Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

On the Decay of the Triplet State of Thionucleobases

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S1. Molecular orbitals in the active space for CASPT2 calculations

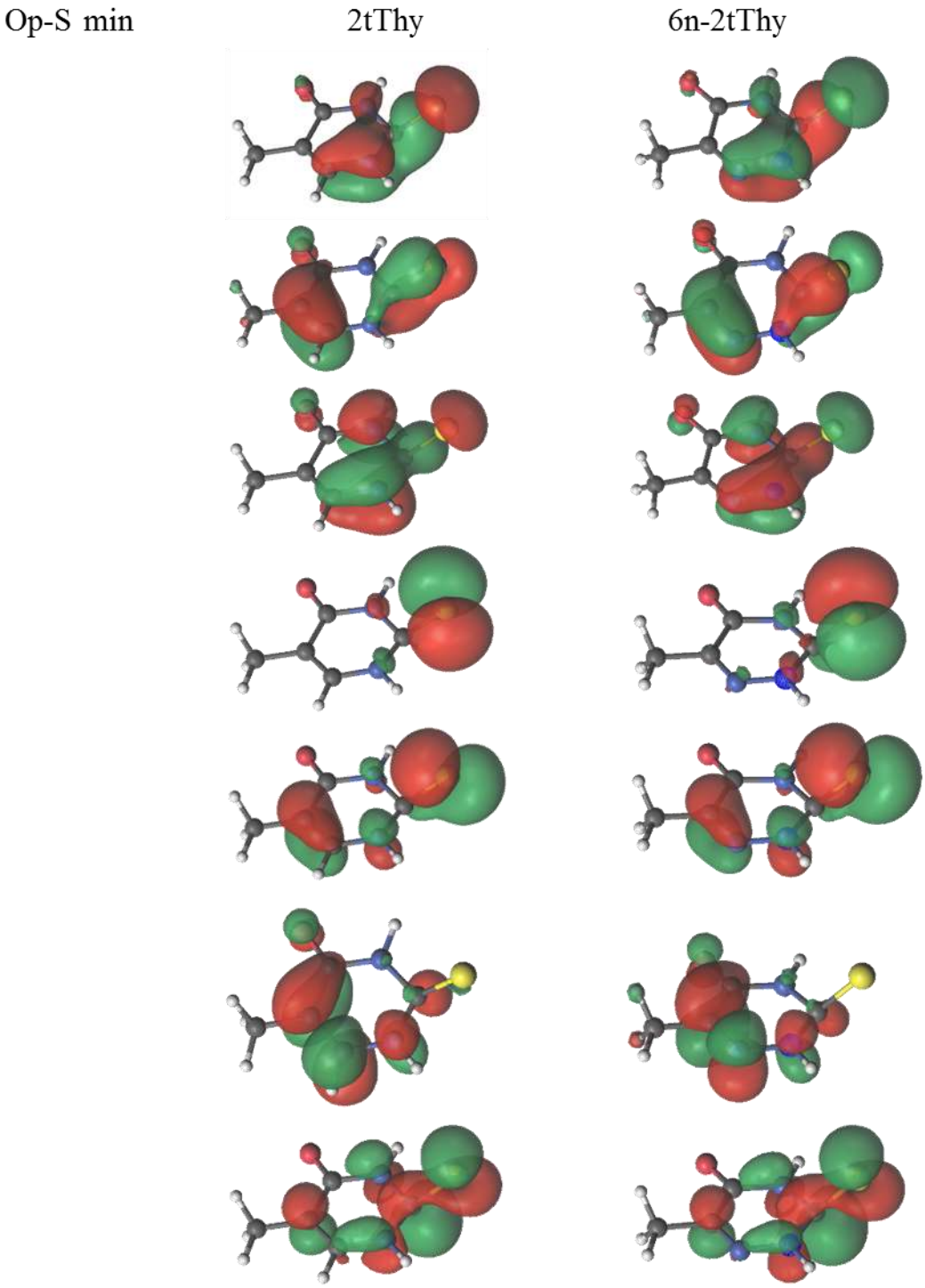


Figure S1. Molecular orbitals in the (10,7) active space used in CASPT2 and CASSCF calculations of 2tThy and 6n-2tThy at the op-S minimum.

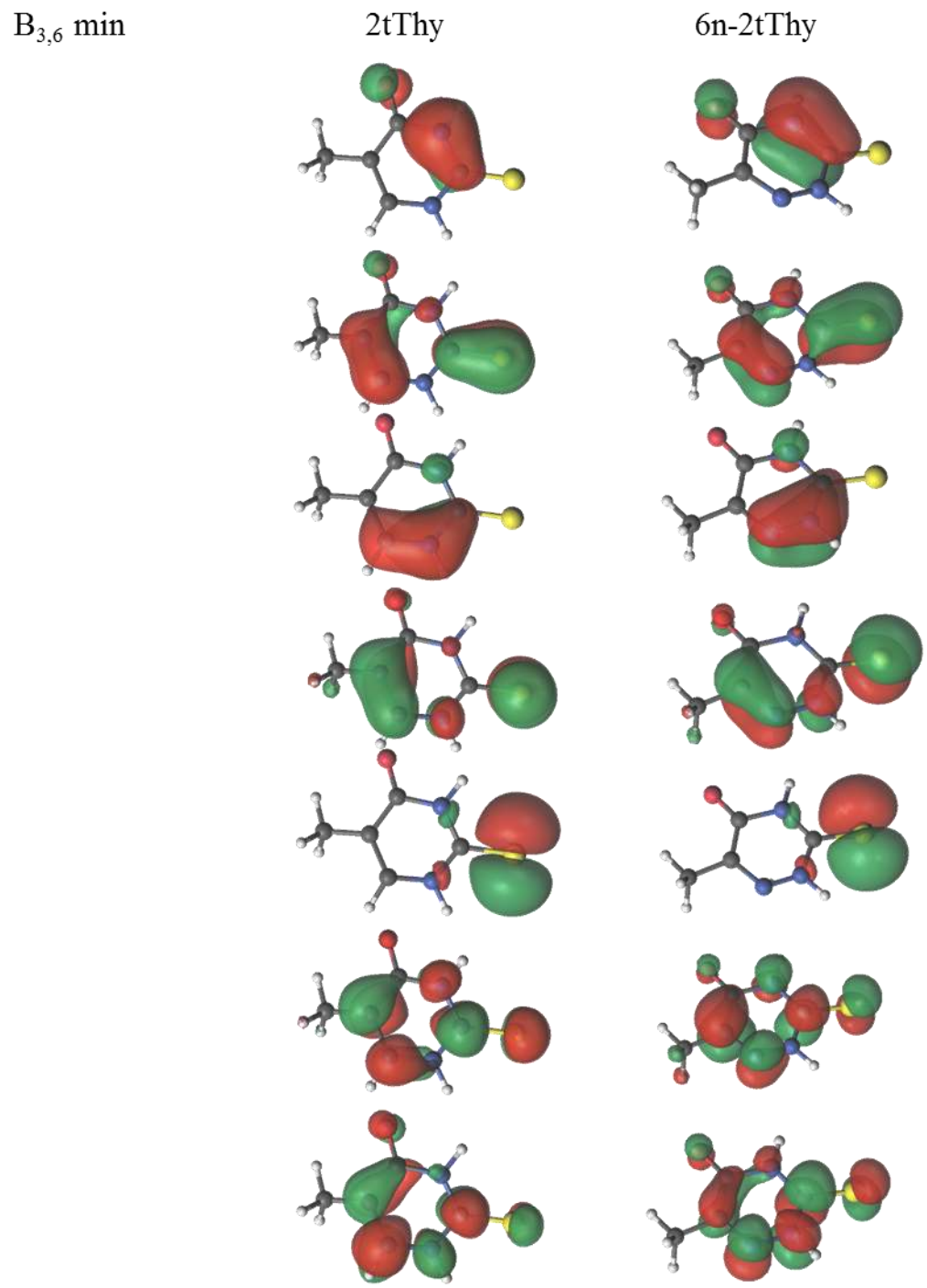


Figure S2. Molecular orbitals in the (10,7) active space used in CASPT2 and CASSCF calculations of 2tThy and 6n-2tThy at the $B_{3,6}$ minimum.

S2. Cartesian coordinates of optimized structures at CASPT2 level

Table S1. 2tThy optimized structures using CASPT2(10,7)/ano-rcc-vdzp calculation (xyz, Angstrom).

S_0

C	-3.12550356	-0.46186309	0.37553996
C	-1.03943832	0.67382799	-0.40210936
C	-1.77989506	1.93559207	-0.44861375
C	-3.09118222	1.91826372	-0.11515271
H	-3.70622335	2.81104870	-0.12087438
O	0.14757042	0.54267847	-0.68297642
C	-1.03382223	3.16407101	-0.86622807
H	-0.19156694	3.34632652	-0.19140520
H	-0.61492577	3.03251070	-1.86883375
H	-1.68695545	4.04016370	-0.86532250
S	-3.91230250	-1.83351319	0.90791225
N	-3.74462879	0.76230469	0.26234386
H	-4.71826023	0.77961252	0.53149026
N	-1.80221372	-0.43249691	0.00956356
H	-1.30496327	-1.31547491	0.07293525

ISC crossing point

C	-3.17388889	-0.66146413	0.10628046
C	-1.06239735	0.59464090	-0.47336412
C	-1.81471028	1.87316856	-0.41005838
C	-3.13446312	1.82364310	-0.18791552
H	-3.76275811	2.71245919	-0.18173767
O	0.14650608	0.54816571	-0.69947123
C	-1.04826720	3.13113194	-0.66543759
H	-0.22024300	3.23139382	0.04379571
H	-0.60280517	3.10543112	-1.66537436
H	-1.69620126	4.00832592	-0.58847132
S	-3.45643919	-0.73377483	1.93785313
N	-3.81539103	0.64206885	0.00448513
H	-4.82189748	0.64179535	0.09638702
N	-1.83463301	-0.54595409	-0.33895467
H	-1.30677742	-1.40791953	-0.37972507

T_1 op-S

C	-3.19942123	-0.52989058	0.09260824
C	-1.04618366	0.64893405	-0.43977648
C	-1.78413405	1.91323767	-0.45743157
C	-3.11143518	1.89341963	-0.14197073
H	-3.71446216	2.79496055	-0.11695721
O	0.15654640	0.54518555	-0.68710621
C	-1.02902811	3.15969566	-0.79673049
H	-0.20294872	3.31253246	-0.09453268
H	-0.58440219	3.08053439	-1.79349072
H	-1.68208369	4.03598013	-0.77158641
S	-3.76051949	-1.59317445	1.45668716
N	-3.77295784	0.74193051	0.16821982
H	-4.76041882	0.76776428	0.37353857
N	-1.80706536	-0.46395024	-0.09345853
H	-1.30579692	-1.34410760	-0.09974378

T_1 $B_{3,6}$

C	-3.16980563	-0.45606759	0.32801671
C	-1.02166360	0.76808111	0.29773640
C	-1.74207627	1.94022081	-0.08054610
C	-3.22409530	1.95009864	0.09828512
H	-3.81988768	2.76593311	-0.29072605
O	0.20481876	0.62305236	0.29846658
C	-1.05229930	3.11703108	-0.65874959
H	0.02534501	2.94740046	-0.69721782
H	-1.42243407	3.32900693	-1.67225971
H	-1.25492547	4.01467261	-0.05734161
S	-3.97818917	-1.92295773	0.31651208
N	-3.79464317	0.70060373	0.00134302
H	-4.77874991	0.59450600	-0.22088273
N	-1.85407227	-0.31926168	0.70635048
H	-1.36067493	-1.18689482	0.88439224

Table S2. 6n-2tThy optimized structures using CASPT2(10,7)/ano-rcc-vdzp calculation (xyz, Angstrom).

S_0

C	-3.10291522	-0.44586745	0.36912952
C	-1.02060302	0.63619153	-0.39678897
C	-1.79992364	1.89842237	-0.43550016
N	-3.05766668	1.95113842	-0.12878225
O	0.16567790	0.55785890	-0.68489080
C	-1.08479716	3.14054917	-0.84964906
H	-0.24784050	3.33370442	-0.17115290
H	-0.66028369	3.01071502	-1.85008272
H	-1.77398864	3.98542290	-0.84222419
S	-3.93938382	-1.78014108	0.90502091
N	-3.66931879	0.79985722	0.24447745
H	-4.64677861	0.89116274	0.48841670
N	-1.77073908	-0.46173700	0.00545755
H	-1.29575404	-1.35768217	0.06412992

ISC crossing point

C	-3.15756804	-0.64374516	0.10110402
C	-1.04213606	0.53887466	-0.43148659
C	-1.84623185	1.82683415	-0.37796849
N	-3.09581486	1.86039650	-0.21269462
O	0.17858313	0.54844520	-0.57567807
C	-1.10973861	3.10181184	-0.65319263
H	-0.28912671	3.24223518	0.05389287
H	-0.66453215	3.05818482	-1.65138591
H	-1.80943100	3.93409744	-0.59609270
S	-3.39939036	-0.68580865	1.90809123
N	-3.75161416	0.66078845	-0.05434897
H	-4.74709783	0.76229226	0.09232285
N	-1.83028059	-0.57971881	-0.42064559
H	-1.32584949	-1.45625835	-0.46667660

T_1 op-S

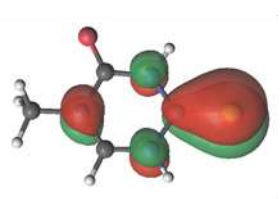
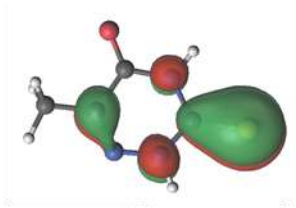
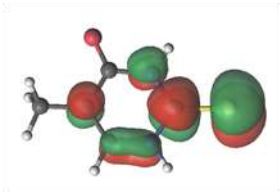
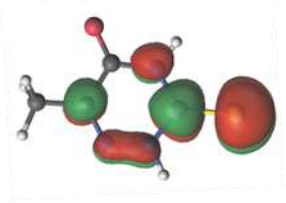
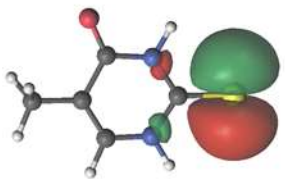
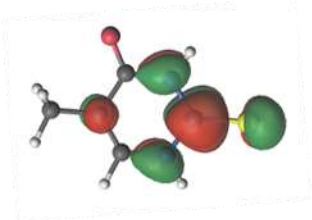
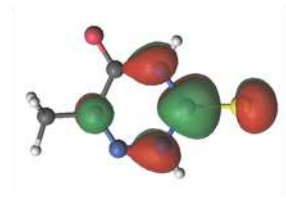
C	-3.15557182	-0.53701696	0.13137622
C	-1.04176218	0.59200502	-0.48217201
C	-1.81549949	1.85935696	-0.44609284
N	-3.09537226	1.90057721	-0.20978952
O	0.15828128	0.54621823	-0.74502925
C	-1.08118491	3.13034963	-0.71977477
H	-0.27875798	3.26866771	0.01156708
H	-0.60732967	3.08752640	-1.70537458
H	-1.77194464	3.97342710	-0.67551274
S	-3.67993011	-1.26531502	1.72188227
N	-3.72151890	0.72712644	0.03507468
H	-4.70919156	0.82076441	0.22009776
N	-1.79708817	-0.52858376	-0.21969862
H	-1.29297844	-1.40701194	-0.20132753

T1 $B_{3,6}$

C	-3.14065956	-0.44866186	0.34175350
C	-1.00672930	0.74682795	0.29402651
C	-1.75023778	1.87930507	-0.13485974
N	-3.19784853	1.94942313	-0.09946238
O	0.22326187	0.64549088	0.35485659
C	-1.09168508	3.10234707	-0.63713185
H	-0.00682667	2.98669458	-0.63064080
H	-1.43591438	3.32802375	-1.65490791
H	-1.37473168	3.96208957	-0.01470804
S	-4.05898001	-1.84853838	0.40520213
N	-3.72337009	0.73650704	0.00719837
H	-4.73157723	0.68854161	-0.12034321
N	-1.81356819	-0.37709839	0.64996400
H	-1.32461338	-1.24723999	0.82269584

S3. Properties of T_1 and T_2 states at the S_0 geometry

Table S3. Properties of the T_1 and T_2 states of 2tThy and 6n-2tThy at ground state minimum (S_0) at CASPT2 (10,7) level.

		2tThy	6n-2tThy
Excitation energy /eV	T_1	3.56	3.49
	T_2	3.99	3.93
SOC /cm^{-1}	T_1	2	2
	T_2	77	78
Character	T_1	ππ*	ππ*
	T_2	nπ*	nπ*
Semi-occupied orbitals	T_1		
			
	T_2		
			

S4. Parameters used in the quasi-Marcus equation

Based on the Golden rule and harmonic vibrational approximation, we can obtain the classic Marcus formula for intersystem crossing rate as:[1,2]

$$k_{isc} = \frac{2\pi}{\hbar}|J_{soc}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \exp\left(-\frac{(\lambda+\Delta G^0)^2}{4\lambda k_b T}\right) \quad (1)$$

where the k_{isc} is the ISC rate, J_{soc} is the spin orbit coupling, λ is the reorganization energy, k_b is the Boltzmann constant, T is the absolute temperature, and ΔG^0 is the total Gibbs free energy variation for the transfer. The term in the exponential is a quadratic approximation for the activation energy $\Delta G^{\ddagger}_{isc}$:

$$\Delta G^{\ddagger}_{isc} \approx \frac{(\lambda+\Delta G^0)^2}{4\lambda}. \quad (2)$$

These parameters are shown in Figure S3:

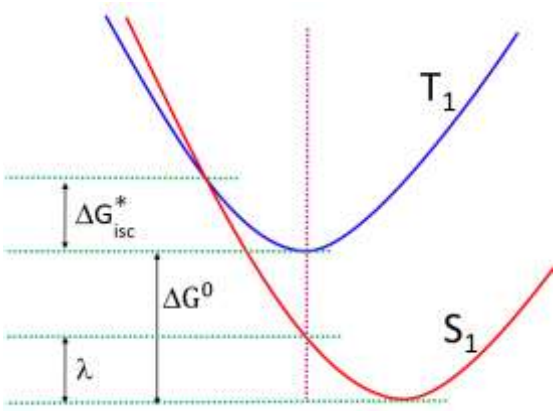


Figure S3. Marcus model in the inverted region.

In the case of small couplings, as it is for triplet/singlet crossings, the diabatic crossing point can be optimized directly because it is practically coincident with the crossing of the adiabatic states. We take advantage of this fact to obtain a more precise estimate of the activation energy $\Delta G^{\ddagger}_{isc}$, and writing a quasi-Marcus formula as follows:

$$K_{isc} = \frac{2\pi}{\hbar}|J_{soc}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \exp\left(-\frac{\Delta G^{\ddagger}_{isc}}{k_b T}\right). \quad (3)$$

(1) Marcus, R. A. *J. Chem. Phys.* **1984**, *81*, 4494.
(2) Ou, Q.; Subotnik, J. E. *J. Phys. Chem. C* **2013**, *117*, 19839.

S5. Semi-occupied orbitals of the T_1 state of 6n-2tThy from CASPT2 calculation

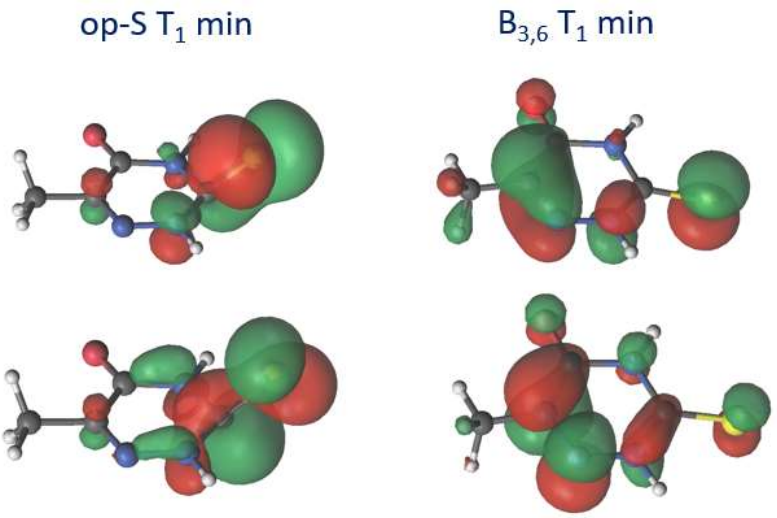


Figure S4. Semi-occupied orbitals of T_1 states of 6n-2tThy from CASPT2 calculations at the two minimum structures.

S6. Optimized T_1 structures with CC2, ADC(2), and B3LYP methods

Table S4. Optimized T_1 minima of 6n-2tThy with B3LYP, CC2, and ADC(2) methods (xyz, Angstrom).

	B3LYP/6-311++g(d,p)	**CC2**/ aug-cc-pVDZ	**ADC(2)**/ aug-cc-pVDZ
op-S min	C -3.156229 -0.534283 0.141503	C -3.145239 -0.569779 0.170017	C -3.142385 -0.560495 0.168758
	C -1.028556 0.588949 -0.462518	C -1.040494 0.570186 -0.516876	C -1.038996 0.572438 -0.511442
	C -1.802559 1.865318 -0.438500	C -1.813712 1.840059 -0.455521	C -1.812191 1.844744 -0.449212
	N -3.083094 1.899814 -0.187358	N -3.125486 1.886820 -0.247094	N -3.117249 1.892733 -0.227909
	O 0.160063 0.537098 -0.720486	O 0.178013 0.529312 -0.773640	O 0.165073 0.535334 -0.789992
	C -1.085000 3.137826 -0.740595	C -1.085932 3.128800 -0.678767	C -1.084951 3.129724 -0.690173
	H -0.279340 3.304605 -0.019162	H -0.310889 3.263140 0.093243	H -0.299118 3.266744 0.069776
	H -0.611345 3.088012 -1.725445	H -0.569241 3.104420 -1.651912	H -0.581408 3.099155 -1.669374
	H -1.782297 3.974075 -0.709114	H -1.797685 3.964799 -0.645577	H -1.793166 3.967649 -0.652342
	S -3.731444 -1.347314 1.633429	S -3.585374 -1.020419 1.850266	S -3.632414 -1.089967 1.794192
	N -3.711416 0.751161 0.067904	N -3.752314 0.700885 -0.037410	N -3.741001 0.713074 -0.008808
	H -4.697872 0.846029 0.263292	H -4.743191 0.788161 0.182533	H -4.735662 0.795542 0.185833
	N -1.784846 -0.528964 -0.188139	N -1.808890 -0.570533 -0.304908	N -1.794086 -0.559363 -0.263773
	H -1.295914 -1.414234 -0.199584	H -1.289415 -1.447758 -0.269129	H -1.282293 -1.439220 -0.240306
$B_{3,6}$ min	C -3.151430 -0.465684 0.365157	C -3.143921 -0.474642 0.325390	C -3.144457 -0.469838 0.329445
	C -1.004201 0.730604 0.241313	C -0.999014 0.740702 0.309283	C -1.001270 0.736279 0.299473
	C -1.740345 1.877065 -0.177163	C -1.741183 1.891940 -0.114670	C -1.745022 1.889221 -0.122602
	N -3.182406 1.921255 -0.213448	N -3.203601 1.981211 -0.028523	N -3.203995 1.974555 -0.060122
	O 0.216985 0.637357 0.327106	O 0.250178 0.636275 0.357067	O 0.238745 0.640178 0.358668
	C -1.080933 3.124443 -0.607337	C -1.089123 3.111653 -0.649920	C -1.087539 3.111035 -0.642668
	H 0.002094 3.032584 -0.551990	H 0.001274 2.982746 -0.674599	H 0.003232 2.989522 -0.646300
	H -1.380789 3.378097 -1.632962	H -1.470558 3.329413 -1.664333	H -1.449798 3.326406 -1.664505
	H -1.416406 3.961940 0.019050	H -1.353824 3.981150 -0.020013	H -1.370695 3.979742 -0.020438
	S -4.091580 -1.832639 0.583938	S -4.066307 -1.873107 0.362065	S -4.064530 -1.859094 0.395293
	N -3.732270 0.712903 -0.024483	N -3.734796 0.736386 -0.010710	N -3.732483 0.734323 -0.005546
	H -4.740724 0.682563 -0.125632	H -4.748302 0.692055 -0.141350	H -4.745231 0.689577 -0.129522
	N -1.809342 -0.403317 0.565653	N -1.812799 -0.380219 0.668221	N -1.808687 -0.384752 0.640987
	H -1.322134 -1.253459 0.814440	H -1.321504 -1.251851 0.865735	H -1.321743 -1.253447 0.851482

Table S5. Optimized T_1 minima of 2t-Cyt and 6t-Gua with ADC(2)/ aug-cc-pVDZ method (xyz, Angstrom).

	2t-Cyt				6t-Gua			
op-S min	N	3.9472210	4.0451363	-4.4282725	C	-0.442472	0.903609	0.000699
	C	4.3849133	4.0146576	-3.1031010	C	-0.218328	3.297675	0.563456
	N	3.3788029	3.9146338	-2.0853339	C	-2.344569	2.072365	0.060856
	C	2.1876489	3.3228551	-2.3705363	H	-2.174465	4.057628	0.506644
	C	1.8375373	3.0724050	-3.6799649	C	0.392004	2.006898	0.325080
	C	2.7415096	3.5801939	-4.7000158	N	0.409728	-0.171751	-0.095782
	S	5.6267495	5.2872062	-2.8978813	H	0.137192	-1.124895	-0.311855
	N	2.3532813	3.5045496	-6.0292953	N	1.711015	1.613499	0.408467
	H	1.5352987	3.0876094	-1.5259124	C	1.683356	0.300094	0.148446
	H	0.8917180	2.5880583	-3.9262149	N	-1.800778	0.869457	-0.137543
	H	2.9446551	4.0387794	-6.6599855	N	-1.646269	3.204224	0.341131
	H	1.3590871	3.5876558	-6.2127109	N	-3.729669	2.172459	0.038343
	H	3.6308380	4.1187889	-1.1238116	H	-4.105181	3.039585	-0.335034
					H	-4.156490	1.347686	-0.374289
					S	0.633222	4.658854	-0.177801
					H	2.554708	-0.350702	0.125878
Ring distorted min	N	3.5330565	3.6748949	-2.0380618	N	-1.559581	3.259117	-0.096386
	C	2.2119291	3.1966168	-2.2846297	C	-0.245990	3.302131	0.283177
	H	1.5300715	3.1869561	-1.4336256	C	0.389001	2.010569	0.210705
	C	1.8086507	3.2568126	-3.6510147	C	-0.492332	0.845874	0.050036
	H	0.7657402	3.0395763	-3.9063816	N	-1.746315	0.828044	-0.294024
	C	2.7306483	3.5384528	-4.6362747	C	-2.140237	2.144917	-0.776526
	N	2.4790343	3.5188385	-6.0205182	N	1.645298	1.630419	0.613468
	H	3.1678498	4.0678101	-6.5316009	C	1.571094	0.300182	0.710748
	H	1.5317038	3.7953923	-6.2677125	N	0.321022	-0.218339	0.433608
	N	4.1234416	3.6688354	-4.3372236	S	0.486528	4.684940	0.894058
	C	4.4160109	3.7822540	-3.0707048	N	-3.542172	2.269165	-0.966186
	H	3.8626293	3.8567947	-1.0952099	H	-2.107818	4.113285	0.012726
	S	6.0789274	4.1790306	-2.7001375	H	0.056977	-1.197722	0.410023
					H	-3.773655	2.811906	-1.798273
					H	-3.949191	1.337953	-1.053658
					H	2.408666	-0.341096	0.981424