Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

pH Dependence of the Speciation and Optical Properties of 4-Benzoylbenzoic Acid

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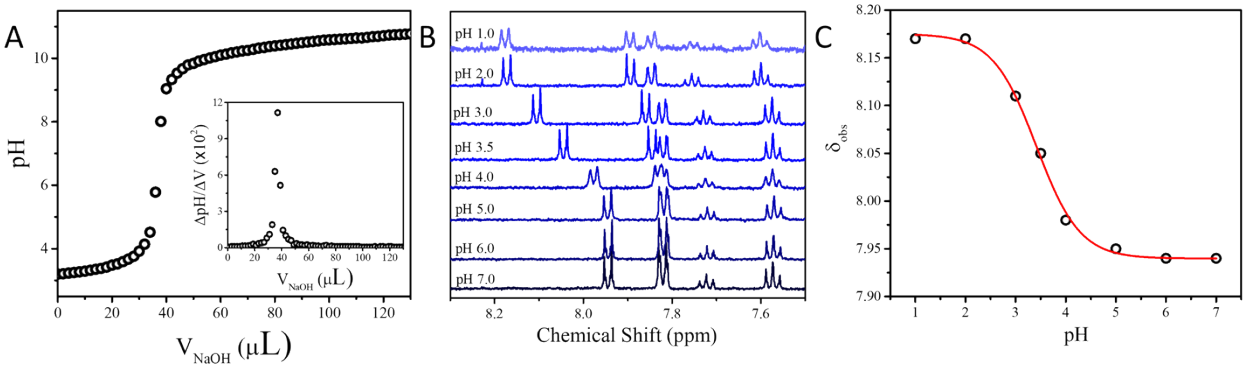

Figure S1: (A) potentiometric titration curve, with the insert showing the first order derivative of the titration. (B) $_1$H-NMR data with respect of pH. (C) Fitting of δ_{obs} vs pH to equation (S1).

Calculation of pKa were conducted by the chemical shift of the doublet signal assigned to the hydrogens in the β-carbon with respect to the ketone group. At low pHs, this doublet shows downfield

at around 8.14 ppm. As pH increases, the doublet shits upfield to 7.94 ppm. This chemical shift can be expressed in terms of the mole fractions of the species in equilibrium:

$$\delta_{obs} = f_{HA}\delta_{HA} + f_{A^-}\delta_{A^-} \quad \text{(S1)}$$

where δ_{obs} is the observed chemical shift, and δ_{HA} and δ_{A^-}, are the chemical shift of protonated and deprotonated 4BBA forms, respectively. f is the mole fraction:

$$f_{HA} = \frac{[H^+]}{[H^+] + K_a} \quad \text{(S2)}$$

$$f_{A^-} = \frac{K_a}{[H^+] + K_a} \quad \text{(S3)}$$

The acid-base equilibrium constant, K_a, is extracted from the fitting of δ_{obs} vs pH to equation (1), as shown in **Figure 1SC**, with the red line represents the fitting of the data. The fitting yields a $K_a = (3.9 \pm 0.3)\times10^{-4}$, for a pKa of 3.41 ± 0.03. This value is statistically similar to that found potentiometrically, as shown in **Figure 1SA**: 3.41 ± 0.04.

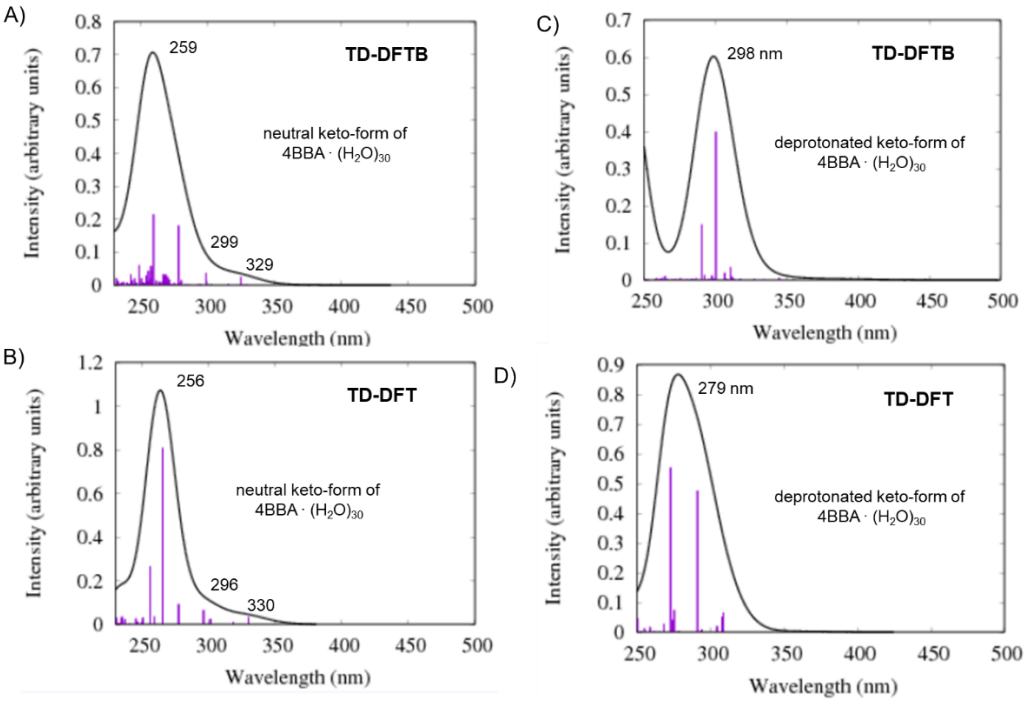

Figure S2. Comparison optical spectrum obtained with TD-DFTB and TD-DFT (B3LYP/6-311++G**) for selected structure of 4BBA · $(H_2O)_{30}$ from the MD-DFTB trajectories: (A) neutral keto-form with TD-DFTB, (B) neutral keto-form with TD-DFT, (C) deprotonated keto-form with TD-DFTB and (D) deprotonated keto-form with TD-DFT. (**Note**: exactly the same geometries were used for TD-DFTB and TD-DFT. No additional geometry optimization was done).

DFT Calculation of the population of speciated forms of 4BBA at different pH:

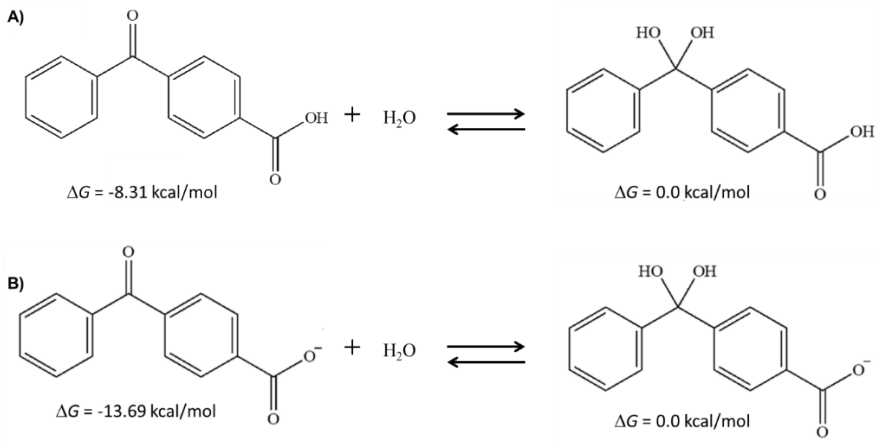

Figure S3. Calculated free Gibbs energy of speciated forms of 4BBA in water at different pH: (A) low pH, and (B) high pH. (B3LYP/6-311++G**)

$$\text{population} = \exp(-\Delta G/RT) * 100$$

where ΔG is the difference in free Gibbs energy between the two species (kcal/mol),

R is the gas constant (1.987 cal/(mol*K)),

T is the temperature in Kelvin.

The population of neutral keto- and diol- forms of 4BBA in water at low pH:

- Population(neutral keto-form) = exp(-(-8.31 kcal/mol) / (1.987 cal/(mol*K) * 298 K)) * 100 = 91.76%
- Population(neutral diol-form) = 8.24%

Therefore, at room temperature in water at low pH, neutral keto-form is expected to be present in a majority (91.76%), while neutral diol-form is present in a minority (8.24%).

The population of ionized keto- and diol- forms of 4BBA in water at high pH:

- Population(ionized keto-form) = exp(-(-13.69 kcal/mol) / (1.987 cal/(mol*K) * 298 K)) * 100 = 99.98%
- Population(ionized diol-form) = 0.02%

Therefore, at room temperature, an ionized keto-form is expected to be present almost exclusively (99.98%), while ionized diol-form is present in a negligible amount (0.02%).

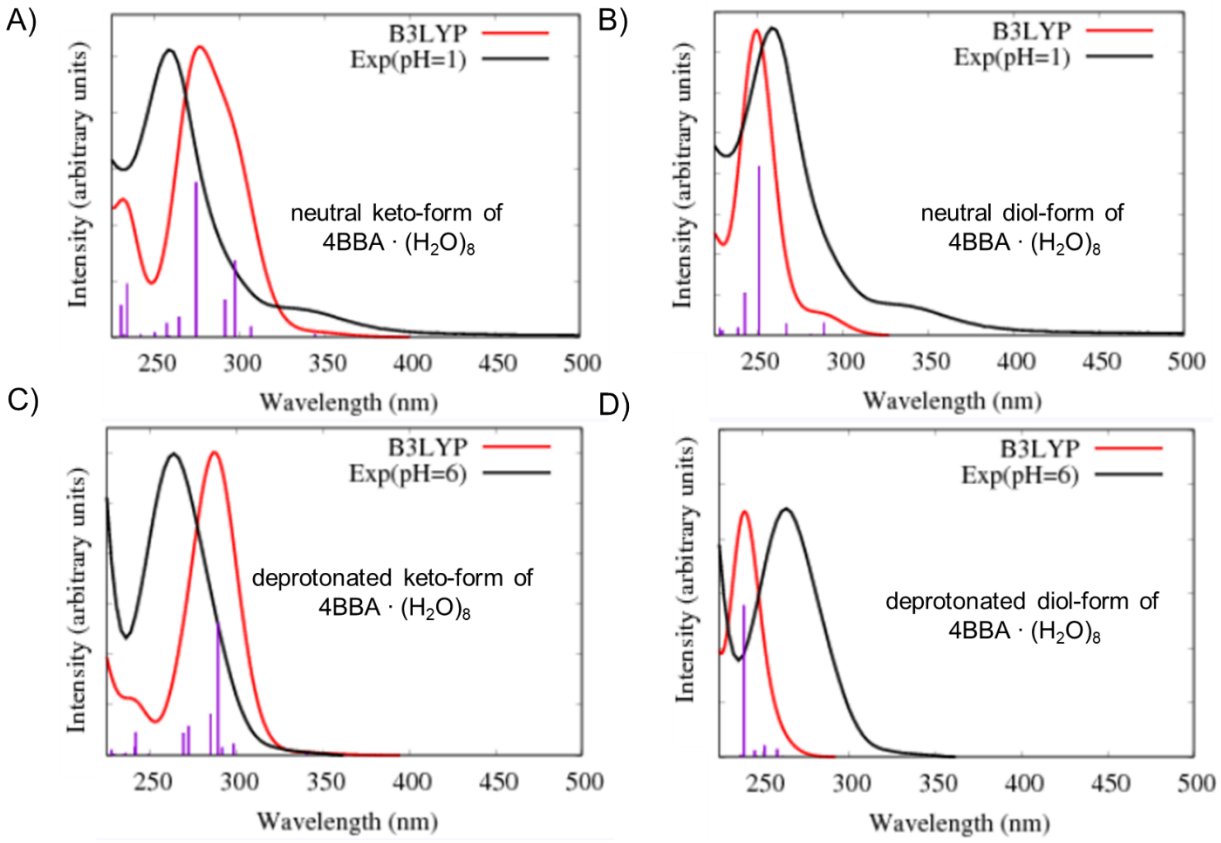

Figure S4: Comparison of the theoretical (red line) and experimental (black line) optical absorption spectra at different pH. Level of theory is B3LYP/6-311++G** (C-PCM).

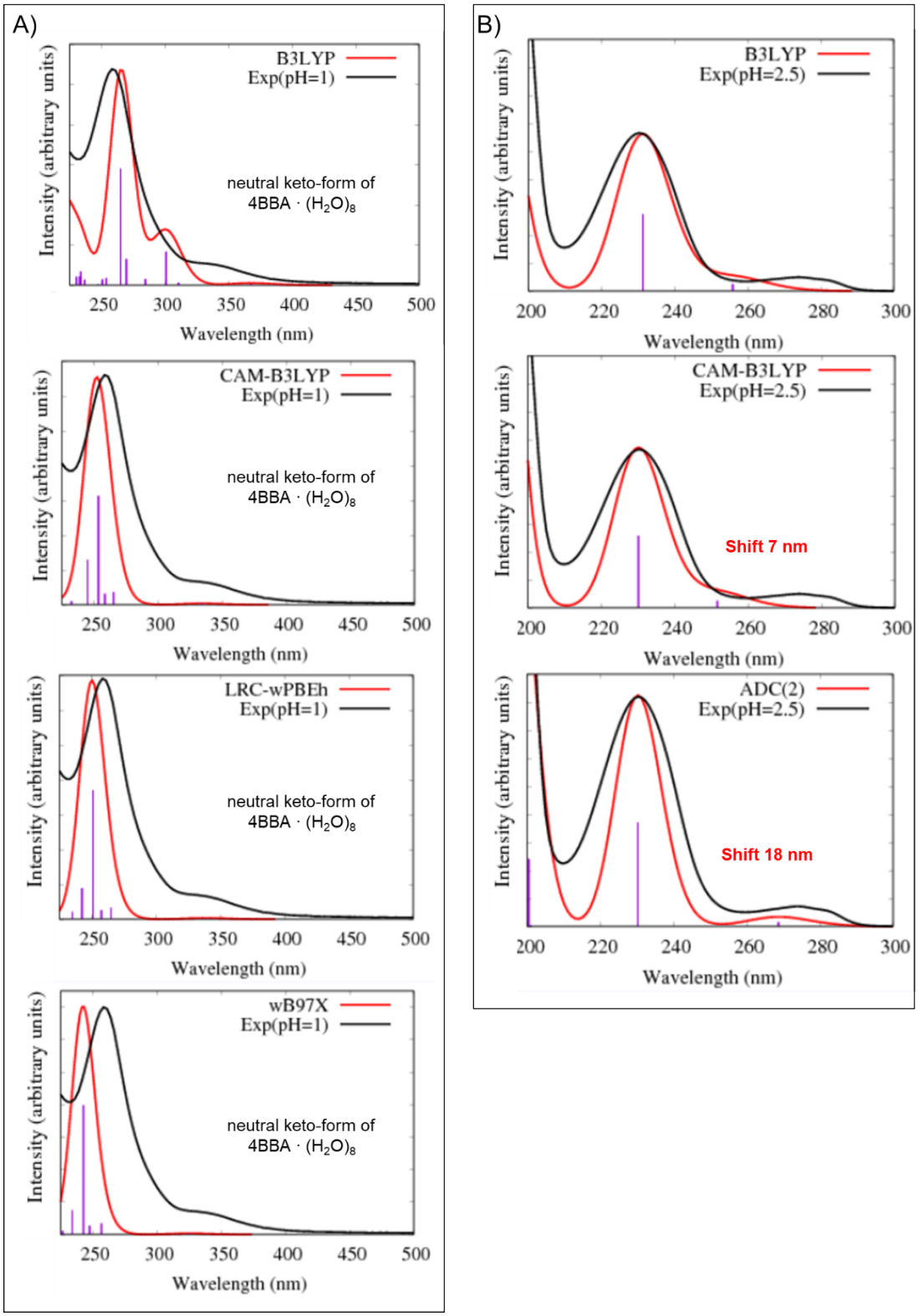

Figure S5: (**A**) Comparison of the theoretical optical absorption (red line) of the neutral keto-form of 4BBA·$(H_2O)_8$ obtained using different functionals (B3LYP, CAM-B3LYP, LRC-wPBEh, wB97X) with experimental spectrum at pH=1 (black line). (Gas phase calculations with 6-311++G** basis set). (**B**) Comparison of the theoretical optical absorption (red line) of the neutral benzoic acid

molecule obtained using different methods (B3LYP, CAM-B3LYP, and ADC(2)) with experimental spectrum at pH=2.5 (black line). (Gas phase calculations with 6-311++G** basis set).

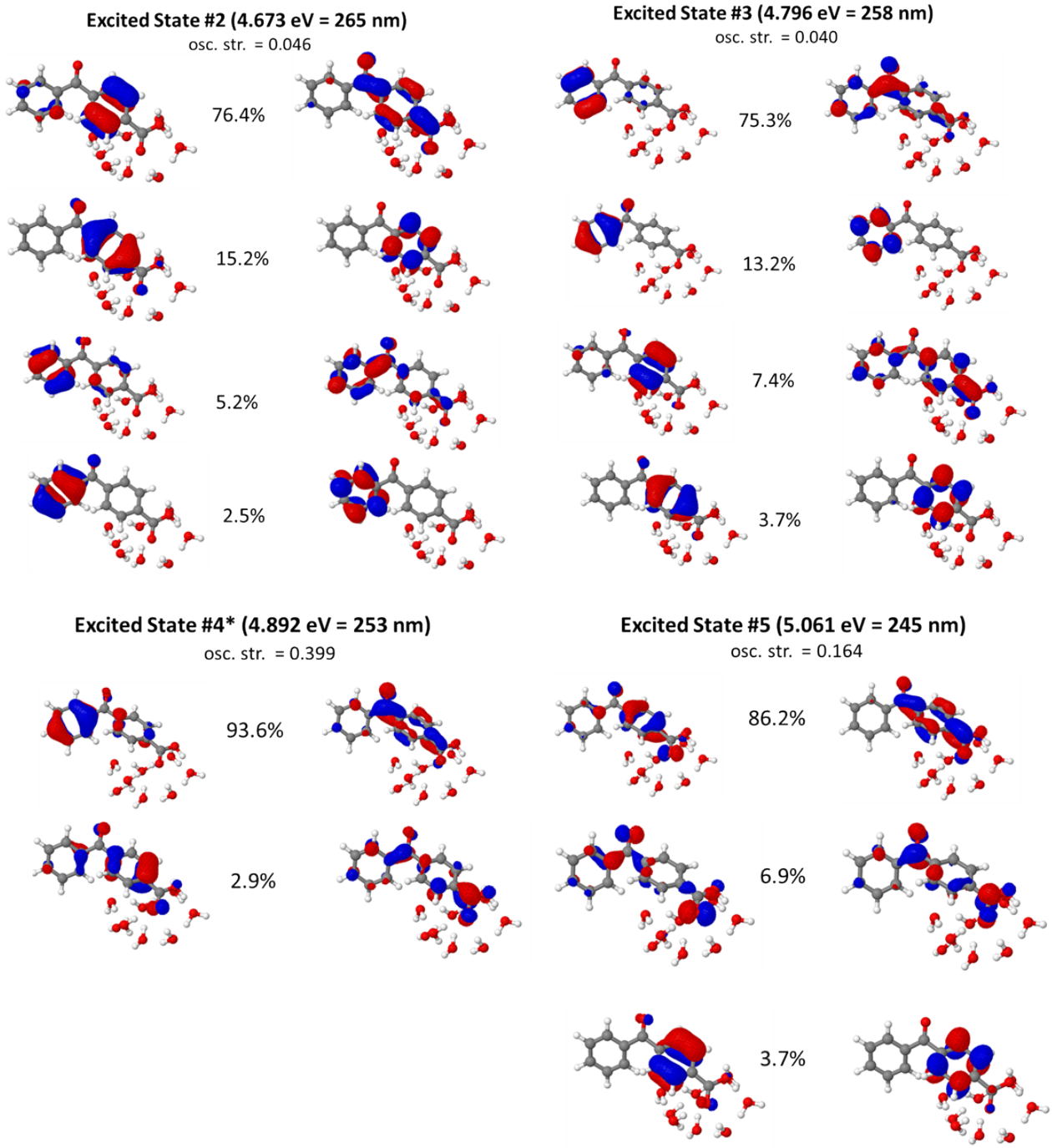

Figure S6. NTO of the selected excited states of neutral keto-form of 4BBA·(H2O)8 calculated at the CAM-B3LYP/6-311++G** (gas phase).

Geometry neutral keto-form of 4BBA with 30 waters selected from DFTB-MD trajectory (tr1-21500):

O	-1.64239967	-5.54937220	-0.23748095
H	-0.77332145	-5.96755838	-0.36149272
H	-1.50670075	-4.70565796	-0.70866203
O	0.83180404	-1.34355736	-3.53198957
H	0.41459826	-1.64079535	-4.35357237
H	0.67081296	-0.38470414	-3.45011640
O	0.68150657	3.55911851	-3.87624454
H	0.85042125	3.56610847	-2.93493319
H	-0.26799515	3.90363646	-3.95574784
O	-2.01950979	2.87485886	-4.77949333
H	-2.29930711	3.31552672	-3.94974351
H	-2.69050932	2.21642733	-4.75631762
O	-2.63594890	1.13046217	-1.62044907
H	-3.02620935	1.67718375	-0.90204316
H	-1.82163143	1.56237388	-1.92366743
O	-4.06982613	2.91305780	2.61258078
H	-4.52947855	3.44978380	3.26655364
H	-3.92292166	2.00102615	2.94776559
O	-0.52823710	-3.47268248	4.57430029
H	-1.04589331	-2.70075822	4.82683229
H	-1.14097691	-4.09892225	4.12824726
O	2.12777567	-3.32607508	-1.88512719
H	2.01129246	-2.88638806	-2.76675653
H	2.52852631	-2.78020215	-1.19917417
O	-1.42163479	3.47920179	-2.06885147
H	-1.98491645	3.71494007	-1.31080437
H	-0.52001625	3.73580241	-1.70392704
O	-0.60616773	-0.43838754	3.70950627

H	-1.53120852	-0.70628583	3.58419132
H	-0.60636073	0.53575057	3.98360252
O	-1.44452548	2.26395631	3.97443151
H	-2.15366101	2.86724043	3.59076405
H	-0.56149501	2.48094773	3.63168907
O	-3.41025829	0.55239785	-4.30115747
H	-3.24715137	0.24688213	-3.38584447
H	-2.77045274	0.01205193	-4.80305195
O	2.05955315	-0.69121903	2.50492001
H	2.33276939	-1.28233600	3.26122403
H	1.10342062	-0.80096048	2.47727132
O	-1.11870730	-0.71882528	-5.39081717
H	-0.95371389	-1.66488254	-5.50966501
H	-0.62212151	-0.14321563	-5.98761082
O	-3.33763480	3.42770267	-0.15100537
H	-3.97664881	3.56057191	-0.88580066
H	-3.75894785	3.29879999	0.72812885
O	-0.50793380	1.07101595	-3.34464741
H	-1.02761412	0.90517551	-4.17958021
H	-0.29963553	2.03134990	-3.49959397
O	-0.91924483	-3.73251796	-2.45763969
H	-0.46037370	-2.95498490	-2.89241982
H	-1.55329394	-3.33385181	-1.84924281
O	1.50184977	-2.00830674	4.84795094
H	1.28080702	-2.93981099	4.69603443
H	0.65788531	-1.54002142	4.64144087
O	2.83283854	0.64017338	5.01636648
H	3.67587018	0.66339427	5.45368195
H	2.28879166	-0.07751867	5.36112356
O	1.12714958	1.83231044	3.50057316
H	1.71144080	2.16634154	4.16673803

H	1.53221822	0.96217769	3.26106334
O	0.55300707	-4.32196760	-0.05018117
H	0.21172220	-3.98661637	-0.91036999
H	1.51511180	-4.19487047	-0.11652918
O	-0.35285586	-3.42844915	-5.10233641
H	0.45609346	-3.83186030	-5.42490292
H	-0.77765149	-4.02572632	-4.46946192
O	0.15391907	-2.52206922	2.15737748
H	0.06748013	-3.25609136	2.77108479
H	0.01330535	-2.90322137	1.27713561
O	2.90953279	-2.62385273	0.82265288
H	3.16453218	-1.66868711	0.97781289
H	2.06352615	-2.63953424	1.35244858
O	-1.91096509	-1.34188437	-2.58251166
H	-1.22664583	-0.77354181	-3.00805497
H	-2.46235514	-0.68408978	-2.08867025
O	-4.79702663	2.74518085	-2.56377625
H	-4.25614643	1.93393373	-2.71072459
H	-5.64240789	2.54564857	-2.97337508
O	-3.28389692	0.33374175	3.45938826
H	-3.05877185	-0.61717510	3.28910708
H	-2.55564547	0.70303351	3.95275688
O	-1.34885287	-4.51832151	2.17396951
H	-1.00892615	-4.21862030	1.22709024
H	-1.79788744	-5.33797932	1.92438173
O	0.21846628	1.61771667	-5.81358576
H	-0.44895804	2.30554557	-5.75790024
H	0.92484528	1.85408866	-5.19360685
O	-2.39834809	-2.38397813	3.20661306
H	-1.42506957	-2.36444592	3.01543403
H	-2.76951313	-3.22919130	2.85077119

C	-0.24555136	1.65130270	0.75701708
C	-1.22385597	0.65911496	0.73621058
C	-0.95979834	-0.59448981	0.11626345
C	0.25030345	-0.71454805	-0.56887662
C	1.07634556	0.33734640	-0.72540915
C	0.87326127	1.52999747	-0.03036506
C	-1.95542085	-1.67955089	0.31589037
O	-1.65792692	-2.85656524	-0.00408120
O	-3.11385369	-1.42106354	0.80990952
H	1.92720771	0.21820848	-1.40474570
C	1.81490684	2.74071097	-0.24503596
H	-0.43967316	2.60284781	1.31229031
H	-2.19112659	0.77590346	1.27941692
C	3.11981082	2.77581978	0.43844041
C	3.93625522	3.92154408	0.36815196
C	3.54232144	1.71438134	1.23902512
C	5.17100477	3.97699094	1.05578077
C	5.58879423	2.87983561	1.82274055
C	4.77676868	1.76052749	1.90032852
H	3.57385564	4.74126387	-0.21904033
H	2.87318754	0.85865617	1.33986115
H	4.98633003	0.95881194	2.58513236
H	6.54140902	2.88215685	2.31978035
H	5.79757929	4.90069246	1.06981075
O	1.43518496	3.65289068	-0.97002947
H	-3.47980618	-2.36610389	0.99964529
H	0.47206238	-1.67510653	-1.02491856
H	-4.19921303	-4.78309155	1.66155350
O	-3.81517649	-4.12551641	1.07579720
H	-2.94554067	-4.42787123	0.77257228
O	-3.13595533	-6.80159044	1.67490327

H	-2.82631421	-7.63685083	1.99208748
H	-2.96241021	-6.67533016	0.72360986