Macropolyhedral Boron-containing Cluster Chemistry. The Isolation and Characterisation of the Eighteen-vertex Azaborane *anti*-[9-$NB_{17}H_{20}$]†

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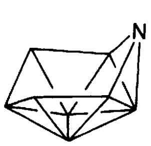
Reaction of *n*-butylnitrite with *anti*-$B_{18}H_{22}$ yields the first macropolyhedral cluster azaborane, eighteen-vertex *anti*-[9-$NB_{17}H_{20}$].

Although carbaborane cluster chemistry is extensive, the chemistry of polyhedral boron-containing compounds that incorporate other first-row main-group elements as cluster constituents is poorly developed. Thus, there is but one example of a contiguous oxaborane,[1] beryllaborane chemistry is essentially limited to two polyhedral types,[2] and, until recently, azaborane chemistry was also only sparsely reported.[3] There is now, however, a contemporary accelerating interest and activity in azaboranes.[3,4] Previously the only unsubstituted cluster azaborane building-blocks described were nine-vertex *arachno*-4-NB_8H_{13} (structure I),[5] ten-vertex *nido*-6-NB_9H_{12} (structure II),[6] and ten-vertex *closo*-1-NB_9H_{10} (structure III),[7] but this short series has now recently been augmented by the ten-vertex diazaborane *arachno*-6,9-$N_2B_8H_{12}$ (structure IV),[8] eleven-vertex *nido*-7-$NB_{10}H_{13}$ (structure V),[9] and twelve-vertex *closo*-1-$NB_{11}H_{12}$ (structure VI).[10] We are interested in developing larger contiguous azaborane building blocks as part of a chemistry that is precursive to tailored boron-containing ceramics and precursive to tailored macromolecules for possible nanotechnological applications, and in this context we now report the isolation of the larger eighteen-vertex 'macropolyhedral' azaborane *anti*-[9-$NB_{17}H_{20}$],† which also constitutes the first



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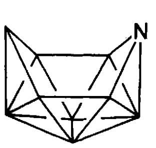

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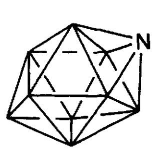

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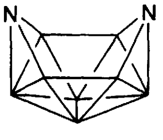

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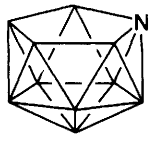

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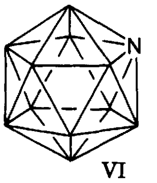

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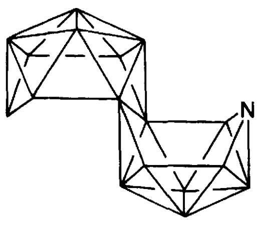

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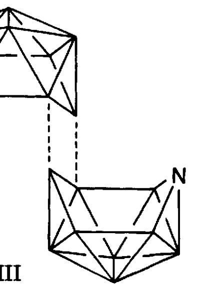

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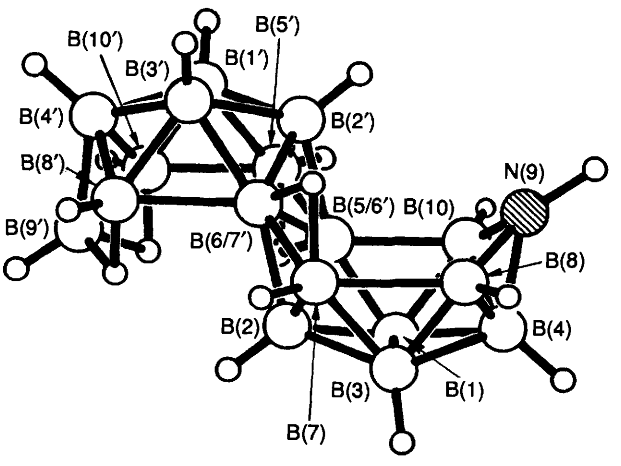

Fig. 1 Representation of the proposed molecular structure of *anti*-[9-$NB_{17}H_{20}$] showing the numbering scheme as *nido*-decaborano-[6′,7′:5,6]-*nido*-9-azadecaborane (compare ref. 11)

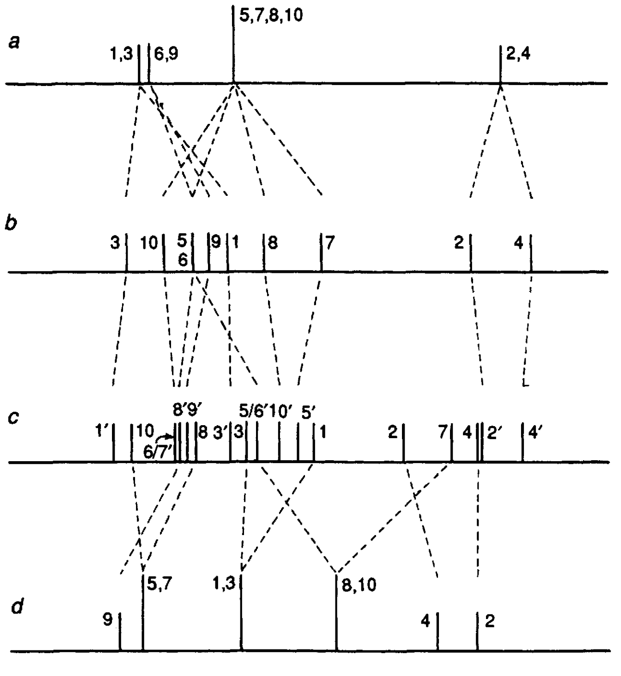

Fig. 2 Stick diagrams of the chemical shifts and relative intensities in the ^{11}B NMR spectra of (from top to bottom): (*a*) *nido*-$B_{10}H_{14}$, (*b*) *anti*-$B_{18}H_{22}$,[11] (*c*) *anti*-[9-$NB_{17}H_{20}$] (this work), and (*d*) *nido*-6-NB_9H_{12} (assignment as in ref. 14). Hatched lines join equivalent positions among the subclusters (note that because of numbering conventions *nido*-6-NB_9H_{12} and the {*nido*-9-NB_9} subcluster of $NB_{17}H_{20}$ have different numberings). The shielding pattern of the {B_{10}} subcluster of $NB_{17}H_{20}$ is readily traced to that of *anti*-$B_{18}H_{22}$, which in turn is readily traced to that of *nido*-$B_{10}H_{14}$ (upper two diagrams). Likewise the shielding pattern of the {NB_9} subcluster can be readily traced to that of *nido*-6-NB_9H_{12} (lower diagram); the magnitude of the differentiation of the (1,3), (5,7), and (8,10) resonances as well as the other shielding changes are very similar for both $B_{10}H_{14}$ and NB_9H_{12} when they are compared to the {B_{10}} and {NB_9} subclusters of $B_{18}H_{22}$ and $NB_{17}H_{20}$.

contiguous macropolyhedral heteroborane to be unequivocally characterised.[12]

We have made use of the recently developed organyl nitrite route for the placement of nitrogen vertices in boron-containing clusters under homogeneous reaction conditions.[13] Treatment of *anti*-$B_{18}H_{22}$ (*ca.* 1.4 mmol) with a threefold excess of *n*-butylnitrite, BuONO (*ca.* 0.5 cm^3), either in diethyl ether (20 cm^3) at room temp., or in benzene (30 cm^3) at reflux temp., for 24 h, followed by repeated chromatography, and then recrystallisation from hot hexane, gave *anti*-[9-$NB_{17}H_{20}$] (Fig. 1) as a colourless, reasonably air-stable, crystalline solid in 15% (diethyl ether route) or 10% yield (benzene route). The compound (structure VII) consists of {*nido*-B_{10}} and {*nido*-6-NB_9} subclusters fused with two-boron edges in common (structure VIII), and was readily characterised as such by mass spectrometry and NMR spectroscopy.‡ In particular the parallels in NMR ^{11}B shielding behaviour among the {NB_9} and {B_{10}} subclusters, and the parent *nido*-$B_{10}H_{14}$ and *nido*-6-NB_9H_{12} cluster models, are very useful in this identification (Fig. 2).

The chromatography required acidic conditions, and was carried out on a silica gel column that had been prepared using an acetic acid–hexane–dichloromethane mixture (5:4:1) as the initial gel–particle suspension medium. The viscous residue that remained after evaporation of the solvents, *etc.*, from the reaction mixture was extracted with a hexane–dichloromethane mixture (3:1; 2 × 20 cm^3), the extract filtered, and then separated chromatographically using hexane–dichloromethane (3:1) as the liquid phase. The major fraction (analytical R_F 0.27; 3:1 hexane–dichloromethane; silica gel G on analytical foil-backed sheets that had been treated with acetic acid and dried in air) was collected and rechromatographed using hexane (100%) as the liquid phase to yield *anti*-[9-$NB_{17}H_{20}$] (analytical R_F 0.10; 100% hexane) as a white solid.

So far these chromatographic conditions for the separation of products in this macropolyhedral azaborane system appear to be quite critical. NMR spectroscopy on as yet unseparable crude fractions suggests other interesting macropolyhedral species which we hope to be able to purify and to report upon in the future.

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Footnotes

† Using the IUPAC-recommended nomenclature for the *anti*-$B_{18}H_{22}$ system (see ref. 11), the formal naming is *nido*-decaborano[6′,7′:5,6]-*nido*-9-azadecaborane. Note that the compound is chiral; the other enantiomer is numbered as the [5′,6′:6,7]-9-aza isomer.

‡ *Selected spectroscopic data:* NMR data as follows {ordered as: assignment $\delta(^{11}B)$/ppm [$\delta(^{1}H)$/ppm in square brackets]} for $CDCl_3$ solution at 294–303 K: azadecaborane subcluster: BH(1) −10.4 [+2.53], BH(2) −22.41 [+0.76], BH(3) −1.2 [+3.00], BH(4) *ca.* −32.9 [+1.24 or −0.25], BH(7) −28.9 [+1.68], BH(8) +5.2 [+3.75], NH(9)- [+6.24 (broad singlet)], BH(10) +14.2 [+4.39]; unsubrogated decaborane subcluster: BH(1′) +16.4 [+3.91], BH(2′) *ca.* −32.9 [−0.25 or +1.24], BH(3′) +0.6 [+2.94], BH(4′) −38.3 [+0.53], BH(5′) −8.3 [+3.00], BH(8′) +7.7 [+3.94], BH(9′) +6.5 [+3.49], BH(10′) −6.6 [+2.90]; common atoms: B(5/6′) −2.3 [−], B(6/7′) +8.8 [−]; bridging H atoms: μH(5′, 5/6′) −2.04, μH(7, 6/7′) −1.50, μH(8′,9′) −0.83, μH(9′,10′) −2.77. Mass spectrometry (70 eV EI ionisation) gave m/z_{max} 221 corresponding to the highest isotopomer of the proposed molecular ion. NMR assignments by [^{11}B–^{11}B]-COSY experiments and ^{1}H-{^{11}B(selective)} spectroscopy.

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