**Support information**

# Photosensitive Damage of Dipeptides: Mechanism and Influence of Structure

Cheng Yang[a], Kai Yi[a], Meirou Zhu[a], Jiangxue Yang[a], Yaxiong Wei*[a], Yongjia Shang[b], Xinsheng Xu*[a]

†

[a] Anhui Province Key Laboratory of Optoelectric Materials Science and Technology, School of Physics and Electronic Information, Anhui Normal University, Wuhu 241002, China. E-mails: davidl@mail.ustc.edu.cn; xxsheng@mail.ahnu.edu.cn

[b] Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, China

# Contents

## Figures and Tables

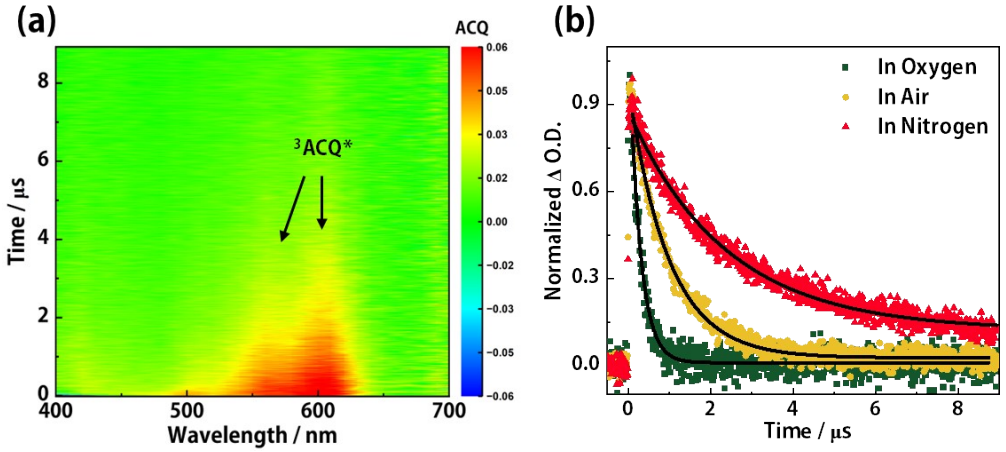


**Figure S1.** (a) Transient absorption spectra of ACQ in $N_2$-saturated ACN-$H_2O$ solution under photoexcitation at 355 nm. (b) The kinetic decay curves at 610 nm with Oxygen, Air and Nitrogen.

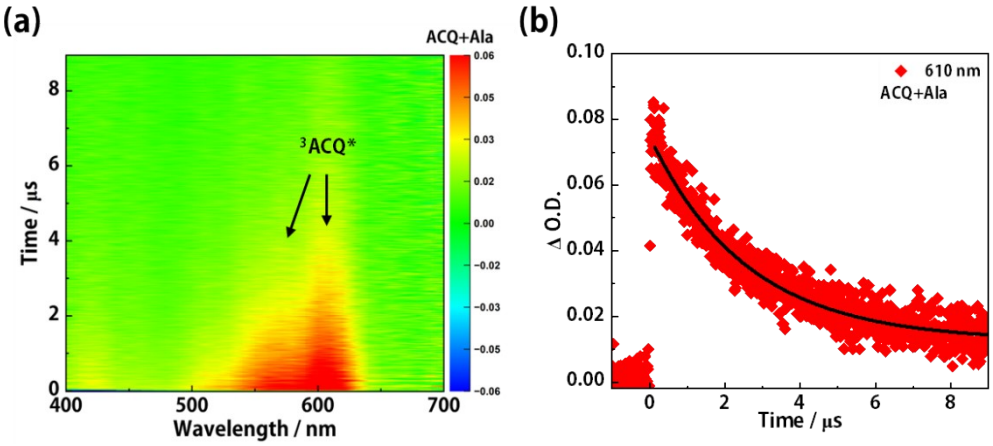


**Figure S2.** Transient absorption spectra (a) and kinetic decay curve (b) of ACQ+Ala measured in $N_2$-saturated ACN-$H_2O$ (1:1, v/v) solution under photoexcitation at 355 nm, *c*[ACQ] = 1.0 mM, *c*[Ala] = 1.0 mM.

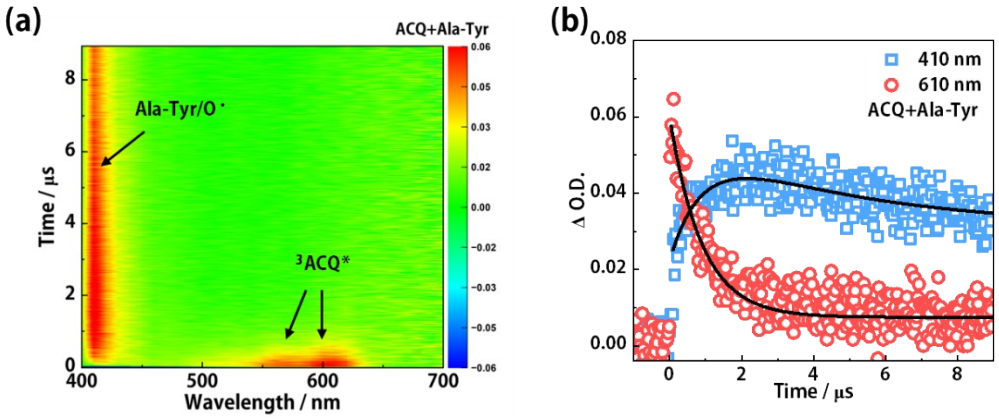


**Figure S3.** Transient absorption spectra (a) and kinetic decay curves (b) of ACQ+Ala-Tyr measured in $N_2$-saturated ACN-$H_2O$ (1:1, v/v) solution under photoexcitation at 355 nm, *c*[ACQ] = 1.0 mM, *c*[Ala-Tyr] = 1.0 mM

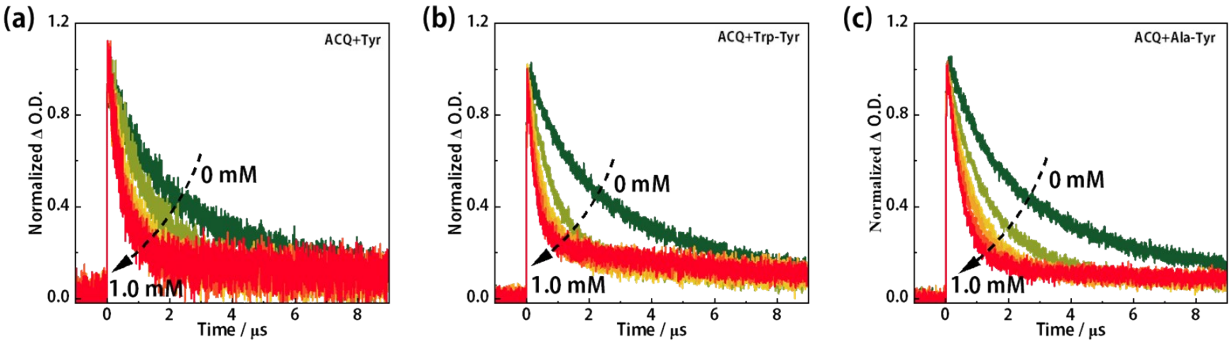


**Figure S4.** Kinetic decay curves of $^3$ACQ* measured at 610 nm with different concentrations of Tyr (a), Trp-Tyr (b), Ala-Tyr (c), *c*[ACQ] = 1.0 mM.

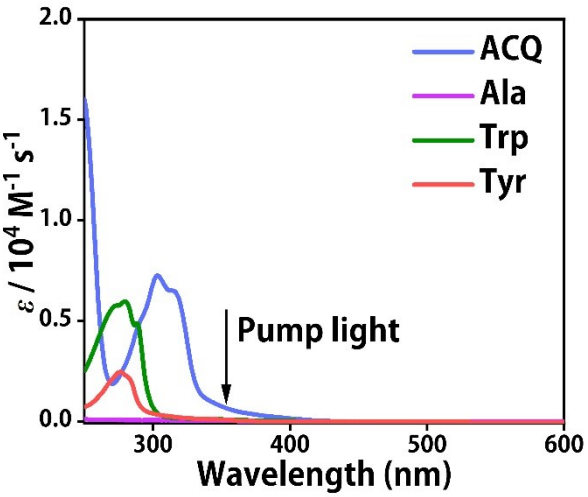


**Figure S5.** The steady-state UV-visible absorption spectra of ACQ, Ala, Trp, Tyr measured in ACN-$H_2O$ (1:1, v/v) solution.

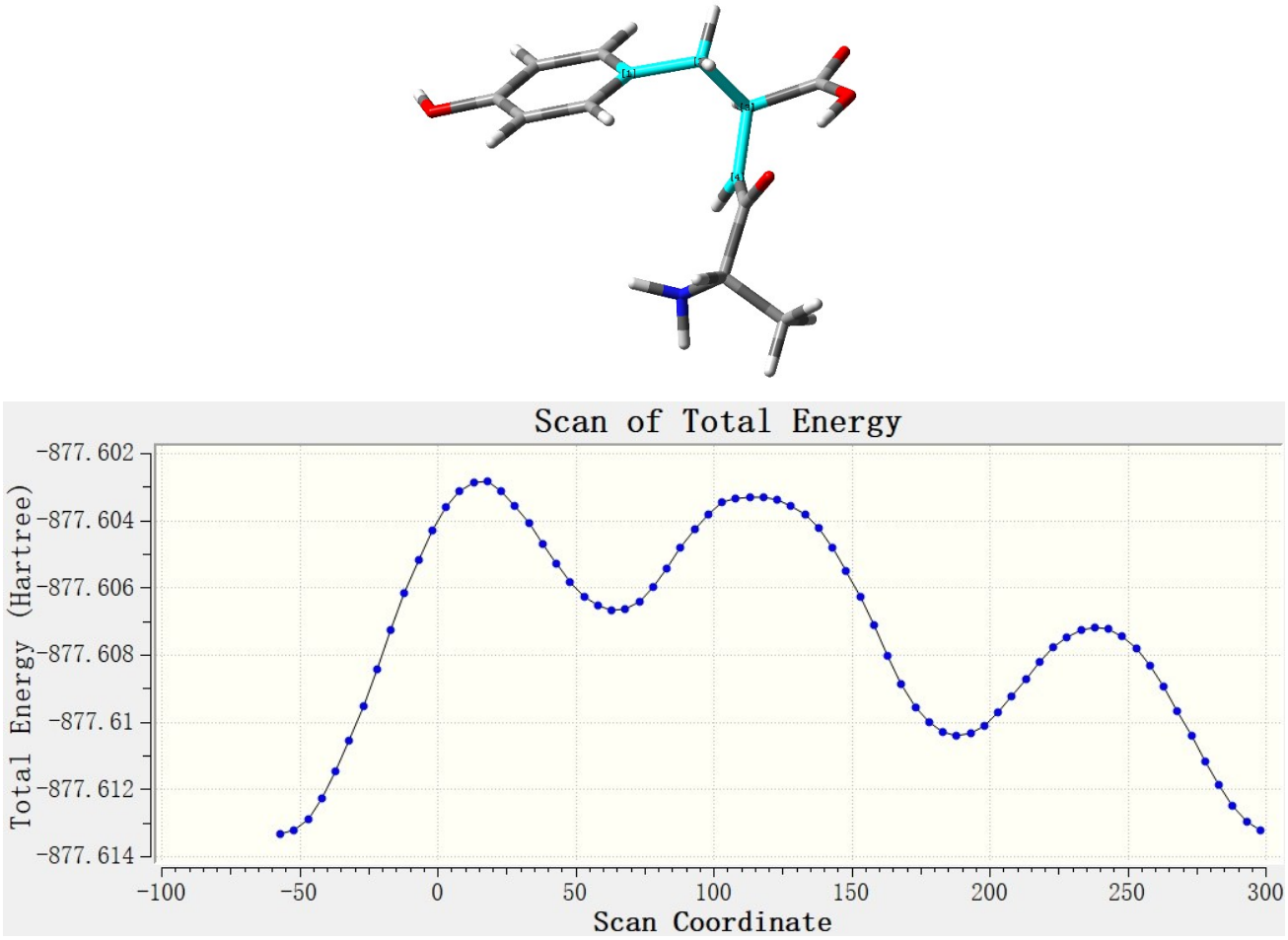


**Figure S6.** Scan of total energy of Ala-Tyr with the dihedral angle (carbon atom 1, 2, 3, 4).

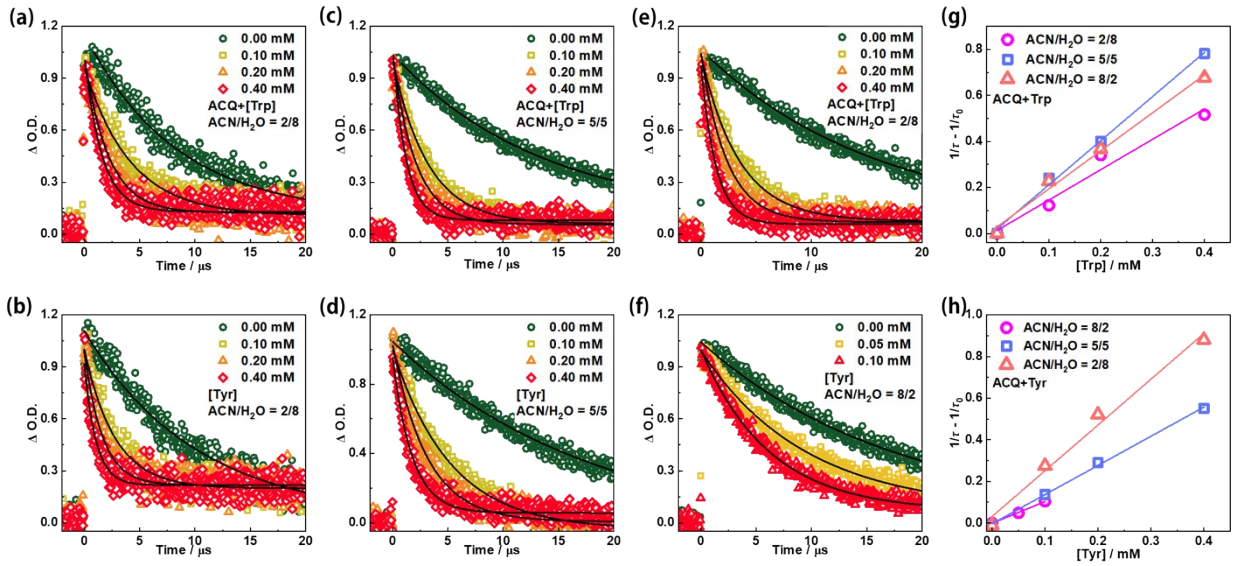


**Figure S7.** Transient absorption spectra (a-f) and kinetic decay curves (g-h) of ACQ+Trp (or Tyr) measured in $N_2$-saturated ACN-$H_2O$ solution under photoexcitation at 355 nm, *c*[ACQ] = 1.0 mM.

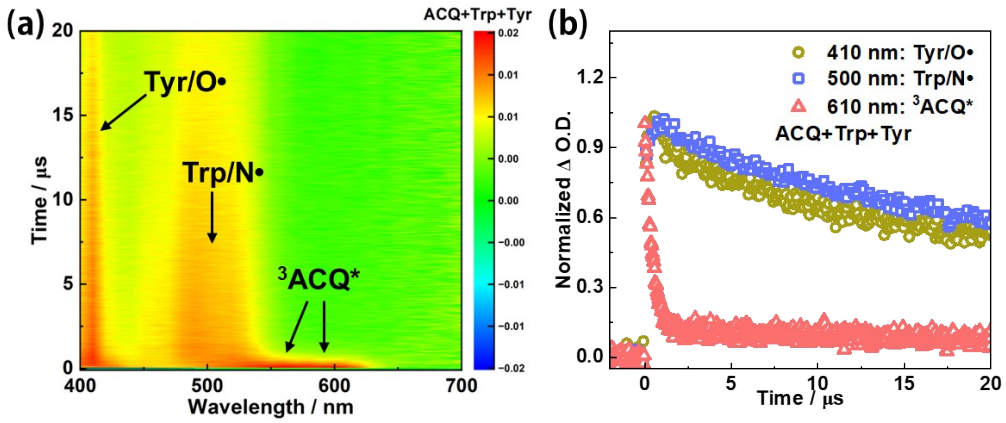


**Figure S8.** Transient absorption spectra (a) and kinetic decay curves (b) of ACQ+Trp+Tyr measured in $N_2$-saturated ACN-$H_2O$ (1:1, v/v) solution under photoexcitation at 355 nm, *c*[ACQ] = 1.0 mM, *c*[Trp] = 0.5 mM, *c*[Tyr] = 0.5 mM.

**Table S1.** Summary of bimolecular quenching rate.

| **Amino acid** | **$k_q$ / $10^9$ $M^{-1}$ $s^{-1}$** |
|---|---|
| Tyr | 1.55 ± 0.08 |
| Trp | 2.11 ± 0.12 |
| Trp-Tyr | 3.65 ± 0.06 |
| Ala-Tyr | 0.83 ± 0.03 |
| Tyr-Ala | 1.41 ± 0.04 |

**Table S2.** Summary of bimolecular quenching rate in different solvents.

| [ACN] (%) | $\eta$ (mpa s)[1,2] | $\varepsilon$ (F/m) [1,2] | $k_{diffuse}$ [a] | $k_q$ [a] | | $k_q$ / $k_{diffuse}$ | |
|---|---|---|---|---|---|---|---|
| | | | | ACQ+Tyr | ACQ+Trp | ACQ+Tyr | ACQ+Trp |
| 20 | 0.87 | 70 | 7.5 | 2.2 | 1.4 | 0.29 | 0.19 |
| 50 | 0.56 | 57 | 11.6 | 1.4 | 1.9 | 0.12 | 0.17 |
| 80 | 0.38 | 44 | 17.1 | 1.0 | 1.7 | 0.06 | 0.10 |

[a] bimolecular quenching rate, $10^9$ $M^{-1}$ $s^{-1}$, $k_{diffuse} = 8k_BT/(3\eta)$.

# DFT Calculation results

### The optimal ground state structures of Trp

0 1

| | | | |
|---|---|---|---|
| C | 4.13061000 | -0.97179600 | -0.17752000 |
| C | 3.81439800 | 0.37589000 | -0.28258700 |
| C | 2.48065800 | 0.74452200 | -0.09196700 |
| C | 1.46317300 | -0.20421100 | 0.19863000 |
| C | 1.81672400 | -1.56042700 | 0.29908900 |
| C | 3.14026000 | -1.93095900 | 0.11089700 |
| N | 1.87718800 | 1.98292800 | -0.13354900 |
| C | 0.52464700 | 1.84505700 | 0.11891800 |
| C | 0.22267600 | 0.52259300 | 0.32750000 |
| C | -1.11773200 | -0.07995100 | 0.64371800 |
| C | -2.24833500 | 0.32400500 | -0.33803400 |
| C | -3.43720600 | -0.61774900 | -0.13368700 |
| N | -2.60395400 | 1.72745900 | -0.16697800 |
| O | -3.22884900 | -1.83099100 | -0.70040200 |
| O | -4.44446700 | -0.34845000 | 0.47298100 |
| H | 5.15679200 | -1.29123400 | -0.31914800 |
| H | 4.57806600 | 1.11369400 | -0.50418300 |
| H | 1.06763700 | -2.31288700 | 0.52093000 |
| H | 3.42095800 | -2.97539900 | 0.18628200 |
| H | 2.34173300 | 2.85359800 | -0.32819600 |
| H | -0.13443700 | 2.69722900 | 0.11815200 |
| H | -1.02413600 | -1.16829200 | 0.63489400 |
| H | -1.44354700 | 0.19250400 | 1.65563100 |
| H | -1.87971700 | 0.17518300 | -1.35620400 |
| H | -3.20697400 | 2.03767900 | -0.92243700 |
| H | -3.13959500 | 1.84031500 | 0.69020300 |
| H | -4.00214000 | -2.38141800 | -0.50261000 |

### The optimal ground state structures of Tyr

0 1

| | | | |
|---|---|---|---|
| C | -2.64108500 | -1.12990600 | 0.17628300 |
| C | -3.31836500 | 0.05300900 | -0.12211300 |
| C | -2.62983200 | 1.26513000 | -0.11493300 |
| C | -1.26952500 | 1.28531900 | 0.19042700 |
| C | -0.57191000 | 0.11244500 | 0.48999600 |
| C | -1.28476700 | -1.09390200 | 0.47688800 |
| O | -4.65584400 | -0.03816900 | -0.40914900 |
| C | 0.90599700 | 0.16094900 | 0.80210800 |
| C | 1.80907900 | -0.26132600 | -0.39372500 |
| C | 3.23434900 | 0.22392000 | -0.12380000 |
| O | 3.37463000 | 1.55153300 | -0.35953900 |
| O | 4.14066600 | -0.46399600 | 0.27628800 |
| N | 1.73248600 | -1.69703800 | -0.61746100 |
| H | -3.18842700 | -2.06488200 | 0.16920200 |
| H | -3.15093000 | 2.19124700 | -0.34050600 |
| H | -0.74779700 | 2.23732800 | 0.19838400 |
| H | -0.76448500 | -2.01901300 | 0.69180500 |

| | | | |
|---|---|---|---|
| H | -5.00924400 | 0.83923700 | -0.58837700 |
| H | 1.17502300 | 1.17623000 | 1.10410600 |
| H | 1.14424300 | -0.49701900 | 1.64472600 |
| H | 1.44820000 | 0.25662500 | -1.28589800 |
| H | 4.28611000 | 1.79259900 | -0.13300000 |
| H | 2.07832300 | -1.93993800 | -1.53959000 |
| H | 2.32233400 | -2.18191000 | 0.05377400 |

**The optimal ground state structures of Trp-Tyr**

0 1

| | | | |
|---|---|---|---|
| C | 5.74694600 | 1.63036100 | -1.13431800 |
| C | 6.80455200 | 1.31008700 | -0.28119400 |
| C | 6.54981000 | 0.65329400 | 0.92167600 |
| C | 5.24067800 | 0.31486900 | 1.26183800 |
| C | 4.16977700 | 0.62098500 | 0.42081900 |
| C | 4.44832800 | 1.28897300 | -0.77943800 |
| O | 8.06586300 | 1.67107000 | -0.67626700 |
| C | 2.75084100 | 0.25563600 | 0.78540000 |
| C | 2.13275200 | -0.92554100 | -0.02974500 |
| N | 0.70862900 | -1.05058900 | 0.22858800 |
| C | 2.78383600 | -2.24864300 | 0.33155400 |
| O | 2.33922000 | -3.02893800 | 1.14130200 |
| O | 3.93300900 | -2.45276100 | -0.33384400 |
| C | -0.21284800 | -0.28331300 | -0.42660900 |
| C | -1.66728200 | -0.53122200 | 0.01170900 |
| C | -2.63205700 | -0.18853100 | -1.13751900 |
| O | 0.10832700 | 0.54066300 | -1.26781600 |
| N | -1.93067500 | 0.32087700 | 1.18061100 |
| C | -4.07871000 | -0.44002000 | -0.81587300 |
| C | -5.02054600 | 0.47723800 | -0.21516100 |
| C | -6.26537200 | -0.20064700 | -0.11145000 |
| N | -6.08205400 | -1.46764500 | -0.62324600 |
| C | -4.77270700 | -1.60054500 | -1.04908500 |
| C | -4.93723200 | 1.80957900 | 0.22734200 |
| C | -6.06837600 | 2.41614300 | 0.75308800 |
| C | -7.29018300 | 1.72148200 | 0.85086800 |
| C | -7.40557800 | 0.40697000 | 0.42063400 |
| H | 5.95729000 | 2.15024400 | -2.06115600 |
| H | 7.36736600 | 0.41030300 | 1.59443600 |
| H | 5.05669400 | -0.19185500 | 2.20403500 |
| H | 3.63275500 | 1.55385900 | -1.44507700 |
| H | 8.70358100 | 1.41398000 | -0.00237600 |
| H | 2.67808400 | 0.01290300 | 1.84960900 |
| H | 2.08911000 | 1.10525400 | 0.60078600 |
| H | 2.27979300 | -0.72739100 | -1.09273900 |
| H | 0.42081000 | -1.77804900 | 0.86822700 |
| H | 4.31435100 | -3.28557900 | -0.01470600 |
| H | -1.77846600 | -1.60511000 | 0.24036700 |
| H | -2.34179100 | -0.78242800 | -2.00897600 |
| H | -2.47152100 | 0.85685000 | -1.40917400 |
| H | -2.90189300 | 0.23378200 | 1.46496400 |
| H | -1.35618200 | 0.05054800 | 1.97219100 |
| H | -6.79528400 | -2.17130200 | -0.71226100 |

| | | | |
|---|---|---|---|
| H | -4.43691600 | -2.52078000 | -1.50302900 |
| H | -4.00067000 | 2.35142000 | 0.16344200 |
| H | -6.01506100 | 3.44330800 | 1.09558900 |
| H | -8.15637700 | 2.22330400 | 1.26698700 |
| H | -8.34810700 | -0.12495800 | 0.49297200 |

**The optimal ground state structures of Tyr-Ala**

0 1

| | | | |
|---|---|---|---|
| C | 4.50996100 | 0.82323300 | -0.16884600 |
| C | 4.92418500 | -0.49288300 | -0.37797900 |
| C | 4.04578800 | -1.54324200 | -0.11831300 |
| C | 2.75980900 | -1.26893000 | 0.34716800 |
| C | 2.32300100 | 0.04082800 | 0.56091000 |
| C | 3.22547600 | 1.08056700 | 0.29460600 |
| O | 6.20260900 | -0.68988700 | -0.83328100 |
| C | 0.91890600 | 0.30943000 | 1.05269400 |
| C | -0.04184200 | 0.85297900 | -0.04093100 |
| C | -1.49095000 | 0.68665200 | 0.45130000 |
| N | 0.27566400 | 2.24441000 | -0.34928400 |
| N | -2.12196100 | -0.46460200 | 0.06548600 |
| C | -3.50368500 | -0.74149600 | 0.41174200 |
| C | -4.52680700 | -0.13072700 | -0.55162400 |
| O | -2.01862100 | 1.51419800 | 1.17874200 |
| C | -3.75307000 | -2.25160000 | 0.53274600 |
| O | -5.70296600 | -0.05244100 | -0.30790600 |
| O | -3.98803600 | 0.27737400 | -1.72371300 |
| H | 5.20378900 | 1.63047400 | -0.37114000 |
| H | 4.36237700 | -2.57121600 | -0.27090000 |
| H | 2.09105100 | -2.09889300 | 0.55471200 |
| H | 2.90715900 | 2.10519600 | 0.43893900 |
| H | 6.37242700 | -1.63312900 | -0.92400900 |
| H | 0.50268700 | -0.61644000 | 1.46136200 |
| H | 0.92476700 | 1.03582600 | 1.87179800 |
| H | 0.10489800 | 0.26065700 | -0.95042900 |
| H | -0.16372300 | 2.52712200 | -1.21964300 |
| H | -0.11823900 | 2.83503200 | 0.38030900 |
| H | -1.69850500 | -1.01738300 | -0.66486500 |
| H | -3.69530400 | -0.25951000 | 1.37192900 |
| H | -4.79389600 | -2.43963300 | 0.79767300 |
| H | -3.10911000 | -2.67059700 | 1.30780900 |
| H | -3.54147000 | -2.76494600 | -0.41045600 |
| H | -4.71334200 | 0.63596900 | -2.25808000 |

**The optimal ground state structures of Ala-Tyr**

0 1

| | | | |
|---|---|---|---|
| C | 2.99405600 | 0.69653300 | 0.99818100 |
| C | 3.85040600 | 0.21978100 | 0.00611700 |
| C | 3.46828700 | -0.87581900 | -0.77004600 |
| C | 2.23270800 | -1.48128400 | -0.55450200 |
| C | 1.35473600 | -1.01405700 | 0.42855300 |
| C | 1.76245500 | 0.08057700 | 1.19995800 |

| | | | |
|---|---|---|---|
| O | 5.04978800 | 0.86022900 | -0.15538500 |
| C | 0.00192200 | -1.65516500 | 0.63726300 |
| C | -1.02285600 | -1.28602300 | -0.47217100 |
| N | -1.21978800 | 0.16205100 | -0.61115600 |
| C | -2.32230500 | -2.10337900 | -0.28559800 |
| O | -2.51446900 | -3.09675700 | -0.94081100 |
| O | -3.17220200 | -1.69884900 | 0.65871300 |
| C | -1.67858800 | 1.00314200 | 0.32973700 |
| C | -1.59913700 | 2.49649300 | -0.01636300 |
| C | -3.00265400 | 3.00720900 | -0.36437100 |
| O | -2.17487200 | 0.63824700 | 1.40406300 |
| N | -0.67410800 | 2.72856600 | -1.13328900 |
| H | 3.30942500 | 1.53529000 | 1.60737300 |
| H | 4.13616400 | -1.26088200 | -1.53524800 |
| H | 1.95690300 | -2.33871400 | -1.16085500 |
| H | 1.11019800 | 0.45105700 | 1.98434600 |
| H | 5.56497400 | 0.42230300 | -0.84096200 |
| H | 0.09111000 | -2.74560600 | 0.63362600 |
| H | -0.39974400 | -1.36806900 | 1.61066700 |
| H | -0.62692300 | -1.61983800 | -1.43019600 |
| H | -0.82993900 | 0.62918100 | -1.42378200 |
| H | -2.85403100 | -0.86665300 | 1.09641400 |
| H | -1.27552900 | 2.98341000 | 0.91204600 |
| H | -3.70315500 | 2.76071500 | 0.43385900 |
| H | -3.35781100 | 2.55544300 | -1.29468500 |
| H | -2.98999200 | 4.09373100 | -0.48736600 |
| H | 0.28754900 | 2.80134100 | -0.81720600 |
| H | -0.90206400 | 3.58196000 | -1.63009400 |

Reference


1. H. Wode, W. Seidel, *Berichte der Bunsengesellschaft für physikalische Chemie*, 1994, **98**, 927.
2. A. M. Katti, N. E. Tarfulea, C. J. Hopper, K. R. Kmiotek, *Journal of Chemical Engineering Data*, 2008, **53**, 2865.