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Structure of σ(+)-5-Bromo-6,9-bis(dimethylsulphido)-*nido*-decaborane(12), C₄H₂₃B₁₀BrS₂, Determined with a Twinned Crystal

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Abstract. $M_r = 323.5$, orthorhombic, $P2_12_12_1$, $a = 9.181$ (3), $b = 9.181$ (3), $c = 19.447$ (5) Å, $V = 1639.2$ (8) Å^3, $Z = 4$, $D_m = 1.31$, $D_x = 1.31$ Mg m^{-3}, Mo $K\alpha$ ($\lambda = 0.71073$ Å), $\mu = 2.70$ mm^{-1}, $F(000) = 656$, room temperature, final $R = 0.069$ for 1232 observed reflections. The crystal used for structure determination was a twin [twin fraction $\alpha = 0.377$ (4)] with coinciding tetragonal lattices. The crystal structure of this twin was solved by a modified heavy-atom method. Determination of the absolute configuration was based upon the anomalous scattering of the Br atom.

Introduction. The present study reports on the X-ray investigation of BrB₁₀H₁₁[S(CH₃)₂]₂ previously prepared (Plešek, Heřmánek & Štíbr, 1969). This compound is the first example of optical isomerism in the decaborane series.

Experimental. Colourless crystals, stable in air and to X-rays, flotation method for D_m, crystal 0.4 × 0.4 × 0.3 mm, preliminary lattice constants and space group from photographs (Cu $K\alpha$ radiation), all parameters refined from 29 reflections centred on the diffractometer; lattice exhibits tetragonal symmetry because a and b are equal within the limits of the error of measurement; differences in intensities of a few pseudotetragonal equivalent reflections (see Fig. 1) exceeded the measuring error, so crystallographic system and space group are as in *Abstract*; Hilger & Watts four-circle diffractometer, Mo $K\alpha$ radiation, ω–2θ scan, $2\theta \le 54°$, scan speed 1 to 4° min^{-1}, rapid

prescan, scanning interval 2°, one standard reflection, no significant variation, 2058 measured independent reflections, 826 unobserved reflections [$I < 1.96\sigma(I)$]; for unobserved reflections $F_{unobs} = \frac{2}{3}F_{min}$ and $\sigma(F_{unobs}) = (1/\sqrt{18})F_{min}$ (F_{min} is the minimum observable value of F); Lp correction, no absorption or extinction correction.

Heavy-atom method was used, but all the main peaks and their heights in a three-dimensional Patterson synthesis could not be explained satisfactorily.

The consequence of the equality of the a and b parameters as mentioned above is that the point symmetry of the lattice is $4/m\ 2/m\ 2/m$ (D_{4h}) and therefore higher than the point symmetry of the structure, which is 222 (D_2). This means that the necessary condition for twinning with superimposed reciprocal lattices is fulfilled. No sample showed disorder effects, such as splitting of the diffraction spots or diffuse reflections either on Weissenberg photographs or in the diffractometer measurements. Therefore we assumed the existence of two individuals related by a fourfold axis in the **c** direction (this rotation as twinning operation). These two individuals contribute independently to each measured intensity I_{hkl} (Catti & Ferraris, 1976). Thus we have

$$I_{hkl} = (1 - \alpha)J_{hkl} + \alpha J_{\bar{k}hl}, \qquad (1)$$

where J_{hkl} are the intensities which an untwinned crystal of the same total volume would give, α is the fraction of the smaller individual.

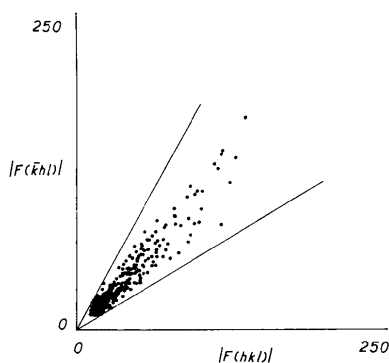The relation (1) leads to the conclusion that our Patterson map is a weighted sum of Patterson maps of

Fig. 1. Diagram of $F_o(\bar{k}hl)$ plotted against $F_o(hkl)$. The straight lines limit the area of occurrence of points.

the two individuals with weights $1 - \alpha$ and α, respectively. This fact allows us to locate the Br atom and satisfactorily explain all the main peaks of the Patterson function. The twin fraction was estimated ($\alpha = 0.25$) from the F_{hkl} to $F_{\bar{k}hl}$ plot (Murray-Rust, 1973), see Fig. 1.

The Br atoms cannot form a framework common to both individuals. Hence positions of the remaining non-hydrogen atoms were determined using a successive Fourier method with coefficients

$$G_{hkl} = \exp(i\varphi^c_{hkl})\,(|F^o_{hkl}|^2 - \alpha|F^c_{\bar{k}hl}|^2)^{1/2}, \qquad (2)$$

where $|F^o_{hkl}|$ is the absolute value of the observed structure factor derived from the measured I_{hkl}, $|F^c_{hkl}|$ is the absolute value of the structure factor calculated on the basis of the known atoms for an untwinned crystal of the same total volume and φ^c_{hkl} is its phase. This synthesis gradually corrects the observed data for crystal twinning as new atoms are located. The reliability and meaning of this correction depend on the portion of the scattering power of the structure which is known. Therefore this correction is useful only in heavy-atom methods. On the other hand, the correction would be unsubstantial if the set of the known atoms forms a substructure of tetragonal symmetry. The main advantage of this correction is that it can be used in the cases for α near to $\frac{1}{2}$ where the direct correction (Zachariasen & Plettinger, 1965) cannot be satisfactorily used (Fisher & Sweet, 1980). We tested this method also on a second set of data which was obtained from another sample of this compound. The twin fraction of this crystal was nearly $\frac{1}{2}$ and the intensities were collected seven years ago as if the crystal system were tetragonal. Nevertheless the solution of the structure on this set of data using the method described above was straightforward.

The refinement was carried out with a local modification of the full-matrix least-squares program *ORFLS* with F magnitudes, $w = 1/\sigma^2$ (Busing, Martin & Levy, 1962), which was adapted for coincidence of reflections following (1) in a similar way to the Kennicott (1963) method. The program enables us to

refine directly the twin fraction and all positional and vibrational parameters.

The initial scale factor and overall temperature parameter were estimated from the Wilson plot. The initial twin fraction was chosen as mentioned above.

The positions of 11 decaborane hydrogen atoms were obtained from difference synthesis, but we were unsuccessful in our attempts to refine them. The methyl group hydrogens were not clearly established.

The reported configuration and its enantiomorph (obtained by changing the signs of x, y and z) were refined to $wR = 0.085$ and $wR = 0.092$ (for all reflections), respectively. Hamilton's R-factor ratio indicates that we may reject the absolute configuration of the enantiomorph (Hamilton, 1965). This result was confirmed by measuring Bijvoet pairs $(hkl-\bar{h}\bar{k}\bar{l})$.*

Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). The calculations were carried out on a Tesla 200 computer.

Discussion. Table 1 gives the final coordinates of the non-hydrogen atoms.

Fig. 2 shows the molecule of $\sigma(+)$-5-bromo-6,9-bis(dimethylsulphido)-*nido*-decaborane(12). The atoms were numbered according to Plešek, Heřmánek & Štíbr (1969). Important bond distances, together with mean values for angles, are reported in Table 2.

The Br atom in position 5 of decaborane destroys both planes of symmetry, which as a consequence produces the chirality. The distance Br—B(5) $1.95\,(1)$ Å agrees with the distance in 1,12-dibromo-1,2-dicarba-*closo*-dodecaborane(10) (Šubrtová, Línek & Novák, 1975). Mean values of the lengths in the

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (*Hamilton*, 1959) *of the non-hydrogen atoms*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Br	0.1475 (2)	0.4002 (2)	0.56072 (8)	5.36 (4)
S(1)	0.0792 (4)	0.1180 (4)	0.4366 (2)	4.58 (8)
S(2)	0.5487 (5)	0.6673 (6)	0.3148 (3)	6.6 (1)
C(1)	0.221 (2)	0.009 (2)	0.464 (1)	9.0 (7)
C(2)	0.015 (2)	0.016 (2)	0.3629 (8)	5.4 (4)
C(3)	0.646 (3)	0.542 (3)	0.261 (1)	14 (1)
C(4)	0.687 (2)	0.693 (3)	0.376 (1)	9.6 (8)
B(1)	0.127 (2)	0.601 (2)	0.4234 (7)	4.4 (4)
B(2)	0.054 (2)	0.424 (2)	0.4005 (7)	3.8 (4)
B(3)	0.088 (2)	0.562 (2)	0.334 (1)	5.3 (5)
B(4)	0.245 (2)	0.647 (2)	0.3574 (8)	4.5 (5)
B(5)	0.188 (1)	0.432 (2)	0.4632 (7)	3.3 (4)
B(6)	0.178 (2)	0.287 (1)	0.4003 (8)	3.5 (4)
B(7)	0.121 (2)	0.371 (2)	0.3187 (7)	4.1 (4)
B(8)	0.246 (2)	0.520 (2)	0.2935 (7)	4.7 (5)
B(9)	0.405 (2)	0.543 (2)	0.3519 (8)	4.1 (4)
B(10)	0.315 (2)	0.591 (2)	0.4372 (7)	4.1 (4)

borane cage and the average S—B distance of 1·91 Å agree with previous results observed for $B_{10}H_{12}^-$ $[S(CH_3)_2]_2$ (Sands & Zalkin, 1962). We observed distinctly shorter (by 0·08–0·1 Å) B(3)—B(4), B(4)—B(8), B(3)—B(8) and longer B(2)—B(5) distances compared with those in $B_{10}H_{12}$ $[S(CH_3)_2]_2$. The S—C distances range from 1·73 (2) to 1·81 (2) Å with mean value of 1·77 (2) Å. The arrangement of the molecules in the unit cell is illustrated in Fig. 3.

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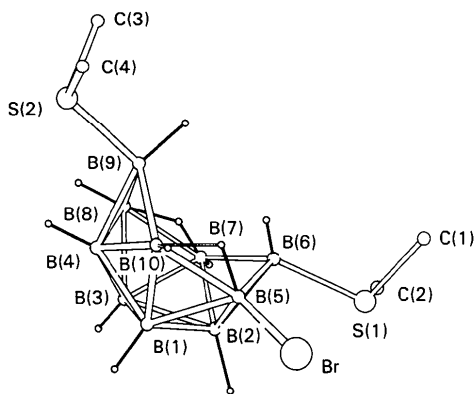

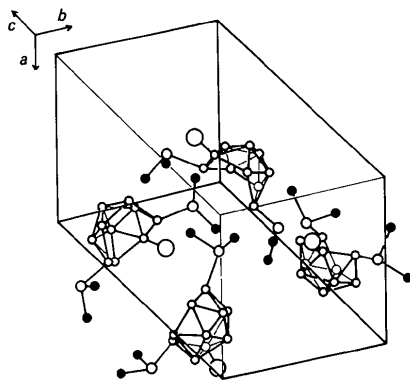Fig. 2. Structure and numbering of $\sigma(+)$-$BrB_{10}H_{11}[S(CH_3)_2]_2$.

Fig. 3. Packing of the molecules in the unit cell.

Table 2. *Interatomic distances* (Å) *and bond angles* (°), *e.s.d.'s* (*in parentheses*) *refer to the last decimal place*

(a) Bond distances

Br—B(5)	1·95 (1)		
S(1)—C(1)	1·73 (2)	S(2)—C(3)	1·79 (3)
S(1)—C(2)	1·81 (2)	S(2)—C(4)	1·76 (2)
S(1)—B(6)	1·93 (1)	S(2)—B(9)	1·89 (2)
B(1)—B(2)	1·81 (3)	B(3)—B(8)	1·70 (3)
B(1)—B(3)	1·81 (2)	B(4)—B(8)	1·70 (2)
B(1)—B(4)	1·73 (2)	B(4)—B(9)	1·76 (3)
B(1)—B(5)	1·82 (2)	B(4)—B(10)	1·76 (2)
B(1)—B(10)	1·75 (3)	B(5)—B(6)	1·81 (2)
B(2)—B(3)	1·84 (2)	B(5)—B(10)	1·94 (2)
B(2)—B(5)	1·73 (2)	B(6)—B(7)	1·84 (2)
B(2)—B(6)	1·70 (2)	B(7)—B(8)	1·85 (3)
B(2)—B(7)	1·77 (2)	B(8)—B(9)	1·86 (2)
B(3)—B(4)	1·70 (3)	B(9)—B(10)	1·90 (2)
B(3)—B(7)	1·80 (3)		

(b) Angles

	Range	Mean	Number of angles
Angles around the Br atom			
Br—B(5)—B	118·4 (8)–122·8 (8)	120·6 (8)	4
Angles around the S atom			
C(1)—S(1)—C(2)	–	101·0 (9)	1
C(3)—S(2)—C(4)	–	97·0 (10)	1
B—S—C	100·6 (9) –109·1 (9)	104·7 (9)	4
Cage angles			
B—B—B	55·2 (11)– 65·7 (11)	60·0 (11)	36
B—B—B	102·6 (11)–116·3 (11)	109·9 (11)	34

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