

Supplementary Information

A molecular insight into the photophysics of Barbituric Acid, a candidate for canonical nucleobases' ancestor

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1. Tautomers of Barbituric Acid (BA)

1.1. Deprotonated Barbituric Acid (BA⁻)

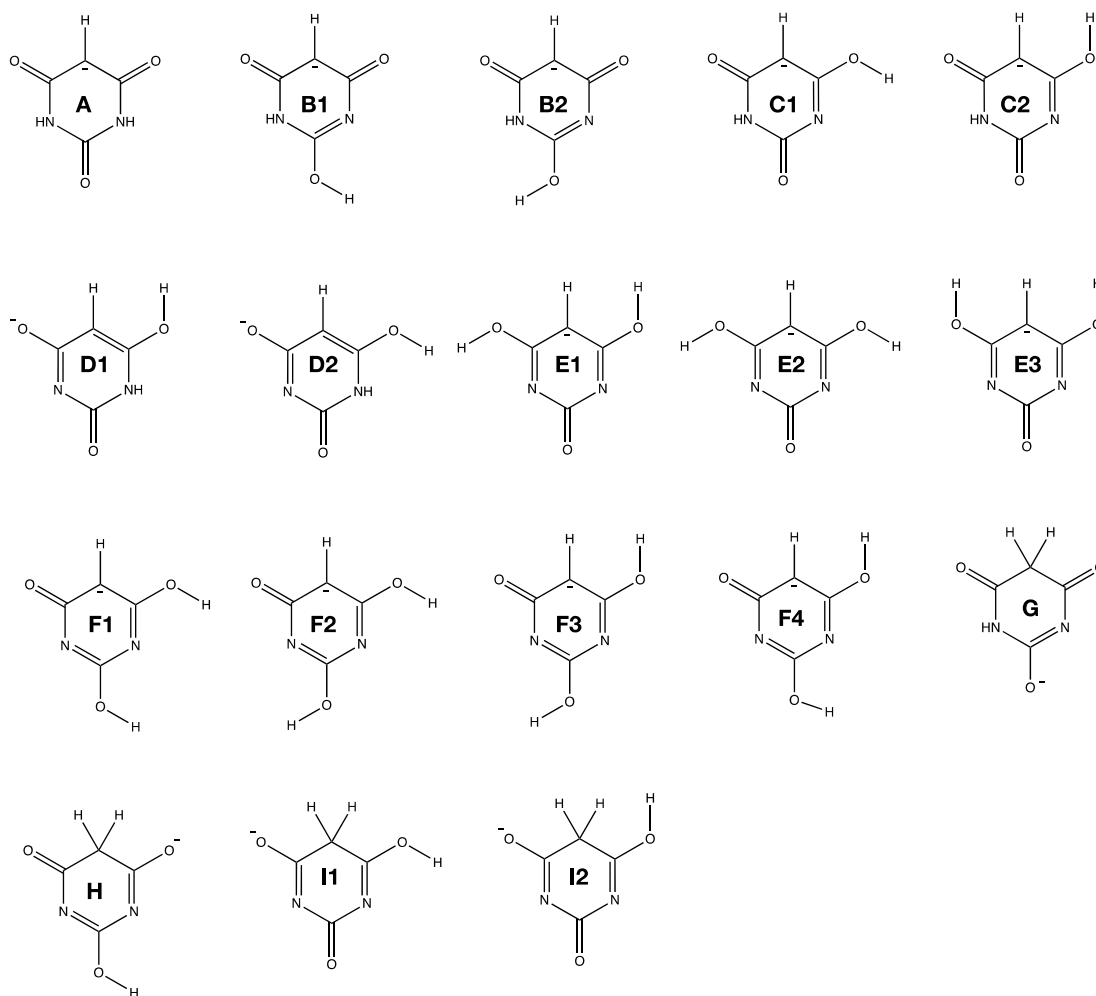


Figure S1: Tautomers for BA⁻.

Table S1: CCSD/aug-cc-pVTZ// MP2/cc-pVTZ relative Gibbs Free Energy for each of the BA⁻ tautomers at room temperature (T=298 K) considering a water PCM continuum, and its corresponding population according to a Boltzmann distribution at T=298K. Tautomers labelling corresponds to that indicated in Figure S1.

Deprotonated Species	ΔG° (kcal/mol)	Population (%)
A	0.00	100
G	4.63	0
C1	8.65	0
C2	10.45	0
H	16.93	0
B1	17.64	0
D1	18.25	0
D2	19.95	0
F2	20.13	0
F1	20.50	0
E2	20.85	0
B2	21.27	0
I1	21.38	0
F3	21.41	0
F4	21.70	0
E1	22.70	0
I2	23.73	0
E3	24.74	0

1.2. Neutral Barbituric Acid (BAH)

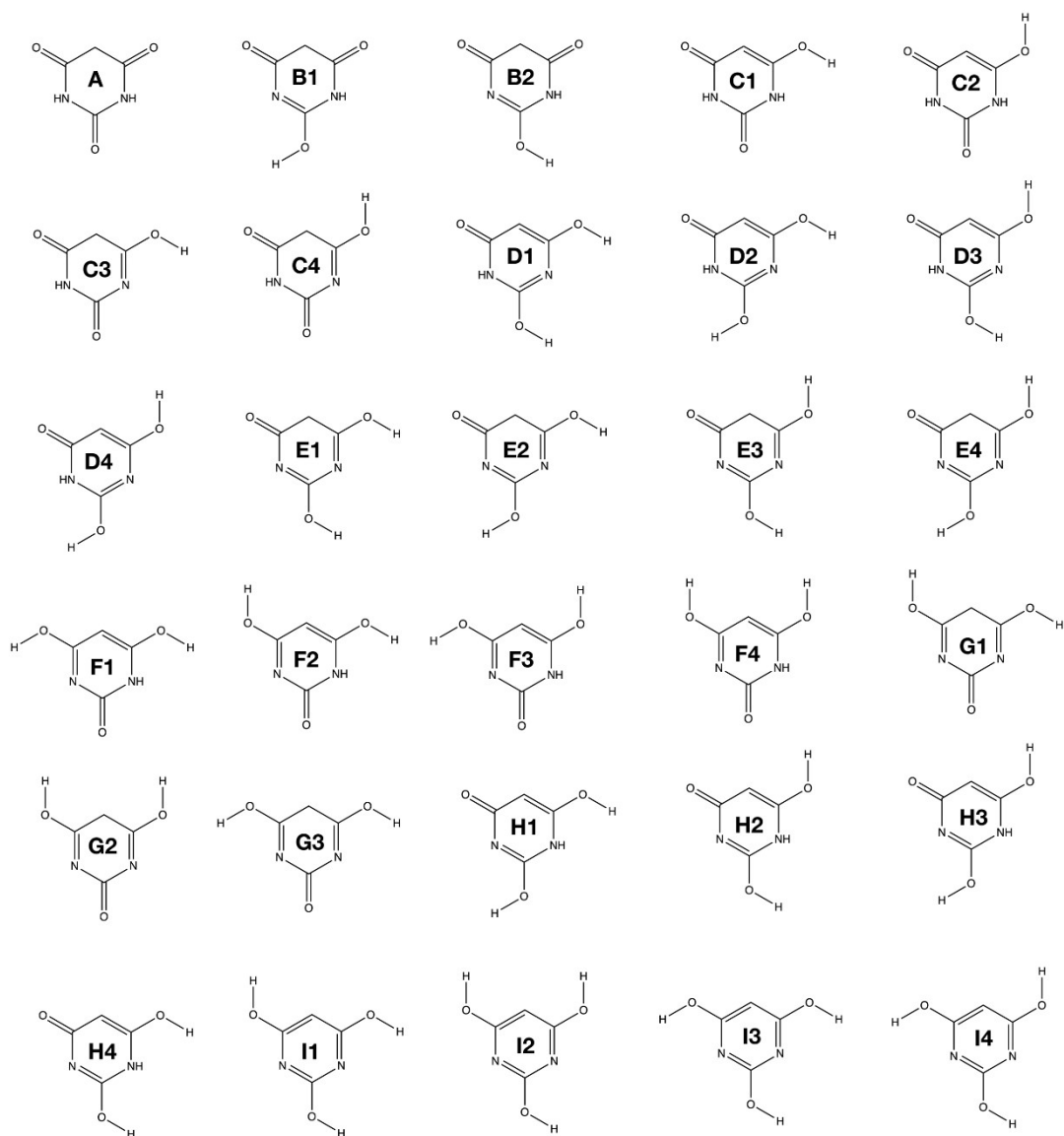


Figure S2: Tautomers for BAH.

Table S2: CCSD/aug-cc-pVTZ// MP2/cc-pVTZ relative Gibbs Free Energy for each of the BAH tautomer at room temperature (T=298 K) considering a water PCM continuum, and its corresponding population according to a Boltzmann distribution at T=298K. Tautomers labelling correspond to that indicated in Figure S2.

Neutral Species	ΔG° (kcal/mol)	Population (%)
A	0	100
C2	9.67	0
C1	12.06	0
C3	13.19	0
C4	16.03	0
B1	17.23	0
D1	18.20	0
D3	19.23	0
F3	19.38	0
I1	20.10	0
B2	21.29	0
F1	21.40	0
D2	21.52	0
I4	21.55	0
I3	21.69	0
F4	21.94	0
D4	22.68	0
I2	23.16	0
F2	23.77	0
H2	25.19	0
H3	27.62	0
G3	27.90	0
H1	28.38	0
E2	28.38	0
E1	29.03	0
G2	30.23	0
E4	30.78	0
H4	31.01	0
E3	31.08	0
G1	33.89	0

2. CASSCF orbitals

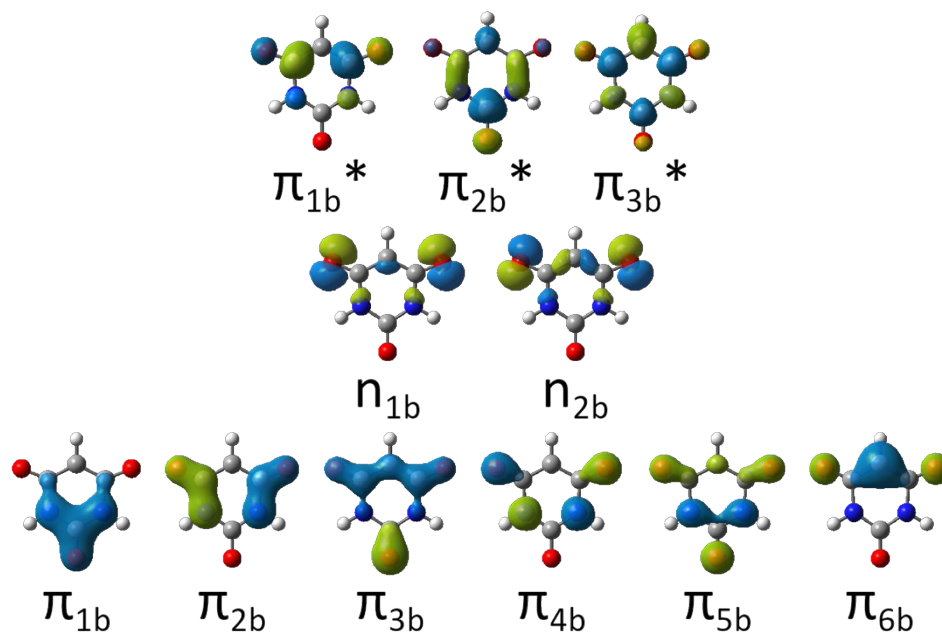


Figure S3: SA3-CASSCF molecular orbitals included in the active space for the calculations of the BA- predominant tautomer at the GS minimum.

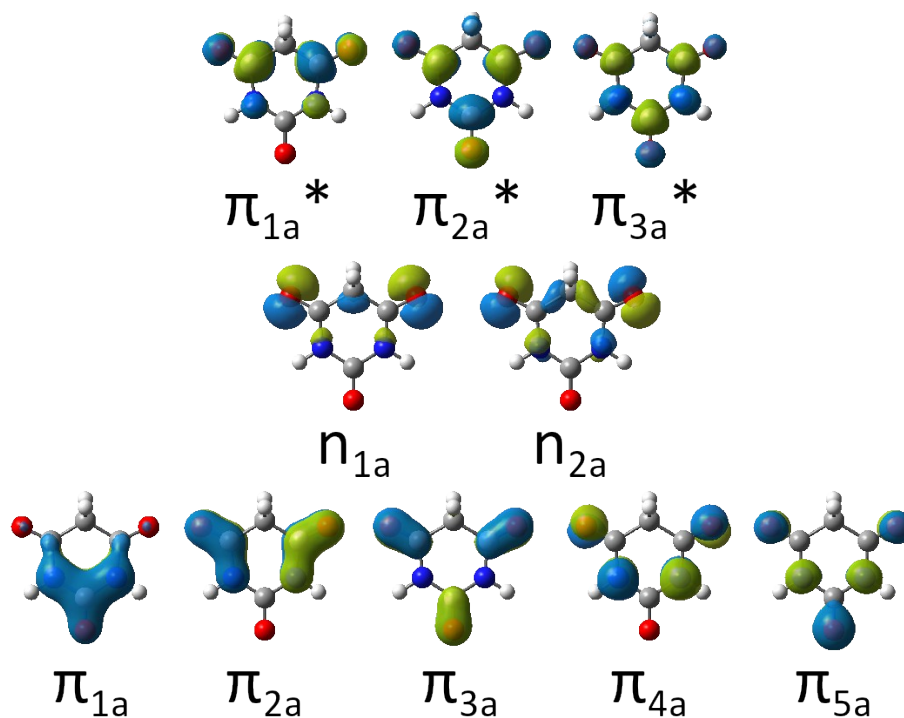


Figure S4: SA4-CASSCF molecular orbitals included in the active space for the calculations of the BAH predominant tautomer at the GS minimum.

3. Geometries of stationary points

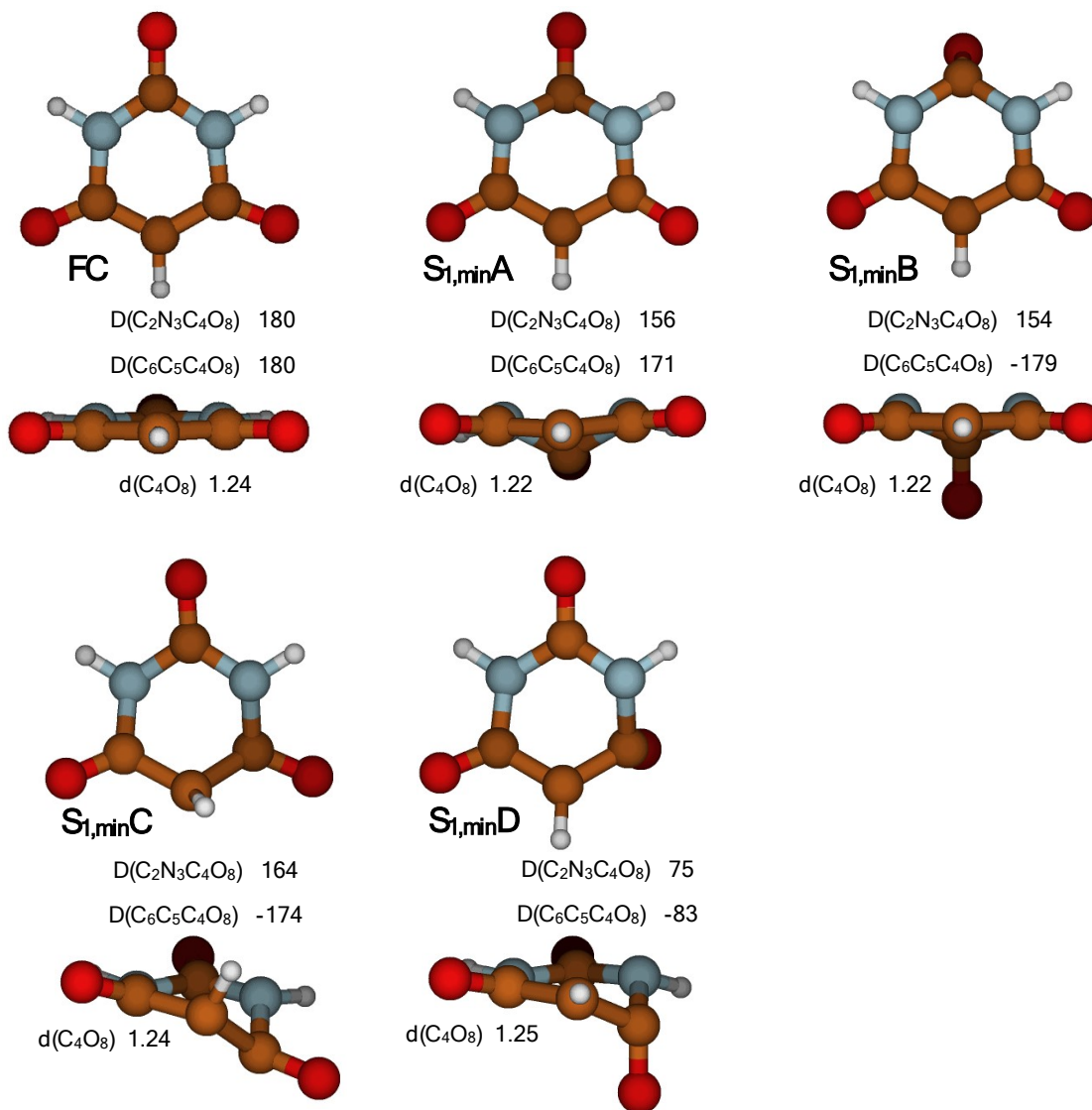


Figure S5: Top and side views of the geometries of the S₀ minimum (top-left), S_{1,min}A (top-center), S_{1,min}B (top-right), S_{1,min}C (bottom-left) and S_{1,min}D (bottom-center) for BA⁻ species. Most relevant distances are reported in Å and angles in degrees. Atom numbering corresponds to that indicated in Figure 1.

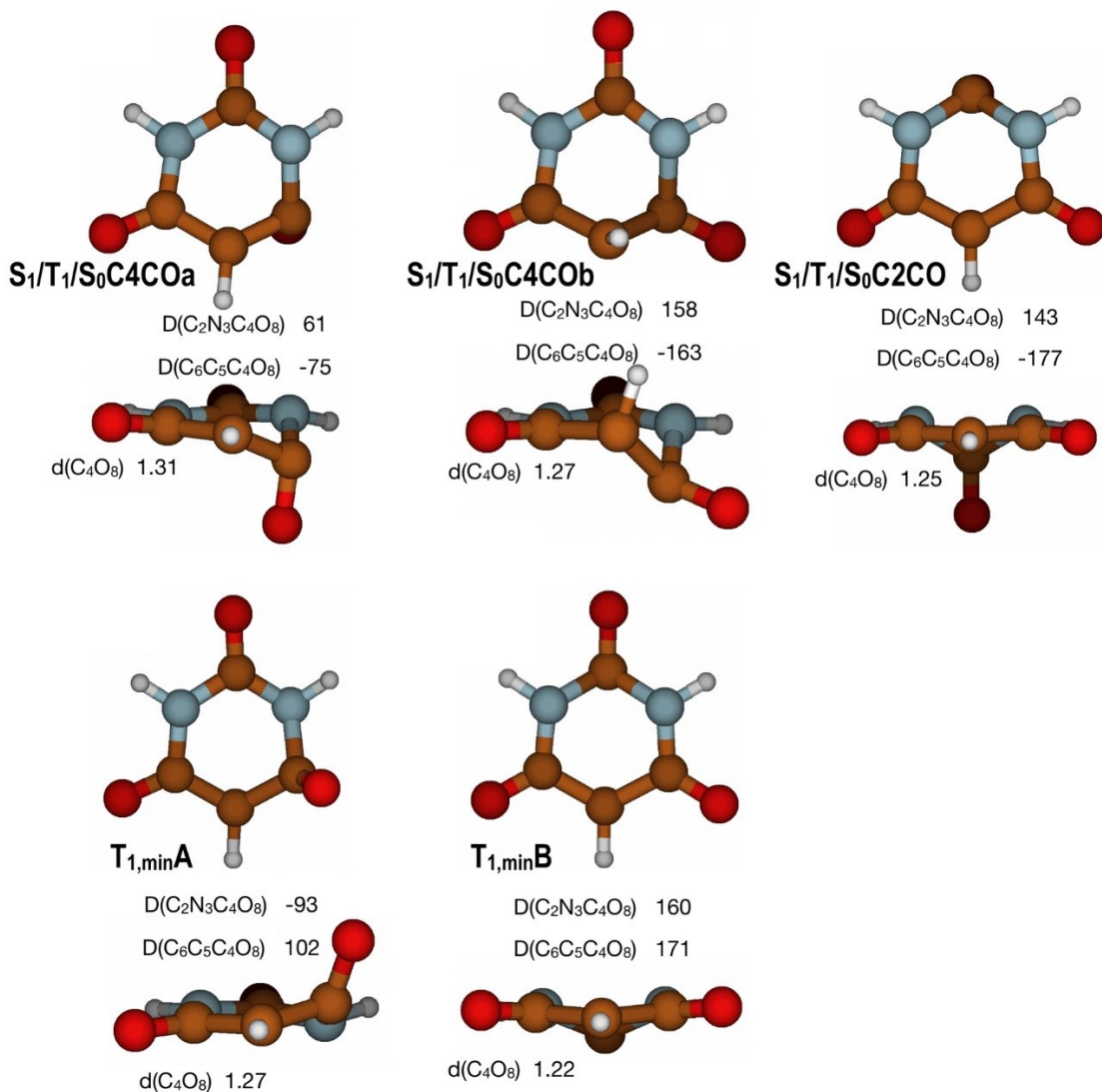


Figure S6: Top and side views of the geometries of the S₁/T₁/S₀ C4COa crossing point (top-left), S₁/T₁/S₀ C4COb crossing point (top-center), S₁/T₁/S₀ C2CO crossing point (top-right), T_{1,min}A(bottom-left) and T_{1,min}B (bottom-center) for BA⁻species. Most relevant distances are reported in Å and angles in degrees. Atom numbering corresponds to that indicated in Figure 1.

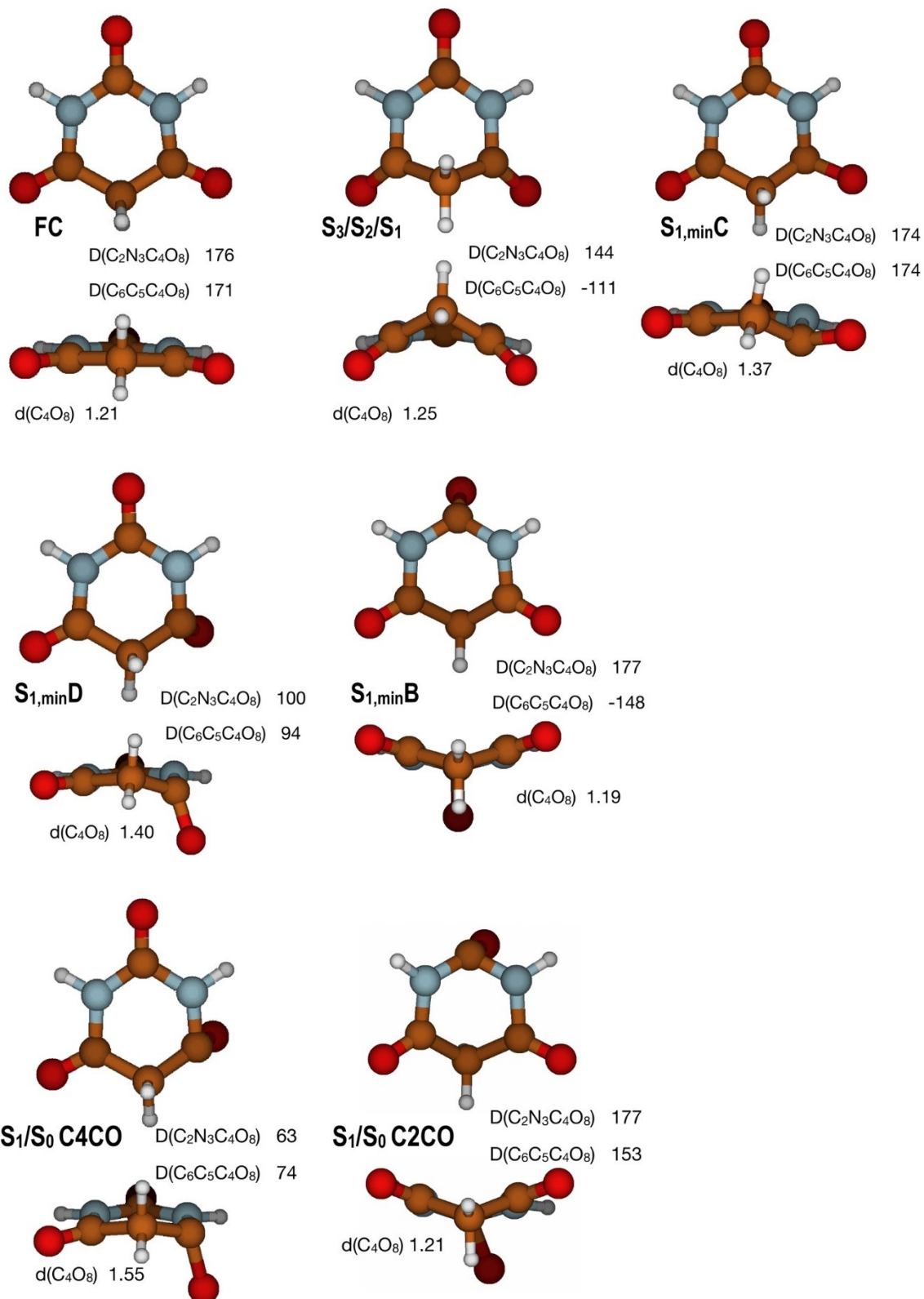


Figure S7: Top and side views of the geometries of S_0 minimum (top-left), $S_3/S_2/S_1$ CI (top-center), $S_{1,\text{min}}\text{C}$ (top-right), $S_{1,\text{min}}\text{D}$ (center-left), $S_{1,\text{min}}\text{B}$ (center-center), S_1/S_0 C4CO crossing (bottom-left) and S_1/S_0 C2CO crossing (bottom-left) for BAH species. Most relevant distances are reported in Å and angles in degrees. Atom numbering corresponds to that indicated in Figure 1.

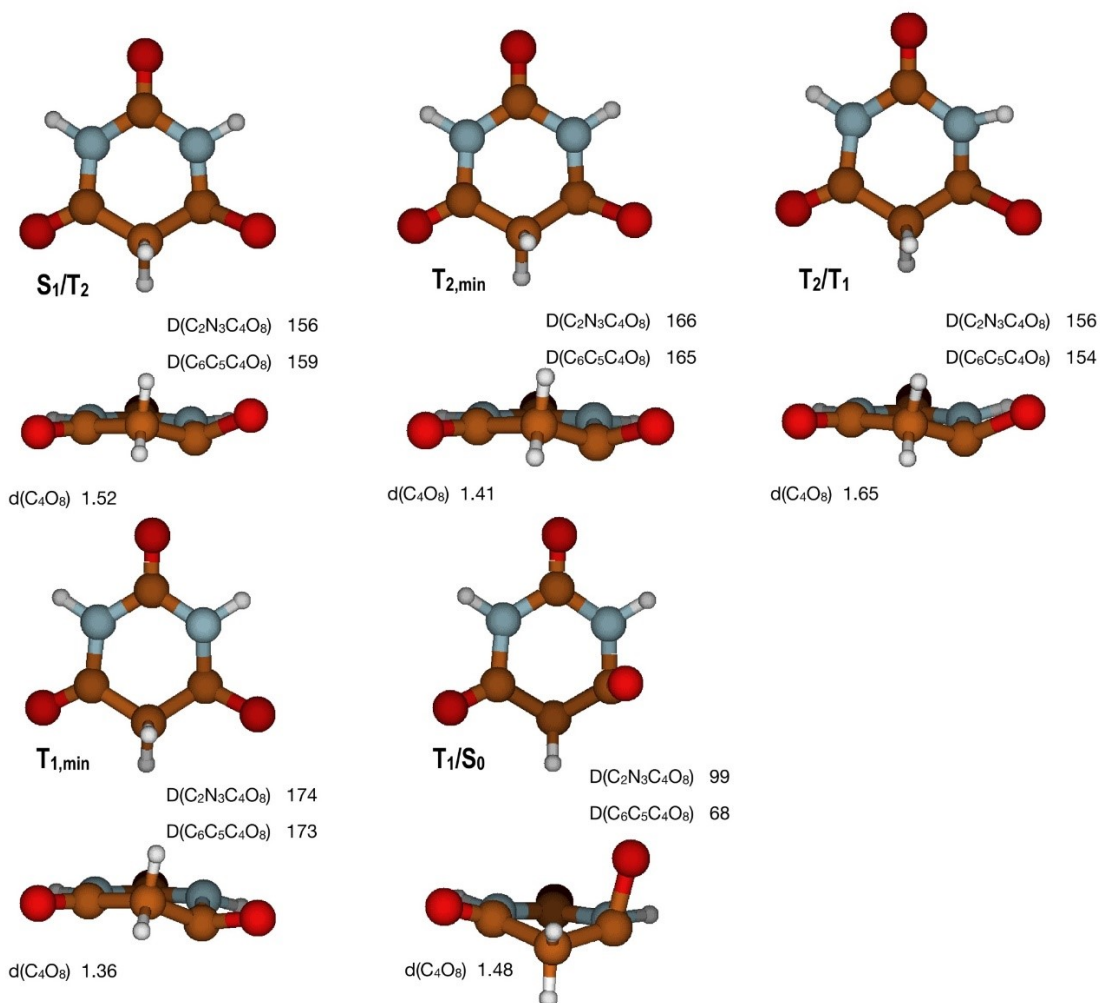


Figure S8: Top and side views of the geometries of the S_1/T_2 crossing point (top-left), $T_{2,min}$ (top-center), T_2/T_1 CI (top-right), $T_{1,min}$ (bottom-left), and T_1/S_0 crossing point (bottom-right) for BAH species. Most relevant distances are reported in Å and angles in degrees. Atom numbering corresponds to that indicated in Figure 1.

4. Individual Transient Absorption Spectra

To replicate the TAS signals recorded experimentally for BA⁻ (PBS pH 7.4, excitation wavelength of 268 nm), we calculated the absorption spectra at the position of all S₁ and T₁ minima, to reproduce excited state absorption (S₁→S_n or T₁→T_n), and at the position of the S₁/S₀ conical intersections, to account for vibrationally hot ground state (S_{0,v>0}→S_n). The individual spectra were obtained from the vertical excitation energies and oscillator strengths by convolution to Gaussian functions, using a half-width of 60 nm. Finally, based on the topography of the potential energy surfaces, these spectra were manually combined until reaching qualitative agreement with the experimental signals at the selected pump-probe time delays.

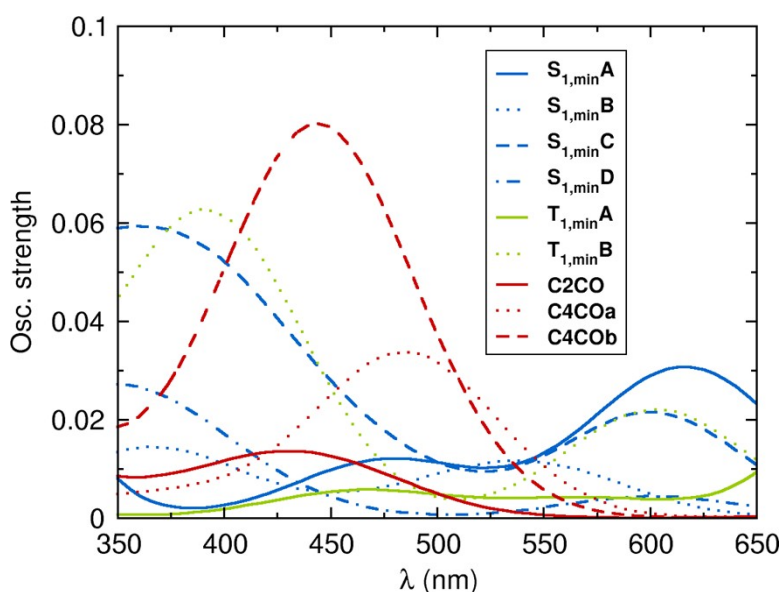


Figure S9: Simulated TAS spectra for all singlet minima (blue), triplet minima (green) and S₁/S₀ conical intersections (red) of BA⁻, calculated at the MS15-CASPT2/ANO-L-VTZ level of theory using a (16,11) active space.