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1,2-Bis(methylsulfanyl)-1,2-dicarba-*closo*-dodecaborane(12)

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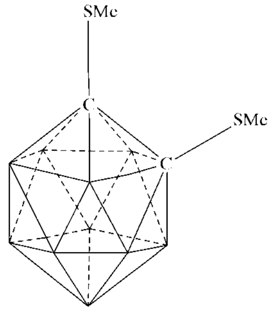
In the title compound, 1,2-$(SCH_3)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ or $C_4H_{16}B_{10}S_2$, the methylsulfanyl groups are bonded to the C atoms of the 1,2-dicarba-*closo*-dodecaborane cage. The $C_{cage}-C_{cage}$ distance is 1.8033 (18) Å and the $S-C_{cage}-C_{cage}-S$ torsion angle is 1.07 (13)°. The $C_{cage}-C_{cage}$ distance is compared with those in other 1,2-dicarba-*closo*-dodecaborane derivatives.

Comment

The contribution of substituents at the cluster C atoms on the lengthening of the $C_{cage}-C_{cage}$ or C1—C2 bond in 1,2-*closo*-$C_2B_{10}H_{12}$ or *o*-carborane derivatives is well known (Kivekäs, Sillanpää *et al.*, 1995; Sillanpää *et al.*, 1996). Different C1—C2 distances in icosahedral *o*-carborane derivatives can be achieved by modifying the substituents at the C atoms of the cluster compound. This is important both from the theoretical point of view and also in order to understand the isomerization process that takes place from *ortho*-, *meta*- and *para*-carborane isomers.

The C1—C2 distance is strongly dependent on the number of substituents connected to the cluster C atoms and the atomic species of those substituents. Accordingly, shortest distances of 1.629 (6) and 1.630 (6) Å have been reported for two crystallographically independent molecules of the unsubstituted parent compound 1,2-*closo*-$C_2B_{10}H_{12}$, carrying H atoms at both cluster C atoms (Davidson *et al.*, 1996). Dealing with one atomic species, it is observed that a substituent at only one of the cluster C atoms does not increase the distance significantly, or affects the distance only slightly, but increased lengthening is observed if both cluster C atoms are substituted. Table 1 lists the C1—C2 bond lengths for a wide range of comparable compounds and the following observations have been noted. Firstly, the lengthening caused by aliphatic C substituents at both cluster C atoms is smaller than that of aromatic C. Secondly, in Si-substituted compounds, the C1—C2 distance is approximately comparable with that in the compound bearing two aliphatic C atoms at the cluster C atoms. Thirdly, the contribution of two P-substituents is comparable with that of two aryl groups. Finally, the longest C1—C2 distances (*ca* 1.80–1.86 Å) have been reported for 1,2-S_2-disubstituted *o*-carborane derivatives (Llop *et al.*, 2002; Teixidor, Viñas *et al.*, 1990; Teixidor, Romerosa *et al.*, 1990). As far as we know, no crystallographic data are available for 1,2-N_2- and 1,2-O_2-disubstituted *o*-carborane compounds. However, a C1—C2 distance as long as 2.001 (3) Å has been reported for the $[1\text{-O-2-}C_6H_5\text{-1,2-}closo\text{-}C_2B_{10}H_{10}]^-$ anion, containing a C═O bond (Brown *et al.*, 1987).



(I)

We have suggested an empirically derived equation (Kivekäs, Sillanpää *et al.*, 1995; Kivekäs, Teixidor *et al.*, 1995) to calculate the C1—C2 distance, as well as carrying out computational analyses to understand the nature of the bond (Llop *et al.*, 2002; Paavola, 2002). As this kind of lengthening is exceptional and unique in chemistry, we have continued our research on this topic and now report the crystal structure of the title compound, (I), the preparation of which has been reported previously by Llop *et al.* (2001).

In compound (I), the SCH_3 groups are oriented in approximately the same direction from the cluster (Fig. 1). This is also indicated by the torsion angles of 101.13 (11) and −92.41 (11)° for C1—C2—S2—C14 and C2—C1—S1—C13, respectively. The molecule has approximately C_s symmetry,

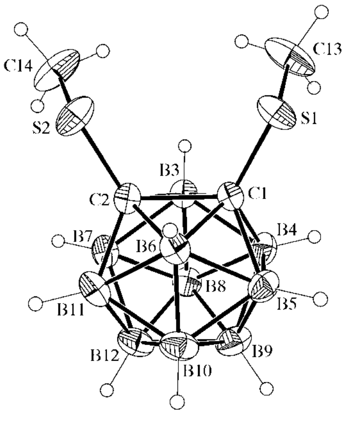


Figure 1
A view of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

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with the pseudo-mirror plane passing through the mid-point of the C1—C2 bond and through atoms B3, B6, B8 and B10. The intramolecular S1···S2 distance of 3.4359 (6) Å is only 0.16 Å shorter than the sum of the corresponding van der Waals radii (Bondi, 1964), thus indicating only minor interaction between the atoms. The free electron pairs of the S atoms are oriented away from each other to avoid steric repulsion. The S1—C1—B6 and S2—C2—B6 angles of 112.05 (9) and 112.45 (9)°, respectively, are narrower than the mean S—C_{cage}—*X* (*X* is C_{cage} or B) angles of *ca* 119.5°, thus indicating that the S atoms are displaced slightly from their ideal radial orientation towards atom B6.

The main interest of (I) is in its C1—C2 bond. The bond length of 1.8033 (18) Å is in line with the previously observed distances in 1,2-disubstituted *o*-carborane derivatives. The bond is clearly longer than the relevant bond in the C-, Si- and P-1,2-disubstituted compounds and is comparable with the distances in the 1,2-S_2-disubstituted compounds. Thus, the C1—C2 distance in (I) is equal to the distance of 1.799 (3) Å in 1,2-$(SC_6H_5)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (Llop *et al.*, 2002) and is equal to or slightly shorter than the distances of 1.816 (6), 1.826 (5) and 1.858 (5) Å in 1,2-μ-$SCH_2CH_2OCH_2CH_2S$-1,2-*closo*-$C_2B_{10}H_{10}$ (Teixidor, Romerosa *et al.*, 1990) and 1,2-μ-$SCH_2(CH_2OCH_2)_2CH_2S$-1,2-*closo*-$C_2B_{10}H_{10}$ (Teixidor, Viñas *et al.*, 1990). The C1—C2 distance in (I) is also equal to the distance of 1.792 (5) Å observed in the [2-CH_3-1-S-1,2-*closo*-$C_2B_{10}H_{10}$]$^-$ anion (Kivekäs *et al.*, 1999), thus indicating that the contribution of methyl and sulfide groups is comparable with that of two SCH_3 groups. The C1—C2 distance found in (I) is a further confirmation that the S atoms in 1,2-disubstituted *o*-carborane derivatives lengthen the C1—C2 distance considerably.

In the [2-CH_3-1-S-*closo*-$C_2B_{10}H_{10}$]$^-$ anion, there is a short intramolecular distance of 2.68 Å between a methyl H atom and the sulfide group, indicating a hydrogen bond between the atoms (Kivekäs *et al.*, 1999). In (I), containing neutral SCH_3 substituents at the cluster C atoms, the shortest S···H(CH_3) distance between different SCH_3 substituents is intermolecular and as long as 3.24 Å, *ca* 0.2 Å longer than the sum of the corresponding van der Waals radii (Bondi, 1964). The shortest intermolecular (S2···H12) contact is 2.95 Å. These distances indicate that there are only weak van der Waals packing forces between the molecules.

Experimental

Compound (I) was synthesized from 1,2-$(SH)_2$-1,2-$C_2B_{10}H_{10}$ and CH_3I, and crystallized from petroleum ether (b.p. 313–333 K; Llop *et al.*, 2001).

Crystal data

$C_4H_{16}B_{10}S_2$
$M_r = 236.39$
Monoclinic, $P2_1/n$
$a = 7.16670$ (10) Å
$b = 15.1733$ (2) Å
$c = 11.8894$ (2) Å
$\beta = 92.9760$ (10)°
$V = 1291.14$ (3) Å^3
$Z = 4$

$D_x = 1.216$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2472 reflections
$\theta = 2.9$–25.7°
$\mu = 0.37$ mm^{-1}
$T = 173$ (2) K
Prism, colourless
0.22 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
4565 measured reflections
2397 independent reflections
2208 reflections with $I > 2\sigma(I)$

$R_{int} = 0.013$
$\theta_{max} = 25.7°$
$h = -8 \rightarrow 8$
$k = -18 \rightarrow 16$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.086$
$S = 1.07$
2397 reflections
147 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.5289P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
C1—C2 distances (Å) for selected C_{cage}-substituted 1,2-dicarba-*closo*-dodecaborane(12) derivatives (compounds containing metal ions or strained rings are not included).

Compound	C1—C2	Reference
(1,2-*closo*-$C_2B_{10}H_{12}$·hmpa)$_2$	1.629 (6) and 1.630 (6)	*a*
1-COOH-*closo*-$C_2B_{10}H_{11}$	1.631 (2)	*b*
1,2-$(COOH)_2$-*closo*-$C_2B_{10}H_{10}$·0.5C_2H_6O	1.651 (2)–1.660 (2)	*c*
1-$P(C_6H_5)_2$-1,2-*closo*-$C_2B_{10}H_{11}$	1.666 (9)	*d*
1-COOH-2-CH_3-*closo*-$C_2B_{10}H_{10}$	1.6694 (17)	*e*
1-CH_2CH_2SH-2-CH_3-1,2-*closo*-$C_2B_{10}H_{10}$	1.670 (3)	*f*
1-COOH-2-C_6H_5-*closo*-$C_2B_{10}H_{10}$	1.678 (3) and 1.691 (3)	*e*
1,1′-$Si(CH_3)_2$-2,2′-$Si(CH_3)_2$-(1,2-*closo*-$C_2B_{10}H_{10}$)$_2$	1.688 (5)	*g*
1-C_6H_5-2-CO(C_6H_5)-*closo*-$C_2B_{10}H_{10}$	1.695 (3)	*e*
1-$P(C_6H_5)_2$-2-CH_3-1,2-*closo*-$C_2B_{10}H_{10}$	1.702 (6)	*h*
1-COOH-2-C_6H_5-*closo*-$C_2B_{10}H_{10}$·2H_2O	1.705 (2)	*e*
1,2-[P(2-C_3H_7)$_2$]$_2$-1,2-*closo*-$C_2B_{10}H_{10}$	1.719 (3)	*i*
1,2-[$P(C_6H_5)_2$]$_2$-1,2-*closo*-$C_2B_{10}H_{10}$	1.722 (4)	*j*
1,2-$(C_6H_5)_2$-1,2-*closo*-$C_2B_{10}H_{10}$	1.720 (4) and 1.733 (4)	*k*
1-P(2-C_3H_7)$_2$-2-CH_3-1,2-*closo*-$C_2B_{10}H_{10}$	1.731 (9)	*j*
1-$P(C_6H_5)_2$-2-S(2-C_3H_7)-1,2-*closo*-$C_2B_{10}H_{10}$	1.747 (5)	*l*
1-$P(C_6H_5)_2$-2-C_6H_5-1,2-*closo*-$C_2B_{10}H_{10}$	1.755 (6)	*m*
1-P(2-C_3H_7)$_2$-2-C_6H_5-1,2-*closo*-$C_2B_{10}H_{10}$	1.769 (4)	*n*
[$PCH_3(C_6H_5)_3$][1-CH_3-2-S-1,2-*closo*-$C_2B_{10}H_{10}$]	1.792 (5)	*o*
1,2-$(SC_6H_5)_2$-1,2-*closo*-$C_2B_{10}H_{10}$	1.799 (3)	*p*
1,2-$(SCH_3)_2$-*closo*-1,2-$C_2B_{10}H_{10}$	1.8033 (18)	*q*
1,2-μ-$SCH_2CH_2OCH_2CH_2S$-1,2-*closo*-$C_2B_{10}H_{10}$	1.816 (6)	*r*
1,2-μ-$SCH_2(CH_2OCH_2)_2CH_2S$-1,2-*closo*-$C_2B_{10}H_{10}$	1.826 (5) and 1.858 (5)	*s*

References: (*a*) Davidson *et al.* (1996) (hmpa is hexamethylphosphoramide); (*b*) Welch *et al.* (2001); (*c*) Venkatasubramanian *et al.* (2003); (*d*) Kivekäs, Teixidor *et al.* (1995); (*e*) Venkatasubramanian *et al.* (2004); (*f*) Kivekäs *et al.* (1998); (*g*) Kivekäs, Romerosa & Viñas (1994); (*h*) Kivekäs, Sillanpää *et al.* (1994); (*i*) Kivekäs, Sillanpää *et al.* (1995); (*j*) Paavola (2002); (*k*) Lewis & Welch (1993); (*l*) Teixidor *et al.* (1997); (*m*) McWhannell *et al.* (1996); (*n*) Sillanpää *et al.* (1996); (*o*) Kivekäs *et al.* (1999); (*p*) Llop *et al.* (2002); (*q*) this work; (*r*) Teixidor, Romerosa *et al.* (1990); (*s*) Teixidor, Vĩnas *et al.* (1990).

Methyl groups were refined as rotating groups, with C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. The other H atoms were refined using a riding model, with B—H = 1.12 Å and $U_{iso}(H) = 1.2U_{eq}(B)$, starting from idealized positions.

Table 2
Selected geometric parameters (Å, °).

S1—C1	1.7610 (13)	C1—B6	1.7233 (19)
S1—C13	1.7876 (18)	C1—C2	1.8033 (18)
S2—C2	1.7630 (14)	C2—B6	1.7121 (19)
S2—C14	1.7929 (18)	C2—B3	1.7255 (19)
C1—B3	1.7208 (19)		
C1—S1—C13	104.27 (7)	S1—C1—C2	117.90 (8)
C2—S2—C14	104.25 (8)	B7—C2—S2	126.21 (9)
B4—C1—S1	126.22 (9)	B11—C2—S2	120.03 (10)
B5—C1—S1	119.05 (9)	B6—C2—S2	112.45 (9)
B3—C1—S1	122.47 (9)	B3—C2—S2	121.43 (9)
B6—C1—S1	112.05 (9)	S2—C2—C1	117.29 (9)
S1—C1—C2—S2	1.07 (13)	C2—C1—S1—C13	−92.40 (12)
C1—C2—S2—C14	101.12 (11)		

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; 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.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1059). Services for accessing these data are described at the back of the journal.

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