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Note

Increments for ^{1}H and ^{13}C NMR chemical shifts in areneboronic acids

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A series of areneboronic acids were studied by NMR spectroscopy. Increments for the ^{1}H and ^{13}C chemical shifts caused by the boronic acid substituent $B(OH)_2$ in areneboronic acids were determined.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; areneboronic acids; chemical shift increments

INTRODUCTION

In the last two decades, the Suzuki cross-coupling reaction has proved to be a very useful method in synthetic organic chemistry.[1] Mainly owing to the convenient availability and handling of areneboronic acids, which are used as starting materials, it has found wide applications for the preparation of biaryls.[2] Accordingly, the significance of the areneboronic acids as a class of organic compounds has increased considerably. In the context of our EPR studies on the radical anions of alkyl arenecarboxylates,[3] we were also interested in biarylcarboxylates[4] and have prepared the desired esters by the Suzuki reaction of a series of suitably substituted boronic acids with *tert*-butyl 4-bromobenzoate.[1,2,4] It therefore seemed of interest to develop a set of NMR spectroscopic chemical shift increments for ^{1}H and ^{13}C nuclei in benzene rings with the important boronic acid substituent $B(OH)_2$. To the best of our knowledge, such increments have not previously been reported, although NMR data for benzeneboronic acid[5a,6] and several derivatives[6] and also ^{13}C increments of the BPh_2 substituent[7] are known (in Ref. 5a, the wrong assignments of C-2 and C-3[5b,c] have been corrected).

RESULTS AND DISCUSSION

We used **1, 2** and **3** as the basic compounds for our NMR study.

The room temperature ^{1}H and ^{13}C NMR spectra of **1, 2** and **3** were measured at high resolution (400 and 100 MHz, respectively). A complete and unequivocal assignment of the lines to the nuclei was performed by use of correlation techniques, in particular by ^{1}H–^{13}C-COSY NMR experiments. Increments I^{H}_{B} for the proton chemical shift differences caused by the boronic acid substituent $B(OH)_2$ were then calculated from $\delta(^{1}H)$ by the use of Eqn (1). The increments I^{H}_{S} for the methyl (*ortho* −0.18, *meta* −0.10, *para* −0.20) and *tert*-butyl (*ortho* 0.02, *meta* −0.09, *para* −0.22) substituents were taken from the literature.[8]

$$I^{H}_{B} = \delta(^{1}H) - (7.26 + \Sigma I^{H}_{S}) \quad (1)$$

The results are shown in Table 1, from which the following mean boronic acid increments I^{H}_{B} can be obtained:

$$I^{H}_{B}(ortho) = 1.02 \pm 0.03; I^{H}_{B}(meta) = 0.25 \pm 0.04; I^{H}_{B}(para) = 0.34 \pm 0.04$$

These increments are typical of a strongly electron-withdrawing substituent. They are comparable to the values for a nitro group and exceed those of carboxylic substituents.[8]

In the same way, the corresponding carbon-13 chemical shift increments I^{C}_{B} were calculated from $\delta(^{13}C)$ and I^{C}_{S} (methyl, *ipso* 9.3, *ortho* 0.6, *meta* 0.0, *para* −3.1; *tert*-butyl, *ipso* 22.1, *ortho* −3.4, *meta* −0.4, *para* −3.1)[8] by use of Eqn (2).

$$I^{C}_{B} = \delta(^{13}C) - (128.5 + \Sigma I^{C}_{S}) \quad (2)$$

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Table 1. Proton chemical shifts $\delta(^1H)$ (ppm) and boronic acid increments I^H_B for **1–3**

	1		**2**		**3**	
Position	δ	I^H_B	δ	I^H_B	δ	I^H_B
ortho-H	8.25	0.99	8.22	1.06	8.31	1.03
	8.25	0.99	—	—	8.06	1.02
meta-H	7.52	0.26	7.29	0.21	7.47	0.30
	7.52	0.26	7.29	0.23	—	—
para-H	7.61	0.35	7.45	0.29	7.65	0.37

Table 2. Carbon-13 chemical shifts $\delta(^{13}C)$ (ppm) and boronic acid increments I^C_B for **1–3**

	1		**2**		**3**	
Position	δ	I^C_B	δ	I^C_B	δ	I^C_B
C-2	136.07	7.57	146.69	8.89	133.17	7.77
C-6	136.07	7.57	137.65	9.15	132.70	7.60
C-3	128.41	−0.09	131.00	1.90	150.88	0.28
C-5	128.41	−0.09	125.60	0.20	128.25	0.15
C-4	133.13	4.63	132.62	4.12	130.24	5.14

The data are compiled in Table 2, from which the following mean boronic acid increments I^C_B result:

$$I^C_B(ortho) = 8.1 \pm 0.7; I^C_B(meta) = 0.4 \pm 0.4; I^C_B(para) = 4.6 \pm 0.4$$

They are comparable to the increments of the related BPh_2 substituent.[7]

In Table 3 and 4, the experimental proton and carbon-13 chemical shifts of the boronic acids **1–6** are compared with the values calculated by use of the increments I^H_B and I^C_B. The agreement is very satisfactory. Hence these increments are suitable for the assignment of the NMR chemical shifts to the specific positions of the benzene ring in areneboronic acids.

We were not able to detect the ^{13}C signals of the *ipso*-positions (C-1) in $CDCl_3$ because of line broadening due to the short relaxation time and the quadrupole moment of boron-11 ($I = 3/2$).[6] The use of DMSO as a much better solvent for boronic acids, which allows higher concentrations to be applied, led to a broad signal of C-1 at 138.4 ppm in the spectrum of **1** (Fig. 1). However, this spectrum does not belong to the boronic acid **1** but to its trimeric anhydride triphenylboroxane (**7**). Owing to their quasi-aromatic character, the boroxanes are very easily formed from the corresponding boronic acids by dehydration, even by simply dissolving them in hygroscopic solvents such as anhydrous ethanol[9] or DMSO.

EXPERIMENTAL

Materials

The boronic acids, colourless solids after recrystallization from water, were prepared according to general literature procedures by reaction of the corresponding bromoarenes

Table 3. Calculated and experimental proton chemical shifts δ (ppm) of areneboronic acids

	ortho-H		*meta*-H		*para*-H	
Compound	Calculated	Measured	Calculated	Measured	Calculated	Measured
1	8.28	8.25	7.51	7.20	7.60	7.61
2	8.18	8.22	7.33	7.25–7.34[a]	7.50	7.45
			7.31			
3	8.30	8.31	7.42	7.47	7.62	7.65
	8.06	8.06				
4	8.19	8.18	7.29	7.54	—	—
5	—	—	7.13	6.99	7.40	7.16
6	8.08	8.13	—	—	7.16	7.69

[a] This NMR signal is a complex, unresolved multiplet. Therefore, a range is given instead of distinct shift values. All other lines were completely analysed (cf. Experimental).

Table 4. Calculated and experimental carbon-13 chemical shifts δ (ppm) of areneboronic acids

	C-2,6		C-3,5		C-4	
Compound	Calculated	Measured	Calculated	Measured	Calculated	Measured
1	136.6	136.07	128.9	128.41	133.1	133.13
2	145.9	147.69	129.5	131.00	133.1	132.62
	136.6	137.65	125.8	125.60		
3	133.2	132.70	151.0	150.88	129.7	130.24
	133.5	133.17	128.5	128.25		
4	136.2	135.58	125.5	124.95	155.2	155.97
5	145.9	139.91	126.4	126.79	133.1	129.30
6	130.1	127.74	150.6	150.56	129.7	129.85

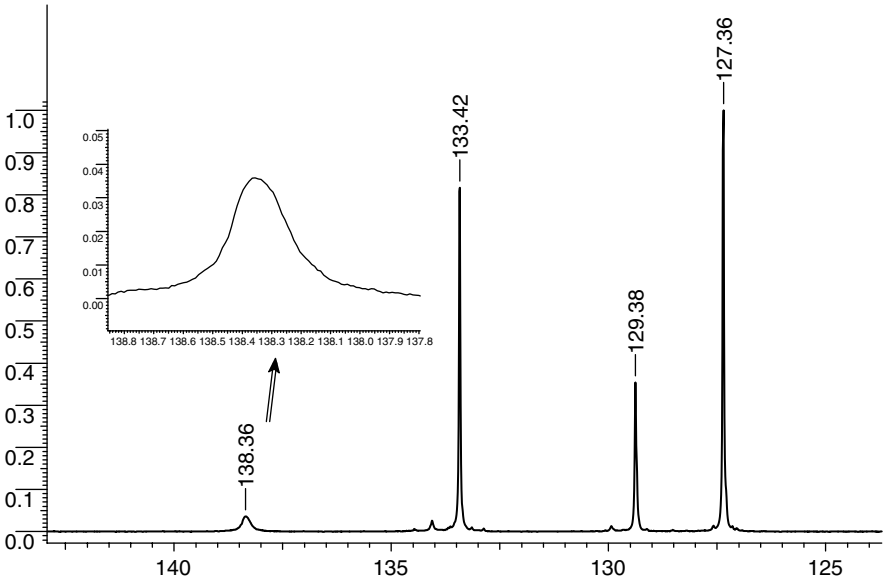

Figure 1. ^{13}C NMR spectrum of triphenylboroxane (**7**) in DMSO.

(5 mmol) with n-butyllithium (5.5 mmol) and subsequently with tri-n-butyl borate (10 mmol).[4,10] The melting-points of boronic acids are questionable since dehydration with the formation of the boroxanes readily occur at elevated temperatures.[9] For the sake of completeness, the high-resolution NMR data for **1**–**6** are given, although **1**, **2** and **5** are known compounds.

*Benzeneboronic acid (**1**)*
Yield 35%, m.p. 219 °C (lit. m.p.[11] 217–220 °C). ^{1}H NMR: $\delta = 7.52$ (dd, $^{3}J = 7.2$, 7.6 Hz, 2H, H-3, H-5), 7.61 (tt, $^{3}J = 7.2$ Hz, $^{4}J = 1.5$ Hz, 1H, H-4), 8.25 (dd, $^{3}J = 7.6$ Hz, $^{4}J = 1.5$ Hz, 2H, H-2, H-6). ^{13}C NMR: $\delta = 128.41$ (C-3, C-5), 133.13 (C-4), 136.07 (C-2, C-6).

*2-Methylbenzeneboronic acid (**2**)*
Yield 30%, m.p. 158 °C (lit. m.p.[12] 171 °C). ^{1}H NMR: $\delta = 2.81$ (s, 3H, CH_3), 7.25–7.34 (m, 2H, H-3, H-5), 7.45 (ddd, $^{3}J = 7.5$, 7.5 Hz, $^{4}J = 1.4$ Hz, 1H, 4-H), 8.22 (dd, $^{3}J = 7.5$ Hz, $^{4}J = 1.4$ Hz, 1H, H-6). ^{13}C NMR: $\delta = 23.5$ (CH_3), 125.60 (C-5), 131.00 (C-3), 132.62 (C-4), 137.65 (C-6), 146.69 (C-2).

*3-tert-Butylbenzeneboronic acid (**3**)*
Yield 37%, m.p. 221 °C. ^{1}H NMR: $\delta = 1.43$ [s, 9H, $C(CH_3)_3$], 7.47 (dd, $^{3}J = 7.6$, 7.4 Hz, 1H, H-5), 7.65 (ddd, $^{3}J = 7.6$ Hz, $^{4}J = 1.2$, 1.1 Hz, 1H, H-4), 8.06 (ddd, $^{3}J = 7.4$ Hz, $^{4}J = 1.2$, 1.1 Hz, 1H, H-6), 8.31 (dd, $^{4}J = 1.2$, 1.2 Hz, 1H, H-2). ^{13}C NMR: $\delta = 31.77$ [$C(CH_3)_3$], 35.1 [$C(CH_3)_3$], 128.25 (C-5), 130.24 (C-4), 132.70 (C-2), 133.17 (C-6), 150.88 (C-3).

*4-tert-Butylbenzeneboronic acid (**4**)*
Yield 40%, m.p. 160 °C. ^{1}H NMR: $\delta = 1.38$ [s, 9H, $C(CH_3)_3$], 7.54 (d, $^{3}J = 8.2$ Hz, 2H, H-3, H-5), 8.18 (d, $^{3}J = 8.2$ Hz, 2H, H-2, H-6). ^{13}C NMR: $\delta = 31.20$ [$C(CH_3)_3$], 35.07 [$C(CH_3)_3$], 124.95 (C-3, C-5), 135.58 (C-2, C-6), 155.97 (C-4).

*2,6-Dimethylbenzeneboronic acid (**5**)*
Yield 21%, m.p. 120 °C (lit. m.p.[13] 125–130 °C). ^{1}H NMR: $\delta = 2.38$ (s, 6H, CH_3), 6.99 (d, $^{3}J = 7.7$ Hz, 2H, H-3, H-5), 7.16 (t, $^{3}J = 7.7$ Hz, 1H, H-4). ^{13}C NMR: $\delta = 22.57$ (CH_3), 126.79 (C-3, C-5), 129.30 (C-4), 139.91 (C-2, C-6).

*3,5-Di-tert-butylbenzeneboronic acid (**6**)*
Yield 34%, m.p. 182 °C. ^{1}H NMR: $\delta = 1.42$ [s, 18H, $C(CH_3)_3$], 7.69 (t, $^{4}J = 2.0$ Hz, 1H, H-4), 8.13 (d, $^{4}J = 2.0$ Hz, H-2, H-6). ^{13}C NMR: $\delta = 31.83$ [$C(CH_3)_3$], 35.22 [$C(CH_3)_3$], 127.74 (C-2, C-6), 129.85 (C-4), 150.56 (C-3, C-5).

NMR spectra

The NMR spectra of saturated (ca 10^{-2}M) $CDCl_3$ solutions of **1**–**6** were measured at 300 K on a Bruker AMX 400 spectrometer (^{1}H 400.13 MHz: ^{13}C, 100.62 MHz). ^{1}H NMR spectra were recorded with a sweep width of 20 ppm with 64K data points and a digital resolution of 0.25 Hz per point. ^{13}C NMR spectra were recorded with a sweep width of 331 ppm with 64K data points and a digital resolution of 0.51 Hz per point after zero filling with 64 K. The ^{13}C NMR spectrum of **7** (Fig. 1) was observed when a solution of 100 mg of **1** in 2 ml of dry DMSO-d_6 was measured at 300 K on a Bruker GMX 500 spectrometer (125.77 MHz, 5000 scans). The assignments are based on ^{1}H–^{13}C-COSY experiments (^{1}H) and the DEPT method (^{13}C).

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