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Synthesis and Structure of Triethylammonium 2-(Acetonitrile)nonahydro-*closo*-decaborate(1−)

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Introduction

Substitution and protonation chemistries of $[B_{10}H_{10}]^{2-}$ have enjoyed continuous attention[1] ever since an efficient synthesis of this *closo* anion was developed by Hawthorne in 1959.[2] Reaction of $[B_{10}H_{10}]^{2-}$ with the strong acid CF_3COOH[3] or HCl[4] in solution produces $[B_{10}H_{11}]^-$. Stable salts of $[B_{10}H_{11}]^-$ with phosphonium cations have been isolated.[5] However, single crystal X-ray structure determinations of these species have been frustrated by crystallographic disorder.[6] More recently, $B_{10}H_{12}$ and $[B_{10}H_{13}]^+$ were proposed as reaction intermediates when the stronger acid CF_3SO_3H was employed as a proton source.[7]

Acid-mediated hydride displacement on $[B_{10}H_{10}]^{2-}$ by substituents containing O, S, and N as donating elements has been described.[8] In this laboratory we have observed the reaction of $[Et_3NH]_2[B_{10}H_{10}]$ with CH_3CN in the presence of CF_3COOH to give $[Et_3NH][2\text{-}B_{10}H_9NCCH_3]$, in contrast to an earlier report[8c] that $[1\text{-}B_{10}H_9NCCH_3]^-$ is produced by a similar reaction but in the presence of *p*-toluenesulfonic acid. Herein we report the synthesis, NMR spectra, and X-ray structure of $[Et_3NH][2\text{-}B_{10}H_9NCCH_3]$.

Experimental Section

All syntheses and reactions were performed under an N_2 atmosphere or under vacuum. All solvents were predried and distilled prior to use. CF_3COOH and *p*-toluenesulfonic acid were obtained from Aldrich and used as received. Boron-11 ($\delta(Et_2O{\cdot}BF_3) = 0.0$ ppm) and proton (δ(tms) = 0.0 ppm) NMR spectra were recorded on a Bruker AM250 spectrometer operating at 80.253 and 250 MHz for ^{11}B and ^1H, respectively. IR spectra were recorded with 2 cm^{-1} resolution using a Mattson-Polaris FT-IR spectrometer.

Synthesis of $[Et_3NH][2\text{-}B_{10}H_9NCCH_3]$. A sample of $[Et_3NH]_2[B_{10}H_{10}]$, 0.20 g (0.62 mmol), was dissolved in 10 mL of CH_3CN. This solution was combined with 1 mL of CF_3COOH in a glovebag at room temperature, and the reaction mixture was warmed to 60 °C for 30 min. Then the solution was cooled to −196 °C, 0.6 mmol of H_2 (identified by mass spectroscopy) was collected by a Toepler pump. Approximately 5 mL of solvent was slowly pumped away. Colorless crystals (0.15 g, 0.58 mmol, yield 93%) of $[Et_3NH][2\text{-}B_{10}H_9NCCH_3]$ were obtained upon cooling the solution to −10 °C for 16 h. IR (CH_2Cl_2): 2493 (m, CN), 1700 (w), 1684 (w), 1669 (w), 1654 (w), 1648 (w), 1617 (w), 1474 (w), 1464 (w), 1460 (w), 1450 (w), 1430 (w), 1399 (w), 1272 (w), 1261 (w), 717 (w) cm^{-1}. ^{11}B NMR (CD_3CN, 20 °C): 1.2 (d, $J_{B-H} = 143.3$ Hz, apical B), −1.5 (d, $J_{B-H} = 163.7$ Hz, apical B), −19.9 (broad s, B(2)), −25.2 (eq B, overlap), −26.6 (eq B, overlap), −27.8 (d, $J_{B-H} = 135.9$ Hz eq B) ppm.

In a similar reaction, 0.161 g (0.5 mmol) of $[Et_3NH]_2[B_{10}H_{10}]$ was combined with 0.57 g of *p*-toluenesulfonic acid in 10 mL of CH_3CN. The reaction solution was refluxed for 4 h, and 0.46 mmol of noncondensable gas was released. The remaining colorless solution was studied by ^{11}B NMR spectroscopy, and the data are completely consistent with formation of $[Et_3NH][2\text{-}B_{10}H_9NCCH_3]$. ^{11}B NMR (CH_3CN, 20 °C): 0.1, −2.2, −20.9, −26.0, −28.6 ppm. Another reaction of $[Me_4N]_2[B_{10}H_{10}]$ with *p*-toluenesulfonic acid in CH_3CN was carried out in the same fashion. The ^{11}B NMR spectrum is also consistent with the formation $[Me_4N][2\text{-}B_{10}H_9NCCH_3]$. ^{11}B NMR (CH_3CN, 20 °C) : 0.0, −2.8, −20.8, −26.7, −28.8 ppm.[9]

X-ray Crystal Structure Determination. A crystal of suitable size (0.4 × 0.3 × 0.4 mm) was mounted in a glass capillary under N_2. Crystallographic data were collected on a Siemens R3m/V four-circle diffractometer with graphite-monchromated MoKα radiation (λ = 0.710 73 Å). Lattice parameters were obtained by least-squares refinement of the angular settings from 25 refections lying in a 2θ range of 30−35°. Symmetry-equivalent data were averaged, and 3972 unique refections were corrected for Lorentz and polarization effects.

The structure was solved by a combination of direct methods using SHELXTL PLUS[10] and the difference Fourier technique and refined by full-matrix least squares including the refinement of the extinction coefficient. Analytical atomic scattering factors were used throughout the structure refinement with both the real and imaginary components of the anomalous dispersion included for all non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms attached to the boron atoms were located directly and their positions refined. The remaining hydrogen atom positions were calculated and allowed to ride on their respective atoms at a distance of 1.00 Å. Crystallographic data are summarized in Table 1. Atomic positional parameters are listed in Tables 2 and 3.

Results and Discussion

In CH_3CN solution and in the presence of CF_3COOH at 60 °C $[Et_3NH]_2[B_{10}H_{10}]$ was completely converted to $[Et_3NH][2\text{-}B_{10}H_9NCCH_3]$ within 30 min as determined by the ^{11}B NMR spectrum of the solution. One equivalent of H_2 gas was formed in the reaction. Subsequent recrystallization from CH_3CN yielded $[Et_3NH][2\text{-}B_{10}H_9NCCH_3]$ in 93% yield. Isomeric species were not detected by NMR spectroscopy. Similar reaction of $K_2[B_{10}H_{10}]$ with CF_3COOH in CH_3CN solution resulted in the formation of $K[2\text{-}B_{10}H_9NCH_3]$[11] (eq 1).

$$[B_{10}H_{10}]^{2-} + CH_3CN + CF_3COOH \rightarrow [2\text{-}B_{10}H_9NCCH_3]^- + H_2 \quad (1)$$

The molecular structure of $[Et_3NH][2\text{-}B_{10}H_9NCCH_3]$ was determined by single crystal X-ray crystallography from crystals

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(9) Small variations are observed in the chemical shifts of the ^{11}B NMR spectra of $[2\text{-}B_{10}H_9NCCH_3]^-$ in the three examples discussed in this section. These differences are probably due to the fact that two of the samples employed undeuterated acetonitrile and excess *p*-toluenesulfonic acid, showing the best agreement in chemical shifts, while the third sample employed deuterated acetonitrile and no excess acid.

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(11) ^{11}B NMR data for $K[2\text{-}B_{10}H_9NCCH_3]$ in CH_3CN at 20 °C: 1.4 (d, $J_{B-H} = 151.7$ Hz), −1.5 (d, $J_{B-H} = 141.4$ Hz), −19.8 (broad, s), −25.1 and −27.6 (d, $J_{B-H} = 137.2$ Hz) ppm.

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Table 1. Crystallographic Data for $(Et_3NH)[2\text{-}B_{10}H_9NCCH_3]$

formula	$C_8H_{28}B_{10}N_2$
fw	260.4
space group	$P2_1/n$
a, Å	9.022(1)
b, Å	13.819(2)
c, Å	13.805(2)
β, deg	92.63(1)
V, Å^3	1719.3(4)
Z	4
ϱ(calcd), g cm^{-3}	1.006
μ(Mo Kα), cm^{-1}	0.47
T, °C	20
scan mode	$2\theta-\theta$
2θ limits	3.5−50°
no. of reflns collected	4393
no. of unique reflns [$I \geq 3.0\sigma(I)$]	3972
no. of variables	209
R_F ($R_F = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$)	0.0874
R_{wF} ($R_{wF} = [\sum w[\lvert F_o\rvert - \lvert F_c\rvert]^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.0638

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	U(eq)[a]
B(1)	2007(5)	6673(3)	3522(3)	42(2)
B(2)	2298(5)	5925(3)	4462(3)	35(2)
B(3)	3577(5)	6876(3)	4199(3)	44(2)
B(4)	2017(5)	7718(3)	4143(3)	43(2)
B(5)	736(5)	6742(3)	4385(3)	39(2)
B(6)	3471(5)	6390(3)	5424(3)	39(2)
B(7)	3288(5)	7684(3)	5201(3)	38(2)
B(8)	1283(5)	7588(3)	5330(3)	39(2)
B(9)	1467(5)	6292(3)	5559(3)	38(2)
B(10)	2537(5)	7130(3)	6152(4)	45(2)
N(1)	2412(3)	4845(2)	4289(2)	36(1)
C(1)	2529(4)	4041(3)	4167(3)	39(1)
C(2)	2662(4)	3019(3)	3990(3)	59(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. H Atom Coordinates ($\times 10^4$) and Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	U, Å^2
H(1)	1883(33)	6507(24)	2735(24)	50
H(3)	4686(35)	6883(24)	3882(23)	50
H(4)	1854(34)	8386(25)	3761(23)	50
H(5)	−473(35)	6624(22)	4192(22)	50
H(6)	4377(35)	5886(24)	5691(23)	50
H(7)	4150(33)	8312(24)	5314(22)	50
H(8)	439(34)	8110(24)	5532(22)	50
H(9)	749(33)	5723(24)	5958(22)	50
H(10)	2674(34)	7268(23)	6904(24)	50

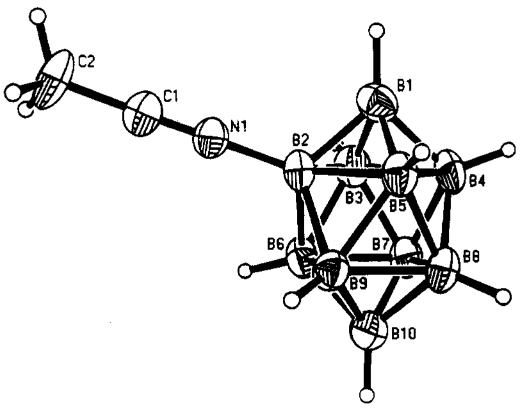

Figure 1. ORTEP plot for $[2\text{-}B_{10}H_9NCCH_3]^-$.

Table 4. Selected Bond Lengths (Å)

B(1)−H(1)	1.11(3)	B(1)−B(5)	1.694(7)
B(1)−B(2)	1.670(6)	B(1)−B(4)	1.680(7)
B(1)−B(3)	1.684(6)	B(2)−B(3)	1.797(6)
B(2)−N(1)	1.515(5)	B(2)−B(9)	1.794(6)
B(2)−B(6)	1.780(6)	B(3)−H(3)	1.11(3)
B(3)−B(7)	1.807(7)	B(3)−B(6)	1.826(7)
B(4)−H(4)	1.07(3)	B(4)−B(8)	1.804(7)
B(4)−B(3)	1.826(7)	B(4)−B(7)	1.816(6)
B(5)−H(5)	1.12(3)	B(5)−B(8)	1.804(6)
B(5)−B(2)	1.806(6)	B(5)−B(9)	1.830(6)
B(5)−B(4)	1.817(6)	B(6)−H(6)	1.12(3)
B(6)−B(10)	1.686(7)	B(7)−B(10)	1.687(7)
B(7)−H(7)	1.17(3)	B(7)−B(6)	1.820(6)
B(8)−H(8)	1.10(3)	B(8)−B(7)	1.831(6)
B(8)−B(10)	1.688(7)	B(9)−B(10)	1.695(6)
B(9)−H(9)	1.17(3)	B(9)−B(8)	1.824(6)
B(9)−B(6)	1.831(6)	B(10)−H(10)	1.06(3)
N(1)−C(1)	1.129(5)	C(1)−C(2)	1.440(6)
C(2)−H(2A)	1.000	C(2)−H(2B)	1.000
C(2)−H(2C)	1.000		

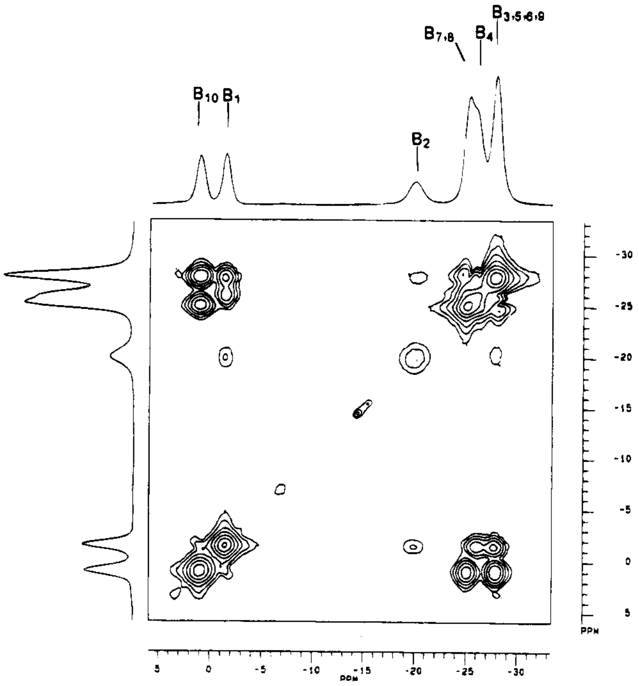

Figure 2. $^{11}B-^{11}B$ COSY spectrum of $(Et_3NH)[2\text{-}B_{10}H_9NCCH_3]$.

grown at −10 °C. An ORTEP plot of the $[2\text{-}B_{10}H_9NCCH_3]^-$ anion is shown in Figure 1 . Selected bond distances and bond angles are given in Tables 4 and 5. The molecular structure of $[2\text{-}B_{10}H_9NCCH_3]^-$ defines a slightly distorted bicapped square antiprism with one acetonitrile molecule coordinated through the N atom to one equatorial boron atom. The *exo* B−N distance, 1.515(5) Å, in $[2\text{-}B_{10}H_9NCCH_3]^-$ is comparable to that in $[2\text{-}B_{10}H_9NCCH{=}CH_2]^-$, 1.523(4) Å.[12] The average apical−equatorial distances are B_1-B_{eq} = 1.682[4] Å,[13] and $B_{10}-B_{eq}$ = 1.689[2] Å. They compare favorably with 1.693(5) and 1.686(5) Å found in $[2\text{-}B_{10}H_9NCCH{=}CH_2]^-$.[11] The average $B_{eq}-B_{eq}$ distance defined by B2, B3, B4, and B5 is 1.811[6] Å and that defined by B6, B7, B8, and B9 is 1.826[2] Å. The average B−B distance between the equatorial planes is 1.808[5] Å. These distances are very close to the corresponding connectivities observed in $[2\text{-}B_{10}H_9NCCH{=}CH_2]^-$.[12]

The ^{11}B NMR data for $[Et_3NH][2\text{-}B_{10}H_9NCCH_3]$ given in the Experimental Section are fully consistent with the X-ray structure of the anion. The resonance at δ −19.9 ppm is a broad singlet which is unaffected by proton coupling. It is assigned

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[12] Sirivardane, U.; Chu, S. S. C.; Hosmane, N. S.; Zhang, G.; Zhu, W.; Zhu, H. *Acta Crystallogr.* **1989**, *C35*, 294.

[13] The error estimate shown in brackets for the average distance d was obtained from the expression $[\sum_{i=1}^{n}(d_i - d)^2/(n^2 - 1)]^{1/2}$.

Table 5. Selected Bond Angles (deg)

H(1)–B(1)–B(5)	131.1(16)	H(1)–B(1)–B(2)	129.6(17)
B(5)–B(1)–B(2)	64.9(3)	H(1)–B(1)–B(4)	132.4(17)
B(5)–B(1)–B(4)	65.2(3)	B(2)–B(1)–B(4)	98.0(3)
H(1)–B(1)–B(3)	128.4(16)	B(5)–B(1)–B(3)	100.4(3)
B(2)–B(1)–B(3)	64.8(3)	B(4)–B(1)–B(3)	65.7(3)
B(1)–B(2)–B(9)	115.1(3)	B(5)–B(2)–B(9)	61.1(2)
B(1)–B(2)–B(3)	58.0(3)	B(5)–B(2)–B(3)	92.1(3)
B(9)–B(2)–B(3)	105.1(3)	B(1)–B(2)–B(6)	115.0(3)
B(5)–B(2)–B(6)	104.7(3)	B(9)–B(2)–B(6)	61.6(2)
B(3)–B(2)–B(6)	61.4(2)	B(1)–B(2)–N(1)	119.8(3)
B(5)–B(2)–N(1)	131.7(3)	B(9)–B(2)–N(1)	116.5(3)
B(3)–B(2)–N(1)	129.7(3)	B(6)–B(2)–N(1)	115.6(3)
B(1)–B(2)–B(5)	58.2(3)	B(1)–B(3)–B(4)	57.0(3)
B(2)–B(3)–B(4)	88.5(3)	B(1)–B(3)–H(3)	122.2(16)
B(2)–B(3)–H(3)	133.2(17)	B(4)–B(3)–H(3)	133.2(17)
B(1)–B(3)–B(7)	112.4(3)	B(2)–B(3)–B(7)	100.4(3)
B(4)–B(3)–B(7)	60.0(3)	H(7)–B(3)–B(7)	117.4(17)
B(1)–B(3)–B(6)	112.0(3)	B(2)–B(3)–B(6)	58.8(2)
B(4)–B(3)–B(6)	101.5(3)	H(7)–B(3)–B(6)	117.1(16)
B(7)–B(3)–B(6)	60.1(2)	B(1)–B(3)–B(2)	57.2(3)
B(1)–B(4)–B(5)	57.8(3)	B(1)–B(4)–H(4)	119.5(18)
B(5)–B(4)–H(4)	131.0(17)	B(1)–B(4)–B(8)	112.6(3)
B(5)–B(4)–B(8)	59.7(3)	H(4)–B(4)–B(8)	119.1(18)
B(1)–B(4)–B(3)	57.2(3)	B(5)–B(4)–B(3)	90.8(3)
H(4)–B(4)–B(3)	131.2(17)	B(8)–B(4)–B(3)	102.3(3)
B(1)–B(4)–B(7)	112.1(3)	B(5)–B(4)–B(7)	102.5(3)
H(4)–B(4)–B(7)	119.1(17)	B(8)–B(4)–B(7)	60.8(3)
B(3)–B(4)–B(7)	59.5(2)	B(1)–B(5)–H(5)	120.5(16)
B(1)–B(5)–B(2)	56.9(3)	H(5)–B(5)–B(2)	132.1(16)
B(1)–B(5)–B(9)	112.0(3)	H(5)–B(5)–B(9)	117.8(16)
B(2)–B(5)–B(9)	59.1(2)	B(1)–B(5)–B(4)	57.1(3)
H(5)–B(5)–B(4)	133.1(16)	B(2)–B(5)–B(4)	88.5(3)
B(9)–B(5)–B(4)	102.0(3)	B(1)–B(5)–B(8)	112.0(3)
H(5)–B(5)–B(8)	119.8(16)	B(2)–B(5)–B(8)	100.1(3)
B(9)–B(5)–B(8)	60.3(2)	B(4)–B(5)–B(8)	59.8(3)
B(2)–B(6)–B(9)	59.6(2)	B(2)–B(6)–B(3)	59.8(2)
B(9)–B(6)–B(3)	102.5(3)	B(2)–B(6)–B(7)	100.6(3)
B(9)–B(6)–B(7)	90.4(3)	B(3)–B(6)–B(7)	59.4(3)
B(2)–B(6)–H(6)	114.8(17)	B(9)–B(6)–H(6)	128.9(17)
B(3)–B(6)–H(6)	117.6(17)	B(7)–B(6)–H(6)	136.3(17)
B(2)–B(6)–B(10)	111.6(3)	B(9)–B(6)–B(10)	57.4(3)

to the substituted boron atom B_2 which is bonded to CH_3CN. The remaining ^{11}B resonances are doublets in the proton-coupled spectrum. Resonances at δ 1.2 and δ −1.5 ppm are assigned to the two apical boron atoms B_1 and B_{10}. Resonances at δ −25.2, −26.6, and −27.8 ppm are assigned to the remaining equatorial boron atoms. These assignments are consistent with the $^{11}B-^{11}B$ COSY spectrum shown in Figure 2. Further examination of the $^{11}B-^{11}B$ COSY spectrum revealed that the resonance at 1.2 ppm may be assigned to the apical boron B_{10} since it shows two equally intense cross peaks with $B_{7,8}$ at −25.2 ppm and $B_{6,9}$ at −27.8 ppm. On the other hand, apical boron B_1 at −1.5 ppm shows weak cross peaks with B_4 at −26.6 ppm and strong cross peaks with $B_{3,5}$ at −27.8 ppm.

Earlier, a similar hydride displacement reaction was proposed as a possible secondary reaction in a kinetic study of the reaction of $[B_{10}H_{10}]^{2-}$ with benzoylating agents in the presence of CF^3-COOH.[3] However, the product was not characterized and no structure was proposed. Another earlier study reported that $[B_{10}H_{10}]^{2-}$ in the presence of *p*-toluenesulfonic acid forms $[1\text{-}B_{10}H_9NCCH_3]^-$ in refluxing CH_3CN solution[8c] on the basis of the ^{11}B NMR spectrum at 19.25 MHz. When the synthesis was repeated with both $[Me_4N]^+$ and $[Et_3NH]^+$ cations, the ^{11}B NMR spectrum at 80.25 MHz reported here revealed that the $[2\text{-}B_{10}H_9NCCH_3]^-$ isomer is formed rather than $[1\text{-}B_{10}H_9\text{-}NCCH_3]^-$. A survey of the literature indicates that a number of apically and equatorially substituted isomers of $[B_{10}H_{10}]^{2-}$ have been prepared with the site of substitution being dependent upon the reaction conditions employed. It would be of interest to reexamine earlier work, for possible misassignments, in which structural characterization was based primarily upon NMR studies at relatively low field strengths.

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Supplementary Material Available: Listings of bond distances, bond angles, positional parameters, and anisotropic thermal parameters (6 pages). Ordering information is given on any current masthead page.