

The First Cluster Azathiaboranes: Isolation and Characterisation of Eight-vertex *hypho*-7,8-NSB₆H₁₁ and Ten-vertex *arachno*-6,9-NSB₈H₁₁

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Reaction of *n*-butyl nitrite with *arachno*-4-SB₈H₁₂ in diethyl ether or with *nido*-6-SB₉H₁₁ in benzene yields the first cluster azathiaboranes, *hypho*-7,8-NSB₆H₁₁ and *arachno*-6,9-NSB₈H₁₁.

The polyhedral cluster structures that typify the higher boron hydrides should be attainable for any combination of atoms that have the same number of electrons and the same number of atomic orbitals available for cluster bonding. This suggests a very rich and varied heteroborane cluster chemistry. However, main-group heteroborane chemistry is dominated so far by one class of compounds: the dicarbaboranes. In comparison to these, even monocarbaborane chemistry is poorly developed.¹ Borane clusters containing two or more different main-group heteroatoms are even more sparsely represented,^{2,3} and polyheteroboranes with disparate heteroatoms of which none is carbon are previously unreported. Currently, there is increasing interest in the heteroboranes of sulfur²⁻⁴ and nitrogen^{2,5,6}. In this paper we report preliminary results on the isolation of borane cluster compounds containing both these elements as cluster constituents: the first cluster azathiaboranes.

The reaction between nine-vertex *arachno*-4-SB₈H₁₂ **1** (prepared as in ref. 7) and excess *n*-butyl nitrite in diethyl ether (reaction scale 3 mmol) over a period of 24 h at room temp. gives modest yields (as yet unoptimised) of eight-vertex *hypho*-7,8-NSB₆H₁₁ **2** (21%) and ten-vertex *arachno*-6,9-NSB₈H₁₁ **3** (10%). Volatile components are removed from the reaction mixture to leave a pale-yellow solid, from which **3** is obtained by extraction with hexane followed by column chromatography on silica gel using CH₂Cl₂-C₆H₁₂ (1:2) as liquid phase; **3** is then purified by sublimation at 60–70 °C (ca. 0.1 mmHg) to give a white crystalline solid. A second, subsequent, extraction of the pale-yellow solid, now with hot benzene, followed by recrystallisation from benzene–hexane, gives **2**, also as a white crystalline solid [*R*_f values (analytical TLC on silica gel G; CH₂Cl₂-C₆H₁₂, 1:2): **2**, 0.23; **3**, 0.35]. The ten-vertex *arachno* compound **3** can be isolated in better yield (14%; again as yet unoptimised) from the treatment of

ten-vertex *nido*-6-SB₉H₁₁ **4** with *n*-butyl nitrite in benzene solution (5 °C, 10 h); a second product is tentatively identified as its *N*-hydroxy derivative 6-(OH)-*arachno*-6,9-NSB₈H₁₀ **5** (34%). Compounds **3** and **5** are isolated by column chromatography on silica gel, using CH₂Cl₂-C₆H₁₂ (1:1) as liquid phase [*R*_f values (analytical TLC on silica gel G; CH₂Cl₂-C₆H₁₂, 1:1): **3**, 0.50; **5**, 0.33]. Compound **3** is further purified by sublimation as above, and the *N*-hydroxy derivative **5** by crystallisation from a solution in C₆H₆ that is overlaid with C₆H₁₂. Additional white products, as yet unidentified, are also formed.

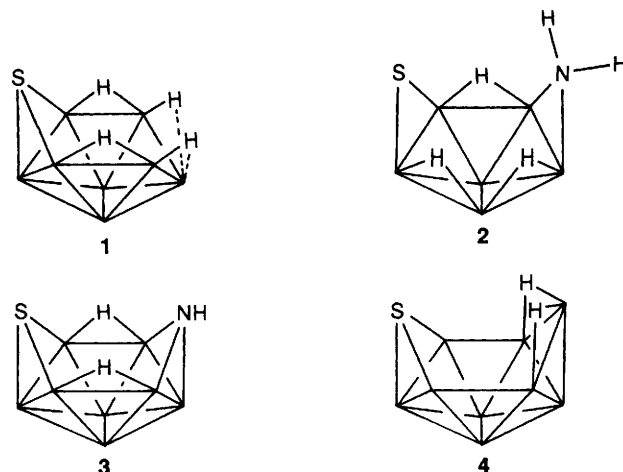


Fig. 1 Schematic representation of the cluster structures of *arachno*-4-SB₈H₁₂ **1**, *hypho*-7,8-NSB₆H₁₁ **2**, *arachno*-6,9-NSB₈H₁₁ **3** and *nido*-6-SB₉H₁₁ **4**. In each case unlabelled vertices correspond to boron atoms, of which each has an *exo*-terminal hydrogen atom bound to it in addition to any others depicted.

The structures of these new azathiaboranes were confirmed by NMR spectroscopy† and also by mass spectrometry (70 eV EI), which in each case showed a value for m/z_{\max} corresponding to the highest isotopomer of the proposed molecular ion. The NMR data for **2**, **3**, and **5** are in agreement with the proposed structures, the observed characteristics correlating with those for the isostructural dicarba- and dihetero-boranes [hypho-7,8-C₂B₆H₁₃]⁻,⁸ [hypho-7,8-CSB₆H₁₁]⁻² and [hypho-7,8-S₂B₆H₉]⁻³ (for **2**), together with arachno-6,9-C₂B₈H₁₄,⁹ arachno-6,9-CNB₈H₁₃² and arachno-6,9-CSB₈H₁₂³ (for **3** and **5**).

This ready synthesis of the hitherto elusive mixed nitrogen-sulfur diheteroboranes (albeit in modest yield) demonstrates a reasonably straightforward entry into the previously unrepresented area of mixed heteroborane chemistry in which none of the cluster atoms is carbon.

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† Selected spectroscopic data: NMR parameters in CDCl₃ solution at 294–297 K, ordered as: assignment, $\delta(^{11}\text{B})$ [approx. $^1J(^{11}\text{B}-^1\text{H})/\text{Hz}$ in parenthesis] $\delta(^1\text{H})$. **2**: BH(5) +1.8 (159) +3.33, BH(2) -1.6 (155) +3.10, BH(4) -20.8 (156 and 42) +2.33, BH(6) -22.4 (180) +2.39, BH(3) -25.6 (145 and 59) +2.48, BH(1) -55.1 (146) -0.57. Additional $\delta(^1\text{H})$ data: NH₂ +2.20 and +1.96, $\mu\text{-H}$ +0.69, -0.48 and -1.59. **3**: BH(2) -13.9 (178) +4.22, BH(4) +7.4 (174) +3.54, BH(8, 10) -23.6 (134 and 38) +2.04, BH(5,7) -24.6 (142 and 44) +1.85, BH(1,3) -38.0 (147) +1.00. Additional $\delta(^1\text{H})$ data: NH(6) +3.50, $\mu\text{-H}$ (5,10; 7,8) +0.20. **5**: BH(2) +12.4 (179) +3.93, BH(4) + 10.2 (178) +4.04, BH(8, 10) -22.0 (accurate J not measured because of peak overlap) +2.35, BH(5,7) -23.9 (accurate J not measured because of peak overlap) +1.99, BH(1,3) -39.6 (150) +0.98. Additional $\delta(^1\text{H})$ data: N(OH) (6) +3.14 (br, tentative assignment), $\mu\text{-H}$ (5,10; 7,8) +0.67. MS (70 eV EI ionization) highest-mass envelope m/z_{\max} 161 (¹H₁₁¹¹B₈¹⁴N³²S¹⁶O), with principal significant fragment envelopes at m/z_{\max} 145 (¹H₁₁¹¹B₈¹⁴N³²S) and 132 (¹H₉¹¹B₇¹⁴N³²S).