

non-H atoms) = 0.46; max. and min. electron densities in final difference map 0.10 and $-0.12 \text{ e } \text{Å}^{-3}$; H atoms calculated and kept unrefined for the last two cycles; all non-H atoms refined anisotropically; $R = 0.043$; $wR = 0.040$; block-diagonal least-squares refinement using *XTAL* (Stewart & Hall, 1985).

Discussion. Table 1 gives the atomic coordinates of the structure shown in Fig. 2.* Bond lengths and angles are given in Table 2. Ring *B* adopts a 'chair' conformation with C(9) 0.6 Å above and C(12) 0.7 Å below the least-squares plane of C(1), C(13), C(11) and C(10). The middle ring *C* adopts a boat-like conformation with C(9) and C(6), respectively, 0.61- and 0.63 Å above the least-squares plane of C(1), C(2), C(7) and C(8). Ring *D* can be described as a β -envelope similar to the other five-membered rings found in polycyclic structures (Cox, Mkandawire & Mallinson, 1981; Précigoux, Busetta & Geoffre, 1981; Précigoux, Leroy & Geoffre, 1980). The *BC* and *CD* junctions are both *trans*, and the methyl and methoxymethoxy groups are *syn*, leading to the *trans-syn-trans* stereochemistry. Such a

conformation for the major isomer obtained by trans-annular Diels–Alder reaction is compatible with a boat-like transition state wherein the *C* ring would adopt a boat conformation.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51042 (60 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 10,11- μ -Hydro-9-dimethylsulphido-7,8-dicarba-*nido*-undecaborane(11)

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Abstract. C₄H₁₇B₉S, $M_r = 194.53$, triclinic, $P\bar{1}$, $a = 8.7912$ (14), $b = 12.093$ (5), $c = 12.5617$ (19) Å, $\alpha = 107.53$ (3), $\beta = 101.019$ (13), $\gamma = 106.10$ (3)°, $V = 1167.2$ (8) Å³, $Z = 4$, $D_x = 1.107 \text{ Mg m}^{-3}$, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.213 \text{ mm}^{-1}$, $F(000) = 408$, 291 K, $R = 0.0480$ for 3580 observed reflections. There are two crystallographically independent molecules in the asymmetric fraction of the unit cell, which differ in respect of the torsion about the B(9)–S bond. The μ -H atom bridges the B(10)–B(11) connectivity asymmetrically, favouring B(10), the less positively charged boron [average μ -H–B(10) 1.165, average μ -H–B(11) 1.35 Å].

Introduction. The synthesis of the title compound (1) was reported ten years ago (Plessek, Janousek & Hermanek, 1978). Spectroscopic study indicated that the SMe₂ unit was bound to B(9) of the *nido*-icosahedral {7,8-C₂B₉} polyhedron, but the position of the bridging H atom (shown to be either 9,10 or 10,11 bridging) was not unambiguously determined.

We are interested in (1) as a precursor of [9-SMe₂-*nido*-7,8-C₂B₉H₁₀][−], a monoanionic carbaborane fully analogous to the ubiquitous [C₃H₃][−] ligand. Since the position of the μ -H atom in (1) may be important in the formation and structure of metal complexes of its anion, we have undertaken the present study.

Table 1. Coordinates of refined atoms and equivalent isotropic thermal parameters

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
S(a)	0.28339 (6)	0.50594 (6)	0.74844 (5)	0.0543 (4)
CS(1a)	0.4092 (3)	0.5721 (3)	0.89584 (21)	0.0680 (19)
CS(2a)	0.3532 (4)	0.6307 (4)	0.7025 (3)	0.125 (4)
B(1a)	-0.2536 (3)	0.4679 (3)	0.6394 (3)	0.0592 (19)
B(2a)	-0.3199 (3)	0.4313 (3)	0.7506 (3)	0.0651 (21)
B(3a)	-0.2555 (3)	0.3274 (3)	0.6577 (3)	0.0676 (21)
B(4a)	-0.0869 (3)	0.4149 (3)	0.62429 (25)	0.0571 (19)
B(5a)	-0.0453 (2)	0.57396 (25)	0.70139 (22)	0.0502 (17)
B(6a)	-0.1908 (3)	0.5851 (3)	0.78330 (25)	0.0562 (18)
C(7a)	-0.1847 (3)	0.37267 (25)	0.8065 (3)	0.0729 (21)
C(8a)	-0.0531 (3)	0.36857 (23)	0.74344 (24)	0.0630 (18)
B(9a)	0.0701 (3)	0.49794 (23)	0.75785 (21)	0.0453 (16)
B(10a)	0.0197 (3)	0.6129 (3)	0.85526 (23)	0.0501 (17)
B(11a)	-0.1544 (4)	0.5147 (3)	0.8862 (3)	0.0680 (22)
S(b)	-0.22948 (7)	0.87045 (6)	0.66900 (6)	0.0658 (5)
CS(2b)	-0.3046 (4)	0.9752 (3)	0.6194 (3)	0.0884 (24)
CS(1b)	-0.2613 (4)	0.7515 (3)	0.5314 (3)	0.0815 (22)
B(1b)	0.2735 (4)	1.1753 (3)	0.8471 (3)	0.0690 (22)
B(2b)	0.3982 (4)	1.0923 (3)	0.8717 (3)	0.0773 (24)
B(3b)	0.2494 (5)	1.0956 (3)	0.9435 (3)	0.0805 (25)
B(4b)	0.0719 (4)	1.0921 (3)	0.8466 (3)	0.0665 (21)
B(5b)	0.1156 (3)	1.08273 (25)	0.71294 (24)	0.0551 (18)
B(6b)	0.3212 (4)	1.0805 (3)	0.7275 (3)	0.0673 (21)
C(7b)	0.2717 (3)	0.9598 (3)	0.8719 (3)	0.0751 (21)
C(8b)	0.0923 (3)	0.95489 (24)	0.85366 (21)	0.0628 (18)
B(9b)	0.0036 (3)	0.94901 (23)	0.72891 (22)	0.0483 (16)
B(10b)	0.1446 (3)	0.9414 (3)	0.64557 (25)	0.0579 (19)
B(11b)	0.3233 (4)	0.9442 (3)	0.7531 (4)	0.0776 (25)
H(1a)	-0.347 (4)	0.472 (3)	0.564 (3)	
H(2a)	-0.444 (4)	0.397 (3)	0.7522 (25)	
H(3a)	-0.330 (4)	0.236 (3)	0.601 (3)	
H(4a)	-0.064 (4)	0.386 (3)	0.545 (3)	
H(5a)	-0.003 (4)	0.644 (3)	0.667 (3)	
H(6a)	-0.238 (4)	0.664 (3)	0.800 (3)	
H(7a)	-0.219 (4)	0.310 (3)	0.832 (3)	
H(8a)	-0.012 (4)	0.285 (3)	0.731 (3)	
H(10a)	0.107 (4)	0.709 (3)	0.913 (3)	
H(11a)	-0.186 (4)	0.547 (3)	0.965 (3)	
H(*a)	0.006 (4)	0.545 (3)	0.900 (3)	
H(1b)	0.327 (4)	1.274 (3)	0.875 (3)	
H(2b)	0.524 (4)	1.127 (3)	0.917 (3)	
H(3b)	0.272 (4)	1.130 (3)	1.037 (3)	
H(4b)	-0.024 (4)	1.128 (3)	0.883 (3)	
H(5b)	0.064 (4)	1.123 (3)	0.653 (3)	
H(6b)	0.399 (4)	1.118 (3)	0.670 (3)	
H(7b)	0.303 (4)	0.926 (3)	0.922 (3)	
H(8b)	0.031 (4)	0.913 (3)	0.893 (3)	
H(10b)	0.116 (4)	0.902 (3)	0.548 (3)	
H(11b)	0.416 (4)	0.900 (3)	0.727 (3)	
H(*b)	0.170 (4)	0.860 (3)	0.677 (3)	

Experimental. Compound prepared according to the literature (Pleseck, Janousek & Hermanek, 1978), and purity checked by microanalysis (C, H) and NMR spectroscopies (^1H , $^{11}\text{B}\{^1\text{H}\}$); crystals suitable for diffraction study obtained by solvent diffusion (CH_2Cl_2 -*n*-hexane) at 291 K; colourless block, *ca* $0.3 \times 0.3 \times 0.4$ mm mounted on glass fibre and set on Enraf-Nonius CAD-4 diffractometer (Mo $K\alpha$ X-radiation, graphite monochromator); cell parameters and orientation matrix from least-squares refinement of θ values ($14 < \theta < 15^\circ$) of 25 centred reflections; data collection by ω - 2θ scans in 96 steps with ω scan width ($0.8 + 0.34 \tan \theta$) $^\circ$; data (*h*: 0 to 10, *k*: -14 to 14, *l*: -14 to 14) measured for $1 \leq \theta \leq 25^\circ$ over 92 X-ray hours; no detectable crystal decay or movement; corrections for Lorentz and polarization effects applied (Gould & Smith, 1986), but not for absorption; 4390 independent reflections measured, 3580 [$F \geq 2.0\sigma(F)$]

Table 2. Interatomic distances (\AA)

S(a)-CS(1a)	1.768 (3)	S(b)-CS(2b)	1.792 (4)
S(a)-CS(2a)	1.770 (4)	S(b)-CS(1b)	1.797 (3)
S(a)-B(9a)	1.879 (3)	S(b)-B(9b)	1.889 (3)
B(1a)-B(2a)	1.740 (5)	B(1b)-B(2b)	1.724 (5)
B(1a)-B(3a)	1.778 (5)	B(1b)-B(3b)	1.769 (5)
B(1a)-B(4a)	1.774 (4)	B(1b)-B(4b)	1.777 (5)
B(1a)-B(5a)	1.777 (4)	B(1b)-B(5b)	1.768 (5)
B(1a)-B(6a)	1.795 (4)	B(1b)-B(6b)	1.793 (5)
B(1a)-H(1a)	1.15 (3)	B(1b)-H(1b)	1.07 (3)
B(2a)-B(3a)	1.740 (5)	B(2b)-B(3b)	1.728 (6)
B(2a)-B(6a)	1.762 (5)	B(2b)-B(6b)	1.757 (5)
B(2a)-C(7a)	1.690 (5)	B(2b)-C(7b)	1.679 (5)
B(2a)-H(11a)	1.800 (5)	B(2b)-H(11b)	1.796 (5)
B(2a)-H(2a)	1.06 (3)	B(2b)-H(2b)	1.04 (3)
B(3a)-B(4a)	1.769 (5)	B(3b)-B(4b)	1.768 (5)
B(3a)-C(7a)	1.712 (5)	B(3b)-C(7b)	1.704 (5)
B(3a)-C(8a)	1.740 (5)	B(3b)-C(8b)	1.738 (5)
B(3a)-H(3a)	1.05 (3)	B(3b)-H(3b)	1.08 (3)
B(4a)-B(5a)	1.767 (4)	B(4b)-B(5b)	1.771 (5)
B(4a)-C(8a)	1.752 (4)	B(4b)-C(8b)	1.744 (5)
B(4a)-B(9a)	1.749 (4)	B(4b)-B(9b)	1.757 (4)
B(4a)-H(4a)	1.03 (3)	B(4b)-H(4b)	1.16 (3)
B(5a)-B(6a)	1.797 (4)	B(5b)-B(6b)	1.790 (5)
B(5a)-B(9a)	1.736 (4)	B(5b)-B(9b)	1.736 (4)
B(5a)-H(10a)	1.779 (4)	B(5b)-H(10b)	1.776 (4)
B(5a)-H(5a)	1.07 (3)	B(5b)-H(5b)	1.11 (3)
B(6a)-B(10a)	1.785 (4)	B(6b)-B(10b)	1.788 (5)
B(6a)-B(11a)	1.775 (5)	B(6b)-B(11b)	1.777 (5)
B(6a)-H(6a)	1.13 (3)	B(6b)-H(6b)	1.19 (3)
C(7a)-C(8a)	1.525 (4)	C(7b)-C(8b)	1.531 (4)
C(7a)-B(11a)	1.623 (5)	C(7b)-B(11b)	1.613 (5)
C(7a)-H(7a)	0.91 (3)	C(7b)-H(7b)	0.88 (3)
C(8a)-B(9a)	1.571 (4)	C(8b)-B(9b)	1.582 (4)
C(8a)-H(8a)	1.14 (3)	C(8b)-H(8b)	0.94 (3)
B(9a)-B(10a)	1.775 (4)	B(9b)-B(10b)	1.773 (4)
B(10a)-B(11a)	1.843 (5)	B(10b)-B(11b)	1.851 (5)
B(10a)-H(10a)	1.12 (3)	B(10b)-H(10b)	1.12 (3)
B(10a)-H(*a)	1.11 (3)	B(10b)-H(*b)	1.22 (3)
B(11a)-H(11a)	1.07 (3)	B(11b)-H(11b)	1.14 (3)
B(11a)-H(*a)	1.31 (3)	B(11b)-H(*b)	1.39 (3)

retained; structure solution using automatic direct methods (Sheldrick, 1986), and iterative full-matrix least-squares refinement (on F)/ ΔF syntheses (Sheldrick, 1976); cage C atoms assigned by a combination of short C-C distance and low isotropic thermal parameters after refinement as B; weights assigned according to $w^{-1} = [\sigma^2(F) + 0.00002F^2]$; all non-H atoms allowed anisotropic thermal motion; cage H atoms positionally refined, and methyl H atoms treated as part of rigid groups (giving sensible S-C-H angles); all H atoms given an overall isotropic thermal parameter, $0.095(16)\text{\AA}^2$ at convergence; No. of variables 320; data:variable ratio >11:1; $R = 0.0480$, $R' = 0.0650$, $S = 1.714$; max. shift/e.s.d. in final cycle < 0.1 ; max. and min. residues in final ΔF synthesis 0.522 and $-0.233 \text{ e}\text{\AA}^{-3}$; scattering factors inlaid in *SHELX76*; all calculations performed on Amdahl 470 V/8 computer.

Discussion. Table 1* lists final atomic coordinates and (for non-H atoms) equivalent isotropic thermal parameters. Interatomic distances are given as Table 2. There

* Lists of structure factors, idealized H-atom coordinates, anisotropic thermal parameters and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51017 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

are two crystallographically independent molecules in the asymmetric unit, *a* and *b*. The root-mean-square misfit (Gould & Taylor, 1986) of the {C₂B₉S} fragments of *a* and *b* is only 0.016 Å, but this increases substantially (0.209 Å) if the C_{methyl} atoms are also included. Hence *a* and *b* differ only in respect of the torsion about the B(9)–S bond. For *a* C(8)–B(9)–S–CS(1) is –100.01 (20)°; for *b* the equivalent torsion is –123.22 (21)°. Plešek *et al.* (1978) noted two CH₃ resonances in the ¹H NMR spectrum of (1), and interpreted this as indicating no free rotation of the SMe₂ unit about the B(9)–S bond. However, the methyl groups of (1) are magnetically inequivalent whatever the torsion about the B–S bond (as long as inversion at S does not occur), so the extent of rotation about this bond in solution remains unknown. It would be surprising, however, if such rotation were restricted at ambient temperature.

In the crystal there are no intermolecular contacts closer than the van der Waals sums of atoms. Fig. 1 presents a perspective view of molecule *a*, and Fig. 2 views the same molecule from a position directly above

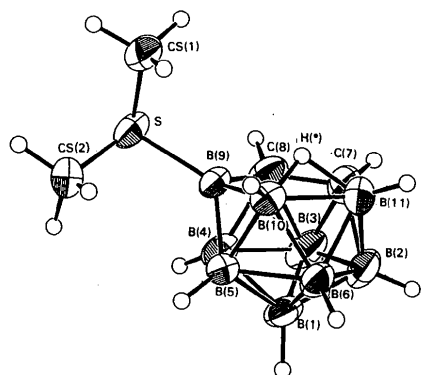


Fig. 1. Perspective view of molecule *a* of [9-SMe₂-nido-7,8-C₂B₉H₁₁] (1) (Mallinson, 1982) showing the atomic numbering scheme.

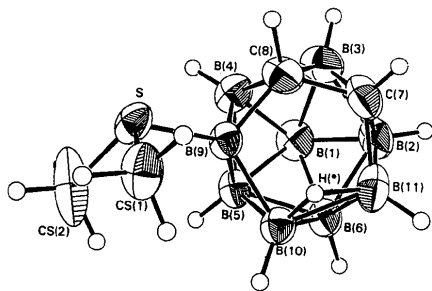


Fig. 2. View of molecule *a* from above the open five-atom face, clearly demonstrating the conformation of the pendant SMe₂ group. In molecule *b* there is a *ca* 23° relative twist about the B(9)–S bond.

the open five-atom face. The crystallographic study clearly defines the H-bridging site as the B(10)–B(11) connectivity. The bridges are significantly asymmetric, favouring B(10) in both independent molecules. Specifically, H(*)–B(10) is 1.11 (3) and H(*)–B(11) 1.31 (3) Å in *a*, and 1.22 (3) and 1.39 (3) Å respectively in *b*. In contrast, the B–H–B bridge in [8-SMe₂-nido-7,9-C₂B₉H₁₁] [a structural isomer of (1)] is symmetric (Šubrtová, Novák, Líněk & Hašek, 1984). The asymmetry in (1) can be readily understood in terms of the protonic nature of bridging H atoms and the relative electronegativity of the (cage) C atoms. Charge-iterated extended Hückel molecular orbital calculations (Howell, Rossi, Wallace, Haraki & Hoffmann, 1977) on idealized models of [nido-7,8-C₂B₉H₁₁]²⁻ and [9-SH₂-nido-7,8-C₂B₉H₁₀]⁻ suggest that in (1) B(10) is substantially more negative than B(11), but indicate that this arises primarily from the non-adjacency of cage carbon atoms rather than any effect caused by the SMe₂ group pendant to B(9).

All other molecular parameters in (1) are as expected. The B–S distance [ave. 1.884 (4) Å] agrees well with those previously reported (*e.g.* Šubrtová *et al.*, 1984; Schramm & Ibers, 1977; Mizusawa, Rudnick & Eriks, 1980). Future contributions will report the structural consequences of deprotonation and isolobal substitution of the μ -H atom of (1), and the results of synthetic and structural studies on η -bonded transition metal and actinide complexes of [9-SMe₂-nido-7,8-C₂B₉H₁₀]⁻.

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