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Correlations between Carbon-13 and Boron-11 Chemical Shifts. II. Chemical Shift Parameters for Amine Boranes and Related Compounds[1]

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Received May 16, 1968

In a recent paper[3] we showed that a linear correlation exists between carbon-13 chemical shift values in alkanes and boron-11 shifts in the analogous isoelectronic amine boranes. This correlation led to the formulation of empirical parameters for the prediction of boron-11 chemical shifts in amine boranes based on constitutive additivity of groups immediately adjacent to the resonance nucleus.[4] Boron-11 chemical shifts for some amine boranes and related compounds were calculated using these parameters with a standard deviation of 2 ppm in chemical shift. However, this method did not account for small variations in chemical shifts of closely related compounds indicating that positions further removed from the resonance nucleus and other factors were affecting the chemical shift values.

Presented below are parameters which not only allow the estimation of chemical shifts for amine boranes and related compounds close to experimental accuracy but which also further emphasize the close correlation between carbon-13 and boron-11 chemical shifts. In order to obtain good results using simple additivity relationships, it was necessary to incorporate parameters involving skeletal positions four atoms removed from the resonance nucleus as well as steric interactions. Grant and Paul[5] also found similar parameters necessary to obtain good prediction of the carbon-13 chemical shifts of alkanes.

The parameters and constant presented in Table I were calculated with the aid of a computer program for the least-squares solution of simultaneous equations. Greek letters denote positions of atoms with respect to the resonance nucleus. The subscripts "C" and "N" were used to denote carbon and nitrogen, respectively. For this analysis only α positions were distinguished. To facilitate comparison of boron-11 and carbon-13 parameters the notation used by Grant and Paul[5] for steric interaction terms was adopted [*e.g.*, 2°(3°) represents secondary boron attached to a tertiary center].

Table I

Parameters for the Estimation of Boron-11 Chemical Shifts in Amine Boranes and Related Compounds

Parameter	Value, ppm[a]	No. of detns
Constant	31.91	23
α_C	4.36	5
α_N	−8.98	23
β	−2.97	20
γ	1.09	8
δ	0.49	3
1°(3°)	−1.99[b]	1
1°(4°)	−4.28	6
2°(3°)	−2.26[b]	1
2°(4°)	0.16	7
4°(1°)	−6.63	4
4°(2°)	−6.45	2
4°(3°)	−5.54	2
4°(4°)	−6.40[b]	1

[a] From $BF_3\cdot(C_2H_5)_2O$. [b] Only one observation; value not included in evaluation of standard deviation.

Using these parameters, values were calculated and compared with the observed values as shown in Table II. For example, to evaluate the boron-11 chemical shift of $H_3BNH(CH_3)_2$ one adds the values from Table I for one α_N, two β's, and one 1°(3°) steric interaction and adds this sum to the constant. The standard deviation between the observed and calculated boron-11 shifts was found to be 0.92, a value exceeding the usual error in boron-11 nmr by only 0.42 ppm.

Figure 1 compares the parameters β, γ, and δ found in this work for boron-11 chemical shifts with the corresponding carbon-13 parameters determined by Grant and Paul.[5] It is interesting to note that the anomalous positive γ-carbon effect (*i.e.*, with respect to β and δ) observed by Grant and Paul for carbon-13 shifts in alkanes is also observed here for the boron-11 shifts of the amine boranes. Recently Cheney and Grant[6] have proposed that for carbon-13 this effect mainly results from a coiling of the chain to a *gauche* configuration causing the γ position to interact directly with the resonance nucleus. These authors considered the γ-carbon effect in *n*-butane and calculated values for this effect for the *gauche* and *trans* configurations. Using the energy difference between these configurations, a weighted average was obtained for the equilibrating *n*-butane system which compared reasonably well with the empirical value for the γ-carbon effect.

The spatial orientation of the atoms in amine boranes is expected to be quite similar to that of the atoms in alkanes, for boron–nitrogen and carbon–carbon are isoelectronic and the boron–nitrogen and carbon–carbon bond distances are similar.[7] This similarity,

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[1] Presented at the Southwest Regional Meeting of the American Chemical Society, Little Rock, Ark., Dec 1967. The support of the University of North Carolina Research Center under Contract SD-100 with the Advanced Research Projects Agency and the U. S. Army Research Office (Durham) is gratefully acknowledged.

[2] Author to whom inquiries should be addressed.

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[4] J. M. Purser and B. F. Spielvogel, *Chem. Commun.*, 386 (1968).

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[6] B. V. Cheney and D. M. Grant, *ibid.*, **89**, 5319 (1967).

[7] K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Springer-Verlag, Berlin, 1965, p 2.

TABLE II
COMPARISON BETWEEN CALCULATED AND OBSERVED BORON-11 CHEMICAL SHIFTS (PPM)

Compound[a]	Obsd shift[b]	Calcd shift	Diff
H_3BNH_3	23.8,[c] 24.0[d]	22.9	−0.97
$H_3BNH_2(t\text{-}C_4H_9)$	22.1[c]	23.2	1.12
$H_3BNH_2CH_3$	20.5,[c] 19.6[d]	19.9	−0.15
$H_3BNH(CH_3)_2$	14.7,[c] 15.0,[d] 15.4[e]	15.0	0.00
$H_3BN(C_2H_5)_3$	14.3[d]	12.9	−1.31
$(CH_3)_3BNH_3$	8.7[d]	9.5	0.79
$H_3BN(CH_3)_3$	8.5,[d] 8.1[f]	9.7	1.42
$(CH_3)_3BNH_2CH_3$	7.5[d]	6.7	−0.79
$H_3B^*N(CH_3)_2BH_2NH_3$	10.2[g]	10.8	0.61
$H_3B^*N(CH_3)_2BH_2NH_2CH_3$	12.1[g]	11.3	−0.79
$H_3B^*N(CH_3)_2BH_2NH(CH_3)_2$	12.4[g]	11.8	−0.59
$H_3B^*N(CH_3)_2BH_2N(CH_3)_3$	11.65[g]	12.3	0.66
$H_3BN(CH_3)_2B^*H_2NH_3$	2.9[g]	5.2	2.28
$H_3BN(CH_3)_2B^*H_2NH_2CH_3$	3.18[g]	2.21	−0.97
$H_3BN(CH_3)_2B^*H_2NH(CH_3)_2$	−3.0[g]	−3.0	0.00
$H_3BN(CH_3)_2B^*H_2N(CH_3)_3$	−3.45[g]	−3.58	−0.13
$(C_2H_5)_3BNH(CH_3)_2$	−4.0[c]	−3.7	0.26
$(CH_3)_3BNH(CH_3)_2$	4.9[d]	4.6	−0.26
$(CH_3)_3BN(CH_3)_3$	0.8[d]	0.8	0.00
$H_2B(NH_3)_2^+$	14.6[c]	13.9	−0.65
$H_2B[N(CH_3)_3]_2^+$	−2.9[h]	−3.6	−0.68
$H_2B[N(CH_3)_2C_2H_5]_2^+$	−1.4[h]	−1.4	0.00
$H_2B[N(CH_3)(C_2H_5)_2]_2^+$	0.6[h]	0.7	0.17

[a] B* indicates observed boron. [b] Boron-11 shifts are relative to $BF_3\cdot(C_2H_5)_2O$. Where more than one value is reported the average was used. When necessary, values were converted by $\delta[BF_3\cdot(C_2H_5)_2O] = \delta[B(OCH_3)_3] - 17.4$. See J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press Inc., New York, N. Y., 1966. [c] R. Schaeffer, "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McCloskey, Ed., The Macmillan Co., New York, N. Y., 1964, p 417. [d] C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965). [e] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959). [f] D. F. Gaines and R. Schaeffer, *ibid.*, **86**, 1505 (1964). [g] G. A. Hahn and R. Schaeffer, *ibid.*, **86**, 1503 (1964). [h] N. E. Miller and E. L. Muetterties, *ibid.*, **86**, 1036 (1964).

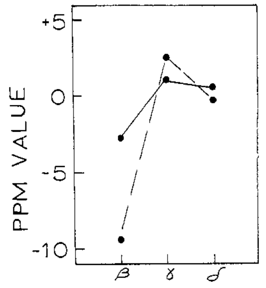

Figure 1.—Comparison of β, γ, and δ parameters for C^{13} (– – – –) and B^{11} (———) shifts.

coupled with the fact that indications exist[8] that the energy difference between the *gauche* and *trans* forms of amine boranes is similar to that for the corresponding alkanes, suggests that the positive γ-carbon effect observed in both the carbon-13 and the boron-11 systems arises from similar phenomena.

Acknowledgment.—We wish to thank Professor C. N. Reilley and Mr. J. R. Layton of the University of North Carolina for the computer program.

(8) R. Hoffmann, "Boron-Nitrogen Chemistry," Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 82.

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The Reaction of Silicon Difluoride with Germane

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Received August 28, 1967

Gaseous silicon difluoride, prepared at high temperatures from silicon and silicon tetrafluoride, has been shown to react with many volatile compounds upon cocondensation at low temperatures.[2-4]

These reactions of silicon difluoride provide a convenient way of preparing types of compounds containing one or, more commonly, two or three $-SiF_2-$ groups, which are difficult to synthesize by other methods.[4] A reaction between germane and silicon difluoride thus suggested itself as a method of making compounds which would be analogs of the known silicon–germanium hydrides[5,6] but with $-SiH_2-$ groups replaced by $-SiF_2-$ groups. An attempt to make fully fluorinated germanium–silicon compounds from silicon difluoride and germanium tetrafluoride had led to the explosive formation of silicon tetrafluoride and germanium fluoride polymers instead of the desired products.[7]

Results

Condensation of a low-pressure gaseous mixture containing silicon difluoride, silicon tetrafluoride, and germane in a roughly 4:2:3 mole ratio, at −196°, gave an orange-yellow solid. When this solid was warmed under vacuum, unreacted silicon tetrafluoride and germane were pumped off first, followed by a mixture of reaction products. The solid became colorless as it warmed up, and at about 0° it melted and foamed vigorously. The residue at room temperature was an air-sensitive, viscous liquid, containing mainly silicon and fluorine with a little germanium and hydrogen. At least 80% of the silicon difluoride which had been condensed was retained in this residue, and the remainder was combined in the volatile products.

Reaction also occurred if a mixture of silicon difluoride and tetrafluoride in a 2:1 mole ratio was first condensed at −196°, and then germane was condensed on top of it. The behavior of the combined condensate on warming was similar to that observed when the components were cocondensed. However, the yield of volatile reaction products was lower than with cocondensation.

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(6) P. L. Timms, C. C. Simpson, and C. S. G. Phillips, *J. Chem. Soc.*, 279, 1467 (1964).

(7) P. L. Timms and J. L. Margrave, unpublished work, Rice University.