Arachno-6,9-Diazadecaborane(12), [6,9-$N_2B_8H_{12}$], an Unsubstituted Contiguous Cluster Diazaborane

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The contiguous diazaborane cluster compound, [*arachno*-6,9-$N_2B_8H_{12}$], has been isolated from the reaction between Na(NO_2) and either [*arachno*-6-(MeCN)-9-NB_9H_{12}] or [*nido*-6-NB_9H_{12}] in tetrahydrofuran (THF) solution.

There is considerable scope for the development of contiguous azaborane chemistry, but the only known unsubstituted azaborane building blocks are limited to the three monoazaboranes [*arachno*-4-NB_8H_{13}],[1] [*nido*-6-NB_9H_{12}],[2,3] and [*closo*-1-NB_9H_{10}][4] (**I**, **II** and **III** respectively). Of these, only [*arachno*-4-NB_8H_{13}][1] and [*nido*-6-NB_9H_{12}],[2,3] can be made in yields reasonable enough for convenient further work. Our two laboratories have for some time been developing their chemistry and that of their metal derivatives,[5–7] and have been interested in extending the work to contiguous polyazaboranes, *i.e.* those that have more than one electron-rich nitrogen centre in the cluster. The only viable method that has so far proved effective for the introduction of the (NH) vertex into borane clusters is that based on the reaction of sodium nitrite with borane[1,3] or carbaborane[6,8] substrates. We now report preliminary findings on the reactions of sodium nitrite with representatives of the ten-vertex *nido*- and *arachno*-families of monoazaboranes, from which we have isolated the first unsubstituted contiguous polyhedral diazaborane, [*arachno*-6,9-$N_2B_8H_{12}$] (Fig. 1 and structure **IV**). As far as we are aware, the only previously characterised cluster diazaboranes are the completely substituted *nido*-type species [$Bu^t_2N_2B_4R_2R'_2$] (where R : R' = Me : Me, Pr^i : Pr^i, and Bu^t : Pr^i, structure **V**),[9] in which the chemistry will be largely dictated by the peralkylation.

Treatment of [*arachno*-9-(MeCN)-6-NB_9H_{12}][2,3] or [*nido*-6-NB_9H_{12}][2,3] (reaction scale *ca.* 20 mmol) with a threefold excess of sodium nitrite (THF solution, 6 h, ambient temperature), followed by acidification (CF_3CO_2H), extraction with n-hexane, and chromatographic separation (TLC; silica-gel; benzene–hexane 1 : 2) gave two products. One of these was the known[1] [*arachno*-4-NB_8H_{13}] [compound **1**; 31%; R_F 0.41 (anal.), *ca.* 0.45 (prep.); identified by NMR spectroscopy]. Vacuum sublimation of the second TLC component gave the second product [compound **2**; 4% (as yet unoptimised); R_F 0.31 (anal.), 0.35 (prep.); m.p. 23 °C], which was identified by NMR and mass spectrometry as [*arachno*-6,9-$N_2B_8H_{12}$]. The NMR data† are clearly compatible with the C_{2v} symmetry and the *arachno* ten-vertex [6,9-$N_2B_8H_{12}$] cluster configuration proposed for compound **2** (Fig. 1 and structure **IV**), and additionally they show the two mutually equivalent bridging hydrogen atoms at B(5)B(10) and B(7)B(8) and the two mutually equivalent cluster (NH) units. These latter are reasonably positioned[10] at the cluster vertices of least connectivity. In addition there is excellent correlation between the ^{11}B and ^1H shielding patterns of individual (BH) units in compound **2** and equivalent positions in the known isoelectronic and isostructural *arachno* ten-vertex series[11] [$B_{10}H_{14}$]$^{2-}$, [6-CB_9H_{14}]$^-$, and [6,9-$C_2B_8H_{14}$]. The observed high-mass cut-off in the mass spectrum‡ at *m/z* 126 is consistent with ready loss of dihydrogen from the molecular ion, a phenomenon often encountered with *arachno* cluster compounds, such as, for example, [4-CB_8H_{14}][10] and [4,5-$C_2B_7H_{13}$].[12]

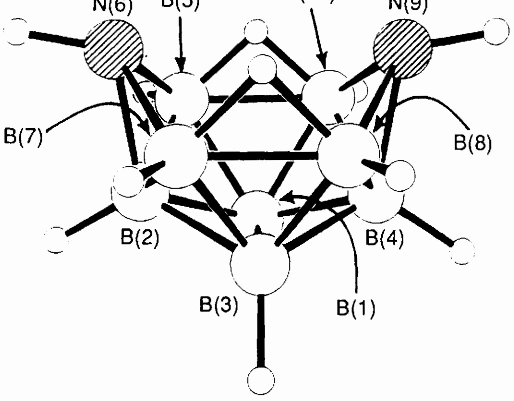
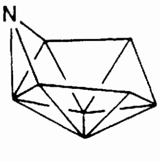


Fig. 1 Proposed molecular structure for [*arachno*-6,9-$N_2B_8H_{12}$] (compound **2**). The *exo*-type nitrogen-bound hydrogen atoms on N(6) and N(9) are so positioned in accord with the *exo* position found for the equivalent hydrogen atom on N(6) in the metalla-azaborane analogue [9,9-$(PMe_2Ph)_2$-*arachno*-9,6-$PtNB_8H_{11}$], in which it takes up a position very close to that of the *exo* hydrogen atom on C(6) in the equivalent metallacarbaborane [9,9-$(PMe_2Ph)_2$-*arachno*-9,6-$PtCB_8H_{12}$].[16] This implies stereochemically active lone pairs in the *endo* positions on N(6) and N(9) [*cf.* Se(6) in reference 17], which in turn has implications for further chemistry



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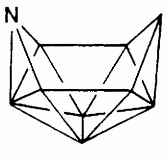

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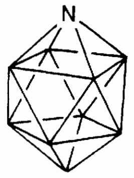

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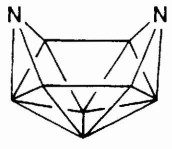
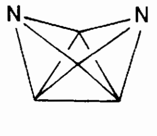


IV



V

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* Work by B.Š. carried out on leave of absence at Leeds from the Institute of Inorganic Chemistry of the Czechoslovak Academcy of Sciences at Řež u Prahy.

† Measured NMR parameters for compound **2**, ordered as assignment, δ (^{11}B) ±0.5 (ppm rel. F_3BOEt_2) [$^1J(^{11}B–^1H)$ ±8 Hz] [δ (^1H) ±0.05 (ppm rel. $SiMe_4$)]: BH (2.4) +7.3{169} [+3.53], BH (5, 7, 8, 10) −25.7{147 and 42} [+1.91 (H_t) and −0.07 (H_μ)], BH (1.3) −41.0{143} [+0.47], NH (6.9) – [+3.10, broadened 1 : 1 : 1 triplet, splitting *ca.* 45 Hz arising from $^1J(^{14}N–^1H)$]; $CDCl_3$ solution at 294–297 K; assignments based on $^1H–\{^{11}B(selective)\}$ experiments, and comparison with equivalent parameters for the isoelectronic *arachno* species[10] [$B_{10}H_{14}$]$^{2-}$, [6–CB_9H_{14}]$^-$ and [6,9–$C_2B_8H_{14}$].

‡ Mass spectrum of compound **2** (70 eV EI ionization): high-mass cut-off at *m/z* 126 (M-2, corresponding to [$^{14}N_2{}^{11}B_8{}^1H_{10}$]$^+$), most intense peaks at *m/z* 123, 124 and 125.

In cluster terms,[13,14] compound **2** is thus isoelectronic with the parent $[B_{10}H_{14}]^{2-}$ anion,[15] in that the two formal $(BH_2)^-$ units at the 6- and 9-positions have been notionally replaced by two isolobal and isoelectronic (NH) vertices. Compound **2** constitutes the first known unsubstituted contiguous cluster diazaborane system, and, as far as we are aware, the first known ten-vertex diheteroborane (carbaboranes and metal-containing species excluded). It is a stable compound that can be stored under nitrogen without any noticeable change, and can be reasonably handled for short periods in air. Further studies aimed at improving the yield of this potentially useful compound, in the systematic synthesis of other novel mono- and poly-heteroboranes of the main-group elements, and in the preparation of their metalla-heteroborane derivatives, are in progress.

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