Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Photophysics and Photochemistry of cis- trans-Hydroquinone, Catechol and Their Ammonia Clusters: A Theoretical Study

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This supplementary material section contains one Figure and two Tables:

Figure SM1: Optimized structures of HQ and CTC monomers and their cluster systems with 1-4 ammonia molecules at the CC2/aug-cc-pVDZ level of theory. Only the S_2 ($^1A''$) excited state, which is accompanied with hydrogen detachment (or transfer) has been depicted. The circles or ellipses have been used to specify HD/HT phenomena.

Table SM1: Vertical transition energies of HQ/CTC monomers, and their ammoniated clusters, computed at the CC2/TZVP level of theory.

Table SM2: xyz coordinates of the optimized ground state geometry of HQ/CTC monomers, and their ammoniated clusters.

Figure SM1:

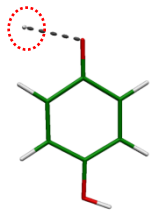
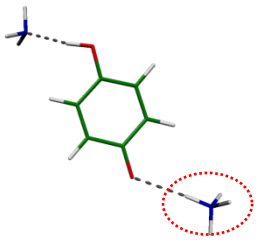
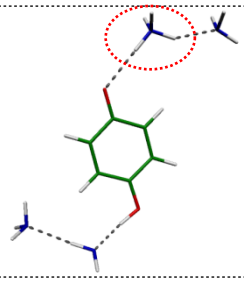
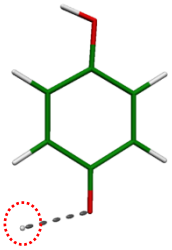
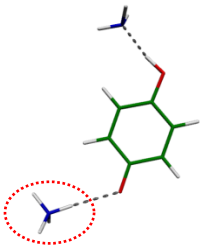
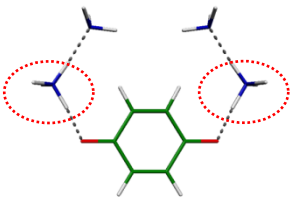
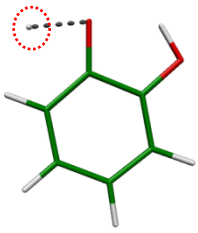
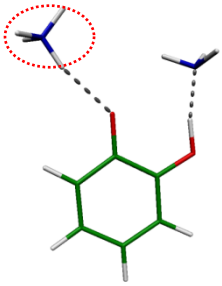
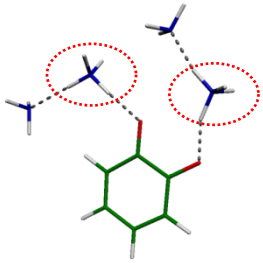
$tHQ-(NH_3)_n$		
n=0	n=2	n=4
		
$cHQ-(NH_3)_n$		
		
$CTC-(NH_3)_n$		
		

Table SM1:

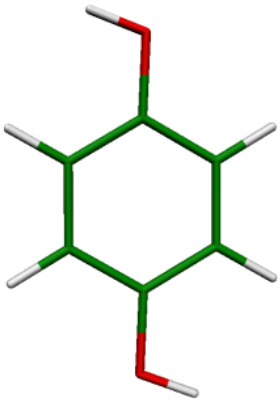
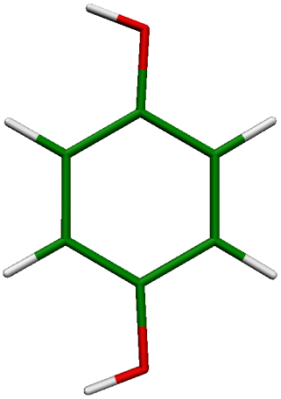
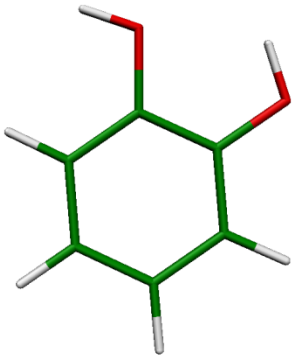
State	Energy/eV	Oscillator Strength	Configuration
tHQ			
A'1 (π_1/π_1^*),(π_2/π_2^*)	4.63	0.0629	5a"-6a"(84.1%),4a"-7a"(12.2%)
A'2 (π_1/π_1^*),(π_2/π_2^*)	6.25	0.1697	5a"-7a"(79.2%),4a"-6a"(15.1%)
A'3 (π_1/π_1^*),(π_2/π_2^*)	7.20	0.6970	4a"-6a"(80.5%),5a"-7a"(12.4%)
A'4 (π_1/π_1^*),(π_2/π_2^*)	7.48	0.4225	4a"-7a"(80.9%),5a"-6a"(10.3%)
A'5 (π_1/π^*),(π_2/π^*)	7.72	0.0000	3a"-6a"(94.5%),1a"-6a"(2.0%)
A"1 (π_1/σ^*),(π_2/σ^*)	6.06	0.00009	5a"-25a'(86.2%),2a"-25a'(4.1%)
A"2 (π_1/σ_1^*),(π_2/σ_2^*)	6.32	0.0000	5a"-26a'(84.2%),3a"-25a'(5.5%)
A"3 (π/σ_1^*),(π/σ_2^*)	7.04	0.0000	5a"-27a'(87.0%),5a"-36a'(2.7%)
A"4 (π/σ_1^*),(π/σ_2^*)	7.79	0.0002	5a"-28a'(89.0%),5a"-32a'(1.7%)
A"5 (π/σ_1^*),(π/σ_2^*)	8.00	0.0041	4a"-25a'(92.9%),4a"-37a'(1.2%)
tHQA			
A'1(π_1/π_1^*),(π_2/π_2^*)	4.54	0.0670	6a"-7a"(85.0%),5a"-8a"(10.7%)
A'2(π_1/π_1^*),(π_2/π_2^*)	6.16	0.2192	6a"-8a"(80.3%),5a"-7a"(12.6%)
A'3(π_1/π_1^*),(π_2/π_2^*)	7.15	0.7593	5a"-7a"(80.6%),6a"-8a"(9.3%)
A'4(π_1/π_1^*),(π_2/π_2^*)	7.42	0.2784	5a"-8a"(62.9%),4a"-7a"(21.9%)
A'5(σ_1,n_H,n_A/σ_A^*),(π_2,n_H,n_A/σ_A^*)	7.57	0.0734	28a'-29a'(79.2%),27a'-29a'(14.1%)
A"1(π/σ_H^*),(π/σ_A^*)	5.95	0.00001	6a"-30a'(75.0%),6a"-29a'(11.3%)
A"2(π/σ_A^*),(π/σ_H^*)	6.13	0.00008	6a"-29a'(73.3%),6a"-30a'(12.0%)
A"3(π/σ_{H1}^*,σ_A^*),(π/σ_{H2}^*,σ_A^*)	6.88	0.000004	6a"-31a'(61.9%),6a"-32a'(21.9%)
A"4(π/σ_{H1}^*,σ_{A1}^*),(π/σ_{H2}^*,σ_{A2}^*)	7.54	0.0003	6a"-33a'(51.8%),6a"-32a'(31.5%)
A"5(π/σ_{A1}^*),(π/σ_H^*,σ_{A2}^*)	7.89	0.0024	5a"-29a'(69.0%),5a"-31a'(17.8%)

tHQ-A2			
A’1(π_1/π_1^*),(π_2/π_2^*)	4.46	0.0704	7a"-8a"(85.1%),6a"-9a"(9.3%)
A’2(π_1/π_1^*),(π_2/π_2^*)	6.09	0.2618	7a"-9a"(78.4%),6a"-8a"(11.2%)
A’3(π_1/π_1^*),(π_2/π_2^*)	7.11	0.8389	6a"-8a"(79.3%),7a"-9a"(7.2%)
A’4(π_1/π_1^*),(π_2/π_2^*)	7.45	0.3733	6a"-9a"(78.8%),7a"-8a"(8.3%)
A’5($n_H,n_A/\sigma_{A1}^*$),($\sigma_2,n_H,n_A/\sigma_{A2}^*$)	7.53	0.1338	31a’-34a’(42.7%),32’-33a’(35.6%)
A”1(π_1/σ_A^*),(π_2/σ_A^*)	5.81	0.00007	7a"-33a’(89.0%),4a"-33a’(3.0%)
A”2(π/σ_{A1}^*),($\pi/\sigma_H^*,\sigma_{A2}^*$)	5.83	0.0000	7a"-34a’(84.7%),7a"-35a’(5.9%)
A”3($\pi/\sigma_{H1}^*,\sigma_{A1}^*$),($\pi/\sigma_{H2}^*,\sigma_{A2}^*$)	6.73	0.0000	7a"-35a’(60.2%),7a"-37a’(23.1%)
A”4(π/σ_{A1}^*),($\pi/\sigma_H^*,\sigma_{A2}^*$)	7.66	0.00000004	6a"-34a’(65.7%),6a"-35a’(17.7%)
A”5(π/σ_1^*),(π/σ_2^*)	7.73	0.0000005	7a"-40a’(61.2%),7a"-41a’(21.7%)
cHQ			
A’1(π_1/π_1^*),(π_2/π_2^*)	4.64	0.0619	5a"-6a"(84.2%),4a"-7a"(12.3%)
A’2(π_1/π_1^*),(π_2/π_2^*)	6.25	0.1648	5a"-7a"(78.9%),4a"-6a"(15.5%)
A’3(π_1/π_1^*),(π_2/π_2^*)	7.20	0.6967	4a"-6a"(79.8%),5a"-7a"(12.8%)
A’4(π_1/π_1^*),(π_2/π_2^*)	7.47	0.4237	4a"-7a"(81.0%),5a"-6a"(10.5%)
A’5(π_1/π^*),(π_2/π^*)	7.73	0.0021	3a"-6a"(94.2%),1a"-6a"(2.0%)
A”1(π_1/σ^*),(π_2/σ^*)	6.12	0.00004	5a"-25a'(85.7%),2a"-25a'(4.2%)
A”2(π_1/σ_1^*),(π_2/σ_2^*)	6.18	0.0000	5a"-26a'(86.6%),3a"-25a'(4.7%)
A”3(π/σ_1^*),(π/σ_2^*)	7.03	0.0000	5a"-27a'(85.5%),5a"-28a'(2.3%)
A”4(π/σ_1^*),(π/σ_2^*)	7.87	0.0000	5a"-28a'(82.0%),5a"-31a'(6.8%)
A”5(π/σ_1^*),(π/σ_2^*)	7.99	0.0033	4a"-26a'(83.3%),4a"-27a'(9.3%)
cHQ-A			
A’1(π_1/π_1^*),(π_2/π_2^*)	4.55	0.0659	6a"-7a"(85.4%),5a"-8a"(10.9%)
A’2(π_1/π_1^*),(π_2/π_2^*)	6.16	0.2123	6a"-8a"(80.6%),5a"-7a"(13.0%)
A’3(π_1/π_1^*),(π_2/π_2^*)	7.15	0.7534	5a"-7a"(79.8%),6a"-8a"(9.7%)
A’4(π_1/π_1^*),(π_2/π_2^*)	7.42	0.3148	5a"-8a"(66.2%),4a"-7a"(18.1%)
A’5($\sigma_1,n_{H1},n_A/\sigma_A^*$),($\sigma_2,n_{H2},n_A/\sigma_A^*$)	7.57	0.0543	28a'-29a'(78.3%),27a'-29a'(15.0%)
A”1(π_1/σ^*),(π_2/σ^*)	5.91	0.00002	6a"-30a'(85.0%),4a"-30a'(3.3%)
A”2(π/σ_{A1}^*),(π/σ_H^* ,σ_{A2}^*)	6.07	0.000001	6a"-29a'(79.9%),6a"-31a'(6.7%)

A”3(π/σ_{H1}* ,σ_{A1}*),(π/σ_{H2}* ,σ_{A2}*)	6.87	0.00001	6a"-31a'(55.6%),6a"-32a'(19.1%)
A”4(π/σ_{H1}* ,σ_{A1}*),(π/σ_{H2}* ,σ_{A2}*)	7.59	0.000005	6a"-32a'(56.7%),6a"-33a'(24.5%)
A”5(π/σ_1*),(π/σ_{A1}*)	7.77	0.0024	5a"-30a'(44.0%),5a"-29a'(33.4%)
cHQ-A2			
A’1(π_1/π_1*),(π_2/π_2*)	4.47	0.0690	7a"-8a"(86.2%),6a"-9a"(9.9%)
A’2(π_1/π_1*),(π_2/π_2*)	6.10	0.2518	7a"-9a"(81.3%),6a"-8a"(11.6%)
A’3(π_1/π_1*),(π_2/π_2*)	7.10	0.8155	6a"-8a"(78.6%),7a"-9a"(7.8%)
A’4(π_1/π_1*),(π_2/π_2*)	7.45	0.4197	6a"-9a"(81.2%),7a"-8a"(7.9%)
A’5(π_1/π*),(π_2/π*)	7.45	0.0119	5a"-8a"(90.1%),3a"-8a"(2.2%)
A”1(π/σ_{A1}*),(π/σ_H*,σ_{A2}*)	5.70	0.0000	7a"-33a'(82.8%),7a"-35a'(7.8%)
A”2(π_1/σ_A*),(π_2/σ_A*)	5.84	0.0000002	7a"-34a'(89.2%),4a"-34a'(3.1%)
A”3(π/σ_{H1}*,σ_A*),(π/σ_{H2}*)	6.70	0.0000	7a"-35a'(60.9%),7a"-37a'(13.8%)
A”4(π/σ_{H1}*),(π/σ_{H1}*,σ_A*)	7.36	0.0000	7a"-37a'(73.8%),7a"-39a'(7.3%)
A”5(π/σ_{A1}*),(π/σ_H*,σ_{A2}*)	7.52	0.0016	6a"-33a'(67.9%),6a"-35a'(18.6%)
CTC			
A’1(π_1/π_1*),(π_2/π_2*)	4.97	0.0414	5a"-6a"(71.4%),4a"-7a"(23.3%)
A’2(π_1/π_1*),(π_2/π_2*)	6.17	0.0703	5a"-7a"(69.5%), 4a"-6a"(21.5%)
A’3(π_1/π_1*),(π_2/π_2*)	6.99	0.4753	4a"-6a"(62.6%), 5a"-7a"(19.4%)
A’4(π_1/π_1*),(π_2/π_2*)	7.07	0.6516	4a"-7a"(61.2%), 5a"-6a"(16.4%)
A’5(π_1/π_1*),(π_2/π_2*)	8.55	0.0895	3a"-6a"(84.8%), 4a"-7a"(4.4%)
A”1(π_1/σ*),(π_2/σ*)	6.00	0.0002	5a"-25a'(74.4%), 3a"-25a'(5.1%)
A”2(π_1/σ_1*),(π_2/σ_2*)	6.86	0.0002	5a"-26a'(53.5%), 4a"-25a'(21.3%)
A”3(π_1/σ_1*),(π_2/σ_2*)	7.14	0.0024	4a"-25a'(50.2%), 5a"-26a'(26.4%)
A”4(π_1/σ_1*),(π_2/σ_2*)	7.66	0.0003	5a"-27a'(65.7%), 4a"-25a'(7.5%)
A”5(π/σ_1*),(π/σ_2*)	7.74	0.000026	4a"-26a'(84.3%), 4a"-25a'(3.8%)
CTC-A			
A’1(π_1/π_1*),(π_2/π_2*)	4.91	0.0495	6a"-7a"(72.3%), 5a"-8a"(21.8%)
A’2(π_1/π_1*),(π_2/π_2*)	6.05	0.0824	6a"-8a"(72.5%), 5a"-7a"(18.6%)
A’3(π_1/π_1*),(π_2/π_2*)	6.90	0.4771	5a"-7a"(72.0%), 6a"-8a"(16.8%)
A’4(π_1/π_1*),(π_2/π_2*)	6.96	0.6549	5a"-8a"(66.0%), 6a"-7a"(17.3%)

A’5(σ_{H1},n_{H1}, $n_{A\ 1}$/σ_A*),(σ_{H2},n_{H2},n_{A2}/σ_A*)	7.68	0.1149	28a'-29a'(78.0%), 27a'-29a'(14.9%)
A”1(π/σ_{A1}*),(π/σ*)	6.13	0.00004	6a"-29a'(79.3%), 6a"-32a'(7.5%)
A”2(π/σ_{H1}*,σ_A*),(π/σ_{H2}*)	6.56	0.0001	6a"-30a'(55.5%), 6a"-32a'(24.7%)
A”3(π_1/σ_{A1}*),(π_2/σ*)	7.14	0.0025	5a"-29a'(67.2%), 6a"-32a'(9.2%)
A”4(π/σ_{H1}*),(π/σ_{H2}*,σ_A*)	7.28	0.0006	6a"-32a'(40.1%), 6a"-30a'(17.3%)
A”5(π/σ_{H1}*,σ_A*),(π/σ_{H2}*)	7.57	0.000001	5a"-30a'(63.3%), 5a"-32a'(9.8%)
CTC-A2			
A’1(π_1/π_1*),(π_2/π_2*)	4.84	0.0613	7a"-8a"(72.0%), 6a"-9a"(19.3%)
A’2(π_1/π_1*),(π_2/π_2*)	5.94	0.0995	7a"-9a"(70.5%), 6a"-8a"(17.6%)
A’3(π_1/π_1*),(π_2/π_2*)	6.79	0.4501	6a"-8a"(62.8%), 7a"-9a"(16.6%)
A’4(π_1/π_1*),(π_2/π_2*)	6.89	0.6681	6a"-9a"(61.1%), 7a"-8a"(12.3%)
A’5(σ_H,n_H, n_A /σ_{A1}*),(σ_H,n_H, n_A /σ_{A2}*)	7.46	0.0562	32a'-34a'(74.4%), 32a'-33a'(10.8%)
A”1(π_1/σ_A*),(π_2/σ_A*)	5.77	0.00009	7a"-33a'(83.9%), 5a"-33a'(3.5%)
A”2(π/σ_{A1}*),(π/σ_H*,σ_{A2}*)	6.34	0.00003	7a"-34a'(57.7%), 7a"-35a'(14.2%)
A”3(π_1/σ_{A1}*),(π_2/σ_H*,σ_{A2}*)	6.82	0.0016	6a"-33a'(77.5%), 7a"-35a'(4.1%)
A”4(π/σ_{H1}*,σ_{A1}*),(π/σ_{H2}*,σ_{A2}*)	7.00	0.0011	7a"-36a'(33.0%), 7a"-35a'(31.3%)
A”5(π/σ_{A1}*),(π/σ_H*,σ_{A2}*)	7.39	0.00008	6a"-34a'(34.9%), 6a"-35a'(25.4%)

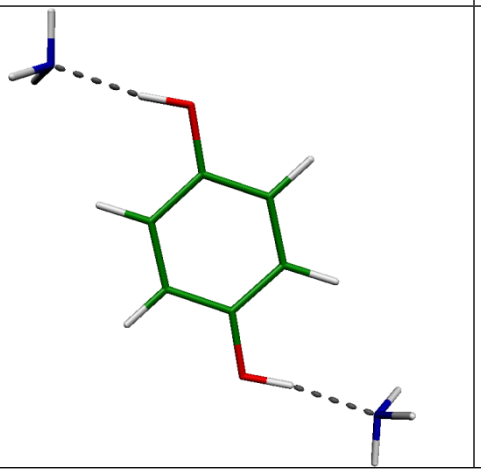
Table SM2

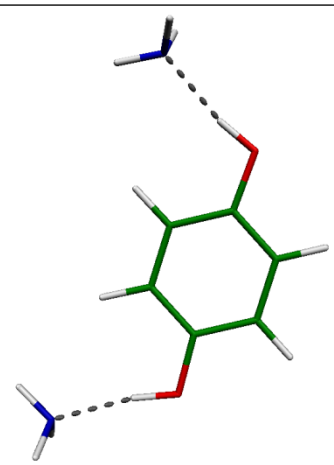
tHQ				cHQ				CTC			
C	-0.71115	-1.19334	0	C	-1.51042	-0.55426	0	C	-1.74137	-0.55675	0
C	0.68016	-1.21508	0	C	-0.30307	-1.25402	0	C	-1.72364	0.83476	0
C	1.39516	-0.02145	0	C	0.90401	-0.56245	0	C	-0.51111	1.52222	0
C	0.71115	1.19334	0	C	0.90142	0.83199	0	C	0.68667	0.82000	0
C	-0.68016	1.21508	0	C	-0.29918	1.52783	0	C	0.66536	-0.57950	0
C	-1.39515	0.02145	0	C	-1.51039	0.83690	0	C	-0.54041	-1.26685	0
H	-1.26154	-2.12838	0	H	-2.44712	-1.10156	0	H	-2.68068	-1.09406	0
H	1.22039	-2.15281	0	H	-0.31233	-2.33885	0	H	-2.65246	1.39039	0
O	2.76701	-0.10900	0	O	2.12794	-1.18811	0	H	-0.47413	2.60409	0
H	1.26154	2.12838	0	H	1.84724	1.35805	0	O	1.86965	1.50024	0
H	-1.22038	2.15281	0	H	-0.31289	2.61001	0	O	1.90778	-1.17817	0
O	-2.76700	0.10900	0	O	-2.66171	1.58787	0	H	-0.54036	-2.35195	0
H	3.12659	0.78545	0	H	-3.41516	0.98646	0	H	2.57754	0.84103	0
H	-3.12659	-0.78545	0	H	1.98067	-2.14084	0	H	1.79617	-2.13543	0
											

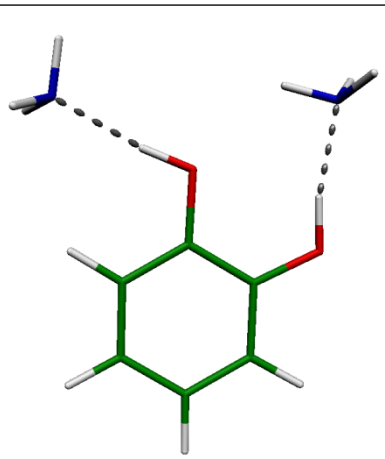
tHQ-A2			
C	-0.09389	1.38464	0
C	-1.26223	0.62370	0
C	-1.15551	-0.77039	0
C	0.09389	-1.38465	0
C	1.26223	-0.62370	0
C	1.15551	0.77039	0
H	2.05180	1.37928	0
H	-0.17815	2.46438	0
O	-2.45551	1.28594	0
H	-3.19298	0.63739	0
H	-2.05180	-1.37928	0
H	0.17814	-2.46439	0
O	2.45551	-1.28595	0
H	3.19298	-0.63739	0
H	4.88622	0.97262	0.81362
N	4.76508	0.38048	0
H	5.53823	-0.27525	0
H	4.88622	0.97262	-0.81362
H	-4.88622	-0.97261	0.81362
N	-4.76508	-0.38048	0
H	-5.53823	0.27525	0
H	-4.88622	-0.97261	0.81362

cHQ-A2			
H	-0.19129	-2.03553	0
H	0.85391	2.79613	0
C	0.6354	1.73548	0
C	-0.70071	1.32775	0
C	-0.98580	-0.03800	0
C	0.04621	-0.97838	0
C	1.37966	-0.56789	0
C	1.66169	0.80033	0
H	2.69751	1.11622	0
O	2.43364	-1.43519	0
H	2.10300	-2.35917	0
H	-2.01642	-0.37235	0
O	-1.66216	2.29664	0
H	-2.55134	1.88142	0
H	2.23857	-4.62359	0.81422
H	0.83408	-4.55117	0
N	1.79121	-4.21800	0
H	2.23857	-4.62359	-0.81422
H	-4.81783	1.80821	-0.81422
H	-4.61871	0.41607	0
N	-4.37340	1.39940	0
H	-4.81783	1.80821	0.81422

CTC-A2			
C	-2.15770	1.08246	0
C	-2.94463	-0.06562	0
C	-2.33846	-1.31737	0
C	-0.94719	-1.40547	0
C	-0.15380	-0.25837	0
C	-0.76460	1.01028	0
H	-2.60438	2.06913	0
H	-4.02385	0.02245	0
H	-2.93463	-2.22123	0
H	-0.46405	-2.37542	0
O	1.21638	-0.30510	0
H	1.50999	-1.24556	0
O	-0.07813	2.17657	0
H	0.90314	2.06113	0
N	2.27349	-2.93127	0
H	2.00955	-3.47664	0.81310
H	3.28650	-2.88738	0
H	2.00955	-3.47664	-0.81310
N	2.71444	2.22246	0
H	3.16618	2.61679	0.81564
H	3.16618	2.61679	-0.81564
H	2.87702	1.22299	0







tHQ-A4			
H	-3.03708	-2.27905	0
O	-2.65534	-1.36749	0
C	-1.29479	-1.43989	0
C	-0.57209	-0.24666	0
H	-1.12202	0.68728	0
C	0.82056	-0.25364	0
H	1.36831	0.67917	0
C	1.52644	-1.46134	0
O	2.88697	-1.53380	0
H	3.26883	-0.62228	0
C	0.80377	-2.65453	0
C	-0.58897	-2.64754	0
H	-1.13671	-3.58035	0
H	1.35375	-3.58844	0
H	3.49856	1.80918	0
N	4.12041	0.99921	0
H	4.72051	1.08737	0.81231
H	4.72051	1.08737	-0.81231
H	2.03807	3.99365	-0.81270
N	1.99730	3.38937	0
H	2.03807	3.99365	0.81270
H	1.07119	2.97654	0
H	-3.26661	-4.71022	0
N	-3.88880	-3.90052	0
H	-4.48880	-3.98881	0.81235
H	-4.48880	-3.98881	-0.81235
H	-1.80628	-6.89535	-0.81272
N	-1.76627	-6.29110	0
H	-1.80628	-6.89535	0.81272
H	-0.84042	-5.87761	0

cHQ-A4			
H	-3.19928	-0.42798	0
O	-2.88157	-1.36282	0
C	-1.52026	-1.40162	0
C	-0.71178	-0.26291	0
H	-1.17798	0.71525	0
C	0.68162	-0.37910	0
H	1.30346	0.50824	0
C	1.29071	-1.63579	0
O	2.63969	-1.82241	0
H	3.10755	-0.95293	0
C	0.47705	-2.77251	0
C	-0.90582	-2.65728	0
H	-1.53424	-3.53936	0
H	0.95084	-3.74643	0
H	3.76589	1.42144	0
N	4.21295	0.50462	0
H	4.81815	0.46843	0.81239
H	4.81815	0.46843	-0.81239
H	2.61033	3.79379	-0.81424
N	2.52222	3.19734	0
H	2.61033	3.79379	0.81424
H	1.57377	2.84190	0
H	-3.45323	2.02281	0
N	-4.04659	1.19312	0
H	-4.64936	1.25806	-0.81241
H	-4.64936	1.25806	0.81241
H	-1.93603	4.17794	0.81417
N	-1.94094	3.57491	0
H	-1.93603	4.17794	-0.81417
H	-1.05827	3.07811	0

CTC-A4			
H	-0.83705	3.75722	0
C	-1.07310	2.70007	0
C	-0.00322	1.80429	0
O	1.24538	2.31869	0
H	1.97358	1.64516	0
C	-0.27726	0.42306	0
C	-1.60114	-0.01656	0
C	-2.65969	0.89146	0
C	-2.39288	2.25647	0
H	-3.20239	2.97581	0
H	-3.68181	0.53140	0
H	-1.78861	-1.08186	0
O	0.78888	-0.43301	0
H	0.45190	-1.36372	0
H	0.36901	-3.63132	0.81082
H	-1.00695	-3.29668	0
N	0.00416	-3.14307	0
H	0.36901	-3.63132	-0.81082
H	4.20386	1.52152	-0.81159
H	4.20386	1.52152	0.81159
N	3.72924	1.14318	0
H	3.88698	0.13658	0
H	2.83584	-1.88896	-0.80683
H	3.89048	-2.84965	0
N	3.44505	-1.94105	0
H	2.83584	-1.88896	0.80683
H	-3.52894	-3.94318	0.81242
H	-3.57229	-2.54066	0
N	-3.15579	-3.46526	0
H	-3.52894	-3.94318	-0.81242