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Synthesis and Structural Characterization of $[(CH_3)_3NH][$*nido*$\text{-}9,11\text{-}I_2\text{-}7,8\text{-}C_2B_9H_{10}]$ and $[(CH_3)_3NH][$*nido*$\text{-}9\text{-}I\text{-}7,8\text{-}C_2B_9H_{11}]$

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Introduction

Electrophilic halogenation of the boron atom vertices of *closo*-carboranes is a well-known reaction[1] which leads to a variety of isomeric products containing fluoro,[2] bromo,[3] chloro,[4] and iodo[5] substituents. Few halogenated *nido*-carborane compounds are known. Among the halogenated *nido*-carboranes,[6−8] the products of the relatively rapid electrophilic attack by formal I^+ upon the open face of the *nido*-$[7,8\text{-}C_2B_9H_{12}]^-$ ion and its derivatives have been most widely studied.

The use of these easily formed iodinated *nido*-carborane derivatives as both radioiodine carriers and as potential boron neutron capture therapy (BNCT) reagents[7] remains under investigation. Earlier structural characterization[6] of halogenated *nido*-carborane anions was performed by ^{11}B NMR, and only one single-crystal X-ray diffraction study of an iodinated *nido*-carborane anion has been reported.[7] This fact coupled with the recent interest in the presence of $\{BH_2\}$ vertices in certain *nido*-carborane anions[9−12] prompted us to investigate the structures of $[(CH_3)_3NH][$*nido*-$9,11\text{-}I_2\text{-}7,8\text{-}C_2B_9H_{10}]$ (**1**) and $[(CH_3)_3NH]$-$[$*nido*-$9\text{-}I\text{-}7,8\text{-}C_2B_9H_{11}]$ (**2**) using X-ray diffraction methods. We here report the first synthesis and structural characterization of a diiodinated *nido*-carborane anion (**1**) which contains an *endo* B-H bond in the open five-membered face, as well as the structure of the previously reported[6] monoiodinated *nido*-carborane anion (**2**).

Experimental Section

Reagents were purchased from Aldrich Chemical Co., Milwaukee, WI. The compounds $[(CH_3)_3NH][$*nido*-$7,8\text{-}C_2B_9H_{12}]$[13,14] and $[(CH_3)_3$-$NH][$*nido*-$9\text{-}I\text{-}7,8\text{-}C_2B_9H_{11}]$ (**2**),[6] were obtained by literature methods. The ^{11}B NMR spectra (160.4 MHz) were obtained using a Bruker AM 500 spectrometer. Boron chemical shift values were externally referenced to $BF_3{\cdot}OEt_2$ in $CDCl_3$ and resonances upfield of the standard are designated as negative. High resolution fast atom bombardment (FAB^-) mass spectral data were obtained by the UCLA Center for Molecular and Medical Sciences Mass Spectrometry using a VG ZAB-SE instrument (Fisons Instruments, VG Analytical, Manchester, U.K.).

Synthesis of $[(CH_3)_3NH][$*nido*$\text{-}9,11\text{-}I_2\text{-}7,8\text{-}C_2B_9H_{10}]$ (1). In a 250 mL round-bottom flask was placed a magnetic stir bar, $[(CH_3)_3NH]$-$[$*nido*-$7,8\text{-}C_2B_9H_{12}]$ (1.0 g, 5.15 mmol), and 50 mL of MeOH. A solution of I_2 (3.268 g, 12.88 mmol, 2.5 eq) in 50 mL of MeOH was added to the reaction flask, and the mixture was refluxed overnight. Addition of 25 mL of H_2O and subsequent evaporation of the MeOH/H_2O solvent resulted in the precipitation of a white crystalline solid from the aqueous layer. Recrystallization from boiling H_2O yielded 2.030 g (88.0%) of product. Mp: 140−141 °C. $^{11}B\{^1H\}$ NMR (EtOH, ppm): −13.9 (2B, B−H), −16.6 (1B, B−H), −19.6 (2B, B−H), −21.2 (2B, B−I), −29.2 (1B, B−H), −36.5 (1B, B−H). HRMS (FAB^-) calculated for $C_2B_9H_{10}I_2$: 384.9783 (calcd); 384.9780 (obsd) ($\Delta = 0.3$ mmu, 0.8 ppm).

X-ray Structural Characterization of 1. A colorless crystal, obtained from a $EtOH/H_2O$ solution, was mounted on a fiber with epoxy cement and placed on a Huber diffractometer constructed by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 50 accurately centered reflections ($9.7° < 2\theta < 20.4°$). The crystallographic data are summarized in Table 1. Data were collected at 25 °C in the $\theta-2\theta$ scan mode. Intensities of three reflections were monitored and did not decay during the course of the experiment. Of the 2808 unique reflections measured, 2425 were considered observed and were used in the subsequent structure analysis. Atoms were located by use of heavy atom methods. All nonhydrogen atoms were refined with anisotropic parameters. Positions of H were refined. H atoms were assigned isotropic displacement values based approximately on the value for the attached atom. Positional and thermal parameters for selected atoms are given in Table 2. Selected bond lengths and bond angles are given in Table 4. Species **1** contains a nido 11-vertex icosahedral fragment comprised of two terminal iodine atoms, nine terminal hydrogen atoms, and one hydrogen atom bonded to an open face boron atom and directed toward the empty twelfth vertex.

X-ray Structural Characterization for 2. A colorless crystal, obtained from a H_2O solution, was mounted on a fiber with epoxy and placed on a Huber diffractometer constructed by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 25 accurately centered reflections ($9.7° < 2\theta < 18.7°$). Selected crystallographic data are summarized in Table 1. Data were collected at 25 °C in the $\theta-2\theta$ scan mode. Intensities of three reflections were monitored and did not decay during the course of the experiment. Of the 2399 unique reflections measured, 1312 were considered observed ($I > 3.0\sigma(I)$) and were used in the subsequent structure analysis. Atoms were located by use of heavy atom methods. The structure of the C_2B_9 fragment is a 12-vertex icosahedron because of disorder involving the C(8) position. This atom has been refined at 0.65% and 0.35% occupancy for atoms labeled C(8) and C(8′) respectively. These are the only non-hydrogen atoms not refined with anisotropic parameters. Despite the noncentrosymmetric space group, this disorder allows the crystal to contain a racemic mixture of anions. Positions of cage hydrogen atoms and the H on nitrogen were refined. All other hydrogen atoms were included in calculated positions with C−H = 1.0 Å. Hydrogen atoms were assigned isotropic displacement values based approximately on the value for the attached atom. Final positional and thermal parameters for nonhydrogen and selected hydrogen atoms are given in Table 3. Selected bond lengths and bond angles are given in Table 5. Further crystallographic details, hydrogen atom parameters, and anisotropic thermal parameters are available as supplementary material.

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(1) Grimes, R. N. *Carboranes*; Academic Press: New York, NY, 1970.

(2) (a) Roscoe, J. S.; Kongprich, S. *Inorg. Chem.* **1970**, *9*, 1561. (b) Lebedev, V. N.; Balagurova, E. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T.; Zakharkin, L. I. *J. Organomet. Chem.* **1990**, *385*, 307.

(3) Zakharkin, L. I.; Ol'shevskaya, V. A.; Poroshina, T. Yu.; Balagurova, E. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1987**, *57*, 1800. Translated from: *Zh. Obshch. Khim.* **1987**, *57* (9), 2012.

(4) Zakharkin, L. I.; Kalinin, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, *11*, 2577.

(5) Li, J.; Logan, C. F.; Jones, Jr., M. *Inorg. Chem.* **1991**, *30*, 4866.

(6) Olsen, F. P.; Hawthorne, M. F. *Inorg. Chem.* **1965**, *4*, 1839.

(7) Mizusawa, E. A.; Thompson, M. R.; Hawthorne, M. F. *Inorg. Chem.* **1985**, *24*, 1911.

(8) Tomita, H.; Luu, H.; Onak, T. *Inorg. Chem.* **1991**, *30*, 812.

(9) Buchanan, J.; Hamilton, E. J. M.; Reed, D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 677.

(10) Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Nestor, K.; Thornton-Pett, M.; Hermanek, S.; Jelinek, T.; Stibr, B. *J. Chem. Soc., Dalton Trans.* **1990**, 681.

(11) Beck, J. S.; Quintana, W.; Sneddon, L. G. *Organometallics* **1988**, *7*, 1015.

(12) Getman, T. D.; Krause, J. A.; Shore, S. G. *Inorg. Chem.* **1988**, *27*, 2399.

(13) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 2295.

(14) Hawthorne, M. F.; Young, D. C.; Garrett, P. M.; Owen, D. A.; Schwerin, S. G.; Tebbe, F. N.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 862.

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Table 1. Selected Crystallographic Data for $[(CH_3)_3NH][\textit{nido}\text{-}9,11\text{-}I_2\text{-}7,8\text{-}C_2B_9H_{10}]$ (**1**) and $[(CH_3)_3NH][\textit{nido}\text{-}9\text{-}I\text{-}7,8\text{-}C_2B_9H_{11}]$ (**2**)

	1	**2**
empirical formula	$C_5H_{20}B_9NI_2$	$C_5H_{21}B_9NI$
fw	445	319
cryst dimens (mm)	0.15 × 0.45 × 0.48	0.04 × 0.4 × 0.22
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
a, Å	7.525(1)	6.913(1)
b, Å	10.006(1)	10.586(2)
c, Å	21.343(3)	19.592(3)
β, deg	94.685(4)	
V, Å^3	1601.74	1434
Z	4	4
T, °C	25	25
density(calcd), g/cm^{-3}	1.85	1.48
μ, cm^{-1}	38.59	21.8
resid[a]: R_F; R_w	0.027; 0.038	0.033; 0.038

[a] The functions minimized during least-squares cycles were $R_F = \Sigma(F_o - F_c)/\Sigma F_o$ and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for $[(CH_3)_3NH][C_2B_9H_{10}I_2]$ (**1**)

	x	y	z	U_{eq}[a]
B(1)	0.5484(6)	0.4518(5)	−0.2041(2)	0.046(3)
B(2)	0.4631(6)	0.5932(5)	−0.1673(2)	0.046(3)
B(3)	0.3862(7)	0.4353(5)	−0.1493(3)	0.049(3)
B(4)	0.5663(6)	0.3217(5)	−0.1489(2)	0.046(3)
B(5)	0.7587(6)	0.4113(5)	−0.1627(2)	0.042(3)
B(6)	0.6936(6)	0.5853(5)	−0.1752(2)	0.044(3)
C(7)	0.4543(5)	0.5445(5)	−0.0908(2)	0.046(3)
C(8)	0.5110(6)	0.3972(4)	−0.0798(2)	0.045(2)
B(9)	0.7192(6)	0.3747(5)	−0.0848(2)	0.042(3)
B(10)	0.8167(6)	0.5336(5)	−0.1034(2)	0.046(3)
B(11)	0.6195(6)	0.6402(4)	−0.1029(2)	0.042(3)
C(1M)	0.9084(9)	0.1472(5)	0.1570(4)	0.070(4)
C(2M)	1.0963(8)	−0.0326(7)	0.2036(3)	0.068(4)
C(3M)	0.8144(9)	−0.0858(8)	0.1416(4)	0.085(5)
N(1)	0.9715(5)	0.0070(4)	0.1501(2)	0.046(2)
I(9)	0.86881(5)	0.22116(3)	−0.02854(2)	0.062(1)
I(11)	0.62858(4)	0.85025(3)	−0.07224(2)	0.051(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for $[(CH_3)_3NH][C_2B_9H_{11}I]$ (**2**)

	x	y	z	U_{eq}[a]
I(1)	0.83734(8)	0.11143(5)	0.00822(2)	0.0548(1)
B(1)	0.5142(16)	−0.0542(11)	0.2103(5)	0.055(2)
B(2)	0.3401(18)	−0.1521(9)	0.1747(5)	0.049(2)
B(3)	0.3194(16)	0.0124(9)	0.1616(5)	0.048(2)
B(4)	0.5589(15)	0.0731(10)	0.1529(5)	0.050(2)
B(5)	0.7204(14)	−0.0534(12)	0.1562(4)	0.055(3)
B(6)	0.5855(15)	−0.1975(11)	0.1710(5)	0.054(3)
C(7)	0.2997(12)	−0.0898(9)	0.0971(4)	0.052(2)
C(8)	0.4240(20)	0.0275(13)	0.0816(7)	0.046(3)[b]
C(8′)	0.4883(36)	−0.0930(21)	0.0526(12)	0.048(6)[b]
B(9)	0.6487(14)	0.0015(9)	0.0771(4)	0.043(2)
B(10)	0.6798(19)	−0.1626(10)	0.0887(5)	0.056(3)
B(11)	0.4326(18)	−0.2180(10)	0.0986(6)	0.066(3)
N(1C)	0.9103(12)	−0.5551(8)	0.1693(4)	0.064(2)
C(1C)	1.0242(14)	−0.6751(8)	0.1718(5)	0.057(2)
C(2C)	1.0389(16)	−0.4423(9)	0.1683(6)	0.075(3)
C(3C)	0.7632(15)	−0.5524(9)	0.1123(5)	0.064(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Value for an atom refined isotropically. C(8) and C(8′) have occupanies of 0.65 and 0.35, respectively.

Results and Discussion

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) in $[(CH_3)_3NH][\textit{nido}\text{-}9,11\text{-}I_2\text{-}7,8\text{-}C_2B_9H_{10}]$ (**1**)

Bond Lengths (Å)			
I(9)−B(9)	2.203(5)	B(5)−B(6)	1.822(7)
I(11)−B(11)	2.201(5)	B(5)−B(9)	1.751(7)
B(1)−B(2)	1.764(7)	B(5)−B(10)	1.789(7)
B(1)−B(3)	1.766(7)	B(6)−B(10)	1.801(7)
B(1)−B(4)	1.754(8)	B(6)−B(11)	1.770(7)
B(1)−B(5)	1.795(7)	C(7)−C(8)	1.547(6)
B(1)−B(6)	1.802(7)	C(7)−B(11)	1.607(6)
B(2)−B(3)	1.736(7)	C(8)−B(9)	1.595(6)
B(2)−B(6)	1.758(7)	B(9)−B(10)	1.809(7)
B(2)−C(7)	1.710(7)	B(10)−B(11)	1.828(7)
B(2)−B(11)	1.798(7)	N(1)−C(1M)	1.492(6)
B(3)−B(4)	1.768(7)	N(1)−C(2M)	1.472(7)
B(3)−C(7)	1.706(7)	N(1)−C(3M)	1.503(7)
B(3)−C(8)	1.732(7)	B(10)−H(10A)	1.043(56)
B(4)−B(5)	1.748(7)	B(9)−H(10B)	1.85(5)
B(4)−C(8)	1.738(6)	B(10)−H(10B)	1.067(57)
B(4)−B(9)	1.794(7)	B(11)−H(10B)	1.497(54)
Bond Angles (deg)			
I(9)−B(9)−B(4)	118.5(3)	I(9)−B(9)−B(10)	122.3(3)
I(9)−B(9)−B(5)	123.0(3)	I(11)−B(11)−B(2)	118.7(3)
I(9)−B(9)−B(8)	121.5(3)	I(11)−B(11)−B(6)	123.5(3)
I(11)−B(11)−C(7)	121.8(3)	B(11)−C(7)−C(8)	112.6(3)
I(11)−B(11)−B(10)	123.6(3)	H(10B)−B(10)−H(10A)	111.1(41)
C(7)−C(8)−B(9)	112.6(3)	H(10B)−B(10)−B(11)	55.0(29)
C(8)−B(9)−B(10)	108.0(3)	H(10B)−B(10)−B(9)	75.2(30)
B(9)−B(10)−B(11)	99.6(3)	H(10B)−B(10)−B(5)	125.7(29)
B(10)−B(11)−C(7)	107.0(3)	H(10B)−B(10)−B(6)	111.9(29)

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) in $[(CH_3)_3NH][\textit{nido}\text{-}9\text{-}I\text{-}7,8\text{-}C_2B_9H_{11}]$ (**2**)

Bond Lengths (Å)			
I(1)−B(9)	2.209(9)	B(5)−B(10)	1.779(15)
B(1)−B(2)	1.734(16)	B(6)−B(10)	1.778(14)
B(1)−B(3)	1.795(15)	B(6)−B(11)	1.782(16)
B(1)−B(4)	1.782(15)	C(7)−C(8)	1.540(16)
B(1)−B(5)	1.776(14)	C(7)−C(8′)	1.57(3)
B(1)−B(6)	1.771(16)	C(7)−B(11)	1.639(14)
B(2)−B(3)	1.766(13)	C(8)−B(9)	1.58(2)
B(2)−B(6)	1.765(16)	C(8′)−B(9)	1.57(3)
B(2)−C(7)	1.681(12)	C(8′)−B(10)	1.67(3)
B(2)−B(11)	1.766(15)	C(8′)−B(11)	1.65(3)
B(3)−B(4)	1.784(15)	B(9)−B(10)	1.764(14)
B(3)−C(7)	1.668(13)	B(10)−B(11)	1.82(2)
B(3)−C(8)	1.733(16)	N(1C)−C(1C)	1.495(12)
B(4)−B(5)	1.744(16)	N(1C)−C(2C)	1.489(13)
B(4)−C(8)	1.748(17)	N(1C)−C(3C)	1.510(13)
B(4)−B(9)	1.779(13)	H(1BR)−B(10)	1.26(18)
B(5)−B(6)	1.812(16)	H(1BR)−B(11)	1.55(17)
B(5)−B(9)	1.726(12)		
Bond Angles (deg)			
I(1)−B(9)−B(4)	119.4(6)	I(1)−B(9)−C(8)	121.5(7)
I(1)−B(9)−B(5)	123.8(6)	I(1)−B(9)−C(8′)	124.5(10)
I(1)−B(9)−B(10)	121.7(6)	B(9)−B(10)−B(11)	102.5(7)
C(7)−C(8)−B(9)	114.8(9)	B(10)−B(11)−C(7)	104.9(8)
C(7)−C(8′)−B(9)	113.8(15)	B(11)−C(7)−C(8)	111.0(8)
C(8)−B(9)−B(10)	106.5(8)	B(11)−C(7)−C(8′)	61.7(10)
C(8′)−B(9)−B(10)	59.9(10)	B(10)−H(1BR)−B(11)	80(9)

Addition of 1 mole equiv of I_2 to an ethanol solution of $[(CH_3)_3NH][\textit{nido}\text{-}7,8\text{-}C_2B_9H_{12}]$ at room temperature resulted in the formation of $[(CH_3)_3NH][\textit{nido}\text{-}9\text{-}I\text{-}7,8\text{-}C_2B_9H_{11}]$ (**2**) while addition of 2.5 equiv of I_2 with heating resulted in an 88% yield of the corresponding diiodo species $[(CH_3)_3NH][\textit{nido}\text{-}9,11\text{-}I_2\text{-}7,8\text{-}C_2B_9H_{10}]$ (**1**). These reactions are believed to comprise electrophilic iodination by formal I^+ at the most nucleophilic B(9) (B(11)) positions available in the nido monoanion.

The salt $[(CH_3)_3NH][\textit{nido}\text{-}9,11\text{-}I_2\text{-}7,8\text{-}C_2B_9H_{10}]$ (**1**) was characterized by ^{11}B NMR, HRMS, and single-crystal X-ray diffraction methods. The ^{11}B NMR spectrum of **1** exhibits a singlet at −21.1 ppm that corresponds to 2 boron atoms, thus indicating diiodination at symmetry equivalent boron vertices. The high resolution mass spectrum (FAB$^-$) of the anion is in

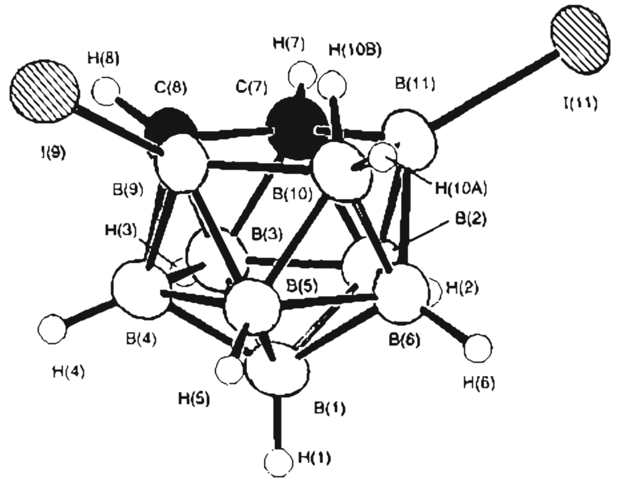

Figure 1. ORTEP diagram showing the structure of the [*nido*-9,11-I_2-7,8-$C_2B_9H_{10}$]$^-$ ion.

agreement with the expected diiodo *nido*-carborane cage structure. Compound **1** crystallized as clear, colorless monoclinic crystals which gave the molecular structure shown in Figure 1. The anion of **1** has the expected *nido*-icosahedral fragment geometry with an *exo*-polyhedral H atom attached to each cage atom. Iodination occurred at the B(9) and B(11) boron atom positions. The B(9)−I(9) bond length is 2.203(5) Å and the B(11)−I(11) bond length is 2.201(5) Å. The B(10) boron atom is bonded to two different hydrogen atoms, *exo*-H(10A) and *endo*-H(10B), with B−H bond lengths of 1.043(56) and 1.067(57) Å, respectively. The *endo*-hydrogen atom, which penetrates the open pentagonal face of the *nido*-carborane cage, is directed toward the empty 12th vertex with a H(10A)−B(10)−H(10B) bond angle of 111.1(41)°, approaching tetrahedral geometry about the B(10) atom. These characteristics are consistent with previous studies of structures[9−12] which contain {BH_2} vertices.

In this present study, the monoiodinated 11-vertex carborane cage anion was demonstrated to be an enantiomeric mixture by X-ray structural characterization. Single crystals of the trimethylammonium salt of **2** suitable for X-ray diffraction were obtained. The two enantiomers of **2** were found to coincidentally crystallize in the unit cell, and the molecular structure of one of these enantiomers, [$(CH_3)_3NH$][*nido*-9-I-7,8-$C_2B_9H_{11}$], is shown in Figure 2. From this structure, the electrophilic substitution by formal I^+ can be seen to have taken place on B(9), the boron atom in the top belt of the [*nido*-7,8-$C_2B_9H_{12}$]$^-$ cage that is adjacent to a carbon atom. The B−I bond length is 2.209(9) Å. An important influence of this I-substitution upon the open face of the nido-cage is the placement of an asymmetric B−H−B bridge between B(10) and B(11). The H(1BR)−B(10) bond length is 1.26(18) Å and the H(1BR)−B(11) bond length is 1.55(17) Å. It had previously been shown by X-ray crystallography and NMR studies that the unsubstituted [*nido*-7,8-$C_2B_9H_{12}$]$^-$ ion exhibits a symmetrical *endo*-H atom at the B(10) position.[9,10] Here we see the result of an electronegative halogen substituent on the B(9) atom inducing B−H−B bridge formation at the B(10)−B(11) positions of the boron cage as opposed to the formation of an *endo*-H atom on the adjacent B(10) position as previously found in the unsubstituted *nido*-carborane anion.[10]

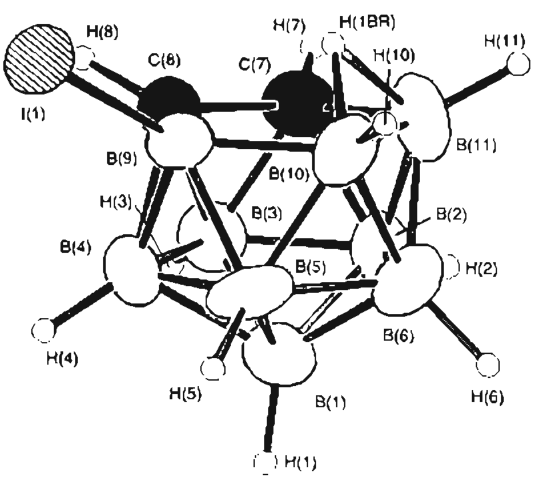

Figure 2. ORTEP diagram showing the structure of the [*nido*-9-I-7,8-$C_2B_9H_{11}$]$^-$ ion.

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Supplementary Material Available: Text giving full crystallographic details of the crystallographic structure determination and tables of final fractional atomic coordinates, non-H atom anisotropic temperature factors, H atom isotropic temperature factors, bond lengths, and bond angles (21 pages). Ordering information is given on any current masthead page.