Bis(dimethyl sulfide)–*closo*-Nonaborane(7)

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Abstract. $C_4H_{19}B_9S_2$, orthorhombic, $P2_12_12_1$, $a = 7.879$ (2), $b = 9.014$ (2), $c = 19.436$ (4) Å, $V = 1379.4$ Å^3, $Z = 4$, $D_x = 1.101$ Mg m^{-3}. The structure has been refined by block-diagonal least-squares methods using 1538 observed independent diffractometer-measured intensity data to $R = 0.079$, $R_w = 0.087$. The boron cage is a tricapped trigonal prism with one dimethyl sulfide group bonded to a capping B atom and the other to a trigonal prismatic B atom.

Introduction. The title compound was prepared by the reaction of $Na_2B_9H_9.2H_2O$ with dimethyl sulfoxide and acetic anhydride. Precipitation from water and recrystallization from warm benzene/hexane gave light-yellow crystals of $B_9H_7[S(CH_3)_2]_2$. The low-temperature ^1H and ^{11}B NMR data suggested 1:1 substitution at a capping boron and at a trigonal prismatic boron. Variable-temperature ^1H NMR suggested cage rearrangement at ambient temperatures (Wong, Kabbani & Gatter, 1981). An X-ray determination was undertaken to locate the exact positions of the substituents and to establish the cage geometry of the nine-boron cluster in the solid state.

The X-ray data were measured on an Enraf–Nonius CAD-4 automated diffractometer using monochromated Cu $K\alpha$ radiation and a crystal measuring $0.15 \times 0.22 \times 0.45$ mm. The unit-cell parameters were determined by a least-squares fit of the angular settings for 15 high-angle reflections. The ω–2θ scanning mode was used with $\theta < 75°$. The intensities were corrected for Lorentz–polarization effects, but not for absorption $[\mu(Cu K\alpha) = 3.27$ mm$^{-1}]$. Of 1694 possible independent reflections 1538 were accepted as observed on the criterion $I > 1.5\sigma(I)$.

The structure was solved by the heavy-atom method and refined by Fourier and block-diagonal least-squares methods. A difference electron density map showed the positions of all the H atoms. Refinement was then continued on all positional parameters, anisotropic thermal parameters for the non-H atoms and isotropic thermal parameters for the H atoms.

Anisotropic effects were significant for the S and C atoms only. The most important part of the structure, the boron cage, did not contribute significantly to the anisotropic refinement. In the final cycles of refine-

Table 1. *Fractional coordinates* ($\times 10^4$ *for non*-H *atoms*, $\times 10^3$ *for* H *atoms*), *equivalent isotropic thermal parameters for non*-H *atoms, and isotropic thermal parameters for* H *atoms*

The form of the isotropic thermal factors used was
$$\exp(-B \sin^2 \theta / \lambda^2).$$

	x	y	z	B (Å^2)
S(1)	3995 (2)	7468 (2)	1685 (1)	4.0 (1)
S(2)	1729 (2)	974 (2)	1214 (1)	3.5 (1)
C(1)	6073 (11)	7067 (15)	1343 (6)	8.5 (6)
C(2)	4236 (15)	7054 (17)	2575 (5)	9.3 (7)
C(3)	2191 (11)	298 (10)	371 (5)	4.8 (4)
C(4)	−419 (11)	302 (11)	1324 (5)	5.4 (4)
B(1)	2562 (10)	5964 (9)	1334 (4)	3.2 (3)
B(2)	1796 (10)	4204 (9)	1810 (4)	3.2 (3)
B(3)	3318 (10)	4084 (9)	970 (4)	3.1 (3)
B(4)	619 (10)	5776 (10)	1684 (5)	3.6 (4)
B(5)	1626 (9)	3016 (8)	1148 (4)	2.9 (3)
B(6)	2737 (11)	5599 (10)	490 (5)	3.7 (4)
B(7)	770 (11)	6001 (10)	807 (5)	3.6 (4)
B(8)	−34 (9)	4216 (10)	1268 (5)	3.4 (3)
B(9)	1468 (10)	4100 (10)	428 (4)	3.5 (3)
H(2)	206 (10)	382 (9)	234 (4)	3.3
H(3)	472 (11)	358 (9)	95 (4)	3.1
H(4)	16 (11)	647 (9)	204 (4)	3.4
H(6)	330 (11)	627 (10)	11 (4)	3.6
H(7)	41 (11)	705 (9)	60 (4)	3.7
H(8)	−133 (10)	387 (9)	130 (4)	3.1
H(9)	121 (11)	367 (10)	−7 (4)	3.5
H(1,1)	630 (15)	598 (12)	152 (5)	7.6
H(1,2)	640 (14)	796 (12)	139 (5)	7.6
H(1,3)	602 (14)	716 (12)	83 (6)	7.6
H(2,1)	530 (16)	791 (13)	268 (6)	8.3
H(2,2)	460 (16)	617 (14)	250 (7)	8.3
H(2,3)	336 (16)	714 (13)	289 (6)	8.3
H(3,1)	215 (12)	−85 (10)	48 (4)	4.7
H(3,2)	300 (12)	85 (11)	19 (5)	4.7
H(3,3)	162 (12)	91 (10)	9 (4)	4.7
H(4,1)	−62 (13)	−96 (11)	131 (5)	6.0
H(4,2)	−84 (13)	69 (11)	183 (6)	6.0
H(4,3)	−92 (13)	71 (11)	89 (5)	6.0

ment, the H atoms were assigned isotropic thermal parameters similar to those of the C or B atoms to which they are bonded. Holding these parameters constant resulted in smaller oscillations in the positional parameters for the hydrogens. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where w was obtained from counting statistics for the observed reflections, while the unobserved reflections were weighted zero. In the final cycle $R = 0.079$ and $R_w = 0.087$ for the observed reflections only. The atomic coordinates, equivalent isotropic B's for the non-H atoms (Willis & Pryor, 1975) and the B's used for the H atoms are given in Table 1.* The scattering factors for the non-H atoms are those given in *International Tables for X-ray Crystallography* (1962), and that for H is from Stewart, Davidson & Simpson (1965). All structural calculations were performed with the NRC system (Ahmed, Hall, Pippy & Huber, 1973).

Discussion. The structure of $B_9H_7[S(CH_3)_2]_2$ is as presented in Fig. 1; one of the dimethyl sulfide ligands is bonded to a capping boron and the other to a trigonal prismatic boron. This mode of substitution supports the interpretation of the low-temperature ^1H NMR spectrum (two singlets of equal intensity at 2·24 and 2·86 p.p.m.) as arising from two distinct dimethyl sulfide groups (Wong *et al.*, 1981).

Several structure determinations of *nido*-borane–dimethyl sulfide derivatives are available for comparison. These include $B_{10}H_{12}[S(CH_3)_2]_2$ (Sands &

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* Lists of structure factors, anisotropic thermal parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36373 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Zalkin, 1962), $B_{10}H_{11}[S(CH_3)_2]C_6H_{11}$ (Mizusawa, Rudnick & Ericks, 1980) and $B_9H_{12}[S(CH_3)_2]OCH_3$ (Plíšek, Heřmánek & Štíbr, 1970). The B–S distances reported are 1·92 (1), 1·89 (1) and 1·94 Å respectively. The *closo*-borane–$S(CH_3)_2$ derivatives have been shown to be inert towards ligand displacement reactions which are facile in the *nido*- derivatives (Knoth, Hertler & Muetterties, 1965). This may suggest stronger B–S bonds in the *closo*- derivatives. The B–S distances of 1·891 (8) and 1·848 (8) Å in our *closo*- compound, however, are not significantly shorter than the above values. It should be noted that the S(1)–B(1) distance is longer than the S(2)–B(5) distance as would be expected for a bond to the cage atom exhibiting the higher coordination number. All C–H and B–H bond distances fall within the range of standard values (see Table 2).

The nine-boron cage itself approximates the tri-capped trigonal prismatic geometry common to B_9 boranes (Guggenberger, 1968). The general trend for cage B–B distances follows the order p–$p > p$–$p' > p$–c, where p represents a trigonal prismatic B, c represents a capping B, and p' is a prismatic B on an opposite triangular face. Average values are 1·97 (1) (p–p), 1·77 (1) (p–p') and 1·70 (1) Å (p–c). These trends compare well with those in the parent $Rb_2B_9H_9$ structure (Guggenberger, 1968): 1·90 (2) (p–p), 1·81 (2) (p–p') and 1·70 (2) Å (p–c). Significant features are the long distances of the B(2)–B(3) and B(8)–B(9) of 2·03 (1) and 2·02 (1) Å in our structure. Variable-temperature NMR results (Wong *et al.*, 1981) indicate a cage nonrigidity at ambient temperatures and a likely mechanism would involve a diamond to square to diamond rearrangement (Lipscomb, 1966). The bond elongations in this structure would be consistent with the two diamond faces already distorting towards two square faces on the polyhedral surface. This distortion in the solid-state structure may account for the facile cage rearrangement of the compound in solution.

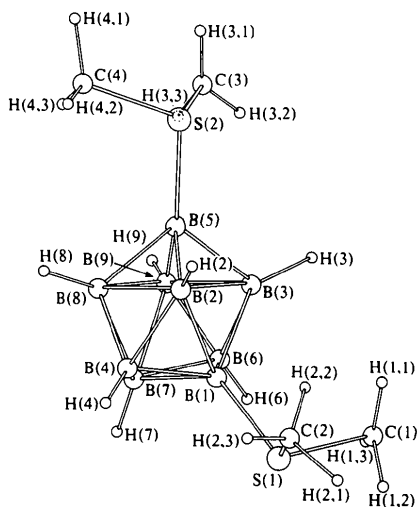The tricapped trigonal prism of the boron cage shows little distortion. The dihedral angle between

Fig. 1. Structure of $B_9H_7[S(CH_3)_2]_2$.

Table 2. *Bond distances* (Å)

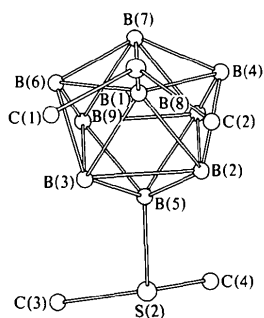|			
S(1)–C(1)	1·80 (1)	B(2)–B(8)	1·78 (1)
S(1)–C(2)	1·78 (1)	B(3)–B(5)	1·68 (1)
S(1)–B(1)	1·891 (8)	B(3)–B(6)	1·72 (1)
S(2)–C(3)	1·786 (9)	B(3)–B(9)	1·80 (1)
S(2)–C(4)	1·809 (9)	B(4)–B(7)	1·72 (1)
S(2)–B(5)	1·848 (8)	B(4)–B(8)	1·70 (1)
B(1)–B(2)	1·93 (1)	B(5)–B(8)	1·71 (1)
B(1)–B(3)	1·93 (1)	B(5)–B(9)	1·71 (1)
B(1)–B(4)	1·68 (1)	B(6)–B(7)	1·70 (1)
B(1)–B(6)	1·68 (1)	B(6)–B(9)	1·69 (1)
B(1)–B(7)	1·74 (1)	B(7)–B(8)	1·95 (1)
B(2)–B(3)	2·03 (1)	B(7)–B(9)	1·95 (1)
B(2)–B(4)	1·71 (1)	B(8)–B(9)	2·02 (1)
B(2)–B(5)	1·68 (1)		

Fig. 2. Projection onto the plane of B(6), B(4), B(2), B(3).
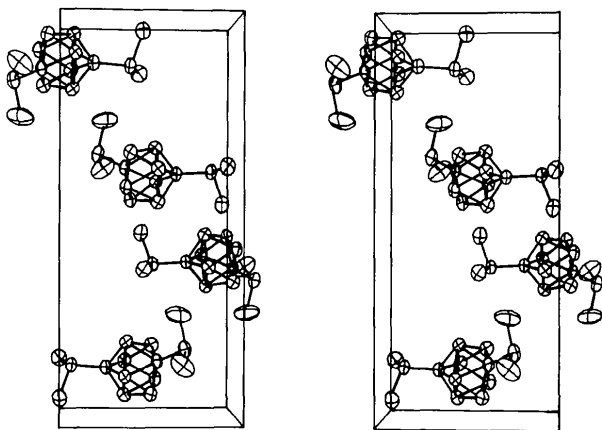
Fig. 3. Stereoscopic drawing (Johnson, 1965) of the contents of one unit cell.

There are no significant intermolecular contacts. The shortest nonbonded distances, excluding hydrogens, are $3 \cdot 743$ (8) Å between S(1) and S(2) related by $x,y,z \rightarrow x$, $y - 1, z$; and $3 \cdot 75$ (1) Å between B(9) and C(3) related by $x,y,z \rightarrow \frac{1}{2} + x, \frac{1}{2} - y, -z$.

A projection onto the plane of B(6), B(4), B(2), B(3) is shown in Fig. 2 and a stereoview is shown in Fig. 3.

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opposite triangular faces is $1 \cdot 4$ (3)°, and those between adjacent rectangular faces $62 \cdot 9$ (3), $58 \cdot 6$ (3) and $58 \cdot 5$ (3)°. The bond angles within the cage are similar to those that would be expected for idealized D_{3h} symmetry and are in good agreement with those given by Guggenberger (1968).

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Structure of Flavanthrene*

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Abstract. $C_{28}H_{14}N_2$, monoclinic, $P2_1/a$, $a = 16 \cdot 179$ (2), $b = 3 \cdot 7996$ (2), $c = 15 \cdot 818$ (1) Å, $\beta = 119 \cdot 192$ (6)°, $U = 848 \cdot 87$ (13) Å^3, $Z = 2$, $D_m = 1 \cdot 47$ (by flotation in carbon tetrachloride/*n*-hexane), $D_x = 1 \cdot 48$ Mg m^{-3}, $M_r = 378 \cdot 43$, μ(Cu $K\alpha$) = 0·69 mm^{-1}. The final R is 0·041 for 1445 independent observed amplitudes. The flavanthrene molecule is planar, and the interplanar distance is $3 \cdot 4711$ (5) Å. The propor-

* Alternative name: 5,13-diazapyranthrene.

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