Three-membered Boron–Nitrogen Heterocycles: Amino Derivatives of 1,2-Diaza-3-boririne and 1-Aza-2,3-diboririne

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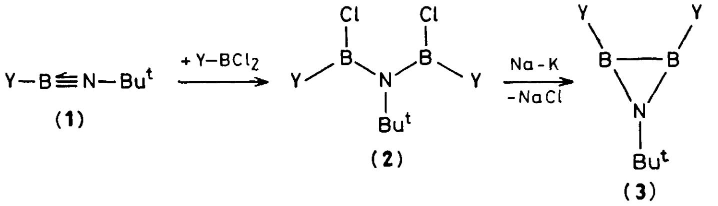
N.m.r. evidence for the novel 1-t-butyl-2,3-bis-(2,2,6,6-tetramethylpiperidino)-1-aza-2,3-diboririne (**3**) and 1,2-di-isopropyl-3-(2,2,6,6-tetramethylpiperidino)-1,2-diaza-3-boririne (**6**) suggests a 2π-electron system for (**3**) and nonplanar nitrogen atoms in (**6**).

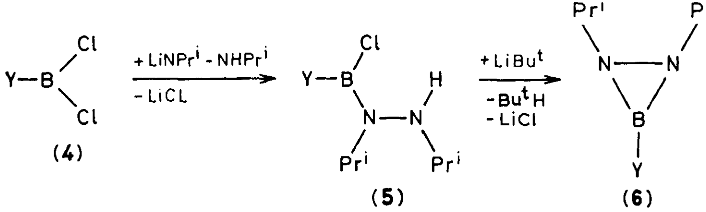
There is considerable interest in small-ring boron–carbon heterocycles; borirenes,[1] boriranes,[2] and dihydrodiboretes[3—5] have only recently been characterized. The latter proved to be non-planar[4] as predicted by theoretical studies.[6,7] In addition, a derivative of a 1,2-diphospha-3-boracyclopropane[8] is known. The BN analogue of borirene is the 2π-electron system 1-aza-2,3-diboririne, and that of the boritene dianions the formal 4π-electron system 1,2-diaza-3-boririne. The former can be regarded as a Hückel-type aromatic system. Both new heterocycles have now been synthesized.

As shown in equation (1) the 1-aza-2,3-diboririne (**3**) is obtained in 90% yield by dehalogenation of the diborylamine (**2**)[†] with sodium–potassium alloy in boiling hexane. Compound (**2**) may be obtained in quantitative yield by chloroboration of compound (**1**)[9] with the dichloro compound (**4**).

[†] Colourless, hydrolytically sensitive solid, m.p. 83—85 °C, *m/z* 443 (^{11}B and ^{35}Cl) calc. 444.13; correct isotopic pattern for M^+; $\delta(^{11}B)$ 31.2 p.p.m. (*vs.* $BF_3{\cdot}OEt_2$); $\delta(^{13}C)$ 56.2 (br., CMe_3), 38.6 (br., C-2, C-4), 33.0 (CMe_3), 32.5 (br., C-6, C-7), and 17.2 (C-3).



(1)



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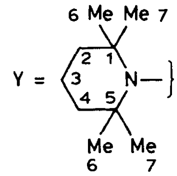
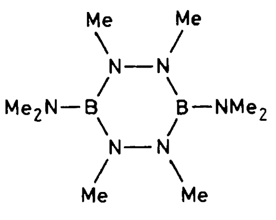


Compound (3) crystallizes from pentane as large plates, m.p. 88 °C. The M_r value in cyclohexane (calc. 375.2, found 370) as well as by mass spectrometry (15 eV, m/z 375 for ^{11}B, correct isotopic pattern) confirms the molecular formula and excludes a six-membered N_2B_4 system like (8).[10]

The 1,2-diaza-3-boririne (6) was prepared in 70% yield from the hydrazino(chloro)borane (5) and t-butyl-lithium in boiling hexane. The precursor (5)‡ was obtained in 80% yield from (4) and lithium di-isopropylhydrazide. Compound (6) is a colourless liquid, b.p. 56—60 °C at 10^{-2} Torr. Mass spectrometry at 15 eV showed no higher masses than calculated for (6) (M_r 265.2, m/z 265, ^{11}B, correct isotopic pattern), and in cyclohexane a molecular mass of 262 ± 5 was determined. Therefore, the presence of a dimer of (6), *i.e.* a derivative of a 1,2,4,5-tetra-aza-3,6-diboracyclohexane (7)[11] can be excluded. Both (3) and (6) are stable to at least 120 °C; their formation and stability are controlled kinetically by the bulky substituents. Electronic factors play a less significant role because the permethylated compounds are six-membered, compounds (7) and (8).[10,11]



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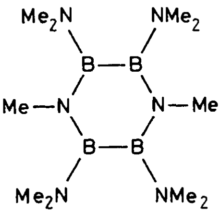

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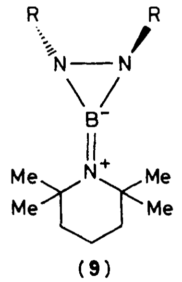

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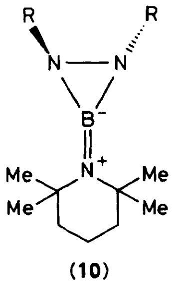

(10)

N.m.r. data for compound (3)§ suggest that the atoms bonded to the ring are coplanar. Compound (3) can be regarded as a cyclic diborylamine, and it would be expected that the methyl groups of the piperidino substituents would be pairwise magnetically nonequivalent as is the case for the amino groups R_2N in a diaminodiborane(4) of type $R_2N(X)B$–$B(X)NR_2$ owing to hindered rotation resulting from strong BN π-bonding. However, no hindered rotation was observed by ^{13}C n.m.r. spectroscopy, even at −100 °C. This would be in accord with compound (3) possessing a 2π- electron aromatic system. If its boron atoms are electronically saturated, exocyclic BN π-bonding would be weak and hence rotation at these bonds would not be hindered.

The boron atom in compound (6)¶ is shielded as in a triaminoborane.[12] The intensities and multiplicities of the ^{1}H n.m.r. signals are as expected, with the methyl groups of the piperidino and isopropyl groups being magnetically equivalent. However, the ^{13}C n.m.r. spectrum recorded in CD_2Cl_2 at ambient temperature shows that the methyl substituents of the piperidino group are pairwise nonequivalent: two broad signals are observed at δ 24.6 and 21.4. These signals are sharp at −40 °C, and the methyl groups of the isopropyl substituents are also split into two sharp signals of equal intensity (δ 33.0 and 31.5). This is due to the isopropyl groups becoming prochiral as inversion at nitrogen slows down sufficiently.

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‡ Colourless liquid, b.p. 65—68 °C at 5 × 10^{-4} Torr, δ(^{11}B) 33.4 p.p.m.; δ(^{13}C) 50.8, 51.6 (H*C*Me$_2$), 52.0 (C-1, C-5), 40.6 (C-2, C-4), 33.9, 28.0 (HC*Me*$_2$), 22.2, 22.0 (C-6, C-7), and 18.7 (C-3).

§ δ(^{11}B) 39.9 p.p.m.; δ(^{13}C): 57.3 (*C*Me$_3$), 52.7 (C-2, C-4), 41.1 (C-2, C-4), 32.5 (C*Me*$_3$), 33.2 (C-6, C-7), and 18.3 (C-3), in CD_2Cl_2.

Note added in proof: The *X*-ray structure analysis confirms the B_2N ring.

¶ δ(^{11}B) 26.5 p.p.m.; δ(^{13}C) 53.8 (C-1, C-5), 52.1 (*C*HMe$_2$), 39.8 (C-2, C-4), 32.5 (br., CH*Me*$_2$), 24.6—21.4 (br., C-6, C-7), and 17.2 (C-3); δ(^{1}H) 3.28 (septet, C*H*Me$_2$, $^3J_{HH}$ 6.4 Hz), 1.57 (br. m, CH$_2$), 1.34 (6- and 7-H), and 1.08 (d, CH*Me*$_2$).

Consequently there are also two sets of methyl groups on the piperidino substituent, as shown in structures (**9**) and (**10**). Coalescence of the ^{13}C n.m.r. signals was observed at 23 °C, and the activation energy (E_A) for inversion at nitrogen was determined to be 58 ± 2 kJ mol^{-1}. The barrier for inversion is much lower in (**6**) than in 1,2-diethyl-1,2-diaziridine[13] (E_A 87 kJ mol^{-1}) and may be attributed to ring BN π-bonding assisting the inversion process.

At present no firm evidence is available for the configuration of (**6**). We assume that the isopropyl groups adopt a *gauche* conformation as represented in structures (**9**) and (**10**). This assumption is based on preliminary geometry-optimized MO calculations using the STO-3G method.[14] The $\delta(^{11}B)$ value suggests that the C_2N moiety of the piperidino substituents is coplanar with the BN_2 ring. A strong i.r. band at 1580 cm^{-1} (with a ^{10}B shoulder at 1610 cm^{-1}) supports this conclusion.

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14 Calculations by Dr H.-U. Wagner, Institute of Organic Chemistry, University of Munich, show that the *cis*-conformation of $H_2N\overline{BNHN}H$ is less stable than the *gauche* conformation by 27.2 kJ mol^{-1}.