Table I. Vibrational Structures for $Mo_2(gly)_4(SO_4)_2 \cdot 4H_2O$ (cm^{-1})

c polarization		a polarization				
ν	$\Delta\nu$	ν_1	$\Delta\nu_1$	ν_2	$\Delta\nu_2$	$\nu_2 - \nu_1$
1st Series						
20 570		21 790		21 930		140
	350		350		350	
20 920		22 140		22 280		140
	350		350		350	
21 270		22 490		22 630		140
	(330)		340		330	
(21 600)		22 830		22 960		130
			340		340	
2nd Series						
		23 170		23 300		130
			350		350	
21 510		23 520		(23 650)		130
	360		320			
21 870		(23 840)				
	360					
22 230						
	340					
22 570		21 510 − 20 570 = 940				
	340	21 790 − 20 570 = 1220				
22 910		21 930 − 20 570 = 1360				
	350					
23 260						
	340					
23 600						
	330					
23 930						
	340					
24 270						

is an order of magnitude more intense than the weak progression in z polarization but somewhat weaker than the intense lines in z. The first progression in x, y begins at 21 790 cm^{-1} and consists of seven lines with an average separation of 342 ± 11 cm^{-1} while the second begins at 21 930 cm^{-1} and six lines can be discerned with an average separation of 344 ± 8 cm^{-1}.

We propose to assign the first, weak progression in z polarization to an electronic transition, forbidden in D_{4h} symmetry but allowed in the S_4 symmetry of the crystal field. Since the deviation from D_{4h} is small, this progression is weak. The peak at 20 570 cm^{-1} is presumably the 0–0 line. The other progression in z polarization and the progression in x, y polarization are attributed to vibronic transitions involving the same electronic excitation having asymmetric vibrations, under

D_{4h}, with frequencies in the excited electronic state of 940, 1220, and 1360 cm^{-1}, respectively. That such a simple spectral picture occurs in an extended polyatomic ion with its many vibrational modes imples that the electronic excitation is quite localized. It probably involves orbitals concentrated on the molybdenum atoms. The vibrational spacings of the progressions averaging 340–345 cm^{-1} are attributed to that normal mode which consists chiefly of Mo–Mo stretching. Since this mode has a frequency of 393 cm^{-1} in the ground state, the transition presumably involves a transition from an Mo–Mo bonding orbital or into an Mo–Mo antibonding orbital or both. The exciting frequencies are probably those of vibrations within the $Mo_2(O_2C-)_4$ tetracyclic core.

Possible assignments for this transition, forbidden in D_{4h} and allowed in z polarization under S_4, in accordance with the spectra are $^1A_{1g} \rightarrow {}^1A_{1u}$, $^1B_{1g}$ and $^1B_{2g}$. The most significant point, however, is that the observations reported here are inconsistent with an assignment of this absorption band to the $\delta \rightarrow \delta^*$ transition which would be electric dipole allowed under D_{4h} symmetry.[14]

Registry No. $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$, 57214-97-8.

References and Notes

(1) Part 1: F. A. Cotton, B. A. Frenz, B. R. Stults, and T. R. Webb, *J. Am. Chem. Soc.*, in press.
(2) (a) Texas A&M University, with support from the National Science Foundation under Grant No. 33142X. (b) Iowa State University of Science and Technology, under U.S. Energy and Research Development Administration Contract No. W-7405-eng-82.
(3) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975).
(4) C. D. Cowman and H. B. Gray, *J. Am. Chem. Soc.*, **95**, 8177 (1973).
(5) F. A. Cotton, C. Oldham, and W. R. Robinson, *Inorg. Chem.*, **5**, 1708 (1966).
(6) L. Dubicki and R. L. Martin, *Aust. J. Chem.*, **22**, 1571 (1969).
(7) (a) D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965); (b) F. A. Cotton, Z. C. Mester, and T. R. Webb, *Acta Crystallogr., Sect. B*, **30**, 2768 (1974).
(8) F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, **1**, 161 (1971).
(9) F. A. Cotton, J. G. Norman, Jr., and T. R. Webb, unpublished studies of $Mo_2(O_2CH)_4$.
(10) M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, **7**, 1570 (1968).
(11) C. Calvo, N. C. Jayadevay, C. J. L. Lock, and R. Restivo, *Can. J. Chem.*, **48**, 219 (1970).
(12) F. A. Cotton and T. R. Webb, *Inorg. Chem.*, **15**, 68 (1976).
(13) D. S. Martin, *Inorg. Chim. Acta, Rev.*, **5**, 107 (1971).
(14) A referee has raised the possibility of an assignment in which the weak progression in z polarization is assigned to a singlet–triplet $\delta \rightarrow \delta^*$ transition. It is then not at all evident why the singlet–singlet transition should be present in both z and x, y polarization. More serious is the fact that a $^1A_{1g} \rightarrow {}^3A_{2u}$ transition would not be z polarized! It would be x, y polarized.

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611

High-Yield Synthesis of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane and Syntheses of Some Halo Derivatives

B. R. GRAGG* and G. E. RYSCHKEWITSCH

The reduction of bis(trimethylamine)dihydroboronium iodide $[[(CH_3)_3N]_2BH_2^+][I^-]$ with potassium metal in 1,2-dimethoxyethane produced a 74% yield of 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane ($B_2N_2C_5H_{18}$). The reactivity of this new small-ring heterocycle was briefly investigated with most of the attention centered on its reactivity toward some halogenating agents (HCl, HBr, HI, Cl_2, Br_2, I_2). A clear-cut halogenation sequence was observed. The hydrogen halides monohalogenated 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane at the boron atom in ring position 4.

This new small-ring boron heterocycle 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane ($B_2N_2C_5H_{18}$),[1]

* To whom correspondence should be addressed at the Department of Chemistry, University of Kentucky, Lexington, Ky. 40506.

I, is the missing link between the six-membered ring II produced by Miller and Muetterties[2] and the four-membered ring formed by the dimerization of $(CH_3)_2NBH_2$, III.

The purpose of this research was to improve the yield and find a more convenient procedure to obtain I from the reaction
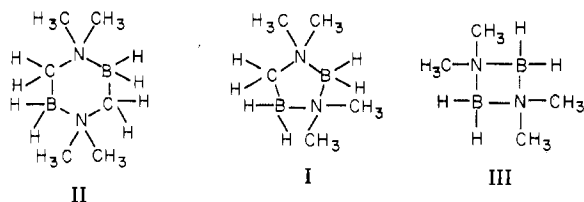
mixture than that reported in the earlier communication. In addition, confirmatory data were sought to support the NMR spectral assignments made previously. Thus, several halogenated derivatives of I were prepared and their properties were investigated.

Experimental Section

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 available electrons for reduction purposes.

Heptane and glyme (1,2-dimethoxyethane) 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 on a vacuum manifold in 1-l. quantities.

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

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

Melting points were recorded on a Thomas-Hoover apparatus.

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

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

Mass spectra were obtained at 70 eV on a Hitachi Perkin-Elmer RMU-6E mass 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.

A. Reaction of Bis(trimethylamine)dihydroboronium Iodide with Sodium–Potassium Alloy. A sample of bis(trimethylamine)dihydroboronium iodide (51.6 g, 200 mmol) and Na–K (9.94 g, 300 mmol of available electrons) were allowed to react in 150 ml of glyme between 67 and 77 °C until CH_4 evolution ceased.

Approximately 150 ml of glyme solution was obtained by filtration. Approximately 35 ml of this solution had the glyme removed by distillation. The residue was treated with 50 ml of deionized water and a liquid, immiscible in water, was collected and washed with three 10-ml portions of deionized water, was dried over $MgSO_4$, was weighed (1.28 g), and was shown to be I in excellent purity.

The remaining 115 ml of glyme solution was treated directly with 500 ml of deionized water, and a liquid, immiscible in water, was collected and washed with three 20-ml portions of deionized water, dried, and filtered. A sample weighing 4.87 g was obtained and was shown to be I. The combined yield was 48% based on the amount of cation added.

B. Reaction of Bis(trimethylamine)dihydroboronium Iodide with Sodium–Potassium Alloy. A sample of bis(trimethylamine)dihydroboronium iodide (103.25 g, 400 mmol) and Na–K (15 g, 450 mmol of available electrons) were allowed to react in 175 ml of refluxing glyme for 2 h. A 33% yield of I was obtained from an aqueous workup. A large ball of solid metal weighing 4.46 g was obtained which was mostly Na.

Reaction of Bis(trimethylamine)dihydroboronium Iodide with Potassium Metal in Glyme. A sample of bis(trimethylamine)dihydroboronium iodide (217 mmol), K (227 mmol), and 75 ml of glyme were added to a 500 ml three-necked flask in the drybox. This mixture was removed to the hood and equipped with a mechanical stirrer (avoid Teflon blades) and a reflux condenser. The third neck was stoppered. A gas-collecting and separating system was set up. The mixture of

$(CH_3)_3N$ and CH_4 was bubbled through a solution containing 300 mmol of HCl(aq). The CH_4, scrubbed of $(CH_3)_3N$, was collected over mineral oil in a graduated cylinder.

The glyme solution was heated to gentle reflux (approximately 85 °C). Methane evolution stopped after 55 min. The amount of CH_4 collected corresponded to 110 ± 4 mmol.

The solution was refluxed for 3 h while a slow stream of N_2 was passed above the solution to remove $(CH_3)_3N$. The solution was then taken into the drybox and filtered. A bluish-white solid weighing 36.45 g, assumed to be KI (218 ± 0.5 mmol), was obtained.

The glyme was removed by atmospheric pressure distillation. The distillation residue was treated with deionized water and a viscous liquid floated to the top. This liquid was placed in a separatory funnel and washed with three 20-ml portions of deionized water. The turbid liquid weighed 10.22 g and corresponded to a 74% yield of I (80 mmol). After drying over $MgSO_4$ and filtering, 8.70 g (62% yield) of I was obtained.

The amount of unreacted H_3O^+ from the HCl solution was found to be 107 mmol. Thus, 193 mmol of $(CH_3)_3N$ had passed into the HCl solution.

Reaction of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane with Anhydrous Hydrogen Chloride. A sample of I (1.39 g, 10.9 mmol) and excess HCl were allowed to react in CH_2Cl_2 by bubbling HCl through a solution of I until the NMR spectrum of the CH_2Cl_2 solution did not change with time.

The CH_2Cl_2 was removed by vacuum evaporation. The solid thus obtained was purified by dissolving it in heptane, filtering the resulting solution, and then removing the heptane by vacuum evaporation. Anal. Calcd for $B_2N_2C_5H_{17}Cl$: C, 37.01; H, 10.56; N, 17.26; B, 13.32; Cl, 21.85. Found: C, 37.19; H, 10.62; N, 17.19; B, 13.16; Cl, 21.70.

The mass spectrum was obtained and the parent – 1 ion (m/e 163) appeared as the heaviest species. The most abundant species (m/e 161) in the parent ion region corresponded to the parent – 3 ion. The base peak appeared at m/e 56.

Anhydrous HCl monochlorinated I to produce a 92% yield of a material with elemental composition $B_2N_2C_5H_{17}Cl$.

Reaction of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane with Anhydrous Hydrogen Bromide. A sample of I (1.44 g, 11.3 mmol) and excess HBr were allowed to react in CH_2Cl_2 solution by bubbling HBr through a solution of I until the ^1H NMR spectrum did not change with time. Solvent was removed by vacuum evaporation and a white solid was obtained (2.30 g). The solid (recrystallized from heptane) had a melting point of 53–55 °C. Anal. Calcd for $B_2N_2C_5H_{17}Br$: C, 29.05; H, 8.29; N, 13.55; B, 10.46; Br, 38.65. Found: C, 29.11; H, 8.26; N, 13.38; B, 10.54; Br, 38.72.

The mass spectrum was obtained. The heaviest isotopic species found corresponds to the parent – 1 ion (m/e 207) with an intensity of 8.2% compared to the base peak (m/e 127) assigned to $[^{11}B_2{}^{12}C_5{}^{14}N_2{}^1H_{17}]^+$. The two remaining peaks in the parent ion region can be assigned to the parent – 2 ion. The pattern of relative intensities in the region below m/e 127, which corresponds to molecular ions resulting from bromide loss, is essentially the same as in the parent ion region of I.

Anhydrous HBr formed a monobromo derivative of I in 99% yield.

Reaction of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane with Anhydrous Hydrogen Iodide. A sample of I (1.28 g, 10 mmol) and excess HI were allowed to react in CH_2Cl_2 solution. The procedure was the same as for the reactions of I with HCl and HBr.

The solid obtained was dissolved in CH_2Cl_2 and then precipitated with heptane. A white solid (2.50 g, 98% yield) was obtained in this manner. The solid melted between 77.5 and 79.5 °C. Anal. Calcd for $B_2N_2C_5H_{17}I$: C, 23.67; H, 6.76; N, 11.04; B, 8.52; I, 50.02. Found: C, 23.69; H, 6.77; N, 10.99; B, 8.52; I, 50.08.

The mass spectrum was obtained and did not show any peaks in the parent ion region (m/e 254). The first set of peaks of significant intensity appeared between m/e 208 and m/e 202.

Reaction of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane with excess Bromine. A sample of I (1.36 g, 10.6 mmol) and excess Br_2 were allowed to react in CH_2Cl_2 solution. Bromine was added dropwise over a 30-min period to the CH_2Cl_2 solution of I until a red color persisted; then 5 drops more of Br_2 was added.

After 4 h the reaction mixture was filtered to remove a small amount of insoluble material and the CH_2Cl_2 was removed by vacuum evaporation.

A yellow solid weighing 3.47 g was obtained. This solid was recrystallized from CH_2Cl_2 by adding heptane. A white solid weighing

3.28 g (90% yield) was obtained with a melting point of 119–121 °C. Anal. Calcd for $B_2N_2C_5H_{15}Br_3$: C, 16.47; H, 4.15; N, 7.68; B, 5.93; Br, 65.76. Found: C, 17.36; H, 4.36; N, 7.73; B, 5.99; Br, 64.51.

Reaction of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane with Iodine. Solid iodine was added in portions to 8.9 mmol of I in 50 ml of CH_2Cl_2. When a solution with a slowly fading yellow color was produced and gas evolution had slowed considerably, a ^1H NMR spectrum was obtained and a pattern identical with that of the monoiodo derivative of I was observed.

To this solution, solid iodine (9 mmol) was added in one portion. This mixture was refluxed until the solution acquired a persistent color (3 days). The reaction mixture was filtered from a small amount of reddish brown solid.

Unreacted iodine was removed by the addition of Hg. The resulting solution was filtered. The CH_2Cl_2 was removed by vacuum evaporation and a viscous liquid which slowly solidified (4.02 g) was obtained.

This solid was extracted with heptane. The heptane-soluble material gave a melting point of 143–145 °C. Anal. Calcd for $B_2N_2C_5H_{15}I_3$: C, 11.88; H, 2.99; N, 5.54; B, 4.26; I, 75.33. Found: C, 12.02; H, 3.04; N, 5.61; B, 4.43; I, 75.56. A weight of 3.48 g was obtained corresponding to a 77% yield.

Synthesis of a Diiodo Derivative of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane. After refluxing of 14.7 mmol of I in the presence of excess HI in CH_2Cl_2 solution for 17 h, the reaction of HI with the monoiodo derivative (produced in the first hour) had consumed only 5–10% of the monoiodo derivative based on the ^1H NMR spectrum. Solid I_2 was added in unweighed portions on three occasions.

The ^1H NMR spectrum was monitored to observe the reaction process. The reaction was stopped after 22 h when the first appearance of the triiodo derivative was detected in the ^1H NMR spectrum.

The reaction mixture was treated with Hg to remove excess I_2 and HI. After filtration and removal of the CH_2Cl_2 by vacuum evaporation, 5.26 g of a slightly reddish liquid was obtained.

This liquid was dissolved in a mixture of CH_2Cl_2 and heptane. A clear reddish liquid (4.33 g) was obtained after concentrating the solvent mixture. The liquid was extracted with heptane and 2.76 g (49% yield) of a slightly yellow liquid was obtained. Anal. Calcd for $B_2N_2C_5H_{16}I_2$: C, 15.82; H, 4.25; N, 7.38; B, 5.70; I, 66.86. Found: C, 15.89; H, 4.27; N, 7.28; B, 5.69; I, 66.97.

Reaction of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane with Chlorine. A sample of I (1.47 g, 11.5 mmol) and Cl_2 were allowed to react in CH_2Cl_2 solution. The solution took on a yellow color after approximately 1 h. A sample was removed and the NMR spectrum was obtained. Chlorine gas was passed for 2 h more. Samples were removed at 1-h intervals and the NMR spectra were obtained. The pattern in the NMR spectrum did not change after 2 h of reaction. After a total of 3 h of exposure to Cl_2 gas the reaction mixture was filtered. The CH_2Cl_2 was removed by vacuum evaporation.

A yellow solid weighing 2.76 g was obtained. This solid was dissolved in a CH_2Cl_2–heptane solvent mixture and filtered. The filtrate was concentrated by vacuum evaporation and a white solid slowly crystallized out of solution. The white needles were dried by vacuum evaporation. A sample weighing 2.32 g (76% yield) was obtained. The melting point of the recrystallized material was 147–149 °C. Anal. Calcd for $B_2N_2C_5H_{14}Cl_4$: C, 22.61; H, 5.31; N, 10.55; B, 8.14; Cl, 53.39. Found: C, 23.21; H, 5.63; N, 10.15; B, 7.86; Cl, 51.76.

The mass spectrum was obtained and gave a parent ion (in 10% relative abundance to the other peaks in the parent ion region) assigned to the isotopic species $[^{11}B_2{}^{14}N_2{}^{12}C_5{}^1H_{14}{}^{35}Cl_3{}^{37}Cl]^+$ at m/e 266. The base peak of the tetrachloro derivative appeared at m/e 193.

Results and Conclusions

Yield Improvements of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane. Two points were found to be important in improving the yield of I. First, the amount of K present should not exceed a 1:1 ratio with $[[(CH_3)_3N]_2BH_2^+][I^-]$; if it does the yield will decrease because of the overproduction of $H_2BN(CH_3)_2$. Second, the closing of the cyclopentane-like ring is a transamination reaction and is slowed if excess $(CH_3)_3N$ is allowed to accumulate in the system. This can be prevented by passing N_2
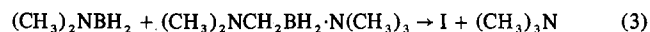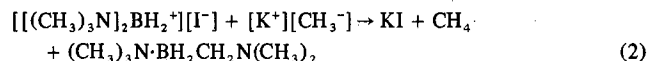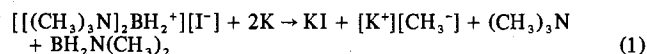
Table I. Infrared Data (cm^{-1}) for $B_2N_2C_5H_{18}$ and Some Halo Derivatives[a]

$B_2N_2C_5H_{18}$: 3000 m, 2940 s, 2415 s, 2340 s, 2265 m, 1463 s, 1402 w, 1360 w, 1290 m, 945 m, 878 w, 830 w, 791 m, 720 w

$B_2N_2C_5H_{17}Cl$: 3000 s, 2945 s, 2890 sh, 2850 w, 2430 s, 2370 sh, 2330 sh, 1463 s, 1443 sh, 1433 sh, 1408 w, 1308 w, 1295 m, 1238 m, 1193 s, 1145 s, 1118 m, 1063 s, 1030 sh, 1019 s, 985 m, 968 s, 948 s, 878 sh, 863 m, 843 s

$B_2N_2C_5H_{17}Br$: 3010 s, 2950 s, 2890 w, 2440 s, 2370 m, 2330 w, 1468 s, 1435 m, 1410 w, 1295 w, 1235 m, 1190 s, 1145 s, 1120 w, 1080 w, 1045 s, 1020 s, 995 m, 965 m, 945 m, 870 w, 840 m

$B_2N_2C_5H_{17}I$: 3005 s, 2950 s, 2450 s, 2370 m, 2330 w, 1466 s, 1432 m, 1406 m, 1366 w, 1293 w, 1236 m, 1191 s, 1142 s, 1117 w, 1077 w, 1039 m, 1017 s, 1002 s, 974 s, 941 m, 873 m, 833 s

$B_2N_2C_5H_{15}Br_3$: 3028 m, 3008 sh, 3000 sh, 2948 s, 2888 w, 2540 s, 1463 s, 1408 w, 1313 w, 1302 w, 1233 m, 1198 m, 1173 s, 1138 m, 1116 w, 1089 m, 1068 s, 1018 m, 990 m, 950 s, 938 s, 900 sh, 888 w, 846 s

$B_2N_2C_5H_{15}I_3$: 3025 w, 3010 w, 2955 m, 2545 m, 1470 s, 1460 sh, 1435 m, 1410 w, 1298 w, 1232 w, 1197 m, 1172 s, 1137 m, 1115 w, 1088 w, 1050 s, 1014 m, 986 m, 952 s, 932 m, 887 m, 839 s

$B_2N_2C_5H_{16}I_2$: 3005 m, 2950 m, 2510 m, 2458 m, 1470 s, 1460 sh, 1435 m, 1410 m, 1297 w, 1232 w, 1197 s, 1175 m, 1140 w, 1119 m, 1094 w, 1054 s, 1019 s, 1012 sh, 978 s, 957 s, 820 s

$B_2N_2C_5H_{14}Cl_4$: 3015 w, 2960 m, 1478 s, 1458 s, 1442 s, 1308 w, 1223 w, 1195 w, 1186 sh, 1136 sh, 1126 m, 1024 m, 996 s, 953 s, 923 s, 908 sh, 851 s, 838 s

[a] Key: s, strong; m, medium; w, weak; sh, shoulder.

through the system while heating it to gentle reflux.

The best reaction sequence that can be proposed from these data is one that produces the unstable $(CH_3)_3N$ adduct of dimethylaminoborane, $(CH_3)_3N \cdot BH_2N(CH_3)_2$, and trimethylamine–(dimethylaminomethyl)borane, $(CH_3)_3N \cdot BH_2CH_2N(CH_3)_2$.[3,4] A logical sequence of reactions that will produce these two compounds is given by eq 1–3.

$$[[(CH_3)_2N]_2BH_2^+][I^-] + 2K \rightarrow KI + [K^+][CH_3^-] + (CH_3)_3N + BH_2N(CH_3)_2 \quad (1)$$

$$[[(CH_3)_3N]_2BH_2^+][I^-] + [K^+][CH_3^-] \rightarrow KI + CH_4 + (CH_3)_3N \cdot BH_2CH_2N(CH_3)_2 \quad (2)$$

$$(CH_3)_2NBH_2 + (CH_3)_2NCH_2BH_2 \cdot N(CH_3)_3 \rightarrow I + (CH_3)_3N \quad (3)$$

^1H NMR and ^{11}B NMR Assignments for 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane. The ^1H NMR spectral peaks of I can be assigned to specific moieties by comparing the chemical shifts observed for I to the chemical shifts observed for II and III.

In the ^1H spectrum of II the methyl groups appear at 154 Hz with a width at half the peak height of 3 Hz, and the methylene protons appear as a broad peak at 127 Hz. The methyl groups in the ^1H NMR spectrum of III appear at 146 Hz with a broadness of 9 Hz at half the peak height.

The $N(CH_3)_2$ unit in ring position 3 of I should be more like the $N(CH_3)_2$ units in III than the $N(CH_3)_2$ units in II. One of the $N(CH_3)_2$ units of I appears at 144 Hz with a broadness of 9 Hz at half the peak height. This absorption is assigned to the $N(CH_3)_2$ unit in ring position 3. The other $N(CH_3)_2$ unit of I should be more like the $N(CH_3)_2$ units of II. The remaining $N(CH_3)_2$ unit of I appears at 159 Hz with a broadness of 5 Hz at half the peak height and is assigned to the $N(CH_3)_2$ unit in ring position 1.

The methylene protons of compound I are assigned to the shoulder appearing at 134 Hz based on broadness and intensity relative to the other two peaks in the spectrum.

The boron nuclei responsible for the ^{11}B NMR spectrum of I are assigned to specific ring positions by comparing the

Table II. Chemical Shift Changes of Methylene Protons in the Halo Derivatives of I

| Compd	a	b	Compd	a	b
I	134		VI	(164–159)	–(30–25)
IV	146 sh	–12	VII	188	–54
V	156, 148 ± 2	–22, –14	VIII	217, 212	–83, –78

[a] The chemical shift of the methylene protons, in Hz downfield from internal TMS. [b] The change in chemical shift of the methylene protons of the halo derivative of I when compared to the NMR spectrum of I, in Hz.

chemical shifts observed to those of the [11]B nuclei in II and III. The boron atom in ring position 2 (between the two nitrogen atoms) of I should have a chemical shift similar to that of the [11]B nuclei of III. The ^{11}B NMR spectrum of III[5] shows a triplet at +14.5 ppm vs. $B(OCH_3)_3$. The peak appearing at +12.3 ppm vs. $B(OCH_3)_3$ in the ^{11}B NMR spectrum of I is therefore assigned to the boron atom in ring position 2.

The boron nuclei of II appear as a triplet at +27.4 ppm vs. $B(OCH_3)_3$. The triplet centered at +25.2 ppm in the ^{11}B NMR spectrum of I is therefore assigned to the boron atom in ring position 4.

Although the assignments made for I are reasonable when compared with NMR spectra of known compounds, the present authors prepared derivatives of I to obtain conclusive data to substantiate the NMR assignments made herein. The presence of two dihydroboryl units, in different environments, in I produced an interesting halogenation sequence.

Halogenation Sequence of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane. Compound I is monohalogenated in greater than 90% yield under mild conditions by the hydrogen halides. Halogenation occurs on the boron atom occupying the number 4 position of the cyclopentane-like ring system. No evidence was obtained supporting a monohalogenated derivative in which the halogen was attached to the boron atom in ring position 2. (See IV–IX.)
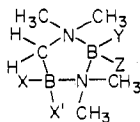
IV: X = Cl, X′ = Y = Z = H   VII: X = X′ = Y = Br, Z = H
V: X = Br, X′ = Y = Z = H   VIII: X = X′ = Y = I, Z = H
VI: X = I, X′ = Y = Z = H   IX: X = X′ = Y = Z = Cl

The monoiodo derivative of I was found to be slowly converted to a diiodo derivative by HI in refluxing CH_2Cl_2. After 17 h only 5–10% of the monoiodo derivative of I had been iodinated by HI.

The second halogen bonds to the boron atom in ring position 2 and produces a mixture of cis and trans isomers. This

statement is based on an extrapolation of the data obtained from the preparation of a material with composition B_2N_2-$C_5H_{16}I_2$ and found to be a mixture of cis and trans isomers of a diiodo derivative of I.

The third halogen substitutes on the boron atom in ring position 4, thus producing a derivative with a BX_2 (X = I, Br, Cl) unit at ring position 4 and a BHX unit at ring position 2.

The fourth halogen replaces the last remaining hydrogen atom in position 2. The only example of a tetrahalo derivative at the moment is the tetrachloro derivative of I. Whether or not the tetrabromo and tetraiodo derivatives can be prepared will depend on the extent of steric crowding[6] around the boron in ring position 2 and the lowered reactivity of the remaining boron–hydrogen bond.

Effect As Seen in the ^{1}H NMR Data on the Methylene Group Protons in Ring Position 5 by Halogenation of One or Three of the Boron–Hydrogen Bonds of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane. The chemical shift of the methylene protons of I (Table II) is affected to the greatest extent of all the carbon-attached hydrogens when compound I is mono- or trihalogenated. The shift is downfield in all cases with the effect for the monohalo derivatives increasing in the order Cl < Br < I. This same order is found for the tribromo and triiodo derivatives of I.

In two cases magnetic nonequivalence of the methylene protons is observed. The monobromo derivative of I and the triiodo derivative of I show this nonequivalence. The methylene protons in the monochloro and monoiodo derivatives of I may or may not be magnetically equivalent. The methylene protons in both cases are too close to peaks due to methyl groups to be resolved. The tribromo derivative of I clearly shows the methylene protons to be magnetically equivalent.

The two trihalo derivatives of I show an interesting difference in the methylene proton region of the ^{1}H NMR spectra. Both trihalo derivatives of I show the methylene protons shifted from the most upfield position in the NMR spectrum of compound I to the most downfield position. The tribromo derivative of I shows the methylene protons to be equivalent, as one would expect if they were adjacent to a BBr_2 unit. The triiodo derivative, on the other hand, shows the methylene protons to be nonequivalent by 5 Hz. This means one of two things: that the BI_2 unit is in ring position 2, which cannot be rationalized considering the available data, or that the presence of two iodines on the same side of the ring system produces an effect large enough to make the methylene protons nonequivalent. Since, of the halo derivatives prepared so far, the iodine-containing ones produce the largest effect in any series, this is a reasonable supposition.

Chemical Shift Trends of Some Halo Derivatives of 1,1,-3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane. A good review of current theories concerning the chemical shift

Table III. Comparison of the ^{1}H NMR Data of Some Halo Derivatives of I to the Assignments Made in the ^{1}H NMR Spectrum of I

Compd	Chem shifts, Hz					
	$N(CH_3)_2$[a]	$N(CH_3)_2$[b]	CH_3[c]	$N(CH_3)_2$[d]	$N(CH_3)_2$[e]	CH_3[f]
I	159		0	144		0
IV	159	0	0	142	+2	0
V	161, 159	–2, 0	2	148, 143	–4, +1	5
VI	164, 160	–5, –1	4	153, 142	–9, +2	11
VII	175, 169	–16, –10	6	162, 157	–18, –13	5
VIII	179, (175 or 174)	–20, (–16 or –15)	4 or 5	(175 or 174), 161	(–31 or –30), –17	14 or 13

[a] The chemical shift of the protons of the methyl groups assigned to the $N(CH_3)_2$ unit in ring position 1 vs. TMS. Solvent is CH_2Cl_2. [b] The change in the chemical shifts of the protons of the methyl groups on the nitrogen atom in ring position 1 compared to the NMR spectrum of I. [c] The absolute value of the chemical shift difference between the methyl groups bonded to nitrogen atom 1. [d] The chemical shift of the protons of the methyl groups assigned to the $N(CH_3)_2$ unit in ring position 3. [e] The change in the chemical shifts of the protons of the methyl groups on the nitrogen atom in ring position 3 compared to the NMR spectrum of I. [f] The absolute value of the chemical shift difference between the methyl groups bonded to nitrogen atom 3.

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.

References and Notes

(1) B. R. Gragg and G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **96**, 4717 (1974).
(2) N. E. Miller and E. L. Muetterties, *Inorg. Chem.*, **3**, 1196 (1964).
(3) A. B. Burg and C. L. Randolph, Jr., *J. Am. Chem. Soc.*, **73**, 953 (1951).
(4) N. E. Miller, *J. Am. Chem. Soc.*, **88**, 4284 (1966).
(5) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).
(6) W. H. Myers, Doctoral Dissertation, University of Florida, 1972.
(7) T. Schaefer, W. F. Reynolds, and T. Yonemoto, *Can. J. Chem.*, **41**, 2969 (1963).

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

B. R. GRAGG* and G. E. RYSCHKEWITSCH

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

* To whom correspondence should be addressed at the Department of Chemistry, University of Kentucky, Lexington, Ky. 40506.