Indirect Nuclear Spin-Spin Coupling Constants $^{n}J(^{11}B, ^{1}H)$ and $^{n}J(^{11}B, ^{11}B)$ in Some Boron Hydrides - Density Functional Theory (DFT) Calculations

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

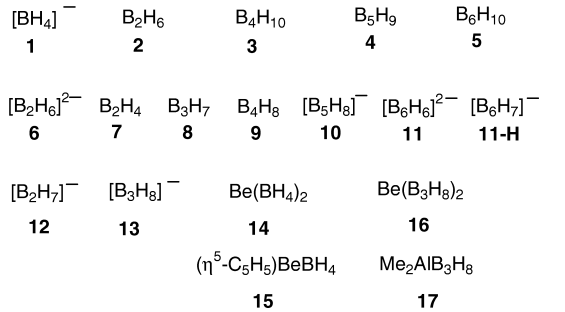
Indirect nuclear spin-spin coupling constants $J(^{11}B,^{1}H)$ and $J(^{11}B, ^{11}B)$ in neutral and anionic boron hydrides **1** – **17**, calculated at the B3LYP/6-311+G(d,p) level of theory, are in good agreement with experimental data if available. This is shown for $[BH_4]^-$ (**1**), B_2H_6 (**2**), B_4H_{10} (**3**), B_5H_9 (**4**), or $[B_2H_7]^-$ (**12**). The calculations can be used to obtain values for those coupling constants for which experimental information is hardly accessible. This applies to complex spin systems involving the quadrupolar ^{11}B nuclei such as in $[B_6H_6]^{2-}$(**11**), to fast dynamic processes such as in B_6H_{10} (**5**), $[B_5H_8]^-$ (**10**), $[B_6H_7]^-$ (**11-H**), $[B_3H_8]^-$ (**13**), $Be(BH_4)_2$ (**14**), (η^5-C_5H_5)$BeBH_4$ (**15**), $Be(B_3H_8)_2$ (**16**), $Me_2AlB_3H_8$ (**17**), or to instable species such as $[B_2H_6]^{2-}$ (**6**), B_2H_4 (**7**), B_3H_7 (**8**), and B_4H_8 (**9**). The experimental ^{11}B NMR spectrum reported in the literature for the dianion **6** does not resemble the spectrum predicted on the basis of the calculated coupling constants.

Key words: Boranes, Hydroborate Anions, NMR, Coupling Signs, DFT Calculations

Introduction

Based on the pioneering work by Alfred Stock in the beginning of the 20th century [1], major developments during the last five decades in the chemistry of boron hydrides and boranes in general have been accompanied by NMR spectroscopy focusing particularly on the nuclei ^{1}H and ^{11}B [2 – 5]. The determination of chemical shifts $\delta^{1}H$ or $\delta^{11}B$ did not pose problems, although the accurate determination of $\delta^{1}H(BH)$ values often required ^{11}B decoupling which was available for NMR spectrometers only as optional equipment until the eighties of the 20th century. In contrast to chemical shifts $\delta^{11}B$, reliable data sets of coupling constants involving the ^{11}B nucleus, $^{n}J(^{11}B,X)$, are still difficult to obtain in many cases, because of the efficient quadrupole-induced relaxation of the ^{11}B nuclei (I = 3/2; ^{10}B: I = 3) which may lead to partial or even complete decoupling. There are serious problems also for coupling constants $^{n}J(^{1}H, ^{1}H)$ in boron hydrides, since the spin-systems are complex in most cases (*e. g.*, ^{1}H and ^{11}B nuclei may be chemically equivalent but magnetically non-equivalent), and the accurate computational simulation of the respective ^{1}H NMR spectra is hampered by the broadening effects exerted by the quadrupolar ^{11}B nuclei. Moreover, many boron hydrides, neutral or anionic, are fluxional, at least in the temperature range usually accessible to NMR experiments. These fluxional properties are frequently related to intramolecular exchange processes, which means that splitting of NMR signals due to spin-spin coupling, if it can be observed at all, reflects averaged values.

This situation is clearly a challenge for the application of quantum chemistry to the calculation of indirect nuclear spin-spin coupling constants. Recent progress in this field has shown that density-functional-theory (DFT) methods, together with a sufficiently large basis set for optimising the molecular geometries, provides $^{n}J(A,X)$ values which are close to experimental data [6 – 9]. There have been already numerous applications to hydrocarbons [$^{n}J(^{13}C,^{1}H)$, $^{n}J(^{13}C,^{13}C)$] [10 – 12], and also first promising attempts for boron compounds aiming at the calculation of $^{n}J(^{11}B,^{1}H)$, $^{n}J(^{11}B,^{11}B)$, and $^{n}J(^{13}C,^{11}B)$ values have been made [13 – 15]. In the present work, it is shown that the calculations work very well for non-fluxional boron hydrides such as **1** – **5**, **10**, **11** but also for the fluxional



Scheme 1. Neutral and anionic boranes considered for B3LYP/6-311+G(d,p) calculations for optimised geometries and NMR parameters.

compounds **5**, **10**, **11-H**, and **13**–**17**. Moreover, coupling constants of unstable species such as **6**, **7**–**9** can be predicted (Scheme 1).

Results and Discussion

Calculated chemical shifts δ^{11}B and coupling constants $J(^{11}\mathrm{B},^{11}\mathrm{B})$ and $J(^{11}\mathrm{B},^{1}\mathrm{H})$ for **1**–**17** are listed in Table 1, together with experimental data if available. The promising performance of the calculations can be seen by inspection of the data for the tetrahydroborate anion **1**, diborane(6) **2**, *arachno*-tetraborane(10) **3**, *nido*-pentaborane(9) **4**, and the heptahydrodiborate **12**, for which numerous experimental data have been determined [2, 4, 5]. This has already been noted previously [13], when calculations were restricted to the Fermi contact term (FC). The present calculations of coupling constants include also the spin-orbital (SO) and spin-dipole terms (SD) [16]. The overall agreement with experimental coupling constants is satisfactory, considering that the latter are associated with fairly large errors owing to experimental shortcomings. All other compounds or ions studied are fluxional (**5**, **10**, **11-H**, **13**–**17**). Their existence has been proposed (*e. g.* **6**), but they are insufficiently stable for measurement (*e. g.* **7**–**9**) or important coupling constants cannot be straightforwardly deduced from the NMR spectra (*e. g.* **11**).

$[B_2H_6]^{2-}$ **6** and B_2H_4 **7**: The formation of the dianion **6** has been proposed [17] in the course of homogenous reduction of diborane(6), mainly on the basis of the ^{11}B NMR spectrum. This spectrum shows a fairly sharp quartet ($^1J(^{11}\mathrm{B},^1\mathrm{H}) = 80$ Hz) at δ^{11}B -26.8 [17]. Although the calculated value $^1J(^{11}\mathrm{B},^1\mathrm{H})$ is similar, the calculated δ^{11}B value is rather far away from the experimental value. More seriously, the ^{11}B NMR spectrum of **6** should be rather complex taking into account the $A_3A'_3XX'$ spin system present in the $[^1H_3\,^{11}B\text{-}^{11}B^1H_3]^{2-}$ isotopomer with a substantial ^{11}B-^{11}B spin-spin coupling (calcd: +64.9 Hz). This is in strong contrast with the experimental ^{11}B NMR spectrum assigned to **6** [17]. Therefore, convincing evidence for the existence of **6** is still missing. Considering the results for spin-spin coupling in B_2H_4 **7** with $^1J(^{11}\mathrm{B},^{11}\mathrm{B}) = 72.0$ Hz and experimental evidence for other diborane(4) derivatives and polyhedral boranes containing a 2c/2e B-B bond [18, 19], the calculated value $^1J(^{11}\mathrm{B},\ ^{11}\mathrm{B}) = 64.9$ Hz for **6** appears to be realistic.

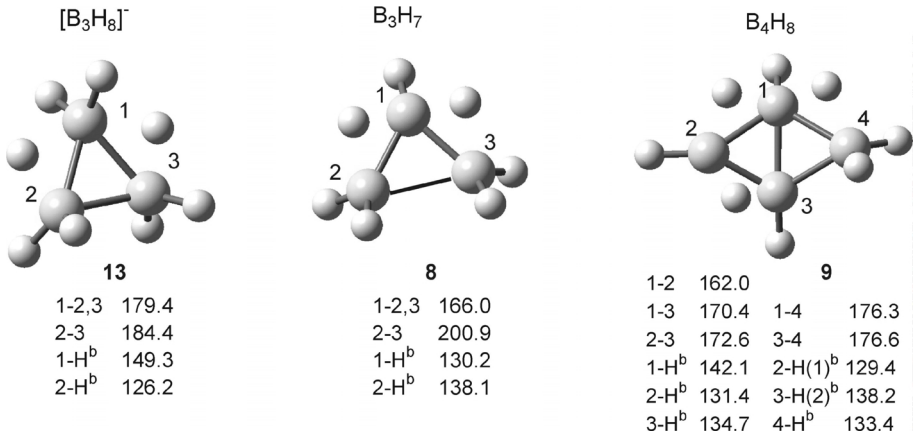
$[B_3H_8]^-$ **13**, B_3H_7 **8**, and B_4H_8 **9**: The anion $[B_3H_8]^-$ **13** is well known as a highly fluxional species [20], in which the three boron atoms are in the same surroundings since all hydrogen atoms become equivalent owing to fast exchange between terminal and bridging positions. This means that the ^{1}H coupled ^{11}B NMR signal consists of nine lines (seven lines are readily observable) separated by averaged ^{11}B-^{1}H spin-spin coupling [$J(^{11}\mathrm{B},^1\mathrm{H}) = 33.0$ Hz]. This is in good agreement with the averaged calcd value $J(^{11}\mathrm{B},\ ^1\mathrm{H}) = +32.2$ Hz which results from dividing the algebraic sum of all calcd ^{11}B-^{1}H couplings ($\Sigma = 772.5$ Hz) by all (24) conceivable ^{11}B-^{1}H coupling interactions. The optimised geometry of **13** (Scheme 2) shows that the bridging hydrogen atoms occupy unsymmetrical positions as is also indicated by the different values $^1J(^{11}\mathrm{B},\ ^1\mathrm{H^b})$ [+45.1 Hz for B(2,3) and only +12.6 Hz for B(1)]. The values $^1J(^{11}\mathrm{B(1)},\ ^{11}\mathrm{B(2,3)})$ (+15.4 Hz) and $^1J(^{11}\mathrm{B(2)},^{11}\mathrm{B(3)})$ (+17.2 Hz) differ little. The small value of $^1J(^{11}\mathrm{B(2)},^{11}\mathrm{B(3)})$, in the absence of a bridging hydrogen atom, points towards a rather weak B(2)-B(3) bonding character.

The transient boron hydrides B_3H_7 **8** and B_4H_8 **9** have been in the centre of several synthetic attempts [21] and theoretical considerations [22–24]. The most stable structures found in this work are those shown in Scheme 2, in agreement with the early work of Lipscomb *et al.* [22] for **8** and **9** and a more recent study by Korkin *et al.* dealing with **8** [24]. Although application of Bader's theory of atoms in molecules [25] did not reveal two bridging hydrogen atoms in **8** [23], the type of bridging shown for **8** with C_2 symmetry (Scheme 2) seems to provide a satisfactory picture, and it is in complete agreement with calcd coupling constants. Thus, the $^1J(^{11}\mathrm{B(1)},\ ^1\mathrm{H^b}) = 50.1$ Hz and $^1J(^{11}\mathrm{B(2,3)},\ ^1\mathrm{H^b}) = 27.0$ Hz values are characteristic of bridging hydrogen atoms. The small value of the calcd coupling constant $^1J(^{11}\mathrm{B(2)},\ ^{11}\mathrm{B(3)}) = +3.7$ Hz is in agreement

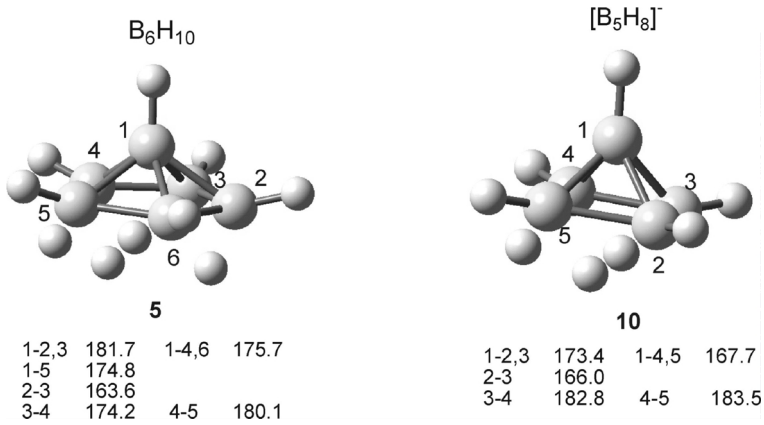
Table 1. Calculated and experimental chemical shifts δ^{11}B and coupling constants in some boron hydrides[a] (see Scheme 1).

Compound	δ^{11}B calcd [found]	$^1J(^{11}B, ^1H)$ calcd [found] [Hz]	$J(^{11}B, ^{11}B)$ calcd [found] [Hz]
1 $[BH_4]^-$	52.9 [−42.0]	+79.1 [81.0]	–
2 B_2H_6	18.0 [18.0][b]	+128.0 [133.5]; +46.4 [46.3] (H^b)	−5.3 [−3.8]
		+4.8 [+4.0] (^2J)	
3 B_4H_{10}	−46.1 [−41.6] (B1,3)	153.1 [155.0] (B1); 121.2 (B2-H^{endo})	+21.2 [20.4] (B1,B3)
	−8.7 [−6.9] (B2,4)	129.0 (B2-H^{exo}); +50.4 (B1-H^b)	2.2 (B1,B2)
		+31.9 [30.0] (B2,H^b); −2.3 (^2J(B(1),H(3))	−0.7 (B2,B4)
		+2.7 (^2J(B(1),H(2)); +4.4 (^2J(B(2),H^t))	
4 B_5H_9	−59.1 [−53.1] (B1)	+169.7 [175.0] (B1)	+21.6 [19.5]
	−16.5 [−13.4] (B2-5)	+160.1 [166.0] (B2)	+8.3 (B2,B3)
		+35.5 [33.0] (H^b); −1,5 (^2J(B(1),H^t)	−0.8 (^2J(B(2),B(4)
		+2.9 (^2J(B(2),H(1)); +5.6 (^2J(B(2),H^t)	
		+2.7 (^2J(B(1),H^b); +0.3 (^2J(B(2),H^b)	
5 B_6H_{10}	−55.9 [−51.8] (B1)	+151.2 [155.0] (B1); +148.4 (B2)	+7.0 (B1,B2); +20.9 (B1,B4); +15.9 (B1,B5)
	+20.2 (B2,3), +16.8 (B4,6)	+158.2 (B(4); +152.2 (B5);	+58.0 (B2,B3); +3.4 (B3,B4); +7.2 (B4,B5)
	−11.5 (B5)	+40.6 (B2,H^b); +46.1 (B4,H^b)	
		+28.0 (B4,H(5)^b); +44.9 (B5,H^b)	
6 $[B_2H_6]^{2-}$	−40.5 [−26.8]	+77.1 [80.0]; −4.3 (^2J)	+64.9
7 B_2H_4	+105.6	+110.8; +5.5 (^2J)	72.0
8 B_3H_7	+28.1 (B1)	+173.1 (B1); +127.3 (B2,H^{endo})	+18.5 (B1,B2,3)
	+4.9 (B2,3)	+130.6 (B2,H^{exo}); +50.1 (B1,H^b)	+3.7 (B2,B3)
		+27.0 (B2,H^b); +9.5 (^2J(B(1),H(2)^{exo}))	
		+1.3 (^2J(B(1),H(2)^{endo}))	
		+4.1 (^2J(B(2),H(1))	
		+0.9 (^2J(B(2),H(3)^{endo}); −3.4 (^2J(B(2),H(3)^{exo})	
9 B_4H_8	0.0 (B1)	+177.1 (B1); +175.5 (B2);+152.8 (B3)	+19.5 (B1,B2); + 33.8 (B1,B3); +21.9 (B1,B4)
	+13.8 (B2)	+125.8 (B4); +26.0 (B1,H^b)	+12.6 (B2,B3); +5.5 B(3,B4); +1.2 (B2,B4)
	+10.3 (B3)	+54.6 (B2,H(1)^b)	
	-13.1 (B4)	+39.8 (B2,H(3)^b); +33.1 (B3,H(3)^b)	
		+55.2 (B3,H(4)^b); +28.3 (B4,H^b)	
10 $[B_5H_8]^-$	−61.8 [−52.6] (B1)	+144.3 [152.0] (B1); +127.6 (B2,3)	+12.4 (B1,B2,3); +28.5 (B1,B4,5)
	−19.3 (B2,3); -24.3 (B3,4)	+137.6 (B4,5)	+61.9 (B2,B3); +6.1 (B4,B5)
		+37.3 (B2,H^b); +42.0 (B4,H^b)	+1.9 (^2J(B(2),B(4))
11 $[B_6H_6]^{2-}$	−18.0 [−17.0]	+114.9 [123.0]; +1.0 (^2J(B(1),H(2))	+18.1; +11.5 (^2J(B(1),B(6))
		+14.7 (^3J(B(1),H(6)	
11-H $[B_6H_7]^-$	−23.0 (B1,2,3)	+143.6 (B1,2,3); +133.7 (B4,5,6)	+0.2 (B1,B2); +23.6 (B1,B4); +16.5 (B4,B5)
	−13.6 (B4,5,6)	+17.4 (H^b)	+6.2 (^2J(B(1),B(6))
12 $[B_2H_7]^-$	−25.2 [−23.0]	100.2 [105.0]; 36.3 (H^b)	−5.7
13 $[B_3H_8]^-$	−37.6 (B1); −48.6 (B2,3)	+108.2 (B1,H^t); +103.7 (B2,H^t)	+15.4 (B1,B2,3); +17.2 (B2,B3)
	[−30.0] (averaged shift)	+12.6 (B1,H^b); +45.1 ((B2,H^b);	
14	−49.7 [n.r.]	+150.7; +64.3 (B,H^b) [87.0 (mean value)]	−7.6 (B,^{9}Be); +0.8 (B,B)
$Be(BH_4)_2$[c]	−1.1 (δ^9Be)	−10.9 (^{9}Be,H^b); −15.2 (^{9}Be,H^t)	
15[d]	−58.7 [n.r.]	+112.2; +54.3 (H^b); -17.6 (^{9}Be,H^b)	−3.9 [3.6] (B,^{9}Be)
η^5-$CpBeBH_4$	−20.0 [−22.1] (δ^9Be)	−3.7 (^{9}Be,H^t)	
16[c]	−47.0, -47.6 [-43.6] B(1,3)	+131.4 [132.0] (B1,H^t)	+19.2 (B1,B3); +4.1 (B1,B2)
$Be(B_3H_8)_2$	−13.1 [−11.8] (B2)	+121.0, +128.1 [122.0] (B2,H^t)	−4.9 (B1,^{9}Be); +0.5 (B2,^{9}Be)
	+7.3 [+2.9] (δ^9Be)	+61.1 [57.0] (B1,H(Be)^b); +50.1 (B1,H^b)	
		+27.4 (B2,H^b); −12.0 (^{9}Be,H^b)	
17	−45.4 [−41.4] (B1,3)	+137.0 (B1,H^t); +119.9, 125.0 (B2,H^t)	+4.6 (B1,B2); +22.6 (B1,B3)
$Me_2AlB_3H_8$	−15.4 [−14.0] (B2)	+48.1 ((B1,H(2)^b); +29.8 (B2,H(2)^b)	−6.8 (B1,^{27}Al); -1.4 (B2,^{27}Al)
		+63.3 (B1,H(Al)^b); +29.0 (Al,H^b)	

[a] Experimental data [in brackets] taken from reviews [2, 3, 5] if not mentioned otherwise; n. r. means not reported. Assignment of data is given in parentheses. Calculated [GIAO-B3LYP/6-311+G(d,p)] chemical shifts: $\sigma(^{11}B)$ data are converted to δ^{11}B data by $\delta^{11}B = \sigma^{11}B)$ $[B_2H_6] - \sigma(^{11}B) + 18.0$, with $\sigma(^{11}B)$ $[B_2H_6] = 84.2$, $\delta^{11}B$ $[B_2H_6] = 18.0$ and $\delta^{11}B$ $[BF_3\text{-}OEt_2] = 0$; $\sigma(^9Be)$ data are converted to δ^9Be data by $\delta^9Be = \sigma(^9Be)$ $[Be(H_2O)_4{}^{2+}] - \sigma(^9Be)$, with $\sigma(^9Be)$ $[Be(H_2O)_4{}^{2+}] = +110.6$, δ^9Be $[Be(H_20)_4{}^{2+}] = 0$. [b] Reference for calculations of $\sigma(^{11}B)$. [c] Data taken from ref. [32]. [d] Data taken from refs. [32, 33].



Scheme 2. Optimised geometries of $[B_3H_8]^-$, B_3H_7 and B_4H_8; bond lengths in [pm].



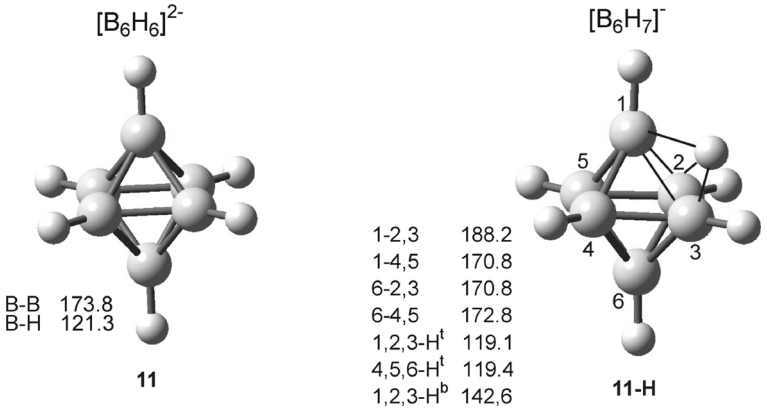
Scheme 3. Optimised geometries of B_6H_{10} and $[B_5H_8]^-$; bond lengths in [pm].

with the large B-B distance (200.9 pm), whereas the other value $^1J(^{11}B(1), ^{11}B(2,3)) = 18.5$ Hz is in the typical range for multi-centre B-B bonds.

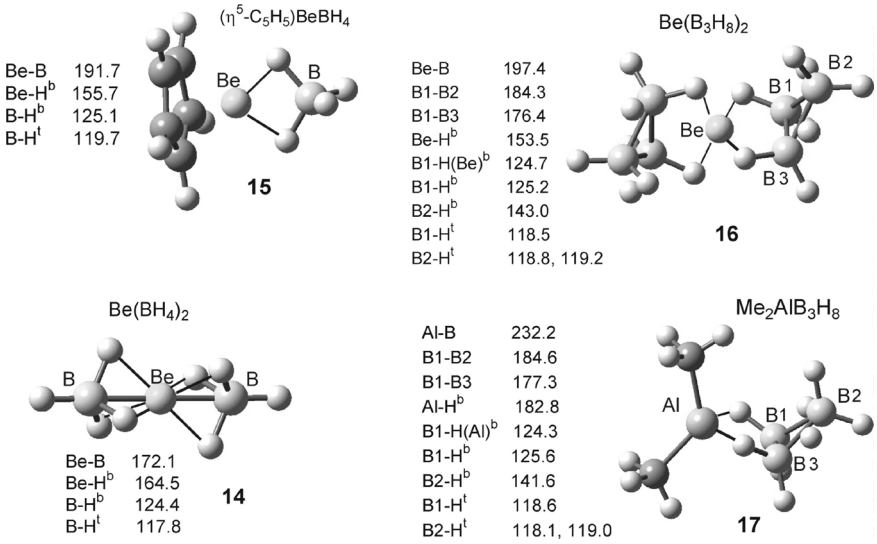
The optimised geometry of **9** with C_1 symmetry shows a fairly short B1-B3 bond (170.4 pm) which is reflected by a large value of $^1J(^{11}B(1), ^{11}B(3)) = +33.8$ Hz. Although, the B(1)-B(2) bond length is even shorter (162.0 pm), the value $^1J(^{11}B,(1), ^{11}B(2)) = +19.5$ Hz is smaller as a result of the B(1)-H-B(2) bridge. Six different ^{11}B-H^b spin-spin couplings are calculated for **9** which range from +26.0 to 55.2 Hz. There is no straightforward relationship between these values and the respective bond lengths B-H^b, although here and in most other examples studied small values $^1J(^{11}B, ^1H^b)$ go together with greater B-H^b distances.

B_6H_{10} **5** and $[B_5H_8]^-$ **10**: The expected and optimised geometries of the *nido*-species **5** and **10** are shown in Scheme 3. Both compounds are fluxional at room temperature [26, 27] because of tautomerism of the bridging hydrogen atoms. Although these exchange processes can be slowed down at low temperature, the determination of a complete NMR data set is difficult, in particular with respect to all coupling constants involving ^{11}B nuclei. In both **5** and **10**, the static structures possess a strong basal B-B bond which should give rise to a large value of $^1J(^{11}B, ^{11}B)$. Indeed the calcd values $^1J(^{11}B(2), ^{11}B(3)) = +58.0$ (**5**) and $+61.9$ Hz (**10**) come close to the range known [18, 19] for 2c/2e B-B bonds. All other values $^1J(^{11}B, ^{11}B)$ in **5** and **10** are much smaller, being in the typical range of multi-centre B-B bonds.

$[B_6H_6]^{2-}$ **11** and $[B_6H_7]^-$ **11-H**: In the series of *closo*-borate dianions $[B_nH_n]^{2-}$, the octahedral **11** [28] is the smallest known cluster (Scheme 4), and its properties and chemistry have been extensively studied [29]. The six ^{11}B and six ^1H nuclei in the $[^{11}B_6^1H_6]^{2-}$ isotopomer are both chemically equivalent but magnetically non-equivalent. However, the information on coupling constants, in principle available by analysis of the $[AX]_6$ spin system, is not accessible owing to



Scheme 4. Optimised geometries of $[B_6H_6]^{2-}$ and $[B_6H_7]^{-}$; bond lengths in [pm].



Scheme 5. Optimised geometries for $Be(BH_4)_2$, $(\eta^5\text{-}C_5H_5)BeBH_4$, $Be(B_3H_8)_2$, and $Me_2AlB_3H_8$; bond lengths in [pm].

effects caused by the quadrupole-induced relaxation of the ^{11}B nuclei. Data given for $^1J(^{11}B, ^1H)$ in the literature for this anion, and also for many other polyborane derivatives, are associated with a large error, since most of the data have been measured assuming first order spin systems. There are two types of ^{11}B-^{11}B spin-spin couplings in **11**, one formally across one bond and a second one formally across two bonds. The calculation gives $^1J(^{11}B, ^{11}B) = +18.1$ Hz and $^2J(^{11}B,^{11}B) = +11.5$ Hz, both values being typical of multi-centre B-B bonds. It is also noteworthy that there is a rather large value $^3J(^{11}B, ^1H) = +14.7$ Hz which is the result of four equivalent coupling pathways. The coupling constants $^3J(^1H,^1H)$ are small (+1.2 Hz), and there is also a small value $^4J(^1H,^1H) = +4.7$ Hz for the antipodal ^{1}H nuclei. The access to fairly accurate calcd coupling constants is encouraging for obtaining experimental evidence by simulation of the complex NMR spectra of the *closo*-borate dianions using the calculated data.

Protonation of the dianion **11** leads to the highly fluxional monoanion $[B_6H_7]^-$ **11-H** (Scheme 4). The optimised geometry indicates that one triangular face is bridged by a hydrogen atom, and the remaining structure is only slightly distorted when compared with **11**. The calcd coupling constants reveal the bridging interactions by the fairly small values $^1J(^{11}B(1,2,3), ^1H^b) = +17.4$ Hz and the very small values $^1J(^{11}B(1), ^{11}B(2,3)) = +0.2$ Hz. Both values for $^1J(^{11}B(1,2,3), ^1H^t) = +143.6$ Hz and $^1J(^{11}B(4,5,6), ^1H^t) = +133.7$ Hz are somewhat larger than in **11** (+114.9 Hz). The magnitude of the values $^1J(^{11}B, ^{11}B) = +16.5$ and +23.6 Hz, not involving the bridge, are similar as in **11** (+18.1 Hz), whereas the

coupling across two bonds is smaller (+6.2 Hz), since one coupling pathway (across the bridge) in **11-H** appears to be less efficient. On the other hand, the magnitude of $^4J(^1H(1), ^1H(6)) = +7.6$ Hz is larger than in **11** (+4.7 Hz).

$Be(BH_4)_2$ **14**, $(\eta^5\text{-}C_5H_5)BeBH_4$ **15**, $Be(B_3H_8)_2$ **16** and $Me_2AlB_3H_8$ **17**: Four examples of main group element boron hydrides **14**, **15**, **16** and **17** have been selected in order to calculate coupling constants for other types of fluxional molecules. The "simple" $[BH_4]^-$ anion is known as an extremely versatile ligand since it can offer a variable number of hydrogen atoms for M-H-B bridges [30], and the same is true, in an increasingly sophisticated manner, for polyborane anions [31]. NMR data of **14** have been obtained in the gas phase and in solution [32], and liquid-state NMR data are available for **15** [33], **16** [32] and **17** [34]. The optimised geometries for **14**–**17** (Scheme 5) suggest that beryllium is coordinated by the $[BH_4]^-$ anions *via* three (**14**) or two bridging hydrogen atoms (**15**), and that the $[B_3H_8]^-$ anion is linked to beryllium in **16** or aluminium in **17** by two B-H-Be or B-H-Al bridges, respectively. The triple bridging in **14** has already been predicted, although unequivocal experimental proof is missing, by *ab initio* studies at a lower level of theory [35]. The double bridge in **15** is in agreement with IR and Raman spectra reported for the liquid and the solid state [36]. The calculated structures of **16** and **17** correspond closely to experimental data [37, 38].

In the case of **15**, the magnitude of the experimentally determined coupling constant $^1J(^{11}B, ^9Be) = 3.6$ Hz is accurately reproduced by the calculations (-3.9 Hz), and the same is true for the averaged experimental data $J(^{11}B,^1H)$ (found: 84.0; calcd +83.3 Hz) and $J(^9Be, ^1H)$ (found: 10.2; calcd. -10.7 Hz). The negative sign of coupling constants involving ^9Be results from $\gamma(^9Be) < 0$. It should be noted that the calculated chemical shifts $\delta\,^9Be$ for **15** and **16** are in good agreement with the experimental values. All this suggests that the calculated data for **14** are reliable. In contrast with **15**, experimental ^1H and ^{11}B NMR spectra for **14** in solution or in the gas phase do not show any signs of ^9Be-^1H or ^{11}B-^9Be spin-spin coupling [32]. This can be interpreted as the result of fast intermolecular exchange, considering the calcd data for **14**–**16** and also the complete experimental data set for **15**. One advantage of the calculation is clearly that it provides information on the relative magnitude of coupling constants involving bridging and terminal ^1H nuclei. This information is lost in the NMR experiment because of the molecular dynamics. The triple hydrogen bridges in **14** cause larger magnitudes of $^1J(^{11}B, ^9Be)$ and also of $^1J(^{11}B, ^1H^t)$ and $^2J(^9Be, ^1H^t)$ when compared with **15**. On the other hand, the magnitude of $J(^9Be, ^1H^b)$ is smaller in **14** than in **15**, and consequently, the magnitude of $^1J(^{11}B, ^1H^b)$ is larger in **14** than in **15**.

The calculated data for coupling constants in **16** and **17** are best compared with data for the $[B_3H_8]^-$ anion **13**. Major changes are induced by the B-H-Be or B-H-Al bridges which lead to an increase in the magnitude of the respective coupling constant $^1J(^{11}B, ^1H^t)$. However, the averaged values of $^1J(^{11}B, ^1H) = 100.3$ in **16** and 100.1 Hz in **17** are slightly smaller than that of $^1J(^{11}B, ^1H^t)$ in **13** for the analogous ^{11}B nuclei (108.2 Hz). This indicates that electron density has been passed on to beryllium or aluminium. The calculated values $J(^{11}B, ^{11}B)$ also indicate some changes in the electron densities in the multi-centre B-B bonds as a result of the coordination of $[B_3H_8]^-$ to Be or aluminium.

Conclusions

DFT calculations provide valuable information on magnitudes and signs of coupling constants in neutral and anionic borane derivatives. These data can be useful for assessing the bonding situation in static structures representing minima on the potential energy surface of otherwise highly fluxional molecules. The bonding in unstable species, not suitable for experimental NMR studies, can be better understood. Moreover, the analysis of exceedingly complex spin systems involving the quadrupolar ^{11}B nuclei can be facilitated using the calculated coupling constants as a starting point for simulation of experimental spectra.

Experimental Section

All calculations were performed using the Gaussian 03 program package [39]. The gas phase geometries were optimized with DFT methods (B3LYP) [40] and the 6-311+G(d,p) basis set [41]. Frequencies were calculated analytically to characterize the stationary points of the optimised geometries as minima (absence of imaginary frequencies) on the respective potential energy surface. Expectedly [6–9], HF calculations of the coupling constants gave poor results, pure DFT methods gave better results, but somewhat less close to experimental data when compared with the B3LYP method. This was checked for **1**–**4**, for which fairly accurate experimental data are available [2–5, 26, 42–44]. The paramagnetic spin-orbital term (PSO) and the spin-dipole term (SD) contributed up to 10% to the magnitude of

some of the coupling constants $J(^{11}B, ^{11}B)$, $J(^{11}B, ^{9}Be)$ or $J(^{27}Al, ^{11}B)$, whereas these contributions to all values $J(^{11}B, ^{1}H)$ were small ($< 2\%$). The diamagnetic spin-orbital term (DSO) was negligible (< 1 Hz) in all cases studied.

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