

## Photostability of 2,6-Diaminopurine and its 2'-Deoxyriboside Investigated by Femtosecond Transient Absorption Spectroscopy

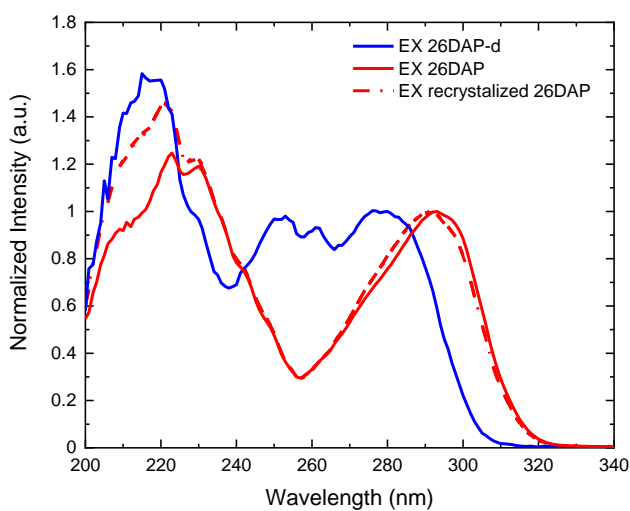
Naishka E. Caldero-Rodríguez,<sup>1‡</sup> Luis A. Ortiz-Rodríguez,<sup>1‡</sup> Andres A. Gonzalez,<sup>1⊥</sup> Carlos E. Crespo-Hernández\*

<sup>1</sup>Department of Chemistry, Case Western Reserve University, Cleveland, OH 44106

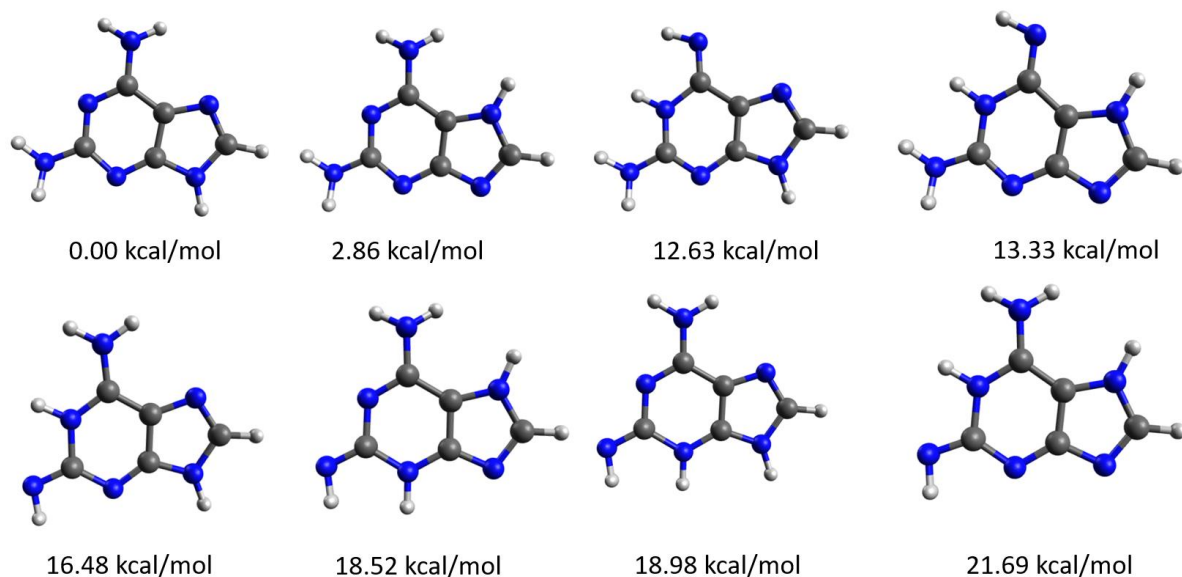
\*Corresponding author; E-mail: carlos.crespo@case.edu; ORCID: 0000-0002-3594-0890

‡ contributed equally to this work; ⊥ participated as an undergraduate research assistant.

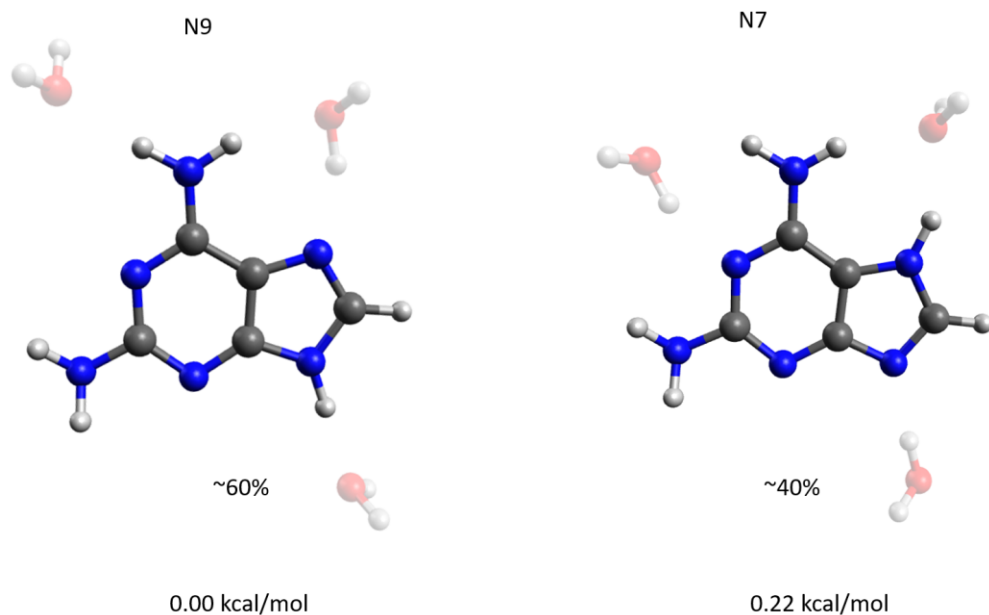
### Electronic Supporting Information



**Figure S1.** Normalized ground state excitation spectra ( $\lambda_{em} = 351$  nm) of 2,6-diaminopurine (26DAP, solid red line), recrystallized 26DAP (dashed red line) and 2,6-diaminopurine-2'-deoxyribose (26DAP-d, solid blue line) in phosphate buffer pH 7.4.



**Figure S2.** Optimized ground state structures of 8 possible tautomers of 26DAP with their relative energies calculated at the B3LYP/cc-pVDZ/CPCM level of theory in water.



**Figure S3.** Optimized ground state structures of the N9 and N7 tautomers of 26DAP microsolvated with three water molecules with their relative energies and percentage ground state contribution calculated at the B3LYP/cc-pVDZ/CPCM level of theory in water.

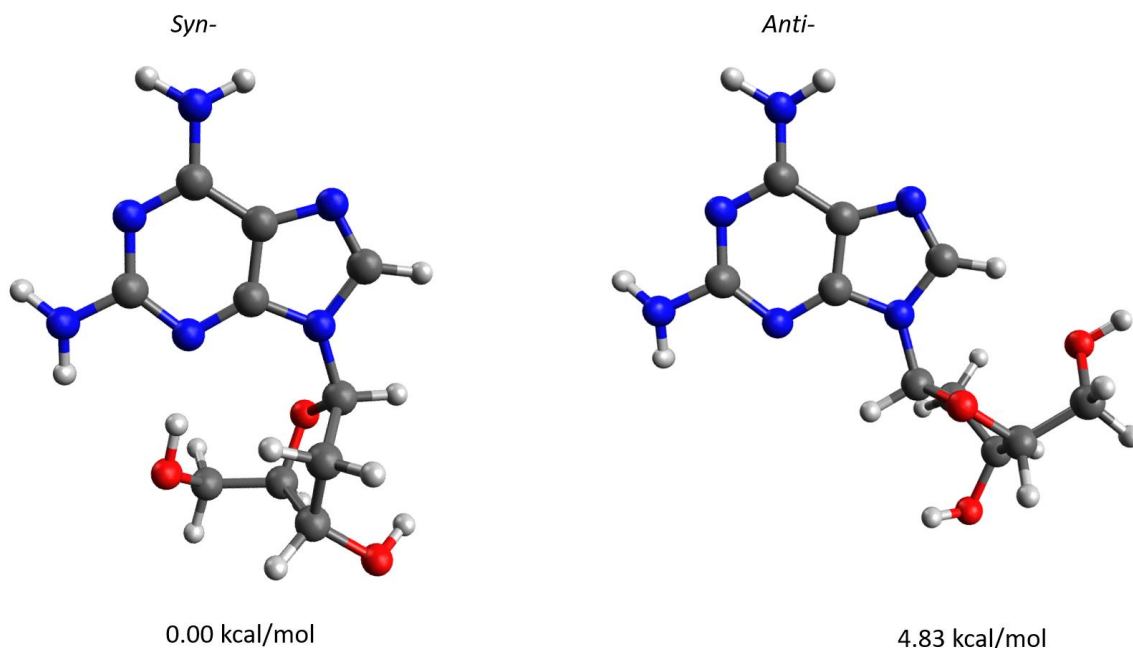
All electronic-structure calculations were performed in ORCA 5.0.<sup>1</sup> Ground state optimizations presented in Figure S3 were performed using density functional theory (DFT), employing the B3LYP hybrid functional<sup>2</sup> and the cc-pVDZ<sup>3</sup> basis set. The percentage of the ground state

contribution (P) of the N9 and N7 tautomers of 26DAP was calculated at room temperature with the relative energies obtained ( $\Delta E$ , eV) for these tautomers. The following equations were considered:<sup>4</sup>

$$P = e^{-\Delta E/kT} / Z \quad (1)$$

$$Z = \sum e^{-\Delta E/kT} \quad (2)$$

where,  $e^{-\Delta E/kT}$  is the ratio of the population of a particular species, Z is the sum of the possible species, k is the Boltzmann's constant (units: eV K<sup>-1</sup>), and T is the temperature (298 K).



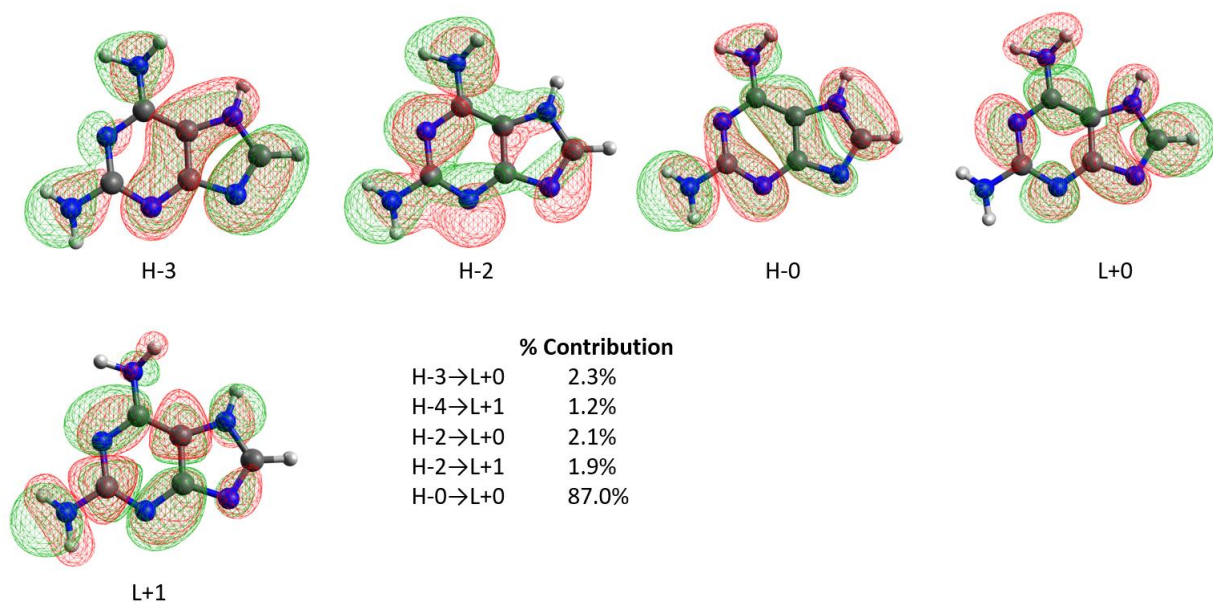
**Figure S4.** Optimized ground state structures of *syn*- and *anti*-sugar conformations of 26DAP-d with their relative energies calculated at the B3LYP/cc-pVDZ/CPCM level of theory in water.

**Table S1.** Vertical excitation energies of the N9 tautomer of 26DAP and 26DAP-d calculated at the TD-X/CPCM/def2-TZVP//B3LYP/cc-pVDZ level of theory in water, where X is the hybrid functional used.

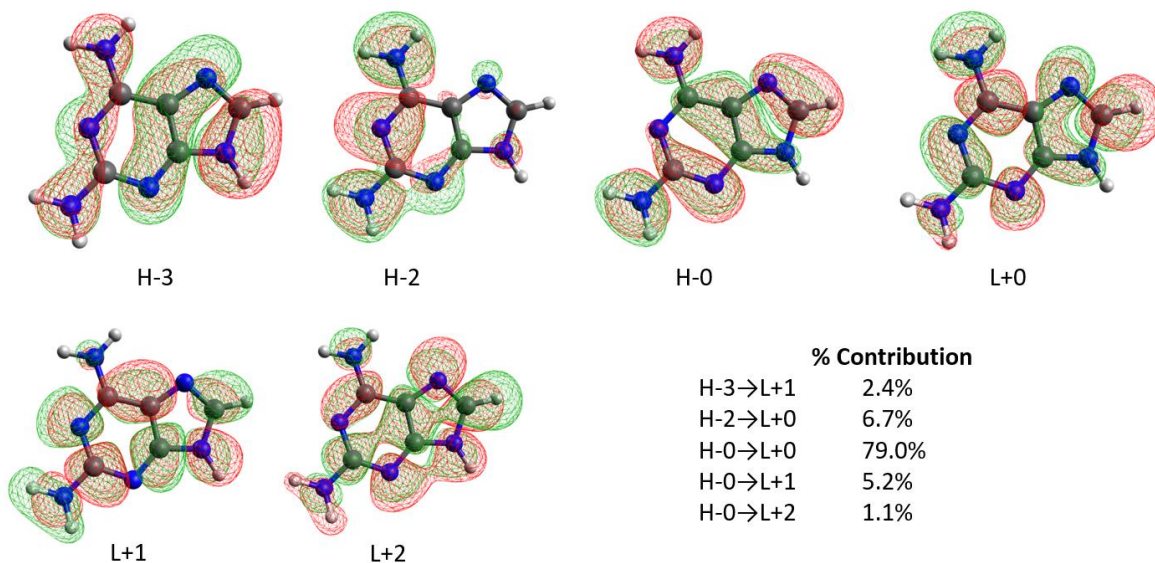
Functional	26DAP/N9	26DAP-d
B3LYP	4.88 (0.25)	4.79 (0.25)
PBE0	4.99 (0.26)	4.90 (0.27)
$\omega$ B97X	5.29 (0.29)	5.20 (0.30)

Table S1 shows that the hybrid functionals B3LYP, PBE0, and  $\omega$ B97X severely overestimate the energy of the lowest-energy singlet state (i.e., 4.43 eV based on the maximum of the

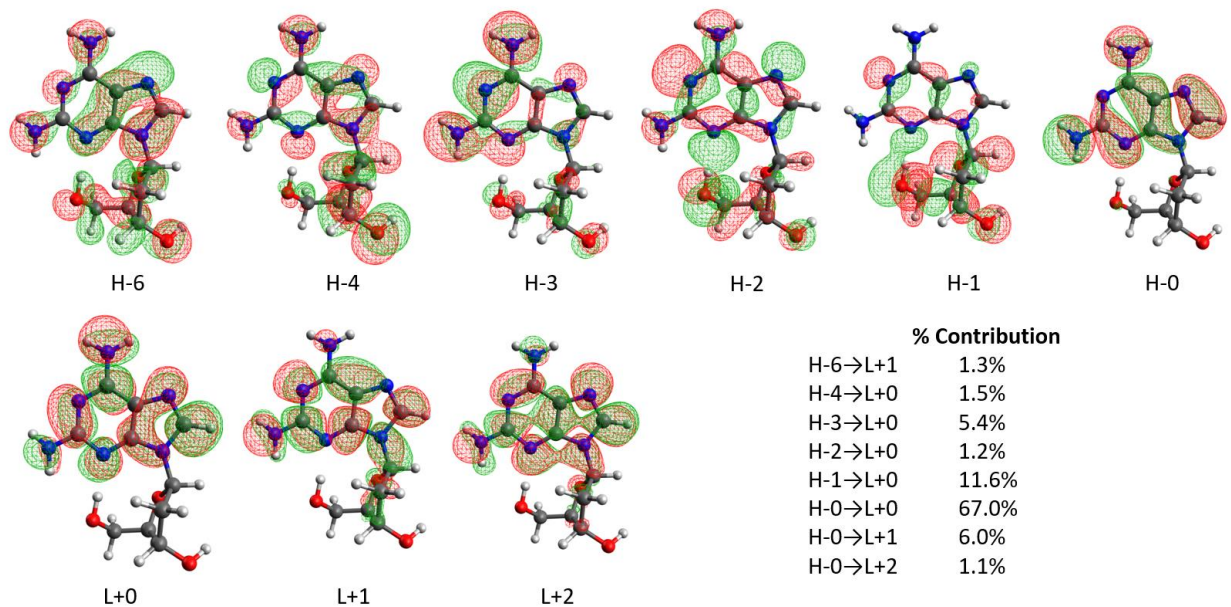
experimental absorption spectra) and thus, justifies the use of the BP86 functional for the vertical excitation energies.



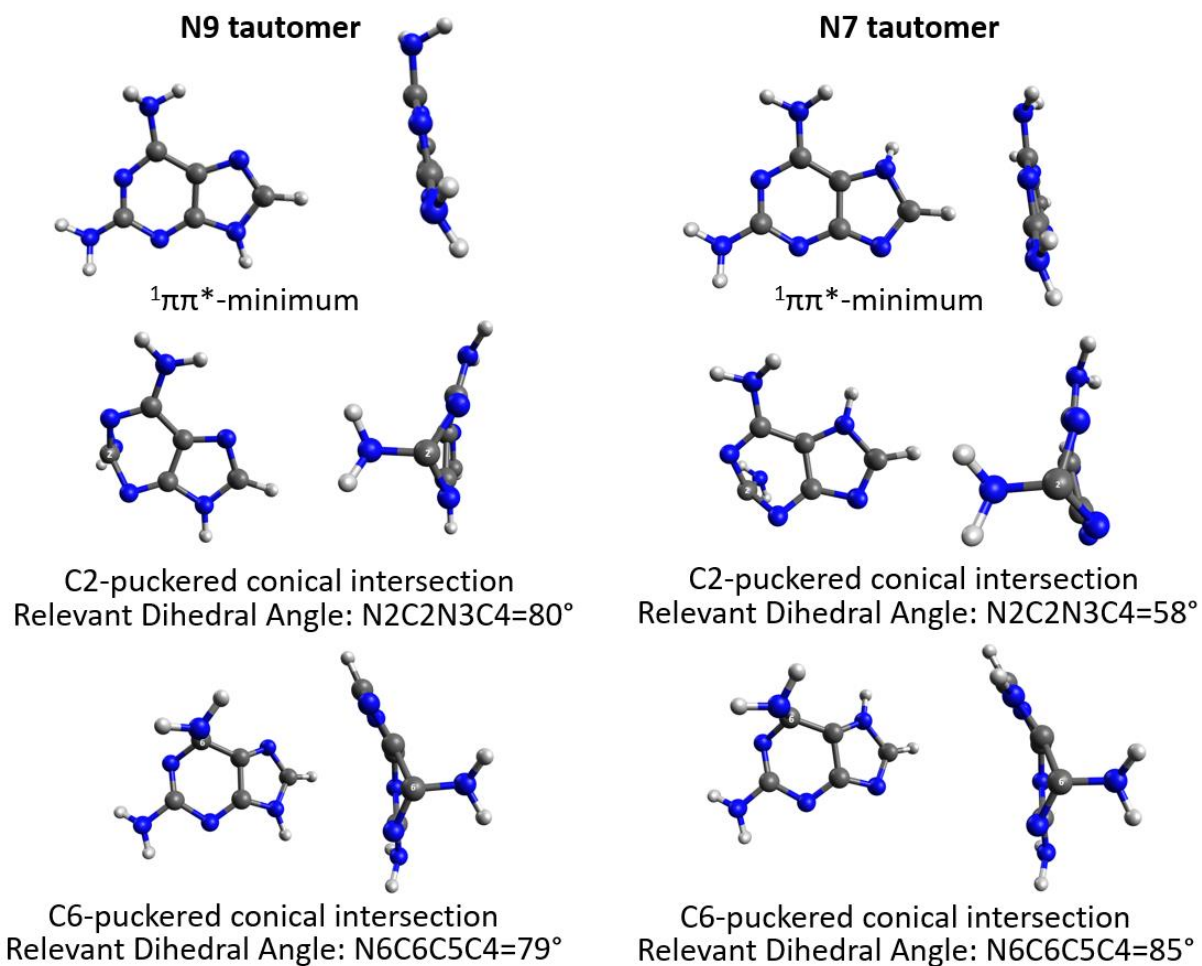
**Figure S5.** Relevant Kohn-Sham orbitals obtained at the TD-BP86/def2-TZVP/CPCM in water for the first excited singlet state of the N7 tautomer of 26DAP with the percentage contribution of single-electron transitions.



**Figure S6.** Relevant Kohn-Sham orbitals obtained at the TD-BP86/def2-TZVP/CPCM in water for the first excited singlet state of the N9 tautomer of 26DAP with the percentage contribution of single-electron transitions.

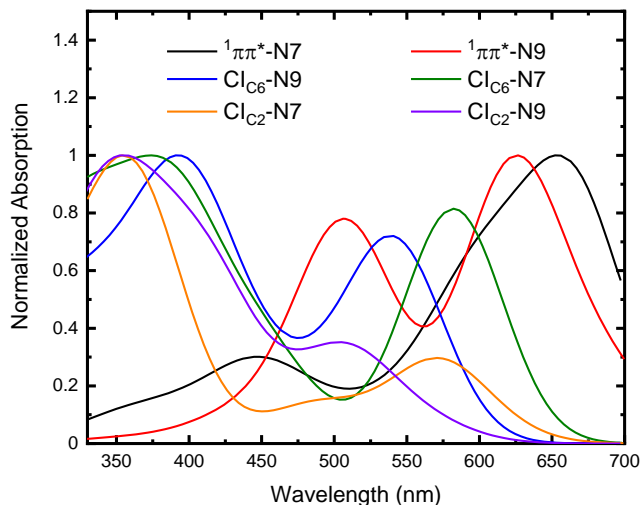


**Figure S7.** Relevant Kohn-Sham orbitals obtained at the TD-BP86/def2-TZVP/CPCM in water for the first excited singlet state of the N9 tautomer of 26DAP-d with the percentage contribution of single-electron transitions.



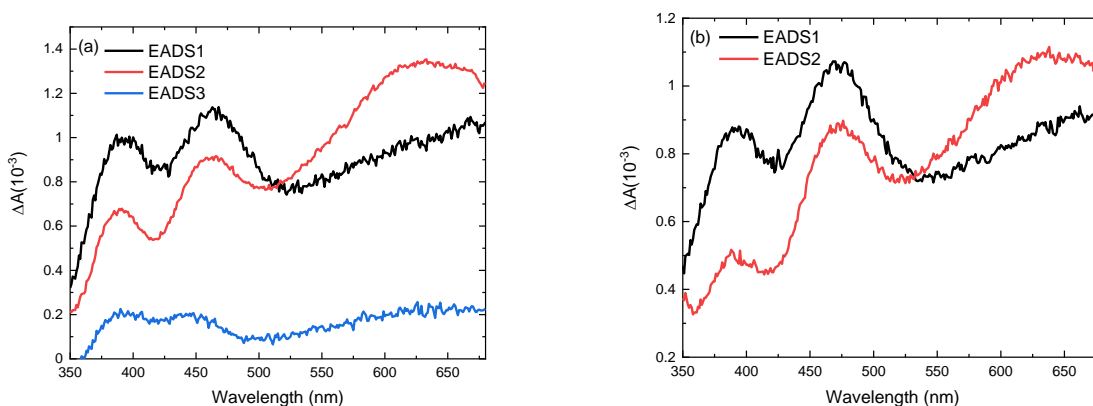
**Figure S8.** Optimized geometry of the  $1\pi\pi^*$  state and relevant conical intersection found in the C2- and C6-coordinates for the N9 and N7 tautomers of 26DAP at the TD-B3LYP/cc-pVDZ level of theory.





**Figure S9.** Excited state absorption spectra of the  $1\pi\pi^*$  minimum and  $Cl_{C6}$  and  $Cl_{C2}$  calculated at the TD-BP86/CPCM/def2-TZVP in water for the N9 and N7 tautomers of 26DAP. Relevant transitions were convoluted with a Gaussian function (FWHM=40 nm).

As shown in Figure S7, the excited state absorption spectra of the  $1\pi\pi^*$  state and the relevant conical intersections of 26DAP significantly overlap in the spectral range of 320 to 700 nm. Therefore, it is likely that the evolution-associated spectra (EADS) extracted from the global and target analyses of the transient absorption data consists of a linear combination of the absorption spectra of the  $1\pi\pi^*$  minima and the C2 and C6 conical intersections rather than to the “pure” species-associated spectra of specific transient species. Therefore, the EADS reported in Figure S6 may not be easily assigned as the expected or calculated absorption spectra of any particular transient species.



**Figure S10.** Evolution-associated difference spectra extracted from the global and target analyses of the transient absorption data for (a) 26DAP and (b) 26DAP-d.

## Supporting References

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