Polyhedral Thiaborane Chemistry: a Comparative Nuclear Magnetic Resonance Study of *arachno*-$[6\text{-}SB_9H_{12}]^-$ and *nido*-6-SB_9H_{11}

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A nuclear magnetic resonance study of *nido*-6-SB_9H_{11} and *arachno*-$[6\text{-}SB_9H_{12}]^-$ using ^{11}B, ^{11}B-{^{1}H}, ^{1}H-{^{11}B}, [^{11}B–^{11}B]-COSY, and [^{1}H–^{1}H]-COSY techniques has enabled unequivocal assignment of the ^{11}B and ^{1}H spectra, and has thereby shown that the basic known behavioural patterns of their binary borane analogues (*arachno*-$[B_{10}H_{14}]^{2-}$ and *nido*-$B_{10}H_{14}$) also hold for the 6-thiadecaborane system. Interestingly, the effects on cluster nuclear shielding upon replacement of the decaborane B(6) centres with sulphur are very similar for both systems in spite of the fundamentally different *arachno versus nido* electronic structures. A long-term hydrolysis product of $[6\text{-}SB_9H_{12}]^-$ is confirmed as [*endo*-9-(OH)-*arachno*-6-$SB_9H_{11}]^-$.

The factors that influence nuclear magnetic shielding in polyhedral boron compounds are not understood, and few reliable structure–shielding correlations that are useful in the general case have emerged.[1–4] An exception to this generalization is in the C_{2v} open ten-vertex cluster type (Figure 1), in which a change from *nido* character, exemplified by $B_{10}H_{14}$, to *arachno* character, exemplified by $[B_{10}H_{14}]^{2-}$, is characterized by an inversion of the ordering of the ^{11}B resonance positions and an increase in the mean ^{11}B shielding of several p.p.m.[5–8] We have found these criteria are useful in assessing *nido versus arachno* character in a variety of ten-vertex non-heteroborane[8–10] and metallaborane[11–15] systems, and also in assessing *nido versus arachno* character in ten-boron fragments in polyhedral systems with more than ten vertices,[16,17] thereby providing insights into bonding patterns[18] within these larger polyhedral types. With the current resurgence of general interest in polyhedral heteroborane types other than those containing metal or carbon atoms, it is of value to examine the n.m.r. properties of other ten-vertex *nido–arachno* pairs to see whether the overall shielding differences apply also to them, and whether any other interesting features emerge. This has been carried here out for the open SB_9 fragment in the *nido*-6-SB_9H_{11}–*arachno*-$[6\text{-}SB_9H_{12}]^-$ pair [schematic structures (**I**) and (**II**) respectively; note that, in (**I**) and (**II**), BH(*exo*) H atoms, except for H(9) in (**II**), are not represented]. Only the ^{11}B n.m.r. spectra for these compounds have been previously reported, and only for the *arachno* species were these reasonably definitively assigned.[19,20]

Experimental

Samples of 6-SB_9H_{11} [compound (**1**)] and Cs[6-SB_9H_{12}] [compound (**2**)] were prepared according to literature procedures[21] and examined under the conditions specified in the Tables of n.m.r. data. N.m.r. spectroscopy was performed at 9.4 T (400 MHz, ^{1}H; 128 MHz, ^{11}B) using commercially available instrumentation. The techniques of ^{1}H-{^{11}B},[10,22,23] [^{11}B–^{11}B]-COSY,[16,24–28] and [^{1}H–^{1}H]-COSY[27–29] spectroscopy used in this work were essentially as described elsewhere; use being made in the ^{1}H-{^{11}B} experiments of the procedure[10,11,30] in which a ^{1}H-{^{11}B(off-resonance)} spectrum is subtracted from a ^{1}H-{^{11}B(on-resonance)} spectrum in order to remove lines arising from ^{1}H resonances not coupled to the ^{11}B nucleus of interest. In the [^{11}B–^{11}B]-COSY and [^{1}H–^{1}H]-COSY[29] experiments, {^{1}H(broad-band noise)} and {^{11}B(broad-band noise)} decoupling, respectively, were applied, with the {^{11}B} decoupling gated off during the relaxation periods between the pulse–acquire sequences to minimise r.f.

Table 1. Details for the two-dimensional n.m.r. experiments

Compound	SB_9H_{11} (**1**)		Cs[SB_9H_{12}] (**2**)	
COSY experiment	[^{11}B–^{11}B]	[^{1}H–^{1}H]	[^{11}B–^{11}B]	[^{1}H–^{1}H]
Data size (t_2,t_1/words)	512,128	1 024,128	256,64	512,128
Transform size (F_2,F_1/words)	512,256	1 024,512	256,128	512,256
t_2 sweepwidth (=2 × t_1 sweepwidth)/Hz	9 615.0	4 854.4	6 493.5	2 604.2
Digital resolution for F_2 and F_1/Hz	37.6	9.5	50.7	10.2
No. of transients per t_1 increment	64	256	64	144
Recycling time/s	0.12	1.1	0.12	1.1
Mixing pulse/°	45	45	45	45
Window (both t_2 and t_1)	sine-bell squared	sine-bell squared	sine-bell squared	sine-bell squared
Decoupling	{^{1}H}-continuous	{^{11}B}gated	{^{1}H}-continuous	{^{11}B}gated

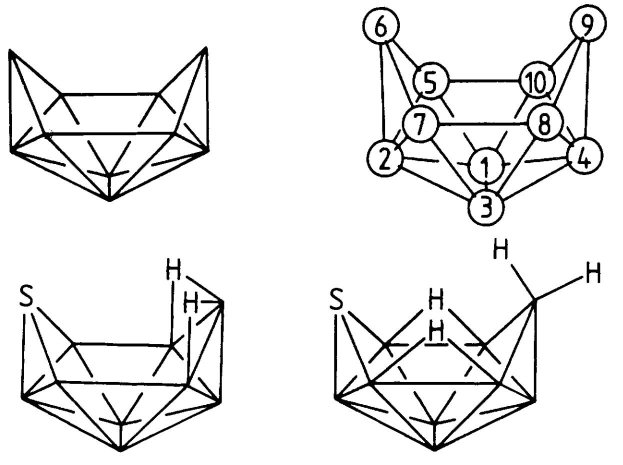


Figure 1. Schematic representation of the ten-vertex *nido–arachno* decaboranyl cluster geometry showing the numbering scheme. *nido*-6-SB_9H_{11} (**1**) has bridging H atoms at B(8)B(9) and B(9)B(10) [see structure (**I**)] and *arachno*-$[6\text{-}SB_9H_{12}]^-$ (**2**) has bridging atoms at B(5)B(10) and B(7)B(8), together with an *endo*-terminal H atom at B(9) [see structure (**II**)]

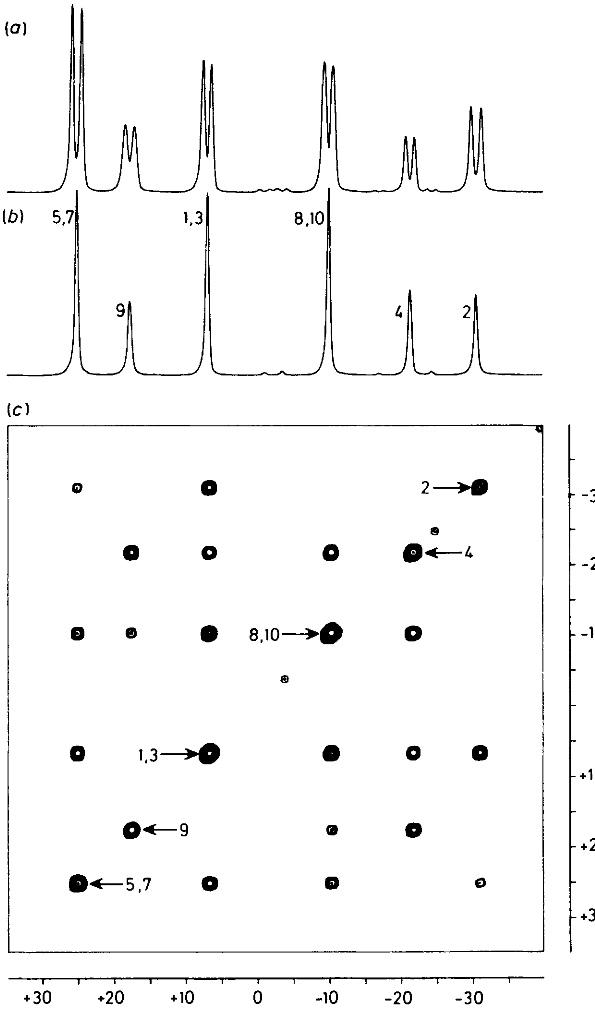


Figure 2. 128-MHz ^{11}B n.m.r. spectra for *nido*-6-SB_9H_{11} (**1**) in CD_2Cl_2 solution. (*a*) Normal ^{11}B spectrum, (*b*) normal spectrum with $\{^1H$(broad-band noise)$\}$ decoupling. In (*a*) a short pre-pulse delay time together with a long $T_1[^{11}B(4)]$ (see Table 2) has resulted in an artificially reduced intensity for the $^{11}B(4)$ resonance. Additional fine structure arising from $^1J(^{11}B-^1H_\mu)$, was apparent for B(9) and B(8,10) in the ^{11}B spectrum [(*a*)] by use of resolution-enhancement techniques (Table 2, footnote *g*). (*c*) $[^{11}B-^{11}B]$-COSY 45 spectrum recorded with $\{^1H$(broad-band noise)$\}$ decoupling

(radio frequency) warming of the sample. The experimental parameters for these COSY experiments are summarized in Table 1. Other spectroscopy was straightforward, longitudinal relaxation times $T_1(^{11}B)$ being measured by the π–delay–$\frac{\pi}{2}$–acquire inversion–recovery method, and chemical shifts, δ, being quoted positive to low field (high frequency) of Ξ 100 for ^1H and Ξ 32.083 971 MHz [nominally $BF_3(OEt_2)$ in $CDCl_3$][4] for ^{11}B (Ξ being defined as in ref. 31). Chemical shifts were measured using solvent deuteron or residual proton resonances as internal secondary standards.

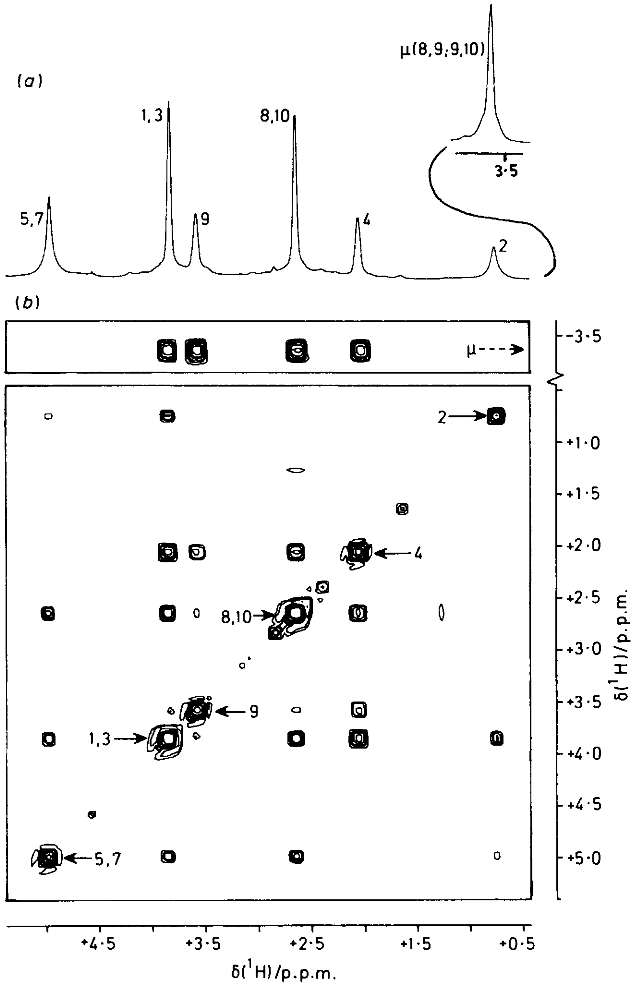


Figure 3. Sections of a 400-MHz $[^1H-^1H]$-COSY 45 spectrum for *nido*-6-SB_9H_{11} (**1**) in CD_2Cl_2 solution, recorded with $\{^{11}B$(broad-band noise)$\}$ decoupling, together with (*a*) the corresponding sections of the ^1H-$\{^{11}B$(broad-band noise)$\}$ spectrum

Results

N.M.R. Behaviour of nido-6-SB_9H_{11} (**1**).—The ^{11}B n.m.r. spectrum of *nido*-6-SB_9H_{11} (**1**) showed a 2:1:2:2:1:1 relative intensity pattern consistent with[19,20] the molecular structure represented in (**I**) (Table 2 and Figure 2). The observation of coupling from the bridging protons to $^{11}B(9)$ and $^{11}B(8,10)$ (see footnote *g* in Table 2) assigned them to these positions and thence the observed $[^{11}B-^{11}B]$-COSY[24] cross-peaks unambiguously assigned the whole ^{11}B spectrum (Figure 2). Definitive $[^{11}B-^{11}B]$-COSY correlations were observed for all nearest-neighbour connectivities, although that between the hydrogen-bridged $^{11}B(9)$ and $^{11}B(8,10)$ positions was somewhat weaker. This, however, is expected since internuclear spin–spin coupling constants between hydrogen-bridged boron atoms are generally small in magnitude.[4,24,32,33] The correlation between the $^{11}B(2)$ and $^{11}B(5,7)$ positions that flank the electronegative sulphur atom S(6) was also weaker. Again, however, a weaker coupling has been generally noted before for interboron connectivities that flank more electronegative cluster atoms,[4] for example carbon in carboranes,[34,35] and sulphur, selenium, and tellurium in chalcogenaborane species,[36,37] and may well result from a diversion of bonding electron density towards bonds with the electronegative element. Conversely, the observed strong correlation $^{11}B(9)-^{11}B(4)$ was manifested by a partially resolvable coupling constant $^1J[^{11}B(9)-^{11}B(4)]$ with a magnitude of *ca.* 30 Hz. As far as we are aware, this is the largest intracluster interboron coupling constant yet observed; much larger, for example, than has been observed for $^1J[^{11}B(9)-^{11}B(4)]$ in ten-boron *nido* ten-vertex species, in which it takes values up to 19 Hz in the examples reported so far.[4,38–40] This

Table 2. Measured ^{11}B and ^{1}H n.m.r. parameters for *nido*-6-SB_9H_{11} (**1**), at 297 K unless otherwise indicated

Assignment[a]	$\delta(^{11}B)$/p.p.m.[b,c] CD_2Cl_2 solution	$\delta(^{11}B)$/ p.p.m.[b] C_6D_6 solution	Observed [^{11}B–^{11}B]-COSY[d,e] correlations, CD_2Cl_2 solution	Approximate $T_1(^{11}B)$/ms saturated CD_2Cl_2 solution[f]	$^1J(^{11}B$–$^1H)$/ Hz[g]	$\delta(^1H)$/ p.p.m.[h] CD_2Cl_2 solution	$\delta(^1H)$/ p.p.m.[h] C_6D_6 solution	a.s.i.s.(^1H)-(C_6D_6)/ p.p.m.[i]	Observed [^1H–^1H]-COSY correlations, CD_2Cl_2 solution[e,j]
(5,7)	+25.3 (2 B)	+25.0	(1,3)s (8,10)s (2)w	17	170	+5.04	+4.97	+0.07	(1,3)m (8,10)s (2)w
(9)	+17.7 (1 B)[k]	+17.7	(8,10)mw (4)s	13	167, 38	+3.88	+3.57	+0.31	(8,10)w (4)m (μ)vs$_2$
(1,3)	+6.6 (2 B)	+6.8	(5,7)s (8,10)vs (4)m (2)s	42	148	+3.55	+3.85	−0.30	(5,7)m (8,10)s (4)s (2)m (μ)vs
(8,10)	−9.9 (2 B)	−10.05	(5,7)s (9)mw (1,3)vs (4)s	28	158, 42	+2.64	+2.65	−0.01	(5,7)s (9)w (1,3)s (4)s (2)vw?$_4$ (μ)vs$_2$
(4)	−21.5 (1 B)[l]	−21.4	(9)s (1,3)m (8,10)s	55	157	+1.76	+2.08	−0.32	(9)m (1,3)s (8,10)s (μ)vs
(2)	−30.7 (1 B)	−30.6	(5,7)w (1,3)s	17	182	+0.64	+0.78	−0.14	(5,7)w (1,3)m (8.10)vw
μ(8,9;9,10)					38, 42	−2.86	−3.40	+0.54	(9)vs$_2$ (1,3)vs (8,10)vs$_2$ (4)vs

[a] By relative intensities, incidence of couplings to μ-H, and two-dimensional [^{11}B–^{11}B]-COSY experiments. [b] ±0.2 p.p.m. to low field (high frequency) of $BF_3(OEt_2)$. [c] Relative intensities in parentheses. [d] {^1H(broad-band noise)} decoupling applied continuously (Table 1). [e] s = Strong, w = weak, m = intermediate, v = very. [f] 298 K. [g] ±2 Hz agreement from both ^1H and ^{11}B spectra with resolution enhancement by apodization. [h] ±0.05 Hz to low field of $SiMe_4$; ^1H resonances related to directly bound B atoms by ^1H-{^{11}B(selective)} experiments. [i] a.s.i.s. = aromatic solvent induced shielding (ref. 42) = [$\delta(^1H)(CD_2Cl_2)$ − $\delta(^1H)(C_6D_6)$]. [j] Recorded with gated {^{11}B(broad-band noise)} decoupling (Table 1); subscripts refer to *n* in $^nJ(^1H$–$^1H)$ when $n \neq 3$. [k] Multiplet structure, splitting *ca.* 31 Hz, presumably arising from $^1J[^{11}B(4)$–$^{11}B(9)]$ in view of strong [^{11}B–^{11}B]-COSY correlation. [l] Unresolved multiplet structure apparent; see footnote *k*.

Table 3. Measured ^{11}B and ^1H n.m.r. parameters for Cs[*arachno*-6-SB_9H_{12}] (**2**) in $(CD_3)_2CO$ solution at 294 K

Assignment[a]	$\delta(^{11}B)$/p.p.m.[b]	Observed [^{11}B–^{11}B]-COSY correlations[c,d]	$^1J(^{11}B$–$^1H)$/Hz[e]	$\delta(^1H)$/p.p.m.[f]	Observed[^1H–^1H]-COSY correlations[c,g]
(4)	+3.6 (1 B)	(9)m (8,10)s (1,3)m	138	+2.79	(9*exo*)s (9*endo*)ms, (8,10)m (1,3)m (μ)w
(5,7)	−8.4 (2 B)[h]	(2)w (8,10)vw? (1,3)s	149 (and *ca.* 41)	+2.43	[(8,10)m (1,3)s (μ)s][i]
(2)	−11.9 (1 B)	(5,7)w (1,3)s	166	+2.42	[(8,10)m (1,3)s (μ)s][i]
(9)	−14.9 (1 B)	(4)m (8,10)s	117 114	+1.42(*exo*)[j] +0.56(*endo*)[k]	(4)s (9*endo*)vs (8,10)m (μ)vw? (4)ms (9*exo*)vs (μ)w?
(8,10)	−33.8 (2 B)[l]	(4)s (5,7)w? (9)s (1,3)s	140 (and *ca.* 47)	+0.37	(4)m [(5,7)(2)]m[i] (9*exo*)m (1,3)s (μ)vs$_2$
(1,3)	−37.1 (2 B)	(4)m (5,7)s (2)s (8,10)s	140	+0.76	(4)m [(5,7)(2)]s[i] (8,10)s (μ)m
μ(7,8;5,10)			*ca.* 36, *ca.* 47	−1.83	(4)w [(5,7)(2)]s[i] (9*exo*)vw? (9*endo*)w? (8,10)vw$_2$ (1,3)m

[a] By relative intensities, incidence of couplings to μ-H, and two-dimensional [^{11}B–^{11}B]-COSY experiments. [b] ±0.5 p.p.m. to low field (high frequency) of $BF_3(OEt_2)$; relative intensities in parentheses. [c] s = Strong, w = weak, m = intermediate, v = very, ? = uncertain. [d] {^1H(broad-band noise)} decoupling applied continuously (Table 1). [e] ±5 Hz; measured from resolution-enhanced ^{11}B and ^1H spectra. [f] ±0.05 Hz to low field of $SiMe_4$; unresolved multiplet structure on most peaks arising from various $^nJ(^1H$–$^1H)$ of ⩽ *ca.* 5 Hz or so. See also footnotes *j* and *k*. [g] Recorded with gated {^{11}B(broad-band noise)} decoupling (Table 1); subscripts refer to *n* in $^nJ(^1H$–$^1H)$ when $n \neq 3$. [h] Fine structure, splitting *ca.* 31 Hz, probably arising from $^1J[^{11}B(5,7)$–$^{11}B(1,3)]$. [i] $\delta[^1H(5,7)]$ and $\delta[^1H(2)]$ accidentally near-coincident, therefore any correlation between these resonances is not observed, and correlations from each resonance not specific. [j] Triplet structure in ^1H-{^{11}B} spectrum, splitting 7.8 Hz, probably arising from couplings $^2J[^1H(9exo)$–$^1H(9endo)]$ and $^3J[^1H(9exo)$–$^1H(4)]$. [k] Triplet structure in ^1H-{^{11}B} spectrum, splitting 6.8 Hz, probably arising from couplings $^2J[^1H(9endo)$–$^1H(9exo)]$ and $^3J[^1H(9endo)$–$^1H(4)]$. [l] Unresolved fine structure, splitting ⩽*ca.* 25 Hz, probably arising from $^1J[^{11}B(8,10)$–$^{11}B(1,3)]$.

may be indicative of a stronger B(4)–B(9) bond in SB_9H_{11} than in $B_{10}H_{14}$, or at least indicative of a linkage containing more boron 2*s* character. It will be instructive to have quantum-mechanical calculations in this area. {See also large $^1J[^{11}B(1,3)$–$^{11}B(5,7)]$ in *arachno*-[6-SB_9H_{12}]$^-$ mentioned below.}

It was evident from smaller observed $^{11}B(4)$ intensities in the initial ^{11}B accumulations that the relaxation time for this resonance was quite long [see (*a*) in Figure 2], and the subsequent measurement of $T_1(^{11}B)$ values for compound (**1**) (Table 2) showed that although they generally parallel those reported previously[41] for *nido*-$B_{10}H_{14}$ they were, with the exception of $T_1[^{11}B(2)]$, in general much longer. However, the solution conditions differed (CD_2Cl_2 for 6-SB_9H_{11} in the present work, $CD_3C_6D_5$ for $B_{10}H_{14}$ in ref. 41), and so the two sets of results are not strictly comparable. It is nevertheless apparent that $T_1(^{11}B)$ for the 2-position is much shorter than would otherwise be expected, which can be accounted for by additional electric field gradient asymmetry at this nucleus presumably induced by the electronegative sulphur atom at the adjacent 6-position.

The proton resonances were traced to their directly bound boron positions by ^1H-{^{11}B} selective double-irradiation experiments. The ^{11}B and *exo*-^1H nuclear shieldings showed the expected[4] parallel (see Figure 5, later), with the slope $\delta(^{11}B)$:$\delta(^1H)$ being *ca.* 14:1, and with the bridging protons at B(8)B(9) and B(9)B(10) resonating at $\Delta\sigma$ *ca.* +6 p.p.m. above this general trend. In [^1H–^1H]-COSY experiments (Table 2 and Figure 3) the interproton correlations arising from $^3J(^1H$–$^1H)$ and $^2J(^1H$–$^1H_\mu)$ confirmed the positional assignments estab-

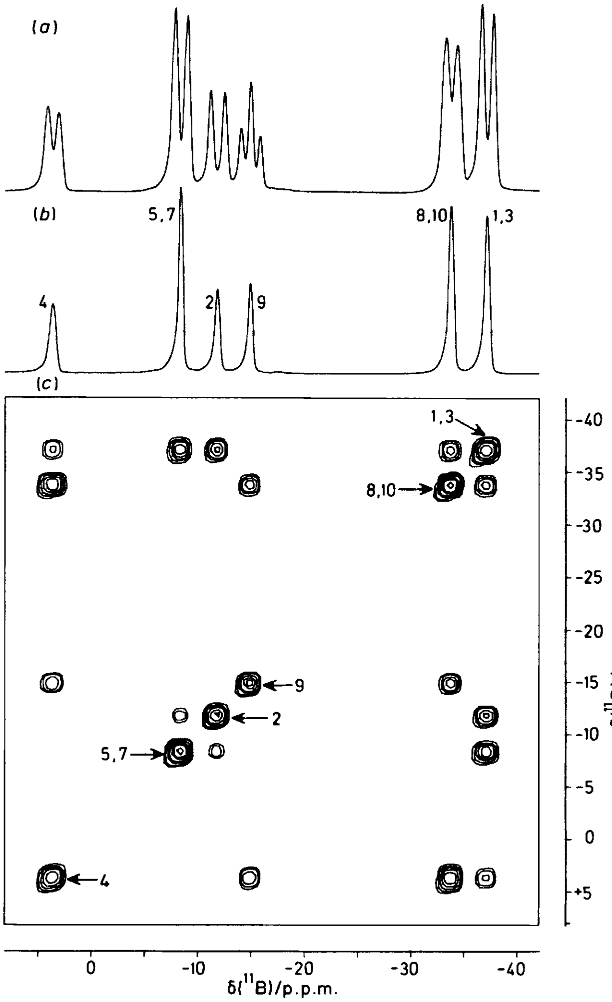


Figure 4. 128 MHz ^{11}B n.m.r. spectra for Cs[*arachno*-6-SB$_9$H$_{12}$] (**2**) in (CD$_3$)$_2$CO solution. (*a*) The straightforward ^{11}B spectrum, (*b*) the straightforward spectrum with {^{1}H(broad-band noise)} decoupling, and (*c*) a [^{11}B-^{11}B]-COSY 45 spectrum recorded with {^{1}H(broad-band noise)} decoupling

lished from the [^{11}B–^{11}B]-COSY results. Interestingly, the relative intensities of the observed correlations often mirrored those of the corresponding ^1J(^{11}B–^{11}B) correlations, with, for example, the ^3J[^{1}H(2)–^{1}H(5,7)] and ^3J[^{1}H(9)–^{1}H(8,10)] cross-peaks being significantly weaker than the others. A second point of interest was the observation of a possible (weak) long-range interproton correlation corresponding to ^4J[^{1}H(2)–^{1}H(8,10)].

The ^{11}B and ^{1}H n.m.r. spectra for *nido*-6-SB$_9$H$_{11}$ (**1**) were also measured in C$_6$D$_6$ solution (Table 2). The aromatic-solvent induced shielding (a.s.i.s.)[42] effects on the ^{11}B shifts were relatively small (*cf.* refs. 40 and 43), but those in the ^{1}H spectrum were relatively more significant. In general the latter ^{1}H a.s.i.s. effects were similar in sign and relative magnitude to those previously reported[23,41,43–45] for B$_{10}$H$_{14}$, but their absolute magnitudes were not so large as for B$_{10}$H$_{14}$ under similar conditions, presumably because the more asymmetric SB$_9$H$_{11}$ molecule does not fit so comfortably in the liquid lattice.

N.M.R. Behaviour of Cs[*arachno*-6-SB$_9$H$_{12}$] (**2**).—Table 3 summarizes the measured ^{11}B and ^{1}H n.m.r. data for the *arachno* species [6-SB$_9$H$_{12}$]$^-$ in a (CD$_3$)$_2$CO solution of Cs[SB$_9$H$_{12}$] (**2**). Again the ^{11}B n.m.r. relative intensity pattern, 1:2:1:1:2:2, was consistent with the molecular symmetry

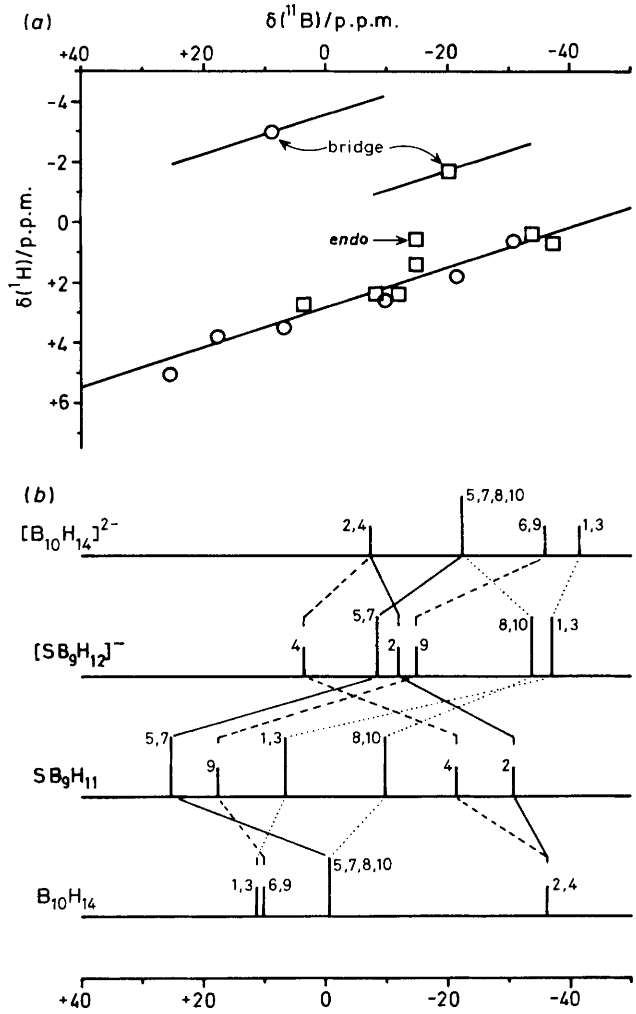


Figure 5. (*a*) A plot of δ(^{11}B) *versus* δ(^{1}H) for directly bound boron and hydrogen atoms in the *nido* compound (**1**) (○) and the *arachno* compound (**2**) (□); the line drawn has intercept δ(^{1}H) +2.8 p.p.m. and slope δ(^{11}B):δ(^{1}H) = 16:1, the slope of the correlation for (**2**) being somewhat greater than this at *ca.* 18:1 and that for (**1**) somewhat smaller at *ca.* 14:1. Points for the bridging protons are plotted *versus* the mean δ(^{11}B) values for their directly bound boron atoms. (*b*) Stick representations of the chemical shifts and relative intensities of (**1**) and (**2**), together with B$_{10}$H$_{14}$ and [B$_{10}$H$_{14}$]$^{2-}$ for comparison; (——) adjacent (α) to the sulphur atom, (– – – –) antipodal and γ to the sulphur atom, and (· · · ·) *meta* (β) to the sulphur atom (*cf.* refs. 28 and S. Heřmánek, J. Fusek, B. Štíbr, J. Plešek, and T. Jelínek, *Polyhedron*, 1986, **5**, 1873)

[structure (**II**)]. The ^{11}B(9) and ^{11}B(5,7)–^{11}B(8,10) resonances were identified as such by the bridge and *endo* ^1J(^{11}B–^{1}H) couplings, and the entire ^{11}B spectrum was thence assigned by [^{11}B–^{11}B]-COSY cross-correlations (Figure 4). As with the *nido* species (**1**) (Table 2 and Figure 2), [^{11}B–^{11}B]-COSY correlations were observed for all nearest-neighbour boron positions, although the relative intensities of cross-peaks for particular cluster-site pairs were generally different for (**1**) *versus* (**2**), as expected from the different *nido versus arachno* cluster electronic structures. Again, however, the ^{11}B(2)–^{11}B(5,7) correlation for the linkage that flanks electronegative sulphur was weak, and the B–H–B bridged linkage, now at ^{11}B(5,7)–^{11}B(8,10) in the *arachno* species (**2**), also exhibited only a weak correlation. Fine structure presumably arising from interboron coupling was observable in the ^{11}B-{^{1}H(broad-band noise)} spectrum for ^{11}B(5,7) and ^{11}B(8,10), the relative strengths of the [^{11}B–^{11}B]-COSY cross-peaks from each of these positions reasonably ascribing the splittings to the couplings ^1J[^{11}B(5,7)–^{11}B(1,3)] and, probably ^1J[^{11}B(8,10)–^{11}B(1,3)] respectively. The apparent magnitudes of these were *ca.* 30 and $\leqslant$ *ca.* 25 Hz respectively, again very large for observed interboron couplings within contiguous borane polyhedra.

The ^{1}H resonances of compound (**2**) were traced to their directly bound boron atoms by ^{1}H-{^{11}B} selective double-irradiation experiments (Table 3) and as with compound (**1**) there was a general parallel between $\delta(^{11}\mathrm{B})$ and $\delta(^1\mathrm{H})$(*exo*), the slope of the correlation, at $\delta(^{11}\mathrm{B}):\delta(^1\mathrm{H})$ *ca.* 18:1, being somewhat greater than observed for the *nido* species (**1**) (Figure 5). A higher $\delta(^{11}\mathrm{B}):\delta(^1\mathrm{H})$ slope for *arachno versus nido* species has been observed elsewhere,[10,13] whereas *closo* species often have a lower value for $\delta(^{11}\mathrm{B}):\delta(^1\mathrm{H})$ (*e.g.* refs. 27, 36, and 37). However, an insufficient number of compounds has been examined to assess the generality of this behaviour. The *endo*-terminal proton on B(9) resonates at $\Delta\sigma$ *ca.* +1 p.p.m. above this general trend, and *exo*-^{1}H(9) at $\Delta\sigma$ *ca.* +3 p.p.m., both within expected[4,9] ranges (note that shielding, σ, takes the opposite sign to chemical shift, δ). Interproton correlations were observed for all the $^3J(^1\mathrm{H}–^1\mathrm{H})$ paths in the [^{1}H–^{1}H]-COSY experiments (Table 3). These, together with the observed $^2J(^1\mathrm{H}–^1\mathrm{H})$ correlations involving the bridging protons, confirm the positional assignments. Fine structure arising from these interproton couplings was apparent on most of the ^{1}H resonance lines in the ^{1}H spectra that were recorded with complete {^{11}B(broad-band noise)} decoupling, some of the fine structure for ^{1}H(9)(*exo*) and ^{1}H(9)(*endo*) being better resolved (footnotes *i* and *j* in Table 3).

Discussion

Comparison of N.M.R. Properties.—It is of interest to compare the n.m.r. shielding patterns of *nido*-6-$\mathrm{SB_9H_{11}}$ (**1**) and *arachno*-$[6\text{-}\mathrm{SB_9H_{12}}]^-$ (**2**) with those of their binary borane analogues, *nido*-$\mathrm{B_{10}H_{14}}$ and *arachno*-$[\mathrm{B_{10}H_{14}}]^{2-}$ respectively, in order to assess the effects of replacing the 6-boron positions with the sulphur heteroatom, and also to compare the shielding pattern of (**1**) with that of (**2**) to see whether the inversion of the ordering of the shielding pattern observed[4–8] for $\mathrm{B_{10}H_{14}} \rightarrow [\mathrm{B_{10}H_{14}}]^{2-}$ is also observed for $\mathrm{SB_9H_{11}} \rightarrow [\mathrm{SB_9H_{12}}]^-$. These comparisons are summarized in Figure 5(*b*) and Figure 5(*a*) shows the $\delta(^{11}\mathrm{B})$–$\delta(^1\mathrm{H})$ correlation data as mentioned above.

There are marked effects upon replacement of BH(6) (plus its associated bridging hydrogen atoms) in $\mathrm{B_{10}H_{14}}$ by sulphur to give the *nido*-6-$\mathrm{SB_9H_{11}}$ species (**1**). The principal effect is a *ca.* 25 p.p.m. deshielding of the ^{11}B(5,7) resonance adjacent to the sulphur, with the other adjacent site, at ^{11}B(2), being relatively little affected; this could be a consequence of the removal of bridging (5,6; 6,7) hydrogen atoms as well as the introduction of the heteroatom, changes in protonation and in effective protonation of polyhedral systems being known to produce significant consequential changes in electronic structure in particular cases.[2–4,7,46,47] Similar changes in $\delta[^{11}\mathrm{B}(5,7)]$, but not generally so marked, occur in the replacement of *nido*-decaboranyl BH(6) (but now not also of its associated bridging hydrogen atoms) by a variety of transition-metal centres.[25,48,49] Associated with this α-deshielding effect at B(5,7) is a significant β-shielding increase at the ^{11}B(8,10) nuclei, and there are also significant γ decreases at the more distant antipodal ^{11}B(4) and open-face ^{11}B(9) positions. A large antipodal effect is not unexpected,[2–4,50–52] but the decrease at the ^{11}B(9) position is of interest, and the occurrence of significant electronic changes at these sites distant from the sulphur atom is also manifested in the anomalously large value for ^1J[^{11}B(4)–^{11}B(9)] as discussed above.

Interestingly, the shielding changes in the *arachno*-$[\mathrm{B_{10}H_{14}}]^{2-}$ skeleton upon replacement of a boron centre by sulphur to give the *arachno*-$[6\text{-}\mathrm{SB_9H_{12}}]^-$ species (**2**) are largely similar to those in the *nido* skeleton in spite of their markedly different electronic structures. Thus there are marked adjacent and antipodal deshielding effects at B(5,7) and B(4) respectively, with a β-shielding effect at B(8,10), whereas the adjacent B(2) and β-B(1,3) positions are relatively little affected. The change at B(5,7) is not so large as in the *nido* species, however, perhaps because no change in bridging hydrogen atoms is involved in the replacement. By contrast the most distant open-face γ position at B(9) undergoes a profound deshielding, of >20 p.p.m., which is unexpected and, taken with the marked changes for ^{11}B(5,7) and ^{11}B(8,10), may well reflect a substantial concerted electronic change in an extended open-face molecular orbital in the *arachno* ten-vertex system.

It can also be seen from Figure 5 that the basic *nido versus arachno* ten-vertex cluster-shielding patterns are retained in the two thiaboranes examined. Although the substituent effects discussed in the last two paragraphs tend to perturb the pattern somewhat, the basic inversion of the cluster nuclear magnetic shielding pattern on effecting the *nido–arachno* interconversion is retained, and the weighted mean ^{11}B chemical shift in the *arachno* species (**2**), at −20.2 p.p.m., is at significantly higher field than that of the *nido* species (**1**), at +1.1 p.p.m. The corresponding values for *arachno*-$[\mathrm{B_{10}H_{14}}]^{2-}$ and *nido*-$\mathrm{B_{10}H_{14}}$ are −26.0 and −2.6 p.p.m. respectively.

Identification of arachno-$[\mathrm{SB_9H_{11}(OH)}]^-$ (**3**).—After standing in acetone solution for some months, partial decomposition of compound (**2**) was noted. The n.m.r. spectra of the products were obtained by difference spectroscopy and were interpretable in terms of only one polyhedral boron-containing product [species (**3**), Table 4, and Figure 6], together with, probably, small amounts of borate products giving rise to resonances[53] with $\delta(^{11}\mathrm{B})$ *ca.* +19 p.p.m. Apart from these borate resonances, the overall ^{11}B n.m.r. behaviour of species (**3**) was very similar to that of (**2**), but with the COSY correlations indicating a different shielding ordering of the three resonances of relative intensity 1 B, the incidence and intensity of the COSY correlations between the numbered cluster positions then being essentially the same as those observed for (**1**).

Table 4. Measured n.m.r. properties for the species identified as [*endo*-9-(OH)-*arachno*-6-$\mathrm{SB_9H_{11}}]^-$ (**3**) in $\mathrm{(CD_3)_2CO}$ solution at 297 K

Assignment[a]	$\delta(^{11}\mathrm{B})$/p.p.m.[b]	$\Delta\sigma(^{11}\mathrm{B})$/p.p.m.[c]	$\delta(^1\mathrm{H})$/p.p.m.[d]
(9)	+7.9 (1 B)	−22.8	+3.89(OH),[e] +2.02
(5,7)	−5.6 (2 B)	−2.8	+2.62
(4)	−7.9 (1 B)	+11.5	+1.98
(2)	−23.9 (1 B)	+12.0	+1.83
(8,10)	−34.4 (2 B)	+0.6	+0.52
(1,3)	−39.9 (2 B)	+2.3	+0.60
μ(5,10;7,8)			−1.79

[a] By relative intensities and observed [^{11}B–^{11}B]-COSY correlations, the latter being similar in incidence and relative intensity to those observed for the unsubstituted species (**2**) (Table 3). [b] ±0.5 p.p.m.; relative intensities in parentheses. [c] $\Delta\sigma = [\delta(^{11}\mathrm{B})(\mathbf{2}) - \delta(^{11}\mathrm{B})(\mathbf{3})]$, and is the increase in ^{11}B shielding observed on substituting compound (**2**) (Table 3) with *endo*-9-hydroxy. [d] ±0.05 p.p.m., $\delta(^1\mathrm{H})$ related to directly bound boron positions by ^{1}H-{^{11}B(selective)} experiments. [e] Only weakly sharpened in ^{1}H-{^{11}B} experiments, indicating a small coupling ascribable to $^2J(^{11}\mathrm{B}–\mathrm{O}–^1\mathrm{H})$.

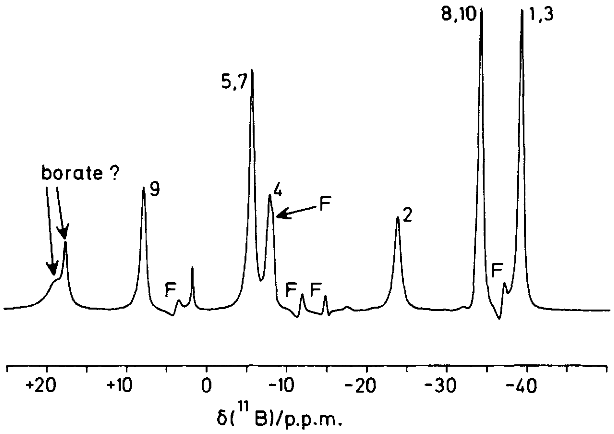
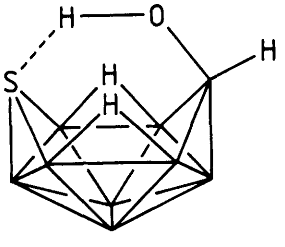


Figure 6. 128 MHz ^{11}B-{^1H(broad-band noise)} difference spectrum showing the [*endo*-9-(OH)-*arachno*-6-SB_9H_{11}]$^-$ anion [species (**3**), numbered as in Figure 1] and borate resonance peaks arising from the hydrolysis of the [*arachno*-6-SB_9H_{12}]$^-$ anion (**2**) in acetone solution. The spectrum was obtained by the subtraction of a spectrum of compound (**2**) (*e.g.* Figure 4) from a partially hydrolysed mixture. The features at the chemical shifts of species (**2**) (marked 'F') arise from an imperfect subtraction that arose because of unsuspected field homogeneity changes that occurred in the months between recording the two spectra



(**III**)

This consideration, together with the absence of an *endo*-terminal ^1H resonance associated with $^{11}B(9)$ (see ref. 10) then indicated that species (**3**) is a 9-*endo*-substituted *arachno*-[6-SB_9H_{11}]$^-$ cluster anion closely related to (**2**). The substituent is reasonably indentifiable as *endo*-9-hydroxy on the basis of the *ca.* 20 p.p.m. negative substituent chemical shift effect $\Delta\sigma$ (reasonably ascribable to alkoxy, hydroxy, or oxy),[4,11,23,54,55] together with a marginal sharpening of the resonance at $\delta(^1H)$ +3.89 [1 H, reasonably ascribable to OH] in ^1H-{$^{11}B(9)$} selective irradiation experiments. An anion of this [9-(OH)-*arachno*-6-SB_9H_{11}]$^-$ formulation has previously been reported.[20] The essential identity of the ^{11}B shielding behaviour of (**3**) with this previously reported species confirms the formulation. This proposed identification of (**3**) as [*endo*-9-(OH)-*arachno*-6-SB_9H_{11}]$^-$ together with the other observed ^{11}B data would imply positive hydroxy substituent shielding effects $\Delta\sigma$ of *ca.* + 10 p.p.m. for $^{11}B(8,10)$ (adjacent) and $^{11}B(2)$ (antipodal) [both within reasonably expected ranges],[23,54] the other positions being largely unperturbed from those of the unsubstituted species (**2**).

The hydroxy anion (**3**) is probably formed *via* hydrolysis by fortuitous moisture in the samples of acetone solvent used. Its incidence and the formation of the *endo* configuration, as opposed to the *exo* configuration and/or a general decomposition to borate, being presumably stabilized by O–H $\cdots$ S interaction with the 6-sulphur *endo* lone pair as indicated in (**III**). The *endo,endo* chelating effect resulting in cluster stabilization has been noted elsewhere in ten-vertex *arachno* chemistry.[8,10,56]

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