Electronic Supporting information for

Evolution of the excitonic state of DNA stacked thymines: intra-base ππ*→S_0 decay paths account for ultrafast (sub-ps) and longer (>100 ps) deactivations

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S1. Computational methods

The system studied by the CASPT2//CASSCF/MM calculations is a double strand B-fragment 5'-C-C-T-T^5-T^3-A-A-A-G-G-3' (1ikk.pdb[4]) solvated in a box of water molecules, including also Na^+ counter ions (Scheme 1). Ground state minimum (Min-S_0) is obtained from 150 ns molecular dynamics at 7°C temperature (280 K, enough lower than melting temperature, which ensure the duplex form), starting from the solvated 1ikk.pdb B-conformation, to evaluate a large amount of different conformations, in which all the atoms are free to move. The extracted centroid of the most populated cluster was then optimized at the QM/MM level.

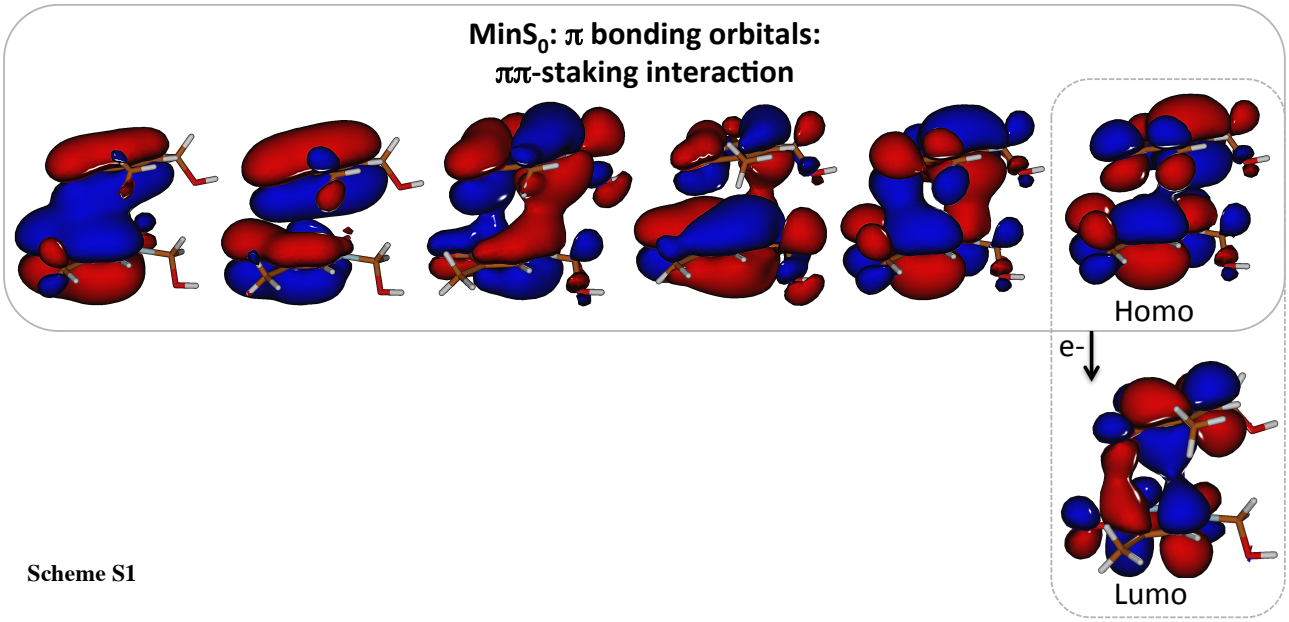
The energies for each critical point or Conical Intersection (CI) are corrected at the QM(CASPT2//CASSCF(16,14))/MM(Amber) level, with a 6-31g* basis set and a state average (five states) Multi-State (MS) approach. The (16,14) active space includes two n orbital (one per base) and the complete set of π and π* orbitals. CASPT2 energies are calculated with Molcas8[5]. Ground and ππ* excited states optimization have been done with a (8,8) active space of 4 π and 4 π* orbitals. CASSCF ππ* states topologies are, indeed, better described without including n orbitals, because of the coupling with nπ* states that emerges at the CASSCF level, tested before, which disappears in the Multi-State (MS) CASPT2//CASSCF(16,14) SP correction. Two n orbitals (on O_4 atoms of each QM Thy) have been then included in the optimization of the nπ* states, leading to a (12,10) active space.

The movable part employed in geometry optimizations consists of eight bases (-T-T^5-T^3-A- and their four paired bases) and all the water molecules H-bonded with these bases. The QM region consists of the two T^3 and T^5 bases plus a small fragment of the sugar ring (see Scheme 1) to better preserve the chromophores charge distribution. The rest of the movable part is treated at the MM level by using Amber12[6] force field. The remaining MM parts (far enough to not influence the QM region) are kept fixed at optimized ground state minimum geometry.

Conical Intersections optimizations were performed with the gradient projection algorithm of Bearpark et al.[7, 8]

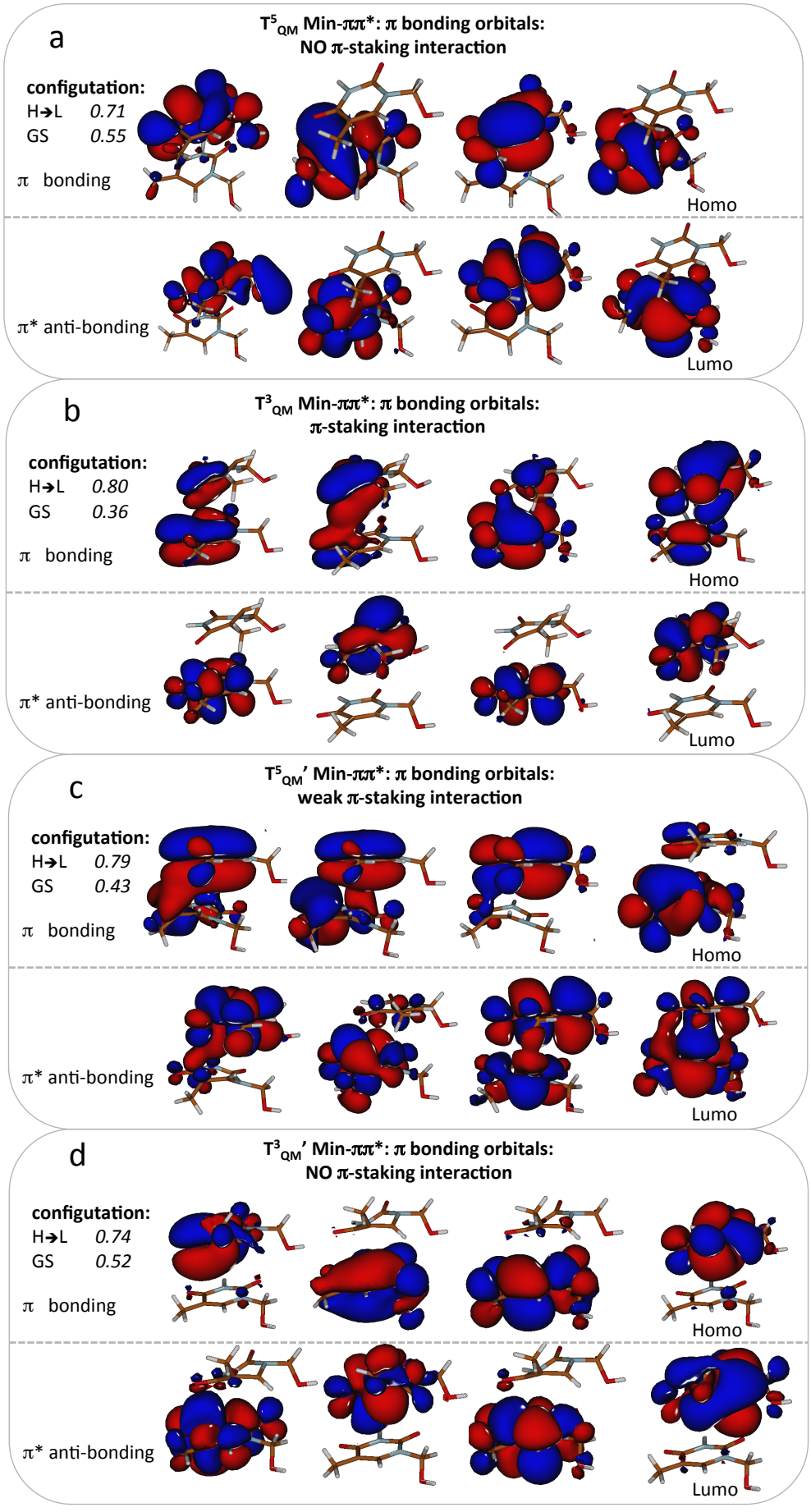
S2. Orbitals of the ππ* minima and π-stacking interactions.

Scheme S1 shows the π orbitals of Min-S_0 structure, showing as the ππ-stacking interactions plays a non-negligible importance to fix a particular distance and orientation in DNA sequences. The dashed line square shows the main electronic transition configuration involved in the T^3_{QM} and T^5_{QM}' ππ* decay path. This picture explain that the excited state nature of these excited states enforces ππ–stacking interaction, because of the electronic transition from a π orbital characterized by low inter-base bonding character to a π* with pronounced bonding properties.



Scheme S1

Scheme S2 displays the orbitals characterizing T^5_{QM} Min–ππ* (a), T^3_{QM} Min–ππ* (b), T^5_{QM}' Min–ππ* (c) and T^3_{QM}' Min–ππ* minima. Only where the π orbitals (not π*) are still shared between bases, the π-stacking stabilization contribution stabilize the excited state minimum, enforced by a great GS configuration component (considerable in all of them). This scheme give the reason why in the T^3_{QM} Min–ππ* (Scheme 2b) the p-stacking stabilize in part the energy. A reduced π orbital delacalization is also observable in T^5_{QM}' Min–ππ* (Scheme 2c). Where π orbitals are fully localized on a single base, the π-interaction stabilization disappears (Scheme 2a and d).

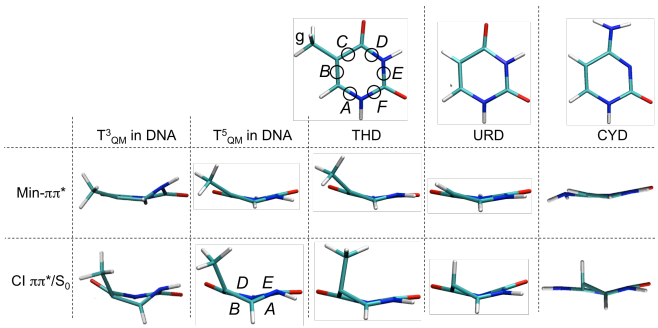

a
T5QM Min-ππ*: π bonding orbitals:
NO π-staking interaction
configutation:
H➔L 0.71
GS 0.55
π bonding
Homo
π* anti-bonding
Lumo
b
T3QM Min-ππ*: π bonding orbitals:
π-staking interaction
configutation:
H➔L 0.80
GS 0.36
π bonding
Homo
π* anti-bonding
Lumo
c
T5QM' Min-ππ*: π bonding orbitals:
weak π-staking interaction
configutation:
H➔L 0.79
GS 0.43
π bonding
Homo
π* anti-bonding
Lumo
d
T3QM' Min-ππ*: π bonding orbitals:
NO π-staking interaction
configutation:
H➔L 0.74
GS 0.52
π bonding
Homo
π* anti-bonding
Lumo

Scheme S2

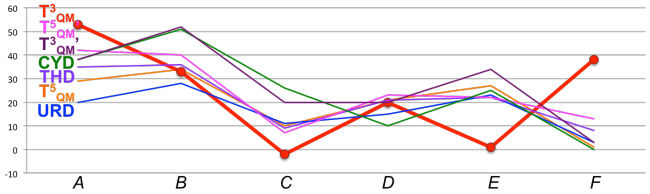
S3. ππ* minima and ππ*/S_0 CIs structures and torsional parameters.

Table S1 corresponds to Table1 in the main text, here integrated with the torsional parameters values for each ππ* minima or ππ*/S_0 CIs discussed in the manuscript.

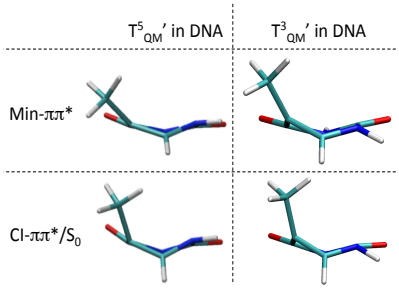
Table S1. Torsional parameters (A, B, C, D, E, F, g: see definition in the top picture) for the two ππ* minima (Minππ*) and ππ*/S_0 CI found in DNA along the T^5_{QM} and T^3_{QM} ππ* decay paths and in solvated pyrimidines (THD, URD and CYD)[1]. The bottom picture displays the trend in the torsional values. T^5_{QM}' and T^3_{QM}' minima (Min-ππ*) and CIs (CI-ππ*/S_0) structures are largely resembling T^5_{QM} Min-ππ* and CI-ππ*/S_0 structures, see Scheme S3.



		A	B	C	D	E	F	g
T^5_{QM} in DNA	Min-ππ*	29	34	10	21	27	1	134
	CI-ππ*/S_0	55	60	14	24	26	12	79
T^3_{QM} in DNA	Min-ππ*	**53**	**33**	**-2**	**20**	**1**	**38**	**133**
	CI-ππ*/S_0	64	50	1	30	15	33	81
T^5_{QM}' in DNA	Min-ππ*	42	40	7	23	22	13	115
	CI-ππ*/S_0	54	53	6	35	32	14	81
T^3_{QM}' in DNA	Min-ππ*	38	52	20	20	34	-3	101
	CI-ππ*/S_0	50	62	19	24	35	1	76
THD[1]	Min-ππ*	35	36	9	21	22	8	123
	CI-ππ*/S_0	38	52	24	15	28	-1	62
URD[1, 2]	Min-ππ*	20	28	11	15	23	3	142
	CI-ππ*/S_0	33	52	23	21	40	-11	64
CYD[1, 3]	Min-ππ*	19	22	10	7	11	2	155
	CI-ππ*/S_0	38	51	26	10	25	0	68



Scheme S3 shows T^5_{QM}' and T^3_{QM}' minima (Min-ππ*) and CIs (CI-ππ*/S_0) structures, which are largely resembling T^5_{QM} Min-ππ* and CI-ππ*/S_0 structures.

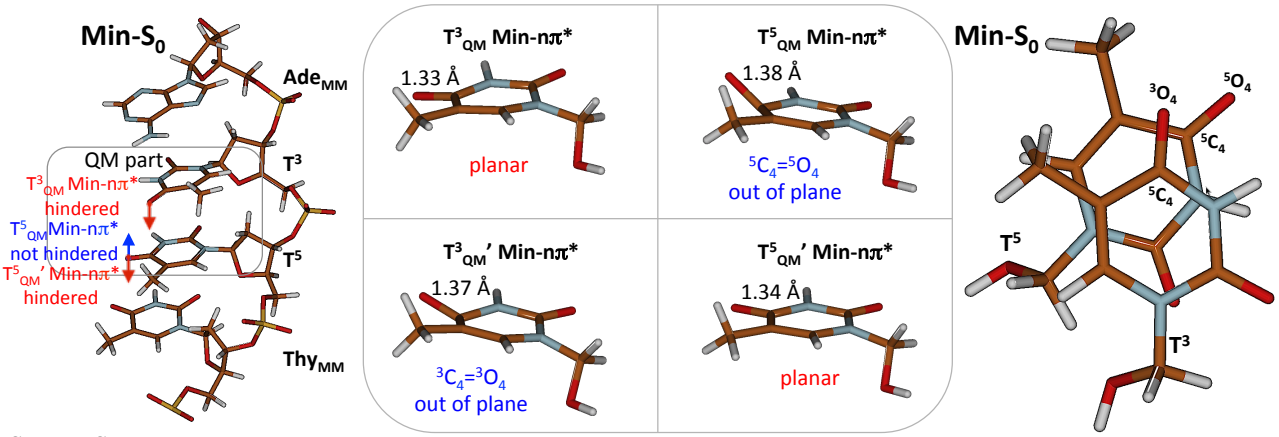


Scheme S3

S4. nπ* minima and the reproducible behaviour along the Thys strand.

Figure 1, in the main text, shows the calculated minima (Min-nπ*) energies together the different ππ* decay paths. All of these minima are roughly isoenergetic with the respective Min-ππ* minima, resembling the Thymine and Thymidines behaviour already seen in previous works[1, 9].

Here, in the central picture of Scheme S4, we show the nπ* calculated minima structures:



Scheme S4

In the case of the T^3_{QM} Min-nπ* where the $^3C_4$=$^3O_4$ should bend vs. T^5, the molecule stays nearly planar because the out of plane motion is hindered by T^5, due to the particular DNA orientation, shown in the Min-S_0 picture on the right side. Looking at the Thys strand of our system (left part of Scheme S4), we se three adjacent Thys, two of them are the QM part and the third is at MM level (Thy_{MM}). The $^5C_4$=$^5O_4$ motion versus the Thy_{MM} suffers the same steric hindrance of T^3_{QM} vs. T^5_{QM}, and so the minimum (T^5_{QM}' Min-nπ*) stays planar as T^3_{QM} Min-nπ*, confirming that the 'two QM staked model' should be reproduced along Thys staked sequences. Instead, T^5_{QM} Min-nπ* shows the classical $^5C_4$=$^5O_4$ out of plane bending, because its orientation allows a larger bending motion.

S5. Min-S_0 vertical excitation energies and oscillator strengths.

Table S2. Min-S_0 vertical excitation energies calculated with QM/MM method. The QM part is at MS-CASPT2//CASSCF(16,14))/6-31g* level, averaged on five states. CT states are evaluated with a state average on ten states. CT_{53} and CT_{35} are CT states involving an electron transfer from T_5 to T_3 and the opposite, respectively. Brightest state in bold characters.

State	Energy (eV)	O.S.
ππ* (exciton)	5.05	0.15
ππ* (exciton)	**5.31**	**0.82**
T^3 nπ*	5.55	0.00
T^5 nπ*	5.67	0.00
CT_{53}	6.55	0.00
CT_{35}	6.90	0.01

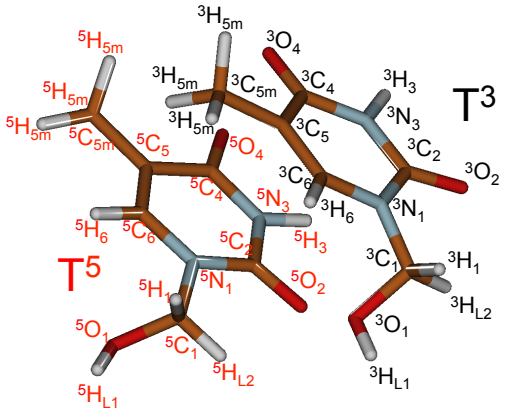
S6. T^3_{QM} decay path, CT and ππ* states energies and charge distributions.

In Table S3 we document together the vertical energies of Min-S_0 and T^3_{QM} Min-ππ* minima to clearly show that the lowest CT state is enough higher in energy than the ππ* exciton state in Min-S_0 and than the ππ* in T^3_{QM} Min-ππ*. Additionally, below we show the T^5 and T^3 bases charges and the respective atom charges (see Scheme S5 and the following values) to evidence that the states described in the main text (T^3_{QM} ππ*) have not CT nature, because T^5 and T^3 are null charged. The opposite charges are simply localized on atoms in the adjacent Thys: $^5C_4$ and $^3O_4$ in Min-S_0 ππ* state (S_2) and in T^3_{QM} Min-ππ*. Aloned charge values are the same reported in Figure 1b and in the main text discussion.

Table S3. Min-S_0 and T^3_{QM} Min-ππ* energies calculated with QM/MM method. The QM part is at MS-CASPT2//CASSCF(16,14))/6-31g* level, averaged on five states. CT_{53} and CT_{35} are CT states involving an electron transfer from T_5 to T_3 and the opposite, respectively. Min-S_0 absorbing state, T^3_{QM} Min-ππ* and the lowest CT states are in bold characters.

	Min-S_0	T^3_{QM} Min-ππ*
State	Energy (eV)	
ππ*	5.05 (exciton)	7.51[a] ($\pi\pi^*T^5_{QM}$)
ππ*	**5.31 (exciton)**	**4.76 ($\pi\pi^*T^3_{QM}$)**
T^3 nπ*	5.55	6.27
T^5 nπ*	5.67	7.94[a]
CT_{53}	**6.55[a]**	**7.28[a]**
CT_{35}	6.90[a]	

[a] Evaluated with 10-states state average calculations



Scheme S5

Min-S_0

• ***ππ* (exciton, S_2)***

T^5=0.00
$^5O_1$=-0.7594 $^5C_1$=0.2196 $^5H_1$=0.2331 $^5N_1$=-0.6987 $^5C_6$=0.1537 $^5H_6$=0.2819 $^5C_5$=-0.1722 $^5C_{5m}$=-0.5034 $^5H_{5m}$=0.2053 $^5H_{5m}$=0.2080 $^5H_{5m}$=0.1905 $^5C_4$=0.7256 $^5O_4$=-0.6388 $^5N_3$=-0.9637 $^5H_3$=0.4995 $^5C_2$=1.1281 $^5O_2$=-0.7312 $^5H_{L1}$=0.4427 $^5H_{L2}$=0.1772

T^3=0.00
$^3O_1$=-0.7520 $^3C_1$=0.2117 $^3H_1$=0.2275 $^3N_1$=-0.6975 $^3C_6$=0.1332 $^3H_6$=0.2879 $^3C_5$=-0.1769 $^3C_{5m}$=-0.5274 $^3H_{5m}$=0.1962 $^3H_{5m}$=0.2091 $^3H_{5m}$=0.2153 $^3C_4$=0.7547 $^3O_4$=-0.6203 $^3N_3$=-0.9508 $^3H_3$=0.5021 $^3C_2$=1.0951 $^3O_2$=-0.7271 $^3H_{L1}$=0.4395 $^3H_{L2}$=0.1818

• ***CT_{53}***

T^5=+0.93
$^5O_1$=-0.7543 $^5C_1$=0.2235 $^5H_1$=0.2336 $^5N_1$=-0.5131 $^5C_6$=0.3032 $^5H_6$=0.2813 $^5C_5$=0.0828 $^5C_{5m}$=-0.5025 $^5H_{5m}$=0.2066 $^5H_{5m}$=0.2173 $^5H_{5m}$=0.1980 $^5C_4$=0.8212 $^5O_4$=-0.4978 $^5N_3$=-0.9456 $^5H_3$=0.4996 $^5C_2$=1.1405 $^5O_2$=-0.6971 $^5H_{L1}$=-0.7388 $^5H_{L2}$=0.4431

T^3=-0.93
$^3O_1$=-0.7548 $^3C_1$=0.2078 $^3H_1$=0.2261 $^3N_1$=-0.8512 $^3C_6$=-0.0989 $^3H_6$=0.2867 $^3C_5$=-0.3511 $^3C_{5m}$=-0.5308 $^3H_{5m}$=0.1978 $^3H_{5m}$=0.2088 $^3H_{5m}$=0.2154 $^3C_4$=0.6039 $^3O_4$=-0.7666 $^3N_3$=-0.9807 $^3H_3$=0.5015 $^3C_2$=1.0853 $^3O_2$=0.1850 $^3H_{L1}$=0.4388 $^3H_{L2}$=0.1754

• ***CT_{35}***

T^5=-0.96
$^5O_1$=-0.7621 $^5C_1$=0.2154 $^5H_1$=0.2322 $^5N_1$=-0.8667 $^5C_6$=-0.1294 $^5H_6$=0.2808 $^5C_5$=-0.3366 $^5C_{5m}$=-0.5067 $^5H_{5m}$=0.2057 $^5H_{5m}$=0.2062 $^5H_{5m}$=0.1913 $^5C_4$=0.5891 $^5O_4$=-0.7627 $^5N_3$=-0.9947 $^5H_3$=0.4988 $^5C_2$=1.1167 $^5O_2$=-0.7467 $^5H_{L1}$=0.4420 $^5H_{L2}$=0.1703

T^3=+0.96
$^3O_1$=-0.7480 $^3C_1$=0.2153 $^3H_1$=0.2278 $^3N_1$=-0.5455 $^3C_6$=0.3022 $^3H_6$=0.2879 $^3C_5$=0.1142 $^3C_{5m}$=-0.5280 $^3H_{5m}$=0.1979 $^3H_{5m}$=0.2179 $^3H_{5m}$=0.2250 $^3C_4$=0.8195 $^3O_4$=-0.4287 $^3N_3$=-0.9298 $^3H_3$=0.5025 $^3C_2$=1.1050 $^3O_2$=-0.7064 $^3H_{L1}$=0.4398 $^3H_{L2}$=0.1883

T^3_{QM} Min-ππ*

• ***ππ* T^3_{QM}***

T^5=-0.01
$^5O_1$=-0.7654 $^5C_1$=0.2246 $^5H_1$=0.2303 $^5N_1$=-0.7956 $^5C_6$=0.1317 $^5H_6$=0.2818 $^5C_5$=-0.1761 $^5C_{5m}$=-0.5031 $^5H_{5m}$=0.2091 $^5H_{5m}$=0.2117 $^5H_{5m}$=0.1954 $^5C_4$=0.8494 $^5O_4$=-0.6322 $^5N_3$=-0.9700 $^5H_3$=0.5029 $^5C_2$=1.1305 $^5O_2$=-0.7462 $^5H_{L1}$=0.4410 $^5H_{L2}$=0.1734

T^3=+0.01
$^3O_1$=-0.7423 $^3C_1$=0.2327 $^3H_1$=0.2155 $^3N_1$=-0.4975 $^3C_6$=0.2253 $^3H_6$=0.2760 $^3C_5$=-0.2991 $^3C_{5m}$=-0.5325 $^3H_{5m}$=0.1974 $^3H_{5m}$=0.2154 $^3H_{5m}$=0.2135 $^3C_4$=0.7244 $^3O_4$=-0.7327 $^3N_3$=-0.9750 $^3H_3$=0.5067 $^3C_2$=1.0564 $^3O_2$=-0.6873 $^3H_{L1}$=0.4365 $^3H_{L2}$=0.1734

• ***CT_{53}***

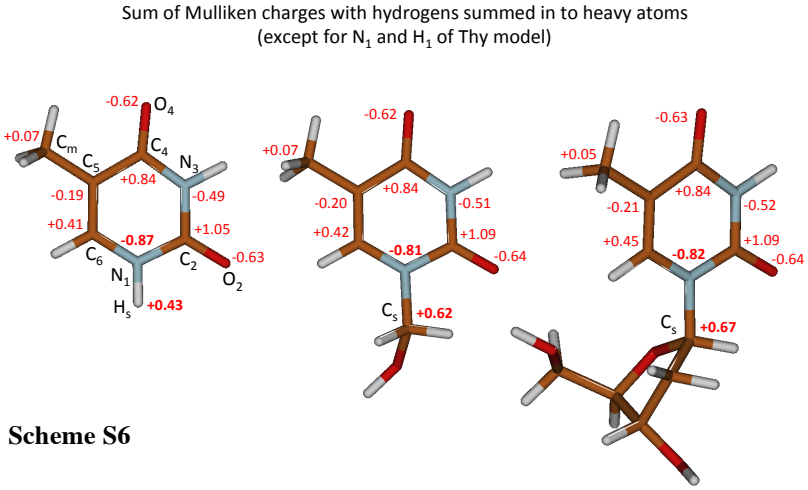
T^5=+0.95
$^5O_1$=-0.7585 $^5C_1$=0.2230 $^5H_1$=0.2381 $^5N_1$=-0.5312 $^5C_6$=0.3133 $^5H_6$=0.2879 $^5C_5$=0.0860 $^5C_{5m}$=-0.5099 $^5H_{5m}$=0.2122 $^5H_{5m}$=0.2260 $^5H_{5m}$=0.1982 $^5C_4$=0.8200 $^5O_4$=-0.4937 $^5N_3$=-0.9448 $^5H_3$=0.5023 $^5C_2$=1.1480 $^5O_2$=-0.7059 $^5H_{L1}$=0.4444 $^5H_{L2}$=0.1933

T^3=-0.95
$^3O_1$=-0.7497 $^3C_1$=0.2317 $^3H_1$=0.2120 $^3N_1$=-0.7620 $^3C_6$=-0.0727 $^3H_6$=0.2684 $^3C_5$=-0.4108 $^3C_{5m}$=-0.5451 $^3H_{5m}$=0.1942 $^3H_{5m}$=0.2027 $^3H_{5m}$=0.2071 $^3C_4$=0.6296 $^3O_4$=-0.8303 $^3N_3$=-0.9422 $^3H_3$=0.4990 $^3C_2$=1.0417 $^3O_2$=-0.7144 $^3H_{L1}$=0.4317 $^3H_{L2}$=0.1601

S7. Validation of the QM/MM fragmentation

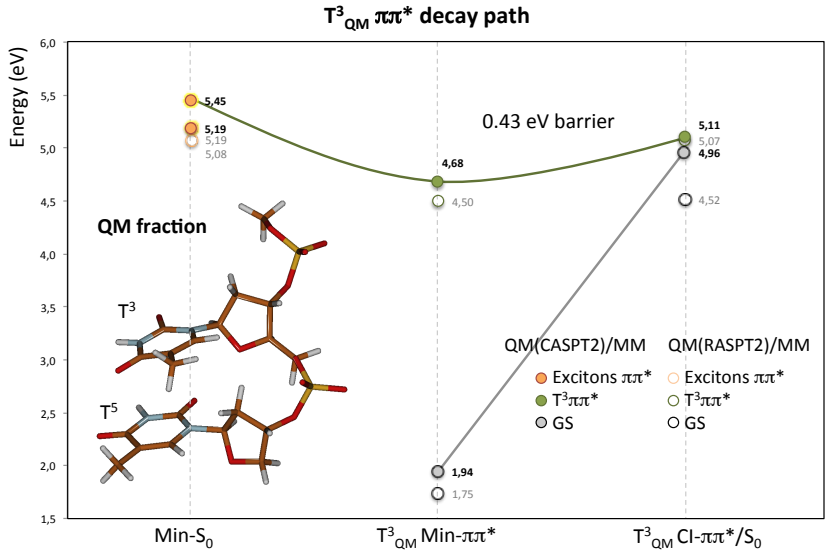
Here we show the computational double-check we did to ensure that the QM fraction we included in the QM/MM calculations (the bases plus part of the relative sugar ring) is large enough to reproduce charges and energy values obtained in QM systems including also the entire sugar or even the phosphate group.

1. First check: charges distribution.
   We ran different HF/6-31g* calculations on three QM model to check that the charges of the base (photoreactive part) are resembling the charge of the entire Nucleotide. The systems are:
   a) the simple base (often used as QM part in QM/MM claculations)
   b) the base plus a fraction of the sugar (here adopted)
   c) the Thimidine.
   Scheme S6 shows the results: we decided to include a part of the sugar in the QM fraction because N_1 and C_S (the sugar atom directly linked to the base) charges are strongly reproducing the Thimidine ones, even if the base model is also well resembling the largest system.



Scheme S6

2. Second check: QM(CASPT2)/MM calculations including sugar and phosphate groups.
To verify the energies of the stationary points of the ππ* T^3_{QM} path (Figure 1b), the one showing a different behaviour (leading to longer lifetimes, τ_3) comparing with the classical previously documented monomer-like path[1], we run supplementary vertical calculations on the important points (Min-S_0, Min-ππ* and CI ππ*/S_0) including the sugar for each base and additionally the phosphate group. We did this because of recent publications (concerning UV induced self-repair of DNA photolesions)[10, 11], which are documenting the importance of the sugar inclusion in the QM part of QM/MM calculations: in same case, the states energies are shifting enough to change the decay path profiles.
Scheme S7 shows the T^3_{QM} ππ* energy profile and the QM part adopted in these supporting calculations, which includes the two stacked Thys plus the relative sugars and phosphate groups. The black-bold character numbers, together with the full circles are QM(MS-CASPT2)//SA5-CASSCF(16,14)/6-31g*/MM energies. The decay path strongly resemble (0.43 eV barrier vs 0.47 eV in the main text) the one obtained with the reduced QM fraction used in the present work (just a part of the sugar ring included in the QM region). This ensures the validity of our work. We ran a supplementary test, using the same enlarged QM part but at the lower RASPT2 level, where RAS1 and RAS3 include 8 and 6 orbitals, respectively and four excitations are allowed in each one. The corresponding results are documented with grey values and empty circles in Scheme S7. They also roughly resemble the equivalent CASPT2 profile, even if in the crossing geometry S_0 and S_1 are showing a larger energy gap, probably due to the lower calculation level.
The QM model utilized in the present manuscript (base plus a part of the sugar ring) was time after time used in different published works, confirming its validity[12-14].



Scheme S7

S8. Cartesian coordinates

Below, we document the Cartesian coordinates of all the QM structures documented in the text. We also created a zip directory (CartesianCoordinates.zip) containing all of them in xyz format files.

Min-S_0
O 16.894778 19.706817 25.296501

C	18.105462	20.217215	25.799571
H	18.584759	19.524449	26.467154
N	19.000683	20.442302	24.688150
C	18.527812	21.054597	23.514873
H	17.563498	21.504533	23.608087
C	19.224700	21.092107	22.364978
C	18.758278	21.750055	21.095741
H	17.708453	21.993916	21.144413
H	19.312878	22.662775	20.910142
H	18.911668	21.093972	20.248432
C	20.545531	20.458372	22.356985
O	21.271241	20.375763	21.395477
N	20.936599	19.909182	23.556971
H	21.860306	19.503487	23.592659
C	20.223902	19.845957	24.712009
O	20.689982	19.304754	25.687047
O	20.608974	20.823236	28.417620
C	21.902838	21.358518	28.297871
H	22.637856	20.582029	28.177222
N	21.946228	22.179756	27.115218
C	20.910571	23.081438	26.832230
H	20.272570	23.301934	27.661060
C	20.730481	23.634549	25.620092
C	19.638671	24.618133	25.295265
H	19.060543	24.856076	26.180001
H	20.054960	25.536196	24.895840
H	18.966745	24.221984	24.543002
C	21.663047	23.237255	24.556817
O	21.563789	23.530639	23.389847
N	22.729277	22.470139	24.977914
H	23.457909	22.304100	24.300508
C	22.932438	21.945145	26.209953
O	23.928477	21.308671	26.466387
H	16.246018	19.845014	25.963153
H	17.840698	21.111254	26.359790
H	20.475574	20.611009	29.320876
H	22.114809	21.901846	29.213623

T^5_{QM} Min-$\pi\pi^*$

O	16.993777	19.697137	25.323746
C	18.191730	20.248912	25.805848
H	18.707313	19.584476	26.473063
N	19.057281	20.458725	24.639914
C	18.513303	20.824751	23.465983
H	17.488289	21.104849	23.473561
C	19.461460	21.147447	22.328161
C	19.263595	22.378071	21.495031
H	19.096411	23.249268	22.118174
H	20.153285	22.561982	20.905475
H	18.414804	22.284755	20.821721
C	20.608096	20.411811	22.296749
O	21.533512	20.419128	21.442203
N	20.870582	19.590292	23.451842
H	21.798569	19.193585	23.480715
C	20.318937	19.807439	24.650600
O	20.799738	19.445213	25.695793
O	20.617321	20.829078	28.433893
C	21.913725	21.361891	28.317180
H	22.646278	20.583977	28.191990
N	21.959008	22.191654	27.142146
C	20.928419	23.099732	26.875463
H	20.294909	23.312200	27.709304
C	20.749978	23.675102	25.673713
C	19.659716	24.667412	25.371412
H	19.114274	24.923920	26.271853
H	20.073542	25.572932	24.943060
H	18.956457	24.269852	24.648471
C	21.685459	23.303295	24.603453
O	21.612557	23.666401	23.460033
N	22.719847	22.486374	24.996016
H	23.440287	22.317946	24.308436
C	22.931883	21.950478	26.224441
O	23.923995	21.304228	26.467452
H	16.328572	19.845991	25.970611
H	17.904643	21.146009	26.349678
H	20.482117	20.614123	29.336201

H	22.126085	21.899968	29.235517

T^5_{QM} Min-nπ*

O	16.884283	19.684358	25.328538
C	18.095911	20.210164	25.829235
H	18.577384	19.526252	26.503666
N	18.981311	20.435940	24.717591
C	18.487046	21.045009	23.547641
H	17.528553	21.503933	23.659410
C	19.148514	21.062171	22.400590
C	18.686948	21.726318	21.130493
H	17.638906	21.974882	21.170892
H	19.242348	22.639905	20.944546
H	18.834987	21.069444	20.279504
C	20.417878	20.346030	22.360446
O	21.425732	20.960503	21.640204
N	20.896194	19.860145	23.578523
H	21.806904	19.432337	23.614245
C	20.204970	19.833990	24.735747
O	20.663843	19.304543	25.706282
O	20.608954	20.818714	28.418038
C	21.903579	21.352646	28.292745
H	22.636476	20.574190	28.171669
N	21.944479	22.173542	27.111133
C	20.904930	23.071928	26.828295
H	20.262795	23.285724	27.655650
C	20.729674	23.628009	25.618056
C	19.634607	24.603728	25.283946
H	19.046096	24.837696	26.162999
H	20.047480	25.524810	24.887804
H	18.973081	24.200497	24.526151
C	21.677011	23.255594	24.562501
O	21.610806	23.599031	23.419189
N	22.735449	22.474722	24.980063
H	23.467257	22.319801	24.304259
C	22.933813	21.938038	26.208752
O	23.898994	21.295005	26.457540
H	16.228969	19.835276	25.990888
H	17.825014	21.107414	26.381676
H	20.476044	20.609984	29.321603
H	22.118037	21.895599	29.209016

T^5_{QM} CI-ππ*/S_0

O	17.075372	19.787404	25.319738
C	18.258069	20.375643	25.790469
H	18.811039	19.712025	26.427464
N	19.104965	20.699800	24.619431
C	18.600433	20.609844	23.399317
H	17.712703	20.020516	23.334634
C	19.363341	21.052872	22.264240
C	19.423420	22.549930	21.964412
H	18.652093	22.792134	21.243433
H	19.267964	23.179205	22.829990
H	20.380860	22.788281	21.525231
C	20.569215	20.366511	22.138124
O	21.479267	20.460903	21.333659
N	20.876777	19.645705	23.355340
H	21.804265	19.241296	23.381114
C	20.409748	19.969197	24.573025
O	20.853556	19.576986	25.606668
O	20.700873	20.771424	28.421827
C	22.017160	21.262750	28.305027
H	22.721452	20.462677	28.156573
N	22.083285	22.116759	27.151685
C	21.092275	23.083095	26.934507
H	20.482065	23.296189	27.785994
C	20.928456	23.711511	25.759236
C	19.886877	24.770791	25.519677
H	19.400067	25.040238	26.449285
H	20.334894	25.657541	25.087038
H	19.127583	24.429250	24.826169
C	21.834859	23.338517	24.663601
O	21.784304	23.765656	23.539863
N	22.830549	22.440032	25.005311
H	23.537296	22.271415	24.303422
C	23.032714	21.861329	26.211334

O	23.996026	21.160893	26.424102
H	16.409427	19.904738	25.972776
H	17.957133	21.245119	26.364855
H	20.554442	20.570369	29.326106
H	22.257567	21.775211	29.231756

T^5_{QM} Min-nπ*$_{1.34}$

O	16.884000	19.684000	25.329000
C	18.096000	20.210000	25.829000
H	18.577000	19.526000	26.504000
N	18.981000	20.436000	24.718000
C	18.487000	21.045000	23.548000
H	17.529000	21.504000	23.659000
C	19.149000	21.062000	22.401000
C	18.687000	21.726000	21.130000
H	17.639000	21.975000	21.171000
H	19.242000	22.640000	20.945000
H	18.835000	21.069000	20.280000
C	20.418000	20.346000	22.360000
O	21.394000	20.941000	21.662000
N	20.896000	19.860000	23.579000
H	21.807000	19.432000	23.614000
C	20.205000	19.834000	24.736000
O	20.664000	19.305000	25.706000
O	20.609000	20.819000	28.418000
C	21.904000	21.353000	28.293000
H	22.636000	20.574000	28.172000
N	21.944000	22.174000	27.111000
C	20.905000	23.072000	26.828000
H	20.263000	23.286000	27.656000
C	20.730000	23.628000	25.618000
C	19.635000	24.604000	25.284000
H	19.046000	24.838000	26.163000
H	20.047000	25.525000	24.888000
H	18.973000	24.201000	24.526000
C	21.677000	23.256000	24.563000
O	21.611000	23.599000	23.419000
N	22.735000	22.475000	24.980000
H	23.467000	22.320000	24.304000
C	22.934000	21.938000	26.209000
O	23.899000	21.295000	26.458000
H	16.229160	19.835117	25.991228
H	17.825286	21.107143	26.381857
H	20.476017	20.610123	29.321344
H	22.118286	21.895857	29.209429

T^3_{QM} Min-ππ*

O	16.915509	19.695382	25.312334
C	18.115305	20.235411	25.812249
H	18.605117	19.561502	26.491304
N	19.008212	20.463354	24.697961
C	18.526248	21.061416	23.520115
H	17.556847	21.500269	23.608506
C	19.237392	21.109690	22.360814
C	18.780209	21.777006	21.095177
H	17.726227	22.006323	21.130468
H	19.328206	22.699090	20.940503
H	18.958717	21.135748	20.241650
C	20.561402	20.484766	22.363791
O	21.280267	20.376229	21.406179
N	20.948815	19.953668	23.566851
H	21.877753	19.560223	23.602640
C	20.246161	19.909359	24.728683
O	20.739737	19.406850	25.716731
O	20.461163	20.906881	28.410136
C	21.771941	21.344201	28.224006
H	22.433461	20.524625	28.013668
N	21.817703	22.233308	27.064972
C	21.261263	23.454051	26.993486
H	20.651032	23.766917	27.815761
C	20.834149	23.791485	25.525004
C	19.467075	24.359817	25.265891
H	18.881630	24.467214	26.172752
H	19.613403	25.364589	24.867797
H	18.894835	23.813891	24.527516
C	21.629031	23.267824	24.506297
O	21.501417	23.367187	23.287627
N	22.758346	22.527691	24.958565

H	23.501401	22.394935	24.289944
C	22.911577	21.995614	26.152103
O	23.863922	21.381227	26.546855
H	16.258199	19.835660	25.971148
H	17.826876	21.131850	26.357219
H	20.391242	20.644504	29.308948
H	22.088837	21.827736	29.149839

T^3_{QM} Min-nπ*

O	16.894430	19.708350	25.296390
C	18.109877	20.217461	25.796052
H	18.585412	19.524897	26.466135
N	18.987406	20.433402	24.691422
C	18.523618	21.058075	23.530586
H	17.556489	21.504121	23.620543
C	19.214703	21.083874	22.381654
C	18.750367	21.721154	21.102144
H	17.700075	21.965342	21.143718
H	19.303959	22.629975	20.895554
H	18.906518	21.050169	20.267328
C	20.539764	20.460086	22.372906
O	21.262860	20.409529	21.429669
N	20.921838	19.910792	23.563437
H	21.847100	19.508418	23.602646
C	20.201399	19.828545	24.711259
O	20.661529	19.259819	25.668019
O	20.627224	20.769350	28.426819
C	21.917525	21.326232	28.307697
H	22.659611	20.556393	28.185403
N	21.943732	22.157285	27.140566
C	20.943540	23.149310	26.946186
H	20.312490	23.348666	27.778993
C	20.697383	23.643552	25.644114
C	19.575347	24.609547	25.326054
H	19.020512	24.858494	26.221986
H	19.959502	25.535351	24.910148
H	18.875224	24.200034	24.605244
C	21.587753	23.229388	24.702250
O	21.484967	23.510904	23.403844
N	22.707991	22.458442	25.001624
H	23.480129	22.431132	24.356933
C	22.924489	21.933940	26.230026
O	23.905213	21.299274	26.464070
H	16.247305	19.847730	25.963733
H	17.848318	21.110801	26.359877
H	20.481718	20.578236	29.334412
H	22.126716	21.868140	29.225919

T^3_{QM} CI-ππ*/S_0

O	16.835410	19.588845	25.313069
C	18.026129	20.150808	25.808245
H	18.521008	19.494952	26.500285
N	18.931030	20.384008	24.703726
C	18.472236	20.990813	23.518852
H	17.496856	21.418920	23.590609
C	19.210633	21.089112	22.399267
C	18.773796	21.777859	21.136138
H	17.712873	21.975014	21.144473
H	19.297036	22.720573	21.022517
H	18.996525	21.165497	20.271299
C	20.555998	20.511941	22.427487
O	21.305028	20.444364	21.484053
N	20.937782	19.982769	23.643491
H	21.868969	19.596618	23.692973
C	20.187830	19.873414	24.769645
O	20.657295	19.360957	25.764366
O	20.377665	21.005065	28.440271
C	21.708720	21.343098	28.202822
H	22.271220	20.481589	27.899659
N	21.746545	22.267985	27.072001
C	21.512308	23.571285	27.031580
H	21.653402	24.188840	27.902198
C	21.062222	24.025739	25.698201
C	19.578038	23.768857	25.479106
H	19.054343	23.652914	26.419976
H	19.194587	24.693984	25.055192
H	19.339866	22.972811	24.793261

C	21.852943	23.620230	24.620538
O	21.648210	23.630121	23.415928
N	22.934613	22.809229	25.078555
H	23.648117	22.578474	24.402884
C	22.876359	22.026628	26.147428
O	23.721567	21.260033	26.507782
H	16.174096	19.740747	25.968546
H	17.715108	21.047066	26.335691
H	20.339206	20.705498	29.328032
H	22.130703	21.722213	29.136587

T^5_{QM}' Min-ππ*

O	16.807308	19.759578	25.178105
C	18.045230	20.176835	25.672507
H	18.512503	19.417569	26.270831
N	18.930790	20.429211	24.536013
C	18.792304	21.430621	23.673624
H	18.180741	22.272267	23.937842
C	19.483838	21.271530	22.338818
C	18.659571	21.169864	21.098486
H	17.711651	20.685339	21.264995
H	18.418768	22.158678	20.716522
H	19.208805	20.639697	20.331515
C	20.745163	20.692235	22.365219
O	21.468130	20.386439	21.427145
N	21.106544	20.198789	23.648274
H	22.012666	19.758693	23.707126
C	20.244996	19.857305	24.617549
O	20.551046	19.213539	25.581165
O	20.626817	20.777121	28.410060
C	21.910594	21.338967	28.296758
H	22.660973	20.577702	28.175625
N	21.937818	22.165368	27.117292
C	20.899127	23.064166	26.853495
H	20.251264	23.253266	27.683027
C	20.725053	23.652957	25.663088
C	19.640518	24.652387	25.360687
H	19.051719	24.863739	26.244931
H	20.066309	25.578938	24.993388
H	18.974799	24.294033	24.585077
C	21.675762	23.304379	24.598562
O	21.577119	23.627673	23.441919
N	22.759437	22.551984	25.010702
H	23.484736	22.398604	24.326019
C	22.942448	21.971868	26.216191
O	23.930951	21.320622	26.465693
H	16.200310	19.852507	25.892016
H	17.839681	21.041816	26.308204
H	20.481903	20.578568	29.315280
H	22.111145	21.886060	29.212831

T^5_{QM}' Min-nπ*

O	16.883617	19.681139	25.326556
C	18.097192	20.200648	25.824290
H	18.578402	19.509110	26.491055
N	18.979129	20.443438	24.715911
C	18.476931	21.137845	23.583717
H	17.533385	21.614180	23.697566
C	19.220080	21.126179	22.364100
C	18.726287	21.797311	21.105665
H	17.656298	21.936568	21.133311
H	19.184538	22.771904	20.977193
H	18.949911	21.197667	20.230253
C	20.398931	20.499056	22.407610
O	21.212542	20.351040	21.355042
N	20.903243	19.909513	23.564006
H	21.853275	19.580323	23.604564
C	20.200232	19.847069	24.722721
O	20.667353	19.299444	25.674418
O	20.604430	20.810342	28.418345
C	21.895097	21.352377	28.295256
H	22.632487	20.578460	28.172776
N	21.933454	22.177307	27.115785
C	20.890593	23.072181	26.831379
H	20.239426	23.273663	27.654467
C	20.721938	23.638626	25.624383
C	19.627293	24.615672	25.292285

H	19.029341	24.835786	26.168485
H	20.042527	25.543770	24.914881
H	18.974919	24.220512	24.523000
C	21.672100	23.267394	24.572674
O	21.604051	23.592256	23.421552
N	22.737313	22.500945	24.995805
H	23.472371	22.350616	24.323317
C	22.930651	21.958560	26.221750
O	23.901055	21.319439	26.471142
H	16.228647	19.829748	25.988562
H	17.826847	21.093482	26.385965
H	20.470821	20.601606	29.322544
H	22.107609	21.895361	29.211412

T^5_{QM}' CI-ππ*/S_0

O	16.902568	20.008710	25.184135
C	18.126157	20.437865	25.708161
H	18.592986	19.667228	26.291249
N	19.023069	20.716567	24.588030
C	19.179302	21.836457	23.900976
H	19.003845	22.783869	24.380807
C	19.654205	21.658528	22.527107
C	18.534205	21.277520	21.575646
H	17.699989	20.846320	22.106814
H	18.167048	22.166369	21.076539
H	18.896428	20.589530	20.823918
C	20.810486	20.899986	22.392964
O	21.350801	20.426639	21.401700
N	21.188047	20.336286	23.659764
H	22.023105	19.767962	23.643982
C	20.277819	19.942733	24.566725
O	20.472394	19.158465	25.441677
O	20.726357	20.760706	28.410259
C	22.059529	21.199702	28.292827
H	22.726797	20.376630	28.104887
N	22.143954	22.088541	27.166322
C	21.225251	23.139063	27.021980
H	20.651777	23.363101	27.896320
C	21.088230	23.823413	25.875335
C	20.173081	25.005229	25.707763
H	19.553179	25.134219	26.586117
H	20.750838	25.909063	25.553297
H	19.532904	24.900115	24.840552
C	21.921077	23.399648	24.738074
O	21.773143	23.757199	23.597496
N	22.956418	22.547149	25.070745
H	23.618916	22.333493	24.339685
C	23.096146	21.854226	26.221919
O	24.008014	21.076479	26.385900
H	16.295676	20.034093	25.904998
H	17.894625	21.272929	26.367388
H	20.572297	20.565989	29.315714
H	22.339643	21.671630	29.231359

T^3_{QM}' Min-ππ*

O	16.813177	19.649432	25.251667
C	18.029452	20.128285	25.762539
H	18.505056	19.402404	26.397418
N	18.937844	20.396779	24.672865
C	18.490122	21.042038	23.509284
H	17.537930	21.516536	23.605207
C	19.197155	21.085012	22.368984
C	18.761186	21.780238	21.109833
H	17.709673	22.018886	21.139261
H	19.319098	22.698421	20.967954
H	18.937482	21.146873	20.249573
C	20.506283	20.427708	22.359074
O	21.247020	20.358969	21.408445
N	20.869378	19.831015	23.547908
H	21.805009	19.457952	23.601340
C	20.166479	19.808399	24.705022
O	20.634047	19.301243	25.700282
O	20.725333	20.883895	28.398041
C	21.969883	21.527999	28.313241
H	22.762124	20.815488	28.169579
N	21.947764	22.410975	27.148799
C	20.788049	22.865840	26.672921

H	19.919762	22.454242	27.113141
C	20.800607	23.734476	25.492627
C	20.642153	25.227941	25.651874
H	21.026634	25.599300	26.602295
H	21.096436	25.752607	24.821538
H	19.580324	25.470477	25.631621
C	21.535422	23.202077	24.405119
O	21.639402	23.569808	23.256043
N	22.453471	22.194140	24.842394
H	23.178558	22.003541	24.163265
C	22.885957	22.068384	26.123996
O	23.936477	21.583951	26.420865
H	16.171937	19.775138	25.931146
H	17.768910	20.991816	26.366304
H	20.553117	20.666137	29.294092
H	22.131011	22.052747	29.243854

T^3_{QM}' Min-nπ*

O	16.896979	19.708689	25.297047
C	18.108741	20.215465	25.802588
H	18.588010	19.517817	26.464664
N	19.001902	20.447745	24.691601
C	18.534371	21.064812	23.525533
H	17.562605	21.499899	23.612401
C	19.238403	21.112133	22.378901
C	18.774531	21.752154	21.099367
H	17.721005	21.983671	21.135812
H	19.317373	22.669728	20.901655
H	18.944483	21.088153	20.261791
C	20.560030	20.488748	22.376125
O	21.291354	20.439394	21.434224
N	20.935219	19.920676	23.557962
H	21.861177	19.518808	23.588497
C	20.224666	19.848914	24.720302
O	20.667851	19.290995	25.662572
O	20.615980	20.763950	28.435467
C	21.904288	21.323197	28.307766
H	22.648789	20.556796	28.187082
N	21.928194	22.149635	27.137070
C	20.880871	23.073311	26.910272
H	20.263921	23.286901	27.751783
C	20.684727	23.622213	25.676522
C	19.596455	24.619322	25.367608
H	19.017654	24.849486	26.253322
H	20.018060	25.543480	24.985435
H	18.917364	24.239388	24.612146
C	21.544182	23.154097	24.660335
O	21.689245	23.869672	23.500838
N	22.734701	22.510895	25.023826
H	23.459718	22.362773	24.341553
C	22.926917	21.954358	26.234614
O	23.906453	21.313513	26.481484
H	16.248470	19.844039	25.964634
H	17.845804	21.105588	26.368934
H	20.475705	20.572915	29.346148
H	22.110385	21.872649	29.222574

T^3_{QM}' CI-ππ*/S_0

O	16.805683	19.644701	25.272822
C	18.011919	20.145689	25.786433
H	18.490629	19.430825	26.432433
N	18.925132	20.411421	24.693650
C	18.470719	21.047411	23.520016
H	17.521139	21.525796	23.616392
C	19.181549	21.087251	22.378300
C	18.757217	21.792982	21.119915
H	17.702616	22.018795	21.133228
H	19.306287	22.720409	21.004599
H	18.958132	21.175213	20.253672
C	20.492959	20.435149	22.373429
O	21.232744	20.358508	21.423663
N	20.863101	19.854659	23.569682
H	21.799910	19.483520	23.619281
C	20.155431	19.827839	24.723875
O	20.630444	19.330891	25.724059
O	20.719182	20.885272	28.393636
C	21.954500	21.533838	28.305231

H	22.756535	20.835000	28.154976
N	21.918194	22.446338	27.143886
C	20.785669	22.674742	26.518729
H	20.037565	21.956705	26.736449
C	20.696439	23.615298	25.441055
C	20.691119	25.109237	25.779184
H	21.296325	25.382715	26.643212
H	21.027715	25.657881	24.906961
H	19.678042	25.439289	25.984121
C	21.524604	23.204995	24.381926
O	21.677442	23.610011	23.249660
N	22.525642	22.259130	24.841151
H	23.263605	22.087948	24.171249
C	22.945375	22.180766	26.121188
O	23.984823	21.731487	26.487205
H	16.155732	19.769437	25.945074
H	17.730920	21.017529	26.376270
H	20.546985	20.672981	29.290197
H	22.110541	22.071759	29.229654

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