# Signatures of $n \rightarrow \pi^*$ interactions in proteins

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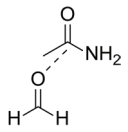


| Parameter | Value |
|---|---|
| $O_{aldehyde}$–$C_{amide}$ distance (*d*) | 2.5–3.5 Å |
| $O_{aldehyde}$–$C_{amide}$–$O_{amide}$ angle | 110° |
| $C_{aldehyde}$–$O_{aldehyde}$–$C_{amide}$–$O_{amide}$ dihedral | 180° |
| $H_{aldehyde}$–$C_{aldehyde}$–$O_{aldehyde}$–$C_{amide}$ dihedral | 180° |

**Figure S1.** Optimization parameters of formamide as approached by formaldehyde (**1**).

**Table S1.** Cartesian coordinates of **1** at *d* = 2.75 Å

| | | | |
|---|---|---|---|
| C | 2.21955600 | 0.13416200 | 0.12859200 |
| O | 1.46735700 | -0.70820000 | -0.27323400 |
| H | 3.31315700 | 0.06878400 | -0.02535400 |
| H | 1.86483300 | 1.02939700 | 0.67981700 |
| C | -1.12407700 | -0.05808800 | 0.37817000 |
| N | -0.89655000 | 1.16483000 | -0.18088700 |
| H | -0.68059200 | -0.16989000 | 1.38216400 |
| H | -1.23029300 | 1.32754000 | -1.11901700 |
| H | -0.21152900 | 1.79416100 | 0.20047400 |
| O | -1.88643200 | -0.87433000 | -0.08832300 |

**Table S2.** Cartesian coordinates of **1** at *d* = 2.80 Å

| | | | |
|---|---|---|---|
| C | 2.24354900 | 0.13741800 | 0.13139500 |
| O | 1.49615000 | -0.70793200 | -0.27340800 |
| H | 3.33797500 | 0.07643000 | -0.01847800 |
| H | 1.88243600 | 1.03092800 | 0.68131200 |
| C | -1.14749300 | -0.05652500 | 0.37991000 |
| N | -0.90929300 | 1.16184800 | -0.18381700 |
| H | -0.70718100 | -0.16613100 | 1.38568000 |
| H | -1.23337100 | 1.32152200 | -1.12587000 |
| H | -0.22213300 | 1.78762700 | 0.19970700 |
| O | -1.90477700 | -0.87565100 | -0.08952500 |

**Table S3.** Cartesian coordinates of **1** at *d* = 2.85 Å

| | | | |
|---|---|---|---|
| C | 2.26746800 | 0.14030900 | 0.13392600 |
| O | 1.52494500 | -0.70758700 | -0.27352900 |
| H | 3.36314500 | 0.08434200 | -0.01108400 |
| H | 1.90117000 | 1.03317900 | 0.68296300 |
| C | -1.17079300 | -0.05470600 | 0.38163700 |
| N | -0.92187900 | 1.15855300 | -0.18669100 |
| H | -0.73377200 | -0.16324500 | 1.38924400 |
| H | -1.23712600 | 1.31432200 | -1.13245000 |
| H | -0.23328800 | 1.78223700 | 0.19808500 |
| O | -1.92332300 | -0.87670300 | -0.09063300 |

**Table S4.** Cartesian coordinates of **1** at *d* = 2.90 Å

| | | | |
|---|---|---|---|
| C | 2.29195500 | 0.14384600 | 0.13652700 |
| O | 1.55407200 | -0.70713100 | -0.27354600 |
| H | 3.38821500 | 0.09167500 | -0.00495400 |
| H | 1.92011500 | 1.03498900 | 0.68391500 |
| C | -1.19389700 | -0.05337200 | 0.38316000 |
| N | -0.93597200 | 1.15574500 | -0.18933700 |
| H | -0.75990500 | -0.15947100 | 1.39241400 |
| H | -1.24114700 | 1.30741800 | -1.13910600 |
| H | -0.24464700 | 1.77559600 | 0.19661600 |
| O | -1.94146900 | -0.87827800 | -0.09165900 |

**Table S5.** Cartesian coordinates of **1** at $d$ = 2.95 Å

| | | | |
|---|---|---|---|
| C | 2.31651600 | 0.14736500 | 0.13890600 |
| O | 1.58330700 | -0.70669200 | -0.27341300 |
| H | 3.41343200 | 0.09908700 | 0.00113000 |
| H | 1.93903200 | 1.03710700 | 0.68448100 |
| C | -1.21691800 | -0.05212700 | 0.38445000 |
| N | -0.95003600 | 1.15295000 | -0.19204000 |
| H | -0.78593900 | -0.15582100 | 1.39544700 |
| H | -1.24634600 | 1.30120300 | -1.14516400 |
| H | -0.25751000 | 1.77010900 | 0.19620400 |
| O | -1.95955900 | -0.88002900 | -0.09258200 |

**Table S6.** Cartesian coordinates of **1** at $d$ = 3.00 Å

| | | | |
|---|---|---|---|
| C | 2.34130300 | 0.15095100 | 0.14113000 |
| O | 1.61274100 | -0.70616500 | -0.27322100 |
| H | 3.43888300 | 0.10668800 | 0.00708000 |
| H | 1.95830900 | 1.03943900 | 0.68485300 |
| C | -1.23973600 | -0.05099000 | 0.38565900 |
| N | -0.96469400 | 1.15018100 | -0.19466600 |
| H | -0.81170100 | -0.15219400 | 1.39832900 |
| H | -1.25240500 | 1.29476900 | -1.15100000 |
| H | -0.27125500 | 1.76506200 | 0.19569200 |
| O | -1.97753700 | -0.88193500 | -0.09340700 |

**Table S7.** Cartesian coordinates of **1** at $d$ = 3.05 Å

| | | | |
|---|---|---|---|
| C | 2.36635400 | 0.15466200 | 0.14320700 |
| O | 1.64241400 | -0.70552900 | -0.27299100 |
| H | 3.46457100 | 0.11443200 | 0.01281200 |
| H | 1.97796900 | 1.04196200 | 0.68501500 |
| C | -1.26232700 | -0.05003200 | 0.38678500 |
| N | -0.98003100 | 1.14746000 | -0.19719500 |
| H | -0.83715800 | -0.14864700 | 1.40106400 |
| H | -1.25982300 | 1.28836600 | -1.15644400 |
| H | -0.28610300 | 1.76065500 | 0.19505500 |
| O | -1.99533900 | -0.88406800 | -0.09414500 |

**Table S8.** Cartesian coordinates of **1** at $d$ = 3.10 Å

| | | | |
|---|---|---|---|
| C | 2.39167000 | 0.15850100 | 0.14514500 |
| O | 1.67232700 | -0.70479100 | -0.27272900 |
| H | 3.49048200 | 0.12227900 | 0.01829500 |
| H | 1.99798100 | 1.04464000 | 0.68496800 |
| C | -1.28469300 | -0.04927300 | 0.38782300 |
| N | -0.99604200 | 1.14481800 | -0.19961500 |
| H | -0.86231400 | -0.14519900 | 1.40365200 |
| H | -1.26866300 | 1.28210100 | -1.16147200 |
| H | -0.30202200 | 1.75689800 | 0.19431700 |
| O | -2.01295500 | -0.88643500 | -0.09480400 |

**Table S9.** Cartesian coordinates of **1** at $d$ = 3.15 Å

| | | | |
|---|---|---|---|
| C | 2.41722800 | 0.16243100 | 0.14695600 |
| O | 1.70244400 | -0.70396800 | -0.27244200 |
| H | 3.51659000 | 0.13018000 | 0.02354100 |
| H | 2.01831900 | 1.04743000 | 0.68474000 |
| C | -1.30685800 | -0.04869400 | 0.38878100 |
| N | -1.01267200 | 1.14228000 | -0.20191800 |
| H | -0.88719800 | -0.14185100 | 1.40610200 |
| H | -1.27869200 | 1.27595900 | -1.16615100 |
| H | -0.31877200 | 1.75363300 | 0.19346400 |
| O | -2.03041500 | -0.88899800 | -0.09539500 |

**Table S10.** Cartesian coordinates of **1** at $d$ = 3.20 Å

| | | | |
|---|---|---|---|
| C | 2.44300400 | 0.16641800 | 0.14865100 |
| O | 1.73273100 | -0.70308100 | -0.27212900 |
| H | 3.54287500 | 0.13809000 | 0.02856700 |
| H | 2.03896600 | 1.05030300 | 0.68434400 |
| C | -1.32884700 | -0.04827100 | 0.38965800 |
| N | -1.02983500 | 1.13985400 | -0.20410900 |
| H | -0.91184200 | -0.13860600 | 1.40842100 |
| H | -1.28970600 | 1.26996000 | -1.17052900 |
| H | -0.33620400 | 1.75076200 | 0.19254500 |
| O | -2.04775500 | -0.89171600 | -0.09592500 |

**Table S11.** Cartesian coordinates of **1** at $d$ = 3.25 Å

| | | | |
|---|---|---|---|
| C | 2.46898000 | 0.17044000 | 0.15023500 |
| O | 1.76316200 | -0.70214400 | -0.27179100 |
| H | 3.56932200 | 0.14598200 | 0.03338400 |
| H | 2.05991000 | 1.05324000 | 0.68379100 |
| C | -1.35067900 | -0.04798400 | 0.39045400 |
| N | -1.04746500 | 1.13753900 | -0.20619300 |
| H | -0.93627200 | -0.13546500 | 1.41061200 |
| H | -1.30157800 | 1.26413400 | -1.17463100 |
| H | -0.35423400 | 1.74823100 | 0.19160800 |
| O | -2.06500000 | -0.89455900 | -0.09640100 |

**Table S12.** Cartesian coordinates of **1** at $d$ = 3.30 Å

| | | | |
|---|---|---|---|
| C | 2.49525800 | 0.17462600 | 0.15166200 |
| O | 1.79390400 | -0.70110500 | -0.27141700 |
| H | 3.59603600 | 0.15406900 | 0.03791900 |
| H | 2.08120000 | 1.05637100 | 0.68297400 |
| C | -1.37223200 | -0.04796300 | 0.39114200 |
| N | -1.06588600 | 1.13531100 | -0.20818800 |
| H | -0.96035000 | -0.13241500 | 1.41266500 |
| H | -1.31523000 | 1.25874800 | -1.17828700 |
| H | -0.37412800 | 1.74685600 | 0.19094000 |
| O | -2.08196400 | -0.89774300 | -0.09679800 |

**Table S13.** Cartesian coordinates of **1** at $d$ = 3.35 Å

| | | | |
|---|---|---|---|
| C | 2.52177300 | 0.17881300 | 0.15300300 |
| O | 1.82478600 | -0.69997800 | -0.27112200 |
| H | 3.62294100 | 0.16205500 | 0.04218700 |
| H | 2.10302300 | 1.05956000 | 0.68223200 |
| C | -1.39359200 | -0.04808200 | 0.39188000 |
| N | -1.08442600 | 1.13292300 | -0.21017600 |
| H | -0.98422100 | -0.12974800 | 1.41456500 |
| H | -1.33154000 | 1.25435700 | -1.18109900 |
| H | -0.39556700 | 1.74691000 | 0.19031200 |
| O | -2.09887800 | -0.90101900 | -0.09716000 |

**Table S14.** Cartesian coordinates of **1** at $d$ = 3.40 Å

| | | | |
|---|---|---|---|
| C | 2.54836000 | 0.18302700 | 0.15418300 |
| O | 1.85576600 | -0.69894600 | -0.27058600 |
| H | 3.64990800 | 0.17005200 | 0.04643500 |
| H | 2.12460600 | 1.06283700 | 0.68087600 |
| C | -1.41490600 | -0.04829000 | 0.39224700 |
| N | -1.10388300 | 1.13119600 | -0.21187800 |
| H | -1.00798200 | -0.12678900 | 1.41636900 |
| H | -1.34495400 | 1.24903200 | -1.18479100 |
| H | -0.41594100 | 1.74538300 | 0.19005300 |
| O | -2.11566300 | -0.90446800 | -0.09746200 |

**Table S15.** Cartesian coordinates of **1** at $d$ = 3.45 Å

| | | | |
|---|---|---|---|
| C | 2.57520300 | 0.18724500 | 0.15530800 |
| O | 1.88689300 | -0.69778800 | -0.27017100 |
| H | 3.67708200 | 0.17800500 | 0.05036100 |
| H | 2.14684400 | 1.06611200 | 0.67969200 |
| C | -1.43600500 | -0.04865300 | 0.39275200 |
| N | -1.12331800 | 1.12909400 | -0.21370000 |
| H | -1.03146500 | -0.12404500 | 1.41803600 |
| H | -1.36167000 | 1.24481300 | -1.18751600 |
| H | -0.43887300 | 1.74602900 | 0.19002800 |
| O | -2.13237800 | -0.90797800 | -0.09771000 |

**Table S16.** Cartesian coordinates of **1** at $d$ = 3.50 Å

| | | | |
|---|---|---|---|
| C | 2.60220200 | 0.19143700 | 0.15635100 |
| O | 1.91808100 | -0.69661500 | -0.26975500 |
| H | 3.70439800 | 0.18580800 | 0.05418000 |
| H | 2.16931200 | 1.06935700 | 0.67840600 |
| C | -1.45700000 | -0.04906300 | 0.39319700 |
| N | -1.14292800 | 1.12699300 | -0.21543200 |
| H | -1.05479700 | -0.12155700 | 1.41969300 |
| H | -1.37911700 | 1.24084500 | -1.18998700 |
| H | -0.46247700 | 1.74719500 | 0.18995600 |
| O | -2.14908600 | -0.91149100 | -0.09793300 |

**Table S17.** Energies of **1** optimized at various values of $d$.

| $d$ (Å) | Energy (Hartree) |
|---|---|
| 2.75 | -284.4950067740 |
| 2.80 | -284.4957078650 |
| 2.85 | -284.4963193460 |
| 2.90 | -284.4968531970 |
| 2.95 | -284.4973185180 |
| 3.00 | -284.4977250820 |
| 3.05 | -284.4980812470 |
| 3.10 | -284.4983937100 |
| 3.15 | -284.4986676930 |
| 3.20 | -284.4989073750 |
| 3.25 | -284.4991165440 |
| 3.30 | -284.4992991080 |
| 3.35 | -284.4994588180 |
| 3.40 | -284.4995995940 |
| 3.45 | -284.4997246160 |
| 3.50 | -284.4998364470 |