The Effect of Methyl Ring Substituents on the ^{11}B-NMR Chemical Shift of Pyrazineboranes

CAROLYN M. MERKEL and DONALD R. MARTIN

Department of Chemistry, The University of Texas at Arlington, Arlington, Tex. 76019, U.S.A.

Received August 20, 1984

The ^{11}B-NMR chemical shift has proved to be a tool useful for examining borane–Lewis base complexes [1]. The relationship between structure and substituents on the borane and the Lewis base, and the ^{11}B-NMR chemical shift has been studied [2]. Additivity parameters have been developed for varying substitution on tricoordinate [3, 4] and tetracoordinate [3, 5, 6] boron atoms; however, changing substituents on the Lewis base [5], or several bonds away [7] has been shown to have little or no effect on the chemical shift.

Recently, this laboratory reported a quantitative relationship between the ^{11}B-NMR chemical shift and the number and position of substituents in borane adducts of methyl substituted pyrazines [8]. This relationship would allow calculation of the exact chemical shift of any methyl-substituted pyrazine–borane adducts.

Inasmuch as this relationship was derived for substitution of one to three methyl groups in the pyrazine ring, it was of interest to evaluate the validity of this relationship for the substitution of four methyl groups. Consequently the ^{11}B-NMR chemical shift of tetramethylpyrazine borane was determined and compared to the calculated chemical shift.

Experimental

Under an atmosphere of dry nitrogen in a glove box, 0.2 ml (2 mmol) of borane methyl sulfide complex was added to a solution of 0.136 g (1 mmol) of tetramethylpyrazine in 15 ml 70% C_6H_6/30% C_6D_6. After 1 h at room temperature, over 1100 scans of the ^{11}B-NMR spectrum were taken at 64.19 mHz on a Nicolet NT-200 wide bore spectrometer. Trimethylborane (TMB) was used as an external standard.

Results and Discussion

An equation

$$\delta_{^{11}\mathrm{B}}\ (\mathrm{ppm}) = -26.9 + a\,(-1.8) + b\,(-0.4) + c + d \quad (1)$$

for calculating the ^{11}B chemical shift for BH_3 adducts with methyl-substituted pyrazines was previously determined in this laboratory [8]. Terms *a* and *b* represent the number of methyl groups *ortho* and *meta* respectively, to the donor nitrogen atoms. Term *c* represents the effect of two methyl groups *ortho* to the nitrogen donor atom, such as for N(1) in 2,6-dimethylpyrazinebis(borane) and has a value of −2.6. Term *d* represents the effect of *cis*-methyl groups *ortho* and *meta* to the nitrogen donor (*e.g.* 2,3-dimethylpyrazine) and has a value of +1.15 ppm. The effect of two sets of *cis*-methyl groups (*e.g.* 2,3,5,6-tetramethylpyrazinebis(borane)) was not known.

Consequently, 2,3,5,6-tetramethylpyrazinebis(borane) was synthesized as previously described [8] and its ^{11}B-NMR spectrum obtained. The ^{11}B-NMR spectrum of 2,3,5,6-tetramethylpyrazinebis(borane) has a single pyrazineborane resonance at −35.56 ppm. This is in good agreement with the chemical shift value of −35.45 ppm calculated with term *d* assumed to be the same when either one or two sets of *cis*-methyl groups are present. Clearly, an additional pair of *cis*-methyl groups neither enhances nor diminishes the effect of the first pair of *cis*-methyl groups.

The quantitative correlation of ^{11}B-NMR chemical shift data for the effect on the boron-nitrogen bond of substituents several bonds away has been shown to be valid for predicting the chemical shift of an unknown pyrazineborane adduct. Experiments are currently underway to determine if a similar correlation can be developed for other substituents and/or heterocyclic molecular donors.

Acknowledgement

The support of The Robert A. Welch Foundation is gratefully acknowledged.

References

1 H. Nöth and B. Wrackmeyer, 'NMR Basic Principles and Progress, Vol. 14', Springer-Verlag, New York, 1978, p. 9.
2 W. G. Henderson and E. F. Mooney, *Annu. Rev. NMR Spectrosc., 2,* 219 (1969).
3 J. M. Purser and B. F. Spielvogel, *Inorg. Chem., 7,* 2156 (1968).
4 K. N. Scott and W. S. Brey, Jr., *Inorg. Chem., 8,* 1703 (1969).
5 B. F. Spielvogel and J. M. Purser, *J. Am. Chem. Soc., 93,* 4418 (1971).
6 J. S. Hartman and G. J. Schrobilgen, *Inorg. Chem., 11,* 940 (1972).
7 F. A. Davis, M. J. S. Dewar and R. Jones, *J. Am. Chem. Soc., 90,* 706 (1968).
8 D. R. Martin, C. M. Merkel, J. U. Mondal and C. R. Rushing, Jr., *Inorg. Chim. Acta,* submitted for publication.

0020-1693/85/$3.30