Table S1. Calculated geometric parameters and energies for B_5H_9 (distances in pm, angles in degrees, energy in Hartrees) from the molecular orbital study.[a]

	HF/3-21G*	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*
$B_{(a)}$-$H_{(a)}$	117.5	118.1	118.5	118.3
$B_{(b)}$-$B_{(b)}$	182.8	181.1	179.9	178.6
$B_{(b)}$-$B_{(a)}$	170.9	170.2	169.5	169.0
$B_{(b)}$-$H_{(t)}$	117.4	117.9	118.6	118.7
$B_{(b)}$-$H_{(br)}$	134.9	134.5	134.8	134.3
$B_{(a)}$-$B_{(b)}$-$H_{(t)}$	132.1	132.1	131.9	131.4
$H_{(br)}$ drop from basal plane	63.8	62.9	62.9	63.3
Energy	-127.82196	-128.57853	-129.66273	-129.05091

[a] Subscript (b) = base position, (a) = apex position, (t) = terminal and (br) = bridging.

Table S2. Calculated geometric parameters and energies for 1-F-B_5H_8 (distances in pm, angles in degrees, energy in Hartrees) from the molecular orbital study.[a]

	HF/3-21G*	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*
B-F	138.7	135.9	136.6	137.3
$B_{(b)}$-$B_{(b)}$	182.7	181.4	180.1	178.9
$B_{(b)}$-$B_{(a)}$	170.7	170.7	170.2	169.7
$B_{(b)}$-$H_{(t)}$	117.3	117.9	118.5	118.6
$B_{(b)}$-$H_{(br)}$	134.4	134.3	134.6	134.1
$B_{(a)}$-$B_{(b)}$-$H_{(t)}$	131.7	131.6	131.2	130.6
$H_{(br)}$ drop from basal plane	64.0	62.8	62.5	62.9
Energy	-226.20862	-227.47597	-228.94273	-228.11597

[a] Subscript (b) = base position, (a) = apex position, (t) = terminal and (br) = bridging.

Table S3. Calculated geometric parameters and energies for 1-Cl-B_5H_8 (distances in pm, angles in degrees, energy in Hartrees) from the molecular orbital study.[a]

	HF/3-21G*	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*
B-Cl	179.7	180.6	180.4	178.1
$B_{(b)}$-$B_{(b)}$	182.9	181.5	180.1	178.9
$B_{(b)}$-$B_{(a)}$	170.6	169.8	169.5	168.9
$B_{(b)}$-$H_{(t)}$	117.3	117.8	118.4	118.6
$B_{(b)}$-$H_{(br)}$	134.5	134.3	134.6	134.2
$B_{(a)}$-$B_{(b)}$-$H_{(t)}$	131.7	131.6	131.3	130.5
$H_{(br)}$ drop from basal plane	63.5	62.6	62.4	62.8
Energy	-584.68845	-587.52104	-589.29616	-588.12114

[a] Subscript (b) = base position, (a) = apex position, (t) = terminal and (br) = bridging.

Table S4. Calculated geometric parameters and energies for 1-Br-B_5H_8 (distances in pm, angles in degrees, energy in Hartrees) from the molecular orbital study.[a]

	HF/3-21G*	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*	MP2(fc)/6-311+G*	MP4(fc)(SDQ)/6-31G*
B-Br	192.7	195.2	194.6	193.3	194.0	193.3
$B_{(b)}$-$B_{(b)}$	182.5	181.5	180.1	178.9	179.7	179.5
$B_{(b)}$-$B_{(a)}$	170.7	169.7	169.3	168.8	169.7	168.8
$B_{(b)}$-$H_{(t)}$	117.3	117.8	118.4	118.6	118.5	118.6
$B_{(b)}$-$H_{(br)}$	134.4	134.3	134.7	134.2	135.1	134.2
$B_{(a)}$-$B_{(b)}$-$H_{(t)}$	131.9	131.7	131.4	130.7	131.3	130.7
$H_{(br)}$ drop from basal plane	64.2	62.6	62.5	62.9	63.5	62.7
Energy	-2687.56334	-2697.92979	-2700.80452	-2698.51162	-2701.0457	-2698.5633

[a] Subscript (b) = base position, (a) = apex position, (t) = terminal and (br) = bridging.

Table S5. Calculated geometric parameters and energies for 2-F-B_5H_8 (distances in pm, angles in degrees, energy in Hartrees) from the molecular orbital study.

	HF/3-21G*	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*
B(1)-H(7)	117.5	118.1	118.5	118.3
B(2)-F(6)	136.1	132.8	134.1	135.2
B(3)-H(8)	117.3	117.8	118.4	118.5
B(4)-H(9)	117.3	117.9	118.5	118.6
B(2)-B(4)	182.8	181.6	180.5	179.4
B(4)-B(3)	182.9	181.7	180.7	179.2
B(1)-B(2)	167.0	167.3	166.7	166.7
B(1)-B(3)	170.1	170.0	169.2	168.6
B(1)-B(4)	172.6	171.6	171.0	170.2
B(2)-H(11)	142.0	141.2	142.9	141.1
B(4)-H(11)	130.3	130.4	130.4	130.3
B(4)-H(13)	136.2	136.4	137.2	136.5
B(3)-H(13)	133.3	132.9	132.9	132.7
B(1)-B(2)-F(6)	137.5	136.8	136.9	136.4
B(1)-B(2)-B(4)	58.9	58.8	58.8	58.8
B(4)-B(2)-B(5)	90.7	90.6	90.6	90.5
B(1)-B(3)-H(8)	128.6	128.3	127.6	127.2
B(1)-B(3)-B(4)	58.4	58.3	58.4	58.5
B(5)-B(3)-B(4)	90.7	90.6	90.6	90.6
B(1)-B(4)-H(9)	130.4	130.7	130.3	130.1
B(1)-B(4)-B(2)	55.9	56.5	56.5	56.9
B(1)-B(4)-B(3)	57.1	57.4	57.4	57.6
B(2)-B(4)-B(3)	89.2	89.3	89.4	89.4
F(7)-B(1)-B(4)	131.1	131.2	131.3	131.5
F(7)-B(1)-B(2)	131.3	131.8	132.0	132.3
F(7)-B(1)-B(3)	129.4	129.7	129.8	130.1
B(2)-H(11)-B(4)	84.2	83.8	82.6	82.6
B(4)-H(13)-B(3)	85.5	84.9	84.0	83.5
Energy	-226.21383	-227.48506	-228.95005	-228.12524

Table S6. Calculated geometric parameters and energies for 2-Cl-B_5H_8 (distances in pm, angles in degrees, energy in Hartrees) from the molecular orbital study.

	HF/3-21G*	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*
B(1)-H(7)	117.4	118.0	118.4	118.3
B(2)-Cl(6)	177.6	178.5	178.8	177.1
B(3)-H(8)	117.3	117.8	118.4	118.6
B(4)-H(9)	117.3	117.8	118.4	118.6
B(2)-B(4)	183.4	181.3	180.4	178.9
B(4)-B(3)	182.3	181.0	179.9	178.8
B(1)-B(2)	170.1	169.3	168.7	168.0
B(1)-B(3)	170.8	170.1	169.4	168.8
B(1)-B(4)	171.1	170.4	169.8	169.3
B(2)-H(11)	135.6	135.2	136.8	136.3
B(4)-H(11)	134.4	133.9	133.6	133.0
B(4)-H(13)	135.3	135.0	135.7	135.2
B(3)-H(13)	134.4	134.0	134.3	133.7
B(1)-B(2)-Cl(6)	131.9	131.9	132.6	131.8
B(1)-B(2)-B(4)	57.7	58.0	58.1	58.3
B(4)-B(2)-B(5)	90.1	90.4	90.3	90.4
B(1)-B(3)-H(8)	130.9	130.8	130.2	129.8
B(1)-B(3)-B(4)	57.9	58.0	58.1	58.2
B(5)-B(3)-B(4)	90.8	90.6	90.6	90.5
B(1)-B(4)-H(9)	132.2	132.2	131.7	131.1
B(1)-B(4)-B(2)	57.2	57.5	57.5	57.6
B(1)-B(4)-B(3)	57.7	57.8	57.8	57.9
B(2)-B(4)-B(3)	89.6	89.5	89.5	89.5
Cl(7)-B(1)-B(4)	130.7	131.0	131.1	131.4
Cl(7)-B(1)-B(2)	130.7	131.1	131.2	131.2
Cl(7)-B(1)-B(3)	131.1	131.5	131.6	131.9
B(2)-H(11)-B(4)	85.6	84.7	83.7	83.2
B(4)-H(13)-B(3)	85.1	84.5	83.6	83.4
Energy	-584.68317	-587.51943	-589.29587	-588.12202

Table S7. Calculated geometric parameters and energies for 2-Br-B_5H_8 (distances in pm, angles in degrees, energy in Hartrees) from the molecular orbital study.

	HF /3-21G*	HF /6-31G*	B3LYP /6-31G*	MP2(fc) /6-31G*	MP2(fc) /6-311+G*	MP4(fc)(SDQ) /6-31G*	MP4(SDQ) /6-31G*
B(1)-H(7)	117.4	117.9	118.4	118.3	118.2	118.6	118.6
B(2)-Br(6)	197.1	193.8	193.6	193.0	193.6	193.7	193.2
B(3)-H(8)	117.3	117.8	118.5	118.6	118.5	118.8	118.8
B(4)-H(9)	117.2	117.8	118.4	118.6	118.5	118.8	118.8
B(2)-B(4)	182.2	181.2	180.2	178.8	179.5	179.5	179.1
B(4)-B(3)	182.4	180.8	179.8	178.7	179.6	179.2	178.9
B(1)-B(2)	169.9	169.5	168.6	168.1	169.2	168.3	168.0
B(1)-B(3)	170.8	170.2	169.6	169.0	169.9	169.2	168.9
B(1)-B(4)	170.8	170.2	169.7	169.3	170.2	169.4	169.1
B(2)-H(11)	133.4	134.1	136.0	135.5	136.2	135.6	135.5
B(4)-H(11)	135.7	134.7	133.9	133.5	134.5	133.9	133.9
B(4)-H(13)	135.0	134.7	135.5	135.0	135.9	135.2	135.1
B(3)-H(13)	134.9	134.3	134.3	133.8	134.6	134.1	134.1
B(1)-B(2)-Br(6)	130.4	130.8	131.9	131.0	131.4	131.1	131.1
B(1)-B(2)-B(4)	57.9	58.0	58.1	58.3	58.4	58.2	58.2
B(4)-B(2)-B(5)	90.7	90.3	90.3	90.4	90.5	90.4	90.4

B(1)-B(3)-H(8)	131.6	131.4	130.5	130.1	130.7	130.2	130.3
B(1)-B(3)-B(4)	57.7	57.9	58.0	58.2	58.2	58.1	58.1
B(5)-B(3)-B(4)	90.5	90.6	90.5	90.5	90.5	90.5	90.5
B(1)-B(4)-H(9)	132.3	132.4	131.9	131.4	131.9	131.5	131.5
B(1)-B(4)-B(2)	57.4	57.6	57.5	57.7	57.8	57.6	57.6
B(1)-B(4)-B(3)	57.7	57.9	58.0	58.0	58.1	58.0	58.0
B(2)-B(4)-B(3)	89.4	89.5	89.6	89.5	89.5	89.5	89.6
H(7)-B(1)-B(4)	130.6	131.0	131.2	131.4	131.5	131.3	131.3
H(7)-B(1)-B(2)	130.7	131.0	131.2	131.3	131.3	131.2	131.2
H(7)-B(1)-B(3)	131.6	131.8	131.6	132.0	132.3	131.9	131.9
B(2)-H(11)-B(4)	85.2	84.8	83.8	83.3	83.1	83.5	83.3
B(4)-H(13)-B(3)	85.1	84.5	83.6	83.3	83.2	83.4	83.3
Energy	-2687.33212	-2697.92630	-2700.80275	-2698.51037	-2701.0455	-2698.5616	-2698.6161

Table S8. Calculated geometric parameters and energies for 1,2-Br_2-B_5H_7 (distances in pm, angles in degrees, energy in Hartrees) from the molecular orbital study.

	HF/3-21G*	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*
B(1)-Br(7)	197.6	194.5	194.1	192.6
B(2)-Br(6)	196.0	192.8	192.7	192.1
B(3)-H(8)	117.2	117.7	118.4	118.5
B(4)-H(9)	117.1	117.6	118.3	118.5
B(2)-B(4)	182.4	181.7	180.5	179.1
B(4)-B(3)	182.7	181.1	180.0	179.0
B(1)-B(2)	168.9	169.3	168.9	168.3
B(1)-B(3)	169.5	169.6	169.1	168.5
B(1)-B(4)	169.8	169.9	169.6	169.1
B(2)-H(11)	133.7	134.3	135.9	135.4
B(4)-H(11)	135.3	134.4	133.9	133.7
B(4)-H(13)	134.8	134.5	135.1	134.7
B(3)-H(13)	134.9	134.2	134.4	134.1
B(1)-B(2)-Br(6)	130.5	130.3	130.9	129.0
B(1)-B(2)-B(4)	57.6	57.8	58.0	58.2
B(4)-B(2)-B(5)	90.6	90.2	90.2	90.4
B(1)-B(3)-H(8)	131.5	131.1	130.3	130.1
B(1)-B(3)-B(4)	57.5	57.8	58.0	58.1
B(5)-B(3)-B(4)	90.5	90.6	90.5	90.4
B(1)-B(4)-H(9)	132.0	131.8	131.2	130.6
B(1)-B(4)-B(2)	57.2	57.5	57.6	57.7
B(1)-B(4)-B(3)	57.4	57.7	57.8	57.8
B(2)-B(4)-B(3)	89.5	89.6	89.7	89.6
Br(7)-B(1)-B(4)	130.2	130.7	131.1	131.3
Br(7)-B(1)-B(2)	130.3	130.4	130.4	129.7
Br(7)-B(1)-B(3)	130.9	131.6	132.1	133.2
B(2)-H(11)-B(4)	85.4	85.1	84.0	83.4
B(4)-H(13)-B(3)	85.3	84.8	83.8	83.5
Energy	-5246.84750	-5267.27637	-5271.94377	-5267.97099

Table S9. Interatomic distances (r/pm) and amplitudes of vibration (u/pm) for the refined GED structure of 1-Br-B_5H_8.[a]

No.	Atom pair	r_a/pm	u/pm[b]	Restraint[c]
1	H(6)-B(2)	120.2	7.3(6)	8.1(8)
2	H(11)-B(2)	135.0	11.1(7)	11.0(10)
3	B(2)-B(1)	170.4	7.1(3)	
4	B(4)-B(2)	176.2	7.9(4)	
5	Br(10)-B(1)	189.7	4.7(4)	5.0(5)
6	H(12)…H(11)	190.7	15.5(fixed)	
7	H(11)…H(6)	204.5	14.5(fixed)	
8	H(11)…B(1)	247.4	10.6(fixed)	
9	B(3)…B(2)	249.0	9.8(10)	
10	H(11)…B(3)	256.3	11.9(8)	12.4(10)
11	H(6)…B(1)	264.0	11.4(fixed)	
12	H(13)…H(11)	269.0	18.3(fixed)	
13	H(6)…B(4)	273.3	11.5(9)	
14	Br(10)…B(2)	329.7	10.6(2)	
15	H(8)…H(6)	343.1	17.7(fixed)	
16	H(11)…H(7)	366.3	14.6(fixed)	
17	H(6)…B(3)	367.6	9.8(fixed)	
18	Br(10)…H(6)	379.4	18.5(15)	19.0(20)
19	H(11)…Br(10)	418.5	12(7)	11.7(10)
20	H(7)…H(6)	485.4	12.5(fixed)	

[a] Estimated standard deviations, obtained in the least-squares refinement, are given in parentheses.

[b] Amplitudes not refined were fixed at the values obtained using the B3LYP/6-31G* force field.

[c] Restraints were also applied to the ratios of u_3/u_4 [0.94(5)] and u_{10}/u_{13} [1.06(5)]. Uncertainties are 5% of the amplitude ratios.

Table S10. Least-squares correlation matrix (x100) for 1-Br-B_5H_8.[a]

	p_2	p_3	u_3	u_4	u_{11}	k_2
p_1	62	-73	11	-64		
p_2			-57			
p_3				63		
u_1						65
u_{10}					81	

[a] Only elements with absolute values ≥ 50% are shown.

Table S11. Interatomic distances (r_a/pm) and amplitudes of vibration (u/pm) for the refined GED structure of 2-Br-B_5H_8.[a]

No.	Atom pair	r_a/pm	u/pm[b]	Restraint[c]
1	H(10)-B(5)	125.4(8)	8.2(fixed)	
2	H(7)-B(1)	125.7(8)	8.3(fixed)	
3	H(8)-B(3)	125.8(8)	8.3(fixed)	
4	H(12)-B(5)	134.3(13)	10.9(fixed)	
5	H(14)-B(3)	134.7(6)	11.0(fixed)	
6	H(14)-B(5)	135.8(6)	11.2(fixed)	
7	H(12)-B(2)	136.3(13)	11.5(fixed)	
8	B(5)-B(1)	170.5(6)	8.1(4)	
9	B(3)-B(1)	171.1(6)	8.1(tied to u_8)	
10	B(2)-B(1)	171.7(6)	8.1(tied to u_8)	
11	B(5)-B(2)	180.3(4)	8.0(6)	6.7(7)
12	B(5)-B(3)	180.8(5)	7.9(tied to u_{11})	
13	H(12)…H(14)	190.1(19)	16.1(fixed)	
14	Br(6)-B(2)	195.0(4)	5.9(6)	
15	H(11)…H(12)	197.2(37)	16.3(fixed)	
16	H(13)…H(14)	197.9(27)	16.1(fixed)	
17	H(12)…H(10)	207.0(63)	15.0(fixed)	
18	H(14)…H(10)	208.5(65)	15.2(fixed)	
19	H(14)…H(8)	209.2(15)	15.0(fixed)	
20	H(14)…B(1)	244.7(11)	10.7(fixed)	
21	H(12)…B(1)	245.0(11)	10.7(fixed)	
22	B(3)…B(2)	253.1(8)	6.3(7)	
23	H(12)…B(3)	256.4(13)	12.5(fixed)	
24	B(4)…B(5)	257.6(13)	6.2(tied to u_{22})	
25	H(14)…B(2)	258.8(10)	12.7(fixed)	
26	H(12)…B(4)	262.1(17)	12.7(fixed)	
27	H(14)…B(4)	263.3(16)	12.6(fixed)	
28	H(8)…B(1)	269.1(15)	12.0(fixed)	
29	H(7)…B(5)	269.2(12)	11.8(fixed)	
30	H(7)…B(2)	270.8(10)	11.8(fixed)	

31	H(10)…B(1)	271.9(64)	11.8(fixed)	
32	H(7)…B(3)	272.3(13)	11.8(fixed)	
33	H(12)…H(13)	273.6(21)	19.1(fixed)	
34	H(12)…Br(6)	274.3(21)	13.8(12)	14.4(14)
35	H(8)…B(5)	281.9(8)	11.8(fixed)	
36	H(10)…B(2)	282.3(9)	11.8(fixed)	
37	H(10)…B(3)	283.4(9)	11.7(fixed)	
38	Br(6)…B(1)	328.0(12)	11.3(tied to u_{41})	
39	H(7)…H(8)	336.7(27)	20.6(fixed)	
40	H(7)…H(10)	337.7(104)	20.2(fixed)	
41	Br(6)…B(5)	343.7(3)	11.4(6)	
42	H(7)…H(12)	354.5(13)	13.8(fixed)	
43	H(7)…H(14)	354.7(15)	13.9(fixed)	
44	H(10)…H(8)	355.9(14)	18.2(fixed)	
45	H(12)…H(8)	371.9(17)	14.9(fixed)	
46	H(7)…Br(6)	375.7(23)	21.0(20)	20.9(20)
47	H(8)…B(2)	376.9(11)	10.2(fixed)	
48	H(12)…H(9)	377.1(41)	15.1(fixed)	
49	H(14)…H(9)	378.4(37)	15.0(fixed)	
50	H(10)…B(4)	381.3(15)	10.1(fixed)	
51	H(10)…Br(6)	404.9(15)	15.2(16)	18.4(20)
52	H(14)…Br(6)	442.3(11)	17.6(12)	
53	Br(6)…B(3)	445.2(6)	9.2(5)	
54	H(9)…H(10)	504.7(26)	12.8(fixed)	
55	H(8)…Br(6)	567.6(10)	10.7(fixed)	

[a] Estimated standard deviations, obtained in the least-squares refinement, are given in parentheses.

[b] Amplitudes not refined were fixed at the values obtained using the B3LYP/6-31G* force field.

[c] A restraint was also applied to the ratio u_{53}/u_{52} [0.53(3)]. The uncertainty is 5% of the amplitude ratio.

Table S12. Least-squares correlation matrix (x100) for 2-Br-B_5H_8.[a]

	p_{14}	u_1	u_5	u_6	u_{10}
p_1	-68			69	
p_4			-59		
p_{19}		68			
u_2			54	72	
u_4					61
u_5				53	

[a] Only elements with absolute values ≥ 50% are shown.

Figure S1. Experimental and final weighted difference (experimental – theoretical) molecular-scattering intensities for 1-Br-B_5H_8.

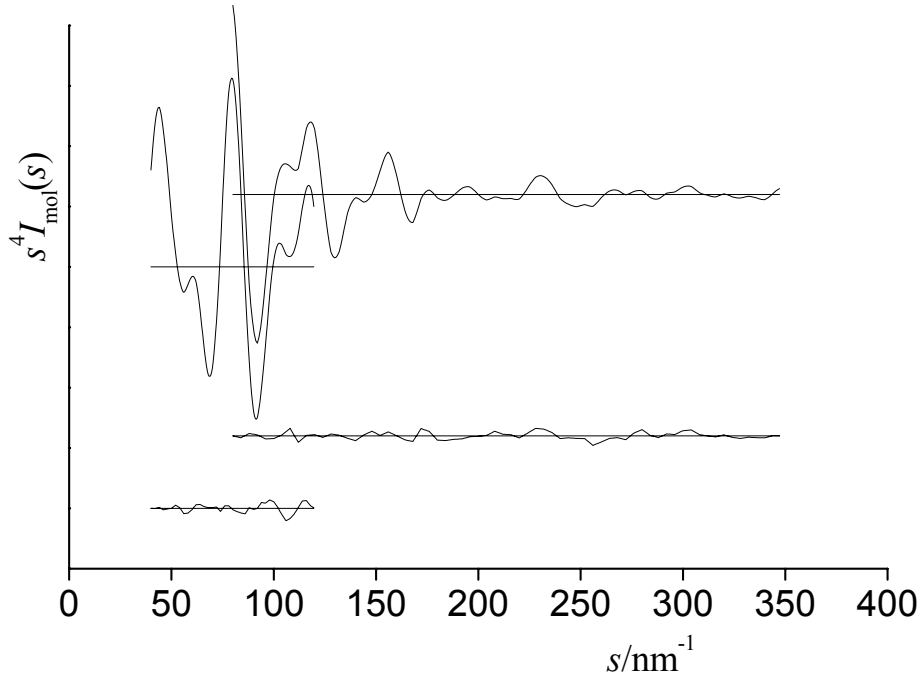

Figure S2. Experimental and final weighted difference (experimental – theoretical) molecular-scattering intensities for 2-Br-B_5H_8.