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Structural Studies of Bis-Catecholate, Bis-Dithiocatecholate, and Tetraalkoxy Diborane(4) Compounds

William Clegg, Mark R. J. Elsegood, Fiona J. Lawlor, Nicholas C. Norman,*,†
Nigel L. Pickett, Edward G. Robins, and Andrew J. Scott

Department of Chemistry, The University of Newcastle upon Tyne,
Newcastle upon Tyne, NE1 7RU, UK

Paul Nguyen, Nicholas J. Taylor, and Todd B. Marder*,‡

Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada

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X-ray structures are described for the bis-catecholate, bis-dithiocatecholate, and tetraalkoxy diborane(4) compounds $\mathrm{B_2(1,2\text{-}O_2C_6H_4)_2}$ (**1**), $\mathrm{B_2(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)_2}$ (**2**), $\mathrm{B_2(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t{}_2C_6H_2)_2}$ (**3**), $\mathrm{B_2(1,2\text{-}S_2C_6H_4)_2}$ (**4**), $\mathrm{B_2(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)_2}$ (**5**), and $\mathrm{B_2(OCH_2CMe_2CH_2O)_2}$ (**6**). All the compounds adopt structures in the solid-state in which the $\mathrm{B_2O_4}$ or $\mathrm{B_2S_4}$ units are planar or very nearly so. In compounds **2** and **3**, the dihedral angles between the two $\mathrm{BO_2C_2}$ planes are 17.3 and 31.8° respectively whereas in **1**, **4** and **5** these angles are exactly 0°. In **6**, a 3-fold disorder precluded our obtaining accurate positions for the two boron atoms, yet a dihedral angle of 0° is required by the $\bar{3}$ site symmetry. The structure of the bis(Lewis base) adduct of $\mathrm{B_2Cl_4}$, $\mathrm{[B_2Cl_4(NHMe_2)_2]}$ (**7**), is also described and structures of the salt $\mathrm{[NH_2Me_2][B(1,2\text{-}O_2C_6H_4)_2]}$ (**8**) and the $\mathrm{NMe_2}$-bridged dimer $\mathrm{[\{BCl_2(\mu\text{-}NMe_2)\}_2]}$ (**9**) are available in the Supporting Information. Compound **1** crystallized in the monoclinic space group $P2_1/c$ with $a = 4.746(1)$ Å, $b = 16.427(3)$ Å, $c = 7.053(2)$ Å, $\beta = 98.59(2)°$, and $Z = 2$. Crystals of **2** were monoclinic, space group $P2_1/c$ with $a = 6.847(1)$ Å, $b = 18.871(5)$ Å, $c = 15.270(2)$ Å, $\beta = 93.16(2)°$, and $Z = 4$. Crystals of **3** were triclinic, space group $P\bar{1}$ with $a = 9.478(4)$ Å, $b = 10.355(4)$ Å, $c = 15.082(7)$ Å, $\alpha = 105.71(3)°$, $\beta = 100.31(4)°$, $\gamma = 94.58(3)°$, and $Z = 2$. Crystals of **4** were monoclinic, space group $P2_1/c$ with $a = 15.364(3)$ Å, $b = 4.0502(4)$ Å, $c = 21.532(3)$ Å, $\beta = 99.320(7)°$, and $Z = 4$. Crystals of **5** were monoclinic, space group $P2_1/c$ with $a = 6.0458(9)$ Å, $b = 7.5319(11)$ Å, $c = 16.552(2)$ Å, $\beta = 96.291(3)°$ and $Z = 2$. Compound **6** crystallized in the rhombohedral space group $R\bar{3}m$ with $a = 8.876(2)$ Å, $c = 13.821(3)$ Å and $Z = 3$. Crystals of **7** were monoclinic, space group $P2_1/c$ with $a = 11.831(3)$ Å, $b = 19.458(5)$ Å, $c = 14.823(5)$ Å, $\beta = 96.63(4)°$, and $Z = 12$.

In the preceding paper,[1] we described the synthesis and spectroscopic characterization of a range of dicatecholate and bis-dithiocatecholate diborane(4) compounds together with one example of an alkoxy derivative. Herein we describe and discuss the X-ray crystal structures of $\mathrm{B_2(1,2\text{-}O_2C_6H_4)_2}$ (**1**), $\mathrm{B_2(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)_2}$ (**2**), $\mathrm{B_2(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t{}_2C_6H_2)_2}$ (**3**), $\mathrm{B_2(1,2\text{-}S_2C_6H_4)_2}$ (**4**), $\mathrm{B_2(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)_2}$ (**5**), and $\mathrm{B_2(OCH_2CMe_2CH_2O)_2}$ (**6**) together with that of the compound $\mathrm{[B_2Cl_4(NHMe_2)_2]}$ (**7**) which has been isolated as a side product from some reactions. The structures of **1**−**3** have been reported in a preliminary communication.[2]

Results and Discussion

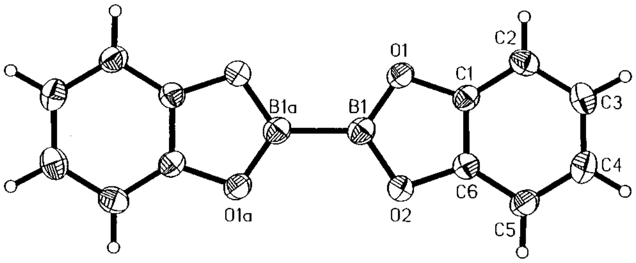

Figure 1. View of the molecular structure of **1** showing the atom numbering scheme. Ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (deg) include B(1)−B(1a) 1.678(3), B(1)−O(1) 1.382(2), B(1)−O(2) 1.394(2), B(1a)−B(1)−O(1) 124.6(1), B(1a)−B(1)−O(2) 124.2(1), O(1)−B(1)−O(2) 111.2(1). Symmetry transformation used to generate equivalent atoms: a, $-x$, $-y$, $1 - z$.

A view of the molecular structure of $\mathrm{B_2(1,2\text{-}O_2C_6H_4)_2}$ (**1**) is shown in Figure 1, and a packing diagram is shown in Figure 2. Molecules of **1** (Figure 1) are essentially planar, with no deviations of more than 0.009 Å from the mean plane of all the atoms, and comprise a crystallographically centrosymmetric central diboron unit with each boron bonded to a 1,2-catecholate group; the crystallographic center requires that the dihedral angle between the $\mathrm{O_2B}$ planes along the B−B bond is strictly zero. In the crystal, molecules of **1** are arranged in parallel stacks (Figure 2 shows a view looking down the *a* axis) with a

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† Present address: The University of Bristol, School of Chemistry, Bristol BS8 1TS, U.K.

‡ Present address: Department of Chemistry, University of Durham, Durham DH1 3LE, U.K.

(1) Previous paper in this issue: Lawlor, F. J.; Norman, N. C.; Pickett, N. L.; Robins, E. G.; Nguyen, P.; Lesley, G.; Marder, T. B.; Ashmore, J. A.; Green, J. C. *Inorg. Chem.* **1998**, *37*, 5282.

(2) Nguyen, P.; Lesley, G.; Taylor, N. J.; Marder, T. B.; Pickett, N. L.; Clegg, W.; Elsegood, M. R. J.; Norman, N. C. *Inorg. Chem.* **1994**, *33*, 4623.

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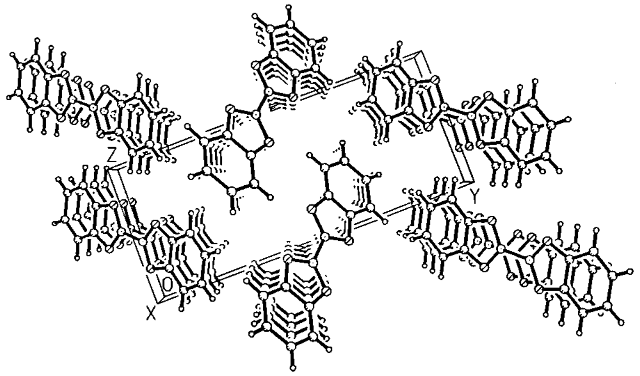

Figure 2. Packing diagram showing the stacking of molecules of **1** in the crystal.

Table 1. Selected Structural Data for Diborane(4) Compounds

compound	B−B (Å)	dihedral angle (deg)	ref
B_2F_4	1.67(5)	0	3
B_2Cl_4	1.75(5)	0	4
$B_2(OMe)_4$[a]	1.720(6)	49.5	5
$B_2(NMe_2)_4$[a]	1.762(1)	90.0(1)	5
$B_2\{N(Me)CH_2CH_2(Me)N\}_2$[b]	1.690(9), 1.696(9)	61.65, 56.78	6
$B\{N(Cy)CH_2CH_2(Cy)N\}_2$[c]	1.721(12)	80.7	7
$B_2(mes)_2(OMe)_2$[d]	1.724(9)	74.9	8
$B_2(mes)_3(OMe)$	1.703(16)	79.0	8
$B_2(mes)_3Ph$	1.706(12)	79.1	8
$B_2(mes)_3(CH_2SiMe_3)$	1.711(20)	85.4	8
$B_2Br_2(NMe_2)_2$	1.682(16)	83.7	9
$B_2Br(NMe_2)_2(mes)$	1.703(14)	74.7	9
$B_2(NMe_2)_2(mes)_2$	1.717(15)	58.9	9
$B_2(NMe_2)_2Ph_2$	1.714(4)	88.7	9
$B_2(pinacol)_2$ (**10**)	1.711(6)	0	10
$B_2(1,2\text{-}O_2C_6H_4)_2$ (**1**)	1.678(3)	0	this work
$B_2(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)_2$ (**2**)	1.687(3)	17.3	this work
$B_2(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t{}_2C_6H_3)_2$ (**3**)	1.684(3)	31.8	this work
$B_2(1,2\text{-}S_2C_6H_4)_2$ (**4**)[b]	1.675(5), 1.670(5)	0	this work
$B_2(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_4)_2$ (**5**)	1.680(4)	0	this work
$B_2(OCH_2CMe_2CH_2O)_2$ (**6**)	2.029(10)	0	this work

[a] Gas-phase electron diffraction structure. [b] Two crystallographically independent molecules. [c] Cy = cyclohexyl. [d] mes = 2,4,6-$Me_3C_6H_2$.

separation between adjacent planes of 3.30 Å. Of particular note is the trigonal planar geometry around the boron atom and the B−B bond distance of 1.678(3) Å which is comparable to, although somewhat shorter than, values for other diborane(4) compounds, some of which are collected in Table 1. It is also clear from Table 1 that the dihedral angle of 0° in **1** is unusual since only B_2F_4, B_2Cl_4, and $B_2(OCMe_2CMe_2O)_2$ (**10**) have previously been found to have angles of 0° in the solid-state, i.e., have what may be described as eclipsed geometries.[3−10] The other examples all have dihedral angles which lie between about 50° and 90°, i.e., geometries which are better described as staggered. The matter of eclipsed vs staggered conformations for diborane(4) compounds is addressed in ref 1. Briefly, calculations indicate that the barrier to rotation around the B−B bond is small, but that for **1**, the eclipsed geometry is marginally more stable. For most of the compounds listed in Table 2, however, the staggered conformation is preferred on steric grounds. The B−O bond lengths in **1** average 1.388 Å which is essentially the same within experimental error as the C−O bonds [av 1.387 Å]. Of the C−C bonds, C(1)−C(2) and C(5)−C(6) are the shortest [av 1.374 Å] with C(1)−C(6) being the next shortest [1.384(2) Å] and C(2)−C(3), C(3)−C(4), and C(4)−C(5) being very similar to each other with an average value of 1.393 Å.

Views of the molecular structures of $B_2(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)_2$ (**2**) and $B_2(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t{}_2C_6H_2)_2$ (**3**) are shown in Figures 3 and 4. There is no crystallographically imposed symmetry on either **2** or **3**. Both compounds are similar to **1** with similar B−B bond distances [**2**, 1.687(3); **3**, 1.684(3) Å]. There is, however, a slight twist around the B−B bond of 17.3° and the packing of molecules of **2** in the crystal is quite different from that in **1** (centrosymmetric pairs in **2** vs infinite stacks [Figure 2] in **1**), both probably the result of the Bu^t groups present in **2**. For **3**, the distortion around the B_2 unit is now more pronounced due to the presence of two Bu^t groups. In fact, the molecules distort such that there is both a twist about the B−B bond and a slight pyramidalization at each boron center, this distortion being best quantified as an angle between the planes defined by B(1), O(1), C(6), C(1), O(2) and B(2), O(3), C(20), C(15), O(4) which is 31.8°.

The structures of the dithiocatecholate compounds $B_2(1,2\text{-}S_2C_6H_4)_2$ (**4**) and $B_2(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)_2$ (**5**) are also similar and are shown in Figures 5−7. In crystals of **4**, there are two crystallographically independent molecules in the unit cell but, as both molecules reside on crystallographic centers of symmetry, each asymmetric unit contains two independent half molecules; the molecular structure of one molecule of **4** is shown in Figure 5. The B−B distances [B(1)−B(1a) 1.675(5), B(2)−B(2b) 1.670(5) Å] are both similar to the B−B bond in **1** but there is a greater difference between the B−S and C−S bond lengths [for both molecules, av. B−S 1.794, av. C−S 1.757 Å] in **4** compared to the B−O and C−O bond lengths in **1**. The C−C bond distances in **4** are also a little different from those in **1**. Thus for molecule 1 (molecule 2 is very similar), the shortest C−C bonds are C(2)−C(3) and C(4)−C(5) [av. 1.378 Å] followed by C(3)−C(4) [1.393(3) Å] with C(1)−C(2), C(5)−C(6) and C(1)−C(6) being similar and slightly longer with an average value of 1.399 Å.

As crystals of **4** are not isomorphous with crystals of **1**, molecules of **4** pack somewhat differently from **1** but the essential feature of parallel stacks is again evident as shown in Figure 6. Interstack distances in **4** are shorter than in **1**, however, with C−H···S and S···S contacts of 2.905 and 3.634 Å respectively which are indicated as dashed lines in Figure 6. Similar parallel stacks are observed in crystal structures of tetrathiafulvalenes and related compounds which also have interstack C−H···S and S···S contacts of similar magnitude.[11]

Molecules of **5** reside on crystallographic centers of symmetry and there is some disorder of the methyl group positions. One arrangement of approximately 50% occupancy is shown in Figure 7; in the other arrangement, the methyl groups would

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(3) (a) Massey, A. G. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 1. (b) Coyle, T. D.; Ritter, J. J. *Adv. Organomet. Chem.* **1972**, *10*, 237.
(4) Atsoji, M.; Wheatley, P. J.; Lipscomb, W. N. *J. Phys. Chem.* **1957**, *27*, 196.
(5) Brain, P. T.; Downs, A. J.; MacCallum, P.; Rankin, D. W. H.; Robertson, H. E.; Forsyth, G. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1195.
(6) Fusstetter, H.; Huffman, J. C.; Nöth, H.; Schaeffer, R. *Z. Naturforsch., Teil B* **1976**, *31*, 1441.
(7) Ferguson, G.; Parvez, M.; Brint, R. P.; Power, D. C. M.; Spalding, T. M.; Lloyd, R. M. *J. Chem. Soc., Dalton Trans.* **1986**, 2283.
(8) (a) Moezzi, A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 2715. (b) Moezzi, A.; Olmstead, M. M.; Bartlett, R. A.; Power, P. P. *Organometallics* **1992**, *11*, 2383.
(9) Moezzi, A.; Olmstead, M. M.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1992**, 2429.
(10) Nöth, H. *Z. Naturforsch., Teil B* **1984**, *39*, 1463.
(11) Novoa, J. J.; Rovira, M. C.; Rovira, C.; Veciana, J.; Tarres, J. *Adv. Mater.* **1995**, *7*, 233.

Table 2. Crystallographic and Structure Solution Data for Compounds **1**–**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
compound formula	$C_{12}H_8B_2O_4$	$C_{20}H_{24}B_2O_2$	$C_{28}H_{40}B_2O_2$	$C_{12}H_8B_2S_4$	$C_{14}H_{12}B_2S_4$	$C_{10}H_{20}B_2O_4$	$C_{12}H_{42}B_6Cl_{12}N_6$
M_r	237.8	350.0	462.2	302.0	330.1	225.9	760.8
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$R\bar{3}m$	$P2_1/c$
crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	rhombohedral	monoclinic
a/Å	4.746(1)	6.847(1)	9.478(4)	15.364(3)	6.0458(9)	8.876(2)	11.831(3)
b/Å	16.427(3)	18.871(5)	10.355(4)	4.0502(4)	7.5319(11)		19.458(5)
c/Å	7.053(2)	15.270(2)	15.082(7)	21.532(3)	16.552(2)	13.821(3)	14.823(5)
α/deg			105.71(3)				
β/deg	98.59(2)	93.16(2)	100.31(4)	99.320(7)	96.291(3)		96.63(4)
γ/deg			94.58(3)				
V/Å^3	543.7(2)	1970.1(6)	1389(1)	1322.2(3)	749.2(2)	943.0(3)	3389(2)
Z	2	4	2	4	2	3	12
D_{calc}/g cm^{-3}	1.453	1.180	1.105	1.517	1.463	1.193	1.491
F(000)	244	744	500	616	340	366	1560
μ(Mo Kα)/mm^{-1}	0.105	0.079	0.071	0.691	0.617	0.086	0.100
T/K	200(2)	200(2)	298(2)	160(2)	160(2)	160(2)	165(10)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
final R^a	0.0385 [0.0456 all data]	0.0495 [0.0657 all data]	0.0446 [0.0670 all data]	0.0324 [0.0349 all data]	0.0302 [0.0319 all data]	0.0389 [0.0416 all data]	0.0420 [0.0640 all data]
final R_w^a	0.0358 [0.0361 all data]	0.0497 [0.0503 all data]	0.1180 [0.1414 all data]	0.0924 [0.0953 all data]	0.0846 [0.0870 all data]	0.0959 [0.0979 all data]	0.0967 [0.1193 all data]

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ in all cases; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ for **1** and **2**; $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for **3**–**7**.

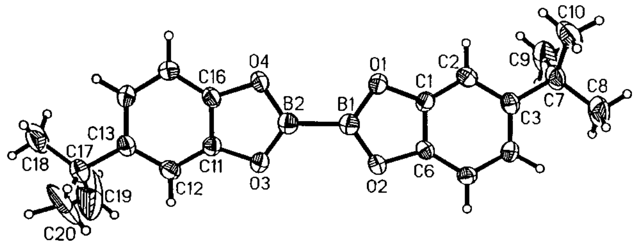

Figure 3. View of the molecular structure of **2** showing the atom numbering scheme. Ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (deg) include B(1)–B(2), 1.687(3); B(1)–O(1), 1.389(3); B(1)–O(2), 1.381(3); B(2)–O(3), 1.391(3); B(2)–O(4), 1.379(3); B(2)–B(1)–O(1), 124.6(2); B(2)–B(1)–O(2), 124.1(2); O(1)–B(1)–O(2), 111.3(2); B(1)–B(2)–O(3), 124.2(2); B(1)–B(2)–O(4), 124.5(2); O(3)–B(2)–O(4), 111.2(2); sum of angles at B(1), 360.0; sum of angles at B(2), 359.9.

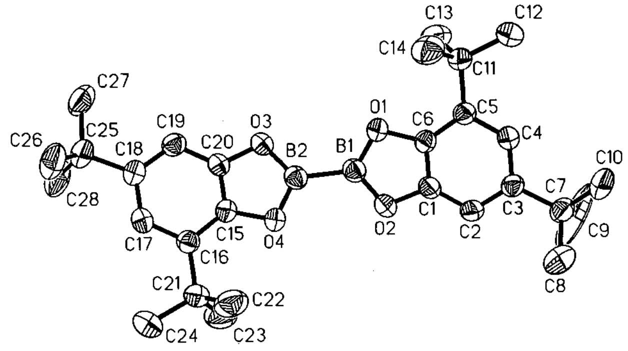

Figure 4. View of the molecular structure of **3**, with H atoms omitted, showing the atom numbering scheme. Ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (deg) include B(1)–B(2), 1.684(3); B(1)–O(1), 1.385(3); B(1)–O(2), 1.381(3); B(2)–O(3), 1.384(3); B(2)–O(4), 1.385(3); B(2)–B(1)–O(1), 124.4(2); B(2)–B(1)–O(2), 123.8(2); O(1)–B(1)–O(2), 111.1(2); B(1)–B(2)–O(3), 126.9(2); B(1)–B(2)–O(4), 121.8(2); O(3)–B(2)–O(4), 110.8(2); sum of angles at B(1), 359.3; sum of angles at B(2), 359.5.

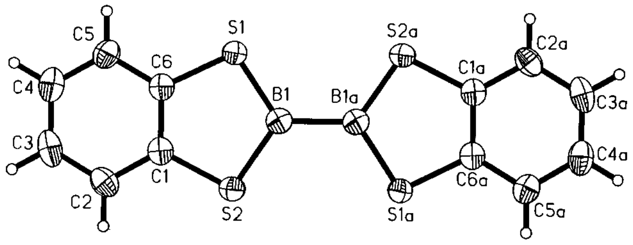

Figure 5. View of the molecular structure of **4** showing the atom numbering scheme. Ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (deg) include B(1)–B(1a), 1.675(5); B(1)–S(1), 1.788(2); B(1)–S(2), 1.796(2); B(2)–B(2b), 1.670(5); B(2)–S(3), 1.798(2); B(2)–S(4), 1.794(2); B(1a)–B(1)–S(1), 123.3(2); B(1a)–B(1)–S(2), 124.2(2); S(1)–B(1)–S(2), 112.5(1); B(2b)–B(2)–S(3), 124.4(2); B(2b)–B(2)–S(4), 123.4(2); S(3)–B(2)–S(4), 112.1(1). Symmetry transformations used to generate equivalent atoms: a, $-x + 2, -y + 3, -z + 1$; b, $-x + 1, -y + 1, -z + 1$.

be attached to carbons labeled C(5) and C(5a). The B–B and B–S bond lengths are similar to those in **4** [B–B 1.680(4), av B–S 1.789 Å].

The structure of $B_2(OCH_2CMe_2CH_2O)_2$ (**6**) is shown in Figure 8. However, while the results of the structure determination for **6** establish that the anticipated structure is correct, severe disorder problems were encountered. Molecules of **6** are, in fact, disordered over three sites as they lie on crystallographic C_3 axes with site symmetry of $\bar{3}$ at the center of the B–B bond. Thus, the methyl carbon C(1) and quaternary carbon C(2) lie on the C_3 axis, but atom C(3) comprises both methylene and

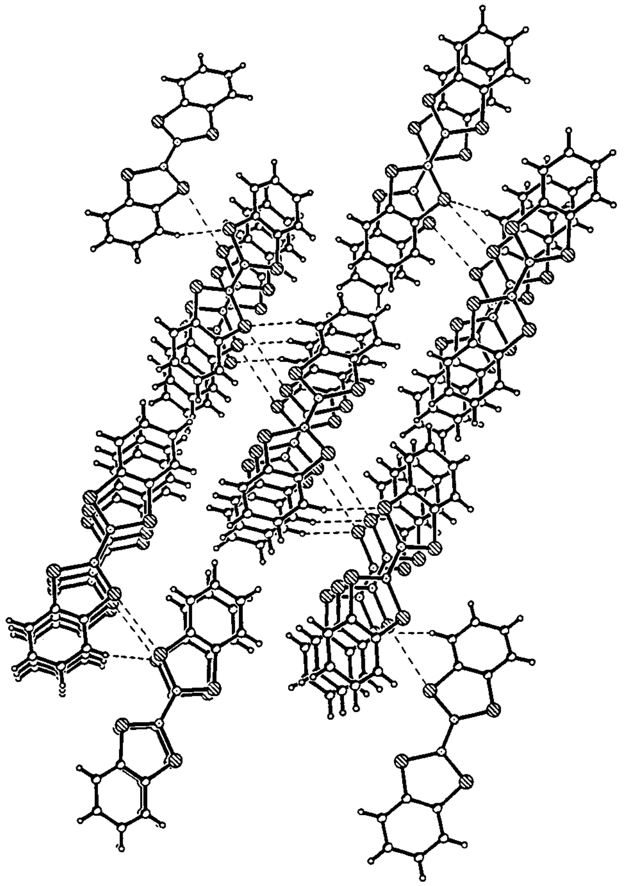

Figure 6. Packing diagram showing the stacking of molecules of **4** in the crystal.

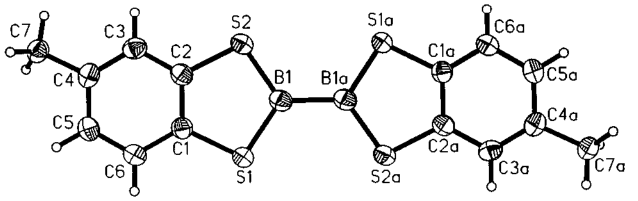

Figure 7. View of the molecular structure of **5** showing the atom numbering scheme. Ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (deg) include B(1)−B(1a), 1.680(4); B(1)−S(1), 1.790(2); B(1)−S(2), 1.788(2); B(1a)−B(1)−S(1), 124.0(2); B(1a)−B(1)−S(2), 123.4(2); S(1)−B(1)−S(2), 112.6(1). Symmetry transformation used to generate equivalent atoms: a, $-x$, $-y+1$, $-z$.

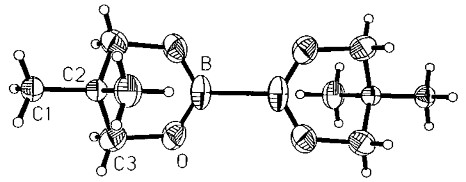

Figure 8. View of the molecular structure of **6** showing the atom numbering scheme. Ellipsoids are drawn at the 50% level. Only one component of the disorder is shown. Selected bond lengths (Å) and angles (deg) include B−B(b), 2.029(10); B−O, 1.315(3); O−B−O(a), 119.8(4); O−B−B(b), 117.3(2). Symmetry transformations used to generate equivalent atoms: a, $-y$, $x-y$, z; b, $-x$, $-y$, $-z+1$.

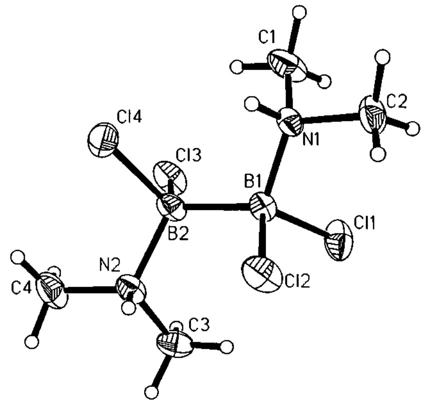

Figure 9. View of the molecular structure of one of the crystallographically independent molecules of **7** showing the atom numbering scheme. Ellipsoids are drawn at the 50% level. Selected bond lengths (Å) include B(1)−B(2), 1.737(5); B(3)−B(4), 1.731(5); B(5)−B(6), 1.740(6).

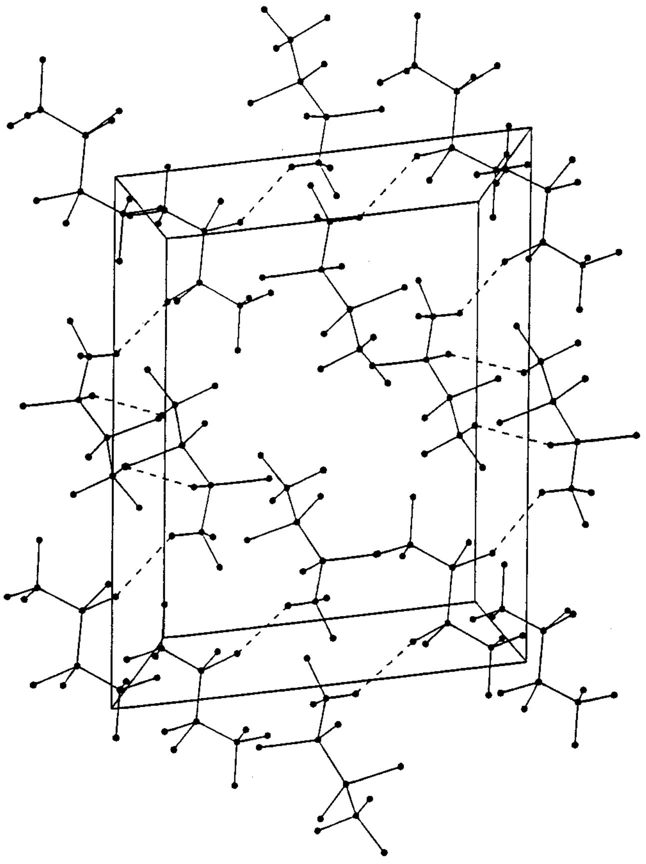

Figure 10. View down the *b* axis of the unit cell of **7** showing the arrangement of molecules and the N−H···Cl interactions.

methyl carbons and the oxygen and boron atoms are fully disordered over three sites. Bond distance and angle data associated with the boron and oxygen atoms must therefore be treated with considerable caution such that the long B−B bond [B−B 2.029(10) Å], short B−O bonds [B−O 1.315(3) Å] and slight pyramidalization at boron are undoubtedly artifacts and not genuine. A dihedral angle of 0° is, however, required by the $\bar{3}$ site symmetry. One component of the disorder constituting a sensible molecular structure for **6** is shown in Figure 8.

The bis(dimethylamine) adduct of B_2Cl_4, $[B_2Cl_4(NHMe_2)_2]$ (**7**) crystallizes with three molecules in the asymmetric unit, one of which is shown in Figure 9; a packing diagram viewed down the crystallographic *b* axis is shown in Figure 10. All three crystallographically independent molecules of **7** are similar and comprise a B_2Cl_4 unit with each boron center having a coordinated $NHMe_2$ ligand; the conformation around the B−B bond is anti with respect to the amine ligands [torsion angles N(1)−B(1)−B(2)−N(2), −154.2°; N(3)−B(3)−B(4)−N(4), −152.4°; N(5)−B(5)−B(6)−N(6), 153.0° for the three molecules]. The B−B bond distances are all similar [av B−B 1.738 Å] and somewhat longer than those found in most diborane(4) compounds (although slightly shorter than in B_2Cl_4 itself[4]) consistent with the greater coordination number around the boron centers; the geometry is close to regular tetrahedral. A related compound $[B_2Cl_4(NMe_3)_2]$ has previously been structurally characterized[12] and has a very similar molecular structure to **7**, but a rather different crystal structure as there is an extensive network of N−H···Cl hydrogen bonds in **7** as shown in Figure 10. While the H···Cl distances are not especially short (they range from 2.693 to 3.000 Å), they are undoubtedly influencial in the packing of molecules of **7**.

The structures of the salt, $[NH_2Me_2][B(1,2\text{-}O_2C_6H_4)_2]$ (**8**) and the NMe_2-bridged dimer $[\{BCl_2(\mu\text{-}NMe_2)\}_2]$ (**9**) mentioned in ref 1 are available in the Supporting Information.

Experimental Section

X-ray Crystallography. A summary of the crystal data for compounds **1**−**7** is given in Table 2. The following section deals with the crystal structure analysis for **1**; details for **2**, are given in parentheses. Data were collected on a Nicolet-Siemens R3m/V diffractometer equipped with graphite-monochromated Mo Kα radiation and a Nicolet LT2 low temperature device. Unit-cell parameters were derived from 25 general reflections well distributed in reciprocal space. Background measurements were made at the beginning and end of each scan for a total time equal to half the scan time. Crystal stability was monitored by measuring two standard reflections every 100 data; only statistical fluctuations (±2%) were observed. Data were corrected for Lorentz and polarization effects and for absorption using a face-indexed numerical method. The structures were solved by Patterson (direct methods for **2**) and Fourier techniques, and refined by full-matrix least-squares methods using Siemens SHELXTL PLUS software,[13] the function minimized being $\sum w(|F_o| - |F_c|)^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Difference Fourier synthesis provided the location of all hydrogen atoms, which were included in the refinement with isotropic displacement parameters (for **2**, a riding model was used with a refined isotropic displacement parameter). During the final cycles of refinement, a weighting scheme of the form $w^{-1} = \sigma^2(F)$ was included. Scattering factors used were taken from the *International Tables*, Vol. 4.[14]

Data for **3**, **6**, and **7** were collected on a Stoe-Siemens diffractometer using on-line profile fitting[15] with all machine control calculations performed using Stoe DIF4 software. Other features different from those described above were as follows. Unit cell parameters were determined by refinement of 2θ angles of 32 (36 for **6**) selected reflections. No absorption correction was made. The variation of standard reflections was also used, together with normal counting statistics, to estimate standard deviations of intensities. For **7**, a decay in intensities of 12% was noted and corrected for.

Data for **4** and **5** were collected on a Siemens SMART CCD area-detector diffractometer. Cell parameters were refined from several hundred reflections selected from the complete data set. Semiempirical absorption corrections were applied, based on sets of equivalent measurements contained in the primary data set.

For structures **3**−**7**, programs were beta release versions of SHELXTL and SHELXL-93.[16] The structures were solved with direct methods. Least-squares refinement was based on F^2 values for all measured reflections, with a weighting scheme $w^{-1} = \sigma^2(F_o^2)$, the σ^2 values having contributions from an analysis of variance as well as counting statistics. The observation threshold $I > 2\sigma(I)$ was used only in calculating R indices for "observed" reflections, for comparison with conventional refinements based on F values, and had no influence on the refinement itself. All non-hydrogen atoms were refined with anisotropic displacement parameters, and isotropic H atoms were included with a riding model in the refinement. For **6**, the 3-fold disorder about the crystallographic C_3 axes was successfully modeled, though individual CH_3 and CH_2 groups could not be resolved and the positions of the boron atoms in particular, with a low electron density, are not well determined. Other refinement models, including different possible space groups, were unsuccessful.

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Supporting Information Available: Tables of bond distances and angles, atomic positional and anisotropic displacement parameters for the structures of **1**, **2**, **8**, and **9**, together with details of data collection, structure solution, refinement, figures and discussion for **8** and **9** (14 pages). X-ray crystallographic files, in CIF format, for structure determinations of compounds **3**, **4**, **5**, **6**, and **7** are available on the Internet only. Ordering and access information is given on any current masthead page.

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[12] Johnson, Q.; Kane, J.; Schaeffer, R. *J. Am. Chem. Soc*. **1970**, *92*, 7614.

[13] Sheldrick, G. M. *SHELXTL PLUS*; Siemens Analytical Instruments: Madison, WI, 1990.

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

[15] Clegg, W. *Acta Crystallogr., Sect. A.* **1981**, *37*, 22.

[16] Sheldrick, G. M. *SHELXL-93*; University of Göttingen: Germany, 1993.