

Spin-Spin Coupling Constants $^1J(^{15}\text{N}, ^{11}\text{B})$ in Boron-Nitrogen Compounds. Experimental Data and DFT Calculations

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Boron-nitrogen compounds were studied with respect to indirect nuclear ^{15}N - ^{11}B spin-spin coupling ($^1J(^{15}\text{N}, ^{11}\text{B})$). Some new experimental data were determined for aminoboranes and tetra-N-pyrrolylborate, and a variety of compounds with B-N single, double and triple bonds were examined using DFT methods for the calculation of $^1J(^{15}\text{N}, ^{11}\text{B})$ at the B3LYP/6-311+G(d,p) level of theory. The calculations predict magnitude and sign of $^1J(^{15}\text{N}, ^{11}\text{B})$ reasonably well, and the Fermi contact term was found to be dominant. A positive sign of $^1J(^{15}\text{N}, ^{11}\text{B})$ was calculated in the case of 1-azacloso-dodecaborane(12), in contrast to all other compounds studied.

Key words: ^{15}N NMR, ^{11}B NMR, Boron-Nitrogen Compounds, Coupling Constants, DFT Calculations

Introduction

Boron-nitrogen chemistry comprises important research areas in molecular chemistry [1], solid state chemistry [2] and materials research [3]. The isoelectronic nature of B-N and C-C units has been an attractive topic for more than six decades [4], and this analogy has gained further attraction since the discovery of fullerenes considering the potential isoelectronic replacement of C-C by B-N units [5].

From the NMR point of view, much work has been done using the quadrupolar ^{11}B nucleus ($I = 3/2$) [6–8], and complementary data, as far as nuclear magnetic shielding is concerned, have been obtained mainly by using ^{14}N NMR spectroscopy (^{14}N : $I = 1$) [9, 10]. The spin-1/2 nucleus ^{15}N has rarely been considered in this context because of its low natural abundance (0.37 %), although indirect nuclear scalar ^{11}B - ^{15}N spin-spin coupling ($^1J(^{15}\text{N}, ^{11}\text{B})$) could in principle provide further information on the bonding situation. Indeed, only a few attempts have been made so far to measure $^1J(^{15}\text{N}, ^{11}\text{B})$ in natural abundance of the isotopes [11, 12], and the sign (< 0) has been determined for only one example, $\text{B}(\text{NHMe})_3$ [12].

In this work, we report on some new experimental data and in particular on the use of DFT calculations carried out in order to predict $^1J(^{15}\text{N}, ^{11}\text{B})$ data in both magnitude and sign. The compounds considered are

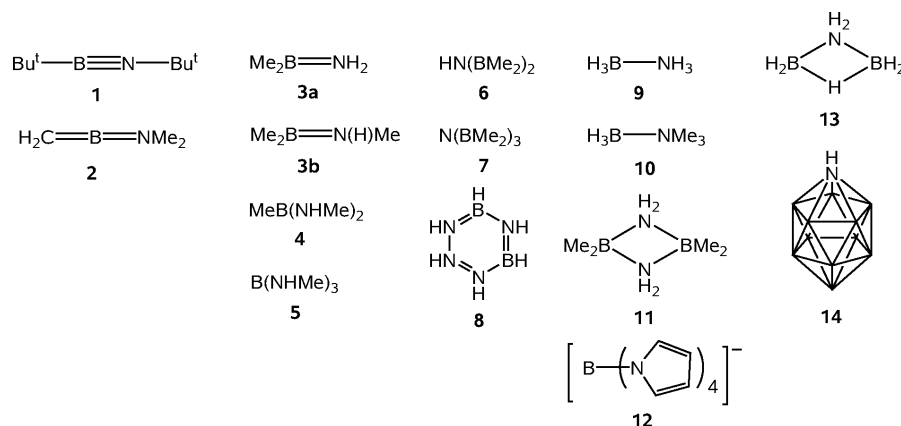
shown in Scheme 1, and experimental data are available for **3–5**, **9–12** and **14**.

Results and Discussion

Measurement of ^{15}N NMR spectra of boron nitrogen compounds in natural abundance

The line widths of the ^{15}N NMR signals of boron-nitrogen compounds depend on the magnitude of $|^1J(^{15}\text{N}, ^{11}\text{B})|$ and the ^{11}B nuclear spin relaxation rate. Since quadrupolar ^{11}B relaxation is efficient with few exceptions, resolved splitting of the ^{15}N NMR signals due to ^{15}N - ^{11}B spin-spin coupling is rarely observed. Thus, fairly small molecules with relatively long relaxation times $T_2(^{11}\text{B})$ and substantial values of $|^1J(^{15}\text{N}, ^{11}\text{B})|$ are required in order to observe the splitting, as found previously in the case of the tris(methylamino)borane **5** [12]. Here, this is shown (Fig. 1) for the mixture of compound **3a** and its dimer **11**. In the former the coupling is resolved as a partially relaxed 1 : 1 : 1 : 1 quartet, whereas in the latter the coupling constant $|^1J(^{15}\text{N}, ^{11}\text{B})|$ is too small to be observed. Similarly, there is no resolved splitting due to ^{15}N - ^{11}B spin-spin coupling in the parent ammine-borane adduct **9** [11b].

In the cases of borates, where the boron atom bears four identical substituents, and where ion pairs are well separated, quadrupolar ^{11}B relaxation rates become



Scheme 1.

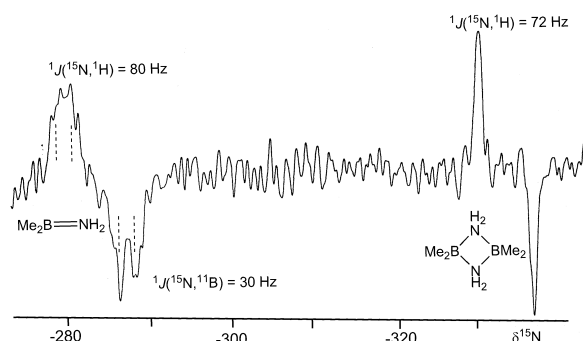


Fig 1. 25.4 MHz ^{15}N NMR spectrum of the monomer/dimer mixture **3a/11** (20 % v/v at 23 °C in $[\text{D}_8]\text{toluene}$) using the basic INEPT pulse sequence without ^1H decoupling [31]. The central signals of the triplets are eliminated as a consequence of the pulse sequence. The broad signal for the aminoborane **3a** shows the partial splitting due to $^1J(^{15}\text{N}, ^{11}\text{B})$, whereas this is not resolved in the case of the dimer **11**.

slow and spin-spin coupling to spin-1/2 nuclei X is frequently resolved, as has been shown for $X = ^1\text{H}$, ^{13}C , ^{19}F [6, 7, 13, 14]. Solutions of the lithium salt of **12** in THF fulfil all required conditions for the purpose of observing spin-spin coupling involving the ^{11}B nucleus, for ^{15}N and also for ^{13}C across two and three bonds (Fig. 2). Unfortunately, the signal-to-noise ratio of the ^{15}N NMR spectra of the sparingly soluble compound was low. This prevented the measurement of $^1J(^{15}\text{N}, ^{10}\text{B})$ and the isotope-induced chemical shift $^1\Delta^{10/11}\text{B}(^{15}\text{N})$. For ^{13}C , the ^{13}C - ^{10}B coupling across three bonds is clearly visible. The isotope effect $^3\Delta^{10/11}\text{B}(^{13}\text{C})$, however, is expectedly very small, since the magnitude of these isotope effects decreases in general significantly with the number of intervening bonds [15].

In the case of the azaborane **14** (the N-Me derivative has been studied by ^{15}N NMR [16]), the ^{15}N NMR signal is observed as a broad singlet in spite of the rather slow quadrupolar ^{11}B relaxation. The line width of the ^{15}N NMR signal suggested that $|^1J(^{15}\text{N}, ^{11}\text{B})| < 8 \text{ Hz}$ [16].

There are some examples for which the ^{14}N - ^{11}B spin-spin coupling can be observed, *e.g.* in the ^{11}B NMR spectra. This is possible if both relaxation times $T_2(^{11}\text{B})$ and $T_2(^{14}\text{N})$ are relatively long, as has been reported for isothiocyanatoborates [17]. In the case of **3a**, the ^{11}B NMR signal measured at r. t. is a broad singlet, whereas at elevated temperature (100 °C) both ^{11}B and ^{14}N relaxation rates slow down, typical of quadrupolar nuclei [18], and a partially relaxed 1 : 1 : 1 triplet is resolved (Fig. 3). The splitting as a result of $|^1J(^{14}\text{N}, ^{11}\text{B})| = 22.5 \pm 3 \text{ Hz}$, observed here for the first time for an aminoborane, compares well with the experimental value $|^1J(^{15}\text{N}, ^{11}\text{B})| = 30.0 \pm 3 \text{ Hz}$ (see Fig. 1), considering the ratio $\gamma(^{15}\text{N})/\gamma(^{14}\text{N}) = -1.403$.

DFT Calculations of $^1J(^{15}\text{N}, ^{11}\text{B})$

Experimental and calculated NMR data of boron-nitrogen compounds are given in Table 1. The comparison with experimental data indicates that the performance of the calculations is reasonably good, as has been shown for various other coupling constants involving the ^{11}B nucleus [19–22], and signs and approximate magnitude of $^1J(^{15}\text{N}, ^{11}\text{B})$ can be predicted with some confidence. The calculations also provide the experimentally inaccessible individual contributions [23] to the total coupling constant $^1J(^{15}\text{N}, ^{11}\text{B})$. Apparently, the non-contact contributions play a minor role even for compounds where B-N multiple bonding

Table 1. ^{11}B and $^{14/15}\text{N}$ NMR parameters^a of the boron-nitrogen compounds **1**–**14**.

	$\delta^{11}\text{B}$ calcd. (found)	$\delta^{15}\text{N}, \delta^{14}\text{N}$ calcd. (found)	$J(^{15}\text{N}, ^{11}\text{B})$ (Hz) ^b calcd. (found)	FC (Hz) calcd.	SD (Hz) calcd.	PSO (Hz) calcd.
1	3.7 (2.4)	–251.2 (–254)	–83.0	–77.6	–3.2	–2.1
2	59.3	–313.0	–51.1	–53.9	–0.4	+2.8
3a	47.3 (47.1)	–297.0 (–281)	–27.2 (30.0)	–29.7	–0.3	+2.8
3b	46.1 (45.7)	–284.8 (–271)	–28.3 (31.5)	–30.7	–0.4	+2.8
4	29.8 (31.7)	–328.9 (–351)	–31.7 (34.0)	–34.1	–0.1	+2.4
5	22.7 (24.2)	–354.4 (–352)	–35.8 (–45)	–37.6	–0.1	+2.0
6	56.6 (56.1)	–221.1 (–250)	–22.0	–24.4	–0.1	+2.5
7	65.3 (61.5)	–177.4 (–185)	–18.4	–20.6	–0.1	+2.4
8	28.5 (29.1)	–269.0 (–278)	–24.1	–26.4	–0.1	+2.4
9	–20.3 (–22.5)	–366.3 (–370)	–0.7 (< 3)	–0.1	–0.4	–0.1
10	–10.2 (–8.1)	–338.7 (–340)	–2.7 (< 6) ^c	–2.5	–0.4	+0.3
11	–4.8 (–3.0)	–347.5 (–333)	–6.0 (< 8)	–5.6	–0.4	0.0
12^d	–1.7 (0.8)	–181.4 (–196)	–24.3 (24.5)	–24.7	–0.3	+0.7
13	–29.3 (–26.7)	–393.6	–6.0	–6.3	–0.1	+0.4
14^e	–10.7 (–9.8) (B2-6) –11.8 (–11.9) (B7-11) 5.8 (2.8) (B-12)	–282.8	+7.6 (< 8) ^f	+7.2	–0.1	+0.6

^a Calcd. $\sigma(^{11}\text{B})$ data are converted to $\delta^{11}\text{B}$ data by $\delta^{11}\text{B} = \sigma(^{11}\text{B}) (\text{B}_2\text{H}_6) - \sigma(^{11}\text{B}) + 18$, with $\sigma(^{11}\text{B}) (\text{B}_2\text{H}_6) = 84.1$, $\delta^{11}\text{B} (\text{B}_2\text{H}_6) = 18.0$ and $\delta^{11}\text{B} (\text{BF}_3\text{--OEt}_2) = 0$; calcd. $\sigma(\text{N})$ data are converted to δN data by $\delta\text{N} = \sigma(\text{N}) (\text{NH}_3) - \sigma(\text{N}) - 399.3$, with $\sigma(\text{N}) (\text{NH}_3) = 259.4$, $\delta\text{N} (\text{NH}_3) = -399.3$ and $\delta\text{N} (\text{neat MeNO}_2) = 0$; experimental chemical shifts were taken from refs. [6, 7] if not mentioned otherwise. FC: Fermi contact term; SD: spin-dipole term; PSO: paramagnetic spin-orbital term; ^b because $\gamma(^{15}\text{N}) < 0$, the sign of $^1J(^{15}\text{N}, ^{11}\text{B})$ is opposite to that of the reduced coupling constant $^1K(^{15}\text{N}, ^{11}\text{B})$; ^c measured for $\text{H}_3\text{B--NEt}_3$; ^d $^2J(^{13}\text{C}, ^{11}\text{B}) = +2.1$ Hz (calcd.) (found: 1.8 Hz), $^3J(^{13}\text{C}, ^{11}\text{B}) = +2.6$ Hz (calcd.) (found: 2.5 Hz); ^e $\delta^{11}\text{B}$ data taken from J. Müller, J. Runsink, P. Paetzold, *Angew. Chem. Int. Ed.* **1991**, 30, 175; ^f measured for the NMe derivative [16].

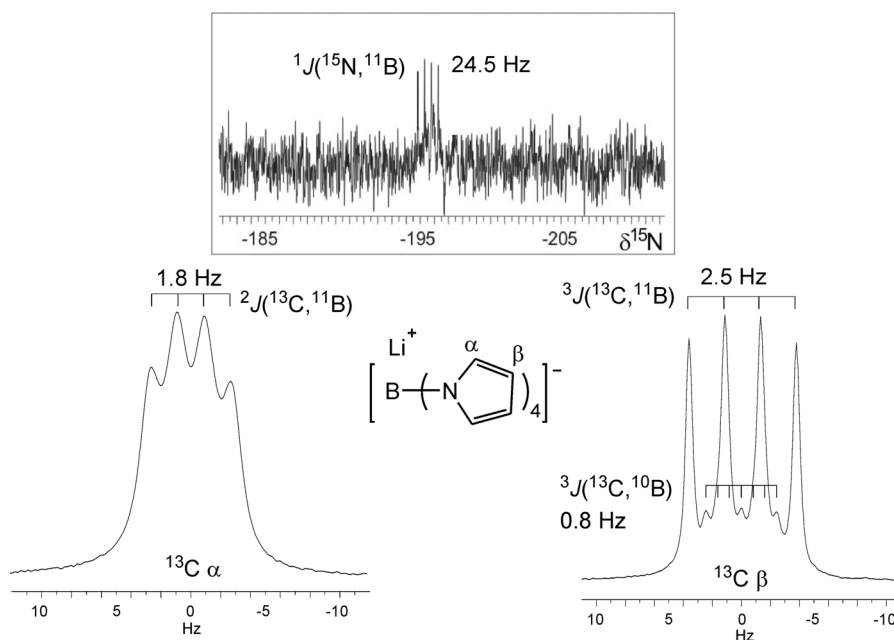


Fig. 2. 50.8 MHz $^{15}\text{N}\{^1\text{H}\}$ and 100.6 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR signals of the tetra-1-pyrrolylborate anion **12** (saturated solution in $[\text{D}_8]\text{THF}$ at 23 °C), showing resolved $^{15}\text{N--}^{11}\text{B}$ and $^{13}\text{C--}^{11}\text{B}$ coupling, respectively.

is of greatest importance. For $^1J(^{13}\text{C}, ^{13}\text{C})$ of alkenes and alkynes, the non-contact contributions are more important [24, 25], and this is also true for $^1J(^{15}\text{N}, ^{13}\text{C})$ of nitriles [26].

The sign of $^1J(^{15}\text{N}, ^{11}\text{B})$ is negative (reduced coupling constants $^1K(^{14}\text{N}, ^{11}\text{B}) > 0$!) except for the polyhedral azaborane **14**. Changes in the magnitude of $^1J(^{15}\text{N}, ^{11}\text{B})$ follow the trend of increasing “s charac-

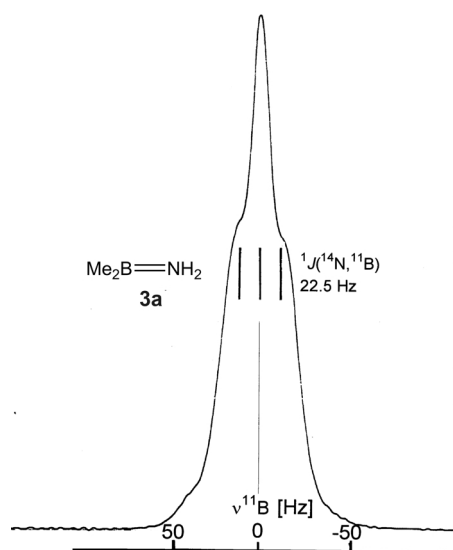


Fig. 3. 80.3 MHz $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of the aminoborane **3a** (20 % v/v at 100 °C in $[\text{D}_8]\text{toluene}$). Quadrupolar relaxation of both ^{11}B and ^{14}N becomes less efficient at high temperature [18]. Thus, the broad singlet (23 °C) changes into a partially relaxed 1 : 1 : 1 triplet (100 °C), revealing ^{14}N - ^{11}B coupling.

ter” of the B–N bond hybrid orbitals (see the data for **9**, **3a**, **2** and **1**), although this is certainly just a crude qualitative explanation. The inversion of the coupling sign in **14**, when compared with **1**–**13**, appears to be a unique feature of the polyhedral boranes. Experimentally, one observes $^1J(^{11}\text{B}, ^{11}\text{B})$ values for polyhedral boranes between 0 and +25 Hz [21c, 26, 27], with ca. 12 Hz for icosahedral species such as **14** [16]. The greater number of valence electrons of heteroatoms such as nitrogen in the polyhedron gives rise to more negative contributions to the Fermi contact term, finally causing sign inversion of the spin-spin coupling, as suggested on the basis of the calculations for **14**. Work is in progress to determine experimen-

tally the sign of $^1J(^{13}\text{C}, ^{13}\text{C})$ in 1,2-dicarba-*closo*-dodecaborane(**12**) (“*ortho*-carborane”), for which a negative sign $^1J(^{13}\text{C}, ^{13}\text{C})$ has been calculated [28], in analogy with the calculated $^1K(^{15}\text{N}, ^{11}\text{B}) < 0$ of **14** which is isoelectronic with *ortho*-carborane.

Experimental Section

The aminoboranes **3** and **4** were prepared as described [29], and samples of **12** [30] and **14** (the NME derivative) [16] were available. ^{11}B , ^{13}C , ^{14}N and ^{15}N NMR spectra were recorded using Bruker ARX 250, DRX 500 and Varian Inova 400 NMR spectrometers, equipped with multinuclear probe heads and variable temperature units. The refocused INEPT pulse sequence with and without ^1H decoupling [31] served for measuring ^{15}N NMR signals after careful calibration of the 90° pulses for the ^1H and ^{15}N frequency channels. Chemical shifts are given relative to $\text{Et}_2\text{O}-\text{BF}_3$ ($\delta^{11}\text{B} = 0$ with $\Xi(^{11}\text{B}) = 32.083971$ MHz) and neat MeNO_2 ($\delta^{15}\text{N} = 0$ with $\Xi(^{15}\text{N}) = 10.136767$ MHz).

The calculations were performed using the program package Gaussian 03, revision B.02 [32]. Gas phase structures were optimised with DFT methods (B3LYP) [33] and the 6-311+G(d,p) basis set [34], and the NMR parameters were calculated using the optimised structures at the same level of theory. The optimised structures were confirmed as minima on the respective potential energy surface by the absence of imaginary frequencies. Table 1 contains the paramagnetic spin-orbital (PSO) contribution; the diamagnetic spin-orbital (DSO) contribution was $\ll 1$ Hz in all cases studied. Nuclear magnetic shielding constants $\sigma(^{11}\text{B})$ and $\sigma(^{15}\text{N})$ were calculated by the GIAO method (gauge-including atomic orbitals) [35], and coupling constants by the coupled perturbed DFT methods [36] as implemented in the Gaussian 03 program. Calculated values $\sigma(^{11}\text{B})$ and $\sigma(^{15}\text{N})$ were converted to $\delta^{11}\text{B}$ and $\delta^{15}\text{N}$ as noted in Table 1, footnote a).

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