Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

The stability of the acetic acid dimer in microhydrated environment and in aqueous solution

Supporting Information

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Table S1. Interaction energies (ΔE), relative interaction energies (ΔE_{rel}), BSSE and the differential relative interaction energies ($\Delta\Delta E_{rel}$) for the HAc dimer conformers (S1 to S4, and S6) at the MP2, PBE, and PBE-D levels using the TZVPP+sp basis set. BSSE corrected values are indicated by the respective index. All values are given in kcal/mol.

	MP2					
structure	ΔE	ΔE_{rel} [a]	ΔE_{BSSE}	$\Delta E_{BSSE, rel}$ [a]	BSSE	$\Delta\Delta E_{rel}$ [b]
S1	-16.51	0.00	-14.81	0.00	1.69	0.00
S2	-7.91	8.60	-6.88	7.93	1.02	0.67
S3	-9.11	7.40	-8.13	6.69	0.98	0.72
S4	-6.44	10.07	-5.52	9.30	0.92	0.77
S6	-4.43	12.08	-3.46	11.35	0.97	0.73
	PBE					
structure	ΔE	ΔE_{rel} [a]	ΔE_{BSSE}	$\Delta E_{BSSE, rel}$ [a]	BSSE	$\Delta\Delta E_{rel}$ [b]
S1	-17.25	0.00	-17.13	0.00	0.12	0.00
S2	-7.26	9.99	-7.18	9.95	0.08	0.04
S3	-8.65	8.60	-8.56	8.57	0.09	0.03
S4	-5.30	11.95	-5.21	11.93	0.09	0.03
S6	-3.16	14.09	-3.10	14.04	0.07	0.05
	PBE-D					
structure	ΔE	ΔE_{rel} [a]	ΔE_{BSSE}	$\Delta E_{BSSE, rel}$ [a]	BSSE	$\Delta\Delta E_{rel}$ [b]
S1	-19.37	0.00	-19.25	0.00	0.12	0.00
S2	-9.01	10.37	-8.92	10.32	0.08	0.04
S3	-10.27	9.10	-10.17	9.07	0.09	0.03
S4	-7.01	12.36	-6.91	12.34	0.10	0.02
S6	-4.27	15.11	-4.19	15.05	0.07	0.05

[a] ΔE_{rel} and $\Delta E_{BSSE, rel}$ with respect to S1

[b] $\Delta\Delta E_{rel} = \Delta E_{rel} - \Delta E_{BSSE, rel}$

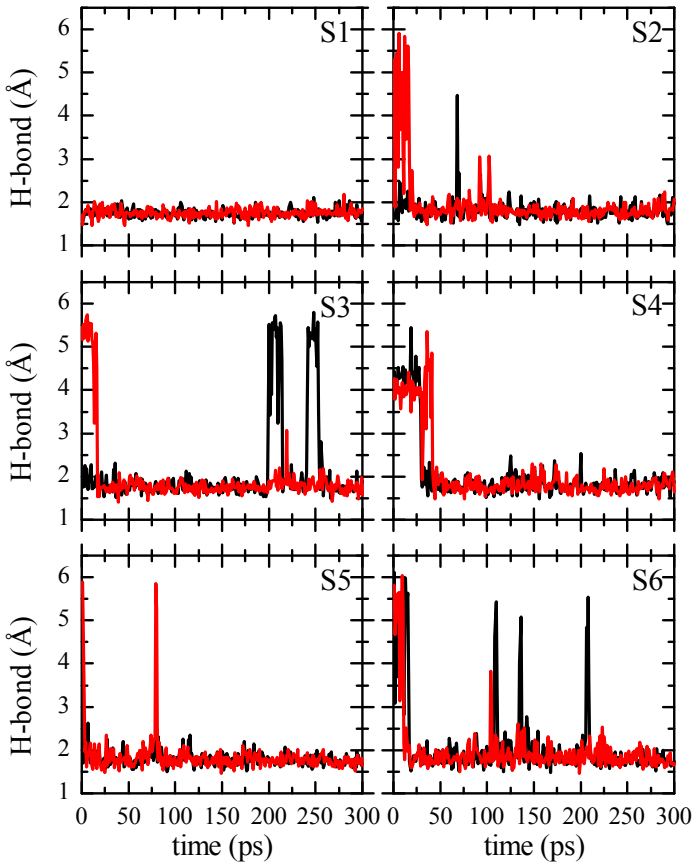

Figure S1. Time evolution during the initial 300 ps of the two C=O···H–O hydrogen bonds of the resulting cyclic dimer (indicated by the red and black lines) for the HAc dimer conformers (S1 to S6) from DFTB-D MD simulations.

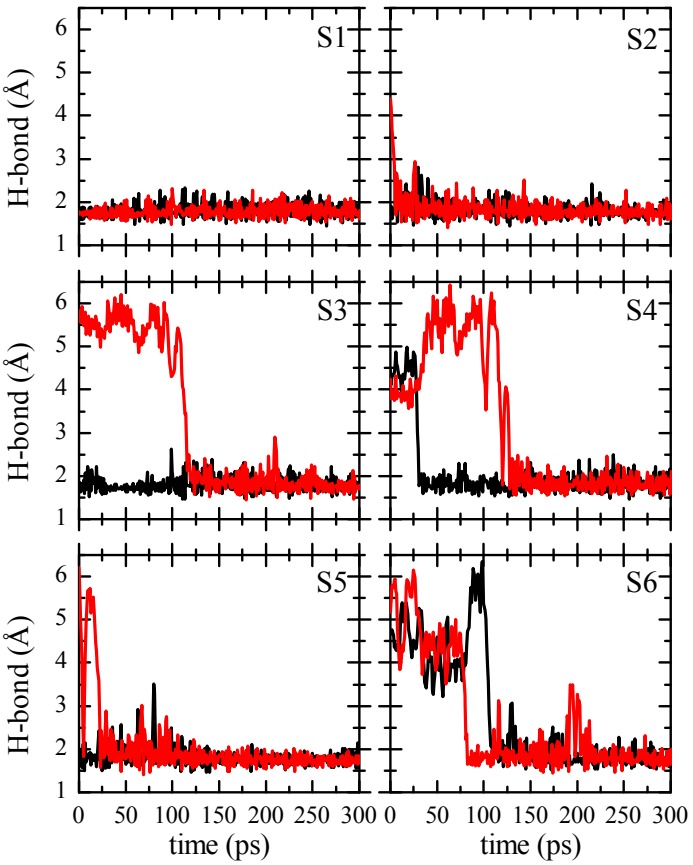

Figure S2. Time evolution during the initial 300 ps of the two C=O···H–O hydrogen bonds of the resulting cyclic dimer (indicated by the red and black lines) for the HAc dimer conformers (S1 to S6) from OPLS MD simulations.

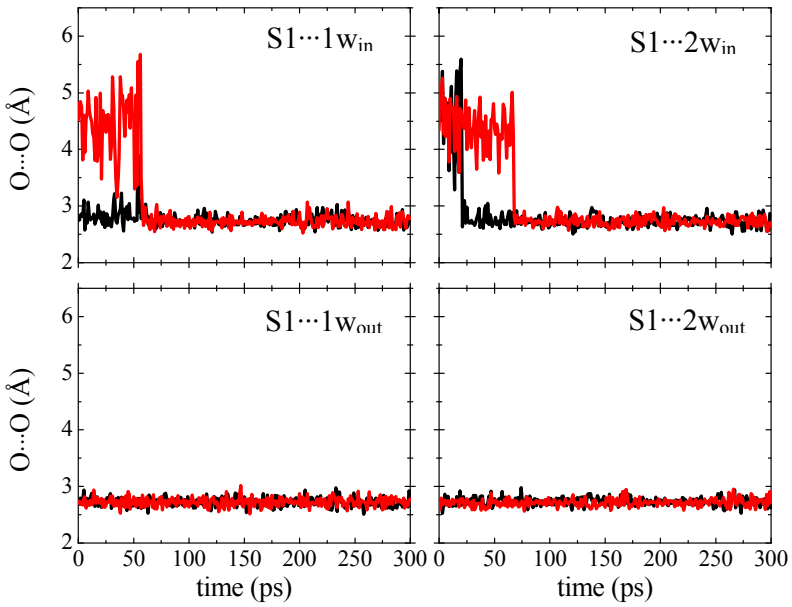

Figure S3. Time evolution during the initial 300 ps of the two intermolecular (C=)O···O(-H) distances of the cyclic dimer (indicated by the red and black lines) hydrated with one (1w) and two (2w) water molecules from DFTB-D MD simulations.

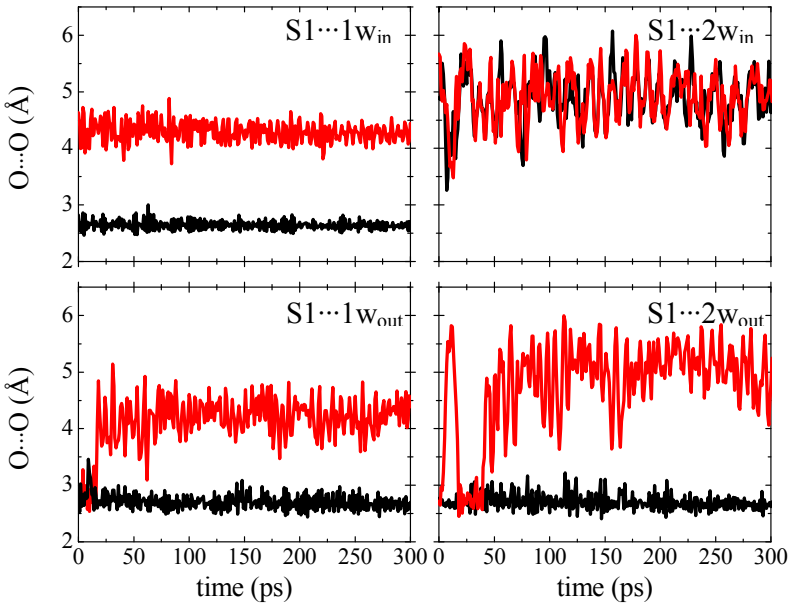

Figure S4. Time evolution during the initial 300 ps of the two intermolecular (C=)O···O(-H) distances of the cyclic dimer (indicated by the red and black lines) hydrated with one (1w) and two (2w) water molecules from OPLS MD simulations.

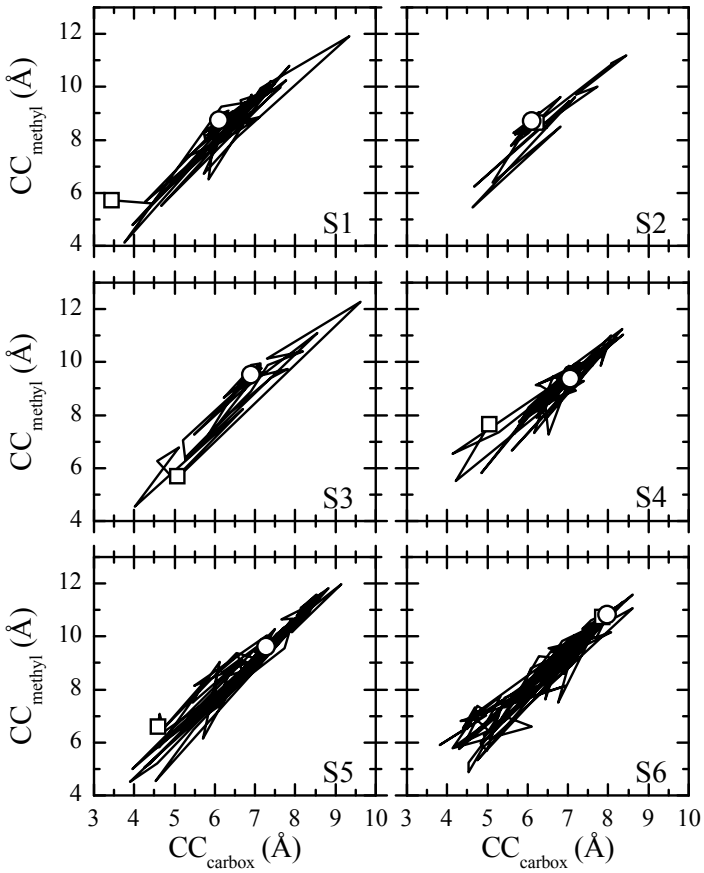

Figure S5. Correlation plots between the carboxyl (CC_{carbox}) and methyl (CC_{methyl}) CC distances for the HAc dimer conformers (S1 to S6) hydrated with four water molecules from OPLS MD simulations. Initial and final structures are indicated with squares and circles, respectively.

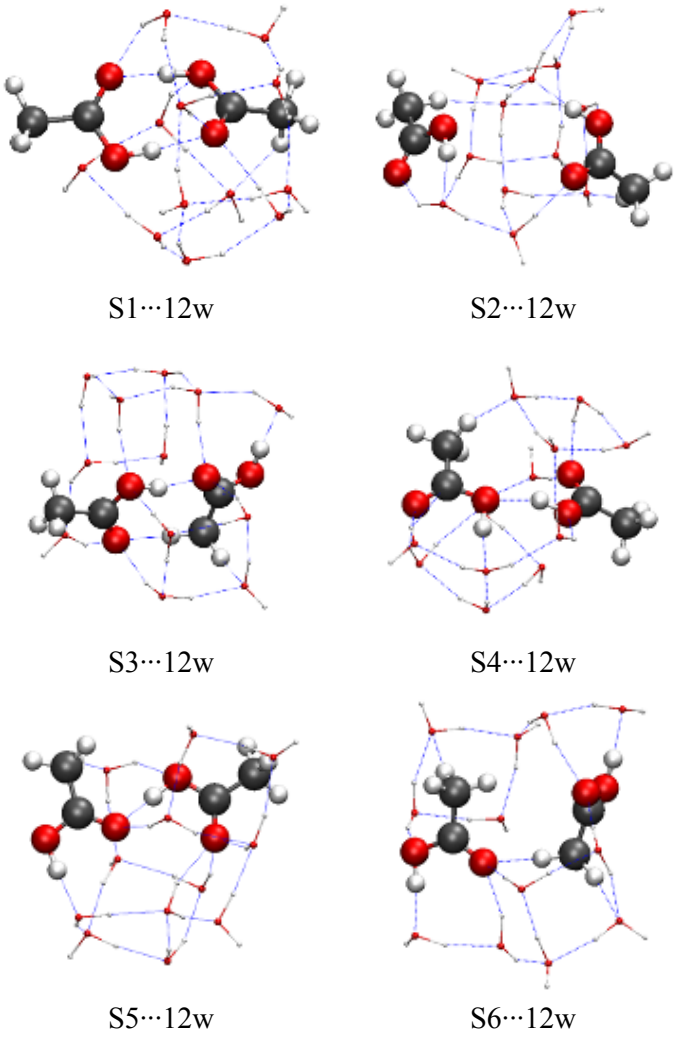

Figure S6. DFTB-D optimized structures of the microhydrated HAc dimer conformers (S1 to S6) with twelve water molecules (12w).

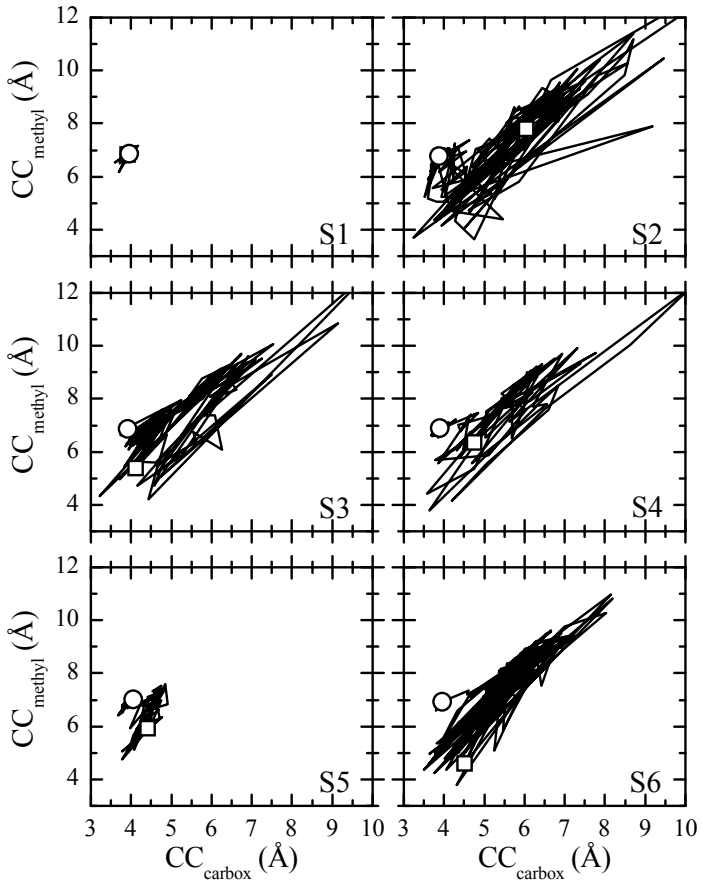

Figure S7. Correlation plots between the carboxyl (CC_{carbox}) and methyl (CC_{methyl}) CC distances for the HAc dimer conformers (S1 to S6) hydrated with twelve water molecules from DFTB-D MD simulations. Initial and final structures are indicated with squares and circles, respectively.

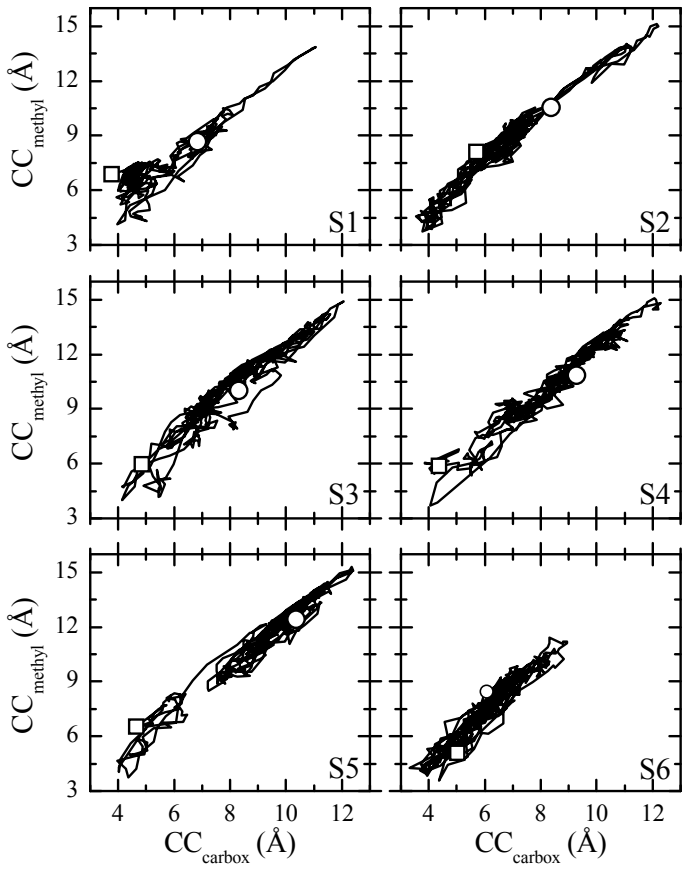

Figure S8. Correlation plots between the carboxyl (CC_{carbox}) and methyl (CC_{methyl}) CC distances for the HAc dimer conformers (S1 to S6) hydrated with twelve water molecules from OPLS MD simulations. Initial and final structures are indicated with squares and circles, respectively.

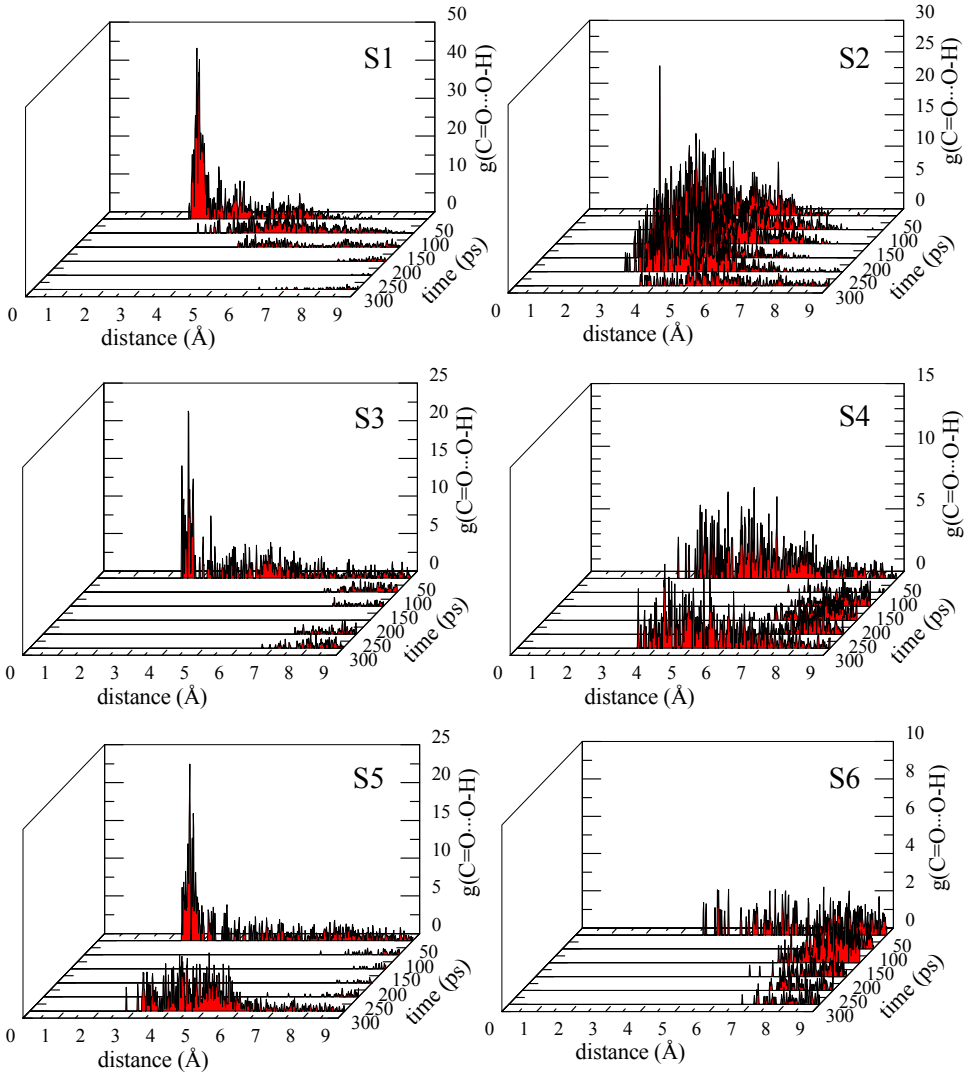

Figure S9. Radial distribution functions (RDFs) of intermolecular (C=)O···O(-H) distances for the HAc dimer conformers (S1 to S6) in aqueous solution from OPLS MD simulations.

Table S2. Cartesian coordinates (Å) for the micorhydrated HAc dimer conformers (S1 to S6) with four water molecules (4w) optimized at the DFTB-D level and total energies (Hartree)

S1···4w

C	7.72060919	1.22049403	-1.25821805
C	6.31488991	0.73217702	-1.19848597
O	5.80663395	0.20317100	-0.19333500
O	5.58784723	0.91834003	-2.31138611
H	7.70117283	2.31514001	-1.10468102
H	8.16796303	1.01999497	-2.23814702
H	8.33183861	0.76405001	-0.47339201
H	4.62670803	0.68523002	-2.14071798
C	1.03633404	-0.47433701	-0.75542003
C	2.45090103	0.00560600	-0.78300601
O	2.93658710	0.68453300	-1.69590497
O	3.20313311	-0.34984899	0.27901700
H	0.44080800	0.01645400	-1.53095603
H	0.58062398	-0.28832299	0.22413900
H	1.01528299	-1.55761194	-0.93121201
H	4.16449785	-0.06996900	0.12402300
O	3.77286005	3.33477497	-0.97325599
H	3.30875111	3.39494205	-0.12512200
H	3.48529506	2.50221395	-1.39542794
O	6.52900314	3.98653793	-0.81405300
H	6.62095308	4.83618116	-1.27077794
H	5.57914782	3.74399805	-0.86658502
O	6.12079811	-2.62823892	-0.29670200
H	6.53020906	-2.97547007	0.50976002
H	6.08697605	-1.65616202	-0.20424600
O	3.34727001	-3.14822888	-0.54245400
H	4.31994915	-3.18637705	-0.64463401
H	3.18302703	-2.47596502	0.13887399

Energy: -39.569501

S2···4w

C	-5.58610296	2.35718799	0.32617801
C	-5.37168407	3.46854401	1.31083906
O	-5.66405010	4.64918613	1.08051598
O	-4.83202314	3.10279703	2.48406291
H	-5.79202318	1.41001201	0.83578801
H	-4.68264389	2.22138095	-0.28266999
H	-6.41360998	2.59227991	-0.35157999
H	-4.73036289	3.92131805	3.08956909
C	-5.42332077	8.81601143	3.13236403
C	-6.72756481	8.09827328	2.96916389
O	-7.63295794	8.43827248	2.22575593
O	-6.85487509	6.96138287	3.74120307
H	-5.45116997	9.78837013	2.63088298
H	-5.19323778	8.96688366	4.19398022
H	-4.61175013	8.21611023	2.69189191
H	-7.77978802	6.58010292	3.55174398
O	-9.29827785	6.33102417	2.87888098
H	-9.25275517	7.21139002	2.45533609
H	-9.15185165	5.67668819	2.15627909
O	-8.48060799	4.52943707	0.93580401

H	-8.54052544	3.63872504	1.31256497
H	-7.52935696	4.75025320	0.86698401
O	-3.69914198	6.59071493	1.67414606
H	-2.91811204	6.49054289	1.10861099
H	-4.41694593	6.04801798	1.28455198
O	-4.54936695	5.31126881	3.96262598
H	-3.99498510	5.85586596	3.36235404
H	-5.40200806	5.79106092	4.03567314

Energy: -39.573983

S3···4w

C	-7.37396383	4.38112497	1.63612998
C	-5.88688087	4.29417706	1.51188195
O	-5.10248518	4.91718388	2.24708605
O	-5.42742920	3.48167491	0.55058300
H	-7.67091894	5.40445614	1.91157806
H	-7.86771202	4.08691311	0.70404601
H	-7.71796799	3.70550609	2.43088198
H	-4.41314316	3.50579906	0.51027000
C	-6.69999886	9.48484516	3.30863190
C	-6.63515615	8.03171539	2.95168304
O	-7.56954288	7.37210512	2.51144099
O	-5.41034794	7.45628405	3.14471698
H	-6.18465090	10.07931137	2.54246211
H	-6.19810295	9.67212677	4.26502085
H	-7.73786783	9.82588768	3.37153292
H	-5.43995714	6.48640490	2.86282206
O	-9.95010281	8.82245255	3.08832192
H	-10.76096058	8.48094559	2.68342495
H	-9.22952366	8.20893478	2.83876610
O	-2.79264593	8.01555920	2.06224799
H	-2.28476501	8.55133533	2.68948293
H	-3.70358706	7.95541096	2.40737700
O	-2.28548598	5.27828693	2.36945391
H	-2.25998712	6.23130608	2.13120604
H	-3.21421504	5.09875488	2.61766911
O	-2.72888708	3.51523304	0.34976000
H	-2.41601205	4.21760607	0.97577500
H	-2.26499104	2.69935393	0.59554303

Energy: -39.572617

S4···4w

C	-6.20215511	3.73783994	-1.47378004
C	-6.80634022	4.98641300	-0.91331297
O	-7.83947706	5.04667807	-0.26168200
O	-6.09315920	6.13012505	-1.17845905
H	-6.89989519	2.89853191	-1.39624000
H	-5.92468596	3.88282108	-2.52452302
H	-5.28706121	3.48517489	-0.92218798
H	-6.55889797	6.91502094	-0.75851703
C	-9.10679436	7.66186285	0.92848402
C	-7.79100323	8.32483673	1.18433905
O	-7.41326523	8.75815582	2.26237011
O	-6.98347616	8.40886211	0.07052600
H	-9.71148491	7.62600279	1.83974695
H	-9.66287899	8.20341110	0.15301500
H	-8.93604660	6.63716793	0.56306398
H	-6.08954287	8.85795975	0.31132901
O	-9.16746044	2.54100108	-0.57643402

H	-8.85690403	3.44762993	-0.38072100
H	-9.91570663	2.36769009	0.01365600
O	-4.85780716	9.31201744	3.27541304
H	-4.90868807	10.17276478	3.71827507
H	-5.78125811	9.03701687	3.09123492
O	-4.53735495	9.31274414	0.55281800
H	-4.45691109	9.39391232	1.53487301
H	-3.99300504	8.53618336	0.28776801
O	-3.43111110	6.91656590	-0.39194000
H	-2.82043600	6.99121380	-1.14026403
H	-4.24829578	6.50098896	-0.72565299

Energy: -39.569114

S5···4w

C	-6.66470003	6.30116510	-0.56788802
C	-5.38460684	6.98528385	-0.93111402
O	-4.88660622	7.91182518	-0.26497000
O	-4.77457809	6.53179598	-2.02950692
H	-7.47006083	7.03758383	-0.39877799
H	-6.53165579	5.74023485	0.36677799
H	-6.97327518	5.59974623	-1.34949505
H	-3.90323710	7.04587317	-2.19087005
C	-7.04417181	12.09360981	1.14995301
C	-6.17698383	11.04953671	0.51104498
O	-5.40378284	11.25898933	-0.41309300
O	-6.32360697	9.79953861	1.04406798
H	-8.09783363	11.91059875	0.90230501
H	-6.95081282	12.06064224	2.24186492
H	-6.77414417	13.09385872	0.79809803
H	-5.72804022	9.14426994	0.55515403
O	-8.73896027	8.47364902	0.26595300
H	-9.26501942	8.16189766	1.01699102
H	-8.02380085	9.03084660	0.62712801
O	-2.13377094	8.46366596	0.24418600
H	-3.06158710	8.16976166	0.33120000
H	-2.18495488	9.35474300	-0.15268400
O	-2.49025202	7.86434412	-2.37560201
H	-2.06995296	7.78012514	-1.48900795
H	-2.71792793	8.81738186	-2.43241596
O	-2.98688412	10.49300385	-1.57672596
H	-3.88236594	10.62973785	-1.19702494
H	-2.68792605	11.35938931	-1.89374900

Energy: -39.575095

S6···4w

C	-3.39038992	12.45828724	-0.84551501
C	-3.84355688	13.78937721	-0.33286300
O	-4.33980417	13.96162319	0.78488702
O	-3.66798806	14.82375526	-1.18404400
H	-2.47698998	12.15025425	-0.31933799
H	-3.17182112	12.49905491	-1.91773999
H	-4.15789890	11.68973827	-0.65362501
H	-4.00304794	15.68465424	-0.77387500
C	-6.41972685	11.79282761	1.57073402
C	-5.98844481	10.45313454	1.06111395
O	-5.44857121	10.27629948	-0.03539800
O	-6.24045086	9.41595459	1.88924694
H	-5.63893223	12.54863930	1.38423204
H	-6.64681911	11.75538158	2.64128208

H	-7.32547617	12.11550522	1.03984201
H	-5.91904020	8.54758358	1.48385203
O	-4.47944307	17.21376038	-0.14957599
H	-3.75618410	17.85320282	-0.05600400
H	-4.78716707	16.99608040	0.76397699
O	-5.06209803	16.16867828	2.30990696
H	-5.99354315	16.02058411	2.53478694
H	-4.72861385	15.32486153	1.93171704
O	-4.80445623	8.05219841	-1.57139802
H	-3.86300397	8.15499210	-1.77907801
H	-5.10088110	8.90752506	-1.18793702
O	-5.47848320	7.00656080	0.86380601
H	-5.14535284	7.21963596	-0.04194600
H	-6.22151613	6.39324617	0.75175202

Energy: -39.574476