Ab initio and density functional study of structure and bonding of cage compounds containing Boron, Phosphorous and group 14 atoms

Sofia Pachini and Michael P. Sigalas*

Laboratory of Applied Quantum Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

Supplementary Material

Table S1 Absolute (hartrees) and Zero Point Energies (kcal/mol) of *closo*-heteroboranes.

Molecule	sym	6-311G++(d,p)				3-21G++(d,p)			
		MP2		B3LYP		MP2		B3LYP	
		E	ZPE	E	ZPE	E	ZPE	E	ZPE
$P_2(HB)_3$	D_{3h}	-757.81424	26.5	-759.14039	25.6	-754.13696	26.0	-755.44438	25.7
$P_2(HB)_2CH_2$[a]	C_{2v}	-771.56491	33.7	-772.93238	33.6	-767.82566	33.9	-769.17494	33.8
$P_2(HB)_2CH_2$	C_s	-771.59150	33.6	-772.95228	33.9	-767.84963	34.2	-769.19267	33.9
$P_2(HB)_2SiH_2$	C_{2v}	-1022.63633	28.4	-1024.38959	28.6	-1017.63832	28.7	-1019.36271	28.8
$P_2(HB)_2GeH_2$	C_{2v}	-2809.01692	27.3	-2811.87851	27.2	-2795.70752	27.5	-2798.52710	27.6
$P_2(HB)_2SnH_2$	C_{2v}					-6726.92385	26.3	-6730.65249	26.1
$P_2(H_2NB)_3$	D_{3h}	-923.64680	61.2	-925.41187	61.1	-919.16017	61.0	-920.90587	60.9
$P_2(H_2NB)_2CH_2$	C_{2v}	-882.15709	58.7	-883.81470	58.3	-877.87653	58.4	-879.51549	58.5
$P_2(H_2NB)_2SiH_2$	C_{2v}	-1133.21522	52.8	-1135.25923	52.7	-1127.67612	52.5	-1129.69086	52.8
$P_2(H_2NB)_2GeH_2$	C_{2v}	-2919.59805	51.7	-2922.75087	51.5	-2905.74842	51.6	-2908.85878	51.7
$P_2(H_2NB)_2SnH_2$	C_{2v}					-6836.96267	50.8	-6840.98208	50.5

[a] Transition state at all levels (one imaginary frequency). All other structures are real minima.

Table S2 Optimized at the MP2 and B3LYP levels bond lengths (Å) and angles (°) for $P_2(HB)_3$ and $P_2(H_2NB)_3$ using the 6-311G++(d,p) and 3-21G++(d,p) basis sets.

	$P_2(HB)_3$				$P_2(H_2NB)_3$				Exp[a]
	6-311G++(d,p)		3-21G++(d,p)		6-311G++(d,p)		3-21G++(d,p)		
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	
B···B	1.863	1.894	1.875	1.906	2.079	2.144	2.087	2.147	2.190
B-P	1.914	1.914	1.916	1.915	1.944	1.952	1.943	1.952	1.952
B-H	1.185	1.182	1.188	1.190					
B-N					1.406	1.400	1.414	1.409	1.400
N-H					1.009	1.008	1.009	1.013	
B-P-B	58.2	59.3	58.6	59.7	64.6	66.6	64.9	66.7	69.6
P-B-P	111.7	110.3	111.2	109.8	103.7	101.3	103.4	101.2	97.5
P-B-H	124.2	124.8	124.4	125.1					
B-B-H	150.0	150.0	150.0	150.0					
P-B-N					128.1	129.3	128.3	129.4	131.2
H-N-H					114.4	114.0	114.6	114.1	

[a] Mean values for $P_2(^iPr_2NB)_2((Me_3Si)_2NB)$ and $P_2(tmpB)_3$ (ref.34).

Table S3 Optimized at the MP2 and B3LYP levels bond lengths (Å) and angles (º) for $P_2(HB)_2EH_2$, (E = C, Si, Ge) using the 6-311G++(d,p) basis set.

	$P_2(HB)_2CH_2$ (C_{2v})		$P_2(HB)_2CH_2$ (C_s)[a]		$P_2(HB)_2SiH_2$ (C_{2v})		$P_2(HB)_2GeH_2$ (C_{2v})	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
B···B	1.971	2.028	1.892	1.924	1.941	1.991	1.946	1.996
B-P	1.922	1.933	1.906	1.910	1.924	1.933	1.931	1.939
			1.898	1.899				
E···B	2.243	2.305	1.717	1.730	2.330	2.386	2.445	2.501
			2.436	2.462				
E-P	1.942	1.951	1.991	2.005	2.267	2.279	2.361	2.369
B-H	1.190	1.187	1.184	1.182	1.190	1.187	1.191	1.188
			1.190	1.187				
E-H	1.091	1.088	1.091	1.089	1.476	1.485	1.531	1.537
			1.089	1.084				
B-P-B	61.7	63.3	59.7	60.7	60.6	62.0	60.5	62.0
E-P-B	70.9	72.8	52.2	52.4	66.9	68.4	68.6	70.2
			77.5	78.1				
P-B-P	99.9	97.6	104.2	103.7	111.0	109.0	111.0	108.9
			104.9	104.5				
P-E-P	98.5	96.4	98.2	97.0	88.7	87.3	84.8	83.4
B-E-B	52.1	52.2	50.7	51.1	49.2	49.3	46.9	47.2
P-B-H	130.0	131.2	127.0	127.5	124.2	125.2	124.0	125.1
			126.6	126.7				
B-B-H	143.4	142.4	156.0	155.2	145.1	145.3	144.1	144.0
			132.2	132.3				
H-E-H	111.1	110.9	112.6	111.5	107.6	107.8	111.5	111.1
α [b]	105.7	105.6	108.8	110.5	125.8	124.9	125.7	124.5

[a] The second value for some geometrical parameters refers to B' (see Fig. 1). [b] α is the angle between the two PEP planes.

Table S4 Experimental and optimized at the MP2 and B3LYP levels bond lengths (Å) and angles (º) for $P_2(H_2NB)_2EH_2$, (E = C, Si, Ge) using the 6-311G++(d,p) basis set.

	$P_2(H_2NB)_2CH_2$ (C_{2v})		$P_2(H_2NB)_2SiH_2$ (C_{2v})			$P_2(H_2NB)_2GeH_2$ (C_{2v})		
	MP2	B3LYP	MP2	B3LYP	Exp[a]	MP2	B3LYP	Exp[b]
B···B	2.071	2.162	2.106	2.183	2.24	2.117	2.193	2.26
B-P	1.947	1.960	1.953	1.967	1.98	1.958	1.970	1.97
E···B	2.350	2.395	2.434	2.496	2.52	2.541	2.599	2.62
E-P	1.920	1.932	2.266	2.280	2.24	2.359	2.370	2.32
B-N	1.396	1.390	1.401	1.394	1.38	1.401	1.394	1.42
E-H	1.093	1.087	1.479	1.487		1.535	1.540	
N-H	1.010	1.010	1.009	1.009		1.010	1.009	
B-P-B	64.2	67.0	65.2	67.4	68.7	65.5	67.6	70.0
E-P-B	74.8	76.0	70.0	71.6	73.0	71.4	72.9	74.6
P-B-P	94.3	92.3	105.3	102.8	100.0	105.3	102.8	99.4
P-E-P	96.1	94.1	86.5	84.8	85.2	82.6	81.0	80.7
B-E-B	52.3	53.7	51.3	51.9	52.6	49.2	49.9	51.2
P-B-N	132.8	133.8	127.3	128.5	129.8	127.2	128.5	130.1
B-B-N	141.0	142.1	149.0	149.6	151.3	148.5	149.1	152.4
H-E-H	110.0	110.0	108.4	108.3		111.1	110.5	
H-N-H	114.4	113.9	114.3	113.9		114.4	113.9	
α [c]	102.9	105.6	125.4	125.6	122.7	126.2	126.3	124.9

[a] Mean values for $P_2(^iPr_2NB)_2(SiPh_2)$ and $P_2(tmpB)_2(SiPh_2)$ (ref. 11). [b] Mean values for $P_2(tmpB)_2(GePh_2)$ (ref. 12).

[c] α is the angle between the two PEP planes.

Table S5 Optimized at the B3LYP level bond lengths (Å) and angles (º) for $P_2(HB)_2SnH_2$,and $P_2(H_2NB)_2SnH_2$ using the SDD effective core potential and basis set

	$P_2(HB)_2SnH_2$	$P_2(H_2NB)_2SnH_2$
B···B	2.043	2.205
B-P	1.973	1.993
Sn···B	2.703	2.721
Sn-P	2.604	2.629
B-H	1.186	
B-N		1.400
N-H		1.014
Sn-H	1.729	1.717
B-P-B	63.3	69.1
Sn-P-B	71.5	73.5
P-B-P	109.8	104.0
P-Sn-P	83.5	74.3
B-Sn-B	48.4	47.8
P-B-H	125.6	
P-B-N		127.8
B-B-H	143.9	
B-B-N		151.3
H-Sn-H	111.8	111.6
H-N-H		115.6
α [a]	128.9	134.1

[a] α is the angle between the two PEP planes.