

Supporting information for

UV-Induced Long-Lived Excited State Decays in Solvated Pyrimidine Nucleosides Resolved at the MS- CASPT2/MM Level

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Table of Contents	Page
S1. Atom Labeling.....	2
S2. Photoelectron Spectroscopy.....	2
S3. Molecular Orbitals.....	3
S4. Linear Interpolations.....	4
S5. H-Transfer in Urd and Cyt.....	5
S6. ¹ n _N π* / ¹ π _H π* state mixing.....	5
S7. Cartesian coordinates.....	6

S1. Atom labeling

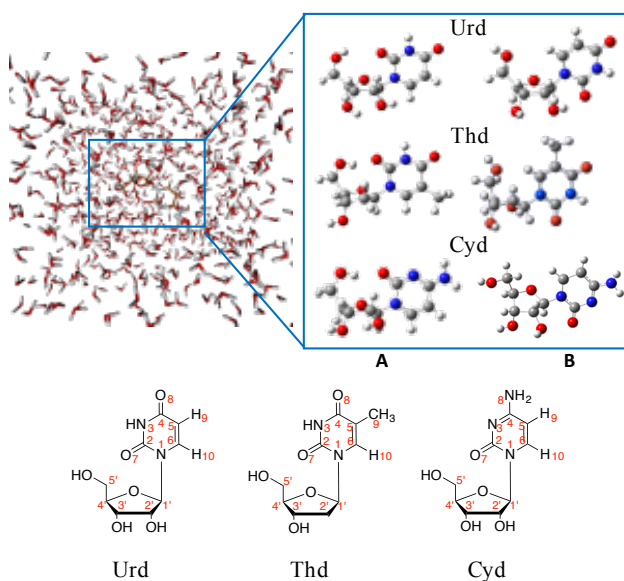


Fig. S1 Main configurations (A and B) along the MM dynamics run obtained through RMS deviation cluster analysis for Uridine (Urd), Thymidine (Thd) and Cytidine (Cyd).

S2. Photoelectron Spectroscopy

Table S1. Scaling factors employed for the cationic states, obtained at the FC region by direct comparison with the experimental evidence.

		Urd	Thd	Cyd
IPEA=0	SS-CASPT2	1.33	1.15	0.7
	MS-CASPT2	1.4	0.85	0.73
IPEA=0.25	SS-CASPT2	1.51	1.34	0.92
	MS-CASPT2	1.57	1.04	0.95

Table S2. AKEs for the different zeroth-order Hamiltonians and excited state minima.

		Thd		Urd		Cyd	
		SS-CASPT2	MS-CASPT2	SS-CASPT2	MS-CASPT2	SS-CASPT2	MS-CASPT2
n₀ Planar	IPEA=0	1.09	0.37	1.61	1.70	1.03	1.31
	IPEA=0.25	1.43	0.67	1.84	1.92	1.41	1.63
n₀ Twisted	IPEA=0	0.33	-0.08	0.36	0.44	0.90	1.28
	IPEA=0.25	0.73	0.23	0.60	0.65	1.36	1.59
T₁	IPEA=0	-0.32	-0.63	-1.47	-1.43	-0.48	-0.17
	IPEA=0.25	-0.08	-0.37	-1.26	-1.22	-0.21	0.08
CT	IPEA=0	2.88	2.20	3.19	3.18	2.49	2.29
	IPEA=0.25	3.10	2.65	3.60	3.60	2.85	2.70
n_N	IPEA=0					1.17	1.48
	IPEA=0.25					1.45	1.65

S3. Molecular Orbitals

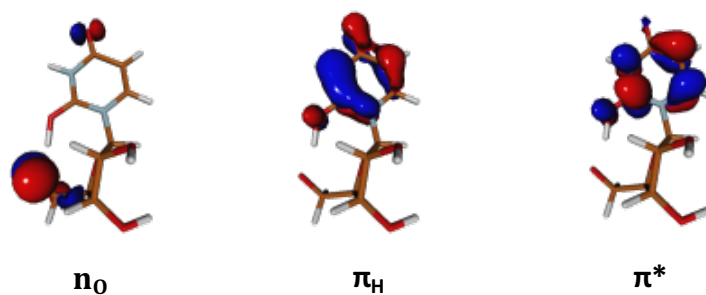


Fig. S12. Molecular orbitals involved in the 5' -O-H $\cdots$ O7 transfer of Uridine (the same for Cytidine and Thymidine). Shown are the lone-pair orbital located at the oxygen atom of the 5' -OH group (involved in the description of the lowest charge-transfer state) as well as the π and π^* orbitals (involved in the description of the $\pi_H\pi^*$ state).

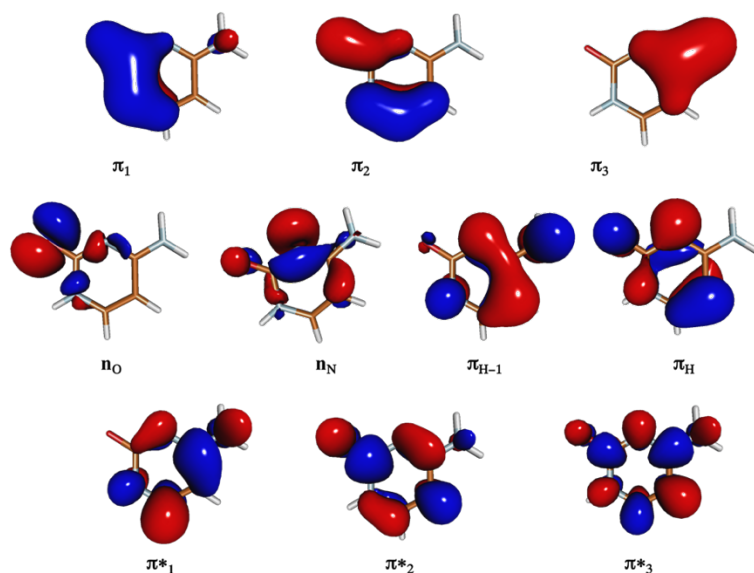


Fig. S13. Orbitals comprising the (14,10) Active Space for Cyd.

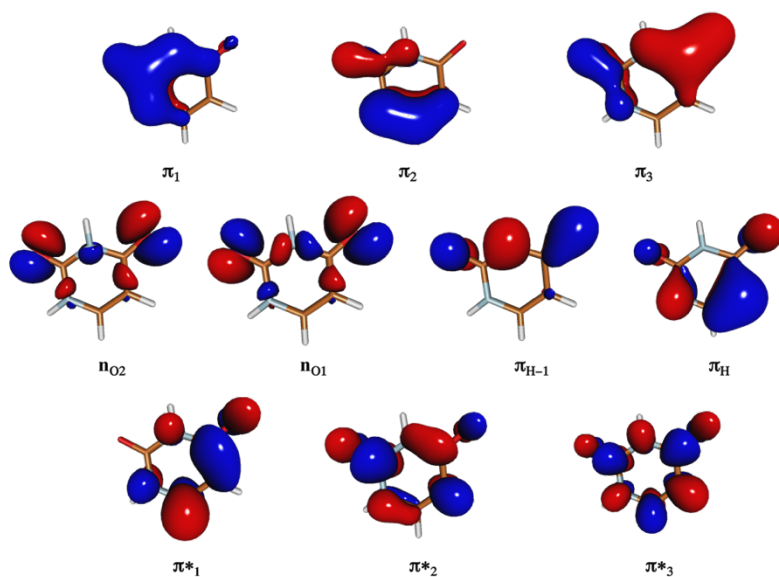


Fig. SI4. Orbitals comprising the (14,10) Active Space for Thd and Urd.

S4. *Linear Interpolations*

Table S3. CIs and maxima obtained from the FC->minima and among the different minima by means of linear interpolation in internal coordinates (LIIC), respectively.

	Urd	Thd	Cyd
CIs (LIIC FC -> min)			
$n_N\pi^*/\pi_H\pi^*$	-	-	4.80
$n_O\pi^*/\pi_2\pi^*$	5.41	5.52	5.60
$n_O\pi^*/n_N\pi^*$	-	-	5.32
$n_O\pi^*/\pi_H\pi^*$	4.95	4.90	5.01
$\pi_2\pi^*/\pi_H\pi^*$	4.75	4.78	4.70
$\pi_2\pi^*/n_N\pi^*$	-	-	5.28
Max (LIICs min -> min)			
$\pi_H\pi^*_{\text{min-pl}} - n_O\pi^*_{\text{min-tw}}$	4.62	4.84	5.49
$\pi_H\pi^*_{\text{min-tw}} - n_O\pi^*_{\text{min-tw}}$	4.91	4.95	5.02
$\pi_H\pi^*_{\text{min-tw}} - \pi_2\pi^*_{\text{min}}$	4.83	4.82	4.80
$\pi_H\pi^*_{\text{min-tw}} - n_N\pi^*_{\text{min}}$	-	-	4.70
$\pi_H\pi^*_{\text{min-tw}} - \pi_H\pi^*_{\text{min-3}}$	-	-	4.97
$\pi_H\pi^*_{\text{min-pl}} - \pi_H\pi^*_{\text{min-3}}$	-	-	5.04

S5. H-transfer

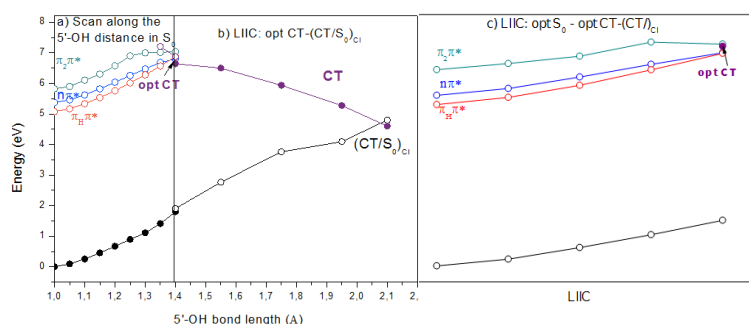


Fig. S15. Energy profiles of the electronic ground state, the lowest bright $\pi\pi^*$ state ($\pi_1\pi^*$), the dark $n\pi^*$ state, the second $\pi\pi^*$ state ($\pi_2\pi^*$) and the charge-transfer (CT) state along the H-transfer coordinate of the 5'-OH group of the ribose moiety **Uridine**. (a) Relaxed scan along the 5'-O–H internuclear distance in the electronic ground state (full black circles) with vertical excitation energies of the $\pi_1\pi^*$, $n\pi^*$, $\pi_2\pi^*$ and CT states (empty red, blue, green and purple circles, respectively). (b) Linear interpolation between the optimised charge-transfer state (full purple circles). (c) Linear interpolation between the ground-state equilibrium geometry (full black circle at the lower left) and the optimised geometry of the charge-transfer state (full purple circle at the right).

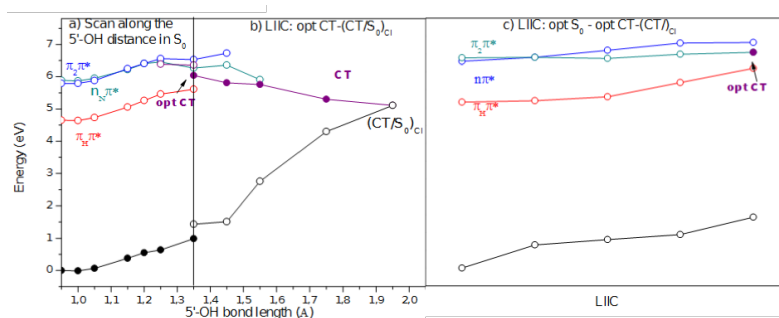


Fig. S16. Energy profiles of the electronic ground state, the lowest bright $\pi\pi^*$ state ($\pi_1\pi^*$), the dark $n\pi^*$ state, the second $\pi\pi^*$ state ($\pi_2\pi^*$) and the charge-transfer (CT) state along the H-transfer coordinate of the 5'-OH group of the ribose moiety **Cytidine**. (a) Relaxed scan along the 5'-O–H internuclear distance in the electronic ground state (full black circles) with vertical excitation energies of the $\pi_1\pi^*$, $n\pi^*$, $\pi_2\pi^*$ and CT states (empty red, blue, green and purple circles, respectively). (b) Linear interpolation between the optimised charge-transfer state (full purple circles). (c) Linear interpolation between the ground-state equilibrium geometry (full black circle at the lower left) and the optimised geometry of the charge-transfer state (full purple circle at the right).

S6. $^1n_N\pi^*/^1\pi_H\pi^*$ wave function mixing

Table S4. Wave function $^1\pi_H\pi^*/^1n_N\pi^*$ mixing along the $^1n_N\pi^*$ decay channel. The weight of the respective configuration state functions representing both $^1n_N\pi^*$ and $^1\pi_H\pi^*$ transitions are given, together with the MS-CASPT2 off-diagonal coupling.

	Cyd		
	WF Weight		MS-CASPT2 Off-diagonal coupling
	n_N	$\pi_H\pi^*$	
FC	0.59	0.02	2.59×10^{-3}
LHC1	0.45	0.28	9.32×10^{-3}
LIIC2	0.39	0.28	2.74×10^{-3}
LHC3	0.49	0.33	1.13×10^{-3}
$n_N\pi^*_{\min}$	0.51	0.32	2.87×10^{-3}
$(n_N\pi^*_{\min} \rightarrow \text{CI})_{\text{TS}}$	0.45	0.16	0.77×10^{-3}
LHC1	0.65	0.23	2.59×10^{-3}
LIIC2	0.38	0.25	6.56×10^{-3}
LHC3	0.36	0.25	9.33×10^{-3}
$(n_N\pi^*/\text{GS})_{\text{CI}}$	0.33	0.26	23.0×10^{-3}

S7. Cartesian coordinates

Table S5. Cartesian coordinates of all the structures (QM part) discussed in the text. (data in Å) for Urd.

Initial nucleoside optimised

H	14.78076523	16.33181813	15.60696563
O	14.49819400	17.08874300	16.14610600
C	13.23564400	17.52142100	15.72331400
H	13.31261700	18.38969200	15.07291100
H	12.69724900	17.82567400	16.61034500
C	12.42917300	16.46558700	14.99878900
H	11.43364700	16.85953400	14.82315900
O	13.04164500	16.16173800	13.76367800
C	12.46464500	14.98597400	13.31156000
H	11.49704800	15.18960700	12.87197400
N	13.26537800	14.38282300	12.25792600
C	12.62895600	13.94461600	11.09893600
H	11.57703900	14.13975600	11.05294100
C	13.27692900	13.30990500	10.10979100
H	12.76953600	12.95116500	9.23823100
C	14.70324900	13.06970700	10.25110400
O	15.40397100	12.49853600	9.44463900
N	15.25163100	13.52914600	11.42388200
H	16.23232400	13.37438700	11.56937700
C	14.59793900	14.14868600	12.45227800
O	15.20269900	14.45454200	13.45512200
C	12.27046600	15.11957900	15.71129600
H	13.12806500	14.92349700	16.33961700
C	12.23681800	14.10082500	14.54812100
H	13.03491000	13.38167200	14.65854000
O	11.00833200	13.44580700	14.47542400
H	11.12766300	12.53125600	14.16795500
O	11.12611800	15.13732400	16.50645400
H	10.56727600	14.39187400	16.29105000

(CT/S₀)_{CI}

H	12.330022	16.778558	13.095461
O	10.984591	16.988958	15.139108
C	10.373337	15.743808	15.337865
H	9.505487	15.639582	14.700985
H	10.084021	15.690274	16.381214
C	11.375642	14.641568	15.040827
H	10.884079	13.696676	15.229355
O	11.707835	14.738890	13.666062
C	12.992401	14.211683	13.480361
H	12.962620	13.129204	13.501927
N	13.499996	14.610186	12.193508
C	13.966770	13.661593	11.321346
H	14.002947	12.663078	11.700388
C	14.393113	13.957515	10.072034
H	14.736641	13.197893	9.400906
C	14.440245	15.351902	9.643802
O	14.940399	15.723578	8.607933
N	13.918156	16.230095	10.533512
H	13.888777	17.187379	10.232080
C	13.152701	15.874935	11.655195
O	13.092597	16.911252	12.544076
C	12.714812	14.694881	15.830107
H	12.779323	15.610517	16.398337
C	13.773134	14.711611	14.694754
H	14.086402	15.733426	14.531212
O	14.889726	13.884287	14.857137
H	15.409348	14.145879	15.629618
O	12.837422	13.675902	16.774455
H	12.980230	12.803910	16.377721

(¹n₀π*/S₀)_{CI-1}

1	N1	12.969321	14.460603	12.022173
2	C2	12.342396	13.757339	10.964167
3	H3	11.268916	13.876693	10.910777

Opt CT

H	12.13045300	16.71606300	13.46522300
O	11.34185600	17.01464400	14.65269900
C	10.56741500	15.97059600	15.09543500
H	9.65675500	15.83404800	14.50547800
H	10.24329900	16.13527500	16.12706900
C	11.32281800	14.65277200	15.06337700
H	10.70951900	13.83018500	15.40441500
O	11.64422900	14.42155900	13.67245100
C	12.96953200	14.11649800	13.51451700
H	13.13225400	13.04800500	13.49035700
N	13.43022100	14.60229600	12.19304200
C	13.94658900	13.67897800	11.29856300
H	13.98123000	12.67766700	11.66517500
C	14.38342300	13.99681600	10.08588700
H	14.74549800	13.25330200	9.40562600
C	14.35138000	15.37678600	9.66519200
O	14.76411600	15.80698100	8.62414000
N	13.78919800	16.23410200	10.61033500
H	13.74184800	17.20733600	10.34842900
C	13.30512400	15.88803100	11.81481100
O	12.79441500	16.78260300	12.51353000
C	12.66914800	14.67347600	15.83184400
H	12.73011000	15.58020700	16.41186500
C	13.72072000	14.71780200	14.69817900
H	13.96115100	15.75645100	14.52026000
O	14.90038200	13.96998900	14.84908600
H	15.37474700	14.21579000	15.65606300
O	12.83534900	13.63565600	16.75536700
H	12.93756500	12.76556900	16.34734800

S₀_{min}

1	N1	12.956704	14.248102	12.369467
2	C2	12.400431	13.818737	11.168092
3	H3	11.336342	13.924758	11.091924
4	C4	13.132908	13.287733	10.172333
5	H5	12.680639	12.940757	9.267564
6	C6	14.572673	13.149366	10.340581
7	O7	15.337083	12.660274	9.536483
8	N8	15.040184	13.630184	11.542710
9	H9	16.030684	13.588188	11.691831
10	C10	14.318366	14.215564	12.554758
11	O11	14.906887	14.641363	13.524635
12	H12	12.374276	14.711267	13.069008

(¹n₀π*)_{min-pl}

N1	12.990712	14.272447	12.313328
C2	12.370295	13.874759	11.143983
H3	11.292137	13.968747	11.086978
C4	13.142020	13.292108	10.118699
H5	12.657902	12.944479	9.215483
C6	14.541009	13.126789	10.252555
O7	15.362209	12.630337	9.410906
N8	15.096177	13.623631	11.497603
H9	16.102073	13.557681	11.647493
C10	14.394692	14.203281	12.496225
O11	14.950052	14.626861	13.530177
H12	12.435316	14.724745	13.038860

(¹n₀π*)_{min-tw}

N1	13.033211	14.304280	12.343285
C2	12.414126	13.866553	11.147412
H3	11.336095	13.940508	11.099656
C4	13.164330	13.334302	10.128039
H5	12.700655	13.017339	9.203174
C6	14.516833	13.165744	10.352502

4	C4	13.067787	13.088937	10.012163
5	H5	12.521449	12.625064	9.199582
6	C6	14.498992	12.963665	10.113848
7	O7	15.158241	12.234530	9.336058
8	N8	15.110963	13.747429	11.079838
9	H9	16.117569	13.946472	10.964157
10	C10	14.416353	14.395230	12.119145
11	O11	15.008797	14.815865	13.107802
12	H12	12.444356	14.944915	12.754898

O7	15.449548	13.024919	9.344926
N8	15.106998	13.666016	11.510389
H9	16.108929	13.578017	11.653947
C10	14.393501	14.265501	12.531681
O11	14.987094	14.677604	13.535275
H12	12.463051	14.755328	13.057162

$(^3\pi_H\pi^*/^1\pi_H\pi^*)_{\text{ISC}}$

1	N1	13.069891	14.406461	12.308402
2	C2	12.485164	13.789665	11.282533
3	H3	11.461509	13.487483	11.405037
4	C4	13.240830	13.621943	10.050749
5	H5	13.307308	14.566046	9.614983
6	C6	14.607919	13.235530	10.203248
7	O7	15.437224	12.853145	9.400001
8	N8	15.112174	13.528980	11.536251
9	H9	16.099956	13.392882	11.679878
10	C10	14.477664	14.250637	12.483317
11	O11	15.046096	14.668216	13.470071
12	H12	12.527811	14.883674	13.032989

$(^1n_O\pi^*/S_0)_{\text{CI-2}}$

1	N1	13.112000	14.375000	12.316000
2	C2	12.533000	13.724000	11.204000
3	H3	11.464000	13.854000	11.118000
4	C4	13.286000	13.109000	10.252000
5	H5	12.762000	12.703000	9.399000
6	C6	14.728000	12.993000	10.378000
7	O7	15.406000	12.362000	9.596000
8	N8	15.271000	13.708000	11.401000
9	H9	16.255000	13.925000	11.322000
10	C10	14.559000	14.280000	12.465000
11	O11	15.113000	14.626000	13.498000
12	H12	12.566655	14.839705	13.037660

$(^3\pi_H\pi^*)_{\text{min}}$

1	N1	12.933419	14.284703	12.308988
2	C2	12.269947	13.809604	11.167345
3	H3	11.365548	13.227073	11.321494
4	C4	13.139794	13.589619	9.988153
5	H5	12.790773	13.777874	8.979709
6	C6	14.513807	13.207152	10.199086
7	O7	15.304595	12.809996	9.329850
8	N8	14.944866	13.377787	11.512905
9	H9	15.946279	13.268111	11.673183
10	C10	14.289249	14.115812	12.498202
11	O11	14.932843	14.523407	13.472224
12	H12	12.394910	14.743104	13.043397

$(^1n_O\pi^*)_{\text{min}}$ and $(^3\pi_H\pi^*/^1n_O\pi^*)_{\text{ISC}}$

1	N1	13.120214	14.357633	12.315429
2	C2	12.535306	13.736208	11.217809
3	H3	11.461014	13.850889	11.123924
4	C4	13.277278	13.106980	10.259145
5	H5	12.767423	12.691814	9.401791
6	C6	14.705187	12.995919	10.384697
7	O7	15.426017	12.356981	9.578424
8	N8	15.272256	13.704706	11.410034
9	H9	16.261269	13.915035	11.325164
10	C10	14.526177	14.324351	12.406689
11	O11	15.140009	14.612848	13.540000
12	H12	12.572506	14.840250	13.036170

$(^3\pi_H\pi^*/^3n_O\pi^*)_{\text{CI}}$

1	N1	13.132838	14.322771	12.338795
2	C2	12.446943	13.856357	11.197375
3	H3	11.372664	13.932904	11.187836
4	C4	13.163063	13.149650	10.211562
5	H5	12.651014	12.692266	9.379072
6	C6	14.528810	13.065506	10.358171
7	O7	15.387596	12.461602	9.494496
8	N8	15.175311	13.690294	11.428925
9	H9	16.194613	13.750868	11.472734
10	C10	14.503262	14.252346	12.496377
11	O11	15.148821	14.645105	13.470295
12	H12	12.602559	14.821046	13.057353

$(^3\pi_H\pi^*/S_0)_{\text{ISC}}$

1	N1	13.058448	14.425943	12.218820
2	C2	12.534344	14.085918	11.035686
3	H3	11.461865	13.900130	10.988777
4	C4	13.461536	14.003808	9.915467
5	H5	13.752711	14.911753	9.619236
6	C6	14.632477	13.229616	10.161872
7	O7	15.506760	12.827089	9.381786
8	N8	14.910048	13.111379	11.565447
9	H9	15.838582	12.769431	11.786038
10	C10	14.413611	14.004511	12.491828
11	O11	15.004797	14.330380	13.515021
12	H12	12.495347	14.847798	12.962466

$(^3n_O\pi^*)_{\text{min}}$

1	N1	13.133414	14.323869	12.341937
2	C2	12.450363	13.859421	11.192798
3	H3	11.373769	13.933757	11.190136
4	C4	13.163123	13.150402	10.212848
5	H5	12.648955	12.694700	9.378981
6	C6	14.529244	13.070970	10.355836
7	O7	15.395566	12.466517	9.491627
8	N8	15.174651	13.689678	11.425364
9	H9	16.192066	13.746414	11.474699
10	C10	14.506030	14.253360	12.489824
11	O11	15.148408	14.649101	13.469364
12	H12	12.603288	14.821356	13.057359

Table S7. Cartesian coordinates of all the structures (QM part) discussed in the text. (data in Å) for Thd.

Initial nucleoside optimised

H	10.20124100	15.65874000	14.25124300
O	9.51986100	15.84260700	13.60953200
C	10.01821900	16.75726300	12.66364300
H	10.15640000	17.73143500	13.11488400
H	9.27270300	16.85596400	11.88612500
C	11.33075200	16.30903300	12.05638700
H	11.62709900	17.00390000	11.28692300
O	12.32737300	16.32439200	13.08003100
C	13.12278500	15.17492800	12.98662100
H	13.94788800	15.37143200	12.32106400
N	13.72799700	14.85102600	14.27711300
C	15.08077600	14.48763800	14.26633800
H	15.55412600	14.56554800	13.30962200
C	15.74093700	14.03942600	15.34781800
C	17.16608600	13.56446900	15.29397400
H	17.20725800	12.50263100	15.50488700
H	17.59305100	13.73291200	14.31258300
H	17.77612700	14.06461100	16.03342700
C	15.01559700	13.96853700	16.60983000
O	15.48886000	13.60478800	17.66537800
N	13.69581100	14.35009200	16.53600300
H	13.18499400	14.36189000	17.40076900
C	12.99832200	14.72561400	15.41543500
O	11.79186400	14.91246900	15.48524700
C	11.30826600	14.88281600	11.46366600
H	10.30359800	14.48529100	11.46476800
C	12.21191600	14.10028300	12.40536200
H	11.62097800	13.65766500	13.19372000
O	11.81920400	14.85937400	10.15038200
H	11.09664700	14.94600200	9.52209800
O	15.66202500	13.26441100	10.90224900
H	14.97939700	12.99554400	10.23393900

Opt CT

H	11.131280	15.288860	14.657481
O	9.937949	15.441611	13.847828
C	10.056240	16.457137	12.941299
H	10.177585	17.422182	13.440660
H	9.183139	16.541621	12.294104
C	11.294508	16.259247	12.077377
H	11.376550	17.049531	11.353583
O	12.436221	16.322701	12.939883
C	13.189638	15.159328	12.847338
H	14.039572	15.320881	12.206442
N	13.766644	14.826484	14.160269
C	15.086107	14.435331	14.175569
H	15.579083	14.462776	13.229149
C	15.712274	13.993559	15.352116
C	17.119984	13.476032	15.333489
H	17.129858	12.424588	15.596103
H	17.569971	13.587584	14.353357
H	17.737837	13.995150	16.055558
C	14.981098	13.982739	16.556428
O	15.365420	13.610494	17.290502
N	13.656086	14.429082	16.458814
H	13.125333	14.469504	17.307726
C	13.037089	14.803558	15.329113
O	11.785451	15.130437	15.439030
C	11.335503	14.884266	11.390170
H	10.349442	14.441187	11.357988
C	12.264039	14.082081	12.290127
H	11.691495	13.625855	13.085506
O	11.868469	14.968295	10.094428
H	11.146422	15.022421	9.461234
O	12.972348	13.061607	11.581728
H	12.379403	12.329754	11.396236

(CT/S₀)_{CI}

H	11.424325	15.329739	14.725445
O	9.652485	15.670088	13.720174
C	10.044447	16.649490	12.824801
H	10.166291	17.612419	13.289777
H	9.205242	16.666101	12.126014
C	11.318397	16.266644	12.081248
H	11.492875	17.018091	11.331443
O	12.369007	16.310257	13.034604
C	13.210513	15.169713	12.925702
H	14.004308	15.383611	12.229610
N	13.826129	14.928836	14.210824
C	15.144899	14.473561	14.217131
H	15.653613	14.535308	13.274945
C	15.757868	13.971033	15.306325
C	17.164884	13.452760	15.285810
H	17.173873	12.402317	15.549937
H	17.604819	13.564350	14.301791
H	17.785327	13.969012	16.006877
C	15.027729	13.942224	16.585286
O	15.522710	13.609325	17.643898
N	13.743095	14.362496	16.509430
H	13.222646	14.373296	17.364767
C	13.035133	14.505954	15.307719
O	11.885398	15.204805	15.556809
C	11.347179	14.867130	11.435332
H	10.360029	14.427618	11.406959
C	12.283342	14.089755	12.356318
H	11.711703	13.625119	13.152280
O	11.873769	14.932195	10.134493
H	11.155340	14.994932	9.499070
O	12.993912	13.062947	11.659428
H	12.401871	12.328920	11.479728

(¹n_Oπ*/S₀)_{CI-1}

1	N1	13.803319	14.958751	14.038648
2	C2	15.208797	14.731042	13.884565
3	H3	15.566019	14.418578	12.933519
4	C4	15.867098	14.167349	15.200231
5	C5	17.242066	13.609709	15.237960

S₀_{min}

1	N1	13.832293	14.904764	14.304384
2	C2	15.141912	14.447900	14.281655
3	H3	15.598362	14.390997	13.297181
4	C4	15.816829	14.083512	15.396520
5	C5	17.216953	13.569626	15.386668
6	H6	17.236199	12.529135	15.718514
7	H7	17.650818	13.630014	14.386733
8	H8	17.834158	14.138001	16.084198
9	C9	15.134408	14.151362	16.668622
10	O10	15.639527	13.841130	17.758442
11	N11	13.817207	14.592339	16.595405
12	H12	13.319100	14.662944	17.483265
13	C13	13.094658	14.949889	15.472639
14	O14	11.899952	15.263135	15.563463
15	H15	13.380231	15.136582	13.420059

(¹n_Oπ*)_{min-pl}

N1	13.779570	14.937989	14.232577
C2	15.086945	14.481671	14.213538
H3	15.535738	14.435530	13.239851
C4	15.756763	14.113798	15.302296
C5	17.165384	13.602935	15.292415
H6	17.194911	12.568151	15.611712
H7	17.593999	13.669870	14.300195
H8	17.781629	14.166297	15.980679
C9	15.058713	14.172118	16.574398
O10	15.617357	13.805605	17.804677
N11	13.754092	14.610360	16.506308
H12	13.261049	14.674837	17.375471
C13	13.055541	14.977487	15.389959
O14	11.889155	15.294168	15.475475
H15	13.333804	15.171378	13.354736

(¹n_Oπ*)_{min-tw}

N1	13.861378	14.904418	14.143414
C2	15.160826	14.403798	14.156150
H3	15.587350	14.222347	13.189497

6	H6	17.248253	12.568296	15.539164
7	H7	17.673691	13.682761	14.250745
8	H8	17.867505	14.181290	15.915355
9	C9	15.082887	14.315055	16.164122
10	O10	15.143439	13.953211	17.804500
11	N11	13.773662	14.601342	16.420408
12	H12	13.605508	15.339250	17.101350
13	C13	13.078851	14.974780	15.179292
14	O14	11.934838	15.362356	15.301822
15	H15	13.354733	15.211898	13.155083

(³π_Hπ*/¹π_Hπ*)_{ISC}

1	N1	13.795597	14.797304	14.288636
2	C2	14.923701	14.051004	14.246472
3	H3	15.236971	13.677165	13.281340
4	C4	15.690591	13.934167	15.493042
5	C5	17.101012	14.381856	15.432626
6	H6	17.612621	13.748925	14.821966
7	H7	17.137939	15.278161	14.984828
8	H8	17.561542	14.444642	16.417084
9	C9	15.005910	13.936973	16.713669
10	O10	15.457531	13.812882	17.886752
11	N11	13.608436	14.280867	16.586046
12	H12	13.120366	14.412095	17.470679
13	C13	13.032701	14.882196	15.510612
14	O14	11.908988	15.394680	15.538135
15	H15	13.372363	15.089770	13.404891

(¹n_Oπ*/S₀)_{CI-2}

1	N1	13.779802	14.831625	14.176294
2	C2	15.114382	14.371109	14.140629
3	H3	15.536639	14.323498	13.152617
4	C4	15.784290	14.079449	15.264487
5	C5	17.278802	14.007030	15.349873
6	H6	17.656055	13.129867	15.858987
7	H7	17.722601	14.058788	14.364590
8	H8	17.593933	14.885512	15.907107
9	C9	15.072736	14.000328	16.497276
10	O10	15.603082	15.051280	17.564833
11	N11	13.806715	14.672958	16.522898
12	H12	13.251299	14.552327	17.318814
13	C13	13.125262	14.986629	15.354070
14	O14	11.953915	15.336576	15.482075
15	H15	13.326262	15.073644	13.294929

(³n_Oπ*)_{min}

1	N1	13.750287	14.801516	14.193828
2	C2	15.111012	14.434724	14.167171
3	H3	15.586678	14.462183	13.210770
4	C4	15.771007	14.014868	15.313557
5	C5	17.204937	13.566621	15.247386
6	H6	17.278377	12.509495	15.467111
7	H7	17.604590	13.731875	14.255273
8	H8	17.825080	14.097411	15.959902
9	C9	15.031048	13.993939	16.467879
10	O10	15.486062	13.578766	17.692928
11	N11	13.667708	14.274880	16.458110
12	H12	13.175000	14.378350	17.320780
13	C13	12.993469	14.690559	15.335296
14	O14	11.800180	14.913068	15.429197
15	H15	13.314415	15.097281	13.321291

(³π_Hπ*/³n_Oπ*)_{CI}

1	N1	13.822711	14.913004	14.100383
2	C2	15.157032	14.453074	14.088593
3	H3	15.619646	14.374121	13.129265
4	C4	15.809522	14.134757	15.268449
5	C5	17.198060	13.559809	15.288011
6	H6	17.158742	12.509938	15.554770
7	H7	17.667013	13.647647	14.317102
8	H8	17.822618	14.061487	16.015972
9	C9	15.114047	14.347287	16.457710

C4	15.842096	14.154504	15.269612
C5	17.216448	13.550004	15.278650
H6	17.184299	12.528047	15.643857
H7	17.639969	13.536002	14.282399
H8	17.887456	14.102929	15.926530
C9	15.200685	14.486358	16.522606
O10	15.604793	13.804644	17.631199
N11	13.766139	14.602867	16.469765
H12	13.314611	14.938196	17.294825
C13	13.111044	14.975580	15.307944
O14	11.947735	15.310837	15.388888
H15	13.426550	15.123721	13.249732

(¹n_Oπ*_{min}→³CI-1)_{ts}

1	N1	13.772514	14.913086	14.270247
2	C2	15.140374	14.581882	14.215200
3	H3	15.611105	14.650799	13.261502
4	C4	15.811580	14.152895	15.359134
5	C5	17.233189	13.657674	15.290447
6	H6	17.245287	12.596680	15.508771
7	H7	17.613080	13.799966	14.286533
8	H8	17.889836	14.167497	15.980637
9	C9	15.074846	14.097529	16.499145
10	O10	15.566530	13.662805	17.712915
11	N11	13.727330	14.423418	16.534301
12	H12	13.273424	14.575599	17.409962
13	C13	13.043562	14.857752	15.425652
14	O14	11.860378	15.115886	15.525266
15	H15	13.317029	15.174126	13.407673

(³π_Hπ*)_{min}

1	N1	13.819185	14.920333	14.316673
2	C2	15.126732	14.466095	14.298250
3	H3	15.576330	14.420825	13.324662
4	C4	15.796206	14.098452	15.386888
5	C5	17.205611	13.589542	15.377864
6	H6	17.236454	12.554693	15.696689
7	H7	17.634788	13.657595	14.386238
8	H8	17.820482	14.153249	16.066640
9	C9	15.097287	14.155249	16.658644
10	O10	15.579809	13.838553	17.721742
11	N11	13.792453	14.591565	16.589848
12	H12	13.298398	14.654905	17.458892
13	C13	13.093734	14.958440	15.473342
14	O14	11.927047	15.273173	15.558155
15	H15	13.373111	15.153640	13.438427

(¹n_Oπ*)_{min} and (³π_Hπ*/¹n_Oπ*)_{ISC}

1	N1	13.812406	14.905315	14.289281
2	C2	15.141192	14.429148	14.231802
3	H3	15.571320	14.322950	13.244548
4	C4	15.810214	14.074206	15.385776
5	C5	17.223136	13.578861	15.377774
6	H6	17.262187	12.530374	15.681640
7	H7	17.654535	13.663698	14.379246
8	H8	17.841819	14.147990	16.074966
9	C9	15.082663	14.086404	16.563169
10	O10	15.682849	14.044452	17.799798
11	N11	13.768175	14.563334	16.588618
12	H12	13.265506	14.637088	17.467066
13	C13	13.076808	14.940784	15.454944
14	O14	11.885443	15.271787	15.551845
15	H15	13.358283	15.144864	13.411592

(³π_Hπ*/S₀)_{ISC}

1	N1	13.894578	14.888567	14.128470
2	C2	15.215867	14.410788	14.072555
3	H3	15.415675	13.738844	13.255330
4	C4	15.870029	14.076369	15.387212
5	C5	17.239545	13.506700	15.375750
6	H6	17.167458	12.424171	15.269379
7	H7	17.806715	13.882427	14.529551
8	H8	17.768346	13.717955	16.295237
9	C9	15.108739	14.122085	16.595596

10	O10	15.521049	13.765180	17.636074	10	O10	15.552725	13.812127	17.701688
11	N11	13.734554	14.573418	16.405865	11	N11	13.823680	14.574831	16.459501
12	H12	13.270449	14.850031	17.245268	12	H12	13.297083	14.690341	17.298004
13	C13	13.085733	14.957866	15.258538	13	C13	13.175080	14.959950	15.296104
14	O14	11.922973	15.299312	15.346381	14	O14	12.019702	15.311870	15.398159
15	H15	13.379649	15.144690	13.214384	15	H15	13.436017	15.104632	13.243680

Table S8. Cartesian coordinates of all the structures (QM part) discussed in the text. (data in Å) for Cyd.

Initial nucleoside optimised

H	12.822914	17.245089	12.340788
O	12.912775	18.103701	12.752515
C	12.042151	18.217826	13.840455
H	11.010550	18.289736	13.511668
H	12.288128	19.139283	14.353640
C	12.183011	17.055783	14.801410
H	11.530825	17.186791	15.650389
O	11.763853	15.845818	14.092891
C	12.668811	14.810952	14.330533
H	12.365925	14.254249	15.208875
N	12.658439	13.857613	13.229811
C	12.545592	12.514465	13.533045
H	12.455647	12.275311	14.572625
C	12.566084	11.570004	12.578709
H	12.514248	10.524950	12.813007
C	12.677266	12.034794	11.209257
N	12.665707	11.149866	10.230518
H	12.653384	11.470700	9.277044
H	12.415444	10.193007	10.413154
N	12.784053	13.319043	10.930029
C	12.850945	14.246763	11.910452
O	13.062141	15.421637	11.651371
C	13.614866	16.798355	15.288437
H	14.286796	17.581668	14.984274
C	14.014025	15.481130	14.617988
H	14.523186	15.691005	13.692110
O	14.840721	14.680854	15.400694
H	14.738398	14.923160	16.317259
O	13.669408	16.649021	16.693202
H	13.984133	17.465937	17.096348

(CT/S₀)_{CI}

H	12.959008	16.106403	12.298391
O	12.930857	18.010333	12.764471
C	12.060016	18.163545	13.861749
H	11.123490	18.147477	13.317600
H	12.245181	19.137165	14.265373
C	12.180047	17.011234	14.836889
H	11.482556	17.206186	15.638320
O	11.863517	15.839595	14.163000
C	12.848439	14.797885	14.375348
H	12.566060	14.231956	15.252789
N	12.892696	13.916910	13.293377
C	12.771596	12.487280	13.629672
H	12.869791	12.239352	14.656226
C	12.798863	11.596040	12.541773
H	12.784682	10.544293	12.757821
C	12.791180	12.026313	11.261138
N	12.914172	11.185257	10.115359
H	12.628248	11.604979	9.256964
H	12.481456	10.293088	10.275638
N	12.875941	13.415732	10.956532
C	12.947824	14.239083	11.953269
O	13.110588	15.542283	11.595840
C	13.601750	16.851066	15.409234
H	14.222595	17.701519	15.185278
C	14.114234	15.597158	14.705785
H	14.610831	15.859084	13.784109
O	15.042272	14.898721	15.458267
H	14.824707	14.961102	16.381097
O	13.581013	16.667100	16.795920
H	13.907910	17.463981	17.229611

Opt CT

H	13.00407787	16.35833891	12.23579290
O	13.08245993	17.70379280	12.74295174
C	12.13587393	17.98263380	13.67822474
H	11.11439993	18.01335680	13.28182674
H	12.29030993	18.95449580	14.16305874
C	12.17049293	16.93453580	14.78050174
H	11.46008793	17.10529580	15.57204774
O	11.83141893	15.65691780	14.17343474
C	12.81900993	14.72619080	14.38411874
H	12.58983693	14.09688180	15.23501774
N	12.87676693	13.79618980	13.23270374
C	12.83494493	12.45063680	13.49233774
H	12.82717693	12.18471380	14.52946674
C	12.80994893	11.52949880	12.52562674
H	12.78725993	10.48045880	12.74261174
C	12.81053193	12.01708780	11.17902874
N	12.73964293	11.18569080	10.16344974
H	12.66769393	11.54001280	9.22409074
H	12.53119493	10.21652180	10.31471974
N	12.88903593	13.32382880	10.93934474
C	12.93966693	14.18749780	11.93134874
O	13.06158493	15.40716680	11.58967474
C	13.57785593	16.75582480	15.35125674
H	14.19550593	17.59870680	15.10821674
C	14.10869293	15.50017380	14.66539674
H	14.59197093	15.78576480	13.74768974
O	15.01318993	14.76160780	15.42354574
H	14.83492693	14.91144180	16.34583574
O	13.58261093	16.55484380	16.75372674
H	13.88877493	17.36433980	17.17501774

S₀_{min}

1	N1	12.638115	13.806058	13.271954
2	C2	12.635098	12.467311	13.562856
3	H3	12.615329	12.195104	14.614332
4	C4	12.650491	11.538398	12.578021
5	H5	12.660963	10.478692	12.799133
6	C6	12.677258	12.025459	11.229643
7	N7	12.700738	11.143029	10.224288
8	H8	12.637856	11.481072	9.261917
9	H9	12.489729	10.161782	10.416559
10	N10	12.687825	13.330414	10.941435
11	C11	12.725447	14.262379	11.936282
12	O12	12.819338	15.477503	11.671131
13	H13	12.644243	14.475712	14.040490

(¹n_Oπ*)_{min-pt}

N1	12.623627	13.746390	13.432476
C2	12.704192	12.355047	13.730569
H3	12.627245	12.094803	14.776948
C4	12.618059	11.476540	12.651329
H5	12.676479	10.407636	12.823641
C6	12.605209	11.937605	11.344506
N7	12.763656	11.119172	10.247235
H8	12.508953	11.507433	9.343467
H9	12.462901	10.157285	10.408703
N10	12.622526	13.337912	11.071452
C11	12.651550	14.116088	12.109112
O12	12.823990	15.404623	11.790476
H13	12.644359	14.429466	14.180508

$(^1n_O\pi^*)_{\text{min-tw}}$

N1	12.668585	13.713581	13.425553
C2	12.749541	12.368763	13.689610
H3	12.817570	12.071908	14.731513
C4	12.749962	11.454814	12.641065
H5	12.808736	10.393262	12.840875
C6	12.725204	11.937918	11.293140
N7	12.718131	11.070904	10.239629
H8	12.523053	11.453872	9.314806
H9	12.417457	10.112674	10.425224
N10	12.686038	13.272693	11.001335
C11	12.689180	14.170397	12.045774
O12	13.226198	15.329617	11.811668
H13	12.663601	14.398506	14.177922

 $(^3\pi_H\pi^*)_{\text{min}}$

1	N1	12.598348	13.745689	13.380736
2	C2	12.435964	12.417815	13.738036
3	H3	12.817203	12.131934	14.718413
4	C4	12.640039	11.466677	12.600302
5	H5	12.655162	10.396574	12.791936
6	C6	12.684223	11.965337	11.282067
7	N7	12.763022	11.095879	10.237579
8	H8	12.621906	11.469440	9.307482
9	H9	12.505767	10.124040	10.411096
10	N10	12.645746	13.277179	11.003327
11	C11	12.704372	14.179712	12.062700
12	O12	12.855503	15.386197	11.779108
13	H13	12.626071	14.438726	14.134604

 $(^3\pi_H\pi^*/^3\pi_2\pi^*)_{\text{CI}}$

1	N1	12.652366	13.778790	13.377748
2	C2	12.639818	12.387623	13.657940
3	H3	12.670740	12.101859	14.686268
4	C4	12.646882	11.508213	12.587331
5	H5	12.665488	10.449330	12.775932
6	C6	12.655072	11.966489	11.280963
7	N7	12.792917	11.141469	10.176468
8	H8	12.500020	11.535453	9.302718
9	H9	12.434062	10.212546	10.320633
10	N10	12.692482	13.359901	11.042159
11	C11	12.712694	14.123460	12.051932
12	O12	12.840374	15.433679	11.745829
13	H13	12.651511	14.460765	14.131848

 $(^1\pi_H\pi^*/n_O\pi^*/S_0)_{\text{CI}}$

1	N1	12.439870	13.698436	13.560756
2	C2	12.310810	12.263320	13.946762
3	H3	13.038210	12.033632	14.727686
4	C4	12.407195	11.411572	12.706412
5	H5	12.408515	10.338471	12.867709
6	C6	12.669071	11.867161	11.480080
7	N7	13.002026	11.172696	10.324094
8	H8	12.590638	11.582332	9.484614
9	H9	12.763125	10.179975	10.402832
10	N10	12.636026	13.323701	11.207609
11	C11	12.570182	13.956235	12.279916
12	O12	12.823490	15.398956	11.823746
13	H13	12.518389	14.423973	14.273618

 $(^1n_N\pi^*)_{\text{min}}$ and $(^1n_N\pi^*/^3\pi_H\pi^*)_{\text{ISC}}$

1	N1	12.665714	13.795885	13.362656
2	C2	12.599092	12.410568	13.675123
3	H3	12.541039	12.163056	14.726476
4	C4	12.608069	11.451942	12.665889
5	H5	12.568185	10.395240	12.908292
6	C6	12.737287	11.814930	11.323440
7	N7	13.013789	10.999687	10.228382
8	H8	12.667197	11.385293	9.345729
9	H9	12.617022	10.066434	10.388140
10	N10	12.840936	13.198711	11.193623
11	C11	12.879053	14.234917	12.050333
12	O12	13.045187	15.417125	11.701826
13	H13	12.670822	14.478462	14.116100

 $(^1,3\pi_H\pi^*)_{\text{ISC}}$

1	N1	12.822146	13.671727	13.447301
2	C2	12.441915	12.394630	13.648876
3	H3	11.844637	12.177141	14.490070
4	C4	12.843374	11.465066	12.612680
5	H5	13.792737	11.171169	12.682477
6	C6	12.577624	11.963215	11.287342
7	N7	12.578547	11.144411	10.231114
8	H8	12.525153	11.531455	9.288971
9	H9	12.446767	10.145304	10.387499
10	N10	12.479973	13.300014	11.061042
11	C11	12.832511	14.151302	12.050614
12	O12	13.095712	15.342933	11.843944
13	H13	12.790924	14.341843	14.216568

 $(^3\pi_2\pi^*)_{\text{min}}$

1	N1	12.611830	13.739382	13.426086
2	C2	12.605616	12.339151	13.720060
3	H3	12.661605	12.063648	14.763399
4	C4	12.657921	11.462806	12.638005
5	H5	12.683421	10.395533	12.823763
6	C6	12.674601	11.920484	11.326771
7	N7	12.899112	11.118117	10.212240
8	H8	12.547172	11.518038	9.340592
9	H9	12.561724	10.161708	10.354173
10	N10	12.656345	13.317891	11.069465
11	C11	12.654085	14.082715	12.108574
12	O12	12.699860	15.383577	11.765063
13	H13	12.629880	14.432350	14.167323

 $(^3\pi_H\pi^*/S_0)_{\text{ISC}}$

1	N1	12.617736	13.730506	13.474931
2	C2	12.750608	12.372127	13.792896
3	H3	13.518588	12.133177	14.510340
4	C4	12.584462	11.453859	12.628783
5	H5	12.358643	10.419552	12.787779
6	C6	12.689368	11.995670	11.296858
7	N7	12.696423	11.145727	10.264193
8	H8	12.599569	11.499781	9.331436
9	H9	12.489710	10.177347	10.425735
10	N10	12.711291	13.282682	11.094591
11	C11	12.718922	14.178732	12.159825
12	O12	12.814822	15.354526	11.872392
13	H13	12.640569	14.401497	14.241522

 $(^1n_O\pi^*)_{\text{min}}$

1	N1	12.643332	13.742054	13.428033
2	C2	12.698590	12.366033	13.736899
3	H3	12.620550	12.103802	14.775659
4	C4	12.605756	11.487607	12.640858
5	H5	12.672846	10.423925	12.811819
6	C6	12.602179	11.957417	11.347150
7	N7	12.724018	11.150715	10.257163
8	H8	12.532065	11.531557	9.341046
9	H9	12.479522	10.180517	10.418373
10	N10	12.576661	13.353862	11.067922
11	C11	12.606562	14.119433	12.123864
12	O12	12.862508	15.391997	11.781052
13	H13	12.651331	14.422331	14.182059

 $(^1n_O\pi^*_{\text{min}} \rightarrow \text{CI-3-st})_{\text{ts}}$

1	N1	12.539885	13.662794	13.595230
2	C2	12.450197	12.234607	13.889972
3	H3	13.076658	11.947414	14.729325
4	C4	12.503657	11.367066	12.653487
5	H5	12.490377	10.296964	12.828410
6	C6	12.710049	11.793066	11.403962
7	N7	12.922388	11.134033	10.216266
8	H8	12.563813	11.610907	9.390420
9	H9	12.615565	10.158843	10.269325
10	N10	12.682107	13.281245	11.282375
11	C11	12.546634	13.938014	12.305365
12	O12	12.504719	15.155486	11.544800
13	H13	12.588367	14.386175	14.305765

$(^1n_O\pi^*/CI)_{is}$

1	N1	12.669249	13.767462	13.412235
2	C2	12.749200	12.418401	13.649514
3	H3	12.847337	12.115416	14.674149
4	C4	12.675579	11.537882	12.636325
5	H5	12.772268	10.483949	12.793150
6	C6	12.561551	12.075193	11.278830
7	N7	12.621613	11.197915	10.260197
8	H8	12.445673	11.530793	9.331887
9	H9	12.467153	10.224385	10.445363
10	N10	12.435169	13.343985	11.049596
11	C11	12.406209	14.225303	12.113677
12	O12	13.166655	15.367865	11.788968
13	H13	12.646355	14.420591	14.178894

$(^1n_N\pi^*/S_0)_{CI}$

1	N1	13.007225	13.716532	13.293486
2	C2	12.944956	12.314367	13.481002
3	H3	12.856148	11.987306	14.512281
4	C4	12.896686	11.463962	12.421350
5	H5	12.715180	10.403958	12.546542
6	C6	12.968312	12.117102	11.117677
7	N7	11.822918	12.379639	10.334614
8	H8	12.041442	12.313501	9.329729
9	H9	11.046116	11.747388	10.551114
10	N10	13.876840	13.229848	11.218681
11	C11	13.305957	14.228014	12.034616
12	O12	13.236095	15.419524	11.706590
13	H13	12.886615	14.345697	14.086545

