Electronic Supplementary Information

A combined experimental and computational study on the deactivation of a photo-excited 2,2'-pyridylbenzimidazole-water complex via excited-state proton transfer

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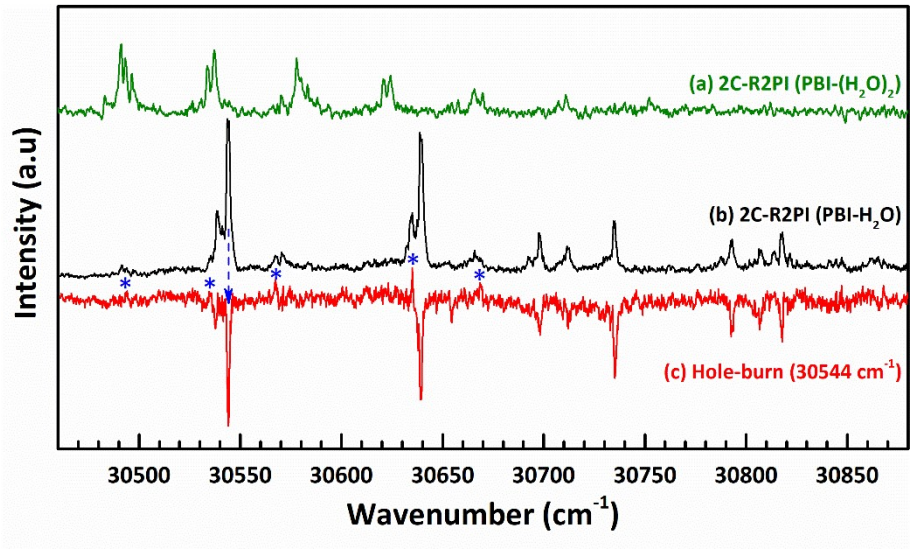
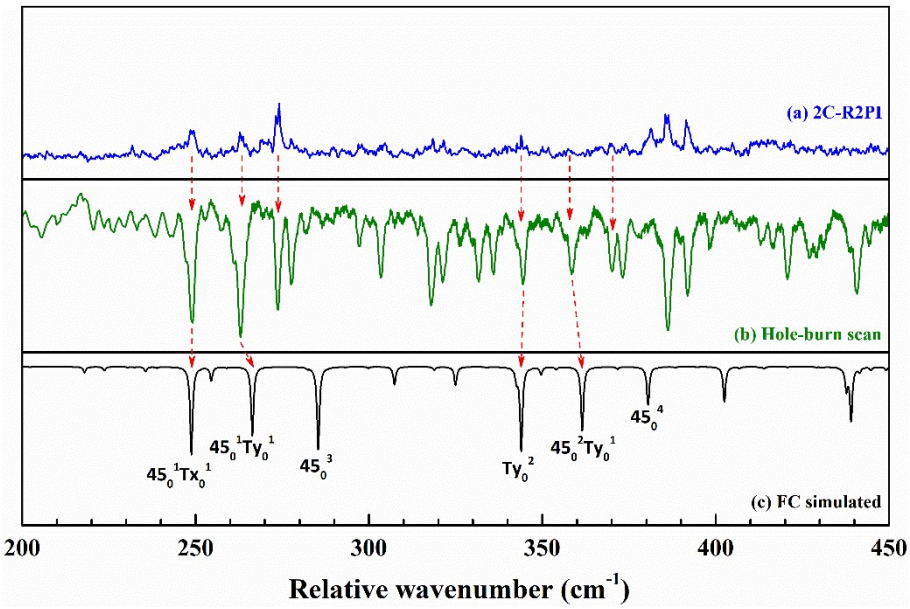
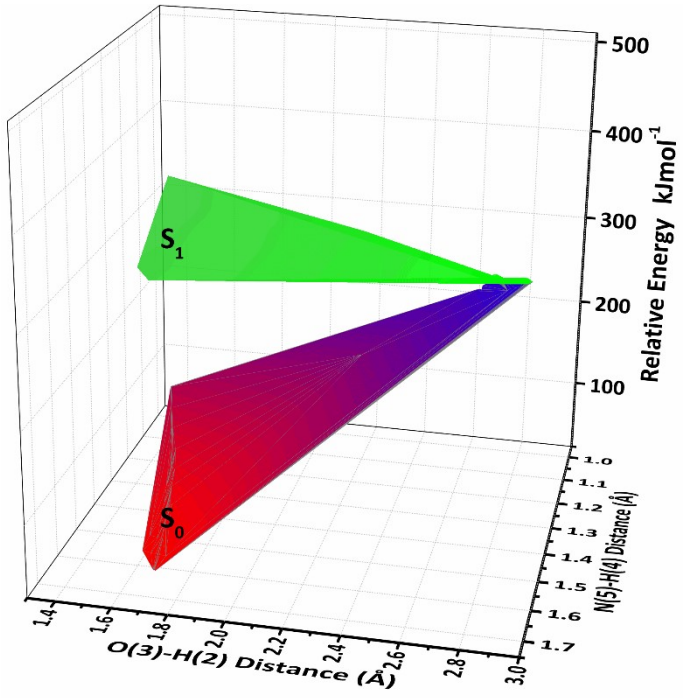


SI Figure S1: (a) Two-color resonant two-photon ionization (2C-R2PI) spectrum of PBI-$(H_2O)_2$ (b) 2C-R2PI spectrum of PBI-H_2O and UV/UV hole-burning spectrum of PBI-H_2O (ionization at 266 nm). The UV hole-burning laser was fixed at the most intense band at 30544 cm^{-1}, shown with the blue dotted arrow. The * indicates the presence of fragmentation bands originating from the larger cluster present in the molecular beam.

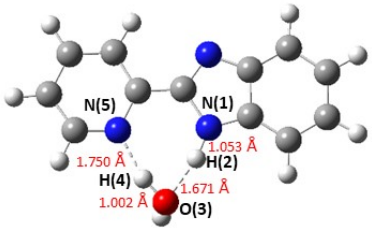
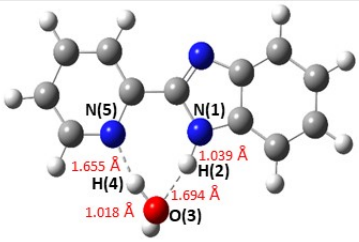
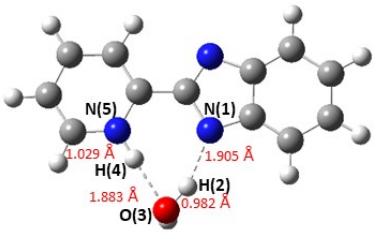
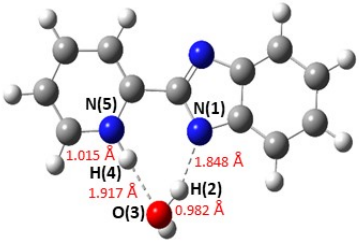
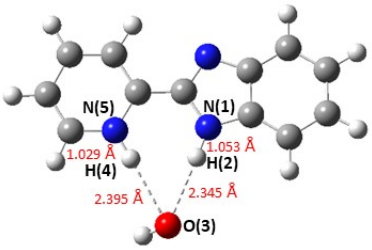
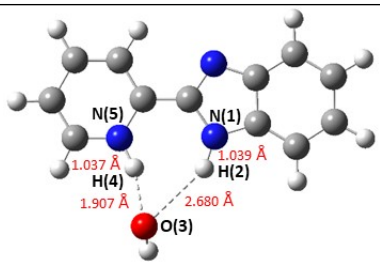
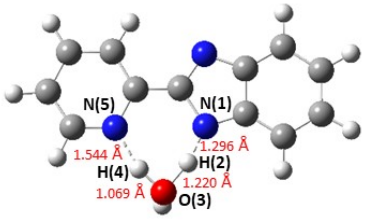
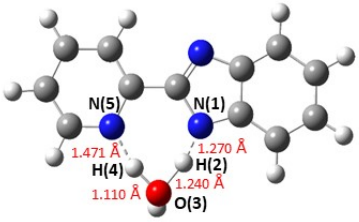
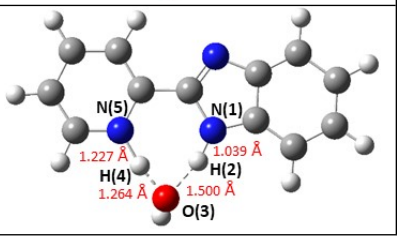


SI Figure S2: (a) Two-color resonant two-photon ionization (2C-R2PI) spectrum of PBI-H_2O (b) UV–UV hole-burn spectrum obtained by scanning hole-burning laser coming 100 ns prior to the 2C-R2PI measurement (probe laser is fixed at $S_1 \leftarrow S_0$ transition 30544 cm^{-1}) and (c) Franck–Condon vibronic spectrum with suggested band assignment, simulated using *FC-LabWin* software based on the DFT-D4(B3LYP)/def2-TZVPP calculation. The relative zero is the band origin of the PBI-H_2O complex at 30544 cm^{-1}.



SI Figure S3: 2D potential energy surface scan (S_0: red and S_1: green) along the O(3)-H(2) and the N(5)-H(4) distance. The relative energies for the surface are given in kJ mol^{-1}, calculated at the DFT-D4/B3-LYP (def2-TZVPP) level of theory. The relative zero is the electronic energy of the relaxed geometry-optimized PBI-H_2O (normal form) complex in the ground state.

SI Figure S4: Geometry optimized structures of PBI-H_2O in the S_1 state calculated using B3LYP-D4/def2-TZVPP and ADC(2) (MP2)/cc-pVDZ level of theory.

	ADC(2) (MP2)/cc-pVDZ	B3LYP-D4/def2-TZVPP
Structure ‘a’ (Normal form)		
Structure ‘b’ (Tautomer product)		
Structure ‘c’ (proton transfer product)		
TS_{ab} (highest energy structure along the path a → b)		
TS_{ac} (highest energy structure along the path a → c)		

SI Table S1: Excited State NBO analysis of structure 'a', 'b', 'c', 'TS_{ab}' and 'TS_{ac}' calculated at DFT-D4/B3-LYP (def2-TZVPP) level of theory. ρ_R is the absolute charge on the solvent molecule. Structure 'c' and 'TS_{ac}' show charge accumulation on the solvent molecule, depicting the formation of charge separated complex.

Structure	ρ_R (charge on solvent)
a	-0.02146
b	-0.01661
c	**-0.86533**
TS_{ab}	0.05517
TS_{ac}	**-0.61561**

SI Table S2: Coordinates of the optimized structures of PBI–H_2O complexes in ground state S_0 and excited state S_1, calculated using B3LYP-D4/def2-TZVPP and ADC(2) (MP2)/cc-pVDZ level of theory. Here 'a': normal form, 'b': tautomer form and 'c': proton transferred form of PBI–H_2O cluster.

PBI-H_2O complex structures calculated at DFT-D4 (B3LYP)/def2-TZVPP level of theory											
Structure 'a' (S_0)				Structure 'b' (S_0)				Structure 'c' (S_0)			
C	2.9805	1.3342	-0.081	C	2.9931	1.395	-0.0827	C	3.0016	1.3592	-0.0281
H	-5.5761	0.248	0.0603	H	-5.5612	0.2877	0.0739	H	-5.5618	0.2003	-0.0165
H	5.0378	-1.3688	0.0851	H	5.0232	-1.3291	0.0863	H	5.0543	-1.3519	0.0018
C	-3.7929	-0.9424	0.0913	C	-3.8053	-0.9105	0.079	C	-3.7825	-0.9759	0.0102
C	-1.7617	0.1341	0.0176	C	-1.6929	0.1821	0.0108	C	-1.7143	0.1446	0.0136
C	4.1414	0.5836	-0.0374	C	4.1396	0.6357	-0.0376	C	4.1577	0.6064	-0.0229
N	-2.4612	-1.0098	0.0765	N	-2.4586	-0.938	0.0554	N	-2.4444	-0.9893	0.0196
C	-4.4957	0.2508	0.045	C	-4.4827	0.2773	0.0529	C	-4.4827	0.2074	-0.0057
C	2.9092	-1.5159	0.1001	C	2.898	-1.4642	0.096	C	2.9291	-1.5032	0.019
H	3.0035	2.4129	-0.1488	H	3.0285	2.474	-0.149	H	3.0259	2.4398	-0.0466
H	5.1009	1.0817	-0.0717	H	5.1058	1.1217	-0.069	H	5.1187	1.1026	-0.0375
H	-4.3168	-1.8896	0.1448	H	-4.2906	-1.8742	0.1204	H	-4.2492	-1.9507	0.0135
H	-1.7771	2.2692	-0.0796	H	-1.7465	2.3071	-0.06	H	-1.7791	2.2727	-0.0072
C	-2.3903	1.3825	-0.033	C	-2.3603	1.421	-0.0221	C	-2.3783	1.3756	-0.0011
C	1.7416	-0.7582	0.0552	C	1.7137	-0.7099	0.0491	C	1.7565	-0.7451	0.0144
N	0.4121	-1.1004	0.0814	N	0.4121	-1.0938	0.0744	N	0.438	-1.0985	0.0258
C	4.106	-0.8205	0.052	C	4.0917	-0.7793	0.0514	C	4.1209	-0.8051	2.00E-04
H	0.0238	-2.042	0.1298	H	-0.3319	-2.6092	0.1533	H	0.0073	-2.0056	0.0644
H	-4.2795	2.3907	-0.0577	H	-4.239	2.4208	-0.0245	H	-4.2767	2.3512	-0.0225
H	2.8855	-2.5945	0.1721	H	2.8696	-2.5434	0.1679	H	2.9028	-2.5836	0.0334
C	-0.3011	0.0689	0.0102	C	-0.2646	0.0864	0.005	C	-0.268	0.0708	0.0103
C	-3.771	1.4367	-0.0198	C	-3.7318	1.4658	-0.0014	C	-3.7571	1.4027	-0.0103
C	1.7605	0.6544	-0.0339	C	1.7585	0.7222	-0.0386	C	1.7783	0.6763	-0.0091
N	0.4718	1.1347	-0.0589	N	0.4923	1.203	-0.0633	N	0.4962	1.1556	-0.011
O	-1.1659	-3.4881	0.1831	O	-1.0809	-3.285	0.1756	H	-1.9876	-1.8877	0.0694
H	-1.7712	-2.7139	0.1275	H	-1.9931	-1.8729	0.0631	O	-1.176	-3.0793	0.0454
H	-1.292	-3.9873	-0.6276	H	-0.9544	-3.8592	-0.5838	H	-1.2558	-3.7983	0.6724
Structure 'a' (S_1)				Structure 'b' (S_1)				Structure 'c' (S_1)			
C	2.999	1.2986	-0.0575	C	3.0259	1.357	-0.1752	C	3.162	1.6192	0.1096
H	-5.5843	0.0888	0.0951	H	-5.6023	0.2126	0.0553	H	-5.4312	0.456	-0.041
H	5.024	-1.4864	0.0908	H	5.0186	-1.4144	0.1705	H	5.2556	-1.0517	-0.1171
C	-3.7481	-0.9949	0.1254	C	-3.8157	-0.9177	0.0255	C	-3.6872	-0.724	-0.094
C	-1.762	0.1979	0.0021	C	-1.757	0.3059	0.028	C	-1.5511	0.3979	-0.047
C	4.1869	0.4776	-0.0121	C	4.2021	0.5397	-0.0779	C	4.3355	0.8827	0.0539

N	-2.4088	-1.0315	0.0953	N	-2.4318	-0.8877	0.0147	N	-2.3163	-0.7723	-0.1082
C	-4.5066	0.1537	0.0638	C	-4.5219	0.2634	0.0487	C	-4.3527	0.456	-0.0489
C	2.8705	-1.5383	0.0827	C	2.8612	-1.4538	0.1894	C	3.1225	-1.2175	-0.1585
H	3.0843	2.3746	-0.1113	H	3.1107	2.4255	-0.3168	H	3.1702	2.6947	0.2192
H	5.1496	0.9683	-0.0312	H	5.1706	1.0146	-0.1472	H	5.2885	1.3906	0.1165
H	-4.2386	-1.9598	0.2064	H	-4.2693	-1.8939	0.018	H	-4.1926	-1.6727	-0.135
H	-1.8995	2.3241	-0.1354	H	-1.859	2.3911	0.0673	H	-1.6221	2.5025	0.0568
C	-2.462	1.4038	-0.0649	C	-2.4265	1.4749	0.0577	C	-2.2301	1.6125	0.0061
C	1.7174	-0.7313	0.0369	C	1.7172	-0.657	0.0965	C	1.9526	-0.4751	-0.107
N	0.4116	-1.038	0.047	N	0.4023	-0.9946	0.1512	N	0.6165	-0.824	-0.1686
C	4.1192	-0.8986	0.0559	C	4.1179	-0.822	0.0989	C	4.319	-0.5127	-0.0771
H	-0.009	-1.9877	0.0654	H	-0.2877	-2.7091	0.1684	H	0.2648	-1.7997	-0.2285
H	-4.3939	2.3344	-0.0897	H	-4.4141	2.4161	0.0812	H	-4.1139	2.6237	0.0359
H	2.7917	-2.6147	0.1406	H	2.7844	-2.5232	0.332	H	3.1147	-2.2952	-0.2504
C	-0.3198	0.1854	-0.0086	C	-0.2545	0.214	0.0041	C	-0.1243	0.3437	-0.0502
C	-3.8401	1.4089	-0.0383	C	-3.87	1.4863	0.0653	C	-3.6073	1.6715	8.00E-04
C	1.7796	0.6867	-0.0308	C	1.8132	0.7418	-0.0848	C	1.9488	0.9326	0.0266
N	0.4939	1.2129	-0.0571	N	0.5053	1.2615	-0.1447	N	0.6606	1.4061	0.0603
O	-1.0664	-3.318	0.1707	O	-0.9619	-3.4218	0.13	O	-1.6466	-3.5446	0.4695
H	-1.7085	-2.5296	0.156	H	-1.9335	-1.7724	0.0086	H	-1.8928	-1.7134	-0.0031
H	-1.258	-3.8359	-0.6147	H	-0.792	-3.9056	-0.6819	H	-1.5452	-4.2797	-0.1474
PBI-H_2O complex structures calculated at ADC(2) (MP2)/cc-pVDZ level of theory											
Structure 'a' (S_0)				Structure 'b' (S_0)				Structure 'c' (S_0)			
C	2.9861	1.3388	-0.0863	C	2.9803	1.3395	-0.11	C	2.997	1.3228	-0.0971
H	-5.6262	0.2617	0.062	H	-5.6206	0.2416	0.0841	H	-5.6236	0.1864	0.0847
H	5.0646	-1.3962	0.0895	H	5.0479	-1.4024	0.1105	H	5.0614	-1.4213	0.1115
C	-3.8284	-0.9482	0.1124	C	-3.8505	-0.9815	0.0918	C	-3.8257	-1.0079	0.1031
C	-1.7776	0.125	0.0239	C	-1.7182	0.1044	0.0138	C	-1.743	0.1137	0.0067
C	4.1572	0.5792	-0.041	C	4.1448	0.5762	-0.0508	C	4.1616	0.5573	-0.0393
N	-2.4798	-1.0346	0.1005	N	-2.4946	-1.0158	0.0646	N	-2.477	-1.0253	0.0747
C	-4.5324	0.2615	0.0476	C	-4.5287	0.2295	0.0604	C	-4.5312	0.1933	0.0588
C	2.9138	-1.5443	0.1078	C	2.8967	-1.544	0.1254	C	2.9115	-1.5635	0.1193
H	3.0077	2.4306	-0.1587	H	3.0103	2.4306	-0.1981	H	3.0253	2.4138	-0.1784
H	5.1291	1.0823	-0.0787	H	5.1198	1.0744	-0.0932	H	5.1365	1.055	-0.0755
H	-4.3658	-1.9016	0.1789	H	-4.348	-1.9534	0.1403	H	-4.3002	-1.9913	0.1648
H	-1.7666	2.2772	-0.1052	H	-1.742	2.246	-0.0692	H	-1.7872	2.2588	-0.0969
C	-2.4023	1.3901	-0.0454	C	-2.3803	1.3603	-0.0248	C	-2.4063	1.3602	-0.0425
C	1.7336	-0.7747	0.0606	C	1.7005	-0.7863	0.0649	C	1.7307	-0.7918	0.0603
N	0.4015	-1.1162	0.0896	N	0.392	-1.1893	0.0995	N	0.4062	-1.1431	0.0855
C	4.1213	-0.841	0.0549	C	4.1039	-0.8478	0.0658	C	4.1194	-0.8644	0.0676
H	4.00E-04	-2.0687	0.144	H	-0.4099	-2.6912	0.2263	H	-0.0654	-2.044	0.1329
H	-4.3077	2.4256	-0.0861	H	-4.2741	2.394	-0.0311	H	-4.3245	2.3587	-0.0551
H	2.8889	-2.636	0.185	H	2.8719	-2.6355	0.2179	H	2.8795	-2.654	0.2041
C	-0.3098	0.0593	0.0146	C	-0.2805	0.006	0.0057	C	-0.2884	0.0353	-0.0039
C	-3.7981	1.458	-0.0339	C	-3.7696	1.4229	-0.0031	C	-3.8013	1.398	-0.0182
C	1.7511	0.6519	-0.0346	C	1.7381	0.6554	-0.0511	C	1.7571	0.6399	-0.0466
N	0.4645	1.1509	-0.0613	N	0.4653	1.1499	-0.0859	N	0.4774	1.1432	-0.084
O	-1.0826	-3.5017	0.1702	O	-1.1867	-3.3309	0.1593	O	-1.2008	-3.0663	0.1659
H	-1.7376	-2.7685	0.2138	H	-2.0222	-1.9759	0.0762	H	-1.9991	-1.9286	0.0869
H	-1.183	-3.8093	-0.7416	H	-1.0426	-3.7272	-0.7125	H	-1.2019	-3.5721	-0.6599
Structure 'a' (S_1)				Structure 'b' (S_1)				Structure 'c' (S_1)			
C	3.0011	1.327	-0.0725	C	3.0106	1.33	-0.0908	C	3.1477	1.6479	-0.1098
H	-5.6264	0.1345	0.0742	H	-5.6467	0.1625	0.1251	H	-5.5222	0.4740	0.1341
H	5.0535	-1.4823	0.0925	H	5.0512	-1.468	0.1235	H	5.2392	-1.0690	0.2278
C	-3.7727	-0.9895	0.1263	C	-3.8495	-0.9808	0.1649	C	-3.7520	-0.7044	0.1324
C	-1.7565	0.1776	0.0153	C	-1.7554	0.2078	0.0027	C	-1.6038	0.4422	0.0192
C	4.17	0.5061	-0.0252	C	4.1986	0.5089	-0.0276	C	4.3282	0.8901	-0.0152
N	-2.4245	-1.0464	0.1095	N	-2.4686	-0.9987	0.1264	N	-2.3669	-0.7458	0.0866

C	-4.5335	0.1865	0.0542	C	-4.5532	0.2034	0.0856	C	-4.4292	0.4849	0.0884
C	2.8861	-1.5815	0.0975	C	2.8671	-1.5373	0.1244	C	3.0777	-1.2097	0.2294
H	3.0727	2.4165	-0.1362	H	3.0826	2.4193	-0.1729	H	3.1723	2.7343	-0.2418
H	5.1505	0.9948	-0.0536	H	5.1766	1.001	-0.0629	H	5.2964	1.3992	-0.0748
H	-4.281	-1.9607	0.2052	H	-4.3311	-1.9575	0.2668	H	-4.2514	-1.6748	0.2020
H	-1.8709	2.3469	-0.1304	H	-1.8454	2.3202	-0.1625	H	-1.6869	2.5717	-0.1025
C	-2.4603	1.4267	-0.0605	C	-2.4473	1.4084	-0.0759	C	-2.3057	1.6704	-0.0382
C	1.7188	-0.7732	0.05	C	1.7169	-0.7418	0.0632	C	1.9087	-0.4466	0.1378
N	0.416	-1.0848	0.0653	N	0.3943	-1.1067	0.0868	N	0.5594	-0.7846	0.1512
C	4.1199	-0.9131	0.0575	C	4.1313	-0.8773	0.0766	C	4.2990	-0.5126	0.1511
H	-0.0142	-2.0452	0.0965	H	-0.3643	-2.8513	0.181	H	0.1688	-1.7467	0.3247
H	-4.3995	2.3772	-0.0989	H	-4.3986	2.4037	-0.1092	H	-4.2161	2.6872	-0.0486
H	2.8153	-2.6715	0.1659	H	2.7973	-2.6274	0.2083	H	3.0544	-2.2973	0.3589
C	-0.3386	0.1698	-1.00E-04	C	-0.2887	0.1392	0.0016	C	-0.1666	0.3957	0.0294
C	-3.8461	1.4334	-0.0421	C	-3.86	1.4538	-0.0444	C	-3.6915	1.7282	-0.0098
C	1.7621	0.6935	-0.0334	C	1.7963	0.6884	-0.0422	C	1.9146	0.9736	-0.0282
N	0.4893	1.2315	-0.0633	N	0.4824	1.2174	-0.0803	N	0.6260	1.4785	-0.0919
O	-1.0229	-3.3758	0.1715	O	-1.0558	-3.5437	0.1031	O	-0.8350	-3.7820	-0.2671
H	-1.686	-2.6276	0.2338	H	-1.9875	-1.9078	0.1546	H	-1.9072	-1.6656	0.0633
H	-1.1999	-3.7193	-0.7161	H	-1.0504	-3.7164	-0.849	H	-1.6435	-4.0076	-0.7857