

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

Op-S min

2tThy

6n-2tThy

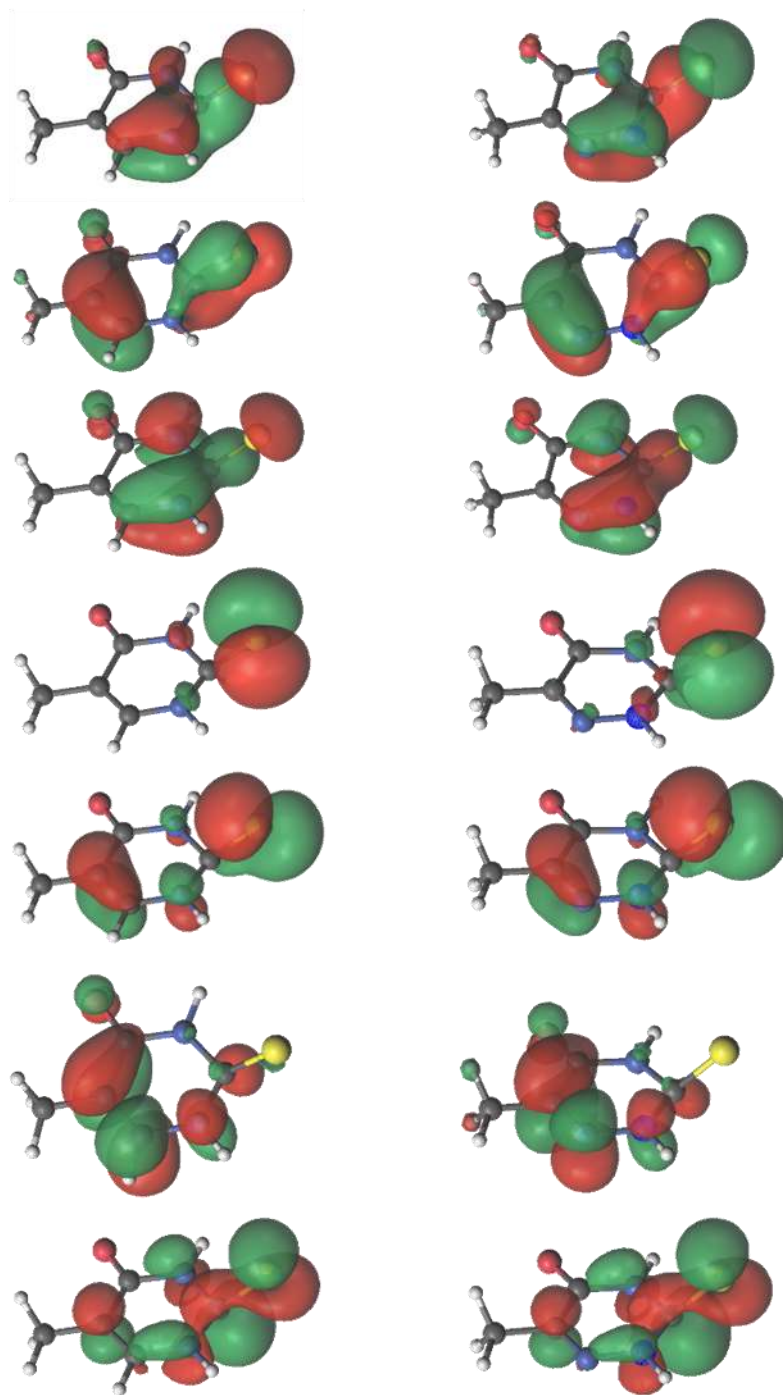


Figure S1. Molecular orbitals in the (10,7) active space used in CASPT2 and CASSCF calculations of 2tThy and 6n-2tThy at the op-S minimum.

B_{3,6} min

2tThy

6n-2tThy

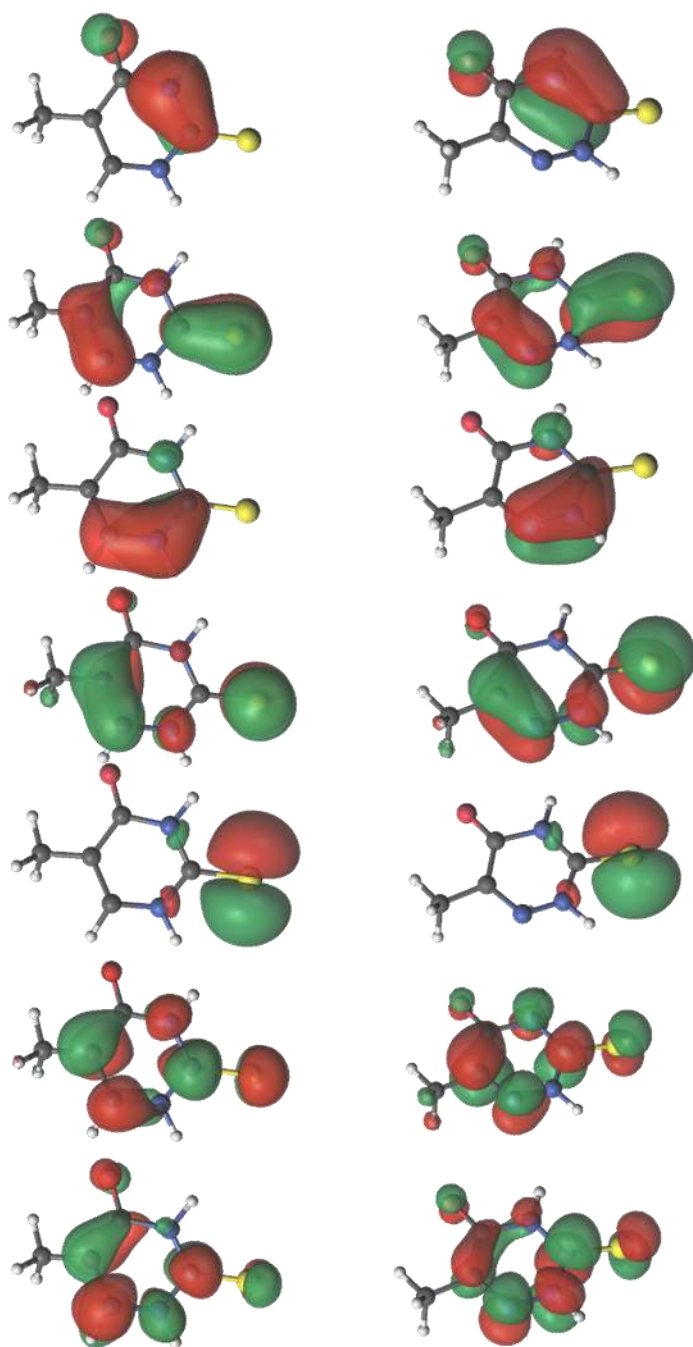


Figure S2. Molecular orbitals in the (10,7) active space used in CASPT2 and CASSCF calculations of 2tThy and 6n-2tThy at the B_{3,6} minimum.

S2. Cartesian coordinates of optimized structures at CASPT2 level

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

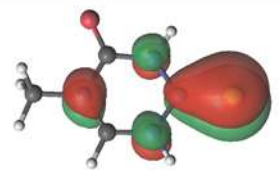
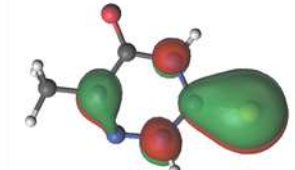
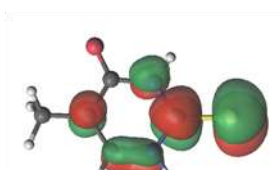
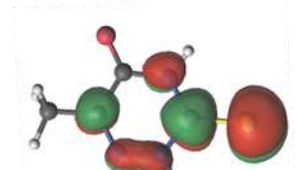
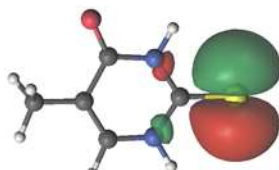
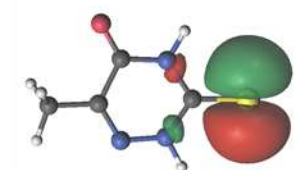
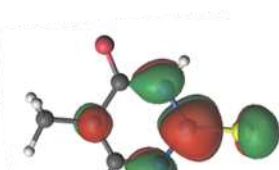
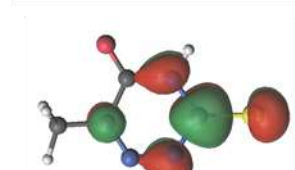
S ₀	ISC crossing point
C -3.12550356 -0.46186309 0.37553996	C -3.17388889 -0.66146413 0.10628046
C -1.03943832 0.67382799 -0.40210936	C -1.06239735 0.59464090 -0.47336412
C -1.77989506 1.93559207 -0.44861375	C -1.81471028 1.87316856 -0.41005838
C -3.09118222 1.91826372 -0.11515271	C -3.13446312 1.82364310 -0.18791552
H -3.70622335 2.81104870 -0.12087438	H -3.76275811 2.71245919 -0.18173767
O 0.14757042 0.54267847 -0.68297642	O 0.14650608 0.54816571 -0.69947123
C -1.03382223 3.16407101 -0.86622807	C -1.04826720 3.13113194 -0.66543759
H -0.19156694 3.34632652 -0.19140520	H -0.22024300 3.23139382 0.04379571
H -0.61492577 3.03251070 -1.86883375	H -0.60280517 3.10543112 -1.66537436
H -1.68695545 4.04016370 -0.86532250	H -1.69620126 4.00832592 -0.58847132
S -3.91230250 -1.83351319 0.90791225	S -3.45643919 -0.73377483 1.93785313
N -3.74462879 0.76230469 0.26234386	N -3.81539103 0.64206885 0.00448513
H -4.71826023 0.77961252 0.53149026	H -4.82189748 0.64179535 0.09638702
N -1.80221372 -0.43249691 0.00956356	N -1.83463301 -0.54595409 -0.33895467
H -1.30496327 -1.31547491 0.07293525	H -1.30677742 -1.40791953 -0.37972507
T ₁ op-S	T ₁ B _{3,6}
C -3.19942123 -0.52989058 0.09260824	C -3.16980563 -0.45606759 0.32801671
C -1.04618366 0.64893405 -0.43977648	C -1.02166360 0.76808111 0.29773640
C -1.78413405 1.91323767 -0.45743157	C -1.74207627 1.94022081 -0.08054610
C -3.11143518 1.89341963 -0.14197073	C -3.22409530 1.95009864 0.09828512
H -3.71446216 2.79496055 -0.11695721	H -3.81988768 2.76593311 -0.29072605
O 0.15654640 0.54518555 -0.68710621	O 0.20481876 0.62305236 0.29846658
C -1.02902811 3.15969566 -0.79673049	C -1.05229930 3.11703108 -0.65874959
H -0.20294872 3.31253246 -0.09453268	H 0.02534501 2.94740046 -0.69721782
H -0.58440219 3.08053439 -1.79349072	H -1.42243407 3.32900693 -1.67225971
H -1.68208369 4.03598013 -0.77158641	H -1.25492547 4.01467261 -0.05734161
S -3.76051949 -1.59317445 1.45668716	S -3.97818917 -1.92295773 0.31651208
N -3.77295784 0.74193051 0.16821982	N -3.79464317 0.70060373 0.00134302
H -4.76041882 0.76776428 0.37353857	H -4.77874991 0.59450600 -0.22088273
N -1.80706536 -0.46395024 -0.09345853	N -1.85407227 -0.31926168 0.70635048
H -1.30579692 -1.34410760 -0.09974378	H -1.36067493 -1.18689482 0.88439224

Table S2. 6n-2tThy optimized structures using CASPT2(10,7)/ano-ccc-vd3p calculation (xyz, Angstrom).

S ₀	ISC crossing point
C -3.10291522 -0.44586745 0.36912952	C -3.15756804 -0.64374516 0.10110402
C -1.02060302 0.63619153 -0.39678897	C -1.04213606 0.53887466 -0.43148659
C -1.79992364 1.89842237 -0.43550016	C -1.84623185 1.82683415 -0.37796849
N -3.05766668 1.95113842 -0.12878225	N -3.09581486 1.86039650 -0.21269462
O 0.16567790 0.55785890 -0.68489080	O 0.17858313 0.54844520 -0.57567807
C -1.08479716 3.14054917 -0.84964906	C -1.10973861 3.10181184 -0.65319263
H -0.24784050 3.33370442 -0.17115290	H -0.28912671 3.24223518 0.05389287
H -0.66028369 3.01071502 -1.85008272	H -0.66453215 3.05818482 -1.65138591
H -1.77398864 3.98542290 -0.84222419	H -1.80943100 3.93409744 -0.59609270
S -3.93938382 -1.78014108 0.90502091	S -3.39939036 -0.68580865 1.90809123
N -3.66931879 0.79985722 0.24447745	N -3.75161416 0.66078845 -0.05434897
H -4.64677861 0.89116274 0.48841670	H -4.74709783 0.76229226 0.09232285
N -1.77073908 -0.46173700 0.00545755	N -1.83028059 -0.57971881 -0.42064559
H -1.29575404 -1.35768217 0.06412992	H -1.32584949 -1.45625835 -0.46667660
T ₁ op-S	T ₁ B _{3,6}
C -3.15557182 -0.53701696 0.13137622	C -3.14065956 -0.44866186 0.34175350
C -1.04176218 0.59200502 -0.48217201	C -1.00672930 0.74682795 0.29402651
C -1.81549949 1.85935696 -0.44609284	C -1.75023778 1.87930507 -0.13485974
N -3.09537226 1.90057721 -0.20978952	N -3.19784853 1.94942313 -0.09946238
O 0.15828128 0.54621823 -0.74502925	O 0.22326187 0.64549088 0.35485659
C -1.08118491 3.13034963 -0.71977477	C -1.09168508 3.10234707 -0.63713185
H -0.27875798 3.26866771 0.01156708	H -0.00682667 2.98669458 -0.63064080
H -0.60732967 3.08752640 -1.70537458	H -1.43591438 3.32802375 -1.65490791
H -1.77194464 3.97342710 -0.67551274	H -1.37473168 3.96208957 -0.01470804
S -3.67993011 -1.26531502 1.72188227	S -4.05898001 -1.84853838 0.40520213
N -3.72151890 0.72712644 0.03507468	N -3.72337009 0.73650704 0.00719837
H -4.70919156 0.82076441 0.22009776	H -4.73157723 0.68854161 -0.12034321
N -1.79708817 -0.52858376 -0.21969862	N -1.81356819 -0.37709839 0.64996400
H -1.29297844 -1.40701194 -0.20132753	H -1.32461338 -1.24723999 0.82269584

S3. Properties of T₁ and T₂ states at the S₀ geometry

Table S3. Properties of the T₁ and T₂ states of 2tThy and 6n-2tThy at ground state minimum (S₀) 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	$\pi\pi^*$	$\pi\pi^*$
	T ₂	$n\pi^*$	$n\pi^*$
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 $\Delta G_{isc}^\ddagger$:

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

These parameters are shown in Figure S3:

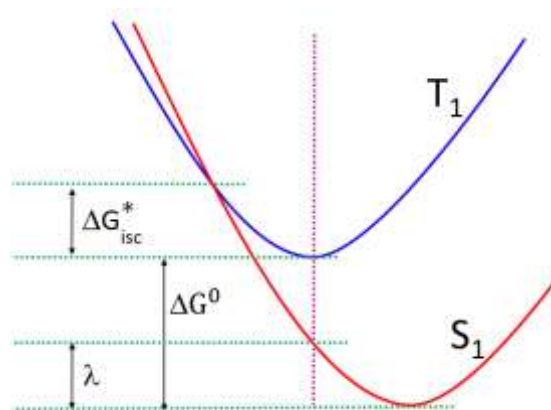


Figure S3. Marcus model in the inverted region.

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 $\Delta G_{isc}^\ddagger$, and writing a quasi-Marcus formula as follows:

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

- (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

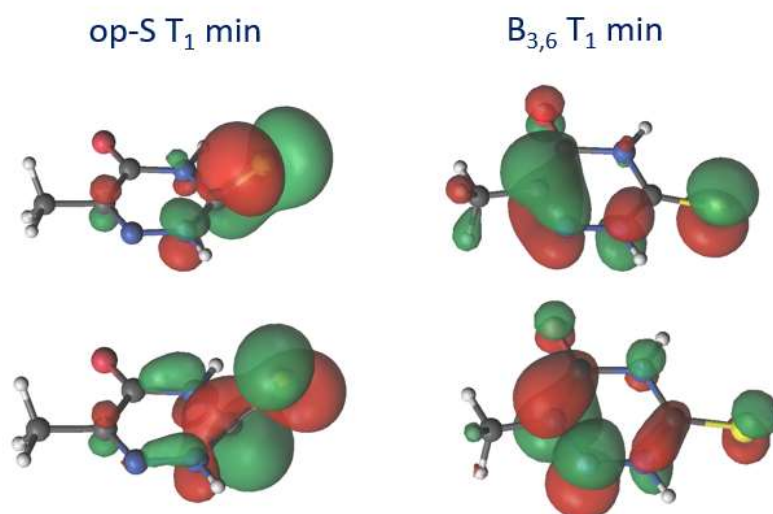


Figure S4. Semi-occupied orbitals of T_1 states of 6n-2tThy from CASPT2 calculations at the two minimum structures.

S6. Optimized T₁ structures with CC2, ADC(2), and B₃LYP methods

Table S4. Optimized T₁ minima of 6n-2tThy with B₃LYP, CC2, and ADC(2) methods (xyz, Angstrom).

	B ₃ LYP/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
	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
B _{3,6} min	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 T₁ 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