Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information for

Microhydration of Benzoic Acid Molecule and its Dissociation

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Cartesian coordinates of $C_6H_5COOH.nH_2O$, n = 0-8

C_6H_5COOH

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.395570
C	1.205094	0.000000	2.090686
C	2.415330	0.000000	1.389560
C	2.414768	0.000021	-0.009210
C	1.206059	0.000063	-0.700884
C	3.679208	0.000023	2.175826
O	4.786907	0.000454	1.403142
O	3.741612	-0.000322	3.383916
H	-0.942288	-0.000016	1.942872
H	1.226683	0.000016	3.179422
H	3.358000	0.000038	-0.551943
H	1.204785	0.000096	-1.790513
H	-0.944733	0.000000	-0.544233
H	5.539526	0.000462	2.008717

$C_6H_5COOH.1H_2O$

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.395570
C	1.205350	0.000000	2.090582
C	2.415525	0.000169	1.389689
C	2.414695	0.000571	-0.008971
C	1.206188	0.000380	-0.700837
C	3.685519	-0.000065	2.167149
O	4.780781	0.000759	1.409743
O	3.721153	-0.001773	3.388619
O	6.468337	0.048995	3.537310
H	-0.942440	0.000363	1.942631
H	1.225683	0.000684	3.179212
H	3.359292	0.001707	-0.549202

H	1.205104	0.000940	-1.790497
H	-0.944817	0.000000	-0.544128
H	5.564704	-0.002085	2.006712
H	6.937125	-0.718669	3.873165
H	5.576498	0.013796	3.928257

$C_6H_5COOH.2H_2O$

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.395600
C	1.205544	0.000000	2.090275
C	2.416137	0.000148	1.390663
C	2.414916	0.000084	-0.008106
C	1.206431	-0.000126	-0.700212
C	3.688304	0.001104	2.169149
O	4.773875	0.010231	1.418231
O	3.701658	-0.006137	3.393445
O	7.044002	0.003891	2.804336
O	5.780660	-0.043651	5.177088
H	-0.942674	0.000709	1.942137
H	1.225459	0.000440	3.178913
H	3.360022	-0.000790	-0.547164
H	1.206203	-0.000176	-1.790012
H	-0.944977	0.000000	-0.543891
H	5.602464	0.015593	1.972164
H	6.776734	-0.039410	3.749012
H	7.596770	0.784366	2.721931
H	4.959157	-0.031159	4.645031
H	5.719583	-0.822840	5.733767

$C_6H_5COOH.3H_2O$

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.395710
C	1.205764	0.000000	2.090204

C	2.416616	-0.000634	1.391062
C	2.415078	-0.001268	-0.007707
C	1.206701	-0.000845	-0.699920
C	3.691015	-0.001758	2.168256
O	4.772238	-0.016952	1.415503
O	3.706495	0.010160	3.391280
O	7.147841	0.042300	2.533902
O	7.580086	-0.403560	5.156422
O	4.982782	-0.144029	5.814231
H	-0.942978	-0.000362	1.941742
H	1.226517	-0.002280	3.178884
H	3.360556	-0.003906	-0.545906
H	1.205921	-0.001339	-1.789780
H	-0.945034	-0.000940	-0.543770
H	5.610129	-0.003350	1.957552
H	7.337889	-0.152903	3.480185
H	7.656869	0.828074	2.324333
H	4.532703	-0.102099	4.948485
H	4.642979	0.600042	6.315205
H	7.872106	-1.275348	5.431516
H	6.668725	-0.303446	5.511361

$C_6H_5COOH.4H_2O$

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.395680
C	1.205835	0.000000	2.090131
C	2.416736	0.000000	1.391073
C	2.415101	0.000000	-0.007756
C	1.206704	0.000000	-0.699895
C	3.694401	0.000000	2.163118
O	4.770336	0.000000	1.417550
O	3.699488	-0.000018	3.392858
O	7.051413	-0.000396	2.597828
O	5.364594	-0.000034	5.474151

O	7.174643	-1.939174	4.604161
O	7.175350	1.938486	4.603836
H	-0.942949	0.000000	1.941783
H	1.225370	0.000000	3.178775
H	3.360733	0.000000	-0.545627
H	1.206362	0.000000	-1.789745
H	-0.945073	0.000000	-0.543683
H	5.629675	-0.000163	1.957511
H	7.214306	-0.770762	3.173457
H	7.214656	0.769965	3.173364
H	4.774736	0.000316	4.683087
H	4.782234	-0.000214	6.236534
H	6.767732	-2.799855	4.482625
H	6.522877	-1.405057	5.092524
H	6.768296	2.799127	4.482498
H	6.523901	1.404372	5.092607

$C_6H_5COOH.5H_2O$

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.395460
C	1.205007	0.000000	2.090947
C	2.415959	0.004059	1.391328
C	2.413743	0.004306	-0.007460
C	1.206253	0.001144	-0.700490
C	3.686124	0.005687	2.170058
O	4.777819	0.063624	1.420953
O	3.709678	-0.045814	3.390625
O	7.070063	0.158561	2.706041
O	7.745561	2.532077	1.630681
O	5.879284	-0.045019	5.112639
O	6.747495	1.196130	-0.546229
O	8.107373	-1.033498	0.441889
H	-0.942360	-0.000033	1.942518
H	1.223740	0.000880	3.179375

H	3.355530	0.003515	-0.552336
H	1.206338	-0.000802	-1.789998
H	-0.944332	0.000659	-0.544749
H	5.606540	0.082878	1.986073
H	7.408527	1.064415	2.530188
H	6.876718	0.076290	3.662472
H	7.222682	0.357417	-0.391317
H	5.850497	1.009477	-0.247249
H	8.635670	2.865565	1.501270
H	7.446965	2.206571	0.753623
H	5.850336	-0.803552	5.699080
H	5.037552	-0.055789	4.616480
H	7.848522	-0.831649	1.359538
H	7.880363	-1.954416	0.298047

$C_6H_5COOH.6H_2O$

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.399010
C	1.211610	0.000000	2.097660
C	2.416020	-0.004204	1.401793
C	2.414295	-0.005129	0.006154
C	1.207328	-0.001699	-0.693286
C	-1.268046	0.001395	2.180215
O	-1.288724	0.048835	3.401279
O	-2.362431	-0.051907	1.434770
O	-4.629599	-0.204681	2.724978
O	-3.447190	0.074532	5.131521
O	-5.541766	-2.650256	1.799882
O	-7.831696	-1.613541	0.911146
O	-6.141849	0.413853	0.337273
O	-4.166115	-1.465745	-0.417333
H	-3.193909	-0.070888	2.000257
H	-4.434180	-0.081934	3.677203
H	-4.958548	-1.116089	2.606672

H	-5.585204	-3.498391	2.245328
H	-6.457810	-2.434734	1.498559
H	-3.442673	0.862683	5.678519
H	-2.607357	0.089306	4.632022
H	-7.356411	-0.792426	0.638928
H	-8.307102	-1.912329	0.133150
H	-5.446677	-0.111627	-0.101876
H	-5.761649	0.585768	1.210625
H	-4.495352	-2.078162	0.259733
H	-3.341101	-1.125033	-0.051786
H	1.191833	0.001680	3.186089
H	3.359685	-0.006508	1.946713
H	3.358409	-0.008589	-0.538862
H	1.207357	-0.000073	-1.782815
H	-0.942931	0.006732	-0.543033

$C_6H_5COOH.7H_2O$

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.398940
C	1.211461	0.000000	2.097307
C	2.415577	0.005635	1.400940
C	2.413778	0.007910	0.005303
C	1.206908	0.002652	-0.693812
C	-1.271355	0.008714	2.174566
O	-2.355617	0.102099	1.424306
O	-1.294232	-0.061783	3.395288
O	-4.652003	0.406068	2.594488
O	-4.256755	2.471063	4.211408
O	-2.938993	0.277812	5.512354
O	-2.704874	4.014437	2.571521
O	-3.106644	2.706750	0.208772
O	-5.133626	-1.235616	4.741393
O	-5.652651	1.587770	0.313914
H	-3.199989	0.149809	1.973605

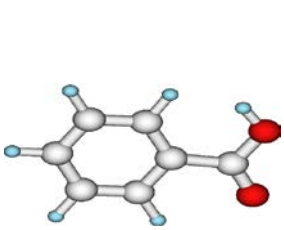
H	-2.355436	0.124167	4.737744
H	-2.381007	0.154465	6.283130
H	-4.571332	1.215906	3.167373
H	-4.955174	-0.286101	3.215873
H	-5.921534	-1.034869	5.251768
H	-4.400297	-0.779938	5.197979
H	-3.688060	3.104832	3.726225
H	-3.688623	2.020973	4.852116
H	-2.836901	4.957603	2.459047
H	-2.850223	3.617508	1.683704
H	-4.034793	2.412381	0.129040
H	-2.624903	1.883106	0.348992
H	1.194079	-0.000747	3.185708
H	3.359102	0.011447	1.945837
H	3.357926	0.015163	-0.539557
H	1.205928	0.003115	-1.783302
H	-0.943687	-0.008191	-0.541678
H	-5.479678	1.045732	1.107445
H	-5.984983	0.984271	-0.353461

$C_6H_5COOH.8H_2O$

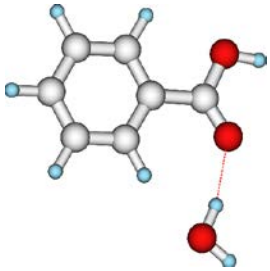
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.393120
C	1.209402	0.000000	2.097037
C	2.417475	0.010160	1.394031
C	2.416876	0.001517	0.001368
C	1.208969	-0.004684	-0.696988
C	1.222052	-0.019420	3.601289
O	2.296519	0.215311	4.199266
O	0.123261	-0.310760	4.179428
O	-0.133410	-0.339453	6.656862
O	1.753412	0.717873	7.989549
O	0.364446	-2.767264	7.404482
O	2.985209	2.114076	6.024033

O	-0.633804	-2.769749	3.253595
O	1.115080	-3.896191	4.950504
O	3.223168	-2.052400	5.512441
O	2.914766	-1.829154	8.121166
H	-0.033724	-1.306230	6.935045
H	0.573246	-3.294008	6.611250
H	-0.524847	-1.838942	3.542490
H	-0.459801	-2.750087	2.308612
H	0.031654	-0.282045	5.624216
H	0.599488	0.164754	7.169171
H	3.150201	-1.918025	7.159497
H	3.653309	-2.174911	8.625737
H	2.298136	1.290067	7.408396
H	2.302133	-0.060918	8.189827
H	3.351394	0.021509	1.953241
H	3.361241	0.002898	-0.542781
H	1.208702	-0.008139	-1.787173
H	-0.944276	0.009724	-0.544218
H	-0.938899	0.015759	1.945084
H	3.900404	2.367460	5.892277
H	2.769705	1.490500	5.301701
H	2.958135	-1.224973	5.066822
H	1.221799	-2.626772	7.843831
H	2.588620	-2.720075	5.203902
H	1.217422	-4.837266	4.795434
H	0.479205	-3.570567	4.268533

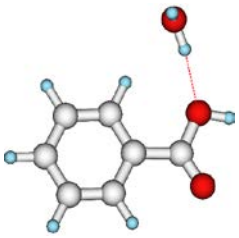
Equilibrium structure and relative energy of conformers for different size of hydrated clusters of benzoic acid clusters



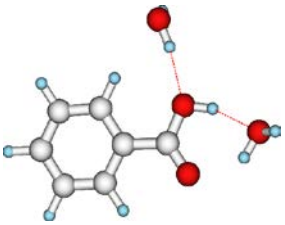
b0-1 (5.8 kcal/mol)



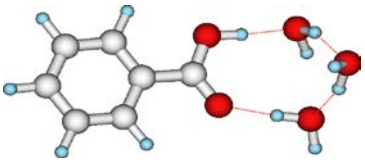
b1-1 (3.9 kcal/mol)



b1-2 (6.4 kcal/mol)



b2-1 (6.9 kcal/mol)



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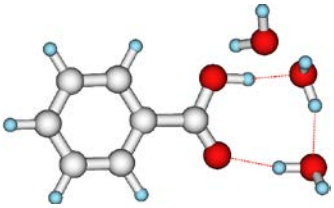

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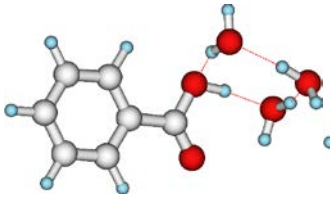
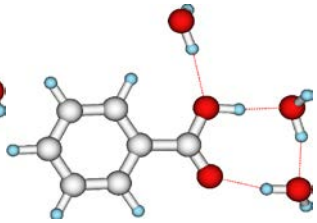


b3-3 (3.6 kcal/mol)



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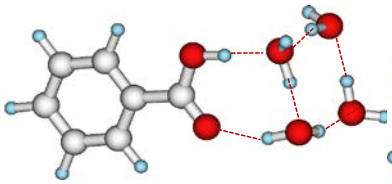

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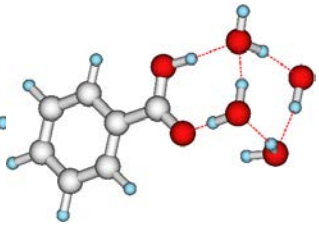
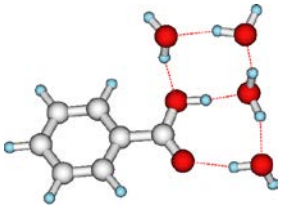
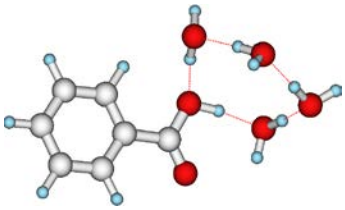


b4-2 (1.7 kcal/mol)



b4-3 (2.3 kcal/mol)



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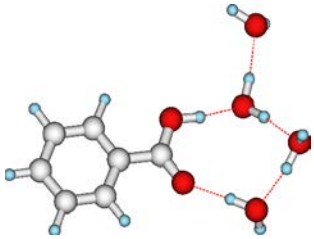

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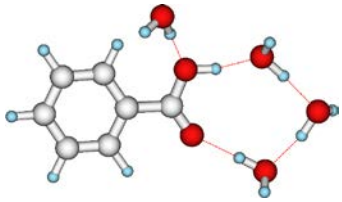
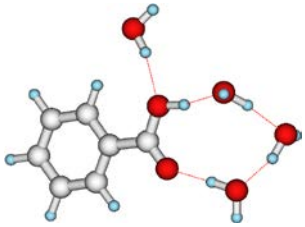


b4-6 (4.6 kcal/mol)



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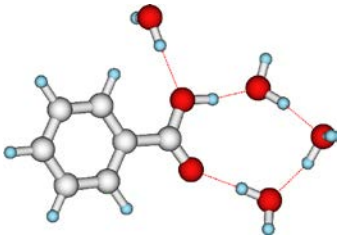

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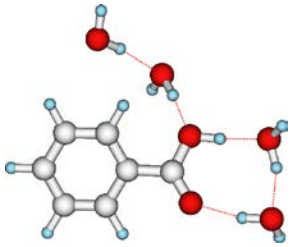
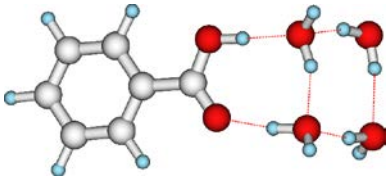
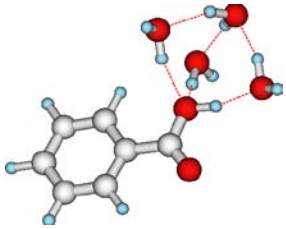


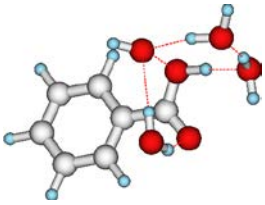
b4-9 (5.8 kcal/mol)



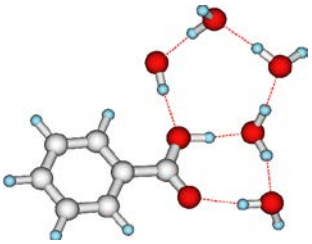
b4-10 (6.2 kcal/mol)



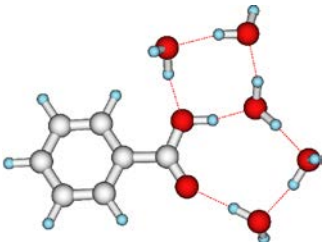
b4-11 (6.5 kcal/mol)



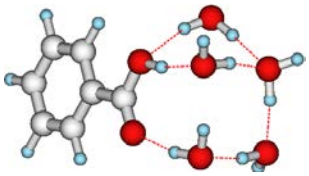
b4-12 (7.0 kcal/mol)



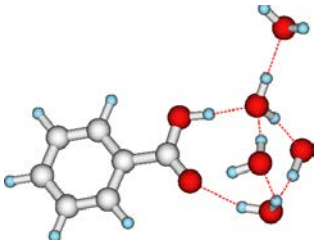
b5-1 (0.5 kcal/mol)



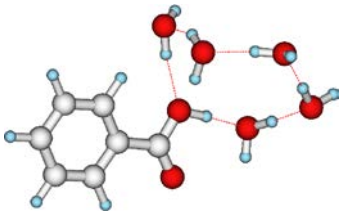
b5-2 (0.8 kcal/mol)



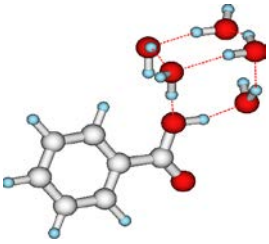
b5-3 (2.5 kcal/mol)



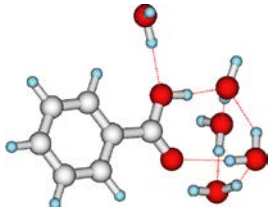
b5-4 (2.6 kcal/mol)



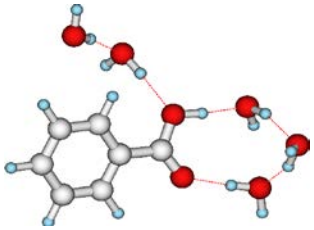
b5-5 (3.2 kcal/mol)



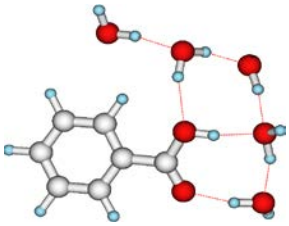
b5-6 (4.6 kcal/mol)



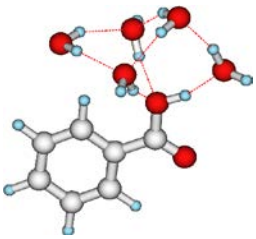
b5-7 (4.9 kcal/mol)



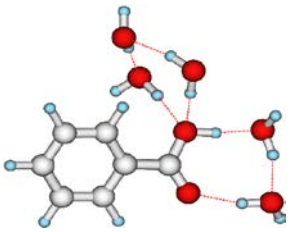
b5-8 (5.2 kcal/mol)



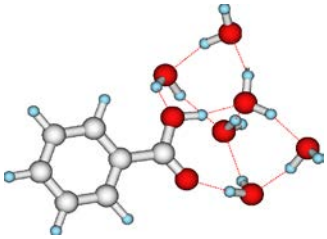
b5-9 (5.3kcal/mol)



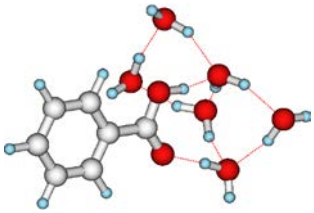
b5-10 (6.2 kcal/mol)



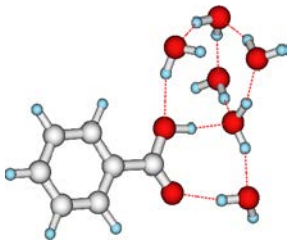
b5-11 (6.5 kcal/mol)



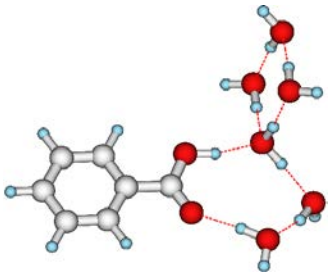
b6-1 (0.2 kcal/mol)



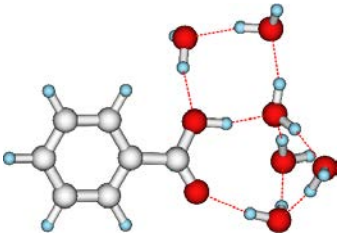
b6-2 (0.5 kcal/mol)



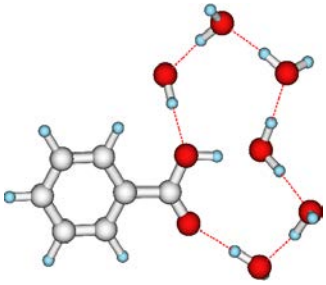
b6-3 (0.9 kcal/mol)



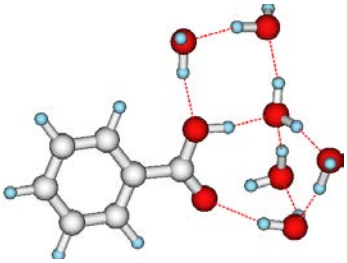
b6-4 (1.2 kcal/mol)



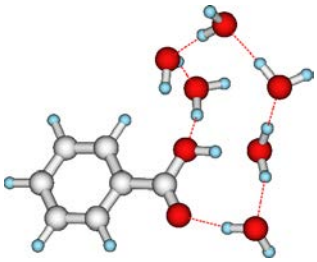
b6-5 (1.3 kcal/mol)



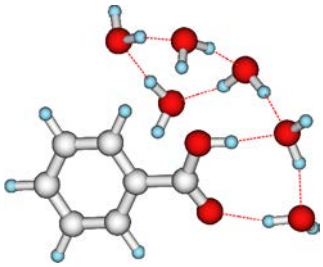
b6-6 (1.7 kcal/mol)



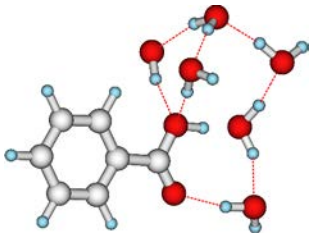
b6-7 (1.9 kcal/mol)



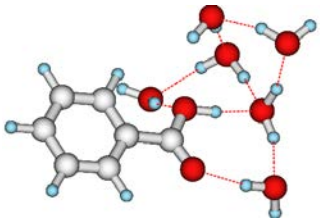
b6-8 (1.9 kcal/mol)



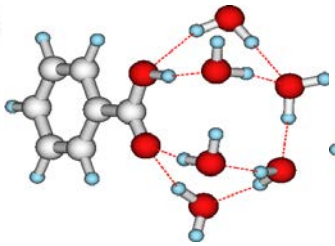
b6-9 (2.0 kcal/mol)



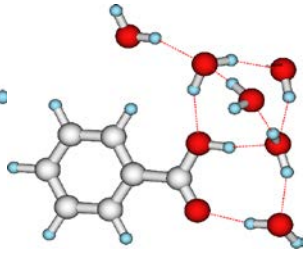
b6-10 (2.1 kcal/mol)



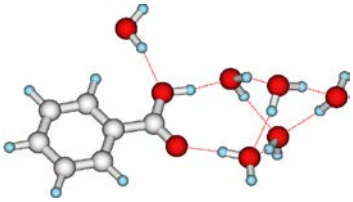
b6-11 (2.1 kcal/mol)



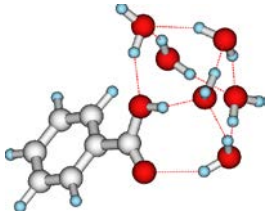
b6-12 (2.7 kcal/mol)



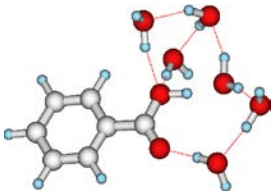
b6-13 (2.9 kcal/mol)



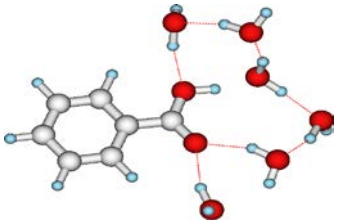
b6-14 (3.1 kcal/mol)



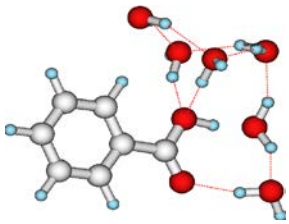
b6-15 (3.1 kcal/mol)



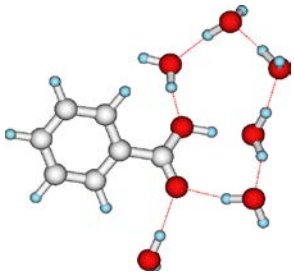
b6-16 (3.9 kcal/mol)



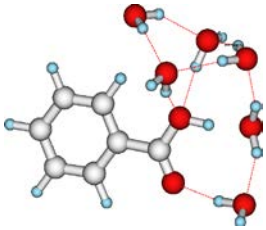
b6-17 (4.2 kcal/mol)



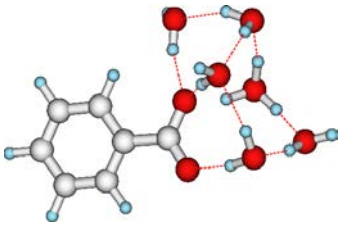
b6-18 (4.6 kcal/mol)



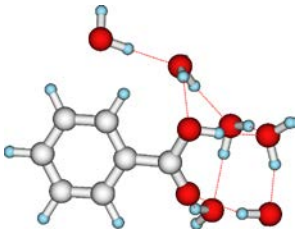
b6-19 (4.8 kcal/mol)



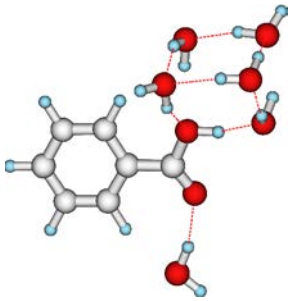
b6-20 (5.0 kcal/mol)



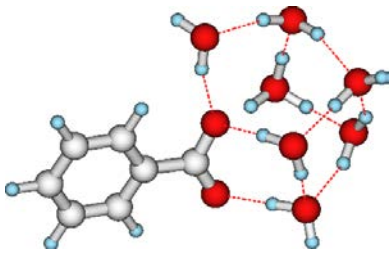
b6-21 (5.4 kcal/mol)



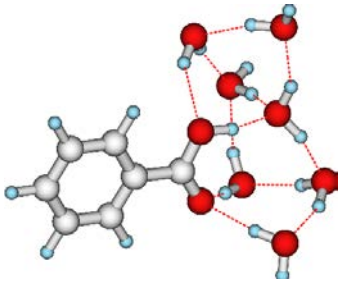
b6-22 (5.4 kcal/mol)



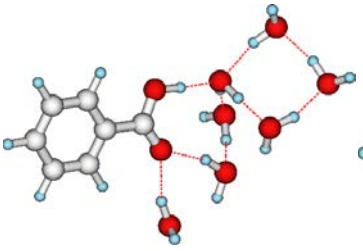
b6-23 (7.7 kcal/mol)



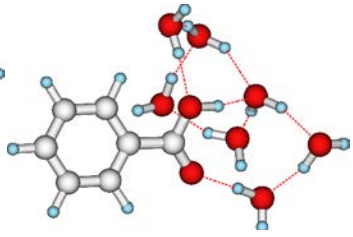
b7-1 (1.5 kcal/mol)



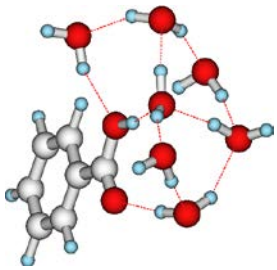
b7-2 (1.6 kcal/mol)



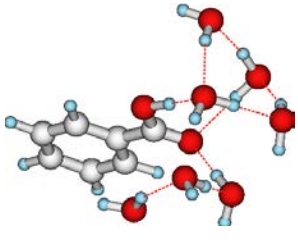
b7-3 (2.6 kcal/mol)



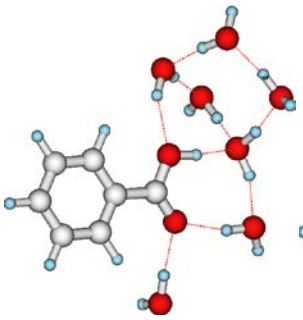
b7-4 (3.1 kcal/mol)



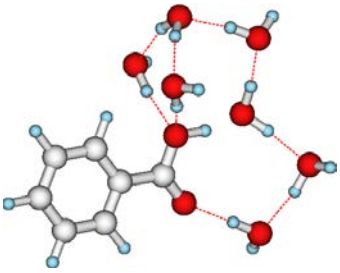
b7-5 (3.4 kcal/mol)



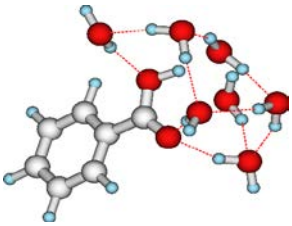
b7-6 (3.5 kcal/mol)



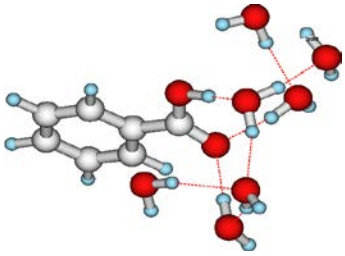
b7-7 (4.1 kcal/mol)



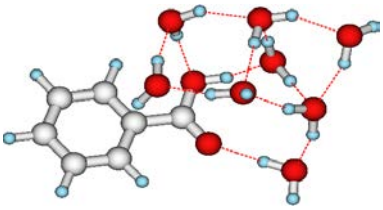
b7-8 (4.3 kcal/mol)



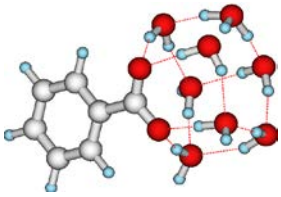
b7-9 (5.4 kcal/mol)



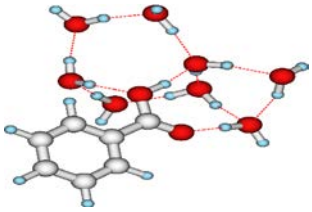
b7-10 (6.3 kcal/mol)



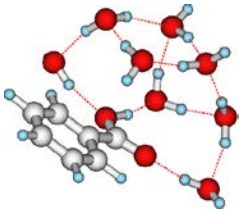
b8-1 (0.3 kcal/mol)



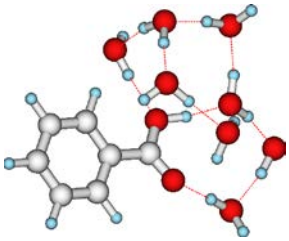
b8-2 (0.6 kcal/mol)



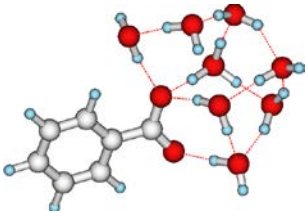
b8-3 (2.3 kcal/mol)



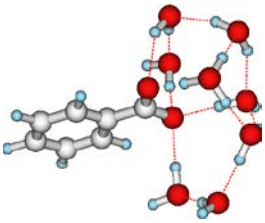
b8-4 (3.0 kcal/mol)



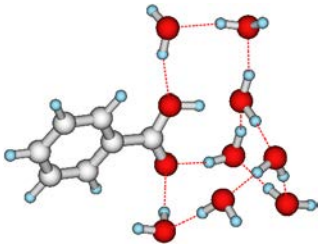
b8-5 (3.2 kcal/mol)



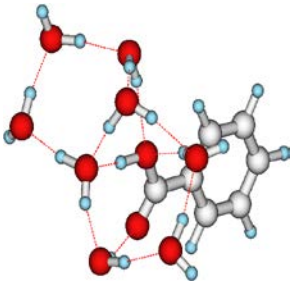
b8-6 (3.8 kcal/mol)



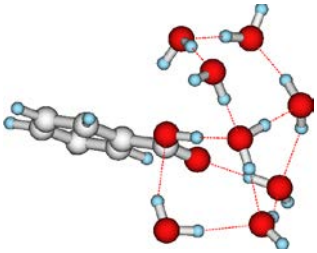
b8-7 (4.0 kcal/mol)



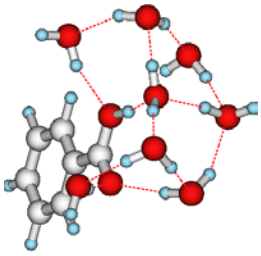
b8-8 (4.4 kcal/mol)



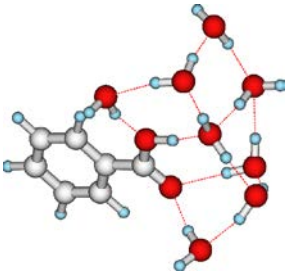
b8-9 (4.5 kcal/mol)



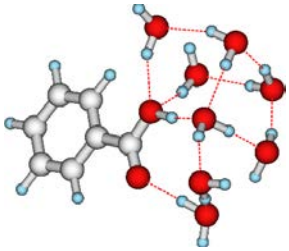
b8-10 (5.2 kcal/mol)



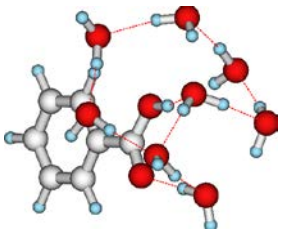
b8-11 (5.5 kcal/mol)



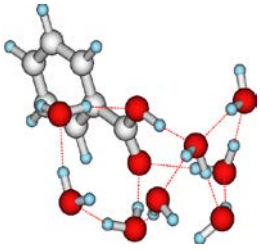
b8-12 (5.7 kcal/mol)



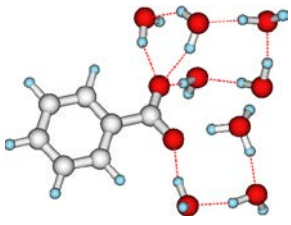
b8-13 (5.7 kcal/mol)



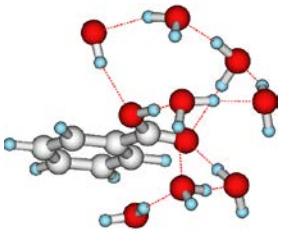
b8-14 (6.4 kcal/mol)



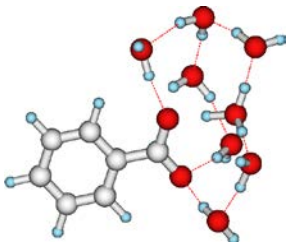
b8-15 (6.4 kcal/mol)



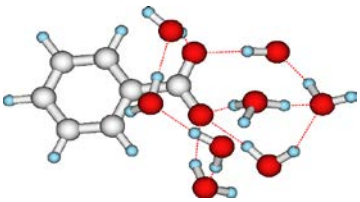
b8-16 (6.5 kcal/mol)



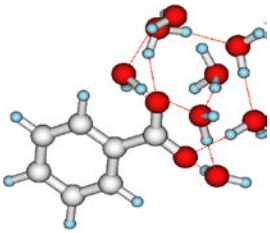
b8-17 (6.7 kcal/mol)



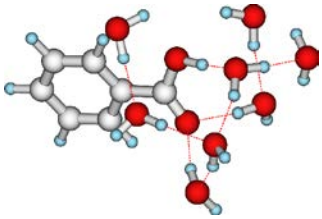
b8-18 (8.0 kcal/mol)

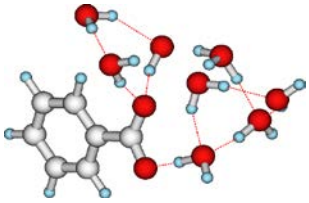


b8-19 (8.4 kcal/mol)



b8-20 (8.5 kcal/mol)





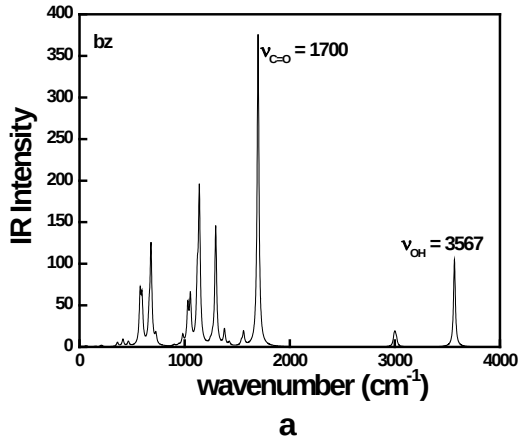
b8-21 (9.5 kcal/mol)

b8-22 (18.0 kcal/mol)

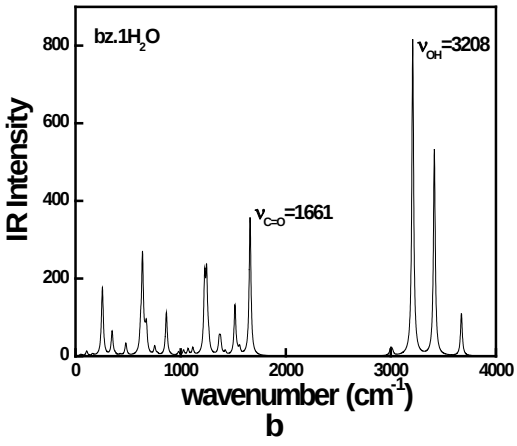
Table1. Comparison of enthalpy and entropy of formation of hydrated clusters of benzoic acid calculated at 100 K

System	” H	” S
	(kcal mol^{-1})	(kcal $mol^{-1}K^{-1}$)
$C_6H_5COOH.1H_2O$	-9.2	0.1
$C_6H_5COOH.2H_2O$	-19.5	0.1
$C_6H_5COOH.3H_2O$	-26.6	0.2
$C_6H_5COOH.4H_2O$	-35.2	0.2
$C_6H_5COOH.5H_2O$	-41.8	0.3
$C_6H_5COOH.6H_2O$	-50.3	0.4
$C_6H_5COOH.7H_2O$	-60.0	0.4
$C_6H_5COOH.8H_2O$	-70.1	0.5

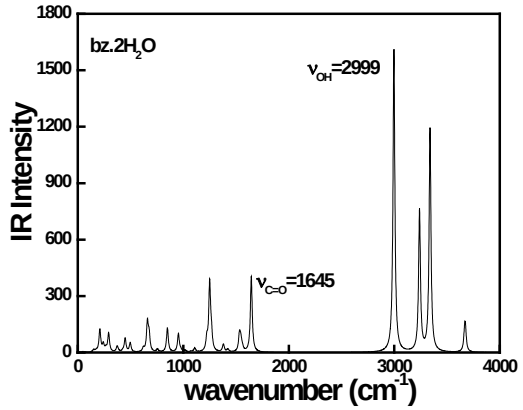
Simulated, scaled (scaling factor 0.93) IR spectra of the most stable structure of a) C_6H_5COOH; b) $C_6H_5COOH.1H_2O$; c) $C_6H_5COOH.2H_2O$; d) $C_6H_5COOH.3H_2O$; e) $C_6H_5COOH.4H_2O$; f) $C_6H_5COOH.5H_2O$; g) $C_6H_5COOH.6H_2O$; h) $C_6H_5COOH.7H_2O$ and i) $C_6H_5COOH.8H_2O$ calculated at É B97X-D/aug-cc-pVDZ level of theory.



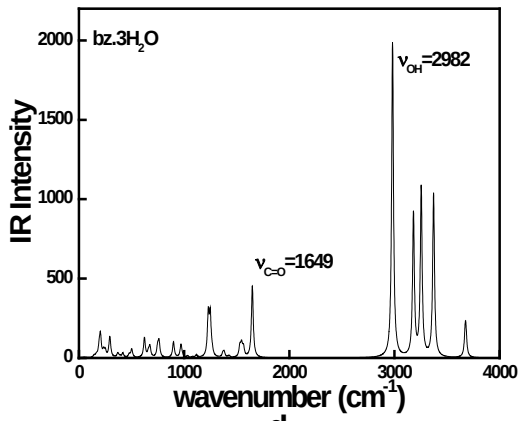
a



b



c



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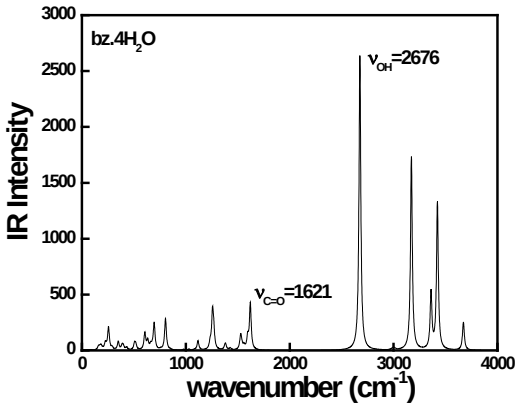
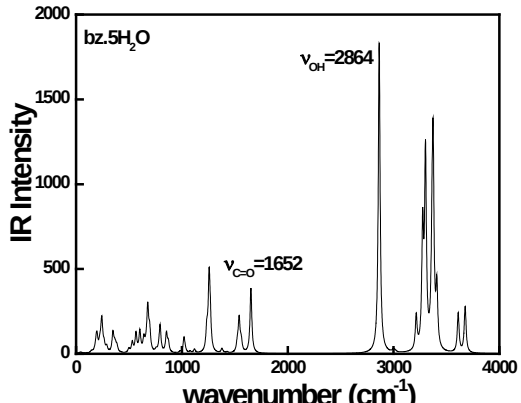
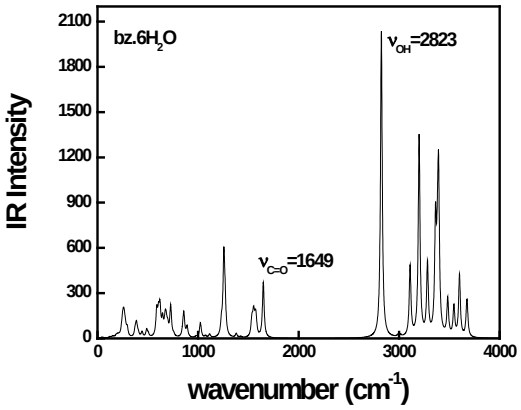


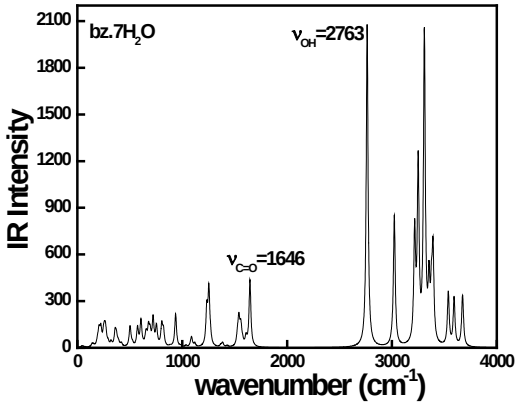
e



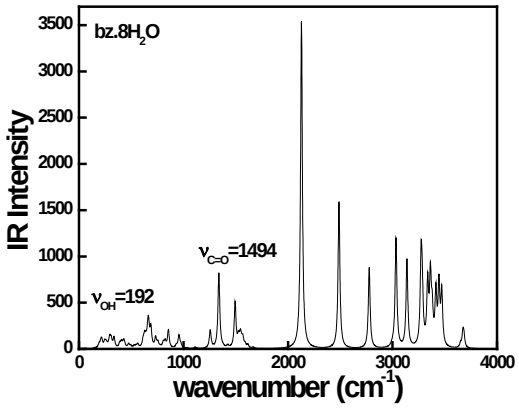
f


bz.6H2O
νOH=2823
νC=O=1649
IR Intensity
wavenumber (cm-1)

g


bz.7H2O
νOH=2763
νC=O=1646
IR Intensity
wavenumber (cm-1)

h


bz.8H2O
νC=O=1494
νOH=192
IR Intensity
wavenumber (cm-1)

i