POLYHEDRAL AZABORANE CHEMISTRY: NMR PARAMETERS FOR THE UNIQUE EIGHT-BORON POLYHEDRAL SPECIES [(C₂H₅NH₂)B₈H₁₁NHC₂H₅]

Peter MacKinnon, Xavier L. R. Fontaine, John D. Kennedy[1] and Paul A. Salter

School of Chemistry, University of Leeds, Leeds LS2 9JT, England;
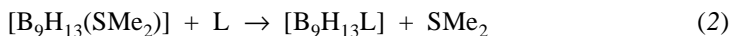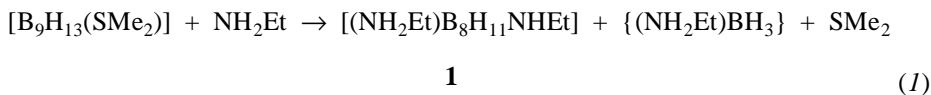*e-mail: [1] johnk@chem.leeds.ac.uk*

Boron (^{11}B) and hydrogen (^{1}H) NMR parameters have been measured for the unique polyhedral aza-borane species [(NH₂Et)B₈H₁₁NHEt)] using single- and double-resonance experiments and two-dimensional shift-correlation methods. Comparison with the NMR properties of other eight-boron species, in particular *arachno*-[B₈H₁₂(PMe₂Ph)], suggests that cluster of [(NH₂Et)B₈H₁₁NHEt] may be better regarded as being of *hypho* character, rather than of *arachno* character as previously supposed.

Key words: Borane; Azaborane; Cluster; NMR.

A principal hindrance to the development of the chemistry of polyhedral boron-cluster compounds that contain about eight boron atoms is the difficulty of obtaining suitable eight-boron starting materials. An important exception to this generalization is the unique synthesis of the unusually structured species [(NH₂Et)B₈H₁₁NHEt] (compound **1**, Fig. 1), readily obtainable in 70% yield by the treatment of *arachno*-[B₉H₁₃(SMe₂)] with ethylamine (idealized stoichiometry as in Eq. (*1*), refs[1,2]). This is generally re-garded as a maverick synthesis, because other ligands L (where L = MeCN, PPh₃, NEt₃, NC₅H₅ and NHEt₂) merely displace SMe₂ from the starting substrate to give *arachno* nine-vertex species [B₉H₁₃L] (Eq. (*2*), refs[1,2]).

$$[B_9H_{13}(SMe_2)] + NH_2Et \rightarrow [(NH_2Et)B_8H_{11}NHEt] + \{(NH_2Et)BH_3\} + SMe_2$$

$$\mathbf{1} \tag{1}$$

$$[B_9H_{13}(SMe_2)] + L \rightarrow [B_9H_{13}L] + SMe_2 \tag{2}$$

Since [B₉H₁₃(SMe₂)] itself can be readily obtained in yields of at least 70% (refs[1,3]) from readily available *nido*-decaborane, B₁₀H₁₄, the octaborane species [(NH₂Et)B₈H₁₁NHEt] (**1**) constitutes a potentially important starting material for eight-boron work, particularly so in view of its unique constitution. In this regard, for

example, we have found in preliminary experiments in our laboratories that it reacts with [PtCl$_2$(PMe$_2$Ph)$_2$] to give the novel seven-boron *arachno*-type azaplatinaborane[4,5] [(PMe$_2$Ph)$_2$PtB$_7$H$_{10}$NHEt] (**2**) and with [Rh(C$_5$Me$_5$)Cl$_2$]$_2$ and NaH to give the seven-boron *closo*-type azadirhodaborane[6] [(C$_5$Me$_5$)RhB$_7$H$_7$NEt] (**3**). However, since the initial synthesis and structural characterization of compound **1**, now nearly 35 years ago[1,2], no further studies have been reported, and, in particular, no NMR investigations have since been carried out. NMR delineation of structural types is an important feature in the development of polyhedral boron chemistry[7–10]. Here we therefore report the detailed NMR analysis that we have carried out on compound **1** in order to assess its relationship with other known[11–17] open eight-vertex and eight-boron systems, and for its ultimate comparison with novel eight-vertex heteroborane types, such as the metallaborane [(CO)$_4$WB$_7$H$_{12}$]$^-$ anion[18] and the azaplatinaborane[4,6] **2** mentioned above.

EXPERIMENTAL

Preparation of [(NH$_2$Et)B$_8$H$_{11}$NHEt] (**1**)

Compound **1** was prepared by the treatment of [B$_9$H$_{13}$(SMe$_2$)] with NH$_2$Et as in ref.[1]. The [B$_9$H$_{13}$(SMe$_2$)] was made from B$_{10}$H$_{14}$ *via* [B$_{10}$H$_{12}$(SMe$_2$)$_2$] as described in the same reference. The results for [(PMe$_2$Ph)B$_8$H$_{12}$] (**4**) were measured for a sample obtained as a by-product in yields of up to 2% from the thermolysis of [4,4-(PMe$_2$Ph)$_2$-*arachno*-4-PtB$_8$H$_{12}$] in refluxing benzene or toluene solution, as described in ref.[5].

Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy was carried out on commercially obtained Bruker AM 400 (*ca* 9.4 T) and JEOL FX100 (*ca* 2.35 T) instruments using general techniques as described elsewhere[19–22] and as sum-
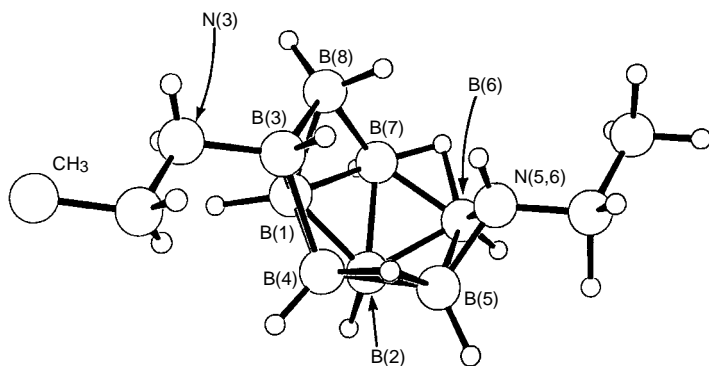

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Molecular structure of [(NH$_2$Et)B$_8$H$_{11}$NHEt] (**1**) as determined by single-crystal X-ray diffraction analysis (data from ref.[2]). Interboron distances were found to be in the range 172.6(9)–191.9(0) ppm, except for B(1)–B(3) at 170.9(10) and B(5)–B(6) at 198.9(9) ppm. There was no asymmetry in the bridging hydrogen-atom positions within crystallographic experimental error

marised and exemplified by Reed[9]. ^{11}B relaxation times $T_1(^{11}\text{B})$ were determined at 9.4 T using the inversion-recovery method under conditions of complete {^{1}H} decoupling. Chemical shifts δ are given in ppm to high field of Ξ 100 MHz (TMS) for ^{1}H (quoted ±0.05 ppm) and Ξ 32.083 971 MHz (nominally F_3BOEt_2 in $CDCl_3$) (ref.[8]) for ^{11}B (quoted ±0.5 ppm), Ξ being defined as in ref.[23].

RESULTS

At 128 MHz the ^{11}B NMR spectrum of $[(NH_2Et)B_8H_{11}NHEt]$ (**1**) showed eight distinct resonance positions of relative intensity one (Table I). All except ^{11}B(8) exhibited 1 : 1 doublet structure arising from couplings $^1J(^{11}\text{B}-^1\text{H})$. The ^{11}B(8) resonance had an effective 1 : 2 : 1 triplet structure arising from couplings to the two protons in the BH_2 group in that position (see Fig. 1) and identified it as such. The results of $[^{11}\text{B}-^{11}\text{B}]$-COSY experiments (Table II and Fig. 2) identified the resonances of the apical B(1) and B(2) positions, since each was correlated with five other positions. The strong correlation between ^{11}B(8) and ^{11}B(1) identified the latter as ^{11}B(1) rather than ^{11}B(2), and interboron correlations thence assigned the other positions, ^{11}B(2), ^{11}B(3), ^{11}B(4) and ^{11}B(7), around the base of the pentagonal pyramidal fragment that has B(1) as apex. In some $[^{11}\text{B}-^{11}\text{B}]$-COSY experiments, very weak (4)–(5) and (6)–(7) cross peaks were observable, thereby assigning the two remaining positions, ^{11}B(4) and ^{11}B(5), of the pentagonal pyramidal fragment based on B(2) as apex (although their distinction is perhaps not too critical in terms of current theory, since BH(5) and BH(6) have very similar ^{11}B and ^{1}H chemical shifts, and $\delta(^1\text{H})(\mu\text{-}4,5)$ and $\delta(^1\text{H})(\mu\text{-}6,7)$ are also very
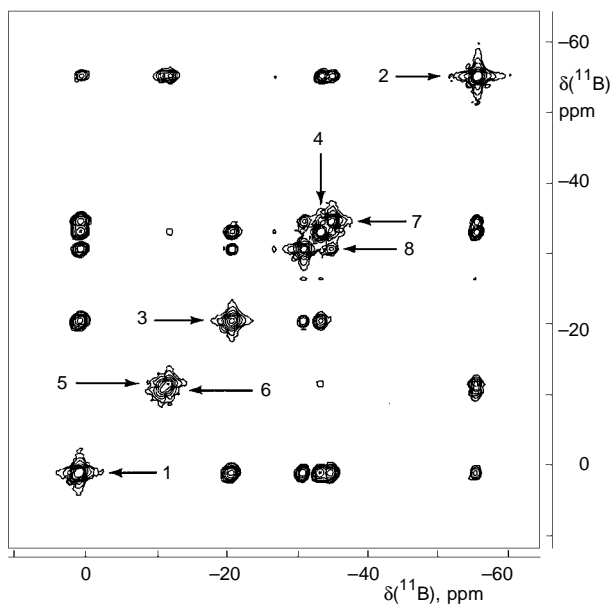

Fig. 2
128 MHz two-dimensional $[^{11}\text{B}-^{11}\text{B}]$-COSY spectrum of $[(NH_2Et)B_8H_{11}NHEt]$ (**1**), recorded under conditions of complete {^{1}H} broad-band noise decouping

similar). Some differential [^{11}B-^{11}B]-COSY effects were noted either side of the plane passing through B(1), B(2) and the midpoints of B(3)–B(8) and B(5)–B(6), for example the (3,4) correlation appeared to be much stronger than the (7,8) one. Selective ^{1}H-{^{11}B} decoupling experiments assigned the terminal and bridging ^{1}H resonances (Table I and Fig. 3) to their corresponding boron positions, and in these experiments stronger couplings of the μ(4,5) and μ(6,7) bridging hydrogen atoms to the "hinge" (4) and (7) ^{11}B resonances, compared to those to the (5) and (6) ^{11}B resonances, were apparent. A similar differential coupling was also apparent for the analogous positions in [(PMe$_2$Ph)B$_8$H$_{12}$] (**4**). In compound **1** these differential coupling effects to the bridging positions were parallelled in the relative strengths of the correlations in two-dimensional [^{11}B-^{1}H]-HETCOR[7] experiments, which also generally confirmed the other ^{1}H assignments from the one-dimensional ^{1}H-{^{11}B(selective)} work. The proton assign-

TABLE I
Measured ^{11}B and ^{1}H NMR parameters for [(NH$_2$Et)B$_8$H$_{11}$NHEt] (**1**) (saturated (CD$_3$)$_2$CO solution at 292 K) together with those for [(PMe$_2$Ph)B$_8$H$_{12}$] (**4**) (CDCl$_3$ solution at 294–297 K)

Assigment	Compound **1**[a]			Compound **4**[b]	
	δ(^{11}B)	≈T_1(^{11}B), ms	δ(^{1}H)	δ(^{11}B)	δ(^{1}H)
(1)	+1.1	17.3	+2.55	–0.8	+2.38
(2)	–55.2	31.0	–0.69	–53.0	–0.45
(3)	–20.5[c]	6.7	+1.09[d]	–37.9[e]	+0.34[d,f]
(4)	–33.1	11.1	+0.59	–7.3	+2.56
(5)	–11.5	4.4	+2.28	+5.3	+3.47
(6)	–10.7	4.0	+2.32	+0.2	+3.19
(7)	–34.6	8.6	+0.50	–2.8	+2.94
(8)	–30.7	7.6	+0.55, –0.56	–25.6	+1.09,+1.13
(4,5)	–	–	–2.22		–1.91
(5,6)	–	–	–1.08[g]		–2.46
(6,7)	–	–	–2.14		–1.76

[a] For details of assignment see text. [b] Assigned by [^{11}B-^{11}B]-COSY correlations (Table II), together with the identification of ^{11}B(3) by its coupling to ^{31}P, and by the selective sharpening of ^{1}H(bridge) resonances in ^{1}H-{^{11}B(selective)} experiments. [c] {NH$_2$Et} substituent site; δ(^{1}H)(NH$_2$) at +5.49 and +5.39; δ(^{1}H)(CH$_2$) at +3.04 and +3.05 [AB part of ABMNX$_3$ system, ^3J(^{1}H-N-C-^{1}H) *ca* 8 Hz], δ(^{1}H)(CH$_3$) at +1.35 ppm. [d] *endo*-Type positions. [e] {PMe$_2$Ph} substituent site; 1 : 1 doublet in ^{11}B-{^{1}H} spectrum, ^1J(^{31}P-^{11}B) 115 ± 10 Hz. [f] Also δ(^{1}H)(PMe$_2$) at +1.71 and +1.73 ppm; ^2J(^{31}P-^{1}H) *ca* 10.5 Hz in each case. [g] Refers to δ(^{1}H)(NH) of the {NHEt} group; additionally δ(^{1}H)(CH$_2$) at +2.62 and +2.63 ppm (AB part of ABMX$_3$ system, ^3J(^{1}H-N-C-^{1}H) *ca* 8 Hz); δ(^{1}H)(CH$_3$) at +1.03 ppm.

TABLE II
Observed [^{11}B-^{11}B]-COSY correlations for [(NH$_2$Et)B$_8$H$_{11}$NHEt] (**1**) (saturated (CD$_3$)$_2$CO solution at 292 K) and for [(PMe$_2$Ph)B$_8$H$_{12}$] (**4**) (CDCl$_3$ solution at 294–297 K)

Position	Compound **1**		Compound **4**	
	$\delta(^{11}\text{B})$	[^{11}B-^{11}B]-COSY	$\delta(^{11}\text{B})$	[^{11}B-^{11}B]-COSY
(1)	+1.1	(2)m (3)vs (4)s (7)vs (8)s	–0.8	(2)w (3)m (4)s (7)ms (8)m
(2)	–55.2	(1)m (4)s (5)s (6)s (7)m	–53.0	(1)w (4)m (5)m (6)s (7)w
(3)	–20.5	(1)vs (4)s (8)w	–37.9	(1)m (4)m
(4)	–33.1^b	(1)s (2)s (3)s	–7.3	(1)s (2)m (3)m
(5)	–11.5^b	(2)s	+5.3	(2)m
(6)	–10.7^b	(2)s	+0.2	(2)s
(7)	–34.6^b	(1)vs (2)m (8)w	–2.8	(1)m (2)w
(8)	–30.7	(1)s (3)w (7)w	–25.6	(1)m

^{a} Correlations weaker for compound **4** because of greater relaxation-induced broadening arising from larger molecular bulk. ^{b} In some experiments very weak (4)–(5) and (6)–(7) correlations were observed for compound **1**.

Fig. 3
The lower two diagrams are stick representations of the chemical shifts in the ^{11}B NMR spectra of [(NH$_2$Et)B$_8$H$_{11}$NHEt] (compound **1**, upper trace) and [B$_8$H$_{12}$(PMe$_2$Ph)] (compound **4**, lower trace), with hatched lines joining equivalent positions in the two molecules (for numbering see Figs 1 and 4). The upper diagram is a plot of $\delta(^1\text{H})$ *versus* $\delta(^{11}\text{B})$ for directly attached B–H *exo* units (○ compound **1**; □ compound **4**), with the solid line having gradient $\delta(^1\text{H}) : \delta(^{11}\text{B})$ *ca* 1 : 16.5 and the hatched line *ca* 1 : 13.
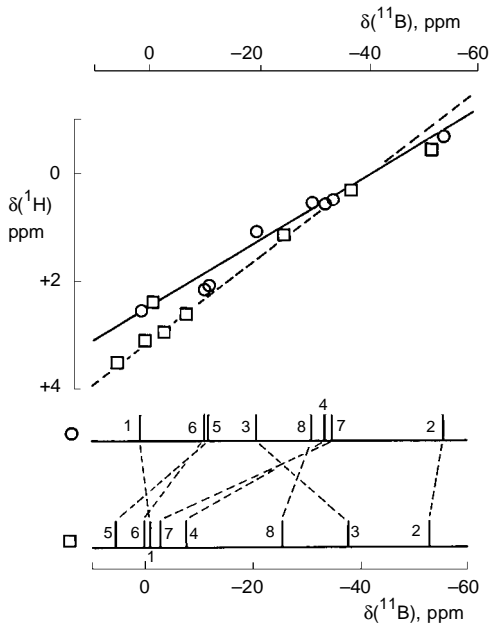
ments revealed a general parallel between $\delta(^1H)$ and $\delta(^{11}B)$ for the BH(*exo*) units. It is of interest that the *endo* BH protons of the B(3) positions of both **1** and **4**, and of the B(8) position of compound **4**, are also close to these BH(*exo*) correlation lines, whereas the *endo* B(8) position in compound **1** is more shielded at *ca* 1 ppm above the general correlation, as is more typical of *endo*-type hydrogen positions[8]. The (4,5) and (6,7) bridging hydrogen atoms, on the other hand, have ^1H shieldings *ca* 4 ppm above the general BH(*exo*) correlation, as is typical for bridging hydrogen atoms.

The ^1H-{^{11}B} selective decoupling experiments also generated selective sharpening of the CH_2 protons of the µ-(5,6)-NHEt group upon irradiation of the $^{11}B(5)$ and $^{11}B(6)$ resonances, and of the CH_2 protons of the 3-NH_2Et group upon irradiation of the $^{11}B(3)$ resonance. These results indicate small but finite couplings $^3J(^{11}B$-N-C-$^1H)$ in each case. The assignments of the CH_2 protons implicit in these last experiments were confirmed by the results of [^1H-^1H]-COSY work, which correlated the protons of the CH_2 group of the µ-(5,6)-NHEt moiety with its corresponding CH_3 protons and with the NH proton resonance of relative intensity 1 H, and which similarly correlated the protons of the CH_2 group of the 3-NH_2Et moiety with its corresponding CH_3 protons and with the NH_2 proton resonance of relative intensity 2 H. There is a marked difference in the shielding of the nitrogen-bound amine protons when the two positions are compared. That of the µ-(5,6)-NHEt group, which is held in an *endo* position above and close to the open face, is considerably shielded, at $\delta(^1H)$ –1.08 ppm. As noted in ref.[2], this position is sterically quite restricted. It is also noted that, because of the asymmetry of compound **1**, the two hydrogen atoms associated with each of the two CH_2 groups are chemically distinct and have slightly different proton chemical shifts. The same consideration applies to the two hydrogen atoms on the NH_2 grouping on the (3)-position (Table I and its footnotes).

Inversion-recovery experiments were carried out to determine the spin-lattice relaxation times T_1 of the ^{11}B nuclei of compound **1** (Table I). The apical $^{11}B(1)$ and $^{11}B(2)$ nuclei had significantly longer relaxation times than the other positions, indicating a greater symmetry of electron distribution about the apical positions. Of the two, the much more highly shielded $^{11}B(2)$ nucleus has a significantly longer relaxation time. Within the set of non-apical positions, there also appears to be a general increase in T_1 (^{11}B) as the nuclear shielding increases, suggesting a parallel between the symmetry of electronic distribution and the electronic circulation about a particular nucleus, as noted elsewhere for other compounds (see, for example, ref.[8]).

DISCUSSION

In the first instance, it is of interest to compare the ^{11}B cluster shielding pattern of [$(NH_2Et)B_8H_{11}NHEt$] (**1**) with those of the substituted eight-vertex *arachno* boranes [$B_8H_{12}L$], where L = NMe_3, MeCN, [NCS]$^-$, *etc*., since it has been suggested that they have closely related structures[2,13,17]. Relevant data are gathered in Table I. The lower

two diagrams in Fig. 3 compare the shielding pattern for compound **1** with that for the ligand derivative *arachno*-[$B_8H_{12}(PMe_2Ph)$] (**4**), the latter being a typical neutral *arachno*-[$B_8H_{12}L$] species for which we also present the results here for comparison purposes (Tables I and II). Figure 4 shows the *connectivity* (as distinct from *bonding*) topologies for the two compound types. Although the structures of the *arachno* octaboron [$B_8H_{12}L$] species have not been confirmed crystallographically, they are reasonably presumed[17,24] to have the [3-L-B_8H_{12}] *arachno* configuration as shown in Fig. 4. This connectivity topology is related to that[1,2] of compound **1**, but with a three-centre two-electron B–H–B link between B(5) and B(6) (compound **4**) rather than the two two-electron two-centre B–N links observed[1,2] in compound **1**.

It can be seen that, whereas the [11]B shielding at the BH$_2$(8) position and at the apical BH(1) and BH(2) positions are very similar for compounds **1** and **4**, there are significant differences (*a*) at the ligand-substituted B(3) positions, (*b*) at the bridged BH(5)BH(6) positions, and (*c*) at the "hinge" BH(4)BH(7) positions. These differences are discussed briefly as follows:

(*a*) The downfield shift at BHL(3) upon change from a phosphine ligand substituent L in compound **4** to an amine in compound **1** is within expected α-substituent effect ranges, and is thereby not remarkable (compare BH$_3$L species, where L = NR$_3$, NHR$_2$, PR$_3$, *etc.*, listed in ref.[25], and also nine-vertex eight-boron species SB$_8$H$_{10}$L and HNB$_8$H$_{10}$L in refs[26,27]). By contrast, (*b*) the upfield shifts for BH(5) and BH(6) upon notional replacement of B–H–B in compound **4** by B–N–B (compound **1**) are much smaller (*ca* 10–15 ppm) than those usually encountered upon the replacement of a three-centre two-electron B–H–B link by a B–N–B link that involves two two-electron two-centre B–N bonds (compare, for example[28], B_2H_6 with $B_2H_5NH_2$, B_2H_5NHR and $B_2H_5NR_2$; differences *ca* 40–45 ppm). This could imply a relief of steric strain, and/or
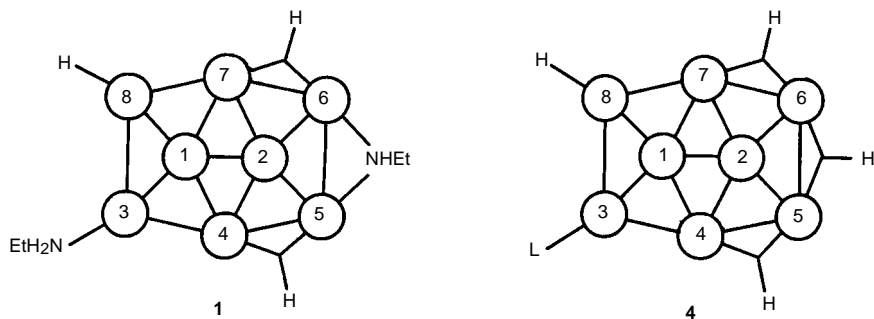

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Schematic connectivity diagrams for (top) [(NH$_2$Et)B$_8$H$_{11}$NHEt] (compound **1**) (see also Fig. 1) and (bottom) the reasonably supposed structure[2,13,17] for *arachno* octaboranes B$_8$H$_{12}$L, where L = NMe$_3$, CH$_3$CN, PMe$_2$Ph (compound **4**), [NCS]$^-$, *etc.* In addition to the *endo*-terminal and bridging hydrogen atoms shown, and in addition to the substituents shown, each boron atom is bound to an *exo*-terminal hydrogen atom *via* one two-electron two-centre σ-bond each

a concomitant more fundamental change in cluster electronic structure. The latter explanation tends to be supported (*c*) by the dramatic (*ca* 30 ppm) increase in [11]B shielding at the "hinge" BH(4) and BH(7) units which are β to the substituted boron atoms: if the structures are isostructural in electronic as well as in geometric terms they should also be "isospectral" (ref.[10]): this is clearly not so.

One significant net effect of these differences is one of a large overall shielding increase for the cluster [11]B atoms in the azaborane [(NH$_2$Et)B$_8$H$_{11}$NHEt] (**1**) compared to [B$_8$H$_{12}$(PMe$_2$Ph)] (**4**). The mean [11]B chemical shift for compound **1** is *ca* –24 ppm, which is some 10 ppm per boron site more shielded than the mean cluster [11]B shieldings for the *arachno* octaborane compound **4**, as well as for other *arachno* octaboranes[4,5,11,14,17] B$_8$H$_{12}$L, and for *arachno*-B$_8$H$_{14}$ itself[11,16], of which each averages in the approximate range δ([11]B) –14 to –16 ppm. The [11]B shieldings[11,13,14] of *nido*-B$_8$H$_{12}$ average even lower, at about δ([11]B) –3 ppm. Taken with the specific site effects discussed in the previous paragraph, these overall shielding differences suggest that the azaborane [(NH$_2$Et)B$_8$H$_{11}$NHEt] (**1**) is not of straightforward *arachno* eight-vertex structural type. In this context we note that the species B$_8$H$_{16}$ (ref.[12]) of formally *hypho*-B$_n$H$_{n+8}$ formulation (but of as yet unknown structure), also has a higher average [11]B shielding, at δ([11]B) *ca* –28 ppm. This is comparable to that of the azaborane **1**. Additionally, the better characterised eight-vertex *hypho* species [C$_2$B$_6$H$_{13}$]$^-$ and [CSB$_6$H$_{11}$]$^-$ also have such higher δ([11]B)(mean) values, of –27.4 and –23.7 ppm, respectively[29,30]. These factors suggest that the electronic structure of the azaborane **1** corresponds more closely to a *hypho* type species rather than an *arachno* one. In accord with this idea, notional replacement of (i) the three two-electron two-centre bonds from the two nitrogen atoms to the B(3), B(5) and B(6) atoms with (ii) three two-electron two-centre bonds to three hydrogen atoms, results in the compound being better regarded as an analogue of the *hypho* binary borane equivalent {B$_8$H$_{14}$}$^{2-}$ and not an analogue of *arachno*-{B$_8$H$_{13}$}$^-$ as originally[2] suggested. Further in accord with this, there is some resemblance to the *hypho* eight-vertex species CH$_2$S$_2$B$_6$H$_9$ (δ([11]B)(mean) –24.7 ppm) that also has a bridge (albeit involving C rather than N) that involves two two-electron two-centre bonds[22]. Here it may also be noted that the *arachno*-{B$_8$H$_{13}$}$^-$ anion, not yet isolated, would also be in the *arachno*-[B$_8$H$_{12}$L] category: in this case the two-electron ligand L would be H$^-$, the hydride ion. These ^{11}B NMR shielding differences suggest that the principal electronic differences between the two cluster types, *arachno* and *hypho*, are not only at the nitrogen-bridged B(5) and B(6) positions (which is not surprising), but also, more interestingly, at the "hinge" B(4) and B(7) sites, both β to the site of the bridging nitrogen substituent. In cluster-geometry terms, the boron-atom arrangement of compound **1** (Figs 1 and 4) is compatible with a *hypho* formalism as well as with an *arachno* formalism. This is because it may be generated by removal of a vertex from an *arachno* nine-vertex geometry such as that of the *iso* type of B$_9$H$_{15}$

skeleton, as well as by removal of a vertex from the classical *nido* nine-vertex geo-
metry.

There might also be differing trends in the ^1H shielding between the *arachno*-
$[B_8H_{12}L]$ species typified by the phosphine compound **4** and the *hypho* structure type of
the azaborane species **1**. Thus, within the overall general parallel between the ^1H and
^{11}B shieldings for BH(*exo*) units for the two compounds (Fig. 3, upper trace), it appears
that the $\delta(^1H) : \delta(^{11}B)$ correlation slope of *ca* 1 : 16.5 (solid line) for compound **1** may
be somewhat smaller than that of the *arachno* compound **4** (*ca* 1 : 13 (hatched line)). It
is often found that in a set of otherwise closely related systems there is a decrease in the
coefficient for this type of $\delta(^1H) : \delta(^{11}B)$ correlation as compounds on a *closo* → *nido*
→ *arachno* sequence are successively examined for this effect[8,21,32]. The further
possible decrease from *arachno* to *hypho*, as suggested here, would be in accord with
an extension of this progressive effect to include *hypho*. However, these sorts of trends
are not always clear cut, and it should also be recognised that ^1H shifts in particluar will
be subject to local ligand-induced anisotropic field variations[8] independent of the basic
individual cluster shielding patterns.

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