Charged H-bonds data set

Complexes. The data set contains following hydrogen-bonded complexes:

1) anions: acetate – water, acetate – methanol, acetate – methylamine
2) cations: methylammonium – water, methylammonium – methanol, methylammonium – methylamine, methylammonium – formaldehyde, guanidinium – water, guanidinium – methanol, guanidinium – methylamine, guanidinium – formaldehyde, imidazolium – water, imidazolium – methanol, imidazolium – methylamine, imidazolium – formaldehyde,

Methods. Geometries of the complexes had been optimized using MP2 in cc-pVTZ basis set with counterpoise correction. The CCSD(T)/CBS interaction energy consist of HF term calculated in aug-cc-pVQZ basis set, MP2/CBS term extrapolated from aug-cc-pVTZ and aug-cc-pVQZ and CCSD(T) correction calculated in aug-cc-pVDZ basis set. All the interaction energies are counterpoise corrected; MP2 calculations use density fitting.

Benchmark results. Table S1 lists the CCSD(T)/CBS interaction energies.

Table S1. *CCSD(T)/CBS interaction energies in the data set of charged H-bonds.*

complex	ΔE (kcal/mol)
acetate ... methanol	-19.753
acetate ... water	-21.062
acetate ... methylamine	-11.455
methylammonium ... formaldehyde	-19.096
methylammonium ... methylamine	-28.560
methylammonium ... methanol	-21.225
methylammonium ... water	-18.514
guanidinium ... formaldehyde	-18.090
guanidinium ... methylamine	-20.196
guanidinium ... methanol	-19.788
guanidinium ... water	-17.467
imidazolium ... formaldehyde	-16.410
imidazolium ... methylamine	-25.977
imidazolium ... methanol	-18.914
imidazolium ... water	-16.485

Structures. Here we list the structures of the complexes in XYZ format:

```
14
carboxyl_mNH2
  C   -1.067681101  -0.271098200   0.098425590
  C    0.361871421   0.290569279  -0.103737259
  O    1.279845864  -0.562993045  -0.089531722
  O    0.451018532   1.538347265  -0.258903660
  H   -1.274226455  -1.017247821  -0.669620680
  H   -1.122005113  -0.781585539   1.060825043
  H   -1.819051732   0.515321513   0.058342297
  H    2.358591571   2.032036918  -0.577059564
  N    3.325234668   2.378226272  -0.618915071
  C    4.203764407   1.272238900  -0.244130768
  H    5.247634052   1.596828130  -0.264891127
  H    3.997944581   0.831075775   0.736038541
  H    4.088828419   0.471128339  -0.970243143
  H    3.366565887   3.073767217   0.116943522

13
carboxyl_mOH
  C   -1.006215463  -0.203566404   0.039323585
  C    0.487100228   0.185923820  -0.030061282
  O    1.301564189  -0.757785383   0.052857808
  O    0.724973696   1.422331940  -0.159634962
  H   -1.223648142  -0.940991754  -0.733559633
  H   -1.208099576  -0.678638500   0.999935449
  H   -1.654410613   0.661570766  -0.082684221
  H    2.323552151   1.971306366  -0.246411344
  O    3.242038147   2.349020688  -0.304495292
  C    4.120013665   1.257459426  -0.234121540
  H    5.142912972   1.638285367  -0.294028876
  H    4.022512629   0.692111931   0.697386417
  H    3.976696841   0.542589358  -1.049974871

10
carboxyl_wat
  C   -0.808438821  -0.243062083   0.038574485
  C    0.533554652   0.513743610  -0.070281243
  O    1.560611869  -0.214420190  -0.027568739
  O    0.465298866   1.764998179  -0.183236969
  H   -0.854283812  -1.014973034  -0.729785233
  H   -1.656064871   0.431570596  -0.062379061
  H   -0.857515936  -0.748947615   1.003461116
  H    2.420729014   2.348323562  -0.279518048
  O    3.332761822   2.015770751  -0.268681517
  H    3.075886493   1.082062820  -0.178457540

14
gua_fmdh
  C   -0.105081656   0.282413741   0.022074441
  N   -0.785227591  -0.820652291  -0.288990507
  N   -0.745585479   1.421570007   0.253246903
  N    1.219250263   0.252146159   0.103458752
  H   -1.744037401   1.479987848   0.172685895
  H    1.727462291  -0.601259621  -0.038822645
  H    1.721470076   1.097144758   0.339497536
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  H    -0.216089211    2.249292326    0.491002112
  H    -1.787472355   -0.815092404   -0.340300985
  H    -0.312365218   -1.684834579   -0.480883846
  O     1.602569103    3.050868682    0.808678982
  C     2.224226383    4.058749214    1.099297255
  H     3.315952442    4.050092152    1.175259403
  H     1.711178461    5.005655912    1.293917723

17
gua_mNH2
  C    -0.022632781    0.158889311   -0.003491152
  N    -1.034258337   -0.697533791    0.152948303
  N    -0.072073363    1.381821873    0.487979803
  N     1.062328053   -0.233142965   -0.675554069
  H    -0.920522620    1.713004355    0.912119915
  H     1.204431006   -1.196369662   -0.918176231
  H     1.826844953    0.406007458   -0.798617863
  H    -1.049138495   -1.576370701   -0.331757120
  H     0.758041219    2.014066447    0.417577832
  H    -1.851470832   -0.438033553    0.674514141
  N     2.136801513    3.149948876    0.362090548
  C     1.629375355    4.251371630    1.207893294
  H     2.372571515    3.530476168   -0.548121952
  H     2.329470033    5.077982821    1.310170076
  H     0.708278821    4.636038784    0.777439086
  H     1.407495363    3.866068655    2.199747335
  H     3.019205595    2.833474292    0.749409056

16
gua_mOH
  C    -0.081972325    0.353680588    0.028076102
  N    -0.781386068   -0.780045332   -0.011075941
  N    -0.700530775    1.527575229    0.063558364
  N     1.245079059    0.328413353    0.036872021
  H    -1.701484618    1.589975232    0.033190952
  H     1.750062669   -0.538343991    0.016503262
  H     1.745755146    1.209639567    0.055791883
  H    -0.322300090   -1.672024252   -0.041041434
  H    -0.137793105    2.370660847    0.078458926
  H    -1.784932170   -0.770876464   -0.005828173
  O     1.662952247    3.184748790    0.158770895
  C     2.081912462    3.852481778    1.365617693
  H     1.981926316    3.707541256   -0.584132688
  H     3.165794687    3.907782802    1.424027822
  H     1.658082817    4.851495416    1.425337117
  H     1.711514317    3.260194559    2.195510760

13
gua_wat
  C    -0.071100547    0.351296503    0.027408194
  N    -0.894833573   -0.694824870   -0.016588211
  N    -0.552894884    1.582189052    0.148368366
  N     1.242556704    0.176740483   -0.048607484
  H    -1.539110307    1.749324362    0.227945668
  H     1.640248335   -0.737740076   -0.159997553
  H     0.091723707    2.360878453    0.177288781
  H    -0.541272484   -1.630581091   -0.099062272
  H    -1.890242352   -0.573671076    0.026661967
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```
  H     1.848157063    0.985745123   -0.011055350
  O     2.018670957    3.007993255    0.136861195
  H     2.419466865    3.415761631    0.911181729
  H     2.349723896    3.533314917   -0.598704323

14
hip_fmdh
  C     4.992080318    5.502206312    0.460294537
  C     4.142932018    5.064052621    1.440422070
  N     4.048348407    6.071858981    2.363217606
  C     4.803200065    7.101898305    1.985225154
  N     5.381732667    6.764409591    0.827845316
  H     3.615689853    4.134288605    1.542678623
  H     3.490538328    6.073564561    3.229990672
  H     5.336891356    5.028852818   -0.439807530
  H     6.011779025    7.360007188    0.309997930
  H     4.923000524    8.029870783    2.513374890
  O     2.771227219    6.581015579    4.736846747
  C     2.031585673    6.290675285    5.660647292
  H     1.521615021    5.322491983    5.706176359
  H     1.853805525    6.994950386    6.478785336

17
hip_mNH2
  C     4.999742982    5.656478915    0.500699101
  C     4.164862142    5.017473257    1.379027829
  N     3.939509304    5.868794127    2.428963225
  C     4.608365297    6.999915738    2.218084680
  N     5.256490848    6.884805521    1.050371362
  H     3.728431744    4.037328478    1.328268100
  H     3.316944545    5.657789713    3.312404450
  H     4.631794200    7.858375587    2.863794077
  H     5.416541405    5.343987339   -0.438462413
  H     5.844006700    7.599873278    0.647217331
  N     2.360413089    5.321240076    4.545257334
  H     2.684644328    4.503728539    5.051765441
  C     0.977807410    5.081780014    4.078478631
  H     0.620679571    5.964248669    3.555286665
  H     0.976672511    4.249143917    3.380678467
  H     0.289084969    4.854400601    4.888818694
  H     2.348465955    6.064511230    5.236002027

16
hip_mOH
  C     5.149867812    5.781166695    0.454915895
  C     4.310331875    4.996348260    1.199035769
  N     3.949484344    5.726378549    2.300513163
  C     4.535679925    6.921018621    2.255243186
  N     5.268418880    6.964890399    1.136262329
  H     3.954151378    3.997818400    1.027940865
  H     3.315215265    5.411421924    3.069161162
  H     4.439502186    7.706358470    2.982065199
  H     5.654340822    5.595095678   -0.474727925
  H     5.822762606    7.757809794    0.847037700
  O     2.287274462    4.997059418    4.277698675
  H     2.537181293    4.540754240    5.086349443
  C     0.852612058    5.085444264    4.230014684
  H     0.600364555    5.592921938    3.305190746
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  H     0.401774603    4.096692297    4.227095080
  H     0.472893936    5.665090054    5.066954029

13
hip_wat
  C     5.082425230    5.694110213    0.467816815
  C     4.219648710    4.994294021    1.267596178
  N     3.928118405    5.797286100    2.338420520
  C     4.577383461    6.954219633    2.222006001
  N     5.282709241    6.901057178    1.086603578
  H     3.803644392    4.010622797    1.155484436
  H     5.553083545    5.435055031   -0.462004958
  H     4.542504567    7.778104465    2.910688070
  H     5.872413711    7.646727047    0.745823201
  H     3.300294311    5.554620966    3.125722341
  O     2.273799414    5.176654089    4.427454544
  H     2.504832168    4.716982810    5.239367142
  H     1.322383844    5.303900651    4.477382132

12
mNH3_fmdh
  C     0.687364580   -0.177705402    0.322869765
  N    -0.735021639    0.201185335    0.055690011
  H    -1.380118913   -0.452570111    0.496181898
  H    -0.945342769    1.128728697    0.420157622
  H    -0.914689681    0.199140171   -0.968987117
  H     0.856655158   -1.164072485   -0.091484742
  H     1.326952365    0.545866029   -0.167734951
  H     0.859676716   -0.176826300    1.392473464
  O    -0.688387552   -0.006827961   -2.671205700
  C    -1.151543972    0.108573219   -3.793715602
  H    -0.570905471   -0.192905158   -4.669883563
  H    -2.154311482    0.514294330   -3.962474775

15
mNH3_mNH2
  C     0.744768151   -0.082282053   -0.019173554
  N    -0.728438635    0.112146543    0.091161198
  H    -1.127753599   -0.526162012    0.776374088
  H    -0.947980520    1.055774181    0.403402411
  H    -1.224663286   -0.064847586   -0.881903869
  H     0.932732220   -1.093480816   -0.362003654
  H     1.212925665    0.074803757    0.945875964
  H     1.132071711    0.628965038   -0.739788431
  N    -1.869193765   -0.320933795   -2.339816000
  C    -1.024136456    0.203286382   -3.437481685
  H    -2.039293972   -1.308126579   -2.505594757
  H    -1.464672792    0.048252935   -4.419381823
  H    -0.870277928    1.269094010   -3.293172401
  H    -0.057160632   -0.291250085   -3.411849851
  H    -2.786883617    0.109107046   -2.404975756

14
mNH3_mOH
  C     0.687041485   -0.021348442    0.158244910
  N    -0.796548184    0.105617965    0.039344613
  H    -1.270243847   -0.509648168    0.698373151
  H    -1.103958172    1.055158108    0.241676877
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  H    -1.110658397   -0.147584181   -0.934324277
  H     0.958993985   -1.044759456   -0.070634654
  H     0.990678267    0.235706496    1.166097459
  H     1.144634560    0.652587758   -0.556167114
  O    -1.407504631   -0.585095302   -2.489010770
  C    -1.068005632    0.161392585   -3.674026593
  H    -1.997797922   -1.300085292   -2.745755652
  H    -1.953332227    0.608017004   -4.117664846
  H    -0.388154864    0.949189504   -3.367554340
  H    -0.566848884   -0.475482436   -4.397112815

11
mNH3_wat
  C     0.729910353   -0.067791535    0.057095373
  N    -0.757044007    0.087897962    0.041272775
  H    -1.200812907   -0.569235636    0.680770653
  H    -1.033508938    1.024135700    0.332440612
  H    -1.137879313   -0.081658460   -0.916293500
  H     1.155255605    0.657321778   -0.626319371
  H     1.094665015    0.102560205    1.062985612
  H     0.969275613   -1.072917859   -0.268483642
  O    -1.621902384   -0.405938406   -2.518774555
  H    -1.424849813    0.103890660   -3.310162799
  H    -2.253608383   -1.070520461   -2.809529101
```

Supplementary error measures

Table S2. *Mean unsigned errors (in kcal/mol) of the studied methods in multiple benchmark data sets.*

	S66	S66x8	S66a8	S22	HB104	Charged HB	HC12	AA24
PM6	2.67	1.99	1.89	3.34	2.67	3.40	2.56	3.07
PM6-DH2	0.64	0.51	0.50	0.39	1.14	1.69	0.62	0.74
PM6-DH+	0.62	0.55	0.49	0.60	1.20	1.51	0.62	1.00
PM6-D3H4	0.47	0.45	0.48	0.61	0.84	0.88	0.58	0.59
DFTB	2.74	2.10	2.12	3.05	2.68	4.29	2.80	2.87
DFTB-D	1.25	1.07	0.98	1.35	1.81	3.85	0.41	1.41
DFTB-D,γ	0.98	0.89	0.79	1.01	1.44	3.16	0.39	1.13
DFTB-DH2	1.08	0.76	0.69	1.32	1.11	1.80	0.41	0.90
DFTB-D3H4	0.52	0.46	0.43	0.79	0.57	1.10	0.48	0.50
RM1	4.75	3.43	3.54	5.84	5.12	4.99	3.53	4.13
RM1-D3H4	0.67	0.64	0.55	0.76	0.70	1.50	0.18	0.46
RM1-D3H4*	0.67	0.64	0.56	0.75	0.70	1.63	0.18	0.50
OM3	3.08	2.22	2.29	3.56	2.69	2.57	3.78	3.83
OM3-DH2	0.63	0.61	0.46	0.67	0.65	1.42	0.97	0.86
OM3-D3H4	0.37	0.39	0.31	0.43	0.44	1.16	0.57	1.10
AM1	5.15	3.76	3.40	6.77	5.10	6.57	3.49	4.65
AM1-DH2	1.39	1.19	1.13	0.69	1.56	2.45	3.23	2.49
AM1-D3H4	0.96	1.08	0.99	1.25	1.72	2.35	0.76	1.18
PM3	4.29	3.32	3.17	5.88	4.75	6.38	1.51	3.25
PM3-D3H4	0.94	0.76	0.67	1.45	0.67	1.53	0.29	0.72

Table S3. *Maximum unsigned errors (in kcal/mol) of the studied methods in multiple benchmark data sets.*

	S66	S66x8	S66a8	S22	HB104	Charged HB	HC12	AA24
PM6	7.99	9.14	6.00	7.61	8.96	7.29	4.01	9.93
PM6-DH2	3.53	4.80	3.46	1.47	4.67	6.45	1.00	4.53
PM6-DH+	2.47	3.09	2.39	1.79	3.37	4.82	1.00	5.82
PM6-D3H4	2.45	3.16	2.76	2.16	3.09	3.06	1.34	4.06
DFTB	5.17	5.31	4.03	7.44	4.71	9.64	4.15	6.82
DFTB-D	3.17	4.36	3.84	2.88	3.86	8.93	1.60	5.50
DFTB-D,γ	2.52	3.14	3.35	2.38	3.35	8.39	1.50	4.45
DFTB-DH2	4.60	6.67	3.83	5.53	5.32	5.29	1.60	4.70
DFTB-D3H4	2.36	2.47	2.51	2.00	1.70	5.09	1.03	2.64
RM1	12.50	13.31	11.69	13.18	12.99	10.52	5.46	11.84
RM1-D3H4	2.95	4.50	3.25	2.89	2.53	6.99	0.53	1.96
RM1-D3H4 no s	2.95	4.50	3.25	2.89	2.53	6.60	0.53	3.63
OM3	7.21	8.31	6.95	8.56	7.41	6.15	6.23	12.76
OM3-DH2	2.26	4.91	2.65	2.26	2.45	6.22	1.94	5.31
OM3-D3H4	1.29	3.06	1.46	1.54	1.41	4.55	1.23	8.10
AM1	20.02	28.20	13.42	20.29	23.05	17.93	6.25	15.77
AM1-DH2	5.27	9.70	5.08	2.08	7.34	11.60	7.14	11.38
AM1-D3H4	3.97	12.67	7.63	4.63	7.14	10.29	1.16	5.52
PM3	16.09	22.86	11.49	19.22	10.99	16.05	5.12	10.08
PM3-D3H4	7.06	9.96	4.33	7.72	2.17	10.39	1.06	2.68

***Table S4**. Coefficients of the polynomial radial function used in the H-bond correction.*

power	c
7	-0.00303407407407313510
6	0.07357629629627092382
5	-0.70087111111082800452
4	3.25309629629461749545
3	-7.20687407406838786983
2	5.31754666665572184314
1	3.40736000001102778967
0	-4.68512000000450434811

***Figure S1.** The repulsive H-H correction (E_{rep}) and its effect on the PM6-D3H4 dissociation curve of T-shaped dimer of hydrogen molecules.*