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9-Methylsulphonyl-1,7-dicarba-closo-dodecaborane(12)

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Abstract. $C_3H_{14}B_{10}O_2S$, $M_r = 222.41$, orthorhombic, $Pnma$, $a = 13.440$ (2), $b = 8.539$ (2), $c = 10.525$ (3) Å, $V = 1207.9$ (5) Å³, $Z = 4$, $D_x = 1.223$, $D_m = 1.220$ Mg m⁻³ (by flotation), $\mu(\text{Mo } K\alpha) = 0.21$ mm⁻¹. The structure was refined to $R = 0.059$ for 1105 counter reflections. The methylsulphonyl group is attached to a B atom of an icosahedral cage containing two C and ten B atoms at its vertices. The molecule exhibits m crystallographic symmetry.

Introduction. The present study reports on the X-ray investigation of 9-CH₃SO₂-1,7-C₂B₁₀H₁₁ previously prepared at the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences in Řež near Prague (Plešek, Janoušek & Heřmánek, 1978). This work deals with the first example of a structure with a methylsulphonyl group attached to a B atom of a borane skeleton.

The colourless crystals are air-stable and do not decompose in X-rays. Preliminary lattice constants and space group ($Pnma$ or $Pn2_1a$) were obtained from photographs (Cu $K\alpha$ radiation). Refined cell parameters were obtained from the orientation matrix calculated by least squares (Shoemaker, 1970) from 40 reflections centred on the diffractometer. A crystal 0.5 × 0.45 × 0.4 mm was used for intensity measurements on a Hilger & Watts four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The ω - 2θ scan technique was used with a constant scan speed of 2°

min⁻¹ over a range of 2° to measure 1708 independent reflections with $2\theta \leq 58^\circ$. 603 of these were classified as unobserved on the criterion $I < 2\sigma_1(I)$, where $I = TC - B_1 - B_2$ and $\sigma_1(I) = (TC + B_1 + B_2)^{1/2}$ (TC = total count, B_1 and B_2 = backgrounds measured at the scan limits for half the scan time). No unobserved reflections were used in the refinement. The intensity of

Table 1. Fractional atomic coordinates

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

	x	y	z
S	0.44017 (7)	0.75	0.61244 (9)
O(1)	0.4527 (1)	0.8948 (2)	0.6826 (2)
C	0.5284 (3)	0.75	0.4895 (4)
C(1)	0.1632 (2)	0.9043 (4)	0.4122 (3)
B(2)	0.0842 (4)	0.75	0.4189 (5)
B(3)	0.1897 (4)	0.75	0.3184 (5)
B(4)	0.2857 (2)	0.8534 (4)	0.3970 (3)
B(5)	0.2380 (2)	0.9171 (4)	0.5442 (3)
B(6)	0.1164 (2)	0.8477 (5)	0.5571 (3)
B(9)	0.3134 (3)	0.75	0.5377 (4)
B(10)	0.2089 (4)	0.75	0.6367 (5)
H(1C)	0.591 (3)	0.75	0.531 (4)
H(2C)	0.518 (2)	0.833 (3)	0.441 (2)
H(C1)	0.133 (3)	0.008 (4)	0.370 (3)
H(B2)	0.012 (3)	0.75	0.374 (4)
H(B3)	0.178 (3)	0.75	0.218 (4)
H(B4)	0.338 (2)	0.926 (3)	0.340 (2)
H(B5)	0.257 (2)	0.026 (3)	0.584 (2)
H(B6)	0.074 (2)	0.903 (4)	0.593 (3)
H(B10)	0.214 (3)	0.75	0.734 (4)

one standard measured after every ten reflections showed no significant variation. The data were corrected for Lorentz and polarization effects, but not for absorption or extinction.

The structure was solved by the heavy-atom method. The *x* and *z* coordinates of the S atom were determined from a Patterson map and the *y* coordinate was fixed at $\frac{1}{2}$. At this stage we chose space group *Pn2₁a*. A Fourier synthesis based on these input parameters provided the positions of all remaining non-hydrogen atoms and showed *Pnma* to be the most likely space group. Refinement was carried out with a local version of the full-matrix least-squares program *ORFLS*

(Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$ {derived from $\sigma_2(I) = [\sigma_1(I) + (0.015I)^2]^{1/2}$ }. The scale and overall temperature factor were estimated from a Wilson plot. Refinement with isotropic temperature factors converged to $R = 0.102$ and with anisotropic to $R = 0.075$ (for observed reflections). A subsequent difference synthesis revealed the positions of all H atoms. Final refinement was carried out in two blocks: the first consisted of parameters of the non-hydrogen atoms, the second of parameters of the H atoms. The final R was 0.059 for the observed reflections. The maximum residual electron density in

Table 2. *Interatomic distances (Å) and bond angles (°)*

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

Distances within the CH ₃ SO ₂ group				C—H methyl distances			
S—O(1)	1.450 (2)	S—B(9)	1.876 (4)	C—H(1C)	0.94 (4)	C—H(2C)	0.89 (3)
S—C	1.755 (4)						
Icosahedral-cage distances				Angles within the CH ₃ SO ₂ group			
C(1)—B(2)	1.694 (4)	B(4)—B(5)	1.763 (5)	O(1)—S—O(2)	117.01 (12)	S—B(9)—B(4)	122.95 (18)
C(1)—B(3)	1.684 (4)	B(4)—B(8)	1.765 (5)	O(1)—S—C	107.25 (11)	S—B(9)—B(5)	120.58 (16)
C(1)—B(4)	1.710 (4)	B(4)—B(9)	1.763 (5)	O(1)—S—B(9)	108.62 (10)	S—B(9)—B(10)	118.63 (23)
C(1)—B(5)	1.719 (5)	B(5)—B(6)	1.744 (5)	C—S—B(9)	107.73 (18)		
C(1)—B(6)	1.720 (5)	B(5)—B(9)	1.752 (4)				
		B(5)—B(10)	1.771 (4)	Icosahedral-cage angles			
B(2)—B(3)	1.769 (7)	B(6)—B(10)	1.716 (6)	B(2)—C(1)—B(3)	63.1 (3)	B(6)—B(2)—B(11)	57.6 (2)
B(2)—B(6)	1.732 (6)	B(6)—B(11)	1.669 (6)	B(2)—C(1)—B(6)	61.0 (3)	B(4)—B(3)—B(8)	59.9 (2)
B(3)—B(4)	1.770 (5)	B(9)—B(10)	1.749 (6)	B(3)—C(1)—B(4)	62.8 (3)	B(3)—B(4)—B(8)	60.1 (2)
C—H and B—H icosahedral-cage distances				B(4)—C(1)—B(5)	61.9 (2)	B(5)—B(4)—B(9)	59.6 (2)
C(1)—H(C1)	1.07 (3)	B(5)—H(B5)	1.05 (3)	B(5)—C(1)—B(6)	61.0 (2)	B(8)—B(4)—B(9)	60.0 (2)
B(2)—H(B2)	1.08 (4)	B(6)—H(B6)	0.83 (3)	B(2)—C(1)—B(4)	114.2 (2)	B(4)—B(5)—B(9)	60.2 (2)
B(3)—H(B3)	1.06 (4)	B(10)—H(B10)	1.03 (4)	B(2)—C(1)—B(5)	112.5 (3)	B(6)—B(5)—B(10)	58.4 (3)
B(4)—H(B4)	1.12 (3)			B(3)—C(1)—B(5)	113.6 (3)	B(9)—B(5)—B(10)	59.5 (2)
				B(3)—C(1)—B(6)	112.2 (2)	B(2)—B(6)—B(11)	61.2 (2)
				B(4)—C(1)—B(6)	111.3 (2)	B(5)—B(6)—B(10)	61.6 (2)
Angles involving H atoms				B(10)—B(6)—B(11)	60.9 (2)	B(4)—B(9)—B(5)	60.2 (2)
S—C—H(1C)	105.0 (23)	B(3)—B(2)—H(B2)	117.1 (21)	C(1)—B(2)—C(7)	102.1 (2)	B(4)—B(9)—B(8)	60.1 (2)
S—C—H(2C)	108.5 (17)	B(6)—B(2)—H(B2)	126.6 (17)	C(1)—B(3)—C(7)	103.0 (2)	B(5)—B(9)—B(10)	60.8 (2)
		B(2)—B(3)—H(B3)	118.2 (23)	C(1)—B(2)—B(3)	58.2 (2)	B(5)—B(10)—B(6)	60.0 (3)
B(2)—C(1)—H(C1)	114.8 (19)	B(4)—B(3)—H(B3)	124.8 (18)	C(1)—B(2)—B(6)	60.2 (3)	B(5)—B(10)—B(9)	59.7 (2)
B(3)—C(1)—H(C1)	118.7 (17)	B(3)—B(4)—H(B4)	119.0 (13)	C(1)—B(3)—B(2)	58.7 (2)	B(6)—B(10)—B(11)	58.2 (2)
B(4)—C(1)—H(C1)	122.6 (19)	B(5)—B(4)—H(B4)	122.4 (13)	C(1)—B(3)—B(4)	59.3 (3)	B(3)—B(2)—B(6)	107.6 (3)
B(5)—C(1)—H(C1)	120.6 (18)	B(8) B(4) H(B4)	123.5 (13)	C(1)—B(4)—B(3)	57.9 (2)	B(2)—B(3)—B(4)	107.8 (3)
B(6)—C(1)—H(C1)	117.6 (18)	B(9)—B(4)—H(B4)	126.7 (13)	C(1)—B(4)—B(5)	59.3 (2)	B(3)—B(4)—B(5)	107.5 (2)
		B(4)—B(5)—H(B5)	122.4 (14)	C(1)—B(5)—B(4)	58.8 (2)	B(3)—B(4)—B(9)	107.3 (2)
C(1)—B(2)—H(B2)	123.0 (8)	B(6)—B(5)—H(B5)	119.6 (15)	C(1)—B(5)—B(6)	59.6 (2)	B(5)—B(4)—B(8)	108.0 (2)
C(1)—B(3)—H(B3)	123.2 (8)	B(9)—B(5)—H(B5)	126.9 (15)	C(1)—B(6)—B(2)	58.8 (2)	B(4)—B(5)—B(6)	107.7 (2)
C(1)—B(4)—H(B4)	121.4 (13)	B(10)—B(5)—H(B5)	123.3 (14)	C(1)—B(6)—B(5)	59.5 (2)	B(4)—B(5)—B(10)	108.3 (2)
C(1)—B(5)—H(B5)	121.1 (14)	B(2)—B(6)—H(B6)	119.1 (20)	C(1)—B(2)—B(11)	104.6 (3)	B(6)—B(5)—B(9)	105.6 (2)
C(1)—B(6)—H(B6)	119.6 (20)	B(5)—B(6)—H(B6)	118.9 (20)	C(1)—B(3)—B(8)	105.7 (3)	B(2)—B(6)—B(5)	109.4 (3)
		B(10)—B(6)—H(B6)	123.5 (20)	C(1)—B(4)—B(8)	104.7 (2)	B(2)—B(6)—B(10)	110.9 (2)
H(1C)—C—H(2C)	114.0 (20)	B(11)—B(6)—H(B6)	124.8 (20)	C(1)—B(4)—B(9)	104.6 (2)	B(5)—B(6)—B(11)	109.9 (2)
H(2C)—C—H(3C)	106.6 (23)	B(5)—B(10)—H(B10)	122.2 (7)	C(1)—B(5)—B(9)	104.8 (2)	B(4)—B(9)—B(10)	109.3 (2)
		B(6)—B(10)—H(B10)	122.6 (18)	C(1)—B(5)—B(10)	105.3 (2)	B(5)—B(9)—B(8)	108.6 (2)
		B(9)—B(10)—H(B10)	122.5 (22)	C(1)—B(6)—B(10)	107.7 (3)	B(5)—B(9)—B(12)	109.1 (2)
				C(1)—B(6)—B(11)	106.3 (2)	B(5)—B(10)—B(11)	106.5 (3)
						B(5)—B(10)—B(12)	107.4 (2)
						B(6)—B(10)—B(9)	106.9 (3)

the final difference synthesis was $0.28 \text{ e } \text{\AA}^{-3}$. Final coordinates are given in Table 1.* Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The calculations were carried out on a Tesla 200 computer.

Discussion. The cage C atom was distinguished from B atoms by its lower temperature factors and shorter bond distances. The structure is built up of an *m*-carborane icosahedron with the methylsulphonyl group attached to B(9). Fig. 1 shows the molecule viewed down the vector [001], the numbering following the IUPAC system (Adams, 1972). The crystal structure has a mirror plane at $y = \frac{1}{4}$. Within one molecule, the atom pairs O(1) and O(2), C(1) and C(7), B(4) and B(8), B(5) and B(12), and B(6) and B(11) are related by the mirror plane. S, C, B(2), B(3), B(9), and B(10) are situated on this mirror plane.

Interatomic distances and bond angles are given in Table 2. Distances within the methylsulphonyl group are in excellent agreement with those in dimethyl sulphone (Sands, 1963). The S—B distance is 1.876 \AA . Mean values of lengths in the borane cage are B—C = $1.705 (1.684\text{--}1.720) \text{ \AA}$ and B—B = $1.749 (1.669\text{--}1.771) \text{ \AA}$. These mean values are shorter by 0.02 \AA (B—C) and 0.04 \AA (B—B) than those in $5,12\text{-Cl}_2\text{-1,7-(CH}_3)_2\text{-1,7-C}_2\text{B}_{10}\text{H}_8$ (Hart & Lipscomb, 1973), and

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34760 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

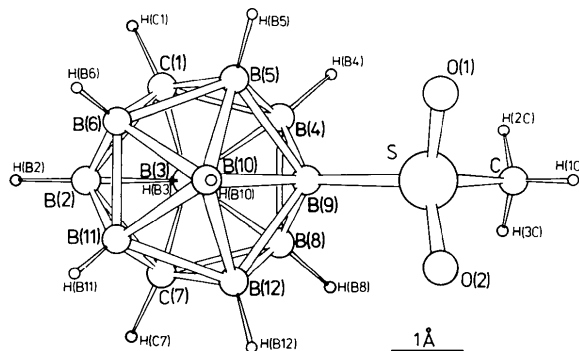


Fig. 1. View of the molecule down the vector [001].

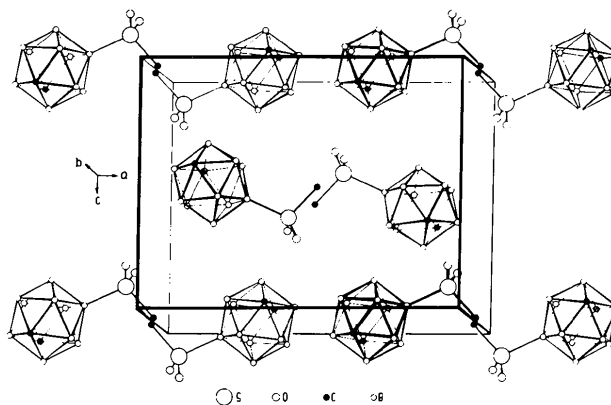


Fig. 2. Packing of the molecules in the unit cell.

longer by 0.03 \AA (B—C) and 0.03 \AA (B—B) than those in $9,10\text{-Br}_2\text{-1,7-C}_2\text{B}_{10}\text{H}_{10}$ (Beall & Lipscomb, 1967). We have not found an abnormally long B(2)—B(3) distance such as those of 1.89 \AA found in $9,10\text{-Br}_2\text{-1,7-C}_2\text{B}_{10}\text{H}_{10}$ and $2,3,4,5,6,8,9,10,11,12\text{-Cl}_{10}\text{-1,7-C}_2\text{B}_{10}\text{H}_2$ (Potenza & Lipscomb, 1966); however, we observed distinctly shorter (by $0.09\text{--}0.12 \text{ \AA}$) B(6)—B(10), B(6)—B(11), and B(9)—B(10) distances compared with those in $5,12\text{-Cl}_2\text{-1,7-(CH}_3)_2\text{-1,7-C}_2\text{B}_{10}\text{H}_8$. For terminal H atoms the average C—H = 1.07 , B—H = $1.02 (0.83\text{--}1.12)$ and methyl C—H = $0.91 (0.89\text{--}0.94) \text{ \AA}$. The packing of molecules within one unit cell is shown in Fig. 2.

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