A computational analysis of the apparent *nido* vs. *hypho* conflict: are we dealing with six- or eight-vertex open-face diheteroboranes?

João Pedro F. Nunes, Josef Holub, David W. H. Rankin, Derek A. Wann and Drahomír Hnyk*[b]

Supplementary Information

Table S1 Cartesian coordinates (in Å) for *closo*-$[B_{11}H_{11}]^{2-}$ (**cB11**) calculated using MP2/6-311G(d,p).

	x	*y*	*z*
B(1)	0.9122	0.0000	1.2360
B(2)	0.0000	1.4949	0.8373
B(3)	-0.9122	0.0000	1.2360
B(4)	0.0000	-1.4949	0.8373
B(5)	1.3391	0.9339	-0.2314
B(6)	0.0000	1.6825	-0.9181
B(7)	-1.3391	0.9339	-0.2314
B(8)	-1.3391	-0.9339	-0.2314
B(9)	0.0000	-1.6825	-0.9181
B(10)	1.3391	-0.9339	-0.2314
B(11)	0.0000	0.0000	-1.4166
H(12)	1.6318	0.0000	2.2017
H(13)	0.0000	2.4385	1.5873
H(14)	-1.6318	0.0000	2.2017
H(15)	0.0000	-2.4385	1.5873
H(16)	2.4572	1.3599	-0.3820
H(17)	0.0000	2.6480	-1.6335
H(18)	-2.4572	1.3599	-0.3820
H(19)	-2.4572	-1.3599	-0.3820
H(20)	0.0000	-2.6480	-1.6335
H(21)	2.4572	-1.3599	-0.3820
H(22)	0.0000	0.0000	-2.6231

Table S2 Cartesian coordinates (in Å) for *nido*-$[B_{10}H_{10}]^{4-}$ (**nB10**) calculated using MP2/6-311G(d,p).

	x	*y*	*z*
B(1)	-0.9158	0.0000	-1.1902
B(2)	0.0000	1.4000	-0.4487
B(3)	0.9158	0.0000	-1.1902
B(4)	0.0000	-1.4000	-0.4487
B(5)	-1.5726	0.8642	0.2574
B(6)	0.0000	0.9042	1.2932
B(7)	1.5726	0.8642	0.2574
B(8)	1.5726	-0.8642	0.2574
B(9)	0.0000	-0.9042	1.2932
B(10)	-1.5726	-0.8642	0.2574
H(11)	-1.4769	0.0000	-2.2917
H(12)	0.0000	2.5427	-0.9231
H(13)	1.4769	0.0000	-2.2917
H(14)	0.0000	-2.5427	-0.9231
H(15)	-2.4934	1.7014	0.0349
H(16)	0.0000	1.6429	2.2991
H(17)	2.4934	1.7014	0.0349
H(18)	2.4934	-1.7014	0.0349
H(19)	0.0000	-1.6429	2.2991
H(20)	-2.4934	-1.7014	0.0349

Table S3 Cartesian coordinates (in Å) for *arachno*-$[B_9H_9]^{6-}$ (**aB9**) calculated using MP2/6-311G(d,p).

	x	*y*	*z*
B(1)	-0.9165	0.5291	0.8276
B(2)	0.0000	-1.0583	0.8276
B(3)	0.9165	0.5291	0.8276
B(4)	0.0000	1.7106	-0.3792
B(5)	-1.4814	-0.8553	-0.3792
B(60	0.0000	-1.8947	-0.7715
B(7)	1.4814	-0.8553	-0.3792
B(8)	1.6409	0.9473	-0.7715
B(9)	-1.6409	0.9473	-0.7715
H(10)	-1.4349	0.8284	1.9750
H(11)	0.0000	-1.6569	1.9750
H(12)	1.4349	0.8284	1.9750
H(13)	0.0000	2.9841	0.0465
H(14)	-2.5843	-1.4920	0.0465
H(15)	0.0000	-3.1820	-0.4058
H(16)	2.5843	-1.4920	0.0465
H(17)	2.7557	1.5910	-0.4058
H(18)	-2.7557	1.5910	-0.4058

Table S4 Cartesian coordinates (in Å) for *hypho*-7,8-$[C_2B_6H_{13}]^-$ (**1a**) calculated using MP2/6-311+G(d,p).

	x	*y*	*z*
B(1)	-0.7070	0.8842	0.0000
B(2)	0.3778	0.6028	-1.4850
B(3)	-1.0051	-0.6697	-0.9171
B(4)	-1.0051	-0.6697	0.9171
B(5)	0.3778	0.6028	1.4850
B(6)	0.9208	1.4880	0.0000
C(7)	0.3778	-0.9718	-1.6889
C(8)	0.3778	-0.9718	1.6889
H(9)	-1.5387	1.7417	0.0000
H(10)	0.1832	1.3503	-2.4044
H(11)	-2.0499	-0.5989	-1.5038
H(12)	-2.0499	-0.5989	1.5038
H(13)	0.1832	1.3503	2.4044
H(14)	1.0197	2.6760	0.0000
H(15)	1.6261	0.9555	-0.9336
H(16)	-1.1724	-1.6058	0.0000
H(17)	1.6261	0.9555	0.9336
H(18)	0.3228	-1.3334	-2.7159
H(19)	1.0987	-1.5449	-1.1026
H(20)	1.0987	-1.5449	1.1026
H(21)	0.3228	-1.3334	2.7159

Table S5 Cartesian coordinates (in Å) for *hypho*-7,8-$[CSB_6H_{11}]^-$ (**1b**) calculated using MP2/6-311+G(d,p).

	x	*y*	*z*
B(1)	-0.5446	0.6591	0.9934
B(2)	-1.8394	0.3861	-0.3396
B(3)	-1.0786	-1.0797	0.6986
B(4)	0.6819	-0.6575	0.9920
B(5)	1.0037	1.1154	0.1445
B(6)	-0.6257	1.7297	-0.3755
C(7)	-1.6369	-1.1080	-0.8110
S(8)	1.8536	-0.4258	-0.4818
H(9)	-0.8234	1.1790	2.0304
H(10)	-2.9239	0.8081	-0.0493
H(11)	-1.7261	-1.4562	1.6349
H(12)	1.1515	-0.8333	2.0790
H(13)	1.6621	1.9809	0.6474
H(14)	-0.9584	2.8458	-0.1246
H(15)	-1.3056	1.2151	-1.3342
H(16)	0.0247	-1.7816	0.7174
H(17)	0.4616	1.7131	-1.0386
H(18)	-2.5361	-1.6902	-1.0092
H(19)	-0.8492	-1.2858	-1.5445

Table S6 Cartesian coordinates (in Å) for *hypho*-7,8-$[S_2B_6H_9]^-$ (**1c**) calculated using MP2/6-311+G(d,p).

	x	*y*	*z*
B(1)	-0.7162	1.1995	0.0000
B(2)	0.3096	0.8905	-1.4958
B(3)	-1.1631	-0.3015	-0.9199
B(4)	-1.1631	-0.3015	0.9199
B(5)	0.3096	0.8905	1.4958
B(6)	0.9553	1.6939	0.0000
S(7)	0.3096	-0.9178	-1.9269
S(8)	0.3096	-0.9178	1.9269
H(9)	1.1407	2.8699	0.0000
H(10)	0.1923	1.7024	-2.3680
H(11)	-2.2275	-0.1766	-1.4521
H(12)	-2.2275	-0.1766	1.4521
H(13)	0.1923	1.7024	2.3680
H(14)	-1.4926	2.1035	0.0000
H(15)	1.5969	1.1079	-0.9298
H(16)	-1.3425	-1.2281	0.0000
H(17)	1.5969	1.1079	0.9298

Table S7 Cartesian coordinates (in Å) for *hypho*-7,8-[NSB_6H_{11}] (**1d**) calculated using MP2/6-311+G(d,p).

	x	*y*	*z*
B(1)	-0.6284	0.6558	1.0130
B(2)	-1.7818	0.3139	-0.3702
B(3)	-0.9824	-1.0902	0.7500
B(4)	0.7220	-0.5771	1.0526
B(5)	0.9387	1.1782	0.1507
B(6)	-0.7020	1.7202	-0.3681
N(7)	-1.3029	-1.1024	-0.7828
S(8)	1.7896	-0.3621	-0.4782
H(9)	-0.9790	1.1583	2.0273
H(10)	-2.9533	0.4650	-0.2626
H(11)	-1.7838	-1.5775	1.4766
H(12)	1.2020	-0.6662	2.1364
H(13)	1.5760	2.0398	0.6655
H(14)	-1.1475	2.7969	-0.1602
H(15)	-1.3494	1.1736	-1.3555
H(16)	0.1114	-1.7708	0.9284
H(17)	0.3979	1.7674	-1.0062
H(18)	-1.9928	-1.7547	-1.1400
H(19)	-0.4260	-1.1245	-1.3170

Table S8 Cartesian coordinates (in Å) for *exo*-7-Me-*hypho*-7,8-[NCB_6H_{12}] (**1e**) calculated using MP2/6-311+G(d,p).

	x	*y*	*z*
B(1)	-0.7986	0.5837	1.0100
B(2)	-2.0114	0.3104	-0.3098
B(3)	-1.0936	-1.1504	0.6861
B(4)	0.6083	-0.6257	0.9019
B(5)	0.7639	1.1671	0.0956
B(6)	-0.9017	1.6953	-0.3228
N(7)	-1.5851	-1.1080	-0.8120
C(8)	1.4580	-0.1814	-0.3735
H(9)	-1.1159	1.0358	2.0592
H(10)	-3.1774	0.4678	-0.1524
H(11)	-1.8217	-1.7052	1.4427
H(12)	1.1055	-0.7386	1.9797
H(13)	1.3730	2.0256	0.6558
H(14)	-1.3313	2.7716	-0.0787
H(15)	-1.6180	1.1878	-1.2962
H(16)	0.0326	-1.8179	0.7060
H(17)	0.1725	1.7298	-1.0276
H(18)	-2.3359	-1.7354	-1.0804
H(19)	-0.8321	-1.1488	-1.4944
H(20)	1.0727	-0.5625	-1.3274
C(21)	2.9788	-0.2781	-0.3152
H(22)	3.4530	0.2934	-1.1219
H(23)	3.3226	-1.3167	-0.3888
H(24)	3.3413	0.1242	0.6357

Table S9 Cartesian coordinates (in Å) for *endo*-7-Me-*hypho*-7,8-[NCB_6H_{12}] (**1f**) calculated using MP2/6-311+G(d,p).

	x	*y*	*z*
B(1)	-0.8541	0.9928	0.6579
B(2)	-1.7313	0.0505	-0.6176
B(3)	-1.0032	-0.7406	1.0745
B(4)	0.5819	0.0502	1.3692
B(5)	0.8683	1.3881	-0.0560
B(6)	-0.6549	1.4059	-1.0156
N(7)	-1.2314	-1.4022	-0.3406
C(8)	1.7454	0.1024	0.2740
H(9)	-1.4244	1.7940	1.3205
H(10)	-2.8997	0.1638	-0.7972
H(11)	-1.8254	-1.0035	1.8902
H(12)	0.7558	0.4256	2.4871
H(13)	1.2258	2.5022	0.1683
H(14)	-1.1530	2.4135	-1.3889
H(15)	-1.0933	0.4358	-1.7818
H(16)	0.1435	-1.2044	1.5177
H(17)	0.5699	1.2831	-1.4035
H(18)	-1.9397	-2.1265	-0.3956
H(19)	-0.3851	-1.7057	-0.8130
H(20)	2.7076	0.3665	0.7124
C(21)	1.9165	-1.0026	-0.7732
H(22)	1.1524	-0.9644	-1.5641
H(23)	1.9094	-2.0112	-0.3366
H(24)	2.8716	-0.8879	-1.2973

Table S10 Cartesian coordinates (in Å) for *nido*-$[B_6H_{11}]^+$ (**nB6**) calculated using MP2/6-311+G(d,p).

	x	*y*	*z*
B(1)	-0.0000	-0.0001	0.8592
B(2)	0.4239	-1.4441	-0.1072
B(3)	1.5045	-0.0430	-0.1068
B(4)	0.5058	1.4176	-0.1067
B(5)	-1.1918	0.9191	-0.1070
B(6)	-1.2424	-0.8494	-0.1072
H(7)	-0.0002	-0.0003	2.0366
H(8)	0.7383	-2.5152	0.2689
H(9)	2.6202	-0.0750	0.2695
H(10)	0.8809	2.4688	0.2697
H(11)	-2.0758	1.6007	0.2693
H(12)	-2.1639	-1.4795	0.2688
H(13)	-0.5578	-1.5633	-1.0009
H(14)	1.3146	-1.0136	-1.0006
H(15)	1.3705	0.9371	-1.0003
H(16)	-0.4675	1.5930	-1.0004
H(17)	-1.6593	0.0476	-1.0008

Table S11 The s character (in %) for heteroboranes **1a-1f** calculated using a full Natural Bond Orbital analysis.

	Bond	B2PLYP	MP2	B98	B97D	PBE	PW91	HFS	Average
1a	B(4)-C(8)	27.07	27.03	27.59	26.23	26.53	26.60	26.85	26.84 ± 0.44
	B(5)-C(8)	28.46	28.45	28.50	28.36	28.34	28.35	28.66	28.45 ± 0.11
	B(2)-C(7)	28.46	28.45	28.50	28.36	28.34	28.35	28.66	28.45 ± 0.11
	B(3)-C(7)	27.07	27.03	27.59	26.23	26.53	26.60	26.85	26.84 ± 0.44
1b	B(4)-S(8)	17.67	18.82	17.60	15.68	16.23	16.26	16.46	16.96 ± 1.10
	B(5)-S(8)	19.09	19.92	18.91	17.69	17.90	17.94	17.96	18.49 ± 0.83
	B(2)-C(7)	28.60	28.61	28.63	28.57	28.53	28.54	28.88	28.62 ± 0.12
	B(3)-C(7)	26.34	26.25	26.96	25.45	25.74	25.82	26.01	26.08 ± 0.49
1c	B(4)-S(8)	17.36	18.45	17.36	15.55	16.04	16.06	16.24	16.72 ± 1.03
	B(5)-S(8)	19.07	19.87	18.85	17.73	17.93	17.97	18.07	18.50 ± 0.79
	B(2)-S(7)	19.07	19.87	18.85	17.73	17.93	17.97	18.07	18.50 ± 0.79
	B(3)-S(7)	17.36	18.45	17.36	15.55	16.04	16.06	16.24	16.72 ± 1.03
1d	B(4)-S(8)	17.28	18.14	17.11	15.62	15.98	16.00	16.14	16.61 ± 0.91
	B(5)-S(8)	17.83	18.65	17.58	16.44	16.39	16.42	16.22	17.08 ± 0.94
	B(2)-N(7)	29.52	29.62	29.50	29.30	29.14	29.17	29.44	29.38 ± 0.18
	B(3)-N(7)	27.80	27.90	27.97	27.05	27.02	27.07	27.43	27.46 ± 0.43
1e	B(4)-N(7)	28.91	29.03	29.25	28.08	28.35	28.42	28.76	28.69 ± 0.42
	B(5)-N(7)	29.57	29.73	29.50	29.27	29.29	29.32	29.69	29.48 ± 0.19
	B(2)-C(8)	26.40	26.29	26.66	26.19	26.13	26.17	26.13	26.28 ± 0.19
	B(3)-C(8)	25.99	25.93	26.39	25.40	25.49	25.56	25.83	25.80 ± 0.35
1f	B(4)-N(7)	28.77	28.83	29.11	27.84	28.19	28.25	28.46	28.49 ± 0.44
	B(5)-N(7)	29.54	29.68	29.46	29.27	29.20	29.22	29.52	29.41 ± 0.18
	B(2)-C(8)	26.27	26.25	26.49	25.89	25.95	25.99	25.99	26.12 ± 0.22
	B(3)-C(8)	26.23	26.06	26.68	25.59	25.70	25.79	25.93	26.00 ± 0.37

Table S12 The p character (in %) for heteroboranes **1a-1f** calculated using a full Natural Bond Orbital analysis.

	Bond	B2PLYP	MP2	B98	B97D	PBE	PW91	HFS	Average
1a	B(4)-C(8)	72.92	72.88	72.39	73.77	73.46	73.39	73.14	73.14 ± 0.45
	B(5)-C(8)	71.53	71.45	71.48	71.62	71.65	71.63	71.33	71.53 ± 0.12
	B(2)-C(7)	71.53	71.45	71.48	71.62	71.65	71.63	71.33	71.53 ± 0.12
	B(3)-C(7)	72.92	72.88	72.39	73.77	73.46	73.39	73.14	73.14 ± 0.45
1b	B(4)-S(8)	82.14	80.96	82.23	84.17	83.62	83.59	83.39	82.87 ± 1.13
	B(5)-S(8)	80.72	79.86	80.03	82.16	81.95	81.91	81.89	81.22 ± 0.99
	B(2)-C(7)	71.32	71.28	71.34	71.41	71.46	71.44	71.10	71.34 ± 0.12
	B(3)-C(7)	73.60	73.65	73.03	74.54	74.26	74.18	73.99	73.89 ± 0.51
1c	B(4)-S(8)	82.44	81.33	82.46	84.29	83.81	83.78	83.60	83.10 ± 1.05
	B(5)-S(8)	80.73	79.91	80.88	82.11	81.91	81.88	81.77	81.31 ± 0.82
	B(2)-S(7)	80.73	79.91	80.88	82.11	81.91	81.88	81.77	81.31 ± 0.82
	B(3)-S(7)	82.44	81.33	82.46	84.29	83.81	83.78	83.60	83.10 ± 1.05
1d	B(4)-S(8)	82.52	81.63	82.69	84.21	83.85	83.83	83.69	83.20 ± 0.94
	B(5)-S(8)	81.95	81.10	82.13	83.38	83.44	83.40	83.59	82.71 ± 0.98
	B(2)-N(7)	70.47	70.37	70.49	70.70	70.86	70.82	70.56	70.61 ± 0.19
	B(3)-N(7)	72.20	72.09	72.03	72.94	72.98	72.93	72.57	72.53 ± 0.43
1e	B(4)-N(7)	71.08	70.97	70.75	71.92	71.65	71.58	71.24	71.31 ± 0.42
	B(5)-N(7)	70.43	70.26	70.50	70.73	70.71	70.68	70.31	70.52 ± 0.19
	B(2)-C(8)	73.58	73.69	73.32	73.79	73.86	73.81	73.86	73.70 ± 0.20
	B(3)-C(8)	73.99	74.05	73.58	74.60	74.51	74.43	74.16	74.19 ± 0.36
1f	B(4)-N(7)	71.23	71.16	70.89	72.16	71.80	71.75	71.54	71.50 ± 0.44
	B(5)-N(7)	70.46	70.32	70.54	70.73	70.80	70.78	70.48	70.59 ± 0.18
	B(2)-C(8)	73.71	73.67	73.49	74.09	74.03	74.00	73.99	73.85 ± 0.23
	B(3)-C(8)	73.75	73.87	73.29	74.40	74.30	74.20	74.06	73.98 ± 0.38

Table S13 Hybridisation for heteroboranes **1a-1f** calculated using a full Natural Bond Orbital analysis.

	Bond	B2PLYP	MP2	B98	B97D	PBE	PW91	HFS	Average
1a	B(4)-C(8)	2.69	2.70	2.62	2.81	2.77	2.76	2.72	2.73 ± 0.06
	B(5)-C(8)	2.51	2.51	2.51	2.53	2.53	2.53	2.49	2.51 ± 0.01
	B(2)-C(7)	2.51	2.51	2.51	2.53	2.53	2.53	2.49	2.51 ± 0.01
	B(3)-C(7)	2.69	2.70	2.62	2.81	2.77	2.76	2.72	2.73 ± 0.06
1b	B(4)-S(8)	4.65	4.30	4.67	5.37	5.15	5.14	5.07	4.91 ± 0.37
	B(5)-S(8)	4.23	4.01	4.23	4.64	4.58	4.57	4.56	4.40 ± 0.24
	B(2)-C(7)	2.49	2.49	2.49	2.50	2.50	2.50	2.46	2.49 ± 0.01
	B(3)-C(7)	2.79	2.81	2.71	2.93	2.89	2.87	2.84	2.83 ± 0.07
1c	B(4)-S(8)	4.75	4.41	4.75	5.42	5.23	5.22	5.15	4.99 ± 0.36
	B(5)-S(8)	4.23	4.02	4.29	4.63	4.57	4.56	4.53	4.40 ± 0.23
	B(2)-S(7)	4.23	4.02	4.29	4.63	4.57	4.56	4.53	4.40 ± 0.23
	B(3)-S(7)	4.75	4.41	4.75	5.42	5.23	5.22	5.15	4.99 ± 0.36
1d	B(4)-S(8)	4.78	4.50	4.83	5.39	5.25	5.24	5.19	5.02 ± 0.32
	B(5)-S(8)	4.60	4.35	4.67	5.07	5.09	5.08	5.15	4.86 ± 0.32
	B(2)-N(7)	2.39	2.38	2.39	2.41	2.43	2.43	2.40	2.40 ± 0.02
	B(3)-N(7)	2.60	2.58	2.58	2.70	2.70	2.69	2.65	2.64 ± 0.06
1e	B(4)-N(7)	2.46	2.44	2.42	2.56	2.53	2.52	2.48	2.49 ± 0.05
	B(5)-N(7)	2.38	2.36	2.39	2.42	2.41	2.41	2.37	2.39 ± 0.02
	B(2)-C(8)	2.79	2.80	2.75	2.82	2.83	2.82	2.83	2.80 ± 0.03
	B(3)-C(8)	2.85	2.86	2.79	2.94	2.92	2.91	2.87	2.88 ± 0.05
1f	B(4)-N(7)	2.48	2.47	2.44	2.59	2.55	2.54	2.51	2.51 ± 0.05
	B(5)-N(7)	2.39	2.37	2.39	2.42	2.42	2.42	2.39	2.40 ± 0.02
	B(2)-C(8)	2.81	2.81	2.77	2.86	2.85	2.85	2.85	2.83 ± 0.03
	B(3)-C(8)	2.81	2.83	2.75	2.91	2.89	2.88	2.86	2.85 ± 0.05

Table S14 Heteroatom charge for heteroboranes **1a-1f** calculated using a full Natural Bond Orbital analysis.

	Atom	B2PLYP	MP2	B98	B97D	PBE	PW91	HFS	Average
1a	C(7)	-0.91	-0.90	-0.93	-0.89	-0.90	-0.90	-0.94	-0.92 ± 0.02
	C(8)	-0.91	-0.90	-0.93	-0.89	-0.90	-0.90	-0.94	-0.92 ± 0.02
1b	C(7)	-0.91	-0.90	-0.93	-0.89	-0.90	-0.90	-0.94	-0.91 ± 0.02
	S(8)	-0.28	-0.31	-0.28	-0.26	-0.23	-0.24	-0.23	-0.27 ± 0.03
1c	S(7)	-0.24	-0.27	-0.23	-0.21	-0.19	-0.19	-0.18	-0.22 ± 0.03
	S(9)	-0.24	-0.27	-0.23	-0.21	-0.19	-0.19	-0.18	-0.22 ± 0.03
1d	N(7)	-0.95	-0.97	-0.94	-0.93	-0.93	-0.93	-0.97	-0.95 ± 0.02
	S(8)	-0.20	-0.23	-0.19	-0.17	-0.14	-0.14	-0.12	-0.18 ± 0.04
1e	C(8)	-0.74	-0.74	-0.75	-0.71	-0.71	-0.71	-0.73	-0.73 ± 0.02
	N(7)	-0.93	-0.95	-0.93	-0.92	-0.91	-0.91	-0.94	-0.93 ± 0.02
1f	C(8)	-0.74	-0.75	-0.76	-0.72	-0.72	-0.72	-0.74	-0.74 ± 0.02
	N(7)	-0.94	-0.96	-0.93	-0.92	-0.91	-0.92	-0.95	-0.94 ± 0.02

Figure S1 The molecular structures of eight-vertex diheteroboranes **1a**-**1f** with full atom numbering.

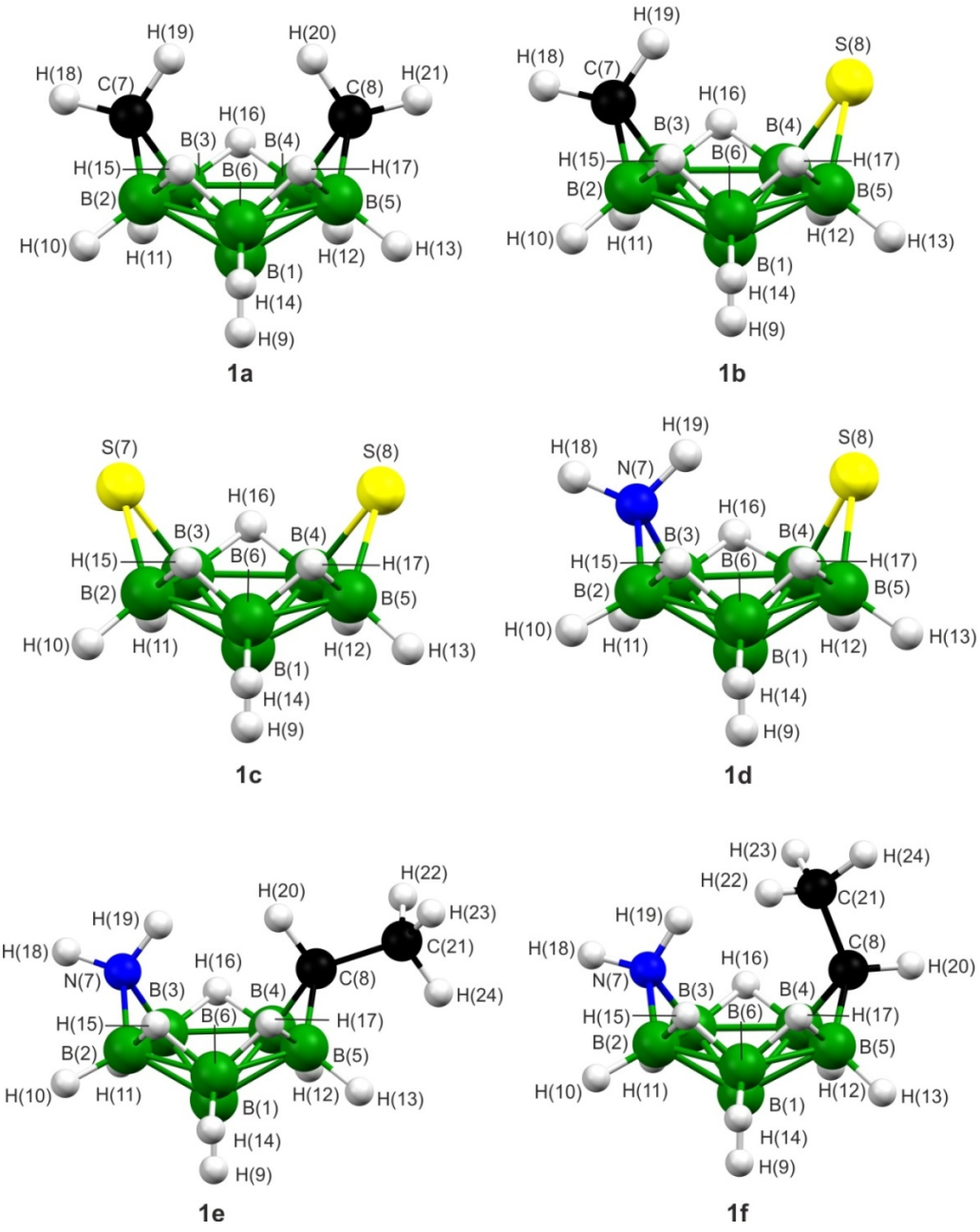

Figure S2 Schematic representation of the *closo-nido-arachno-hypho* relationship for $n = 11$ containing all atom numbering.

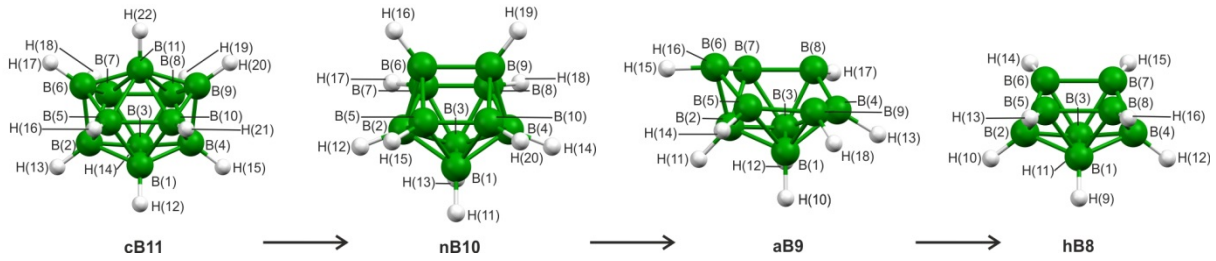

Figure S3 The molecular structure of *nido*-$[B_6H_{11}]^+$, whose structure resembles a *hypho* eight-vertex heteroborane with full atom numbering.