Constitutive Chemical-shift Parameters for Amineboranes and Related Compounds

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BORON-11 chemical shifts in donor–acceptor complexes are often used to measure the relative stability of the complexes. However, Heitsch[1] has shown, for a number of amineboranes, that, unless the variations in structures of the compounds compared are small, boron-11 shifts are a poor criterion of stability.

We have shown[2] that a linear relationship exists between carbon-13 chemical-shift values in alkanes and boron-11 shifts in the analogous iso-electronic amineboranes, and have calculated carbon-13 and boron-11 shifts from each other to within a few p.p.m.

Parameters were obtained which, in addition to providing insight into the factors governing boron-11 shifts, have value in allowing chemical-shift values to be associated with specific structures.

Savitsky and Namikawa[3] showed that carbon-13 shifts in a large number of unsubstituted hydrocarbons can be estimated, to within 2 p.p.m., by constitutive additivity using a small number of bond-parameters. These parameters were assigned to structural fragments immediately surrounding the resonance carbon in a molecule. Similarly, we have found that the chemical shift of a given boron in an amineborane or related compound may be estimated by adding the values for the structural fragments shown in Table 1.

TABLE 1

*Constitutive bond-parameters for boron-*11 *chemical shifts in amineboranes and related compounds*

Bond type	No. of determinations	Value*
$-H$	22	6·73
$-CH_3$	4	2·84
$-CH_2-$	2	0·78
$-NH_3$	4	0·56
$-NH_2-$	6	−0·65
$-NH<$	6	−3·76
$-N\equiv$	15	−8·33

* In p.p.m. relative to BF_3,Et_2O.

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The values in Table I were obtained by a computer programme for the least-square solution of simultaneous equations using the 28 boron-11 shifts given in Table 2. All shifts were obtained from the literature. Values for the groups, $-CH<$ and $-C\equiv$ do not appear since boron-11 shifts for boron–nitrogen compounds containing these groups were not available.

Table 2

*Comparison between calculated and observed boron-*11 *chemical shifts*

No.	Compound[a]	Obs.[b]	Calc.	Diff.
1	H_3BNH_3	23·8[c], 24·0[d]	20·76	−3·14
2	$H_3BNH_2Bu^t$	22·1[c]	19·55	−2·55
3	H_3BNH_2Me	20·5[c], 19·6[d]	19·55	−0·55
4	H_3BNHMe_2	14·7[c], 15·0[d], 15·4[e]	16·44	1·43
5	H_3BNEt_3	14·3[d]	11·86	−2·43
6	Me_3BNH_3	8·7[d]	9·08	0·38
7	H_3BNMe_3	8·5[d], 8·1[f]	11·86	3·56
8	Me_3BNH_2Me	7·5[d]	7·87	0·37
9	Et_3BNHMe_2	−4·0[c]	−1·42	2·58
10	Me_3BNHMe_2	4·9[d]	4·76	−0·14
11	Me_3BNMe_3	0·8[d]	0·19	−0·61
12	$H_3B^*NMe_2BH_2{\cdot}NH_3$	10·2[g]	11·86	1·66
13	$H_3B^*NMe_2BH_2{\cdot}NH_2Me$	12·1[g]	11·86	−0·23
14	$H_3B^*NMe_2BH_2{\cdot}NHMe_2$	12·4[g]	11·86	−0·53
15	$H_3B^*NMe_2BH_2{\cdot}NMe_3$	11·65[g]	11·86	0·21
16	$H_3BNMe_2{\cdot}B^*H_2{\cdot}NH_3$	2·9[g]	5·69	2·79
17	$H_3BNMe_2{\cdot}B^*H_2{\cdot}NH_2Me$	3·18[g]	4·48	1·30
18	$H_3BNMe_2{\cdot}B^*H_2{\cdot}NHMe_2$	−3·0[g]	1·37	4·37
19	$H_3BNMe_2{\cdot}B^*H_2{\cdot}NMe_3$	−3·45[g]	−3·20	0·25
20	$B_3H_6{\cdot}N_3H_3Me_3$	6·2[c]	5·94	−0·25
21	$(H_2BNMe_2)_2$	−2·9[c], −4·6[c]	−3·20	0·60
22	$(Et_2BNHMe)_2$	−2·1[h]	−5·96	−3·86
23	$(H_2BNH_2)_3$	11·8[i]	12·16	0·36
24	$(H_2BNH_2)_2$	11·8[i]	12·16	0·36
25	$H_2B[NH_3]_2^+$	14·6[c]	14·58	−0·01
26	$H_2B[NMe_3]_2^+$	−2·9[j]	−3·20	−0·30
27	$H_2B[NMe_2Et]_2^+$	−1·4[j]	−3·20	−1·80
28	$H_2B[NMeEt_2]_2^+$	0·6[j]	−3·20	−3·80

[a] B* indicates observed boron.

[b] Boron-11 shifts are in p.p.m. relative to BF_3Et_2O. Where more than one value is reported the average was used. When necessary, values were converted[4] by: $\delta BF_3,Et_2O = \delta B(OMe)_3 - 17{\cdot}4$.

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With these parameters, calculated chemical shifts were obtained and compared with those observed (Table 2). The standard deviation in chemical shift is 2·0 p.p.m. over a range in shift of close to 30 p.p.m. The usual error reported for observed values is ±0·5 p.p.m.

Table 2 shows a number of boron–nitrogen compounds containing four-co-ordinate boron: amineboranes (1—11); diborazanes (12—19); four- and six-membered ring compounds, cycloborazanes (20—24); and diaminedihydroboron(+1) cations (25—28).

Table 3 compares the values of the parameters found in this study for boron-11 with those found by Savitsky for carbon-13. It is clear that for both boron-11 and carbon-13 nuclei, increasing substitution on the group adjacent to the resonance nucleus results in decreased shielding of this nucleus.

The results show that, within the accuracy of a few p.p.m., the boron-11 shifts may be obtained by addition of a small number of bond-parameters assigned to the structural fragments immediately surrounding the boron nucleus. This observation

TABLE 3

*Comparison of constitutive bond-parameters for carbon-*13 *shifts in hydrocarbons and boron-*11 *shifts in amineboranes and related compounds*

Carbon-13[a]		Boron-11[b]			
$-H$	31·8	$-H$	6·73	$-H$	6·73
$-CH_3$	24·7	$-CH_3$	2·84	$-NH_3$	0·56
$-CH_2-$	16·2	$-CH_2-$	0·78	$-NH_2-$	−0·65
$-CH<$	9·3	$-CH<$	—	$-NH<$	−3·76
$-C\equiv$	3·5	$-C\equiv$	—	$-N\equiv$	−8·33

[a] Determined by Savitsky[3]; shift in p.p.m. from benzene.
[b] Shift in p.p.m. from BF_3,Et_2O.

is in agreement with that of Savitsky for carbon-13 shifts in hydrocarbons. From these data it is clear that positions further removed from the boron are affecting the chemical shift, for although this method predicts identical shifts for the cations (25—28) the observed shifts vary slightly.

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