059–3065.

[2] M. J. Frisch and G. W. Trucks and H. B. Schlegel and G. E. Scuseria and M. A. Robb and J. R. Cheeseman and G. Scalmani and V. Barone and B. Mennucci and G. A. Petersson and H. Nakatsuji and M. Caricato and X. Li and H. P. Hratchian and A. F. Izmaylov and J. Bloino and G. Zheng and J. L. Sonnenberg and M. Hada and M. Ehara and K. Toyota and R. Fukuda and J. Hasegawa and M. Ishida and T. Nakajima and Y. Honda and O. Kitao and H. Nakai and T. Vreven and Montgomery, Jr., J. A. and J. E. Peralta and F. Ogliaro and M. Bearpark and J. J. Heyd and E. Brothers and K. N. Kudin and V. N. Staroverov and R. Kobayashi and J. Normand and K. Raghavachari and A. Rendell and J. C. Burant and S. S. Iyengar and J. Tomasi and M. Cossi and N. Rega and J. M. Millam and M. Klene and J. E. Knox and J. B. Cross and V. Bakken and C. Adamo and J. Jaramillo and R. Gomperts and R. E. Stratmann and O. Yazyev and A. J. Austin and R. Cammi and C. Pomelli and J. W. Ochterski and R. L. Martin and K. Morokuma and V. G. Zakrzewski and G. A. Voth and P. Salvador and J. J. Dannenberg and S. Dapprich and A. D. Daniels and ÃŰ. Farkas and J. B. Foresman and J. V. Ortiz and J. Cioslowski and D. J. Fox, Gaussian 09 Revision D.01, Gaussian Inc. Wallingford CT 2009.


# Comparison of $S_1$ Equilibrium Geometries at the ADC(2) and TDDFT Levels of Theory

To elucidate the absence of the ring-amino-twist mechanism in the dynamics simulations, we reoptimized the $n\pi^*$ equilibrium geometry obtained at the ADC(2) level (whose location on the interpolated path is shown by the arrow in Figure 7 in the article) at the TDDFT level of theory. An analogous $n\pi^*$ equilibrium geometry was obtained, which differs from the equilibrium geometry obtained at the ADC(2) level: the C=O bond length of the keto group is 0.084 Å shorter than it is in the ADC(2) minimum. This structural difference leads to a large $S_1/S_0$ energy gap of 1.47 eV in the TDDFT-optimized equilibrium geometry, which is in stark contrast to the almost nonexistent energy gap at the ADC(2) level (cf. Figure S3 where the $S_1$ state exhibits $\pi\pi^*$ character in the Franck–Condon region and $n\pi^*$ character at the equilibrium geometry). The discrepancy in the description of this part of the potential-energy surface at the ADC(2) and TDDFT levels of theory

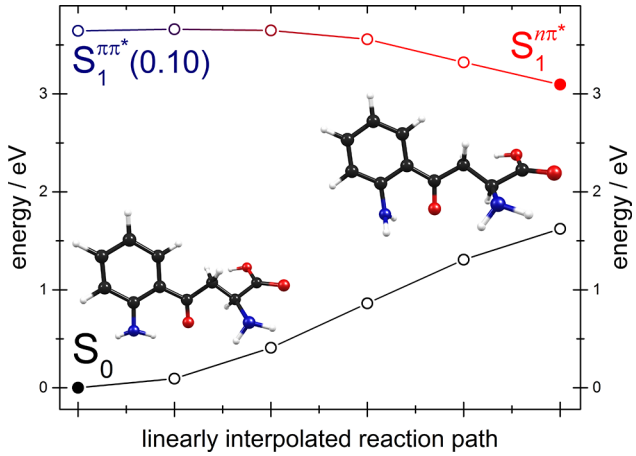


**Figure S3** Energy profiles (in eV), computed at the TDDFT level, of the electronic ground state (empty black circles) and the first excited singlet state (empty blue/red circles) along the linearly interpolated reaction path connecting the ground-state equilibrium geometry of the *cis* conformer (full black circle at the left bottom) with the local $S_1$ equilibrium geometry (TDDFT-optimized $S_1$ equilibrium geometry started from the ADC(2)-optimized $S_1$ equilibrium geometry, full red circle at the right). The physical character of the $S_1$ state changes adiabatically from a $\pi\pi^*$ nature (blue region) to an $n\pi^*$ nature (red region). The insets show the ground-state and the $S_1$ equilibrium geometries (left and right, respectively). For details consult the Computational Methods section in the article.

may be the reason why excited-state deactivation via the ring-amino-twist mechanism has not been observed in the dynamics simulations.

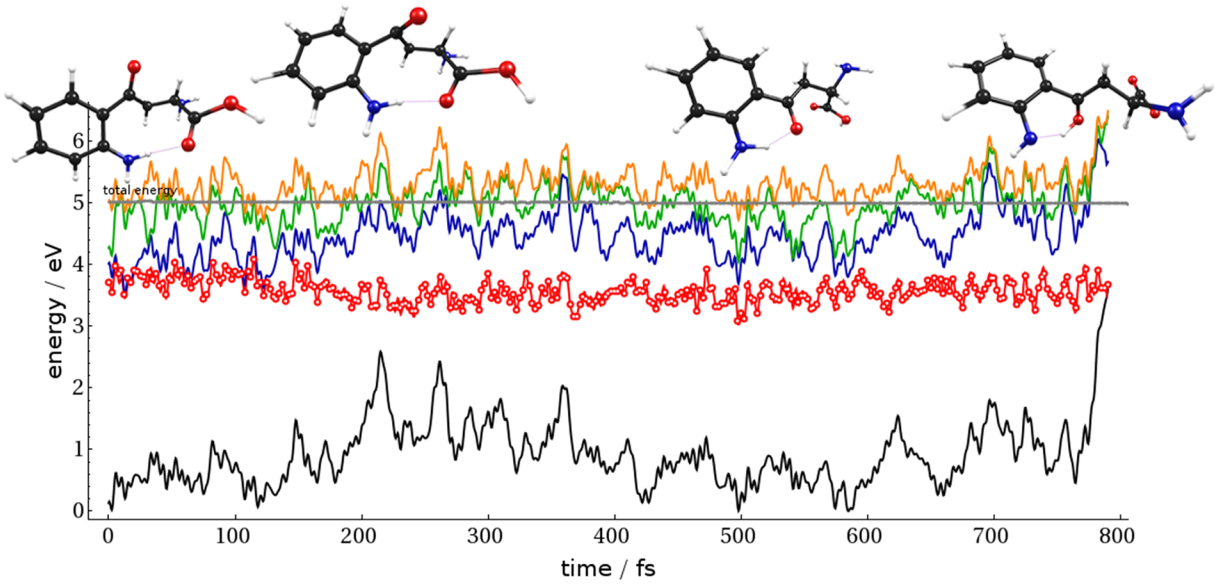


**Figure S4** Instantaneous energies of the electronic ground state ($S_0$, black curve) and the first four excited singlet states ($S_1$–$S_4$, red, blue, green, and orange curves) for a selected trajectory of *trans* kynurenine, obtained with nonadiabatic trajectory-surface-hopping dynamics simulations. The red dots indicate the populated state at a given time. At 790 fs, the trajectory hops to the $S_0$ state at the $S_1/S_0$ conical intersection. The insets show selected molecular structures during the time evolution of the trajectory. The value of the total energy of the system is given by the horizontal line. This trajectory shows *trans*→*cis* isomerization and subsequent deactivation via ring-N–H···O=C proton transfer. For details consult the Computational Methods section in the article.

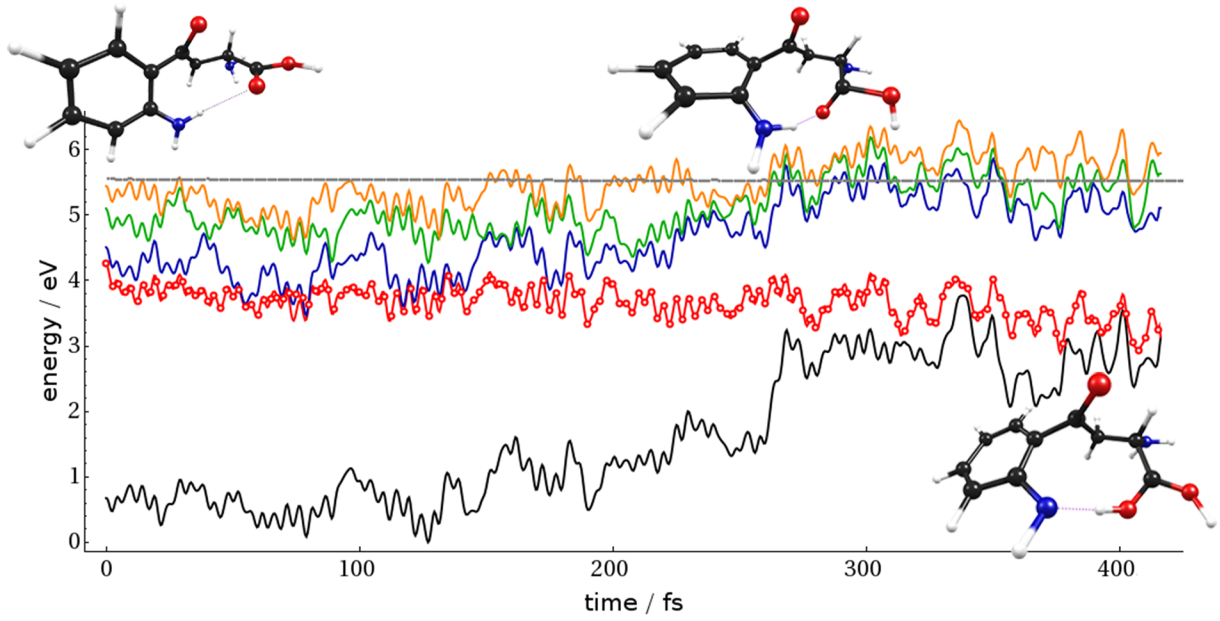


**Figure S5** Instantaneous energies of the electronic ground state ($S_0$, black curve) and the first four excited singlet states ($S_1$–$S_4$, red, blue, green, and orange curves) for a selected trajectory of *trans* kynurenine, obtained with nonadiabatic trajectory-surface-hopping dynamics simulations. The red dots indicate the populated state at a given time. At 420 fs, the trajectory hops to the $S_0$ state at the $S_1/S_0$ conical intersection. The insets show selected molecular structures during the time evolution of the trajectory. The value of the total energy of the system is given by the horizontal line. This trajectory shows deactivation via ring-N–H$\cdots$O=COH proton transfer. For details consult the Computational Methods section in the article.

**Table S3** Cartesian coordinates of the MP2/cc-pVDZ optimized ground-state equilibrium geometry of the ring-N–H···O=C intramolecularly hydrogen-bonded *cis* conformer of kynurenine (energy: $-721.432801\ E_h$).

```
27

C    0.014139  -3.956112   0.194255
C   -0.264887  -4.100583  -1.164846
C   -0.446501  -2.963365  -1.977022
C   -0.327279  -1.696068  -1.404602
C   -0.032054  -1.522060  -0.027809
C    0.133624  -2.678152   0.798875
C    0.148406  -0.155961   0.527161
C   -0.004924   1.039196  -0.416495
C    0.100210   2.362845   0.353878
C    0.131335   3.561942  -0.595823
O   -0.630236   4.499425  -0.529022
N    0.327691  -2.592563   2.162394
O    0.456694   0.049856   1.709399
N   -1.055426   2.480785   1.234758
O    1.115588   3.539400  -1.538311
H    1.652797   2.746326  -1.394050
H    0.139845  -4.844903   0.823870
H   -0.348809  -5.104998  -1.593444
H   -0.675711  -3.068590  -3.041256
H   -0.466690  -0.816373  -2.038067
H    0.770675  -3.400274   2.588715
H    0.644689  -1.682748   2.489566
H   -0.994652   1.004202  -0.902542
H    0.757632   0.937798  -1.211735
H    1.075353   2.369123   0.889502
H   -1.226991   3.475238   1.399043
H   -0.817477   2.053977   2.130803
```

**Table S4** Cartesian coordinates of the ADC(2)/cc-pVDZ minimum-energy conical intersection for the ring-N–H$\cdots$O=C proton-transfer process of the *cis* conformer of kynurenine (energy: $-721.321412\ E_h$).

```
27

C   -0.1233517892  -3.2303974850  -1.9457079536
C    0.1566662527  -1.8751621604  -1.5057512634
C    0.0868151568  -1.5567611707  -0.1728923524
C   -0.1579201550  -2.5840303764   0.7947999714
C   -0.4140522882  -3.8855123748   0.3688139714
C   -0.4058836351  -4.2128611929  -1.0303028421
C    0.3057535006  -0.1563001917   0.3573151598
C    0.0004560647   1.0540255583  -0.4574381305
C    0.1681287530   2.3367656575   0.3777595422
C   -0.1589691398   3.5992324097  -0.4248620438
O   -0.8720452740   4.4902689310  -0.0207706419
N   -0.0380273749  -2.1703215133   2.1241276263
O    1.2196608464  -0.0343097883   1.3461319848
N   -0.7219081254   2.2695619828   1.5294223633
O    0.4467603167   3.7002677294  -1.6408481472
H    0.9885540765   2.9073266849  -1.7708740178
H   -0.6265426752  -4.6660710998   1.1100476394
H   -0.6330266939  -5.2347671879  -1.3502990058
H   -0.1280842177  -3.4468223320  -3.0189200910
H    0.3699619547  -1.1048470662  -2.2550927364
H   -0.2119900403  -2.9649893953   2.7566242491
H    0.9817597286  -0.8373962658   1.9297742326
H   -1.0354088823   0.9942090576  -0.8428726301
H    0.6768377737   1.0680706600  -1.3465207044
H    1.2470226067   2.4187923694   0.6408548174
H   -0.8494143044   3.2212321609   1.8819516425
H   -0.2484995428   1.7349304463   2.2598443078
```

**Table S5** Cartesian coordinates of the MP2/cc-pVDZ optimized ground-state equilibrium geometry of the tail-N–H$\cdots$O=C intramolecularly hydrogen-bonded *trans* conformer of kynurenine (energy: $-721.435203$ $E_h$).

```
27

C   -1.307780  -0.203056  -2.686724
C   -0.303194  -0.049053  -1.700148
C    1.047239   0.137512  -2.117937
C    1.324099   0.116454  -3.506754
C    0.320181  -0.051810  -4.463247
C   -1.016005  -0.208113  -4.051315
C   -0.797838  -0.125523  -0.277825
C    0.171469   0.021740   0.884232
C   -0.492317  -0.229169   2.232678
C    0.573076  -0.296940   3.316833
O    1.776034  -0.298236   3.145174
N    2.142342   0.232883  -1.238374
O   -1.993512  -0.326691  -0.054254
N   -1.416272   0.867486   2.552306
O    0.001845  -0.374457   4.546759
H    2.363635   0.247622  -3.831140
H    0.581715  -0.054884  -5.526691
H   -1.816018  -0.333268  -4.787163
H   -2.333326  -0.333825  -2.331179
H    2.974861   0.563509  -1.723886
H    1.980035   0.823100  -0.426712
H    0.563836   1.056689   0.893264
H    1.030440  -0.652641   0.738075
H   -0.979698  -1.228322   2.206248
H    0.750561  -0.402329   5.169722
H   -2.196275   0.776282   1.895866
H   -1.815077   0.681905   3.476200
```

**Table S6** Cartesian coordinates of the ADC(2)/cc-pVDZ minimum-energy conical intersection for the tail-N–H$\cdots$O=C proton-transfer process of the *trans* conformer of kynurenine (energy: $-721.335407\ E_h$).

```
27

C   -1.3235483752  -0.0015493336  -2.4108471452
C   -0.2199946094   0.2925695184  -1.5614966428
C    1.1008672274   0.1877244126  -2.1029022427
C    1.2602807058  -0.2920168239  -3.4172881454
C    0.1623029990  -0.6200117935  -4.2259788457
C   -1.1393183703  -0.4642063109  -3.7156715669
C   -0.5082930190   0.7137258439  -0.2056735312
C    0.3661970574   0.5235679834   0.9927018932
C   -0.3851764689  -0.2889775087   2.0650045572
C    0.4791023938  -0.4301109475   3.3225623481
O    1.5473174260   0.1059292773   3.5138039776
N    2.2423543508   0.4972021081  -1.3224517702
O   -1.7482803551   1.1583723150   0.0393758355
N   -1.6043282088   0.4006136967   2.4302822024
O   -0.1558832996  -1.2022079931   4.2406957617
H    2.2755563006  -0.3806681185  -3.8241455106
H    0.3237046927  -0.9784697577  -5.2479380367
H   -2.0099035797  -0.7061060427  -4.3339342764
H   -2.3283703157   0.1119697591  -1.9943306688
H    3.0658805766   0.6158183555  -1.9130916558
H    2.1127879087   1.3616878340  -0.7941598755
H    0.6109195317   1.4929596650   1.4732134287
H    1.3053884988   0.0173422765   0.7337128825
H   -0.5877384213  -1.3196609313   1.6894619346
H    0.4259259785  -1.1947927248   5.0236271169
H   -1.8873054513   1.0642488782   1.0612752064
H   -2.1847881895  -0.2220603658   3.0114434739
```

**Table S7** Cartesian coordinates of the ADC(2)/cc-pVDZ minimum-energy conical intersection (C2 up) for the ring-puckering process of the *trans* conformer of kynurenine (energy: $-721.298206\ E_h$).

```
27

C   -6.8825180132   7.6077997752   5.2747033988
C   -7.8935213316   7.8271517316   4.1958905167
C   -8.7461744689   6.7636147560   4.0197670034
C   -8.8288590227   5.7239140742   5.0358702020
C   -8.2641290057   5.9151055735   6.3124110632
C   -7.4626665065   7.0536515050   6.5288670944
N   -5.7457904770   6.9208563394   4.8452193776
H   -7.9305736638   8.7255592988   3.5691537673
H   -9.4838340193   6.7630621350   3.2067439562
H   -9.4831209117   4.8633787301   4.8574424776
H   -8.5914047436   5.3099860912   7.1675587555
H   -5.3814463174   6.2112986753   5.4846486311
H   -5.7096716224   6.6599994100   3.8571353064
C   -7.2825530057   7.6525698815   7.8599498262
C   -6.5932330111   9.0107912628   7.8989697483
C   -6.7614464186   9.6807765527   9.2552031130
C   -6.0125805033   8.8977057679  10.3247984200
O   -7.6821932923   7.1009098308   8.8924929685
O   -4.9570458922   8.3145802846  10.1599304272
O   -6.6091757843   9.0235571081  11.5375855714
N   -6.2828818888  11.0741536255   9.1829121475
H   -7.0021186973   9.6591835278   7.1041891554
H   -5.5180117214   8.8705450472   7.6818863712
H   -7.8276309850   9.7012883374   9.5322604908
H   -6.0265590798   8.5404108938  12.1519942493
H   -5.2672005300  11.0472201214   9.0395937307
H   -6.4047056889  11.5029237238  10.1061784620
```

**Table S8** Cartesian coordinates of the MP2/cc-pVDZ ground-state equilibrium geometry of the *trans* conformer of kynurenine used for the construction of the linearly interpolated reaction path to the C2-up ring-puckered minimum-energy conical intersection (energy: $-721.435273\ E_h$).

```
27

C    -7.131808   7.535814   5.143223
C    -7.634769   6.942733   3.961130
C    -8.669504   6.003566   3.987227
C    -9.235075   5.621289   5.217466
C    -8.756827   6.202762   6.393209
C    -7.727393   7.174312   6.384830
N    -6.127040   8.516413   5.016637
H    -7.184029   7.226360   3.002252
H    -9.026982   5.567035   3.048630
H   -10.039667   4.880707   5.254755
H    -9.177722   5.934918   7.366231
H    -5.409898   8.456429   5.736070
H    -5.674525   8.457545   4.105242
C    -7.383390   7.749585   7.733454
C    -6.499674   8.982096   7.859677
C    -6.604296   9.587024   9.254339
C    -6.022475   8.621103  10.274889
O    -7.856244   7.252646   8.756784
O    -5.023481   7.948583  10.093058
O    -6.667550   8.688124  11.463080
N    -5.884759  10.872567   9.278947
H    -6.747053   9.733270   7.093396
H    -5.447382   8.672442   7.705132
H    -7.659241   9.775698   9.506130
H    -6.176925   8.079610  12.045997
H    -4.883972  10.666966   9.183827
H    -5.979381  11.272414  10.217758
```

**Table S9** Cartesian coordinates of the ADC(2)/cc-pVDZ minimum-energy conical intersection (C2 down) for the ring-puckering process of the *trans* conformer of kynurenine (energy: $-721.296071\ E_h$).

```
27

C   -6.9801839593   7.7085068738   5.2314147705
C   -6.4949820853   6.3683523832   4.7628001277
C   -7.5124267311   5.4776114762   4.5336275280
C   -8.8448412118   5.7407946721   5.0687370177
C   -9.0446978121   6.7387501601   6.0376478264
C   -7.9642999114   7.5936462830   6.3472040149
N   -7.4793421195   8.4864289693   4.1891096631
H   -5.4410557569   6.1263686511   4.5803036862
H   -7.3077498939   4.4845563905   4.1122351258
H   -9.6494295676   5.0302191001   4.8515878526
H   -9.9299518667   6.7196914219   6.6850863967
H   -7.9067432896   9.3736467233   4.4504224027
H   -6.9483705783   8.4961146307   3.3195537363
C   -7.7937283752   8.2222198269   7.6604586473
C   -6.5492667403   9.0883694825   7.8309006660
C   -6.4397241241   9.6304904024   9.2461811496
C   -6.2279956831   8.4807598150  10.2220526998
O   -8.6093632014   8.0775939307   8.5807413375
O   -5.6785832281   7.4265141536   9.9620662235
O   -6.6386326505   8.8134108061  11.4729737239
N   -5.3443704479  10.6135260198   9.3220303289
H   -6.5768018918   9.9293013402   7.1157557052
H   -5.6629755299   8.4756255454   7.5792546656
H   -7.3786865356  10.1391013050   9.5176571586
H   -6.4074638571   8.0403838610  12.0201074624
H   -4.4623380526  10.1113046638   9.1718325775
H   -5.2910308901  10.9557669109  10.2863128668
```

**Table S10** Cartesian coordinates of the ADC(2)/cc-pVDZ minimum-energy conical intersection (C1 up) for the ring-puckering process of the *trans* conformer of kynurenine (energy: $-721.266376\ E_h$).

```
27

C   -6.8127950491   6.4269439183   4.4030541115
C   -7.5709563420   5.2447683250   4.5437532612
C   -7.1949349999   7.5439963204   5.2644799074
C   -7.6484025344   7.3521639378   6.6416289826
C   -8.6631682005   5.4296589958   5.3741067683
C   -8.7983908561   6.7663587846   6.0192606465
C   -7.5723265824   8.1861211722   7.8250127052
C   -6.2688891760   8.9398042954   8.0637406193
C   -6.3257462699   9.7580500820   9.3463211127
C   -6.4047652242   8.8374901389  10.5564040382
N   -6.8967912143   8.8306040698   4.7837792657
N   -5.1408244807  10.6323286637   9.4245816147
O   -5.9012729606   7.7327984985  10.6389595388
O   -8.4980309398   8.2257344632   8.6562717373
O   -7.0040745336   9.4588947927  11.6060220768
H   -6.9432394642   8.8195577707  12.3393376647
H   -6.0065185750   6.5665424561   3.6759950927
H   -7.3088687716   4.2963026270   4.0697794299
H   -9.3788766397   4.6378487018   5.6233867917
H   -9.8025774533   7.1697186682   6.2337501266
H   -7.1548512473   8.9510473602   3.8028692938
H   -7.3234992769   9.5695743960   5.3423129310
H   -6.0232811141   9.6078356444   7.2192665907
H   -5.4535180256   8.1945025595   8.1328278375
H   -7.2243814488  10.3953488921   9.3496919795
H   -5.2002699047  11.1759002312  10.2911059149
H   -4.3162627664  10.0329150971   9.5421673068
```

**Table S11** Cartesian coordinates of the ADC(2)/cc-pVDZ minimum-energy conical intersection for the ring-amino-twist process of the *cis* conformer of kynurenine (energy: $-721.320905\ E_h$).

```
27

C     0.000000    0.000000    0.000000
C     1.411983    0.000000    0.000000
C    -0.687146    1.211354    0.000000
H    -0.559392   -0.943356   -0.003108
C     0.000119    2.473507    0.007483
C     2.106990    1.234258   -0.005983
H     1.959796   -0.946761    0.001461
C     1.435042    2.454465   -0.000188
H     3.202708    1.230129   -0.011915
H     1.997453    3.393352    0.001229
N    -2.118569    1.335400   -0.007351
H    -2.588497    1.091358   -0.879967
H    -2.606077    0.950954    0.803602
C    -0.838054    3.593978    0.048669
C    -0.421031    5.029243    0.026684
C    -1.252591    5.804830   -1.021757
H     0.648324    5.104736   -0.226615
H    -0.578161    5.452006    1.040858
C    -0.749080    7.235384   -1.215642
O    -0.569474    7.746596   -2.297296
O    -2.229627    3.413132    0.069331
N    -1.177564    5.096365   -2.292884
H    -2.286042    5.893096   -0.617963
H    -1.408292    5.760792   -3.035753
H    -1.908909    4.381609   -2.286400
O    -0.539675    7.947228   -0.073666
H    -0.753073    7.377242    0.680158
```

**Table S12** Cartesian coordinates of the ADC(2)/cc-pVDZ $S_1$ equilibrium geometry of the *cis* conformer of kynurenine (energy: $-721.321494\ E_h$).

```
27

C   -0.1815971  -3.8023500   0.3396180
C   -0.6884292  -4.0635039  -0.9511705
C    0.2172623  -2.5098673   0.6817146
H   -0.0987184  -4.6069968   1.0799873
C    0.1259490  -1.4226416  -0.2535340
C   -0.7893873  -3.0019160  -1.8830847
H   -1.0026728  -5.0753666  -1.2255597
C   -0.3937866  -1.7048933  -1.5602009
H   -1.1857655  -3.2035615  -2.8846354
H   -0.4786583  -0.9058763  -2.3035936
N    0.7442320  -2.1380616   1.9635746
H    0.0810466  -2.1442852   2.7394073
H    1.6317505  -2.5690666   2.2258856
C    0.5945518  -0.1840368   0.2201939
C    0.6021897   1.1117649  -0.5335469
C    0.0636549   2.2394259   0.3775937
H   -0.0299105   1.0318354  -1.4325372
H    1.6460425   1.3239346  -0.8483894
C   -0.1107070   3.5576408  -0.3747995
O   -1.1025435   4.2477591  -0.3065432
O    1.0809408  -0.0734846   1.5108746
N   -1.2235757   1.8231791   0.9195115
H    0.8370057   2.4281089   1.1556231
H   -1.7285973   2.6650839   1.2063456
H   -1.0384493   1.2775248   1.7643822
O    0.9551161   3.9531542  -1.1243557
H    1.6500973   3.2838640  -1.0355657
```

**Table S13** Cartesian coordinates of the TDDFT/cc-pVDZ-optimized $S_1$ equilibrium geometry (started from the ADC(2)/cc-pVDZ-optimized $S_1$ equilibrium geometry) of the *cis* conformer of kynurenine used for the construction of the linearly interpolated reaction path to the ground-state equilibrium geometry (energy: $-723.004464\ E_h$).

```
27

C   -0.0522519  -3.9271823   0.2392192
C   -0.4345519  -4.1720974  -1.0941067
C    0.1774996  -2.6320044   0.6614748
H    0.0635707  -4.7554556   0.9420595
C    0.0416680  -1.4953118  -0.2074589
C   -0.5741280  -3.0823157  -1.9709948
H   -0.6165151  -5.1920809  -1.4333202
C   -0.3435568  -1.7783629  -1.5530372
H   -0.8701380  -3.2617201  -3.0079786
H   -0.4592381  -0.9566736  -2.2614329
N    0.5645381  -2.3666717   2.0170174
H   -0.1113513  -2.0180318   2.6904934
H    1.5337366  -2.1766241   2.2544332
C    0.3184613  -0.2218018   0.3564464
C    0.2390658   1.0536388  -0.4638185
C    0.0853610   2.3057153   0.4244690
H   -0.6173980   1.0011441  -1.1556717
H    1.1577236   1.1177939  -1.0869398
C    0.0602843   3.6103967  -0.3795448
O   -0.7212205   4.5054030  -0.1766509
O    0.6840554  -0.1248209   1.6004917
N   -1.1435901   2.2077862   1.1996519
H    1.0004739   2.3726959   1.0543713
H   -1.4333816   3.1490985   1.4700699
H   -0.9538309   1.6710737   2.0459659
O    1.0203002   3.7544172  -1.3299871
H    1.5614540   2.9493615  -1.3680258
```

**Table S14** Cartesian coordinates of the MP2/cc-pVDZ optimized ground-state equilibrium geometry of the 6′-O–H$\cdots$ intramolecularly hydrogen-bonded conformer of 3-hydroxykynurenine O-$\beta$-D-glucoside (energy: $-1405.590684$ $E_h$).

```
49

C    0.025409  -4.032552   0.079049
C   -0.243953  -3.159600  -1.165637
O   -1.356977  -2.315457  -1.053250
C   -2.066968  -2.260150   0.206836
C   -1.066361  -2.102130   1.342467
C   -0.222973  -3.366608   1.453392
O    0.893194  -2.415337  -1.645895
C    1.410924  -1.452158  -0.795078
C    0.945150  -0.114793  -0.912375
C    1.502613   0.868981  -0.051214
C    2.554065   0.509531   0.823466
C    3.056204  -0.794616   0.869123
C    2.482405  -1.781043   0.046122
N   -0.063653   0.151764  -1.861727
C    1.067936   2.316871   0.039639
O    1.793933   3.123669   0.619292
C   -3.003858  -1.066861   0.085184
O   -2.295774   0.147191  -0.051166
O   -1.787760  -1.872450   2.541917
O    0.931061  -3.161676   2.255685
O   -0.910026  -5.115087   0.037900
C   -0.281076   2.766678  -0.493729
C   -0.648292   4.153043   0.030054
C    0.359683   5.226212  -0.351324
O    0.831377   5.039736  -1.620393
N   -1.991756   4.504036  -0.460797
O    0.636342   6.202237   0.314720
```

*Continued on next page*

| | | | |
|---|---|---|---|
| H | −0.421599 | −1.234962 | 1.093520 |
| H | −0.829376 | −4.104810 | 2.003749 |
| H | 1.068243 | −4.398797 | 0.035830 |
| H | −0.413954 | −3.842180 | −2.019738 |
| H | −2.652487 | −3.188687 | 0.347862 |
| H | −1.703386 | 0.046186 | −0.823718 |
| H | 3.892389 | −1.046095 | 1.529184 |
| H | 2.867355 | −2.805155 | 0.026393 |
| H | 2.970798 | 1.297982 | 1.455702 |
| H | 0.112654 | 1.009862 | −2.383176 |
| H | −0.132765 | −0.637334 | −2.507531 |
| H | −1.069527 | 2.046698 | −0.218558 |
| H | −0.237313 | 2.810952 | −1.597086 |
| H | −0.679608 | 4.138869 | 1.130909 |
| H | −2.238168 | 5.421683 | −0.076885 |
| H | −1.926637 | 4.651947 | −1.473586 |
| H | −1.122631 | −1.908208 | 3.246924 |
| H | 1.402670 | −2.408615 | 1.864234 |
| H | −0.773259 | −5.577322 | −0.802601 |
| H | −3.602467 | −1.003605 | 1.006326 |
| H | −3.686673 | −1.248742 | −0.769265 |
| H | 1.410499 | 5.807820 | −1.777194 |

**Table S15** Cartesian coordinates of the ADC(2)/cc-pVDZ minimum-energy conical intersection for the 6′-O–H···N2 proton-transfer process of the intramolecularly hydrogen-bonded conformer of 3-hydroxykynurenine O-$\beta$-D-glucoside (energy: $-1405.473957$ $E_h$).

```
49

C    2.8391435446  -1.9745337155  -0.1620610341
C    1.6711976858  -1.6761723100  -0.8673239957
C    1.1707103392  -0.3608536840  -0.9329613203
C    1.8275412066   0.7436026912  -0.2663115566
C    3.0975266568   0.4233946218   0.3396088283
C    3.5847206291  -0.8725475086   0.3924617372
O    0.9949847127  -2.6733652340  -1.5825150912
C   -0.1766838181  -3.2016623827  -0.9634004674
C   -0.0203344427  -3.5978766418   0.5201704035
C   -0.3021297707  -2.4888941001   1.5643988404
C   -1.1740282558  -1.3693237734   0.9953872761
C   -2.0764767660  -1.9381735694  -0.0880491278
O   -1.2838827950  -2.3386965713  -1.2144060428
O   -1.0008659568  -4.6085384935   0.7898466624
C   -3.0776680203  -0.9280554998  -0.6260023108
O   -2.5260605815   0.1032077523  -1.3972021658
O   -2.0013063408  -0.7761007705   1.9840887205
O    0.8266698104  -1.9857402942   2.2470121739
N    0.2096862087  -0.1073020914  -2.0233018862
C    1.2441192725   2.0526981654  -0.0356674126
C   -0.2502481269   2.2337644810  -0.2983105277
C   -0.8275309319   3.3631875833   0.5475359260
N   -2.2924432824   3.3890127070   0.3612356806
O    1.8821830383   3.0226839171   0.4404911979
C   -0.2135831217   4.7168809948   0.2326702197
O   -0.0382844082   5.6127905750   1.0338169458
O   -0.0362835514   4.8826632241  -1.1115388371
```

*Continued on next page*

| | | | |
|---|---|---|---|
| H | −0.5077708941 | −0.6207854057 | 0.5283884226 |
| H | −0.9087716245 | −2.9964278532 | 2.3342185244 |
| H | 1.0062494263 | −3.9754680700 | 0.6764205772 |
| H | −0.3486896001 | −4.1242229048 | −1.5474798839 |
| H | −2.6466767354 | −2.7963274484 | 0.3159589685 |
| H | −0.7885309672 | 0.0349041869 | −1.7009209780 |
| H | 4.5454547255 | −1.0735878374 | 0.8800675991 |
| H | 3.1958902604 | −3.0074775883 | −0.1096153871 |
| H | 3.6489997929 | 1.2573359178 | 0.7875265610 |
| H | 0.5119315615 | 0.7121107506 | −2.5711440949 |
| H | 0.1940463161 | −0.9475960712 | −2.6205390020 |
| H | −0.8206081233 | 1.3220425234 | −0.0497090837 |
| H | −0.4557357767 | 2.4732055676 | −1.3604970886 |
| H | −0.6208929004 | 3.1738514636 | 1.6127871748 |
| H | −2.6710431521 | 4.1350684210 | 0.9545972605 |
| H | −2.4729521819 | 3.7075880583 | −0.5975068305 |
| H | −1.3919207601 | −0.4747648656 | 2.6780845797 |
| H | 1.4513998824 | −1.6561453540 | 1.5752895952 |
| H | −0.7865276291 | −5.3672276600 | 0.2261996863 |
| H | −3.6151259065 | −0.4365734020 | 0.2074603457 |
| H | −3.8367373904 | −1.4151407078 | −1.2696354281 |
| H | 0.3156816969 | 5.7873402463 | −1.1942444877 |