Supporting Information

σ - and π -Bond strengths in Main Group 3-5 Compounds

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Supporting Information Available: Optimized CCSD(T) geometry parameters for AH₂, XH₂, and planar NH₃ and PH₃, calculated vibrational frequencies, and total CCSD(T) energies (E_h) as a function of basis set extrapolated to the complete basis set limit.

Table S1. Optimized CCSD(T) Bond Lengths (Å) and Bond Angles (°) for AH₂, XH₂, and planar NH₃ and PH₃.

Molecule	Basis	$r_{M(VA)H}$	$\angle HNH$	$\angle HPB$	$r_{M(IIIA)H}$	$\angle HBH$	$\angle HBP$	$r_{M(VA)M(II)}$
BH ₂	aVDZ	1.2059				128.3		
	aVTZ	1.1893				128.9		
AlH ₂	aVDZ				1.6090	118.70		
	aVTZ				1.6010	118.46		
PH ₂	aVDZ	1.4103	122.24					
	aVTZ	1.3981	122.09					
NH ₃ (planar)	aVDZ	1.0055	120.00					
	aVTZ	0.9975	120.00					
PH ₃ (planar)	aVDZ	1.3943	120.00					
	aVTZ	1.3820	120.00					

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Table S2. Calculated vibrational MP2/(cc-pVTZ) frequencies (cm⁻¹)

Molecule	symmetry	calcd	Expt. ^a
BH ₂	a ₁	2538.7	
	a ₁	1042.6	
	b ₂	2697.0	
AlH ₂	a ₁	1818.4	1766
	a ₁	786.5	760
	b ₂	1844.8	1799
PH ₂	a ₁	2459.3	2310
	a ₁	1143.2	1101.9
	b ₂	2470.4	
BH ₂ NH ₂ (rot)	a'	3342.1	
	a'	2562.4	
	a'	2478.4	
	a'	1561.4	
	a'	1331.2	
	a'	1082.6	
	a'	1021.5	
	a'	727.7	
	a''	3410.6	
	a''	1178.0	
	a''	778.9i	
	a''	728.4	
BH ₂ NH ₂ (rot-planar)	a ₁	3522.6	
	a ₁	2463.4	
	a ₁	1560.3	
	a ₁	1348.4	
	a ₁	1124.9	
	a ₂	1186.2i	

	b ₁	3625.4
	b ₁	1168.8
	b ₁	651.0
	b ₂	2516.7
	b ₂	1009.6
	b ₂	631.5i
BH ₂ PH ₂	a'	2626.8
(rot)	a'	2535.6
	a'	2308.5
	a'	1244.9
	a'	1068.5
	a'	851.7
	a'	675.2
	a'	586.1
	a''	2313.5
	a''	1024.7
	a''	632.7
	a''	393.1i
BH ₂ PH ₂	a ₁	2542.5
(rot-planar)	a ₁	2507.6
	a ₁	1264.0
	a ₁	1035.5
	a ₁	700.7
	a ₂	1150.7i
	b ₁	2548.8
	b ₁	1021.3
	b ₁	460.8
	b ₂	2635.4
	b ₂	825.3
	b ₂	870.7i
AlH ₂ NH ₂	a'	3454.4

(rot)	a'	1891.5
	a'	1870.5
	a'	1566.9
	a'	846.4
	a'	772.5
	a'	571.9
	a'	238.8
	a''	3541.5
	a''	727.9
	a''	516.2i
	a''	514.4
AlH ₂ NH ₂	a ₁	3478.9
(rot-planar)	a ₁	1883.6
	a ₁	1565.9
	a ₁	851.1
	a ₁	784.3
	a ₂	549.3i
	b ₁	3568.6
	b ₁	719.0
	b ₁	507.2
	b ₂	1871.4
	b ₂	578.4
	b ₂	164.2i
AlH ₂ PH ₂	a'	2303.8
(rot)	a'	1889.3
	a'	1879.8
	a'	1089.5
	a'	804.6
	a'	610.8
	a'	431.9
	a'	381.6

AlH ₂ PH ₂ (rot-planar)	a''	2311.7
	a''	673.5
	a''	477.2
	a''	186.5i
	a ₁	2481.7
	a ₁	1901.5
	a ₁	1059.4
	a ₁	819.4
	a ₁	464.2
	a ₂	532.7i
	b ₁	2502.6
	b ₁	631.3
	b ₁	378.0
	b ₂	1903.2
	b ₂	525.3
	b ₂	641.8i

^a Jacox, M.E., J. Phys. Chem. Ref. Data, Monograph 3, 1994.

Table S3. Total CCSD(T) Energies (E_h) as a Function of Basis Set and Extrapolations to the CBS Limit Using Equation 3.

System	Basis Set	E_h
BH ₂ NH ₂ (rot)	aVDZ	-81.76893
	aVTZ	-81.845504
	aVQZ	-81.866507
	CBS	-81.878051
BH ₂ NH ₂ (rot-planar)	aVDZ	-81.761047
	aVTZ	-81.837999
	aVQZ	-81.859204
	CBS	-81.870871
BH ₂ PH ₂ (rot)	aVDZ	-367.989422
	aVTZ	-368.054623
	aVQZ	-368.072073
	CBS	-368.081609
BH ₂ PH ₂ (rot-planar)	aVDZ	-367.930755
	aVTZ	-367.999761
	aVQZ	-368.018339
	CBS	-368.028506
AlH ₂ NH ₂ (rot)	aVDZ	-299.011641
	aVTZ	-299.087723
	aVQZ	-299.108769
	CBS	-299.120359
AlH ₂ NH ₂ (rot-planar)	aVDZ	-299.011384
	aVTZ	-299.086965
	aVQZ	-299.107958
	CBS	-299.119530
AlH ₂ PH ₂ (rot)	aVDZ	-585.236575
	aVTZ	-585.300398
	aVQZ	-585.317912
	CBS	-585.327540
AlH ₂ PH ₂ (rot-planar)	aVDZ	-585.201306
	aVTZ	-585.266256
	aVQZ	-585.284172

	CBS	-585.294032
NH ₃ (planar)	aVDZ	-56.416255
	aVTZ	-56.471739
	aVQZ	-56.487220
	CBS	-56.495762
AlH	aVDZ	-242.534088
	aVTZ	-242.547218
	aVQZ	-242.550697
	CBS	-242.552594
AlH ₂	aVDZ	-243.109759
	aVTZ	-243.127383
	aVQZ	-243.13233
	CBS	-243.135063
PH	aVDZ	-341.404295
	aVTZ	-341.436111
	aVQZ	-341.444275
	CBS	-341.448692
PH ₂ (² B ₁)	aVDZ	-342.023126
	aVTZ	-342.061892
	aVQZ	-342.072059
	CBS	-342.077588
PH ₃ (planar)	aVDZ	-342.599972
	aVTZ	-342.645620
	aVQZ	-342.657892
	CBS	-342.664605