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The Molecular Structure of (PSH^+)(*nido*-7,8-$C_2B_9H_{12}^-$) Determined by Neutron Diffraction (PS = Proton Sponge, 1,8-Bis(dimethylamino)naphthalene)

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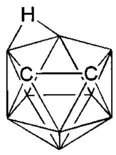
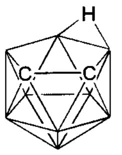
Introduction

The icosahedral carborane, *closo*-1,2-$C_2B_{10}H_{12}$, is the most widely researched of all carboranes and has an extensive derivative chemistry.[1] Its most important reaction is that with Lewis bases[2−5] removing one boron vertex to generate the anion (*nido*-7,8-$C_2B_9H_{12}^-$), the intermediate through which vast numbers of closo carboranes, heteroboranes, and metallacarboranes have been prepared.[6] The icosahedral fragment structure of its C_2B_9 framework and the location of its eleven exo-terminal hydrogen atoms are undisputed. However, the location of the endo hydrogen atom has remained contentious over the $3^1/_2$ decades since the anion was first reported.[2] Calculations of various degrees of sophistication[7,8] have shown that the energy difference between terminal [on B(10), **II**] and bridging [between B(10) and B(9) or B(11), **I** or **III**] sites is small. X-ray studies of salts with the cation $[(Me_2SO)_2H]^+$ (in the case of the parent species *nido*-7,8-$C_2B_9H_{12}^-$), and assorted cations (in the case of species bearing substituents) have indicated endo-terminal (**II**)[9] and asymmetric bridging (**III**)[10] sites, respectively. We have recently reported the structure of $[(Me_2N)_3PNH_2^+]$-(*nido*-7,8-$C_2B_9H_{12}^-$) where the endo hydrogen was located by X-ray diffraction in a very asymmetrical bridging position between B9 and B10 (**IIIa**).[11] Solution-state NMR studies suggest that (*nido*-7,8-$C_2B_9H_{12}^-$) either is fluxional in solution with the bridging hydrogen flipping between the B9/B10 and B10/B11 bonds (**Ia**)[12] or is static with structure **II**.[13]



Ia



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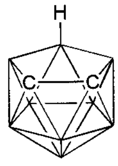

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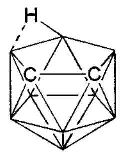
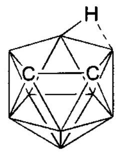


IIIa



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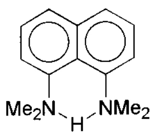

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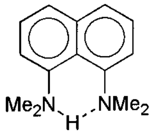

V

Experimental Section

Synthesis of (PSH^+)(*nido*-7,8-$C_2B_9H_{12}^-$). Addition of a hexane solution (40 mL) of Proton Sponge (1,8-*N*,*N*,*N*′,*N*′-tetramethylnaphthalenediamine = PS) (0.214 g, 1 mmol) to a hexane solution of *nido*-7,8-$C_2B_9H_{13}$ (0.134 g, 1 mmol) afforded a precipitate. This solid was filtered and recrystallized from dichloromethane with slow diffusion of hexane at −30 °C to yield crystals of (PSH^+)(*nido*-7,8-$C_2B_9H_{12}^-$) (0.27 g, 77%). Found: C, 54.70; H, 8.87; N, 7.92. $C_{16}H_{31}B_9N_2$ requires C, 55.11; H, 8.96; N, 8.03.

NMR data for the (PSH^+) cation (acetone-d_6): δ_H (300 MHz) 18.79 (1H, s, NH), 7.97 (2H, d, J_{HH} = 8 Hz; H4,5), 7.91 (2H, d, 8; H2,7),

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10.1021/ic000961e CCC: $20.00

Table 1. Summary of Crystallographic Data for $(PSH^+)(\textit{nido}\text{-}7,8\text{-}C_2B_9H_{12}^-)$

	X-ray diffraction	neutron diffraction
empirical formula	$C_{16}H_{31}B_9N_2$	
fw	348.72	
a (Å)	8.129(1)	8.110(2)
b (Å)	11.251(2)	11.134(2)
c (Å)	12.392(2)	12.342(2)
α (deg)	68.524(5)	68.34(1)
β (deg)	86.359(7)	86.55(1)
γ (deg)	79.712(8)	79.98(1)
V (Å^3)	1037.7(3)	1019.9(4)
space group	$P\bar{1}$	
Z	2	
μ	0.058 mm^{-1} (Mo Kα)	$1.25 + 14.71\lambda$ cm^{-1}
$R_w(F^2)$ (all data)	0.1284	0.2372
$R_1(F^2)$	0.0561	0.0982
	[2823 reflns $I > 2\sigma(I)$]	[5005 reflns $I > 2\sigma(I)$]

7.63 (2H, t, 8; H3,6), 3.17 (12H, s; CH_3); δ_C (75 MHz) 144.8 (C1,8), 135.8 (C10), 129.7 (C4,5), 127.5 (C3,6), 122.0 (C2,7), 119.5 (C9), 46.2 (CH_3).

NMR data for the $(\textit{nido}\text{-}7,8\text{-}C_2B_9H_{12}^-)$ anion (acetone-d_6): δ_H (300 MHz, $^1H\{^{11}B\}$) 1.86 (2H, $B_{9,11}H$), 1.81 (2H, CH), 1.68 (1H, B_3H), 1.14 (4H, $B_{2,4,5,6}H$), 0.46 (1H, B_1H), 0.01 (1H, $B_{10}H$), −2.95 (^1H, μ-H); δ_B (96.2 MHz) −10.4 ($B_{9,11}$), −15.9 ($B_{5,6}$), −16.4, (B_3), −21.4 ($B_{2,4}$), −32.5 (B_{10}), −37.2 (B_1); solid-state δ_B (96.2 MHz) −19.3 (7B), −33.6 (1B), −38.7 (1B). Calculated NMR chemical shifts for neutron diffraction geometry (GIAO−B3LYP/6-311G*): −6.0 (B_9), −8.1 (B_5), −15.3 (B_{11}), −18.2 (B_3), −20.8 (B_2), −25.4 (B_6), −26.4 (B_4), −36.1 (B_{10}), −32.2 (B_1). Calculated NMR chemical shifts for neutron diffraction geometry, averaged for C_s symmetry (GIAO−B3LYP/6-311G*): −10.7 ($B_{9,11}$), −16.8 ($B_{5,6}$), −18.2 (B_3), −23.6 ($B_{2,4}$), −36.1 (B_{10}), −39.2 (B_1).

Description of the X-ray Diffraction Study. The X-ray diffraction experiment was carried out at 150 K, using graphite-monochromated Mo Kα X-radiation (= 0.71073 Å), on a Bruker SMART-CCD detector diffractometer equipped with a Cryostream N_2 flow cooling device.[14] Cell parameters were determined and refined using the SMART software[15] from the centroid values of 279 reflections with 2θ values between 5° and 42°. Raw frame data were integrated using the SAINT program.[16] The structure was solved using direct methods and refined by full-matrix least squares on F^2 using the SHELXTL suite of programs.[17] A shapeless colorless crystal with dimensions 0.36 × 0.32 × 0.28 mm^3 was used for the measurements. A total of 6319 reflections were measured which merged to 3652 unique data with an agreement factor of 0.0458. The monoclinic space group $P\bar{1}$ cannot be determined unambiguously from the systematic absences; however, a clearly satisfactory refinement of the structure in $P\bar{1}$ confirmed this space group assignment. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters (adps). Hydrogen atoms were located from difference Fourier maps and their coordinates and isotropic adps refined. Crystal data are given in Table 1. The atom-numbering scheme with H(12) bridging B(10)−B(11) rather than B(9)−B(10) was chosen for consistency with ref 8.

Description of the Neutron Diffraction Study. A thin plate crystal of size 3 × 2.5 × 1 mm^3 was selected to collect neutron diffraction data on the SXD instrument at the ISIS spallation neutron source, using the time-of-flight Laue diffraction method.[18] Data were collected at a temperature of 30 ± 2 K under experimental conditions described previously.[19] The intensities were extracted and reduced to structure factors using standard SXD procedures.[18] A total of 19586 reflections were observed, reducing to a unique set of 5005 structure factors on merging ($R_{int} = 0.066$). This structure factor set was used for structural refinement using SHELXTL-NT.[17] All non-hydrogen atom positions from the X-ray model were used as a starting point for the refinement. Hydrogen atom positions were located from subsequent difference Fourier maps. All atoms refined with anisotropic displacement parameters. Neutron scattering lengths were taken from *International Tables for Crystallography,* Vol. C, Table 4.4.4.1 (Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, 1992). Crystal data are given in Table 1. Selected bond distances and angles are given in Table 2.

Table 2. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $(PSH^+)(\textit{nido}\text{-}7,8\text{-}C_2B_9H_{12}^-)$ as Determined by Diffraction of X-rays (at 150 K) and Neutrons (at 30 K)

	neutron diffraction	X-ray diffraction
	Distances	
C7−C8	1.570(4)	1.564(3)
C8−B9	1.625(6)	1.623(4)
B9−B10	1.825(6)	1.813(4)
B10−B11	1.871(6)	1.841(4)
B11−C7	1.615(6)	1.620(3)
B11−H12	1.469(11)	
B11−H11	1.207(10)	
B10−H10	1.201(13)	
B10−H12	1.252(10)	
N1−H1N	1.228(13)	
N2···H1N	1.419(13)	
N1···N2	2.599(3)	2.601(2)
	Angles	
B10−H12−B11	86.4(5)	

Results and Discussion

In view of the structural uncertainty, the suspicion that substituents on carbon might favor a bridged site in contrast to a terminal site for the parent anion $(\textit{nido}\text{-}7,8\text{-}C_2B_9H_{12}^-)$, and the knowledge that neutron diffraction methods are usually preferable to X-ray diffraction when hydrogen atom sites are at issue, we embarked on a neutron diffraction study of the Proton Sponge salt $(PSH^+)(\textit{nido}\text{-}7,8\text{-}C_2B_9H_{12}^-)$, though appreciating that the high neutron capture cross section of the boron isotope ^{10}B might thwart the study. The only previous cage borane structurally characterized by neutron diffraction was deuterated ^{10}B-depleted decaborane $(\textit{nido}\text{-}^{11}B_{10}D_{14})$[20] though some smaller boranes[21] and metal tetrahydridoborates[22] have been studied at natural abundance.

We succeeded in growing large crystals of the salt $(PSH^+)(\textit{nido}\text{-}7,8\text{-}C_2B_9H_{12}^-)$ by slow diffusion of hexane into a CH_2Cl_2 solution and obtained good quality neutron diffraction data. Figure 1 shows the structure of $(PSH^+)(\textit{nido}\text{-}7,8\text{-}C_2B_9H_{12}^-)$ as determined by neutron diffraction, and selected metric data from both the X-ray and neutron diffraction studies are in Table 2. The unique hydrogen atom H(12) in the anion is clearly localized in an unsymmetric B−H−B bridging position over

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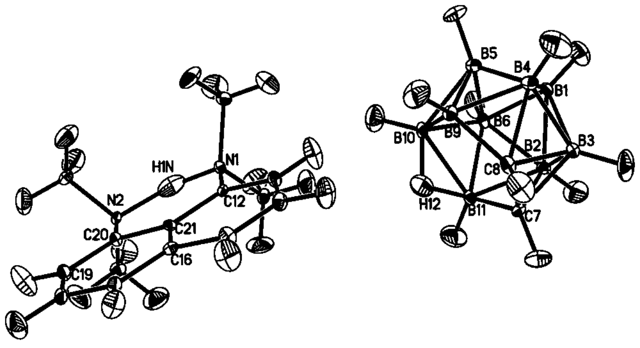

Figure 1. The molecular structure of (PSH^+)(*nido*-7,8-$C_2B_9H_{12}^-$) as determined by single-crystal neutron diffraction; all atoms are shown as 50% probability ellipsoids.

the B(10)−B(11) bond, with B−H distances of 1.252(10) and 1.469(11) Å. On these boron atoms the terminal hydrogens are unaffected by the presence of the bridging atom, with B(9)−H(9) and B(10)−H(10) being insignificantly longer than the other seven B−H units. The bridged cluster edge B(10)−B(11) is longer than its unbridged counterpart;[23] the asymmetry of the open pentagonal face extends to the B−C distances.

The location of the hydrogen between the nitrogen atoms in the (PSH^+) cation may be symmetric (**IV**) or asymmetric (**V**), the latter geometry being more common in reported X-ray structures of salts containing (PSH^+) cations.[24] In our discrete (PSH^+) cation, the bond lengths are 1.228(13) and 1.419(13) Å for N1−H13 and H13···N2, respectively, corresponding to geometry **V**. A previous neutron diffraction study on the complex of PS and 1,2-dichloromaleic acid, (PSH^+)($HO_2CClCClCO_2^-$), reported a more asymmetric hydrogen bond, with N1−H13 = 1.106(5) Å and H13···N2 = 1.608(6) Å.

In agreement with recently reported results at the HF/6-31G* and B3LYP/6-31G* levels, two geometries (**II** and **IIIa**) were located by optimization of (*nido*-7,8-$C_2B_9H_{12}^-$) at the more computationally intensive MP2/6-31G* level using the GAUSSIAN94 package.[25] The energy minimum (geometry **IIIa**) has the endo hydrogen asymmetrically bridging the B9−B10 bond as seen in the neutron diffraction structure reported here; the fitting error between the calculated and experimental structure for all atoms is only 0.03 Å using the *ofit* command of XP.[17] The second geometry (**II**) has a symmetrically bridging endo hydrogen and corresponds to a transition state located a mere 1.5 kcal mol^{-1} above the energy minimum. Energies for the MP2/6-31G* optimized geometries of structures **IIIa**, **II**, **IV**, and **V** are −306.06799, −306.06565, −652.03475, and −652.03618 au, respectively. The resulting energy differences between geometries are **IIIa**/**II** = 1.47 and **IV**/**V** = 0.87 kcal mol^{-1} without zero point energy corrections. These results do not unequivocally rule out the possibility of geometry **II** for (*nido*-7,8-$C_2B_9H_{12}^-$) in a different solid-state phase.

What of the geometry for (*nido*-7,8-$C_2B_9H_{12}^-$) in the solution state? Recently, application of the combined ab initio/IGLO or GIAO/NMR method[26] to (*nido*-7,8-$C_2B_9H_{12}^-$) revealed fluxionality of the asymmetrically bridging hydrogen between geometries **IIIa** and **IIIb** (via geometry **II**) in solution to correspond best with the observed solution-state boron NMR data for (*nido*-7,8-$C_2B_9H_{12}^-$). Our calculated NMR shifts (GAUSSIAN94) generated from the neutron diffraction geometry are in good agreement with observed solution state (assuming that fluxionality takes place in solution between the two geometries **IIIa** and **IIIb**) and the limited solid-state ^{11}B NMR data.

From our neutron diffraction study it is clear that the geometry of (*nido*-7,8-$C_2B_9H_{12}^-$) is best drawn as **IIa**/**IIb** with an asymmetric bridge, while the diagrams **Ia**/**Ib** with symmetric bridges may be used for convenience in the same way as, for example, $B_{10}H_{14}$, where asymmetric bridging hydrogens were also found by neutron diffraction. The same geometry is found in solutions of (*nido*-7,8-$C_2B_9H_{12}^-$) where endo hydrogen fluxionality occurs between the two geometries **IIIa** and **IIIb**.

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Supporting Information Available: Crystallographic data for the X-ray and neutron diffraction studies as a CIF file. Cartesian coordinates of MP2/6-31G* optimized geometries of **II**, **III**, **IV**, and **V.** This material is available free of charge via the Internet at http://pubs.acs.org.

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