

Three sulfur-containing diborane(4)
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Received 25 May 1999

Accepted 15 November 1999

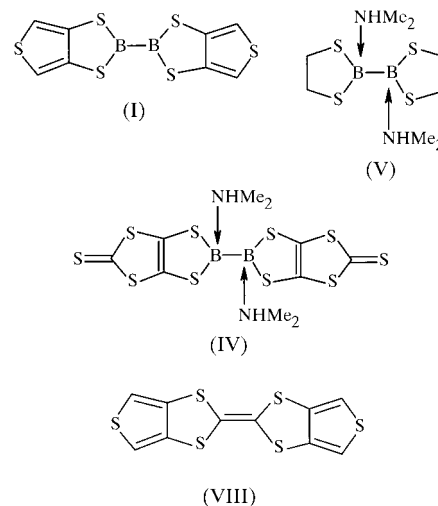
The preparation and structures of three diborane(4) compounds are described. The compound $B_2(3,4-S_2C_4H_2-1-S)_2$ [2,2'-bi(1,3,5,2-trithiaborapentalene), $C_8H_4B_2S_6$] is planar and lies at a crystallographic inversion centre. The amine adducts [$B_2(C_3S_5)_2(NHMe_2)_2$] [2,2'-bis(dimethylamino)-2,2'-bi(1,3,4,6,2-tetrathiaborapentalene-5-thione), $C_{10}H_{14}B_2N_2S_{10}$] and [$B_2(1,2-S_2C_2H_4)_2(NHMe_2)_2$].0.33 CH_2Cl_2] [1,2-bis(dimethylamino)-1,1:2,2-bis(dimethylenedithioxy)diborane(4) dichloromethane solvate, $C_8H_{22}B_2N_2S_4$.0.33 CH_2Cl_2] contain dimethylamine ligands bound to each boron in an *anti* conformation about the B–B bond, with tetrahedral geometry at the B atoms. The crystal structures display a number of $S \cdots S$ interactions, which appear to dictate the packing arrangements.

Comment

The number of diborane(4) compounds containing the B_2E_4 ($E = O$ or S) central core that have been structurally characterized continues to grow (Clegg *et al.*, 1998), especially for $E = O$, largely as a result of interest in these compounds as reagents in metal-catalysed diboration reactions (Marder & Norman, 1998). Here, we report some novel sulfur-containing diborane(4) compounds, 2,2'-bi(1,3,5,2-trithiaborapentalene), (I), 2,2'-bis(dimethylamino)-2,2'-bi(1,3,4,6,2-tetrathiaborapentalene-5-thione), (IV), and 1,2-bis(dimethylamino)-1,1:2,2-bis(dimethylenedithioxy)diborane(4) dichloromethane solvate, (V).

Molecules of (I) (Fig. 1) lie at an inversion centre and have approximate D_{2h} symmetry. The B–B bond length in (I) is 1.672 (12) Å, *cf.* 1.675 (5) Å in $B_2(1,2-S_2C_6H_4)_2$, (II) and 1.680 (4) Å in $B_2(1,2-S_2-4-MeC_6H_3)_2$ (III) (Clegg *et al.*, 1998). Molecules of (II) and (III), like (I), are planar in the solid state, presumably to allow closer packing. The two independent B–S bonds in (I) are 1.800 (6) and 1.807 (6) Å, *cf.* 1.788 (2) and 1.796 (2) Å in (II), and 1.790 (2) and 1.788 (2) Å in (III). Angles around the boron centre range from 114.1 (3)–123.0 (5)°, as expected for an sp^2 hybridized boron centre, with the smaller angle caused by the chelating ring.

Compounds (IV) (Fig. 2) and (V) (Fig. 3) are Lewis base adducts of diborane(4) compounds, in which the amines bind to the Lewis acidic boron centres. The amines are arranged in



an *anti* conformation relative to the B–B bond [N1–B2–B1–N2 = -155.69 (18) for (IV) and N1–B1–B2–N2 = 161.91 (17)° for (V), respectively]. The molecules are staggered, rather than eclipsed, about the B–B bond [S2–B1–B2–S6 = -157.83 (12), S1–B1–B2–S6 = -40.3 (2), S2–B1–B2–S7 = 83.79 (18) and S1–B1–B2–S7 = -158.66 (13)° in (IV), and S3–B2–B1–S1 = 167.64 (12), S3–B2–B1–S2 = 48.1 (2), S4–B2–B1–S1 = -73.49 (17) and S4–B2–B1–S2 = 166.93 (13)° in (V)]. A number of similar adducts of diborane(4) compounds have been structurally characterized (Clegg *et al.*, 1997). The B–B lengths in (IV) and (V) are 1.746 (4) and 1.758 (5) Å, respectively, markedly longer than in the Bsp^2-Bsp^2 cases highlighted in (I)–(III) and consistent with a change in hybridization and a higher coordination number at the boron. The B–B bond lengths in [$B_2(1,2-S_2C_6H_4)_2(4-pic)_2$] (4-pic = 4-picoline) (VI) and [$B_2(1,2-S_2C_6H_4)_2(PMe_2Ph)_2$] (VII) are 1.715 (1) and 1.750 (4) Å, respectively, whilst in the mono-adducts [$B_2(1,2-S_2C_6H_4)_2(4-pic)$] and [$B_2(1,2-S_2C_6H_4)_2(PEt_3)$] the B–B bond lengths are 1.701 (7) and 1.707 (3) Å, respectively (Clegg *et al.*, 1997), intermediate between Bsp^2-Bsp^2 and Bsp^3-Bsp^3 bonds. Interestingly, molecules of (VI) and (VII) lie over an inversion centre and a C_2 axis, respectively; whilst similar

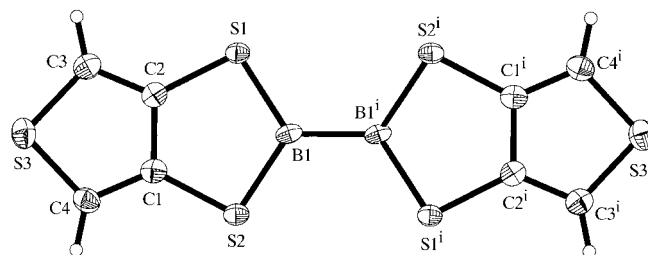


Figure 1

The molecular structure of (I). Ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii [symmetry code: (i) $2 - x, 1 - y, 1 - z$].

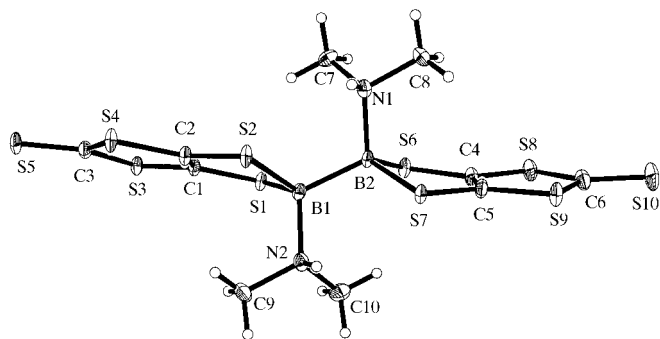


Figure 2

The molecular structure of (IV). Ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

symmetries are possible for (IV) and (V), neither exhibit exact symmetry in the solid state.

Angles around the B atoms [105.29 (13)–113.5 (2)° in (IV) and 104.30 (15)–119.9 (2)° in (V)] are consistent with tetrahedral geometry. The B–S bonds in (IV) [1.933 (3)–1.954 (3) Å] and (V) [1.913 (3)–1.943 (3) Å] are longer by *ca* 0.1 Å than those in (I)–(III), for reasons similar to those referred to above, together with the fact that any B–S π -bonding present in (I)–(III) is likely to be reduced in (IV) and (V). The BS_2C_2 rings in (IV) display an envelope conformation, with B1 and B2 lying 0.14 and 0.17 Å, respectively, out of the mean plane of their respective five-membered rings. Similar deviations are observed in (VI) and (VII). In (V), the BS_2C_2 rings are puckered, with the S–C–C–S torsion angles being –45.0 (6) and 44.4 (8)° for S1–C1–C2–S2 and S3–C3–C4–S4, respectively.

A packing diagram of the molecules of (I) is shown in Fig. 4. The molecules adopt a modified herring-bone packing motif where there is no ring–ring overlap between molecules in the ‘stacks’, such that the distance between planes of molecules in the stacks is 2.44 Å. The angle between the direction of different stacks in the *c* direction is 51.6°. The packing in (II) differs from that of (I) in that molecules of (II) form planar sheets utilizing inter- and intrastack S··S interactions. In (I), exocyclic S··S interactions are present [S3··S3^v = 3.621 (4) Å; (v) $1 - x, 1 - y, -z$] (van der Waals radius of S = 1.8 Å), approximately parallel to the crystallographic *a* axis. There are also interactions between adjacent molecules in

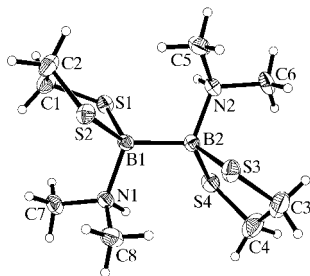


Figure 3

The molecular structure of (V). Ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The dichloromethane solvate is omitted.

stacks [S2··S1ⁱⁱⁱ = 3.618 (3) Å; (iii) $x, y, z + 1$]. π -Stacking appears to have been precluded by the formation of S··S interactions, since these interactions are formed in the direction of the S lone pairs, resulting in a herring-bone arrangement of molecules with no π interactions and short intra-stack distances. There are also possible S··S interactions between molecules in stacks in different directions [S2··S2^{iv} = 3.799 (2) and S1··S1ⁱⁱ = 3.857 (2) Å; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, \frac{3}{2} - y, \frac{1}{2} + z$].

The carbon analogue of (I), $\text{C}_2(\text{S}_3\text{C}_3\text{H}_2)_2$, (VIII), has been structurally characterized (Rovira *et al.*, 1994) in space group $P2_1/a$ with molecules of (VIII) also lying at inversion centres, and whilst there are no striking structural differences in the molecular structure other than those expected, the packing arrangement is slightly different. Although the classic herring-bone packing is observed, the exact arrangement of molecules is different to that of (I), due to the different S··S interactions (Fig. 5). The angle between the direction of non-parallel stacks in (VIII) is 65.6° and there are no short intrastack S··S interactions (the shortest S··S contacts are 3.991 Å), but there are reasonable ring–ring interactions: the π -stacking distance is 3.62 Å. There are, however, two unique sets of S··S contacts between adjacent molecules in differently directed stacks [S2··S1ⁱ = 3.546 and S2··S1ⁱⁱ = 3.606 Å; (i) $x - \frac{1}{2}, -\frac{1}{2} - y, z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$]. Again, there are interactions between the terminal S atoms of adjacent molecules [3.531 (1) Å].

The crystal structures of (I) and (VIII) demonstrate that with a minimal number of H atoms, S··S interactions efficiently mimic hydrogen bonds in playing an important role in the association of molecules.

Fig. 6 shows the packing of molecules of (IV) in the crystal structure, with the NHMe_2 groups omitted. The packing of the molecules is best described as ruffled chains propagating in the *a* direction [S10ⁱ··S10ⁱⁱⁱ = 3.393 (2) and S5··S5ⁱⁱ = 3.552 (1) Å; (i) $1 - x, 1 - y, -z$; (ii) $3 - x, 2 - y, 1 - z$; (iii) $2 + x, 1 + y, z$], and interactions of S atoms in adjacent chains [S4ⁱⁱⁱ··S9ⁱⁱ = 3.787 (1), S4ⁱⁱⁱ··S7ⁱⁱ = 3.437 (1), S2ⁱⁱ··S2ⁱⁱⁱ = 3.417 (1), S2ⁱⁱ··S7ⁱⁱⁱ = 3.438 (1), S3··S8ⁱ = 3.607 (1), S1··

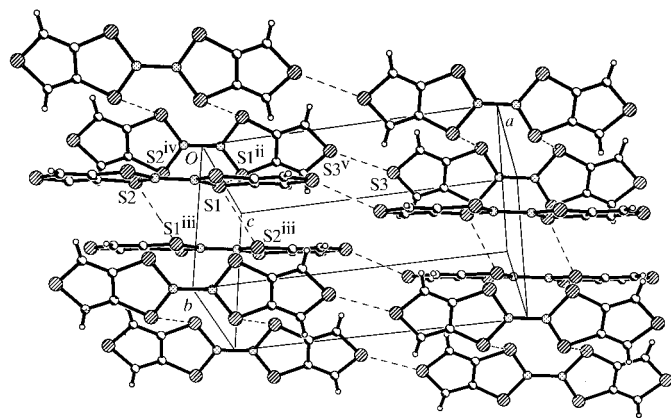


Figure 4

Packing diagram for (I) viewed down the *b* axis [symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $x, y, z + 1$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $1 - x, 1 - y, -z$].

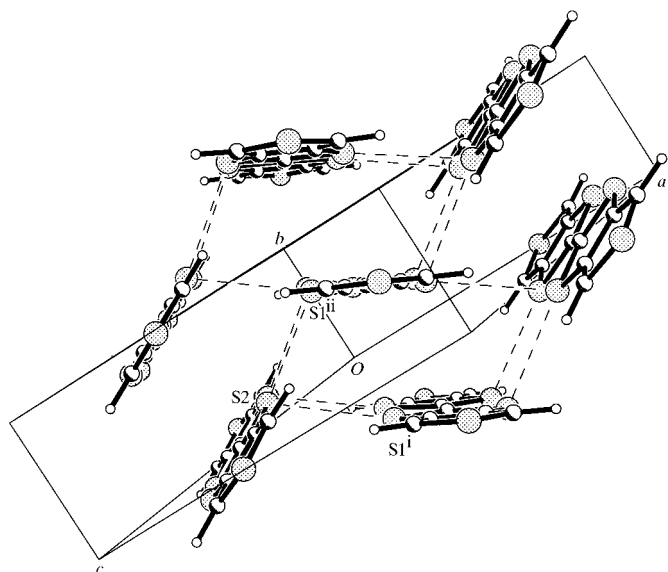


Figure 5
Packing diagram for (VIII) viewed [101] [symmetry codes: (i) $-\frac{1}{2}, -\frac{1}{2} - y, z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$].

$S8^i = 3.410$ (1), $S1 \cdots S6^i = 3.626$ (1) and $S6^i \cdots S6 = 3.877$ (1) Å] create an infinite ruffled sheet. Sheets are stacked in the b direction with one close contact [$S3 \cdots S7^{iv}$ 3.531 (1) Å; (iv) $x + 1, y, z$].

In addition to the $S \cdots S$ interactions in the crystal structures of (I) and (IV), there are a number of $S \cdots H$ hydrogen bonds, though these are long and at the sum of the van der Waals radii of S and H atoms (3.0 Å). In (V), in the absence of $S \cdots S$ contacts, there are a number of (long) $S \cdots H$ hydrogen bonds.

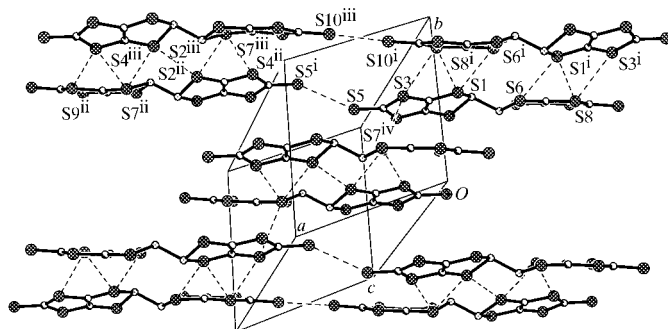


Figure 6
Packing diagram for (IV) viewed down the b axis, with the amine groups omitted for clarity [symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $3 - x, 2 - y, 1 - z$; (iii) $2 + x, 1 + y, z$; (iv) $x + 1, y, z$].

Experimental

For (I), a solution of n -BuLi (2.8 ml of a 1.6 M solution in hexanes) was added to a cooled solution (195 K) of 3,4-dibromothiophene (1.0 g, 4.5 mmol) in Et_2O (10 ml) and the reaction was stirred for 30 min, after which time elemental S (0.144 g, 4.5 mmol) was added. The reaction was then stirred at 195 K for 1 h, after which time the addition of n -BuLi and elemental S was repeated. The reaction was then allowed to warm to room temperature and was stirred for a

further 30 min. After this time the reaction was recooled to 195 K and HCl (10 ml of a 1.0 M solution in Et_2O) was added. Upon warming to room temperature a precipitate formed and the solution became yellow. Filtration afforded a yellow solution which was reduced in volume to ca 10 ml, which also removed any unreacted HCl. The filtrate was then cooled to 273 K and $B_2(NMe_2)_4$ (0.5 ml, 2.5 mmol; Brotherton *et al.*, 1960) was added, resulting in the immediate formation of a yellow precipitate. The reaction was stirred for 12 h, after which time the Et_2O was removed by syringe and the solid washed with hexane (5×5 ml) to give the crude bis-amine adduct [$B_2(3,4-S_2C_4H_2-1-S)_2(NHMe_2)_2$]. To a suspension of [$B_2(3,4-S_2C_4H_2-1-S)_2(NHMe_2)_2$] (0.15 g, 0.37 mmol) in Et_2O (5 ml) HCl (1 ml of a 1.0 M solution in Et_2O) was added and the reaction stirred for 3 h. After this time the solid was removed by filtration and washed with Et_2O (2×5 ml). Combination and evaporation of the Et_2O fractions gave compound (I) as a yellow solid, and this was recrystallized by dissolving in toluene and layering with hexane (yield: 0.8 g, 69%). 1H NMR ($CDCl_3$) δ 7.37 p.p.m.; $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ 62.7 p.p.m.; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 143.3 (C), 115.8 p.p.m. (CH). MS (EI) m/z 314 (M^+).

For (IV), a solution of [$B_2Cl_4(NHMe_2)_2$] (0.26 g, 1.0 mmol; Lawlor *et al.*, 1998) in tetrahydrofuran (2 ml) was added to a stirred suspension of [NET_4] $_2$ [$Zn(C_3S_3)_2$] (0.50 g, 21 mmol) in tetrahydrofuran (10 ml), resulting in a colour change from dark red to light yellow. Crystals of (IV) were isolated by layering this solution with toluene (2 ml), CH_2Cl_2 (2 ml) and hexane (10 ml). $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ 41.8 p.p.m.

For (V), $B_2(NMe_2)_4$ (0.3 ml, 1.5 mmol) was added to a solution of 1,2-ethanedithiol (0.28 g, 3.0 mmol) in hexane (20 ml) and the solution refluxed for 5 h, after which it was allowed to cool to room temperature and then refrigerated at 243 K overnight. The solvent was then removed by syringe, affording (V) as a white crystalline solid (yield: 0.36 g, 81%). $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ 5.8 p.p.m. Addition of HCl affords $B_2(1,2-S_2C_2H_4)_2$ in solution; $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ 65.8 p.p.m.

Compound (I)

Crystal data

$C_8H_4B_2S_6$
 $M_r = 314.10$
Monoclinic, $P2_1/c$
 $a = 13.549$ (2) Å
 $b = 7.525$ (2) Å
 $c = 5.891$ (4) Å
 $\beta = 90.04$ (3)°
 $V = 600.6$ (4) Å³
 $Z = 2$

$D_x = 1.737$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 62 reflections
 $\theta = 5-50^\circ$
 $\mu = 1.10$ mm⁻¹
 $T = 173$ (2) K
Plate, colourless
0.55 \times 0.40 \times 0.01 mm

Data collection

Siemens SMART CCD area detector diffractometer
 ω rotation with narrow frame scans
Absorption correction: SADABS (Sheldrick, 1996)
 $T_{min} = 0.37$, $T_{max} = 0.88$
3856 measured reflections
1383 independent reflections

1150 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.047$
 $\theta_{max} = 27.52^\circ$
 $h = -13 \rightarrow 17$
 $k = -9 \rightarrow 9$
 $l = -7 \rightarrow 7$
Intensity decay: <1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.135$
 $S = 1.06$
1382 reflections
74 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0882P)^2]$
where $P = [\max(F_o^2, 0) + 2F_c^2]/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 1.12$ e Å⁻³
 $\Delta\rho_{min} = -0.71$ e Å⁻³

Table 1Selected geometric parameters (\AA , $^\circ$) for (I).

B1—B1 ⁱ	1.672 (12)	S2—C1	1.753 (6)
B1—S1	1.800 (6)	S3—C4	1.717 (6)
B1—S2	1.807 (6)	S3—C3	1.722 (6)
B1 ⁱ —B1—S1	122.9 (5)	C4—C1—C2	113.8 (5)
B1 ⁱ —B1—S2	123.0 (5)	C4—C1—S2	129.0 (4)
S1—B1—S2	114.1 (3)	C2—C1—S2	117.2 (4)
C2—S1—B1	95.9 (3)	C3—C2—C1	112.5 (5)
B1—S1—S1 ⁱⁱ	63.6 (2)	C3—C2—S1	130.3 (4)
C1—S2—B1	95.6 (3)	C1—C2—S1	117.1 (4)
C4—S3—C3	93.4 (3)	C2—C3—S3	110.5 (4)
C4—S3—S3 ⁱⁱⁱ	153.7 (2)	C1—C4—S3	109.7 (4)
C3—S3—S3 ⁱⁱⁱ	103.9 (2)		

Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (iii) $1-x, 1-y, -z$.**Compound (IV)***Crystal data*

$\text{C}_{10}\text{H}_{14}\text{B}_2\text{N}_2\text{S}_{10}$
 $M_r = 504.45$
 Triclinic, $\bar{P}1$
 $a = 9.578$ (2) \AA
 $b = 9.686$ (2) \AA
 $c = 12.172$ (3) \AA
 $\alpha = 95.56$ (2) $^\circ$
 $\beta = 91.99$ (2) $^\circ$
 $\gamma = 113.349$ (12) $^\circ$
 $V = 1028.5$ (4) \AA^3

$Z = 2$
 $D_x = 1.629$ Mg m^{-3}
 Mo $K\alpha$ radiation
 Cell parameters from 132 reflections
 $\theta = 5-50^\circ$
 $\mu = 1.07$ mm^{-1}
 $T = 123$ (2) K
 Needle, orange
 $0.5 \times 0.1 \times 0.1$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω rotation with narrow frame scans
 Absorption correction: *SADABS* (Sheldrick, 1996)
 $T_{\min} = 0.70$, $T_{\max} = 0.92$
 10 786 measured reflections
 4654 independent reflections

3579 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\text{max}} = 27.48^\circ$
 $h = -12 \rightarrow 12$
 $k = -12 \rightarrow 12$
 $l = -15 \rightarrow 15$
 Intensity decay: $<1\%$

Table 2Selected geometric parameters (\AA , $^\circ$) for (IV).

B1—N2	1.628 (3)	S4—C3	1.720 (2)
B1—B2	1.746 (4)	S4—C2	1.746 (2)
B1—S1	1.938 (3)	S5—C3	1.668 (2)
B1—S2	1.954 (3)	S6—C4	1.739 (2)
B2—N1	1.632 (3)	S7—C5	1.749 (2)
B2—S7	1.933 (3)	S8—C6	1.729 (3)
B2—S6	1.935 (3)	S8—C4	1.745 (2)
S1—C1	1.749 (2)	S9—C5	1.739 (2)
S2—C2	1.744 (2)	S9—C6	1.741 (3)
S3—C3	1.728 (2)	S10—C6	1.645 (2)
S3—C1	1.737 (2)		
N2—B1—B2	113.5 (2)	N1—B2—S6	107.35 (15)
N2—B1—S1	107.4 (2)	B1—B2—S6	113.4 (2)
B2—B1—S1	113.1 (2)	S7—B2—S6	105.57 (12)
N2—B1—S2	106.84 (15)	C7—N1—C8	108.3 (2)
B2—B1—S2	110.2 (2)	C7—N1—B2	114.1 (2)
S1—B1—S2	105.29 (13)	C8—N1—B2	116.2 (2)
N1—B2—B1	112.3 (2)	C9—N2—C10	108.8 (2)
N1—B2—S7	107.2 (2)	C9—N2—B1	115.8 (2)
B1—B2—S7	110.7 (2)	C10—N2—B1	114.1 (2)

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.072$
 $S = 1.04$
 4654 reflections
 224 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2]$
 where $P = [\max(F_o^2, 0) + 2F_c^2]/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.41$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.41$ e \AA^{-3}
 Extinction correction: *SHELXTL* (Siemens, 1997b)
 Extinction coefficient: 0.0012 (5)

Compound (V)*Crystal data*

$\text{C}_8\text{H}_{22}\text{B}_2\text{N}_2\text{S}_4 \cdot 0.33\text{CH}_2\text{Cl}_2$
 $M_r = 324.53$
 Trigonal, $R\bar{3}$
 $a = 29.629$ (3) \AA
 $c = 9.438$ (2) \AA
 $V = 7175.6$ (17) \AA^3
 $Z = 18$
 $D_x = 1.351$ Mg m^{-3}

Mo $K\alpha$ radiation
 Cell parameters from 273 reflections
 $\theta = 5-50^\circ$
 $\mu = 0.69$ mm^{-1}
 $T = 173$ (2) K
 Needle, colourless
 $0.4 \times 0.1 \times 0.1$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω rotation with narrow frame scans
 Absorption correction: none
 15 138 measured reflections
 3658 independent reflections
 2888 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$
 $\theta_{\text{max}} = 27.48^\circ$
 $h = -34 \rightarrow 38$
 $k = -38 \rightarrow 35$
 $l = -12 \rightarrow 11$
 Intensity decay: $<1\%$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.129$
 $S = 1.30$
 3658 reflections
 157 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 20.867P]$
 where $P = [\max(F_o^2, 0) + 2F_c^2]/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.27$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.66$ e \AA^{-3}

Table 3Selected geometric parameters (\AA , $^\circ$) for (V).

B1—N1	1.655 (4)	S1—C1	1.827 (3)
B1—B2	1.758 (5)	S2—C2	1.826 (3)
B1—S1	1.924 (3)	S3—C3	1.815 (4)
B1—S2	1.943 (3)	S4—C4	1.823 (4)
B2—N2	1.662 (4)	C1—C2	1.512 (4)
B2—S3	1.913 (3)	C3—C4	1.513 (6)
B2—S4	1.942 (3)		
N1—B1—B2	108.7 (2)	N2—B2—S4	106.54 (18)
N1—B1—S1	109.22 (19)	B1—B2—S4	108.80 (19)
B2—B1—S1	108.56 (19)	S3—B2—S4	104.97 (16)
N1—B1—S2	105.77 (18)	C7—N1—C8	107.7 (2)
B2—B1—S2	119.9 (2)	C7—N1—B1	116.4 (2)
S1—B1—S2	104.30 (15)	C8—N1—B1	114.0 (2)
N2—B2—B1	110.4 (2)	C5—N2—C6	107.8 (2)
N2—B2—S3	107.99 (19)	C5—N2—B2	112.8 (2)
B1—B2—S3	117.5 (2)	C6—N2—B2	116.2 (2)

H atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} value of their attached C (1.5 U_{iso} for methyl groups), with the exception of H1 and H2 in (IV) which were located from the electron density difference map. During refinement of (I), high residual electron density, poor

agreement factors ($R_1 = 0.240$ and $wR_2 = 0.586$), a β angle close to 90° and unusual shapes of the diffraction peaks all suggested non-merohedral twinning. Addition of the pseudo-orthorhombic twin law (100, $0\bar{1}0$, $00\bar{1}$) improved convergence and greatly reduced the agreement factors and the features in the final difference map. The volume fraction of one of the twin components was found to be 0.383 (3). The twinning is presumably responsible for the rather high electron density residuals (highest peak $1.12 \text{ e}\text{\AA}^{-3}$, 0.81 \AA from S2; deepest trough $-0.71 \text{ e}\text{\AA}^{-3}$, 0.85 \AA from S1). The good agreement between the chemically equivalent bond lengths and angles and the reasonable ellipsoids suggests that the model is satisfactory. In (V), the Cl atoms of the dichloromethane molecule were located on a threefold axis with the C atom disordered over two sets of three sites, each with an occupancy of about 1/6. The atoms C9 [occupancy factor $3 \times 0.178(8)$] and C9' were refined isotropically. Attached H atoms were not included.

For all compounds, data collection: *SMART* (Siemens, 1995a); cell refinement: *SAINTE* (Siemens, 1995a); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Siemens, 1995b); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We thank the EPSRC for a studentship (MJQ), and Laporte plc and the Royal Society for additional funds.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1489). Services for accessing these data are described at the back of the journal.

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