with intermediates of composition BH_4D or BD_4H, respectively, which mainly decompose to give HD and BH_3 or BD_3, but which decompose at a lower rate to H_2 and BH_2D or D_2 and BD_2H. Hence we believe that, of the two plausible mechanisms (6 and 9), the data favor mechanism 9.

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CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM & HAAS COMPANY,
REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALABAMA

The Amine Complexes of Aluminum Hydride. IV. Bis-(dimethylamino borane)-bis-(dimethylamino) Alane

BY JOHN K. RUFF

Received November 22, 1961

A new compound, $HAl[N(CH_3)_2]_2{\cdot}2BH_2N(CH_3)_2$, has been prepared by the reaction of bis-(dimethylamino) alane with dimethylamino borane. The interaction of various other dimethylamino borane derivatives with dimethylamino derivatives of alane produced the same material. Its probable structure is discussed.

Only a few examples of complexes formed between boron and aluminum hydride derivatives have been reported. Perhaps the best known is aluminum borohydride. In this complex the boron and aluminum atoms are believed to be bonded together *via* hydrogen bridges.[1] Burg attempted to prepare amino derivatives of aluminum borohydride in which one of the hydride bridges was replaced by an amino group.[2] He observed that a complex reaction occurred between aluminum borohydride and dimethylamino borane. Although the products were not completely characterized, one fraction was tentatively identified as having the composition $BH_4Al[BH_3N(CH_3)_2]_2$. Based on the information reported, one cannot determine whether the dimethylamino group had been substituted for a terminal or a bridging hydride atom.

Preparation of Bis-(dimethylamino borane)-bis-(dimethylamino) Alane.—The possible existence of compounds containing a dimethylamino group bonded to both boron and aluminum prompted an investigation into the preparation of such materials. The interaction of dimethylamino borane and bis-(dimethylamino) alane[3] was found to produce a single product in excellent yield.

$$HAl[N(CH_3)_2]_2 + 2H_2BN(CH_3)_2 \longrightarrow HAl[N(CH_3)_2]_2{\cdot}2BH_2N(CH_3)_2 \quad (1)$$

Little or no side products were isolated nor did appreciable quantities of starting materials remain in the reaction mixture when the above stoichiometry was followed. The new compound was named bis-(dimethylamino borane)-bis-(dimethylamino) alane for reasons presented in the following section.

Bis-(dimethylamino borane)-bis-(dimethylamino) alane also could be prepared by the reaction of tris-(dimethylamino) alane with trimethylamine borane or by reaction of tris-(dimethylamino) borane with trimethylamine alane. Good yields of bis-(dimethylamino borane)-bis-(dimethylamino)

$$2Al[N(CH_3)_2]_3 + 2BH_3{\cdot}N(CH_3)_3 \longrightarrow HAl[N(CH_3)_2]_2{\cdot}2BH_2N(CH_3)_2 + HAl[N(CH_3)_2]_2 + 2N(CH_3)_3 \quad (2)$$

$$2B[N(CH_3)_2]_3 + 2AlH_3{\cdot}N(CH_3)_3 \longrightarrow HAl[N(CH_3)_2]_2{\cdot}2BH_2N(CH_3)_2 + HAl[N(CH_3)_2]_2 + 2N(CH_3)_3 \quad (3)$$

alane were obtained in both reactions. Although the amount of trimethylamine liberated was in close agreement with the above stoichiometry, only fair yields of bis-(dimethylamino) alane were isolated, so that the presence of small amounts of other dimethylamino derivatives is not precluded.

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[1] W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949).

[2] A. B. Burg and C. L. Randolph, *J. Am. Chem. Soc.*, **73**, 953 (1951).

[3] The nomenclature in this paper is an extension of that proposed in part I [*ibid.*, **82**, 2141 (1960)]. See *ibid.*, **83**, 1798 (1961) for Part III.

The isolation of bis-(dimethylamino) alane in reaction 2 perhaps is unexpected in that it represents one of the few known examples of exchange of hydride from boron to aluminum.[4]

Several other related reactions also were found to produce bis-(dimethylamino borane)-bis-(dimethylamino) alane

$$Al[N(CH_3)_2]_3 + 3BH_2N(CH_3)_2 \longrightarrow HAl[N(CH_3)_2]_2 \cdot 2BH_2N(CH_3)_2 + HB[N(CH_3)_2]_2 \quad (4)$$

$$3HAl[N(CH_3)_2]_2 + 2BH_2N(CH_3)_3 \longrightarrow HAl[N(CH_3)_2]_2 \cdot 2BH_2N(CH_3)_2 + 2H_2AlN(CH_3)_2 \quad (5)$$

$$3AlH_2N(CH_3)_2 + 2B[N(CH_3)_2]_3 \longrightarrow HAl[N(CH_3)_2]_2 \cdot 2BH_2N(CH_3)_2 + HAl[N(CH_3)_2]_2 \quad (6)$$

The complex was isolated in fair yield in each of these reactions and the co-products in reactions 4 and 5, bis-(dimethylamino) borane and dimethylamino alane, also were identified. Since the yields of the isolated products were low, the stoichiometry represented in the above equations must be considered to be postulated rather than demonstrated.

The formation of bis-(dimethylamino borane)-bis-(dimethylamino) alane in six reactions differing for the most part only in the distribution of hydride and dimethylamino groups between boron and aluminum suggests that it is a unique chemical entity in this system. Undoubtedly a large number of reaction paths exist for its formation due to the known disproportionation reactions among the dimethylamino boranes[2] and the possibility of analogous behavior of the dimethylamino alanes.[5]

Constitution and Structure of Bis-(dimethylamino borane)-bis-(dimethylamino) Alane.—The formulation of bis-(dimethylamino borane)-bis-(dimethylamino) alane as an adduct between dimethylamino borane and bis-(dimethylamino) alane is based primarily on spectral evidence. Four of the five hydridic hydrogens in bis-(dimethylamino borane)-bis-(dimethylamino) alane are bonded to the borons in terminal positions as BH_2 groups, since a triplet was observed in the B^{11} n.m.r. spectrum of the complex (see Fig. 1).[6] Three types of bonding are thought to be likely for the remaining hydridic hydrogen; an Al–H bond, an Al–H–B bridge bond, or a B–H–B bridge bond.[7] No effect on the multiplicity of the B^{11} n.m.r. spectrum of the complex would arise from the presence of an Al–H bond. However, coupling of the boron with the bridge proton might occur if either an Al–H–B or a B–H–B bridge bond was present. Although boron has not been observed to couple with bridge hydrogens in the higher boron hydrides (*i.e.*, B_5H_9 and $B_{10}H_{14}$), such coupling does occur in diborane and in dimethylamino diborane.[8] This results in each member of the triplet, due to the two terminal hydrogens, being split into a doublet. The B^{11} n.m.r. spectrum of the latter compound exhibits a temperature dependence suggesting that exchange of the bridge and terminal hydrogens takes place. Since the lack of splitting at 25° of the observed triplet could arise from rapid exchange of bridge and terminal hydrogens, the B^{11} n.m.r. spectrum of bis-(dimethylamino borane)-bis-(dimethylamino) alane was obtained at $-55°$. No splitting of the triplet was detected at this temperature either. This suggests that a B–H–B bond is not present in the complex.

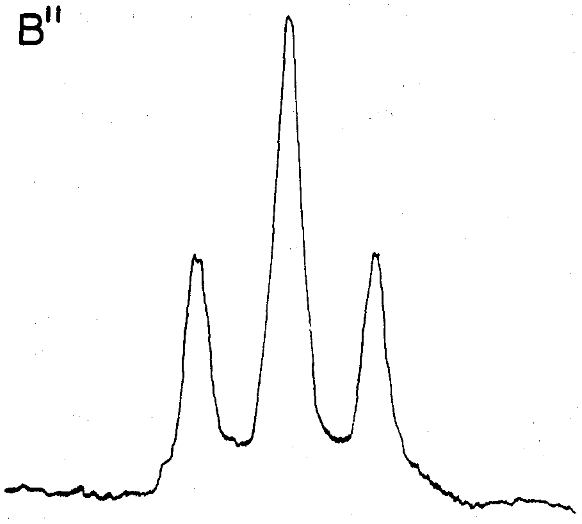

Fig. 1.—The B^{11} n.m.r. spectrum of bis-(dimethylamino borane)–bis-dimethylamino alane.

A comparison of the chemical shift of the boron resonance with those reported for similar compounds can yield information as to the probable coördination number of the boron. The B^{11} n.m.r. spectra of a number of simple boron compounds demonstrates that when boron is tetra-

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[4] The preparation of aluminum borohydride from aluminum trialkyls and diborane might formally be considered as an example of this type of exchange.

[5] J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 535 (1961).

[6] The single bond observed in the B^{11} n.m.r. spectrum of $AlB_2D_5[N(CH_3)_2]_4$ eliminated the possibility that the observed spectrum of the light compound was due to two overlapping doublets.

[7] The author is indebted to one of the reviewers for suggesting this type of bonding and for structure V.

[8] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

hedrally bonded, the B^{11} resonance occurs at a higher field than when it is bonded to only three groups.[8] In fact, the resonance bands for all the boron–nitrogen compounds investigated, in which the boron has a coördination number of four, occur on the high field side of methyl borate. Recently a similar correlation was found between the chemical shift of the B^{11} resonance and the degree of association for several dialkylamino alkyl boranes.[9] The high field position of the triplet in the B^{11} n.m.r. of bis-(dimethylamino borane)-bis-(dimethylamino) alane suggests, therefore, that the borons are bound to four groups.

The infrared spectrum of bis-(dimethylamino borane)-bis-(dimethylamino) alane consists of several bands in the B–H and Al–H stretching region (see Fig. 2). The bands at 4.15, 4.30, 4.4, 4.5, and 4.8 μ are quite similar to those found in the infrared spectra of trimethylamine borane and dimethylamino borane and are attributed to the presence of terminal hydrogens on boron. The stretching frequency of these bands underwent an isotopic shift by a factor of 1.35 to 1.40 when deuterium was substituted for the hydridic hydrogen in the complex. No strong bands are present that can be assigned to Al–H–B bridges as are present in aluminum borohydride.[1]

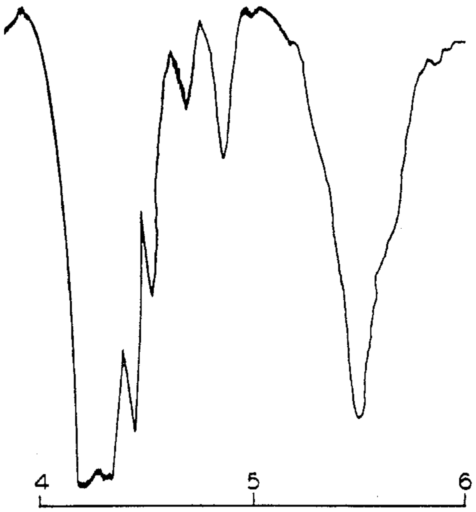

Fig. 2.—The infrared spectrum of bis-(dimethylamino borane)–bis-dimethylamino alane in the B–H and Al–H stretching region.

The absorption band at 5.45 μ is more difficult to assign since both the Al–H[10] and B–H–B bridge stretching modes appear in this region. The band shifted to 7.57 μ upon deuterium substitution so it is associated with either of the above two possibilities. Assignments have not been made for the B–H–B stretching frequencies in all of the boron hydrides. However, two stretching modes were assigned in diborane[11] (5.22 and 6.24 μ), dimethylamino diborane[12] (5.31 and 6.12 μ), and aluminum borohydride[1] (4.64 and 6.67 μ). Thus if a B–H–B bridge is present in bis-(dimethylamino borane)-bis-(dimethylamino) alane, a stretching band might be expected in the 6–7.5 μ region. Since both of the bridge stretching bands in diborane and dimethylamino diborane undergo an isotopic shift upon deuteration,[11,12] a comparison of the spectra of $AlB_2H_5[N(CH_3)_2]_4$ and $AlB_2D_5[N(CH_3)_2]_4$ was made. No change in the spectra was observed in this region so it is concluded that no strong absorption band due to a hydridic hydrogen–metal stretching mode is present.

The reactivity of the B–H–B bridge toward nucleophiles has been amply demonstrated. Dimethylamino diborane is reported to form a stable complex with trimethylamine,[13] while other B–H–B bridge systems undergo cleavage reactions. No interaction was observed when bis-(dimethylamino borane)-bis-(dimethylamino) alane was treated with trimethylamine at 25°, and in fact trimethylamine is liberated in the preparation of the complex (reactions 2 and 3) in almost quantitative fashion. A B–H–B bridge, if it is present in the compound, is either much longer than the bridge in diborane or is involved in a rapid exchange process (as indicated by the lack of coupling observed in the B^{11} n.m.r. spectrum), so that it would be expected to be labile toward attack by trimethylamine.

On the basis of the above arguments it is felt that the fifth hydridic hydrogen is bound to aluminum and that the compositional formula $HAl[N(CH_3)_2]_2 \cdot 2BH_2N(CH_3)_2$ probably is correct. Furthermore, since the B^{11} n.m.r. spectrum of the complex suggests that boron is bonded to four groups, there are four possible structures for

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(9) M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2671 (1961).

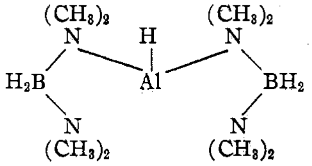
(10) The Al–H stretching frequency is assigned to a band occurring at 5.50 μ and 5.45 μ for $H_2AlN(CH_3)_2$ and $HAl[N(CH_3)_2]_2$, respectively. This frequency also is reported to be 5.46 μ and 5.48 μ for $H_2AlN(C_2H_5)_2$ and $HAl[N(C_2H_5)_2]_2$. [G. Schomburg and E. G. Hoffman, *Z. Elektrochem.*, **61**, 1110 (1957).]

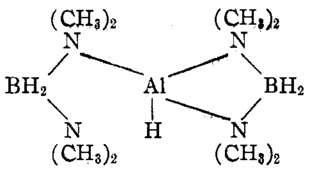
(11) R. C. Lord and E. Nielsen, *J. Chem. Phys.*, **19**, 1 (1951).

(12) D. E. Mann, *ibid.*, **22**, 70 (1954).

(13) A. B. Burg and C. L. Randolph, *J. Am. Chem. Soc.*, **71**, 3451 (1949).

the compound. The first three are closely related and differ only in the coördination number of the aluminum


I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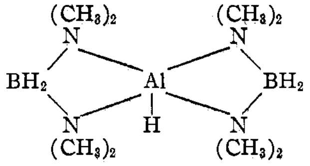
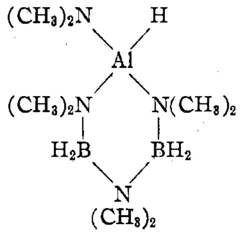
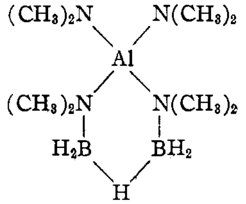

III


IV

If a B—H—B bridge were present, then a fifth structure probably would be the correct one.


V

In an effort to distinguish between the proposed structures, the proton n.m.r. spectrum of bis-(dimethylamino borane)-bis-(dimethylamino) alane was obtained, since in all the structures except III the nitrogen exists in two different degrees of coördination. The spectrum, however, consisted of a single band that could be attributed to the methyl groups even when the solution was cooled to -40° (rapid exchange of the dimethylamino groups was thought possible, especially for structures I and II). The effect of the coördination number of nitrogen on the shielding of the protons in dimethylamino groups was demonstrated in the proton n.m.r. spectrum of dimeric tris-(dimethylamino) alane.[14] Two methyl resonance bands were observed which had area ratios of two to one, as would be predicted for a structure involving two bridging dimethylamino groups and four terminal ones.[15] The apparent equivalence of the methyl groups in bis-(dimethylamino borane)-bis-(dimethylamino) alane and the field position of the resonance band is compatible with structure III. However, this evidence is not conclusive.

An attempt was made to utilize the difference in reactivity that exists between terminal dimethylamino groups and bridging dimethylamino groups toward boron trichloride in such compounds as tris-(dimethylamino) alane and bis-(dimethylaminochloro) alane[15] to distinguish between some of the proposed structures. A tensiometric titration of bis-(dimethylamino borane)-bis-(dimethylamino) alane with boron trichloride resulted in a sharp linear pressure increase at a mole ratio of boron trichloride to the complex of 2.2. The reaction

$$HAl[N(CH_3)_2]_2\cdot 2BH_2N(CH_3)_2 + 2BCl_3 \longrightarrow HAlCl_2 + 2BH_2N(CH_3)_2 + 2BCl_2N(CH_3)_2$$

is postulated to explain the observed stoichiometry. Further exchange of chloride and hydride probably occurs, producing chlorodiboranes. Since the number of moles of volatile materials is not appreciably decreased, this exchange would not be readily detected in the titration. The consumption of one boron trichloride for each dimethylamino group formally associated with the aluminum in bis-(dimethylamino borane)-bis-(dimethylamino) alane suggests that complete degradation of the Al–N bonds probably occurred. Therefore, this method cannot be used to distinguish between the proposed structures, I through IV. The observed stoichiometry also is compatible with structure V.

In view of the unsuccessful attempts to eliminate any of the proposed structures as possibilities or to demonstrate conclusively the absence of a B–H–B bridge, it probably will remain for the crystallographer to elucidate the structure of bis-(dimethylamino borane)-bis-(dimethylamino) alane.

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(14) The proton spectrum was taken at 40 Mc. on a 11.7% solution in chlorobenzene. The spectrum consisted of two methyl bands at $\tau = 8.58$ (relative area $= 1.00$ and assigned to the bridging dimethylamino groups) and $\tau = 8.38$ (relative area $= 2.04$ and assigned to the terminal dimethylamino groups) relative to tetramethylsilane.

(15) J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 2835 (1961).

Experimental

Since the product and some of the starting materials react with oxygen and moisture, all operations were performed in a conventional vacuum line or in an inert atmosphere.

Materials.—The preparation of trimethylamine alane and the dimethylamino alanes was reported recently.[3,15] Trimethylamine borane and dimethylamino borane were prepared by the method of Schaeffer and Anderson.[16] Tris-(dimethylamino) borane was prepared from tri-*n*-butyl borate and tris-(dimethylamino) alane.[17]

Preparation of $HAl[N(CH_3)_2]_2 \cdot 2BH_2N(CH_3)_2$.—The same procedure was used in all the preparations of bis-(dimethylamino borane)-bis-(dimethylamino) alane. The reactants were weighed and added to a 100-ml. flask containing hexane in the drybox. The solution was filtered and then refluxed under nitrogen for 1 hr. Upon cooling, the product crystallized out and was filtered off either in the drybox or by means of the vacuum filtration apparatus. It was easily recrystallized from hexane.

(a) A mixture of 1.20 g. of bis-(dimethylamino) alane and 1.21 g. of dimethylamino borane in 40 ml. of hexane was refluxed for 1 hr. A yield of 1.78 g. of bis-(dimethylamino borane)-bis-(dimethylamino) alane (I) was obtained, m.p. 120°. The solvent was removed from the filtrate under reduced pressure. An infrared spectrum of the solid residue was identical to that of the purified product, m.p. 115–117°. This melting point is higher than those of the starting materials.

(b) Tris-(dimethylamino) alane, 5.39 g., was allowed to react with 2.50 g. of trimethylamine borane at reflux in 60 ml. of hexane for 1.5 hr. During reflux, nitrogen gas was allowed to sweep through the reactor and bubble into a standard solution of hydrochloric acid. After reaction was complete, a back-titration by sodium hydroxide (to a methyl red end point) showed the consumption of 32.3 meq. of acid (calcd. 34.2 meq.). Hence, virtually all the trimethylamine had been liberated. The mixture was filtered and a 3.05 g. sample of I was isolated, m.p. 120°. The solvent was removed from the filtrate *in vacuo* and the residue was sublimed slowly at 40°. A 1.35 g. sample of bis-(dimethylamino) alane was obtained, m.p. 62° (lit. 63°). Its infrared spectrum was identical to that of a known sample.

(c) The reaction of 2.80 g. of tris-(dimethylamino) borane with 1.79 g. of trimethylamine alane in 40 ml. of hexane produced a 1.84-g. sample of $HAl[N(CH_3)_2]_2 \cdot 2BH_2N(CH_3)_2$, m.p. 121°. The filtrate was treated as in (b). Bis-(dimethylamino) alane, 0.90 g., was obtained, m.p. 61°. Its identity also was confirmed by infrared spectrum. The amount of trimethylamine liberated in the reaction was determined as described above; found 21.1 meq., calcd. 20.2 meq.

Bis-(dimethylamino borane)-bis-(dimethylamino) alane-D_5 was prepared from 1.85 g. of trimethylamine alane-D_3 and 2.86 g. of tris-(dimethylamino) borane. A 1.62-g. sample of the deuterated complex was obtained, m.p. 122°. Hydrolysis of a 0.2561-g. sample of the complex produced 5.28×10^{-3} mole of HD (mass spectrum of the gas gave a H/D ratio of 1.06); calcd. 5.45×10^{-3} mole.

(d) Trimethylamine borane, 1.30 g., was treated with 3.18 g. of bis-(dimethylamino) alane in 50 ml. of hexane. A 1.72-g. sample of I was produced, m.p. 119°. The residue from the filtrate was sublimed at 50°. Dimethylamino alane, 0.69 g., was obtained, m.p. 85° (lit. 89°). The infrared spectrum of the sublimate showed no B–H absorption.

(e) Tris-(dimethylamino) alane, 4.81 g., and dimethylamino borane, 5.13 g., were allowed to react in 60 ml. of hexane. A 51% yield (3.89 g.) of I was obtained. The hexane was distilled off of the filtrate at 33° under reduced pressure until approximately 5 ml. of liquid remained and this was fractionated in the vacuum line through −45 and −78° baths. Approximately 0.6 g. of liquid trapped in the −78° bath was identified as bis-(dimethylamino) borane by comparison of its infrared spectrum with that of a known sample.

(f) The reaction of 2.60 g. of dimethylamino alane with 3.50 g. of tris-(dimethylamino) borane in 50 ml. of hexane yielded 1.41 g. of I, m.p. 121°. No attempt was made to isolate any products from the filtrate.

Analysis.—Nitrogen analysis was performed as described previously for similar compounds.[15] Active hydrogen was determined by a two-step hydrolysis procedure. The material was hydrolyzed under vacuum with a methanol–ether mixture. When the reaction had ceased, trifluoroacetic acid was added and the mixture was warmed to 50° for 1 hr. The amount of hydrogen evolved was measured by means of a Toepler pump and a calibrated storage bulb system. The remaining solution then was treated as already described[5] to determine the aluminum content. An aliquot was titrated for boric acid by the conventional mannitol titration procedure.

Anal. Calcd. for $AlB_2H_5N_4(CH_3)_8$: Al, 11.73; B, 9.41; N, 24.4; active H, 2.17. Found: Al, 11.55; B, 9.30; N, 24.3; active H, 2.12. B/Al = 2.01; H/Al = 4.94; N/Al = 4.06.

Reaction of BCl_3 with $HAl[N(CH_3)_2]_2 \cdot 2BH_2N(CH_3)_2$.—A solution of 0.3940 g. of bis-(dimethylamino borane)-bis-(dimethylamino) alane in 4 ml. of *n*-decane was treated with known amounts of gaseous boron trichloride in a constant-volume apparatus. After each addition, the reaction flask was allowed to warm to ambient temperature. The pressure was recorded when no further change was noted. A sharp linear increase in pressure occurred at a mole ratio of boron trichloride to I of 2.19.

A similar titration was performed with trimethylamine and a 0.2872-g. sample of I in 5 ml. of *n*-decane. A linear increase in pressure was observed after the initial addition of 2.7×20^{-4} mole of the amine.

Molecular Weight Determination.—The apparent molecular weight of bis-(dimethylamino borane)-bis-(dimethylamino) alane was determined cryoscopically in benzene. The procedure and apparatus were described previously.[5] The three values found, 248, 254, 253 (theory, 230), indicate that the degree of association in benzene is low.

Infrared Spectrum.—The infrared spectra of bis-(dimethylamino borane)-bis-(dimethylamino) alane and bis-(dimethylamino borane)-bis-(dimethylamino) alane-D_5 were obtained on Nujol mulls that were prepared in the drybox. The observed bands are listed in Table I. Figure 2 shows the infrared spectrum in the B–H and Al–H region. The infrared spectra of both compounds also were

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[16] G. W. Schaeffer and E. R. Anderson, *J. Am. Chem. Soc.*, **71**, 2143 (1949).

[17] J. K. Ruff, *J. Org. Chem.*, **27**, 1020 (1962).

TABLE I

INFRARED SPECTRA OF $AlB_2H_5[N(CH_3)_2]_4$ AND $AlB_2D_5[N(CH_3)_2]_4$

$AlB_2H_5[N(CH_3)_2]_4$	$AlB_2D_5[N(CH_3)_2]_4$
3.4 vs	3.4 vs
3.5 m	3.5 m
4.15 vs^a	5.55 vs^a
4.30 vs^a	5.87 vs^a
4.4 m^a	6.25 vw^a
4.5 w^a	6.8 vs
4.65 vw^a	6.95 m
4.8 w^a	7.05 w
5.45 s^a	7.12 m
6.8 vs	7.55 s^a
6.95 m	8.1 s
7.05 w	8.5 w
7.10 m	8.6 vs
7.90 w	9.1 m
8.1 s	9.65 s
8.4 w^a	10.35 s
8.6 vs	10.6 s,^{a} broad
8.95 s^a	10.85 w
9.1 m	11.0 s
9.65 w	12.8 w
10.3 s	13.0 m
10.7 s	13.8 s^a
12.2 s^a	
12.5 w^a	
12.9 m	

^{a} Bands that clearly underwent isotopic shift upon deuteration.

obtained in a tetrachloroethylene solution (0.21 g. of compound per 5 ml. of solvent) in 0.1-mm. matched cells. No differences in the spectra of the light and the heavy compounds were observed in the 6–7-μ region.

Unless great care was taken in the preparation of the samples, especially the solutions, a new absorption band at 6.5 μ appeared in the spectrum. The intensity of the band was dependent upon the history of the sample. Both the light and heavy compounds exhibited similar behavior, so that it is felt that this band is due to a non-hydridic impurity which probably is formed by hydrolysis.

N.m.r. Spectrum.—The B^{11} and proton n.m.r. spectra of bis-(dimethylamino borane)-bis-(dimethylamino) alane were obtained on a 14.3% solution in chlorobenzene with a Varian Model V-4300 B spectrometer operating at 12.8 and 40 Mc., respectively. The B^{11} n.m.r. spectrum of bis-(dimethylamino borane)-bis-(dimethylamino) alane-D_5 was obtained on a 9.3% solution in benzene. The low temperature B^{11} n.m.r. spectrum of the light compound was obtained on a 4.7% solution in toluene employing a double-wall dewar insert of approximately 10 mm. i.d. A few drops of tetramethylsilane were added to the solutions as an internal standard for the proton n.m.r. and methyl borate was used as an external standard for the B^{11} n.m.r. spectra. Chemical shifts were measured by the sideband technique. The B^{11} n.m.r. spectrum of bis-(dimethylamino borane)-bis-(dimethylamino) alane consisted of a triplet centered at $\delta = 16.6 \times 10^{-6}$ relative to methyl borate (see Fig. 1) and with a $J_{BH} = 107$ c.p.s. The B^{11} n.m.r. spectrum of the deuterated complex consisted of a single band at $\delta = 17.7 \times 10^{-6}$. No splitting of the observed triplet occurred when the B^{11} n.m.r. spectrum of bis-(dimethylamino borane)-bis-(dimethylamino) alane was obtained at $-55° \pm 3°$. The proton n.m.r. spectrum consisted of single bands attributable to chlorobenzene, tetramethylsilane, and the methyl groups on the nitrogen, $\tau = 8.58$.[18] No splitting of the methyl resonance was observed when the solution was cooled to $-39 \pm 1°$. It was not possible to distinguish the bands due to the Al–H and B–H bonds due to the quadrupole broadening and spin–spin coupling of the aluminum and hydrogen and the spin–spin coupling of the bonded boron and hydrogen.

Acknowledgment.—The author wishes to thank Mr. R. D. Strahm for the chemical analyses, and Mrs. C. P. Haney for the n.m.r. spectra. This work was performed under contract DA-01-021-ORD-784.

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(18) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).