

## Structural characteristics of dibromoborylated benzene derivatives

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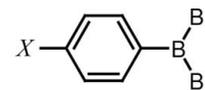
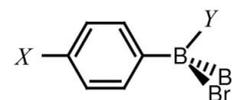
The crystal structures of five dibromobenzene derivatives, namely dibromoborylbenzene,  $C_6H_5BBr_2$ , (I), 1-dibromoboryl-4-(trimethylsilyl)benzene,  $C_9H_{13}BBr_2Si$ , (II), 4-bromo-1-(dibromoboryl)benzene,  $C_6H_4BBR_3$ , (III), dibromo(dimethylamino)(phenyl)borane,  $C_8H_{12}BBR_2N$ , (IV), and dibromo(dimethylsulfanyl)[4-(trimethylsilyl)phenyl]borane,  $C_{11}H_{19}BBR_2SSi$ , (V), have been determined. Compounds (I)–(IV) crystallize with one molecule in the asymmetric unit, but the molecule of (V) is located on a crystallographic mirror plane, implying twofold disorder of the central aromatic ring, the S atom and one of the methyl groups bonded to the S atom. In (I), (II) and (III), the B atom is three-coordinated, and in (IV) and (V) it is four-coordinated. The geometric parameters of the  $-BBr_2$  group in these five structures agree well with those of comparable structures retrieved from the Cambridge Structural Database. The C–B and B–Br bond lengths in the molecules with a three-coordinated B atom are significantly shorter than those in the molecules with a four-coordinated B atom. In the compounds with a three-coordinated B atom, the  $-BBr_2$  group tends to be coplanar with the aromatic ring to which it is attached.

### Comment

In the past few decades, dihaloboryl-substituted arenes have gained significant importance as starting materials for aryl(hydro)boranes (Lorbach *et al.*, 2012) and BN addition compounds (Heilmann-Brohl *et al.*, 2011), for example. Both classes of substance feature intriguing optoelectronic behaviour. We present here the crystal structures of a series of dibromoborylated benzene derivatives and a comparison of their molecular structures.

Dibromoborylbenzene, (I) (Fig. 1), features an essentially planar molecule (r.m.s. deviation for all non-H atoms = 0.007 Å) and a dihedral angle of 3.7 (3)° between the  $-BBr_2$  group and the aromatic ring. The packing (Fig. 2) shows pairs of centrosymmetrically related molecules, with the B atom

located almost directly over the C atom in the *para* position of the ring [ $B1-C4^i = 3.584(9)$  Å; symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ ].

(I)  $X = H$ (II)  $X = Me_3Si$ (III)  $X = Br$ (IV)  $X = H, Y = HNMe_2$ (V)  $X = Me_3Si, Y = SMe_2$ 

In 1-dibromoboryl-4-(trimethylsilyl)benzene, (II), the *para* position of the dibromobenzene ring is substituted with a trimethylsilyl residue (Fig. 3). The dihedral angle between the aromatic ring and the  $-BBr_2$  group is 6.4 (3)°. As for (I), the

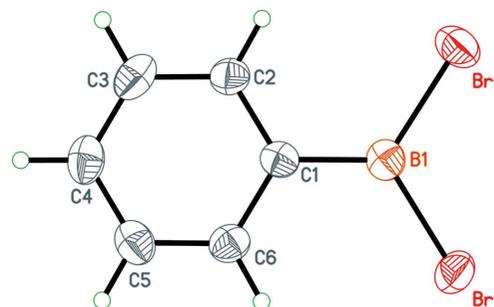


Figure 1

A perspective view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

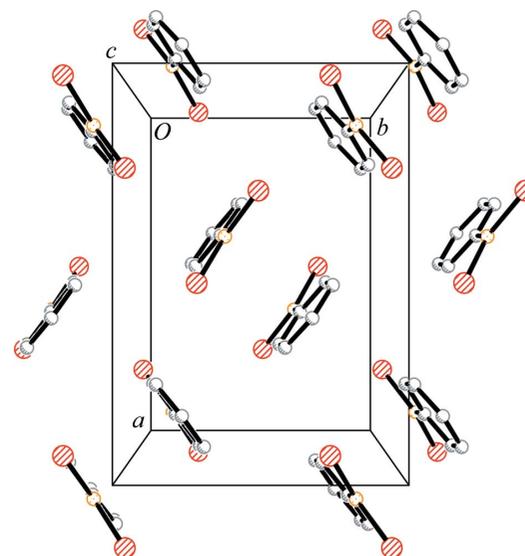
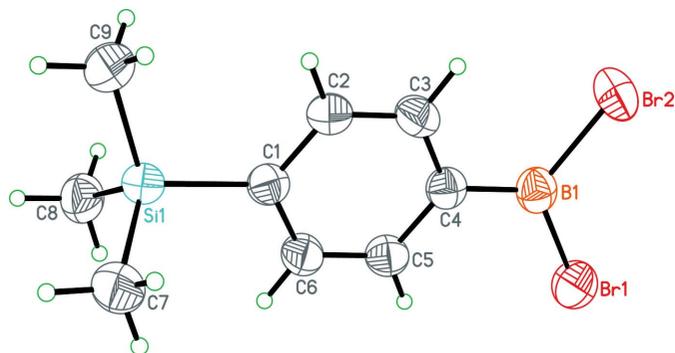


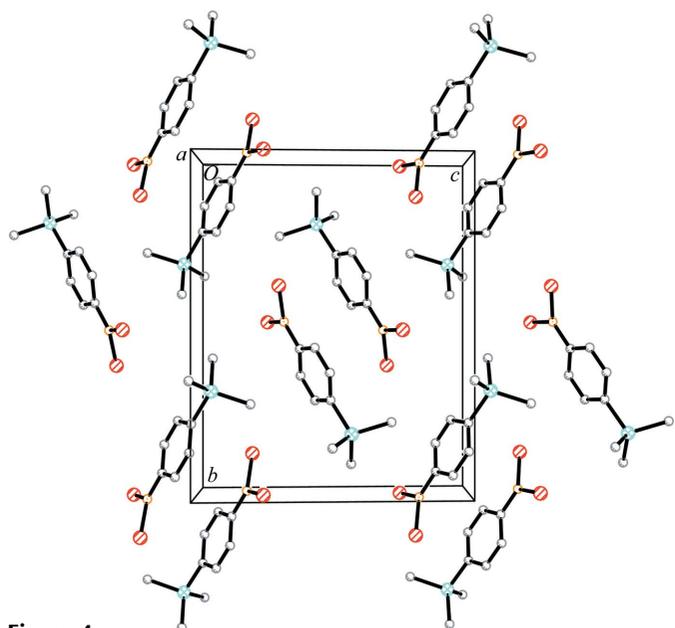
Figure 2

A packing diagram for (I), viewed in the *ab* plane. H atoms have been omitted for clarity.



**Figure 3**

A perspective view of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.



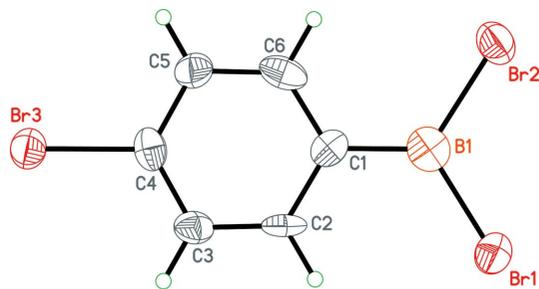
**Figure 4**

A packing diagram for (II), viewed in the *bc* plane. H atoms bonded to C atoms have been omitted for clarity.

packing (Fig. 4) shows pairs of centrosymmetrically related molecules, which are slightly displaced from one another. The B atom is located over (but with a slight displacement from) the C atom in the *ortho* position of the ring [B1–C5<sup>i</sup> = 3.626 (5) Å; symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ ].

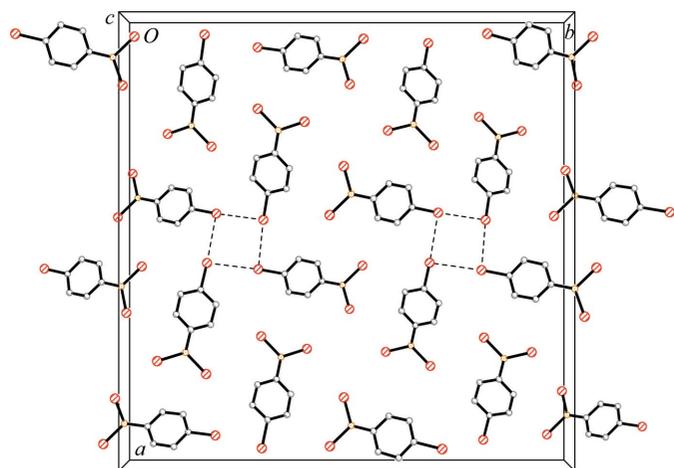
In 4-bromo-1-(dibromoboryl)benzene, (III), a bromine residue is located in the the *para* position of the dibromobenzene ring (Fig. 5), decreasing the electron density of the C atom to which it is bonded. The dihedral angle between the aromatic ring and the  $-BBr_2$  group is 3.0 (9)°. The packing (Fig. 6) shows intermolecular contacts between the Br atoms in the *para* position of the ring [Br3···Br3<sup>i</sup> = Br3···Br3<sup>ii</sup> = 3.663 (2) Å; symmetry codes: (i)  $y - \frac{3}{4}, -x + \frac{3}{4}, -z - \frac{1}{4}$ ; (ii)  $-y + \frac{3}{4}, x + \frac{3}{4}, -z - \frac{1}{4}$ ].

Dibromo(dimethylamino)(phenyl)borane, (IV) (Fig. 7), is the product of the reaction of (I) with dimethylamine. Whereas the B atom is still located in the plane of the aromatic ring [it deviates by just 0.034 (9) Å from the ring plane], the two Br atoms deviate by  $-0.976$  (9) (Br1) and  $-0.819$  (10) Å



**Figure 5**

A perspective view of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

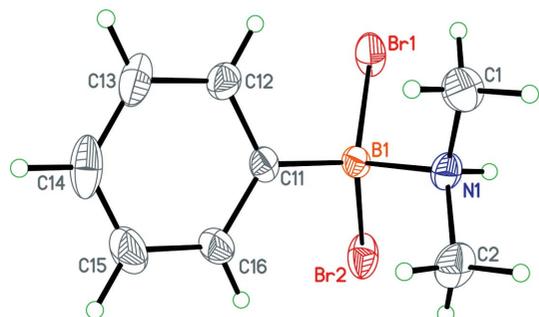


**Figure 6**

A packing diagram for (III), viewed in the *ab* plane. Br···Br contacts are shown as dashed lines. H atoms have been omitted for clarity.

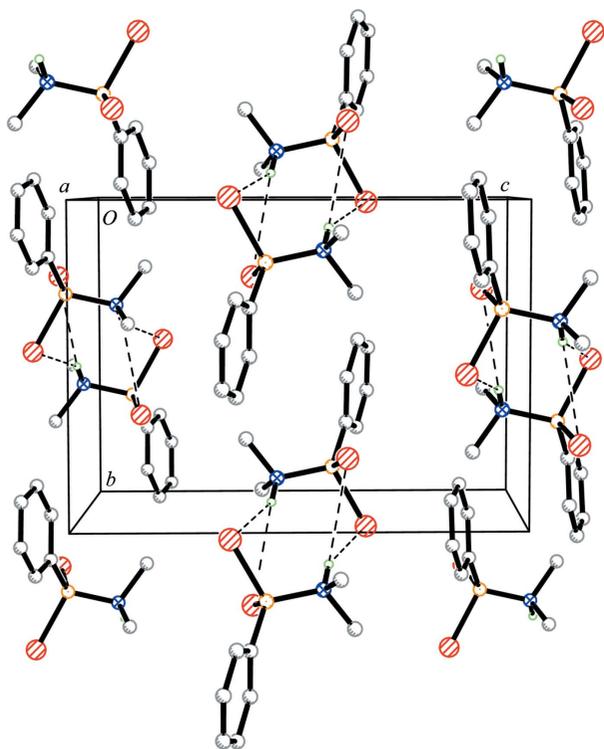
(Br2) from the ring plane. The N atom is displaced even further [1.538 (9) Å] from the ring plane in the opposite direction to the Br residues. The crystal packing (Fig. 8) shows that the molecules are connected by N–H···Br hydrogen bonds to form centrosymmetric dimers. It is remarkable that the amino H atom forms two almost equal hydrogen bonds to the two Br atoms of another molecule (Table 1).

Dibromo(dimethylsulfanyl)[4-(trimethylsilyl)phenyl]borane, (V) (Fig. 9), is the product of the reaction of (II) with dimethyl sulfide. The molecule is located on a crystallographic mirror plane. As a result, the central ring, the S atom and one

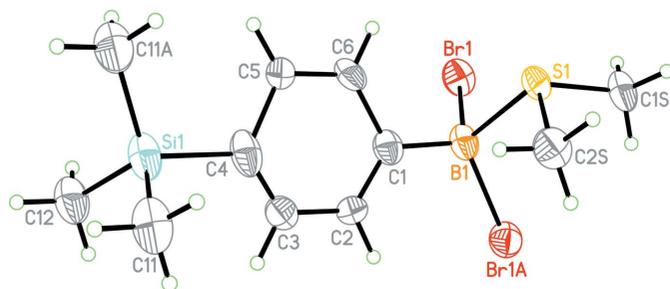


**Figure 7**

A perspective view of (IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 8**  
A packing diagram for (IV), viewed in the *bc* plane. H atoms bonded to C atoms have been omitted for clarity. Hydrogen bonds are shown as dashed lines.



**Figure 9**  
A perspective view of (V), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Only one of the two disordered orientations of the central ring is shown. [Symmetry code: (A)  $x, -y + \frac{1}{2}, z$ .]

of the methyl groups bonded to the S atom are disordered over two equally occupied orientations. Due to this disorder, the deviation of the B, Br and S atoms from the ring plane(s) is not discussed.

In order to compare these five structures with similar compounds, a search of the Cambridge Structural Database (CSD, Version 5.33 of November 2011, plus one update; Allen, 2002) was performed for an aromatic ring carrying a  $-\text{BBr}_2$  residue. Eight entries were found, namely 4-(dibromoboryl)-toluene (AYUHIL), 1,3-bis(dibromoboryl)benzene (AYUHOR), 1,4-bis(dibromoboryl)benzene (AYUHUX), 1,3,5-tris(dibromoboryl)benzene (AYUJAF) and 4,4'-bis(dibromoboryl)biphenyl (AYUJEJ) (Haberecht *et al.*, 2004), dibromo(2,4,6-triisopropylphenyl)borane (EHUBEO) (Olmstead *et al.*, 2003), and dibromo(2,6-dimesitylphenyl)borane (TIZ-

XAB) and [2,6-bis(2,4,6-triisopropylphenyl)phenyl]dibromoborane (TIZXEF) (Grisby & Power, 1996), with a mean C—B bond length of 1.55 (3) Å and a mean B—Br bond length of 1.91 (1) Å. These values agree well with those in (I), (II) and (III) (Table 2).

If the substituents of the ring in the *ortho* position with respect to the  $-\text{BBr}_2$  group are H atoms, the  $-\text{BBr}_2$  group is coplanar with the ring. The dihedral angle between the ring and the  $-\text{BBr}_2$  group ranges from 1.4 (in AYUJEJ) to 8.8° (in AYUJAF). In three of the structures, the *ortho* substituents are very bulky and force the  $-\text{BBr}_2$  group into an almost perpendicular position with respect to the aromatic ring (dihedral angles:  $\text{BBr}_2/\text{ring} = 87.3^\circ$  in EHUBEO,  $77.5^\circ$  in TIZXAB and  $90.0^\circ$  in TIZXEF).

A search of the CSD for an aromatic ring carrying a  $-\text{BBr}_2$  residue with a four-coordinated B atom revealed only two structures, dibromo(2-dimethylaminomethylphenyl)borane (CEJWUJ; Brown *et al.*, 1998) and bromo(bromo{4-[dibromo(tricyclohexylphosphino)boranyl]phenyl}boranyl)-B-bis(tricyclohexylphosphino)platinum benzene *n*-hexane solvate (QOMLEK; Braunschweig *et al.*, 2008). The C—B bond lengths of 1.559 (CEJWUJ) and 1.609 Å (QOMLEK), and the B—Br bond lengths (2.019 and 2.020 Å in CEJWUJ, and 2.046 and 2.056 Å in QOMLEK) are in good agreement with those of (IV) and (V) (Table 2). Apart from these distances, the two database structures differ too much from (IV) and (V) for further comparison.

In conclusion, it can be said that the C—B and B—Br bonds are significantly elongated if the number of substituents at the B atom is increased from three to four. Molecules containing a three-coordinated B atom carrying two Br atoms tend to have the  $-\text{BBr}_2$  group coplanar with the aromatic ring, as long as no bulky substituents in the *ortho* position of the aromatic ring prevent coplanarity. The crystal packing of these structures depends on the substitution pattern. Compounds (I) and (II), with electron-rich residues in the position *para* to the  $-\text{BBr}_2$  group, feature a B— $\pi$  interaction in their crystal structures, whereas no such interaction is observed in the structures of (III), (IV) and (V).

## Experimental

All experiments were carried out under dry nitrogen or argon with strict exclusion of air and moisture using standard Schlenk techniques. The starting materials were purchased from commercial sources and used without further purification. The solvents were distilled from sodium/benzophenone prior to use.  $\text{C}_6\text{D}_6$  was dried over molecular sieves and stored under dry nitrogen. The NMR spectra were recorded on Bruker AM 250, DPX 250, Avance 300 and Avance 400 spectrometers. Abbreviations: *s* = singlet, *d* = doublet, *t* = triplet, *vtr* (virtual triplet), *q* = quartet, *quin* = quintet, *mult* = multiplet and *br* = broad.

For the synthesis of (I), trimethylphenylsilane (8.5 ml, 49.2 mmol, 1 equivalent) was dissolved in hexane (10 ml) and cooled to 273 K.  $\text{BBr}_3$  (5 ml, 52.9 mmol, 1.1 equivalents) was added rapidly *via* a syringe. The mixture was allowed to warm slowly to room temperature and was then heated under reflux for 2 h. During removal of all volatile components *in vacuo*, dibromoborylbenzene was obtained as

colourless crystals (yield 11.46 g, 94%).  $^1\text{H}$  NMR (250.1 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.95 (*vt*,  $^3J_{\text{HH}} = 7.5$  Hz, 2H, Ph—H<sup>meta</sup>), 7.11 (*t*,  $^3J_{\text{HH}} = 7.4$  Hz, 1H, Ph—H<sup>para</sup>), 8.04 (*d*,  $^3J_{\text{HH}} = 7.6$  Hz, 2H, Ph—H<sup>ortho</sup>).  $^{11}\text{B}$  NMR (128.4 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  57.4 ( $h_{1/2} = 90$  Hz).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  128.3 (Ph—C<sup>meta</sup>), 135.3 (Ph—C<sup>para</sup>), 138.0 (Ph—C<sup>ortho</sup>). When a benzene (0.6 ml) solution of (I) (0.1 mmol) in the presence of an excess of  $\text{HNMe}_2$  was left to stand for one week, single crystals of the composition  $\text{PhBBr}_2\cdot\text{HNMe}_2$ , (IV), could be isolated.

For the synthesis of (II), 1,4-bis(trimethylsilyl)benzene (4.95 g, 21.8 mmol, 1 equivalent) and  $\text{BBr}_3$  (2.3 ml, 23.9 mmol, 1.1 equivalents) were dissolved in hexane (15 ml) and stirred for 24 h at room temperature. The solution was evaporated to dryness *in vacuo* to give (II) as colourless crystals (yield 6.13 g, 86%).  $^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  0.13 (*s*, 9H, SiMe<sub>3</sub>), 7.34 (*d*,  $^3J_{\text{HH}} = 8.1$  Hz, 2H, Ph—H<sup>2/6</sup>), 8.08 (*d*,  $^3J_{\text{HH}} = 8.1$  Hz, 2H, Ph—H<sup>3/5</sup>).  $^{11}\text{B}$  NMR (128.4 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  57.0 ( $h_{1/2} = 280$  Hz).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -1.5 (SiMe<sub>3</sub>), 133.3 (C<sup>Ar</sup>), 136.8 (C<sup>Ar</sup>), 150.1 (SiC<sup>Ar</sup>). When a benzene (0.6 ml) solution of (II) (0.1 mmol) in the presence of an excess of  $\text{SMe}_2$  was left to stand for one week, single crystals of the composition  $\text{Me}_3\text{SiC}_6\text{H}_4\text{BBR}_2\cdot\text{SMe}_2$ , (V), could be isolated.

For the synthesis of (III), 4-bromo-1-(trimethylsilyl)benzene (4.3 ml, 21.8 mmol, 1 equivalent) was added to a solution of  $\text{BBr}_3$  (2.3 ml, 23.9 mmol, 1.1 equivalents) and hexane (15 ml). After the mixture had been heated under reflux for 4 h, the solvent was removed *in vacuo* to give single crystals of (III) (yield 5.87 g, 82%).  $^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.12 (*d*,  $^3J_{\text{HH}} = 8.3$  Hz, 2H, Ph—H<sup>2/6</sup>), 7.66 (*d*,  $^3J_{\text{HH}} = 8.3$  Hz, 2H, Ph—H<sup>3/5</sup>).  $^{11}\text{B}$  NMR (128.4 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  57.4 ( $h_{1/2} = 180$  Hz).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  131.6 (C<sup>Ar</sup>), 131.7 (BrC<sup>Ar</sup>), 139.0 (C<sup>Ar</sup>).

## Compound (I)

### Crystal data

$\text{C}_6\text{H}_5\text{BBR}_2$	$V = 1537.6$ (4) $\text{\AA}^3$
$M_r = 247.73$	$Z = 8$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 11.0841$ (16) $\text{\AA}$	$\mu = 10.45$ $\text{mm}^{-1}$
$b = 7.8287$ (12) $\text{\AA}$	$T = 173$ K
$c = 17.720$ (2) $\text{\AA}$	$0.29 \times 0.17 \times 0.09$ mm

### Data collection

Stoe IPDS II two-circle diffractometer	14258 measured reflections
Absorption correction: multi-scan (MULABS; Spek, 2009; Blessing, 1995)	1517 independent reflections
$T_{\min} = 0.152$ , $T_{\max} = 0.453$	1089 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.081$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	82 parameters
$wR(F^2) = 0.110$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{\max} = 0.59$ $\text{e \AA}^{-3}$
1517 reflections	$\Delta\rho_{\min} = -1.07$ $\text{e \AA}^{-3}$

## Compound (II)

### Crystal data

$\text{C}_9\text{H}_{13}\text{BBR}_2\text{Si}$	$V = 1273.00$ (17) $\text{\AA}^3$
$M_r = 319.91$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 6.7452$ (5) $\text{\AA}$	$\mu = 6.42$ $\text{mm}^{-1}$
$b = 15.2390$ (12) $\text{\AA}$	$T = 173$ K
$c = 12.4123$ (10) $\text{\AA}$	$0.29 \times 0.25 \times 0.25$ mm
$\beta = 93.841$ (6)°	

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ , °) for (IV).

$D\text{—H}\cdots A$	$D\text{—H}$	$\text{H}\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
$\text{N1—H1}\cdots\text{Br1}^i$	0.85 (7)	2.96 (7)	3.705 (6)	147 (6)
$\text{N1—H1}\cdots\text{Br2}^i$	0.85 (7)	2.96 (7)	3.684 (5)	143 (6)

Symmetry code: (i)  $-x, -y, -z + 1$ .

### Data collection

Stoe IPDS II two-circle diffractometer	19196 measured reflections
Absorption correction: multi-scan (MULABS; Spek, 2009; Blessing, 1995)	2235 independent reflections
$T_{\min} = 0.258$ , $T_{\max} = 0.297$	1942 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.064$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	119 parameters
$wR(F^2) = 0.084$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\max} = 0.46$ $\text{e \AA}^{-3}$
2235 reflections	$\Delta\rho_{\min} = -0.37$ $\text{e \AA}^{-3}$

## Compound (III)

### Crystal data

$\text{C}_6\text{H}_4\text{BBR}_3$	$Z = 16$
$M_r = 326.63$	Mo $K\alpha$ radiation
Tetragonal, $I4_1/a$	$\mu = 13.80$ $\text{mm}^{-1}$
$a = 29.446$ (3) $\text{\AA}$	$T = 173$ K
$c = 4.0228$ (4) $\text{\AA}$	$0.26 \times 0.11 \times 0.11$ mm
$V = 3488.0$ (8) $\text{\AA}^3$	

### Data collection

Stoe IPDS II two-circle diffractometer	12710 measured reflections
Absorption correction: multi-scan (MULABS; Spek, 2009; Blessing, 1995)	1544 independent reflections
$T_{\min} = 0.124$ , $T_{\max} = 0.312$	1111 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.097$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.070$	91 parameters
$wR(F^2) = 0.149$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\max} = 0.90$ $\text{e \AA}^{-3}$
1544 reflections	$\Delta\rho_{\min} = -1.08$ $\text{e \AA}^{-3}$

## Compound (IV)

### Crystal data

$\text{C}_8\text{H}_{12}\text{BBR}_2\text{N}$	$V = 1069.1$ (2) $\text{\AA}^3$
$M_r = 292.82$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.9095$ (9) $\text{\AA}$	$\mu = 7.53$ $\text{mm}^{-1}$
$b = 9.2874$ (13) $\text{\AA}$	$T = 173$ K
$c = 12.9306$ (13) $\text{\AA}$	$0.19 \times 0.09 \times 0.05$ mm
$\beta = 92.249$ (8)°	

### Data collection

Stoe IPDS II two-circle diffractometer	6363 measured reflections
Absorption correction: multi-scan (MULABS; Spek, 2009; Blessing, 1995)	2004 independent reflections
$T_{\min} = 0.329$ , $T_{\max} = 0.705$	1413 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.082$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.104$   
 $S = 0.99$   
 2004 reflections  
 113 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.98 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.96 \text{ e } \text{Å}^{-3}$

## Compound (V)

### Crystal data

$\text{C}_{11}\text{H}_{10}\text{BBr}_2\text{SSi}$   
 $M_r = 382.04$   
 Orthorhombic, *Pnma*  
 $a = 6.6950 (5) \text{ Å}$   
 $b = 11.0880 (8) \text{ Å}$   
 $c = 21.6870 (16) \text{ Å}$

$V = 1609.9 (2) \text{ Å}^3$   
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 5.21 \text{ mm}^{-1}$   
 $T = 173 \text{ K}$   
 $0.20 \times 0.10 \times 0.05 \text{ mm}$

### Data collection

Stoe IPDS II two-circle diffractometer  
 Absorption correction: multi-scan (*MULABS*; Spek, 2009; Blessing, 1995)  
 $T_{\min} = 0.422$ ,  $T_{\max} = 0.781$

22983 measured reflections  
 1705 independent reflections  
 1146 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.073$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.083$   
 $S = 0.90$   
 1705 reflections

110 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.40 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.56 \text{ e } \text{Å}^{-3}$

The H atoms were initially located by difference Fourier synthesis. Subsequently, H atoms bonded to C atoms were refined using a riding model, with methyl C–H = 0.98 Å, aromatic C–H = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl or  $1.2U_{\text{eq}}(\text{C})$  for aromatic H atoms. The coordinates of the H atom bonded to the N atom in (IV) were refined with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ . Due to imposed crystallographic mirror symmetry, the central ring of (V), the S atom and one of the methyl groups bonded to the S atom are disordered over two equally occupied positions.

**Table 2**

Bond lengths (Å) for (I)–(V).

Bond	(I)	(II)	(III)	(IV)	(V)
C–B	1.533 (9)	1.535 (5)	1.53 (2)	1.600 (9)	1.592 (8)
B–Br	1.917 (7)	1.906 (4)	1.911 (16)	2.049 (6)	2.022 (4)
B–Br	1.919 (7)	1.915 (4)	1.926 (16)	2.058 (7)	2.022 (4)

For all compounds, data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3438). Services for accessing these data are described at the back of the journal.

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