Supplementary Material

Adsorption of Helium on large, planar polycyclic aromatic hydrocarbons: Cationic and anionic hexabenzocoronene

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Data provided in this file (HBC_SI_220901f.docx):

- Fig. S1. Mass spectra of positively and negatively charged $Hbc^{\pm}$ ions complexed with helium.
- Fig. S2. First derivatives of logarithmic ion abundances for cation and anions, and second derivatives of computed energies.
- Fig. S3. Computed front and side views of He_nHbc^+ for $n \leq 90$. For each size, the helium densities obtained from the PIMD simulations are superimposed on the structure of Hbc^+.
- Table S1. Computed classical and quantum energies *versus* size *n* for $He_nHbc^{\pm}$.
- Table S2. Cartesian coordinates (*x*,*y*,*z*) and partial charges (*q*) on each atom of bare Hbc^+ computed using DFT at the M06-2X/6-31+G* level.
- Table S3. Cartesian coordinates (*x*,*y*,*z*) and partial charges (*q*) on each atom of bare Hbc^- computed using DFT at the M06-2X/6-31+G* level.

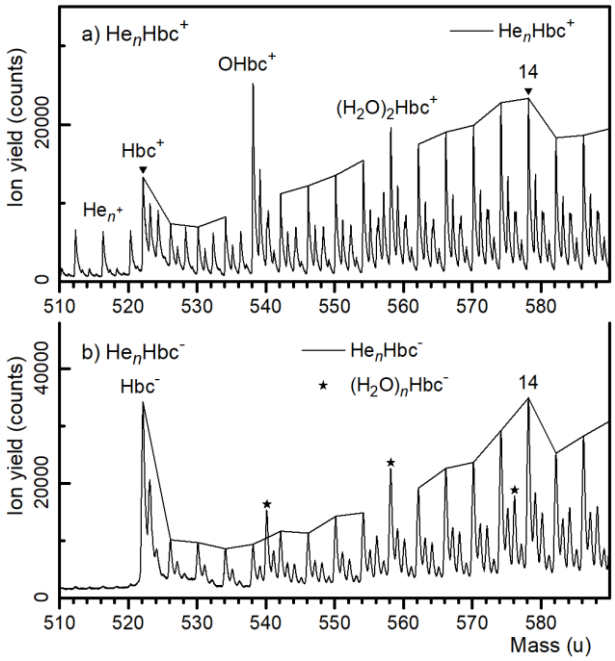


Figure. S1. Mass spectra of positively and negatively charged $Hbc^{\pm}$ ions complexed with helium (panels and b, respectively). Mass peaks due to isotopically pure $He_nHbc^{\pm}$ (i.e. $^4He_n{}^{12}C_{42}{}^1H_{18}$, mass 522.141 u for $n = 0$) are connected by solid lines. Contributions due to ^{16}O and $^1H_2{}^{16}O$ contaminants are labeled. In agreement with mass spectra obtained by laser-induced desorption [1], there is no evidence for the "fairly facile loss of up to four hydrogen atoms" from Hbc cations reported by Reed and Tennent upon electron ionization of bare Hbc [2].

1. Mavrinskaya, N.; Räder, H. J.; Müllen, K. Nonlinear behavior during semi-quantitative analysis of thin organic layers by laser desorption mass spectrometry. *Rapid Commun. Mass Spectrom.* **2011**, *25*, 2196-2200, doi:10.1002/rcm.5102.
2. Reed, R. I.; Tennent, A. Mass spectrum of 1-12, 2-3, 4-5, 6-7, 8-9, 10-11-hexabenzocoronene. *Org. Mass Spectrom.* **1971**, *5*, 619-621, doi:10.1002/oms.1210050513.

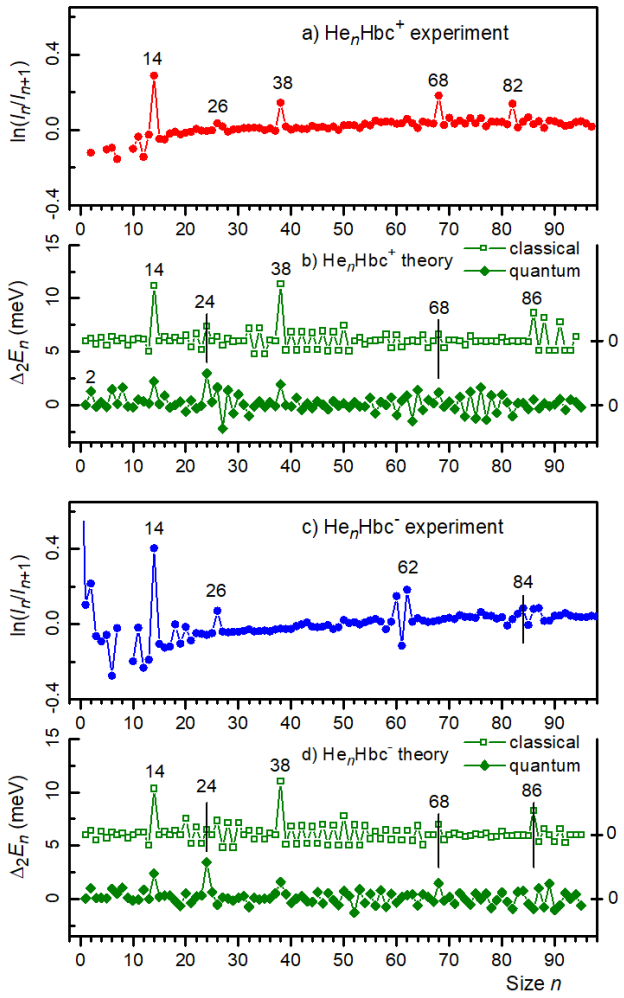
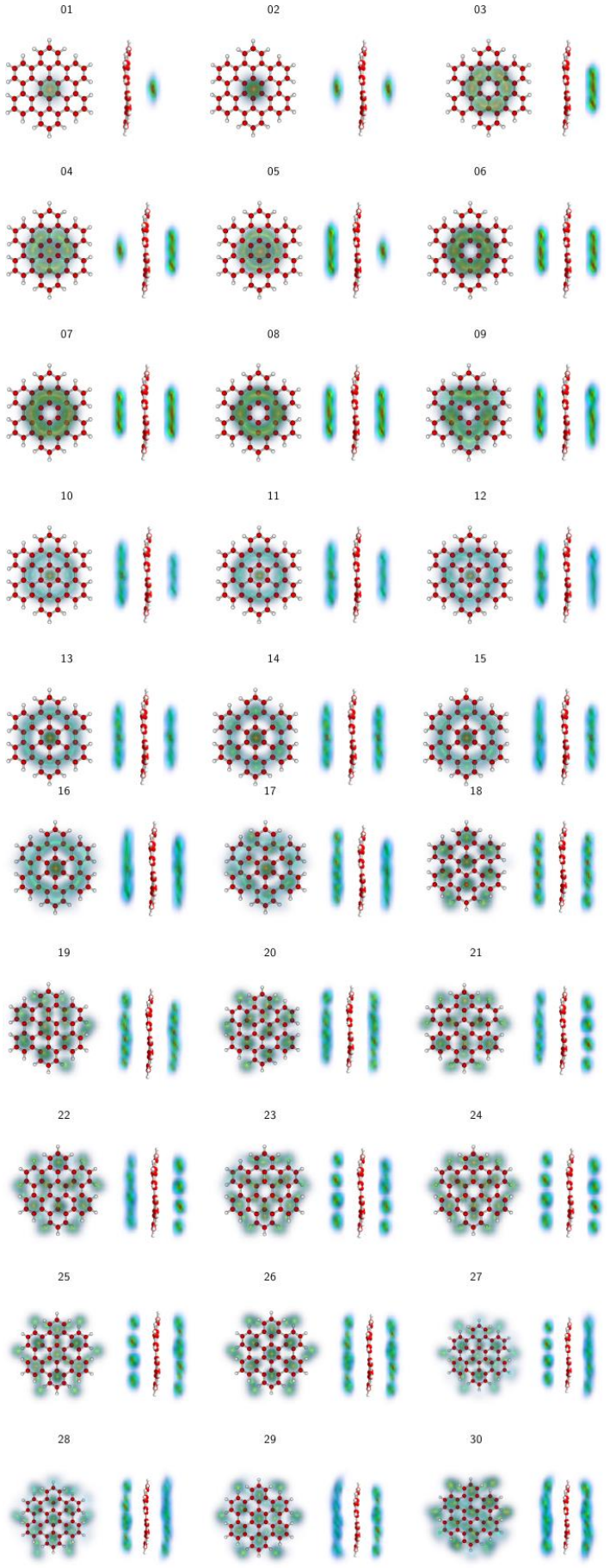


Figure. S2. Panels a and c: First derivatives of logarithmic ion abundances for cation and anions, respectively. The corresponding second derivatives of computed energies are displayed in panels b and d, respectively.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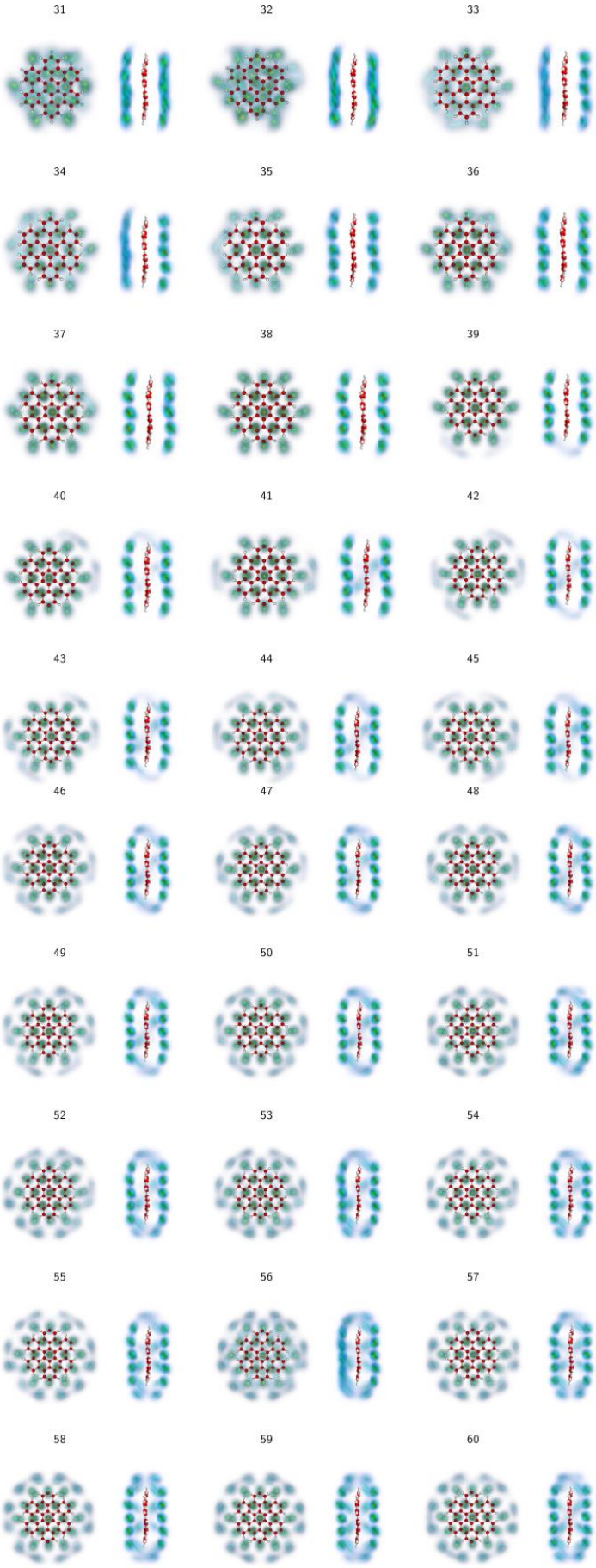
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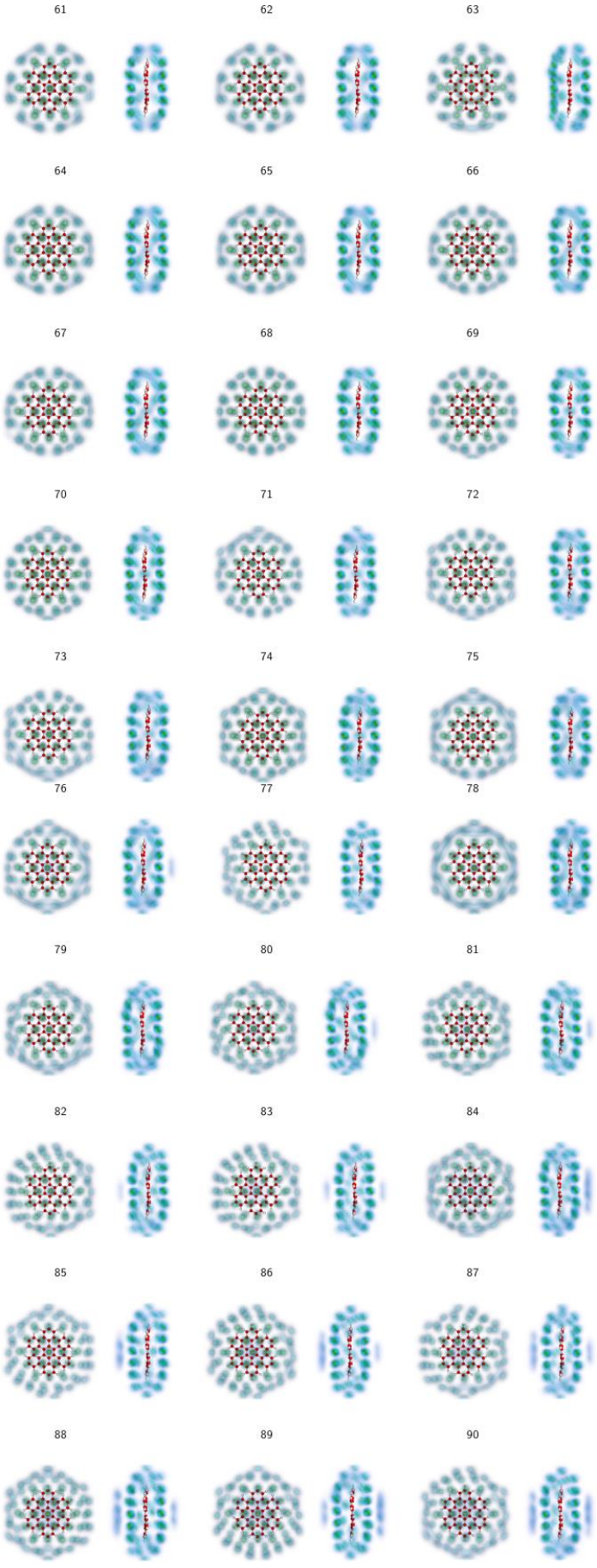

Figure. S3. Computed front and side views of He_nHbc^+ for $n < 90$. For each size, the helium densities obtained from the PIMD simulations are superimposed on the structure of Hbc^+.

Table S1. Computed energies *versus* size *n* for He_nHbc^+ and He_nHbc^-. Classical energies E_c are listed in meV per atom; total quantum energies E_q are listed in Hartree. The number of He atoms on either side of $Hbc^{\pm}$ is indicated for some sizes *n* as *p*+*q*, with *p*+*q* = *n*.

He_nHbc^+

n	E_c/n (meV)	arrangement	E_q (Hartree)	arrangement
0	0	0+0	0	
01	24.18947	1+0	-6.819429100869068E-004	
02	24.19581	1+1	-1.363778672277615E-003	
03	24.11157	3+0	-1.998802168255109E-003	
04	24.13835	3+1	-2.640218261895236E-003	
05	24.08661	4+1	-3.272270324304337E-003	
06	24.12241	3+3	-3.912133948980715E-003	
07	24.09351	4+3	-4.549746412557004E-003	
08	24.07104	4+4	-5.079374470285785E-003	
09	24.02515	5+4	-5.600732300559383E-003	
10	24.02920	7+3	-6.127710283877961E-003	6+4
11	24.02170	7+4	-6.661496498089828E-003	
12	23.99329	7+5	-7.176870273546458E-003	
13	23.95650	7+6	-7.680213892810647E-003	
14	23.99517	7+7	-8.178316826467170E-003	
15	23.68208	8+7	-8.594846555222033E-003	
16	23.40806	8+8	-9.007970570167983E-003	
17	23.14412	9+8	-9.388366269025264E-003	
18	22.90958	9+9	-9.777444754939824E-003	
19	22.68241	10+9	-1.016709739443137E-002	
20	22.47793	10+10	-1.054526561792713E-002	
21	22.26732	12+9	-1.094660765538418E-002	
22	22.10127	12+10	-1.133218722458680E-002	
23	21.91985	12+11	-1.172992129189334E-002	
24	21.78641	12+12	-1.212923421536824E-002	
25	21.60853	13+12	-1.242021590341250E-002	
26	21.44460	13+13	-1.270098125667590E-002	
27	21.27876	15+12	-1.292155947695439E-002	
28	21.13848	15+13	-1.322285608835159E-002	
29	21.00088	16+13	-1.347309807775598E-002	
30	20.87340	15+15	-1.375225445625423E-002	
31	20.75339	16+15	-1.399631084894553E-002	
32	20.64117	16+16	-1.423801823902286E-002	
33	20.49945	17+16	-1.451829660747848E-002	
34	20.40148	18+16	-1.480433530552930E-002	
35	20.27480	18+17	-1.507808802768300E-002	
36	20.18857	18+18	-1.535869692998750E-002	
37	20.10423	19+18	-1.562981070083166E-002	
38	20.02457	19+19	-1.590588835335648E-002	
39	19.81153		-1.611094388771822E-002	
40	19.63046		-1.631686923352261E-002	
41	19.43745		-1.652772420447603E-002	
42	19.27381		-1.671359438330699E-002	
43	19.09801		-1.691731672340760E-002	
44	18.94805		-1.711576472219008E-002	
45	18.78734		-1.732388974104613E-002	
46	18.65057		-1.751956933468870E-002	
47	18.49989		-1.771429968054831E-002	
48	18.37484		-1.792383864483180E-002	
49	18.23722		-1.812082086013770E-002	
50	18.12235		-1.832024239610316E-002	
51	17.98294		-1.851379333162801E-002	
52	17.86687		-1.871593138730249E-002	
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54	17.64200		-1.910562087637529E-002	
55	17.53831		-1.930730725308037E-002	
56	17.43836		-1.948405924848980E-002	

57	17.34131	-1.968955056717587E-002
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65	16.64776	-2.117387344673725E-002
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67	16.49722	-2.151313499707107E-002
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73	16.10601	-2.222127109581134E-002
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82	15.62308	-2.313263927907334E-002
83	15.57345	-2.324467600953441E-002
84	15.52542	-2.335066321096539E-002
85	15.47864	-2.345006016868611E-002
86	15.43367	-2.356367943430589E-002
87	15.35938	-2.365896120213054E-002
88	15.29695	-2.376677654177332E-002
89	15.21125	-2.386909272527251E-002
90	15.13719	-2.397523672418906E-002
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92	14.99417	-2.416516938158190E-002
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94	14.86647	-2.435018307739516E-002
95	14.80525	-2.442364401995693E-002
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98	14.62306	-2.465169939497332E-002
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106	14.19422	-2.524355803577767E-002
107	14.14439	-2.530135509026720E-002
108	14.08999	-2.538342302369289E-002
109	14.03484	-2.544163331445132E-002
110	13.97784	-2.549908934545182E-002

He$_n$Hbc$^-$

n	E_c/n (meV)	arrangement	E_q (Hartree)	arrangement
01	25.12082	1+0	-7.116418775573115E-004	
02	25.12654	1+1	-1.420823471528046E-003	
03	24.98347	3+0	-2.092734140784047E-003	
04	25.02482	3+1	-2.761061024997960E-003	
05	24.97763	4+1	-3.425169514403443E-003	
06	24.99146	3+3	-4.086675045542022E-003	

07	24.96376	4+3	-4.713170824590654E-003	
08	24.93732	4+4	-5.320962083349337E-003	
09	24.89609	5+4	-5.889301144537721E-003	
10	24.88995	7+3	-6.452584862180117E-003	6+4
11	24.88397	7+4	-7.021205408035449E-003	
12	24.85830	7+5	-7.592436840325503E-003	
13	24.81747	7+6	-8.131017591997584E-003	
14	24.85175	7+7	-8.668839725736503E-003	
15	24.59070	8+7	-9.118123245984990E-003	
16	24.36182	8+8	-9.559279636643185E-003	
17	24.14161	9+8	-9.988352733290639E-003	
18	23.94585	9+9	-1.040492682996538E-002	
19	23.74842	10+9	-1.082741184497784E-002	
20	23.56941	10+10	-1.127319321144245E-002	
21	23.33293	11+10	-1.169906479332637E-002	
22	23.15235	12+10	-1.213826256198835E-002	
23	22.95443	12+11	-1.256896080431156E-002	
24	22.80534	12+12	-1.298700397331822E-002	
25	22.64714	13+12	-1.327810897679332E-002	
26	22.50022	13+13	-1.354490643642256E-002	
27	22.31444	14+13	-1.383051108387034E-002	
28	22.18341	15+13	-1.411122453405846E-002	
29	22.02168	15+14	-1.438980830387840E-002	
30	21.90924	15+15	-1.467417803147202E-002	
31	21.76729	16+15	-1.495397979838546E-002	
32	21.63409	16+16	-1.522273530177608E-002	
33	21.49686	17+16	-1.551794644929291E-002	
34	21.37936	18+16	-1.580781118422390E-002	
35	21.25754	18+17	-1.609886636420984E-002	
36	21.15299	18+18	-1.638847259402568E-002	
37	21.04948	19+18	-1.667607376498591E-002	
38	20.95144	19+19	-1.694406147064903E-002	
39	20.72935		-1.715319494178007E-002	
40	20.53933		-1.734537116521886E-002	
41	20.33814		-1.755044758327909E-002	
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69	16.88755		-2.259290531412278E-002	
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86	15.72440	-2.435703919853898E-002
87	15.64417	-2.448896294933279E-002
88	15.57270	-2.458333781336249E-002
89	15.49617	-2.470573599658040E-002
90	15.42119	-2.477529602900300E-002
91	15.35449	-2.488238792425066E-002
92	15.28288	-2.501107982285475E-002
93	15.22044	-2.511849080237368E-002
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100	14.80973	-2.575392003558161E-002
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102	14.69633	-2.588519289899248E-002
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104	14.58803	-2.604027193291135E-002
105	14.53292	-2.612242078174365E-002
106	14.47821	-2.619641851302456E-002
107	14.42389	-2.625011528166922E-002
108	14.36767	-2.633887879637835E-002
109	14.31131	-2.637339141697072E-002
110	14.25455	-2.644290495505031E-002

Table S2. Cartesian coordinates (*x*,*y*,*z*) and partial charges (*q*) on each atom of bare Hbc^+ computed using DFT at the M06-2X/6-31+G* level

Atom	*x*	*y*	*z*	*q*
C	1.427694	0.000000	0.002383	-0.067403
C	0.721205	-1.227473	0.003547	0.048757
C	-0.721205	-1.227473	-0.003547	0.042697
C	-1.427694	0.000000	-0.002383	-0.082617
C	-0.721205	1.227473	-0.003547	0.042697
C	0.721205	1.227473	0.003547	0.048757
C	2.870123	0.000000	0.028184	0.016042
C	1.435537	-2.469514	-0.015514	0.003980
C	-1.435537	-2.469514	0.015514	0.030115
C	-2.870123	0.000000	-0.028184	0.068476
C	-1.435537	2.469514	0.015514	0.030115
C	1.435537	2.469514	-0.015514	0.003980
C	4.984395	-1.197447	0.146065	-0.143655
C	2.860433	-2.476789	-0.035041	0.055677
C	0.730751	-3.705819	-0.040789	0.067793
C	-0.730751	-3.705819	0.040789	0.006919
C	-2.860433	-2.476789	0.035041	0.085660
C	-4.984395	-1.197447	-0.146065	-0.113540
C	-4.984395	1.197447	-0.146065	-0.113540
C	-2.860433	2.476789	0.035041	0.085660
C	-0.730751	3.705819	0.040789	0.006919
C	0.730751	3.705819	-0.040789	0.067793
C	2.860433	2.476789	-0.035041	0.055677
C	4.984395	1.197447	0.146065	-0.143655
C	3.583942	-1.222002	0.044938	0.052757
C	1.445769	-4.890617	-0.157635	-0.181232
C	-1.445769	-4.890617	0.157635	-0.160580
C	-3.583942	-1.222002	-0.044938	-0.005018
C	-3.583942	1.222002	-0.044938	-0.005018
C	-1.445769	4.890617	0.157635	-0.160580
C	1.445769	4.890617	-0.157635	-0.181232
C	3.583942	1.222002	0.044938	0.052757
C	3.536758	-3.702472	-0.144961	-0.189055
C	2.839193	-4.888746	-0.215789	-0.056921
C	-2.839193	-4.888746	0.215789	-0.059379
C	-3.536758	-3.702472	0.144961	-0.200515
C	-5.676612	0.000000	-0.206223	-0.123959
C	-3.536758	3.702472	0.144961	-0.200515
C	-2.839193	4.888746	0.215789	-0.059379
C	2.839193	4.888746	-0.215789	-0.056921
C	3.536758	3.702472	-0.144961	-0.189055
C	5.676612	0.000000	0.206223	-0.100632
H	-5.547269	2.119522	-0.201337	0.150474
H	5.547269	-2.119522	0.201337	0.151183
H	4.616101	-3.734044	-0.200691	0.153170
H	-4.616101	-3.734044	0.200691	0.153368
H	-4.616101	3.734044	0.200691	0.153368
H	4.616101	3.734044	-0.200691	0.153170
H	0.933133	-5.840847	-0.226938	0.157573
H	-0.933133	-5.840847	0.226938	0.149897
H	-5.547269	-2.119522	-0.201337	0.150474
H	-0.933133	5.840847	0.226938	0.149897
H	0.933133	5.840847	-0.226938	0.157573
H	5.547269	2.119522	0.201337	0.151183
H	3.373547	-5.826632	-0.319393	0.146595
H	-3.373547	-5.826632	0.319393	0.148317
H	-6.756334	0.000000	-0.301180	0.151021
H	-3.373547	5.826632	0.319393	0.148317
H	3.373547	5.826632	-0.319393	0.146595
H	6.756334	0.000000	0.301180	0.149000

Table S3. Cartesian coordinates (*x*,*y*,*z*) and partial charges (*q*) on each atom of bare Hbc^- computed using DFT at the M06-2X/6-31+G* level

Atom	*x*	*y*	*z*	*q*
C	1.425635	0.000000	0.007585	-0.008020
C	0.720650	-1.229313	0.005254	-0.053014
C	-0.720650	-1.229313	-0.005254	-0.052301
C	-1.425635	0.000000	-0.007585	-0.032544
C	-0.720650	1.229313	-0.005254	-0.052301
C	0.720650	1.229313	0.005254	-0.053014
C	2.875561	0.000000	0.037419	-0.017661
C	1.436193	-2.465684	-0.021342	0.021926
C	-1.436193	-2.465684	0.021342	0.046947
C	-2.875561	0.000000	-0.037419	0.047310
C	-1.436193	2.465684	0.021342	0.046947
C	1.436193	2.465684	-0.021342	0.021926
C	4.992916	-1.202170	0.172772	-0.267114
C	2.861685	-2.480965	-0.038745	-0.041590
C	0.733022	-3.708523	-0.052933	0.068006
C	-0.733022	-3.708523	0.052933	0.001256
C	-2.861685	-2.480965	0.038745	-0.005936
C	-4.992916	-1.202170	-0.172772	-0.226459
C	-4.992916	1.202170	-0.172772	-0.226459
C	-2.861685	2.480965	0.038745	-0.005936
C	-0.733022	3.708523	0.052933	0.001256
C	0.733022	3.708523	-0.052933	0.068006
C	2.861685	2.480965	-0.038745	-0.041590
C	4.992916	1.202170	0.172772	-0.267114
C	3.591650	-1.229065	0.057202	0.105057
C	1.446235	-4.893847	-0.193078	-0.220207
C	-1.446235	-4.893847	0.193078	-0.196015
C	-3.591650	-1.229065	-0.057202	0.034750
C	-3.591650	1.229065	-0.057202	0.034750
C	-1.446235	4.893847	0.193078	-0.196015
C	1.446235	4.893847	-0.193078	-0.220207
C	3.591650	1.229065	0.057202	0.105057
C	3.532873	-3.708838	-0.168296	-0.166399
C	2.840612	-4.898010	-0.258953	-0.153656
C	-2.840612	-4.898010	0.258953	-0.159794
C	-3.532873	-3.708838	0.168296	-0.176256
C	-5.676387	0.000000	-0.238748	-0.130540
C	-3.532873	3.708838	0.168296	-0.176256
C	-2.840612	4.898010	0.258953	-0.159794
C	2.840612	4.898010	-0.258953	-0.153656
C	3.532873	3.708838	-0.168296	-0.166399
C	5.676387	0.000000	0.238748	-0.094779
H	-5.553554	2.125551	-0.243011	0.126360
H	5.553554	-2.125551	0.243011	0.127815
H	4.614037	-3.730319	-0.233867	0.116569
H	-4.614037	-3.730319	0.233867	0.115359
H	-4.614037	3.730319	0.233867	0.115359
H	4.614037	3.730319	-0.233867	0.116569
H	0.921357	-5.837712	-0.279613	0.129206
H	-0.921357	-5.837712	0.279613	0.119747
H	-5.553554	-2.125551	-0.243011	0.126360
H	-0.921357	5.837712	0.279613	0.119747
H	0.921357	5.837712	-0.279613	0.129206
H	5.553554	2.125551	0.243011	0.127815
H	3.375397	-5.834287	-0.386429	0.107523
H	-3.375397	-5.834287	0.386429	0.110518
H	-6.757541	0.000000	-0.348535	0.108078
H	-3.375397	5.834287	0.386429	0.110518
H	3.375397	5.834287	-0.386429	0.107523
H	6.757541	0.000000	0.348535	0.103556