

## **Quantum mechanics/molecular mechanics studies on the excited-state decay mechanisms of cytidine aza-analogues: 5-azacytidine and 2'-deoxy-5-azacytidine in aqueous solution**

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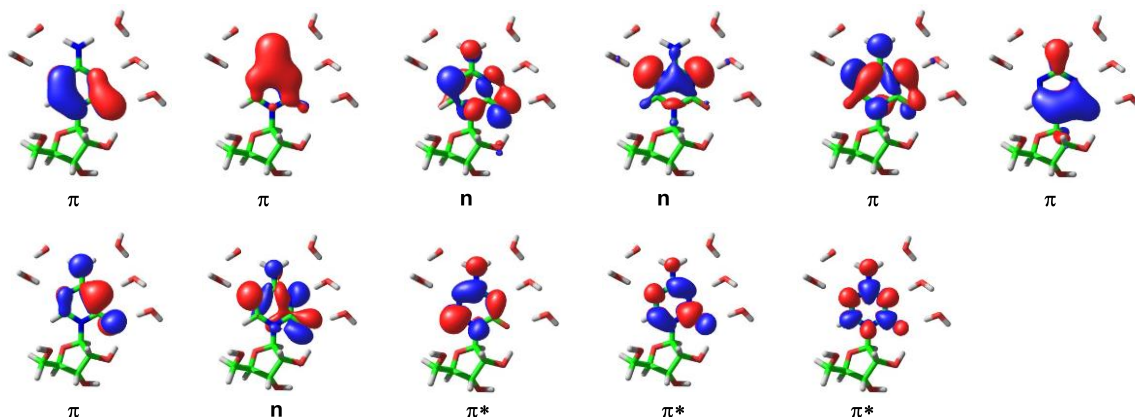
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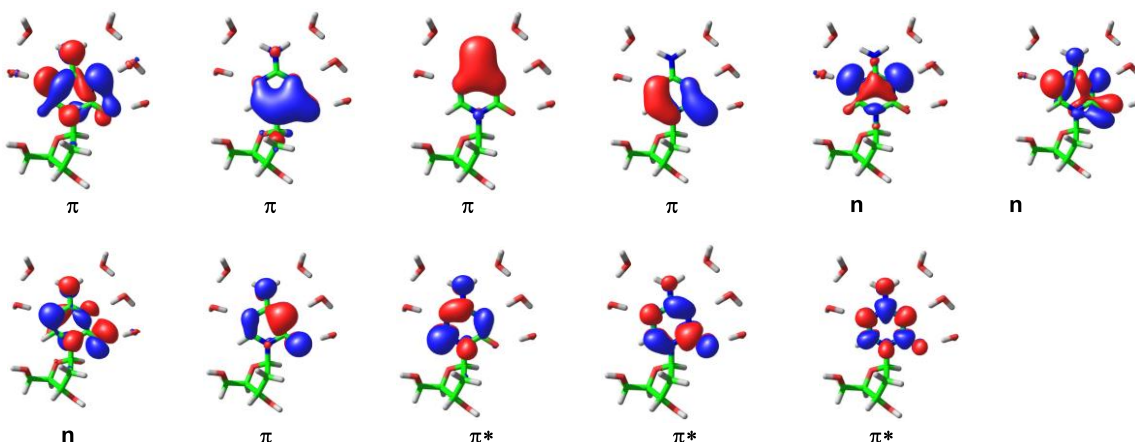
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## 1. Active Orbitals



**Figure S1.** Molecular orbitals included in the active space for 5ACyd used for QM/MM calculations.



**Figure S2.** Molecular orbitals included in the active space for 5AdCyd used for QM/MM calculations.

## 2. The Effective Spin–Orbit Couplings Expression

Spin-orbit couplings are obtained at the QM(CASPT2)/MM level within the atomic mean-field (AMFI) approximation. The effective spin-orbit couplings are expressed as follows:

$$\langle \psi_I | H_{eff}^{so} | \psi_J \rangle = \sqrt{\frac{|\langle \psi_I | H_x^{so} | \psi_J \rangle|^2 + |\langle \psi_I | H_y^{so} | \psi_J \rangle|^2 + |\langle \psi_I | H_z^{so} | \psi_J \rangle|^2}{3}}$$

in which  $\psi_I$  and  $\psi_J$  are the perturbatively modified electronic wave functions of the corresponding singlet and triplet states;  $H_x^{so}$ ,  $H_y^{so}$ ,  $H_z^{so}$  are the  $x$ ,  $y$ , and  $z$  components of the spin-orbit operator.

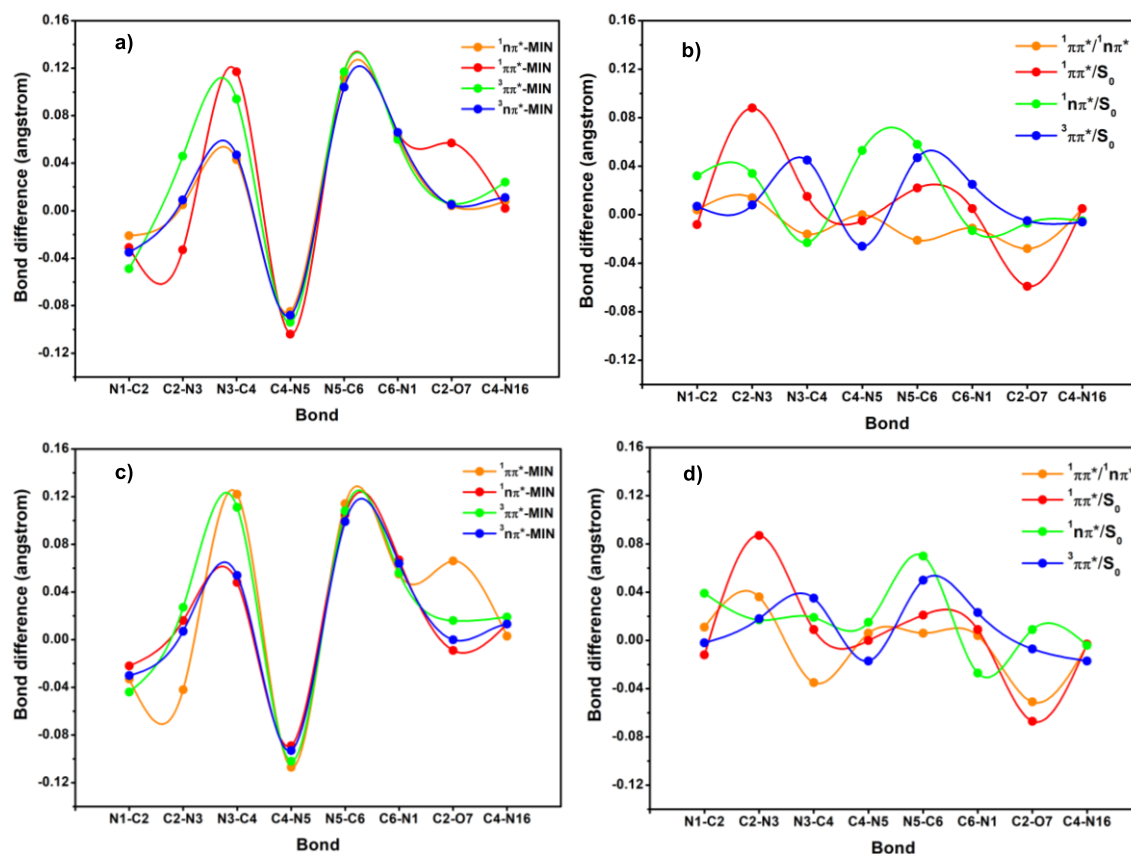
### **3. The 5-Water Hydrogen-Bond Network**

In our 50 ps MD simulations of aqueous 5ACyd and 5AdCyd, we found a compact 5-water hydrogen-bond network always around the N3 and N5 ring atoms and NH and C=O groups. This situation is similar to 5-7 water hydrogen-bonded network used in 5-AC, 2-AT, and 2,4-DT systems recently by our group (refs. 15,30 in main text) and 4-water hydrogen-bonded network used in 2'-Deoxy-5-formylcytidine system (5fdCyd·4H<sub>2</sub>O) by Wang et al. [1] and 5-D<sub>2</sub>O hydrogen-bonded network used in acid form guanosine 5'-monophosphate (9Me-GN7D<sup>+</sup>·5D<sub>2</sub>O) by Zhang et al. [2]. The final MD snapshot that deletes frozen water molecules generates the starting structure for the following QM/MM computations. This strategy has been used in many similar works before (refs. 15,26-30 in main text).

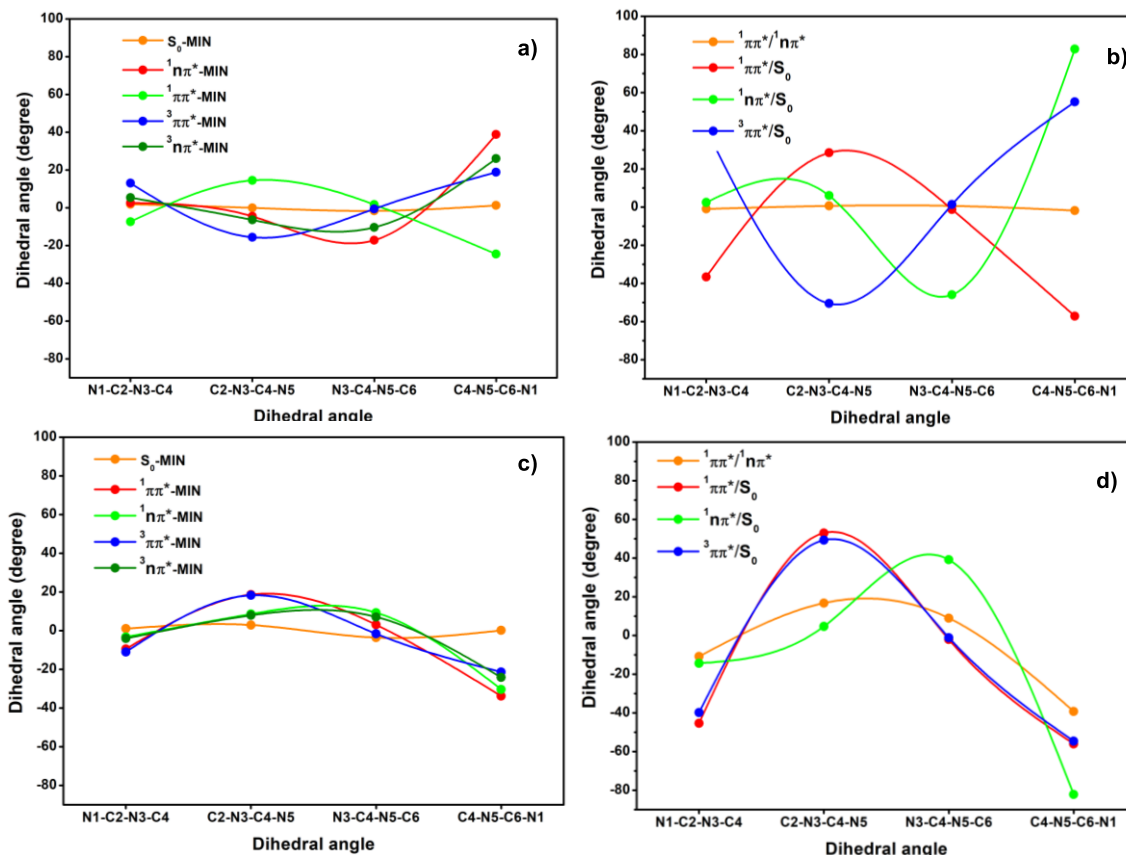
[1] X. Wang, L. Martínez-Fernández, Y. Zhang, K. Zhang, R. Improta, B. Kohler, J. Xu and J. Chen, *Chem. Eur. J.*, 2021, 27, 10932-10940.

[2] Y. Zhang, R. Improta and B. Kohler. *Phys. Chem. Chem. Phys.*, 2014, 16, 1487-1499.

#### 4. Bond-Length Difference and Dihedral Angles of Minima and Conical Intersections and Crossing Points



**Figure S3.** QM(CASSCF)/MM computed bond-length difference (in Å) of excited-state minima compared with the counterparts of the  $S_0$  minimum  $S_0$ -MIN (a) for 5ACyd and (c) for 5AdCyd. The positive and negative values mean they are longer and shorter than those of  $S_0$ -MIN, respectively. Bond-length difference (in Å) of crossing structures compared with the counterparts of the corresponding excited-state minimum (b) for 5ACyd and (d) for 5AdCyd, respectively.



**Figure S4.** QM(CASSCF)/MM computed dihedral angles (in °) of minima and conical intersections and crossing points (a and b) for 5ACyd and (c and d) for 5AdCyd, respectively.

## 4. Tables

**Table S1** QM(CASPT2)/MM computed vertical excitation energies (in kcal/mol [eV]) of the low-lying excited singlet and triplet states at the  $S_0$ -MIN of 5-AC<sup>a</sup>, 5ACyd, and 5AdCyd in aqueous solution.

	$^1n\pi^*$	$^1\pi\pi^*$	$T_1(\pi\pi^*)$	$T_2(\pi\pi^*)$
5-AC <sup>a</sup>	112.0 [4.86]	112.6 [4.88]	103.9 [4.51]	104.9 [4.55]
5ACyd	113.8 [4.93]	114.2 [4.95]	101.7 [4.41]	107.8 [4.67]
5AdCyd	112.4 [4.88]	112.2 [4.86]	101.3 [4.39]	105.4 [4.57]

a. *Phys. Chem. Chem. Phys.*, 2022, 24, 27793-27803.

**Table S2** QM(CASPT2)/MM computed adiabatic excitation energies (in kcal/mol) of the optimized minima, conical intersections and crossing points of 5-AC<sup>a</sup>, 5ACyd, and 5AdCyd in aqueous solution.

	$^1n\pi^*$ - MIN	$^1\pi\pi^*$ - MIN	$^3\pi\pi^*$ - MIN	$^3n\pi^*$ - MIN	$^1\pi\pi^*/^1n\pi^*$	$^1\pi\pi^*/S_0$	$^1n\pi^*/S_0$	$^3\pi\pi^*/S_0$
5-AC	91.6	95.0	83.6	96.8	95.1/95.1	86.5/86.4	97.0/94.1	91.6/86.4
5ACyd	93.7	97.2	90.1	102.6	102.9/102.8	89.8/85.9	99.7/96.2	98.5/93.1
5AdCyd	92.9	91.0	84.3	99.3	95.2/94.3	86.6/82.5	97.8/91.5	91.1/84.7

a. *Phys. Chem. Chem. Phys.*, 2022, 24, 27793-27803.

## 5. Cartesian Coordinates of All Optimized Structures

In xyz format (unit: Ångstrom)

### CASSCF/ANO-L-VDZP

**For 5ACyd**

S<sub>0</sub>-MIN

H	-1.797619131	2.624541187	1.924019139
O	-1.795793131	1.861366135	1.363817096
C	-2.630341187	2.054946147	0.250402017
H	-2.270744164	2.884995207	-0.358938028
H	-3.654808264	2.269821162	0.561631039
C	-2.645495188	0.804988056	-0.602038045
H	-3.340635239	0.961852068	-1.423304101
O	-1.357975096	0.573128039	-1.165083083
C	-0.771668056	-0.588352040	-0.689662050
H	-0.733173052	-1.347334098	-1.467193105
N	0.624552045	-0.286105019	-0.320818025
C	1.138623082	0.963157072	-0.376332026
H	0.455823032	1.747201123	-0.641305045
C	3.182807230	0.162635013	0.170007013
N	4.456137319	0.463038036	0.403965027
H	5.112810370	-0.272614021	0.593381044
H	4.808907347	1.353792098	0.113078008
N	2.767016198	-1.070314078	0.251591021
C	1.460190105	-1.346539099	0.028561003
O	0.994715071	-2.462657178	0.112112011
C	-3.008538219	-0.480789033	0.130357010
H	-3.610087262	-0.290952023	1.018417073
C	-1.643695117	-1.069103077	0.485236037
H	-1.281087091	-0.619357043	1.406447102
O	-3.691781265	-1.306184095	-0.763178053
H	-3.562031258	-2.212120157	-0.509150039
N	2.367940171	1.242646090	-0.135613010
O	-1.756273126	-2.446534174	0.596944042
H	-0.888797064	-2.833578203	0.564620038
O	3.143241224	4.273954308	-0.232466015
H	2.853664205	3.371447241	-0.140367012
H	3.065562222	4.678230338	0.621852045
O	6.447964463	-1.739069124	1.176186084
H	5.926578429	-2.525755183	1.017002074
H	7.344672531	-1.951913141	0.957863066

O	4.517229324	-3.600451262	0.430052031
H	4.026174290	-4.197337301	0.984879073
H	3.928484280	-2.867663208	0.278477019
O	5.625748407	3.038558217	-0.918387068
H	4.947900355	3.702682268	-0.838829063
H	6.029832435	3.135477226	-1.770170125
O	2.110671152	-4.681675335	1.809695131
H	1.722630122	-4.017841288	1.249714088
H	1.622020117	-5.480961395	1.668688121

<sup>1</sup>nπ\*-MIN

H	-1.974440142	2.596005188	2.026466145
O	-2.036223147	1.809401130	1.504118109
C	-2.818245202	2.030402145	0.359534025
H	-2.431008177	2.871973208	-0.215666013
H	-3.854823278	2.242155162	0.633002048
C	-2.804404200	0.804913056	-0.528757040
H	-3.510360253	0.969984072	-1.339470095
O	-1.521337108	0.620539045	-1.106698078
C	-0.891560062	-0.533816038	-0.659523046
H	-0.849214061	-1.270752090	-1.462022106
N	0.476801036	-0.172367011	-0.269217020
C	1.093895079	0.970584069	-0.829648060
H	0.446018034	1.789841131	-1.068960078
C	3.168569230	0.381970029	0.126251008
N	4.432040317	0.620316044	0.494122034
H	5.011162363	-0.171710011	0.705167050
H	4.884983350	1.400869103	0.057016002
N	2.638297192	-0.851674063	0.227198018
C	1.331689094	-1.191618088	0.073445008
O	0.946402066	-2.332096170	0.244244019
C	-3.131422225	-0.509214037	0.166885010
H	-3.739286268	-0.362814024	1.058631078
C	-1.749268127	-1.063511076	0.504897036
H	-1.395592100	-0.621135047	1.432203101
O	-3.789940274	-1.332218097	-0.749760054
H	-3.631433261	-2.239208163	-0.518145036
N	2.315674165	1.295905091	-0.239391019
O	-1.825114133	-2.448337176	0.594131042
H	-0.945633066	-2.805727202	0.589839044
O	3.214834233	4.458473319	-0.144215009
H	2.821545204	3.598382258	-0.056431001
H	3.155321230	4.872152352	0.707511051

O	6.303048454	-1.676789121	1.072275077
H	5.910722426	-2.524262183	0.867350060
H	7.079129509	-1.845876133	1.586402112
O	5.025703360	-4.066525293	0.350484025
H	4.214576303	-4.280954307	0.807341059
H	4.843603351	-4.157638302	-0.574019041
O	5.618935403	3.088485222	-0.970324069
H	4.972576356	3.773043274	-0.827534060
H	6.018966432	3.238007233	-1.816359129
O	2.449342179	-4.483252324	1.523207109
H	1.917844138	-3.793002273	1.136769083
H	1.884744138	-5.226768378	1.684535123

$^1\Pi\Pi^*$ -MIN

H	-1.845152134	2.620448187	1.880363133
O	-2.004061146	1.810937131	1.416428104
C	-2.704597196	2.044468147	0.222344018
H	-2.250023160	2.858251208	-0.343131022
H	-3.745145271	2.304931168	0.431672033
C	-2.692517196	0.799792059	-0.641675046
H	-3.380973241	0.956134070	-1.468714108
O	-1.402738099	0.573227043	-1.195727086
C	-0.798122055	-0.573005042	-0.702886052
H	-0.768961055	-1.344057099	-1.470081105
N	0.591639040	-0.237105016	-0.364936025
C	0.999357072	1.088740078	-0.071726007
H	0.353328024	1.850242131	-0.475540034
C	3.157826228	0.392538026	0.149005010
N	4.483663325	0.503337037	0.201196016
H	5.056083362	-0.287097020	0.427001028
H	4.923855356	1.360456096	-0.078549007
N	2.729716198	-0.947366068	0.349910026
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O	1.090084077	-2.410840173	0.040127003
C	-3.053846222	-0.487500037	0.086921004
H	-3.676134266	-0.305961019	0.961912071
C	-1.683918123	-1.046451074	0.468706032
H	-1.345754096	-0.587853042	1.393629101
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H	-3.615639263	-2.226641161	-0.535011037
N	2.368672171	1.380696099	-0.070419003
O	-1.792200129	-2.431061174	0.597406046
H	-0.941280070	-2.839315204	0.647506044



O	3.201008229	4.222065304	-0.277008018
H	2.872249206	3.327139240	-0.179157011
H	3.112421222	4.643871335	0.567195041
O	6.447578466	-1.740918128	1.102509079
H	5.939680429	-2.541659182	0.977750071
H	7.350613530	-1.949555138	0.906637063
O	4.442845318	-3.612430258	0.479982032
H	4.024003287	-4.190060304	1.106477078
H	3.866809280	-2.859985206	0.402599030
O	5.711674410	3.080576224	-0.998115071
H	4.967702358	3.664026262	-0.866030065
H	5.952960428	3.132694224	-1.913882135
O	2.120855153	-4.835199349	1.956466140
H	1.689304121	-4.394985315	1.237783088
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${}^3\Pi\Pi^*$ -MIN

H	-1.813810129	2.657381192	1.898950134
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C	-2.686321192	2.062169147	0.256002020
H	-2.294690165	2.876004205	-0.354888023
H	-3.712023268	2.304135164	0.543809037
C	-2.714622194	0.806014057	-0.587869044
H	-3.428030248	0.957333069	-1.394422099
O	-1.443495103	0.569466042	-1.178278086
C	-0.836852062	-0.579189039	-0.699905049
H	-0.825396057	-1.349881097	-1.469964104
N	0.562468038	-0.256572018	-0.369516027
C	1.102805080	1.021218072	-0.633390046
H	0.401432030	1.828332129	-0.602488042
C	3.159322228	0.314416023	0.177913011
N	4.423635321	0.497158035	0.624676047
H	5.017051359	-0.307303024	0.692355049
H	4.878368354	1.338991095	0.325625024
N	2.763631199	-1.023368071	0.080863004
C	1.393635102	-1.270939091	-0.065658006
O	1.021425075	-2.419347174	0.098794006
C	-3.060576218	-0.473792034	0.161404014
H	-3.648618261	-0.280423021	1.057375076
C	-1.685052124	-1.047560076	0.497711036
H	-1.308303095	-0.584678042	1.405973102
O	-3.753108272	-1.310661093	-0.715476052
H	-3.638079262	-2.212504159	-0.442470033

N	2.387276170	1.298521095	-0.149453012
O	-1.792613130	-2.427707174	0.632152046
H	-0.931315069	-2.822155203	0.622890047
O	3.190959227	4.265742308	-0.239533018
H	2.879849207	3.368610242	-0.153025011
H	3.125243223	4.665705337	0.617467044
O	6.436372465	-1.834852133	1.173450084
H	5.960777429	-2.635997192	0.964691067
H	7.354725528	-2.004699143	1.015303071
O	4.558005326	-3.741322267	0.308326024
H	4.031644289	-4.267299306	0.902104067
H	3.991432290	-3.029882218	0.038132005
O	5.674571406	3.020258220	-0.944659067
H	4.968081355	3.651801262	-0.849335062
H	5.982233429	3.067693219	-1.839532134
O	2.184377156	-4.725289340	1.820555129
H	1.717214125	-4.104724297	1.276198091
H	1.698343125	-5.538903398	1.796845130

${}^3n\pi^*$ -MIN

H	-1.918177139	2.608542185	1.958739141
O	-1.951360140	1.825029132	1.429186102
C	-2.758186198	2.021613146	0.296779022
H	-2.385357172	2.853582203	-0.301544019
H	-3.789547275	2.235921163	0.586648041
C	-2.756435198	0.778423057	-0.566807043
H	-3.464916247	0.932375070	-1.377467101
O	-1.476757105	0.573044043	-1.145999083
C	-0.854462059	-0.576437043	-0.680788050
H	-0.820557059	-1.330550098	-1.466944106
N	0.523515037	-0.227680014	-0.311260021
C	1.092316078	1.010689074	-0.703756051
H	0.413791028	1.839677134	-0.723925050
C	3.193301228	0.348602027	0.170666013
N	4.464642319	0.569135042	0.532978038
H	5.046964363	-0.230638015	0.699575048
H	4.911744351	1.365606096	0.122248009
N	2.672386193	-0.897362062	0.212670013
C	1.364165099	-1.238184088	0.039288003
O	0.986758070	-2.384709173	0.197644014
C	-3.091543221	-0.518631037	0.157425014
H	-3.690829264	-0.347956023	1.050804075
C	-1.711946123	-1.078564079	0.496135035

H	-1.350118099	-0.625022044	1.415076104
O	-3.765725271	-1.351923096	-0.737791055
H	-3.615317258	-2.256037164	-0.490112035
N	2.352945171	1.271571093	-0.188400013
O	-1.796295130	-2.461363175	0.606595044
H	-0.920242067	-2.826877205	0.595536044
O	3.220750234	4.457235319	-0.154177009
H	2.830822205	3.594364258	-0.082220005
H	3.159007230	4.854308347	0.703720051
O	6.328350455	-1.777378128	1.147149080
H	5.899594427	-2.593724185	0.892504067
H	7.254556525	-1.961161143	1.238163090
O	4.853759347	-4.011778287	0.249409016
H	4.123341298	-4.286124311	0.795643056
H	4.479003322	-3.812748273	-0.598352045
O	5.620277402	3.058153222	-0.961312069
H	4.974629357	3.744046271	-0.826049062
H	5.989382433	3.175853228	-1.825862131
O	2.374436171	-4.541745328	1.661913118
H	1.857501136	-3.863996280	1.237982091
H	1.839824134	-5.323913383	1.700335122

${}^1\pi\pi^*/{}^1n\pi^*$

H	-1.902106137	2.616296188	1.922209136
O	-1.954184142	1.823074129	1.408919100
C	-2.730588197	2.022522145	0.256411021
H	-2.340778169	2.852272204	-0.334068026
H	-3.768327272	2.240337163	0.520292035
C	-2.712741197	0.776614054	-0.603461045
H	-3.404687245	0.927004069	-1.428760104
O	-1.421152102	0.566472042	-1.158078083
C	-0.810976056	-0.581034042	-0.676543048
H	-0.774184056	-1.341697095	-1.455036104
N	0.567569043	-0.240283016	-0.304358020
C	1.064877079	1.073227078	-0.379452029
H	0.399831031	1.856564132	-0.659625045
C	3.202970233	0.381056028	0.155408012
N	4.507170326	0.530422038	0.403075030
H	5.078844366	-0.272817019	0.588240045
H	4.952985357	1.377242101	0.102208009
N	2.727742197	-0.936557067	0.259016018
C	1.448006106	-1.233906087	0.024987004
O	1.065640078	-2.411313173	0.110928008

C	-3.061796221	-0.516669039	0.122034010
H	-3.679073264	-0.340623024	1.002231070
C	-1.688086119	-1.072272077	0.490193036
H	-1.342640095	-0.613302043	1.412649102
O	-3.716737269	-1.354530099	-0.782386054
H	-3.588534259	-2.257269163	-0.518242039
N	2.400864172	1.332760096	-0.157017013
O	-1.775252127	-2.456363175	0.609829042
H	-0.908670067	-2.839551206	0.596490045
O	3.206297229	4.287278309	-0.250835017
H	2.886153206	3.392076242	-0.174852011
H	3.104962225	4.690796340	0.601217043
O	6.386414461	-1.794090128	1.170595083
H	5.906673426	-2.602184190	0.997482070
H	7.304784526	-1.980790142	1.031399077
O	4.620885331	-3.832215276	0.330602026
H	4.040966291	-4.283967310	0.934880068
H	4.061838291	-3.237651235	-0.152110011
O	5.705541409	3.077454221	-0.948577069
H	4.994264357	3.702705266	-0.842672059
H	5.999594432	3.125780227	-1.849175135
O	2.223738159	-4.709666340	1.847417134
H	1.748722127	-4.058452292	1.345853095
H	1.727948126	-5.516703397	1.797632128

${}^1\pi\pi^*/S_0$

H	-2.236084160	2.622666191	1.959825140
O	-2.111847154	1.867901136	1.402013099
C	-2.779126202	2.042120145	0.175607015
H	-2.369908170	2.895755206	-0.365081025
H	-3.846608278	2.205929159	0.338448026
C	-2.611819190	0.810021061	-0.687123047
H	-3.229073234	0.935412065	-1.574654113
O	-1.257814093	0.686716052	-1.098758081
C	-0.697124048	-0.519108038	-0.702051053
H	-0.667384048	-1.234146090	-1.523110111
N	0.674273047	-0.258601021	-0.308053021
C	1.063954077	0.852192064	0.491073037
H	0.281484021	1.484910107	0.860471063
C	3.165143230	0.464084034	0.240616017
N	4.468625320	0.474037033	-0.050560002
H	5.070070364	-0.213158015	0.364546026
H	4.883530351	1.324412097	-0.384436026

N	2.682715193	-0.822369057	0.658232049
C	1.533860109	-1.267669093	-0.024310001
O	1.372705099	-2.450330174	-0.219915015
C	-2.975906213	-0.511472037	-0.009278001
H	-3.639894261	-0.365302025	0.841454062
C	-1.611348115	-1.046585077	0.414239030
H	-1.326743097	-0.594168042	1.361621100
O	-3.570443255	-1.340746095	-0.962824071
H	-3.462311250	-2.246307161	-0.699811051
N	2.322110167	1.419941101	0.147984010
O	-1.656990119	-2.436532173	0.517184039
H	-0.790947057	-2.813897201	0.457329034
O	3.196302229	4.257147305	-0.295835022
H	2.810536201	3.392998244	-0.154241013
H	3.157896227	4.714134337	0.533644039
O	6.363480458	-1.638287116	1.169748082
H	5.885607425	-2.464737178	1.168386085
H	7.229246522	-1.822948132	0.831840060
O	4.485232325	-3.698417264	0.798900057
H	4.051284290	-4.325523314	1.366937099
H	3.825472277	-3.044935221	0.614409045
O	5.654095406	3.082546224	-1.166458086
H	4.923868352	3.666559264	-0.973593072
H	5.899751423	3.221635230	-2.071084149
O	2.006726146	-4.863641351	1.879332137
H	1.683203120	-4.382555318	1.129710081
H	1.496206110	-5.660413406	1.941677138

${}^1n\pi^*/S_0$

H	-1.961114142	2.672773191	2.017813145
O	-2.114880154	1.868581134	1.544143113
C	-2.782208199	2.119344151	0.335574022
H	-2.302056164	2.930876214	-0.211694014
H	-3.824900273	2.390062172	0.521471037
C	-2.761992200	0.886133064	-0.542418042
H	-3.432859245	1.058078077	-1.381457098
O	-1.460364104	0.667419048	-1.065028079
C	-0.892512063	-0.514245037	-0.601513043
H	-0.876000066	-1.255999089	-1.402775099
N	0.471695032	-0.186649013	-0.191809015
C	1.281137093	0.602434044	-1.020910075
H	0.970985069	1.122474080	-1.904874136
C	3.204108229	0.210589013	0.076986008

N	4.480358322	0.489276036	0.337954023
H	5.093256365	-0.260863021	0.601759042
H	4.884246354	1.314435095	-0.059211002
N	2.695953192	-0.996934069	0.270373019
C	1.327536095	-1.240920088	0.171869013
O	0.904305063	-2.348314167	0.406552032
C	-3.147234227	-0.412252027	0.155765011
H	-3.782488272	-0.242495019	1.023875076
C	-1.792015128	-0.996196074	0.547779041
H	-1.452328103	-0.542997041	1.474837107
O	-3.791155275	-1.232623086	-0.775146058
H	-3.678497265	-2.138960153	-0.516534035
N	2.246489161	1.155701082	-0.086901006
O	-1.914388140	-2.377309169	0.664560046
H	-1.052644078	-2.766263200	0.735194054
O	3.103421224	4.432353320	-0.029700004
H	2.643311189	3.619977262	0.147818013
H	3.066476222	4.942988357	0.769188056
O	6.406805459	-1.728478123	1.033835075
H	5.997264433	-2.568936184	0.832829061
H	7.141748514	-1.906991136	1.603075117
O	5.093076366	-4.093950296	0.272438022
H	4.307231312	-4.287159307	0.780121054
H	4.806284348	-3.996110286	-0.625376042
O	5.475905392	3.078176220	-0.937402068
H	4.835236349	3.752039271	-0.729763055
H	6.014827435	3.393333244	-1.650487118
O	2.563396185	-4.506870325	1.590254115
H	2.033743148	-3.790536275	1.255610091
H	2.002890145	-5.267912380	1.656718122

${}^3\Pi\Pi^*/S_0$

H	-1.805696128	2.665017193	1.967870142
O	-1.947923139	1.857120133	1.496320105
C	-2.739885196	2.074903152	0.358526027
H	-2.338211167	2.890399208	-0.243167016
H	-3.766022271	2.320886169	0.643269044
C	-2.772181201	0.829133059	-0.500658035
H	-3.502887255	0.982569072	-1.291364094
O	-1.509729107	0.615618046	-1.115379083
C	-0.890199066	-0.540957041	-0.668283046
H	-0.914812068	-1.302334092	-1.450137103
N	0.501631038	-0.216103013	-0.350218023

C	1.215552087	0.822361062	-1.040345077
H	0.612521046	1.509896110	-1.600626116
C	3.041984221	0.433493033	0.119015006
N	4.092058297	0.464019035	0.962371069
H	4.797341347	-0.240759016	0.845002058
H	4.470615323	1.380118100	1.108168080
N	2.701637195	-0.890561066	-0.342064026
C	1.356621095	-1.236054092	-0.107923006
O	1.086620077	-2.374126173	0.214761014
C	-3.089855220	-0.464387036	0.239531018
H	-3.668082263	-0.288814020	1.145368081
C	-1.701232120	-1.018023074	0.547612038
H	-1.310175097	-0.543990037	1.442905102
O	-3.782697271	-1.304935094	-0.635769047
H	-3.657650263	-2.206331159	-0.366473025
N	2.285867166	1.383077100	-0.244164018
O	-1.778945128	-2.401004171	0.689983049
H	-0.908110065	-2.766338200	0.766909054
O	3.184216228	4.245433305	-0.282542021
H	2.784011202	3.380317241	-0.212705018
H	3.000386217	4.705806341	0.525142040
O	6.254784451	-1.666248122	1.113417079
H	5.887612425	-2.517232180	0.882293063
H	7.188753519	-1.719939123	0.967238071
O	4.887062350	-3.979995288	0.221744016
H	4.200386304	-4.310860310	0.794722060
H	4.460869322	-3.746573272	-0.592078040
O	5.630775406	2.944313215	-1.035143075
H	4.934350354	3.576939255	-0.890249063
H	6.125797444	3.237188231	-1.787962128
O	2.422472172	-4.643083332	1.701459121
H	1.890402139	-3.964600283	1.304941095
H	1.880527135	-5.416653389	1.782873126

For 5AdCyd

S<sub>0</sub>-MIN

H	-1.032382076	4.104704294	1.211232085
O	-1.190596088	3.210034231	0.944792066
C	-2.081939151	3.159214228	-0.140338008
H	-1.687720124	3.720283270	-0.988589071
H	-3.052597220	3.580212259	0.128340009
C	-2.282197163	1.721516124	-0.567323039
H	-3.002288218	1.711295124	-1.382554098
O	-1.052712077	1.193361087	-1.035342077

C	-0.720933050	0.006046998	-0.383664026
H	-0.984606071	-0.849122063	-0.993358070
N	0.728533051	-0.038466005	-0.210980016
C	1.462034103	1.085827079	-0.073187007
H	0.918705066	2.012993145	-0.065465004
C	3.356901243	-0.153790011	0.020228001
N	4.685014337	-0.119517010	0.076798007
H	5.214348376	-0.967522070	-0.012182999
H	5.161763371	0.754962052	0.172291010
N	2.719221195	-1.286160091	-0.045127003
C	1.361943099	-1.285610091	-0.153426011
O	0.692324050	-2.286016166	-0.201462012
C	-2.774195202	0.755673055	0.518771037
H	-3.239073234	1.280970090	1.350958099
C	-1.501621107	0.026096000	0.926087068
H	-0.961506071	0.615188047	1.662773121
O	-3.698785264	-0.101336009	-0.102575009
H	-4.009880287	-0.756702056	0.506263038
H	-1.678266119	-0.971313069	1.318801093
N	2.738761197	1.092351078	0.044677001
O	1.211281087	-5.040425362	-0.888218064
H	0.999253072	-4.144608296	-0.643272044
H	1.043465075	-5.112654368	-1.817821129
O	3.919094284	-4.090045296	0.189929012
H	3.468360249	-3.250645235	0.178319011
H	3.292883237	-4.715865339	-0.158741009
O	6.220181450	2.558736187	0.529974036
H	5.551934399	3.236242231	0.479197035
H	6.761047489	2.753057201	1.284120092
O	3.654118265	3.912395281	0.089154005
H	3.373894241	3.002071218	0.060445007
H	3.545156256	4.258709304	-0.786279058
O	6.295905455	-2.640590191	-0.354640024
H	7.018383506	-2.880421205	0.209411016
H	5.632530406	-3.323475238	-0.259299016

<sup>1</sup>ππ\*-MIN

H	-1.151721082	4.174143303	1.204703086
O	-1.338930096	3.277003236	0.967970071
C	-2.139594155	3.219553230	-0.184689014
H	-1.678871122	3.773291272	-1.003370071
H	-3.127948224	3.642919260	0.007374000
C	-2.310781164	1.780172126	-0.619556045



H	-3.011225217	1.765107127	-1.452299104
O	-1.067678077	1.262897089	-1.052261075
C	-0.752349054	0.068397006	-0.402610032
H	-1.039705075	-0.776077055	-1.018246075
N	0.686453051	0.012390003	-0.239528018
C	1.373697100	1.042107074	0.422466032
H	0.848535063	1.975708141	0.507227035
C	3.331721238	-0.054270006	0.160387009
N	4.652891336	-0.217843017	0.083874007
H	5.037359362	-1.117926082	-0.133214012
H	5.249794378	0.587815041	0.093038007
N	2.619921190	-1.285567090	0.128506012
C	1.337060095	-1.187692085	-0.166382011
O	0.685647050	-2.253828161	-0.399473027
C	-2.825534206	0.815877058	0.457922035
H	-3.317066240	1.340917099	1.274158092
C	-1.557002114	0.098223008	0.896970064
H	-1.034485074	0.692161048	1.640349119
O	-3.727026269	-0.056614002	-0.180435011
H	-4.093963292	-0.669229046	0.441416033
H	-1.744703126	-0.896877066	1.294436095
N	2.760715200	1.091202080	0.268853021
O	1.090381078	-5.190587376	-1.114974082
H	0.775763057	-4.311422312	-0.956340068
H	1.045705077	-5.336081385	-2.051110147
O	3.626918263	-4.287708307	0.376806026
H	3.236612232	-3.422853244	0.427077029
H	2.991087213	-4.832470350	-0.075243004
O	6.385831461	2.368560171	0.363121026
H	5.678300407	3.008281219	0.322666023
H	6.893454495	2.568873185	1.138371083
O	3.846537278	3.759869268	0.146181008
H	3.463271252	2.881982210	0.186709016
H	3.603647260	4.124739299	-0.693732048
O	5.946889426	-2.888495207	-0.559830042
H	6.763128489	-3.105513225	-0.128271009
H	5.311278381	-3.556821254	-0.310506022

<sup>1</sup>nπ\*-MIN

H	-1.177539084	4.230748303	1.178106087
O	-1.334691096	3.333232240	0.922342065
C	-2.168971155	3.275507236	-0.206837014
H	-1.730260122	3.828239276	-1.038634073

H	-3.149993224	3.701902266	0.012772000
C	-2.357954167	1.837407133	-0.637717049
H	-3.069439223	1.831115130	-1.461595108
O	-1.126084079	1.310349096	-1.084136077
C	-0.824851057	0.097619005	-0.451639034
H	-1.128913082	-0.736769055	-1.071897075
N	0.611983043	0.013330001	-0.309833020
C	1.307863095	1.059993074	0.342371023
H	0.860174062	2.031144146	0.257674019
C	3.330554238	-0.134987010	0.212314014
N	4.656798336	-0.286951020	0.357802027
H	5.068655365	-1.115080082	-0.032939003
H	5.207131377	0.550629042	0.341446027
N	2.527713181	-1.200287086	0.009395002
C	1.182538084	-1.240494090	-0.288280022
O	0.584910043	-2.253215162	-0.506018034
C	-2.873495207	0.877340064	0.443455033
H	-3.337059239	1.407776099	1.272823094
C	-1.615408117	0.127233007	0.855187064
H	-1.072915080	0.701903053	1.600358114
O	-3.810653276	0.035457003	-0.184127012
H	-4.135586295	-0.612154046	0.425359028
H	-1.814604128	-0.869944061	1.240609091
N	2.692193191	0.997675071	0.280140022
O	1.322848093	-4.946095358	-0.719600052
H	1.052079075	-4.030995290	-0.660646050
H	1.081062076	-5.251872377	-1.584233115
O	3.959325286	-4.961765355	0.374027025
H	3.868975277	-5.187631376	1.289186091
H	3.086133220	-5.016197363	-0.012943003
O	6.311422456	2.407290172	0.449207031
H	5.642430408	3.077520220	0.343005025
H	6.822068489	2.645136189	1.211970087
O	3.764960271	3.833059276	0.035103005
H	3.389866244	2.961548211	0.084586004
H	3.537930256	4.175496298	-0.819399061
O	5.712700410	-2.924741213	-0.593658042
H	6.537055470	-3.294020238	-0.875595065
H	5.169546373	-3.646322261	-0.279708018

$^3\Pi\Pi^*$ -MIN

H	-1.208007089	4.214001304	1.108155078
O	-1.361297096	3.306111239	0.888997066

C	-2.174243157	3.196521229	-0.250798017
H	-1.735382124	3.734459267	-1.091836077
H	-3.168735227	3.606056260	-0.060289005
C	-2.323873168	1.740982126	-0.637908044
H	-3.019081218	1.688431121	-1.473386108
O	-1.072222075	1.222016088	-1.046276075
C	-0.755451054	0.048177006	-0.357680026
H	-1.033278074	-0.816493057	-0.949027066
N	0.682121047	-0.008295002	-0.172452013
C	1.372217097	1.106121079	0.333604022
H	0.887354066	2.050033149	0.185239015
C	3.353264240	-0.054727003	0.181822011
N	4.693073336	-0.208617012	0.214618015
H	5.080694364	-1.070581075	-0.119355008
H	5.261043379	0.614493047	0.151031013
N	2.649818191	-1.279330091	0.157136009
C	1.294936094	-1.217592087	-0.144593011
O	0.723287052	-2.273659163	-0.364948026
C	-2.836117206	0.809094059	0.468756034
H	-3.332410237	1.357856100	1.266330089
C	-1.565442111	0.114583009	0.934521068
H	-1.047157076	0.739338051	1.655953122
O	-3.732181270	-0.086545008	-0.143857010
H	-4.082599296	-0.694117051	0.492268035
H	-1.745419124	-0.867783065	1.365485100
N	2.761222199	1.086338079	0.281911019
O	1.119052081	-5.125606368	-1.089901077
H	0.870322063	-4.222553306	-0.936502070
H	1.035434074	-5.280826379	-2.021455144
O	3.677374266	-4.389512316	0.362701029
H	3.272505235	-3.552072253	0.549314041
H	3.014992218	-4.889876350	-0.104350007
O	6.406474459	2.433831173	0.397241031
H	5.707070409	3.080917220	0.355272026
H	6.901346496	2.614231190	1.185511087
O	3.845623278	3.815786275	0.154874009
H	3.471992252	2.938713212	0.213823016
H	3.602811260	4.159663299	-0.694025048
O	5.900098426	-2.880513208	-0.676958050
H	6.735652485	-3.124844224	-0.303228020
H	5.274806379	-3.554496255	-0.417431032

<sup>3</sup>nπ\*-MIN

H	-1.192785088	4.244721308	1.125042082
O	-1.359575100	3.342769242	0.892138067
C	-2.188038157	3.264382237	-0.239569018
H	-1.745346124	3.800784274	-1.079820076
H	-3.169769229	3.695790264	-0.032709001
C	-2.377423170	1.818247133	-0.643517048
H	-3.087375220	1.796099128	-1.468336106
O	-1.146187084	1.278035093	-1.078490079
C	-0.840354062	0.087841005	-0.406995027
H	-1.138721081	-0.766637057	-1.002395073
N	0.593804042	0.008736002	-0.247539020
C	1.311102094	1.087090077	0.316339021
H	0.868673062	2.053493148	0.171492011
C	3.327411237	-0.109906008	0.190378014
N	4.654167336	-0.266754018	0.332052024
H	5.062747365	-1.099134077	-0.052227006
H	5.210312373	0.566859040	0.324500025
N	2.532085180	-1.189270087	-0.007982999
C	1.189095088	-1.225052089	-0.271001020
O	0.601227044	-2.252408162	-0.496292037
C	-2.894436211	0.881582065	0.456543031
H	-3.370475243	1.427949103	1.268137092
C	-1.633331117	0.153703009	0.896303062
H	-1.094562081	0.755289052	1.622423118
O	-3.817017273	0.014915004	-0.158782010
H	-4.146439297	-0.616630044	0.464977031
H	-1.827188132	-0.832066061	1.312952092
N	2.689928191	1.017489071	0.276592021
O	1.313104093	-4.964473356	-0.772633053
H	1.044420076	-4.050855291	-0.705432051
H	1.078823079	-5.260134379	-1.641990119
O	3.943719283	-4.960368359	0.361526028
H	3.846584279	-5.184089376	1.277550092
H	3.075581219	-5.026156362	-0.034494001
O	6.341415455	2.408465173	0.442602031
H	5.662690408	3.071260222	0.350863027
H	6.851516494	2.639648192	1.207712088
O	3.789954270	3.820759276	0.069968006
H	3.410551243	2.950689213	0.130912011
H	3.562072258	4.154367298	-0.787633058
O	5.693423409	-2.919790209	-0.613058045
H	6.530373469	-3.291051236	-0.854596063
H	5.146799371	-3.636054259	-0.293429023

${}^1\pi\pi^*/{}^1n\pi^*$

H	-1.167875085	4.147265301	1.185339083
O	-1.326343097	3.245290231	0.946143066
C	-2.155510156	3.167730230	-0.186279012
H	-1.725954122	3.728099271	-1.017540073
H	-3.145858228	3.574420255	0.029789001
C	-2.314191167	1.724975123	-0.617109045
H	-3.038919216	1.702092123	-1.428955101
O	-1.077226075	1.227943090	-1.088531079
C	-0.711322053	0.045111006	-0.438039031
H	-0.982226069	-0.813255059	-1.042098078
N	0.730439052	0.034698004	-0.305431022
C	1.397083099	1.108731082	0.315454020
H	0.869118063	2.048806146	0.321690025
C	3.421413247	0.039866002	0.134381012
N	4.744714342	-0.085606004	0.138709009
H	5.162055371	-0.976607070	-0.069355007
H	5.311296384	0.743747056	0.132013007
N	2.685440191	-1.136533081	0.153032012
C	1.369647100	-1.179095082	-0.173577012
O	0.792407057	-2.241851160	-0.330882024
C	-2.781296199	0.750475052	0.472373035
H	-3.262571234	1.266437089	1.301214094
C	-1.489242105	0.057301006	0.878657065
H	-0.961162068	0.660438046	1.611242116
O	-3.683853263	-0.137429009	-0.142893013
H	-3.990323288	-0.782190058	0.479163035
H	-1.645592117	-0.941913066	1.278221094
N	2.784219200	1.161677086	0.118430006
O	1.202924087	-5.065285363	-1.038736077
H	0.952281067	-4.161784300	-0.877629064
H	1.043231073	-5.237000375	-1.958363140
O	3.766811269	-4.424861319	0.394963029
H	3.313315236	-3.684522265	0.784286055
H	3.106125224	-4.863117349	-0.135192007
O	6.325085453	2.534724182	0.454668034
H	5.634896405	3.186972231	0.359662027
H	6.786690487	2.736471198	1.258076088
O	3.782841271	3.915976282	0.036210001
H	3.425875248	3.031149217	0.007799999
H	3.562747256	4.324697310	-0.791059058
O	6.000608431	-2.773372199	-0.475571033
H	6.805788489	-3.044456220	-0.056467007

H 5.352871385 -3.454491249 -0.295766023

${}^1\Pi\Pi^*/S_0$

H	-0.871495063	4.041397290	1.502870108
O	-1.169618084	3.196441228	1.197627087
C	-1.832406132	3.319531238	-0.035385003
H	-1.225333087	3.884137279	-0.743754051
H	-2.789491202	3.831867278	0.088563004
C	-2.092671151	1.949201139	-0.623197044
H	-2.693476192	2.084981153	-1.519921109
O	-0.865274061	1.345545098	-0.978397070
C	-0.712052053	0.083341003	-0.401382028
H	-0.946199068	-0.695916052	-1.121487080
N	0.669114050	-0.097254005	-0.039601001
C	1.407918104	0.756729054	0.809805056
H	0.847073062	1.507478109	1.337009098
C	3.315334238	-0.041922004	0.224635017
N	4.560352327	-0.243550019	-0.198675015
H	4.954285355	-1.165869085	-0.191098012
H	5.170829374	0.548580041	-0.274555022
N	2.563095184	-1.220644090	0.534542037
C	1.317437097	-1.284271093	-0.117419007
O	0.910387067	-2.313987169	-0.589530041
C	-2.818679201	0.953320069	0.292938020
H	-3.333201241	1.454046103	1.110588081
C	-1.688746119	0.055956007	0.778082055
H	-1.223662089	0.494590034	1.655627117
O	-3.739953270	0.257723021	-0.512593035
H	-4.223262303	-0.371955026	0.003864999
H	-2.016704143	-0.953565068	1.017119075
N	2.720511196	1.084644077	0.388870029
O	1.111622078	-5.145264371	-1.213157089
H	0.938738066	-4.212802305	-1.156471083
H	1.102895077	-5.374059388	-2.133385154
O	3.508389253	-4.660788333	0.538749039
H	3.090852222	-3.961240283	1.023911076
H	2.834982205	-5.004704358	-0.042407005
O	6.264888450	2.354893168	0.163500011
H	5.559195398	2.997748215	0.157944010
H	6.780353489	2.517724183	0.942150069
O	3.726221268	3.783290272	0.028985001
H	3.321498237	2.920204211	0.126458011
H	3.452526250	4.118088298	-0.814499059

O	5.654228409	-3.033090218	-0.452687032
H	6.513069468	-3.367519243	-0.234955016
H	5.017641360	-3.697172268	-0.192264012

${}^1n\pi^*/S_0$

H	-1.156305085	4.205066305	1.218536086
O	-1.322364097	3.313516239	0.947862066
C	-2.164087156	3.289698235	-0.179354013
H	-1.723283127	3.856675277	-0.999917073
H	-3.139025227	3.720373267	0.057089002
C	-2.369294171	1.865387136	-0.646350046
H	-3.105441226	1.884745133	-1.448208103
O	-1.153856085	1.354440096	-1.146078084
C	-0.816231056	0.136651007	-0.550877041
H	-1.132029084	-0.690498050	-1.176286082
N	0.630427045	0.077755003	-0.475177034
C	1.358904098	0.941773067	0.331621025
H	0.956862069	1.822424130	0.794618055
C	3.297077236	-0.117104009	0.239953016
N	4.620098333	-0.254405016	0.390704030
H	5.029562364	-1.145371082	0.179604012
H	5.194860376	0.560322039	0.294957022
N	2.512744180	-1.234843091	0.330255023
C	1.212193087	-1.178358087	-0.171662014
O	0.593386045	-2.193875157	-0.366486027
C	-2.849117207	0.873247063	0.421187032
H	-3.295375238	1.378022097	1.275864091
C	-1.573075111	0.123538011	0.781777056
H	-1.029047074	0.679519051	1.539106113
O	-3.795352275	0.037921000	-0.201653013
H	-4.104677295	-0.622419042	0.402263029
H	-1.759422128	-0.884283065	1.145736082
N	2.699621194	0.954093070	-0.238514019
O	1.307236094	-4.943114354	-0.691062052
H	1.052560076	-4.032824291	-0.579744040
H	1.061131075	-5.200504374	-1.569804113
O	3.970203286	-5.003689359	0.362250027
H	3.890219278	-5.261769378	1.270792091
H	3.087430223	-5.008157361	-0.003726001
O	6.271075453	2.409886173	0.444585032
H	5.580104403	3.056006223	0.331347023
H	6.766095485	2.660067190	1.213681086
O	3.715363266	3.785880272	-0.092188006

H	3.341726239	2.953205213	-0.363229026
H	3.572608257	4.385700313	-0.813099057
O	5.718848413	-2.900937206	-0.455822032
H	6.500228469	-3.278360237	-0.832954058
H	5.147300370	-3.622915259	-0.198031012

${}^3\Pi\Pi^*/S_0$

H	-0.978226071	4.121049299	1.478386108
O	-1.214131088	3.260163234	1.163789085
C	-1.871417132	3.346098243	-0.074898007
H	-1.277997093	3.921887281	-0.785762057
H	-2.845798207	3.827708278	0.036083004
C	-2.080843151	1.960811140	-0.647607049
H	-2.680759195	2.065824148	-1.548848112
O	-0.831998062	1.396111101	-0.986414073
C	-0.651894046	0.134757008	-0.413395029
H	-0.884540066	-0.641872048	-1.137016082
N	0.739864054	-0.013062000	-0.070532003
C	1.398339101	0.852315060	0.855701059
H	0.833695059	1.715445123	1.152314083
C	3.354367241	-0.044915004	0.398992031
N	4.631108332	-0.294304023	0.110795010
H	4.933675356	-1.229279088	-0.083919008
H	5.227567377	0.482464032	-0.102040005
N	2.559613187	-1.228750091	0.644662045
C	1.334767096	-1.228927090	-0.048671003
O	0.924409068	-2.281609162	-0.492124036
C	-2.779708202	0.952335069	0.275829021
H	-3.310400237	1.445799103	1.087800079
C	-1.624236116	0.092627006	0.769337057
H	-1.168540086	0.556848038	1.638475117
O	-3.680282264	0.224783018	-0.525652040
H	-4.143591297	-0.416273028	-0.005329000
H	-1.924969139	-0.921798065	1.022803074
N	2.778378200	1.083050078	0.513983036
O	1.116490080	-5.120996371	-1.290904091
H	0.920828067	-4.196952303	-1.197438086
H	1.190204084	-5.298153383	-2.219599162
O	3.466004251	-4.869863348	0.524744040
H	3.059454220	-4.429525318	1.259494093
H	2.757598198	-5.084982367	-0.077344007
O	6.325068456	2.336067169	0.159050011
H	5.622672406	2.982028217	0.125607009



H	6.816553489	2.508661181	0.950811070
O	3.792459274	3.749624270	0.025048002
H	3.408503243	2.886292210	0.181348011
H	3.463677247	4.050962291	-0.810674060
O	5.437380394	-3.117152225	-0.580685039
H	6.299667455	-3.508860253	-0.549121040
H	4.827299347	-3.768409274	-0.235386015