The Structure of 1,2-Diaryl-1,2-bis(dimethylamino)diboron Compounds and Related Species: Boron–Nitrogen Analogues of Buta-1,3-dienes†

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The 1,2-dihalogenodiborane(4) compound $Br(Me_2N)BB(NMe_2)Br$ **1** reacts with Li(mes) (mes = C_6H_2-Me_3-2,4,6) or LiPh to form the derivatives $Br(Me_2N)BB(NMe_2)(mes)$ **2**, $(mes)(Me_2N)BB(NMe_2)(mes)$ **3**, and the previously reported (synthesised by a different route) species $Ph(Me_2N)BB(NMe_2)Ph$ **4** in moderate yields. Compounds **2**–**4** are thermally stable, colourless, crystalline solids. All compounds were characterized by X-ray crystallography and NMR spectroscopy. Their structures have B–B bond lengths that vary from 1.682(16) Å in **1** to 1.717(15) Å in **3**. In addition, all compounds display high angles (from 58.9 to 88.7°) between the planes at the boron atoms and short B–N distances that are near 1.39 Å. The structures of **1**–**4** represent, apparently, the first such acyclic examples for diborane(4) derivatives of the type $B_2X_2(NR_2)_2$ where X = halogen or aryl group. Crystal data: 130 K: **1**, $Br(Me_2N)BB(NMe_2)Br$, monoclinic, space group $P2_1$, $a = 6.789(2)$, $b = 7.720(2)$, $c = 10.012(4)$, $\beta = 103.06(3)°$, $Z = 2$, $R = 0.048$ for 1109 $[I > 2.0\sigma(I)]$ data; **2**, $Br(Me_2N)BB(NMe_2)(mes)$, monoclinic, space group $C2/c$, $a = 24.890(14)$, $b = 7.662(4)$, $c = 18.500(12)$, $\beta = 116.36(4)°$, $Z = 8$, $R = 0.063$ for 1910 $[I > 2.0\sigma(I)]$ data; **3** $(mes)(Me_2N)BB(NMe_2)(mes)$, orthorhombic, space group $Pbcn$, $a = 37.983(14)$, $b = 14.167(5)$, $c = 12.282(4)$ Å, $Z = 12$, $R = 0.095$ for 1829 $[I > 3.0\sigma(I)]$ data; **4**, $Ph(Me_2N)BB(NMe_2)Ph$, orthorhombic, space group $P2_12_12_1$, $a = 8.579(2)$, $b = 12.920(4)$, $c = 13.925(3)$ Å, $Z = 4$, $R = 0.045$ for 1776 $[I > 4.0\sigma(I)]$ data.

Derivatives of diborane(4) (*i.e.* B_2H_4) are the simplest catenated boron compounds.[1,2] Yet, in spite of the very large amount of information now available for B–B bonded, three-dimensional polyboron species, diborane(4) species have received relatively little attention. The main reason for this has probably been their perceived instability.[1,2] For example, diborane(4) itself is stable only when it is complexed with Lewis bases such as amines or phosphines.[3] In addition, its halide derivatives, *e.g.* B_2Cl_4.[4] are difficult to synthesise in large quantities and, with the exception of B_2F_4,[5] have marginal stability under ambient conditions. Until recently, the only well known stable diborane(4) compounds were those that involved good π-donor substituents *e.g.* $-NR_2$, $-OR$ groups (R = alkyl or aryl), a phenomenon that was first recognized thirty years ago.[6,7] Two simultaneous reports[8,9] in 1980 disclosed the first isolable tetraorganodiborane(4) compounds which were stabilized by bulky alkyl groups such as Bu^t or CH_2Bu^t. Yet, in spite of the presence of these large groups, it was shown that they decomposed between about 50 and 90 °C.

Recent work in this research group and others has demonstrated that diaryl boryl groups [*e.g.* $-B(mes)_2$, mes = C_6H_2-Me_3-2,4,6] were very effective in stabilizing unusual inorganic boron compounds.[10] It was thought that the use of similar groups might prove to be effective in the enhancement of the stability of organodiborane(4) species. This reasoning has led to the isolation and the structural characterization of the species $(mes)_2BB(mes)Ph$[11] and $(mes)_2BB(mes)(CH_2SiMe_3)$[11] which have higher (up to *ca.* 200 °C) thermal stability than the pure alkyls. As in the case of the alkyl derivatives the synthesis of these species was achieved by the conversion of $B_2(NMe_2)_4$ to $B_2(OMe)_4$ which may then be treated with aryl or alkyl lithium reagents to afford partial or total substitution of the –OMe groups. In this paper, attention is focussed on the structure and stability of compounds containing amino, and aryl or halide substituents. Such compounds, for example, those of the general formula $B_2R_2(NR'_2)_2$[12–14] have been synthesised previously and they have been used as precursors for other diborane(4) compounds. With the exception of some cyclic species[15,16] the acetylenic species $(PhCC)(Me_2N)BB(NMe_2)(CCPh)$[17] and the bulky alkyl derivative $B_2(fluorenyl)_2[\overline{NCH_2(CH_2)_2CH_2}]_2$[17] there are almost no structural data available. In this paper the structures of three aryl substituted 1,2-bis(diethylamino)diboron compounds and the related precursor 1,2-dibromo species are described.

Experimental

Starting Materials.—The compounds BBr_3, $NHMe_2$, LiBu (1.6 mol dm^{-3} solution in hexane) were purchased from commercial suppliers. The compounds $B_2(NMe_2)_4$,[6] $Br(Me_2N)BB(NMe_2)Br$,[18] Li(mes)[19] and LiPh[20] were prepared by literature methods.

General procedures. All work was performed by using Schlenk techniques under N_2 or in an Vacuum Atmospheres HE-43 Dry Box. Solvents were freshly distilled under N_2 from Na–K alloy and degassed twice immediately before use. Proton and ^{11}B NMR spectra were obtained on a General Electric QE-300 spectrometer. The ^{11}B chemical shifts were referenced to a $BF_3 \cdot Et_2O$ standard. All the compounds gave satisfactory H, C and N analyses.

Syntheses.—$Br(Me_2N)BB(NMe_2)Br$ **1**. This compound was prepared by a method very similar to that described in the literature.[18] A solution of BBr_3 (25.35 g, 101 mmol) in pentane (50 cm^3) was added dropwise to a stirred solution of $B_2(NMe_2)_4$ (20 g, 101 mmol) in pentane (40 cm^3) cooled in a solid CO_2–acetone bath. The mixture was allowed to reach room temper-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: mmHg ≈ 133 Pa.

Table 1 Selected crystal data for compounds **1**–**4**

	1	**2**	**3**	**4**
Compound	Br(Me$_2$N)BB(NMe$_2$)Br	(mes)(Me$_2$N)BB(NMe$_2$)Br	(mes)(Me$_2$N)BB(NMe$_2$)(mes)	Ph(Me$_2$N)BB(NMe$_2$)Ph
Empirical formula	$C_4H_{12}B_2Br_2N_2$	$C_{13}H_{23}B_2BrN_2$	$C_{22}H_{34}B_2N_2$	$C_{16}H_{22}B_2N_2$
M	269.6	308.9	348.1	264.0
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$C2/c$	$Pbcn$	$P2_12_12_1$
Crystal dimensions (mm)	0.56 × 0.6 × 0.4	0.05 × 0.1 × 0.12	0.12 × 0.22 × 0.6	0.46 × 0.72 × 0.92
a/Å	6.789(2)	24.890(14)	37.983(14)	8.579(2)
b/Å	7.720(2)	7.662(4)	14.167(5)	12.920(4)
c/Å	10.012(4)	18.500(12)	12.282(4)	13.925(3)
β/°	103.06(3)	116.36(4)	—	—
U/Å^3	510.3(3)	3141(3)	6615(4)	1543.4(7)
Z	2	8	12	4
D_c/Mg m^{-3}	1.75	1.31	1.05	1.14
2θ range/°	0–55	0–50	0–50	0–55
μ/mm^{-1}	7.808	2.576	0.037	0.061
F(000)	260	1280	1520	568
Independent reflections	1253	2768	5827	2032
Observed reflections	1109($I > 2\sigma I$)	1910($I > 2\sigma I$)	1829($I > 3\sigma I$)	1776($I > 2\sigma I$)
No. of parameters	0.048	163	158	181
$R(F)$	90	0.063	0.095	0.045
$R'(F)$	0.050	0.060	0.099	0.054

Table 2 Atomic coordinates (× 10^4) for Br(Me$_2$N)BB(NMe$_2$)Br **1**

Atom	x	y	z
Br(1)	2 778(2)	6 787	8 333(1)
Br(2)	7 133(2)	3 482(2)	7 304(1)
N(1)	2 477(11)	3 142(11)	8 880(8)
N(2)	3 294(12)	3 779(12)	5 347(7)
C(1)	1 728(15)	3 495(19)	10 100(9)
C(2)	2 562(16)	1 246(15)	8 611(12)
C(3)	4 328(19)	3 494(19)	4 209(11)
C(4)	1 101(13)	4 064(15)	4 843(8)
B(1)	3 053(13)	4 293(16)	7 988(10)
B(2)	4 170(17)	3 844(13)	6 690(11)

Table 3 Atomic coordinates (× 10^4) for (mes)(Me$_2$N)BB(NMe$_2$)Br **2**

Atom	x	y	z
Br	3347(1)	1817(1)	9023(1)
N(1)	4593(2)	−1010(7)	8738(3)
N(2)	3084(2)	−1725(8)	8405(3)
C(1)	3977(3)	1003(9)	7511(4)
C(2)	3637(3)	430(10)	6702(4)
C(3)	3557(3)	1519(9)	6055(4)
C(4)	3792(3)	3217(11)	6177(4)
C(5)	4124(3)	3759(10)	6973(4)
C(6)	4221(3)	2709(9)	7631(4)
C(7)	3354(3)	−1344(10)	6528(4)
C(8)	3689(3)	4379(11)	5471(4)
C(9)	4592(3)	3410(10)	8471(4)
C(10)	5127(3)	−925(11)	8596(4)
C(11)	4706(3)	−2031(9)	9459(4)
C(12)	3178(3)	−3410(10)	8117(5)
C(13)	2557(3)	−1785(12)	8561(5)
B(1)	4051(3)	−174(10)	8255(5)
B(2)	3472(3)	−333(10)	8506(5)

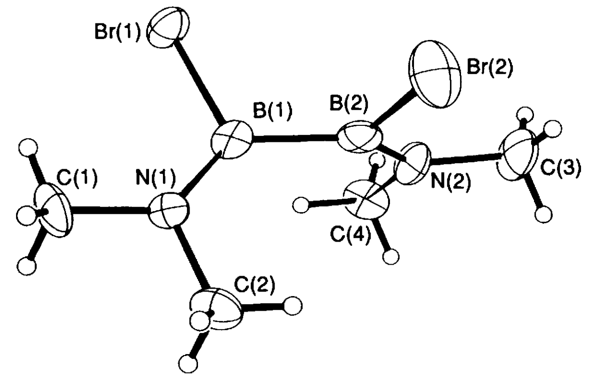

Fig. 1 Computer generated drawing of compound **1**

ature and stirred overnight. The pentane was then distilled off at atmospheric pressure and after distilling some B(NMe$_2$)$_2$Br by-product at 32–38 °C (0.2 mmHg), Br(Me$_2$N)BB(NMe$_2$)Br was distilled at 70–73 °C (0.2 mmHg); lit. 76–77 °C (1.5 mmHg).[18] Yield 19.1 g, 70%; m.p. 42 °C. NMR (C_6D_6): ^{11}B, δ 37.7, lit. 38.0;[21] ^{1}H, δ 2.5 (d, 12 H).

(mes)(Me$_2$N)BB(NMe$_2$)Br **2**. A solution of Br(Me$_2$N)BB(NMe$_2$)Br (1.0 g, 3.7 mmol) in hexane (40 cm^3) was added dropwise to a stirred slurry (1.0 g, 7.9 mmol) of Li(mes) in diethyl ether (40 cm^3) with cooling in a solid CO$_2$–acetone bath. The mixture was allowed to warm to room temperature and stirred overnight. The volatile components were then removed under reduced pressure and the residue was extracted with hexane (30 cm^3). Filtration and reduction of the filtrate to about 3–4 cm^3 and cooling at −20 °C gave colourless crystals of **2**. Yield 0.74 g, 65%, m.p. 63–64 °C. NMR (C_6D_6): ^{11}B, δ 47.4 and 41.4; ^{1}H, δ 1.754 (s, 3 H), 1.884 (s, 6 H), 1.931 (s, 3 H), 2.14 (s, 3 H), 2.195 (s, 3 H), 2.286 (s, 3 H) and 6.36 (s, 2 H).

(mes)(Me$_2$N)BB(NMe$_2$)(mes) **3**. A solution of (mes)(Me$_2$N)BB(NMe$_2$)Br (1.02 g, 3.3 mmol) in pentane (40 cm^3) was added rapidly by a double-tipped needle to a stirred slurry of Li(mes) (0.6 g, 4.7 mmol) in pentane (40 cm^3), and cooled at −78 °C. The mixture was allowed to reach room temperature and was refluxed overnight. Filtration and reduction of the filtrate to *ca.* 2–3 cm^3 and subsequent cooling at −20 °C gave crystals of compound **3**. Yield 0.57 g, 50%; m.p. 117–119 °C. NMR (C_6D_6): ^{11}B, δ 50.2; ^{1}H, δ 1.988 (s, 3 H), 2.202 (s, 6 H), 2.68 (d, 12 H) and 6.717 (s, 4 H).

Ph(Me$_2$N)BB(NMe$_2$)Ph **4**. A solution of Br(Me$_2$N)BB(NMe$_2$)Br (1.0 g, 3.7 mmol) in hexane (40 cm^3) was added to a rapidly stirred slurry of LiPh (0.70 g, 8.3 mmol) in hexane (40 cm^3), and cooled in a solid CO$_2$–acetone mixture. The mixture was allowed to warm to room temperature and stirred overnight. Filtration and reduction of the volume of

Table 4 Atomic coordinates ($\times 10^4$) for (mes)(Me_2N)BB(NMe_2)(mes) **3**

Atom	x	y	z
Molecule 1			
N(1)	5430(2)	660(6)	2045(7)
C(1)	5439(3)	−147(7)	2796(9)
C(2)	5734(3)	630(8)	1295(9)
C(3)	5217(2)	2223(7)	1234(8)
C(4)	5037(3)	2279(7)	233(9)
C(5)	5081(3)	3041(7)	−486(9)
C(6)	5295(3)	3790(8)	−178(9)
C(7)	5465(3)	3775(8)	814(9)
C(8)	5429(2)	3011(7)	1506(9)
C(9)	4795(3)	1491(8)	−74(9)
C(10)	5351(3)	4598(9)	−977(10)
C(11)	5619(3)	3027(8)	2588(8)
B(1)	5172(3)	1379(9)	2043(10)
Molecule 2			
N(2)	3231(2)	5007(6)	2663(6)
N(3)	3657(2)	6892(5)	1466(6)
C(12)	2982(2)	4250(7)	2901(8)
C(13)	3589(2)	4619(7)	2524(9)
C(14)	2735(2)	6224(6)	2778(7)
C(15)	2510(2)	6334(6)	1895(7)
C(16)	2154(2)	6549(6)	2060(8)
C(17)	2025(2)	6662(7)	3112(8)
C(18)	2251(3)	6584(7)	3971(9)
C(19)	2608(2)	6391(7)	3832(8)
C(20)	2639(2)	6194(7)	754(7)
C(21)	1636(3)	6865(8)	3282(9)
C(22)	2845(3)	6351(7)	4799(8)
C(23)	3647(2)	6223(7)	563(8)
C(24)	3921(2)	7633(7)	1278(9)
C(25)	3482(2)	7635(6)	3282(8)
C(26)	3268(2)	8439(7)	3250(8)
C(27)	3297(2)	9131(7)	4051(8)
C(28)	3537(3)	9046(7)	4887(9)
C(29)	3745(3)	8246(7)	4925(9)
C(30)	3721(2)	7540(7)	4144(8)
C(31)	2996(2)	8558(7)	2358(8)
C(32)	3572(3)	9830(8)	5724(10)
C(33)	3956(3)	6690(7)	4228(9)
B(2)	3140(3)	5952(8)	2587(9)
B(3)	3444(3)	6833(8)	2391(10)

Table 5 Atomic coordinates ($\times 10^4$) for Ph(Me_2N)BB(NMe_2)Ph **4**

Atom	x	y	z
B(1)	529(3)	9 040(2)	7 632(2)
B(2)	−1 435(3)	8 860(2)	7 479(2)
N(1)	1 107(2)	9 803(1)	8 255(1)
N(2)	−2 270(2)	9 340(1)	6 747(1)
C(1)	92(3)	10 492(2)	8 798(2)
C(2)	2 748(3)	10 003(2)	8 457(2)
C(3)	1 698(3)	8 274(2)	7 111(2)
C(4)	1 770(3)	8 204(2)	6 100(2)
C(5)	2 778(3)	7 523(2)	5 641(2)
C(6)	3 718(3)	6 870(2)	6 175(2)
C(7)	3 649(3)	6 904(2)	7 170(2)
C(8)	2 661(3)	7 596(2)	7 624(2)
C(9)	−3 918(3)	9 149(2)	6 514(2)
C(10)	−1 596(3)	10 088(2)	6 083(2)
C(11)	−2 310(3)	8 118(2)	8 209(1)
C(12)	−1 938(3)	7 063(2)	8 292(2)
C(13)	−2 725(3)	6 420(2)	8 929(2)
C(14)	−3 881(3)	6 814(2)	9 518(2)
C(15)	−4 251(3)	7 861(2)	9 467(2)
C(16)	−3 492(3)	8 494(2)	8 822(2)

the filtrate and cooling at 10 °C gave colourless crystals of Ph(Me_2N)BB(NMe_2)Ph **4**. Yield 0.48 g, 50%; m.p. 98–101 °C (lit. 101–102 °C).[13] NMR (C_6D_6): ^{11}B, δ 49.3; ^1H, δ 2.26 (d, 12 H), 6.702 (d, 2 H), 6.815 (t, 4 H) and 6.882 (d, 4 H).

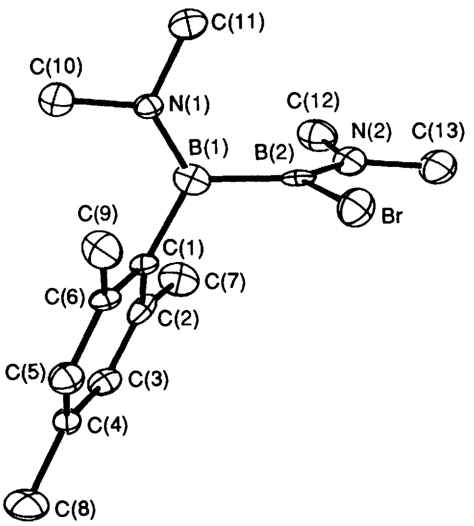

Fig. 2 Thermal ellipsoidal drawing of compound **2**. Hydrogen atoms are omitted for clarity

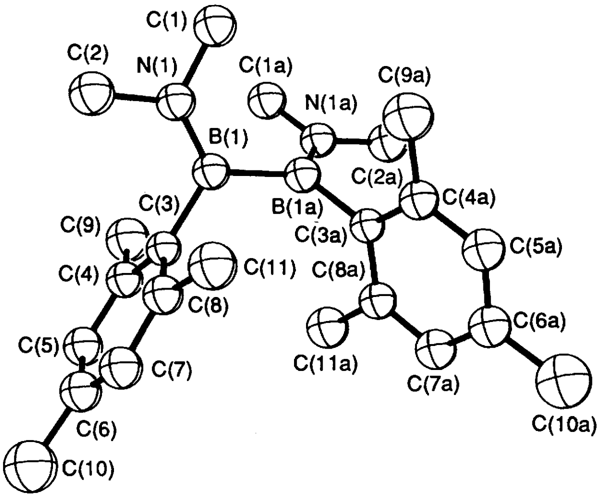

Fig. 3 Thermal ellipsoidal plot of compound **3**. Hydrogen atoms are omitted for clarity

X-Ray Data Collection and Solution Refinement of the Structures.—Crystals of the compounds **1**–**4** were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of hydrocarbon oil. A single crystal was selected, mounted on a glass fibre and immediately placed in the low-temperature N_2 stream. X-Ray data were collected at 130 K with Mo-Kα radiation (λ = 0.710 69 Å) on a Siemens R3m/v diffractometer equipped with a locally modified low-temperature device. Computer programs were from SHELXTL-PLUS (version 4)[22] installed on a micro VAX 3200. The atom form factors including anomalous scattering were from ref. 23. Some details of the data collection and refinement are given in Table 1. The structures were solved by direct methods and subsequently refined by full-matrix least-squares refinement. The H atoms were included by use of a riding model with C–H distances of 0.96 Å and fixed isotropic thermal parameters. All non-hydrogen atoms were refined anisotropically except for compound **3** for which isotropic thermal parameters were employed. An absorption correction* was applied to all

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* The absorption correction was made by using the program XABS by Hope and Moezzi,[24] from $F_o - F_c$ differences.

Table 6 Selected bond angles (°) and bond lengths (Å) for compounds **2**–**4**

1		**2**		**3***		**4**	
B(1)–B(2)	1.682(16)	B(1)–B(2)	1.703(14)	B(2)–B(3)	1.717(15)	B(1)–B(2)	1.714(4)
B(1)–N(1)	1.378(14)	B(1)–N(1)	1.399(8)	B(2)–N(2)	1.385(13)	B(1)–N(1)	1.405(3)
B(1)–Br(1)	1.972(12)	B(2)–N(2)	1.395(10)	B(2)–C(14)	1.604(13)	B(2)–N(2)	1.392(3)
B(2)–Br(2)	1.986(11)	B(1)–C(1)	1.586(11)	B(3)–N(3)	1.397(13)	B(1)–C(3)	1.584(3)
B(2)–N(2)	1.342(12)	B(2)–Br	1.998(9)	B(3)–C(25)	1.584(15)	B(2)–C(11)	1.586(3)
Br(1)–B(1)–N(1)	117.7(7)	C(1)–B(1)–N(1)	121.5(8)	C(14)–B(2)–N(2)	117.4(8)	C(3)–B(1)–N(1)	119.9(2)
B(2)–B(1)–N(1)	127.7(9)	B(2)–B(1)–N(1)	119.0(7)	C(14)–B(2)–B(3)	119.3(8)	C(3)–B(1)–B(2)	118.8(2)
B(2)–B(1)–Br(1)	114.4(7)	B(2)–B(1)–C(1)	119.4(6)	N(2)–B(2)–B(3)	123.1(8)	N(1)–B(1)–B(2)	121.2(2)
Br(2)–B(2)–N(2)	119.5(8)	Br–B(2)–N(2)	116.6(6)	N(3)–B(3)–C(25)	117.8(8)	N(2)–B(2)–C(11)	119.7(2)
B(1)–B(2)–N(2)	127.4(9)	B(1)–B(2)–N(2)	129.6(7)	N(3)–B(3)–B(2)	123.1(9)	N(2)–B(2)–B(1)	122.4(2)
B(1)–B(2)–Br(2)	113.1(6)	B(1)–B(2)–Br	113.7(7)	C(25)–B(3)–B(2)	119.0(8)	C(11)–B(2)–B(1)	117.9(2)
B(1)–N(1)–C(1)	129.0(10)	B(1)–N(1)–C(11)	124.7(7)	B(2)–N(2)–C(13)	125.4(8)	B(1)–N(1)–C(1)	122.6(2)
B(1)–N(1)–C(2)	119.2(9)	B(1)–N(1)–C(10)	124.0(5)	B(2)–N(2)–C(12)	124.3(7)	C(1)–N(1)–C(2)	111.7(2)
C(1)–N(1)–C(2)	111.8(9)	C(11)–N(1)–C(10)	111.3(5)	C(13)–N(2)–C(12)	110.3(7)	B(1)–N(1)–C(2)	125.7(2)
B(2)–N(2)–C(3)	126.5(9)	C(12)–N(2)–C(13)	110.4(7)	B(3)–N(3)–C(24)	124.4(8)	B(2)–N(2)–C(10)	123.8(2)
B(2)–N(2)–C(4)	121.4(9)	C(12)–N(2)–B(2)	120.9(7)	B(3)–N(3)–C(23)	124.4(8)	B(2)–N(2)–C(9)	125.5(2)
C(3)–N(2)–C(4)	112.0(7)	C(13)–N(2)–B(2)	128.7(7)	C(23)–N(3)–C(24)	111.2(7)	C(9)–N(2)–C(10)	110.7(2)

Compound		**1**		**2**			**3***		**4**
Angle between planes at B		83.7		74.7			58.9		88.7
Angle between plane at B(1) and plane at N(1)		4.1		4.5	Angle between plane at and plane at atoms	B(2) N(2)	4.3	N(1)	4.7
						C(14)	85.1	C(3)	66.3
Angle between plane at B(2) and the plane at the atoms	N(2)	6.2	N(2)	6.5	Angle between plane at and plane at atoms	B(3) N(3)	1.4	N(2)	5.4
			C(1)	77.2		C(25)	88.5	C(11)	62.8

* Distances for one of the two molecules are provided.

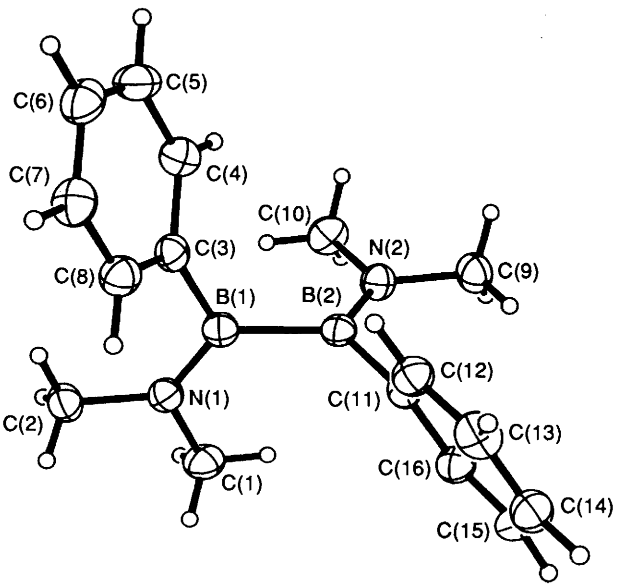


Fig. 4 Computer generated drawing of compound **4**

compounds. Fractional coordinates for non-hydrogen atoms for compounds **1**–**4** are given in Tables 2–5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis.—The compounds **2**–**4** may be synthesised by the treatment of **1** with the appropriate number of equivalents of aryllithium as illustrated by equations (1) and (2).[17] The previously reported[18] compound **1** was obtained by the reaction of BBr_3 with $B_2(NMe_2)_4$. The latter species is obtainable in good yield by the reduction of $B(NMe_2)_2X$ (X = Cl or Br) with sodium in a hydrocarbon solvent.[6]

$$\underset{\mathbf{1}}{\mathrm{Br(Me_2N)BB(NMe_2)Br}} + \mathrm{Li(mes)} \longrightarrow \underset{\mathbf{2}}{\mathrm{Br(Me_2N)BB(NMe_2)(mes)}} + \mathrm{LiBr} \quad (1)$$

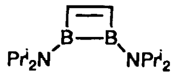
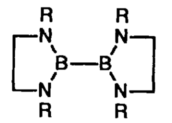
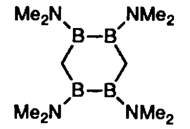
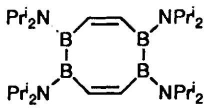
$$\mathrm{Br(Me_2N)BB(NMe_2)Br} + 2\mathrm{LiR} \longrightarrow \mathrm{R(Me_2N)BB(NMe_2)R} + \mathrm{LiBr} \quad (2)$$

$$(\mathrm{R} = \text{mes } \mathbf{3} \text{ or Ph } \mathbf{4})$$

Compounds of the type $B_2R_2(NMe_2)_2$ (R = alkyl or aryl) similar to **3** and **4** have been obtained by reduction of the precursor $BR(NMe_2)X$ (X = halide, R = alkyl or aryl) with alkali metals.[12–14] Similar reactions, in this laboratory, using the precursor $B(mes)(NMe_2)Br$ did not give good yields of **3** although the related species **4** was reported to be obtainable by this route. It may be that a bulky group at boron (*i.e.* mesityl) prevents an efficient reduction. In effect, equations (1) and (2) offer an alternative route to such compounds with the advantage that differentially substituted products like **2** can be readily isolated. The steric crowding in **3** is underlined by the fact that it is only obtained upon overnight refluxing. Stirring a mixture of **1** with 2 equivalents of Li(mes) at room temperature affords only the monosubstituted derivative **2**.

Structures.—The structures of compounds **1**–**4** are illustrated in Figs. 1–4. Selected bond distances, angles and structural parameters are given in Table 6. The following major structural features are common to the four structures: (*i*) the B–B distances display relatively minor variation and are all within 0.02 Å of 1.7

Table 7 Selected bond distances (Å) and angles (°) for some diborane(4) amido derivatives and related species

Compound	B–B	B–X	B–N	B–C	Ref.
B_2Br_4	1.689(16)	1.902(4)	—	—	28
1 $B_2(NMe_2)_2Br_2$	1.682(16)	1.979(13)	1.360(13)	—	This work
2 $B_2(mes)(NMe_2)_2Br$	1.703(14)	1.998(12)	1.397(9)	1.585(11)	This work
3 $B_2(mes)_2(NMe_2)_2$	1.717(15)	—	1.391(13)	1.594(14)	This work
4 $B_2Ph_2(NMe_2)_2$	1.714(4)	—	1.399(3)	1.585(3)	This work
5 $B_2(CCPh)_2(NMe_2)_2$	1.696(8)	—	1.387(6)	1.548(6)	17
6 $B_2(fluorenyl)_2[NCH_2(CH_2)_2CH_2]_2$	1.697( )	—	1.393(3)	1.614(3)	17
7 $(Me_2N)_2B–B(NMe_2)_2$	1.762(11)	—	1.408(3)	—	29
8 	1.748		1.409(2)	1.579(2)	15
					
9 R = Me	1.690(9) 1.696(9)	 —	1.417(8) 1.414(7)	— —	30
10 R = C_6H_{11}	1.721(2)	—	1.402(7) 1.383(7)	—	31
11 	1.711	—	1.405	1.59	32
12 	1.718	—	1.409	1.579	16
$B_2(mes)_3Ph$	1.706(12)	—	1.412	1.565(Ph) 1.580(9)(mes)	11

Å, (*ii*) there are large angles (58.9–88.7°) between the planes at the boron atoms, (*iii*) the B–N distances are short and average about 1.39 Å in length. The compounds **1**–**4** are in effect analogues of substituted buta-1,3-dienes with localized B–N double bonds and low angles (4–6.5°) between the planes at boron and nitrogen. The B–N distances are typical for bonding between three-co-ordinate nitrogen and boron centres[25,26] and a π interaction and substantial rotation barriers about the B–N bond confirmed by the observation of magnetically inequivalent methyl groups in their room-temperature ^1H NMR spectra. In addition, the structures of **1**–**4** are closely related to the 1,2-diborylhydrazines *e.g.* $(mes)_2B(H)NN(H)B(mes)_2$ which also display localized multiple boron–nitrogen bonding and magnetically inequivalent organic substituents on boron.[27]

The B–B distances in **1**–**4** show only minor variation across the series. The average distance is 1.704 Å and this is what is expected from the sum of the radii for three-co-ordinate boron (0.85 Å).* The B–B distances of **1**–**4** may be compared with those found in B_2Br_4,[28] tetraorganodiboranes(4) and various tetra-amido derivatives (Table 7). It can be seen that, with the exceptions of $B_2(NMe_2)_4$ **7**[29] [B–B 1.762(11) Å] and $Pr^i_2NBCHCHBNPr^i_2$ **8**[15] the B–B distances fall in the range 1.70 ± 0.02 Å. The longer B–B distance in **8**[15] may be the result of the strain in the four-membered B_2C_2 ring. The longer distance in **7** was partly rationalized on the basis of steric effects.[29] This argument notwithstanding, the B–B distances observed in the closely related **5**,[17] **6**,[17] **9**[30] and **10**[31] species are shorter (Table 7). It may be that, since the structure of **7** was determined by electron diffraction at high temperature, its higher thermal and rotation energy, and the absence of restrictions owing to the acyclic nature of the $-NR_2$ groups, contribute to a lengthening of the B–B bond. Overall, the data in Table 7 indicate that any π interaction involving the B–B bond is either very small or non-existent. The relatively minor variations in the B–B and B–N bond lengths can, to a large extent, be rationalized on the basis of steric crowding, ring strain, variable Coulombic repulsion across the B–B bonds and the changes in the strength of the B–N π bond. For example, the lengths of the B–B and the B–N bonds in **3** and **4** are very similar (Table 7). The fairly short B–N bonds point to a strong B–N π interaction and the B–B bond lengths fall at the longer end of the range for B–B bonds in this class of compound. The structures of **5** and **6** also have short B–N bonds although the lengths of the B–B bonds are also reduced, perhaps because of electron withdrawing character of the –CCPh and fluorenyl substituents. If the organo groups are replaced by bromines, the electron withdrawing character of the halide may reduce the negative charge density on boron and decrease the B–B Coulombic repulsion. This should also enhance π-electron donation by nitrogen and the B–N distances ought to be shorter. The B–B (1.682 Å) and B–N (av. 1.36 Å) bond distances observed for **1** are in accord with this rationale. Interestingly the corresponding bond distances in **2** also correlate with this view but the uncertainties in the structural parameters render this comparison less meaningful. The structure of the tetra-aminodiborane(4) derivatives **9** and **10** lends further support to

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* The radius for boron quoted in the literature varies from about 0.8 to 0.9 Å. However, a value of 0.85 Å is consistent with structures for a variety of three-co-ordinate boron compounds including those in refs. 10 and 11.

this description of the bonding. The competitive π interaction of the two amino groups with the boron p orbital reduces the strength of the B–N π bonds such that the B–N bonds are near 1.4 Å. The average B–B distance in **9** is 1.693 Å which is slightly shorter than expected. A more extreme example involves the more crowded species **10** which shows a longer B–B bond 1.721(12) Å and shorter B–N distances (≈ 1.39 Å). In this case the B–N interaction has apparently been strengthened at the expense of weakening the B–B bond. Ultimately, a situation can be envisaged in which this bond could be cleaved to give an aminoboryl radical.

The compounds **2**–**4** have moderate air and moisture sensitivity. The major feature in their ^{1}H NMR spectra is the observation of separate resonances for the $-NMe_2$ methyl groups. In the case of **2** two different sets of NMe_2 peaks were observed owing to the different boron substitution. Two separate ^{11}B NMR peaks (at δ 47.4 and 41.4) were also observed. The downfield peak appears to be due to a mesityl-substituted boron compound since **3** and **4** display single peaks at δ 50.2 and 49.3.

In summary, it has been shown that the boron–nitrogen analogues of buta-1,3-dienes are structurally very similar to the corresponding organic species. Current work in this laboratory demonstrates that they have an interesting chemistry. For example, **4** readily undergoes a two-electron reduction in donor solvents to give dianions with multiple B–B bonds. This and other aspects of their chemistry will be described in a subsequent publication.

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