Supplementary Material (ESI) for PCCP

ESI

Comparison of the non-radiative decay mechanisms of 4-pyrimidinone and uracil: an *ab initio* study

Vassil B. Delchev, Andrzej L. Sobolewski and Wolfgang Domcke

Table S1 Vertical excitation energies of 4Py and U (eV), calculated with the ground state geometries of the compounds, studied at CASPT2//CASSCF level

State	Ur				Exp.
	CASPT2(10,9)		CC2		
	cc-pVDZ	aug-cc-pVDZ	cc-pVDZ	aug-cc-pVDZ	
$^1n_O\pi^*$	4.930	4.740	4.914	4.706	
$^1\pi\pi^*$	5.301	4.826	5.540	5.226	5.08
$^1\pi\sigma^*$	7.109	5.690	7.221	5.814	
	4Py				
	CASPT2(8,7)		CC2		
$^1n_O\pi^*$	4.903	4.679	4.770	4.594	
$^1\pi\pi^*$	5.028	4.515	4.879	4.672	4.51
$^1\pi\sigma^*$	7.504	5.936	7.519	5.882	

Table S2 Vertical excitation energies of 4Py and U (eV), calculated with the ground state geometries of the compounds, studied at CASPT2//MP2 level

State	U				Exp.
	CASPT2(10,9)		CC2		
	cc-pVDZ	aug-cc-pVDZ	cc-pVDZ	aug-cc-pVDZ	
$^1n_O\pi^*$	4.77	4.74	4.91	4.71	
$^1\pi\pi^*$	5.18	4.80	5.54	5.23	5.08
$^1\pi\sigma^*$	-	5.66	-	5.81	
	4Py				
	CASPT2(8,7)		CC2		
$^1n_O\pi^*$	4.87	4.77	4.77	4.59	
$^1\pi\pi^*$	4.47	4.30	4.88	4.67	4.51
$^1\pi\sigma^*$	-	5.84	-	5.88	

Table S3 Adiabatic excitation energies (in eV) of the $^1n_O\pi^*$ (A"), $^1\pi\pi^*$ (A'), and $^1\pi\sigma^*$ (A") states of U and 4Py, studied at CASPT2//CASSCF level.

State	U	
	CASPT2(10,9)/aug-cc-pVDZ	CC2/aug-cc-pVDZ
$^1n_O\pi^*$	3.06	2.37
$^1\pi\pi^*$	3.72	4.34
$^1\pi\sigma^*$	5.15	5.31
	4Py	
	CASPT2(8,7)/aug-cc-pVDZ	CC2/aug-cc-pVDZ
$^1n_O\pi^*$	3.18	2.09
$^1\pi\pi^*$	2.77	2.85
$^1\pi\sigma^*$	5.22	5.24

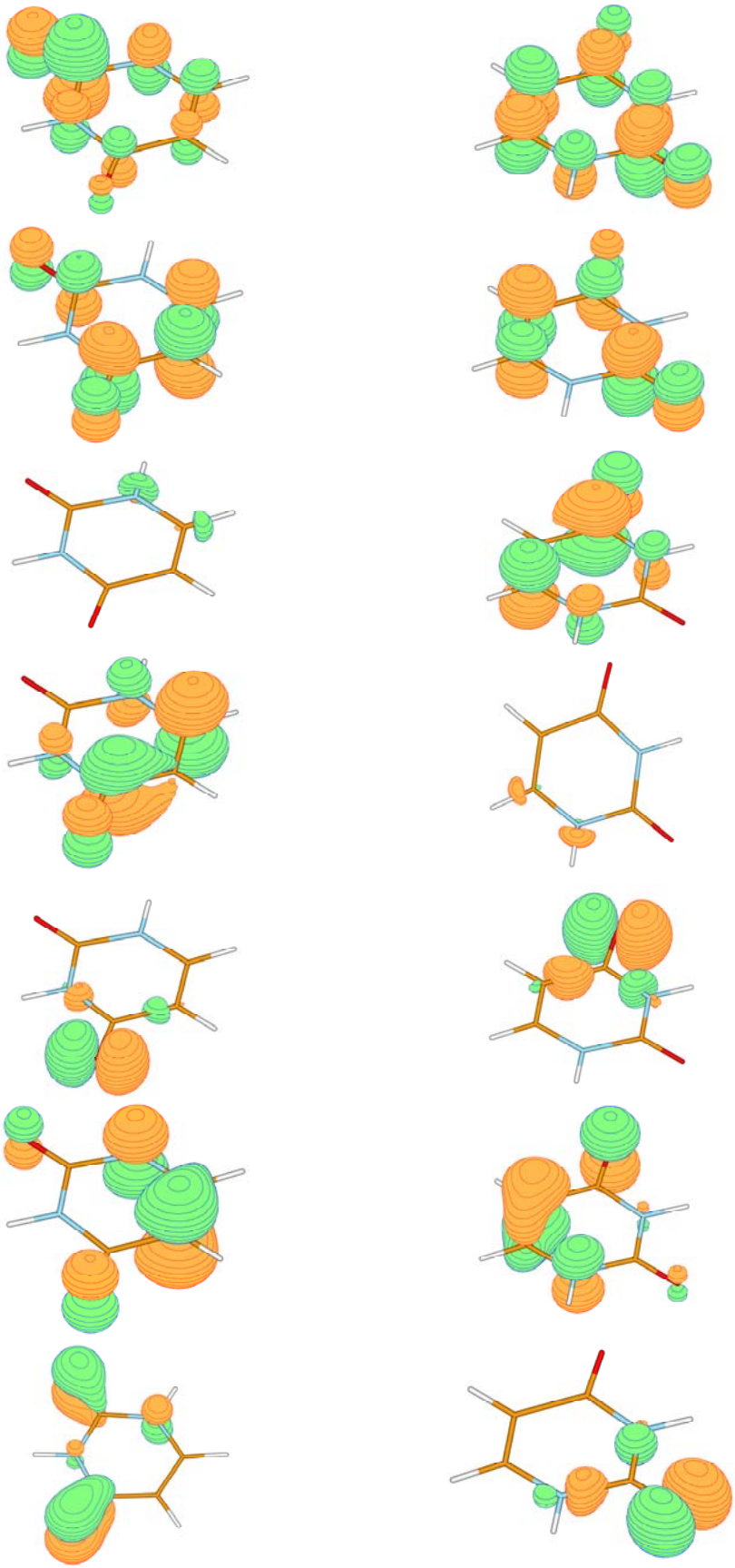
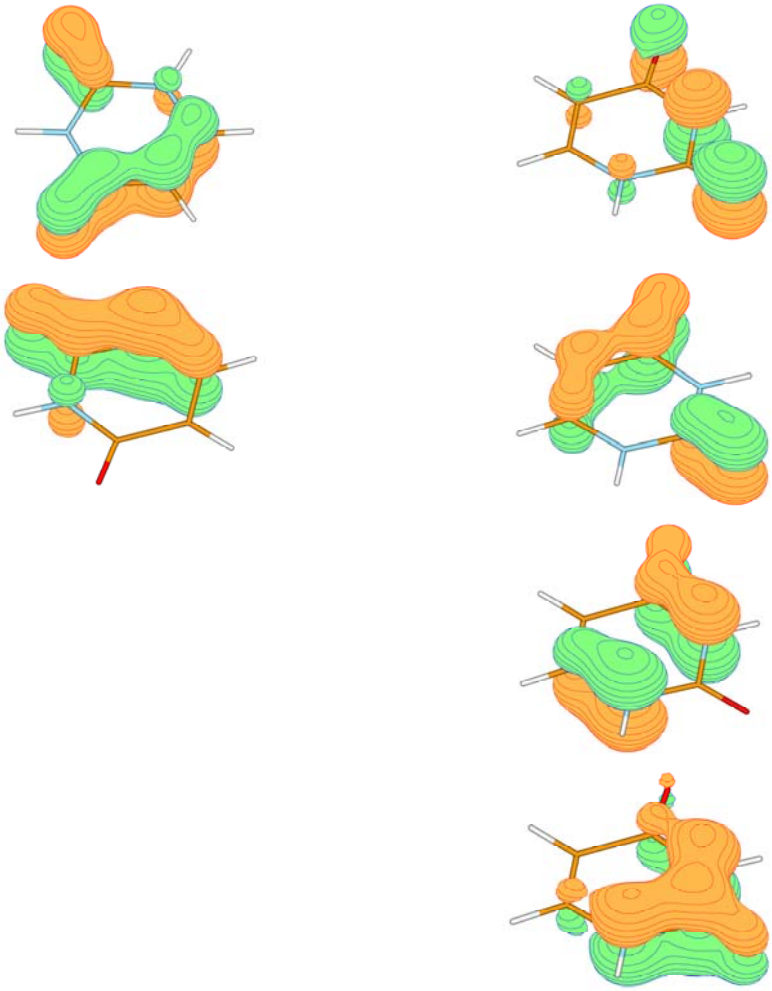


Fig. S1 *(Continued)*



CASSCF(10,9) CASSCF(14,11)

Fig. S1 State-averaged active molecular orbitals of U, obtained with the aug-cc-pVDZ basis set at the ground-state equilibrium geometry.

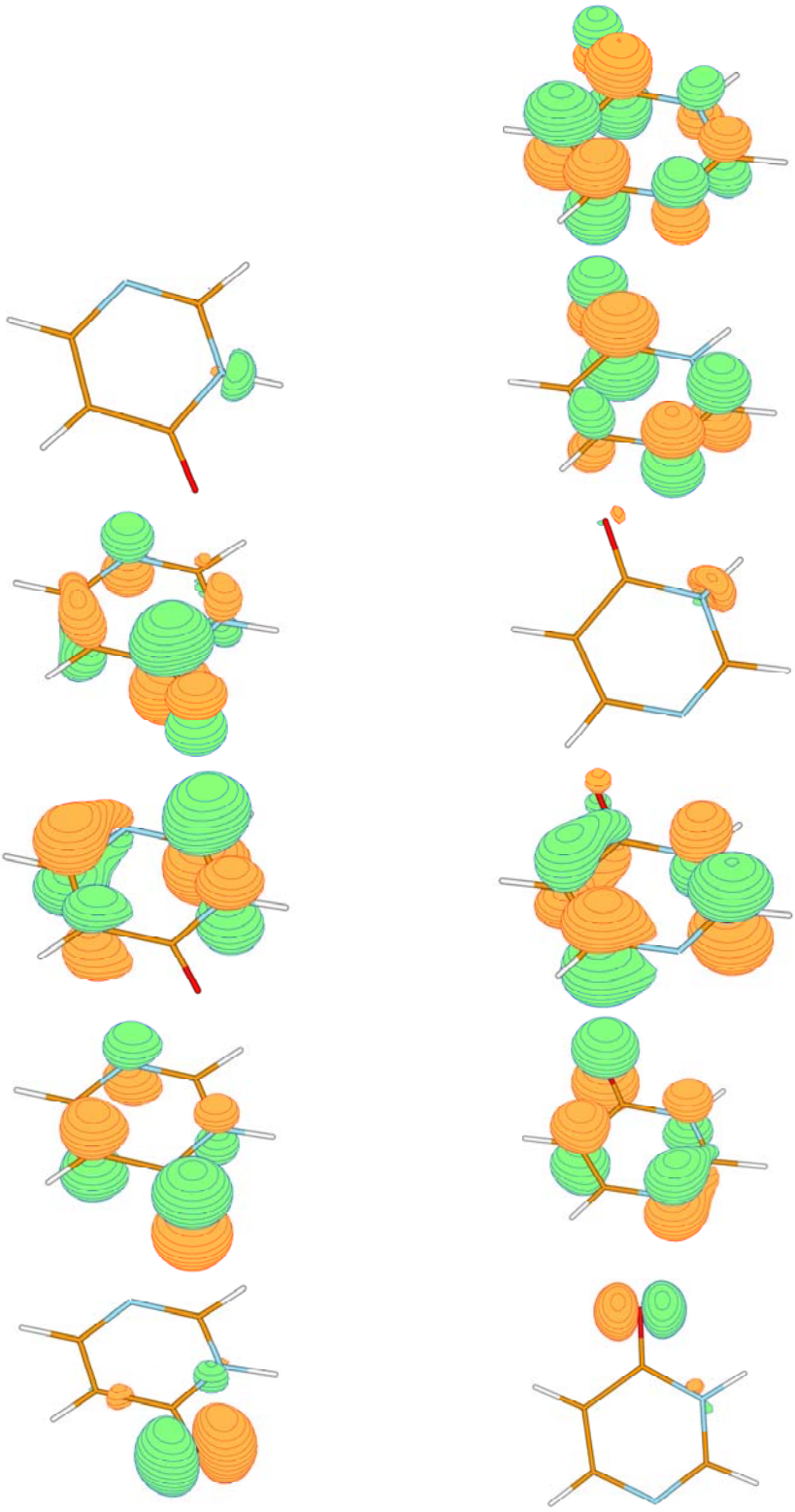
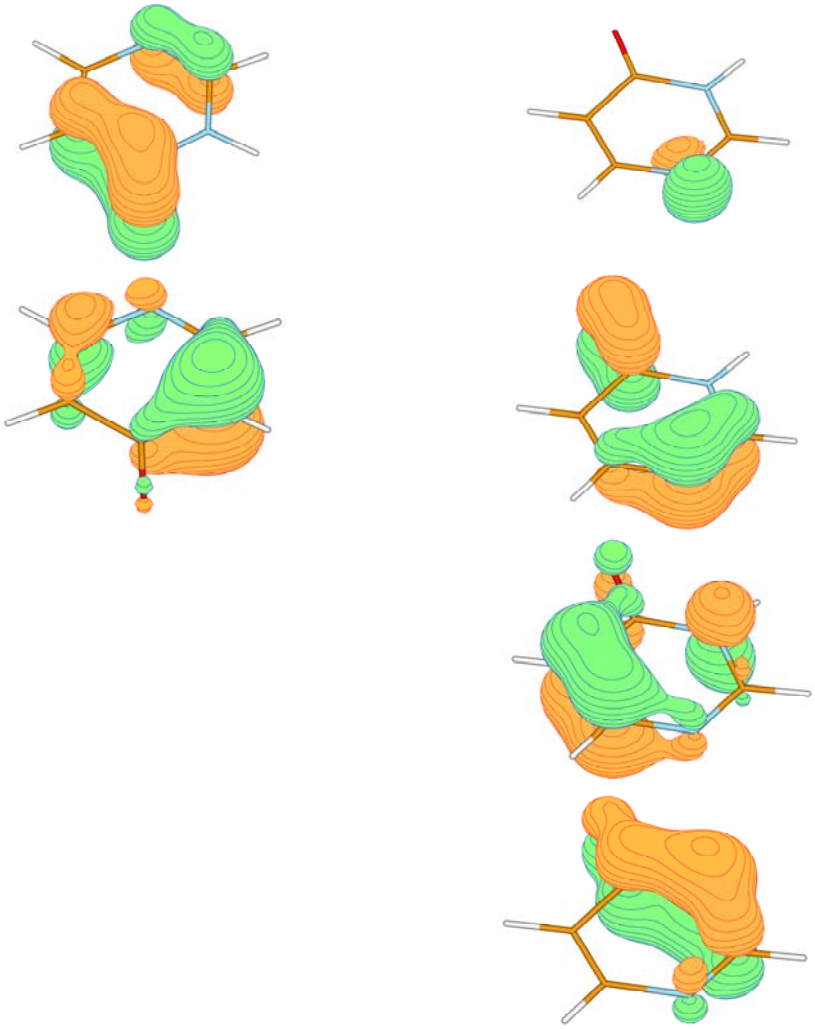


Fig. S2 *(Continued)*



CASSCF(8,7) CASSCF(12,10)

Fig. S2 State-averaged active molecular orbitals of 4Py, obtained with the aug-cc-pVDZ basis set at the ground-state equilibrium geometry.

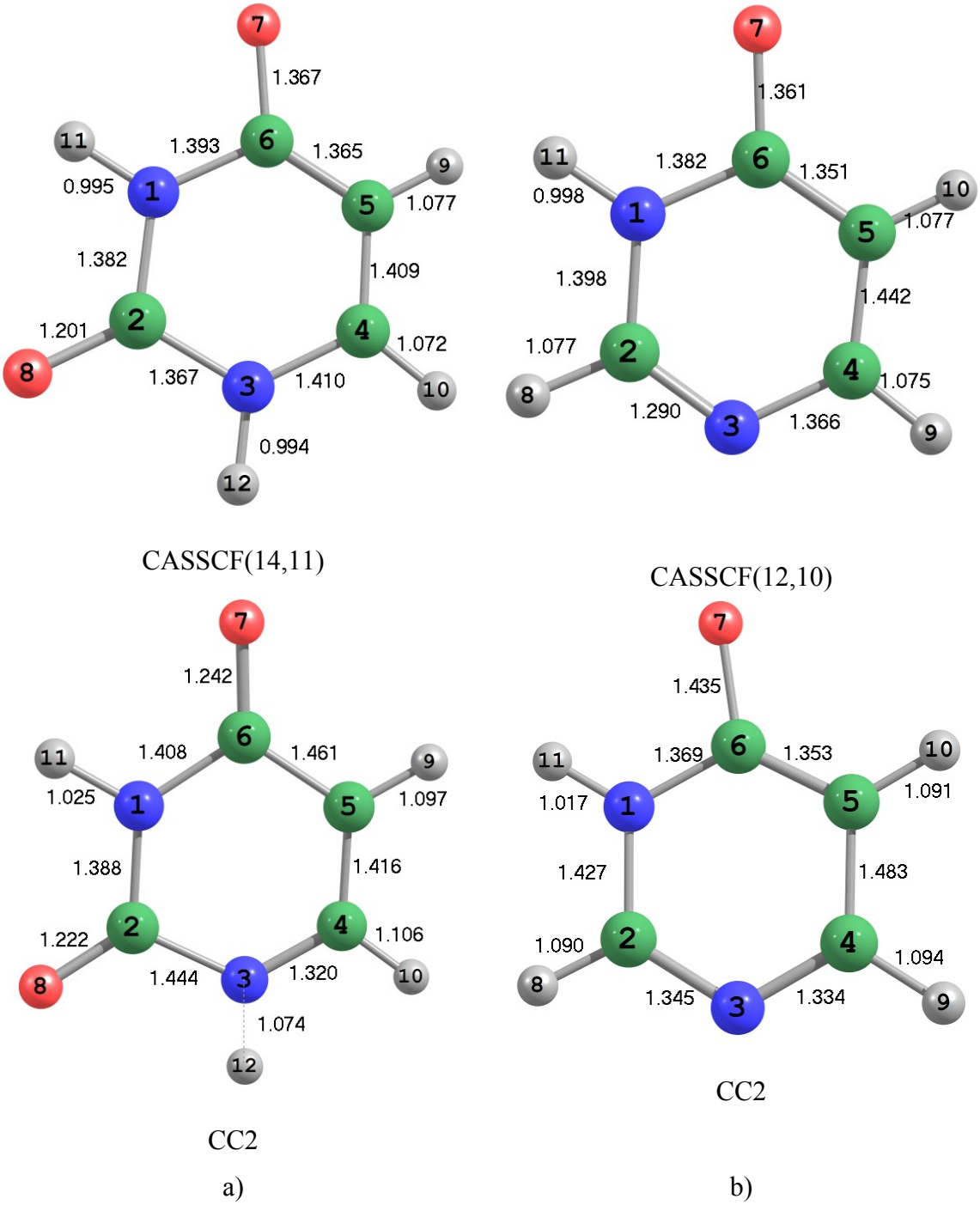


Fig. S3 Optimized structures (C_S) of the $^1n_O\pi^*$ state of a) U and b) 4Py at CASSCF and CC2 levels

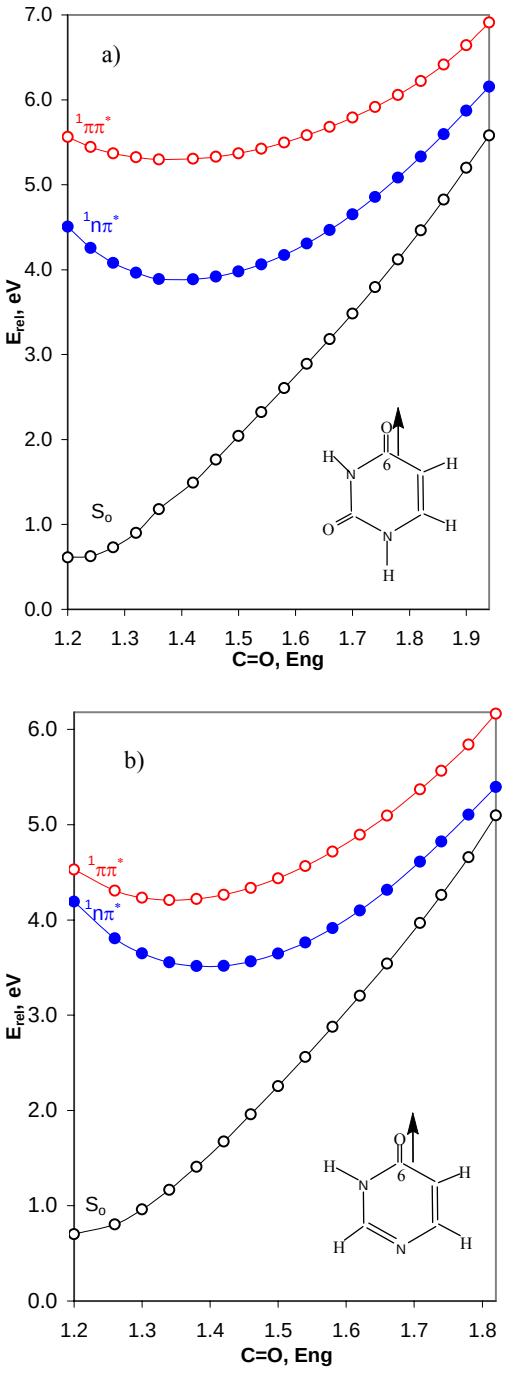


Fig. S4 Potential-energy profiles of C=O elongation for U (a) and 4Py (b). The geometry optimization was carried out for the $^1n_O\pi^*$ state (closed circles) at the CC2/cc-pVDZ level. The energies are referred to the energies of the ground-state equilibrium geometries

Optimized {CASSCF(6,6)/6-31G*} S_o/S_1 conical intersection related to C=C twisting in U

7	0.120612	-0.924401	-0.115620
6	-0.055799	-0.460961	1.143920
7	-0.004618	0.962440	1.264188
6	0.174602	1.708526	0.187361
6	-0.357699	1.250583	-1.076020
6	0.043700	-0.157785	-1.330198
8	0.183143	-0.746980	-2.359037
8	-0.137486	-1.118454	2.129435
1	0.696608	2.641091	0.348150
1	-1.436063	1.162349	-0.904285
1	0.232926	-1.914219	-0.192377
1	0.194028	1.275015	2.196521

Optimized {CASSCF(6,6)/6-31G*} S_o/S_1 conical intersection related to the C=C twisting in 4Py

7	0.074145	-0.236734	0.044290
6	0.133579	0.074344	1.333842
7	1.276734	0.310605	2.036448
6	2.311535	0.078145	1.228061
6	2.287488	0.601684	-0.093378
6	1.156572	0.286916	-0.853795
8	0.803968	0.663421	-1.934718
1	-0.792407	0.005772	1.901816
1	2.230592	1.663752	-0.079058
1	3.047316	-0.680390	1.521392
1	-0.798099	-0.469258	-0.393829

Optimized {CASSCF(6,6)/6-31G*} S_o/S_1 conical intersection related to C=N twisting in 4Py

7	-0.039747	0.056397	0.037884
6	-0.019370	-0.034925	1.423154
7	1.239930	-0.021464	1.945563
6	1.629789	1.215610	1.846764
6	0.967414	2.055815	0.922523
6	0.355954	1.441207	-0.205115
8	0.031249	1.984366	-1.228644
1	-0.913376	-0.149606	2.063582
1	1.252557	3.070419	0.789150
1	2.506168	1.536212	2.391990
1	-0.874469	-0.145426	-0.485191