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Mechanisms and Energetics for Hydrogen Abstraction of Thymine Photosensitized by Benzophenone from Theoretical Principle

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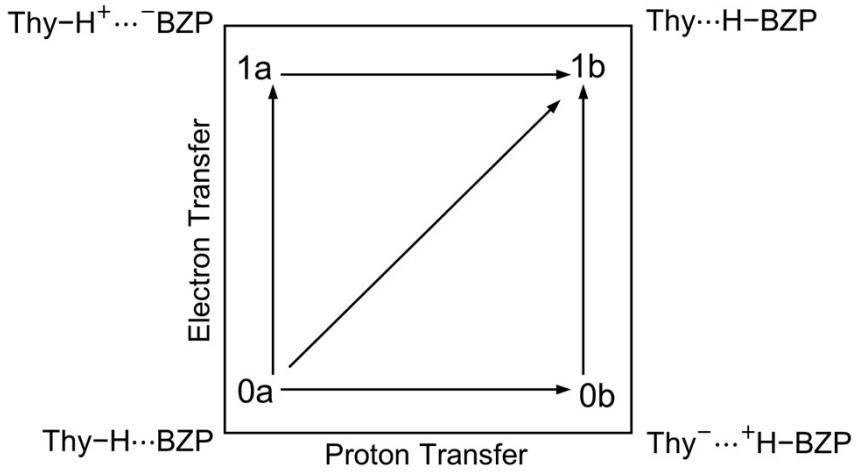
Table of Contents

Multistate Density Functional Theory (MSDFT)



Scheme S1. Two-dimensional More O'Ferrall-Jencks diagram for the hydrogen abstraction reaction between benzophenone (BZP) and thymine (Thy-H) moieties. The horizontal and vertical coordinates stand for proton transfer (PT) and electron transfer (ET) pathways, and the diagonal line implies the concerted PT-ET pathway. The four corners (0a, 1a, 0b, 1b) of the diagram stand for the reactant state, electron transfer state, proton transfer state, and product state, respectively.

For exploring the essence of intramolecular hydrogen abstraction occurred in the BZP-Thy compound, the benzophenone (BZP) and thymine (Thy-H) molecules were adopted in the MSDFT approach. The preference for the concerted and sequential ET/PT mechanisms can be characterized by the four valence-bond structures from the two-dimensional More O'Ferrall-Jencks diagram[1] in Scheme S1. Herein, 0 and 1 stand for the localized electronic configurations, while a and b represent the initial state and final state in the proton-transfer process, respectively. The four diabatic states corresponding to Lewis configurations can be expressed by a single determinant of block-localized Kohn-Sham (BLKS) orbitals in DFT framework, *i.e.* reactant state (0a, Thy - H···BZP), electron transfer state (1a, $^{\text{Thy - H}^{+}\cdots{}^{-}\text{BZP}}$), proton transfer state (0b, $^{\text{Thy}^{+}\cdots{}^{-}\text{H - BZP}}$) and product state (1b, Thy···H - BZP).[2-5]

$$\Psi_{0a}^{BLKS} = \hat{A}\left\{\Omega_{0a}^{1}(\text{Thy - H})\Omega_{0a}^{1}(\text{BZP})\right\} \tag{S1}$$

$$\Psi_{1a}^{BLKS} = \hat{A}\left\{\Omega_{1a}^{1}(\text{Thy - H}^{+})\Omega_{1a}^{2}(^{-}\text{BZP})\right\} \tag{S2}$$

$$\Psi_{0b}^{BLKS} = \hat{A}\left\{\Omega_{0b}^{1}(\text{Thy}^{-})\Omega_{0b}^{2}(^{+}\text{H - BZP})\right\} \tag{S3}$$

$$\Psi_{1b}^{BLKS} = \hat{A}\left\{\Omega_{1b}^{1}(\text{Thy}^{\bullet})\Omega_{1b}^{2}(^{\bullet}\text{H - BZP})\right\} \tag{S4}$$

In Equations (S1)-(S4), $\hat{A}$ is the antisymmetrizer, and Ω_{γ}^{k} stands for the occupied BLKS orbital for the k^{th} (k = 1, 2) fragment in diabatic state γ (γ=0a, 1a, 0b, 1b). The two fragments Thy-H and BP denotes thymine and the triplet excited benzophenone molecules, respectively. The total spin multiplicity is three. The BLKS orbitals are orthogonal within each block, but orbitals between different blocks are non-orthogonal. According to multistate density functional theory (MSDFT), the configuration interaction of the above four diabatic states yields the adiabatic ground and excited states for the coupled ET and PT reaction:

$$\Phi^{\text{MSDFT}} = \sum_{\gamma}^{4} c_{\gamma} \Psi_{\gamma}^{\text{BLKS}} \tag{S5}$$

where c_{γ} is the coefficient for state γ (ground or excited states). Meanwhile, the simplification of the four-state theory into a pair of two-state models can be achieved by linearly combining these four diabatic states of Equations (S1)-(S4). Specifically, for the hydrogen atom transfer (HAT) mechanism, the electronically valence-bond configurations are localized on the donor (a) and acceptor (b) position of the hydrogen nuclear, corresponding to the effective diabatic states of the HAT reactant and product, $\Phi_{\text{R}}^{\text{HAT}}$ and $\Phi_{\text{P}}^{\text{HAT}}$, respectively.

$$\Phi_{\text{R}}^{\text{HAT}} = c_{0\text{a}} \Psi_{0\text{a}}^{\text{BLKS}} + c_{1\text{a}} \Psi_{1\text{a}}^{\text{BLKS}} \tag{S6}$$

$$\Phi_{\text{P}}^{\text{HAT}} = c_{0\text{b}} \Psi_{0\text{b}}^{\text{BLKS}} + c_{1\text{b}} \Psi_{1\text{b}}^{\text{BLKS}} \tag{S7}$$

For the concerted-asynchronous electron-proton transfer (CEPT) mechanism, electron and proton migrate separately but each of its diabatic states is stabilized by the accompanying proton tunneling. Note that the CEPT mechanism is different from the proton coupled electron transfer reaction (abbreviated as PCET), which isn't necessarily concerted. The effective diabatic CEPT reactant and product configurations, $\Phi_{\text{R}}^{\text{CEPT}}$ and $\Phi_{\text{P}}^{\text{CEPT}}$, should be localized on the electron donor (0) and acceptor (1) by combining the two proton configurations (a and b), respectively.

$$\Phi_{\text{R}}^{\text{CEPT}} = c_{0\text{a}} \Psi_{0\text{a}}^{\text{BLKS}} + c_{0\text{b}} \Psi_{0\text{b}}^{\text{BLKS}} \tag{S8}$$

$$\Phi_{\text{R}}^{\text{CEPT}} = c_{1\text{a}} \Psi_{1\text{a}}^{\text{BLKS}} + c_{1\text{b}} \Psi_{1\text{b}}^{\text{BLKS}} \tag{S9}$$

In Equations (6)-(9), the qualities c_{γ} are configurational coefficients determined by the

two diabatic states in each equation.

Calculations of decay rates

The fluorescent radiative rate was calculated by[6]

$$k_{\mathrm{FL}} = \frac{e^2 f \Delta E^2}{2\pi\varepsilon_0 m_{\mathrm{e}} c^3 \hbar^2} \tag{S10}$$

where e is the electron charge. f is the oscillator strength of S_1. ΔE is the energy gap between S_1 and S_0 at the S_1 minimum geometry (unit in cm^{-1}). ε_0 is the vacuum permittivity. m_{e} is the electron mass. c is the speed of light.

Based on the Marcus theory[7], the ISC rate from S_1 to a neighbor triplet state T_{m} can be estimated by

$$k_{\mathrm{ISC}} = \frac{2\pi}{\hbar}|V_{\mathrm{SOC}}|^2 \frac{1}{\sqrt{4\pi\lambda k_{\mathrm{B}} T}} \exp\left(-\frac{\left(\Delta G_{\mathrm{ST}} + \lambda\right)^2}{4\lambda k_{\mathrm{B}} T}\right) \tag{S11}$$

where V_{SOC} is the spin-orbit coupling (SOC) matrix element. λ is the reorganization energy and ΔG_{ST} is the vertical free Gibbs energy.

The phosphorescent rate was calculated by[8]

$$k_{\mathrm{PH}} = \frac{16\pi^3 10^6 n^3 E\left(T_i\right)^3}{3h\varepsilon_0} \left\{ \sum_j \frac{\left\langle T_i|H_{\mathrm{SOC}}|S_j\right\rangle}{E\left(S_j\right) - E\left(T_i\right)} \left\langle S_j|M|S_0\right\rangle \right\} \tag{S12}$$

Here, n and ε_0 are refractive index of the solvent medium and the vacuum permittivity, respectively. $E(S_j)$ and $E(T_i)$ denote the excitation energy from the jth singlet state (S_j) and ith triplet state (T_i) to S_0. $\left\langle T_i|H_{\mathrm{SOC}}|S_j\right\rangle$ is the spin orbit coupling constants between selected states. $\left\langle S_j|M|S_0\right\rangle$ is the transition dipole moment from S_j to S_0.

Table S1. Relative energy (RE, kcal/mol), vertical excitation energy (ΔE, eV), absorption wavelength (λ, nm) and oscillator strength f of main excited states of the ^{1}RC geometry. The reference energy is the ground-state energy of ^{1}RC.

State	RE (kcal/mol)	ΔE (eV)	λ (nm)	f
S_0	0.00			
S_1	84.42	3.6607	339	0.001
S_2	95.84	4.1562	298	0.000
S_3	102.71	4.4541	278	0.022
S_4	105.53	4.5762	271	0.030
S_5	108.55	4.7073	263	0.201

Table S2. Natural transition orbital (NTO, hole and electron wave functions) pairs for excited states of the ^{1}RC geometry (isovalue = 0.05 e·Å^{-3}). *w* denotes the square of the singular value for a given NTO pair, i.e. the associated weight for each NTO pair.

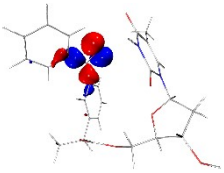
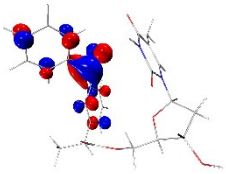
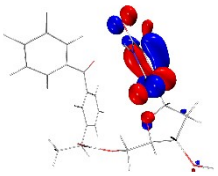
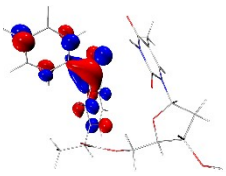
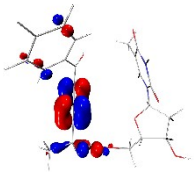
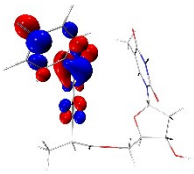
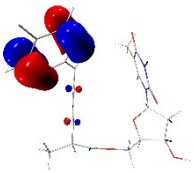
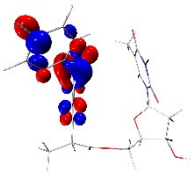
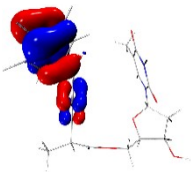
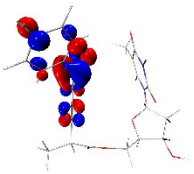
Excited State	Nature	*w*	Hole-NTO	Electron-NTO
S_1	$^{1}(n\pi^{*})$	99.5%		
S_2	$^{1}(\pi\pi^{*})$	100.0%		
S_3	$^{1}(\pi\pi^{*})$	92.8%		
S_4	$^{1}(\pi\pi^{*})$	92.4%		
S_5	$^{1}(\pi\pi^{*})$	94.5%		

Table S3. Natural transition orbital (NTO, hole and electron wave functions) pairs for main excited state of optimized geometry in the hydrogen abstraction reaction (isovalue = 0.05 e·Å^{-3}). *w* denotes the square of the singular value for a given NTO pair, i.e. the associated weight for each NTO pair.

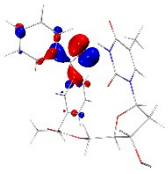
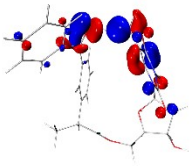
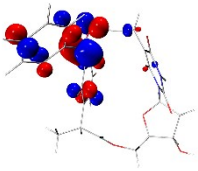
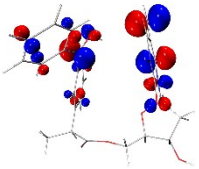
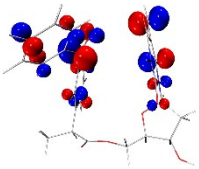
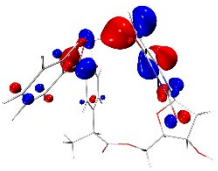
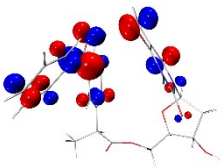
Geometry	Excited State	Nature	*w*	Hole-NTO	Electron-NTO
$^{3}RC^{*}$	T_1	$^{3}(n\pi^{*})$	98.4%		
$^{3}TS^{*}$	T_1	$^{3}(\pi\pi^{*})$	100.5%		
$^{3}IM^{*}$	T_1	$^{3}(\pi\pi^{*})$	172.2%		
ISC^{T_1/S_0}	T_1	$^{3}(\pi\pi^{*})$	100.5%		

Table S4. Mulliken charges and spin densities of main intermediates in the hydrogen abstraction reaction of BZP-Thy dyad.

		H	Thy	BZP	Bridge
$^{3}RC^{*}$	Charges	0.18	-0.40	0.04	0.18
	Spin densities	0.00	0.00	2.00	0.00
$^{3}TS^{*}$	Charges	0.31	-0.20	-0.30	0.20
	Spin densities	-0.02	0.56	1.46	0.00
$^{3}IM^{*}$	Charges	0.43	-0.23	-0.38	0.18
	Spin densities	0.00	1.00	1.00	0.00

Bridge stands for the covalently linked fragment in BZP-Thy structure, except the BZP and thymine fragments. On the bridge, Mulliken charge values of these intermediates are almost unchanged and the spin density is zero. This indicates that all electrons on this part are paired. Thy represents the remaining part after the H3 atom on the methyl of thymine loses.

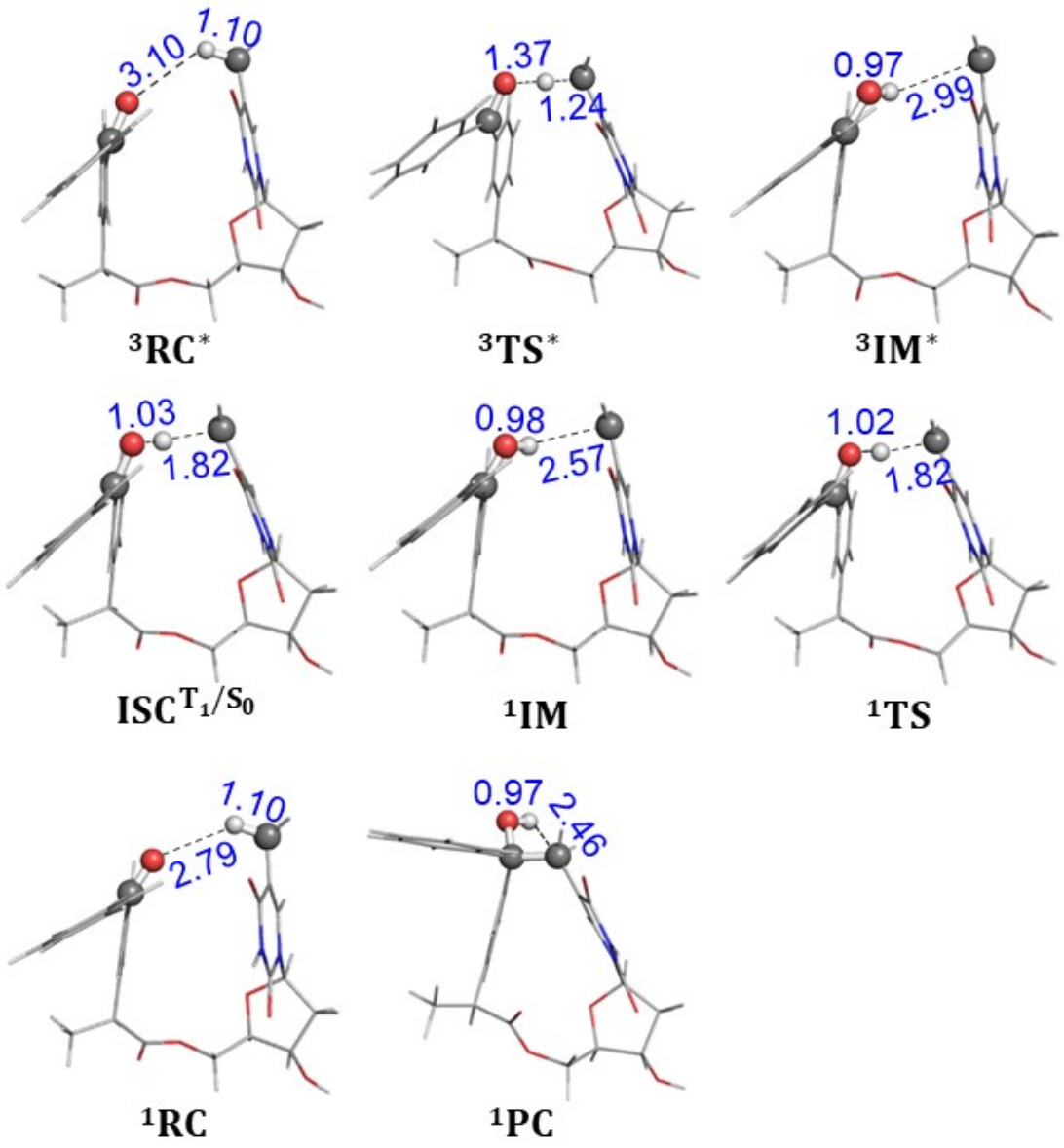


Figure S1. Optimized geometries of the hydrogen abstraction reaction with the bond lengths of O2-H3 and C4-H3 (Units in Å).

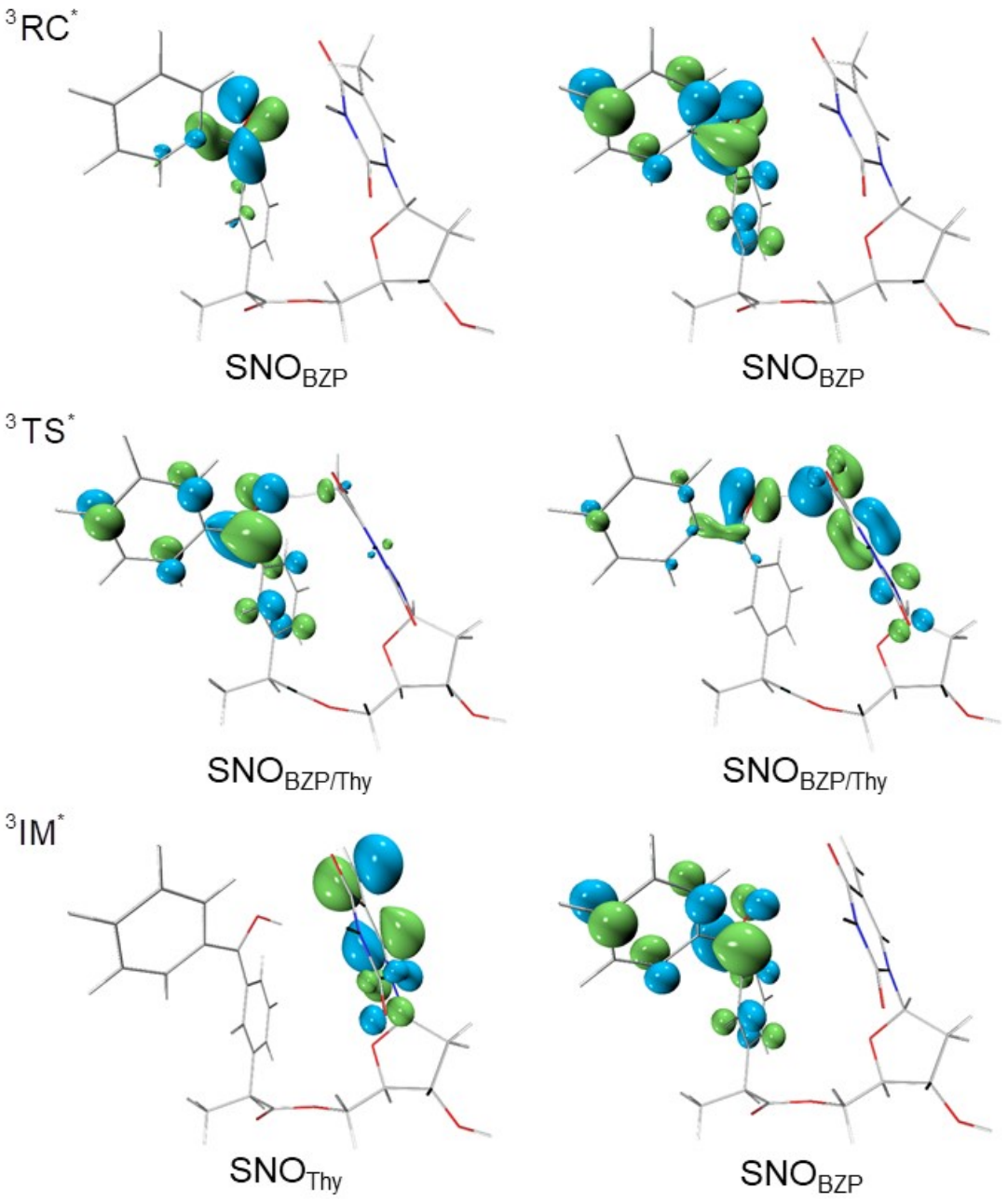


Figure S2. Spin natural orbitals (SNO) of $^3RC^*$, $^3TS^*$ and $^3IM^*$ in the hydrogen abstraction reaction and their occupation numbers are 1.00. The positive occupation numbers refer to α spin.

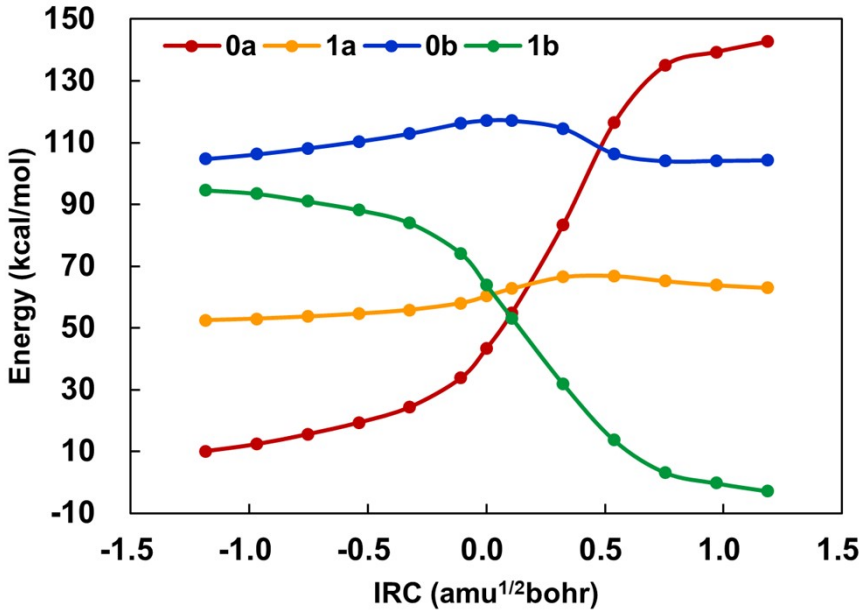


Figure S3. Diabatic potential energy surfaces along with IRC in the hydrogen abstraction reaction between BZP and thymine molecules. 0a (red line), 1a (yellow line), 0b (blue line) and 1b (green line) represent reactant state, electron transfer state, proton transfer state and product state, respectively. The energy is relative to the first structure of the Eg ground-state potential energy profile. The linking bridge of BZP-Thy was omitted in the MSDFT calculation.

From the adiabatic perspective of Born-Oppenheimer approximation, DFT calculation provides evidence of spin natural orbitals, Mulliken charges, spin densities, etc for HAT mechanistic investigation. In MSDFT, static electron correlation is treated through configuration interaction and the various diabatic states can be applied to further analysis of hydrogen abstraction with electronically non-adiabatic character. The reaction mechanism of hydrogen abstraction is divided into HAT and concerted-asynchronous electron-proton transfer (CEPT)[9-11]. The energy for the electron transfer state (1a) is always lower than that for the proton transfer state (0b).

Cartesian Coordinates

^{1}RC				^{1}RC*			
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C	-1.039332	4.788615	-0.465493	C	4.878051	-2.540192	-0.217671
H	-1.604195	5.333751	0.296722	H	5.658752	-2.430255	0.540964
H	-0.537095	5.516479	-1.111203	H	4.973371	-3.531775	-0.672427
H	-1.743151	4.218641	-1.078469	H	5.041242	-1.788987	-0.995624
O	1.981668	2.703777	-0.328211	O	1.210776	-2.834012	-0.024746
C	2.781296	1.805204	-1.131781	C	0.068507	-2.904807	-0.907636
H	2.126427	1.178322	-1.738326	H	-0.026779	-1.964566	-1.456214
H	3.431192	2.396800	-1.785312	H	0.209272	-3.723952	-1.619806
O	2.737921	0.172329	0.630170	O	-1.417528	-2.023856	0.770449
C	4.545533	-0.018590	-0.940420	C	-2.425262	-3.365353	-0.930189
C	4.445301	-1.316146	-0.114111	C	-3.537213	-2.741617	-0.067831
H	4.181396	-0.190697	-1.956684	H	-2.332722	-2.821928	-1.874925
H	5.300065	-1.352865	0.568219	H	-4.011190	-3.538307	0.513495
H	4.453551	-2.218401	-0.727355	H	-4.307503	-2.238262	-0.654548
O	5.847455	0.557501	-0.968413	O	-2.570370	-4.760901	-1.164064
H	6.371018	0.069048	-1.622808	H	-3.206547	-4.874744	-1.887270
N	2.031802	-2.062784	0.340685	N	-3.073575	-0.342295	0.689232
C	1.564832	-2.066253	-0.969636	C	-2.798656	0.240577	-0.543538
O	2.097745	-1.449717	-1.885686	O	-2.373642	-0.380994	-1.512729
N	0.436283	-2.840181	-1.165780	N	-3.050415	1.598513	-0.593857
H	0.087435	-2.858043	-2.118543	H	-2.852852	2.041605	-1.484992
C	3.614384	0.955135	-0.193268	C	-1.165974	-3.156486	-0.071531
H	4.227084	1.596720	0.454093	H	-1.019573	-4.049680	0.552591
C	1.343886	-2.733218	1.338778	C	-3.526479	0.422110	1.751885
H	1.775775	-2.629557	2.328099	H	-3.685010	-0.134476	2.669030
C	-0.015960	3.859547	0.206162	O	2.659757	3.758906	0.916414
H	0.690330	4.457840	0.790682	C	3.493755	-2.363109	0.427861
C	-0.674938	2.858636	1.155996	H	3.345484	-3.143020	1.183097
C	-1.441124	1.796599	0.657366	C	3.362549	-1.010818	1.131511
C	-0.538413	2.997083	2.541727	C	2.977657	0.126236	0.429944
C	-2.044475	0.872420	1.522564	C	3.698400	-0.905029	2.494162
H	-1.536357	1.668940	-0.416243	C	2.896207	1.394384	1.070533
C	-1.142162	2.085984	3.414038	H	2.759843	0.051532	-0.629907
H	0.047238	3.820112	2.943383	C	3.664311	0.342093	3.129570
C	-1.878152	1.019168	2.909595	H	3.994311	-1.791521	3.048174
H	-1.025623	2.208137	4.487065	C	3.273314	1.481167	2.442070
H	-2.333527	0.291944	3.573699	H	3.936565	0.417573	4.179060
C	3.157242	-1.177433	0.715725	H	3.226827	2.438573	2.951298
H	3.346417	-1.422868	1.763615	C	2.485586	2.569806	0.374383

C	-0.306697	-3.551306	-0.215242	C	1.802184	2.663423	-0.922489
O	-1.313389	-4.171157	-0.554884	C	2.059507	3.776651	-1.758951
C	0.223496	-3.466376	1.138675	C	0.823397	1.723076	-1.315841
C	-0.515995	-4.166806	2.242411	C	1.391903	3.911122	-2.973781
H	0.014334	-4.070096	3.193968	H	2.804100	4.506760	-1.460959
H	-1.518688	-3.740119	2.359562	C	0.177783	1.860446	-2.539745
H	-0.638466	-5.232746	2.019800	H	0.566699	0.899689	-0.658620
C	0.797323	3.094430	-0.834307	C	0.455737	2.954243	-3.373008
O	0.416725	2.828024	-1.958292	H	1.608176	4.762544	-3.612691
O	-2.803988	-1.359409	1.695295	H	-0.561325	1.119329	-2.830755
C	-2.787230	-0.329434	1.021108	H	-0.060604	3.058556	-4.322734
C	-3.504902	-0.286544	-0.291730	C	-2.809415	-1.781318	0.893484
C	-3.639802	-1.484397	-1.015147	H	-3.116830	-1.965026	1.926353
C	-4.107917	0.883467	-0.782018	C	-3.523941	2.436275	0.425883
C	-4.342282	-1.503319	-2.217277	O	-3.694094	3.633805	0.213857
H	-3.173611	-2.387306	-0.633428	C	-3.768538	1.752377	1.689310
C	-4.830185	0.855554	-1.975784	C	-4.267551	2.558256	2.854517
H	-4.035631	1.808771	-0.219632	H	-4.405646	1.929096	3.738127
C	-4.941748	-0.334285	-2.698364	H	-3.563652	3.359728	3.107033
H	-4.426532	-2.428919	-2.779853	H	-5.224572	3.037835	2.618215
H	-5.305191	1.762051	-2.339798	C	2.387185	-2.530569	-0.606087
H	-5.495759	-0.352352	-3.632857	O	2.520109	-2.380137	-1.805989

^{3}RC *

C	-0.665646	5.007428	-0.169188
H	-1.174907	5.527750	0.647630
H	-0.115311	5.746117	-0.761029
H	-1.421211	4.549216	-0.813553
O	2.125835	2.597741	-0.241004
C	2.796499	1.676194	-1.130279
H	2.053962	1.133392	-1.717883
H	3.455626	2.235395	-1.802776
O	2.714487	-0.018538	0.570089
C	4.392015	-0.305359	-1.120476
C	4.258792	-1.609197	-0.309487
H	3.929805	-0.425576	-2.103790
H	5.156577	-1.722465	0.305964
H	4.155096	-2.496761	-0.935491
O	5.727742	0.169380	-1.251379
H	6.150461	-0.335513	-1.963633
N	1.841077	-2.197273	0.317411
C	1.271029	-2.138859	-0.950672

^{3}TS *

C	-0.693144	4.295000	-0.412201
H	-1.324852	4.766953	0.346536
H	-0.180124	5.084387	-0.972353
H	-1.334892	3.749694	-1.109252
O	2.490026	2.667578	-0.433941
C	3.386413	1.777459	-1.135971
H	2.826214	1.221538	-1.888581
H	4.158707	2.384461	-1.616908
O	2.937335	0.195720	0.601897
C	4.887453	-0.264392	-0.720984
C	4.499383	-1.523513	0.085968
H	4.647199	-0.405637	-1.778024
H	5.240368	-1.659500	0.879402
H	4.469349	-2.430545	-0.518410
O	6.247357	0.124699	-0.566242
H	6.783536	-0.439962	-1.144844
N	1.949442	-1.902149	0.216832
C	1.717320	-1.970848	-1.165970

O	1.761930	-1.525193	-1.891330	O	2.500114	-1.540744	-1.998261
N	0.089823	-2.847402	-1.072266	N	0.529356	-2.582724	-1.514006
H	-0.336291	-2.818750	-1.992803	H	0.361485	-2.656285	-2.512717
C	3.605184	0.717460	-0.280101	C	4.005014	0.840843	-0.109702
H	4.315275	1.274817	0.346009	H	4.605060	1.412382	0.610009
C	1.206758	-2.868450	1.349026	C	0.985180	-2.280629	1.107886
H	1.723040	-2.817597	2.301271	H	1.230354	-2.113908	2.150448
C	0.287291	3.945944	0.400050	C	0.325536	3.359452	0.259843
H	1.047497	4.433615	1.019594	H	0.995639	3.950538	0.890241
C	-0.433040	2.918300	1.274352	C	-0.320313	2.283847	1.139750
C	-1.252021	1.951453	0.695222	C	-1.323505	1.455738	0.635643
C	-0.264764	2.933927	2.670905	C	0.122241	2.099882	2.459866
C	-1.933983	0.996397	1.489107	C	-1.934334	0.451054	1.430288
H	-1.346945	1.907922	-0.385158	H	-1.623314	1.559545	-0.400944
C	-0.915324	1.986039	3.467779	C	-0.435788	1.086801	3.248872
H	0.378696	3.680540	3.128082	H	0.903604	2.738075	2.863551
C	-1.735913	1.022407	2.896397	C	-1.440858	0.268202	2.749496
H	-0.780349	2.005520	4.545785	H	-0.088429	0.947942	4.269592
H	-2.252554	0.300067	3.519431	H	-1.890725	-0.491891	3.379682
C	3.047645	-1.394096	0.615736	C	3.149354	-1.190004	0.738862
H	3.296528	-1.665425	1.644781	H	3.157691	-1.448762	1.800386
C	-0.601889	-3.561197	-0.085842	C	-0.494654	-3.033730	-0.675174
O	-1.659101	-4.128095	-0.357774	O	-1.513670	-3.526348	-1.141081
C	0.041102	-3.545311	1.220728	C	-0.216768	-2.844322	0.754220
C	-0.630965	-4.261150	2.357278	C	-1.241011	-3.185110	1.723501
H	-0.045303	-4.177836	3.276986	H	-0.901898	-3.212471	2.760191
H	-1.627047	-3.842211	2.540896	H	-2.131966	-2.318705	1.692504
H	-0.766739	-5.324366	2.128094	H	-1.841019	-4.055609	1.447279
C	1.023678	3.208842	-0.714678	C	1.186068	2.656800	-0.786579
O	0.650835	3.131451	-1.869642	O	0.753234	2.128987	-1.792308
O	-2.875393	-1.156611	1.617299	O	-3.269219	-1.566820	1.515222
C	-2.738724	-0.047621	0.896125	C	-3.015405	-0.376942	0.938017
C	-3.431088	-0.059584	-0.377180	C	-3.979680	-0.002219	-0.080612
C	-3.708473	-1.298741	-1.017344	C	-4.700004	-1.021564	-0.761159
C	-3.914556	1.133117	-0.974222	C	-4.297686	1.346061	-0.393984
C	-4.406299	-1.327336	-2.219880	C	-5.651985	-0.706561	-1.723243
H	-3.333372	-2.218877	-0.581728	H	-4.472463	-2.056704	-0.532887
C	-4.592767	1.086711	-2.184203	C	-5.247745	1.649156	-1.361434
H	-3.760324	2.084628	-0.476231	H	-3.810915	2.151176	0.145827
C	-4.848401	-0.141244	-2.815632	C	-5.932344	0.628996	-2.037109
H	-4.596536	-2.281598	-2.703765	H	-6.176396	-1.506755	-2.239558
H	-4.941209	2.011302	-2.636383	H	-5.471554	2.689931	-1.581437
H	-5.388277	-0.168087	-3.757515	H	-6.676066	0.872890	-2.790351

^{3}IM*				^{1}IM			
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C	-0.648919	4.947340	-0.180670	C	-0.699752	4.748895	-0.294688
H	-1.156675	5.463916	0.639499	H	-1.236976	5.267779	0.504999
H	-0.114487	5.691357	-0.780575	H	-0.173372	5.495693	-0.898631
H	-1.405231	4.478150	-0.816197	H	-1.430240	4.247803	-0.935768
O	2.185711	2.595077	-0.274958	O	2.259213	2.596544	-0.340183
C	2.860027	1.666153	-1.153032	C	3.003468	1.672138	-1.165591
H	2.121800	1.137395	-1.758576	H	2.312394	1.106294	-1.792131
H	3.542223	2.217257	-1.808941	H	3.694196	2.237563	-1.799897
O	2.710574	-0.024001	0.543339	O	2.833540	0.040735	0.583413
C	4.419997	-0.347354	-1.105513	C	4.611256	-0.302023	-0.993912
C	4.259855	-1.640040	-0.280613	C	4.403874	-1.587658	-0.166849
H	3.968898	-0.473532	-2.093274	H	4.228343	-0.441250	-2.008333
H	5.145756	-1.754737	0.351494	H	5.254779	-1.696269	0.512602
H	4.157518	-2.534216	-0.897175	H	4.333821	-2.487002	-0.779930
O	5.762627	0.109554	-1.223678	O	5.958100	0.157773	-1.028266
H	6.188370	-0.406867	-1.925775	H	6.433011	-0.372059	-1.687585
N	1.825422	-2.198501	0.319193	N	1.931535	-2.120209	0.305935
C	1.289913	-2.171768	-0.962314	C	1.486033	-2.128433	-1.010585
O	1.805320	-1.586308	-1.907117	O	2.086729	-1.601075	-1.938978
N	0.105330	-2.881543	-1.105454	N	0.289553	-2.802784	-1.208975
H	-0.280757	-2.879189	-2.044133	H	-0.026525	-2.832351	-2.173102
C	3.634711	0.693580	-0.286958	C	3.771863	0.747531	-0.241029
H	4.341323	1.238607	0.353894	H	4.440150	1.330812	0.406396
C	1.167844	-2.823600	1.360111	C	1.165488	-2.650312	1.323879
H	1.653661	-2.748245	2.324929	H	1.580986	-2.542803	2.318133
C	0.323177	3.900680	0.382838	C	0.289985	3.740458	0.308074
H	1.082856	4.399817	0.993598	H	1.030055	4.273198	0.913300
C	-0.373608	2.862489	1.265373	C	-0.392981	2.708522	1.209960
C	-1.222453	1.912611	0.696660	C	-1.290238	1.784853	0.672679
C	-0.152349	2.845375	2.650794	C	-0.113309	2.675403	2.584620
C	-1.865604	0.923767	1.481239	C	-1.938314	0.818461	1.481854
H	-1.352029	1.897608	-0.380439	H	-1.460930	1.777631	-0.398392
C	-0.776596	1.879321	3.445561	C	-0.731552	1.723142	3.400776
H	0.508293	3.579980	3.103192	H	0.585534	3.388931	3.012613
C	-1.615286	0.927155	2.877870	C	-1.627184	0.804559	2.866328
H	-0.609099	1.874139	4.519229	H	-0.517312	1.705766	4.466005
H	-2.114391	0.205387	3.518167	H	-2.124001	0.096476	3.522925
C	3.036378	-1.398712	0.621352	C	3.138242	-1.337139	0.669700
H	3.266011	-1.653842	1.658787	H	3.310502	-1.598141	1.716572
C	-0.625945	-3.566598	-0.139383	C	-0.550869	-3.387809	-0.265562
O	-1.661600	-4.147941	-0.437693	O	-1.591405	-3.932912	-0.610207

C	-0.035693	-3.508618	1.218225	C	-0.062289	-3.274350	1.128531
C	-0.710146	-4.128562	2.270799	C	-0.853500	-3.778437	2.163266
H	-0.311720	-4.114522	3.279053	H	-0.524834	-3.730174	3.195549
H	-2.009192	-1.441115	2.117333	H	-2.188876	-1.581793	2.091380
H	-1.641440	-4.646992	2.082540	H	-1.787910	-4.274335	1.933520
C	1.057869	3.168972	-0.736192	C	1.052265	2.997320	-0.784457
O	0.664740	3.063858	-1.882185	O	0.619784	2.751706	-1.894290
O	-2.791490	-1.308908	1.554452	O	-3.007147	-1.347003	1.615324
C	-2.686714	-0.111042	0.891252	C	-2.838955	-0.170151	0.930859
C	-3.461055	-0.037337	-0.322722	C	-3.651593	-0.057212	-0.256824
C	-3.869031	-1.230384	-0.976389	C	-4.144084	-1.230045	-0.887435
C	-3.886118	1.196547	-0.880327	C	-4.033857	1.194135	-0.805506
C	-4.635660	-1.182380	-2.135089	C	-4.950404	-1.148914	-2.016850
H	-3.550851	-2.185622	-0.573964	H	-3.857749	-2.197062	-0.489776
C	-4.651955	1.230940	-2.040244	C	-4.841102	1.262521	-1.935766
H	-3.638607	2.126182	-0.379219	H	-3.721697	2.112106	-0.319374
C	-5.031332	0.045058	-2.680407	C	-5.304075	0.094922	-2.553805
H	-4.923727	-2.110275	-2.622847	H	-5.303001	-2.063005	-2.487935
H	-4.968454	2.190322	-2.441245	H	-5.124036	2.235030	-2.330162
H	-5.630218	0.077132	-3.586131	H	-5.934940	0.153714	-3.436186

^{1}TS

C	-0.473429	4.552459	-0.463180
H	-1.022378	5.109052	0.302423
H	0.082239	5.268488	-1.078367
H	-1.194588	4.040237	-1.105898
O	2.532701	2.579465	-0.500123
C	3.312126	1.601612	-1.226205
H	2.668031	1.082994	-1.937444
H	4.109170	2.128372	-1.758810
O	2.811299	0.052341	0.521186
C	4.686483	-0.526866	-0.849420
C	4.314188	-1.733916	0.036733
H	4.352316	-0.698254	-1.876218
H	5.095476	-1.855139	0.793263
H	4.224824	-2.666104	-0.521884
O	6.067448	-0.185154	-0.821363
H	6.533441	-0.790739	-1.418899
N	1.775802	-2.049547	0.340805
C	1.451616	-2.176427	-1.007510
O	2.174651	-1.802736	-1.922637
N	0.229336	-2.785399	-1.242939

ISC$^{T_1/S_0}$

C	-0.699752	4.748895	-0.294688
H	-1.236976	5.267779	0.504999
H	-0.173372	5.495693	-0.898631
H	-1.430240	4.247803	-0.935768
O	2.259213	2.596544	-0.340183
C	3.003468	1.672138	-1.165591
H	2.312394	1.106294	-1.792131
H	3.694196	2.237563	-1.799897
O	2.833540	0.040735	0.583413
C	4.611256	-0.302023	-0.993912
C	4.403874	-1.587658	-0.166849
H	4.228343	-0.441250	-2.008333
H	5.254779	-1.696269	0.512602
H	4.333821	-2.487002	-0.779930
O	5.958100	0.157773	-1.028266
H	6.433011	-0.372059	-1.687585
N	1.931535	-2.120209	0.305935
C	1.486033	-2.128433	-1.010585
O	2.086729	-1.601075	-1.938978
N	0.289553	-2.802784	-1.208975

H	-0.003138	-2.908915	-2.223229	H	-0.026525	-2.832351	-2.173102
C	3.896586	0.631772	-0.214531	C	3.771863	0.747531	-0.241029
H	4.556972	1.165300	0.482807	H	4.440150	1.330812	0.406396
C	0.869823	-2.381495	1.324967	C	1.165488	-2.650312	1.323879
H	1.197861	-2.177610	2.337036	H	1.580986	-2.542803	2.318133
C	0.484818	3.549738	0.202001	C	0.289985	3.740458	0.308074
H	1.226540	4.094272	0.792920	H	1.030055	4.273198	0.913300
C	-0.236694	2.573629	1.136204	C	-0.392981	2.708522	1.209960
C	-1.219045	1.712414	0.644615	C	-1.290238	1.784853	0.672679
C	0.087561	2.530780	2.500581	C	-0.113309	2.675403	2.584620
C	-1.913338	0.816542	1.492873	C	-1.938314	0.818461	1.481854
H	-1.423085	1.701958	-0.419731	H	-1.460930	1.777631	-0.398392
C	-0.569563	1.637053	3.352624	C	-0.731552	1.723142	3.400776
H	0.852208	3.194450	2.895294	H	0.585534	3.388931	3.012613
C	-1.555989	0.788874	2.863968	C	-1.627184	0.804559	2.866328
H	-0.313835	1.613432	4.408452	H	-0.517312	1.705766	4.466005
H	-2.082015	0.119342	3.536351	H	-2.124001	0.096476	3.522925
C	3.007714	-1.331558	0.742032	C	3.138242	-1.337139	0.669700
H	3.080047	-1.516617	1.816727	H	3.310502	-1.598141	1.716572
C	-0.741623	-3.182360	-0.323514	C	-0.550869	-3.387809	-0.265562
O	-1.790176	-3.688574	-0.705343	O	-1.591405	-3.932912	-0.610207
C	-0.378236	-2.925056	1.084418	C	-0.062289	-3.274350	1.128531
C	-1.325296	-3.196132	2.098210	C	-0.853500	-3.778437	2.163266
H	-1.034279	-3.114143	3.141413	H	-0.524834	-3.730174	3.195549
H	-2.407316	-1.738194	1.996880	H	-2.188876	-1.581793	2.091380
H	-2.172120	-3.830043	1.859364	H	-1.787910	-4.274335	1.933520
C	1.240692	2.744474	-0.850171	C	1.052265	2.997320	-0.784457
O	0.738692	2.282948	-1.856875	O	0.619784	2.751706	-1.894290
O	-3.225897	-1.182124	1.734004	O	-3.007147	-1.347003	1.615324
C	-2.929524	-0.094049	0.998192	C	-2.838955	-0.170151	0.930859
C	-3.711793	0.063956	-0.215499	C	-3.651593	-0.057212	-0.256824
C	-4.267473	-1.081331	-0.838090	C	-4.144084	-1.230045	-0.887435
C	-4.003607	1.330366	-0.778890	C	-4.033857	1.194135	-0.805506
C	-5.046239	-0.963288	-1.983634	C	-4.950404	-1.148914	-2.016850
H	-4.050726	-2.058409	-0.421640	H	-3.857749	-2.197062	-0.489776
C	-4.791760	1.438641	-1.920648	C	-4.841102	1.262521	-1.935766
H	-3.641046	2.231190	-0.295725	H	-3.721697	2.112106	-0.319374
C	-5.313934	0.295392	-2.535060	C	-5.304075	0.094922	-2.553805
H	-5.447217	-1.857888	-2.453020	H	-5.303001	-2.063005	-2.487935
H	-5.010139	2.422553	-2.327130	H	-5.124036	2.235030	-2.330162
H	-5.927326	0.384373	-3.427211	H	-5.934940	0.153714	-3.436186

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^{1}PC

C	-0.774234	3.121522	-2.243084
H	-1.493693	3.875533	-1.909737
H	-0.266868	3.500637	-3.136937
H	-1.322047	2.216732	-2.520060
O	2.510633	2.159711	-1.354159
C	3.541336	1.151681	-1.451397
H	3.132864	0.259151	-1.924838
H	4.342951	1.567830	-2.067345
O	2.934251	0.593489	0.827073
C	4.993553	-0.365169	0.024068
C	4.338101	-1.285785	1.080031
H	5.037572	-0.871042	-0.944564
H	4.874555	-1.140843	2.022845
H	4.371514	-2.341806	0.815127
O	6.288671	0.096785	0.399194
H	6.910289	-0.636568	0.266791
N	1.799885	-1.500608	0.638724
C	1.934802	-2.159745	-0.580927
O	2.969232	-2.196223	-1.236194
N	0.788141	-2.813472	-0.988554
H	0.884382	-3.357039	-1.840080
C	4.050579	0.856012	-0.042399
H	4.564635	1.735604	0.358685
C	0.556571	-1.376947	1.224909
H	0.552159	-0.778160	2.128670
C	0.241722	2.833380	-1.121510
H	0.808719	3.743604	-0.908533
C	-0.426947	2.375656	0.176805
C	-1.229627	1.228806	0.207726
C	-0.258346	3.111732	1.356341
C	-1.875147	0.809796	1.379616
H	-1.356058	0.652203	-0.702238
C	-0.892218	2.707323	2.530882
H	0.360220	4.005675	1.352567
C	-1.699041	1.566852	2.544161
H	-0.767442	3.288382	3.440624
H	-2.208373	1.291229	3.461557
C	2.917079	-0.744283	1.272538
H	2.644384	-0.729622	2.329115
C	-0.484806	-2.802009	-0.405348
O	-1.375394	-3.501178	-0.887183
C	-0.591639	-1.934569	0.760979
H	-3.137448	-0.617593	3.296435

C	1.236925	1.766918	-1.567728
O	0.920730	0.693851	-2.045416
O	-3.658704	-0.464005	2.491023
C	-2.757789	-0.454790	1.365174
C	-3.711754	-0.403521	0.160860
C	-3.761130	-1.371884	-0.845202
C	-4.611647	0.675465	0.096984
C	-4.682036	-1.260025	-1.895253
H	-3.085687	-2.219622	-0.831590
C	-5.532974	0.782307	-0.941511
H	-4.586857	1.434473	0.872907
C	-5.570689	-0.188576	-1.948274
H	-4.699174	-2.021868	-2.670513
H	-6.220807	1.623523	-0.967473
H	-6.285414	-0.106168	-2.762820
C	-1.896786	-1.770737	1.506562
H	-2.546750	-2.622321	1.289544
H	-1.662308	-1.829281	2.575961

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