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The Structure of 9,12-Isopropylidenedithio-1,2-dicarba-*closo*-dodecaborane(12)

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Abstract

$C_5H_{16}B_{10}S_2$, $[(CH_3)_2CS_2]C_2B_{10}H_{10}$, is monoclinic, space group $C2/c$, with $a = 22{\cdot}331$ (4), $b = 9{\cdot}326$ (1), $c = 13{\cdot}138$ (1) Å, $\beta = 105{\cdot}39$ (1)°, $Z = 8$. The structure was solved by direct methods and refined to $R = 0{\cdot}029$ for 1730 counter reflections. The isopropylidenedithio group is bonded to the two adjacent B atoms of the *ortho*-carbaborane icosahedral cage with mean B—S = 1·846 (2) Å, mean C—S = 1·863 (2) Å. The whole molecule has a noncrystallographic plane of symmetry.

Introduction

X-ray structure analysis of the title compound was undertaken as part of our continuing study of the structures of the carbaboranes and their derivatives. The compound investigated is the first known dithio derivative. Crystals were prepared in the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences (Plešek, Janoušek & Heřmánek, 1979) and kindly supplied by Dr Plešek.

Experimental

Oscillation and Weissenberg photographs (Cu $K\alpha$ radiation) revealed the crystal to be monoclinic. Systematic extinctions indicated the space groups $C2/c$ or Cc. Cell dimensions were refined by least squares from twenty reflections, centred on the diffractometer. The density was measured by flotation in a tetrachloromethane–hexane mixture. Crystal data are summarized in Table 1.

Table 1. *Crystal data*

$[(CH_3)_2CS_2]C_2B_{10}H_{10}$	Monoclinic, $C2/c$
$a = 22{\cdot}331$ (4) Å	$Z = 8$
$b = 9{\cdot}326$ (1)	$M_r = 248{\cdot}53$
$c = 13{\cdot}138$ (1)	$F(000) = 1024$
$\beta = 105{\cdot}39$ (1)°	$D_m = 1{\cdot}24$ Mg m^{-3}
$V = 2637{\cdot}8$ (7) Å^3	$D_c = 1{\cdot}25$

A crystal 0·4 × 0·4 × 0·5 mm was mounted on a Syntex $P2_1$ diffractometer (Mo $K\alpha$ radiation, graphite monochromator) and the intensities of 1730 independent reflections were measured in the $\omega/2\theta$ scan mode to $2\theta = 45°$. The scan speed varied from 1·40 to 29·3° min^{-1} and was determined from a rapid pre-scan. The scanning interval ranged from 1° below $K\alpha_1$ to 1° above $K\alpha_2$ of the Mo $K\alpha$ doublet. 1554 intensities with $I > 1{\cdot}96\sigma(I)$ [where $\sigma(I)$ was calculated from counting statistics] were regarded as observed and included in further calculations. The intensities of four standard reflections measured after every 36 reflections showed no significant changes. The data were scaled with the reference reflections and corrected for Lorentz and polarization factors. No absorption correction was applied.

Structure determination and refinement

The structure was solved with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). For the solution we used the known configuration of the twelve atoms in the icosahedral carbaborane cage (Šubrtová, Línek & Novák, 1975) with random position and orientation.

The statistical test showed that the crystal is centrosymmetric (Table 2) and the appropriate space group is $C2/c$. The phases of 300 strong reflections ($E > 1{\cdot}87$) were then determined and the E map calculated from the solution with the best figure of merit showed the positions of all the nonhydrogen atoms. Refinement of the overall scale factor, of positions and of isotropic thermal parameters for the nonhydrogen atoms was carried out by block-diagonal least squares with a modified NRC 10 program (Ahmed, Hall, Pippy & Huber, 1966). The function minimized was $w(|F_o| - |F_c|)^2$, with $w^{-1} = \sigma^2(F) + (0{\cdot}022F_o)^2$. R reduced to 0·100. A difference map at this stage showed all 16 H atoms in their expected positions. The C atoms of the polyhedron were

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Table 2. *Statistical distribution of the normalized structure factor amplitudes (E) compared with theoretical values*

	Experimental	Centro-symmetric	Noncentro-symmetric
$\langle\lvert E\rvert\rangle$	0·815	0·798	0·886
$\langle\lvert E\rvert^3\rangle$	1·504	1·596	1·329
$\langle\lvert E^2-1\rvert\rangle$	0·924	0·968	0·736

Table 3. *Fractional coordinates* ($\times 10^4$) *and equivalent* $\bar{B}$ *values (Hamilton,* 1959) *with e.s.d.'s in parentheses*

	x	y	z	$\bar{B}$ (Å^2)
C(1)	1925 (1)	5261 (2)	7687 (2)	3·4
C(2)	1242 (1)	5034 (2)	7895 (2)	3·6
B(3)	1785 (1)	3715 (3)	8284 (2)	3·7
B(4)	2191 (1)	3721 (3)	7283 (2)	3·2
B(5)	1887 (1)	5151 (3)	6381 (2)	3·0
B(6)	1289 (1)	6018 (3)	6816 (2)	3·4
B(7)	989 (1)	3324 (3)	7663 (2)	3·5
B(8)	1592 (1)	2468 (3)	7253 (2)	3·0
B(9)	1643 (1)	3346 (2)	6057 (2)	2·5
B(10)	1096 (1)	4794 (3)	5782 (2)	2·9
B(11)	684 (1)	4747 (3)	6754 (2)	3·4
B(12)	914 (1)	3105 (3)	6287 (2)	2·8
S(1)	432 (0)	1837 (1)	5343 (1)	3·8
S(2)	1730 (0)	2232 (1)	4937 (0)	2·8
C(3)	1034 (1)	1056 (2)	4763 (2)	3·0
C(4)	1241 (1)	−392 (2)	5252 (2)	4·3
C(5)	738 (1)	898 (3)	3582 (2)	4·4

Table 4. *Fractional coordinates* ($\times 10^3$) *and isotropic temperature factors for hydrogen atoms with e.s.d.'s in parentheses*

	x	y	z	$B_{\rm iso}$ (Å^2)
H(C1)	221 (1)	589 (2)	816 (2)	3·8 (5)
H(C2)	115 (1)	565 (2)	843 (2)	4·5 (5)
H(B3)	199 (1)	362 (2)	911 (2)	5·1 (5)
H(B4)	270 (1)	356 (2)	753 (2)	4·0 (5)
H(B5)	220 (1)	580 (2)	609 (2)	4·1 (5)
H(B6)	121 (1)	720 (2)	685 (2)	4·4 (5)
H(B7)	72 (1)	283 (3)	813 (2)	5·4 (6)
H(B8)	169 (1)	136 (2)	737 (1)	3·4 (4)
H(B10)	88 (1)	524 (2)	503 (2)	5·4 (5)
H(B11)	25 (1)	526 (3)	672 (2)	5·0 (5)
H(C41)	154 (1)	−75 (2)	496 (2)	5·6 (6)
H(C42)	146 (1)	−26 (3)	600 (2)	5·0 (6)
H(C43)	89 (1)	−107 (3)	510 (2)	6·9 (7)
H(C51)	104 (1)	44 (3)	320 (2)	8·2 (8)
H(C52)	58 (1)	190 (2)	322 (2)	5·0 (5)
H(C53)	39 (1)	26 (2)	349 (2)	4·6 (5)

distinguished from the B atoms by their lower temperature factors and shorter bond distances.

Subsequent least-squares calculations, with isotropic thermal parameters for the H atoms and anisotropic parameters for the other atoms, reduced $R = \sum \lvert\lvert F_c\rvert - \lvert F_o\rvert\rvert / \sum \lvert F_o\rvert$ to a final value of 0·029 and $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum (w\lvert F_o\rvert^2)]^{1/2}$ to 0·037. The highest parameter shifts in the last cycle were $<0{\cdot}2\,\sigma$. The highest residual peak in the final difference map was 0·6 e Å^{-3} and was located in the vicinity of a S atom. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974), except for H (Stewart, Davidson & Simpson, 1965).*

The final positional and thermal parameters for the nonhydrogen atoms are given in Table 3, and for H atoms in Table 4. All calculations were carried out on an IBM 370/135 computer.

Results and discussion

Fig. 1 shows a view of a molecule of 9,12-$(CH_3)_2$-CS_2-1,2-$C_2B_{10}H_{10}$ and the numbering of the atoms. The bond distances and angles are given in Table 5. The basis of the molecule is an *ortho*-carbaborane polyhedron with ten B and two C atoms at the vertices. The H atoms are terminally attached to the C and B atoms by bonds directed radially from the centre of the polyhedron. The two S atoms of the isopropylidenedithio group are bonded to the adjacent B(9) and B(12) with a mean B—S = 1·846 (2) Å. The five-membered ring B(9)—B(12)—S(1)—C(3)—S(2) with S—C—S = 112·9 (1)° is not planar, as expected. The angle between the planes B(9)—B(12)—S(1)—S(2) and S(1)—

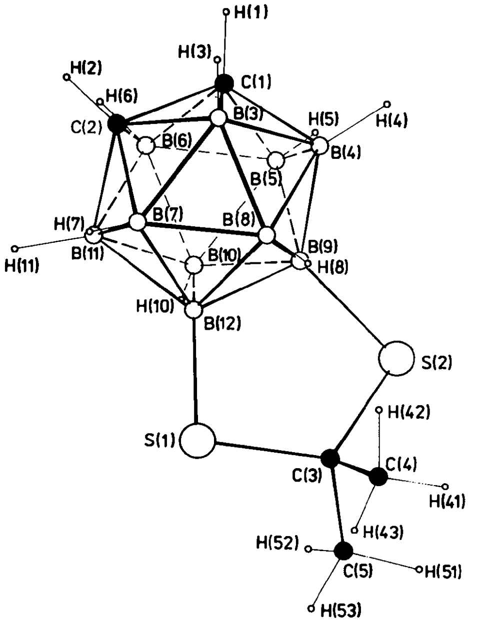

Fig. 1. Structure and numbering of the $[(CH_3)_2CS_2]C_2B_{10}H_{10}$ molecule.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34978 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Interatomic distances* (Å) *and angles* (°)

E.s.d.'s (in parentheses) refer to the last decimal place.

(*a*) Distances in the polyhedron

Non-hydrogen atoms, arranged to show the C_s symmetry of the polyhedron

C(1)–B(3)	1·710 (3)	C(2)–B(3)	1·708 (4)
C(1)–B(4)	1·693 (3)	C(2)–B(7)	1·692 (3)
C(1)–B(5)	1·697 (3)	C(2)–B(11)	1·697 (3)
C(1)–B(6)	1·720 (3)	C(2)–B(6)	1·714 (3)
B(3)–B(4)	1·784 (4)	B(3)–B(7)	1·786 (4)
B(4)–B(5)	1·794 (3)	B(7)–B(11)	1·794 (4)
B(4)–B(8)	1·770 (4)	B(7)–B(8)	1·768 (4)
B(4)–B(9)	1·780 (3)	B(7)–B(12)	1·781 (3)
B(5)–B(6)	1·779 (4)	B(6)–B(11)	1·784 (4)
B(5)–B(9)	1·785 (3)	B(11)–B(12)	1·775 (4)
B(5)–B(10)	1·764 (4)	B(10)–B(11)	1·760 (4)
B(8)–B(9)	1·802 (3)	B(8)–B(12)	1·798 (3)
B(9)–B(10)	1·793 (3)	B(10)–B(12)	1·797 (3)

C(1)–C(2)	1·634 (3)
B(3)–B(8)	1·751 (3)
B(6)–B(10)	1·739 (3)
B(9)–B(12)	1·748 (3)

Hydrogen atoms

C(1)–H(C1)	0·97 (2)	C(2)–H(C2)	0·97 (2)
B(5)–H(B5)	1·07 (2)	B(11)–H(B11)	1·08 (2)
B(4)–H(B4)	1·10 (2)	B(7)–H(B7)	1·07 (2)
B(3)–H(B3)	1·07 (2)	B(8)–H(B8)	1·06 (2)
B(6)–H(B6)	1·12 (2)	B(10)–H(B10)	1·06 (2)

(*b*) Isopropylidenedithio distances

B(12)–S(1)	1·840 (2)	B(9)–S(2)	1·853 (2)
S(1)–C(3)	1·859 (2)	S(2)–C(3)	1·867 (2)
C(3)–C(4)	1·514 (3)	C(3)–C(5)	1·525 (3)
C(4)–H(C41)	0·92 (2)	C(5)–H(C51)	1·03 (3)
C(4)–H(C42)	0·99 (2)	C(5)–H(C52)	1·07 (2)
C(4)–H(C43)	0·98 (2)	C(5)–H(C53)	0·96 (2)

(*c*) Cage angles

Type	Range	Mean value	Number of angles
B–B–B	58·1 (1)–61·3 (1)	60·0 (1)	36
	106·7 (2)–109·6 (2)	108·1 (2)	34
C–B–B	57·9 (1)–59·3 (1)	58·3 (1)	12
	103·2 (2)–104·1 (2)	103·7 (2)	16
B–C–B	62·7 (1)–63·9 (2)	63·4 (1)	6
	115·6 (2)–116·5 (2)	116·2 (2)	6
C–C–B	61·4 (1)–61·8 (1)	61·5 (1)	4
	111·2 (2)–112·0 (2)	111·6 (2)	4
B–B–H	112·2 (1·2)–135·0 (1·2)	123·7 (1·2)	32
B–C–H	110·5 (1·3)–124·2 (1·3)	118·1 (1·3)	8
C–B–H	114·5 (1·1)–121·2 (1·2)	117·4 (1·1)	8
C–C–H	115·7 (1·2)–117·7 (1·2)	116·7 (1·2)	2

(*d*) Angles in the isopropylidenedithio group

B(7)–B(12)–S(1)	129·7 (2)	B(4)–B(9)–S(2)	129·6 (1)
B(8)–B(12)–S(1)	119·7 (1)	B(5)–B(9)–S(2)	128·9 (1)
B(9)–B(12)–S(1)	111·7 (1)	B(8)–B(9)–S(2)	118·8 (1)
B(10)–B(12)–S(1)	117·6 (1)	B(10)–B(9)–S(2)	118·2 (1)
B(11)–B(12)–S(1)	128·1 (2)	B(12)–B(9)–S(2)	111·4 (1)
B(12)–S(1)–C(3)	99·9 (1)	B(9)–S(2)–C(3)	99·6 (1)
S(1)–C(3)–S(2)	112·9 (1)	S(2)–C(3)–C(4)	108·7 (1)
S(1)–C(3)–C(4)	110·4 (1)	S(2)–C(3)–C(5)	107·7 (1)
S(1)–C(3)–C(5)	106·9 (1)	C(4)–C(3)–C(5)	110·3 (2)

Table 6. *Important planes in the molecule and atomic deviations* (Å) *from them*

Atoms marked with an asterisk were not included in the least-squares calculation.

(*a*) Plane B(9), B(12), S(1), S(2)

$$-0{\cdot}1978x + 0{\cdot}7528y - 0{\cdot}6279z + 2{\cdot}7828 = 0$$

B(9)	0·007 (2)	S(1)	0·0003 (6)
B(12)	−0·008 (2)	S(2)	−0·0002 (5)

(*b*) Plane B(3), B(6), B(8), B(10), C(3), C(4), C(5)

$$0{\cdot}9773x + 0{\cdot}1263y - 0{\cdot}1700z + 0{\cdot}2679 = 0$$

B(3)	−0·006 (3)	C(1)*	0·814 (2)
B(6)	−0·001 (3)	C(2)*	−0·819 (2)
B(8)	−0·002 (3)	B(4)*	1·438 (3)
B(10)	0·008 (3)	B(5)*	1·443 (3)
C(3)	−0·001 (2)	B(7)*	−1·444 (3)
C(4)	0·009 (3)	B(9)*	0·879 (2)
C(5)	−0·008 (3)	B(11)*	−1·437 (3)
		B(12)*	0·869 (2)
		S(1)*	−1·544 (1)
		S(2)*	1·561 (1)

S(2)—C(3) is 157·6°. The two B—S—C angles, 99·9 (1) and 99·6 (1)°, have the expected values for divalent S linked to two atoms (Abrahams, 1956).

C(3), C(4), C(5) together with the four atoms of the carbaborane cage B(3), B(6), B(8) and B(10) form a plane which is perpendicular to both previous planes and at the same time is identical to a noncrystallographic plane of symmetry for the whole molecule. Table 6 indicates equations of the mean planes and deviations of the atoms from these planes. Distances in Table 5 are arranged with respect to the noncrystallographic plane of symmetry.

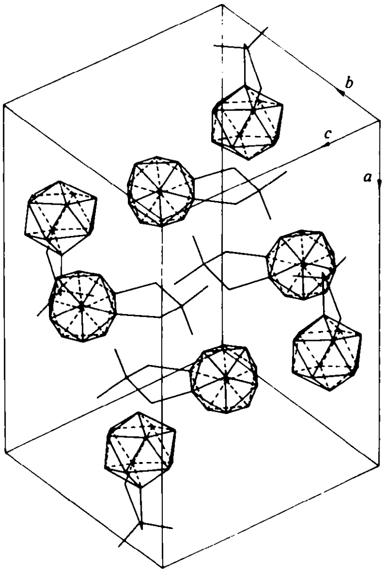

Fig. 2. Packing of the molecules within the unit cell.

The carbaborane cage $C_2B_{10}H_{10}$ forms a very regular icosahedron with C—C = 1·634 (3) Å; the B—C bonds range from 1·692 (3) to 1·720 (3) Å, B—B bonds from 1·739 (3) to 1·802 (3) Å, both C—H bonds = 0·97 (2) Å and B—H bonds range from 1·06 (2) to 1·12 (2) Å. The S—C bonds in the isopropylidenedithio ring, 1·859 (2) and 1·867 (2) Å, are slightly longer than the mean distance for a single C—S bond of 1·83 (2) Å (Abrahams, 1956). On the other hand, S—B bonds in the same ring, 1·840 (2) and 1·853 (2) Å, are shorter than the S—B = 1·92 (2) Å known for the ligand derivatives of boron compounds (Sands & Zalkin, 1962; Šubrtová, 1971).

C(3) has a tetrahedral configuration with an average C—C = 1·519 (3) Å and an average value of six angles of 109·4 (1)°. C—H distances in the methyl groups range from 0·92 (2) to 1·07 (2) Å.

The shortest H—H intermolecular distance is 2·49 (3) Å. The arrangement of the molecules in the unit cell is shown in Fig. 2.

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The Structure Determination and Molecular-Mechanics Calculation of 1,6-Anhydro-β-D-galactopyranose*

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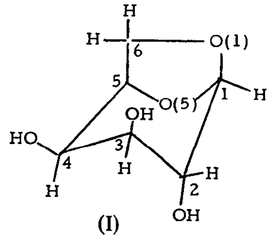
Abstract

1,6-Anhydro-β-D-galactopyranose, $C_6H_{10}O_5$, M_r = 162·08, m.p. = 498 K, is orthorhombic, $P2_12_12_1$, a = 11·073 (3), b = 28·890 (5), c = 6·396 (1) Å ($\lambda_{\mathrm{Cu}K\alpha}$ = 1·54051 Å), V = 2046·1 Å^3, Z = 12, D_x = 1·578, D_m = 1·584 Mg m^{-3}. The structure was solved by *MULTAN* and refined to $R(F)$ = 0·056 for 2033 independent reflections. The three symmetry-independent molecules have similar molecular dimensions, except for the orientations of the three hydroxyl groups. An extensive system of hydrogen bonds in the crystal structure involves three linear and six bifurcated O—H···O interactions. A molecular-mechanics program, *MMI-CARB*, parameterized for carbohydrates, gave a molecular fit such that the differences in observed and calculated molecular dimensions were comparable to those observed between the symmetry-independent molecules.

Introduction

1,6-Anhydro-β-D-galactopyranose, (I), galactosan, is the tenth in a series of 1,6-anhydropyranose molecules for which crystal structure analyses are reported. Eight of these molecules have also been examined by



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