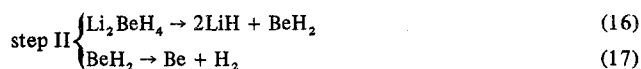
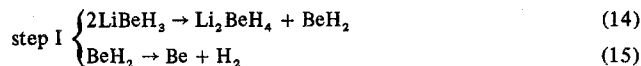


Similarly, the weight loss at 308° (5.1%) corresponds to the weight loss of one atom of hydrogen. Therefore, the thermal decomposition of LiBeH₃ is believed to occur in essentially two steps below 500° (see eq 14–17).



(b) Reaction of AlH₃ with LiBe₂(CH₃)₅ in Diethyl Ether. Attempted Preparation of LiBe₂H₅. The reaction of AlH₃ and LiBe₂(CH₃)₅ resulted in a solid of indefinite analysis. The X-ray powder diffraction of the solid gave very weak lines similar to those of Li₂BeH₄, but with different intensities. The vacuum DTA–TGA of the solid showed three noncondensable gas evolutions at 165, 243, and 308°, respectively. The thermal effect (DTA) of gas evolution at 165° is a small endotherm which probably represents the decomposition of BeH₂ into beryllium and hydrogen. The gas evolution at 243° is accompanied by an exotherm whereas the gas evolution at 308° is accompanied by a small endotherm. The weight loss (1%, 2.8%, and 5.7%, respectively) indicates the presence of one or more species in the sample.

A potential route to complex metal hydrides of beryllium of the type Na_nBe_mH_{2n+m} and K_nBe_mH_{2n} involves the reaction of NaH or KH with (CH₃)₂Be followed by reaction of the resulting complex with LiAlH₄. Attempts to prepare KBe(CH₃)₂H and NaBe(*s*-C₄H₉)₂H in diethyl ether resulted

in incomplete reaction between potassium or sodium hydride and corresponding dialkylberyllium compounds.

Acknowledgment. We wish to acknowledge the financial support of the Office of Naval Research under Contract No. N 00014-67-A-0419-005 AD and ONR Contract Authority No. NR 093-050/7-11-69(473).

Registry No. LiH, 7580-67-8; BeH₂, 7787-52-2; Li₂BeH₄, 19321-21-2; Li₃BeH₅, 56792-70-2; LiBeH₃, 25282-11-5; CH₃Li, 917-54-4; (CH₃)₂Be, 506-63-8; LiAlH₄, 16853-85-3; Li₂Be(CH₃)₄, 20860-58-6; Li₃Be(CH₃)₅, 56829-59-5; LiBe₂(CH₃)₅, 56829-60-8; (*n*-C₄H₉)₂Be, 7367-41-1; Et₂O, 60-29-7; BeBr₂, 7787-46-4; AlH₃, 7784-21-6; LiBe(CH₃)₃, 56792-71-3.

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Trends in the Proton Nuclear Magnetic Resonance Spectra of Some Amine–Haloboranes. Steric Effects¹

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Borane adducts of trimethylamine and diethylamine were halogenated using free halogens or hydrogen halides, and the proton NMR spectra of these amine–haloborane adducts were obtained. The resonances of these adducts showed a shift to lower field with increased size of halogen or with increased number of halogens on boron. This shift to lower field had been previously attributed to inductive effects, but in this work it was shown that the shift to lower field was due to steric interaction between halogens on boron and alkyl groups on nitrogen. Proton NMR spectra for diethylamine–haloboranes were complex and showed patterns attributable to nonequivalent methylene protons. Computer analyses of the spectra allowed assignments consistent with preferred rotational configurations.

Introduction

There can be no question as to the place of nuclear magnetic resonance in chemistry today. NMR has become one of the most powerful tools available for studying a wide variety of chemical systems, including such diverse problems as reaction kinetics, structure, product yields, product identification, and reaction mechanisms. However, in spite of its usefulness, there is still considerable controversy in the literature concerning the origin of chemical shifts.

A variety of physical evidence has established that the acid strengths of the boron trihalides increase in the order BF₃ < BCl₃ < BBr₃ < BI₃. This evidence includes calorimetric studies,³ dipole moment determinations,⁴ gas-phase displacement studies,^{5–7} and structural determinations involving X-ray and microwave techniques.^{8–10} Attempts have been made, with varying success, to correlate this property of the boron trihalides with various spectral properties of their

donor–acceptor complexes. Thus, correlations have been attempted between acidity of the boron trihalides and infrared data,^{11–16} mass spectral data,¹⁷ ¹¹B NMR data,^{18–22} and ¹H NMR data^{23–27} obtained on the donor–acceptor complexes formed by the boron trihalides. The one characteristic common to these various correlations is the assumption that the relative ability of the coordinated boron trihalides to remove electron density from the donor to which they are coordinated is in the same order as the order of acid strengths of the free boron trihalides.

In particular the ¹H NMR spectra of trimethylamine–trihaloboranes have been examined^{25–27} and the conclusion was reached that the trend observed in the spectra, a downfield shift of the methyl resonance with larger halogens on boron, is consistent with an inductive effect due to the increased acidity of the borane. To evaluate this argument, consider first the reason that the order of acid strength is BF₃ < BCl₃ <

$\text{BBr}_3 < \text{BI}_3$. Conventional arguments analyze this fact in terms of three factors. Since the order of electronegativity of the halogens is $\text{F} \gg \text{Cl} > \text{Br} > \text{I}$, one would predict an order of $\text{BF}_3 \gg \text{BCl}_3 > \text{BBr}_3 > \text{BI}_3$. This order is opposite to the order observed. The ability of the halogens to π bond to boron (in the free acid) increases in the order $\text{I} < \text{Br} < \text{Cl} \ll \text{F}$, and since π bonding in the free acid must be destroyed to form the adduct, the strongest acid would be the one which has the least π bonding. Thus on the basis of extent of π bonding, one would predict an order of $\text{BF}_3 \ll \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$. This order is the same as the order observed. The relative steric bulk of the halogens increases in the order $\text{F} < \text{Cl} < \text{Br} < \text{I}$. Since front strain thus introduced into the adduct is a destabilizing influence, one would predict that the acid strength would be in the order $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3 > \text{BI}_3$. This order is opposite to the order observed. If the actual order of acid strengths is determined by these three factors, one must conclude that the predominant effect is π bonding, since only that factor correctly predicts the order. That is, the energy required to break up π bonding in the free acid determines the relative acid strength of the boron trihalides. However, if all the π bonding in the free acid is destroyed in forming the adduct, the inductive withdrawing power of the coordinated borane should be principally determined by the electronegativity of the halogens, and thus the inductive withdrawing power should be in the order $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3 > \text{BI}_3$. To the extent that there is residual π bonding (or hyperconjugation) in the acceptor portion of the adduct, this order may be modified somewhat, but, the arguments of Drago¹⁶ and others notwithstanding, it is difficult to believe that there could be enough residual π bonding in the adduct to cause the order of inductive withdrawal power to be the reverse of that predicted by electronegativity.

One is led, therefore, to conclude that some other factors besides inductive effects are at work in determining these spectral properties. It is our purpose to present ^1H NMR data for a large number of amine-haloboranes and to suggest an alternative explanation for the trends which we have noted in these data. This explanation is based on a factor which has thus far been ignored in this connection, steric interaction between halogens on boron and protons on alkyl groups in bases coordinated to boron.

Experimental Section

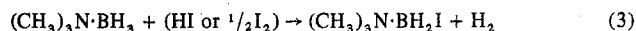
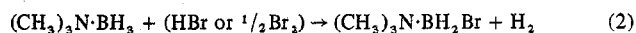
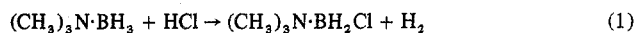
Materials. Trimethylamine-borane, dimethylamine-borane, and triethylamine-borane were obtained from Callery Chemical Co. and were used without further purification. Other chemicals and solvents were reagent grade and except where noted were used without any further purification, but were dried over molecular sieves where appropriate.

Apparatus and Methods. Proton NMR spectra of the amine-boranes and haloboranes were taken at ambient temperature in CH_2Cl_2 solution with tetramethylsilane as an internal standard. The spectra were obtained at 60 MHz, using a Varian Model A-60A spectrometer. The chemical shifts, δ , are reported in ppm, downfield from tetramethylsilane; error limits on these data are ± 2 in the last digit shown. In the case of the diethylamine-haloboranes, nonequivalence of the methylene protons required that some spectra be run on a 100-MHz instrument (Varian Model XL-100) in order that the peaks in the pattern could be sufficiently resolved to allow interpretation. The ABCD₃ pattern was analyzed on an IBM 360-65 computer at the University of Florida Computing Center using a program, LAMP2, supplied by R.W.K. Details of the spectral analysis are discussed in a separate section. The chemical shifts of the diethylamine adducts are reported from the 60-MHz spectra.

Synthesis of Diethylamine-Borane. Diethylamine-borane was synthesized via a transamination reaction of diethylamine with trimethylamine-borane. Trimethylamine-borane was refluxed in a large excess of diethylamine for about 3 hr. The excess diethylamine was pumped off, and the remaining diethylamine-borane was purified by shaking with water and extracting with methylene chloride, the methylene chloride being evaporated to give good yield (ca. 85%) of

liquid diethylamine-borane. The ^1H NMR spectrum of the compound showed a triplet in the methyl region, a broadened quintet in the methylene region, and a broad resonance further downfield which was assigned to N-H. Chemical shifts and coupling constants are given in Table III. The ir spectrum was characterized by a strong peak at 3200 cm^{-1} , assigned to N-H stretch, and a strong doublet centered at 2350 cm^{-1} , assigned to coordinated BH_3 stretch. The ^{11}B NMR spectrum of the compound showed a quartet ($J_{\text{BH}} = 97.5\text{ Hz}$) centered at 34.6 ppm upfield from trimethyl borate.

Synthesis of the Monohaloborane Adducts of Trimethylamine. The procedures for the monohalogenation of trimethylamine-borane have been published previously²⁸ and will thus only be summarized here in eq 1-3. These reactions may be carried out in a variety of solvents,



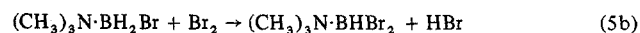
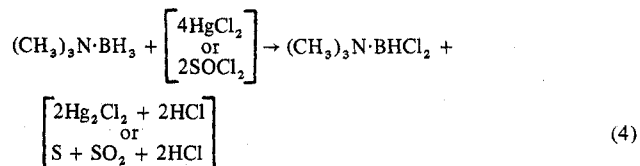
such as benzene, carbon tetrachloride, or methylene chloride. The monochloro- and monobromoborane adducts were stable in air, but the monoiodoborane adduct was both moisture and light sensitive.

Synthesis of the Monohaloborane Adducts of Triethyl-, Dimethyl-, and Diethylamine. (a) The reactivity of triethylamine-borane was similar to that of trimethylamine-borane. Thus, similar reactions produced good yields of the monohaloborane adducts. Triethylamine-borane reacted only slightly slower than did trimethylamine-borane, under the same conditions.

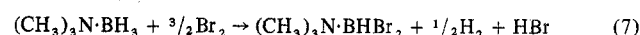
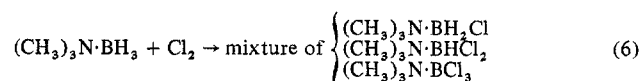
(b) Dimethylamine-borane was much more reactive than trimethylamine-borane, and more stringent reaction conditions were required. To prepare the monochloroborane adduct a stoichiometric amount of HCl was added to a solution of dimethylamine-borane (excess HCl reacted to produce the dichloroborane adduct). The monobromoborane adduct was best prepared by the addition of a stoichiometric amount of HBr to a solution of dimethylamine-borane. (Addition of Br_2 to dimethylamine-borane in a ratio of 1:2 resulted in the formation of ca. 90% monobromoborane adduct, ca. 5% dibromoborane adduct, and ca. 5% unreacted starting material.) The monoiodoborane adduct could be prepared by the addition of I_2 to a solution of dimethylamine-borane in a ratio 1:2. All of the dimethylamine-monohaloboranes were moisture-sensitive solids, the monoiodoborane adduct being extremely unstable. Proton NMR spectra of solutions of dimethylamine-monoiodoborane showed decomposition into uncharacterized products on standing for several days. All of the monohaloborane adducts of dimethylamine fumed on exposure to the atmosphere.

(c) The reactivity of diethylamine-borane was similar to that of dimethylamine-borane. Thus, similar reactions produced good yields of the diethylamine-monohaloboranes. The diethylamine adducts were also very sensitive to moisture, and the monoiodoborane adduct decomposed rapidly, even stored pure in the drybox. All of the diethylamine-monohaloboranes were liquids.

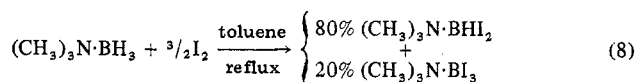
Synthesis of the Dihaloborane Adducts of Trimethylamine. Procedures for the preparation of dichloro- and dibromoborane adducts of trimethylamine have been published elsewhere^{29,30} and thus will be only summarized here in eq 4 and 5. It should be noted that the



dichloroborane adduct was produced in the reaction of Cl_2 with trimethylamine-borane and that the dibromoborane adduct was produced by reaction of Br_2 with trimethylamine-borane in a ratio of 1.5:1, as shown in reactions 6 and 7. Trimethylamine-diiodoborane



was prepared by the reaction of I_2 and trimethylamine-borane (eq 8). The adduct was formed in a mixture of products and was



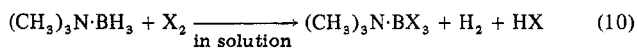
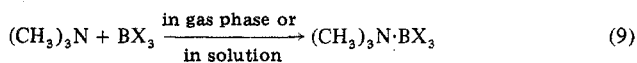
recoverable by sublimation. The ratio of primary products was determined by NMR. The diiodoborane adduct was more volatile, and sublimation produced pure $(CH_3)_3N \cdot BHI_2$ on the cold finger. The dichloro- and dibromoborane adducts were stable in air. The diiodoborane adduct decomposed unless stored in the dark in a desiccator.

Synthesis of the Dihaloborane Adducts of Triethyl-, Dimethyl-, and Diethylamine. (a) The dihaloborane adducts of triethylamine were prepared by reaction of the halogen (Cl_2 , Br_2 or I_2) with triethylamine-borane, in CH_2Cl_2 . When Cl_2 or Br_2 was used, a mixture of products resulted (i.e., mono-, di-, and trihalogenated products), but the dihaloborane adducts could be easily identified by NMR. Triethylamine-diiodoborane was the principal product (ca. 94%) when I_2 and $(CH_3CH_2)_3N \cdot BH_3$ react in a ratio of 1.15:1.00 in CH_2Cl_2 ; gentle reflux and a long exposure time are necessary. The reactivity of triethylamine-borane was thus similar to that of trimethylamine-borane.

(b) The dihaloborane adducts of dimethylamine were prepared by reaction of the halogen (Cl_2 , Br_2 , or I_2) with dimethylamine-borane in CH_2Cl_2 . When Br_2 or I_2 was used, addition of halogen to dimethylamine-borane in 1:1 ratio yielded amine-dihaloborane in high purity. However, when Cl_2 was used, mixtures of products resulted. The dichloroborane adduct was prepared in high purity by reaction of an excess of HCl with dimethylamine-borane. These adducts were moisture sensitive and should be handled only in a drybox.

(c) The dihaloborane adducts of diethylamine were prepared in the same way as the dimethylamine adducts. Br_2 or I_2 added to diethylamine-borane produced diethylamine-dibromoborane or -diiodoborane in high purity. Addition of an excess of HCl to diethylamine-borane produced diethylamine-dichloroborane in high purity. Diethylamine-dichloroborane was a colorless liquid. Diethylamine-dibromoborane and diethylamine-diiodoborane were yellowish solids. All three adducts were extremely sensitive to moisture, and the diiodoborane adduct decomposed on standing.

Synthesis of the Trihaloborane Adducts of Trimethylamine. Two methods were used for preparation of the trihaloborane adducts of trimethylamine^{31,32}



These reactions proceeded at room temperature, except that reaction with I_2 required extended refluxing in toluene. The triiodoborane adduct was unstable and decomposed on storing.

Synthesis of the Trihaloborane Adducts of Triethyl-, Dimethyl-, and Diethylamine. (a) Reaction of an excess of Cl_2 or Br_2 with triethylamine-borane produced triethylamine-trichloroborane and -tribromoborane in high purity. However, reaction of an excess of I_2 with triethylamine-borane with refluxing over a long period of time produced Et_3NH^+ in addition to the previously mentioned triethylamine-diiodoborane.

(b) The addition of an excess of Cl_2 or Br_2 to dimethylamine-borane produced dimethylamine-trichloroborane and -tribromoborane in good yield and high purity.³³ The reaction of I_2 and dimethylamine-borane produced the triiodoborane adduct, but only after long exposure and refluxing. These adducts were white solids when first isolated, although decomposition produced color changes when the product was allowed to stand (Br, yellow; I, dark brown). All three adducts fumed in the atmosphere, but short exposures did not seem to affect the trichloro- or tribromoborane adducts. The triiodoborane adduct was handled in the drybox and exposure to light was avoided. The reaction of dimethylamine with boron trichloride and tribromide has been reported in detail elsewhere.^{33a}

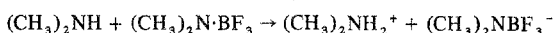
(c) The addition of Cl_2 or Br_2 in excess to diethylamine-borane produced diethylamine-trichloroborane and -tribromoborane in good yield and high purity. Attempts to produce diethylamine-triiodoborane by reaction of an excess of I_2 with diethylamine-borane under reflux over a long period of time first produced $Et_2NH \cdot BHI_2$ and then

$Et_2NH_2^+$. Diethylamine-trichloroborane and -tribromoborane were white solids when first isolated, although the tribromoborane adduct turned yellow on standing. Both compounds could be handled for short periods in the atmosphere without apparent damage, though both fumed slightly.

Synthesis of the Trifluoroborane Adduct of Trimethylamine. Trimethylamine-trifluoroborane was prepared in good yield and high purity by bubbling an excess of trimethylamine into an ether solution of boron trifluoride-etherate. Evaporation of the volatiles left the white, crystalline adduct.

Synthesis of the Trifluoroborane Adducts of Triethylamine, Dimethylamine, and Diethylamine. (a) Triethylamine-trifluoroborane was prepared in the same way as trimethylamine-trifluoroborane. A solution of triethylamine in ether was added dropwise to an ether solution of boron trifluoride-etherate. Evaporation of the volatiles left low-melting, colorless crystals of triethylamine-trifluoroborane. On standing in air, slow decomposition produced a brown oil.

(b) Dimethylamine-trifluoroborane³⁴ was prepared by two methods, the first of which was the same as that used to prepare trimethylamine-trifluoroborane. Dimethylamine was bubbled into an ether solution of boron trifluoride-etherate, and the volatiles were removed to leave clear, colorless crystals of dimethylamine-trifluoroborane. This method did produce dimethylamine-trifluoroborane, however the stoichiometry was difficult to control, and there was NMR evidence for a side reaction as shown by



when dimethylamine was in excess.^{34b} The second method suffers from the same drawback—difficulty in controlling stoichiometry. Dimethylamine and boron trifluoride were bubbled together in an inert solvent such as methylene chloride or benzene. As long as dimethylamine was not present in excess, evaporation of the volatiles produced clear, colorless crystals of dimethylamine-trifluoroborane. The adduct decomposed into a brown oil standing in air but could be kept by storing under vacuum.

(c) Diethylamine-trifluoroborane was prepared by methods similar to those used in the preparation of dimethylamine-trifluoroborane. Diethylamine was added as a solution in ether, methylene chloride, or benzene. On standing in air the low-melting crystals of diethylamine-trifluoroborane rapidly decomposed to a brown oil.

Satisfactory spectral and elemental analyses were obtained on these trifluoroborane adducts without further purification.

Computer Analysis of the Spectra of Eight Diethylamine-Haloboranes. The 1H NMR spectra of the diethylamine-haloborane adducts were analyzed by means of the program LAMP2, a version of LAME³⁵ written for an IBM 360-65 computer with a Calcomp plotter. LAME is a modification of LAOCOON^{36,37} to include magnetic equivalence factoring. The spin system was analyzed as $ABCD_3$ (A, B = nonequivalent methylene protons; C = nitrogen proton; D_3 = methyl protons), since the full 11-proton system was too large for the program as currently dimensioned. Little error should be introduced by this approximation³⁶ since any cross-coupling between the ethyl groups should be exceedingly small, and since the nitrogen-attached proton is only weakly coupled to all others ($J/\Delta\delta$ does not exceed 0.1). The system approximates to $AMNX_3$.

In order to aid the process of analysis, the 100-MHz spectra of the dibromo- and monochloroborane adducts were obtained, and analysis of these, made simpler by the spreading out of the pattern at the higher field strength, allowed initial assignment of the 60-MHz spectra with more certainty. This initial assignment of parameters was made as follows. Values of δ for the various protons were estimated by visual approximation. The centers of mass of the halves of the methylene pattern were used as initial estimates of $\delta_{CH_2(A)}$ and $\delta_{CH_2(B)}$. The two $J_{CH_2-CH_3}$'s were assumed to be approximately equal, since the methyl resonances were, in every case, 1:2:1 triplets; the value used was the spacing of the triplet. Values for J_{NH-CH_2} were assumed to be either zero, by visual observation, or about 5 Hz by analogy to the dimethylamine-haloborane results. Values for J_{AB} were estimated visually on the basis of spacings in the methylene pattern. Signs for the coupling constants were assumed to be positive for the three-bond constants ($J_{CH_2CH_3}$ and J_{NHCH_2}) and negative for the two-bond constant (J_{AB}) by analogy to carbon systems. No fine structure was observed in any of the NH resonances, probably on account of quadrupolar broadening by coupling to nitrogen and/or boron. Accordingly, the approximate chemical shifts assigned to these resonances were not refined. After one spectrum had been fully

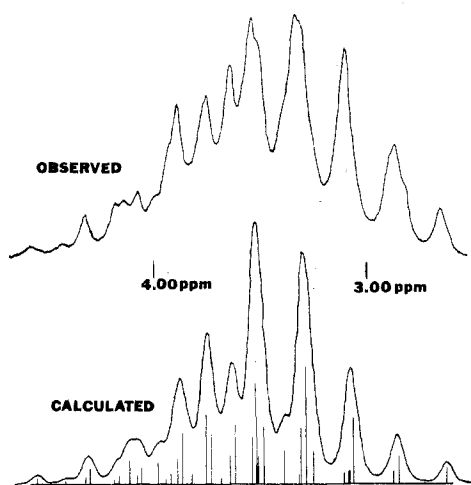


Figure 1. Comparison of observed and calculated proton NMR spectra of the methylene region of $(\text{CH}_3\text{CH}_2)_2\text{NH}\cdot\text{BBr}_2$.

Table I. ^1H NMR Data for $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$ Adducts

Borane	$(\text{CH}_3)_2\text{NH}$ adducts			$(\text{CH}_3)_3\text{N}$ adducts	
	$\delta_{\text{CH}_3}^a$	J_{HNCH}^b	J_{BNCH}^b	$\delta_{\text{CH}_3}^a$	J_{BNCH}^b
BH_3	2.533	5.5		2.583	
BH_2Cl	2.600	5.5		2.633	
BH_2Br	2.692	5.5		2.717	
BH_2I	2.758	5.5		2.817	
BHCl_2	2.700	5.5		2.717	
BHBBr_2	2.808	5.5		2.900	
BHI_2	2.892	5.5		3.050	
BF_3	2.58	5.8	1.9	2.62	1.6 ^c
BCl_3	2.92	5.8	2.9	2.97	2.7
BBr_3	3.03	5.4	3.4	3.13	3.1
BI_3	3.15	5.2	3.7	3.32	3.4

^a In ppm, downfield from internal tetramethylsilane in methylene chloride solvent. ^b In Hz. ^c $J_{\text{FBNCH}} = 0.8$ Hz.

analyzed, the initial assignment of parameters in other spectra were made by a straightforward comparison of patterns and/or by visual estimations.

On the average 20–48 lines (and in no case less than 17) were assigned in the methylene region of a spectrum and were given equal weight. In each case 16 of 32 lines were assigned in the methyl region. In all cases except two to be mentioned the calculated spectra were observed to converge to constancy via the iterative procedure of LAMP2. The root-mean-square error of observed vs. calculated transition frequencies did not exceed 0.25 Hz and averaged 0.16 Hz. Good agreement was found between observed 60-MHz spectra and calculated spectra plotted using Castellano's hybrid line shape function.³⁸ An example of these observed and calculated spectra is shown in Figure 1. The spectra of diethylamine-trichloroborane and -tribromoborane were poorly resolved, probably due to the added feature of coupling to boron, and as a result, it was not possible to carry out full analyses on these two spectra. Approximate values for the parameters were obtained by simulating the spectra. The accuracy of these results is obviously somewhat lower than those for the six mono- and dihaloborane adducts, which were obtained by rigorous analysis.

Results and Discussion

A. General Data. The ^1H NMR data for the haloborane adducts of dimethyl- and trimethylamine are given in Table I and are shown graphically in Figure 2. It is clear that substitution of halogen (Cl, Br, or I) for hydrogen in these amine-boranes produces a downfield shift of the resonance of the methyl groups. It is also clear that this downfield shift is larger, the larger the halogen introduced or the greater the number of halogens introduced. It is significant that the bulkier amine, trimethylamine, shows a greater downfield shift for a given change in borane substituents than does the less hindered dimethylamine. There is no a priori reason for this difference if the shift is determined solely by an inductive

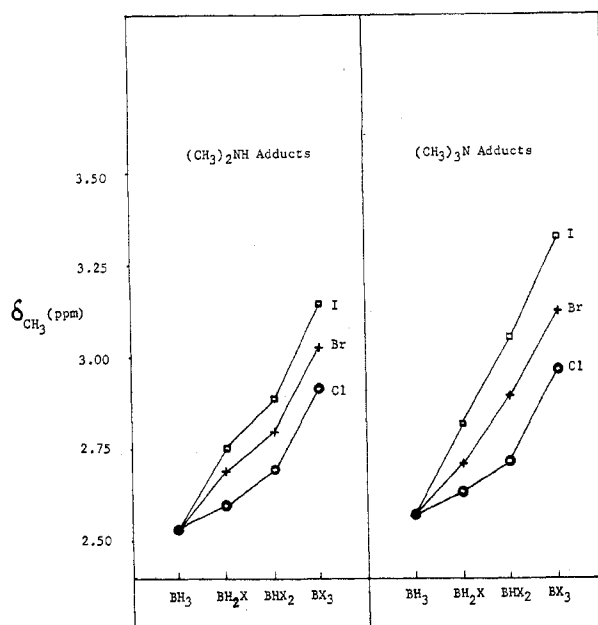


Figure 2. Chemical shift of methyl protons in $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$ adducts as a function of extent of halogen substitution on boron.

Table II. ^1H NMR Data for $(\text{CH}_3\text{CH}_2)_3\text{N}$ Adducts

Borane	$\delta_{\text{CH}_3}^a$	J_{HCCH}^b	$\delta_{\text{CH}_2}^a$	J_{BNCH}^b
BH_3	1.158	7.4	2.758	
BH_2Cl	1.158	7.1	2.883	
BH_2Br	1.158	7.0	2.942	
BH_2I	1.167	7.0	2.992	
BHCl_2	1.275	7.2	3.092	
BHBBr_2	1.300	7.3	3.292	
BHI_2	1.325	7.3	3.358	
BF_3	1.208	7.0	2.942	<2.0 ^c
BCl_3	1.367	7.3	3.383	2.6
BBr_3	1.450	7.3	3.575	2.8

^a In ppm, downfield from internal tetramethylsilane in methylene chloride solvent. ^b In Hz. ^c $J_{\text{FBNCH}} < 1.0$ Hz.

mechanism. It is therefore proposed that the greater steric interaction between halogen and the methyl groups of the trimethylamine adducts results in a greater downfield shift for the methyl protons in the trimethylamine-haloboranes.³⁹ It is also significant that the trifluoroborane adducts show almost no change in chemical shift from that of the BH_3 adducts. Little or no steric interaction would be expected in these cases. (In other work in this laboratory, chemical shifts have been determined for mono- and disubstituted fluoro-⁴¹ and oxo-borane⁴² adducts of trimethylamine. In these cases, small upfield shifts from the borane are noted, probably caused by the anisotropic effects of the B–O and B–F bonds.)

Tables II and III give the ^1H NMR data for the haloborane adducts of triethyl- and diethylamine, respectively. These data are displayed graphically in Figures 3 and 4. From Figure 3, it is again clear that the substitution of a halogen (Cl, Br, or I) for hydrogen in an amine-borane results in a downfield shift of the resonances due to protons in alkyl groups in the amine. The relative changes in chemical shift for the methylene protons in these ethylamine-boranes are greater than for the methyl protons in the methylamine-boranes mentioned above. The relative magnitude of these chemical shift changes, in fact, parallels the order of steric bulk expected for these amines, i.e. $(\text{CH}_3)_2\text{NH} < (\text{CH}_3)_3\text{N} < (\text{CH}_3\text{C}(\text{H}_2)_2\text{NH} < (\text{CH}_3\text{CH}_2)_3\text{N}$.

A similar conclusion is reached when one examines the effect of substitution on the chemical shift of the methyl groups in the two ethylamines. Monohalogenation has almost no effect

Table III. ^1H NMR Data for $(\text{CH}_3\text{CH}_2)_2\text{NH}$ Adducts

Borane	$\delta_{\text{CH}_3}^a$	$\delta_{\text{CH}_2}^{a,b}$	$\text{CH}_2(\text{A})$			J_{AB}	$\text{CH}_2(\text{B})$		
			$\delta_{\text{CH}_2(\text{A})}^a$	$J_{\text{HNCH(A)}}^c$	$J_{\text{H}_3\text{CCH(A)}}^c$		$\delta_{\text{CH}_2(\text{B})}^a$	$J_{\text{HNCH(B)}}^c$	$J_{\text{H}_3\text{CCH(B)}}^c$
BH_3	1.233	2.800	2.800 ^d	7.0	7.2		2.800 ^d	7.0	7.2
BH_2Cl	1.255	2.983	3.070	5.3	7.3	-13.0	2.895	5.7	7.4
BH_2Br	1.273	3.055	3.153	4.3	7.3	-12.9	2.995	5.7	7.2
BH_2I	1.287	3.088	3.152	4.8	7.2	-13.4	3.023	5.5	7.4
BHCl_2	1.335	3.203	3.347	4.8	7.2	-13.2	3.043	-0.5	7.2
BHBr_2	1.373	3.278	3.418	4.6	7.2	-13.1	3.137	-0.5	7.1
BIH_2	1.388	3.280	3.513	4.1	7.2	-13.2	3.047	-0.2	7.1
BF_3	1.267	3.025	^e	^e	7.3	^e	^e	^e	7.3
BCl_3	1.427	3.367	3.743	4.6 ^f	7.5	-13.2 ^f	3.122	-0.2 ^f	7.5
BBr_3	1.487	3.530	3.928	4.6 ^f	7.4	-13.2 ^f	3.130	-0.2 ^f	7.4

^a In ppm, downfield from internal tetramethylsilane in methylene chloride solvent. ^b Average value for nonequivalent protons; actual values for each proton given in other columns. ^c In Hz. ^d Poor resolution; nonequivalence not detectable. ^e Multiplet structure not resolved; values not determinable. ^f Poor resolution; approximate values given.

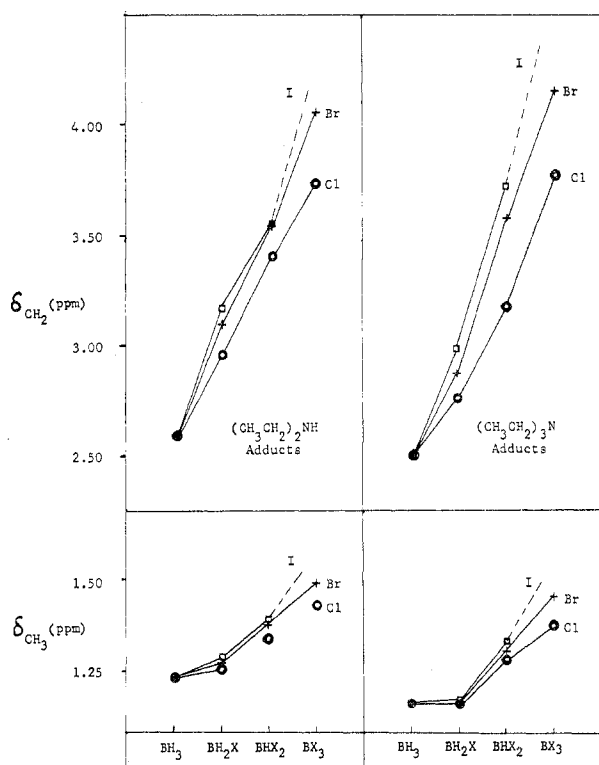


Figure 3. Chemical shift of methyl and methylene protons in adducts of $(\text{CH}_3\text{CH}_2)_2\text{NH}$ and $(\text{CH}_3\text{CH}_2)_3\text{N}$ as a function of extent of halogen substitution on boron. (Chemical shifts shown for methylene protons in $(\text{CH}_3\text{CH}_2)_2\text{NH}$ adducts are averages; see text for discussion.)

at all, dihalogenation produces moderate downfield shifts, and trihalogenation causes larger shifts yet. This suggests increasing interaction between borane halogens and these methyl groups. Consideration of likely conformations in the adducts shows that such interactions should be minimal with only one halogen on boron but of increased importance with two or three halogens on boron.

A comment must be made on the lack of data for the BI_3 adducts of di- and triethylamine. As pointed out in the Experimental Section, reaction of an excess of I_2 with the borane adduct of these two amines produced only ammonium salts in addition to diiodoborane adducts. This implies that there is so much steric interaction in the diiodoborane adducts that attempts to introduce a third iodide in this manner succeed only in destroying the adduct. Similar reactions with the two methylamine-boranes produced triiodoborane adducts in reasonably good yield and with no evidence of ammonium salts as by-products.

B. Steric Effect on Chemical Shift. The ^1H NMR data we

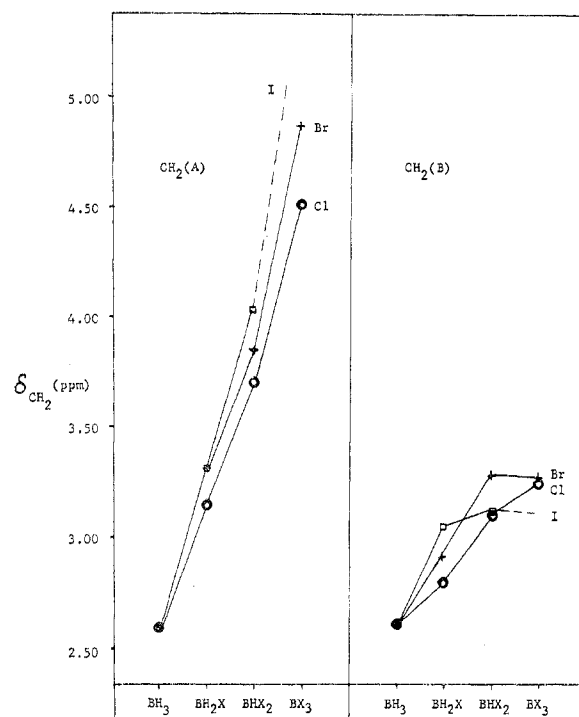


Figure 4. Chemical shift of nonequivalent methylene protons in $(\text{CH}_3\text{CH}_2)_2\text{NH}$ adducts as a function of extent of halogen substitution on boron.

have obtained on various amine-haloboranes clearly show a dependence on extent of halogen substitution on the borane portion of the adduct. Substitution of halogen for hydrogen results in a downfield shift of the NMR signal of the alkyl groups in the amine, and this shift is greater, the greater the number of halogens or the larger the halogens. Studies on alkyl halides have suggested several possible explanations for this phenomenon, all of which certainly contribute to the overall effect, though probably not to the same degree. These include (1) magnetic anisotropy associated with the halogen, including anisotropy in the boron-halogen bond, (2) magnetic anisotropy in C-C or C-N bonds adjacent to the affected proton, induced in some undefined manner by the presence of the halogen groups on boron, and (3) intramolecular van der Waals forces between the halogen on boron and the alkyl protons in the amines. Our analysis of the system favors the third explanation, but the other two are not ruled out by the information available.

Bothner-By and Naar-Colin⁴³ examined ^1H NMR data for a group of alkyl halides and concluded that factors other than electronegativity were at work in determining shifts of groups more than one carbon away from the halogen. They did not make any definite conclusion but suggested that either me-

someric or long-range C-X bond anisotropy effects might be the cause of the observed shifts.

Cavanaugh and Dailey^{44,45} examined the same group of compounds but reached different conclusions. They concluded that the shift could be expressed quantitatively as the result of a linear combination of two effects—the first a contribution due to inductive withdrawing of electron density by the halogen and the second a contribution due to the presence of C-C bonds adjacent to the affected proton. Cavanaugh and Dailey did not attempt to define the origin of this “C-C bond shift” but did say that it was probably not a purely anisotropic effect, since anisotropy played such a small role in determining the shifts of the methyl derivatives and since the “C-C bond shift” is of such a large magnitude for the ethyl and isopropyl derivatives. They pointed out that the magnitude of the “C-C bond shift” is proportional to the size of the substituent, implying a steric origin for the effect.

Spiesecke and Schneider⁴⁶ examined both ¹H and ¹³C NMR data for a series of CH₃X and CH₃CH₂X compounds. Their results contradicted the conclusions of Cavanaugh and Dailey, in that they concluded that the major contributions to these shifts came from the inductive and anisotropic effects of the X substituent. They did comment, however, that their conclusions were incomplete, since several aspects of the problem remained inadequately explained, and suggested the presence of another uncharacterized contribution to the chemical shift as the explanation of these aspects.

Schaeffer, Reynolds, and Yonemoto⁴⁷ pointed out that two major factors disfavor anisotropy playing a role in determining chemical shifts in alkyl halides. One factor is that the equation relating anisotropy to shielding effects (based on the point-dipole approximation by McConnell⁴⁸) is not valid in cases where the radius of the charge distribution giving rise to the anisotropy is of the same order as the distance between the point-dipole and the point of interest. The second factor is that in the case of these alkyl halides, the experimental observations are in many cases *opposite* to what would be predicted on the basis of anisotropic effects. In particular, an *upfield* shift is predicted for several cases where a downfield shift is actually observed. They resolved this quandary by invoking shifts due to van der Waals interactions. Citing the work of Buckingham, Schaeffer, and Schneider⁴⁹ on dispersion forces in intermolecular solvent effects, they pointed out that a downfield shift is expected from each of two types of interaction: (1) interaction in the equilibrium configuration causes a distortion of the electronic environment of the nucleus, probably an expansion; (2) the motion of the molecules at moderate temperatures leads to a time-dependent distortion of the symmetry of the C-H bonds, and for molecules whose C-H bonds are exposed to a “sideways” attack, this effect could be important. The first type of interaction is possible if the molecule is at all crowded, and the second could arise from internal rotations and vibrations of the molecule. These effects should increase as the number of electrons in the perturbing atom increases. That is, the effect should be greater for the larger halogens.

Haigh, Palmer, and Semple⁵⁰ expanded on this idea by observing that three factors involving intramolecular van der Waals forces contribute to the determining of chemical shifts, (much of the argument is derived from the work of Marshall and Pople⁵¹): (1) at all ranges, London dispersion forces polarize the atoms' electron clouds toward each other (according to an inverse sixth-power law), reducing the diamagnetic term, i.e., shifting the absorption downfield; (2) for ranges a little above or below the conventional van der Waals separation, the repulsive overlap forces produce an opposite effect; (3) at very short range, the major interference of the electron clouds hinders procession and thus produces a

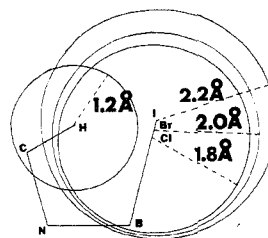


Figure 5. Sketch of approximate bond lengths, bond angles, and van der Waals radii for an H-C-N-B-X system (X = Cl, Br, I) showing the potential for severe overcrowding.

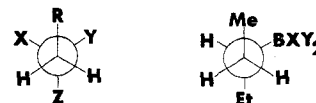


Figure 6. Newman projections showing similarity between RCH₂CXYZ and MeCH₂N(H)(Et)(BXY₂), where Me = CH₃ and Et = CH₃CH₂.

downfield shift. Clearly in severely hindered cases, the third factor will predominate, and experimental evidence has been presented in several cases to support this contention. Nagata, Terasawa, and Tori⁵² reported observing the deshielding of protons as a result of steric interference by other proximate hydrogen atoms. The degree of deshielding was observed to be closely related to the distance between the interfering protons. Winstein, Carter, Anet, and Bourn^{53,54} reported on the effects of steric compression on chemical shifts and coupling constants in half-cage and related molecules. This system involved steric interaction between an -OH group (or -O-) and a proton in another part of the molecule. Large downfield shifts were again noted, the larger shifts noted for the more sterically crowded system.

In our system, there is certainly extremely close approach between the protons in the alkyl portion of the molecule and the halogens attached to boron. This is indicated by a detailed consideration of bond distances and van der Waals radii as shown in Figure 5, as confirmed in a recent report^{10,11} of the direct structure determination on trihaloborane adducts of trimethylamine in which was included the information that the nonbonded carbon (methyl)-halogen distance was 0.6 Å shorter than the sum of the corresponding van der Waals radii. Thus, we believe the NMR results we have obtained reflect the great steric strain inherent in these systems. That is, a downfield shift of the resonance due to the alkyl group is the result of substituting halogen for hydrogen on boron, and a greater downfield shift arises when more or larger halogens are substituted. We believe that these trends have been caused mostly by steric effects and that other effects, such as magnetic anisotropy, are not of sufficient magnitude to be important in determining the direction of chemical shift changes in these compounds.

C. Nonequivalent Methylene Protons in Diethylamine-Haloboranes. The pattern of the ¹H NMR resonance observed for the methylene (CH₂) protons of the diethylamine-haloborane adducts is not a simple doublet of quartets, as one might predict on the basis of first-order coupling to CH₃ and NH protons. Instead the pattern observed is extremely complex, due to the nonequivalence of the two methylene protons.⁵⁵ These spectra were analyzed as the AB portion of an ABCD₃ spectrum, using a computer program as described in the Experimental Section. The results of these analyses are given in Table III and are shown graphically in Figure 4. That the methylene protons of these adducts should be nonequivalent is not surprising. Magnetic nonequivalence of this sort is possible in any system in which a methylene group is attached to a tetrahedral center with three different groups on it. This

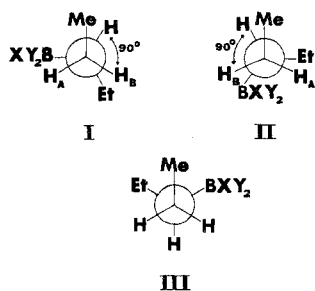


Figure 7. Newman projections showing rotameric isomers of $\text{MeCH}_2\text{N}(\text{H})(\text{Et})(\text{BXY}_2)$, where $\text{Me} = \text{CH}_3$ and $\text{Et} = \text{CH}_3\text{CH}_2$; torsional preferences are shown.

is illustrated in Figure 6, in which Newman projections are shown for RCH_2CXYZ and for $\text{CH}_3\text{CH}_2\text{N}(\text{H})(\text{Et})(\text{BXY}_2)$, where $\text{Et} = \text{CH}_2\text{CH}_3$, and $\text{X}, \text{Y} = \text{H}, \text{Cl}, \text{Br}, \text{I}$. Depending on the differences in size among the three groups, different degrees of nonequivalence may arise as the result of two effects:^{40,57,58} (1) intrinsic nonequivalence—nearly free rotation but with different torsional preferences for similar positions of the methylene protons; (2) nonequal conformer population—the relative rotation population is such as to make one (or two) rotation(s) favored over the other(s). Nonequivalence of methylene protons in a borane system has apparently been observed in two instances; however, in neither case was the resulting pattern analyzed. Coyle and Stone observed²³ a complicated methylene spectrum for $(\text{CH}_3\text{C}(\text{H})_2)_2\text{S}\cdot\text{BH}_3$, which they attributed to nonequivalence of the methylene protons; in that case, the lone pair of electrons on the sulfur acted as a stereochemically significant group. Rothgery and Hohnstedt⁵⁹ observed an AB pattern for the methylene protons between nitrogen and the carbonyl group in $\text{CH}_3\text{CH}_2\text{OC}(\text{O})\text{CH}_2\text{NH}(\text{CH}_3)\cdot\text{BX}_3$ ($\text{X} = \text{H}, \text{Cl}$).

The values for δ_{CH_2} for the diethylamine-haloborane adducts, as shown in Figure 3, are averages of the values for the two nonequivalent protons. Figure 4 shows graphically the actual values for the chemical shifts of these nonequivalent protons. (Using standard notation, the downfield proton is labeled proton A and the upfield proton, proton B.) Examination of Figure 4 shows that proton A is extremely sensitive to halogen substitution on boron, while proton B is relatively insensitive. This implies that proton A is, on the average, very close to the borane moiety, while proton B is insulated from it. (The anomalous changes in the shift of proton B between BH_2I and BHI_2 and between BHBBr_2 and BBBr_3 are significant. More will be said about this later.)

At this point, consider the changes in the coupling constants between the nitrogen-attached proton and the two methylene protons as a function of substitution on boron. The values of $J_{\text{HNCH(A)}}$ are in the range 4.5–5.5 Hz for all of the adducts. On the other hand, the values for $J_{\text{HNCH(B)}}$ drop to about zero when more than one halogen is substituted on boron. The Karplus rule for ethane-type systems⁶⁰ predicts that J_{HNCH} will be at a minimum when the dihedral angle between the two protons is 90° . Thus when more than one halogen is substituted on boron, a rotamer is preferred for the system which has a 90° dihedral angle between the NH bond and the CH(B) bond.

The three possible rotamers for this system are shown, as Newman projections looking down one C–N bond, in Figure 7. Rotamers I and II are shown torsionally twisted by interaction between the methyl group and the nearest bulky group on nitrogen. Protons A and B are labeled according to dihedral angle, proton B being 90° (dihedrally) from the NH group. Rotamer III is ruled out because it has the bulky methyl group between the two bulky groups on nitrogen. Rotamer II is ruled out because it would require that proton B be more sensitive to halogen substitution on boron. Rotamer

I is the preferred rotamer since it has a dihedral angle of about 90° between the NH bond and the CH(B) bond and since it has proton A near and proton B well-insulated from the borane moiety. Recall now the anomalous changes in the chemical shift of proton B between BH_2I and BHI_2 and between BHBBr_2 and BBBr_3 . The fact that proton B is totally insensitive to the new halogen substituted on boron in these cases implies that these are the points at which rotamer I is nearly completely “frozen out”. Thus it takes one iodide or two bromides to freeze the rotation, but even with three chlorides, there is still some freedom of rotation. This trend is perfectly in line with the trends in relative steric bulk of the halogens.⁶¹

When one examines the chemical shifts of the trimethylamine-, triethylamine-, and dimethylamine-haloboranes, both Onyszczuk's inductive argument²⁶ and a steric effect argument appear to be reasonable explanations of the trends one sees. However, the inductive argument is effectively destroyed by the results described here for the diethylamine-haloboranes. The fact that such a large nonequivalence exists between two protons the same number of bonds away from boron *cannot* be rationalized on the basis of our inductive effect transmitted through the bonds. Such an effect must of necessity affect the two protons to the same extent. The data *are*, however, easily and reasonably explained on the basis of steric interference resulting in a downfield shift, which increases with the severity of the interference.

It must be noted that the proposal of a relationship between NMR shift and steric factors does *not* require a relationship between those steric factors and the net stability of the molecule. In other words, the assertion that steric interactions between halogens on boron and alkyl groups on nitrogen increase with increasing size or number of halogens does *not* assert that this increase in steric interaction is accompanied by a net destabilizing of the adduct (or, more correctly, of the BN bond). Indeed, one need only compare the gas-phase dissociation data of Onyszczuk⁶ with the X-ray data of Taylor,^{10,11} both concerning the trimethylamine-trihaloboranes. Onyszczuk showed clearly that boron tribromide forms a more stable adduct than boron trichloride, while Taylor's work showed that the BN bond lengths in the BBBr_3 and BCl_3 adducts were, within experimental error, the same. One must conclude therefore that the bond length is determined by a combination of bonding strength and steric repulsion, both of which increase from the BCl_3 to the BBBr_3 adduct, so that the bond length is not changed. Had the increase in steric repulsion caused a decrease in B–N bond strength, the B–N bond in the BBBr_3 adduct should have been considerably longer than that in the BCl_3 adduct. Had there been no increase in steric repulsion, the increase in bond strength should have caused the BN bond in the BBBr_3 adduct to be considerably shorter than that in the BCl_3 adduct.

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Registry No. $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$, 74-94-2; $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_2\text{Cl}$, 52920-74-8; $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_2\text{Br}$, 52920-75-9; $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_2\text{I}$, 56553-86-7; $(\text{CH}_3)_2\text{NH}\cdot\text{BHCl}_2$, 56553-87-8; $(\text{CH}_3)_2\text{NH}\cdot\text{BHBBr}_2$, 56553-88-9; $(\text{CH}_3)_2\text{NH}\cdot\text{BHI}_2$, 56553-89-0; $(\text{CH}_3)_2\text{NH}\cdot\text{BF}_3$, 811-59-6; $(\text{CH}_3)_2\text{NH}\cdot\text{BCl}_3$, 13072-44-1; $(\text{CH}_3)_2\text{NH}\cdot\text{BBBr}_3$, 54067-18-4; $(\text{CH}_3)_2\text{NH}\cdot\text{BI}_3$, 56553-90-3; $(\text{CH}_3)_3\text{N}\cdot\text{BH}_3$, 75-22-9; $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{Cl}$, 5353-44-6; $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{Br}$, 5275-42-3; $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{I}$, 25741-81-5; $(\text{CH}_3)_3\text{N}\cdot\text{BHCl}_2$, 25741-83-7; $(\text{CH}_3)_3\text{N}\cdot\text{BHBBr}_2$, 32805-31-5; $(\text{CH}_3)_3\text{N}\cdot\text{BHI}_2$, 25741-84-8; $(\text{CH}_3)_3\text{N}\cdot\text{BF}_3$, 420-20-2; $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$, 1516-55-8; $(\text{CH}_3)_3\text{N}\cdot\text{BBBr}_3$, 1516-54-7; $(\text{CH}_3)_3\text{N}\cdot\text{BI}_3$, 5041-59-8; $(\text{CH}_3\text{CH}_2)_3\text{N}\cdot\text{BH}_3$, 1722-26-5; $(\text{CH}_3\text{CH}_2)_3\text{N}\cdot\text{BH}_2\text{Cl}$, 13240-39-6; $(\text{CH}_3\text{CH}_2)_3\text{N}\cdot\text{BH}_2\text{Br}$, 15112-86-4; $(\text{CH}_3\text{CH}_2)_3\text{N}\cdot\text{BH}_2\text{I}$, 15112-87-5; $(\text{CH}_3\text{CH}_2)_3\text{N}\cdot\text{BHCl}_2$, 51006-67-8; $(\text{CH}_3\text{CH}_2)_3\text{N}\cdot\text{BHBBr}_2$,

56553-91-4; $(\text{CH}_3\text{CH}_2)_3\text{N}\cdot\text{BHl}_2$, 56598-29-9; $(\text{CH}_3\text{CH}_2)_3\text{N}\cdot\text{BF}_3$, 368-37-6; $(\text{CH}_3\text{CH}_2)_3\text{N}\cdot\text{BCl}_3$, 2890-88-2; $(\text{CH}_3\text{CH}_2)_3\text{N}\cdot\text{BBR}_3$, 2903-69-7; $(\text{CH}_3\text{CH}_2)_2\text{NH}\cdot\text{BH}_3$, 2670-68-0; $(\text{CH}_3\text{CH}_2)_2\text{NH}\cdot\text{BH}_2\text{Cl}$, 56553-92-5; $(\text{CH}_3\text{CH}_2)_2\text{NH}\cdot\text{BH}_2\text{Br}$, 56553-93-6; $(\text{CH}_3\text{CH}_2)_2\text{N}\cdot\text{H}\cdot\text{BH}_2\text{I}$, 56553-94-7; $(\text{CH}_3\text{CH}_2)_2\text{NH}\cdot\text{BHCl}_2$, 56553-95-8; $(\text{CH}_3\text{CH}_2)_2\text{NH}\cdot\text{BHBBr}_2$, 56553-96-9; $(\text{CH}_3\text{CH}_2)_2\text{NH}\cdot\text{BHI}_2$, 56553-97-0; $(\text{CH}_3\text{CH}_2)_2\text{NH}\cdot\text{BF}_3$, 372-56-5; $(\text{CH}_3\text{CH}_2)_2\text{NH}\cdot\text{BCl}_3$, 56553-98-1; $(\text{CH}_3\text{CH}_2)_2\text{NH}\cdot\text{BBR}_3$, 56553-99-2.

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- (39) The work of Kessler⁴⁰ on barriers to rotation of *tert*-butyl groups in organic molecules suggested that in some mono- and disubstituted trimethylamine-boranes hindered rotation might be observed. If the rate of rotation could be slowed down enough, the methyl groups could become nonequivalent. Accordingly, the NMR spectra of $(\text{CH}_3)_3\text{N}\cdot\text{BHl}_2$, $(\text{CH}_3)_3\text{N}\cdot\text{BHBBr}_2$, and $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{I}$ were examined at low temperature in CH_2Cl_2 and CS_2 . In all cases the signal remained a sharp singlet down to below -80°C . It becomes clear then that the barrier to rotation in these adducts is low; it is probably *not* low because of a low transition state energy but rather because of a high ground-state energy. In other words, these adducts are so highly hindered that there is little energy difference between staggered and eclipsed forms.
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- (55) The CH_2 regions of the ^1H NMR spectra of the diethylamine adducts were quite sensitive to changes in solvent. In methylene chloride, the borane (BH_3) adduct showed a 1:4:6:4:1 quintet in the CH_2 region, which is consistent with the CH_2 protons being equivalent, but in benzene solution, the pattern shifted upfield and showed the complexity associated with nonequivalence. Similarly, on changing from methylene chloride to benzene, the CH_2 region of the spectrum of the dibromoborane (BHBBr_2) adduct showed a large increase in the chemical shift difference between the two nonequivalent protons, an increase from about 17 to about 40 Hz. These two observations would seem to be most logically explained as follows. Changing from CH_2Cl_2 to benzene as a solvent causes the resonances due to the methylene protons to shift upfield, but the B proton (the upfield proton in CH_2Cl_2) is shifted *further* by this solvent change than is proton A. This implies a specific solvation of one of the two protons,⁵⁶ and since the overall shift of both protons is upfield, it would seem reasonable that the more affected proton, proton B, would be the one specifically solvated. Indeed, in general all of the haloborane adducts in this study showed NMR spectra which were sensitive to changes in solvent. In CH_2Cl_2 solution the positions and patterns observed for the various resonances were quite constant with changes in temperature or concentration but in aromatic solvents this was not found to be the case. The gross trends reported in this work are observed in spectra taken in benzene or benzene-like solvents, but specific comparisons are hazardous because of the complicating factors of shift effects resulting from temperature and concentration changes.^{56b}
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- (61) Our conclusion that there is highly hindered rotation in the diethylamine-haloboranes suggested that at higher temperature this rotation might be more likely to occur freely, thus making the methylene protons in these adducts more nearly equivalent. Accordingly, we examined the methylene region of the spectrum of diethylamine-dibromoborane at temperatures up to about 140° in *sym*-tetrachloroethane. (This solvent was chosen because of its high boiling point (149°) and its resemblance to methylene chloride, the solvent for most of our work.) Although the spectrum lost some resolution at higher temperature, probably due to easier relaxation, it did not change in the number or location of peaks. Thus, the methylene region of the spectrum of diethylamine-dibromoborane (in *sym*-tetrachloroethane) is insensitive to increases in temperature. This strongly implies that the molecule is so highly hindered that rotation is not likely, even at 140° . It should be pointed out that this conclusion is not inconsistent with the conclusion reached earlier on trimethylamine adducts,³⁹ though it may at first glance seem to be so. The earlier case examined rotation about a BN bond, the nitrogen end of which is highly symmetric. This case examines rotation about a CN bond, neither end of which is symmetric. Since the two cases examine rotation about very different types of bonds, the conclusions should be examined separately; that is, the one conclusion has no direct bearing on the other.