Electronic Supplementary Information (ESI) for Theoretical insight into photodeactivation mechanisms of adenine-uracil and adenine-thymine nucleobase pairs

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1 Conformational analysis

It is well known that the Watson-Crick conformer of the A-U base pair is not the most stable in the gas phase.¹ Figure S1 presents selected conformers of the A-U base pair optimized using the SCS-MP2 method and the cc-pVTZ basis set. Some of them are more stable than the Watson-Crick conformer (denoted as W:W cis). The most stable is the dimer of the bases that interact through the sugar edges (S:S) with a relative energy difference of 15.5 kJ/mol compared to the WC conformer of the A-U and 16.2 kJ/mol of the A-T base pair (values in parentheses). The presented results translate into a major share of this conformer in the Boltzmann population of the studied set of structures, leaving the remaining isomers in merely 4% of the population.



Fig. S1 Conformers of the adenine-uracil base pair chosen based on previous reports^{2,3} located using the SCS-MP2/cc-pVTZ method. The adopted nomenclature is based on the hydrogen bonding scheme; the "cis / trans" labels refer to the glycosidic bond orientation in nucleoside, and the W/H/C-H/S are accordingly Watson-Crick/Hoogsteen/C-H/sugar interacting sides. The respective relative energy values for the adenine-thymine base pair conformers are shown in parentheses.

For optimized isomers, potential energy profiles were constructed in the Franck-Condon region, and the selected excitation energies are listed in Table S1. Apparently, the WC conformer is not the only one in which the EDPT mechanism is, in principle, possible. Except for the W:S isomer of the A-U base pair, at least one state having a charge-transfer component was found within the 15 lowest-lying excited states. However, in the most stable structure, the CT state lies relatively high and is separated from the lowest-lying bright state by more than 2 eV. This implies that even though geometry optimization at the S₁ excited state PES of $\pi_A \pi_U^*$ CT character leads to proton transfer through a low-lying conical intersection with the ground state, the population of this dark CT state is unlikely, which is consistent with the lack of EDPT spectral features for gas-phase A-T.⁴

Table S1 The vertical excitation energies of the lowest-lying charge-transfer states calculated using the SCS-ADC2/cc-pVTZ method for each investigated conformer of the A-U base pair.

Conformer	State	Energy [eV]	State character	Oscillator strength
W:W cis (WC)	S ₁	5.09	$n_{II}\pi_{II}^*$	0.000
	S_2	5.19	$\pi_A \pi_A^*$	0.013
	S ₃	5.36	$\pi_A \pi_A^* / \pi_U \pi_U^*$	0.330
	S 9	6.60	$\pi_A \pi_A^* / \pi_A \pi_U^* / \pi_U \pi_U^*$	0.372
	S ₁₁	6.67	$\pi_A \pi_U^*$	0.170
W:W trans	S_1	4.94	$n_U \pi_U^*$	0.000
	S_2	5.21	$\pi_A \pi_A^*$	0.012
	S ₃	5.39	$\pi_{\!A}\pi_{\!A}^*$	0.300
	S_{11}	6.85	$\pi_{\!A}\pi_{\!U}^*$	0.016
S:S	S_1	5.05	$n_U \pi_U^*$	0.000
	S_2	5.22	$\pi_A \pi_A^*$	0.000
	S_3	5.34	$\pi_{\!A}^{}\pi_{\!A}^{*}$	0.434
	S_{14}	7.12	$\pi_{\!A}\pi_{\!U}^*$	0.002
S:W	S_1	4.91	$n_U \pi_U^*$	0.000
	S_2	5.24	$\pi_A \pi_A^*$	0.007
	S_3	5.39	$\pi_{\!A}^{}\pi_{\!A}^{*}$	0.275
	S ₁₂	6.89	$\pi_{\!A}\pi_{\!U}^*$	0.003
W:S	S_1	5.05	$n_U \pi_U^*$	0.000
	S_2	5.17	$\pi_A \pi_A^*$	0.043
	S_3	5.35	$\pi_{\!A}\pi_{\!A}^*$	0.503
H:W cis (HS)	S_1	5.09	$n_U \pi_U^*$	0.000
	S_2	5.18	$\pi_A \pi_A^*$	0.040
	S_3	5.32	$\pi_{\!A}\pi_{\!A}^*$	0.132
	S 9	6.43	$\pi_{\!A}\pi_U^*$	0.008
H:W trans	S_1	4.98	$n_U \pi_U^*$	0.000
	S_2	5.19	$\pi_{\!A}\pi_{\!A}^*$	0.032
	S_3	5.34	$\pi_{\!A}\pi_{\!A}^*$	0.137
	S_{10}	6.61	$\pi_{\!A}\pi_{\!U}^*$	0.000
H:S	S_1	5.04	$n_U^{}\pi_U^*$	0.000
	S_2	5.16	$\pi_{\!A}\pi_{\!A}^*$	0.090
	S_3	5.30	$\pi_{\!A}\pi_{\!A}^*$ / $\pi_{\!A}\sigma_{\!A}^*$	0.206
	S ₁₃	6.97	$\pi_{\!A}\pi_{\!U}^*$	0.004
S:C-H	S ₁	5.23	$\pi_A \pi_A^* / \pi_A \sigma_A^*$	0.007
	S_2	5.25	$n_U \pi_U^*$	0.000
	S_3	5.34	$\pi_U \pi_U^*/\pi_A \pi_A^*$	0.409
	S_7	6.26	$\pi_{\!A}\pi_{\!U}^*$	0.001
	S ₁₃	6.99	$n_A \pi_U^*$	0.000

The potential energy profiles of the H:W cis/trans and S:C-H conformers show lower-lying CT states compared to those of the W:W cis conformer. However, only for the S:C-H isomer does the energy gap between the lowest bright state and the CT state decrease to 0.88 eV (compared to 1.27 eV in the W:W cis). In this dimer, another CT state that is characterized by the ${}^{1}n\pi^{*}$ transition was also found. The corresponding weight of CT configuration (Ω_{CT}) for this state approaches unity. In this respect, it differs from the W:W cis conformer, in which the ${}^{1}n\pi^{*}$ state was also located, but with only a partial CT character.

What is unique about the W:W cis (WC) conformer is that the CT state has significant oscillator strength, which justifies its description as a bright state. This implies that only in this structure could the CT state be directly populated, which certainly increases the plausibility of EDPT, especially in the prebiotic context of this study.

2 The details of NEVPT2 calculations for WC A-U and A-T base pairs

The reliability of the SCS-MP2/SCS-ADC(2) protocol was tested against the NEVPT2/ccpVTZ results obtained assuming the state-averaged (SA) CASSCF reference wavefunctions implemented in the ORCA 4.2.1 package.⁵ For the A-U base pair the active space consisted of 10 electrons correlated in 8 orbitals (3 occupied π , 2 occupied n and 3 virtual π^* shown in Fig. S2) and was averaged over the two lowest-lying states.



Fig. S2 The orbitals included in the active space in NEVPT2 calculations for WC A-U base pair.



Fig. S3 The orbitals included in the active space in NEVPT2 calculations for WC A-T base pair.

In the case of A-T base pair the active space consisted of 10 electrons correlated in 8 orbitals (4 occupied π , 1 occupied n, 2 virtual π^* and 1 virtual σ^*) and was averaged over four lowest-lying states. The orbitals included in the active space are presented in Fig S3.

The PE cut along the amino N-H transfer in WC A-T base pair shows EDPT via LE/CT and CT/S₀. Solid lines correspond to the SCS-MP2/SCS-ADC2/cc-pVTZ data, and triangles show the NEVPT2/cc-pVTZ energies at the same geometries.



Fig. S4 The results of SCS-MP2/SCS-ADC2 (solid lines) and NEVPT2 (points) calculations for WC A-T base pair. PE cuts for the states of interest were obtained using LIIC between the FC region and the ${}^{1}\pi\pi_{CT}^{*}$ S₁/S₀ MECP.

3 Solvent effects in the FC region

The SCS-ADC(2)/COSMO approach was used to estimate the solvation effects on the potential energy profile of the A-U base pair. The vertical excitation energies in the FC region were calculated assuming nonequilibrium solvation with a slow part of the solvent apparent charges equilibrated for the ground state and the fast part, depending on the refraction index, for the excited state, according to the iterative PTED scheme implemented in the Turbomole 7.6 package.

The results for both water and chloroform solvents show that the interaction with a polarizable medium changes the order of the low-lying LE states; however, it does not affect the order of LE states localized at a given base. The $S_1 {}^1n_U \pi_U^*$ state is destabilized and becomes S_2 and S_4 in chloroform and water environment, respectively. Still, the ${}^1n_U\pi_U^*$ state remains very close to the bright states. In turn, the ${}^1\pi_A\pi_A^*$ transition localized on adenine is virtually unaffected by the presence of solvent and becomes the S_1 state. The charge transfer state is slightly stabilized, but remains relatively high above the lowest-lying bright state (1.12 eV in chloroform and 1.29 eV in water).

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S	State / Transition	E _{exc}	Transition	Eexc	f	Ω_{CT}	Transition	Eexc	f	Ω_{CT}
	vacum		chlo	proform	$(\varepsilon = 4.80)$		W	ater (E	= 78.34)	
S ₁	$n_{ m U}\pi_{ m U}^*$	5.09	$\pi_A \pi_A^*$	5.19	0.011	0.008	$\pi_A \pi_A^*$	5.19	0.008	0.007
S_2	$\pi_{ m A}^{-}\pi_{ m A}^{*}$	5.19	$n_{ m U}\pi_{ m U}^*$	5.26	$1.1 \cdot 10^{-4}$	0.041	$\pi_A \pi_A^* / \pi_U \pi_U^*$	5.26	0.372	0.009
S ₃	$\pi_{\mathrm{A}}\pi_{\mathrm{A}}^{*}/\pi_{\mathrm{U}}\pi_{\mathrm{U}}^{*}$	5.33	$\pi_A \pi_A^* / \pi_U \pi_U^*$	5.27	0.380	0.007	$\pi_U \pi_U^* / \pi_A \pi_A^*$	5.35	0.251	0.008
S_4	$\pi_{\mathrm{U}}\pi_{\mathrm{U}}^*/\pi_{\mathrm{A}}\pi_{\mathrm{A}}^*$	5.46	$\pi_U \pi_U^*$	5.36	0.241	0.010	$n_{\mathrm{U}}\pi_{\mathrm{U}}^{*}$	5.36	$1.1 \cdot 10^{-4}$	0.052
S_5	$n_A \pi_A^*$	5.65	$n_A \pi_A^*$	5.73	$4.3 \cdot 10^{-4}$	0.046	$n_A^* \pi_A^*$	5.76	$4.3 \cdot 10^{-4}$	0.045
S_6	$n_{\rm A}\pi_{\rm A}^*$	6.17	$n_A \pi_A^*$	6.26	$2.2\cdot10^{-4}$	0.042	$n_A \pi_A^*$	6.31	$2.1\cdot10^{-4}$	0.043
S_7	$\pi_{\mathrm{U}}\pi_{\mathrm{U}}^{*}$	6.28	$\pi_{\rm A}\pi_{\rm U}^*$ (CT)	6.39	0.006	0.935	$\pi_{\!A}\pi_{\!A}^*$	6.44	0.323	0.029
S_8	$n_{\mathrm{U}}^{*}\pi_{\mathrm{U}}^{*}$	6.33	$\pi_A \pi_A^* / \pi_U \pi_U^*$	6.42	0.192	0.052	$\pi_{\rm A}\pi_{\rm U}^*$ (CT)	6.55	0.014	0.887
S9	$\pi_{\rm A}\pi_{\rm U}^*$ (CT)	6.57	$n_{\mathrm{U}}\pi_{\mathrm{U}}^{*}$	6.48	$3.5 \cdot 10^{-7}$	0.014	$n_{ m U}\pi_{ m U}^*$	6.62	$1.9 \cdot 10^{-7}$	0.015
S ₁₀	$n_{ m A}\pi_{ m A}^*$	6.64	$\pi_U \pi_U^* / \pi_A \pi_A^*$	6.56	0.467	0.008	$\pi_U \pi_U^*$	6.74	0.307	0.022
S ₁₁	$\pi_{\rm A}\pi_{\rm A}^*/\pi_{\rm A}\pi_{\rm U}^*$ (CT)	6.65	$n_A \pi_A^*$	6.71	0.002	0.051	$n_A \pi_A^*$	6.75	0.188	0.004
S ₁₂	$\pi_{ m A}\pi_{ m A}^*$	6.88	$\pi_{\!A}\pi_{\!A}^*$	6.78	0.208	0.004	$n_{ m A}\pi_{ m A}^*$	6.85	0.001	0.047

Table S2 Vertical excitation energies (in eV) in Franck–Condon region of adenine-uracil base pair calculated with the SCS-ADC(2)-COSMO/cc-pVTZ method considering the model of bulk water and chloroform with charge distribution equilibrated for the ground state.

4 Substituent effect

The calculations presented in the main article focus on the properties of gas-phase WC base pairs A-T and A-U. The photochemistry of nucleosides is much more complex, as it involves quite a few isomers and the possibility of formation of intramolecular hydrogen bonds and additional deactivation channels. Interesting case studies can be found, for example, in Tuna et al.,⁶ Janicki et al.⁷ or Mansour et al.⁸ Nontheless, to gain some insight into the effects of glycosidic bond formation, we investigated the key stationary points for methylated base pairs. We located minimum energy structures of the ground state, first excited state, and MECPs after introducing the methyl groups at the N1 atom of uracil and N9 of adenine. The results presented in Table S3 show insignificant relative energy differences between the optimized S₁ excited states minima and the respective MECPs associated with the selected deactivation mechanisms.

Table S3 The relative energy difference in eV between the first excited state and MECP geometries with particularsubstituents at the N1(U) and N9(A) positions calculated using the SCS-ADC2/cc-pVTZ method.

Substituent	C2-oop(A)	C2-2-oop(A)	C6-oop(A)	C6-oop(U)	EDPT
-H	0.28	0.04	0.08	0.86	0.08
-CH ₃	0.26	0.05	0.09	0.84	0.12

5 Spin orbit couplings and transition rate calculations for A-U

The transition rates of radiative and nonradiative processes were calculated using the thermal vibration correlation function (TVCF) formalism for excited state decay, developed by Shuai et al.^{9–11} Due to the availability of non-adiabatic coupling terms, these calculations were performed using the TD-DFT approach, assuming ω B97X-D3 exchange-correlation functional and def2-SVP basis set available in the QChem 6.1 package.¹²

The minimum energy structure of the A-U WC base pair in the first excited state of ${}^{1}n\pi^{*}$ character was determined using the ω B97X-D3/def2-SVP method. A comparison of the characters of the low-lying states in this geometry shows different orderings of excited states in the TD-DFT and SCS-ADC(2) results. These are shown in Table S4 and reveal that the order of the T₁ and T₂ states is reversed in the TDDFT calculations. Hovewer, both triplet states lie below the S₁ state in the vicinity of its potential energy minimum.

Table S4 Selected excitation energies calculated at the respective minimum-energy geometries of the first excited ${}^{1}n_{U}\pi_{U}^{*}$ state of A-U dimer using the SCS-ADC(2)/cc-pVTZ and ω B97X-D3/def2-SVP methods (in parentheses, excitation energies obtained using the ω B97X-V/def2-SVP method are shown). Subscripts A and U indicate the localization of a given molecular orbital on a particular nucleobase.

State	e / Transition	$E_{exc}/[eV]$	f	State	/ Transition	$E_{exc}/[eV]$	f
	ωB97X	K-D3/def2-SV	Р		SCS-AD	OC(2)/cc-pV	ΓZ
$ \begin{array}{r} T_1 \\ T_2 \\ T_3 \\ S_1 \\ T_4 \\ S_2 \end{array} $	${}^{3}\pi_{\mathrm{U}}\pi_{\mathrm{U}}^{*}$ ${}^{3}\mathrm{n}_{\mathrm{U}}\pi_{\mathrm{U}}^{*}$ ${}^{3}\pi_{\mathrm{A}}\pi_{\mathrm{A}}^{*}$ ${}^{1}\mathrm{n}_{\mathrm{U}}\pi_{\mathrm{U}}^{*}$ ${}^{3}\pi_{\mathrm{U}}\pi_{\mathrm{U}}^{*}$ ${}^{1}\pi_{\mathrm{U}}\pi_{\mathrm{U}}^{*}$	3.23 (3.28) 3.83 (3.89) 3.98 (4.03) 4.21 (4.30) 4.37 (4.46) 5.44 (5.52)	$\begin{array}{c} 0.00 \\ 0.00 \\ 0.00 \\ 5.98 \cdot 10^{-4} \\ 0.00 \\ 0.25 \end{array}$	$\begin{array}{c} T_1\\S_1\\T_2\\S_2\\T_3\\T_4\end{array}$	${}^{3}n_{U}\pi_{U}^{*}$ ${}^{1}n_{U}\pi_{U}^{*}$ ${}^{3}\pi_{U}\pi_{U}^{*}$ ${}^{1}\pi_{U}\pi_{U}^{*}$ ${}^{3}\pi_{U}\pi_{U}^{*}$ ${}^{3}\pi_{L}\pi_{A}^{*}$	2.77 2.83 2.90 3.79 4.14 4.19	$\begin{array}{c} 0.000 \\ 1.47 \cdot 10^{-4} \\ 0.000 \\ 0.179 \\ 0.000 \\ 0.000 \\ 0.000 \end{array}$



Fig. S5 The S₁ excited state minimum-energy geometries obtained with the SCS-ADC(2)/cc-pvTZ (red structure) and ω B97X-D3/def2-SVP (navy blue one) methods, superimposed with the RMSD 0.127. The inset presents isolated uracil structures from both equilibrium geometries (RMSD 0.117). The structures were aligned based on the positions of the three atoms marked.

The minimum energy structures of the S₁ ${}^{1}n_{U}\pi_{U}^{*}$ state and the T₁ ${}^{3}\pi_{U}\pi_{U}^{*}$ (corresponding to the T₂ state in SCS-ADC(2)/cc-pVTZ calculations) obtained using the TD-DFT approach were very similar to those located at the SCS-ADC(2)/cc-pVTZ level, with RMSD of 0.109



Fig. S6 The triplet T_2 geometry obtained with the SCS-ADC(2)/cc-pvTZ method (red structure) and the triplet T_1 geometry obtained using ω B97X-D3/def2-SVP method (navy blue structure) superimposed with the RMSD 0.189. The inset presents isolated uracil structures from both equilibrium geometries (RMSD 0.255). The structures were aligned based on the positions of the three atoms marked

and 0.184, respectively (cf. Figs. S5-S6). This and a similar character of the respective excited states justify the use of the TD-DFT approach for the transition-rate calculations.

The rotationally invariant spin-orbit coupling constants (SOCC) were computed including mean-field treatment of the two-electron part of the Breit–Pauli Hamiltonian and Wigner-Eckart theorem (as implemented in QChem 6.1)¹³ by summing over all projections *M* of spin *S* according to:

$$SOCC = \sqrt{\sum_{M'M''} |\langle S'M'|H^{SO}|S''M''\rangle|^2}.$$
(1)

The SOCC values computed between the $S_1(n\pi^*)$ and $T_1(\pi\pi^*)$ states amount to 30.3 cm⁻¹ for both the ω B97X-D3/def2-SVP and ω B97X-V/def2-TZVP methods at the respective S_1 minimum energy geometries. These are similar to the corresponding values obtained at the SCS-ADC(2)/cc-pVTZ S₁ minimum energy geometry (39.0 and 38.8 cm⁻¹, respectively) as well as the SA-CASPT2(12,10)/cc-pVTZ-DK estimate of 58.3 cm⁻¹ obtained at the same geometry using RASSI-SO approach implemented in OpenMolcas v22.10 (the active space consisted of 3 n_U, 2 π_A , 1 π_U and 4 virtual orbitals: 2 π_U^* and 2 π_A^* ; and the density was averaged over the two lowest-lying states). In fact, the larger magnitudes of these couplings only strengthen our conclusions.

The transition rate between these states calculated using the TVCF approach in the MOMAP software¹⁴ amounts to $1.60 \times 10^{10} \text{ s}^{-1}$, which is consistent with the k_{ISC} rate calculated for isolated uracil by Etinski et al. $(2.60 \times 10^{10} \text{ s}^{-1})$.¹⁵ The calculated reverse ISC rate k_{RISC} of $3.99 \times 10^{-3} \text{ s}^{-1}$ is negligible. The corresponding internal conversion S_1 - $S_0 k_{IC}$ rate is an order of magnitude smaller $(1.29 \times 10^9 \text{ s}^{-1})$ while the radiative rate of this transition is very small $(1.91 \times 10^3 \text{ s}^{-1})$.

In the ω B97X-D3 method the T₁($\pi\pi^*$) state lies 0.98 eV below the S₁($n\pi^*$) state. However, the geometries obtained from the optimization of T₁ and S₁ in this methodology correspond to the geometries of SCS-ADC(2) T₂ and S₁, for which the energy gap in the potential energy profile calculated in SCS-ADC(2) is smaller than 0.2 eV. In addition, the SA-2-CASPT2(12,10)/ccpVTZ-DK calculations indicate a much more substantial spin-orbit coupling between these states. These results imply that the intersystem crossing to a triplet manifold may be of great importance in WC A-U, especially since the S₁($n\pi^*$)— S_0 k_{IC} rate is an order of magnitude lower than the k_{ISC} rate calculated using the ω B97X-D3/def2-SVP method. Rates of selected radiative and nonradiative transitions calculated at the ω B97X-D3/def2-SVP level are shown in Table S5.

	k_{IC}/k_{ISC} [$\frac{1}{s}$]	Lifetime [s]	$k_r \left[\frac{1}{s}\right]$	Lifetime [s]
S_0/S_1	$1.29\cdot 10^9$	$7.75 \cdot 10^{-10}$	$1.91 \cdot 10^3$	$5.25\cdot 10^{-4}$
S_0/T_1	$1.61 \cdot 10^{8}$	$6.21 \cdot 10^{-9}$	$9.29 \cdot 10^{-2}$	10.7
S_1/T_1	$1.60 \cdot 10^{10}$	$6.23 \cdot 10^{-11}$	$9.31 \cdot 10^{-4}$	$1.07 \cdot 10^{3}$
S_1/T_2	$6.64 \cdot 10^{7}$	$1.51 \cdot 10^{-8}$	$7.73 \cdot 10^{-5}$	$1.29 \cdot 10^4$

Table S5 Rates of selected nonradiative (IC or ISC) and radiative transitions computed using the TVCF approach based on ω B97X-D3/def2-SVP data.

6 Schematic representation of the investigated radiationless deactivation mechanisms in the A-T WC base pair

In general, the geometries and spectra of the low-lying states were qualitatively similar for the WC A-U and A-T. Figure S7 shows a schematic diagram of the deactivation processes studied in A-T which is qualitatively similar to that shown in Fig. 5 of the main article with only small quantitative differences with respect to A-U. The major difference is in the ordering of LE ${}^{1}\pi\pi^{*}$ states, which should not affect the mechanisms discussed.



Fig. S7 Schematic representation of the investigated radiationless deactivation mechanisms in the A-T base pair. Values show energies relative to the ground state in eV. Ring-puckering paths are labeled with puckered base and the most distorted ring atom, e.g. C6-oop(T) indicates thymine atom C6 distorted out of plane.

7 A comment regarding availability of the located conical intersections based on crystallographic and molecular dynamics data.

The distortion of all the intramolecular MECPs discussed from the quasiplanar structure raises the question of the plausibility of these paths in DNA and RNA structures. In particular, MECPs associated with the C2- and C6-atom puckering of adenine feature a significant out-of-plane distortion. To explore whether the puckered structures are accessible in nucleic acid, we performed a search of the experimental B-DNA structures. When the structural deformations of the puckered MECPs are taken into account, the propeller twist parameter seems to reflect the change in the mutual orientation of the nucleobases most reliably.¹⁶ The average value of this parameter for A-T in the experimental results collected (data collected on 29/09/2023) from the nucleic acid database 17,18 is 22.9° , while the BIGNASim molecular dynamics simulations database,¹⁹ employing Nucleic Acids Flexibility Server,²⁰ shows that this parameter can change up to 53.6°. The data presented pertain only to a B-DNA duplex with at least two A-T base pairs in a sequence. The average and extreme values of the propeller twist parameter could be compared to the values of the dihedral angle $\delta([A]N_9C_8 - N_1C_2[U])$ which amounts to 21.8° and 5.1° for the two C2-oop(A) MECPs, 88.8° for the C6-oop(A) and 31.4° and 8.9° for C5-oop(U) and C6-oop(U) MECPs, respectively. Therefore, only the C6-puckered(A) MECP geometry does not fit these ranges and may be unattainable in the larger RNA fragment. However, the discussed mechanisms concern only bare nucleobase pairs, and the experimental data reflect the equilibrium geometries. Thus, the derived ranges of structural parameters are not necessarily limiting and are only a hint regarding availability of a given conical intersection.

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