Enhanced Thermal Stability in Organodiborane(4) Compounds: Synthesis and Structural Characterization of MeO(Mes)BB(Mes)OMe, $Mes_2BB(Mes)OMe$, $Mes_2BB(Mes)Ph$, and $Mes_2BB(Mes)CH_2SiMe_3$ (Mes = 2,4,6-$Me_3C_6H_2$)

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A series of organo-substituted diborane(4) compounds have been prepared and characterized by X-ray crystallography and NMR spectroscopy. The compounds MeO(Mes)BB(Mes)OMe (1), $Mes_2BB(Mes)OMe$ (2), $Mes_2BB(Mes)Ph$ (3), and $Mes_2BB(Mes)CH_2SiMe_3$ (4) were synthesized by the reaction of the stable precursor species $B_2(OMe)_4$ with the appropriate organolithium reagent. All the compounds are thermally stable, air- and moisture-sensitive, colorless crystalline solids. Moreover, the species 3 and 4 exhibit significantly enhanced thermal stability in comparison to previously reported tetraalkyldiborane(4) derivatives. The X-ray structures of 3 and 4 represent the first structural reports for tetraorganodiborane(4) species. Crystal data with Mo Kα (λ = 0.71069 Å) radiation at 130 K are as follows: 1, MeO(Mes)BB(Mes)OMe, a = 8.324 (2) Å, b = 14.744 (3) Å, c = 15.395 (5) Å, Z = 4, orthorhombic, space group $Pc2_1b$, R = 0.059 for 1488 ($I > 2\sigma(I)$) data; 2, $Mes_2BB(Mes)OMe{\cdot}0.5C_5H_{12}$, a = 8.666 (10) Å, b = 12.500 (13) Å, c = 13.858 (16) Å, α = 109.90 (8)°, β = 100.51 (8)°, γ = 99.68 (8)°, Z = 2, triclinic, space group $P\bar{1}$, R = 0.090 for 1554 ($I > 2\sigma(I)$) data; 3, $Mes_2BB(Mes)Ph$, a = 8.911 (3) Å, b = 12.142 (3) Å, c = 13.961 (3) Å, α = 104.04 (2)°, β = 93.88 (3)°, γ = 107.86 (2)°, Z = 2, triclinic, space group $P\bar{1}$, R = 0.075 for 1834 ($I > 2\sigma(I)$) data; 4, $Mes_2BB(Mes)CH_2SiMe_3$, a = 12.221 (8) Å, b = 15.880 (7) Å, c = 16.152 (6) Å, α = 112.26 (3)°, β = 93.96 (4)°, γ = 89.97 (4)°, Z = 4 (two independent molecules), triclinic, space group $P\bar{1}$, R = 0.087 for 2445 ($I > 2\sigma(I)$) data.

Introduction

Tetraorgano derivatives of diborane(6) (i.e., compounds of formula $(HBR_2)_2$) are well-known and have an extensive chemistry.[1] In contrast, tetraorganodiborane(4) species are relatively poorly studied.[2] The first examples of such compounds were isolated only within the last decade and they were stabilized through the use of bulky substituents such as neopentyl and *tert*-butyl groups.[3,4] In a broader context it has been recognized for a number of years that increased electronic and steric shielding of boron in diborane(4) derivatives enhances their stability by hindering their decomposition to BX_3 and polyboron species.[2] Thus, $B_2(NMe_2)_4$[5,6] is considerably more thermally stable than B_2Cl_4[7] owing to the superior π-donor characteristics and the greater size of the NMe_2 ligands. Similarly, $B_2Et_2(NMe_2)_2$ is stable up to about 140 °C,[8] whereas $B_2Cl_2Me_2$ decomposes above −20 °C[9] and B_2Me_4 is unknown. Apparently, π-donor groups such as NMe_2 hinder nucleophilic attack at the borons by increasing the electron density and the steric hindrance at those sites. The isolation of tetraorganodiborone(4) compounds such as $(t\text{-Bu})_2BB(t\text{-Bu})Me$[3] (stable up to ~50 °C), $(t\text{-Bu})(t\text{-BuCH}_2)BB(CH_2\text{-}t\text{-Bu})(t\text{-Bu})$[4] and $(t\text{-Bu})_2BB(t\text{-Bu})(CH_2\text{-}t\text{-Bu})$[4] (stable to ca. 90–100 °C) demonstrates that steric hindrance is, by itself, capable of inducing stability in tetraorganodiboron(4) species. In these alkyl derivatives the boron–carbon bonding is, for the most part, simple σ-bonding. It is possible, however, to have more complex bonding in boron aryls through hyperconjugative interaction involving the boron and aryl ring. Thus, aryl derivatives of diborane(4) might show a marked increase in stability over their alkyl counterparts as a result of the possibility of increased interaction with boron.

In this paper, the synthesis and characterization of several aryl diborane(4) derivatives, including the first example of a tetraaryldiborane(4), are reported. It is shown that, although they display increased thermal stability, there is little evidence of hyperconjugation. Most probably, their stability is due to large size of, and the absence of α-hydrogens in, the aromatic substituents.

Experimental Section

Starting Materials. BBr_3, $HNMe_2$, HCl, and n-BuLi (1.6 M, hexane) were obtained commercially and used as received. The reagents $B_2(NMe_2)_4$,[5] LiPh,[10] LiMes,[11] and $LiCH_2SiMe_3$[12] were prepared according to literature methods.

General Procedures. All experiments were performed either with modified Schlenk techniques or in a Vacuum Atmospheres HE43-2 drybox under a nitrogen atmosphere. Solvents were freshly distilled from a sodium/potassium alloy or magnesium and degassed twice prior to use. ^1H and ^{11}B NMR spectra were recorded in C_6D_6 solution by using a General Electric QE-300 spectrometer and referenced to $BF_3{\cdot}Et_2O$. Infrared spectra were recorded as Nujol mulls between CsI plots with use of a Perkin-Elmer PE-1430 spectrometer.

$B_2(OMe)_4$.[13] This compound was prepared by a slightly modified literature procedure. At room temperature, 12.8 g (404 mmol) of methanol was added to a stirred solution of 19.9 g (101 mmol) of $B_2(NMe_2)_4$ in diethyl ether (100 mL) by a double-tipped needle. The solution was cooled in a dry ice/acetone bath and 14.6 g (404 mmol) of hydrogen chloride gas in diethyl ether (100 mL) was added dropwise. The reaction mixture was stirred for 2 h and was then allowed to reach room temperature and stirred

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Table I. Selected Crystal Data[a] and Collection Parameters for Compounds 1–4

	compound, formula			
	MeO(Mes)BB-(Mes)OMe (1), $C_{20}H_{28}B_2O_2$	$Mes_2BB(Mes)$-$OMe{\cdot}0.5C_5H_{12}$ (2), $C_{30.5}H_{40}B_2O$	$Mes_2BB(Mes)Ph$ (3), $C_{33}H_{38}B_2$	$Mes_2BB(Mes)$-CH_2SiMe_3 (4), $C_{31}H_{44}B_2Si$
fw	322.04	446.27	456.25	466.37
a, Å	8.324 (2)	8.666 (10)	8.911 (3)	12.221 (8)
b, Å	14.744 (3)	12.500 (13)	12.142 (3)	15.880 (7)
c, Å	15.395 (5)	13.858 (16)	13.961 (5)	16.152 (6)
α, deg		109.90 (8)	104.04 (2)	112.26 (3)
β, deg		100.51 (8)	93.88 (3)	93.96 (4)
γ, deg		99.68 (8)	107.86 (2)	89.97 (4)
vol, $Å^3$	1889.4 (7)	1344 (3)	1378.2 (8)	2892 (3)
Z	4	2	2	4
space group	$Pc2_1b$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
d(calcd), $g{\cdot}cm^{-3}$	1.132	1.088	1.099	1.077
2θ range, deg	0–55	0–42	0–45	0–45
no. of obsd reflns	1488 ($I > 2\sigma(I)$)	1554 ($I > 2\sigma(I)$)	1834 ($I > 2\sigma(I)$)	2445 ($I > 2\sigma(I)$)
μ, mm^{-1}	0.069	0.058	0.056	0.093
R(*F*)	5.89%	8.97%	7.45%	8.72%
$R_w(F)$	6.68%	10.77%	7.26%	8.26%

[a] All data were collected at 130 K with Mo Kα radiation (λ = 0.71069 Å).

for a further 4 h. After filtration the precipitate was washed twice with diethyl ether and the combined filtrate was subjected to reduced pressure (0.2 mm) at −60 °C to remove the solvent. The product tetramethoxydiboron was separated from small amounts of trimethylborate byproduct by fractional distillation at −45 °C at 0.01-mm pressure. Yield 11.1 g, 75%; ^{11}B NMR δ 31.2.

(MeO)MesBBMes(OMe) (1). $B_2(OMe)_4$ (1.0 g, 6.8 mmol) in diethyl ether (60 mL) was added by a double-tipped needle to a rapidly stirred slurry of 1.7 g (13.7 mmol) of LiMes in diethyl ether (50 mL) cooled in a dry ice/acetone bath. The mixture was allowed to reach room temperature and stirred overnight. The ether was then removed under reduced pressure and the residue was extracted with hexane. Filtration and reduction of the volume of the filtrate and cooling at −20 °C gave colorless crystals of compound 2. Yield 0.98 g, 45%; mp 105–107 °C; ^{11}B NMR (C_6D_6) δ 61; ^1H NMR (C_6D_6) δ 2.36 (s, 12 H), 2.37 (s, 6 H), 3.42 (s, 6 H(OMe)), 6.73 (s, 4 H). Calcd for $C_{20}H_{28}B_2O_2$: C, 74.59; H, 8.76. Found: C, 74.2; H, 8.73.

$Mes_2BBMes(OMe){\cdot}0.5C_5H_{12}$ (2). A solution of tetramethoxydiborane(4), 0.99 g (6.7 mmol), in diethyl ether (40 mL) was added rapidly by a double-tipped needle to 3.65 g (29 mmol) of LiMes in diethyl ether (60 mL), cooled in a dry ice/acetone bath. The solution was allowed to reach room temperature and stirred overnight. All the volatile materials were removed under reduced pressure and the residue was extracted with several 15-mL portions of pentane. Reduction of the volume of the filtrate to 5–6 mL resulted in an oily precipitate, which, upon cooling in a −20 °C freezer for several days, afforded colorless crystals of compound 2. Yield 55%; ^1H NMR (C_6D_6) δ 1.95 (s, 6 H), 2.00 (s, 3 H), 2.01 (s, 6 H), 2.16 (s, 12 H), 3.34 (s, 3 H), 6.56 (s, 2 H), 6.63 (s, 4 H); ^{11}B NMR (C_6D_6) δ 99.1, 59. Calcd for $C_{30.5}H_{40}B_2O$: C, 82.07; H, 9.03. Found: C, 81.95; H, 8.99.

$Mes_2BB(Mes)Ph$ (3). Compound 3 was synthesized by the addition of a solution of $Mes_2BBMes(OMe)$ (1.15 g, 2.8 mmol) in pentane (50 mL) by a double-tipped needle to a rapidly stirred slurry of LiPh (0.34 g, 4 mmol) in pentane (40 mL) with cooling in a dry ice/acetone bath. The mixture was allowed to reach room temperature and stirred overnight. Filtration and reduction of the volume of the filtrate to ca. 20 mL gave colorless crystals of 3. Yield 0.67 g, 70%; mp 171–83 °C; ^1H NMR (C_6D_6) δ 2.04 (s, 6 H), 2.12 (s, 6 H), 2.16 (s, 3 H), 2.22 (s, 12 H), 6.75 (s, 6 H), 7.11 (t, 3 H), 7.61 (dd, 2 H); ^{11}B NMR (C_6D_6) δ 99. Calcd for $C_{33}H_{38}B_2$: C, 86.87; H, 8.4. Found: C, 86.81; H, 8.1.

$Mes_2BB(Mes)CH_2SiMe_3$ (4). Compound 4 was synthesized by the addition of $Mes_2BBMes(OMe)$ (1.05 g, 2.6 mmol) in pentane (30 mL) by a double-tipped needle to a well-stirred solution of 0.38 g (4 mmol) of $LiCH_2SiMe_3$ in pentane (40 mL) with cooling in a dry ice/acetone mixture. The solution was allowed to reach room temperature and stirred overnight. It was then filtered and reduced to a volume of 4–5 mL under low pressure. Colorless crystals of 4 were obtained from a C_6H_6 solution at room temperature. Yield 0.54 g, 45%; ^{11}B NMR (C_6D_6) δ 100; ^1H NMR δ 0.10 (s, 9 H), 0.19 (s, 2 H), 2.06 (s, 6 H), 2.10 (s, 3 H), 2.20 (s, 12 H), 2.23 (s, 6 H), 6.63 (s, 2 H), 6.70 (s, 4 H). Calcd for $C_{31}H_{44}B_2Si$: C, 79.83; H, 9.51. Found: C, 78.94; H, 9.2.

X-ray Data Collection and Solution and Refinement of the Structures. The crystals of 1–4 were transferred from the Schlenk tube onto a Petri dish and immediately covered with a layer of hydrocarbon oil. A single crystal was selected, mounted on a glass fiber with silicon grease, and immediately placed in the low-temperature N_2 stream.[14] The X-ray data for the compounds 1 and 3 were collected on a Siemens R3m/v diffractometer equipped with a locally modified Enraf-Nonius LT apparatus. Data collection for 2 and 4 was carried out on a Syntex $P2_1$ diffractometer equipped with a locally modified Syntex LT-1 low-temperature device. Computer programs were from SHELXTL-PLUS (Version 5) installed on a microVAX 3200 computer. The atom form factors, including anomalous scattering factors, were from ref 15. Some details of data collection and refinement are given in Table I. Further details are provided in the supplementary material. All structures were solved by direct methods. An absorption correction for 4 was applied by using the method described in ref 16. Hydrogen atoms were included in the refinement at calculated positions by using a riding model with a C–H distance of 0.96 Å and $U_H = 1.2U_C$. Atom coordinates and isotropic thermal parameters are given in Table II. Selected bond distances and angles and other important structural parameters are given in Table III. The structures of 2–4 were somewhat marred by poor crystal quality. This was due primarily to their tendency to crystallize as thin plates. Also, it may be noted that the majority of the atoms have low atomic numbers and in the case of 2 these problems were exacerbated by the presence of solvent molecules in the crystal.

Results and Discussion

Syntheses. The synthetic route to compounds 1–4 begins with the key species $B_2(NMe_2)_4$.[5] Because of the facility with which it can be obtained in large quantities, this compound is currently the most important starting material for the synthesis of diborane(4) compounds. It also possesses high thermal stability, which permits convenient storage for a considerable time.[5] This material can be converted to $B_2(OMe)_4$ via treatment with MeOH/HCl.[13] This somewhat surprising reaction, in which the

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[14] This method is described in: Hope, H. In ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 10.

[15] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[16] The absorption correction was made by using the program XABS by H. Hope and B. Moezzi. The program obtains an absorption tensor from $F_o - F_c$ differences. Moezzi, B. Ph.D. Dissertation, University of California, Davis, CA, 1987.

Table II. Selected Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for 1–4[a]

atom	*x*	*y*	*z*	*U*[a]
		Compound 1		
B(1)	3571 (8)	8973	514	29 (2)
B(2)	1510 (8)	9073 (7)	113 (4)	30 (2)
O(1)	4229 (4)	9405 (5)	−640 (2)	36 (1)
O(2)	933 (4)	9654 (5)	733 (2)	39 (1)
C(1)	4625 (6)	8405 (6)	709 (3)	20 (2)
C(2)	5043 (6)	7494 (6)	533 (3)	29 (2)
C(19)	5904 (6)	9377 (7)	−840 (4)	50 (2)
C(20)	−761 (7)	980 (7)	837 (4)	52 (2)
		Compound 2		
B(1)	1656 (15)	4659 (11)	8169 (10)	34 (6)
B(2)	1064 (14)	3252 (11)	7258 (10)	30 (6)
C(2)	1198 (12)	5731 (9)	7980 (8)	35 (5)
C(11)	−379 (11)	2196 (8)	7081 (8)	26 (5)
C(20)	2338 (11)	3233 (9)	6562 (8)	27 (5)
O(1)	2793 (8)	4796 (6)	9062 (6)	37 (3)
C(1)	3603 (13)	5894 (9)	9915 (8)	48 (6)
		Compound 3		
B(1)	867 (9)	8318 (7)	2224 (6)	42 (4)
B(2)	300 (10)	7265 (6)	2865 (6)	40 (4)
C(1)	334 (8)	9451 (6)	2543 (5)	39 (3)
C(7)	1756 (8)	8245 (6)	1281 (5)	41 (3)
C(16)	−1524 (8)	6490 (5)	2554 (5)	35 (3)
C(25)	133 (8)	706 (8)	3738 (5)	37 (3)
		Compound 4 (Molecule 1)		
B(1)	3251 (11)	9891 (9)	7272 (10)	18 (4)
B(2)	3092 (12)	11044 (10)	7662 (10)	24 (4)
C(1)	3527 (10)	9337 (8)	6288 (8)	24 (3)
C(10)	1786 (10)	11164 (8)	7494 (9)	27 (4)
C(19)	3880 (10)	11878 (8)	8180 (8)	24 (3)
C(28)	2947 (10)	9338 (8)	7864 (8)	29 (4)
		Compound 4 (Molecule 2)		
B(3)	1654 (12)	3217 (9)	2663 (10)	21 (4)
B(4)	1820 (12)	4102 (10)	2329 (10)	27 (4)
C(32)	1412 (10)	3358 (8)	3661 (8)	24 (3)
C(41)	3098 (9)	4361 (8)	2548 (8)	20 (3)
C(50)	1006 (9)	4570 (7)	1865 (8)	17 (3)
C(59)	1942 (10)	2233 (7)	2019 (8)	25 (3)

[a] Equivalent isotropic U defined as one-third the trace of the orthogonalized U_{ij} tensor.

B–B bond is maintained intact, gives a good yield of $B_2(OMe)_4$ with only minor quantities of the $B(OMe)_3$ byproduct. As far as its reactivity with organolithium compounds is concerned, the $B_2(OMe)_4$ species can be viewed as a B_2X_4 (X = halide) substitute. In contrast to tetrahalides, such as B_2Cl_4[7] or B_2Br_2,[17] it has the advantage of much superior thermal stability and gram quantities are isolable by a fairly straightforward synthetic procedure.[13] More importantly perhaps, it undergoes reactions with fairly powerful nucleophiles without cleavage of the B–B bond. This characteristic was recognized with the pioneering synthesis of the tetraalkyl derivatives mentioned in the Introduction.[3,4]

As the Experimental Section shows, $B_2(OMe)_4$ reacts smoothly with LiMes to give products 1 and 2 as shown by eqs 1 and 2. It is notable that reaction with 4 equiv of LiMes did not result in complete substitution of four OMe groups. This behavior parallels that observed in the reaction between Li(*t*-Bu) and $B_2(OMe)_4$.[3,4] For steric reasons, presumably, only a maximum of three Mes group may be added as illustrated by eq 2. The fourth OMe group may, however, be replaced by the less sterically crowding Ph or CH_2SiMe_3 substituents to give 3 or 4 as shown by eq 3. The compounds 1–4 are colorless crystalline solids that react with air and moisture. They possess high thermal stability (up to 200 °C) and appear to be stable for long periods at ambient temperature when stored in an inert atmosphere (N_2).

$$B_2(OMe)_4 + 2LiMes \xrightarrow{Et_2O} \underset{1}{(MeO)MesBBMes(OMe)} + 2LiOMe \quad (1)$$

$$B_2(OMe)_4 + 4LiMes \xrightarrow{Et_2O} \underset{2}{Mes_2BBMes(OMe)} + 3LiOMe + LiMes \quad (2)$$

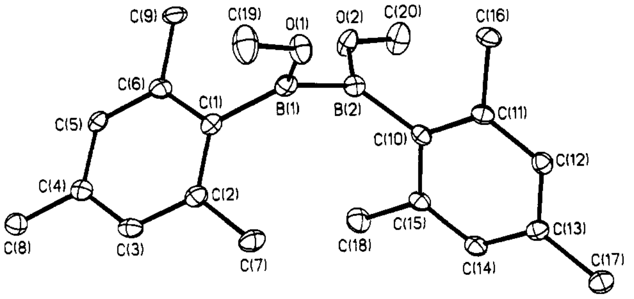

Figure 1. Computer-generated thermal ellipsoid plot of **1**. H atoms are omitted for clarity.

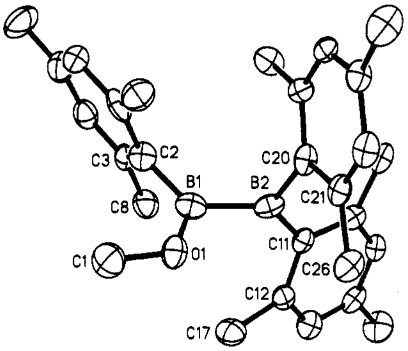

Figure 2. Computer-generated thermal ellipsoid plot of **2**. H atoms are omitted for clarity.

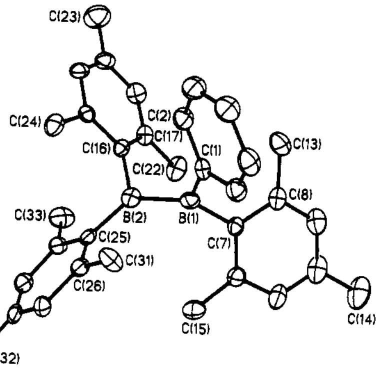

Figure 3. Computer-generated thermal ellipsoid plot of **3**. H atoms are omitted for clarity.

$$Mes_2BBMes(OMe) + 2LiR \rightarrow Mes_2BBMes(R) + LiOMe \quad (3)$$

$$R = Ph\ (3)\ \text{or}\ CH_2SiMe_3\ (4)$$

Structures. The structures of compounds 1–4 were determined by X-ray crystallography. They are illustrated in Figures 1–4. Those of 3 and 4 represent the first such examples for tetraorganodiborone(4) species.[18] The closest

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[17] For a convenient synthesis of B_2Br_4, see in the following reference: Nöth, H.; Pommerening, H. *Chem. Ber.* **1981**, *114*, 398.

[18] Professor A. Berndt has informed us that he and his group have structurally characterized the species $(Me_3Si)_2CH(Mes)BB(Mes)CH(SiMe_3)_2$ and $F_2BB(C_6H\text{-}2,3,5,6\text{-}Me_4)_2$, which have B–B distances of 1.739 (7) and 1.68 (1) Å.

Table III. Selected Bond Distances (Å) and Angles (deg) and Structural Parameters for 1–4

1		2		3		4[a]	
B(1)–B(2)	1.724 (9)	B(1)–B(2)	1.703 (16)	B(1)–B(2)	1.706 (12)	B(1)–B(2)	1.711 (20)
B(1)–O(1)	1.356 (8)	B(1)–O(1)	1.373 (15)	B(1)–C(1)	1.565 (12)	B(1)–C(1)	1.559 (18)
B(1)–C(1)	1.581 (8)	B(2)–C(2)	1.550 (20)	B(1)–C(7)	1.579 (11)	B(1)–C(28)	1.584 (12)
B(2)–O(2)	1.370 (10)	B(2)–C(11)	1.574 (15)	B(2)–C(16)	1.576 (9)	B(2)–C(10)	1.624 (19)
B(2)–C(10)	1.562 (9)	B(2)–C(20)	1.586 (18)	B(2)–C(25)	1.586 (12)	B(2)–C(19)	1.559 (17)
O(1)–B(1)–C(1)	121.9 (5)	O(1)–B(1)–C(2)	121.4 (9)	C(1)–B(1)–C(7)	115.1 (7)	C(1)–B(1)–C(28)	117.6 (10)
O(1)–B(1)–B(2)	113.9 (4)	O(1)–B(1)–B(2)	112.8 (11)	C(1)–B(1)–B(2)	116.9 (6)	C(1)–B(1)–B(2)	121.7 (13)
C(1)–B(1)–B(2)	124.2 (4)	C(2)–B(1)–B(2)	125.2 (10)	C(7)–B(1)–B(2)	127.8 (7)	C(28)–B(1)–B(2)	120.1 (11)
O(2)–B(2)–C(10)	123.2 (5)	C(11)–B(2)–C(20)	122.8 (9)	C(16)–B(2)–C(25)	119.8 (6)	C(10)–B(2)–C(19)	121.6 (11)
O(2)–B(2)–B(1)	116.2 (5)	C(11)–B(2)–B(1)	131.1 (11)	C(16)–B(2)–B(1)	112.0 (6)	C(10)–B(2)–B(1)	104.5 (10)
C(10)–B(2)–B(1)	120.7 (5)	C(20)–B(2)–B(1)	106.1 (9)	C(25)–B(2)–B(1)	128.1 (6)	C(19)–B(2)–B(1)	133.5 (12)
B(1)–O(1)–C(19)	123.4 (5)	B(1)–O(1)–C(1)	125.0 (9)				
B(2)–O(2)–C(20)	121.1 (5)						

	1		2		3		4	
angle between B planes		74.9		79.0		79.1		85.4
angle betwn plane at B(1) and plane at the atoms	C(1)	84.5	C(2)	71.1	C(1)	43.1	C(1)	66.3
	O(1)	2.3	O(1)	3.0	C(7)	56.5		
	O(2)	2.2						
angle betwn plane at B(2) and plane at the atoms	C(11)	87.6	C(11)	33.1	C(6)	65.7	C(10)	76.2
			C(20)	71.1	C(25)	39.3	C(19)	34.3

[a] Distances for one of the two molecules are provided. Data for the remaining molecule are given in the supplementary material.

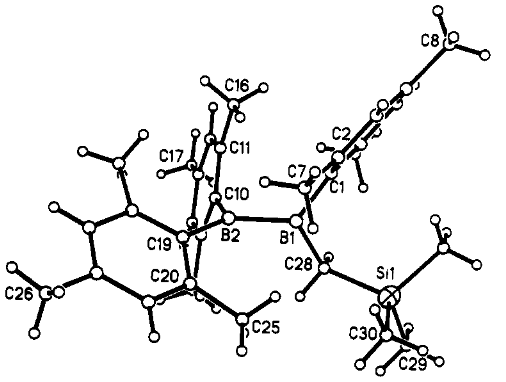
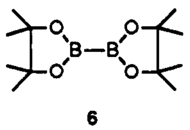


Figure 4. Computer-generated plot of 4. H atoms are omitted for clarity.

forerunners to structures 1 and 2 are an electron diffraction study of $B_2(OMe)_4$[19] (B–B = 1.720 (6) Å), 5, and an X-ray crystal study of the dioxaborolane species, 6,[20] which has



6

a B–B distance near 1.714.[20] The structures of 1–4 are characterized by bond lengths that span the range 1.703–1.724 Å. Moreover, there are very high angles (74.9–85.4°) between the planes at the two boron centers. It is notable that for the methoxy-substituted compounds 1 and 2 the angle between the planes at the borons and at the substituent oxygens are quite low (3° or less). Other noteworthy features of the structures concern the angles at the boron centers. In both 1 and 2 the angles between the boron–ligand bonds are greater than 120°, whereas in 3 and 4 they are less than this value. The angles between the planes of the aromatic ring substituents and the boron centers also display considerable variability. In 1, the mesityl rings are almost perpendicular to the planes at the boron centers. For 2, the C(2) and C(20) ring planes subtend angles of 71.1° with respect to boron planes, whereas the angle for C(11) ring is 33.1°. The variation in the interplanar angles in the compounds 3 and 4 are listed in Table III.

Discussion

Compounds 1–4 were synthesized in a fairly straightforward manner, and in moderate yield, by the route outlined in the synthesis section. This synthetic pathway involves the derivatization of species that have preformed B–B bonds. Currently, there is no broadly established route to tetraorganodiborane(4) compounds that uses monomeric organoboron precursors. It has, however, proved possible to generate diboron(4) compounds containing some B–C bonds by the reduction outlined by eq 4.[8,21,22] Recent work has also indicated that it is possible

$$2Me_2N(R)BX \xrightarrow{2M} Me_2N(R)BB(R)NMe_2 + 2MX \qquad (4)$$

$$R = Et, Pr, Bu, Ph;\ X = Cl, Br;\ M = Na \text{ or } K$$

to generate B–B bonded species by the reduction of $RBCl_2$ and R_2BCl (R = alkyl) if organosubstituents with α-H's are avoided.[23] The organometallic aspects of diboron chemistry were reviewed in 1972.[2] At that time no tetralkyl- or tetraaryldiboron derivatives had been definitely characterized in spite of some attempts to prepare them. The isolation of trialkylboranes and involatile polymeric residues suggested that the disproportionation given by eq 5 occurs readily.[24] The complexation of these com-

$$B_2R_4 \rightarrow BR_3 + (1/n)(BR)_n \qquad (5)$$

pounds with Lewis bases enhances their stability and the parent compound B_2H_4 can only be isolated in this form.[25-27] The simultaneous recognition by two research

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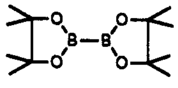
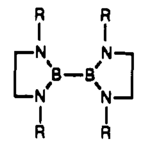
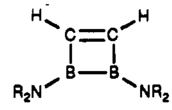
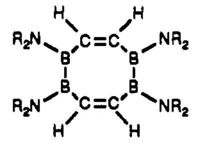
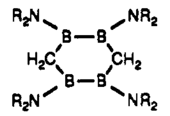
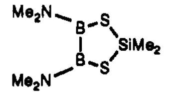
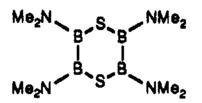
groups[3,4] that bulky substituents such as the *tert*-butyl or neopentyl groups greatly enhance the stability of B_2R_4 species resulted in the isolation of the first tetraorganodiborone compounds. These compounds were stable up to 50–100 °C.[3,4] Their stability in relation to the nonexistence of B_2Me_4 suggested that steric protection of the boron center from attack through the use of large substituents was a key factor in determining stability. The high thermal stability of other diborane(4) derivatives such as $B_2(NMe_2)_4$ also supported this conclusion.[5] In this case the good π-donor characteristics of the NMe_2 in addition to its moderately large size combine to produce an easily prepared and highly stable compound. The relative stability of other diborane(4) derivatives also lends credence to this view. Thus, the species $B_2(OMe)_4$[13] is less stable than $B_2(NMe_2)_4$ owing to the reduced π-donor ability and size of the OMe group relative to NMe_2. Similarly, tetrachlorodiborane(4) (B_2Cl_4) decomposes at room temperature or below to give BCl_3 and polyhaloboron species.[28]

The thermal stability of tetraorganoborane(4) compounds **3** and **4** is greater than that of the previously described tetraalkyl derivatives.[3,4] Clearly, the high steric requirements of the mesityl group contribute greatly to this enhanced stability. In addition, the absence of α-hydrogen substituents in the organic groups is probably a factor in their stabilization.[23] The electronic properties of these groups may also play a role. Although aryl substituents are generally not as powerful σ-donors as the alkyls, they are capable of behaving as π-donors by the use of the aromatic π-electrons. Interactions between the empty p-orbitals on boron and substituent aryl ligands have been well-documented and can in some cases be quite strong.[29,30] The ^{11}B NMR data for **1–4** do not suggest that there is extensive delocalization of this kind. Only one broad resonance was observed in the case of compound **4**, indicating that the bonding for the differentially substituted borons is similar. Also, the shift observed for the tetraaryl species, **3**, is very similar to that observed for the tetraalkyl derivatives,[3,4] which suggests no great change in the electron density at the borons.

There is some structural evidence for compounds **1–4** that could be interpreted in favor of some delocalization. In the case of **1** where there are coplanar and π-bonding OMe groups on each boron the mesityl rings possess an orientation that is almost at right angles to the plane at each boron even though it appears that there is sufficient room for the mesityl group to adopt a much smaller interplanar angle. One interpretation of this result is that multiple interactions at these centers are dominated by the B–O π-bonding[31] so that any similar interaction with the mesityl ring is greatly reduced. In **2**, a similar situation is obtained for B(1), which is also bound to an OMe and a mesityl group (angle 77.1°). For B(2), however, one mesityl ring possesses a rather low interplanar angle of 33.1° whereas the other ring also has a twist angle of 71.1°. Compound **3** also possesses this pattern to some degree, with a low interplanar angle, and presumably a π-interaction to at least one group on each boron. In **4**, there is an unusual situation in that one mesityl ring (C(19)) is oriented to interact more strongly with the B(2) p-orbital. On the alkyl-substituted B(1), however, the C(1) ring maintains a high twist angle, perhaps for steric reasons, so that there appears to be no B–C "π-bonding" possible in this case.

Table IV. Selected Structural Data for Diborane(4) Derivatives

compound	B–B, Å	twist angle, deg	ref
$B_2(OMe)_4$, 5	1.720 (6)	49.5	19
 6	1.711 (6)	0	20
			
R = Me, 7	1.690 (9)	61.65	32
	1.696 (9)	56.78	32
R = Me, 7a ($GaCl_3$ adduct)	1.705 (23)		33
R = c-C_6H_{11}, 8	1.721 (12)	80.7	34
R = $B_2(NMe_2)_4$, 9	1.762 (1.1)	90.0 (1.1)	19
 R = *i*-Pr, 10	1.749	0	35
 R = *i*-Pr, 11	1.718 (2)	82	36
 R = Me, 12	1.711 (2)	not stated	37
cyclo-$(BNMe_2)_6$, 13	1.7 (av)	not stated	38
 14	1.723 (11)	53.4	39
 15	1.68 (2)	64.56	39
$(Me_2NB)_2S_2Fe_2(CO)_6$, 16	1.685 (8)		40
	1.669 (8)		40
B_2F_4, 17	1.720 (4) (gas)	variable	41
	1.67 (5) (solid)	0	28
B_2Cl_4, 18	1.702 (69) (gas)	variable	42
	1.75 (5) (solid)	0	43
B_2Br_4, 19	1.689 (16) (gas)	variable	44

An obvious feature of structures **1–4** is the very high angle between the planes at the boron atoms. In addition the B–B distances show only minor variation (within the limits of accuracy imposed by the standard deviations) across the series. These data suggest that there is essentially no multiple character or π-bonding between the boron centers in these compounds. The high interplanar angle is, of course, indicative of no p–p π-overlap and the

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B–B distances are consistent with a single bond between neutral three-coordinate boron centers. The B–B bond lengths may be compared with those in other diborane(4) systems listed in Table IV.[32–44] It is clear that the majority of these distances (with a few notable exceptions) are within two-hundredths of an angstrom of 1.71 Å. As already mentioned, the B–B distances in **1** and **2** are very similar to those found for the diboron species **5**[19] and **6**[20] (Table IV). In addition it can be seen that, since the O_2BBO_2 array in **6** is planar, there is little correlation between the boron planes and the B–B bond length in this class of compound. Little change in the B–B distances is apparent if all the methoxy groups are all replaced by aryl or alkyl groups as in **3** or **4**. The bonding in the case of the amido derivatives **7–9**[19,32,34] is less clear cut, however. The three compounds all display high twist angles; yet, there is a much greater variation in the B–B bond lengths that fall into no readily discernible pattern. The B–B bond lengths in **7** and **8** are "average" and within the expected range. The B–B bond in **9**, however, appears to be uncharacteristically long and it is not easy to reconcile this distance with the size or electronic properties of the NMe_2 substituents. The B–B distances in **7** and **8** are indeed close to those seen in **1–6**, and it is possible to rationalize the small variation in their bond lengths on the basis of either steric effects or Coulomb repulsion between the boron atoms owing to residual changes arising from the ionic character of the B–ligand bonds. With the exception of the compound **11**, which has a lengthened B–B bond that can be rationalized on the basis of ring strain, the remaining species have B–B distances within the range stated above.[45] Other structures of diborane(4) derivatives have also appeared; however, these involve boron centers that are further coordinated by donors, e.g., $(pz)_2B–B(pz)_2$ (pz = pyrazolyl). These have longer B–B distances of 1.76–1.77 Å.[46]

The structural data currently available for the wide variety of compounds in Table IV suggests that the amount of B–B π–bonding in such compounds is very low or nonexistent, even when the borons are substitutd by π–donor groups. The latter conclusion is also supported by simple molecular orbital considerations of π-bonding. For example, if the hypothetical species $(H_2N)_2BB(NH_2)_2$ is assumed to be planar and to have D_{2h} symmetry, the six p-orbitals generate six molecular orbitals. Only one of these is strongly bonding with respect to all the p-orbitals. One is bonding with respect to the B–B bond and antibonding with respect to the B–N bonds. Of the four remaining π-molecular orbitals, two are nonbonding (HOMO's) and two are antibonding. As a result the molecule may prefer to retain the strong B–N π-interactions within the two $B(NH_2)_2$ units such that any significant B–B π-interaction is excluded. As a result, the molecules may be treated as two essentially independent halves that are linked by a simple σ–bond. This view of the bonding also receives support from the determination of the barriers to internal rotation the diboron tetrahalides B_2X_4 (X = F, Cl, or Br) by electron diffraction,[41,42,44] The values for the fluoride, chloride, and bromide derivatives are 0.42 (16),[41] 1.85 (5),[42] and 3.07 (33)[44] kcal mol^{-1}. Since the most accurate structural determinations[41,42,44] for these three compounds reveal B–B distances that are very similar to those found in the other compounds in Table IV, it can be argued that rotation barriers in these compounds (and by implication the strength of the B–B π-interactions) ought to be similar.

The lack of significant π-bonding between the borons has led to attempts to induce such bonding by the reduction of diborane(4) derivatives. Thus, the reduction of $B_2(CH_2\text{-}t\text{-}Bu)_4$ leads to the persistent radical $[B_2(CH_2\text{-}t\text{-}Bu)_4]^-$, which has an EPR spectrum that is consistent with a one-electron B–B π-bond.[47] In addition, calculations[48] on the diborane(4) dianion $[B_2H_4]^{2-}$ suggest that a two-electron B–B π-bond ought to be quite strong. Preliminary results[49] for the reduction of **3** by powdered lithium in ether show that the species $[\{(Et_2O)Li\}_2\{Mes_2BB(Mes)Ph\}]$ can be isolated as a red crystalline material. This has an essentially planar $B_2\{C(ipso)\}_4$ array, a B–B distance of 1.636 (10) Å, and two Li^+ ions located above and below the $B_2\{C(ipso)\}_4$ plane. These interesting results will be reported in a separate publication.

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Supplementary Material Available: Full tables of data collection and details of refinement, atomic coordinates, bond distances and angles, hydrogen coordinates, and isotropic thermal parameters (34 pages). Ordering information is given on any current masthead page.

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(45) Obviously, the solid-state structural determinations for **17** and **18** give B–B distances outside this range, but in these cases the standard deviations are unusually high (0.05 Å). This statement is true to a lesser extent in the case of **15**.

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