

Exo-substituent Effects in Icosahedral ($B_{12}H_{12}^{2-}$) and Octahedral ($B_6H_6^{2-}$) *closo*-Borane Skeletons: An Experimental and Quantum Chemical Study of Reaction Mechanisms

Supplementary Material

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Table S1. NMR chemical shifts (in ppm) for a) **B12** and b) **B6** skeleton

a)

X	H								F								
	mono				ortho				meta				para				
	B1-12	B1	B2-6	B7-11	B12	B1,2	B3,6	B4,5,7,8	B9,11	B10,12	B1,7	B2,6	B3,5,8,11	B4,12	B9,10	B1,12	B2-11
HF/def2-SVP	-13.8	7.8	-14.9	-16.6	-20.7	5.3	-16.4	-17.5	-20.2	-20.1	5.4	-16.0	-17.6	-21.9	-19.6	5.0	-17.3
MP2/def2-SVP	-13.6	12.1	-14.8	-16.5	-23.2	9.7	-16.0	-17.3	-20.6	-24.4	9.7	-15.5	-17.4	-23.6	-19.8	8.8	-16.9
HF/def2-TZVP	-15.6	7.5	-16.7	-18.4	-22.9	4.8	-18.2	-19.2	-22.1	-24.8	5.2	-17.7	-19.4	-24.0	-21.4	4.8	-19.0
MP2/def2-TZVP	-16.2	11.4	-17.1	-19.2	-26.0	8.6	-18.5	-19.6	-23.4	-27.6	9.0	-17.8	-19.9	-26.9	-22.4	8.3	-19.2
<i>exptl^a</i>	-15.3	10.2	-16.7	-18.5	-24.0	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	6.6	-18.1	-19.5	-25.4	-21.7	<i>n/d</i>	<i>n/d</i>
<i>exptl^b</i>	-14.4	9.8	-16.0	-17.6	-23.3	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>

X	Cl															
	mono		ortho				meta		para							
	B1	B2-6	B7-11	B12	B1,2	B3,6	B4,5,7,8	B9,11	B10,12	B1,7	B2,6	B3,5,8,11	B4,12	B9,10	B1,12	B2-11
HF/def2-SVP	-0.9	-12.4	-11.9	-16.6	-1.3	-11.1	-13.2	-16.2	-17.8	-1.8	-11.0	-13.3	-15.9	-15.8	-2.3	-13.1
MP2/def2-SVP	1.4	-12.1	-14.4	-19.0	1.3	-10.8	-12.8	-15.9	-19.2	0.8	-10.6	-12.9	-17.6	-15.3	-1.0	-12.6
HF/def2-TZVP	-2.6	-14.0	-16.4	-18.9	-3.4	-12.9	-14.7	-18.0	-19.1	-3.3	-12.6	-14.9	-17.3	-17.3	-3.5	-14.7
MP2/def2-TZVP	-0.7	-14.3	-16.8	-21.7	-1.5	-13.0	-14.8	-18.5	-21.3	-1.2	-12.6	-15.0	-19.8	-17.5	-2.6	-14.6
<i>exptl^a</i>	-2.8	-14.8	-16.6	-20.2	-3.7	-13.8	-15.3	-18.3	-20.1	-3.7	-13.8	-15.4	-19.2	-17.5	<i>n/d</i>	<i>n/d</i>

X	Br															
	mono		ortho				meta		para							
	B1	B2-6	B7-11	B12	B1,2	B3,6	B4,5,7,8	B9,11	B10,12	B1,7	B2,6	B3,5,8,11	B4,12	B9,10	B1,12	B2-11
HF/def2-SVP	-1.5	-12.1	-14.3	-15.7	-2.0	-10.6	-12.4	-15.2	-15.8	-2.2	-10.5	-12.6	-14.0	-14.9	-1.7	-12.5
MP2/def2-SVP	-0.3	-11.7	-13.8	-17.6	-0.4	-10.1	-11.7	-14.7	-17.1	-0.6	-9.9	-11.9	-15.7	-14.1	-1.6	-11.7
HF/def2-TZVP	-3.5	-13.7	-16.0	-17.8	-4.2	-12.2	-13.9	-17.1	-17.6	-4.1	-12.0	-14.1	-15.8	-16.6	-3.7	-14.0
MP2/def2-TZVP	-2.3	-13.9	-16.3	-20.6	-2.8	-12.2	-13.9	-17.3	-19.9	-2.5	-11.9	-14.1	-18.3	-16.6	-3.4	-13.9
<i>exptl^a</i>	-8.2	-14.3	-15.9	-18.9	-8.9	-13.3	-14.7	-16.9	-18.7	-9.0	-13.4	-14.6	-16.2	-17.9	<i>n/d</i>	<i>n/d</i>

a. Refs. 43, 44

b. Ref. 45

b)

X	H	F							
		mono			cis			trans	
	B1-6	B1	B2-5	B6	B1,2	B3,5	B4,6	B1,6	B2-5
HF/def2-SVP	-17.0	6.6	-20.7	-36.3	1.9	-24.7	-39.3	-1.6	-23.4
MP2/def2-SVP	-18.6	9.2	-21.9	-41.4	5.1	-25.7	-43.9	-0.1	-24.0
HF/def2-TZVP	-19.2	8.3	-22.9	-40.2	3.1	-26.9	-42.6	-0.5	-25.3
MP2/def2-TZVP	-21.3	11.6	-24.5	-47.2	6.9	-28.3	-48.6	1.5	-26.1
<i>expt^a</i>	"-18.1;-13.2	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>	<i>n/d</i>

X	Cl								
	mono			Cis			trans		
	B1	B2-5	B6	B1,2	B3,5	B4,6	B1,6	B2-5	
HF/def2-SVP	-3.7	-17.5	-27.7	-5.6	-18.0	-27.7	-8.8	-17.6	
MP2/def2-SVP	-3.5	-18.8	-31.9	-4.9	-19.0	-31.4	-10.1	-18.4	
HF/def2-TZVP	-4.1	-18.9	-30.2	-6.2	-19.1	-28.9	-9.2	-18.3	
MP2/def2-TZVP	-3.2	-20.4	-35.9	-4.8	-20.1	-33.6	-10.0	-18.9	
<i>expt^b</i>	-1.0	-14.5	-30.4	-2.4	-15.4	-30.3	-10.4	-13.6	

X	Br							
	mono		cis			trans		
	B1	B2-5	B6	B1,2	B3,5	B4,6	B1,6	B2-5
HF/def2-SVP	-4.3	-16.8	-25.2	-5.9	-16.4	-24.1	-7.7	-16.3
MP2/def2-SVP	-4.9	-18.0	-29.6	-5.9	-17.3	-27.9	-9.8	-17.0
HF/def2-TZVP	-5.6	-18.2	-28.1	-7.3	-17.4	-25.9	-9.6	-17.0
MP2/def2-TZVP	-5.5	-19.5	-33.8	-6.5	-18.2	-30.4	-11.0	-17.5
<i>expt^b</i>	-7.6	-14.0	-27.3	-8.4	<i>n/d</i>	-26.9	-12.6	-15.0

a Ref. 47

b Ref. 46