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A NMR Study on Boron Compounds

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Abstract : ^{1}H NMR spectra of amine borane, $(CH_3)_{3-n}$ $H_nN\cdot BH_3$ and amine boron trifluoride, $(CH_3)_{3-n}H_nN\cdot BF_3$ adducts were observed. ^{1}H chemical shifts of methyl groups occur at a higher field as the methyl group successively substituted for hydrogen on nitrogen. With respect to trimethylamine, both BH_3 and BF_3 bases are considered to be comparable acids. These results lead to a good relation between chemical shifts in BF_3 group and variations in structure on amine boron trifluoride adducts.

Introduction

It is well known that Lewis bases such amines or ethers coordinate their lone pair electrons toward boranes or boron halides to form many interesting addition products (adducts). Chemist have been naturally interested in studying characters of dative bonds in phosphine boranes or amine boranes. In particular, amine borane, $H_3N\cdot BH_3$, which is one of the simplest and the most basic adducts, has been considerably investigated because this adduct is isoelectric and the same configuration with ethane molecule. Furthermore, effects of methyl substituents on nitrogen on base strength and bond length in these adducts have been discussed.1)

Durig, *et. al.*,2) have gone into details the effects of the methyl group on the P-B streching frequency and the P-B bond length in phosphine borane $(CH_3)_{3-n}H_3P\cdot BH_3$ adducts ; the first introduction of the methyl group to phosphorus makes higher in the streching and shorter in the bond length, while the second and third introductions effect nothing beyond that. On the other hand, Taylor1) has been verified to form the correlation between the N-B streching frequency and the number of the methyl group in amine borane $(CH_3)_{3-n}H_nN\cdot BH_3$ adducts (n=0, 1, 2, 3). However, to exact gain informations from IR spectra is considerably difficult because a absorption band frequently involved other mode. Microwave absorption method is also inadequate for nonvolatile adducts.

NMR technique is available for studying on electron density or interactions between two nuclei. Coyle and Stone3) and Heitsch4) observed ^{1}H and ^{11}B chemical shifts in various amine borane adducts and discussed the base strength on the basis of inductive effects by methyl substituents on nitrogen. If such an inductive effect by methyl groups would exist, a series of variation in structures of amine borane adducts naturally occur as methyl group is successively substituted for hydrogen on nitrogen.

A discussion on a relation between variations in structure and number of methyl groups in amine borane adducts has been ever made because these were too air-sensitive adducts to obtain X-rays diffraction patterns except for trimethylamine borane. There are reports on structual parameters of phosphine boranes by M. W.2) and amine boron trifluorides, except $(CH_3)_2HN\cdot BF_3$, by X-rays.5) However, no systematical discussion on these adducts have been made because of complex factors such as behaviors of d orbital in phosphorus or a possibility of $F \rightarrow B$ $p\pi$-$p\pi$ donations in boron trifluoride. Present author attempted to discuss a relation of variations in structure with effects induced by methyl groups on nitrogen from NMR sprctra of amine borane and amine boron trifluoride adducts and to compare base strengths of BH_3 and BF_3.

Experimental

All amine boron trifluoride adducts were prepared by the reaction between amines and boron trifluoride etherate at −78°C and at room temperature, respectively. Ammonia borane and monomethylamine borane were obtained by the reaction of ammonia and monomethylamine gases with diborane in THF

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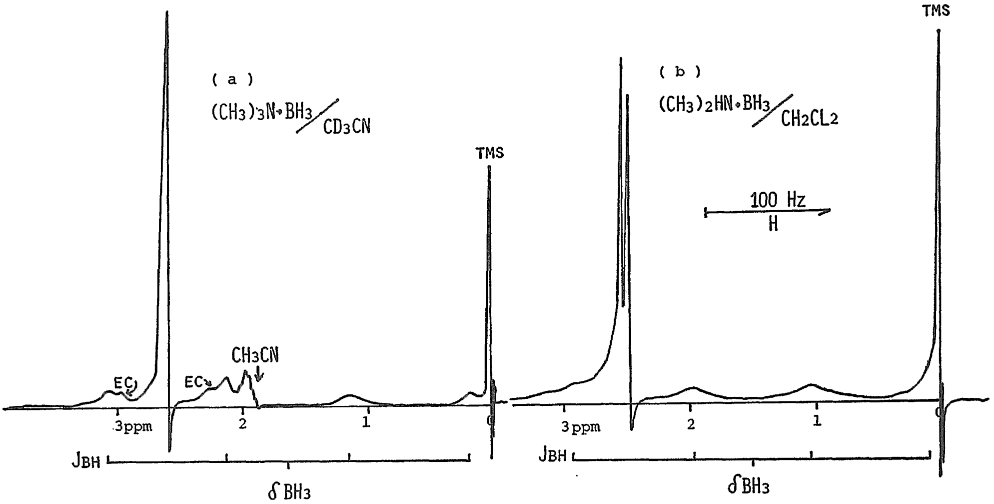

Fig. 1 ^1H NMR spectra of $(CH_3)_3N \cdot BH_3$ (a) and of $(CH_3)_2HN \cdot BH_3$ (b).

at −78°C. Both gases were evoluved from the reaction of amine hydrochloride with NaOH and dried over CaH_2 before use. Diborane, B_2H_6, was prepared by the known method.[6] Dimethylamine and trimethylamine borane were obtained from Ventron Co.. The prepared samples except for ammonia borane were purified by literature procedures.[7] Ammonia borane was recrystallized from ethyl ether. Most NMR samples were prepared in a drybox under N_2 gas atmosphere. Solvents of $CDCl_3$, CH_2Cl_2, and CD_3CN and TMS as an internal standard were purcharsed from E. Merck and used without further purification. NMR spectra were recorded on JEOL A-60. Purity was checked by IR spectrum.

Results and Discussion

A ^1H NMR spectrum of trimethylamine borane in CD_3CN is shown in Fig. 1 (a). The spectrum generally consisted of two components, in which one is a relative intense peak but the other is relative weak peaks. The intense signal is considered to result from methyl groups in trimethylamine although no hyperfine due to mutual interactions between methyl groups is observed. Value of ^1H chemical shift is fair agreement with those reported in literatures.[3,4] Furthermore, as seen from a spectrum of dimethylamine borane in CH_2Cl_2 shown in Fig. 1 (b), this intense peak attributed by trimethyl groups varied to a doublet caused by an interaction between a proton and two methyl groups in dimethylamine.

Relative weak peaks are observed in both Figs. 1(a) and (b). A coupling between two peaks at lower field is about 94-96 Hz and this values are in fair agreement with those of spin-spin coupling constants reported for BH_3.[8] Thus, the weak peaks are interpreted to consist of a quartet although the fourth

		δCH_3 (ppm)		δBX_3	J_{BX} (Hz)		J_{HCNH} (Hz)	
	$CDCl_3$	CH_2Cl_2	CD_3CN	CD_3CN	CD_3CN		CD_3CN	
H_3N BH_3						92*		
$(CH_3)H_2N$ BH_3			−2.16	−1.63	92	93*	5.7	6.1*
$(CH_3)_2HN$ BH_3			−2.40	−1.54	94	94*	5.5	6.0*
$(CH_3)_3N$ BH_3	−2.50	−2.54	−2.56	−1.46	96	96*		
H_3N BF_3	−2.58	−2.60		+147*		13.8*		
$(CH_3)H_2N$ BF_3			−2.52	+153*		15.7*		6.2*
$(CH_3)_2HN$ BF_3	−2.60		−2.56	+159*		15.5*		5.8*
$(CH_3)_3N$ BF_3	−2.60		−2.58	+163*		13.8*		
$(CH_3)_3N$ BCl_3		−2.97						
$(CH_3)_3N$ BBr_3		−3.09						

* data from Ref. 4.

TABLE 1 NMR Parameters in amine boranes and amine haloboranes peak at the highest field is disappeared behind a peak of TMS. Other weak signals except for those in borane are also observed in Fig.1 (a) : that is, one is two echo signal shown in both sides of methyl proton signal and the other is considered to be methyl proton signal of CH_3CN which is involved in CD_3CN as impurity. These values of ^1H chemical shifts and spin-spin coupling constants in $(CH_3)_{3-n}H_nN\cdot BH_3$ and $(CH_3)_{3-n}H_nN\cdot BF_3$ adducts are summarized in Table 1.

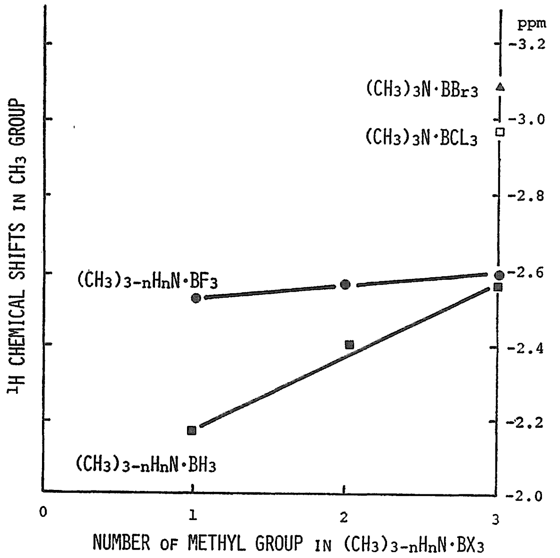

Fig. 2 The variations in the ^1H chemical shifts of methyl protons in amine boranes and amine boron trifluorides.

Considerable solvent shifts were observed between $CDCl_3$ CD_3CN solutions of the same adduct, so comparisons were only made between the shifts in CD_3CN solvent. In a series of $(CH_3)_{3-n}H_nN\cdot BH_3$ adducts, as methyl group is successively substituted for hydrogen on nitrogen, ^1H chemical shifts of borane groups occur at a higher field, while those of methyl groups do at a lower field. As well as the ^1H chemical shifts, spin-spin coupling constants of borane groups gradually increase as the numbers of the methyl group on nitrogen increase. ^1H chemical shifts of methyl group in a series of $(CH_3)_{3-n}H_nN\cdot BF_3$ adducts are, however, all essentially equal.

On the assumption that the chemical shifts of the methyl groups will be sensitive to electron density about proton, the observed chemical shifts can be correlated. The correlation between the ^1H chemical shift of the methyl groups in a series of $(CH_3)_{3-n}H_nN\cdot BH_3$ and $(CH_3)_{3-n}H_nN\cdot BF_3$ adducts and the number of the methyl group are shown in Fig. 2.

As the methyl group is successively substituted for hydrogen on nitrogen, the ^1H chemical shifts decrease linearly. The variation of the chemical shifts with the methyl group in BH_3 adducts is considerably larger than that in BF_3 adducts. This degree is assumed to result from difference in base strength between BH_3 and BF_3, that is, the more electronegative fluorine atom attract stronger than the less electronegative hydrogen atom. The reason why the methyl shifts in BF_3 adducts are all essentially equal can be viewed as a consequence of the strong electron withdrawing power of the fluorine atom. Any increase in the electron density on boron atom donated by amine is passed on to the fluorine atom.

With respect to trimethylamine, BH_3 and BF_3 seem to be acids of comparable strength.[4] In a series of $(CH_3)_3N\cdot BX_3$ (X=H, F, Cl, Br.), The order of the methyl chemical shifts was $BH_3 < BF_3 < BCl_3 < BBr_3$ and was not in accord with that expected from differences in electronegativities of halogen atoms. This can be explained by the difference in the Van der Waals radius of the atom bound to boron atom,[9] and here, tribromoborane adduct may cause a large inductive effect. In contrast to acid strength in borane or boron halide, the inductive effect of methyl group is one of the effectual determinant on base strength in amines.

Furthermore, the inductive effect by the methyl groups resulted in the decrease of the ^1H chemical shift for methyl groups and so may follow by an increase of ^1H chemical shift for borane groups. As seen from Table 1, ^1H chemical shifts in borane group linearly increased (decrease in negative value) with increasing methyl groups on nitrogen. These results are shown in Fig. 3, together literature values on ^{19}F chemical shifts of $(CH_3)_{3-n}H_nN\cdot BF_3$ adducts.[4)] Both the ^1H and ^{19}F chemical shifts occur at higher field as methyl group successively substituted for hydrogen on nitrogen. This corresponds to increase in electron density about BH_3 and BF_3 groups but reversely to decrease in electron density about methyl groups. However, it is diffecult to estimate exactly amounts of electrons induced by methyl groups and those of electrons withdrawed to BH_3 or BF_3 groups because of possibility of $F \rightarrow B$ $p\pi$-$p\pi$ bonding for BF_3.[4)]

Hybrid orbitals of boron atom known to change from sp^2 to sp^3 on adduct formations. Thus, p characters on boron atom would gradually increase by further stronger bases, that is, by amines with increasing inductive effects. Trimethylamine in these adducts shows the largest chemical shifts of ^1H and ^{19}F and is therefore considered to result in the most electron density on boron atom. The increase in p characters on boron atom is appeared to result in structual changes about boron atom, that is, bond angles of $\angle XBX$, or $\angle NBX$ (X=H or F). Therefore, one would be expected variations in the bond angle mentioned above as a measure of electron withdrawed from amines. The more p electron migrate to boron atom, the smaller the XBX bond angle and the larger the NBX bond angle. On the other hand, decrease of electrons result will in structual changes about nitrogen atom that is, decreases of YNB angle and increases of YNY (Y=H or CH_3) angle. Structures of a series of amine boron trifluoride adducts except for $(CH_3)_2HN\cdot BF_3$ were investigated by X-rays diffraction,[5)] and in amine borane adducts only $(CH_3)_3N\cdot BH_3$ was investigated by M. W.[10)] Thus, these data were used to relate the variation in structure with the electron density in nitrogen or boron atom.

From results on various combinations, an excellent relation between variations in NBF bond angle and ^{19}F chemical shifts was found and are shown in Fig. 4. The bond angle in $(CH_3)_2HN\cdot BF_3$ adduct is an assumed value. Accordingly, the successive substitutions of the methyl group for hydrogen on nitrogen result in the ^{19}F chemical shifts in BF_3 groups at higher field and the increases of the NBF bond angle, while it causes no systematical changes in the spin-spin coupling constants for the BF_3 groups. No variation in electron density of a N-B dative bond is appeared to observe since the N-B dative bonds in these adducts are comparable length, on the basis of an increase of s electron resulting in the shorter bond length. The p electron induced by methyl group is assumably withdrawn to the fluorine atom rather than the N-B dative bond, while the s electron donated by BF_3 acid is withdrawn to the hydrogen or methyl group. In amines, increases of each bond

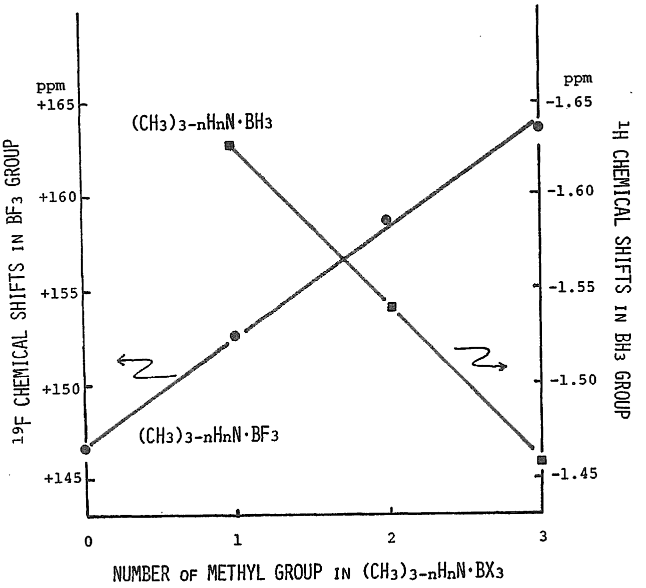

Fig. 3 The variations in the ^1H and ^{19}F chemical shifts of BH_3 and BF_3 in amine boranes and amino boron trifluorides, respecttively.

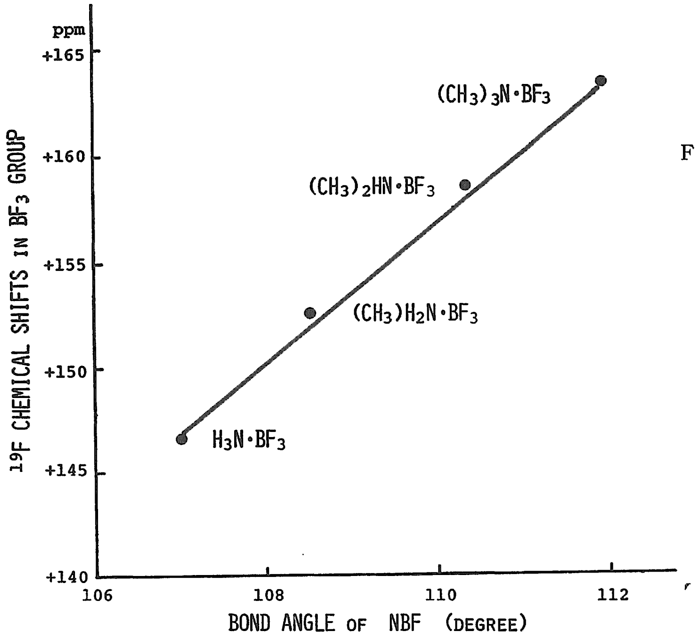

Fig. 4 The correlations between the ^{19}F chemical shifts and the structual variation in amine boron trifluorides.

angles on adduct formations are known to increase s chracters on nitrogen atom, respectively ; for example, an increase in bond angle of trimethylamine from 108.7° to 114° is assumed to correspond to variation from sp^3 to sp^2. This can be viewed as conseqences of an introduction to nitrogen of s electron, in other words, a back donation from BF$_3$ group. Accordingly, the methyl group on nitrogen may be concluded to result in the increase of the electron density at boron atom and of the NBF bond angle.

In $(CH_3)_{3-n}H_nN \cdot BH_3$ adducts, no relation between the ^{1}H chemical shifts and the spin-spin coupling constants or the variation in the structure for BH$_3$ groups are found because of the lack of X-rays data. However, M. W. data in $(CH_3)_3N \cdot BH_3$$^{10)}$ may expect us to obtain such a relation as observed in Fig. 4. Using data on the N-B streching frequency,$^{2)}$ which decreases with increasing methyl group, the good correlation between the N-B streching and the variation in structures may be perhaps obtained. No the N-B streching frequency was also observed in spite of many attempts. To make clear the structures of these boron compounds, further studies on X-rays diffraction, NMR, and IR spectra will be performed.

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References

1) R. C. Taylor, Adv. Chem. Ser., **42**, 59 (1964).
2) J. R. Durig, B. A. Hudgens, Y. S. Li, and J. D. Odom, J. Chem. Phys., **61**, 4890 (1974).
3) T. D. Coyle and F. G. A. Stone, J. Amer. Chem. Soc., **83**, 4138 (1961).
4) C. W. Heitsch, Inorg. Chem., **4**, 1019 (1965).
5) J. L. Hoard, S. Geller, and T. B. Owen, acta. Cryst,, **4**, 405 (1951).
6) G. Zweiffl and H. C. Brown, Org. React., **13**, 1 (1963).
7) S. G. Shore and R. W. Parry, J. Amer. Chem. Soc., **80**, 8 (1958).
8) D. F. Gaines and R. Schaeffer, *ibid.*, **86**, 1505 (1964) : W. D. Phillips, H. C. Miller, and E. L. Muetterties, *ibid.*, **81**, 4496 (1959).
9) W. H. Myers, G. E. Ryschkwitsch, M. A. Mat hur, and R. W. King, Inorg. Chem., **14**, 2874 (1974).
10) J. R. Durig, Y. S. Li, and J. D. Odom, J. Mol. Struct., **16**, 443 (1973).