Table IV. ^{11}B NMR Data for I and Some Halo Derivatives[a]

Compd	B(2) chem shift[b]	M, J_{B-H}[c]	B(4) chem shift[d]	M, J_{B-H}[c]
I	+12.3	t, 110	+25.2	t, 97
IV	+12.6	t, 110	+18.1	d, 110
IX	+5.6	s, . . .	+9.7	s, . . .
V	+12.6	t, 116	+18.8	d, 120
VII	+11.7	d, unresolved	+16.4	s, . . .
VI	+13.1	t, 110	+24.5	d, 120
$B_2N_2C_5H_{16}I_2$	+19.9[e]	bm		
VIII	+17.9	d, 130	+37.5	s, . . .

[a] External $B(OCH_3)_3$ is the reference; CH_2Cl_2 is the solvent in all cases. [b] Chemical shift for the boron atom in ring position 2 in ppm upfield from $B(OCH_3)_3$. [c] M = multiplicity: t, triplet; d, doublet; s, singlet; bm, broad multiplet. *J* is the coupling constant, in Hz. [d] Chemical shift for the boron atom in ring position 4 in ppm. [e] The boron nuclei of this material appear as a broad unresolved multiplet.

changes predicted for a series of amine–haloboranes and their correlation to the chemical shifts actually observed is presented by Myers.[6]

The theory most important in explaining the ^{1}H NMR behavior of amine–haloboranes is set forth by Schaefer, Reynolds, and Yonemoto.[7] Essentially, the argument is made that for a given halo derivative the degree of steric crowding or electron cloud distortion around a proton will determine the extent of change in chemical shift position of that proton when compared with the same proton in the parent compound. The shifts caused by steric interactions are always downfield and increase with an increase in halogen size. This is exactly the trend found for the halo derivatives of I (Tables II and III).

^{11}B NMR Data for the Mono- and Trihalo Derivatives of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane in Relation to the Assignments Made in the ^{11}B NMR Spectrum of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane. If the assignments made in the ^{11}B NMR spectrum of I are correct, then the ^{11}B NMR spectra of the monohalo derivatives of I should show that the peak appearing at +25.2 ppm in the ^{11}B NMR spectrum of I has been shifted more than the peak at +12.3 ppm in the ^{11}B NMR spectrum of I. Also, the peak corresponding to the triplet at +25.2 ppm in the ^{11}B NMR spectrum of I should appear as a doublet.

In all three monohalo derivatives of I the most upfield peak is a doublet. This doublet partially overlaps with a triplet due to a BH_2 unit in the monochloro and the monobromo derivatives but is completely resolved in the monoiodo derivative.

The changes in the chemical shifts of the boron nuclei in the monochloro and the monobromo derivatives are greater for the boron atoms in ring position 4. Both boron atoms are shifted to essentially the same extent but in opposite directions in the monoiodo derivative of I.

If the assignments made in the ^{11}B NMR spectrum of I are correct, then the ^{11}B NMR spectra of the trihalo derivatives of I should show that the triplet at +25.2 ppm assigned in I to the boron atom in ring position 4 is now a singlet and shifted to a larger extent than the peak appearing at +12.3 ppm assigned to the boron atom in ring position 2 of I, which should now be a doublet.

In both trihalo derivatives the absorption assigned to the boron atom in ring position 4 of compound I now appears as a singlet and is shifted to a larger extent than the absorption corresponding to the boron atom in ring position 2 of compound I, which now appears as a doublet.

Thus, the assignments made in the ^{11}B NMR spectrum of I are confirmed by the ^{11}B NMR spectra (Table IV) of the monohalo and the trihalo derivatives of I.

Registry No. I, 53521-47-4; IV, 58438-26-9; V, 58438-27-0; VI, 58485-82-8; VII, 58438-28-1; VIII, 58438-29-2; IX, 58438-31-6; $B_2N_2C_5H_{16}I_2$, 58438-30-5; bis(trimethylamine)dihydroboronium iodide, 19581-80-7.

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Synthesis of a New Class of Boron Cations from 4-Iodo-1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane

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A new class of boron cations has been prepared from 4-iodo-1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane [$B_2N_2C_5H_{17}I$]. The syntheses of four cations using pyridine, 4-methylpyridine, 2-methylpyridine, and trimethylamine as Lewis bases to displace iodide from $B_2N_2C_5H_{17}I$ are demonstrated. A case of tight ion pairing capable of influencing the ^{1}H NMR spectra of the pyridine amine containing cations is discussed.

The monoiodo derivative[1] of 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane [$B_2N_2C_5H_{18}$][2] was allowed to react with several amines to determine if a new class of boron cations containing the five-membered cyclopentane-like ring system could be obtained in a manner analogous to iodide displacement from trimethylamine–iodoborane by a wide variety of Lewis bases.[3,4] In addition, it was of interest to determine if the spectral properties of these derivatives would support the structure proposed for $B_2N_2C_5H_{17}I$.

Experimental Section

All solvents and reagents were purified by conventional means.

Infrared spectra were obtained using a Beckman IR-10 spectrophotometer with standard operating conditions employed. Melting points were recorded on a Thomas-Hoover apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The ^{1}H NMR spectra were obtained at 60 MHz, using a Varian

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Model A-60A spectrometer. All inert-atmosphere work was done in a Vacuum/Atmospheres drybox equipped with Dri-Train HE-93B. Charging of the individual reaction vessels was done in this drybox, unless otherwise noted.

Reaction of 4-Iodo-1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane with Pyridine. A benzene solution containing 7.6 mmol of $B_2N_2C_5H_{17}I$ was prepared in a 125-ml Erlenmeyer flask and to this was added 7.6 mmol of pyridine in benzene solution. When the first drop of pyridine solution was added, the mixture turned intensely yellow and quickly developed a turbidity. The solution was warmed to gentle reflux on a hot plate for 5 min and then stirred for 9 h. At the end of this time a yellow liquid had separated from the benzene solution. The benzene-soluble portion was decanted and the viscous oil remaining was washed with three 20-ml portions of benzene. The resulting yellow liquid was freed of solvent by vacuum evaporation and a slightly sticky, yellow solid weighing 1.92 g was obtained. This solid softened over a wide range and was completely melted at 60 °C.

The yellow solid was dissolved in a mixture of CH_2Cl_2 and heptane and filtered, and the filtrate was concentrated by vacuum evaporation. A yellow liquid separated from the solvent mixture as the percentage of heptane increased. The solvent mixture was decanted and the yellow liquid remaining was washed three times with heptane. The yellow liquid was freed of solvent by vacuum evaporation.

A sample was sent for elemental analysis. Anal. Calcd for $[(B_2N_2C_5H_{17})NC_5H_5]^+,I^-$: C, 36.09; H, 6.66; N, 12.62; B, 6.50; I, 38.13. Found: C, 35.38; H, 6.71; N, 11.87; B, 6.18; I, 37.51.

A sample was converted to the PF_6^- salt. The PF_6^- salt had a sharp melting point at 149–150 °C. The percent conversion was not determined.

A sample of the PF_6^- salt was sent for elemental analysis. Anal. Calcd for $[(B_2N_2C_5H_{17})C_5H_5N]^+,PF_6^-$: C, 34.23; H, 6.32; N, 11.97; B, 6.16; P, 8.83; F, 32.49. Found: C, 34.03; H, 6.32; N, 11.83; B, 6.17; P, 8.69; F, 32.50.

The weight (1.92 g) of product obtained corresponds to a 76% yield of crude material.

Reaction of 4-Iodo-1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane with 4-Methylpyridine. A benzene solution containing 8.4 mmol of $B_2N_2C_5H_{17}I$ was placed in a one-necked 24/40 standard taper 125-ml flask. A benzene solution containing 8.4 mmol of 4-methylpyridine was added to the benzene solution of $B_2N_2C_5H_{17}I$. The reaction mixture was stirred for 30 min.

No benzene-insoluble material had formed at the end of this time. The reaction mixture was heated to gentle reflux for 5 min on a hot plate; then the solution was allowed to cool. A yellow liquid separated from the benzene solution and collected on the bottom of the flask. The above procedure was repeated two times and the solution was stirred for a total of 5.5 h.

After 5.5 h the benzene-soluble portion was decanted from a viscous yellow-green liquid. This liquid was treated as described in the previous reaction. The resulting yellow liquid was freed from solvent by vacuum evaporation and 2.17 g of slightly yellow-green solid was obtained. This solid softened slowly over a wide range and was completely melted at 78 °C.

A sample was sent for elemental analysis. Anal. Calcd for $[(B_2N_2C_5H_{17})C_6H_7N]^+,I^-$: C, 38.09; H, 6.97; N, 12.11; B, 6.23; I, 36.59. Found: C, 37.13; H, 7.08; N, 11.13; B, 5.93; I, 36.00. The weight of cation obtained (2.17 g) corresponds to a 74% yield.

A sample of the iodide salt was converted, in about 10% yield, to the PF_6^- salt. The melting point was sharp, between 126 and 127°C. The PF_6^- salt was a white solid.

Reaction of 4-Iodo-1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane with 2-Methylpyridine. A benzene solution containing 7.8 mmol of $B_2N_2C_5H_{17}I$ was placed in a 125-ml Erlenmeyer flask with a 24/40 standard taper neck. To this solution 7.8 mmol of 2-methylpyridine was added, dropwise, as a solution in benzene. The solution remained clear and colorless and was stirred for 30 min with no change observed. The solution was heated to gentle reflux for 10 min and a yellow color developed. A small amount of white solid precipitated out. The reaction mixture was removed from the drybox and placed in the hood. The solution was refluxed for 24 h and at the end of this time a large amount of white solid was present. The reaction mixture was removed to the drybox and filtered. The white solid obtained was dried by vacuum evaporation. A weight of 1.77 g of material with a sharp melting point at 184–185 °C was obtained. The colorless solid was dissolved in CH_2Cl_2 and heptane was added dropwise to precipitate the product. After filtering and vacuum-drying the solid, a melting point was taken and found to be 184–185 °C, the same as before recrystallization. A sample of the solid was sent for elemental analysis. Anal. Calcd for $[(B_2N_2C_5H_{17})C_6H_7N]^+,I^-$: C, 38.09; H, 6.97; N, 12.11; B, 6.23; I, 36.59. Found: C, 37.95; H, 6.84; N, 11.92; B, 6.22; I, 36.63. The amount of product obtained (1.77 g) corresponds to a yield of 65%.

Reaction of 4-Iodo-1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane with Trimethylamine. A sample of $B_2N_2C_5H_{17}I$ (ca. 11.8 mmol) was prepared in benzene solution by adding solid iodine, in portions, to 1.51 g of $B_2N_2C_5H_{18}$ until a yellow-brown color persisted.

The flask was then removed from the drybox and fitted with a gas bubbling tube and a reflux condensor. Trimethylamine gas was passed just above the surface of the solution. The solution was brought rapidly to gentle reflux. The solution lost the yellow color almost immediately and within 1 min a turbidity had developed; within 5 min substantial amounts of a white, benzene-insoluble material had precipitated. The reaction was continued in the above manner for 2 h and then the mixture was taken into the drybox and filtered. The benzene-insoluble portion was washed three times with 10-ml portions of benzene and then transferred to a tared flask and dried by vacuum evaporation. A white solid weighing 2.55 g was obtained.

The white solid was dissolved in a CH_2Cl_2–heptane mixture and heptane was added dropwise. A finely divided white solid precipitated immediately. The solution was filtered and the solid discarded. The above treatment was repeated. The remaining solution was taken to dryness by vacuum evaporation. A white solid weighing 2.23 g was obtained.

The melting point was taken. The sample began to soften at 138 °C and melted between 153 and 155 °C.

A portion of this sample was sent for elemental analysis. Anal. Calcd for $[(B_2N_2C_5H_{17})N(CH_3)_3]^+,I^-$: C, 30.71; H, 8.38; N, 13.43; B, 6.91; I, 40.57. Found: C, 30.58; H, 8.30; N, 13.38; B, 7.06; I, 40.54. The purified sample (2.23 g) corresponds to a 60.4% yield of $[(B_2N_2C_5H_{17})N(CH_3)_3]^+,I^-$.

The infrared spectra are reported as follows using the notation of Durkin, De Hayes, and Glore[5] and were recorded as solutions in CH_2Cl_2. Peak locations are given in cm^{-1}.

$[B_2N_2C_5H_{17}py]^+,I^-$ (py = pyridine): 3030 (m), 2950 (s), 2450 (s), 1628 (sh), 1621 (m), 1468 (sh), 1459 (s), 1408 (w), 1358 (w), 1236 (w), 1192 (m), 1158 (m), 1115 (m), 1086 (w), 1025 (w), 1017 (w), 994 (w), 970 (w), 943 (w), 878 (w), 853 (w), 808 (m).

$[B_2N_2C_5H_{17}py]^+,PF_6^-$: 3060 (w), 3005 (w), 2955 (w), 2450 (s), 1632 (w), 1621 (m), 1492 (w), 1468 (sh), 1462 (s), 1407 (w), 1356 (w), 1322 (w), 1235 (w), 1200 (sh), 1192 (m), 1159 (m), 1113 (m), 1083 (m), 1028 (sh), 1016 (m), 996 (w), 970 (w), 944 (w), 876 (m), 841 (s), 808 (sh).

$[B_2N_2C_5H_{17}\text{-4-}CH_3py]^+,I^-$: 3030 (m), 2955 (s), 2450 (s), 1633 (s), 1512 (w), 1470 (s), 1443 (s), 1416 (sh), 1235 (w), 1203 (m), 1192 (m), 1157 (m), 1108 (m), 1084 (m), 1018 (w), 971 (w), 946 (w), 877 (w), 838 (w), 824 (m).

$[B_2N_2C_5H_{17}\text{-4-}CH_3py]^+,PF_6^-$: 3060 (w), 3000 (w), 2955 (w), 2450 (s), 1634 (s), 1506 (w), 1468 (s), 1446 (sh), 1416 (sh), 1341 (w), 1321 (w), 1236 (m), 1201 (m), 1192 (s), 1160 (s), 1108 (s), 1084 (m), 1016 (m), 992 (w), 970 (w), 942 (w), 876 (s), 840 (s), 823 (sh).

$[B_2N_2C_5H_{17}\text{-2-}CH_3py]^+,I^-$: 3035 (m), 2955 (s), 2450 (s), 1624 (s), 1572 (w), 1496 (m), 1464 (s), 1416 (w), 1304 (w), 1236 (m), 1203 (sh), 1192 (s), 1169 (m), 1144 (m), 1122 (m), 1112 (sh), 1081 (m), 1059 (w), 1016 (w), 971 (w), 944 (w), 876 (w), 852 (w), 806 (w).

$[B_2N_2C_5H_{17}(CH_3)_3N]^+,I^-$: 3035 (m), 2955 (s), 2450 (s), 1482 (sh), 1468 (s), 1458 (sh), 1411 (w), 1319 (w), 1238 (w), 1214 (w), 1197 (m), 1164 (s), 1128 (w), 1096 (w), 1018 (m), 998 (w), 984 (sh), 970 (m), 945 (sh), 884 (w), 844 (s).

Results and Discussion

The ^1H NMR data are tabulated in Table I for the iodide salts using CH_2Cl_2 as solvent. The 100-MHz ^1H NMR spectrum was obtained for the 4-methylpyridine derivative to be sure that the peaks observed in the 60-MHz spectrum were not due to unexpected coupling from some source that could have caused the observed spectral pattern.

The data listed in Table II demonstrate that the chemical shift changes observed for the methyl groups of the $N(CH_3)_2$ unit in ring position 3 are less than the chemical shift changes

Table I. ^{1}H NMR Data for Four Amine Derivatives of $B_2N_2C_5H_{17}I^a$

	Chem shift				
Cation	1-$[N(CH_3)_2]^b$	2-$[N(CH_3)_2]^c$	$-CH_3{}^d$	Aromatic protons^e	CH^f
$[B_2N_2C_5H_{17}py]^+$	178 (2.6), 170 (3.6)	153 (3.7), 140 (2.8)		514 (5)	215 (1.3)
$[B_2N_2C_5H_{17}\text{-4-}CH_3py]^+$	177 (2.5), 170 (3.3)	152 (3.4), 138 (2.8)	160 (3.9)	539 (2), 474 (2)	218 (0.9)
$[B_2N_2C_5H_{17}\text{-4-}CH_3py]^+$	258, 249	214, 191	231		331
$[B_2N_2C_5H_{17}\text{-2-}CH_3py]^+$	177, 170 (3)	150, 146 (6)	177	515 (4)	213 (1)
$[B_2N_2C_5H_{17}(CH_3)_3N]^+$	169 (6.6)	163 (3.6), 159 (3)	175 (9.3)		

[a] Obtained at 60 MHz, except for the second listing of the 4-methylpyridine-containing product which was obtained at 100 MHz. The anion is iodide in all cases and the chemical shifts, relative to internal TMS, are given in hertz. The number of protons associated with each peak is enclosed in parentheses. Methylene chloride is the solvent in all cases. [b] The chemical shifts of the methyl groups bonded to the nitrogen atom in position 1 of the saturated ring. [c] The chemical shifts of the methyl groups bonded to the nitrogen atom in position 3 of the saturated ring. [d] The chemical shift of the methyl group(s) belonging to the amine. [e] The chemical shift of the protons observed in the aromatic region. The average value is reported for the protons in the aromatic region of the pyridine and 2-methylpyridine derivatives. [f] The chemical shift of the observed methylene proton.

Table II. ^{1}H NMR Data for *N*-Methyl Groups in Amine Derivatives Obtained from $B_2N_2C_5H_{17}I^a$

Derivative	*b*	*c*	*d*	*e*	*f*
$[B_2N_2C_5H_{17}py]^+, I^-$	8	19, 11	13	9, −4	38
$[B_2N_2C_5H_{17}\text{-4-}CH_3py]^+,I^-$	7	18, 11	14	8, −6	39
$[B_2N_2C_5H_{17}\text{-2-}CH_3py]^+,I^-$	7	18, 11	4	6, 2	31
$[B_2N_2C_5H_{17}(CH_3)_3N]^+, I^-$	0	10	4	19, 15	10

[a] All values in hertz. Methylene chloride is the solvent in all cases. [b] The chemical shift difference between methyl groups bonded to the nitrogen atom in ring position 1. [c] The change in chemical shift for the methyl groups bonded to the nitrogen atom in ring position 1 when compared to $B_2N_2C_5H_{18}$. [d] The chemical shift difference between methyl groups bonded to the nitrogen atom in ring position 3. [e] The change in chemical shift for the methyl groups bonded to the nitrogen atom in ring position 3 when compared to $B_2N_2C_5H_{18}$. [f] The total spred of methyl resonances encompassed by the methyl groups bonded to nitrogen atoms of the saturated ring system.

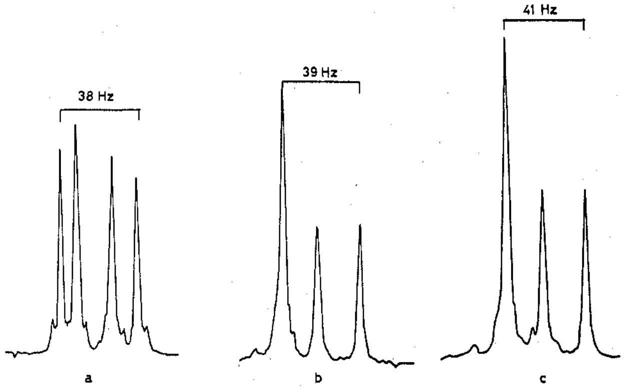


Figure 1. ^{1}H NMR spectra: (a) $[B_2N_2C_5H_{17}py]^+,I^-$ in CH_2Cl_2, aliphatic region; (b) $[B_2N_2C_5H_{17}py]^+,PF_6^-$ in CH_2Cl_2, aliphatic region; (c) $[B_2N_2C_5H_{17}py]^+,I^-$ in D_2O, aliphatic region.

observed for the methyl groups of the $N(CH_3)_2$ unit in ring position 1 for all three pyridine amine containing derivatives when compared with the NMR spectrum of $B_2N_2C_5H_{18}$. This contradicts the expected trend for amine substitution at ring position 4. Figures 1 and 2 show that when iodide is replaced by PF_6^- as the counterion, in the pyridine- and 4-methylpyridine-containing derivatives, the methyl groups bonded to the nitrogen atom in ring position 1 become magnetically equivalent and the resonances of the methyl groups bonded to the nitrogen atom in ring position 3 shift further apart. This is also observed with the 2-methylpyridine-containing derivative.

The data listed in Table III demonstrate that when a solvent with a high enough dielectric constant is used, in this case D_2O, all of the iodide salts show one set of equivalent methyl groups and one set of nonequivalent methyl groups.

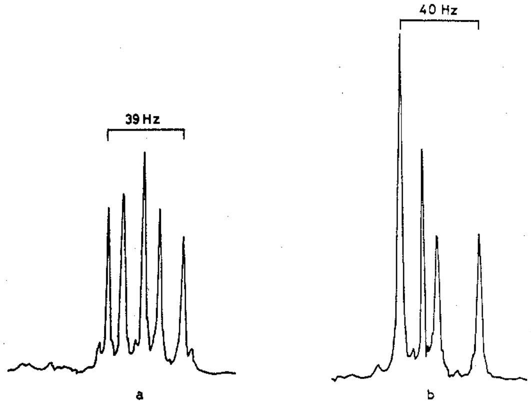


Figure 2. ^{1}H NMR spectra: (a) $[B_2N_2C_5H_{17}\text{-4-}CH_3py]^+,I^-$ in CH_2Cl_2, aliphatic region; (b) $[B_2N_2C_5H_{17}\text{-4-}CH_3py]^+,PF_6^-$ in CH_2Cl_2, aliphatic region.

Table III. ^{1}H NMR Data (Hz) for Two PF_6^- Salts in CH_2Cl_2 Solution and Four I^- Salts in D_2O

Cation	*a*	*b*	*c*
$[B_2N_2C_5H_{17}py]^+,PF_6^-$	0	21	39
$[B_2N_2C_5H_{17}py]^+,I^-$	0	21	41
$[B_2N_2C_5H_{17}\text{-4-}CH_3py]^+,PF_6^-$	0	21	40
$[B_2N_2C_5H_{17}\text{-4-}CH_3py]^+,I^-$	0	21	41
$[B_2N_2C_5H_{17}\text{-2-}CH_3py]^+,I^-$	0	16	34
$[B_2N_2C_5H_{17}(CH_3)_3N]^+,I^-$	0	10	10

[a] The chemical shift difference between methyl groups bonded to the nitrogen atom in position 1 of the saturated ring system. [b] The chemical shift difference between methyl groups bonded to the nitrogen atom in position 3 of the saturated ring system. [c] The total spread of methyl resonances encompassed by the methyl groups bonded to nitrogen atoms of the saturated ring system.

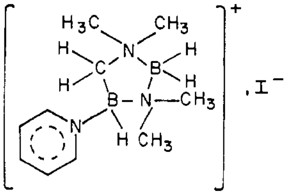
It is of interest to note that the ^{1}H NMR spectra of the pyridine, 4-methylpyridine, and 2-methylpyridine derivatives with PF_6^- as the counterion and CH_2Cl_2 as solvent are essentially identical with the ^{1}H NMR spectra of these derivatives when I^- is the counterion and D_2O is the solvent. An example is given in Figure 1.

Proposed Stuctures for Some Amine Derivatives of $B_2N_2C_5H_{17}I$. The derivative produced when pyridine reacts with $B_2N_2C_5H_{17}I$ does not exhibit the saltlike behavior found for some boron cations. The purified material will dissolve to a small extent in benzene and, in so doing, imparts a yellow color to the solution.

The broad absorption at 215 Hz, spanning approximately 30 Hz and appearing as a doublet, is assigned to one of the methylene protons bonded to the carbon atom in ring position 5. Judging from the values of the integrals the remaining methylene proton appears to fall under the peaks assigned to methyl groups at 153 and 170 Hz.

There is some evidence suggesting that conformational isomers may exist in CH_2Cl_2 solution (note the four small peaks in Figure 1a).

The data agree with a structure in which the pyridine molecule is coordinated to the boron atom in ring position 4. This conclusion is based on the different behavior of the $N(CH_3)_2$ units of the cyclopentane-like ring system observed in the NMR spectrum. The fact that the methylene protons are nonequivalent also supports this conclusion. The structure and name proposed for the derivative produced from the reaction of pyridine with $B_2N_2C_5H_{17}I$ are



1,1,3,3-tetramethyl-4-pyridine-1,3-diazonia-2,4-diboratocyclopentane iodide

The derivative obtained when 4-methylpyridine reacts with $B_2N_2C_5H_{17}I$ separates from benzene solution as a viscous liquid. After isolation and purification the derivative will dissolve to a small extent in benzene imparting a yellow color to the solution.

The broad multiplet (spanning 40 Hz) centered at 218 Hz in the 60-MHz NMR spectrum is assigned to one of the methylene protons bonded to the carbon atom in ring position 5.

The derivative obtained when 2-methylpyridine reacts with $B_2N_2C_5H_{17}I$ precipitates from benzene solution as a very pure material in the form of a white solid, unlike the yellow liquids obtained when pyridine or 4-methylpyridine are used.

The broad absorption centered at 213 Hz (spanning 32 Hz) is assigned to one of the methylene protons bonded to the carbon atom in ring position 5. The remaining methylene proton bonded to this carbon atom cannot be located in the NMR spectrum.

The product obtained when iodide is displaced by $(CH_3)_3N$ from $B_2N_2C_5H_{18}I$ is a white solid exhibiting saltlike characteristics. This derivative behaves like the 2-methylpyridine-containing derivative in that it precipitates as a solid from benzene solution instead of separating as an oil like the 4-methylpyridine- and the pyridine-containing derivatives. The ^1H NMR spectrum in CH_2Cl_2 solution corresponds to what one would expect if substitution occurred at the boron atom in ring position 4. The $N(CH_3)_2$ unit next to the substitution site shows the greatest changes. The position of the methylene protons cannot be assigned. The values of the integrals suggest that they may be hidden under the peaks assigned to the methyl groups.

The proposed structures for the derivatives produced by iodide displacement from $B_2N_2C_5H_{17}I$ by 4-methylpyridine, 2-methylpyridine, or $(CH_3)_3N$ are analogous to that of the pyridine derivative.

The data reported herein pose an interesting question. Why are the NMR spectra of the pyridine amine derivatives different when PF_6^- is substituted for I^- in CH_2Cl_2 solution? Since the only difference in the systems is the anions, an explanation must be based on some interaction available to one anion and not the other. It is well-known that I^- forms charge-transfer complexes with pyridinium ions.[6,7]

Boron cations containing pyridine amines can be viewed just as easily as pyridinium ions. In the research presented here the $[B_2N_2C_5H_{17}]^+$ moiety supplies the positive charge. If the I^- forms charge-transfer complexes with the aromatic ring systems of the pyridine amine derivatives resulting in tight ion pairing, then it could lock in the internal motions of the five-membered ring system so as to produce different time-averaged magnetic environments for the methyl groups bonded to the nitrogen atom in ring position 1. In addition the I^- could be in a position to influence the electron density around the protons of one of the methyl groups bonded to the nitrogen atom in ring position 1 thus producing a measurable chemical shift difference in the methyl groups. Molecular models indicate that this is a definite possibility depending on the proximity of the I^- to the aromatic ring system.

If this proposal of charge-transfer complexes forming tight ion pairs is correct, then for a derivative containing an aliphatic amine the NMR spectrum of its I^- salt in CH_2Cl_2 should be identical in pattern with the NMR spectrum of its I^- salt in D_2O. For this reason the trimethylamine derivative of $B_2N_2C_5H_{17}I$ was prepared. The NMR spectra of the I^- salt in CH_2Cl_2 and D_2O were identical in pattern showing equivalent methyl groups bonded to the nitrogen atom in ring position 1 and nonequivalent methyl groups bonded to the nitrogen atom in ring position 3.

Additional support for this argument is seen in the results obtained by removing the I^- from its association with the aromatic ring systems of the pyridine amine derivatives by using D_2O as the solvent. The nonequivalence of the methyl groups bonded to the nitrogen atom in ring position 1 is destroyed. It is of interest to note that when the nonequivalence is destroyed in the methyl groups bonded to the nitrogen atom in ring position 1 of the pyridine and 4-methylpyridine derivatives, the methyl groups bonded to the nitrogen atom in ring position 3 shift apart further, equal to the degree of nonequivalence originally observed in the methyl groups bonded to the nitrogen atom in ring position 1 (see Tables II and III).

Some comments are in order concerning the differences observed in the NMR spectra of the two types of derivatives investigated. The total number of hertz spanned by the methyl groups of the five-membered ring system in the aromatic amine derivatives is 3–4 times that spanned by the methyl groups of the five-membered ring system in the aliphatic amine derivative. Also, the number of hertz spanned is essentially constant for each derivative regardless of the solvent used or the anion present.

The unexpected chemical shifts observed in the three pyridine amine containing derivatives [the $N(CH_3)_2$ unit in ring position 1 being shifted more than the $N(CH_3)_2$ unit in ring position 3 when compared to the NMR spectrum of $B_2N_2C_5H_{18}$] is proposed to be a consequence of the magnetic lines of force generated by the aromatic ring systems. The small magnetic fields generated by the electrons of the aromatic ring systems are producing an electron density gradient causing the protons of the methyl groups of the saturated ring system to absorb at higher or lower field frequencies than expected.[8-10]

Registry No. $[B_2N_2C_5H_{17}py]^+,I^-$, 58602-42-9; $[B_2N_2C_5H_{17}py]^+,PF_6^-$, 58602-44-1; $[B_2N_2C_5H_{17}\text{-4-}CH_3py]^+,I^-$, 58602-45-2; $[B_2N_2C_5H_{17}\text{-4-}CH_3py]^+,PF_6^-$, 58602-47-4; $[B_2N_2C_5H_{17}\text{-2-}CH_3py]^+,I^-$, 58602-48-5; $[B_2N_2C_5H_{17}(CH_3)_3N]^+,I^-$, 58602-49-6; $B_2N_2C_5H_{17}I$, 58485-82-8; pyridine, 110-86-1; 4-methylpyridine, 108-89-4; 2-methylpyridine, 109-06-8; trimethylamine, 75-50-3.

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Alkali Metal Reductions of Some Trimethylamine–Haloboranes and Bis(trimethylamine)dihydroboronium Iodide

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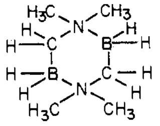
Trimethylamine–bromoborane and trimethylamine–iodoborane were reduced with Na–K alloy in several solvents. The data obtained support the contention that a reactive intermediate, $[(CH_3)_3NBH_2:]^-$, was produced which reacts via two paths, in varying degrees of significance, depending on the solvent used. The synthesis of $(CH_3)_3NBD_2H$ was demonstrated. The synthesis of 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane was improved. An improved synthesis for 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratocyclohexane was also found.

A limited number of diborane(4) adducts have been reported. In 1962 the first adduct of diborane(4), $(C_6H_5)_3P{\cdot}BH_2BH_2{\cdot}P(C_6H_5)_3$, obtained from the cleavage of trimethylamine–triborane(7) was reported.[1]

The bis(trifluorophosphine) adduct of diborane(4), $F_3P{\cdot}BH_2BH_2{\cdot}PF_3$, was prepared by treating the dimethyl ether adduct of triborane(7) with PF_3.[2,3] This adduct is a useful reagent for preparing other substituted fluorophosphine adducts of diborane(4).[4]

The bis(trimethylamine) adduct of diborane(4), $(CH_3)_3N{\cdot}BH_2BH_2{\cdot}N(CH_3)_3$, was reported to be formed by allowing $(CH_3)_3N{\cdot}BH_2Br$ to react with Na–K alloy in $(CH_3)_3N$ as solvent at 0 °C.[5] However, additional work has shown that 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratocyclohexane is the product and not $(CH_3)_3N{\cdot}BH_2BH_2{\cdot}N(CH_3)_3$.[6,7] This interesting product has been prepared previously by two different methods and has been referred to as dimethylaminomethylborane cyclic dimer, $[(CH_3)_2NCH_2BH_2]_2$,[8,9] referred to as I by the present authors.



I

The purpose of the work reported here was to try to prepare $(CH_3)_3N{\cdot}BH_2BH_2{\cdot}N(CH_3)_3$ and elucidate the reaction sequence leading to the production of I from $(CH_3)_3N{\cdot}BH_2Br$.

The coupling of two boron atoms to give a normal two-electron bond by reducing boron–halogen bonds with active metals has met with remarkable success.[10] Therefore, the present authors continued along similar lines using trimethylamine–iodoborane as the starting material instead of trimethylamine–bromoborane, after the iodoborane was found to be more reactive with Na–K alloy than the bromoborane.

Experimental Part

Trimethylamine–borane was obtained from Callery Chemical Co. and was used without further purification.

Sodium–potassium alloy was a 25:75 mixture by weight, respectively, and was prepared by placing clean chunks of the metals into a flask containing benzene and stirring until a liquid formed. One gram of this alloy provided 30 mmol of electrons available for reduction purposes.

Heptane, benzene, diethyl ether, glyme (1,2-dimethoxyethane) and diglyme [bis(2-methoxyethyl) ether] were obtained dry and oxygen free by using a mixture of Na metal and benzophenone in each solvent to react with water and dissolved oxygen. When the solutions turned blue, they were distilled in 1-l. quantities using a vacuum manifold (except for diglyme which was distilled at atmospheric pressure).

Methylene chloride was purified by stirring with $MgSO_4$ and CaH_2 for several weeks and then distilled in 1-l. quantities using a vacuum manifold.

Infrared spectra were obtained using a Beckman IR-10 spectrophotometer.

Melting points were recorded on a Thomas-Hoover apparatus.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

The ^1H NMR spectra were obtained at 60 MHz, using a Varian Model A-60A spectrometer.

All inert atmosphere work was done in a Vacuum/Atmospheres drybox equipped with Dri-Train HE-93B. Charging of the individual reaction vessels was done in this drybox, unless otherwise noted.

A standard vacuum line with a three-trap system was used for all reduced pressure work.

Reaction of Trimethylamine–Bromoborane with Sodium–Potassium Alloy in Trimethylamine at 0 °C. Trimethylamine–bromoborane (5 g, 32.9 mmol) was allowed to react with excess Na–K alloy in trimethylamine for 15 h at 0 °C. The products obtained were trimethylamine–borane ($(CH_3)_3N{\cdot}BH_3$), dimethylaminomethylborane cyclic dimer (I), and 3.77 g of benzene- and CH_2Cl_2-insoluble material that was not investigated.

The weight of $(CH_3)_3N{\cdot}BH_3$ produced (0.426 g) corresponded to a 17.7% yield based on the amount of $(CH_3)_3N{\cdot}BH_2Br$ added. The weight of I produced (0.189 g) corresponded to an 8.2% yield based on the $(CH_3)_3N{\cdot}BH_2Br$ added.

Reaction of Trimethylamine–Iodoborane with Sodium–Potassium Alloy in Trimethylamine at 0 °C. A sample of $(CH_3)_3N{\cdot}BH_2I$ (5.48 g, 27.4 mmol) and Na–K (2.28, 68.4 mmol of available electrons) were allowed to react in $(CH_3)_3N$ at 0 °C for 3 h. The products were $(CH_3)_3N{\cdot}BH_3$, $(CH_3)_3N$ (obtained after warming the nonvolatile residue at 45 °C on the vacuum line), I, bis(trimethylamine)dihydroboronium iodide, noncondensable gas (1.34 mmol), and Na–K (recovered from two sources: a Hg amalgam produced H_2 equivalent to 4.4 mmol of available electrons, and 0.76 g was recovered as a liquid from the reaction residue; this weight corresponded to 22.8 mmol of available electrons).

The reduction of $(CH_3)_3N{\cdot}BH_2I$ proceeded to completion over a 3-h period to produce a 44.4% yield of $(CH_3)_3N{\cdot}BH_3$, a 10.7% yield of I, and 1.8 mmol of $[(CH_3)_3N]_2BH_2{}^+I^-$. No other boron-containing compounds soluble in benzene or CH_2Cl_2 were obtained. Materials

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