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Supporting Information

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Concerted Asynchronous Hula-Twist Photoisomerization in the S65T/H148D Mutant of Green Fluorescent Protein**

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1. Computational Details

1.1 Model Setup: The crystal structure of an S65T/H148D GFP mutant (PDB code: 2DUF)[S1] containing the neutral GFP chromophore *p*-HBDI was used to construct the initial QM/MM model. Its protonation state was checked by visual inspection. Eight Na^+ counterions were added using the xleap module of the AMBER9 package[S2] to neutralize the system in accordance with experimental conditions. The 294 crystal water molecules in the protein were kept in the model.

1.2 Equilibrium Molecular Dynamics (MD): The initially constructed system was equilibrated for 1 ns using classical canonical MD simulations (at 298 K). The general Amber force field (GAFF), the Amber99 force field,[S2] and the TIP3P water model were used for the chromophore, the amino acid residues of the S65T/H148D GFP mutant, and the water molecules, respectively. A cutoff radius of 9.0 Å was used for truncating the electrostatic and van der Waals interactions. All MD simulations were performed with the TINKER4.2 package.[S3] For the starting geometry of the subsequent QM/MM calculations, we selected a snapshot from the end of the MD run with an appropriate intermolecular hydrogen-bonding network.

1.3 QM/MM Computational Protocol: Scheme S1 shows the chosen QM/MM partitioning. The QM subsystem (53 atoms) consisting of Asp148 and the neutral *p*-HBDI chromophore is larger than the QM models used previously.[S4-S7] The MM subsystem includes the remaining amino acid residues, water molecules, and counterions. The boundary separating the QM and MM regions was treated by the hydrogen link-atom scheme (see the wavy lines in Scheme S1). To reduce the strong electrostatic interactions between a link atom and its two nearest MM atoms, the weight-consistent reparameterization scheme introduced by Olivucci et al. was adopted to adjust the MM point charges near the QM/MM boundaries. [S8-S11] Specifically, the two nearest point charges were set to

zero and the other neighboring MM point charges were re-parameterized (see Table S1). Many previous QM/MM excited-state simulations have shown that this simple scheme can achieve satisfactory accuracy. For the remaining MM atoms, standard force-field point charges were used. Please see the original literatures[S8-S11] for the detailed QM/MM protocol.

Scheme S1. *The chosen QM/MM partitioning: the QM subsystem includes the para-chromophore (p-1) and Asp148; the MM subsystem includes the other amino acid residues, counterions, and water molecules. See text for details*.

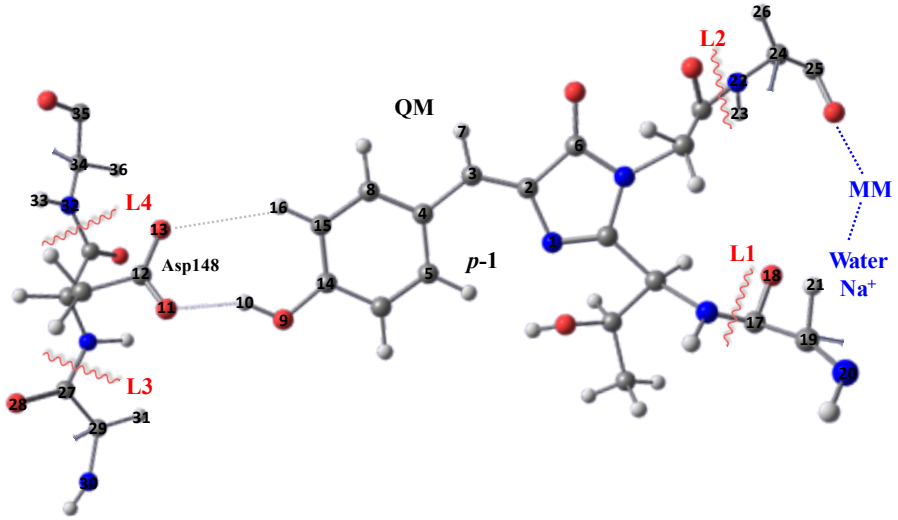


Table S1. *Re-parameterized point charges (a.u.) for the MM atoms near the QM/MM boundary.*

C17	0.0000	C27	0.0000
O18	-0.4179	O28	-0.4179
C19	0.2476	C29	0.2251
N20	-0.2657	N30	-0.2657
H21	0.1451	H31	0.1316
N22	0.0000	N32	0.0000
H23	0.2019	H33	0.2019
C24	-0.2875	C34	-0.1857
C25	0.4973	C35	0.4973
H26	0.0512	H36	0.0591

1.3.1 QM Method: The complete active space self-consistent field (CASSCF) method was chosen as QM electronic structure method. In all CASSCF calculations (geometry optimizations and single-point computations), we used an active space of 12 electrons in 10 orbitals, which included 2 electrons and 2 orbitals (σ and σ*) of the O9-H10 bond of the *p*-HBDI GFP chromophore, 2 electrons and 1 lone-pair n orbital of the O11 atom of Asp148, and 8 π electrons and 7 π/π* orbitals mainly from the GFP chromophore (the highest 4 occupied π and the lowest 3 unoccupied π* orbitals).

Geometry optimizations were performed using a 2-root state-averaged CASSCF approach (S_0 and S_1, equal weights) for the S_1 state and a state-specific approach for the S_0 state. Single-point energies at all optimized structures were determined from 4-root state-averaged CASPT2//CASSCF calculations to include more dynamical electron correlation. These calculations were done without an ionization potential-electron affinity (IPEA) shift, but included an energy-level shift of 0.2 a.u. to avoid intruder-state problems.

The 6-31G* basis set was employed in all electronic structure calculations. In the QM-only calculations of the QM subsystem (see Scheme 1), which are denoted as “in vacuo” in the following, the same computational strategies were applied (CASSCF, CASPT2, basis set, etc.).

1.3.2 Vertical Excitation Energies: Vertical excitation energies, oscillator strengths, and transition dipole moments to the lowest three excited singlet states at the Franck-Condon (**FC)** point were computed using the CASPT2//CASSCF and CASSI//CASSCF methods at the CASSCF optimized S_0 minimum.

1.3.3 Optimizations of Minima and Paths: Local minima on the S_0 and S_1 states were fully optimized at the CASSCF level for the in-vacuo system and at the QM(CASSCF)/AMBER level for

the double mutant, respectively.[S8-S11] At the same computational levels, the minimum-energy paths for proton transfer and photoisomerization were computed by reaction-coordinate-constrained optimizations, in which the chosen reaction coordinate was fixed at a given value while all remaining degrees of freedom were fully relaxed. The O9...H10 distance and the φ and τ dihedral angles (C5-C4-C3-C2 and C4-C3-C2-C6) were selected as the predefined reaction coordinates of the excited-state proton transfer and photoisomerization, respectively (see Scheme 1). Intrinsic reaction coordinate (IRC) calculations were not performed.

1.3.4 S_1/S_0 Conical Intersections: The location of conical intersections was assessed on the basis of the computed S_1-S_0 energy gaps along the optimized minimum-energy reaction paths both for the in-vacuo system and the double mutant.

In the case of the S65T/H148D double mutant, the conical intersection could be located quite precisely in this manner because there is only a small energy gap of 0.5 kcal/mol at this structure at the QM(CASPT2//CASSCF)/AMBER level (see Figure 2a). By contrast, the estimate for the in-vacuo conical intersection is rather approximate, with an energy gap of 6 kcal/mol at the CASPT2//CASSCF level (see Figure 2b).

1.3.5 Packages: The CASSCF calculations were performed using GAUSSIAN03.[S12] The CASPT2 and CASSI calculations were done using MOLCAS7.6;[S13] whereas the MM calculations were conducted using TINKER4.2. The corresponding QM/MM modules were employed for QM/MM computations.[S8-S10]

2. Minimum-Energy Paths

2.1 One-Bond-Flip Path: The minimum-energy profile was scanned along the C5-C4-C3-C2 (φ) dihedral angle of the GFP chromophore (*p*-1) at the CASPT2//CASSCF(12e,10o)/AMBER level. As

can be seen from the results shown in Figure S1, this path is unimportant. There is a high barrier in the S_1 state (> 40 kcal/mol) when the C5-C4-C3-C2 dihedral angle is increased from -11° to 105°. At the end point, the intermolecular O9···H10 hydrogen bond is slightly elongated to 1.70 Å from 1.66 Å of the S_1 keto tautomer. Furthermore, along this C5-C4-C3-C2 (φ) torsion, we did not find an energetically degenerate S_1/S_0 conical intersection region, the smallest energy gap being 23.5 kcal/mol in our computations. We conclude that the isomerization involving only the C5-C4-C3-C2 (φ) torsional reaction coordinate (i.e., a one-bond flip mechanism) is not allowed energetically in the S65T/H148D GFP mutant.

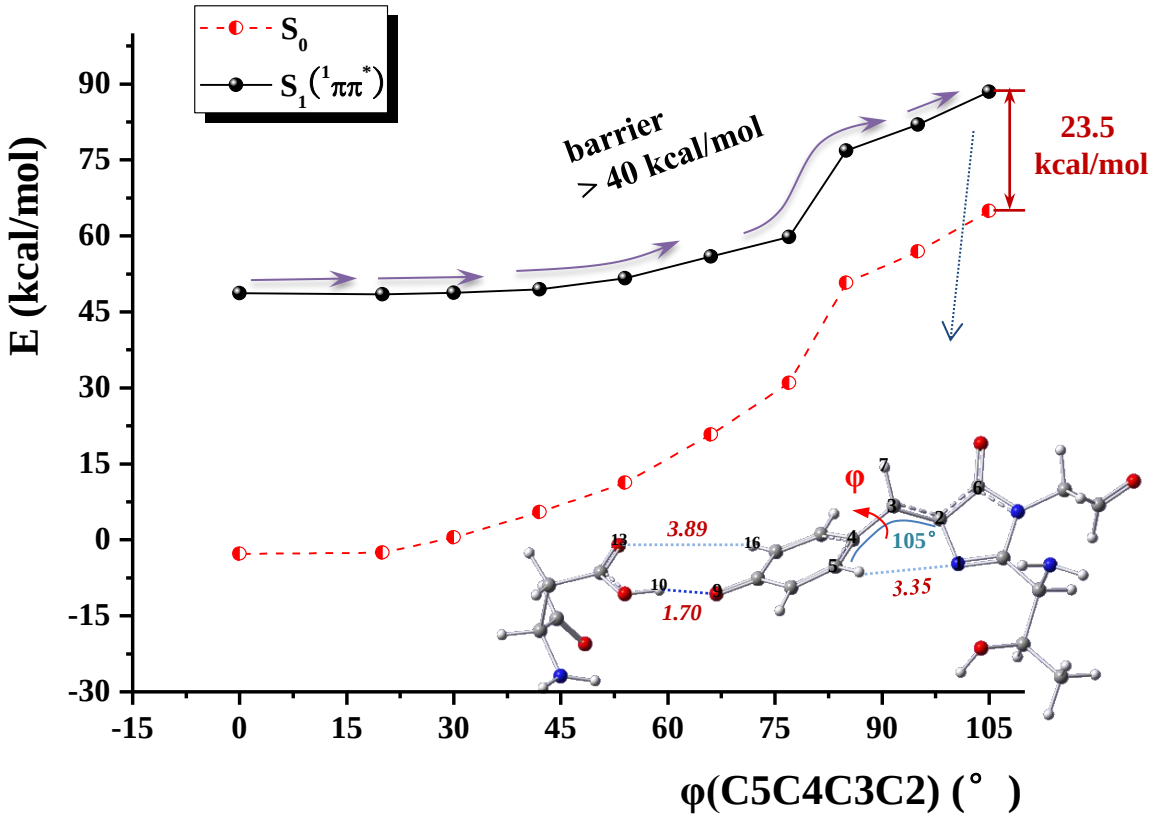


Figure S1. *Minimum-energy profiles (kcal/mol, unrelaxed S_0 and relaxed S_1) with respect to the rotation of the C5-C4-C3-C2 (φ) dihedral angle (C3-C4 P-bond) of the p-HBDI chromophore in the S65T/H148D GFP mutant calculated at the CASPT2//CASSCF(12e,10o)/AMBER level. The chosen reaction coordinate eventually corresponds to the simple one-bond-flip isomerization around P-bond. The related isomerization barrier is also highlighted.*

2.2 Concerted Synchronous Hula-Twist Mechanism: With the use of the minimum-energy path strategy, we also explored the synchronous hula-twist mechanism, i.e., the synchronous rotation around the C5-C4-C3-C2 (φ) and C4-C3-C2-C6 (τ) torsional angles. In our constrained optimizations, these two dihedral angles were simultaneously twisted to ca. 80° (see Figure S2). Along this concerted minimum-energy path, the dihedral angle (C5-C4-C3-H7) associated with the central C-H group is twisted out of the plane by more than 45° and there is a significant barrier in the S_1 state (> 36 kcal/mol). Hence, this synchronous hula-twist mechanism should not contribute to the observed loss of fluorescence in the S65T/H148D GFP mutant. The results for the concerted asynchronous hula-twist mechanism are described in the main article.

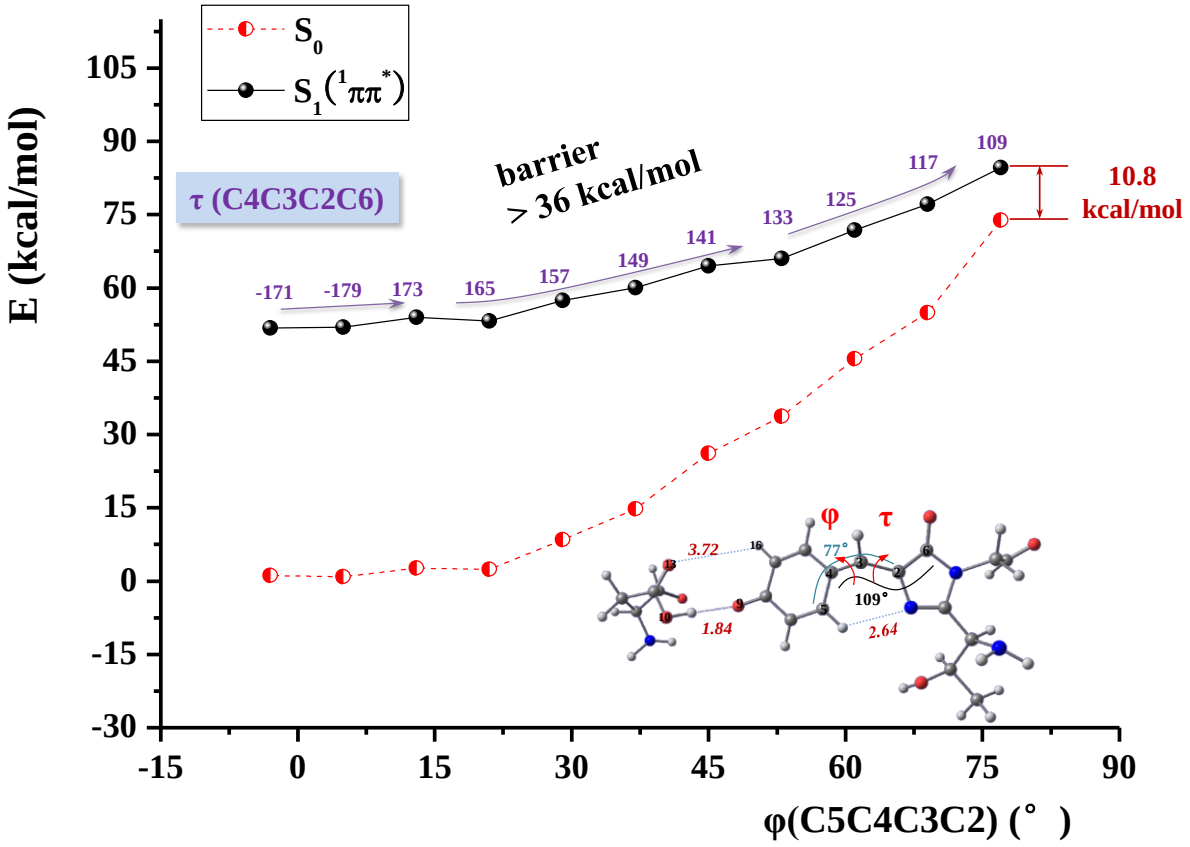


Figure S2. *Minimum-energy profiles (kcal/mol, unrelaxed S_0 and relaxed S_1) with respect to the simultaneous rotation of both C5-C4-C3-C2 (φ) and C4-C3-C2-C6 (τ) dihedral angles (C3-C4 P-bond and C2-C3 I-bond) of the p-HBDI chromophore in the S65T/H148D GFP mutant calculated at the CASPT2//CASSCF(12e,10o)/Amber level. This reaction coordinates correspond to the concerted synchronous hula-twist mechanism. The chosen τ (C4-C3-C2-C6) values are given along the points in the S_1 state. The related isomerization barrier is also highlighted.*

2.3 Role of Hydrogen Out-of-Plane (HOOP) Motion in the Excited-State Decay: The HOOP motion in the central CH unit during the final stage of the photoisomerization is essential for the decay of the anionic fluorescent state. In the beginning stages, when the C4-C3-C2-C6 dihedral angle is increased from -164° to -123°, the CH unit twists out of the plane only slightly (< 20°), and the S_1-S_0 energy gap remains large (on average > 30 kcal/mol). However, when the C4-C3-C2-C6 dihedral angle is further increased from -123° to -115°, the central CH unit is distorted out of the plane significantly (twist > 60°, see C5-C4-C3-H7 dihedral angle in Figure 2a). This strongly raises the S_0 energy and leads to an S_1/S_0 conical intersection (see discussion in the main article).

To further examine the role of this HOOP motion in the formation of the S_1/S_0 conical intersection, we optimized two S_1 structures with the C5-C4-C3-H7 dihedral angle fixed at 160° and 150° (see Figure S3 and relative energies in Table S2). The corresponding S_1-S_0 energy gaps were computed to be 21.5 and 18.4 kcal/mol, respectively; they are much larger than the gap of 0.5 kcal/mol at the S_1/S_0 conical intersection (see Figure 2a). Hence, significant HOOP motion is required to reach an S_1/S_0 conical intersection in the rigid protein surrounding. The HOOP motion is necessitated by the rigid cavity near the GFP chromophore (see discussion in the main article).

It should be stressed that such HOOP motion is not needed in the deactivation of the anionic fluorescent state in vacuo. Due to the missing steric constraints, the double-bond rotation can proceed smoothly without HOOP motion. This exemplifies the importance of the protein environment in choreographing the deactivation pathway of the anionic S_1 fluorescent state.

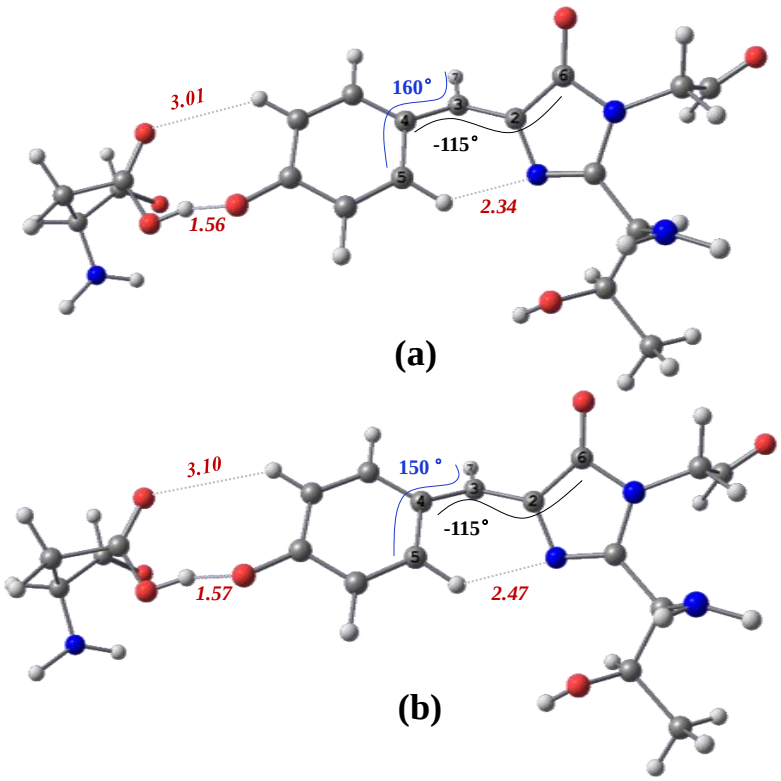


Figure S3. *S_1 structures optimized with the C5-C4-C3-H7 dihedral angle fixed at 160°(a) and 150°(b). See section 2.3 for details.*

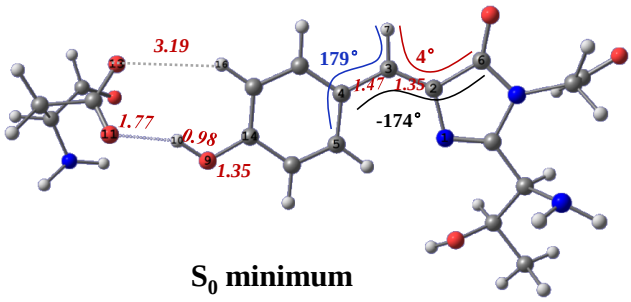
Table S2. *Relative energies (ΔE, kcal/mol) of two S_1 Structures Optimized with Fixed C5-C4-C3-H7 Dihedral Angle (see Figure S3 and section 2.3) and of the S_1/S_0 Conical Intersection in the S65T/H148D Double Mutant*

	160°	150°	S_1/S_0 CI
S_0	22.8	26.1	44.4
$S_1(^1\pi\pi^*)$	44.3	44.5	44.9

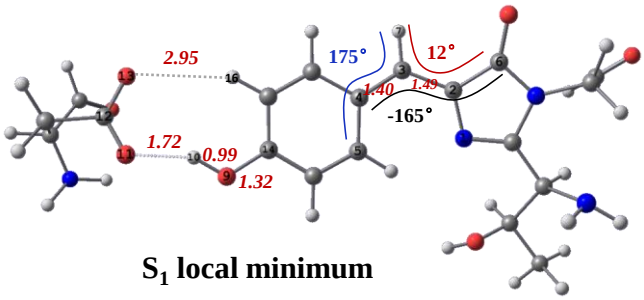
3. Optimized Structures

The structures optimized in the S_0 and S_1 states are schematically shown below: (a) the S65T/H148D GFP mutant, (b) in-vacuo. Selected key geometric parameters that are relevant to the excited-state proton transfer (reaction coordinate: O9-H10 distance) and to the photoisomerization (around the C4-C3-C2-C6 dihedral angle) are also given (see *Sect. 6* for full Cartesian coordinates).

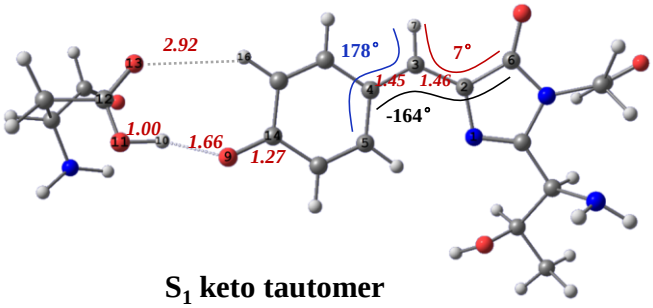
(a)



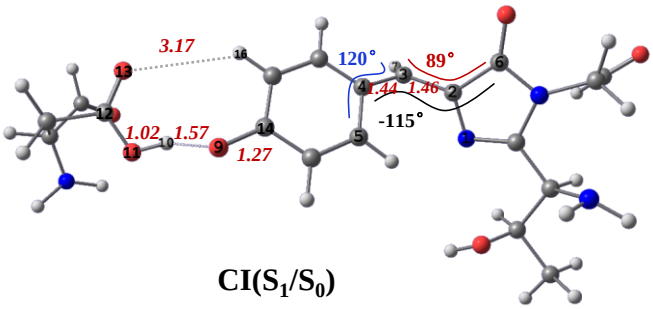
S_0 minimum



S_1 local minimum

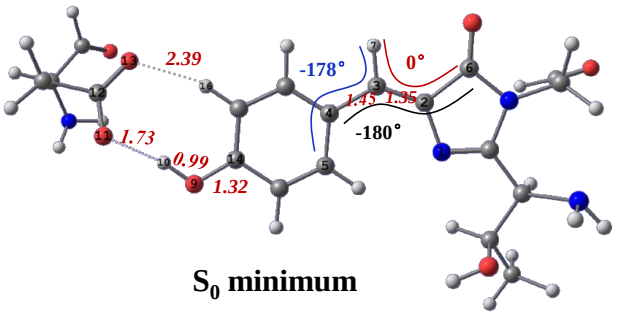


S_1 keto tautomer

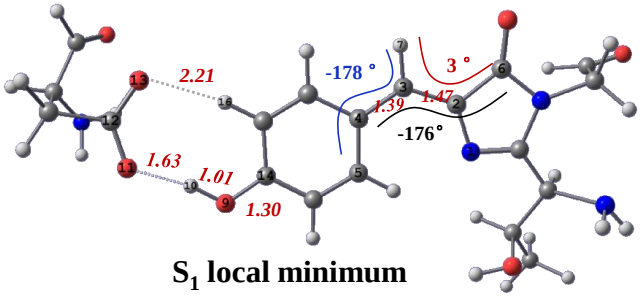


$CI(S_1/S_0)$

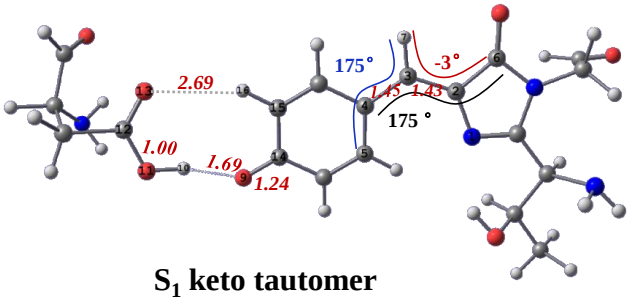
(b)



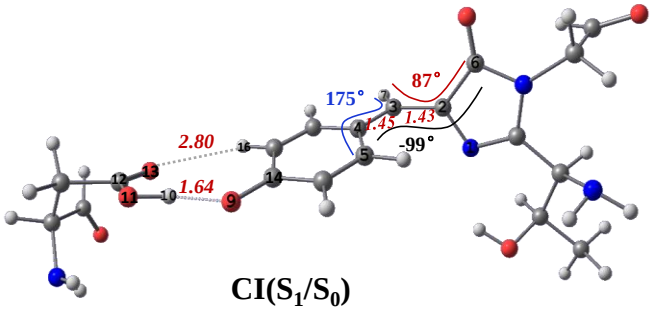
S_0 minimum



S_1 local minimum



S_1 keto tautomer



$CI(S_1/S_0)$

4. Tables

Table S3. *Vertical excitation energies ($E_{\perp}$, kcal/mol), oscillator strengths (f), transition dipole moments (ΔD.M., Debye), and singly occupied orbitals involved in the $S_0 \rightarrow S_1(^1\pi\pi^*)$ electronic transition in the S65T/H148D GFP mutant and in vacuo. The values were computed with the 4-root state-average CASPT2//CASSCF(12e,10o)/AMBER method at the CASSCF(12e,10o)/AMBER optimized S_0 minimum. Orbitals were plotted using GV tool of MOLCAS7.6.*

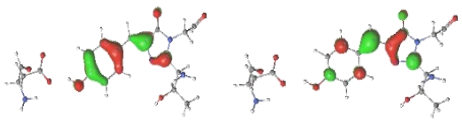
	$E_{\perp}$	*f*	ΔD.M.	singly occupied orbitals
in vacuo	71.6 (399 nm)	1.1769	17.45→13.03	
in protein	71.1 (402 nm)	1.1342	40.52→35.04	

Table S4. *Selected geometric parameters of the optimized structures involved in the proton transfer and isomerization processes in the S65T/H148D GFP mutant and in vacuo (see Scheme S1 for atom numbering).*

	Distance (Å)						Dihedral Angle (°)		
	O_9-H_{10}	H_{10}-O_{11}	O_{13}-H_{16}	O_9-C_{14}	C_2-C_3	C_3-C_4	$C_4C_3C_2C_6$	$C_5C_4C_3H_7$	$H_7C_3C_2C_6$
				In protein					
S_0-min	0.98	1.77	3.19	1.35	1.35	1.47	-174	179	4
S_1-loc min	0.99	1.72	2.95	1.32	1.49	1.40	-165	175	12
keto tautomer	1.66	1.00	2.92	1.27	1.46	1.45	-164	178	7
CI(S_1/S_0)	1.57	1.02	3.18	1.27	1.46	1.44	-115	120	89
				In vacuo					
S_0-min	0.99	1.73	2.39	1.32	1.35	1.45	-180	-178	0
S_1-loc min	1.01	1.64	2.21	1.30	1.47	1.39	-176	-178	3
keto tautomer	1.69	1.00	2.69	1.24	1.44	1.45	175	175	-3
CI(S_1/S_0)	1.64	1.01	2.81	1.25	1.45	1.42	-99	175	87

Table S5. *Absolute energies (A.E., hartree), relative energies (ΔE, kcal/mol), and MM energies (hartree) of optimized structures for proton transfer (reaction coordinate: O9-H10 distance) in the S65T/H148D GFP mutant. The corresponding energy profiles are plotted in Figure 1 (top left) of the main article.*

(O9-H10)	**CASSCF A.E.**	**CASPT2 A.E.**	**MM**	**CASPT2 ΔE**
S_0-min (0.985)				
Root1 (S_0)	-1495.35117	-1479.01739	-20.09461	0.0
Root2 ($S_1(^1\pi\pi^*)$)		-1478.90409		71.1

Root3		-1478.86994		92.5
Root4		-1478.85322		103.0
S_1-loc min (0.99)				
Root1 (S_0)	-1495.31061	-1479.00900	-20.08863	9.0
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18688	-1478.91526		67.8
Root3		-1478.88181		88.8
Root4		-1478.85834		103.6
S_1 (1.06)				
Root1 (S_0)	-1495.30794	-1479.00820	-20.08883	9.4
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18488	-1478.91628		67.1
Root3		-1478.88183		88.7
Root4		-1478.85780		103.8
S_1 (1.13)				
Root1 (S_0)	-1495.30410	-1479.01244	-20.09004	6.0
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18094	-1478.92354		61.8
Root3		-1478.88681		84.8
Root4		-1478.86265		100.0
S_1 (1.19)				
Root1 (S_0)	-1495.30078	-1479.01465	-20.09155	3.6
Root2 ($S_1(^1\pi\pi^*)$)	-1495.17835	-1478.92948		57.1
Root3		-1478.89036		81.6
Root4		-1478.86597		96.9
S_1 (1.27)				
Root1 (S_0)	-1495.30003	-1479.01033	-20.09282	5.6
Root2 ($S_1(^1\pi\pi^*)$)	-1495.17784	-1478.92990		56.0
Root3		-1478.88153		86.4
Root4		-1478.86459		97.0
S_1 (1.33)				
Root1 (S_0)	-1495.30149	-1479.01131	-20.09538	3.3
Root2 ($S_1(^1\pi\pi^*)$)	-1495.17955	-1478.93167		53.3
Root3		-1478.88294		83.9
Root4		-1478.86575		94.7
S_1 (1.40)				
Root1 (S_0)	-1495.30336	-1479.01887	-20.09658	-2.2
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18109	-1478.93641		49.6
Root3		-1478.89152		77.8
Root4		-1478.86748		92.8
S_1 (1.46)				
Root1 (S_0)	-1495.30732	-1479.01932	-20.09740	-3.0
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18534	-1478.93768		48.3
Root3		-1478.88929		78.6
Root4		-1478.86977		90.9
S_1 (1.51)				
Root1 (S_0)	-1495.30627	-1479.01764	-20.09720	-1.8
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18520	-1478.93694		48.9
Root3		-1478.88772		79.7
Root4		-1478.86922		91.4
S_1 (1.59)				
Root1 (S_0)	-1495.30872	-1479.01754	-20.09754	-1.9

Root2 ($S_1(^1\pi\pi^*)$)	-1495.18664	-1478.93695		48.6
Root3		-1478.88680		80.1
Root4		-1478.87039		90.4
S_1-tautomer (1.66)				
Root1 (S_0)	-1495.30869	-1479.01734	-20.09789	-2.0
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18652	-1478.93711		48.3
Root3		-1478.88609		80.3
Root4		-1478.87118		89.7

Table S6. *Absolute energies (A.E., hartree), relative energies (∆E, kcal/mol), and MM energies (hartree) of optimized structures for photoisomerization (reaction coordinate: C4-C3-C2-C6 dihedral angle) in the S65T/H148D GFP mutant. The corresponding energy profiles are plotted in Figure 1 (top right) of the main article.*

(*C4-C3-C2-C6*)	CASSCF A.E.	CASPT2 A.E.	MM	CASPT2 ΔE
S_1 (-156°)				
Root1 (S_0)	-1495.30255	-1479.01239	-20.09725	1.5
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18570	-1478.93730		48.6
Root3		-1478.88216		83.2
Root4		-1478.87311		88.9
S_1 (-153°)				
Root1 (S_0)	-1495.29872	-1479.01027	-20.09708	2.9
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18475	-1478.94121		46.3
Root3		-1478.87465		88.0
Root4		-1478.88363		82.4
S_1 (-146°)				
Root1 (S_0)	-1495.29069	-1479.00179	-20.10272	4.7
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18207	-1478.93586		46.1
Root3		-1478.86831		88.5
Root4		-1478.87694		83.0
S_1 (-145°)				
Root1 (S_0)	-1495.29176	-1478.99656	-20.11166	2.4
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18778	-1478.93351		41.9
Root3		-1478.86476		85.1
Root4		-1478.87397		79.3
S_1 (-141°)				
Root1 (S_0)	-1495.28423	-1478.99346	-20.10998	5.4
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18671	-1478.93438		42.5
Root3		-1478.86487		86.1
Root4		-1478.87310		80.9
S_1 (-137°)				
Root1 (S_0)	-1495.28187	-1478.99328	-20.10830	6.5
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18953	-1478.93727		41.7
Root3		-1478.86834		84.9
Root4		-1478.87215		82.6
S_1 (-132°)				

Root1 (S_0)	-1495.27251	-1478.98545	-20.10988	10.5
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18808	-1478.93405		42.7
Root3		-1478.86349		87.0
Root4		-1478.86603		85.4
S_1 (-128°)				
Root1 (S_0)	-1495.26312	-1478.97938	-20.10855	15.1
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18754	-1478.93355		43.9
Root3		-1478.86079		89.5
Root4		-1478.86190		88.8
S_1 (-123°)				
Root1 (S_0)	-1495.26531	-1478.98069	-20.10773	14.8
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18752	-1478.93316		44.6
Root3		-1478.86019		90.4
Root4		-1478.86081		90.0
S_1 (-117°)				
Root1 (S_0)	-1495.21504	-1478.94251	-20.10606	39.8
Root2 ($S_1(^1\pi\pi^*)$)	-1495.19460	-1478.93499		44.5
Root3		-1478.83117		109.7
Root4		-1478.84533		100.8
CI(S_1/S_0) (-115°)				
Root1 (S_0)	-1495.20628	-1478.93570	-20.10550	44.4
Root2 ($S_1(^1\pi\pi^*)$)	-1495.19536	-1478.93492		44.9
Root3		-1478.82613		113.2
Root4		-1478.84273		102.8

Table S7. *Absolute energies (A.E., hartree), relative energies (∆E, kcal/mol), and MM energies (hartree) of optimized structures for photoisomerization (reaction coordinate: C5-C4-C3-C2 dihedral angle) in the S65T/H148D GFP mutant. The corresponding energy profiles are plotted in Figure S1 of SI.*

(*C5-C4-C3-C2*)	CASSCF A.E.	CASPT2 A.E.	MM	CASPT2 ∆E
S_1 (0°)				
Root1 (S_0)	-1495.30965	-1479.01788	-20.09852	-2.8
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18566	-1478.93587		48.7
Root3		-1478.88584		80.1
Root4		-1478.86911		90.6
S_1 (20°)				
Root1 (S_0)	-1495.30609	-1479.01676	-20.09924	-2.5
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18331	-1478.93553		48.5
Root3		-1478.88391		80.9
Root4		-1478.87111		88.9
S_1 (30°)				
Root1 (S_0)	-1495.30054	-1479.01287	-20.09841	0.5
Root2 ($S_1(^1\pi\pi^*)$)	-1495.18026	-1478.93586		48.8
Root3		-1478.87578		86.5
Root4		-1478.87693		85.8

S_1 (42°)				
Root1 (S_0)	-1495.28985	-1479.00584	-20.09747	5.5
Root2 ($S_1(^1\pi\pi^*)$)	-1495.17585	-1478.93577		49.4
Root3		-1478.86623		93.1
Root4		-1478.87457		87.8
S_1 (54°)				
Root1 (S_0)	-1495.27588	-1478.99769	-20.09633	11.3
Root2 ($S_1(^1\pi\pi^*)$)	-1495.17162	-1478.93335		51.7
Root3		-1478.86077		97.2
Root4		-1478.86524		94.4
S_1 (66°)				
Root1 (S_0)	-1495.25784	-1478.98489	-20.09403	20.8
Root2 ($S_1(^1\pi\pi^*)$)	-1495.16846	-1478.92885		55.9
Root3		-1478.85127		104.6
Root4		-1478.84849		106.3
S_1 (77°)				
Root1 (S_0)	-1495.23419	-1478.97113	-20.09154	31.0
Root2 ($S_1(^1\pi\pi^*)$)	-1495.16515	-1478.92517		59.8
Root3		-1478.84142		112.4
Root4		-1478.83027		119.3
S_1 (85°)				
Root1 (S_0)	-1495.21975	-1478.95715	-20.07407	50.7
Root2 ($S_1(^1\pi\pi^*)$)	-1495.16489	-1478.91544		76.9
Root3		-1478.82837		131.5
Root4		-1478.81185		141.9
S_1 (95°)				
Root1 (S_0)	-1495.20086	-1478.94718	-20.07411	56.9
Root2 ($S_1(^1\pi\pi^*)$)	-1495.15759	-1478.90724		82.0
Root3		-1478.81575		139.4
Root4		-1478.82017		136.6
S_1 (105°)				
Root1 (S_0)	-1495.18333	-1478.93887	-20.06973	64.9
Root2 ($S_1(^1\pi\pi^*)$)	-1495.14892	-1478.90134		88.4
Root3		-1478.80936		146.2
Root4		-1478.81235		144.3

Table S8. *Absolute energies (A.E., hartree), relative energies (ΔE, kcal/mol), and MM energies (hartree) of optimized structures for photoisomerization (reaction coordinates: C5-C4-C3-C2 and C4-C3-C2-C6 dihedral angles) in the S65T/H148D GFP mutant. The corresponding energy profiles are plotted in Figure S2 of SI.*

C5-C4-C3-C2 *C4-C3-C2-C6*	**CASSCF A.E.**	**CASPT2 A.E.**	**MM**	**CASPT2 ΔE**
S_1 (-3°;-171°**)**				
S_0	-1495.31264	-1479.01442	-20.09582	1.1
$S_1(^1\pi\pi^*)$	-1495.18689	-1478.93360		51.8

S_1 (5°; -179°)				
S_0	-1495.31278	-1479.01618	-20.09442	0.9
$S_1(^1\pi\pi^*)$	-1495.18679	-1478.93472		52.0
S_1 (13°; 173°)				
S_0	-1495.30422	-1479.01156	-20.09624	2.6
$S_1(^1\pi\pi^*)$	-1495.17994	-1478.92978		53.9
S_1 (21°; 165°)				
S_0	-1495.30645	-1479.01177	-20.09644	2.4
$S_1(^1\pi\pi^*)$	-1495.18473	-1478.93077		53.2
S_1 (29°; 157°)				
S_0	-1495.29187	-1479.00732	-20.09601	5.4
$S_1(^1\pi\pi^*)$	-1495.17093	-1478.92690		55.9
S_1 (37°; 149°)				
S_0	-1495.27525	-1478.99827	-20.09023	14.8
$S_1(^1\pi\pi^*)$	-1495.16336	-1478.92603		60.1
S_1 (45°; 141°)				
S_0	-1495.26453	-1478.98274	-20.08766	26.1
$S_1(^1\pi\pi^*)$	-1495.16526	-1478.92153		64.5
S_1 (53°; 133°)				
S_0	-1495.24558	-1478.97139	-20.08694	33.7
$S_1(^1\pi\pi^*)$	-1495.16220	-1478.91990		66.0
S_1 (61°; 125°)				
S_0	-1495.22325	-1478.95499	-20.08450	45.5
$S_1(^1\pi\pi^*)$	-1495.15558	-1478.91302		71.8
S_1 (69°; 117°)				
S_0	-1495.20423	-1478.94057	-20.08397	54.9
$S_1(^1\pi\pi^*)$	-1495.14610	-1478.90510		77.1
S_1 (77°; 109°)				
S_0	-1495.18311	-1478.92062	-20.07376	73.8
$S_1(^1\pi\pi^*)$	-1495.15093	-1478.90346		84.6

Table S9. *Absolute energies (A.E., hartree) and relative energies (∆E, kcal/mol) of optimized structures for proton transfer (reaction coordinate: O9-H10 distance*) *in vacuo. The corresponding energy profiles are plotted in Figure 1 (bottom left) of the main article.*

(O9-H10)	**CASSCF**	**CASPT2**	
	A.E.	**A.E.**	**ΔE**
S_0-min (0.99)			
Root1 (S_0)	-1474.85660	-1479.05905	0.0
Root2 ($S_1(^1\pi\pi^*)$)		-1478.94498	71.6
Root3		-1478.91123	92.8
Root4		-1478.89610	102.3
S_1-min (1.01)			
Root1 (S_0)	-1474.82881	-1479.05036	5.4
Root2 ($S_1(^1\pi\pi^*)$)	-1474.70120	-1478.95292	66.6

Root3		-1478.91772	88.7
Root4		-1478.89753	101.4
S_1 (1.08)			
Root1 (S_0)	-1474.82523	-1479.04989	5.7
Root2 ($S_1(^1\pi\pi^*)$)	-1474.69977	-1478.95487	65.4
Root3		-1478.91871	88.1
Root4		-1478.89675	101.8
S_1 (1.15)			
Root1 (S_0)	-1474.82161	-1479.04928	6.1
Root2 ($S_1(^1\pi\pi^*)$)	-1474.69782	-1478.95688	64.1
Root3		-1478.91910	87.8
Root4		-1478.89588	102.4
S_1 (1.20)			
Root1 (S_0)	-1474.82323	-1479.05285	3.9
Root2 ($S_1(^1\pi\pi^*)$)	-1474.70102	-1478.96331	60.1
Root3		-1478.92399	84.7
Root4		-1478.90039	99.6
S_1 (1.26)			
Root1 (S_0)	-1474.82955	-1479.06026	-0.8
Root2 ($S_1(^1\pi\pi^*)$)	-1474.70808	-1478.97253	54.3
Root3		-1478.92513	84.0
Root4		-1478.90058	99.4
S_1 (1.32)			
Root1 (S_0)	-1474.83161	-1479.05660	1.5
Root2 ($S_1(^1\pi\pi^*)$)	-1474.71022	-1478.97377	53.5
Root3		-1478.92235	85.8
Root4		-1478.90730	95.2
S_1 (1.38)			
Root1 (S_0)	-1474.83807	-1479.06370	-2.9
Root2 ($S_1(^1\pi\pi^*)$)	-1474.71601	-1478.97813	50.8
Root3		-1478.92805	82.2
Root4		-1478.91128	92.7
S_1 (1.44)			
Root1 (S_0)	-1474.84043	-1479.06504	-3.8
Root2 ($S_1(^1\pi\pi^*)$)	-1474.71821	-1478.97987	49.7
Root3		-1478.92936	81.4
Root4		-1478.91338	91.4
S_1 (1.52)			
Root1 (S_0)	-1474.84393	-1479.06653	-4.7
Root2 ($S_1(^1\pi\pi^*)$)	-1474.72153	-1478.98277	47.9
Root3		-1478.93000	81.0
Root4		-1478.91898	87.9
S_1 (1.60)			
Root1 (S_0)	-1474.84254	-1479.06510	-3.8
Root2 ($S_1(^1\pi\pi^*)$)	-1474.72025	-1478.98161	48.6
Root3		-1478.92850	81.9
Root4		-1478.91767	88.7
S_1-tautomer (1.69)			
Root1 (S_0)	-1474.84348	-1479.06477	-3.6

Root2 ($S_1(^1\pi\pi^*)$)	-1474.72132	-1478.98134	48.8
Root3		-1478.92829	82.1
Root4		-1478.91697	89.2

Table S10. *Absolute energies (A.E., hartree) and relative energies (∆E, kcal/mol) of all optimized structures for photoisomerization (reaction coordinate: C4-C3-C2-C6 dihedral angle) in vacuo. The corresponding energy profiles are plotted in Figure 1 (bottom right) of the main article.*

(*C4-C3-C2-C6*)	CASSCF	CASPT2	
	A.E.	A.E.	ΔE
S_1 (-170°)			
Root1 (S_0)	-1474.84196	-1479.06312	-2.6
Root2 ($S_1(^1\pi\pi^*)$)	-1474.72033	-1478.97980	49.7
Root3		-1478.92714	82.8
Root4		-1478.91451	90.7
S_1 (-158°)			
Root1 (S_0)	-1474.83791	-1479.06018	-0.7
Root2 ($S_1(^1\pi\pi^*)$)	-1474.72027	-1478.97945	50.0
Root3		-1478.92695	82.9
Root4		-1478.91186	92.4
S_1 (-145°)			
Root1 (S_0)	-1474.82702	-1479.05099	5.1
Root2 ($S_1(^1\pi\pi^*)$)	-1474.72262	-1478.97853	50.5
Root3		-1478.92277	85.5
Root4		-1478.90394	97.3
S_1 (-132°)			
Root1 (S_0)	-1474.81269	-1479.03830	13.0
Root2 ($S_1(^1\pi\pi^*)$)	-1474.72844	-1478.98020	49.5
Root3		-1478.91336	91.4
Root4		-1478.89234	104.6
S_1 (-119°)			
Root1 (S_0)	-1474.78557	-1479.00891	31.5
Root2 ($S_1(^1\pi\pi^*)$)	-1474.74064	-1478.99122	42.6
Root3		-1478.89931	100.2
Root4		-1478.87222	117.2
S_1 (-109°)			
Root1 (S_0)	-1474.77952	-1479.00327	35.0
Root2 ($S_1(^1\pi\pi^*)$)	-1474.74482	-1478.98913	43.9
Root3		-1478.89039	105.8
Root4		-1478.86292	123.1
CI(S_1/S_0) (-99°)			
Root1 (S_0)	-1474.78209	-1479.00418	34.4
Root2 ($S_1(^1\pi\pi^*)$)	-1474.74470	-1478.99460	40.4
Root3		-1478.90011	99.7
Root4		-1478.87087	118.1

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6. Cartesian Coordinates

S_0 minimum (protein)

N	9.916406	7.866508	1.689217
C	10.943106	6.896173	1.418279
C	11.167830	6.731034	-0.081484
O	10.489014	7.282069	-0.895928
C	10.706230	5.518955	2.095777
C	9.510228	4.800068	1.482705
O	9.732119	4.236012	0.391503
O	8.432008	4.819154	2.079645
H	9.088140	7.775514	1.141165
H	9.895389	8.070238	2.685816
H	11.884664	7.272339	1.809918
H	11.957934	6.069376	-0.435109
H	11.583626	4.888248	1.982512
H	10.555008	5.696417	3.151276
C	-0.308958	0.972135	-2.015425
N	0.799927	1.498881	-1.674301
C	1.827216	0.725039	-2.232528
C	-3.289097	3.307086	-1.171434
O	-1.045332	3.261043	-0.355844
C	1.192463	-0.376732	-2.976064
O	1.698137	-1.315723	-3.597585
N	-0.115789	-0.191384	-2.821637
C	-1.723859	1.388102	-1.701378
N	-2.190015	0.473575	-0.681120
C	-1.846405	2.895347	-1.434310

C	-1.120294	-1.114541	-3.306929
C	-1.656425	-0.814272	-4.697655
O	-2.163285	-1.677141	-5.343831
C	3.161294	0.896644	-2.076502
C	3.868948	1.888894	-1.257969
C	3.203587	2.900901	-0.513256
C	3.919137	3.758339	0.284265
C	5.249599	1.816728	-1.162489
C	5.988416	2.707462	-0.371256
C	5.323035	3.658725	0.363951
O	5.921137	4.532873	1.192945
H	-3.317633	4.384528	-1.063626
H	-3.634011	2.862040	-0.245404
H	-3.962556	3.019147	-1.973900
H	-0.792108	4.195507	-0.495238
H	-2.310506	1.202911	-2.594919
H	-1.743836	0.638300	0.204958
H	-3.203926	0.372423	-0.753704
H	-1.510432	3.397439	-2.338723
H	-0.702525	-2.109122	-3.333054
H	-1.941362	-1.130851	-2.605653
H	-1.575784	0.181817	-5.143763
H	3.790774	0.197763	-2.600046
H	2.138873	2.997725	-0.560650
H	3.414706	4.522577	0.845069
H	5.787454	1.072009	-1.721939
H	7.061646	2.649430	-0.341864
H	6.893838	4.418314	1.300637

S_1 local minimum (protein)

N	9.824968	7.967310	1.675008
C	10.843914	6.989395	1.377226
C	11.072708	6.854432	-0.120834
O	10.405000	7.419384	-0.934658
C	10.596114	5.598579	2.015676
C	9.373525	4.916743	1.410608
O	9.573306	4.269108	0.365046
O	8.283315	5.052580	1.977539
H	8.998933	7.881803	1.117773
H	11.788916	7.346755	1.775830
H	11.464849	4.962690	1.874431
H	10.466214	5.751161	3.076871
H	-0.272764	0.871731	-1.976509

H	0.871609	1.444394	-1.717529
C	1.858560	0.659824	-2.233373
N	-3.198268	3.260584	-1.091019
C	-0.952377	3.159971	-0.286514
C	1.268628	-0.452201	-2.869729
O	1.770727	-1.426191	-3.489171
C	-0.065554	-0.292154	-2.707778
O	-1.675260	1.310605	-1.648058
N	-2.177629	0.398526	-0.639113
C	-1.766779	2.816640	-1.366194
N	-1.052465	-1.231898	-3.188255
C	-1.620498	-0.928732	-4.567855
C	-2.156795	-1.784663	-5.200710
C	3.322531	0.932377	-2.122662
O	3.915397	1.855983	-1.258530
C	3.165922	2.803957	-0.452029
C	3.837040	3.709795	0.349731
C	5.372590	1.914083	-1.168985
C	6.005323	2.811849	-0.388726
C	5.229834	3.717547	0.402982
C	5.797021	4.582248	1.222402
C	-3.198041	4.336747	-0.966971
O	-3.556271	2.811990	-0.171310
H	-3.881253	3.003620	-1.895506
H	-0.658791	4.081304	-0.440438
H	-2.269146	1.141092	-2.539987
H	-1.730037	0.546327	0.249809
H	-1.422214	3.319532	-2.265719
H	-0.608396	-2.213718	-3.232015
H	-1.864009	-1.272355	-2.476594
H	3.962860	0.326034	-2.730478
H	2.097598	2.821604	-0.503432
H	3.286401	4.427694	0.930371
H	5.951202	1.229944	-1.762856
H	7.079079	2.869827	-0.351020
H	6.789134	4.556350	1.285967
H	-3.192113	0.369489	-0.686805
H	-1.566560	0.077531	-5.000425
H	9.732439	8.047739	2.680817
H	11.881468	6.212500	-0.478243

S_1 keto tautomer (protein)

N	9.574213	8.222013	1.548849
C	10.659927	7.327531	1.252082

C	10.848020	7.138276	-0.252163
O	10.111994	7.627471	-1.052377
C	10.552970	5.946813	1.967644
C	9.346707	5.188383	1.483751
O	9.390378	4.500834	0.488895
O	8.279129	5.345331	2.195636
H	8.735508	8.069311	1.028217
H	11.584539	7.769382	1.607369
H	11.431244	5.340553	1.782510
H	10.487164	6.132274	3.029198
H	-0.201540	0.729934	-1.869615
H	0.916106	1.347254	-1.629778
C	1.933768	0.598397	-2.167267
N	-3.241318	3.001905	-1.068097
C	-1.023770	3.014401	-0.181786
C	1.368272	-0.547138	-2.786280
O	1.897034	-1.508010	-3.402730
C	0.036120	-0.438643	-2.596004
O	-1.619228	1.108554	-1.531588
N	-2.068882	0.195685	-0.496279
C	-1.782051	2.615924	-1.282110
N	-0.920901	-1.422429	-3.040746
C	-1.505707	-1.183899	-4.424445
C	-2.023777	-2.077079	-5.021868
C	3.356660	0.920255	-2.121412
O	3.967460	1.881331	-1.229036
C	3.248794	2.820163	-0.427811
C	3.924503	3.707928	0.404480
C	5.412562	1.919270	-1.140684
C	6.063176	2.798962	-0.351624
C	5.341587	3.734560	0.486279
C	5.948452	4.528279	1.263704
C	-3.293392	4.079171	-0.964483
O	-3.614322	2.553016	-0.154352
H	-3.881489	2.701054	-1.892882
H	-0.770652	3.947203	-0.332569
H	-2.217067	0.895449	-2.412032
H	-1.616477	0.382402	0.381995
H	-1.427480	3.115979	-2.179582
H	-0.449733	-2.392516	-3.059974
H	-1.728853	-1.466826	-2.325106
H	4.007151	0.297567	-2.696701
H	2.180891	2.847519	-0.470857
H	3.369223	4.414554	0.992814

H	5.981025	1.236138	-1.747947
H	7.138143	2.824092	-0.319681
H	7.485578	4.905398	1.767966
H	-3.082380	0.100749	-0.545856
H	-1.494810	-0.194990	-4.891457
H	9.568968	8.436382	2.545196
H	11.676511	6.533937	-0.619466

CI(S_1/S_0) (protein)

N	9.727467	8.072798	1.806567
C	10.741543	7.092128	1.540548
C	10.961948	6.916297	0.040291
O	10.259936	7.449259	-0.765324
C	10.487940	5.707006	2.207849
C	9.399731	4.902781	1.539676
O	9.672276	4.024778	0.751444
O	8.186654	5.213123	1.861277
H	8.847007	7.909322	1.364873
H	11.678116	7.449171	1.953430
H	11.387904	5.105945	2.180941
H	10.228149	5.893919	3.240377
H	-0.123131	0.418403	-1.851817
H	0.922524	1.200188	-1.853216
C	2.003068	0.444508	-2.190606
N	-3.122787	2.545789	-0.672769
C	-0.836356	2.535361	0.017109
C	1.549732	-0.897075	-2.497021
O	2.152974	-1.869574	-2.988093
C	0.211395	-0.856802	-2.313204
O	-1.518471	0.712813	-1.364217
N	-1.787853	-0.229961	-0.293613
C	-1.685027	2.204297	-1.036732
N	-0.699207	-1.888137	-2.753496
C	-1.300859	-1.676928	-4.142373
C	-1.784779	-2.595362	-4.727804
C	3.363103	0.956583	-2.354513
O	4.149553	1.366981	-1.216118
C	3.508680	2.010964	-0.114664
C	4.224013	2.743825	0.793724
C	5.551840	1.444530	-1.265095
C	6.284609	2.143508	-0.338333
C	5.649391	2.849521	0.718369
C	6.288256	3.540104	1.565400

C	-3.182685	3.611326	-0.483326
O	-3.409332	2.026383	0.234797
H	-3.825847	2.290923	-1.461269
H	-0.496758	3.443392	-0.129483
H	-2.208616	0.476033	-2.169239
H	-1.262655	-0.021501	0.539706
H	-1.415466	2.761412	-1.930473
H	-0.181416	-2.834651	-2.771476
H	-1.504579	-1.974024	-2.037968
H	3.624980	1.381689	-3.300724
H	2.439838	2.024165	-0.061949
H	3.728158	3.296071	1.567730
H	6.069990	0.957252	-2.070878
H	7.355368	2.187642	-0.405019
H	7.537026	4.492924	1.561533
H	-2.790534	-0.387833	-0.223018
H	-1.331075	-0.691432	-4.619684
H	9.798663	8.396150	2.770884
H	11.746266	6.252409	-0.323261

S_0 minimum (vacuo)

N	-8.263697	0.724137	1.431176
C	-8.500886	-0.290162	0.419759
C	-8.114764	-1.658144	0.943266
O	-7.764914	-1.888743	2.055442
C	-7.842419	-0.018234	-0.945044
C	-6.315776	0.096281	-0.806852
O	-5.728344	-0.962981	-0.594521
O	-5.846647	1.243257	-0.891679
H	-7.419713	0.520242	1.932212
H	-9.578977	-0.359962	0.242577
H	-8.084045	-0.833333	-1.622764
H	-8.254589	0.898288	-1.355028
C	4.370287	0.061927	-0.036081
N	3.117687	0.306246	-0.089318
C	2.474108	-0.900909	-0.431389
C	5.738661	3.290169	1.547440
O	4.463179	3.064084	-0.481471
C	3.510587	-1.945602	-0.584918
O	3.421171	-3.111503	-0.849424
N	4.686524	-1.282415	-0.308585
C	5.427551	1.068676	0.344656
N	6.410442	1.154009	-0.722423
C	4.795910	2.419318	0.725182

C	5.966820	-1.939090	-0.329997
C	6.381690	-2.482894	1.020034
O	7.430812	-3.005940	1.209446
C	1.153185	-1.137089	-0.594620
C	0.002383	-0.254537	-0.487905
C	0.081402	1.131132	-0.205928
C	-1.058604	1.893829	-0.130984
C	-1.260495	-0.791568	-0.676788
C	-2.427373	-0.039136	-0.599999
C	-2.333755	1.314214	-0.330551
O	-3.370248	2.127014	-0.238056
H	5.259144	4.233458	1.790598
H	6.641465	3.515410	0.990618
H	6.015430	2.803703	2.477428
H	3.666697	3.563482	-0.376805
H	5.945689	0.680102	1.218086
H	6.008988	1.663330	-1.484434
H	3.897200	2.223434	1.297324
H	5.900522	-2.773540	-1.016992
H	6.725920	-1.257266	-0.680333
H	0.929037	-2.160170	-0.845331
H	1.041730	1.582886	-0.059081
H	-1.012020	2.947460	0.076620
H	-1.357965	-1.842766	-0.891873
H	-3.390747	-0.495471	-0.742740
H	-4.232412	1.689889	-0.466439
H	7.198857	1.681233	-0.403306
H	5.647890	-2.368290	1.828073
H	-8.118563	1.612398	0.988663
H	-8.217384	-2.468938	0.213387

S_1 local minimum (vacuo)

N	-8.085877	0.501953	1.600763
C	-8.379974	-0.312400	0.436137
C	-7.992255	-1.754232	0.688778
O	-7.614093	-2.180743	1.731793
C	-7.773925	0.200726	-0.881978
C	-6.247655	0.285759	-0.786547
O	-5.658626	-0.790654	-0.719005
O	-5.762602	1.432285	-0.734369
H	-7.275612	0.143372	2.067693
H	-9.464077	-0.344112	0.295660
H	-8.040879	-0.480235	-1.686423
H	-8.193033	1.174341	-1.110757

C	4.336087	0.054382	-0.035907
N	3.048714	0.238391	-0.047016
C	2.462518	-0.959903	-0.351069
C	5.616775	3.334719	1.507289
O	4.280543	3.073721	-0.466378
C	3.470150	-1.960579	-0.526331
O	3.403348	-3.149560	-0.787570
N	4.653182	-1.270043	-0.317590
C	5.363999	1.095905	0.309132
N	6.319159	1.237308	-0.785059
C	4.690020	2.419126	0.715068
C	5.938949	-1.905252	-0.395833
C	6.406046	-2.465627	0.931646
O	7.488133	-2.930147	1.095786
C	1.026700	-1.256161	-0.477678
C	-0.035419	-0.359234	-0.396570
C	0.115677	1.063347	-0.178899
C	-1.004155	1.878362	-0.131898
C	-1.394981	-0.856253	-0.544847
C	-2.475190	-0.061560	-0.498738
C	-2.289628	1.352619	-0.295081
O	-3.287335	2.178026	-0.252039
H	5.101296	4.254743	1.763215
H	6.491811	3.602122	0.923633
H	5.945464	2.863551	2.429167
H	3.396268	3.391625	-0.366314
H	5.931486	0.741670	1.168667
H	5.860116	1.684205	-1.555272
H	3.826863	2.175741	1.319920
H	5.859294	-2.734921	-1.086661
H	6.677319	-1.210682	-0.767447
H	0.813445	-2.289324	-0.667662
H	1.098914	1.465413	-0.062926
H	-0.917878	2.939504	0.022611
H	-1.524800	-1.915133	-0.692965
H	-3.476363	-0.446539	-0.594221
H	-4.198091	1.781815	-0.414663
H	7.083396	1.822666	-0.509092
H	5.677907	-2.417919	1.748688
H	-7.872581	1.438652	1.317437
H	-8.143881	-2.419694	-0.165746

S_1 keto tautomer (vacuo)

N	-8.695475	0.431494	1.461436

C	-8.812959	-0.111242	0.124418
C	-8.581367	-1.610737	0.110545
O	-8.473425	-2.272214	1.090988
C	-7.939128	0.608332	-0.913422
C	-6.462536	0.454290	-0.608403
O	-5.942619	-0.621737	-0.595446
O	-5.877547	1.590659	-0.359129
H	-8.368313	-0.270856	2.094728
H	-9.843705	-0.002517	-0.224208
H	-8.118284	0.184000	-1.896735
H	-8.210270	1.655403	-0.948212
C	4.534784	0.068890	-0.094841
N	3.240504	0.209678	-0.134529
C	2.684192	-1.037124	-0.320069
C	5.759938	3.595979	0.900402
O	3.956778	2.949243	-0.464887
C	3.750275	-2.014678	-0.407984
O	3.733738	-3.220089	-0.568510
N	4.899781	-1.262236	-0.259006
C	5.523739	1.184073	0.095364
N	6.326180	1.336513	-1.118169
C	4.800576	2.469575	0.546532
C	6.215579	-1.833617	-0.306196
C	6.713099	-2.286479	1.050485
O	7.862724	-2.478955	1.289524
C	1.299306	-1.389568	-0.447517
C	0.154602	-0.516551	-0.269305
C	0.218773	0.852954	0.120471
C	-0.938092	1.611924	0.282911
C	-1.164414	-1.065045	-0.474477
C	-2.287755	-0.342599	-0.316449
C	-2.240164	1.063364	0.078687
O	-3.276803	1.730099	0.226874
H	5.197970	4.452258	1.254838
H	6.327060	3.913326	0.031880
H	6.453785	3.292774	1.679557
H	3.279225	2.291961	-0.593720
H	6.213392	0.900721	0.889600
H	5.747446	1.725897	-1.838798
H	4.218655	2.222691	1.430284
H	6.172917	-2.712967	-0.938027
H	6.917249	-1.133517	-0.735341
H	1.115393	-2.421286	-0.658973
H	1.172924	1.300388	0.296661

H	-0.879338	2.644847	0.572849
H	-1.239395	-2.100416	-0.765156
H	-3.260259	-0.776242	-0.471916
H	-4.906593	1.492191	-0.160992
H	7.077292	1.981171	-0.962625
H	5.943639	-2.416187	1.817816
H	-8.069820	1.210636	1.497906
H	-8.571354	-2.068906	-0.881752

CI(S_1/S_0) (vacuo)

N	8.690278	1.439016	0.669672
C	8.832207	0.163404	-0.002632
C	8.641596	0.282917	-1.504536
O	8.605832	1.321759	-2.080895
C	7.949094	-0.935751	0.602224
C	6.473260	-0.639741	0.408869
O	6.000816	-0.571840	-0.687704
O	5.845011	-0.465964	1.532907
H	8.537415	2.164006	-0.003613
H	9.862625	-0.187531	0.101185
H	8.160569	-1.880877	0.112099
H	8.178600	-1.043097	1.653913
C	-4.546907	0.274737	-0.220517
N	-3.346956	0.472496	-0.706569
C	-2.715374	-0.739758	-0.803538
C	-6.150775	3.786530	-0.452401
O	-3.926476	3.183065	0.005858
C	-3.651721	-1.787979	-0.296204
O	-3.542485	-2.978502	-0.187859
N	-4.784897	-1.065084	0.043181
C	-5.538187	1.374435	0.075332
N	-5.719670	1.449886	1.519580
C	-5.097704	2.696856	-0.584395
C	-5.960823	-1.670284	0.607309
C	-6.974840	-2.085861	-0.438631
O	-8.131489	-2.222956	-0.201031
C	-1.351360	-0.924666	-1.258194
C	-0.197113	-0.669854	-0.470802
C	-0.215129	-0.228540	0.875159
C	0.933572	0.021585	1.584543
C	1.092581	-0.839151	-1.031546
C	2.247342	-0.603174	-0.354400
C	2.234353	-0.151769	1.010380
O	3.275477	0.075760	1.658741

H	-5.816783	4.677058	-0.973044
H	-6.306040	4.056448	0.586728
H	-7.100623	3.475382	-0.878674
H	-3.203067	2.618581	-0.246897
H	-6.498311	1.089320	-0.354324
H	-4.907788	1.872736	1.933419
H	-4.934715	2.507446	-1.642882
H	-5.655119	-2.568897	1.132742
H	-6.430575	-1.005532	1.318114
H	-1.212241	-1.175885	-2.287058
H	-1.152774	-0.071708	1.367668
H	0.892695	0.359398	2.600573
H	1.154415	-1.170301	-2.053156
H	3.203985	-0.734754	-0.821627
H	4.863551	-0.273246	1.420484
H	-6.498529	2.039933	1.746030
H	-6.577363	-2.270886	-1.441817
H	7.915263	1.437296	1.302944
H	8.615604	-0.663282	-2.050107