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A Comparative Study of Methylamine Adducts of Triborane(7)

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Although the complete series of methylamine adducts of borane(3) has been known,[1] the corresponding series of triborane(7) adducts was not complete. Monomethylamine- and dimethylamine-triborane(7) were missing in the series. Therefore, the preparation of these two adducts was undertaken so that a comparative study of the complete series of compounds, $(CH_3)_nNH_{3-n}\cdot B_3H_7$ (n = 0–3), would become possible. The preparation and characterization of the two new adducts and observations on NMR spectra of the series of compounds are described in this paper.

Results and Discussion

Monomethylamine and dimethylamine adducts of triborane(7), $CH_3NH_2\cdot B_3H_7$ and $(CH_3)_2NH\cdot B_3H_7$, were prepared by a method similar to that reported for $NH_3\cdot B_3H_7$ preparation:[2] tetraborane(10), B_4H_{10}, was first converted to tetrahydrofuran–triborane(7) and a base-exchange reaction was then performed on the tetrahydrofuran adduct in various solvents

$$B_4H_{10} + THF \rightarrow THF\cdot B_3H_7 + {}^1/_2B_2H_6$$

$$THF\cdot B_3H_7 + amine \rightarrow amine\cdot B_3H_7 + THF$$

Like ammonia[3] and unlike trimethylamine,[4] neither monomethylamine nor dimethylamine produces the triborane adduct in its direct reaction with B_4H_{10}.[5] The two new adducts were characterized by elemental analysis and infrared, mass, and NMR spectra with reference to the known adducts, trimethylamine- and ammonia–triborane(7). Monomethylamine–triborane(7) is a colorless liquid at room temperature (25 °C) melting at a temperature around 20 °C. Dimethylamine–triborane(7) is a white solid which melts near 30 °C. Melting points of these compounds are lowered sharply by the presence of a small amount of impurity in the sample. These low melting points contrast with those of $NH_3\cdot B_3H_7$ (73–75 °C)[2] and $(CH_3)_3N\cdot B_3H_7$ (above 200 °C).[4] A similar contrast is observed for the series of methylamine adducts of borane(3): 112–114 (dec),[6] 56, 36, and 94 °C,[1] for $NH_3\cdot BH_3$, $CH_3NH_2\cdot BH_3$, $(CH_3)_2NH\cdot BH_3$, and $(CH_3)_3N\cdot BH_3$, respectively. The newly prepared adducts are stable in dry air and resistant to complete hydrolysis in 6 N HCl. These are comparable to the properties of $NH_3\cdot B_3H_7$[2] and $(CH_3)_3N\cdot B_3H_7$.[4]

Listed in Table I are the ^{11}B and ^1H NMR data obtained in this study for the four triborane(7) adducts. The results are, in general, in agreement with those previously reported for $NH_3\cdot B_3H_7$[7] and $(CH_3)_3N\cdot B_3H_7$[8] and with those expected for the other two methylamine adducts. However, this study, by virtue of complete coverage of the series of compounds, revealed new aspects of the spectral properties which are described below.

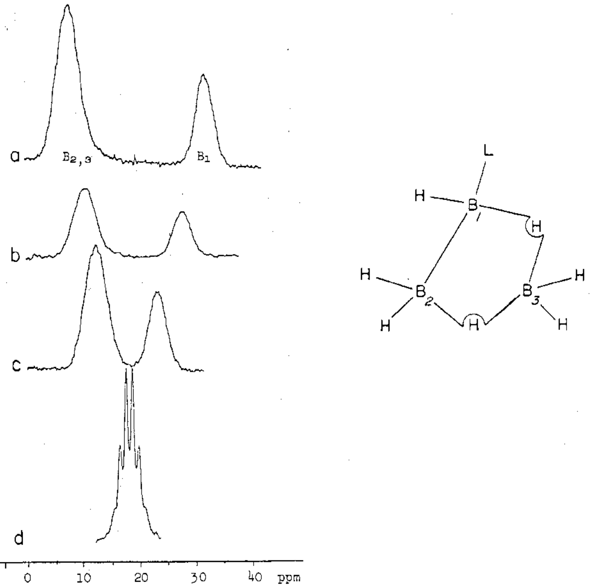

Figure 1. Structure and ^{11}B NMR spectra of methylamine-triboranes(7) in CH_2Cl_2 at 20 °C (32.1 MHz): (a) $NH_3\cdot B_3H_7$, (b) $CH_3NH_2\cdot B_3H_7$, (c) $(CH_3)_2NH\cdot B_3H_7$, (d) $(CH_3)_3N\cdot B_3H_7$. Structure is from the structure of $NH_3\cdot B_3H_7$ (C. E. Nordman and C. Reimann, *J. Am. Chem. Soc.*, **81**, 3538 (1959)); L = amine.

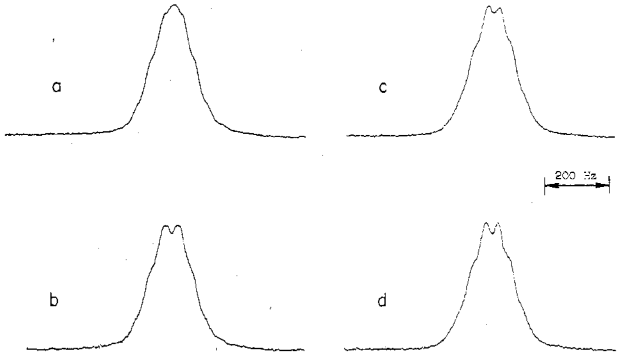

Figure 2. $B_{2,3}$ resonance peaks of $NH_3B_3H_7$ at 20 °C (32.1 MHz): (a) and (b) [CH_2Cl_2 solution], normal and $^{11}B_1$ irradiated spectra, respectively; (c) and (d) [$(C_2H_5)_2O$ solution], normal and $^{11}B_1$ irradiated spectra, respectively.

In going from $NH_3\cdot B_3H_7$ to $(CH_3)_3N\cdot B_3H_7$, the chemical shift for B_1 (amine-attached boron atom) decreases while the $B_{2,3}$ shift increases. (See Figure 1.) The downfield shift trend observed here for the signal of amine-attached boron is consistent with those observed for amine–boranes(3),[9a,c] μ-amino-diboranes(6),[9a] and cycloborazanes.[9b] Shown in Figure 2c is the $B_{2,3}$ resonance peak of $NH_3\cdot B_3H_7$ in diethyl ether solution. The shape of the peak is comparable to that reported previously.[7] A line shape simulation, assuming a Lorentzian curve for each of the component peaks of the multiplet and a value of 35 Hz for the peak separation, revealed that the shape of the multiplet peak is consistent with that of a 1:7:21:35:35:21:7:1 octet and is inconsistent with that of a 1:5:10:10:5:1 sextet. The model in which seven hydrogen atoms are migrating rapidly around the three boron atoms in the $NH_3B_3H_7$ molecule[7] is consistent with this spectrum. The $B_{2,3}$ peak of $NH_3B_3H_7$ in CH_2Cl_2 solution, however, has the appearance of an odd-number multiplet with a hump at the middle (Figure 2a). Upon irradiating the CH_2Cl_2 solution

Table I. ^{11}B and ^{1}H NMR Data for Methylamine–Triboranes(7)[e]

Compd	Solvent	B_1 shift,[a] ppm	$B_{2,3}$ shift,[a] ppm	J_{BH}, Hz	H_B shift,[b] τ	H_C shift,[b] τ	J_{HCNH}, Hz	H_N shift,[b] τ	J_{HN}, Hz
$NH_3 \cdot B_3H_7$	CH_2Cl_2	32.0	8.2	36[c]	8.55 br			6.41 t	48
	$(C_2H_5)_2O$	32.6	9.7	35[c]	8.97 br			6.22 br, t	38
$CH_3NH_2 \cdot B_3H_7$	CH_2Cl_2	27.7	10.8	35[c]	8.70 br	7.55 t	6.2	6.39 br, t	45
	$(C_2H_5)_2O$	28.1	11.2	35[c]					
$(CH_3)_2NH \cdot B_3H_7$	CH_2Cl_2	23.4	12.6	35[c]	8.74 br	7.53 d	5.8	6.44 br, t	35
	$(C_2H_5)_2O$	23.4	13.6	32[c]					
$(CH_3)_3N \cdot B_3H_7$[d]	CH_2Cl_2	18.3	18.3	35	8.88 br	7.46 s			
	$(C_2H_5)_2O$		17.9	37					
	THF		18.4	34					
	Benzene		18.4	35					

[a] Shift for $BF_3 \cdot O(C_2H_5)_2$ was taken as zero. [b] Shift for CH_2Cl_2 was taken as τ 4.72. [c] Measured on the $^{11}B_1$ irradiated spectra. [d] Reported for the boron were 18.6 ± 0.5 ppm, J_{BH} = 35.0 ± 1 Hz,[8a] and 16.2 ± 1 ($B_{2,3}$), 14.4 ± 1 (B_1) ppm, J_{BH} = 35 Hz in benzene solution, and 14.4 ± 1 ($B_{2,3}$), 13.0 ± 1 (B_1) ppm in $(C_2H_5)_2O$ solution.[8b] [e] Abbreviations: br, broad; t, triplet; d, doublet; s, singlet; H_X, proton attached to X.

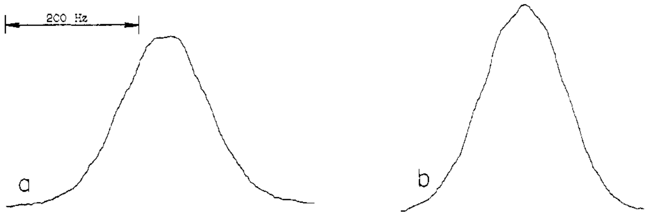

Figure 3. $B_{2,3}$ resonance peaks of (a) $CH_3NH_2 \cdot B_3H_7$ and (b) $(CH_3)_2NH \cdot B_3H_7$ in $(C_2H_5)_2O$ at 20 °C (32.1 MHz).

with the frequency of the B_1 resonance peak, the shape of the $B_{2,3}$ peak changes to an even-number multiplet (Figure 2b) similar to that in Figure 2c. Irradiation of the diethyl ether solution sample with its B_1 peak frequency does not cause an appreciable change in the shape of the $B_{2,3}$ peak (Figure 2d). The apparent odd-number multiplet feature that is observed for the CH_2Cl_2 solution sample must be due to the coupling between B_1 and $B_{2,3}$ atoms, and in diethyl ether solution ether molecules must be interacting with the B_3H_7 moiety (probably at B_2 and B_3 atoms) to reduce the coupling constant between B_1 and $B_{2,3}$. Assuming that the odd-number multiplet (Figure 2a) is a 1:1:1:1 quartet of the multiplet shown in Figure 2b, the coupling constant between B_1 and $B_{2,3}$ is estimated to be in the range of 15–20 Hz. The resonance peak due to B_1 does not show the anticipated octet structure. Irradiation of the sample with the $B_{2,3}$ resonance frequency does not bring about the multiplet structure either. The absence of multiplet structure in the B_1 peak can be attributed to the quadrupole broadening effect of the nitrogen atom attached to the B_1 atom as well as to the N–B_1 spin–spin coupling. Both B_1 and $B_{2,3}$ resonance peaks sharpen to apparent singlet peaks upon irradiating the sample with a radiofrequency noise band which covers the resonance frequencies of protons.

The proton NMR spectrum of $NH_3 \cdot B_3H_7$ contains a broad resonance signal, which is attributed to the seven hydrogens in the B_3H_7 group, centered at τ 8.55. Irradiation with a radiofrequency noise band covering both B_1 and $B_{2,3}$ resonance frequencies changes the broad proton resonance signal to a narrow, sharp singlet. Irradiation of the sample with the B_1 resonance frequency changes the shape of the proton peak to a broad, isosceles triangular shape, which may be interpreted as a broad septet due to the coupling of the two equivalent $B_{2,3}$ atoms to the seven hydrogen atoms. Irradiation of the $B_{2,3}$ atoms, on the other hand, produces a broad trapezoidal shape for the proton signal, which suggests a broad, overlapping 1:1:1:1 quartet due to the coupling of the hydrogens to the B_1 atom which is coupled to the nitrogen atom. These observations provide additional support for the equivalency of the seven hydrogens and two boron atoms (B_2 and B_3) in the B_3H_7 group.

Shown in Figure 3 are the $B_{2,3}$ resonance peaks of $CH_3NH_2 \cdot B_3H_7$ and $(CH_3)_2NH \cdot B_3H_7$ in diethyl ether solutions. In contrast to the $B_{2,3}$ resonance signal of $NH_3 \cdot B_3H_7$, the shapes of these peaks remain the same whether dichloromethane or diethyl ether is used for the solvent. However, irradiation of the B_1 atom brings about the even-number multiplet structure of these $B_{2,3}$ resonance signals, regardless of the solvent used, comparable to that shown in Figure 2d for $NH_3 \cdot B_3H_7$. Apparently the B_1–$B_{2,3}$ decoupling effect of diethyl ether is not operative for these two adducts. This may be correlated with the high chemical shift values of the $B_{2,3}$ atoms of these adducts compared with that of $NH_3 \cdot B_3H_7$. The B_1 peaks are structureless even when the $B_{2,3}$ atoms are irradiated. The results of the ^{1}H spin-decoupling experiments on the ^{11}B spectrum and ^{11}B spin-decoupling experiments on the ^{1}H spectrum are similar to those observed for $NH_3 \cdot B_3H_7$ and indicate the equivalency of the two boron atoms (B_2 and B_3) and seven hydrogen atoms in these compounds. The absence of the odd-number multiplet appearance in the $B_{2,3}$ peak of $CH_3NH_2 \cdot B_3H_7$, in CH_2Cl_2 solution in particular, is inconsistent with the peak shapes of the other two adducts. This may be attributed to different magnitudes of coupling constants and line broadening effects involved in each of the three compounds compared above. The explicit explanation is yet to be worked out. The shapes of the $B_{2,3}$ resonance peaks of the three adducts described above remain the same at higher temperatures (up to 50 °C) as those at 20 °C, and at lower temperatures the fine structures of the multiplets broaden to give featureless, broad peaks.

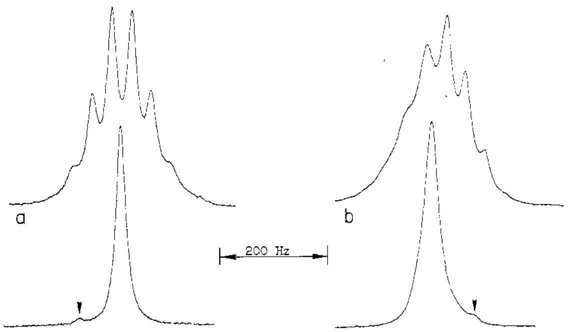

Figure 4. ^{11}B NMR spectra of $(CH_3)_3N \cdot B_3H_7$ at 20 °C (a) in CH_2Cl_2 and (b) in benzene (32.1 MHz): upper, normal spectra; lower, ^{1}H irradiated spectra. The humps indicated by arrowheads are due to impurities in the samples.

Boron-11 NMR spectra of $(CH_3)_3N \cdot B_3H_7$ are unique in that the chemical shift difference between the two resonance signals (B_1 and $B_{2,3}$) is very small and that some of its fine structure is distinctively sharp. Indeed, the CH_2Cl_2 solution sample gives a perfectly symmetrical well-resolved multiplet signal, indicating fortuitous coincidence of B_1 and $B_{2,3}$ chemical shifts. In benzene, diethyl ether, or tetrahydrofuran, the B_1 chemical shift is slightly larger than the $B_{2,3}$ shift and hence the dissymmetry of the resonance peak is observed.

Previously the spectra of $(CH_3)_3N{\cdot}B_3H_7$ in benzene and tetrahydrofuran were interpreted as an overlap of two octets (B_1 and $B_{2,3}$) with the chemical shift difference comparable to the $^{11}B-^{1}H$ coupling constant (about 35 Hz).[8b] The present study has shown that the B_1 resonance peaks for the other three amine adducts are structureless broad peaks. The same would be expected for the B_1 peak of the $(CH_3)_3N{\cdot}B_3H_7$ spectrum if the peak could be seen separated from the $B_{2,3}$ peak. It is therefore difficult to explain the enhanced sharpness of the fine structure peaks on the basis of the simple superposition of the two peaks. Assuming that B_1 and $B_{2,3}$ atoms are coupled to each other and are both coupled to seven hydrogens in the trimethylamine adduct as they are in the other adducts, the well-resolved perfectly symmetric resonance peak for $(CH_3)_3N{\cdot}B_3H_7$ in CH_2Cl_2 would be explained more appropriately as a case of "deceptive simplicity",[10] caused by the coincidence of the B_1 and $B_{2,3}$ chemical shifts. In benzene, diethyl ether and tetrahydrofuran, the chemical shifts of B_1 and $B_{2,3}$ are not equal but the difference is probably similar to the $^{11}B_1-^{11}B_{2,3}$ coupling constant (15–20 Hz) (Figure 4b). Therefore, the resulting spectrum is of complex second order and has a perturbed, dissymmetrical structure.

Experimental Section

Chemicals. Laboratory stock tetraborane(10), which had been prepared by the pyrolysis of diborane(6) in a hot–cold reactor, was purified by trap-to-trap fractionation in a vacuum line. The purified tetraborane(10) had a vapor pressure of 386 mmHg at 0 °C, and no impurity could be detected in the infrared spectrum of the sample. Dimethylamine was taken from a cylinder (Matheson Gas Products) and fractionated in the vacuum line. Monomethylamine and trimethylamine were prepared from their hydrochlorides by treating with concentrated sodium hydroxide solutions, drying the liberated amines with KOH pellets, and then fractionating them in the vacuum line. Ammonia (Matheson Gas Products) was stored over sodium metal. Diethyl ether and tetrahydrofuran were stored over $LiAlH_4$, and dichloromethane and benzene over molecular sieves. These reagents were distilled from the storage containers into the vacuum line as needed.

Amine–Triboranes(7). The method described earlier[2] for the preparation of ammonia–triborane(7) was followed closely for the preparations of the four amine–triboranes(7) described in this paper. The use of diethyl ether or dichloromethane as the solvent for the base-displacement reactions of tetrahydrofuran–triborane(7) with the amines gave results which were comparable to those when tetrahydrofuran was used as the solvent. The compounds are resistant toward complete hydrolysis in acid solutions. When treated with 6 N HCl for 2–3 days in sealed tubes at 95 °C, the monomethylamine and dimethylamine adducts yielded 104 and 85.7 mmol of hydrogen gas/g of the sample, respectively, whereas the calculated values based on the equation $\text{amine}{\cdot}B_3H_7 + H^+ + 9H_2O \rightarrow \text{amine}{\cdot}H^+ + 3B(OH)_3 + 8H_2$ are 113 and 94.6 mmol/g, respectively. Consequently the results of boron analysis on the sample solution after the hydrolyses were lower, but those of nitrogen analysis were consistent with the formulas. Anal. Calcd for $CH_3NH_2{\cdot}B_3H_7$: B, 46.0; N, 19.9. Found: B, 44.3; N, 19.9. Calcd for $(CH_3)_2NH{\cdot}B_3H_7$: B, 38.4; N, 16.6. Found: B, 38.1; N, 16.5. The sample solutions decolorized dilute solutions of iodine.

The mass spectra of the two adducts showed the highest m/e at 69 and 83 for $CH_3NH_2{\cdot}B_3H_7$ and $(CH_3)_2NH{\cdot}B_3H_7$, respectively. These values which are two units less than the molecular ion masses of the adducts are probably due to the facile loss of two hydrogen atoms from each molecule under the conditions employed in the instrument. Similar observations have been reported for other boron hydride compounds, e.g., B_4H_{10}, B_5H_{11}, and B_9H_{15}.[11] Infrared spectra (recorded on a Beckman IR-20 infrared spectrophotometer) are as follows. $CH_3NH_2{\cdot}B_3H_7$ (cm^{-1}) (liquid film): 3285 (s), 3255 (s), 3160 (sh), 3018 (ms), 2960 (ms), 2490 (vs), 2425 (vs), 2340 (sh), 2020 (w, br), 1563 (s), 1451 (s), 1430 (sh), 1304 (s), 1147 (s), 1127 (s), 1035 (sh), 978 (s, br), 920 (sh), 820 (w), 795 (w). $(CH_3)_2NH{\cdot}B_3H_7$ (cm^{-1}) (thin-layer solid): 3240 (vs), 3005 (m), 2960 (m), 2490 (s), 2455 (s), 2430 (s), 2360–2330 (br, sh), 2230 (m), 2060 (w), 2025 (w), 1460 (s), 1435 (sh), 1405 (m), 1305 (s), 1225 (w), 1145 (s), 1050 (w, br), 990 (s), 920 (s). The NMR spectra were recorded on a Varian XL-100-15 instrument equipped with a spin-decoupler unit (Gyrocode). The standard for boron chemical shifts, $BF_3{\cdot}O(C_2H_5)_2$, was used externally.

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Registry No. $NH_3{\cdot}B_3H_7$, 57808-44-3; $CH_3NH_2{\cdot}B_3H_7$, 57808-46-5; $(CH_3)_2NH{\cdot}B_3H_7$, 57808-47-6; $(CH_3)_3N{\cdot}B_3H_7$, 57808-48-7; ^{11}B, 14798-13-1.

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Fluorinated Cyclic Compounds. A Cyclodisilazane and a 1,3-Diaza-2-stanna-4-silacyclobutane with Fluorinated Substituents on Nitrogen

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The existence of four-membered silicon–nitrogen rings (cyclodisilazanes) has been established for some time.[1] However, the analogous tin–nitrogen rings (cyclodistannazanes) have been synthesized only recently[2,3] and the mixed four-membered silicon–tin–nitrogen heterocycles are rarely evident in the literature.[3]

In general, the nitrogen substituents on these four-membered heterocycles are hydrogenated. The only examples of model compounds containing fluorinated substituents are cyclodisilazanes with pentafluorophenyl groups attached to the nitrogens.[4,5] Since the most frequently used methods for preparing totally hydrogenated cyclodisilazanes are not useful for synthesizing the fluorinated analogues, other approaches are required.

This work describes the chemistry involved in our efforts to synthesize four-membered silicon– or tin–nitrogen heterocycles which contain fluorinated nitrogen substituents. Generally, in order to obtain useful precursors, attempts were made to saturate the C=N bond of the hexafluoroisopropylidenimino group of $(CH_3)_2Si[N{=}C(CF_3)_2]_2$ and $(CH_3)_2Sn[N{=}C(CF_3)_2]_2$,[6] via a one-step addition, by small polar molecules.[7] A dilithium salt, $(CH_3)_2Si[NLiC(CF_3)_2CH_3]_2$, was obtained which proved to be an excellent precursor to some heterocycles.