

Structure of Bis[1,2-dicarbaborane(12)-9-thio]methane, $(C_2B_{10}H_{11}S)_2CH_2$

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Abstract. $M_r = 364.6$, $P2_1$, $a = 12.491(7)$, $b = 14.103(19)$, $c = 11.974(9)$ Å, $\beta = 92.52(5)^\circ$, $V = 2107(3)$ Å³, $Z = 4$, $D_x = 1.149(2)$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.234$ mm⁻¹, room temperature, $R = 0.068$ for 2445 independent reflections, $F(000) = 744$. The molecule consists of two *ortho*-carbaborane icosahedra linked by an $-S-CH_2-S-$ chain. There are two rotational isomers in the asymmetric unit. The centroids of the four icosahedra in the asymmetric unit are related by non-space-group pseudo-symmetry. Each icosahedron has 12 nearest neighbours coordinated as in (slightly distorted) hexagonal close packing with the principal axis parallel to [001].

Introduction. The present study reports the results of the X-ray investigation of the title compound and forms part of our continuing studies on structures of the thio derivatives of the carbaboranes.

Experimental. Preliminary oscillation and Weissenberg photographs showed the space group to be $P2_1/m$ or $P2_1$. The $h1l$ reflections were found to be generally weak. Statistical tests (MILTAN, Main, Woolfson, Lessinger, Germain & Declercq, 1974) indicated an acentric distribution.* Final cell parameters calculated by least squares from 23 reflections centred on a Syntex $P2_1$ diffractometer (Shoemaker, 1970). Needle-shaped crystal, ca $0.1 \times 0.1 \times 0.4$ mm used for intensity measurements on the diffractometer (Mo $K\alpha$ radiation, graphite monochromator). Intensities of 2900 independent reflections measured in the $\omega/2\theta$ scan mode up to $2\theta = 45^\circ$ (index range $h 0 \rightarrow 13$, $k 0 \rightarrow 15$, $l -12 \rightarrow +12$). Scan speed varied from 1.40 to $29.3^\circ \text{min}^{-1}$ and was determined from a rapid prescan. 2129 reflections with $I > 1.96 \sigma(I)$ [$\sigma(I)$ from counting statistics] regarded as observed. Intensities of three standards measured after every 22 reflections showed no significant changes. Data scaled according to the reference reflections and corrected for Lorentz and polarization effects, but not for absorption or extinction. Structure solved by heavy-atom method. Coordinates of the four

S atoms in the asymmetric unit found by image-seeking (Buerger, 1959) from the three-dimensional F^2 map. Starting from this phasing model the positions of the remaining 50 non-hydrogen atoms were found by successive electron-density syntheses. Refinement carried out on an IBM 370/135 computer using a modified NRC 10 block-diagonal least-squares program (Ahmed, Hall, Pippy & Huber, 1966). The function minimized was $G = \sum w(|F_o| - |F_c|)^2$, with $w^{-1} = \sigma^2(|F_o|) + (0.02|F_o|)^2$; $\sigma^2(|F_o|)$ from counting statistics. Scattering factors from *International Tables for X-ray Crystallography* (1974). The y coordinate of S(1) was fixed. The eight C atoms of the four carbaborane icosahedra were distinguished from the B atoms by their lower temperature factor B_{iso} and shorter bond distances. In the final stages positional and anisotropic thermal parameters of non-hydrogen atoms were refined and 48 H atoms were inserted in computed positions [bond distance 1.08 Å, $B_{iso} = 6.0$ Å², scattering factors from Stewart, Davidson & Simpson (1965)]. From these only the four CH_2 H atoms were refined (isotropically). The final $wR = 0.055$ for 2445 reflections, of which 316 are unobserved with $\frac{1}{3} < F_o/F_c < 1$. Final maximum electron density residual 0.36 e Å⁻³; shifts in final least-squares cycle $< 0.5 \sigma$.

Discussion. Fig. 1 shows that the molecule is built up of two *ortho*-carbaborane icosahedra $C_2B_{10}H_{11}$ (further denoted as 'cages') linked through an $-S-CH_2-S-$ chain. One of the two neighbouring C atoms in each cage occupies the site at greatest distance from the S atom to which the cage is bonded. The positional and equivalent isotropic thermal parameters of the non-hydrogen atoms are given in Table 1,* and a survey of bond lengths and angles in Fig. 1 and Table 2. The values of the e.s.d.'s are affected by the relatively high

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, interatomic distances in the individual cages and details of the statistical tests have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38635 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

Table 1. Fractional coordinates ($\times 10^4$) and B_{eq} values (Hamilton, 1959) with e.s.d.'s in parentheses

	x	y	z	B_{eq} (\AA^2)
S(1)	615 (1)	9997	1064 (1)	3.54 (4)
S(2)	-747 (1)	10006 (2)	-995 (1)	3.17 (4)
S(3)	4435 (2)	7145 (2)	5794 (2)	3.99 (5)
S(4)	6022 (2)	5730 (2)	4914 (2)	4.75 (5)
C(1)	-76 (6)	9248 (5)	36 (6)	3.6 (2)
C(2)	4706 (6)	6268 (6)	4745 (6)	5.0 (3)
C(101)	2503 (6)	8681 (6)	3836 (6)	4.8 (2)
C(102)	2355 (5)	7553 (6)	3666 (6)	4.4 (2)
B(103)	1318 (8)	8200 (7)	4139 (8)	5.2 (3)
B(104)	1417 (8)	9279 (7)	3455 (7)	4.8 (3)
B(105)	2544 (7)	9239 (7)	2599 (8)	4.4 (3)
B(106)	3153 (7)	8114 (7)	2804 (9)	5.2 (3)
B(107)	1107 (7)	7302 (7)	3162 (8)	4.7 (3)
B(108)	499 (7)	8413 (7)	2966 (8)	4.3 (3)
B(109)	1234 (7)	9074 (6)	2001 (7)	3.7 (3)
B(110)	2326 (8)	8342 (7)	1585 (8)	5.1 (3)
B(111)	2258 (7)	7285 (7)	2312 (7)	4.5 (3)
B(112)	1050 (8)	7825 (6)	1813 (7)	4.2 (3)
C(201)	-3126 (7)	8050 (7)	-2588 (9)	7.8 (4)
C(202)	-2561 (7)	7620 (6)	-3620 (7)	6.3 (3)
B(203)	-2940 (10)	8725 (9)	-3650 (10)	8.5 (5)
B(204)	-2782 (8)	9155 (8)	-2300 (10)	6.8 (4)
B(205)	-2270 (10)	8242 (8)	-1484 (9)	6.9 (4)
B(206)	-2210 (10)	7236 (8)	-2310 (10)	8.4 (4)
B(207)	-1760 (10)	8400 (10)	-4147 (9)	9.8 (5)
B(208)	-1830 (10)	9385 (7)	-3294 (8)	8.1 (5)
B(209)	-1392 (6)	9096 (6)	-1950 (6)	2.8 (2)
B(210)	-1055 (9)	7882 (7)	-1980 (10)	7.2 (4)
B(211)	-1281 (9)	7467 (9)	-3340 (10)	9.3 (5)
B(212)	-800 (10)	8630 (10)	-3130 (10)	8.9 (5)
C(301)	1928 (6)	5823 (8)	7782 (7)	6.5 (3)
C(302)	2584 (7)	5374 (7)	8814 (7)	6.5 (3)
B(303)	2463 (9)	6546 (8)	8764 (8)	5.8 (3)
B(304)	2497 (7)	6820 (8)	7333 (7)	5.1 (3)
B(305)	2631 (8)	5740 (9)	6599 (8)	5.6 (3)
B(306)	2636 (9)	4806 (7)	7580 (10)	6.1 (4)
B(307)	3645 (8)	6016 (8)	9208 (7)	5.5 (3)
B(308)	3677 (8)	6944 (7)	8245 (8)	4.9 (3)
B(309)	3785 (7)	6424 (6)	6894 (7)	3.5 (2)
B(310)	3857 (7)	5205 (7)	7031 (8)	4.8 (3)
B(311)	3777 (8)	4935 (8)	8485 (9)	5.9 (3)
B(312)	4490 (7)	5943 (7)	8071 (7)	4.4 (3)
C(401)	8255 (6)	5660 (7)	2196 (7)	5.8 (3)
C(402)	7533 (6)	5784 (7)	1057 (6)	5.7 (3)
B(403)	7740 (9)	6744 (8)	1867 (9)	6.7 (4)
B(404)	7757 (7)	6313 (8)	3240 (7)	5.2 (3)
B(405)	7606 (8)	5059 (9)	3134 (8)	5.6 (3)
B(406)	7484 (9)	4747 (7)	1720 (9)	6.0 (4)
B(407)	6459 (8)	6495 (8)	1261 (8)	6.0 (3)
B(408)	6581 (8)	6821 (7)	2679 (8)	4.9 (3)
B(409)	6518 (7)	5774 (7)	3467 (6)	3.7 (2)
B(410)	6348 (8)	4800 (7)	2543 (9)	5.0 (3)
B(411)	6338 (8)	5264 (9)	1166 (7)	5.8 (4)
B(412)	5714 (7)	5901 (8)	2229 (7)	4.3 (3)

Table 2. Survey of interatomic distances (\AA) and angles ($^\circ$) in the individual cages with e.s.d.'s in parentheses

The e.s.d.'s of the minimum and maximum values of the ranges are as given by the least-squares program; the e.s.d.'s of the mean values are calculated from the deviations of the individual values from the mean. n is the number of distances/angles of the same type in each cage.

(a) Distances

Molecule 1 (M1)

Type	n	Cage 1 ($i=1$)		Cage 2 ($j=2$)	
		Range	Mean	Range	Mean
C-C	1		1.61 (1)		1.57 (1)
C-B	8	1.64 (1)–1.71 (1)	1.679 (7)	1.61 (2)–1.70 (1)	1.648 (10)
B-B	21	1.70 (1)–1.80 (1)	1.764 (5)	1.67 (2)–1.77 (2)	1.733 (6)

Molecule 2 (M2)

Type	n	Cage 3 ($i=3$)		Cage 4 ($j=4$)	
		Range	Mean	Range	Mean
C-C	1		1.58 (1)		1.61 (1)
C-B	8	1.66 (1)–1.71 (1)	1.680 (7)	1.65 (1)–1.70 (1)	1.681 (6)
B-B	21	1.72 (2)–1.80 (1)	1.765 (5)	1.71 (2)–1.78 (2)	1.757 (4)

Table 2 (cont.)

(b) Angles

Molecule 1 (M1)

Type	n	Cage 1 ($i=1$)		Cage 2 ($j=2$)	
		Range	Mean	Range	Mean
C-C-B	4	60.2 (5)–62.7 (5)	61.5 (6)	60.2 (6)–63.7 (6)	61.5 (8)
B-C-B	6	61.6 (5)–65.0 (5)	63.1 (6)	61.9 (7)–64.0 (7)	63.1 (4)
C-B-B	12	56.7 (5)–59.6 (5)	58.5 (3)	56.3 (6)–59.9 (6)	58.5 (3)
C-B-C	2	57.0 (5), 57.1 (5)	57.05 (9)	56.1 (6), 58.0 (6)	57.05 (10)
B-B-B	36	58.1 (5)–62.4 (6)	60.0 (1)	57.6 (6)–62.0 (6)	60.0 (2)

Molecule 2 (M2)

Type	n	Cage 3 ($i=3$)		Cage 4 ($j=4$)	
		Range	Mean	Range	Mean
C-C-B	4	61.2 (6)–62.9 (6)	61.9 (4)	60.5 (6)–62.1 (6)	61.4 (4)
B-C-B	6	62.3 (7)–63.9 (6)	63.1 (3)	61.8 (6)–64.5 (6)	62.8 (4)
C-B-B	12	57.5 (6)–59.2 (6)	58.5 (2)	56.6 (6)–59.6 (6)	58.6 (3)
C-B-C	2	55.7 (5), 56.8 (6)	56.2 (5)	57.0 (5), 57.3 (5)	57.2 (2)
B-B-B	36	58.4 (5)–61.8 (6)	60.0 (1)	58.0 (6)–61.3 (6)	60.0 (1)

Table 3. Fractional coordinates ($\times 10^4$) of the centroids of the cages in the asymmetric unit with approximate symmetry relations and distances between nearest centroids (e.s.d.'s in parentheses)

(a) Coordinates

Molecule	x	y	z				
CC(1)	1814 (3)	8276 (3)	2861 (3)	x	y	z	(R0)
CC(2)	-2001 (4)	8324 (3)	-2816 (4)	$-x$	y	$-z$	(R1)
Molecule 2							
CC(3)	3164 (3)	5881 (3)	7901 (3)	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}+z$	(R2)
CC(4)	7028 (3)	5780 (3)	2213 (3)	$\frac{1}{2}+x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	(R3)

(b) Distances (\AA)

Column A: centroid in position x,y,z [see part (a) of this table].

Column B: centroid in position derived by space-group symmetry as defined in column C.

Values marked by asterisks are distances between centroids of chain-linked cages.

	A	B	C	
CC(1)–CC(2)	x	y	z	*8.129 (6)
–CC(2)	x	y	$1+z$	7.188 (6)
–CC(2)	$-x$	$-\frac{1}{2}+y$	$-z$	6.987 (6)
–CC(2)	$-x$	$\frac{1}{2}+y$	$-z$	7.124 (6)
–CC(3)	x	y	z	7.054 (5)
–CC(3)	x	$y-1$	$-1+z$	7.101 (5)
–CC(3)	$-x$	$\frac{1}{2}+y$	$1-z$	7.246 (5)
–CC(3)	$1-x$	$\frac{1}{2}+y$	$1-z$	7.361 (5)
–CC(4)	x	y	z	7.473 (5) max.
–CC(4)	$-1+x$	y	z	6.951 (5)
–CC(4)	$1-x$	$\frac{1}{2}+y$	$-z$	7.230 (5)
–CC(4)	$1-x$	$\frac{1}{2}+y$	$1-z$	6.971 (5)
CC(2)–CC(3)	x	y	$-1+z$	7.330 (6)
–CC(3)	$-1+x$	y	$-1+z$	7.038 (6)
–CC(3)	$-x$	$\frac{1}{2}+y$	$-z$	7.170 (6)
–CC(3)	$-x$	$\frac{1}{2}+y$	$1-z$	7.108 (6)
–CC(4)	$-1+x$	y	z	7.159 (6)
–CC(4)	$-1+x$	y	$-1+z$	7.009 (6)
–CC(4)	$-x$	$\frac{1}{2}+y$	$-z$	7.235 (6)
–CC(4)	$1-x$	$\frac{1}{2}+y$	$-z$	7.121 (6)
CC(3)–CC(4)	x	y	z	*8.519 (5)
–CC(4)	x	y	$1+z$	6.913 (5) min.
–CC(4)	$1-x$	$-\frac{1}{2}+y$	$1-z$	7.199 (5)
–CC(4)	$1-x$	$\frac{1}{2}+y$	$1-z$	6.914 (5)

ratio of the number of refined parameters to the number of reflections (502:2445). The mean values of bond lengths and angles are in accord with the lengths and angles in similar compounds (Šubrtová, Linek & Hašek, 1980).

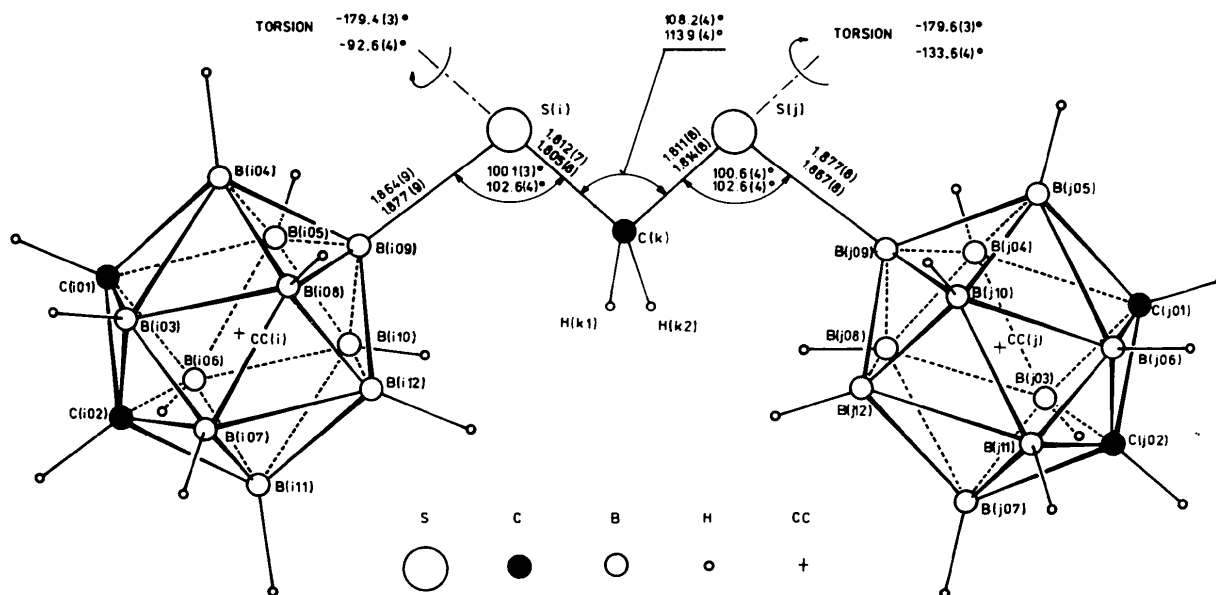


Fig. 1. Schematic view of the molecule with numbering and selected bond distances (\AA), angles and torsion angles for both molecule 1 ($M1$) and molecule 2 ($M2$). For $M1$: numbering with $i = 1, j = 2, k = 1$ and the upper values of distances and angles. For $M2$: numbering with $i = 3, j = 4, k = 2$ and the lower numerical values. The terminal H atoms of the icosahedra (numbering omitted for clarity) have the same numbers as the non-hydrogen atoms to which they are bonded. The points $CC(i), CC(j)$ are the centroids of the icosahedra.

We shall discuss two features of the structure, namely the configuration of the molecules and their packing. The actual molecule is comparatively large and has a complicated shape. Therefore, a 'simplified molecule' is used. Here all H atoms are omitted and each cage of C_2B_{10} is reduced to its unweighted centroid CC . Such a model consists of five points, $CC(i), S(i), C(k), S(j)$ and $CC(j)$ (see Fig. 1).

The configuration. From Fig. 1 it may be seen that it is possible for the molecule to form rotational isomers. Actually two such isomers $M1$ and $M2$ occur in the asymmetric unit. The simplified $M1$ simulates C_{2v} symmetry, being nearly planar and having pair-wise nearly equal values of the bond distances and angles in the chain $B(109)-S(1)-C(1)-S(2)-B(209)$. The simplified $M2$ has a *trans* configuration. The distance $CC(3)-CC(4)$ is slightly greater than $CC(1)-CC(2)$ (see Table 3). The bond angles at the S and C atoms of the linking chain are greater in $M2$ than in $M1$; the corresponding bond distances of both $M1$ and $M2$ are equal to within 1.5σ .

The packing. The coordinates of the centroids of the four cages forming the asymmetric unit are given in Table 3. Also given are the symmetry relations, which hold in fair approximation between these four crystallographically non-equivalent points. It may be seen from Fig. 2 that:

(a) The simplified $M1$ [*cf.* also the positions of $S(1), C(1), S(2)$] is disposed so that the screw axis at $(0, y, 0)$ is, to a good approximation, its twofold axis (this does

not hold for the individual atoms, the vertices of the icosahedra!); see relations (R0) and (R1) in Table 3. Consequently, the pairs of cages of $M1$ form layers normal to the y direction. Each cage has two nearest neighbours in its own layer, one of them belonging to the same molecule.

(b) The operation of the screw axis repeats the layers at separations of $b/2$ and each cage has two more nearest neighbours in adjacent layers.

(c) The centroids $CC(3)$ and $CC(4)$ of $M2$ are disposed so that the screw axis at $(\frac{1}{2}, y, \frac{1}{2})$ of $P2_1$ is to a good approximation their twofold axis [this does not hold for $S(3)$ and $S(4)$, or for the individual vertices of the icosahedra!]; see relations (R2) and (R3). The $M2$ molecules thus form layers and have an arrangement of nearest neighbours analogous to the $M1$ molecules.

(d) Owing to the relations (R0) and (R2) the positions of the centroids simulate the existence of a (skew) glide plane at $x = \frac{1}{4}$ with a translation vector $b/4 + c/2$. For this reason the layers of $M1$ and $M2$ alternate at approximately equal separations (*ca* $b/4$) and consequently each cage has eight more nearest neighbours.

(e) Similarly the positions of the centroids simulate another (skew) glide plane at $z = \frac{1}{4}$ with a translation vector $a/2 + b/4$ [see relations (R0) and (R3)].

This packing arrangement explains the weakness of the $h1l$ reflections. Although the symmetry relations (R0-R3) do not form a group, nevertheless as a consequence of them each carbaborane icosahedron

has 12 nearest neighbours. One of them belongs to the same molecule (chain-linked). The remaining 11 distances between the centroids of the nearest non-linked cages are near to $b/2$ ($=7.05 \text{ \AA}$) and range from

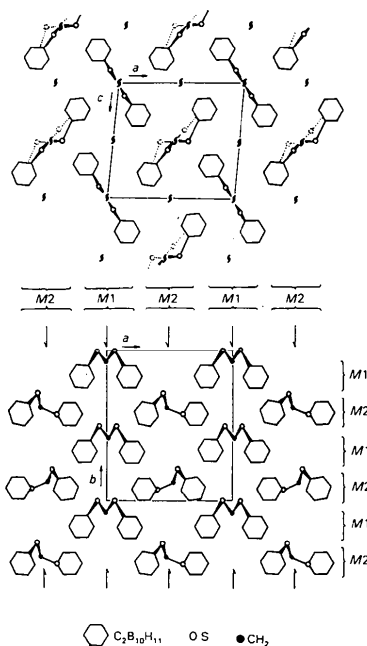


Fig. 2. Schematic view (H atoms omitted, icosahedra represented by hexagons) of the packing showing the positions of the molecules with respect to the screw axes and the layers of molecules 1 and molecules 2. In the projection along **b** (upper part of the figure) the molecules 1 eclipse one another and the molecules 2 are partially eclipsed (dotted lines). The projection along **c** (lower part of the figure) shows the nearly hexagonal close packing of the icosahedra.

6.913 (5) to 7.473 (5) \AA (see Table 3). Owing to this the arrangement of the icosahedra in the crystal simulates hexagonal close packing with the principal axis parallel to [001]. This suggests that the packing of the icosahedra plays a more important role than the bonding properties of the linking $-\text{S}-\text{CH}_2-\text{S}-$ chain in determining the crystal structure.

The shortest intermolecular distances range from 2.50 for H(21)–H(102) to 3.22 \AA .

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Structure of *N*-(3-*tert*-Butyl-2-fluoro-1-indanyl)acetamide, $\text{C}_{15}\text{H}_{20}\text{FNO}$

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Abstract. $M_r = 249.3$, orthorhombic, $Pbca$, $a = 9.740$ (2), $b = 27.692$ (3), $c = 21.460$ (2) \AA , $V = 5788$ (2) \AA^3 , $Z = 16$, $D_x = 1.14 \text{ Mg m}^{-3}$, $\lambda(\text{Cu K}\alpha) = 1.5424 \text{ \AA}$, $\mu = 0.66 \text{ mm}^{-1}$, $F(000) = 2144$, $T = 298 \text{ K}$.

Final $R = 0.031$ for 689 observed reflections. The molecules show a *cis* configuration concerning the F atom and the acetamide group, both of them being in a *trans* position with respect to the *tert*-butyl group.

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