A new cyclic borazine species $B_8(NH)_4(NMe_2)_8$ containing a twelve-membered B_8N_4 ring

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The reaction between $B_2(NMe_2)_4$ and two equivalents of $[NH_4][PF_6]$ in thf at room temperature affords the new cyclic borazine $B_8(NH)_4(NMe_2)_8$ containing a non-planar twelve-membered ring with alternating $B_2(NMe_2)_2$ and NH units.

Tetraamino substituted diborane(4) compounds, $B_2(NR_2)_4$, are important precursors for diborane(4) chemistry, most notably the dimethylamino species $B_2(NMe_2)_4$ (**1**).[1] In a recent paper,[2] we described a subset of this class of compound containing primary amido substituents, $B_2(NHR)_4$,[1b,2] in which the amide was an aniline derivative with R including Ph, 2,6-$Me_2C_6H_3$ and 4-IC_6H_4. The most efficient synthetic route to primary amido species involves transamination reactions between **1** and the corresponding primary amine[1b,2] and we were interested in exploring the potential for transamination with ammonia with a view to preparing the compound $B_2(NH_2)_4$. Little is known of this species but in an early review by Brotherton,[1c] the reaction between **1** and NH_3 under pressure was reported to produce a polymer presumed to result from facile condensation through loss of NH_3 from initially formed $B_2(NH_2)_4$, which was proposed to be unstable by analogy with $B(NH_2)_3$.[3] A similar reaction had also been described by Nöth and co-workers[4] and a polymeric material, assigned the empirical formula BNH, had been obtained somewhat earlier by Schlesinger *et al.*[5] from the reaction between B_2Cl_4 and ammonia. Indeed, well characterised compounds containing the B–NH_2 moiety are scarce but include such species as $(Me_3Si)_3CB(NH_2)_2$,[6] $B\{NH(2,4,6\text{-}Bu^t{}_3C_6H_2)\}(NH_2)_2$[7] and the borazine $B_3(NH_2)_3N_3H_3$.[8] In addition, we note that a number of theoretical studies on $B_2(NH_2)_4$ have been carried out[9] and also that the fully deprotonated form of $B_2(NH_2)_4$, *i.e.* $[B_2N_4]^{8-}$, is known in some solid-state lanthanide nitrido-borate structures with the general formula $Ln_3B_2N_4$;[10] in all cases the B_2N_4 unit is planar.

The reaction between **1** and gaseous ammonia in hexane at room temperature showed no evidence of any reaction after 3 h, as determined by ^1H and ^{11}B NMR spectroscopy.† Similarly, there was no indication of any reaction after **1** had been added to liquid ammonia and allowed to stir for 2 h.† A reaction did take place, however, when **1** was dissolved in an ammonia–thf solution to which four equivalents of $[NH_4][PF_6]$ was added. This reaction afforded an insoluble white polymeric material, elemental analysis for which was consistent with a material close to composition BNH.‡ A reaction scheme consistent with the formation of BNH is shown in eqn (1) and (2), consideration of which led to an expectation that a reaction with less $[NH_4][PF_6]$ might afford an intermediate species. Thus the reaction between **1** and two equivalents of $[NH_4][PF_6]$ in thf at room temperature was carried out, which afforded, after work-up, colourless crystals of a material identified as the cyclic borazine species $B_8(NH)_4(NMe_2)_8$ (**2**) albeit in low isolated yield.§

$$B_2(NMe_2)_4 + 4[NH_4][PF_6] \rightarrow B_2(NH_2)_4 + 4[NH_2Me_2][PF_6] \quad (1)$$

$$B_2(NH_2)_4 \rightarrow \{BNH\}_2 + 2NH_3 \quad (2)$$

The structure of compound **2** was established by X-ray crystallography, the results of which are shown in Fig. 1.¶ Compound **2** has crystallographic C_2 symmetry, although the idealised molecular symmetry is defined by the D_{2d} point group.

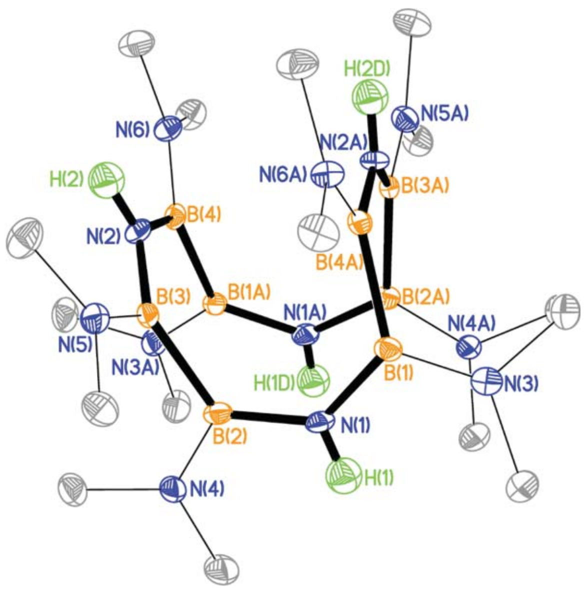

Fig. 1 A view of the molecular structure of compound **2**. Ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°) include: B(1)–B(4A) 1.739(4); B(2)–B(3) 1.718(4); B(1)–N(1) 1.436(4); B(2)–N(1) 1.440(4); B(3)–N(2) 1.440(4); B(4)–N(2) 1.451(4); B(1)–N(3) 1.423(4); B(2)–N(4) 1.424(4); B(3)–N(5) 1.424(4); B(4)–N(6) 1.420(4); B(1)–N(1)–B(2) 130.0(2); B(3)–N(2)–B(4) 130.0(2); N(1)–B(1)–N(3) 118.8(3); N(3)–B(1)–B(4a) 117.6(2); N(1)–B(1)–B(4a) 123.6(2); N(1)–B(2)–N(4) 119.6(2); N(1)–B(2)–B(3) 120.7(2); N(4)–B(2)–B(3) 119.3(2); N(2)–B(3)–N(5) 119.4(2); N(2)–B(3)–B(2) 122.8(2); N(5)–B(3)–B(2) 117.8(2); N(2)–B(4)–N(6) 117.9(2); N(2)–B(4)–B(1a) 122.4(2); N(6)–B(4)–B(1a) 119.5(2).

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The two crystallographically independent B–B distances [1.718(4) and 1.739(4) Å] are typical of those found in the B_2N_4 units of other structurally characterised tetraamino diborane(4) compounds.[2] Likewise the B–N bond lengths are unexceptional, although we note that the B–N distances to the ring NH nitrogens [1.440(4) and 1.451(4) Å] are significantly longer than the B–NMe_2 distances, which average 1.423 Å. Of all the interbond angles at the trigonal planar B and N centres, the ones that deviate most from 120° are the B–N–B angles at the NH nitrogens, which are both 130.0(2)°. The angles at boron are all close to 120°, with the HN–B–B angle being the larger [but only slightly, ranging from 120.7(2) to 123.6(2)°]. Within the NMe_2 groups, the C–N–C angle is typically around 112°, whilst the B–N–C angles are centred around 124°. The conformation of the B_8N_4 ring is of the type encountered for a molecule like cyclo-octatetraene and is defined by the torsion angles between the adjacent ring atom trigonal planes [B(1)–N(1) −10.6(4); N(1)–B(2) 13.8(4); B(2)–B(3) 93.3(3); B(3)–N(2) 3.4(4); N(2)–B(4) 16.1(4); B(4)–B(1a) 87.6(4)°]. The conformations about the B–B bonds in particular are close to ideally staggered as is commonly, although not universally, observed for tetraamino diborane(4) compounds.[2]

The reaction pathway by which compound **2** is formed is unclear, although an equation consistent with its formation is shown in eqn (3). The diborane(4) species $B_2(NH_2)_2(NMe_2)_2$ is a possible intermediate but we obtained no evidence for a six-membered ring compound $B_4(NH)_2(NMe_2)_4$ analogous to species such as $B_4O_2(OH)_4$,[11] $B_4O_2(NR_2)_4$[12] and $B_4S_2(NMe_2)_4$.[13] Substitution of the NMe_2 groups is most likely effected by initial protonation of the NMe_2 nitrogen by the ammonium cation, which then allows replacement of the $NHMe_2$ amine by NH_3. Subsequent deprotonation would result in an NH_2 group bound to boron and the ammonium cation $[NH_2Me_2]^+$.

$$4B_2(NMe_2)_4 + 8[NH_4][PF_6] \rightarrow B_8(NH)_4(NMe_2)_8 + 8[NH_2Me_2][PF_6] + 4NH_3 \qquad (3)$$

Compound **2** represents a new type of cyclic borazine species (perhaps better described as a diborazine). In general, borazines adopt cyclic six-membered ring structures with the general formula $B_3R_3N_3R'_3$, or $\{BRNR'\}_x$ where $x = 3$, and are isoelectronic with arenes;[14] some examples are known where $x = 4$.[15] Fused and linked systems related to naphthalene and biphenyl respectively are also known, the latter including species in which the two rings are linked by a B–B bond.[16] One example is known of a cyclic $B_4R_4N_4R'_4$ species containing two B–B bonds, *i.e.* $[B_4(NMe_2)_4N_4Et_4]$ effectively an isomer of $\{BRNR'\}_x$ ($x = 4$), derived from the reaction between $B_2Cl_2(NMe_2)_2$ and 1,2-diethylhydrazine.[17] Compound **2** constitutes a new class of general formula $\{B(R)B(R)NR'\}_x$ where $x = 4$ and in which B–B bonds are present as well as B–N bonds. Further studies are in progress to determine whether borazines of this type can be prepared and isolated with different ring sizes and to better characterise polymeric forms, particularly in view of the interest in using borazines as precursors to boron nitride and boron carbonitride materials.[18] We note also the possible relevance of compounds such as **2** to hydrogen storage using ammonia–borane species.[19]

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Notes and references

† **Reaction of $B_2(NMe_2)_4$ with gaseous ammonia**: ammonia gas was bubbled though a stirred solution of $B_2(NMe_2)_4$ (0.3 cm^3, 1.295 mmol) in hexane (10 cm^3) at room temperature for 3 h, which resulted in the appearance of a slight cloudiness in the solution. After this time, the hexane was removed by vacuum, resulting in a colourless liquid, which was shown by ^1H and ^{11}B NMR spectroscopy to be unreacted $B_2(NMe_2)_4$. **Reaction of $B_2(NMe_2)_4$ with liquid ammonia**: ammonia gas was condensed into a flask containing a small piece of metallic sodium (to effect drying) for sufficient time to afford 10 cm^3 of liquid. The liquid ammonia was then re-condensed into a Young's tap tube at −78 °C. A sample of $B_2(NMe_2)_4$ (0.210 g, 1.061 mmol) was then added to the Young's tube, forming two immiscible layers which were then stirred. After 2 h, the mixture was allowed to warm to room temperature and the ammonia to boil off. The remaining liquid residue was shown by ^1H and ^{11}B NMR spectroscopy to be unreacted $B_2(NMe_2)_4$.

‡ Ammonia gas was condensed into a flask containing thf (10 cm^3) at −78 °C until the solvent volume had approximately doubled and the resulting mixture was stirred. A sample of $B_2(NMe_2)_4$ (0.313 g, 1.581 mmol) was then added followed by the slow addition of a solution of $[NH_4][PF_6]$ (1.03 g, 6.319 mmol) in thf (5 cm^3). The resulting mixture was allowed to warm to room temperature and the ammonia to boil off, during which the solution became slightly cloudy. After stirring at room temperature for 1 h, a small amount of a colourless precipitate had formed. Vacuum pumping of the mixture to remove the remaining dissolved ammonia and some of the thf caused further precipitation. The reaction mixture was then filtered, affording a colourless solid product (0.113 g). Anal. Calcd for $B_2N_2H_2$: H, 4.28; C, 0.00; N, 50.42%. Found H, 4.86; C, 0.80; N, 47.75%. IR: 3480.0, 3321.8, 3307.7 (N–H).

§ **Preparation of $B_8(NH)_4(NMe_2)_8$.** A solution of $[NH_4][PF_6]$ (0.420 g, 2.577 mmol) in thf (10 cm^3) was added very slowly to a stirred solution of $B_2(NMe_2)_4$ (0.3 cm^3, 1.295 mmol) in thf (40 cm^3) at room temperature. The mixture was stirred for 30 min, during which time a colourless precipitate formed. Removal of all volatiles by vacuum afforded a colourless residue which was extracted with hexane (3 × 3 cm^3). Concentration of the hexane solution followed by cooling to 4 °C for several days yielded a colourless solid (0.01 g, 8%) together with some colourless crystals suitable for X-ray diffraction. ^1H NMR ($CDCl_3$): δ 2.65 (24H, s, Me), $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 35.8, $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 41.2. HREI-MS *m/z* 485.494322 (M^+ − Me), calcd *m/z* for $C_{15}H_{49}{}^{11}B_8N_{12}$: 485.494757.

¶ Crystal data for **2**: $C_{16}H_{52}B_8N_{12}$, M = 499.18, orthorhombic, a = 22.220(4), b = 28.467(6), c = 9.5966(19) Å, V = 6070(2) Å^3, T = 100(2) K, space group *Fdd*2 , Z = 8, μ = 0.066 mm^{-1}, R_{int} = 0.0583 (for 16769 measured reflections), R_1 = 0.0527 [for 1777 unique reflections with $>2\sigma(I)$], wR_2 = 0.1256 (for all 1847 unique reflections).[20–23] CCDC 655805. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711487g

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