TABLE I

CALCULATED AND OBSERVED GAS PHASE SPECTRA AND ASSIGNMENTS[d]

Mode	Symmetry type	Band type[a]		$HB^{10}Cl_2$	$HB^{11}Cl$	$\Delta\nu$ ($B^{10}-B^{11}$)	$DB^{10}Cl$	$DB^{11}Cl$	$\Delta\nu$ ($B^{10}-B^{11}$)
ν_1	A_1	B (⊥)	Calcd.	752	729	23	735	714	21
B–Cl stretch			Obsd.	762[b]	740[b]	22			
ν_2	A_1	B (⊥)	Calcd.	2614	2607	7	1913	1902	11
B–I stretch			Obsd.	2617	[c]		1969[b]	[c]	
ν_3	A_1	B (⊥)	Calcd.	289	287	2	287.5	285	2.5
B–Cl sym.			Obsd.						
ν_4 deformation	B_1	A (‖)	Calcd.	1032	1000	32	1002	962	40
B–Cl asym. stretch			Obsd.	1100[b]	1089[b]	11	1050[b]	1005[b]	45
ν_5	B_1	A (‖)	Calcd.	859.5	851.2	8.3	640.6	639.7	0.9
B–H in-plane deformation			Obsd.		892[b]				
ν_6	B_2	C (⊥)	Calcd.	667.2	654.0	13.2	576.1	560.4	15.7
Out-of-plane deformation			Obsd.	795[b]	784[b]	11	661[b]	645[b]	16

[a] Type A, B, and C refer to vibration–rotation bands whose dipole moment changes are along the axes of least, intermediate, and greatest moments of inertia, respectively. In this case, $I_B \approx I_C$, and ‖ and ⊥ refer to band types of the accidentally symmetric top whose dipole moment changes are along and perpendicular to the top axis, A. [b] Band centers estimated from positions of the observed vibration–rotation envelopes. [c] No B^{10}–B^{11} splitting was observed for this mode. [d] All frequencies are in cm.$^{-1}$.

tion (892 cm.$^{-1}$). In the matrix, a doublet centered at 917 cm.$^{-1}$ is also observed and can be assigned to the B^{10} species. (Interference from ν_3 (958 cm.$^{-1}$) of $B^{11}Cl_3$ prevented observation of this band in the gas phase.) Two bands at 801 and 788 cm.$^{-1}$ can be assigned to the B^{10}–B^{11} splitting of the out-of-plane deformation, which occurs at 795 and 784 cm.$^{-1}$ in the gas phase. The behavior of the remaining bands from 760 to 700 cm.$^{-1}$ cannot yet be correlated with the gas phase observations. (The two intense bands at 995 and 955 cm.$^{-1}$ are ν_3 of B^{10} and $B^{11}Cl_3$.)

In the $HBCl_2$-$DBCl_2$ mixture, all of the bands assigned to $HBCl_2$ show intensity decreases. In addition, two new bands appear at 1007 and 970 cm.$^{-1}$. Although the pattern of frequency shifts is not clear, these bands may be assigned to the B-Cl asymmetric stretch of $DB^{10}Cl_2$ and $DB^{11}Cl_2$ (observed at 1050 and 1005 cm.$^{-1}$ in the gas phase). Again the bands between 700 and 760 cm.$^{-1}$ cannot be assigned except for one possibility: a weak doublet, whose peaks are at 759 and 756 cm.$^{-1}$, which appeared in the $HBCl_2$ spectrum, has disappeared. The B^{10}–Cl symmetric stretch of $HBCl_2$ occurs at 762 cm.$^{-1}$ in the gas phase, and the calculations predict a shift to lower frequency for $DBCl_2$. The behavior of the doublet at 759 and 750 cm.$^{-1}$ indicates that it may be the B^{10} component of this mode.

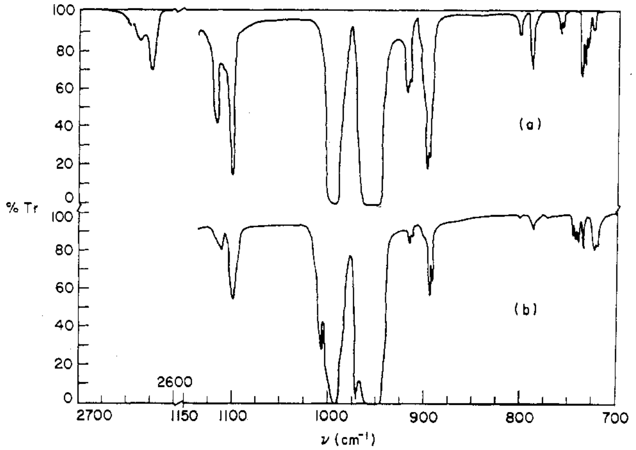

Fig. 1.—Matrix isolation spectra of $HBCl_2$–BCl_3 and $HBCl_2$–$DBCl_2$–BCl_3 mixtures in argon, at ≈10°K.; 700–1150 and 2600–2700 cm.$^{-1}$: (a) $HBCl_2$–BCl_3, ≈25% $HBCl_2$, and mole ratio of A to the mixture = 100; (b) $HBCl_2$–$DBCl_2$–BCl_3, ≈10% each of $HBCl_2$ and $DBCl_2$, and mole ratio of A to the mixture = 100.

Some of the bands observed in the matrix are multiplets, *e.g.*, the high-frequency triplet (B-H stretch), the doublets assigned to the B^{10}- and B^{11}-H in-plane deformation, and possibly the B^{10}–Cl symmetric stretching mode. Other spectra not shown (matrix isolation and mixed crystal) indicate that the relative intensities, frequencies, and line widths of the component of the high-frequency triplet are quite sensitive to concentration, temperature, and deposition effects. This behavior is characteristic of systems which are influenced by intermolecular interactions.[5] It is interesting to note that bands involving H motions are multiplets. Since $HBCl_2$ is the simplest compound available containing a single B-H bond, with refined methods of preparation and separation, it may provide a convenient species with which to investigate boron–hydrogen interactions.

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(5) See, for example, D. Dows, *J. Chem. Phys.*, **31**, 1637 (1959).

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Chemistry of Boranes. XVII.[1] Pyrolysis of $H_2B(NR_3)_2{}^+X^-$ Salts

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Pyrolysis of the borane cation salts,[2] $H_2B(NR_3)_2{}^+X^-$, provides a good route to monosubstituted borane adducts, R_3NBH_2X.

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(1) Paper XVI: N. E. Miller and E. L. Muetterties, *Inorg. Chem.*, in press.

$$H_2B[N(CH_3)_3]_2{}^+X^- \xrightarrow{120\text{–}200°} (CH_3)_3NBH_2X + N(CH_3)_3$$

Trimethylamine azidodihydroborane, $(CH_3)_3NBH_2N_3$, was prepared in 30–40% yield by slow heating of $H_2B[N(CH_3)_3]_2{}^+N_3{}^-$ to 120–150° under vacuum. The azide distilled from the pyrolysis flask as a mobile liquid which froze to a crystalline solid at 13°. On rapid heating the azidoborane detonates near 200°, but otherwise appears to be safe to handle. It is soluble in ethers, benzene, and chloroform and is sparingly soluble in water. On exposure to moist air for a day, partial hydrolysis takes place with formation of small amounts of a nonvolatile white solid.

The infrared spectrum of $(CH_3)_3NBH_2N_3$ shows the expected two BH stretching frequencies at 2400 and 2280 cm.$^{-1}$ and an azide stretching frequency at 2100 cm.$^{-1}$. It is reported in the literature[3] that crystalline $(CH_3)_3NBH_{3-n}(N_3)_n$ compositions, where $n = 1.5$ and 1.9, result when trimethylamine is added to the reaction product of diborane and hydrazoic acid. It is quite apparent that these are gross mixtures, and $(CH_3)_3NBH_2N_3$ is probably not present in significant amounts since it is a liquid.

Trimethylamine azidodihydroborane adds one mole of boron trifluoride, apparently to form $(CH_3)_3NBH_2\text{-}N_3\text{-}BF_3$. The infrared spectrum of the adduct shows an azide stretching absorption shifted toward shorter wave length (2175 cm.$^{-1}$) and strong BF absorption at 1100–1200 cm.$^{-1}$. This type of adduct is not unknown in boron chemistry, as evidenced by the recently reported compound, $R_2NHBH_2CNBH_3$.[4]

Pyrolyses of other salts are being investigated. The chloride salt, $H_2B[N(CH_3)_3]_2{}^+Cl^-$, when heated to near 200°, gives pure $(CH_3)_3NBH_2Cl$; $H_2B[N(CH_3)_3]_2{}^+Br^-$ forms $(CH_3)_3NBH_2Br$; and the carbonate salt yields traces of a liquid which may have the structure $(CH_3)_3NBH_2OCO_2BH_2N(CH_3)_3$. The chlorine and bromine substituted adducts have been reported by Nöth and Beyer,[5] who prepared them by the reaction of trimethylamine borane and the corresponding hydrogen halide, but some difficulty was experienced by us in obtaining pure products by their procedure.

Experimental

A 60-ml. portion of 2.3 M $H_2B[N(CH_3)_3]_2OH$[2] was acidified with aqueous hydrazoic acid, and the water was evaporated *in vacuo* to leave about 26 g. of mushy solid. The residue was transferred to a short-path still equipped with a drip tip and take-off assembly.[6] The remainder of the water in the residue was removed by careful heating to 80° under high vacuum. On further heating, some gas evolution was observed at 100–120°. The solid changed to a liquid after several hours at this temperature, trimethylamine collected in the pump trap, and a clear mobile liquid distilled. Heating was continued for 3–4 hr. at 130–140° until a total of 5.2 g. (32%) of $(CH_3)_3NBH_2N_3$ had collected. The residue still contained some undecomposed $H_2B[N(CH_3)_3]_2{}^+N_3{}^-$.

Anal. Calcd. for $(CH_3)_3NBH_2N_3$: C, 31.6; H, 9.7; N, 49.2; B, 9.5. Found: C, 32.2; H, 9.9; N, 49.1; B, 9.5.

A 0.17-g. portion (1.5 mmoles) of $(CH_3)_3NBH_2N_3$ absorbed 1.27 mmoles of gaseous boron trifluoride from a total of 2.8 mmoles at room temperature to give a liquid adduct which was soluble in benzene without reaction.

An anhydrous sample of $H_2B[N(CH_3)_3]_2{}^+Cl^-$, 6.09 g. (36.6 mmoles), was heated in a vacuum sublimer to 200–250° over a period of 3 hr. The white sublimate was collected on a water jacket cooled to 0°. The pyrolysis gases were collected in a series of traps on a vacuum train. Repeated resublimation of the white sublimate yielded $(CH_3)_3NBH_2Cl$, 2.79 g. (71.2% yield). The pure product melts at 85–86°, lit.[5] 85°.

Anal. Calcd. for $(CH_3)_3NBH_2Cl$: C, 33.6; H, 10.3; N, 13.1; B, 10.1; Cl, 33.0. Found: C, 33.6; H, 10.3; N, 13.1; B, 10.3; Cl, 33.7.

The nonvolatile residue, 0.96 g., was identified by infrared analysis as $(CH_3)_3NH^+Cl^-$. The liquid nitrogen trap contained trimethylamine (83% yield) and a trace of chloroform which had been used in the drying of the original salt.

In the apparatus described above, 9.22 g. (43.6 mmoles) of anhydrous $H_2B[N(CH_3)_3]_2{}^+Br^-$ was decomposed at 200–250° to yield a gas, a sublimate, and a residue. The condensed gas, 2.47 g. (96% yield), was identified as trimethylamine by its infrared spectrum and vapor pressure. The sublimate was resublimed three times at 60–100° to yield a white crystalline product, 5.38 g. (88.4% yield), m.p. 74–75°, lit.[5] 67°.

Anal. Calcd. for $(CH_3)_3NBH_2Br$: C, 23.7; H, 7.30; N, 9.22; B, 7.12; Br, 52.6. Found: C, 24.2; H, 7.42; N, 9.34; B, 7.11; Br, 51.1.

A sample of $[H_2B[N(CH_3)_3]_2{}^+]_2CO_3{}^{-2}$ was prepared by treating one part of $H_2B[N(CH_3)_3]_2{}^+OH^-$ with carbon dioxide (from Dry Ice) until saturated, boiling to expel excess carbon dioxide, and adding one part of $H_2B[N(CH_3)_3]_2{}^+OH^-$. The solution was evaporated with careful mild heating until a white solid formed which decomposed with formation of hydrogen, carbon dioxide, trimethylamine, and a few drops of a clear mobile liquid. The infrared spectrum of the liquid had a BH_2 doublet absorption at 2400 and 2300 cm.$^{-1}$, a strong carbonyl absorption at 1700 cm.$^{-1}$, and bands in the long wave length region at 1180, 1250, and 850 cm.$^{-1}$, characteristic of R_3NBH_2X derivatives. The product was not obtained in pure form.

Anal. Calcd. for $(CH_3)_3NBH_2OCO_2BH_2N(CH_3)_3$: C, 41.2; H, 10.9. Found: C, 38.4; H, 9.9.

This compound is quite sensitive to hydrolysis.

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[2] N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

[3] E. Wiberg and H. Michaud, *Z. Naturforsch.*, **9b**, 497 (1954).

[4] V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **83**, 2471 (1961).

[5] H. Nöth and H. Beyer, *Ber.*, **93**, 2251 (1960).

[6] R. J. McCarter, *Rev. Sci. Instr.*, **33**, 388 (1962).

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Preparation and Properties of the $Ln_2Ti_2O_7$-Type Rare Earth Titanates

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The mineral pyrochlorite $(CaNaNb_2O_6F)$[1] exists as a face-centered cubic structure which can be derived in principle from appropriate substitutions in a material of empirical formula $A_2B_2O_7$. Examples of a true $A_2B_2O_7$ compound are found in the synthetic structures

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[1] O. Rosén and A. Westgren, *Geol. Foren. Stockholm For.*, **60**, 226 (1938).