

Electronic Supplementary Information

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¹¹B-NMR Shielding Effects in the *closo* Borane Series. Sensitivity of Shifts and their Additivity

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$\alpha(^{13}\text{C})$ -Shifts for 1-halosubstituted *n*-pentanes¹ (universal α_{ref} scale)

F- 70.1 Cl- 30.6 Br- 19.3 I- -7.4

Table S1. ¹¹B-NMR data for haloderivatives of the [*closo*-B₆H₆]²⁻ dianion

compound	$\delta(^{11}\text{B})$	multiplicity	$\Delta\delta$	assignment
[B ₆ H ₆] ²⁻	- 13.5	d	0	B1-6
[1-Cl-B ₆ H ₅] ²⁻	-1.0	s	3.1	B1
	-14.5	d	-1.0	B2-5
	-30.4	d	-16.9	B6
[1-Br-B ₆ H ₅] ²⁻	-7.6	s	5.9	B1
	-14.0	d	-0.5	B2-5
	-27.3	d	-13.8	B6
[1-I-B ₆ H ₅] ²⁻	-23.2	m	-9.7	B1
	-13.1	d	0.4	B2-5
	-21.6	m	-8.1	B6
[1,6-Cl ₂ -B ₆ H ₄] ²⁻	-10.4	s	-1.5	B1,6
	-13.6	d	-0.1	B2-5
[1,6-Br ₂ -B ₆ H ₄] ²⁻	-15.0	s	3.1	B1,6
	-12.6	d	0.9	B2-5
[1,6-I ₂ -B ₆ H ₄] ²⁻	-25.2	s	11.7	B1,6
	-13.1	d	0.4	B2-5
[1,2,4,6-Cl ₄ -B ₆ H ₂] ²⁻	-13.8	s	-0.3	B1,2,4,6
	-18.3	d	-4.8	B3,5
[1,2,4,6-Br ₄ -B ₆ H ₂] ²⁻	-15.9	m	-2.4	B3,5
	-16.0	m	-2.5	B1,2,4,6
[1,2,4,6-I ₄ -B ₆ H ₂] ²⁻	-11.7	d	1.8	B3,5
	-26.1	s	-12.6	B1,2,4,6
[B ₆ Cl ₅ H] ²⁻	-13.9	m	-0.4	B1
	-15.7	m	-2.2	B2-5
	-27.4	d	-13.9	B6
[B ₆ Br ₅ H] ²⁻	-15.8	m	-2.3	B1
	-17.6	m	-4.1	B2-5
	-23.4	m	-9.9	B6
[B ₆ I ₅ H] ²⁻	-15.7	d	-2.2	B6
	-22.0	s	-8.5	B1
	-25.6	s	-12.1	B2-5
[B ₆ Cl ₆] ²⁻	- 17.4	s	-3.9	B1-6
[B ₆ Br ₆] ²⁻	- 18.5	s	-5.0	B1-6
[B ₆ I ₆] ²⁻	- 24.7	s	-11.2	B1-6

Data from ref.²

Table S2. ^{11}B -NMR data for 1-haloderivatives of the $[\text{closo-B}_9\text{H}_9]^{2-}$ dianion

compound	$\delta(^{11}\text{B})$	multiplicity	$\Delta\delta$	assignment
$[\text{B}_9\text{H}_9]^{2-}$	-3.8	d	0	B4-6
	-21.0	d	0	B1-3,7-9
$[\text{1-Cl-B}_9\text{H}_8]^{2-}$	0.9	d	4.7	B5
	-5.3	s,d	-1.5	B4,6
	ca. -6.0	d	15.0	B1
	-18.0	d	3.0	B2,3
	-18.5	d	3.5	B7
	-23.2	d	-2.2	B8,9
$[\text{1-Br-B}_9\text{H}_8]^{2-}$	0.6	d	4.4	B5
	-5.0	d	-1.2	B4,6
	-9.7	s	11.3	B1
	-18.0	d	3.0	B2,3,7
	-22.3	d	-1.3	B8,9
$[\text{1-I-B}_9\text{H}_8]^{2-}$	0.1	d	3.9	B5
	-3.8	d	0.0	B4,6
	-16.9	s	4.1	B1
	-18.5	d	2.5	B8,9
	-21.0	d	0.0	B2,3,7

Data from ref. 3

Table S3. ^{11}B -NMR data for haloderivatives of the $[\text{closo-B}_{10}\text{H}_{10}]^{2-}$ dianion

compound	$\delta(^{11}\text{B})$	multiplicity	$\Delta\delta$	assignment
$[\text{B}_{10}\text{H}_{10}]^{2-}$	-0.7	d	0	B1,10
	-28.7	d	0	B2-9
$[\text{2-Cl-B}_{10}\text{H}_9]^{2-}$	-2.0	d	-1.3	B1,10
	-9.2	s	19.5	B2
	-24.4	m	4.3	B3,5/6,9
	-27.6	d	1.1	B7,8
	-30.8	d	-2.1	B4
$[\text{2-Br-B}_{10}\text{H}_9]^{2-}$	-1.6	d	-0.9	B1,10
	-13.2	s	15.5	B2
	-25.6	d	3.1	B3,5/6,9
	-27.6	d	1.1	B3,5/6,9
	-27.3	d	1.4	B7,8
	-30.1	d	-1.4	B4
$[\text{2-I-B}_{10}\text{H}_9]^{2-}$	-0.6	d	0.1	B1,10
	-25.6	m	3.1	B3,5/6,9/2/7,8
	-26.5	m	2.2	B3,5/6,9/2/7,8
	-28.8	m	-0.1	B4
$[\text{1-I-B}_{10}\text{H}_9]^{2-}$	0.0	d	0.7	B10
	-8.9	s	8.2	B1
	-25.2	d	3.5	B2-5
	-28.8	d	-0.1	B6-9

Data from ref.⁴

Table S4. ^{11}B -NMR data for haloderivatives of the $[\text{closo-B}_{12}\text{H}_{12}]^{2-}$ dianion

compound	$\delta(^{11}\text{B})$	multiplicity	$\Delta\delta$	assignment
$[\text{B}_{12}\text{H}_{12}]^{2-}$	-15.3	d	0	B1-12
$[\text{1-F-B}_{12}\text{H}_{11}]^{2-}$	10.2	s	25.1	B1
	-16.7	d	-1.4	B2-6
	-18.5	d	-3.2	B7-11
	-24.0	d	-8.7	B12
$[\text{1-Cl-B}_{12}\text{H}_{11}]^{2-}$	-2.8	s	12.5	B1
	-14.8	d	0.5	B2-6
	-16.6	d	-1.3	B7-11
	-20.2	d	-4.9	B12
$[\text{1-Br-B}_{12}\text{H}_{11}]^{2-}$	-8.2	s	7.1	B1
	-14.3	d	1.0	B2-6
	-15.9	d	-0.6	B7-11
	-18.9	d	-3.6	B12
$[\text{1-I-B}_{12}\text{H}_{11}]^{2-}$	-21.3	s	-6.0	B1
	-13.7	d	1.6	B2-6
	-15.2	d	0.1	B7-11
	-16.9	d	-1.6	B12
$[\text{1,2-Cl}_2\text{-B}_{12}\text{H}_{10}]^{2-}$	-2.3	s	-3.7	B1,2
	-14.3	d	-13.8	B3,6
	-16.1	d	-15.3	B4,5,7,11
	-17.9	d	-18.1	B8,10
	-21.5	d	-20.1	B9,12
$[\text{1,2-Br}_2\text{-B}_{12}\text{H}_{10}]^{2-}$	-7.2	s	-8.9	B1,2
	-13.3	d	-13.3	B3,6
	-14.9	d	-14.7	B4,5,7,11
	-16.5	d	-16.9	B8,10
	-19.5	d	-18.7	B9,12
$[\text{1,2-I}_2\text{-B}_{12}\text{H}_{10}]^{2-}$	-19.7	s	-20.8	B1,2
	-12.1	d	-11.9	B3,6
	-13.6	d	-13.6	B4,5,7,11
	-15.1	d	-15.0	B8,10
	-16.8	d	-16.3	B9,12
$[\text{1,7-F}_2\text{-B}_{12}\text{H}_{10}]^{2-}$	7.0	s	6.6	B1,7
	-18.1	d	-18.1	B2,3
	-19.9	d	-19.5	B4,6,8,11
	-21.7	d	-21.7	B9,10
	-25.4	d	-25.4	B5,12
$[\text{1,7-Cl}_2\text{-B}_{12}\text{H}_{10}]^{2-}$	-4.1	s	-3.7	B1,7
	-14.3	d	-13.8	B2,3
	-16.1	d	-15.4	B4,6,8,11
	-17.9	d	-17.5	B9,10
	-19.7	d	-19.2	B5,12
$[\text{1,7-Br}_2\text{-B}_{12}\text{H}_{10}]^{2-}$	-8.8	s	-9.0	B1,7
	-13.3	d	-13.4	B2,3
	-14.9	d	-14.6	B4,6,8,11
	-16.5	d	-16.2	B9,10
	-17.9	d	-17.9	B5,12
$[\text{1,7-I}_2\text{-B}_{12}\text{H}_{10}]^{2-}$	-21.2	s	-21.8	B1,7
	-12.1	d	-12.0	B2,3
	-13.6	d	-13.3	B4,6,8,11
	-15.1	d	-15.0	B9,10
	-15.3	d	-15.0	B5,12

Data from ref.⁵⁻⁷

Table S5. Gradient values (g) indicating sensitivity to halogen substitution for all positions in the known series of [*closo*-X_m-B_nH_{n-m}]²⁻ derivatives

series	α	β	γ	A
[1-X-B ₆ H ₅] ²⁻	-57.5	9.0 B2-5	-	18.0 B6
[1,6-X ₂ -B ₆ H ₄] ²⁻	-38.8 $\alpha+A$	0.0 $\beta-\beta$	-	-
[1,2,4,6-X ₄ -B ₆ H ₂] ²⁻	-31.3 $\alpha+A+\beta$	18.0 2 β	-	-
[B ₆ X ₆] ²⁻	-19.0 $\alpha+4\beta$	-	-	-
[1-X-B ₉ H ₈] ²⁻	-32.5	-10.1 B2,3,7 4.0 B4,6	-2.5 B5 13.5 B8,9	-
[2-X-B ₁₀ H ₉] ²⁻	-41.3	-1.8, 5.4 B3,5/6,9 3.5 B1	3.5 B10 2.5 B7,8 5.4 B4	-
[1-X-B ₁₂ H ₁₁] ²⁻	-45.0	3.9 B2-6	4.3 B7-11	9.2 B12
[1,2-X ₂ -B ₁₂ H ₁₀] ²⁻	-42.5 $\alpha+\beta$	6.3 $\beta+\beta$ 7.0 $\beta+\gamma$	7.0 $\gamma+\gamma$	11.3 A+ γ
[1,7-X ₂ -B ₁₂ H ₁₀] ²⁻	-43.8 $\alpha+\gamma$	7.9 B2,3 $\beta+\beta$ 8.0 B4,6/8,11 $\beta+\gamma$	8.6 B9,10 $\gamma+\gamma$	13.4 B5,12 A+ γ

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