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A Study on Steric Interactions of Amine Borane Compounds

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Abstract : Chemical shifts of methyl group in amine boranes, $(CH_3)_{3-n}H_nN{\cdot}BF_3$ and $(CH_3)_3N{\cdot}BX_3$ (X = H, F, Cl, Br...) were larger than those of o-halotoluenes, o-$XC_6H_4CH_3$. It is explained by differences in steric effects between sp^3 bybrid in amine boranes and sp^2 bybrid in o-halotoluenes and by a number of methyl groups and halogen atoms. The facts that larger Van der Waals radius of halogen atoms make the B-N bond length shorter in the haloborazines $B_3N_3H_3X_3$ and amine boranes are explained by the steric effect based on sp^3 hybrid.

Introduction

Amine boranes are very interesting addition products (adducts) which involve a N-B dative bond being isoelectric with a C-C covalent bond. The dative bond is expected to be susceptible to influences by strengths of Lewis bases or acids. In $(CH_3)_{3-n}H_nN{\cdot}BH_3$ adducts, Taylor1) has reported a linear correlation between N-B streching frequencies and a number of methyl group. Effects of amines or acids on the N-B bond in various adducts were also investigated by ^1H NMR spectroscopy2). One of present authors (K.S)3) proved an existence of methyl inductive effect on the dative bond by structual variations in $(CH_3)_{3-n}H_nN{\cdot}BF_3$ adducts. Meyer, *et. al.*, 4) have established a order of methyl chemical shifts in $(CH_3)_3N{\cdot}BX_3$ (X = H, F, Cl, Br, I), namely, acid strengths was $BI_3>BBr_3>BCl_3>BF_3>BH_3$, and the methyl chemical shifts were caused by steric interactions between methyl groups and halogen atoms ; the larger the Van der Waals radius of the halogen atom is, the more strong the steric interactions become. They, however, took no thought of the N-B bond length being opposed to the increase of the Van der Waals radius of the halogen atom in $(CH_3)_3N{\cdot}BX_3$ adducts. Futhermore, the steric effect could not explained the methyl chemical shift of $(CH_3)_3N{\cdot}B(CH_3)_3$, in which the methyl group has Van der Waals radius of 0.20 nm.

To reseach conclusive evidences on the tendency of the methyl chemical shifts in $(CH_3)_3N{\cdot}BX_3$, chemical shifts of methyl groups in o-halotoluences, C_7H_7X (X = H, F, Cl, Br) were measured since these compounds involve C-C bonds possessing the same bond length and being isoelectric with N-B dative bond.

Experimental

$(CH_3)_{3-n}H_nN{\cdot}BF_3$ adducts were prepared by reactions of various amines and boron

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Adducts	δCH_3 (*ppm*)	γB-N(*nm*)※	∠NBX※	∠CNB※	Van der Waals[3] radius (*nm*)
$H_3N \cdot BF_3$		0.160	107°		
$CH_3H_2N \cdot BF_3$	−2.52	0.157	108.5°		
$(CH_3)_2HN \cdot BF_3$	−2.56		(110.5° assumed)		
$(CH_3)_3N \cdot BF_3$	−2.60	0.164	112°	105°	0.135
$(CH_3)_3N \cdot BH_3$	−2.58	0.1638	105.3°	109.9°	0.12
$(CH_3)_3N \cdot BCl_3$	−2.97	0.1616	110.0°	110.7°	0.18
$(CH_3)_3N \cdot BBr_3$	−3.07	0.1603	111.7°	110.9°	0.20

※ data fro m Ref. 5, 6, and 7

TABLE 1. NMR chemical shifts and structural parameters in amine borane adducts.

trifluoride etherate. $(CH_3)_3N \cdot BH_3$ adduct was purcharsed from Ventron Co.. $(CH_3)_3N \cdot BCl_3$ and $(CH_3)_3N \cdot BBr_3$ were presented from Mr. K. Ishihara in Hiroshima University. All samples were recrystallized from absolute acetone solution before use. o-halotoluenes and toluene were purcharsed from Eastman Kodak Co., and used after distillations. NMR spectra of all amine boranes in CD_3CN solutions were recorded using TMS as internal standard. Spctra of o-halotoluenes were also measured in neat at room temperature.

Results and Discussion

NMR chemical shifts of methyl groups in $(CH_3)_{3-n}H_nN \cdot BF_3$ adducts tablated in Table 1 linearly decrease as the methyl group is successively substituted for hydrogen in nitrogen. This fact is interpreted to result from the decrease in electron density about methyl group by inductive effects. Then the electron induced by the methyl group is assumably withdraw to a borane group rather than a N-B dative bond since the bond lengths in these adducts are comparable and successive structual variations about borane groups are given rise to. The correlation between the structual variations, bond angle of ∠NBF, and the methyl chemical shifts was concluded in $(CH_3)_{3-n}H_nN \cdot BF_3$ adducts but did not be formed in $(CH_3)_3N \cdot BX_3$ adducts[3]. As shown from Table 1, the order of the chemical shifts for methyl group in $(CH_3)_3N \cdot BX_3$ adducts is against that expected from differences in efectronegativities of Lewis acids. Meyer, *et. al.*, [4] explained it to result from steric interactions between methyl groups and halogen atoms, that is, the oreder of the chemical shift in these adducts was considered to depend on the Van der Waals radius of the halogen atom.

The chemical shifts of the methyl groups in $(CH_3)_3N \cdot BX_3$ adducts are plotted against the Van der Waals radius in Fig. 1. The chemical shifts of these adducts except trimethylamine borane adduct linearly vary with the Van der Waals. The chemical shift of the methyl group in $(CH_3)_3N \cdot B(CH_3)_3$ adduct is abnormal in spite of a methyl group possessing the same Van der Waals radius with a bromine atom. Inductive effects in trimethylamine group were perhaps canseled by effects of methyl groups in trimethylborane. In Fig. 1, chemical shifts of methyl groups in o-halotoluenes are also plotted

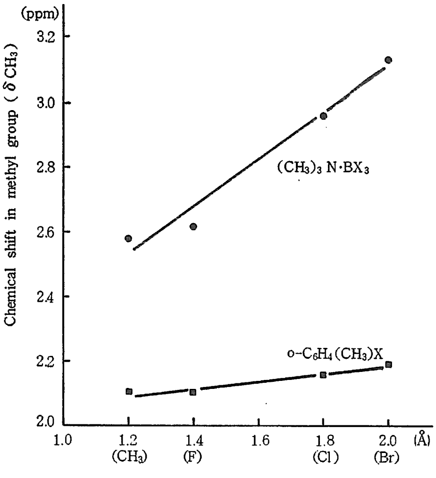

Fig. 1. The relations of the methyl chemical shifts in trimethylamine haloboranes and o-halotoluene with Van der Waals radii of halogen atoms.

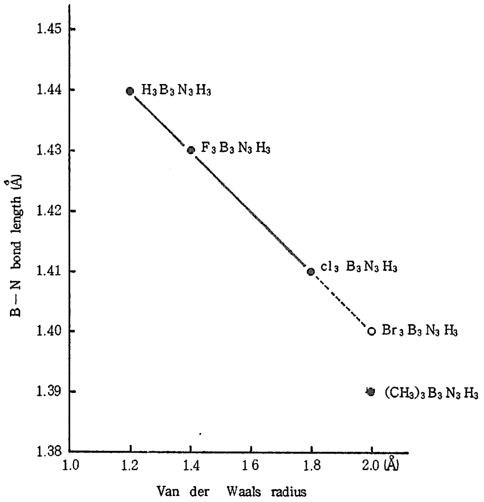

Fig. 2. The relations of the B-N bond lengths in borazine derivatives with Van der Waals radii of halogen substituents.

against Van der Waals radius : δ_{CH_3} of toluene, o-fluorotoluene, o-chlorotoluene, o-bromotoluene and o-xylene are 2.11, 2.10, 2.15, 2.19, and 2.06 ppm, respectively. The chemical shifts show a similar tendency with those of $(CH_3)_3N\cdot BX_3$ adducts, although they slightly vary with inclination.

The differnce between the two lines is considered to be based upon that in the kinds of the bond or the structures ; that is, o-halotoluenes possess the same bond length of 0.139 nm for the C-C bonds but the N-B bond lengths vary 0.160 to 0.164 nm with the decrease of the Van der Waals radius. The N-B bonds in amine boranes possess sp^3 hybrid and the C-C bonds in o-halotoluenes do sp^2 hybrid. As you can see in Fig. 2, the similar variations between the bons length and Van der Waals radius are also shown in B-haloborazines, $X_3B_3N_3H_3$, which are isoelectric compouds with o-halotoluenes and change 0.140 to 0.144 nm with Van der Waals radius except B-trimethyl borazine (0.139 nm)[8], Therefore, tendencies of chemical shifts in o-halotoluenes are considered to present purely the effect of Van der Waals of halogen. The sp^2 hybrid is assumably considered to restict the steric interaction between the methyl group and the halogen atom. Then, the bond length of the C-C bond in o-halotoluene are constant. It shows that chemical shifts in amine boranes are effected by additional factor on sp^3 hybrid.

It is also a very intersting question why the larger the Van der Waals radius is, the shorter the bond length in amine boranes and haloborazine become. By the interaction of the halogen atom with the larger Van der Waals radius, the methyl group probably migrate s electrons into the N-B bond to bring about the shorter bond length and a slight increase of a CNB bond angle. On the other hand, the B-X bond in adducts may be further stabilized by taking of p electron in the halogen atom, a double bond character. In o-halotoluenes, the double bond character (sp^2 hybrid) is interpreted to be attenuated by a benzene ring and so shows few variations in the chemical shifts or bond lengths. The least three combinations of the steric interaction exist in amine boranes and then it is presumably interpreted to bring about the large variations of the methyl chemical shifts in spite of the longer bond length. Accordingly, the chemical shifts of the methyl groups in amine boranes and o-halotoluenes may be effected by both the steric interactions and the double bond character.

References

1) R. C. Taylor, Adv. Chem. Ser., **42**, 59 (1964).
2) C. W. Heisch, Inorg. Chem., **4**, 1019 (1964).
H. Noth and H. Beyer, Ber., **93**, 939 (1960).
3) K. Sogabe, Men. Fac. Educ. Shimane Univ., **11**, 13 (1977).
4) W. H. Myers, G. E. Ryschkewitsch, M. A. Mathur, and R. W. King, Inorg. Chem, **14**. 2874 (1974).
5) J. L. Hoard, S. Geller, and T. B. Owen, Acta. Cryst., **4**, 405 (1951).
6) P. Cassoux, R. L. Kuczkowski, P. S. Bryan, and R. C. Talor, Inorg. Chem., **14**, 126 (1975).
7) P. H. Clippard, J. C. Hanson, and R. C. Talor, J. Cryst. Mol. Struct., **1**, 363 (1971).
8) K. E. Blick, I. A. Boenig, and K. Niedenzu. Inorg. Chem., **10**, 1917 (1971) and thier references.