1109. *Boron Hydride Derivatives. Part IX.*[1] *The Reaction of Decaborane with Ammonia.*

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Ammonia reacts with decaborane in benzene solution to give a triammoniate identical with that formed as a major product from decaborane and ammonia gas. The structure of this compound and of the substance formed from it by the action of heat have been examined. The latter is shown to be diammoniadecaborane, $B_{10}H_{12}(NH_3)_2$, whilst the triammoniate is best formulated as $NH_4^+[B_{10}H_{13}\cdot NH_3,NH_3]^-$.

THE pressure–composition isotherm for the system solid decaborane–ammonia gas has recently been studied by Toeniskoetter.[2] He demonstrated the existence of tri-, tetra-, and hexa-ammoniates, $B_{10}H_{14},nNH_3$ ($n = 3$, 4, and 6), and also showed that there was some evidence for a penta-ammoniate. All these substances had high dissociation pressures with the exception of the triammoniate, which was stable under ambient conditions. On heating to 75—95°, however, the latter lost hydrogen and ammonia to give a substance which Toeniskoetter formulated as $B_{10}H_{14}(NH_2)_2$. Further prolonged heating at 120° resulted in the loss of more hydrogen to give $B_{10}H_{12}(NH_2)_2$. We have re-examined the triammoniate and its primary pyrolysis product in order to obtain more information about their structures.

DISCUSSION

The method of preparation of triammoniadecaborane used by Toeniskoetter is time-consuming and an identical product can be obtained as a white precipitate by bubbling dry ammonia through a solution of decaborane in benzene. Similarly, the formation of the primary pyrolysis product can be more conveniently effected by boiling a suspension of the triammoniate in dry toluene.

Structure of the Primary Pyrolysis Product.—Toeniskoetter showed that the decomposition of triammoniadecaborane took place almost quantitatively according to the equation

$$B_{10}H_{14},3NH_3 \longrightarrow B_{10}H_{18}N_2\ (I) + NH_3 + H_2$$

The composition of (I) is confirmed by its elemental analysis and also the stoicheiometry of the reaction. The conditions for the formation of (I), however, are very mild and one would not expect the B_{10} decaborane cage to be destroyed. Possible structures are therefore $B_{10}H_{14}(NH_2)_2$, as suggested by Toeniskoetter, or $B_{10}H_{12}(NH_3)_2$ in which the ammonia molecules donate electrons to the $B_{10}H_{12}$ unit in a similar way to other donors in the well-characterised $B_{10}H_{12}\longleftarrow M_2$ class of compounds,[3a,b]

The correctness of the second alternative is shown by the ^{11}B nuclear magnetic resonance (n.m.r.) spectrum of the substance (Fig. 1), which is almost identical with that of bisacetonitriledecaborane and bis(dimethyl sulphide)decaborane.[4]

Further confirmation is obtained from the infrared (i.r.) spectrum, Fig. 2. The strong bands at 3282 and 3230 cm.$^{-1}$ are due to the antisymmetric and symmetric stretching modes of the co-ordinating NH_3 groups. Similar bands have been observed in this region in the spectra of, for example, complex ammine salts [5] and in non-hydrogen-bonded mono-alkylammonium ions.[6] An amino-group, on the other hand, should absorb at

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[1] Part VIII, Blay, Pace, and Williams, *J.*, 1962, 3416.

[2] Toeniskoetter, Ph.D. Thesis, 1959, St. Louis Univ., Missouri.

[3] (*a*) Hawthorne and Pitochelli, *J. Amer. Chem. Soc.*, 1959, **81**, 5834; (*b*) Reddy and Lipscomb, *J. Chem. Phys.*, 1959, **31**, 610.

[4] Pace, Williams, and Williams, *J.*, 1961, 2196.

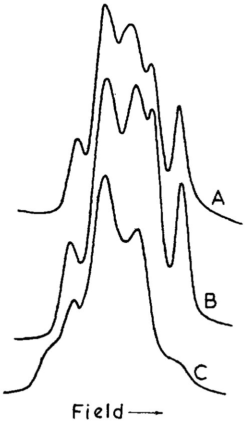
[5] Svatos, Curran, and Quagliano, *J. Amer. Chem. Soc.*, 1955, **77**, 6159; Svatos, Sweeny, Mizushima, Curran, and Quagliano, *ibid.*, 1957, **79**, 3313.

[6] Chevalier and Sandorfy, *Canad. J. Chem.*, 1960, **38**, 2524.

considerably higher frequencies,[7] 3500—3300 cm.$^{-1}$, unless in a strongly hydrogen-bonding environment, which does not occur in this instance.

The band at 1584 cm.$^{-1}$ can be assigned to the antisymmetric $-NH_3$ deformation vibration, with the corresponding symmetric mode absorbing near 1400 cm.$^{-1}$. The splitting of the latter may be due to in- and out-of-phase vibrations of the NH_3 groups.

FIG. 1. The ^{11}B nuclear magnetic resonance spectra of:
A, $B_{10}H_{12}(NH_3)_2$.
B, $B_{10}H_{12}(Me_2S)_2$.
C, $[B_{10}H_{13}OH]^{2-}$.



The frequency is rather higher than usual since the ammines [5] and alkylammonium salts [8] absorb in the range 1355—1150 cm.$^{-1}$ with the antisymmetric mode lying between 1650 and 1550 cm.$^{-1}$. However, the exact position of the symmetric mode appears to be sensitive to the size of the charge on the nitrogen atom, and in the case of the NH_3^+ group of amino-acid hydrochlorides and zwitterions [9] the frequency is reported to be as high as 1550—1485 cm.$^{-1}$.

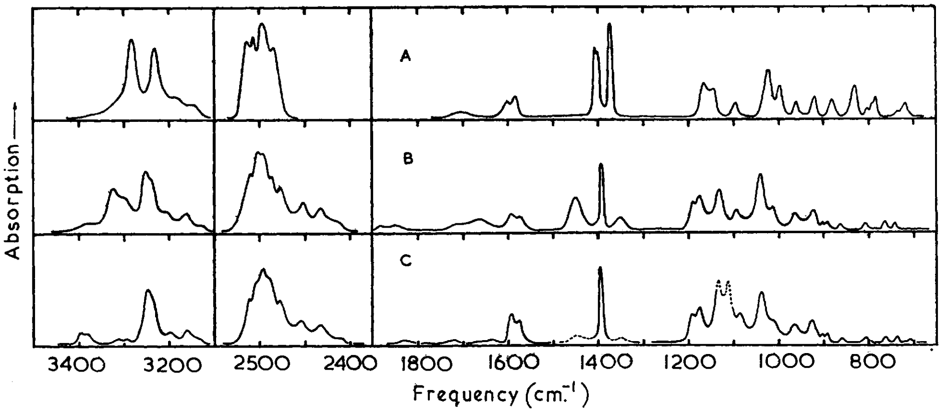


FIG. 2. The infrared spectra of: A, $B_{10}H_{12}(NH_3)_2$; B, $B_{10}H_{14}\cdot 3NH_3$; C, $NaB_{10}H_{13}\cdot 2NH_3$.

The bands assignable to the $-NH_3$ rocking vibration and the $B-NH_3$ stretching vibration [10] should lie in the region below 1000 cm.$^{-1}$, but cannot be picked out with certainty from the large number of B–H deformation and B–B stretching bands which occur in the same region.

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[7] Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 248.
[8] Ref. 7, p. 259.
[9] Ref. 7, p. 236.
[10] Taylor and Cluff, *Nature*, 1958, **182**, 390.

The B–H frequencies of the molecule are also consistent with the $B_{10}H_{12}(NH_3)_2$ formulation. Thus the B–H stretching vibration near 2500 cm.$^{-1}$ lies well within the range, 2507 ± 14 cm.$^{-1}$, observed for other $B_{10}H_{12} \leftarrow M_2$ derivatives,[4] whilst the strong band at 1020 cm.$^{-1}$ is consistent with the range 1000 ± 20 cm.$^{-1}$ for the B–H deformation vibration of these compounds.

The $B_{10}H_{14}(NH_2)_2$ formulation would require the substance to be a substituted $B_{10}H_{16}$ derivative. No spectral data are available for this class of compound, but it might be expected that the B–H stretching frequency would be similar to those of substituted decaboranes, which are near 2570 cm.$^{-1}$.

Structure of Triammoniadecaborane.—Stock[11] showed that decaborane took up six molecules of ammonia in liquid ammonia solution to form a hexa-ammoniate, but that this dissociated completely at room temperature. Toeniskoetter,[2] on the other hand, found that equilibrium in the formation of the triammoniate from decaborane and gaseous ammonia was reached only after 34 days and that once formed the substance, unlike the hex-ammoniate, could not be dissociated into its components by evacuation or heat. He therefore suggested that, although an ammoniate $B_{10}H_{14},3NH_3$ was formed initially, a slow proton-transfer took place to form an ammonium salt, $(NH_4)_2B_{10}H_{12},NH_3$.

This assumption is not necessarily valid, since the formation of triammoniadecaborane is rapid in benzene solution, and also it is possible to sublime decaborane from the compound by heating to 80° and pumping *in vacuo*. There are therefore three possible structures, *viz.*, an ammoniate, $B_{10}H_{14},3NH_3$ (II), a monobasic salt, $(NH_4)[B_{10}H_{13},2NH_3]$ (III), or the dibasic salt, $(NH_4)_2[B_{10}H_{12},NH_3]$ (IV).

The evidence below, however, is consistent with (III) provided that this is modified to the form $NH_4^+[B_{10}H_{13}\cdot NH_3,NH_3]^-$ wherein the second ammonia molecule in the anion is much less tightly bound than the first.

Infrared spectrum. The i.r. spectrum of triammoniadecaborane (Fig. 2) is considerably more complex than that of diammoniadecaborane, $B_{10}H_{12}(NH_3)_2$, and gives good indication of the presence of both the NH_4^+ ion and co-ordinated NH_3, the latter possibly being of two types. Thus the NH_4^+ stretching band, which for weakly hydrogen-bonded salts has been shown[12] to occur near 3300 cm.$^{-1}$, can be assigned to the strong broad peak at 3324 cm.$^{-1}$. The deformation band is the medium-strength absorption at 1450 cm.$^{-1}$, while the combination band observed for many ammonium salts in the 1700—1600 cm.$^{-1}$ region[12] is the weak band at 1665 cm.$^{-1}$. The strongly co-ordinated $-NH_3$ group gives rise to N–H bands in similar positions to those observed for diammoniadecaborane. For example, the N–H stretching vibration can be assigned to the strong band at 3250 cm.$^{-1}$, while the antisymmetric and symmetric deformation modes occur at 1595 and 1395 cm.$^{-1}$, respectively.

The N–H stretching region, in addition to the absorptions mentioned above, contains a number of other bands, which indicate the possibility of a second, more weakly co-ordinated, NH_3 group. Such a group would be expected to possess an absorption approaching that of free ammonia in a condensed phase, *e.g.*, 3420 cm.$^{-1}$ in carbon tetrachloride solution[13] or 3378 cm.$^{-1}$ in the solid.[14] On this basis, the band at 3380 cm.$^{-1}$ can be assigned to such a group and the shoulder at 1575 cm.$^{-1}$ then assigned to its antisymmetric deformation vibration.

Effect of organic solvents. Treatment of triammoniadecaborane at room temperature with dimethylformamide, dimethyl sulphoxide, acetonitrile, dioxan, or diglyme resulted in the liberation of ammonia and the formation of greenish-yellow solutions. Similar behaviour occurred with water and the resulting solution did not evolve hydrogen. Toluene, on the other hand, produced no change. It was quantitatively found that

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[11] Stock, " Hydrides of Boron and Silicon," Cornell University Press, Ithaca, 1957, p. 127.

[12] Waddington, *J.*, 1958, 4340.

[13] Cannon, *Spectrochim. Acta*, 1958, **10**, 425.

[14] Reding and Hornig, *J. Chem. Phys.*, 1951, **19**, 594.

addition of diglyme produced approximately one mole of ammonia per mole of the triammonia-compound. Acetonitrile gave a similar result.

Since ethers do not appear to be very effective donors for decaborane-type compounds [*e.g.*, compounds of the type $B_{10}H_{12}(\leftarrow OR_2)_2$ have not yet been prepared], it must be assumed that the displaced ammonia can only have been very loosely held in the triammoniadecaborane.

Conductivity of the aqueous solution.—The aqueous solution is conducting. It was observed that for *ca.* 0·001M-solutions the molecular conductivity was initially near 100 mhos, but rose rapidly in about 20 min. to 178 mhos (25·4°) and remained constant at this value for at least 24 hr. The shape of the conductivity–time curve enabled an easy extrapolation to zero time of solution to be made, when the conductivity was found to be 112 mhos.

Triammoniadecaborane would be expected to give initially a solution of NH_4^+ and $[B_{10}H_{13}\cdot NH_3,NH_3]^-$ ions, but the presence of free ammonia in strong aqueous solutions shows that the anion immediately loses its loosely held ammonia to give the $[B_{10}H_{13}NH_3]^-$ anion together with dissolved ammonia. The equivalent conductivity of the ammonium ion [15] at this concentration is about 70 mhos, so that the conductivity of the anion is *ca.* 40 mhos. Such a value is completely consistent with an anion of this size; most bulky organic anions have equivalent conductivities in the range 20—40 mhos.[15] Similarly, the conductivity of the $[B_{10}H_{13}Et_2NH]^-$ ion can be calculated to be *ca.* 40 mhos from the observed conductivity of the diethylammonium salt, $\Lambda_{1030} = 80$ mhos at 25°, and the conductivity of the cation,[16] *viz.*, 38 mhos.

The increase in conductivity with time, which was *ca.* 70 mhos, is consistent with the formation of a second ammonium ion such as would be required by the reaction:

$$[B_{10}H_{13}\cdot NH_3]^- + H_2O \longrightarrow NH_4^+ + [B_{10}H_{13}OH]^{2-}$$

The formation of a related anion, *viz.*, $[B_{10}H_{14}OH]^-$, has already been suggested by Guter and Schaeffer [17] to account for the ionisation of decaborane in aqueous solution.

Some support for this hypothesis comes from the conductometric titration of the aged 0·001M-solution with standard 0·01M-sodium hydroxide solution. The curve obtained was typical of those found for the titration of ammonium ion with hydroxyl ion, showing a rapid increase in specific conductivity at two equivalents of alkali, thereby confirming the presence of two ammonium ions per mole of triammoniadecaborane.

Conductometric titration of the aged 0·001M-solution with 0·01M-hydrochloric acid, on the other hand, yielded a sharp end-point at just over one equivalent of acid, in accord with the liberation of one mole of ammonia per mole of compound on dissolution in water.

Ultraviolet spectrum. The change in conductivity of aqueous triammoniadecaborane is paralleled by changes in the ultraviolet (u.v.) spectrum. The spectrum of triammoniadecaborane, measured within 10 sec. of preparation of the solution, consisted of a pronounced shoulder at 225 mμ superimposed on a background which rose steadily to complete absorption at 200 mμ. Within 45 sec. a new maximum appeared at 258 mμ, and grew steadily, whilst that at 225 mμ decreased slowly. After 2½ min., however, the latter began to increase in intensity again, and both this absorption and that at 258 mμ continued to grow, until steady values were reached after 20 min. The extinction coefficients were then $\varepsilon_{258} \geqslant 4600$ and $\varepsilon_{225} \geqslant 5800$, but it is noteworthy that the band at 225 mμ was then considerably sharper than that found in the initial measurement, and it is not unreasonable to assume that both bands originate from the same species, *viz.*, $[B_{10}H_{13}OH]^{2-}$. When the solution was left for several hours, the band at 258 mμ was

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[15] Weissberger, "Physical Methods of Organic Chemistry," Interscience, New York, 1960, Vol. 1, Part IV, p. 3044.

[16] Moore and Winmill, *J.*, 1912, 1635.

[17] Guter and Schaeffer, *J. Amer. Chem. Soc.*, 1956, **78**, 3546.

replaced by a new band at 270 mμ ($\varepsilon \geqslant 3500$) whilst the 225 mμ band was reduced to a slight shoulder on a background absorption which increased steadily towards 200 mμ.

The spectra of a number of ions of the type $[B_{10}H_{13}M]^{2-}$ or $[B_{10}H_{12}M{\cdot}M']^{-}$, where M is a singly charged anion and M′ a neutral electron donor, have been reported by Knoth and Muetterties.[18] These ions are of the same formal type as the $[B_{10}H_{13}OH]^{2-}$ ion postulated above, and they all show u.v. absorption in the region 240—250 mμ. The $[B_{10}H_{14}OH]^{-}$ ion suggested by Guter and Schaeffer[17] also absorbs at 249 mμ. Both this and the $[B_{10}H_{13}]^{-}$ ion are reported[19] to decompose slowly in aqueous solution to give a species which absorbs at 270 mμ, and it is probable that this is the same as that described above which absorbs at 270 mμ.

Diammoniadecaborane, unlike the tri-compound, gave a stable very feebly-conducting, aqueous solution. Absorption maxima for this solution were found at 250, 220, and 193 mμ.

Potentiometric titrations. The reaction of triammoniadecaborane with acid was carried out by adding a known weight of the solid compound, or a known volume of aged 0·01M-solution, to 0·01M-hydrochloric acid and back-titrating the excess of acid potentiometrically with standard alkali. With both methods it was found that one equivalent of acid was consumed per mole of triammoniadecaborane, thereby supporting the conductometric results. However, Dupont and Hawthorne[20] have shown that the titration of disodium decaboranate-(14), $Na_2{}^{2+}B_{10}H_{14}{}^{2-}$, gives a single end-point corresponding to the reaction:

$$B_{10}H_{14}{}^{2-} + H_3O^+ \longrightarrow B_{10}H_{15}{}^{-} + H_2O$$

It would be expected, therefore, that, if the anion $[B_{10}H_{13}OH]^{2-}$ were present in the aged solution, two equivalents of acid would be required, corresponding to neutralisation of the loosely bound ammonia, followed by the reaction:

$$[B_{10}H_{13}OH]^{2-} + H_3O^+ \longrightarrow [B_{10}H_{14}OH]^{-} + H_2O$$

The failure to observe this stoicheiometry is due partly to the very dilute solutions used and partly to the greater acid strength of $H_2[B_{10}H_{13}OH]$ compared with $H_2[B_{10}H_{14}]$, which arises from the electronegative OH group. When the titration was carried out directly with 5N-hydrochloric acid, the end-point occurred at exactly two equivalents, but the reaction was now acccompanied by hydrogen evolution. Hawthorne and his co-workers[21] have shown that B_9 compounds are readily formed from B_{10} compounds with the liberation of hydrogen under these conditions, and they have, in addition, demonstrated the existence[22] of the $[B_9H_{12}]^{-}$ anion. It seems likely, therefore, that the $[B_{10}H_{14}OH]^{-}$ ion is unstable and decomposes according to the equation:

$$[B_{10}H_{14}OH]^{-} + 2H_2O \longrightarrow [B_9H_{12}]^{-} + B(OH)_3 + 2H_2$$

This is supported by the observation that addition of triphenylmethylphosphonium iodide solution or of excess of tetramethylammonium hydroxide to the acidified solution results in the formation of precipitates, in a similar fashion to the precipitation of the corresponding salts[19,20] of $B_{10}H_{13}{}^{-}$, $B_{10}H_{15}{}^{-}$, and $B_{10}H_{14}{}^{2-}$. The reaction is being further investigated.

The potentiometric curve obtained by the addition of an excess of sodium hydroxide solution to the solid triammonia-compound, followed by back-titration with hydrochloric acid, was more complex. The pH was initially greater than 11 and at first decreased very slowly on addition of acid, after which there was a rapid fall in pH of 2 units, followed by another period of slowly decreasing pH, and finally a second end-point with a drop of 6

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[18] Knoth and Muetterties, *J. Inorg. Nuclear Chem.*, 1961, **20**, 66.
[19] Hawthorne, Pitochelli, Strahm, and Miller, *J. Amer. Chem. Soc.*, 1960, **82**, 1825.
[20] Dupont and Hawthorne, *Chem. and Ind.*, 1962, 405.
[21] Graybill, Pitochelli, and Hawthorne, *Inorg. Chem.*, 1962, **1**, 626.
[22] Graybill, Ruff, and Hawthorne, *J. Amer. Chem. Soc.*, 1961, **83**, 2669.

units, typical of an ammonia–hydrochloric acid neutralisation. The initial titre, corresponding to the neutralisation of excess of sodium hydroxide, showed that two equivalents of the alkali had reacted per mole of triammoniadecaborane, whilst the amount of acid consumed from the first to the second end-point was equivalent to three moles of ammonia. Such stoicheiometry can be accounted for by the reaction:

$$NH_4[B_{10}H_{13}NH_3,NH_3] + 2OH^- \longrightarrow 3NH_3 + [B_{10}H_{13}OH]^{2-} + H_2O$$

analogous to the slow hydrolysis of the salt in neutral solution.

Titration of an ethanolic solution of triammoniadecaborane with sodium ethoxide, on the other hand, gave a sharp end-point after the addition of one equivalent of base, indicating that only one ammonium ion per mole of compound was present initially:

$$NH_4[B_{10}H_{13}NH_3,NH_3] + OEt^- \longrightarrow NH_3 + EtOH + [B_{10}H_{13}NH_3,NH_3]^- \text{ or } [B_{10}H_{13}NH_3]^- + NH_3$$

When triammoniadecaborane was dissolved in acetic acid, a pale brown solution was produced and hydrogen was evolved. On subsequent titration with perchloric acid in acetic acid, nearly two equivalents of acid were required for an end-point. This result is explicable in terms of the formation of an ammonianonaborane analogous to the degradation of diethylammonium diethylaminedecaboranate to diethylaminenonaborane reported by Hawthorne and his co-workers:[21]

$$\begin{aligned}[B_{10}H_{13}NH_3,NH_3]^- + HOAc &\longrightarrow [B_{10}H_{13}NH_3]^- + NH_4^+ + OAc^- \\ [B_{10}H_{13}NH_3]^- + 4HOAc &\longrightarrow B_9H_{13}NH_3 + 2H_2 + B(OAc)_3 + OAc^- \\ [B_{10}H_{13}NHEt_2]^- + 4HOH &\longrightarrow B_9H_{13}NHEt_2 + 2H_2 + B(OH)_3 + OH^-\end{aligned}$$

the boron triacetate being present in the $(AcO)_2BOB(OAc)_2$ form.[23] The neutralisation of the acetate ion requires two equivalents compared with one equivalent for the diethylamine compound.

Nuclear Magnetic Resonance Spectrum of $[B_{10}H_{13}OH]^{2-}$.—The ^{11}B nuclear magnetic (n.m.r.) spectrum of an aqueous solution of triammoniadecaborane is shown in Fig. 1. The spectrum is very similar in outline and in magnitude of chemical shift to that of diammoniadecaborane and to the spectra of $Na_2[B_{10}H_{13}CN]^{2-}$, $Na[B_{10}H_{13}{\cdot}Me_2S]^-$, and $Na[B_{10}H_{12}CN{\cdot}Me_2S]^-$ reported by Knoth and Muetterties.[18] The latter ions are all derived from $[B_{10}H_{14}]^{2-}$ and, on this basis, the reaction

$$[B_{10}H_{13}NH_3]^- + H_2O \longrightarrow [B_{10}H_{13}OH]^{2-} + NH_4^+$$

can be regarded as one in which a ligand displaces another on the B_{10} unit in a manner typical of this class of compound.

The Reaction of Sodium Decaboranate with Ammonia.—Sodium hydride reacts with ethereal decaborane to form a solution of sodium decaboranate.[1] When a stream of dry ammonia was bubbled through this solution, a yellow colour was produced which quickly disappeared with the formation of a white precipitate on further passage of ammonia. Analysis of the precipitate was consistent with the presence of one atom of sodium and two molecules of ammonia per B_{10} unit and the reaction can be represented by the equation:

$$Na^+B_{10}H_{13}^- + 2NH_3 \longrightarrow Na^+[B_{10}H_{13}{\cdot}2NH_3]^-$$

The substance dissolved in water to give a solution whose conductivity changed with time in a very similar fashion to that of the triammonia-compound, corresponding initially to two ions and increasing by *ca.* 75 mhos in 25 min. to a value consistent with three ions.

The i.r. spectra of a number of preparations of the substance were measured. Although these were substantially the same, there were some small differences from spectrum to spectrum, which were of two kinds. First, there were a few bands whose intensities were variable. These can be attributed to small quantities of impurity or decomposition product. Secondly, the quality of the spectra was variable; in some cases the bands

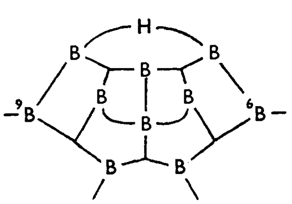
[23] Gerrard and Wheelans, *Chem. and Ind.*, 1954, 758.

were badly resolved and there was considerable background absorption, while in other cases the bands were sharp and typical of a crystalline substance. A spectrum of the latter type (Fig. 2) is almost identical with that of triammoniadecaborane, except for two details. Firstly, bands at 3324, 1668, 1456, and 1353 cm.$^{-1}$, which were assigned to the ammonium ion in the triammoniadecaborane spectrum, are either missing or present as very weak absorptions in the spectrum of the sodium salt. Secondly, there is an extra band at 1113 cm.$^{-1}$ which is of variable intensity, depending apparently on the degree of exposure of the salt to moisture. The similarity of the spectra and conductivity behaviour of the ammonium and sodium compounds is consistent with their being salts of the same anion, *viz.*, $[B_{10}H_{13}{\cdot}2NH_3]^-$. The variability of the spectrum of the sodium salt is probably due to its being hygroscopic. Hawthorne and his co-workers [24] have also observed that the salts $NaB_{10}H_{13}M$, where M is an amine or triphenylphosphine, are extremely hygroscopic. When the salt absorbs moisture it is probable that the reaction:

$$[B_{10}H_{13}{\cdot}2NH_3]^- + H_2O \longrightarrow NH_4^+ + [B_{10}H_{13}OH]^{2-} + NH_3$$

takes place, giving rise to the bands of variable intensity observed in the spectra.

It has been shown [3b,18,24] recently that series of isostructural anions can be derived from decaborane anions by replacement of hydrogen by electron donors, *e.g.*, $B_{10}H_{14}^{2-}$ $B_{10}H_{13}M^-$, and $B_{10}H_{12}M_2$, where M is a neutral ligand. The valency structure of the parent ions has been discussed in detail by Lipscomb.[3b] Diammoniadecaborane is a member of the $B_{10}H_{14}^{2-}$ class, but the triammonia-compound could be derived from either $B_{10}H_{17}^{3-}$, $B_{10}H_{15}^{3-}$, or $B_{10}H_{13}^{3-}$, depending on the validity of formulation II, III, or IV. Lipscomb [25] has suggested a possible structure (I) for the $B_{10}H_{15}^{3-}$ ion and has suggested that the tripyridinedecaborane described by Burkhardt and Fetter [26] should be regarded as a derivative of this ion, *viz.*, $pyH^+[B_{10}H_{13}py_2]^-$. The experimental evidence favours a similar formula for triammoniadecaborane inasmuch as the compound is a uni-univalent electrolyte. However, this structure does not easily account for the weakness of binding of one of the ammonia molecules. The most likely place for the co-ordination of a ligand, on Lipscomb's formulation, would be at the 6-position and symmetry considerations would then require the second ammonia molecule to be at the 9-position with no difference in bonding.



(V)

If compounds of the type $B_{10}H_{14}M_2$ or $B_{10}H_{14}M_3$ are examined, it will be noted that typical substances of the first type have M as diethylamine,[24] 2-bromopyridine,[26] or morpholine.[27] The only stable $B_{10}H_{14}M_3$ compounds reported so far are the pyridine and ammonia derivatives but, in each of these, one molecule of ligand is weakly held. Dimethylamine [28] forms a tri-derivative, but this slowly dissociates at ambient temperature to the di-derivative. Hawthorne and his co-workers [24] have shown that the $B_{10}H_{14}M_2$ compounds are usually ionic, *i.e.*, MH^+ $B_{10}H_{13}M^-$, and it appears therefore that the tri-compounds are derived from this structure by addition of a second M molecule. The criterion of whether this process takes place is not one of base strength, since pyridine and dimethylamine form tri-derivatives and diethylamine does not. However, both pyridine and ammonia are small molecules whereas the three M_2 ligands are comparatively bulky, and this suggests that purely steric considerations govern the formation of a tri-derivative. Dimethylamine is intermediate in size between these two groups and forms a fairly unstable tri-derivative. The B_{10} unit has a double pentagonal pyramid structure [29] of C_{2v}

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[24] Graybill, Pitochelli, and Hawthorne, *Inorg. Chem.*, 1962, **1**, 622.
[25] Lipscomb, *Proc. Nat. Acad. Sci.*, 1961, **47**, 1791.
[26] Burkhardt and Fetter, *Chem. and Ind.*, 1959, 491.
[27] Pace, Williams, and Williams, unpublished work.
[28] Fitch and Laubengayer, *J. Amer. Chem. Soc.*, 1958, **80**, 5911.
[29] Sutton, " Interatomic Distances," *Chem. Soc. Special Publ.* No. 11, 1958, p. M23.

symmetry such that the only approach to the molecule, where steric hindrance would be a less serious factor, is along the C_2 axis towards the bases of the pyramids. It is possible, therefore, that the co-ordination of the third M group is at this point.

Note added October 17th, 1963: Since this paper was submitted, Benjamin, Stafiej, and Takacs (*J. Amer. Chem. Soc.*, 1963, **85**, 2674) have reported the isolation of salts of the $B_9H_{14}^-$ anion from the hydrolysis of aqueous decaborane. The ion has a maximum in the ultraviolet spectrum at 271 mμ ($\varepsilon = 3980$) and is almost certainly the substance which we thought to be $B_9H_{12}^-$ formed on acid titration of aqueous triammoniadecaborane. Benjamin *et al.* also gave evidence from ultraviolet spectra for a precursor to $B_9H_{14}^-$ in the hydrolysis of decaborane which they believed, in agreement with us, to be $(B_{10}H_{13}{\cdot}OH)^{2-}$.

EXPERIMENTAL

Physical Methods.—I.r. spectra were measured as Nujol and Florube mulls using either a Grubb-Parsons G.S.2 or a Unicam S.P. 100 double-beam grating spectrometer. Band positions (cm.$^{-1}$) are as follows:

$B_{10}H_{12}(NH_3)_2$. 3282s, 3230ms, 2526s, 2512s, 2493vs, 2467ms, 1603mw, 1584m, 1406s, 1399s, 1372vs, 1164ms, 1141m, 1095mw, 1022s, 995ms, 960mw, 919m, 880mw, 830ms, 803vw, 791w, 784mw, 744vw, 733w, 719mw, 712w.

$NH_4[B_{10}H_{13}{\cdot}2NH_3]$. 3383w, 3324ms, 3299msh, 3251s, 3237ssh, 3201mw, 3162mw, 3131w, 2518s, 2501vs, 2490vssh, 2473s, 2454ms, 2403m, 2364m, 2323w, 1883vw, 1842vw, 1722vw, 1668w, 1596mw, 1572mw, 1456m, 1391s, 1353mw, 1189m, 1174m, 1130ms, 1090w, 1076wsh, 1044ms, 1012mw, 960mw, 921mw, 901vw, 891vw, 857w, 804w, 759w, 740w, 706vw, 691vw.

$Na[B_{10}H_{13}{\cdot}2NH_3]$. 3396mw, 3380mw, 3322w, 3297w, 3247s, 3236ssh, 3196mw, 3160mw, 3131w, 2523s, 2506sh, 2493vs, 2470ssh, 2455s, 2410m, 2366m, 2323w, 1831vw, 1726vw, 1670vw, 1634vw, 1594m, 1575m, (1461 var), 1395s, (1351 var), 1191m, 1175m, 1133s,var, 1113s,var, 1087w, 1036ms, 1014msh, 964mw, 926mw, 902w, 891w, 857w, 805w, 763w, 739w, 710vw.

U.v. spectra of the aqueous solutions were measured in 1 cm.-cells using a Unicam S.P. 700 recording spectrometer.

A Varian Associates V4300 spectrometer was used to measure the ^{11}B n.m.r. spectra at 12·0 Mc./sec. The spectra of triammoniadecaborane, in aqueous solution, and diammoniadecaborane, in acetonitrile solution, were measured in tubes of 15 mm. diameter. Chemical shifts were measured by the side-band method, relative to boron trichloride, and then adjusted to $\delta_{(MeO)_3B} = 0$, using a value of 29·6 p.p.m. calculated from the data of Onak *et al.*[30] $B_{10}H_{12}(NH_3)_2$, 21, 34, 44, 53, 66 p.p.m. $[B_{10}H_{13}OH]^{2-}$, 8, 19, 34, 47, 65 p.p.m. Diammoniadecaborane was recovered unchanged from the acetonitrile solution.

Conductivity measurements were made initially with a Doran conductivity bridge, but subsequently with a Mullard conductivity bridge, the cells being calibrated with standard potassium chloride solution.

Potentiometric titrations were carried out with an E.I.L. model 23A direct-reading pH meter with glass and calomel electrodes.

Materials.—Decaborane (American Potash and Chemical Corporation) was recrystallised from n-hexane before use. Solvents were " AnalaR " grade, suitably dried.

Triammoniadecaborane.—Ammonia, dried by passage over potassium hydroxide pellets, was bubbled through a solution of decaborane in benzene. The solution developed a pale green colour followed by the formation of a pale green precipitate, which turned pale yellow and eventually white on further passage of ammonia. The precipitate was filtered off, washed well with benzene, and dried by pumping *in vacuo* for 2 hr. An identical *product* was obtained by carrying out the reaction in ethereal solution (Found: H, 12·2; N, 23·9. Calc. for $B_{10}H_{23}N_3$: H, 13·4; N, 24·2%).

On boiling with aqueous caustic soda, the triammoniate gave off 29·7 and 29·2% of ammonia (Calc. for $B_{10}H_{14}{\cdot}3NH_3$: 29·5%).

The substance, on warming, decomposed without melting, giving off ammonia and hydrogen. It was also decomposed by contact with dimethylformamide, dioxan, acetonitrile, diglyme, and dimethyl sulphoxide, with the liberation of ammonia. It was insoluble in benzene, toluene,

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[30] Onak, Landesman, Williams, and Shapiro, *J. Phys. Chem.*, 1959, **63**, 1533.

and n-hexane, but readily soluble in water, the solution smelling of ammonia. Boiling for a short time with a benzene solution of pyridine or triphenylphosphine resulted in the formation of dipyridine- or bistriphenylphosphine-decaborane. Triammoniadecaborane slowly decomposed on standing at ambient temperature, the nitrogen content having fallen to 11·4% in 4 months. This corresponds to the loss of *ca.* two molecules of ammonia per B_{10} unit.

Diammoniadecaborane.—This compound was prepared by boiling a suspension of triammoniadecaborane in toluene, until no more ammonia was evolved. The solid was filtered off and recrystallised from acetone as a white crystalline solid, not melting below 250° (Found: H, 12·0, 11·3; N, 18·1. Calc. for $B_{10}H_{18}N_2$: H, 11·8; N, 18·2%). It was insoluble in benzene, toluene, and n-hexane, but soluble with slight reaction in acetonitrile, acetone, and hot water. It could also be recovered unchanged from solution in boiling dimethylformamide or pyridine and failed to react with triphenylphosphine in boiling acetonitrile solution. Since these substances are very firmly held in compounds of the $B_{10}H_{12}M_2$ type, it can be inferred that the ammonia in diammoniadecaborane is equally strongly bound.

Sodium diammoniadecaboranate.—A solution of sodium decaboranate was prepared by shaking ethereal decaborane with *ca.* twice the theoretical quantity of sodium hydride (50% dispersion in mineral oil, L. Light & Co.). When the evolution of hydrogen ceased, the excess of sodium hydride was filtered off and dry ammonia bubbled through the filtrate. Colour changes similar to those found with ammonia and ethereal decaborane took place and ultimately the precipitate became very pale yellow. It was filtered off, washed well with ether, pumped hard *in vacuo*, and stored in a vacuum desiccator over potassium hydroxide since the *material* is hygroscopic (Found: N, 16·3, 16·4; NH_3, 18·1, 16·9, 20·5, 17·5; Na, 10·6, 10·9, Na $B_{10}H_{19}N_2$ requires N, 15·7; NH_3, 19·10; Na, 12·9%).

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