

Hyperconjugation in Trialkylboranes Shown by Indirect Nuclear Spin-Spin Coupling Constants. Experimental Data and Density Functional Theory (DFT) Calculations

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Trimethylborane (**1**), triethylborane (**2**), 1,3-dimethyl-1-boracyclopentane (**3**), 1-methyl-1-boracyclohexane (**4**), 9-methyl- and 9-ethyl-9-borabicyclo[3.1.1]nonane [**5(Me)** and **5(Et)**], and 1-boraadamantane (**6**) were studied by ¹¹B and ¹³C NMR spectroscopy with respect to coupling constants ¹J(¹³C, ¹¹B) and ¹J(¹³C, ¹³C). Results of DFT calculations at the B3LYP/6-311+g(d,p) level of theory show satisfactory agreement with the experimental data. Hyperconjugation arising from C-C σ bonds adjacent to the tricoordinate boron atom is indicated, in particular for 1-boraadamantane (**6**), by the optimised calculated structures, and by the experimental and calculated data ¹J(¹³C, ¹³C). The calculated magnitude of ¹J(¹³C, ¹H) for carbon atoms adjacent to boron becomes significantly smaller if the optimised structures suggest hyperconjugative effects arising from these C-H bonds.

Key words: Trialkylboranes, Coupling Constants, ¹³C NMR, DFT, ¹¹B NMR Calculations

Introduction

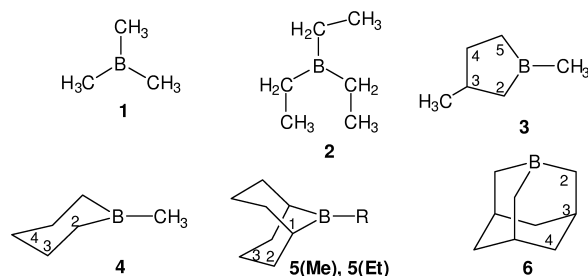
The important concept of hyperconjugation helps to explain structure, stabilisation and reactivity in various fields of organic and organometallic chemistry [1–3]. Since hyperconjugation concerns the electron distribution in σ bonds adjacent to an electron deficient centre, structural parameters such as bond lengths and angles can be indicative [4]. Spectroscopic data are also affected, shown for example by the decrease in the vibrational frequencies for the respective bonds [5] or by the marked changes in nuclear shielding of the nuclei involved [6]. Another NMR parameter, namely indirect X-Y nuclear spin-spin coupling, given as the coupling constants ¹J(X,Y), for nuclei forming σ bonds adjacent

to the electron deficient centre, should also reflect hyperconjugation. Next to carbocations containing tricoordinate carbon atoms, the analogous boranes should exhibit hyperconjugative effects [7–9]. We have studied the trialkylboranes **1–6** (Scheme 1) by ¹³C NMR spectroscopy in order to measure the coupling constants ¹J(¹³C, ¹¹B) and ¹J(¹³C, ¹³C). The geometries of these molecules were optimised at the B3LYP/6-311+G(d,p) level, and the coupling constants were calculated at the same level of theory.

Results and Discussion

NMR measurements

Chemical shifts δ¹³C and δ¹¹B of the boranes **1–6** are given in Table 1. The ¹³C{¹H} NMR spectra of **1–3**, measured at room temperature, show broad signals for the carbon atoms connected to boron with a fine structure according to partially resolved ¹³C-¹¹B spin-spin coupling [10]. The coupling constants ¹J(¹³C, ¹¹B) can be measured fairly accurately (±1 Hz) from the splitting of the two inner lines of the partially relaxed 1:1:1:1 quartet [11]. In the cases of **4–6**, this splitting is not resolved at room temperature. When the ¹³C{¹H} NMR spectrum of **4** is recorded at 80 °C, the splitting appears, since the relaxation rate of the



Scheme 1. Trialkylboranes studied by ¹¹B and ¹³C NMR as well as by DFT calculations.

Table 1. Experimental^a and [calcd.^b] ¹¹B and ¹³C chemical shifts of the trialkylboranes **1–6** (Scheme 1).

	$\delta^{11}\text{B}$	$\delta^{13}\text{C}(\text{BC})$	$\delta^{13}\text{C}(\text{other})$
1	86.0 [89.6]	14.8 [15.5]	–
2	86.5 [87.9]	20.8 [23.6, 25.5, 19.3]	8.3 [9.1, 11.2, 9.2]
3	92.6 [94.6]	40.5 (2), 31.2 (5), 10.1 (BMe) [42.9 (2), 34.7 (5), 8.5 (BMe)]	36.3 (3), 35.8 (4), 22.9 (Me) [43.8 (3), 40.6 (4), 24.2 (Me)]
4	86.0 [86.9]	28.0 (2), 13.0 (BMe) [31.1 (2), 13.9 (BMe)]	24.2 (3), 28.5 (4) [29.5 (3), 32.3 (4)]
5(Me)	88.0 [91.9]	34.8 (1), 12.4 (BMe) [20.5 (1), 12.4 (Bme)]	33.6 (2), 23.7 (3) [39.5 (2), 29.2 (3)]
5(Et)^c	87.7	31.4 (1), 20.3 (BCH ₂)	33.5 (2), 23.7 (3), 8.2 (R)
6^d	82.6 [84.6]	39.0 (2) [43.2 (2)]	45.2 (3), 38.8 (4) [54.9 (3), 43.1 (4)]

^a In C₆D₆ at 23 ± 1 °C; groups or nuclei involved are shown in parentheses; ^b SCF-GIAO: B3LYP/6-311+G(d,p); ^c NMR parameters were not calculated; ^d in CD₂Cl₂ at 23 ± 1 °C.

quadrupolar ¹¹B nucleus slows down at elevated temperatures [10, 11]. In the cases of **5** and **6**, the measurement of the line widths of the ¹³C(BC) NMR signals and of the relaxation time T^Q(¹¹B) enable to calculate [10b, 12] the experimental coupling constants ¹J(¹³C, ¹¹B) (±1 Hz). The result is confirmed by comparison of the data for **4** determined from the observed splitting at 80 °C with those obtained from line widths measurements at room temperature. Coupling constants ¹J(¹³C, ¹³C) for **2–6** were measured by the basic INADEQUATE pulse sequence [13], as shown for 1-boraadamantane (**6**) in Fig. 1. The small differences in the chemical shifts $\delta^{13}\text{C}$ (e.g. for **5**) prevented in some cases the determination of ¹J(¹³C, ¹³C). The experimental and calculated data are listed in Table 2.

Calculated structures

The optimised structures of the fairly rigid frameworks of **3**, **5** and **6** (Scheme 2) are readily obtained either by pure HF methods and also by DFT methods. The C(2)–C(3) bond in **6** is markedly longer than usual C–C bonds, which indicates hyperconjugation via the C(2)–C(3) σ bonds. Some crystal structures of substituted 1-adamantyl cations have been determined [4]. The elongation of the C(2)–C(3) bond is clearly evident, and has been interpreted by hyperconjugation [4]. The calculated structure of the parent 1-adamantyl cation, isoelectronic to **6**, reveals C(2)–C(3) = 162.9 pm, markedly larger than in **6**, as a consequence of stronger hyperconjugation required by the positively charged carbon atom in 1-position. As the result of

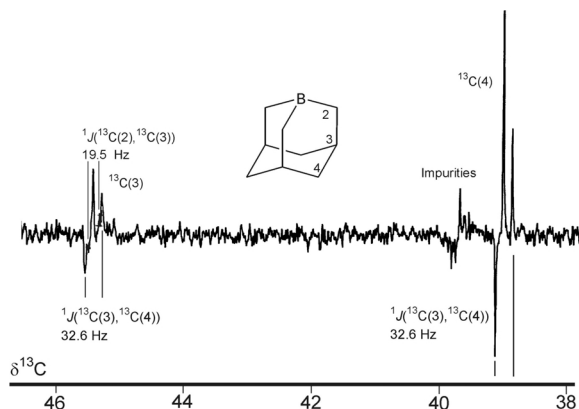
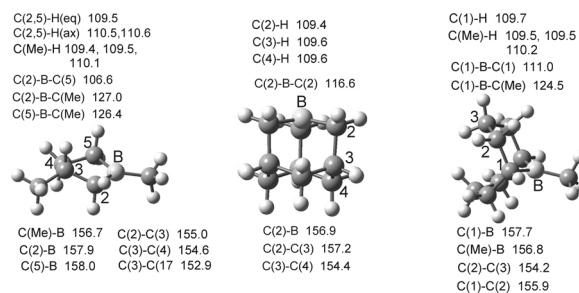


Fig. 1. 125.8 MHz ¹³C{¹H} NMR spectrum (INADEQUATE [13]) of 1-boraadamantane (**6**), in CD₂Cl₂ at 23 °C, showing the typical antiphase doublets corresponding to ¹J(¹³C, ¹³C). The extremely broad ¹³C(2) NMR signal is not visible under these conditions, since the transversal ¹³C(2) magnetisation decays completely in the course of the INADEQUATE pulse sequence. The intensity of the ¹³C(3) NMR signal is reduced, since this nucleus has a fairly short relaxation time T₂ owing to unresolved, partially relaxed ¹³C–¹¹B coupling across two bonds; this effect appears to be much smaller for the ¹³C(4) NMR signal. Therefore, it should hold that |²J(¹³C(3), ¹¹B)| > |³J(¹³C(4), ¹¹B)|, and this is correctly predicted by the calculated data [²J(¹³C(3), ¹¹B) = –3.0 Hz and ³J(¹³C(4), ¹¹B) = +1.7 Hz].



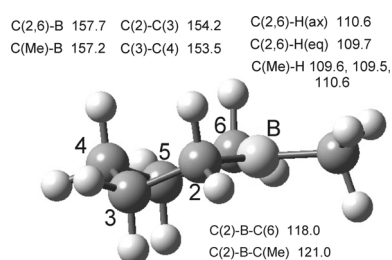
Scheme 2. Optimised structures of 1,3-dimethyl-1-boracyclopentane (**3**), 1-boraadamantane (**6**), and 9-methyl-9-borabicyclo[3.3.1]nonane [**5(Me)**]. Bond lengths are given in [pm] and angles in [°].

the rigid carbon skeleton in **6**, the surroundings of the boron atom are pyramidal ($\sigma[\text{C}(2)\text{--B--C}(2)] = 349.8^\circ$) instead of being planar as in other trialkylboranes. Similarly, in the parent 1-adamantyl cation the sum of the bond angles at C⁺ is calculated as 353.6°. Of the B–Me groups in **3–5**, there is always one C–H bond vector almost parallel to the assumed orientation of the “empty” boron p_z orbital. This corresponds to the finding for the energy minimum of the calculated structure of methylborane [8a].

Table 2. Experimental^a and [calcd.^b] coupling constants $^1J(^{13}\text{C}, ^{11}\text{B})$, $^1J(^{13}\text{C}, ^{13}\text{C})$ and $^1J(^{13}\text{C}, ^1\text{H})$ of the trialkylboranes **1–6** (Scheme 1).

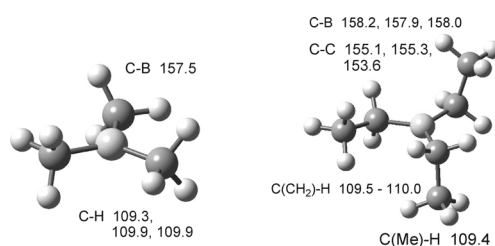
$^1J(^{13}\text{C}, ^{11}\text{B})$	$^1J(^{13}\text{C}, ^{13}\text{C})$	$^1J(^{13}\text{C}, ^1\text{H})^c$	
1	51.0 [49.1]	–	113.5 [117.4, 106.6, 106.8]
2	52.0 ^d [49.7, 49.2, 49.0]	33.0 [26.1, 26.9, 34.3]	[115.1, 114.7, 115.2, 113.2, 101.9, 110.1] (CH_2)
3	48.0 [47.9] (2), 47.0 [44.6] (5), 52.5 [52.0] (Me)	33.5 [32.1] (2-3), 34.0 [33.4] (3-4) ^e , 36.5 [35.9] (3-Me)	[120.0, 103.2 (2), 119.8, 104.5] (5), 111.0 [115.5, 114.8, 101.4] (BMe)
4	49.5 [50.0] (2), 51.5 [50.0] (Me)	32.0 [32.2] (2-3), 24.0 [33.7] (3-4)	112.0 [115.6, 100.6] (2,6), 110.0 [114.7, 114.7, 100.8] (BMe)
5(Me)	48.0 [46.9] (1), 51.0 [49.6] (Me)	28.0 [26.2] (1-2), 33.5 [33.0] (2-3)	[119.8] (1), [123.6, 117.6] (2), 110.0 [115.4, 115.2, 100.0] (BMe)
5(Et)	51.0 (Et)	34.0 (2-3) ^e , 33.0 (Et),	not measured, not calcd.
6^f	49.0 [47.7]	19.5 [17.6] (2-3), 32.6 [31.9] (3-4)	119.0 [121.5] (2), 131.0 [130.1] (3), 123.0 [120.2, 122.6] (4)

^a Given in Hz (± 1 or better); nuclei involved are shown in parentheses; ^b B3LYP/6-311+G(d,p); ^c selected data; ^d L. W. Hall, D. W. Lowman, P. D. Ellis, J. D. Odom, *Inorg. Chem.* **14**, 580 (1975); ^e $^1J(^{13}\text{C}(4), ^{13}\text{C}(5))$ for **3** and $^1J(^{13}\text{C}(1), ^{13}\text{C}(2))$ for **5(Et)** not measured, since the shift differences for the ^{13}C NMR signals are too small; ^f in CD_2Cl_2 at $23 \pm 1^\circ\text{C}$.

Scheme 3. Optimised structure of 1-methyl-1-boracyclohexane (**4**). Bond lengths are given in [pm] and angles in [°].

The situation is somewhat different for the non-cyclic boranes **1** and **2**, and also for the 1-boracyclohexane (**4**). The structure of the latter is found as a minimum at the B3LYP/6-311+G(d,p) level as shown in Scheme 3 with close to parallel orientations of the axial C(2,6)-H bonds relative to the assumed orientation of the “empty” boron p_z orbital, together with one of the C(Me)-H bonds (similar to the structures of **3** and **5**) in the same orientation, however in opposite direction relative to both axial C(2,6)-H bond vectors. These structural features are consistent with hyperconjugative effects mainly *via* the respective C-H bonds. The structure of **4** is analogous to that of one of the “hyperconjomers” of the 1-methyl-1-cyclohexylcation [14]. Similar to the experimental evidence for this cation [15], the low-temperature (-80°C) NMR spectra of **4** do not allow to distinguish between conformers, and since there are also no different ^1H NMR signals for axial and equatorial hydrogen atoms, the relevant dynamic intramolecular processes are fast with respect to the NMR time scale.

The energy differences between most of the numerous possible conformers of both **1** and **2** appear to

Scheme 4. Optimised structures of trimethyl (**1**) and triethylborane (**2**). There are numerous other conformers which all possess almost the same energy. Bond lengths are given in [pm] and angles in [°].

be extremely small (< 0.1 kcal/mol), and no attempt has been made to find the true minima. The structure of **2** has been refined previously at the MP2/6-31G* level assuming C_{3h} symmetry which, however, is not exactly the symmetry found in the solid-state structure [8b]. Scheme 4 shows structures of **1** and **2**, for which the calculations have converged without constraints of symmetry. There are again longer and shorter C-H bonds in both **1** and **2**, and in the case of **2**, the C-C bond lengths are slightly different. This indicates hyperconjugation *via* C-H bonds in **1**, and *via* C-H and C-C bonds in **2**.

Calculations of chemical shifts and coupling constants

The calculated isotropic magnetic shielding constants [16] (converted to the $\delta^{13}\text{C}$ and $\delta^{11}\text{B}$ values) agree reasonably well with experimental data, at least as far as the trend of the data is concerned. The largest deviations in magnitude are found for $\delta^{13}\text{C}$ data of the cyclic derivatives.

There is also agreement for the calculated coupling constants [17] with experimental data. The val-

ues $^1J(^{13}\text{C}, ^{11}\text{B})$ are accurately reproduced in all cases which is important, since these data are sometimes difficult to obtain experimentally. The rather small value of $^1J(^{13}\text{C}, ^{13}\text{C}) = 25.1 \text{ Hz}$ [18] for the trimethylmethyl cation, $[\text{Me}_3\text{C}]^+$, isoelectronic to **1**, is not exactly reproduced by the calculations (34.0 Hz). However, the trend, when compared with other one-bond ^{13}C - ^{13}C couplings [19], is correctly predicted. The calculations give the total coupling constants as the sum of the Fermi-contact term (FC) and the non-contact terms, the spin-dipole (SD) and the spin-orbital terms (diamagnetic, DSO, and paramagnetic PSO). The relative contributions arising from these terms are not available by experimental methods. Although the FC contribution dominates expectedly for nuclei such as ^{11}B or ^{13}C , for planar surroundings of these nuclei the PSO contribution may become noticeable [20]. For the trialkylboranes studied here, the PSO contribution to $^1J(^{13}\text{C}, ^{11}\text{B})$ possesses a negative sign and is in the order of $-2.1 \pm 0.1 \text{ Hz}$. In the case of $^1J(^{13}\text{C}, ^{13}\text{C})$ for $[\text{Me}_3\text{C}]^+$, the PSO contribution amounts even to -5.3 Hz which explains at least partly the rather small magnitude of this coupling constant, considering that an sp^2 hybridised ^{13}C nucleus is involved [19].

In the case of **6**, the unusually small experimental value for $^1J(^{13}\text{C}(2), ^{13}\text{C}(3))$ is reflected by the calculations and fits to the rather long C(2)-C(3) distance. Therefore, a major part of the decrease in the magnitude of $^1J(^{13}\text{C}(2), ^{13}\text{C}(3))$ can be attributed to hyperconjugation. Again the comparison with calculated data (experimental data $^1J(^{13}\text{C}, ^{13}\text{C})$ are not available) for the isoelectronic 1-adamantyl cation is instructive. The value $^1J(^{13}\text{C}^+, ^{13}\text{C}(2)) = 32.6 \text{ Hz}$ is similar to that calculated for $[\text{Me}_3\text{C}]^+$. The calculated value $^1J(^{13}\text{C}(2), ^{13}\text{C}(3)) = 12.0 \text{ Hz}$ is even smaller than in **6**, fully consistent with the larger C(2)-C(3) distance in the cation.

The experimental $^1J(^{13}\text{C}, ^1\text{H})$ values are in general averaged because of fast rotation of the alkyl groups about the respective B-C bond axis or because of fluxionality of the ring systems (*e.g.* in **3** and **4**). It is noteworthy that the calculated values $^1J(^{13}\text{C}, ^1\text{H})$ are significantly smaller for those slightly elongated C-H bonds which are likely to be involved in hyperconjugation.

Conclusions

Hyperconjugation in boranes is reflected by the smaller magnitude of coupling constants $^1J(^{13}\text{C}, ^{13}\text{C})$

for C-C σ bonds adjacent to the electron deficient boron atom. The large effect observed here experimentally for 1-boraadamantane (**6**) is reproduced by DFT calculations. The agreement between calculated and experimental data $^1J(^{13}\text{C}, ^{13}\text{C})$ and $^1J(^{13}\text{C}, ^{11}\text{B})$ for the trialkylboranes, and also for the carbocation $[\text{Me}_3\text{C}]^+$, is certainly promising for similar compounds which are less accessible to experimental studies.

Experimental Section

All trialkylboranes were handled under an atmosphere of Ar excluding traces of oxygen and moisture. The solvents for the NMR samples (C_6D_6 or CD_2Cl_2) were dry and saturated with Ar, and the NMR tubes were sealed after several freeze-pump-thaw cycles. The trialkylboranes were prepared following literature procedures: **1** [21], **2** [22], **3** (from the reaction of 1-chloro-3-methyl-1-boracyclopentane [23a] with tetramethyl tin [23b], **4** [24], **5(Me)** [25], **5(Et)** [26], and **6** [27]. ^{11}B and ^{13}C NMR spectra were recorded for solutions (10–20%) in C_6D_6 at 23 °C (or at 80 °C in the case of **4**) or in CD_2Cl_2 (**6**), using Bruker WP 200, AC 300 and DRX 500 spectrometers.

The calculations were performed using the Gaussian 03 program package [28]. Optimisation of the gas phase geometries was carried out with DFT methods (B3LYP) [29] and the 6-311+G(d,p) basis set [30]. Frequencies were calculated analytically to characterise the stationary points of the optimised geometries as minima (except of **1** and **2**) by the absence of imaginary frequencies. Calculated nuclear shieldings $\sigma(^{13}\text{C})$ and $\sigma(^{11}\text{B})$ were converted into the δ values by $\delta^{13}\text{C} = \sigma(^{13}\text{C})(\text{Me}_4\text{Si}) - \sigma(^{13}\text{C})$ and $\delta^{11}\text{B} = \sigma(^{11}\text{B})(\text{B}_2\text{H}_6) - \sigma(^{11}\text{B}) + 18$, where $\sigma(^{13}\text{C})(\text{Me}_4\text{Si}) = 184.0$ and $\sigma(^{11}\text{B})(\text{B}_2\text{H}_6) = 84.2$. Pure HF calculations of the coupling constants gave poor agreement with experimental data, pure DFT methods gave better results, but somewhat less close to experimental data when compared with the B3LYP method. This was checked for **1** and **6**, for which accurate experimental data are available. The paramagnetic spin-orbital term (PSO) contributed to the magnitude of the coupling constants $^1J(^{13}\text{C}, ^{11}\text{B})$ by < 5% and $^1J(^{13}\text{C}, ^{13}\text{C})$ by up to 15%, whereas these contributions to all values $^1J(^{13}\text{C}, ^1\text{H})$ were small (< 2%). The contributions from the spin-dipole term (SD) and the diamagnetic spin-orbital term (DSO) were small (< 1 Hz) in all cases studied.

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