Indirect Nuclear Spin-Spin Coupling Constants $^{1}J(^{17}O,^{11}B)$. First Observation and Calculation Using Density Functional Theory (DFT)

Bernd Wrackmeyer and Oleg L. Tok

Anorganische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany

Reprint requests to Prof. Dr. B. Wrackmeyer. E-mail: b.wrack@uni-bayreuth.de

Z. Naturforsch. **61b,** 949 – 955 (2006); received March 3, 2006

Dedicated to Professor Dr. Max Herberhold on the occasion of his 70th birthday

Coupling constants $^{1}J(^{17}O,^{11}B)$ of borates, borane adducts and boranes with boron-oxygen bonds have been calculated on the basis of optimised molecular structures using the B3LYP/6-311+G(d,p) level of theory. This indicates that such coupling constants can be of either sign and that their magnitudes can be rather small. Since both ^{11}B and ^{17}O are quadrupole nuclei, it is therefore difficult to measure representative data. In the cases of trimethoxyborane and tetraethyldiboroxanes, it proved possible to obtain experimental data $^{1}J(^{17}O,^{11}B)$ (22 and 18 Hz) by measurement of ^{17}O NMR spectra at high temperature (120 °C and 160 °C) respectively. The magnitude of these coupling constants is in reasonable agreement with calculated data. In the case of the diboroxane, this points towards a bond angle B-O-B more close to 180° than to 140°.

Key words: Boranes, Borates, ^{17}O NMR, Coupling Constants, DFT Calculations

Introduction

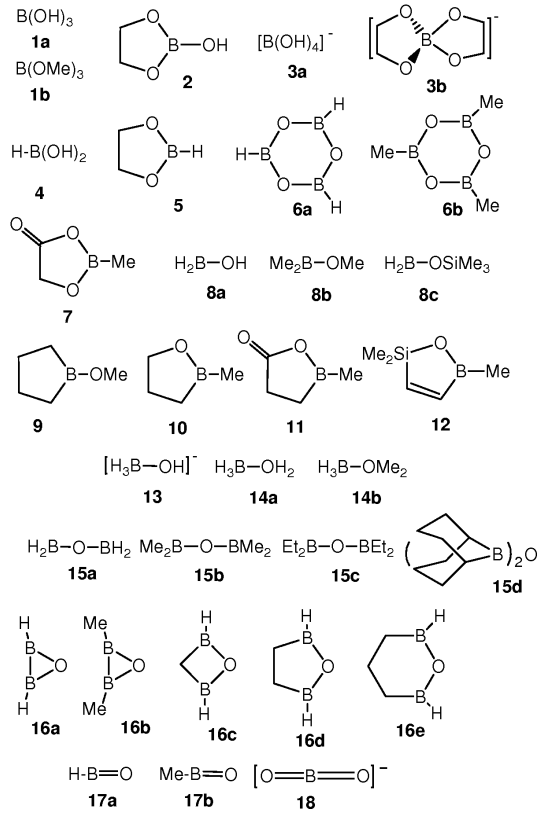
Boron-oxygen compounds are the natural resources of the element boron, and they play an important role in many applications of boranes. In addition to routinely applied ^{1}H and ^{13}C NMR spectroscopy, many boron-oxygen compounds have been studied extensively by ^{11}B NMR [1, 2], allowing to distinguish readily between three- and four-coordinate boron atoms, and revealing information on equilibria and also on the nature of other substituents at the boron atom. Few studies have been carried out on boron-oxygen compounds focusing on ^{17}O NMR at natural abundance in solution [3 – 5], and it has been shown that the chemical shifts $\delta^{17}O$ cover a rather large range (*ca.* 250 ppm). The $\delta^{17}O$ values mirror certain properties of the B-O bond, in particular the potential BO(pp)π interactions in trigonal boranes, complementary to the information from ^{11}B NMR. In contrast to $\delta^{17}O$ [3 – 5] and to the large known data set of spin-spin couplings of ^{11}B with other nuclei $J(^{11}B,X)$ [1, 2], no examples of scalar ^{17}O-^{11}B spin-spin coupling have been reported so far. Sign and magnitude of coupling constants $^{1}J(^{19}F,^{11}B)$ [6] and $^{1}J(^{15}N,^{11}B)$ [7] are known and therefore, data for $^{1}J(^{17}O,^{11}B)$ would be highly welcome to establish trends in spin-spin coupling. We report here on attempts, based on experiments and calculations, to gain the missing information on $^{1}J(^{17}O,^{11}B)$ for the molecules of type **1 – 18** shown in Scheme 1. Many representatives of these compounds have already been prepared. Some have been reported as reactive intermediates in the gas phase (*e.g.* **17**) or may be present in the solid state (**18**).

Results and Discussion

General remarks on ^{17}O NMR and the search for candidates showing resolved ^{17}O-^{11}B coupling in ^{17}O NMR spectra

The nuclear magnetic properties of the ^{17}O nucleus are not particularly inviting for NMR studies [8 – 10] considering its low natural abundance (0.037%) and its sizeable quadrupole moment ($I = 5/2$; $Q = -2.6\ 10^{-2}\ [10^{-28}\ \mathrm{m}^2]$). Enrichment of ^{17}O in boron-oxygen compounds is relatively easy if labelled water $H_2{}^{17}O$ can be used for the synthesis, and applications of such labelled reagents have been demonstrated [11 – 14]. However, the fast quadrupolar relaxation rate – $T^{Q}(^{17}O)$ is generally in the order of a few ms or less – often prevents the observation of resolved ^{17}O-X spin-spin coupling in both ^{17}O and X NMR spectra except in favourable cases [15 – 19]. If X is

0932–0776 / 06 / 0800–0949 $ 06.00



Scheme 1. Boron-oxygen compounds considered in this study for calculations of NMR parameters.

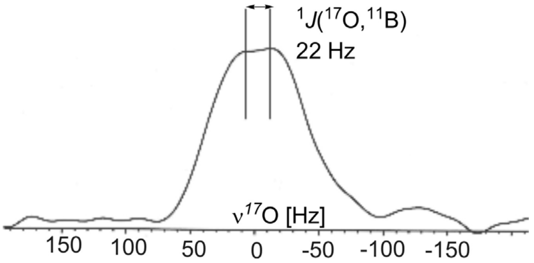


Fig. 1. 54.2 MHz ^{17}O NMR spectrum of trimethoxyborane **1b** in mesitylene (25%, V/V) at 120 °C. The signal shape is typical of a partially relaxed 1 : 1 : 1 : 1 quartet $[2\pi\,^1J(^{17}\text{O},^{11}\text{B})\ T^{\text{Q}}(^{11}\text{B}) \approx 1]$, where the outer lines have collapsed and the distance between the inner lines represents the coupling constant $^1J(^{17}\text{O},^{11}\text{B}) = 22 \pm 4$ Hz.

also a quadrupolar nucleus such as ^{11}B ($I = 3/2$) in an unsymmetrical environment, the situation becomes worse, and even for ^{17}O-enriched compounds resolved splitting due to scalar coupling will be rare, and line shape analysis as an alternative for deducing the coupling information, becomes difficult. In any case, it is advisable to measure the ^{17}O NMR spectra for observation of ^{17}O-X spin-spin coupling since enrichment with $^{17}\text{O} > 10\%$ is rather expensive, and even with 25% enrichment of ^{17}O it may be difficult to analyse the splitting of the X NMR signal (at least six lines of ideally equal intensity).

In our previous ^{17}O NMR studies on boron-oxygen compounds [3–5], we have noted sharpening of ^{17}O NMR signals when the ^{17}O NMR spectra were measured at higher temperature. This is in principle the expected effect for the quadrupolar nucleus ^{17}O, since the enhanced molecular mobility at elevated temperature leads to shorter correlation times τ_c, and by this the quadrupolar relaxation rate slows down $[T^{\text{Q}}(^{17}\text{O})$ becomes longer]. However, if partially relaxed (unresolved) ^{17}O-^{11}B spin-spin coupling contributes to the line widths of the ^{17}O NMR signals, an increase in temperature could eventually lead to broadening of the ^{17}O NMR signals as a result of the longer lifetimes of both ^{17}O and ^{11}B spin states. Several of the compounds shown in Scheme 1 (**1b**, **6b**, **8b**, **9**, the B-ethyl derivatives [4, 5] of **7**, **10** and **12**, and the diboroxanes **15b**, **15c**, **15d**) were studied by ^{17}O NMR at temperatures between +25 to +160 °C. In the cases of the compounds **6b**, **8b**, **9**, and the B-ethyl derivatives of **7**, **10** and **12**, a steady decrease in the line width of the respective ^{17}O NMR signal was observed with increasing temperature. This points towards a rather small magnitude of $^1J(^{17}\text{O},^{11}\text{B})$.

In the case of trimethoxyborane, B(OMe)$_3$ (**1b**), dissolved in mesitylene, the ^{17}O NMR signal (25 °C: $h_{1/2} = 100$ Hz) became slightly sharper up to 70 °C ($h_{1/2}$ = 90 Hz), and at 110 °C, even better discernible at 120 °C, the signal started to split in the top, typical of partially relaxed scalar coupling of an X nucleus with the ^{11}B nucleus of $I = 3/2$, where the resolved splitting corresponds to the distance between the inner lines of the 1 : 1 : 1 : 1 quartet with $^1J(^{17}\text{O},^{11}\text{B}) = 22 \pm 4$ Hz (Fig. 1). The relaxation time $T^{\text{Q}}(^{11}\text{B})$ of **1b** in the same sample was found to increase from 0.011 s at 23 °C to 0.046 s at 110 °C.

The ^{17}O NMR signal of **15b** (δ^{17}O 231.0) did not change markedly in going from 25 °C ($h_{1/2} = 75$ Hz) to 70 °C ($h_{1/2} = 70$ Hz), and then the line width was increasing with increasing temperature, and a new strong signal appeared in the region for **6b** (δ^{17}O 152.0). According to ^{11}B NMR spectra decomposition of **15b** (δ^{11}B 52.0) into **6b** and BMe$_3$ ($\delta^{11}\text{B} = 33.2$ and 86.0) sets in at elevated temperature. Therefore, the changes in the ^{17}O line widths did not provide unambiguous

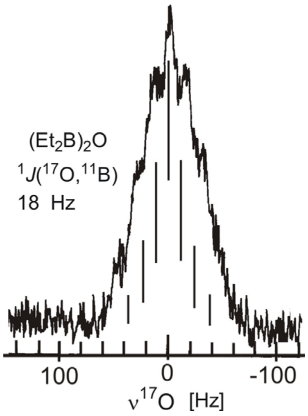


Fig. 2. 27.1 MHz ^{17}O NMR spectrum of ^{17}O enriched (5%) tetraethyldiboroxane **15c** in mesitylene (∼ 3% V/V) at 160 °C.

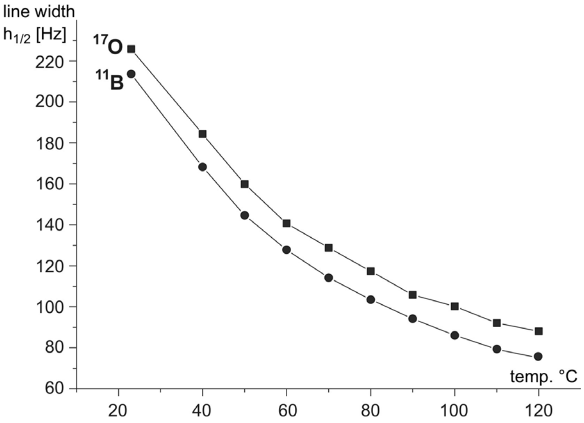


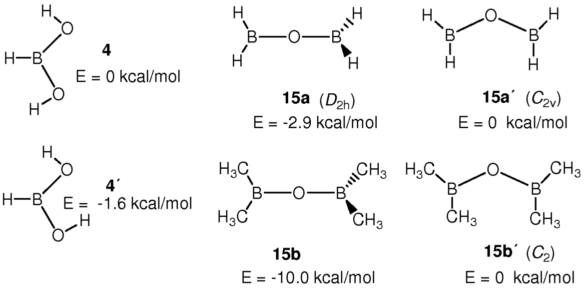
Fig. 3. Changes in the line widths of the 128.3 MHz ^{11}B and 54.2 MHz ^{17}O NMR signals of the diboroxane **15d** as a function of temperature. The almost parallel changes in the functions indicate that contributions from ^{17}O-^{11}B coupling to the line widths of the ^{17}O NMR signals are small, even at 120 °C.

evidence for ^{17}O-^{11}B coupling. The tetraethyl derivative **15c** proved to be thermally more stable than **15b**, in particular in diluted solutions (∼ 3% in benzene, toluene, xylene or mesitylene). In order to observe the ^{17}O NMR signal of such diluted solutions, ^{17}O enriched (5%) **15c** was used. The ^{17}O NMR signal at 25 °C has a line width $h_{1/2} = 90$ Hz, it became slightly sharper ($h_{1/2} = 75$ Hz) at 70 °C, then further heating caused broadening, and at 160 °C (in mesitylene; $T^Q(^{11}B) = 0.042$ s) resolved splitting with the typical pattern due to scalar one-bond spin-spin coupling of ^{17}O with two ^{11}B nuclei [$|^1J(^{17}O,^{11}B)| = 18 \pm 2$ Hz] was observed (Fig. 2).

The measurements of ^{17}O NMR spectra of **15d** at high temperature did not give the same result. The larger molecular size of **15d**, when compared with **15c**, causes more efficient quadrupolar relaxation for both ^{11}B and ^{17}O nuclei as shown by the parallel changes of the line widths of ^{11}B and ^{17}O NMR signals (Fig. 3). The contribution arising from unresolved ^{17}O-^{11}B spin-spin coupling to the line widths of the ^{17}O NMR signals is too small, even above 120 °C.

Optimised geometries of boron-oxygen compounds

The molecules shown in Scheme 1 possess the expected gas phase structures. Major ambiguities arise in the cases of **4** and **15**. There are two isomers **4** and **4’** with a planar arrangement of all atoms (Scheme 2), of which **4** with identical OH groups is slightly less stable. The optimised geometries of the diboroxanes **15a** [20] and **15b** are close to D_{2d} symmetry (almost linear B-O-B units: 179.6° in **15a** and 178.7° in **15b**). In addition to **15a**, the bent structure **15a’** with C_{2v} symmetry has been identified as a minimum on the potential energy surface (PES) by MP4/6-311G(d,p) calculations [20], and the energy difference between **15a** and **15a’** was found to be extremely small [20] (see also Scheme 2). In contrast to the present calculations, which predict a linear structure for **15b**, the electron diffraction study has revealed a B-O-B angle of 144.4° for molecular C_2 symmetry in **15b’** [21]. The calculations predict that **15b** is more stable than **15b’** (C_2 symmetry) by 10 kcal/mol (Scheme 2). The calculated structure of planar bent **15b”** (with C_{2v} molecular symmetry analogous to **15a’**) is only a stationary point on the PES). The calculation based on the experimental geometry [31] of **15b’** leads to linear **15b** as the minimum on the PES. In the solid state, tetramethyldiboroxane is a dimer [22]. Solid tetraphenyldiboroxane is a monomer and has a bent B-O-B unit (angle B-O-B 152.7(2)°) [23], whereas the only example of a solid monomeric tetraalkyldiboroxane, derived from 1-boraadamantane, shows an almost linear B-O-B moi-



Scheme 2. Comparison of the energies of some alternative structures of boron-oxygen compounds.

Table 1. Calculated and experimental ^{17}O and ^{11}B NMR parameters[a,b] of the boron oxygen compounds **1 – 18** (see Schemes 1 and 2 for the structures).

Compound No.	δ^{17}O (exp.)	δ^{17}O (calcd.)	δ^{11}B (exp.)	δ^{11}B (calcd.)	$^1J(^{17}$O,^{11}B) (calcd.) [Hz]	FC (calcd.)	SD (calcd.)	PSO (calcd.)
1a	+51.0	+26.3	+19.6	+19.6	−13.9	−17.8	−1.6	+4.1
1b	+11.0	+14.7	+18.2	+18.1	−17.2	−21.0	−0.2	+4.2
					[(-)22] exp.			
2	–	+15.2	–	+23.2	−21.0 (OH)	−24.8	−0.2	+4.1
		+46.6			−5.3 (*cis* to H)	−9.4	−0.2	+4.5
		+43.3			−11.8 (*trans* to H)	−16.0	−0.2	+4.6
3a	–	+23.0	+1.1	+1.8	−6.9	−8.5	−0.4	+2.1
3b	–	+15.6		+10.7	−5.0	−6.7	−0.3	+2.3
4	–	+89.1	–	+27.6	−12.5	−17.8	−0.2	+5.4
4’	–	+82.0	–	+26.9	−5.6 (OH,BH, *cis*)	−10.7	−0.1	+5.4
		+72.3			−3.3	−8.2	−0.2	+5.3
5	–	+92.8	+28.1	+28.1	+3.7	−1.4	−0.3	+5.6
6a	–	+170.2	–	+27.4	+1.5	−3.3	−1.5	+6.1
6b	+152.0	+160.1	33.2	+34.4	−1.3	−5.7	−0.2	+4.7
7	+88.0	+99.3	+38.6	+38.7	+2.8	−2.7	−0.3	+6.0
	+222.4	+240.3			−3.1	−1.1	−0.2	+4.6
	+360.0 (C=O)	+383.6						
8a	–	+155.9	–	+49.8	+1.3	−6.1	−0.2	+7.7
8b	95.0	+120.2	+53.5	+54.5	−1.8	−7.9	−0.3	+6.6
8c	–	+183.2	–	+49.0	−5.3	−12.3	−0.1	+7.2
9	97.0	+106.4	+60.8	+61.4	−3.3	−9.5	−0.3	+6.6
10	+161.8	+166.0	+57.0	+57.2	+5.5	−5.9	−0.4	+7.0
11	–	+298.8	–	+63.1	+2.5	−3.3	−0.2	+6.2
		+402.8 (C=O)						
12	+135	+145.9	+48.0	+50.0	+0.7	−5.2	−0.2	+6.2
13	–	−35.4		−12.3	+4.4	+4.5	−5.3	+5.0
14a	–	−30.2	–	+9.6	+9.7	+12.0	−1.0	−1.3
14b	–	−71.9	+2.5	+5.7	+13.8	+15.2	−0.6	−0.5
15a	–	+291.7	–	+43.5	−22.5	−28.3	−0.5	+6.3
15a’	–	+259.9	–	+57.5	−1.8	−8.0	0.0	+6.2
15b	+231	+261.8	+52.0	+50.2	−22.4	−27.3	−0.4	+4.4
15b’	+231	+238.3	+52.0	+60.2	−13.0	−18.0	−0.1	+5.2
15c	+235.0[m]	–	+52.0[m]	–	[(-)19.5] (exp)			
15d	+225	–	+56.0	–				
16a	–	+460.7	–	+67.2	+28.4	+16.7	+1.0	+10.7
16b	–	+435.7	–	+69.1	+26.8	+16.3	+0.9	+9.7
16c[c]	–	+332.8	–	+68.2	+12.6	+5.4	0.0	+7.2
16d	–	+279.9	–	+65.2	+5.3	−0.7	−0.1	+6.3
16e	–	+237.2	–	+57.0	+1.9	−4.0	0.0	+6.0
17a	–	+235.6	–	+13.7	−25.1	−22.4	−5.2	+2.6
17b	–	+211.3	–	+21.2	−24.0	−22.5	−4.6	+3.0
18	–	−8.6		+10.8	−16.2	−18.1	−1.2	−2.3

[a] Calculated σ^{17}O) data are converted to δ^{17}O data by $\delta^{17}\text{O} = \sigma(^{17}\text{O})\,[\text{CO}] - \sigma(^{17}\text{O}) + 350.1$, with $\sigma(^{17}\text{O})\,[\text{CO}] = -72.3$, $\delta^{17}\text{O[CO]} = 350.1$ and $\delta^{17}\text{O}\,[\text{H}_2\text{O (liquid)}] = 0$; calculated $\sigma(^{11}\text{B})$ data are converted to δ^{11}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 $\delta^{11}\text{B}\,[\text{BF}_3\text{-OEt}_2] = 0$; experimental δ^{17}O data are taken from ref. [3 – 5], and experimental δ^{11}B data are taken from ref. [1, 2], if not stated otherwise. FC, SD and PSO mean Fermi contact, spin-dipole and paramagnetic spin-orbital term. All contributions to the reduced coupling constant $^1K(^{17}\text{O},^{11}\text{B})$ have the opposite sign to $^1J(^{17}\text{O},^{11}\text{B})$; [b] in some cases, experimental data refer to the B-ethyl derivatives (see text); [c] this work; measured at 160 °C in mesitylene; at 23 °C: δ^{17}O +225.0; δ^{11}B +52.6.

ety (angle B-O-B = 171.8(6)°) [24]. All this indicates a low barrier to the distortion from structures with ideal D_{2d} or C_{2v} molecular symmetry in diboroxanes. The cyclic compounds **16**, of which the structure of **16b** has been calculated previously [25], were included in order to find out about the influence of the angle B-O-B in diboroxanes on the calculated coupling constant $^1J(^{17}\text{O},^{11}\text{B})$.

In both borane adducts **14a** and **14b**, the surroundings of the oxygen atom are pyramidal. The oxides **17** and **18**, isoelectronic with acylium cations [26] and carbon dioxide, respectively, possess the expected linear arrangement at the boron atom.

Calculation of indirect nuclear spin-spin coupling constants $^1J(^{17}O,^{11}B)$

The calculated chemical shifts δ^{11}B and δ^{17}O (Table 1) are close to the experimental values when available [27–30]. It has been shown that calculation of various indirect nuclear coupling constants ^nJ(X,Y) affords fairly reliable data [29–36]. The calculated coupling constants $^1J(^{17}$O,^{11}B) are given in Table 1 together with contributions from the Fermi contact term (FC), the spin-dipole (SD) and the paramagnetic spin-orbital term (PSO). Since $\gamma^{11}\text{B}) > 0$ and $\gamma(^{17}\text{O}) < 0$, the total values $^1J(^{17}$O,^{11}B) as well as the FC-, SD-, PSO contributions have the opposite sign relative to the reduced coupling constants $^1K(^{17}$O,^{11}B) and their respective reduced contributions $[^1K(^{17}\text{O},^{11}\text{B}) = 4\pi^2\ ^1J(^{17}\text{O},^{11}\text{B})\ (\gamma(^{17}\text{O})\ \gamma(^{11}\text{B})\ \text{h})^{-1}]$.

The presence of lone pairs of electrons at the oxygen atom should give rise to pronounced negative contributions to the (reduced) Fermi-contact term [37]. This is obvious in the absence of BO(pp)π interactions, *e.g.* for the borane adducts **14a, b**; the FC term becomes small in the case of the borate **13** and changes its sign in the borates **3a, b**. The situation for the FC contribution to the coupling constants $^1J(^{17}$O,^{13}C) for all sp^3-hybridized carbon atoms [36b] is similar to that for $^1J(^{17}$O,^{11}B) in the borane adducts **14a, b**. The PSO contribution can be of either sign, and cannot be neglected as is evident in the case of **13**. The SD contributions in the molecules containing four-coordinate boron atoms are small, except again for **13**.

Any marked BO(pp)π interactions in the molecules containing three-coordinate boron atoms will change the nature of the lone pairs at the oxygen atom. The inspection of Table 1 shows that the (reduced) FC contributions are fairly large and positive in most cases, except in slightly strained rings such as **5**, **6**, **7**, **10–12**, **16d, e**, and in particular for small rings like **16a–c**. The contribution arising from the PSO term is quite substantial for all trigonal boranes, whereas the SD term is relatively small.

The most intriguing question concerns the bonding in the diboroxanes, where the bond angle B-O-B is a matter of debate. The calculations show that the value of $^1J(^{17}$O,^{11}B) increases from -1.8 to -22.5 Hz ($^1K(^{17}\text{O},^{11}\text{B}) > 0$!) in going from the C_{2v} structure (**15a‘**) to the D_{2d} structure (**15a**). In the latter, both lone pairs at the oxygen atom are involved in BO(pp)π interactions and consequently, negative contributions to the (reduced) FC term are less dominant. This can also be seen by following the trend of the calculated data for **16a–d**, where the structure of **16d** is comparable with that of **15a’**. The calculated magnitude of $^1J(^{17}\text{O},^{11}\text{B}) = -13.0$ for the experimental C_2 structure **15b’** is larger than for **15b’** with C_{2v} structure (-7.6), however, still less negative than for **15b** with D_{2d} symmetry (-22.4 Hz). Interestingly, the calculated chemical shift δ^{11}B of **15b** (50.2) is much closer to the experimental value (+52.0) than the δ^{11}B value (60.2) calculated using the experimental C_2 symmetry of **15b’** or the C_{2v} structure (58.9). In the case of **15c**, an experimental coupling constant $^1J(^{17}\text{O},^{11}\text{B}) = (-)18$ Hz at 160 °C ($\delta^{11}\text{B} = 52.0$) is available (Fig. 2). The experimental δ^{11}B values for **15c** and **15d** remain unchanged with temperature, within the experimental error. The experimental δ^{17}O value for **15c** changes slightly from +225 (23 °C) to +235 (+150 °C), into the direction of the calculated shift of **15b** (gas phase). It is well known that there can be significant changes in δ^{17}O for the gas and the liquid phase [38] and therefore, it is difficult to draw a firm conclusion from the calculated δ^{17}O values of **15**.

Table 2. Comparison of calculated ^{17}O NMR parameters of isoelectronic linear boron- and carbon-oxygen compounds.

Compound No.	δ^{17}O (calcd.)	$^1J(^{17}$O,^{11}B) $^1J(^{17}$O,^{13}C) (calcd.) [Hz]	FC (calcd.)	SD (calcd.)	PSO (calcd.)
17a	+235.6	−25.1 (^{11}B)	−22.4	−5.2	+2.6
[H-C≡O]$^+$	+316.2	−8.2 (^{13}C)	+2.4	−12.2	+1.6
17b	+211.3	−24.0 (^{11}B)	−22.5	−4.6	+3.0
[Me-C≡O]$^+$	+303.2	+0.6 (^{13}C)	+6.5	−9.6	+3.7
18	−8.6	−16.2	−18.1	−1.2	−2.3
O=C=O	+63.4	+17.1 (^{13}C)	+14.8	−2.7	+5.0

The oxides **17** have been proposed as reactive intermediates [39]. The fairly large positive (reduced) FC term indicates that BO(pp)π bonding suppresses most of the usually negative influence of the lone pairs of electrons at the oxygen atom. Table 2 shows a comparison of the calculated NMR data of **17** and **18** with the isoelectronic acylium cations and carbon dioxide. The ^{17}O nuclei in the latter are more deshielded and the (reduced) FC term is significantly less positive, typically of all comparable boron- and carbon-oxygen compounds [36b]. In contrast with the nonlinear species, the SD term becomes important, and its magnitude is larger in the case of carbon because the electrons are more attracted towards the carbon atom in the acylium cations.

Conclusions

The magnitude of the coupling constants $^1J(^{17}O,^{11}B)$ in borates, borane adducts and in most boranes is small, and the coupling constants can be of either sign. Experimental values $^1J(^{17}O,^{11}B)$ were obtained for two examples, trimethoxyborane **1b** and tetraethyldiboroxane **15c**, and the data were found in reasonable agreement with calculated values. Apparently, BO(pp)π bonding leads to less negative contributions of the (reduced) Fermi contact term. Trends for ^{17}O-^{11}B indirect nuclear spin-spin coupling are now established. Expectedly, the data are in between those found for ^{15}N-^{11}B and ^{19}F-^{11}B spin-spin coupling, and experimental and theoretical evidence has become available for the first time.

Experimental Section

The compounds studied were commercial samples (**1b**) or prepared as described previously [3–5, 11–13], and all samples were handled in an atmosphere of dry argon, using carefully dried solvents. The purity of the compounds was checked by ^1H and ^{13}C NMR. Samples for measurements at high temperatures were sealed in NMR tubes (5 mm o. d.). ^{11}B and ^{17}O NMR measurements were carried out using Bruker WP 200, ARX 250 and Varian Inova 400 spectrometers, all equipped with multinuclear probe heads and variable temperature units. Pulse widths were set close to 90° pulses and spectra were recorded without repetition delays. Relaxation times $T^Q(X)$ ($X = {}^{11}B$, ^{17}O) given were determined from the line widths of the ^{11}B or ^{17}O NMR signals. In several cases, the data were confirmed by applying the inversion-recovery technique for determination of $T_1(X)$.

All calculations were performed using the program package Gaussian 03, revision B.02 [38]. Optimisation of the gas phase geometries was done with DFT methods (B3LYP) [39] and the 6-311+G(d,p) basis set [40]. The nature of calculated optimised structures as minima or stationary points on the PES was confirmed by the absence or presence of imaginary frequencies. Table 1 contains the paramagnetic spin-orbital (PSO) contribution; the diamagnetic spin-orbital (DSO) contribution was < 1 Hz in all cases studied.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft. We are grateful to Prof. Dr. R. Köster for a gift of ^{17}O enriched compounds.

---

[1] a) H. Nöth, B. Wrackmeyer, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, in P. Diehl, E. Fluck, R. Kosfeld (eds): NMR – Basic Principles and Progress, Vol. 14, Springer, Berlin (1978); b) B. Wrackmeyer, R. Köster, in R. Köster (ed.): Houben-Weyl – Methoden der Organischen Chemie, Vol. 13/3c, pp. 377–611, Thieme, Stuttgart (1984); c) B. Wrackmeyer, Annu. Rep. NMR Spectrosc. **20**, 61–203 (1988).

[2] J. D. Kennedy, in J. Mason (ed.): Multinuclear NMR, pp. 221–258, Plenum Press, New York (1987).

[3] W. Biffar, H. Nöth, H. Pommerening, B. Wrackmeyer, Chem. Ber. **113**, 333 (1980).

[4] B. Wrackmeyer, R. Köster, Chem. Ber. **115**, 2022 (1982).

[5] R. Köster, G. Seidel, R. Boese, B. Wrackmeyer, Chem. Ber. **121**, 597 (1988).

[6] a) J. W. Emsley, L. Phillips, V. Wray, Progr. NMR Spectroscopy **10**, 83 (1975); b) S. Berger, S. Braun, H.-O. Kalinowski, NMR-Spectroscopy of the Non-Metallic Elements, pp. 619–622, Wiley, Chichester (1997).

[7] B. Wrackmeyer, J. Magn. Reson. **54**, 174 (1983).

[8] J. P. Kintzinger, Oxygen-17 NMR, in P. Diehl, E. Fluck, R. Kosfeld (eds): NMR – Basic Principles and Progress, Vol. 17, Springer, Berlin (1981).

[9] S. Berger, S. Braun, H.-O. Kalinowski, NMR-Spectroscopy of the Non-Metallic Elements, pp. 319–397, Wiley, Chichester (1997).

[10] D. W. Boykin, ^{17}O NMR Spectroscopy in Organic Chemistry, pp. 1–325, CRC Press, Boca Raton (1991).

[11] a) R. Köster, W. Fenzl, Inorg. Synth.**22**, 188 (1983); b) R. Köster, P. Idelmann, Inorg. Synth. **24**, 83 (1986).

[12] R. Köster, G. Seidel, B. Wrackmeyer, K. Horchler, Chem. Ber. **123**, 1253 (1990).

[13] R. Köster, A. Sporzynski, W. Schüßler, D. Blaeser, R. Boese, Chem. Ber. **127**, 1191 (1994).

[14] R. Köster, W. Schüßler, R. Boese, M. Herberhold, S. Gerstmann, B. Wrackmeyer, Chem. Ber. **129**, 503 (1996).

[15] M. Broze, Z. Luz, J. Phys. Chem. **73**, 1600 (1969).

[16] H. C. E. McFarlane, W. McFarlane, J. Chem. Soc. Chem. Commun. 531 (1978).

[17] R. E. Wasylishen, J. O. Friedrich, S. Mooibroek, J. B. Macdonald, J. Chem. Phys. **83**, 548 (1985).

[18] J. Shamir, H. Selig, D. Samuel, J. Reuben, J. Am. Chem. Soc. **87**, 2359 (1965).

[19] T. J. Solomon, J. N. Kieth, A. J. Kacmarek, J. K. Ranay, J. Am. Chem. Soc. **90**, 5408 (1968).

[20] F. Gatti, N. Berthe-Gaujac, I. Demachy, F. Volatron, Chem. Phys. Lett. **232**, 503 (1995).

[21] G. Gundersen, H. Vahrenkamp, J. Mol. Struct. **33**, 97 (1976).

[22] H. Borrmann, A. Simon, H. Vahrenkamp, Angew. Chem. **101**, 182 (1989); Angew. Chem. Int. Ed. Engl. **28**, 180 (1989).

[23] T. Lange, U. Böhme, G. Roewer, Inorg. Chem. Commun. **5**, 377 (2002).

[24] B. Wrackmeyer, E. V. Klimkina, W. Milius, Yu. N. Bubnov, J. Organomet. Chem. **687**, 108 (2003).

[25] M. Bühl, H. F. Schaefer III, P. v. R. Schleyer, R. Boese, Angew. Chem. **105**, 1265 (1993); Angew. Chem. Int. Ed. Engl. **32**, 1154 (1993).

[26] G. A. Olah, A. Burrichter, G. Rasul, R. Gnann, K. O. Christie, G. K. S. Prakash, J. Am. Chem. Soc. **119**, 8035 (1997).

[27] a) M. Bühl, in P. v. R. Schleyer (ed.): Encyclopedia of Computational Chemistry, Vol. 3, pp. 1835 – 1845, Wiley, Chichester (1999); b) M. Bühl, P. v. R. Schleyer, J. Am. Chem. Soc. **114**, 477 (1992).

[28] a) V. G. Malkin, O. L. Malkina, M. E. Casida, D. R. Salahub, J. Am. Chem. Soc. **116**, 5898 (1994); b) E. Fadda, M. E. Casida, D. R. Salahub, J. Chem. Phys. **118**, 6758 (2003).

[29] T. Helgaker, M. Jaszunski, K. Ruud, Chem. Rev. **99**, 293 (1999).

[30] T. W. Keat, D. J. Tozer, T. Helgaker, Chem. Phys. Lett. **391**, 374 (2004).

[31] a) T. Helgaker, M. A. Watson, N. C. Handy, J. Chem. Phys. **113**, 9402 (2000); b) M. A. Watson, P. Salek, P. Macak, M. Jaszunski, T. Helgaker, Chemistry Eur. J. **10**, 4627 (2004).

[32] a) V. Sychrovsky, J. Gräfenstein, D. Cremer. J. Chem. Phys. **113**, 3530 (2000); b) A. Wu, J. Gräfenstein, D. Cremer, J. Phys. Chem. A **107**, 7043 (2003).

[33] V. Barone, J. E. Peralta, R. H. Contreras, J. P. Snyder, J. Phys. Chem. A **106**, 5607 (2002).

[34] a) J. E. Peralta, R. H. Contreras, J. R. Cheeseman, M. J. Frisch, G. E. Scuseria, Chem. Phys. Lett. **375**, 452 (2003); b) T. Helgaker, M. Jaszunski, K. Ruud, A. Gorska, Theoret. Chem. Acc. **99**, 175 (1998); c) J. E. Del Bene, J. Figuero, I. Alkorta, J. Phys. Chem. A **108**, 3662 (2004).

[35] a) L. B. Krivdin, S. P. A. Sauer, J. E. Peralta, R. H. Contreras, Magn. Reson. Chem. **40**, 187 (2002); b) L. B. Krivdin, Magn. Reson. Chem. **41**, 157 (2003); c) L. B. Krivdin, Magn. Reson. Chem. **41**, 885 (2003); d) T. Onak, J. Jaballas, M. Barfield, J. Am. Chem. Soc. **121**, 2850 (1999); e) T. A. Ruden, T. Helgaker, M. Jaszunski, Chem. Phys. **296**, 53 (2004).

[36] a) B. Wrackmeyer, Z. Naturforsch. **58b**, 1041 (2003); b) B. Wrackmeyer, Z. Naturforsch. **59b**, 286 (2004); c) B. Wrackmeyer, Z. Naturforsch. **59b**, 1192 (2004); d) B. Wrackmeyer, Struct. Chem. **16**, 67 (2005); e) B. Wrackmeyer, C. Köhler, Heteroatom Chem. **16**, 85 (2005); f) B. Wrackmeyer, Z. Naturforsch. **60b**, 955 (2005); g) B. Wrackmeyer, Z. Naturforsch. **60b**, 259 (2005).

[37] V. M. S. Gil, W. von Philipsborn, Magn Reson. Chem. **27**, 409 (1989).

[38] Gaussian 03, Revision B.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery (Jr.), T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA (2003).

[39] a) A. D. Becke, J. Chem. Phys. **98**, 5648 (1993); b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988; **41**: 785 (1988); c) P. J. Stevens, F. J. Devlin, C. F. Chablowski, M. J. Frisch, J. Phys. Chem. **98**, 11623 (1994).

[40] a) D. McLean, D. G. S. Chandler, J. Chem. Phys. **72**, 5639 (1980); b) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, J. Chem. Phys. **72**, 650 (1980).