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New polycyclic borazine species†

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The new polycyclic borazines $B_2\{1,2\text{-}N_2C_6H_4\}_2\{B_2(NMe_2)_2\}_2$, $B_2\{1,8\text{-}N_2\text{naph}\}_2\{B_2(NMe_2)_2\}_2$ and $B_2(NPh)_4\{B_2(NMe_2)_2\}_2$ have been prepared from diborate(4) anions and two equivalents of $B_2Cl_2(NMe_2)_2$ and have been structurally characterised. Aspects of their structure and bonding are discussed and comparison made with corresponding polycyclic aromatic hydrocarbons.

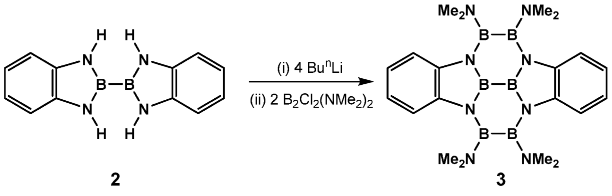
In general, borazines, *i.e.* cyclic species containing alternating BR and NR units, adopt six-membered ring structures with the general formula $\{BNR_2\}_x$; commonly $x = 3$ and the species are isoelectronic with arenes,[1] although some examples are known where $x = 4$.[2] Fused or linked systems related to naphthalene and biphenyl have also been described, the latter including species in which the two rings are linked by a B–B bond.[3] One example has been reported of a cyclic $B_4N_4R_8$ species containing two B–B bonds, *i.e.* $B_4(NMe_2)_4N_4Et_4$, effectively an isomer of $\{BNR_2\}_x$ ($x = 4$), derived from the reaction between $B_2Cl_2(NMe_2)_2$ and 1,2-diethylhydrazine.[4] In a recent paper, we described an example of a new class of boron-rich borazine with the general formula $\{B_2NR_3\}_x$ where $x = 4$, namely $B_8(NH)_4(NMe_2)_8$ (**1**), in which B–B bonds are present as well as B–N bonds (a diborazine).[5] Herein we report examples of two new borazine types constructed from reactions involving diborane(4) compounds. The polycyclic frameworks of these novel borazines can also be seen in relation to those of isostructural polycyclic aromatic hydrocarbons (PAHs), which constitute a highly promising class of photoelectric materials and the substitution of BN units for isoelectronic CC units in PAH manifolds is a topic of considerable current interest owing to the subtly different electronic properties of the resulting materials.[6] In the case of the species reported herein, the B : N ratio is such that the compounds have two electrons fewer than their parent PAH.

We have previously shown that diborane(4) compounds containing primary amido substituents, $B_2(NHR)_4$, can be lithiated by addition of a stoichiometric amount of Bu^nLi to give the tetra-anionic diborate(4) anions $[B_2(NR)_4]^{4-}$.[7] Using this methodology lithiation of the 1,1-isomer of $B_2\{1,2\text{-}(NH)_2C_6H_4\}_2$ (**2**)[8] followed by reaction with two equivalents of $B_2Cl_2(NMe_2)_2$[9] afforded the compound 1,1-$B_2\{1,2\text{-}N_2C_6H_4\}\{B_2(NMe_2)_2\}_2$ (**3**) according to Scheme 1.†

The structure of **3** (as a toluene solvate) was determined by X-ray crystallography (Fig. 1)‡§ which revealed a polycyclic species in which a B–B unit derived from each of the two $B_2Cl_2(NMe_2)_2$ reactants has added in a 1,2-fashion to pairs of nitrogen atoms in the $B_2\{1,2\text{-}(NH)_2C_6H_4\}_2$ precursor.

Compound **3** comprises a mixture of fused C_6, B_4N_2 and BC_2N_2 rings and resembles those borazines which have a naphthalene-type structure, *i.e.* $B_5N_5R_8$[3] but in this case the general formula is $B_6N_4R_8$ and it therefore contains two fewer electrons. Molecules of **3** lie on a crystallographic centre of inversion but adopt a markedly non-planar, twisted conformation due to intramolecular steric interactions between adjacent NMe_2 groups as a result of the conformation about the B–N bonds required to maximise π-bonding. This twisting is reflected in the angle between the N_2B planes, τ, of 58.4° for the peripheral B_2 units, in contrast to the eclipsed conformation (*i.e.*, $\tau = 0$) about the central B_2 unit. Also notable are some of the bond distances. Thus the central B–B bond [B(1)-B(1A) 1.611(4) Å] is extremely short,[8,10] being substantially shorter than the outer B–B lengths [B(2)–B(3A) 1.757(4) Å] and comparable to lengths which have been formally assigned as B═B double bonds.[11] The B–N bond lengths also span a wide range with the exocyclic distances shortest [B(2)–N(3) 1.402(3), B(3)–N(4) 1.402(2) Å] and the endocyclic longer in two groups [B(1)–N(1) 1.427(3), B(1)–N(2) 1.431(3) and B(2)–N(1) 1.500(3), B(3)–N(2) 1.495(3) Å]. These bond lengths are suggestive of exocyclic B═N character, and endocyclic units comprising delocalized N–B–N bonding and formal B–N single bonds respectively.

An analogous reaction starting with 1,1-$B_2\{1,8\text{-}N_2\text{naph}\}_2$ (**4**), derived from the reaction between $B_2(NMe_2)_4$[9b,12] and two



Scheme 1

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† Electronic supplementary information (ESI) available: Syntheses and experimental data for **3–6**; molecular structure of **4**. CCDC 807912–807915. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc10196j

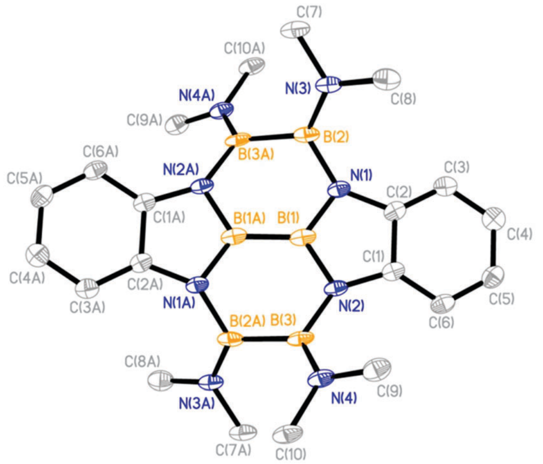
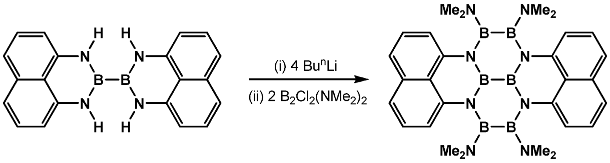


Fig. 1 A view of the molecular structure of compound **3**. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and the solvent of crystallisation (toluene) have been omitted for clarity. Selected bond distances (Å): B(1)–B(1A) 1.611(4), B(2)–B(3A) 1.757(4), B(1)–N(1) 1.427(3), B(1)–N(2) 1.431(3), B(2)–N(1) 1.500(3), B(2)–N(3) 1.402(3), B(3)–N(2) 1.495(3), B(3)–N(4) 1.402(2). Symmetry transformations used to generate equivalent atoms labelled "A" $\frac{1}{2} - x$, $\frac{1}{2} - y$, $2 - z$.



4 **5**

Scheme 2

equivalents of 1,8-diaminonaphthalene, afforded a similar species 1,1-$B_2\{1,8\text{-}N_2naph\}_2\{B_2(NMe_2)_2\}_2$ (**5**) (Scheme 2).†

We note that this diamine has been employed recently as a substituent in diborane(4) compounds used in diboration reactions.[13] Both **4** and **5** were characterised by X-ray crystallography, the latter as a bis-toluene solvate.†‡¶‖ Complex **4** co-crystallises with two molecules of DMF but the structure is unexceptional and is similar to the structure of **2** reported in ref. 8; molecules are strictly planar in the solid state and the B–B distance is typical of a single bond at 1.691(4) Å. The structure of **5** resembles that of **3** and is shown in Fig. 2.

Molecules of **5** also lie on a crystallographic inversion centre and are twisted about the peripheral B_2 vectors [τ = 67.7°] comparable to that found in **3**. In **5**, however, the B–B distances are much more similar [B(1)–B(1A) 1.728(4) and B(2)–B(3A) 1.710(3) Å] reflecting the reduced ring strain in a species composed entirely of six-membered rings. The B–N distances exhibit a similar pattern to those observed in compound **3**.

In order to test whether the short nature of the central B–B bond in **3** is purely due to ring strain in the molecule or whether this is evidence of some B–B π bonding, DFT calculations[14,15] were performed on **3** and **5**** and the molecular orbitals of π-symmetry examined. Whilst **5** showed no evidence of π bonding between the central boron atoms, the HOMO-2 in **3** (see Fig. 3) shows substantial delocalisation of the nitrogen lone pairs across the p-orbitals of both boron atoms, suggesting that the B–B bond order is higher than 1 in this case.

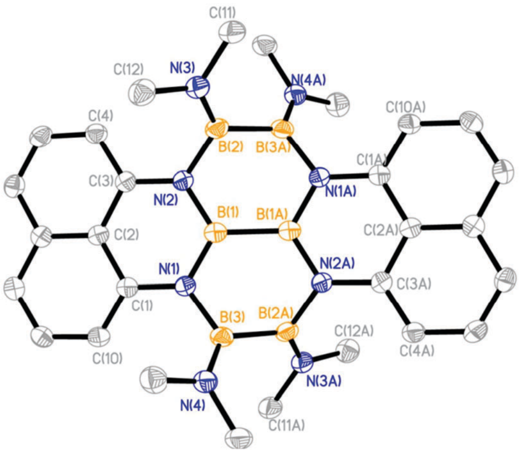


Fig. 2 A view of the molecular structure of compound **5**. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and the solvent of crystallisation (toluene) have been omitted for clarity. Selected bond distances (Å): B(1)–B(1A) 1.728(4), B(2)–B(3A) 1.710(3), B(1)–N(1) 1.439(2), B(1)–N(2) 1.435(2), B(2)–N(2) 1.504(2), B(2)–N(3) 1.393(2), B(3)–N(1) 1.499(2), B(3)–N(4) 1.402(2). Symmetry transformations used to generate equivalent atoms labelled "A" $2 - x$, $2 - y$, $1 - z$.

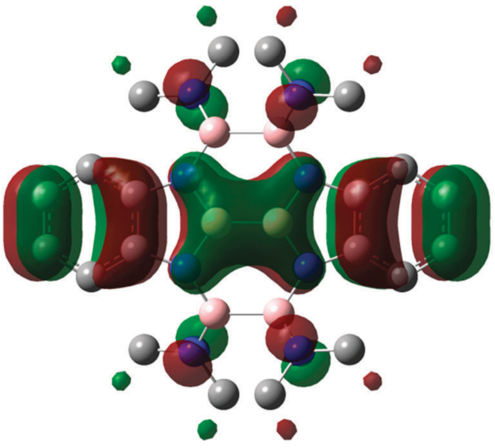
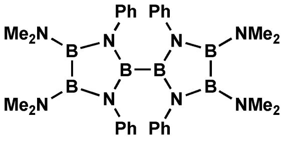


Fig. 3 A contour plot of the HOMO-2 of compound **3** (contour value 0.04) showing a B–B π-bonding interaction.

In looking to explore further the generality of the reactions which afforded **3** and **5**, the reaction between the lithium salt of the diborate(4) anion $[B_2(NPh)_4]^{4-}$ [7] and two equivalents of $B_2Cl_2(NMe_2)_2$ was carried out which afforded the compound $B_2(NPh)_4\{B_2(NMe_2)_2\}_2$ (**6**).†



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Interestingly, the addition of the B–B units occurs in a 1,1-fashion in this case to give a compound containing two B_3N_2 rings linked by an unsupported B–B bond. The structure

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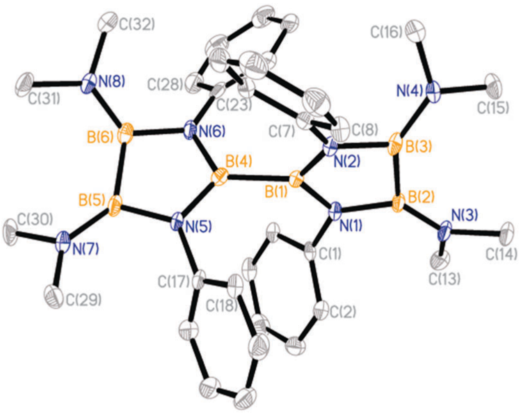

Fig. 4 A view of the molecular structure of compound **6**. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are set at the 50% probability level. Selected bond distances (Å) and angles (deg) include: B(1)–B(4) 1.722(5), B(2)–B(3) 1.723(5), B(5)–B(6) 1.718(5), B(1)–N(1) 1.462(5), B(1)–N(2) 1.440(5), B(2)–N(1) 1.474(5), B(2)–N(3) 1.405(5), B(3)–N(2) 1.475(5), B(2)–N(4) 1.405(5), B(4)–N(5) 1.457(5), B(4)–N(6) 1.451(4).

of **6** was also determined by X-ray crystallography and is shown in Fig. 4.‡†† The two B_3N_2 rings are non-planar and are arranged in an approximately staggered conformation about the central B–B bond, the angle between the two BN_2 planes, τ, being 84.6°. All B–B bonds are similar in length and characteristic of single bonds [B(1)–B(4) 1.722(5), B(2)–B(3) 1.723(5), B(5)–B(6) 1.718(5)].[8,10] The non-planarity of the five-membered rings arises because the $B_2(NMe_2)_2$ units are twisted [τ = 30.2°], but this is significantly less than the twisting observed in **3** and **5**. Compound **6** also constitutes a new class of borazine and is related to a fulvalene but with 2 fewer electrons; 8 *vs.* 10.

In summary, we have shown that BN-rich polycyclic systems, which may be viewed both as new types of borazines and as isostructural with polycyclic aromatic hydrocarbons, may be constructed in comparatively few steps from simple diborane(4) precursors.

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Notes and references

‡ Single crystals of **3–6** were recrystallised from saturated solutions of an appropriate solvent (see ESI†), mounted in inert oil and transferred to the cold gas stream of the diffractometer. Structures were solved using SHELXS and refined using SHELXL.[16]

§ **Crystal data for 3·toluene:** $C_{27}H_{40}B_6N_8$, M = 541.53, monoclinic, space group $C2/c$, a = 27.515(5), b = 12.652(2), c = 8.8516(14) Å, β = 102.852(9)°, U = 3004.2(8) Å^3, Z = 4, D_c = 1.197 Mg m^{-3}, λ = 1.54178 Å, μ(Cu-Kα) = 0.544 mm^{-1}, F(000) = 1152, T = 100(2) K, R_1 = 0.0502 [for 1616 reflections with $I > 2\sigma(I)$], wR_2 = 0.1351 [for all 2129 reflections], R_{int} = 0.0672. CCDC 807912.

¶ **Crystal data for 4·2DMF:** $C_{26}H_{30}B_2N_6O_2$, M = 480.18, monoclinic, space group $P2_1/n$, a = 12.8216(7), b = 13.9708(8), c = 14.5010(8) Å, β = 104.001(3)°, U = 2520.4(2) Å^3, Z = 4, D_c = 1.265 Mg m^{-3}, λ = 0.71073 Å, μ(Mo-Kα) = 0.082 mm^{-1}, F(000) = 1016, T = 100(2) K, R_1 = 0.0569 [for 4239 reflections with $I > 2\sigma(I)$]. wR_2 = 0.2216 [for all 7023 reflections]. R_{int} = 0.0357. CCDC 807913.

‖ **Crystal data for 5·2toluene:** $C_{42}H_{52}B_6N_8$, M = 733.78, orthorhombic, space group $Pbca$, a = 13.4491(4), b = 9.6202(3), c = 31.1212(10) Å, U = 4026.6(2) Å^3, Z = 4, D_c = 1.210 Mg m^{-3}, λ = 1.54178 Å, μ(Cu-Kα) = 0.541 mm^{-1}, F(000) = 1560, T = 100(2) K, R_1 = 0.0453 [for 3170 reflections with $I > 2\sigma(I)$], wR_2 = 0.1161 [for all 3402 reflections]. R_{int} = 0.0741. CCDC 807914.

** Computational energy minimisations for **3** and **5** were carried out using B3LYP/6-31G*, with the geometry of the species in the crystal structure as the starting point for the optimisation. All calculations were performed with the Gaussian03 package using the B3LYP functional and with 6-31G* basis sets on all atoms.[14,15]

†† **Crystal data for 6:** $C_{32}H_{44}B_6N_8$, M = 605.61, triclinic, space group $P\bar{1}$, a = 11.9997(8), b = 12.1731(9), c = 14.0679(13) Å, α = 94.107(6)°, β = 104.802(5)°, γ = 119.494(3)°, U = 1681.0(2) Å^3, Z = 2, D_c = 1.196 Mg m^{-3}, λ = 1.54178 Å, μ(Cu-Kα) = 0.540 mm^{-1}, F(000) = 644, T = 100(2) K, R_1 = 0.0676 [for 4832 reflections with $I > 2\sigma(I)$], wR_2 = 0.1850 [for all 5585 reflections]. The crystal was a partial merohedral twin with two domains. Each domain was indexed independently using the Apex II software and integrated simultaneously using SAINT. The structure was solved using 'detwinned' data and refined against all reflections. This resulted in a ratio of 0.66 : 0.34 for the two domains. CCDC 807915.

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