

Quantum chemical examination of the possibility of forming an adduct and an inclusion compound of quercetin with cucurbit[7]uril

Alexey N. Masliy, Tatiana N. Grishaeva, Denis A. Safin and Andrey M. Kuznetsov

COMPUTATIONAL DETAILS

Preliminary quantum chemical calculations aimed at establishing the most probable structures of the compounds were performed using the Priroda 20 software package at the density functional theory level using the PBE functional of the GGA type.^{S1,S2} The Def2-TZVP atomic basis set of Alrich et al.^{S3} was used for all atoms. Full optimization of the molecular geometry was performed without any symmetry constraints. Upon completion of the optimization, the frequencies of normal vibrations of the systems were calculated. The absence of imaginary frequency values in the calculated spectrum indicated that the energy minimum on the potential energy surface had been reached. Based on the calculation of the frequencies of normal vibrations, a thermochemical analysis was performed, from which the total enthalpies, entropies, and Gibbs free energies of the systems under study were calculated.

Since the Priroda software package does not allow for the solvent effect in continuum models, further calculations were performed using the Orca 5.0.3 software package.^{S4,S5} First, the most stable structures of the compounds selected at the first stage were optimized taking into account the solvent effect at the same calculation level (PBE/Def2-TZVP). The solvent effect was taken into account in the conductor-like continuum polarization model (C-PCM).^{S6} Since hybrid functionals provide a significant improvement in the accuracy of calculating the total energy of chemical systems, as well as their thermodynamic parameters, at the last stage the GGA-type PBE functional was replaced by its hybrid version PBE0.^{S7} In other words, the optimization of geometric parameters and the calculation of normal vibration frequencies at the last stage were performed using PBE0/Def2-TZVP.

Supramolecular structures are usually formed due to many weak bonds, among which dispersion interactions can play a significant role. Therefore, when calculating within the Orca software package, we took into account dispersion interactions using the semi-empirical D4 Grimme model.^{S8} The D4 model is an evolutionary development of the previous models by Grimme et al. Our previous works have shown,^{S9,S10} that the use of the PBE0/def2-TZVP D4 combination in quantum chemical calculations provides the best agreement between the thermodynamic effects of the reactions studied in those works and the experimental data. For this reason, we use this methodology in this and our other studies. As for the choice of the continuum model of solvation, since in this study the molecular-continuum model of the solvent was used at the final stage (water molecules directly interacting with quercetin and cucurbit[7]uril were explicitly taken into account, and further interaction with the solvent of the entire system was taken into account in the continuum model), the choice of a specific model (C-PCM, IEFPCM, COSMO, etc.) did not play a fundamental role, and we took the model that is recommended for use by default in the Orca software package, especially since this model also allowed us to obtain correct results in our other studies.

References

- S1. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151; [https://doi.org/10.1016/S0009-2614\(97\)01206-2](https://doi.org/10.1016/S0009-2614(97)01206-2).
- S2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; <https://doi.org/10.1103/PhysRevLett.77.3865>.
- S3. A. Schiafer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571; <https://doi.org/10.1063/1.463096>.
- S4. F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 73; <https://doi.org/10.1002/wcms.81>.
- S5. F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2018, **8**, E1327; <https://doi.org/10.1002/wcms.1327>.
- S6. V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995; <https://doi.org/10.1021/jp9716997>.
- S7. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158. <https://doi.org/10.1063/1.478522>.
- S8. E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, C. Bannwarth and S. Grimme, *J. Chem. Phys.*, 2019, **150**, 154122; <https://doi.org/10.1063/1.5090222>.
- S9. A. N. Masliy and A. M. Kuznetsov, *Curr. Org. Chem.*, 2023, **27**, 1909; <https://doi.org/10.2174/0113852728278635231127111522>.
- S10. A. N. Masliy, I. G. Akhmetov, A. M. Kuznetsov and I. M. Davletbaeva, *Int. J. Quantum. Chem.*, 2024, **124**, e27462; <https://doi.org/10.1002/qua.27462>.

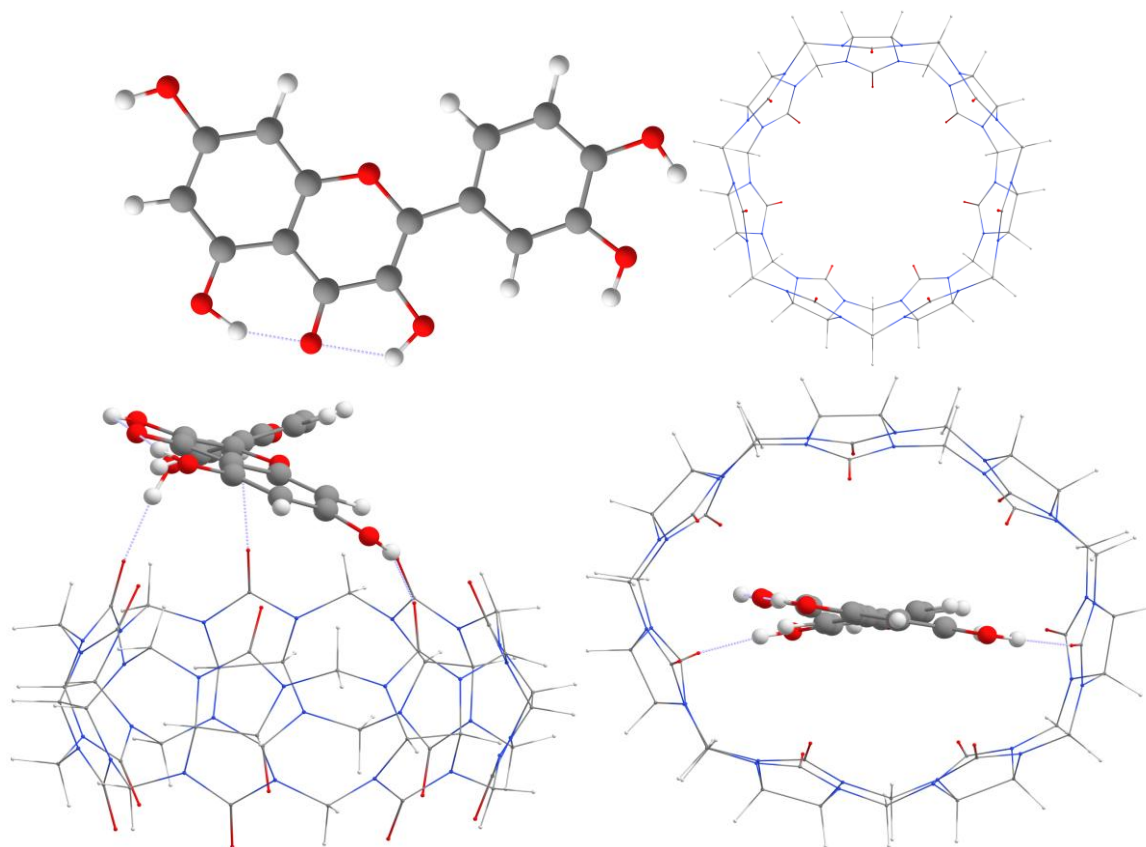


Figure S1. Optimized structures of quercetin and CB[7], as well as the adduct and inclusion compound based on them. The quercetin molecule is shown in the ball-and-stick model, the CB[7] molecule – in the wire model. (atomic Cartesian coordinates of quercetin are given in the **Table S1**).

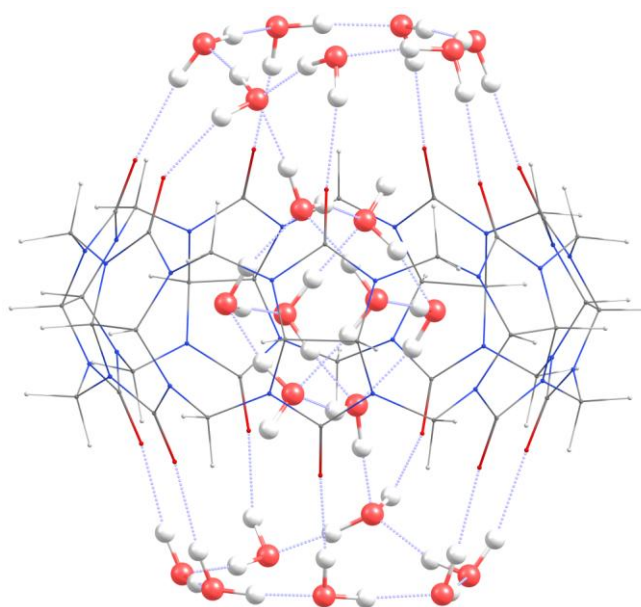


Figure S2. Optimized structure of the supramolecular compound $14\text{H}_2\text{O}-(\text{H}_2\text{O})_8@\text{CB}[7]$. Water molecules are shown in the ball-and-stick model, the CB[7] molecule – in the wire model. (atomic Cartesian coordinates for this complex are given in the **Table S2**).

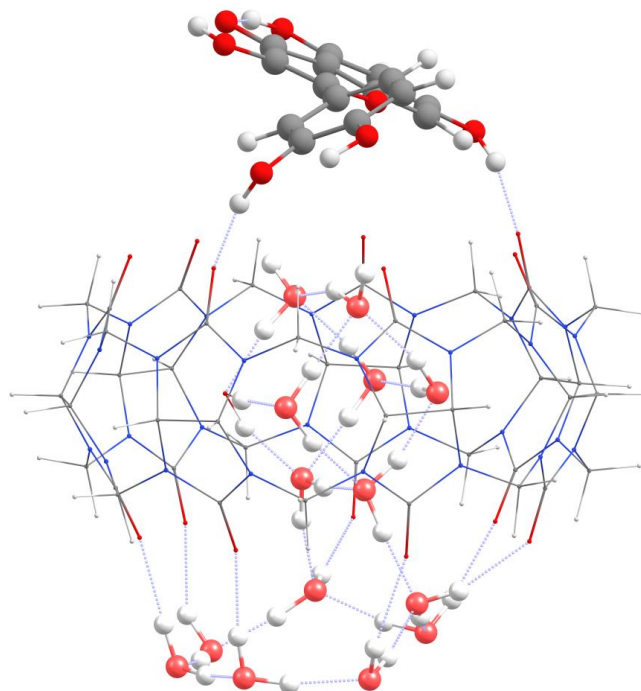


Figure S3. Optimized structures of quercetin and CB[7], as well as the adduct and inclusion compound based on them. The quercetin molecule is shown in the ball-and-stick model, the CB[7] molecule – in the wire model. (atomic Cartesian coordinates of quercetin are given in the Supplementary Materials section, Table S1).ct are given in the Supporting Information section, **Table S3**).

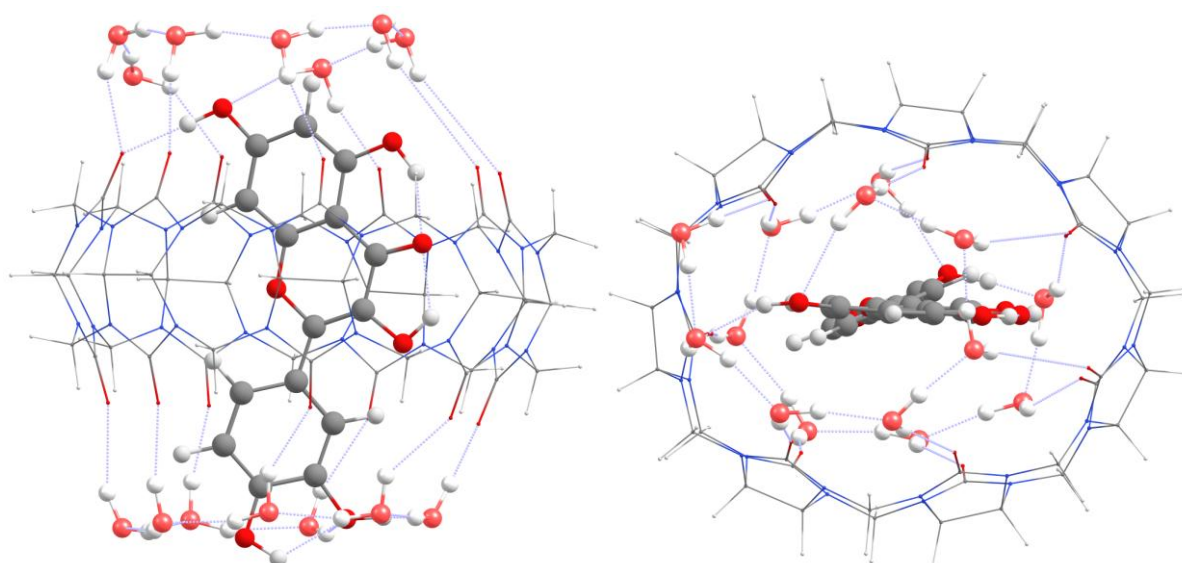


Figure S4. Optimized structure of the supramolecular compound 14H₂O-Q@CB[7] (frontal and vertical projections). Water molecules and the quercetin molecule are shown in the ball-and-stick model, the CB[7] molecule – in the wire model. (atomic Cartesian coordinates for this inclusion compound are given in the **Table S4**).

TABLE S1: Atomic Cartesian coordinates (in Å) for quercetin (Figure S1) optimized at the PBE0/Def2-TZVP C-PCM D4 level

Atom	x	y	z
C	0.15199102690032	1.56316859011224	0.01928135280648
C	1.57399531881870	1.77840392753492	0.02192257377908
C	-0.36962598361071	0.30298481852240	0.00502486186851
C	1.80437569523769	-0.64375195324530	-0.00546902748113
C	2.39980510692104	0.61997268883628	0.00803683614679
C	2.54956705270658	-1.80784627797166	-0.01846352791199
C	3.81110825985645	0.70613391934638	0.00744464573348
C	4.57123468891161	-0.44385821343366	-0.00597072845857
C	3.93350500835599	-1.68927939668617	-0.01833806616611
H	2.07225726461544	-2.77852841192382	-0.02867899351621
H	5.65379191576001	-0.37875288661592	-0.00638656461793
O	4.64083829597622	-2.83197101201909	-0.03047854308421
H	5.58684188164936	-2.63998683436839	-0.03035305762421
O	2.01264176997799	2.95385753829902	0.03487262124873
O	4.39736509931979	1.90540469570931	0.02018475799813
H	3.66760413357519	2.57705280503841	0.02958703075448
O	-0.59744271343309	2.68184246304445	0.03142730877586
H	0.04717103914593	3.41384954055574	0.04016105734980
C	-1.76979766278482	-0.09333942702184	-0.00035301000734
C	-2.80444975904010	0.85370585297089	0.00784695722893
C	-2.10684041382246	-1.45065444908640	-0.01440539325046
C	-4.12157936572504	0.44872599858156	0.00189828896521
C	-3.43023489627220	-1.85118789256912	-0.01997113748252
C	-4.44820477160133	-0.91213152451218	-0.01186536981813
H	-2.58717329017963	1.91248349389475	0.01855660722670
H	-1.32959739561202	-2.20165030554714	-0.02097565935416
H	-3.68964985532847	-2.90354125692646	-0.03065671816275
O	0.46623874084727	-0.76479789220856	-0.00630292108373
O	-5.73473348782819	-1.31200574821317	-0.01735426076981
H	-6.30629583738985	-0.53187640001285	-0.00838965026550
O	-5.17554806486634	1.30181841289981	0.00855246806588
H	-4.86915879108131	2.21575513701557	0.01961527110672

TABLE S2: Atomic Cartesian coordinates (in Å) of the supramolecular compound 14H₂O-(H₂O)₈@CB[7] (Fig. 2) optimized at the PBE0/Def2-TZVP C-PCM D4 level

Atom	x	y	z
N	1.97649248591623	-4.59990943863470	-1.59218777954806
C	2.69636599025387	-5.08249125677814	-0.43836131474882
C	3.96939928302545	-4.19748036839392	-0.42455099383228
N	3.82399659539722	-3.38556953633848	-1.60507595179646
C	2.66175139774784	-3.63636034376034	-2.26441157975908
N	3.86133796217675	-3.48650364486598	0.82033572785287
C	2.76827138305111	-3.86675914885629	1.54437278604291
N	2.08514848014590	-4.80622972029508	0.83139040908512
C	0.97804062233295	-5.54058179524636	1.37020866618455
N	-0.31586804236303	-5.14369401658210	0.88498816037827
C	-0.87444899949683	-5.63920421887209	-0.34296295177523
C	-2.36256763469900	-5.22504850096357	-0.25709180304314

N	-2.44975988797183	-4.56420893812311	1.01634311606374
C	-1.25712233374895	-4.55115900090938	1.68028738527230
N	-0.41000446279816	-4.97395343691280	-1.53018402157075
C	-1.39759682660513	-4.26586577175582	-2.14946821745010
N	-2.53668800148514	-4.37704637709862	-1.40671068108360
C	-3.69317718892899	-4.17353209297395	1.61808691151229
N	-4.23758729930210	-2.92698491642443	1.15881985481944
C	-5.05129246776345	-2.78453430912685	-0.01614060391716
C	-5.58476761899364	-1.33461528425496	0.09321333446325
N	-4.94878871032285	-0.83195266843784	1.28186342319972
C	-4.20149878905407	-1.78968252509137	1.90989308716385
N	-4.34177779676774	-2.77651450529755	-1.27224308291975
C	-4.43065284913680	-1.57999594583587	-1.90994771266447
N	-5.14326649595419	-0.72238775891932	-1.13114988913139
C	-5.37010968522481	0.37258413716169	1.93904834421623
N	-4.80624669537798	1.57924598139815	1.40098052821956
C	-5.32569670583511	2.25471465333578	0.23996860169423
C	-4.59408331970947	3.61823498448487	0.25887919584102
N	-3.75686193849189	3.52494702521797	1.42794668963842
C	-3.92590511967270	2.35190960637995	2.09416867674872
N	-4.93630100596542	1.68308220138765	-1.02049748790278
C	-4.14556994746604	2.52766047737847	-1.74940666388314
N	-3.90084359886641	3.64176692156765	-1.00027665658951
C	-3.02882288067994	4.63756681921600	1.96900552843455
N	-1.76494466364300	4.88371446774705	1.33851583508501
C	-1.61132130812261	5.69485145195178	0.15650604014894
C	-0.08060307317921	5.90254159575444	0.07095703462131
N	0.41206706581543	5.26929844903424	1.26241386120140
C	-0.58251879292732	4.69181210571862	1.99390765360614
N	-1.92712678373525	5.05125324633884	-1.08646308335744
C	-0.82020055916020	4.80264329740004	-1.84293683541084
N	0.27804192647038	5.24636322227172	-1.15926094344656
C	1.75253967133593	5.43307434236999	1.74588706142489
N	2.72293753572178	4.58097973185474	1.12327125433134
C	3.37054789250402	4.88807568775746	-0.12310260264278
C	4.53542732723627	3.86925336198431	-0.18407000174765
N	4.36049635644742	3.09866148734480	1.02147542722073
C	3.32684019170221	3.55253444573593	1.78531394331096
N	2.60396957271705	4.59019942282734	-1.30399463764791
C	3.17153527076494	3.60118377697515	-2.05334329877507
N	4.29706450856417	3.16871618789976	-1.41381720281471
C	5.31639265446662	2.15132300824579	1.51002814561695
N	5.22146247361444	0.84496259701947	0.91923605842549
C	5.86366749445664	0.49279373028110	-0.31747417426244
C	5.73666277597497	-1.04812087417233	-0.35764654882456
N	5.01171206581423	-1.35757396839783	0.84946356464860
C	4.76458171044574	-0.24457316997067	1.59491145357002
N	5.02266009724319	-1.28956607288768	-1.58013073657226
C	4.76282409100459	-0.13823036320490	-2.26900815103151
N	5.17807105638945	0.91728280237844	-1.50907786917857
C	5.23239742938662	2.26320130510081	-2.01212664460101
C	4.88096537287663	-2.59077457303384	-2.16480717793276
O	4.27985989830338	-0.07399057345981	-3.38509346304315

C	4.91163749172423	-2.69067253745539	1.38181906286664
O	4.23759862034634	-0.21900342726447	2.70025384915753
O	3.01453285979560	3.14338933911009	2.89089666988555
O	2.78085177659028	3.20717055438446	-3.13911125145707
C	1.55293669589461	5.43273648159504	-1.79659223667891
O	-0.45427306080656	4.12972826417433	3.06799277132709
O	-0.80374342419213	4.31951424687144	-2.96170726615634
C	-3.26389882017851	4.81119059049407	-1.54299614992101
O	-3.39497192238621	2.04201949150729	3.15411432383758
O	-3.75449893859691	2.34046977522158	-2.88821505478590
C	-5.60489053040193	0.55325571121251	-1.60057977026969
O	-3.63357761278275	-1.66506986861649	2.98068845493367
O	-3.97098251384086	-1.31127994046320	-3.01372081897517
C	-3.81759075086859	-3.95750528331464	-1.89564478432384
O	-1.06150352054730	-4.12249518131026	2.80456738380740
O	-1.29368646113475	-3.65927646761823	-3.20156187196747
C	0.84263319620921	-5.27233288371874	-2.15961744430166
O	2.49293720774250	-3.46893212388347	2.66290902527229
O	2.30191905469287	-3.09957795652814	-3.30547599559074
O	1.26200546685081	-0.58543259065774	-2.27400088962385
O	-1.43945034810579	-0.18989366695259	-2.13378238493129
O	-1.57426131155052	-1.37783039905079	0.22706294982929
O	1.09219424223341	-1.84677991270435	0.21943910423077
O	1.50684567642563	0.32481229688037	1.92242086396079
O	1.71458746478669	1.54887153616378	-0.43500767864173
O	-0.92703097555942	2.05380503565349	-0.54794220280432
O	-1.18673553735491	0.77756261595569	1.92730119199069
H	-2.18270286643518	6.62233862734379	0.25926865471298
H	0.22346950703290	6.95360997055116	0.04637762201264
H	-6.41520950901111	2.33320206163489	0.30343386046508
H	-5.26052578502769	4.48197175503263	0.34272008347033
H	-5.83380845478056	-3.54866927225964	-0.03362133709766
H	-6.67296244827910	-1.26594665739416	0.18250193647878
H	-0.71672299693356	-6.71881906206778	-0.42530234446386
H	-3.06157340117529	-6.06559737062582	-0.29916369386246
H	4.90665508121122	-4.75976768094618	-0.46690485188551
H	2.89700240992747	-6.15282601741253	-0.54130964555251
H	3.69492595544315	5.93316227007176	-0.13381556151280
H	5.52833641844879	4.32857765780470	-0.19482673343117
H	5.82121144113482	-3.13761699579766	-2.04451783155568
H	4.67293909279703	-2.45386527805947	-3.22493251836632
H	1.85667307828461	6.47795291952726	-1.67205892355198
H	1.42533125911599	5.21778830820874	-2.85674413153866
H	-3.87566686133684	5.68381652475887	-1.29482797952764
H	-3.22839427819090	4.69130624276328	-2.62477659600554
H	-6.67558576072714	0.63265090160201	-1.38737193642712
H	-5.44569477963678	0.58733894005075	-2.67725545064615
H	-4.53111333100550	-4.77448514975763	-1.74819922921839
H	-3.71768140568637	-3.75247594033122	-2.96054028802446
H	1.01476615145534	-6.35201242082073	-2.10260894862332
H	0.76925209809962	-4.97266268811101	-3.20401216077195
H	6.32362890911361	2.53795449611653	1.32646362406704
H	5.16026731949502	2.04396002087233	2.58241998309470

H	1.12258258281212	-6.60103769957590	1.14035067837873
H	0.98180617839613	-5.39956211544346	2.45010681166048
H	-4.43030024915415	-4.96025315441623	1.42938212273345
H	-3.52610345045114	-4.08531542031804	2.69058344637689
H	-6.46116843931573	0.44215107840899	1.87796043811508
H	-5.06929289500374	0.30635746357461	2.98361966002024
H	-3.64963713410018	5.53459160844175	1.87706513998536
H	-2.84090692168589	4.43228587038590	3.02187897534011
H	2.05123884452854	6.47488005040982	1.59150633208134
H	1.75210319755893	5.21059602998992	2.81208025526450
H	4.72418231401388	-2.60792638407055	2.45139099872814
H	5.86724399895418	-3.19956726916250	1.21837353536462
H	6.24261877442820	2.65458535078409	-1.85659373859329
H	5.02087849828317	2.22085722715345	-3.07965951187589
H	6.69584169558455	-1.57462202940761	-0.36564123147539
H	6.89652715252551	0.85429178171833	-0.32362930579753
H	1.69340999516744	0.84730433872579	1.09967092414638
H	0.76918198941801	1.82001673803965	-0.51960887245095
H	-1.22750000018780	1.38447528016932	-1.19063685146529
H	-1.56640281907078	-0.68172782843635	-1.27720347164439
H	-0.63691194605176	-1.67941062976863	0.25800869108858
H	1.32191662687149	-1.17106614905540	0.88658769901108
H	1.24251332864734	-1.41334866558617	-0.64311178025557
H	2.33419509002594	0.29552840280986	2.42330001108618
H	1.81301312251587	0.86094600995704	-1.11230558806917
H	-1.13668451352122	1.67740876455116	0.32764496251021
H	-2.20928608913227	-0.41163744933998	-2.67627372203784
H	-1.59836391223934	-0.66205648312258	0.88889521124255
H	-1.71781756325642	1.16308084621507	2.63786334304406
H	-0.26139992937262	0.68745344674219	2.22548782842021
H	1.60596085749677	-1.27161916063396	-2.86368813424547
H	0.29968069600081	-0.50747091789028	-2.43986537793698
O	-2.72340700898366	-0.81647453953905	5.47261892533516
O	-2.14211481939031	1.83104561336621	5.68284423057980
O	0.32800755594008	2.90008767585061	5.44282143988694
O	2.75914962643115	1.71344064875829	5.27367094985943
O	3.41192491154185	-0.93525169874214	5.28302687572174
O	1.63608351611535	-2.99395934307014	5.26656118997491
O	-1.07566383835216	-2.96325007552173	5.35895621771150
H	-1.24471390106339	-3.31511802089934	4.47131427590619
H	-3.12373027420462	-0.90337564399507	4.59346110319776
H	-2.58288475657363	2.11581498597026	4.86926173351446
H	0.24209481514833	3.34955300709115	4.58772458061598
H	3.01901130085558	2.03157605874076	4.39505005099804
H	3.74891176394791	-0.94523786499217	4.37453491360185
H	1.80464030469202	-3.27175625159677	4.35234634436336
H	-1.60242777501250	-2.13444296258823	5.41988102158285
H	-2.44339910102952	0.12258064290862	5.55552086948231
H	-1.21412905698231	2.15279497771332	5.60380013681417
H	1.17201399939606	2.39674536685380	5.39987833548280
H	2.92696076418021	0.74509800567446	5.28126027359937
H	2.71505238519111	-1.62943543509001	5.31349363817134
H	0.65913851814742	-2.89497796793360	5.33107012107383

O	-3.34104312537067	1.33164786758792	-5.45010325491492
O	-3.06708687720148	-1.36956806666058	-5.66552875718069
O	-0.81342425500199	-2.86918394944860	-5.82414997600000
O	1.82103530210959	-2.22205742163159	-5.95910136754604
O	2.70813415541962	0.30506209717915	-5.67475799539972
O	1.34233015992937	2.61750034825656	-5.44304268851397
O	-1.31595087979594	3.15112151901599	-5.42915759563854
H	-1.35979765759666	3.54364428353011	-4.54322569634891
H	-3.61576585242071	1.47434744136706	-4.53074711950814
H	-3.36761188329351	-1.57370348583359	-4.76699798888418
H	-0.87591342368878	-3.25284515913431	-4.93531769347259
H	2.09542814857856	-2.62222024447244	-5.12100269929851
H	3.21057864410853	0.26729107619905	-4.84635753812588
H	1.66963104830330	2.93760943881873	-4.58795148878171
H	0.11494053465072	-2.55213710440307	-5.90210550963862
H	2.08032198006912	-1.27399987592454	-5.87530604421103
H	2.13483349760917	1.10243559253029	-5.60306919191550
H	0.36622535850165	2.73886613762086	-5.43551920194614
H	-1.99966231265020	2.44495701846258	-5.45142660208998
H	-3.16671642800822	0.36820136828113	-5.53676421081677
H	-2.20312816910528	-1.83088327023406	-5.76027853603861

TABLE S3: Atomic Cartesian coordinates (in Å) of the supramolecular compound Q-7H₂O-(H₂O)₈@CB[7] (Figure S3) optimized at the PBE0/Def2-TZVP C-PCM D4 level

Atom	x	y	z
N	1.95913652113185	-4.80164146050174	-2.15013176777022
C	2.68704078247582	-5.25534122557353	-0.98895320396763
C	3.89838257909533	-4.29011505740172	-0.94387431813026
N	3.76219497900562	-3.52226533429642	-2.15390891217980
C	2.63796061004083	-3.85175550581766	-2.85166492272678
N	3.68812251050256	-3.55403547637026	0.27280400221352
C	2.61494229248964	-4.02465922157763	0.98492547829061
N	2.04033167829323	-5.04011280311223	0.26937577669896
C	1.04514908443519	-5.90757539117162	0.82863942621011
N	-0.30939418486211	-5.58418835632811	0.47562455988088
C	-0.88762181369192	-5.91302638580301	-0.79925288688225
C	-2.36540450206971	-5.48813347921149	-0.63891079118591
N	-2.40703337678102	-4.91851035480600	0.68337163153446
C	-1.22414076031699	-5.06922375031862	1.34509925955401
N	-0.42909135723194	-5.12546653192746	-1.91488704174077
C	-1.43902606963487	-4.38348675762152	-2.46553686187902
N	-2.56725331587291	-4.56095109114941	-1.71548854139878
C	-3.62683866402493	-4.52968704141750	1.33800562529449
N	-4.13659443165882	-3.24754170789118	0.94591228877680
C	-5.01707689625891	-3.04871363022717	-0.16772177862099
C	-5.52175849002242	-1.59862175854362	0.02662821895744
N	-4.76282078010730	-1.12892682053115	1.15595289988194
C	-4.01552446902221	-2.12928490630008	1.72648393836042
N	-4.39952465603044	-3.00265564091504	-1.47099409095190
C	-4.60537497921986	-1.81336163487512	-2.09850592967274
N	-5.21991077461173	-0.96298891483688	-1.22810472196745
C	-5.10999754075054	0.06562617230429	1.87136903111321

N	-4.63234248301729	1.28492513076258	1.27344144185579
C	-5.33810404557150	1.95826593526953	0.21114732595248
C	-4.68548601587423	3.35986511636014	0.17738255497367
N	-3.76755679435148	3.32896305109596	1.28084897996783
C	-3.78883216628503	2.13200376785640	1.93867029994224
N	-5.10203485913573	1.44558019046899	-1.10896871809943
C	-4.43357126114736	2.33890992998761	-1.90110155110458
N	-4.08867468190923	3.41435109979108	-1.13206073206465
C	-3.12910852421671	4.50273219790230	1.81000525708500
N	-1.89218802104553	4.86161844287869	1.17502869375110
C	-1.80495280773756	5.58983426290206	-0.06863599673057
C	-0.28154063161899	5.82705403186569	-0.23013337008283
N	0.27676260934163	5.23701515237810	0.95684572650472
C	-0.67781391019570	4.70539301843991	1.76400484163472
N	-2.15272588223114	4.86099709339701	-1.25583361316918
C	-1.07062100347164	4.60752804179046	-2.04703927091649
N	0.03469299406751	5.14686525751905	-1.45684916648306
C	1.63954211397579	5.41273779316143	1.38049029750094
N	2.58590791924145	4.53799321666707	0.75502074447165
C	3.17575648372317	4.81114186681872	-0.52229469695997
C	4.35121894547371	3.80577039129244	-0.60369419471945
N	4.21952487576975	3.05030497708160	0.61479123155949
C	3.20068748825324	3.50142855278283	1.40736747625585
N	2.35367260596659	4.46151452574535	-1.65432225725786
C	2.91192594374874	3.46842080971054	-2.40350108861351
N	4.08363899452457	3.09062136644150	-1.82073431058906
C	5.17776208265784	2.08734019282544	1.06972926865048
N	5.06854867171120	0.77924001737849	0.47927723274258
C	5.67469112279306	0.42544912904720	-0.77460577611692
C	5.54898731675942	-1.11465664552108	-0.81641980950087
N	4.81198098985627	-1.41905090193047	0.38208596789780
C	4.61606606128182	-0.31291152085963	1.16051168886916
N	4.85486739496324	-1.36639095160430	-2.05009869296083
C	4.59032202865134	-0.21245730278461	-2.73525169629232
N	4.96425241903091	0.84478993377404	-1.95469756927002
C	5.00622340159735	2.19278109950442	-2.44833853347648
C	4.78959626536232	-2.66277366681504	-2.66804083706069
O	4.13003560551612	-0.14961692977641	-3.86115547768950
C	4.70281102397945	-2.75633506400935	0.89600400128000
O	4.13817785442737	-0.30870288076421	2.28628287218119
O	2.91832278707895	3.08901941953027	2.51674673243506
O	2.46288110644341	3.01482296162766	-3.44388481017164
C	1.28799615771175	5.29288290618966	-2.14060788979475
O	-0.46323096620062	4.20522069747249	2.86315863138175
O	-1.09827942813921	4.03264378526761	-3.12302819318483
C	-3.49974580418529	4.60505286476388	-1.67803935802503
O	-3.17777652450480	1.87028147121485	2.96202863411009
O	-4.21741952593400	2.20521917426329	-3.09188325476074
C	-5.78051816774735	0.29490088702881	-1.63298285020401
O	-3.38870287863493	-2.05019383173618	2.76521380635136
O	-4.33478983358893	-1.57045946647589	-3.26549980029959
C	-3.87313425134637	-4.14851337778414	-2.15174396343023
O	-1.04081815901814	-4.81090135093370	2.52705484500220

O	-1.35474005815289	-3.70184988417265	-3.47173186039788
C	0.77419678894071	-5.43638471346039	-2.64411152629493
O	2.26808204134550	-3.64135853397564	2.08139228882713
O	2.31284123224947	-3.40948188009261	-3.94355625803124
O	1.16597248590079	-0.31077732038635	-2.49818534352842
O	-1.40004978416098	0.45027631633066	-2.33540752329287
O	-1.82977149004093	-1.29255941003763	-0.35581331545718
O	0.76892520657248	-2.10536465886337	-0.42868592652214
O	1.40492981136143	-0.30974416844627	1.65938228239899
O	1.76411117944039	1.35365484355720	-0.36777831902715
O	-0.77531851315899	2.22296974985255	-0.29051022817328
O	-1.17823851975199	0.41097952311687	1.75341957835504
H	-2.39411158665406	6.50938445752789	-0.00482013971303
H	-0.00062849808591	6.88277748490314	-0.29496953022501
H	-6.41164821201656	1.97702342247481	0.42482600315189
H	-5.39638278993369	4.18291435000589	0.30264366109274
H	-5.81297564565864	-3.79998690734832	-0.15825102090928
H	-6.59471459264417	-1.53014340553164	0.23324840503967
H	-0.75305153386973	-6.97819716747757	-1.01063347917254
H	-3.07570888064472	-6.31690105290776	-0.71643565970569
H	4.86837154689627	-4.79648702225284	-0.92687876146561
H	2.96094094502084	-6.30838717187189	-1.10381735368175
H	3.48392223896187	5.85925645903825	-0.58690733247530
H	5.33733332219750	4.27705963713058	-0.65353879838311
H	5.75563263849200	-3.16150223251849	-2.53990656842162
H	4.59872001809298	-2.51210036254286	-3.72963065900042
H	1.60251449639346	6.33956978949215	-2.06756627236419
H	1.12452206834842	5.04062018088024	-3.18752763078536
H	-4.11475345257057	5.46671055403744	-1.39970277682170
H	-3.49954704014903	4.49926698980781	-2.76206878079474
H	-6.82814850056181	0.32850986326400	-1.31615992527426
H	-5.72991212577336	0.34803609868228	-2.71962101781889
H	-4.55764035295422	-4.99217152729347	-2.01520055267530
H	-3.81515371530458	-3.89829103642645	-3.21008126746977
H	0.91404176437908	-6.52217614704408	-2.62267004644838
H	0.63787690580746	-5.11062679623649	-3.67443075836636
H	6.18395470868176	2.46869767821357	0.86773803194416
H	5.04337331378414	1.97496947519784	2.14478830077662
H	1.25987696231234	-6.92867804417058	0.50010617949958
H	1.12478611437391	-5.85724785532770	1.91301335464939
H	-4.39457312362438	-5.28242434785775	1.13270987696926
H	-3.42395477753506	-4.50210462424658	2.40771998718142
H	-6.20146087828894	0.12397871383379	1.95781434426851
H	-4.67244200963863	-0.00621642624839	2.86631219374817
H	-3.82538970424035	5.34211643583742	1.71804584732178
H	-2.92585793838012	4.32266522712120	2.86400840718156
H	1.93356078560880	6.44729338490143	1.17620046177488
H	1.67409273225560	5.23081461146402	2.45361985133118
H	4.46176390950178	-2.68244481895303	1.95573765429459
H	5.66985952905052	-3.25793581716722	0.77562335808058
H	6.01721662413663	2.59000215934483	-2.31281532466081
H	4.77348227942995	2.15875258426418	-3.51176484332184
H	6.51059253891246	-1.63799946166172	-0.81128229018941

H	6.70761461341795	0.78662289065666	-0.80891015071766
H	1.60222874144902	0.34710086390484	0.93746572426931
H	0.87691067276730	1.78382558048851	-0.36735934681034
H	-1.10620582236060	1.75400241849447	-1.07822379489666
H	-1.69965298238715	-0.24053149023770	-1.69386511281655
H	-0.93887906932227	-1.71003493777262	-0.38616440733185
H	1.07818840342428	-1.60089582063750	0.34722322182977
H	1.01368076726842	-1.55695166236243	-1.20142167982186
H	2.24360909503991	-0.41753092060385	2.13416707270931
H	1.76238896370581	0.80947528303712	-1.17675634887768
H	-1.00108935464743	1.64098972572679	0.46263592269833
H	-1.83931030854952	0.28140686421426	-3.19514284093791
H	-1.77883534434325	-0.72053896937327	0.43163041543765
H	-1.68140668731784	0.78016513395644	2.49396909121111
H	-0.27751655943995	0.16354398302907	2.04125536074647
H	1.36937375460547	-0.53470033941421	-3.42742884885220
H	0.22781262879764	-0.00272224103084	-2.50997470596310
O	-3.19043378907337	2.23292892492340	-5.74505267381597
O	-2.53402143584056	-0.20099093833015	-4.75951672104068
O	-1.02120229830743	-2.15135345212318	-5.79156906786243
O	1.40460930808529	-1.15133976313748	-5.14187617069198
O	3.01427855434856	0.67599869413081	-6.29954994155460
O	1.72114791409761	3.07423280123871	-6.08845359136977
O	-0.92331147539286	3.76132904275202	-5.89871909865865
H	-0.89227232243512	4.02346381155586	-4.96450862072996
H	-3.60217562403644	2.53815328856613	-4.92349174017233
H	-3.27161554911968	-0.66308319132138	-4.32063110936914
H	-1.13204914727398	-2.80900576550511	-5.08716767954389
H	1.94964115911727	-1.90630599260999	-4.85911365708033
H	3.54946529171343	0.67289046679451	-5.49082829841314
H	1.93799892707071	3.18280284164598	-5.14677790644672
H	-0.11660199356748	-1.79220824177891	-5.65015115035742
H	1.97948042718697	-0.53341662953214	-5.65301269698398
H	2.51417444637277	1.52335902572468	-6.28416443482349
H	0.75014342556345	3.21237821874613	-6.12780635904609
H	-1.70869105271565	3.17090051671045	-5.93369374377161
H	-2.93891877987583	1.31161809447214	-5.51555241856522
H	-1.99145134831661	-0.90851424101170	-5.19054370081774
C	1.74634278629364	0.44008925317925	5.88068466604322
C	2.73253334219795	-0.60531903001387	5.81934844453204
C	0.42230163449379	0.15778856441381	5.75317445835546
C	0.88260559546067	-2.12041328552901	5.35161080837504
C	2.24874179528389	-1.92024669575274	5.56422251133992
C	0.36625170163909	-3.34751786245117	4.99128004876864
C	3.11186523920894	-3.03911716080800	5.47927067786949
C	2.61046219228391	-4.27766382811053	5.14913002410065
C	1.25104216919259	-4.40810918809042	4.84801942010304
H	-0.68914878348092	-3.46078322808590	4.78350694420966
H	3.27450204506719	-5.12427337379928	5.02845117462932
O	0.82164965239094	-5.59762878627111	4.39665678652372
H	0.02379244224044	-5.44658516593473	3.84711822117579
O	3.94155717534885	-0.32365287767367	6.00573175380735
O	4.42384332660971	-2.86932353794102	5.68528421907234

H	4.55765640157024	-1.90283579465662	5.86078595786150
O	2.20584362277582	1.68053801265696	6.14274040514117
H	3.16891572994448	1.57641758289266	6.24346287503106
C	-0.69532989228191	1.07477804327228	5.91767767266390
C	-0.59982995767961	2.40532129814673	5.50865954617486
C	-1.88686201939486	0.61609683060762	6.48253925079131
C	-1.68569859882536	3.24671940895769	5.63282252756757
C	-2.96046343078433	1.47288012307322	6.64845447323957
C	-2.87038207177136	2.78615152637612	6.21570503326132
H	0.30543681689236	2.77730126334529	5.04822099940628
H	-1.96999911197612	-0.41421838276376	6.80435626358120
H	-3.88725320857502	1.12403440873496	7.08932005923321
O	0.01260246213634	-1.10155751991385	5.47673218996700
O	-3.93151097058665	3.61141180886313	6.32063807586573
H	-3.69155292106240	4.45115385443016	5.90101731425784
O	-1.68821057550127	4.52807999250238	5.18813007520743
H	-1.18388983557474	4.55279084355830	4.34049194304423

TABLE S4: Atomic Cartesian coordinates (in Å) of the supramolecular compound 14H₂O-Q@CB[7] (Figure S4) optimized at the PBE0/Def2-TZVP C-PCM D4 level

Atom	x	y	z
O	-0.09204672010230	0.13218099114510	0.61529287110741
C	0.50870282655072	0.99228116026557	-0.24327431859946
C	1.20013961162508	0.51290069363816	-1.30539042936429
C	1.31416463469608	-0.89026878213157	-1.54530625383650
C	0.65608778137510	-1.75343392481745	-0.63871139165829
C	-0.05489555785678	-1.20224552735782	0.43048874575898
C	0.67503577373093	-3.15555618788383	-0.80472834440867
C	-0.00460891107703	-3.94781886135355	0.08109320848157
C	-0.70295008009138	-3.36742132957117	1.14285545175251
C	-0.74018872251557	-1.98960247797735	1.33254976540570
O	1.78887358468415	1.29327880742070	-2.22310827117613
O	1.91787437423413	-1.27047939403890	-2.57171678238384
C	0.27902667628434	2.38908377721652	0.06638114571037
C	1.17201128913992	3.38372060406205	-0.35369338413950
C	0.92111487860650	4.70400352351983	-0.04875401216544
C	-0.24035121922138	5.05702903559391	0.64500014569627
C	-1.11143959887012	4.07434546794885	1.07159988024330
C	-0.85169559809547	2.74970546114779	0.79328989066325
O	1.35229567622195	-3.70131321923638	-1.82358097664230
O	-1.31000030740872	-4.21914106590822	1.95700797071787
O	1.76503970765655	5.73077446497214	-0.32461420266225
O	-0.48521755108628	6.35913346536409	0.89251354445383
O	-3.05116618925528	-3.25342880084987	3.63460435380497
C	-3.29300936582242	-2.09075140817223	3.94887143741509
N	-2.57717007216947	-1.34931152203440	4.83164923467950
C	-3.24899804278046	-0.10914936057293	5.15027303190029
C	-4.45567866633902	-0.09575852229341	4.17523887512698
N	-4.33832220722279	-1.35947553671843	3.49455580026102
N	-4.22635602459627	1.08058386254310	3.37922860624146
C	-3.17047787345892	1.81436665297335	3.84102242513264
N	-2.54589755448634	1.09543886464730	4.81895375428397

C	-1.47519663911763	-1.89702386527545	5.57904438588716
N	-0.19130471429187	-1.41527333858995	5.15667188430227
C	0.38217691334214	-0.19312166741756	5.64807882864115
C	1.82013546679260	-0.22396251305243	5.08821244217655
N	1.83751898966063	-1.41239284754091	4.26701010749065
C	0.70215827870198	-2.15776806481259	4.43720621564835
N	1.93673250484515	1.01901213226689	4.38134012036346
C	0.78981216058756	1.75895480594997	4.45048227683083
N	-0.15877497104028	1.02483410111827	5.10413645019287
O	0.65876443915414	2.89158484799295	4.02415194109245
C	-1.40818887192570	1.58976080652161	5.53459854358564
C	3.20038527494710	1.60809582502548	4.03948874757392
N	3.76910424143067	1.11057537338280	2.82279505557490
C	4.45684518069844	-0.14638544479999	2.76439852687238
C	5.21411521926589	-0.07829664769049	1.42409340975267
N	4.80077612958420	1.18240659764893	0.86171274400071
C	4.04777715961680	1.90925227627373	1.74746186596797
N	3.61675335145858	-1.31431510604029	2.62905925223045
C	3.88556841428216	-1.98754586380468	1.46445724799694
N	4.76297938015488	-1.24647018520697	0.72522231826912
C	3.07109507142035	-1.97305383553909	3.78903994467745
O	0.52391058649474	-3.30000553737736	4.04558332264057
C	-5.24418800044683	-1.84543779116398	2.49183527199463
N	-4.99387882465326	-1.32899546281847	1.17619109702332
C	-5.60403595218120	-0.13393968197279	0.66854213504568
C	-5.26225617760109	-0.16934456890758	-0.83797735398225
N	-4.44172104233322	-1.34901387159808	-0.97505935739085
C	-4.38540040804265	-2.05859868364494	0.19479126409668
N	-4.58549793710226	1.07853443241960	-1.06047260569156
C	-4.52230429000089	1.83991321423412	0.07435236181388
N	-5.02182951330685	1.10474184205772	1.10928346410652
O	-2.85844492970241	2.93042517778668	3.46873781045357
C	-5.17235725961321	1.61686513811437	2.44036635735234
C	-4.23230646889237	-1.99563948986589	-2.24420945783324
N	-3.24262819032199	-1.37096349674986	-3.07607460474405
C	-3.53743737964885	-0.18788192502697	-3.83985938049346
C	-2.43281854820320	-0.16183621734219	-4.91417037930288
N	-1.64316686233225	-1.32531334240486	-4.61628669103991
C	-2.17460877724417	-2.06157875764473	-3.59172539891141
N	-1.77945306607324	1.09674255403996	-4.69146000678124
C	-2.35147225161568	1.80829808259029	-3.67698934297795
N	-3.35609464842883	1.05341565724692	-3.13247441906632
O	-3.89915384497039	-3.16491838256239	0.33440660455423
O	-4.11336041636523	2.98505235713085	0.13721477412876
C	-4.41922070493008	1.64353755793675	-2.36673841323231
C	-0.67610507290889	-1.84358894369242	-5.54753930843933
N	0.61208598142646	-1.21480814255199	-5.47875809915912
C	0.94182675196827	0.00851358445950	-6.16640208216893
C	2.47656504685772	0.10884679640506	-5.99421496176793
N	2.82827099382182	-1.14995171924041	-5.41057704120910
C	1.73651037184933	-1.93908128363091	-5.16785403905893
N	2.63315048363754	1.28176969029142	-5.15909548358140
C	1.46499136602702	1.98969223066269	-5.05592473495366

N	0.46126494674939	1.22375468123111	-5.56881610566978
O	-1.78130672152030	-3.15254719410658	-3.21870496197280
C	-0.89130530488234	1.68248099233088	-5.65615692927184
O	-2.03540735079040	2.93583606664348	-3.33608657498572
C	4.16892078853052	-1.55126396710598	-5.08950966631023
N	4.64917200578873	-1.09242355416416	-3.81550686738773
C	5.30599873889738	0.16230109860909	-3.58740492339718
C	5.71692869292725	0.08834336429154	-2.09621607362548
N	5.13459948634927	-1.15086638407903	-1.65376532807855
C	4.63517424886431	-1.88424265060833	-2.70105672627882
N	5.15442750218499	1.28586656503060	-1.52708812972421
C	4.52026123248659	2.05024751518517	-2.46421245700103
N	4.48502328859119	1.34879184086971	-3.63515389020772
O	1.75292987965967	-3.09736312185589	-4.80343273817486
C	3.90911456276354	1.86632999015062	-4.84230017978619
O	1.34938588743516	3.11434004059834	-4.60304514543878
C	5.47057058746948	-1.77477070909003	-0.40918705340164
O	4.30196046840390	-3.05056837143476	-2.64950163163736
C	5.50927633542105	1.79368328628035	-0.23228367243539
O	4.09407508707637	3.17888658829257	-2.28317978479700
O	3.44344692509034	-3.07797477489498	1.14217604645264
O	3.71039129980623	3.07194480614057	1.61276103345614
H	-6.14204971590863	-0.24415403867142	-1.48470920375033
H	-6.67766035930403	-0.14125029467865	0.87908330141244
H	-2.81063605779347	-0.21403154511285	-5.93969847491520
H	-4.55011764252858	-0.24333741273010	-4.25133549588977
H	3.01467886975408	0.25439168231827	-6.93566669406514
H	0.62065872025120	-0.04525367178185	-7.21158367020406
H	6.80064840234244	0.07605754453307	-1.94166389729134
H	6.15180666240107	0.27499725558182	-4.27238116267669
H	5.11168374153535	-0.25996542153286	3.63434278274902
H	6.30314442446954	-0.10145504425221	1.53329938507423
H	-5.42526088181234	-0.03059304179738	4.67630953105366
H	-3.53517593878009	-0.10611653543326	6.20584561755738
H	3.90203373277120	1.42098846570102	4.85979696547939
H	3.05283942107481	2.68107540757539	3.92978654724942
H	-6.18452546783191	1.39918460671090	2.79344485839328
H	-5.02912188019910	2.69572280158329	2.39936507552894
H	-5.35571647522281	1.52669558065985	-2.92418951630046
H	-4.20312106450765	2.70280974657532	-2.24503472108664
H	-1.27405656639550	1.46028869866300	-6.65691716898898
H	-0.89197867179179	2.76018488075175	-5.50316715398769
H	4.59975083435629	1.69093745755994	-5.67234796757226
H	3.76515748885136	2.93846868979117	-4.71566947163131
H	6.58409513869756	1.64744528404666	-0.08108263113693
H	5.28249095682422	2.85846496286573	-0.21898355758555
H	-1.61065337365613	-1.65544823156543	6.63703780227752
H	-1.49394881097678	-2.97811151795175	5.45187800555638
H	6.54457654003353	-1.66533741308564	-0.22229326859666
H	5.22488656870252	-2.83157364139226	-0.49804642426880
H	4.84126301583871	-1.18932828387591	-5.87148493108835
H	4.19012198021010	-2.63990682429331	-5.07386713102816
H	-1.08215379103446	-1.73390609538344	-6.55920408595775

H	-0.53226800975147	-2.90073315390280	-5.32941486931496
H	-5.18447956650090	-2.01876005627204	-2.78818522021598
H	-3.90703327019864	-3.01507515108017	-2.04468233014766
H	-6.26565532397459	-1.58638073434149	2.78175696644461
H	-5.14252821057533	-2.92885587513610	2.45700600293124
H	2.89716286263985	-3.01873679932433	3.54785202192819
H	3.81487451339891	-1.92030065327720	4.59226863733051
H	-1.54126659753284	1.38193148710566	6.60028531697569
H	-1.35998457364395	2.66654417884987	5.38060064635673
H	2.59099894751217	-0.29450448805750	5.86190487378683
H	0.33230186334375	-0.17012619254334	6.74098435481439
H	-1.27965218246285	-1.53564367978482	2.15129423139631
H	-0.02508950028201	-5.02158749571104	-0.02031030491369
H	-1.88144765214220	-3.75446526087159	2.61031933038481
H	1.74924848980214	-2.97075774950890	-2.36451161720762
H	2.17519930196521	0.66368054144160	-2.86310136256848
H	2.07944299130000	3.12685278453611	-0.88106929110186
H	-1.54263933633263	1.99282670930157	1.13628014388893
H	-1.98941473076919	4.34373784743154	1.63016823479911
H	0.22675333604613	6.86504048558799	0.47278885656729
H	2.20502825917450	5.60624655707965	-1.22673609170696
O	-3.55322143955798	-5.92460934826062	0.10788767680068
O	-1.91134914283224	-5.88112242630002	-2.13545175037263
O	0.77656431814668	-6.54151727759157	-1.88746611806719
O	1.17607546590828	-7.12915422469474	0.78761237604877
O	2.06881896129173	-5.12892100531704	2.42454647353239
O	-1.01022382065135	-5.94901698029502	4.46560741248945
O	-3.41811839742056	-6.16528019891579	2.91381481413744
H	-3.67675329066124	-5.26633502719274	3.15183312097106
H	-3.73786317917499	-4.97351895896748	0.15889488937745
H	-1.90230954272347	-4.95994160923720	-2.43426721479643
H	1.13444852362989	-5.64904224106183	-2.00790911856711
H	1.81585279580303	-7.83555441592166	0.91600981182836
H	2.55186185083372	-4.45567441431866	1.91191201035686
H	-0.63424796507013	-5.09040446204466	4.23605381215764
H	-1.77069392063205	-6.05143776920581	3.86499797993149
H	-3.32637070527397	-6.13472759975613	1.93956351994552
H	-2.90092899134458	-5.98417812586698	-0.62114782190331
H	-0.96748294815313	-6.12769367230845	-2.03398250101897
H	0.97368269752256	-6.76459505904917	-0.95251509815472
H	1.47729685044973	-6.39415459688239	1.36856801932238
H	1.41578641400576	-4.60961495346516	2.91896838541805
O	2.51425902999924	5.59329258219482	2.48866897831891
O	2.62659932486360	5.48339315881105	-2.71861338702250
O	0.06399920994516	5.37771819014097	-3.61152253278136
O	-2.32575039763554	5.43081734341734	-2.08740077276967
O	-3.79483219955211	5.78447693777414	0.44551530819566
O	-2.77590878378203	5.85556933229188	3.26299606981040
O	-0.00955990196012	5.60450893634543	3.99583188301592
H	-2.45863184361931	4.49180335599208	-2.28490885485511
H	-4.01104103461143	4.83928806473962	0.43654150544547
H	-3.00915076204106	4.93978708221595	3.47055428203540
H	0.01995181658541	4.64944702258396	4.16207353165926

H	2.82803815406262	4.68054376959704	2.39285667638040
H	3.02367450262528	4.59993455723073	-2.80702227813149
H	0.09183972318524	4.45513600779000	-3.90643350497983
H	-2.64761510032006	5.56466996551757	-1.17923864372072
H	-3.37832488106227	5.91924475287181	1.31359530333105
H	-1.80787794267273	5.87107205601859	3.39635162422379
H	0.74303736196285	5.72844234650581	3.39121136743908
H	2.42581525371664	5.88438831382666	1.56948240163793
H	1.72005609879245	5.43206145658225	-3.10337402737167
H	-0.66421674834763	5.43324632785836	-2.96508099671428