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# Microwave-Assisted Iodination: Synthesis of Heavily Iodinated 10-Vertex and 12-Vertex Boron Clusters

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Microwave-assisted syntheses of heavily iodinated 10-vertex and 12-vertex *closo* boron clusters are reported. Salts of *closo*-B<sub>10</sub>I<sub>10</sub><sup>2-</sup>, 1-carba-*closo*-CHB<sub>9</sub>H<sub>4</sub>I<sub>5</sub><sup>-</sup>, 1-carba-*closo*-CB<sub>11</sub>H<sub>6</sub>I<sub>6</sub><sup>-</sup>, 1-carba-*closo*-CHB<sub>11</sub>I<sub>11</sub><sup>-</sup>, and B<sub>12</sub>I<sub>12</sub><sup>2-</sup> were prepared in yields of 80% or better. All molecules were characterized by NMR and IR spectroscopy and mass spectrometry. The crystal structure of [Et<sub>4</sub>N][CHB<sub>9</sub>H<sub>4</sub>I<sub>5</sub>] was determined by single crystal X-ray diffraction. This salt crystallizes in the monoclinic *P*2(1)/*c* space group, *a* = 9.74427(12) Å, *b* = 20.7512(2) Å, *c* = 13.06589(17) Å, *b* = 101.2176(12)°, *V* = 2591.52(6) Å<sup>3</sup>, *Z* = 4, and *r*<sub>c</sub> = 2.262 g/cm<sup>3</sup>.

**Keywords:** carboranes, boron clusters, iodination, microwave synthesis

## Introduction

Iodinated boron anions are valuable as weakly-coordinating anions,<sup>[1,2]</sup> and as precursors for cross-coupling reactions.<sup>[3–8]</sup> Heavily iodinated boron clusters have been investigated as alternatives to organoiodine contrast agents for X-ray imaging, due to the higher iodine-carrying capacity of the boron clusters and their greater *in vivo* stability which results, in part, from the greater relative strength of boron-iodine vs. carbon-iodine bonds.<sup>[9–11]</sup>

Electrophilic substitution has been employed in the preparation of iodinated derivatives of boron clusters, including *closo*-B<sub>10</sub>H<sub>10</sub><sup>2-</sup> (**1**), *closo*-B<sub>12</sub>H<sub>12</sub><sup>2-</sup> (**2**), 1-carba-*closo*-CHB<sub>11</sub>H<sub>11</sub><sup>-</sup> (**3**), and 1-carba-*closo*-CHB<sub>9</sub>H<sub>9</sub><sup>-</sup> (**4**). These molecules react readily with iodine in dilute solutions at ambient temperature, and the preparation of monoiodinated products is straightforward. However, each attached iodine atom deactivates these boron clusters toward further reactions, and the preparation of highly iodinated clusters (e.g., periodinated at boron) is a challenge. Forceful conditions have been employed to prepare the partly iodinated clusters 1-Ph-CHB<sub>9</sub>H<sub>4</sub>I<sub>5</sub><sup>-</sup> (**12**) and CHB<sub>11</sub>H<sub>5</sub>I<sub>6</sub><sup>-</sup> (**3b**),<sup>[13]</sup> and the periodinated clusters CHB<sub>11</sub>I<sub>11</sub><sup>-</sup> (**3a**),<sup>[9,14]</sup> B<sub>12</sub>I<sub>12</sub><sup>2-</sup> (**2a**),<sup>[15]</sup> B<sub>10</sub>I<sub>10</sub><sup>2-</sup> (**1a**),<sup>[15]</sup> and CHB<sub>9</sub>I<sub>9</sub><sup>-</sup> (**4a**)<sup>[16]</sup>; however, reported approaches have several drawbacks. Typical protocols require heating for multiple days and careful exclusion of oxygen and moisture. Iodine

monochloride, a stronger electrophile than I<sub>2</sub>, is employed for the majority of these reactions. However, the use of ICl risks the formation of chlorinated byproducts and, in attempts to iodinate *closo*-CB<sub>9</sub><sup>-</sup>, heating with ICl gave CHB<sub>9</sub>Cl<sub>9</sub><sup>-</sup> as the exclusive product.<sup>[16]</sup> The reactivity of I<sub>2</sub> has been enhanced by using triflic acid as the solvent, but aggressive heating (>180°C) for several days in sealed heavy-walled glass tubes is still required for reactions to complete.

Microwave irradiation (MWI) has been shown to promote reactions of anionic boron clusters, including electrophilic methylation<sup>[17]</sup> and transition metal-catalyzed cross-coupling reactions.<sup>[5,6]</sup> In this work, a convenient MWI iodination procedure was developed and employed in the synthesis of a family of heavily iodinated 10- and 12-vertex anionic borane and carborane clusters.

## Experimental

### General

All carboranes and boranes prepared are air and moisture stable at room temperature. Except where noted otherwise, reactions were carried out without special measures to exclude air or moisture. All microwave reactions were performed in sealed vials in a Biotage Initiator reactor. Cs[CHB<sub>11</sub>H<sub>11</sub>], Cs[CHB<sub>9</sub>H<sub>9</sub>], and [Et<sub>4</sub>N]<sub>2</sub>[B<sub>10</sub>H<sub>10</sub>] were prepared from decaborane (UCHEM Shanghai, Ltd., China) according to published methods.<sup>[18–20]</sup> Cs<sub>2</sub>B<sub>12</sub>H<sub>12</sub> was purchased from Strem Chemical. Iodine was purchased from Malinkrodt Pharmaceuticals and ICl was purchased from Alfa Aesar. All other chemicals were purchased from Aldrich Chemical Co. and used as received unless noted otherwise. <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C, NMR spectra were collected at 25°C in

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a Bruker Avance III 400 MHz spectrometer operating at 128.37 MHz ( $^{11}\text{B}$ ), 400.13 MHz ( $^1\text{H}$ ), and 100.62 MHz ( $^{13}\text{C}$ ). All samples were dissolved in acetone- $d_6$  and referenced to TMS ( $^1\text{H}$  and  $^{13}\text{C}$ ) and  $\text{BF}_3\cdot\text{OEt}_2$  ( $^{11}\text{B}$ ). IR spectra were collected on a Thermo Nicolet Avatar 360 FT-IR from pressed KBr pellets. Mass spectra were collected by ESI-MS on an Agilent 1620 Quadrupole MS in negative ion mode over a range of  $m/z = 100\text{--}2000$ . Elemental analyses were performed by Micro Analysis, Inc. (Wilmington, DE).

### Syntheses

**Synthesis of tetraethylammonium 1,2,3,4,5,6,7,8,9,10-decaiodo-closo-decaborate  $[\text{Et}_4\text{N}]_2$  **1a**.** A 5 mL microwave vial was loaded with  $[\text{Et}_3\text{NH}]_2$  **1** (0.10 g, 0.31 mmol),  $\text{I}_2$  (0.80 g, 3.2 mmol), and 5 mL of acetic acid. After heating to  $180^\circ\text{C}$  for 45 min, the reaction was verified complete by  $^{11}\text{B}$  NMR, and a light-colored precipitate had settled from the brown reaction solution. The reaction contents were diluted with 5 mL of water and *ca.* 2 mL of a 5% aqueous  $\text{Na}_2\text{SO}_3$  solution was added dropwise until the brown color of iodine disappeared, leaving a yellow solution with a white precipitate.  $\text{Et}_4\text{NBr}$  (0.11 g, 0.52 mmol, 2 eq.) dissolved in 2 mL of water was added, and the solution was cooled to  $0^\circ\text{C}$ . The solid was collected by vacuum filtration, washed with 10 mL of water, and dried overnight in air at ambient temperature, followed by 24 h in an oven at  $120^\circ\text{C}$  to give  $[\text{Et}_4\text{N}]_2$  **1a**, (0.42 g, 0.254 mmol, 82%).  $^{11}\text{B}$  NMR (acetone,  $\delta$  ppm)  $-2.6$  [s, 2B (B1, B10)],  $-19.8$  [s, 8B, (B2-B9)] MS (isotopic abundance, note: half molecular masses were observed,  $m/z$ , for  $z = 2$ ), calcd. for  $\text{B}_{10}\text{I}_{10}^{2-}$  688 (66), 688.5 (100), 689 (90); Found 688 (86), 688.5 (100), 689 (65). Anal Calcd. for  $\text{C}_{16}\text{H}_{40}\text{B}_{10}\text{N}_2\text{I}_{10}$ : C 11.74; H 2.46; N 1.71; I 77.49; Found: C 10.25; H 2.37; N 1.78; I 77.20. IR (KBr;  $\text{cm}^{-1}$ ) 3119 (m), 2975 (m), 2764 (m), 1455 (s), 1390 (m), 1079 (m), 928 (s), 818(m).

**Synthesis of tetraethylammonium 1,2,3,4,5,6,7,8,9,10,11,12-dodecaiodo-closo-dodecaborate  $[\text{Et}_4\text{N}]_2$  **2a**.** A 20 mL microwave vial was loaded with  $[\text{Cs}]_2$  **2** (0.10 g, 0.26 mmol),  $\text{I}_2$  (2.11 g, 8.31 mmol), and 10 mL of acetic acid and was heated to  $230^\circ\text{C}$  for 2.5 h. The contents of the vial were quenched with 1.8 g of  $\text{Na}_2\text{SO}_3$  dissolved in 50 mL of water to give a clear yellow solution that contained a black precipitate. The solid was removed by filtration and a solution of  $[\text{Et}_4\text{N}][\text{Br}]$  (0.10 g [0.47 mmol]) in 2 mL of water was added, giving a yellow precipitate. This precipitate was collected by vacuum filtration and washed with 10 mL water and dried overnight in air at ambient temperature, followed by 24 hours in an oven at  $120^\circ\text{C}$  to give  $[\text{Et}_4\text{N}]_2$  **2a** (0.46 g, 0.24 mmol, 96%).  $^{11}\text{B}$  NMR (acetone,  $\delta$  ppm)  $-15.7$  [s, 12B (B1-B12)]. IR (KBr;  $\text{cm}^{-1}$ ) 3002 (m), 2981 (m), 2942 (m), 1455 (s), 1390 (m), 1168 (m), 997(m), 926 (s), 782 (m). MS (isotopic abundance, note: half molecular masses were observed,  $m/z$ , for  $z = 2$ ) calcd. for  $\text{B}_{12}\text{I}_{12}^{2-}$  825.5 (46), 826 (82), 826.5 (100), 827 (74); Found 825.5 (40), 826 (89), 826.5 (100), 827(71).

**Synthesis of tetramethylammonium 2,3,4,5,6,7,8,9,10,11,12-undecaiodo-1-carba-closo-dodecaborate(1-)  $[\text{Me}_4\text{N}]$  **3a**.** A 5 mL microwave vial was loaded with  $[\text{Cs}]$  **3** (0.24 g,

0.88 mmol) and  $\text{ICl}$  (13.02 g, 80.1 mmol) and was heated at  $120^\circ\text{C}$  for 75 min. The contents of the vial were transferred into a round bottom flask with 20 mL dichloromethane. Dichloromethane and excess iodine monochloride were removed under vacuum at  $100^\circ\text{C}$ , to give a dark brown solid. The solid was treated with aqueous  $\text{NaOH}$  (5%, 30 mL) and aqueous  $\text{NaHSO}_3$  (10%, 15 mL) and extracted with diethyl ether ( $4 \times 20$  mL). The combined ether extracts were concentrated *in vacuo* to give an orange oil.  $\text{Me}_4\text{NCl}$  (0.35 g, 3.2 mmol) in 10 mL water was added, and a white precipitate formed immediately. This solid was collected by vacuum filtration, washed with 100 mL water, followed by 50 mL hexanes, and dried overnight in air at ambient temperature, followed by 24 h in an oven at  $120^\circ\text{C}$  to give  $[\text{Me}_4\text{N}]$  **3a** (1.23 g, 0.769 mmol, 87.3%).  $^{11}\text{B}$  NMR (acetone,  $\delta$  ppm)  $-7.5$  [s, 1B (B12)],  $-11.9$  [s, 5B (B2-B6)],  $-18.8$  [s, 5B (B7-B11)]. IR (KBr;  $\text{cm}^{-1}$ ) 2999 (m), 1478 (s), 1098 (m), 917 (s). MS (isotopic abundance) calcd. for  $\text{CHB}_{11}\text{I}_{11}^-$  1527 (74), 1528 (100), 1529 (81); Found 1527 (75), 1528 (100), 1529 (83).

**Synthesis of cesium 7,8,9,10,11,12-hexaiodo-1-carba-closo-dodecaborate(1-)  $[\text{Cs}]$  **3b**.** A 20 mL microwave vial was loaded with  $[\text{Cs}]$  **3** (0.25 g, 0.91 mmol),  $\text{I}_2$  (4.60 g, 18.1 mmol), and glacial acetic acid (10 mL) to give a dark brown solution that was heated to  $225^\circ\text{C}$  for 75 min.  $^{11}\text{B}$  NMR verified reaction completion. Excess iodine was quenched with saturated aqueous  $\text{Na}_2\text{SO}_3$  (10 mL) to give a yellow solution. The solution was extracted with diethyl ether ( $4 \times 15$  mL). The combined ether extracts were concentrated *in vacuo* to give a brown oil. A solution of  $\text{CsCl}$  (2.0 g, 12 mmol) in 2 mL of water was added to the oil, and a tan precipitate formed immediately. This solid was collected by vacuum filtration, washed with water, and dried overnight in air at ambient temperature followed by 24 h in an oven at  $120^\circ\text{C}$  to give  $[\text{Cs}]$  **3b** (0.82 g, 0.79 mmol, 87.1%).  $^{11}\text{B}$  NMR (acetone,  $\delta$  ppm)  $-6.8$  [s, 1B (B12)],  $-14.8$  [d, 5B (B2-B6)],  $-19.1$  [s, 5B (B7-B11)]. IR (KBr;  $\text{cm}^{-1}$ ) 3040 (m), 2601 (vs), 1605 (m), 918 (s), 853 (vs), 622 (m). MS (isotopic abundance) calcd. for  $\text{CB}_{11}\text{H}_6\text{I}_6^-$  898(74), 899(100), 900(82); Found 898 (76), 899(100), 900(84).

**Synthesis of tetraethylammonium 6,7,8,9,10-pentaiodo-1-carba-closo-decaborate(1-)  $[\text{Et}_4\text{N}]$  **4b**.** A 5 mL microwave vial was loaded with  $\text{Cs}$  **4** (0.10 g, 0.40 mmol),  $\text{I}_2$  (0.60 g, 2.4 mmol), and 5 mL of acetic acid. After heating to  $220^\circ\text{C}$  for 45 min, the reaction was verified complete by  $^{11}\text{B}$  NMR. To this solution, *ca.* 2 mL of a 5% aqueous  $\text{Na}_2\text{SO}_3$  was added dropwise, and 5 mL water were added to give a white solid suspended in a yellow solution. Extraction with diethyl ether ( $4 \times 15$  mL), followed by concentration of the combined ether extracts *in vacuo* gave a brown oil. A solution of  $\text{Et}_4\text{NBr}$  (0.092 g, 0.44 mmol) in 2 mL of water was added to the oil, and a white precipitate formed immediately. The solid was collected by vacuum filtration, washed with 20 mL of water, and dried overnight in air at ambient temperature, followed by 24 h in an oven at  $120^\circ\text{C}$  to give  $[\text{Et}_4\text{N}]$  **4b**, 0.29 g, (84%).  $^{11}\text{B}$  NMR (acetone,  $\delta$  ppm) 17.7 [s, 1B (B10)],  $-11.5$  [d, 4B, (B2-B5)],  $-24.1$  [s, 4B, (B6-B9)]. IR (KBr;  $\text{cm}^{-1}$ ) 3091 (m), 3002

(m), 2986 (m), 2974 (m), 2579 (vs), 1479 (s), 1435 (s), 1390 (s), 1169 (m), 1061 (m), 953 (s), 782 (s) 606 (m). Anal. Calcd. for  $C_9H_{25}B_9NI_5$ : C 12.30; H 2.87; N 1.59; I 72.18; Found: C 12.35; H 2.91; N 1.60; I 70.66. MS (isotope abundance) calcd. for  $CB_9H_5I_5^-$  748 (57), 749 (98), 750 (100), 751 (46); Found 748 (56), 749 (97), 750 (100), 751 (50).

### X-Ray Crystallography

Crystals of  $[Et_4N] \mathbf{4b}$  were grown by slow evaporation of an acetone/water solution and single crystals were selected under a light microscope. A colorless prism ( $0.23 \times 0.17 \times 0.13 \text{ mm}^3$ ) was mounted with a 0.05 mm diameter polyethylene loop (Hampton Research, Aliso Viejo, CA) using NVH oil (Hampton Research). Diffraction measurements were conducted at 298(1) K with an Agilent Xcalibur Nova sealed tube microfocus X-ray source (50 kV/0.8 mA) using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ , 300  $\mu\text{m}$  beam diameter) and an Agilent Onyx CCD detector set 65.0000 mm from the sample ( $2 \times 2$  binning with correlated images).

Data were collected using CrysAlisPRO v171.35.21<sup>[21]</sup> using a strategy based on Laue symmetry 2/m, which was suggested by a short pre-experiment. A total of 1223 frames were collected using a frame width of  $1.000^\circ$  with exposure times of 5.420 or 21.700 s. The data were integrated with CrysAlisPRO v171.35.21, and an empirical absorption correction was applied using ABSPACK ( $\mu = 47.36 \text{ mm}^{-1}$ ; max/min transmission 1.000/0.09614). There were 17,032 total reflections at a maximum  $2\theta$  of  $67.0800$  ( $0.84 \text{ \AA}$  resolution), of which 4637 were independent ( $R_{int} = 0.0845$ ,  $R_{sig} = 0.0479$ , redundancy = 3.7, completeness = 99.98%) and 4,043 reflections (87%) were greater than  $2\sigma(I)$ . Intensity statistics strongly indicated a centric space group, which was  $P2_1/c$ . The unit cell parameters were  $a = 9.74427(12) \text{ \AA}$ ,  $b = 20.7512(2) \text{ \AA}$ ,  $c = 13.06589(17) \text{ \AA}$ ,  $\beta = 101.2176(12)^\circ$ ,  $V = 2591.52(5) \text{ \AA}^3$ ,  $Z = 4$  calculated density  $D_c = 2.262 \text{ g/cm}^3$ .

Olex2<sup>[22]</sup> was used for phase determination and refinement with easily identifiable non-hydrogen peaks for initial model building. Atomic coordinates and isotropic and anisotropic displacement parameters of non-hydrogen atoms were refined via full matrix least-squares on intensities. Hydrogen atoms were added geometrically, riding on the atoms to which they were attached. The refinement converged with  $R_1 = 0.0845$  for intensity  $I > 2\sigma(I)$  and  $wR_2 = 0.2412$  for all data. The largest difference peak/hole was  $2.9/-2.2 \text{ e/\AA}^3$ .

The assignment of electron density in a peak near B19 to an iodine atom with a partial chemical occupancy of 3% was found to improve  $R_1$  for the refined model. This can be explained by slight overiodination of  $\mathbf{4}$  during the preparation of  $\mathbf{4b}$ , and resulting contamination by a small quantity of  $CHB_9H_5I_6^-$ .

## Results and Discussion

### Syntheses

We report here the preparation of heavily iodinated boron and carborane cluster anions in yields of 82–96% using microwave irradiation (MWI). Iodination reactions carried out under MWI showed a dramatic increase in rate compared

**Table 1.** Results of MWI iodination reactions of borane and carborane anions

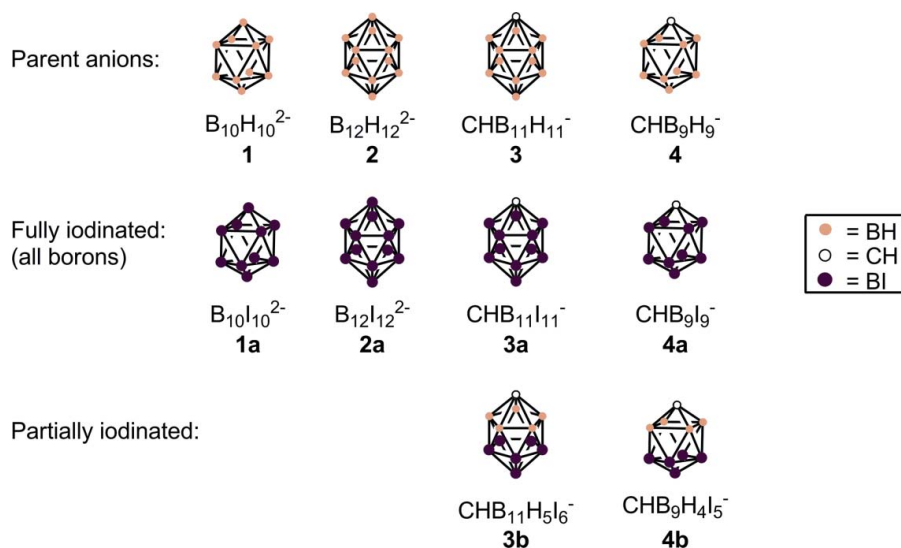
Compound	Iodine Source (Solvent)	Time	Temp. (MWI)	Yield
$B_{10}I_{10}^{2-}$	$I_2$ (HOAc)	45 min	180°C	82%
$B_{12}I_{12}^{2-}$	$I_2$ (HOAc)	2.5 h	230°C	96%
$CHB_{11}H_5I_6^-$	$I_2$ (HOAc)	75 min	225°C	87%
$CHB_{11}I_{11}^-$	ICl (neat)	75 min	120°C	87%
$CHB_9H_4I_5^-$	$I_2$ (HOAc)	45 min	220°C	84%

to conventionally heated reactions. For example, the undeca-iodination of  $\mathbf{3}$ , which requires 48 h of heating with ICl in a sealed tube, proceeds 40 times more rapidly under MWI, and is complete within 75 min. All of the MWI iodination reactions were complete in 2.5 h or less, and the yield of each reaction is comparable or higher than published conventionally heated reactions. Results for all reactions are listed in Table 1.

With conventional heating, elemental iodine only adds a limited number of iodine atoms to the boron clusters in this study (Figure 1). The use of triflic acid as a catalyst and solvent has been shown to increase the reactivity of  $I_2$ ; however, triflic acid is extremely sensitive to moisture and its removal by distillation (bp =  $162^\circ\text{C}$ ) complicates the workup. MWI was found to extend the limit to iodine's use as an iodination agent and avoid or reduce the need for triflic acid. The dianionic borane cluster  $\mathbf{1}$  could be periodinated in under 45 min by MWI using elemental iodine in acetic acid. Similarly,  $\mathbf{2}$  was fully iodinated using iodine in acetic acid in 2.5 h.

**Table 2.** Crystallographic data and structure refinement summary for  $[Et_4N] \mathbf{4b}$

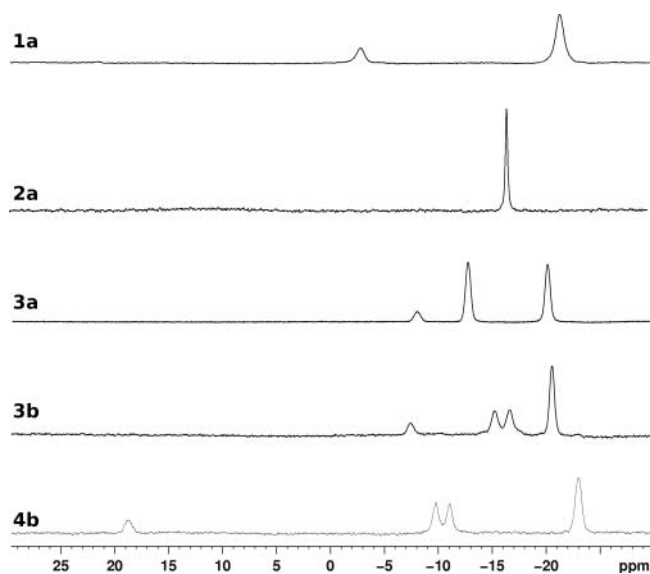
Empirical formula	$C_9H_{25}B_9NI_{11}$
Formula weight	882.99
Crystal system, Space group	Monoclinic, $P2_1/c$
Unit cell dimensions	$a = 9.74427(12)$ $b = 20.7512(2)$ $c = 13.06589(17)$ $a = 90$ $b = 101.2176(12)$ $\gamma = 90$
Volume ( $\text{\AA}^3$ )	2591.52(6)
$Z$	4
Calculated density	2.262
Independent reflections	4637
$F(000)$	1594
$q$ range for data collection	4.05–67.080
Limiting indices	$-11 < h < 11$ , $0 < k < 24$ , $0 < l < 15$
Goodness-of-fit on $F^2$	1.030
$R_1$ , $wR_2$ , $[I > 2\sigma(I)]$	0.0845, 0.2272
$R_1$ , $wR_2$ (all data)	0.0904, 0.2412
Largest diff. peak and hole ( $\text{e/\AA}^3$ )	2.9042 and $-2.1687$



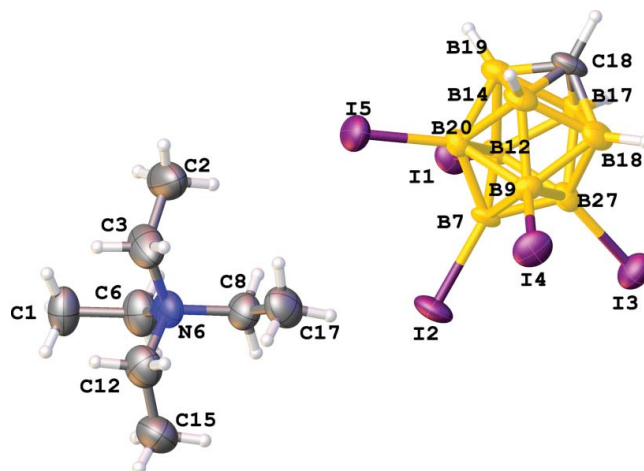
**Fig. 1.** Example parent and iodinated 10- and 12-vertex borane and carborane anions.

Compared to the dinegative borane clusters, the monocarborane anions are less reactive. The MWI reaction of **3** with  $I_2$  in acetic acid regioselectively iodinate only six of the eleven boron vertices, yielding **3b** as the exclusive product. The degree of iodination observed using  $I_2$  under MWI is unprecedented in reactions of **3**, where reports indicate that a maximum of two iodine atoms can be introduced using  $I_2$ .<sup>[23]</sup> The five identical boron atoms adjacent to the apical carbon in **3** are the least amenable to electrophilic substitution.  $^{11}B$  NMR and mass spectra taken for reaction aliquots indicate that iodination of these positions does proceed slowly under MWI, but periodination of all boron vertices was not complete after extended (>24 h) heating with  $I_2$  in acetic acid. However, rapid iodination of all boron vertices in **3** can be achieved by using ICl under MWI, and **3a** was obtained as the sole product in 75 min.

MWI reactions of **4** with iodine in acetic acid gave the penta-iodo species **4b**, with iodination occurring regioselectively at the five borons most distant from the cluster carbon (i.e., positions B6–B10). The preparation of periodinated anion **4a** was attempted as well.  $^{11}B$  NMR monitoring of MWI reactions of **4** using  $I_2$  in acetic acid or in 1,1,2,2-tetrachloroethane indicated that iodination proceeded slowly beyond 5-fold iodination, but extended heating (>12 h) led to gradual degradation of the cluster. Reactions conducted using iodine in triflic acid or sulfuric acid resulted in significant decomposition as well. The use of ICl was explored, and this gave partial iodination of **4** at room temperature, and convergence of the reaction to **4b** was indicated by  $^{11}B$  NMR after 30 min (Figure 2). Heating was required to introduce additional iodine atoms, but MWI heating of solutions of **4** with ICl (or with  $I_2/AlCl_3$ ) led instead to chlorination, giving  $CHB_9Cl_9^-$  as the dominant product after 30 min of MWI heating at



**Fig. 2.**  $^{11}B$  NMR spectra of iodinated boron clusters.



**Fig. 3.** Molecular structure of  $[Et_4N]$  **4b**. The thermal ellipsoids are drawn at 40% probability.

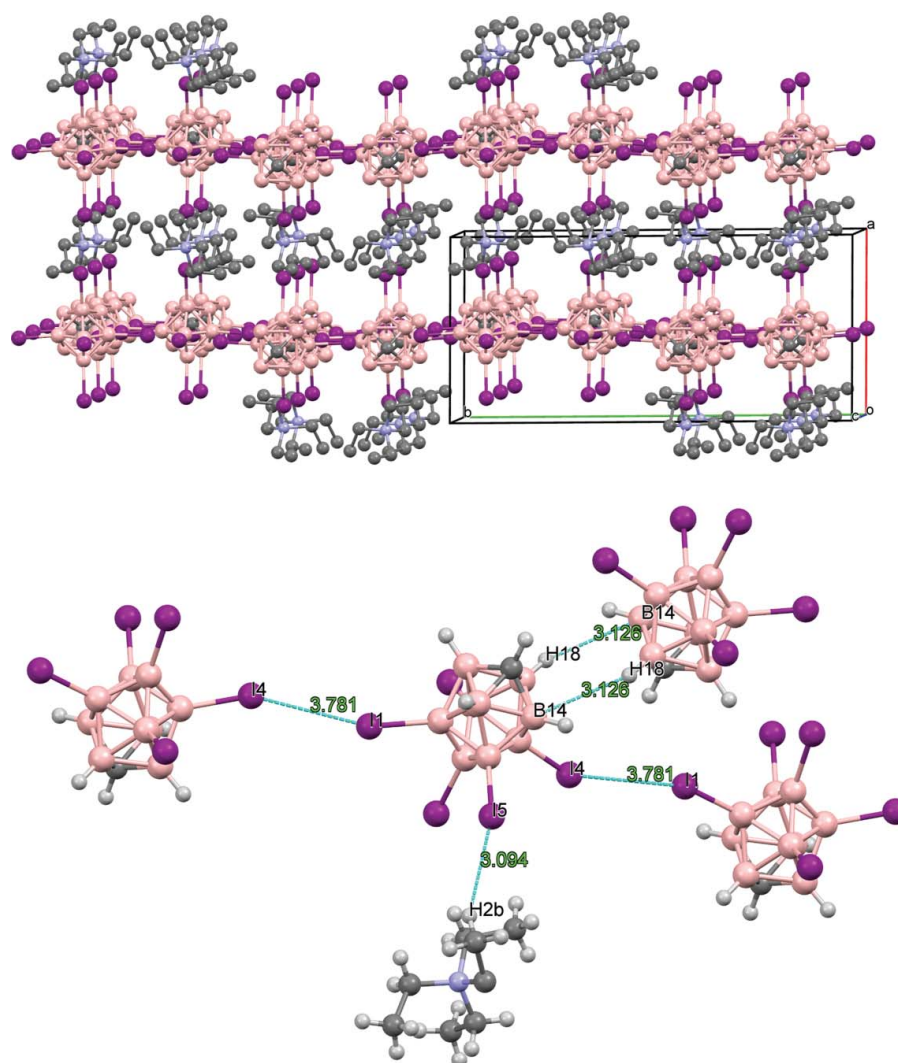
**Table 3.** Selected bond distances (Å) and angles (°) of [Et<sub>4</sub>N] **4b**

Bond	Distance (Å)	Bond	Angle (°)
I2—B7	2.1423 (4)	B17—B18—B14	90.86 (2)
I5—B20	2.1499 (3)	B17—B19—B14	88.996 (19)
B9—I4	2.1634 (5)	B19—B14—B18	90.55 (2)
B12—I1	2.1565 (5)	B19—B17—B18	89.591 (19)
B27—I27a	2.1625 (3)	B12—B20—B9	89.963 (16)
B9—B20	1.8165 (4)	B12—B27—B9	89.849 (16)
B9—B27	1.8339 (4)	B27—B9—B20	90.62 (2)
B12—B20	1.8488 (4)	B27—B12—B20	89.57 (2)
B12—B27	1.8351 (4)		
B14—B18	1.8166 (3)		
B14—B19	1.8612 (6)		
B17—B18	1.8466 (6)		
B17—B19	1.8623 (3)		

Notably, none of the other boron clusters in the present study gave chlorinated products when reacted with ICl.

### Crystal Structure of [Et<sub>4</sub>N] **4b**

The penta-iodinated species **4b** was isolated in 84% yield as a tetraethylammonium salt and high quality crystals of this salt were characterized by X-ray crystallography (Table 2). In the crystal structure, **4b** has near  $C_{4v}$  symmetry (Figure 3). The four chemically-equivalent iodines attached to each boron in the lower belt (i.e., B9, B12, B20, B27) of the anion have an average B-I distance of 2.158 Å, and the unique iodine at the antipodal boron (B7) has a slightly shorter B-I bond of 2.142 Å (Table 3). The lower belt of borons is square planar, with an average distance of 1.845 Å between neighboring borons, B-B-B bond angles of  $90 \pm 0.6^\circ$ , and a maximum torsional angle of  $0.38^\circ$ . The geometry of the upper belt of boron atoms is nearly identical, with an average B-B bond length of 1.847 Å, B-B-B bond angles of  $90 \pm 1.0^\circ$ , and a maximum torsional angle of  $0.47^\circ$ .



**Fig. 4.** Top: crystal packing of [Et<sub>4</sub>N] **4b**, viewed along the *c* crystallographic axis. Bottom: coordination environment of **4b** within the 3D structure.



In the three-dimensional extended structure, each anion contacts three others, forming an approximately planar network perpendicular to the *a* crystallographic axis (Figure 4). Tetraethylammonium cations are arranged in planes that alternate with the anion layers. The anions and cations weakly associate with each other in the structure. The closest contact between these is 3.09 Å between I4 on **4b** and H15a on the tetraethylammonium cation, a distance slightly less than the sum of the van der Waals radii for these atoms (3.18 Å).

## Conclusions

We report here a MWI iodination method for borane and carborane cluster anions, which was used to prepare heavily iodinated derivatives of *closo*-B<sub>10</sub>H<sub>10</sub><sup>2-</sup>, *closo*-B<sub>12</sub>H<sub>12</sub><sup>2-</sup>, 1-carba-*closo*-CHB<sub>9</sub>H<sub>9</sub><sup>-</sup>, 1-carba-*closo*-CHB<sub>11</sub>H<sub>11</sub><sup>-</sup>. These boron clusters were characterized by <sup>11</sup>B NMR, IR, and MS, and the crystal structure of [Et<sub>4</sub>N][CHB<sub>9</sub>H<sub>4</sub>I<sub>5</sub>] was determined by X-ray crystallography.

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