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2-Methyl-1-phenylsulfanyl-1,2-dicarba-*closo*-dodecaborane(12)

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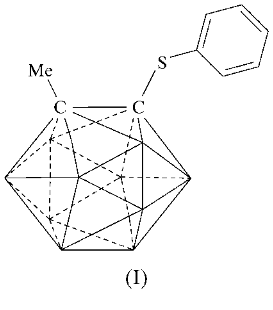
In the title *o*-carborane derivative, $C_9H_{18}B_{10}S$, the methyl and phenylsulfanyl groups are connected to the C atoms of the carborane cage. The $C_{cage}-C_{cage}$ distance is 1.708 (4) Å.

Comment

In 1,2-dicarba-*closo*-dodecaboranes, the $C_{cage}-C_{cage}$ (or C1—C2) bond length is considerably influenced by the number of substituents and atom species connected to the cluster C atoms. These distances are shortest for 1,2-H_2 compounds [1.57 (1)–1.634 (3) Å; Šubrtová *et al.*, 1980; Novák *et al.*, 1983], while much longer distances [1.799 (3)–1.858 (5) Å] are observed for 1,2-S_2-substituted compounds (Llop *et al.*, 2002; Teixidor, Romerosa *et al.*, 1990; Teixidor, Viñas *et al.*, 1990). Continuing our studies of the elongation of the C1—C2 distance caused by different C_{cage} substituents (Kivekäs *et al.*, 1994, 1995, 1998; Sillanpää *et al.*, 1996), and in order to prepare new ligands or ligand precursors for complexation, we have now synthesized and characterized the title compound, (I), and determined its crystal structure.



(I)

In (I), the phenylsulfanyl and methyl groups are connected to the cluster C atoms of the 1,2-dicarba-*closo*-dodecaborane moiety. The phenyl group is oriented away from atom B3 and, in order to reduce the repulsion between the phenyl group and the carborane cage, the S atom is moved slightly from its idealized radial position towards atom B3. As a consequence, the B3—C1—S angle is significantly smaller [113.19 (18)°] than the B6—C1—S angle [122.48 (19)°], and the C13—C2—C1—S torsion angle is −5.3 (3)°. Thus, the variation of the C13—C2—*X* angles [116.8 (3)–121.7 (3)°; *X* is C_{cage} or B] is less than that of the S—C1—*X* angles. The contribution of the phenylsulfanyl and methyl substituents on the cluster C atoms to the C1—C2 bond is indicated by the bond distance of 1.708 (4) Å.

Comparison of (I) with the relevant sulfido-substituted monoanion $[2\text{-Me-1-S-}C_2B_{10}H_{10}]^-$ (Kivekäs *et al.*, 1999) reveals two marked differences. The C1—C2 distance is significantly shorter in (I) than in the latter compound [1.792 (5) Å], but the C1—S distance in (I) [1.784 (3) Å] is significantly longer than in the latter compound [1.735 (4) Å].

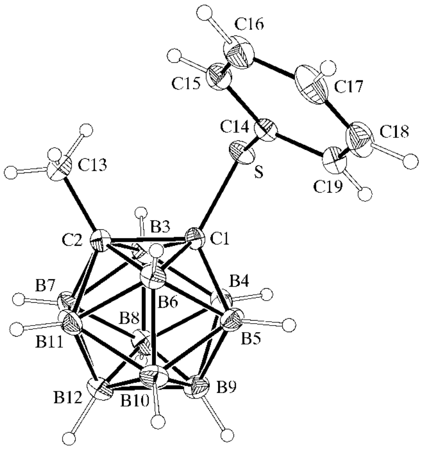


Figure 1
A view of the structure of (I), with displacement ellipsoids at the 20% probability level. H atoms are shown as small spheres of arbitrary radii.

The observed C1—C2 distance in (I) is in line with our earlier results obtained for neutral 1,2-disubstituted *o*-carboranes. The distance is slightly longer than that in compounds with aliphatic C atoms connected to both cluster C atoms [1.670 (3) and 1.684 (6) Å; Kivekäs *et al.*, 1998; Holbray *et al.*, 1993], but is much shorter than the corresponding distance in 1,2-S_2-substituted *closo* compounds [1.799 (3)–1.858 (5) Å; Llop *et al.*, 2002; Teixidor, Romerosa *et al.*, 1990; Teixidor, Viñas *et al.*, 1990].

The C1—C2 distance in (I) is comparable with the corresponding distance of 1.702 (6) Å in 1-Me-2-PPh_2-$C_2B_{10}H_{10}$ (Kivekäs *et al.*, 1994), and indicates that the contribution of one Me and one SPh substituent to the lengthening of the C1—C2 distance is equivalent to that of one Me and one PPh_2 substituent.

Experimental

Reaction of 1-Me-1,2-$C_2B_{10}H_{11}$ in diethyl ether with a solution of *n*-butyllithium in hexane, and subsequent reaction with phenyl disulfide in diethyl ether, resulted in a white solid. After purification, the solid was recrystallized from dichloromethane–*n*-hexane and pale-yellow crystals of (I) were obtained. Full details of the synthesis,

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together with the spectral data and elemental analysis, are given in the archived CIF.

Crystal data

$C_9H_{18}B_{10}S$
$M_r = 266.39$
Monoclinic, $P2_1/n$
$a = 7.2391$ (14) Å
$b = 17.2093$ (11) Å
$c = 12.3461$ (10) Å
$\beta = 98.066$ (10)°
$V = 1522.9$ (3) Å^3
$Z = 4$

$D_x = 1.162$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.1$–15.9°
$\mu = 0.19$ mm^{-1}
$T = 296$ (2) K
Prism, pale yellow
0.38 × 0.26 × 0.24 mm

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.943$, $T_{\max} = 0.956$
2906 measured reflections
2681 independent reflections
1708 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.020$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 20$
$l = -14 \rightarrow 14$
3 standard reflections every 150 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.135$
$S = 1.03$
2681 reflections
183 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.4580P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0060 (16)

Table 1

Selected geometric parameters (Å, °).

S—C1	1.784 (3)	C1—B4	1.718 (4)
S—C14	1.778 (3)	C1—B5	1.702 (4)
C1—C2	1.708 (4)	C1—B6	1.717 (4)
C1—B3	1.726 (4)	C2—C13	1.513 (4)
C14—S—C1	104.33 (12)	C13—C2—C1	118.3 (2)
C2—C1—S	119.59 (18)	C13—C2—B3	116.8 (3)
B3—C1—S	113.19 (18)	C13—C2—B6	117.8 (3)
B5—C1—S	124.1 (2)	C13—C2—B7	121.2 (3)
B4—C1—S	117.93 (19)	C13—C2—B11	121.7 (3)
B6—C1—S	122.48 (19)		
C13—C2—C1—S	−5.3 (3)	C1—S—C14—C15	−99.0 (2)
C2—C1—S—C14	90.4 (2)	C1—S—C14—C19	84.2 (2)

The methyl group was refined as a rotating group, with C—H = 0.96 Å and $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(C). The other H atoms were refined using a riding model, with B—H = 1.10 Å and C—H = 0.93 Å, and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(B or C), starting from idealized positions.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1379). Services for accessing these data are described at the back of the journal.

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