

with $I \geq 2.5\sigma(I)$ used in refinement. Standard reflections 221 (I), 131 (II) checked every 50 reflections: no significant deviation. Empirical absorption correction factor between 0.9 and 1.1 (I), 0.97 and 1.26 (II). Structures solved with *SHELXS86* (Sheldrick, 1985). H atoms from difference Fourier synthesis. Anisotropic least-squares refinement (*SHELX76*; Sheldrick, 1976) using *F*. H isotropic with common refined temperature factor [$B = 6.5$ (I), 4.4 \AA^2 (II)]. $w = 1/(\sigma^2 + gF^2)$, $g = 0.0002$ (I), 0.0037 (II). $R = 0.041$, $wR = 0.046$ for 2801 observed reflections (I) and $R = 0.045$, $wR = 0.053$ for 1537 observed reflections (II). Final $(\Delta/\sigma)_{\max} = 0.07$ (I), 0.5 (II); $S = 2.74$ (I), 1.0 (II). Max. and min. heights in final difference Fourier synthesis = 0.21 and -0.31 e \AA^{-3} (I), 0.17 and -0.45 e \AA^{-3} (II). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic parameters are summarized in Tables 1 and 2,* the bond distances in the rings in Table 3, and the endocyclic torsion angles in Table 4. Figs. 1 and 2 give stereoscopic views of the molecules (Motherwell & Clegg, 1978).

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44111 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The First Structurally Characterized Monoalkylthioborane. Structure of 1,3,5-Tri(*tert*-butyl)cyclotriborathiane

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Abstract. C₁₂H₃₃B₃S₃, $M_r = 306$, orthorhombic, *Pbca*, $a = 15.577$ (3), $b = 18.327$ (4), $c = 27.791$ (5) Å, $V = 7933.7$ (26) Å³, $Z = 16$, D_m (by flotation) = 1.07 (1), $D_x = 1.02 \text{ g cm}^{-3}$, $F(000) = 2688$, $\text{Mo } K\alpha_1$, $\lambda = 0.70926 \text{ \AA}$, $\mu = 3.18 \text{ cm}^{-1}$, $T = 293 \text{ K}$, $R = 0.059$, $wR = 0.058$ for 2918 reflections with $F_o^2 > 3\sigma(F_o^2)$. There are two crystallographically independent (Bu^tSBH₂)₃ molecules per asymmetric unit with no imposed symmetry. The B–S distances range from

In the two compounds the five-membered rings exhibit envelope conformations with C(9) for (I) and C(1) for (II) at the flap. In compound (I), the six-membered ring has a chair conformation flattened in the C(2)–C(1)–C(4) moiety with an approximate mirror plane passing through C(1) and C(4). In compound (II), the seven-membered ring exhibits a twist-chair conformation with a twofold axis passing through C(7) and the middle point of the C(3)–C(4) bond.

The ring fusions in the two compounds are *cis* and the phenylsulfonyl substituents are in *exo* positions.

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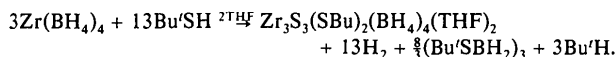
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1.915 (10) to 1.978 (10) Å. The B–S–B angles range from 103.3 (3) to 110.9 (3)° and the S–B–S angles from 102.6 (4) to 111.1 (4)°.

Introduction. Recently, we have been exploring the chemical reactivity of early-transition-metal borohydride complexes toward various thiols with the purpose of synthesizing new complexes that contain *M*–S and/or *M*–SR bonds. In a preliminary communication, we have reported (Coucouvanis, Lester, Kanatzidis & Kessissoglou, 1985) on the synthesis and characterization of $[\text{Zr}_3\text{S}_3(\text{SR})_2(\text{BH}_4)_4]_n(\text{THF})_2$ ($n =$

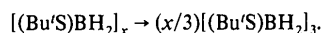
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1,2, $R = \text{Bu}'$) which was obtained (for $n = 1$) by the reaction of $\text{Zr}(\text{BH}_4)_4$ and $\text{Bu}'\text{SH}$:



The by-product of this reaction, $[(\text{Bu}'\text{S})\text{BH}_2]_3$, (I), is obtained in excellent yield (92%). It is an air-stable moisture-sensitive white crystalline compound. The formation of (I) results from a reaction between $\text{Bu}'\text{SH}$ and BH_3 , which are both present in the reaction mixture. The reactions of thiols with boranes are well known, and the alkylthioborane products have been studied in some detail in the last two decades (Mikhailov, 1970). The alkylthioboranes are mostly white moisture-sensitive materials that, depending on stoichiometry and conditions, can exist as polymers, oligomers or monomers. Monoalkylthioboranes of the type RSBH_2 are not known in simple monomeric forms, but primarily as polymers or trimers (e.g. Mikhailov, 1970; Muetterties, Miller, Packer & Miller, 1964).

The title compound was first synthesized by Mikhailov (1970), and its properties were studied. It can exist in a polymeric form which, in tetrahydrofuran solutions, transforms to the trimer:



The structure of the trimeric RSBH_2 compounds is presumed to be cyclic and fairly conclusive spectral evidence has been advanced for such a structure in $[(\text{EtS})\text{BH}_2]_3$ and $[(\text{Bu})\text{SBH}_2]_3$ (Muetterties *et al.*, 1964). To the best of our knowledge, there has been no report of a crystal structure determination of any monoalkylthioborane compound to date. In this paper, we report the crystal and molecular structure of the title compound.

Experimental. Large well shaped colourless crystals of (I) can be grown by the slow cooling of a concentrated pentane solution to 253 K. An irregularly shaped fragment broken off from such a crystal (dimensions $0.40 \times 0.29 \times 0.58$ mm) was used for the structure determination. The crystal was placed into a 0.5 mm glass capillary and mounted on a Nicolet P3 automated four-circle diffractometer. Accurate cell parameters of the orthorhombic cell were obtained from the least-squares refinement of the 2θ , ω , ϕ , χ angles of 25 high-angle ($16 < 2\theta < 45^\circ$) machine-centred reflections. 5758 reflections were collected ($2\theta_{\text{max}} = 45^\circ$) of which 5192 were unique. Data used in the refinement [$F_o^2 > 3\sigma(F_o^2)$], 2918. The minimum and maximum scan speeds were 5.0 and $29.3^\circ \text{min}^{-1}$. The number of variable parameters was 349. The intensities were corrected for Lorentz and polarization effects, but not for absorption, owing to the small absorption coefficient. Intensities were collected only from the unique portions of the reciprocal-lattice sphere (one octant)

with hkl values ranging 0→18, 0→21, 0→32 respectively. The space group was uniquely determined as $Pbca$ from the systematic extinctions ($0kl$ $k = 2n$, $h0l$ $l = 2n$, $hk0$ $h = 2n$). During data collection, three standard reflections were monitored every 90 reflections. No significant crystal decay was detected. The structure was solved by direct methods (*MULTAN*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and routine *SOLV* of the *SHELXTL* (Sheldrick, 1981) system. The six S atoms of the two independent $[(\text{Bu}'\text{S})\text{BH}_2]_3$ molecules were revealed in the E maps. With the locations of these atoms as a starting model, the rest of the non-hydrogen atoms were located *via* successive Fourier difference electron density maps. At this stage it was evident from the difference electron density map that one of the Bu' groups from each crystallographically independent molecule (axially disposed ones – see *Discussion*) showed rotational disorder around the S(3)–C(9) and S(6)–C(21) bonds respectively. The high isotropic thermal parameters of the C atoms of those Bu' groups also supported this observation. The carbon atoms in the twofold-disordered *tert*-butyl groups were assigned occupancy factors of 0.5 and the structure was refined with isotropic temperature factors to an R value of 7.2%. The least-squares refinement continued with all non-disordered atoms assigned anisotropic temperature factors. Finally, the positions of the H atoms were calculated (except those attached to the disordered C atom) and included in the structure-factor calculation, but were not refined. The H atoms were assigned temperature factors of 0.08 (for those attached to the B atoms) and 0.10. The final R values were $R = 5.92\%$ and $wR = 5.81\%$. The least-squares program minimizes the function $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F_o) + 0.002(F_o)^2]^{-1}$. $(\Delta/\sigma)_{\text{max}} = 0.02$; $-0.89 \leq \Delta\rho \leq 0.95 \text{ e } \text{Å}^{-3}$. Atomic scattering factors those of *SHELXTL*.

Discussion. Atomic parameters for the non-hydrogen atoms are listed in Table 1.* Bond distances and angles are given in Table 2. An *ORTEP* drawing (Johnson, 1965) of one of the two crystallographically independent molecules and the numbering scheme are shown in Figs. 1 and 2.

Each of the $[(\text{Bu}'\text{S})\text{BH}_2]_3$ molecules contains a B_3S_3 core which consists of a six-membered cyclic array of alternating B and S atoms. The six-membered B_3S_3 rings are puckered and assume a chair conformation. This conformation has been previously observed in the cyclic boron–nitrogen ring in $[(\text{CH}_3)_2\text{NBH}_2]_3$

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44107 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

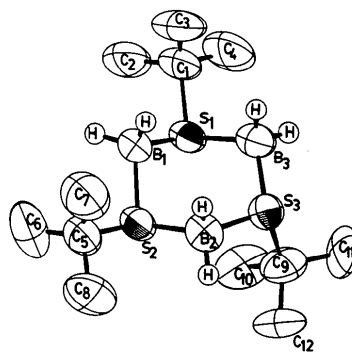
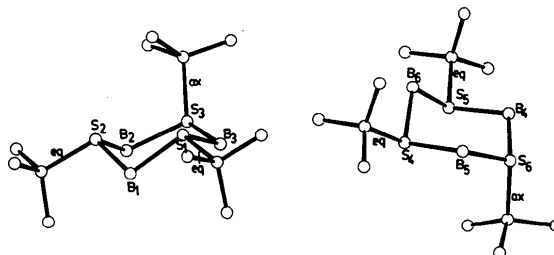
Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i> (Å ²)
S(1)	0.2209 (1)	0.2797 (1)	0.0585 (1)	0.0454
S(2)	0.2242 (1)	0.1593 (1)	-0.0156 (1)	0.0449
S(3)	0.0442 (1)	0.2047 (1)	0.0293 (1)	0.0496
S(4)	0.4292 (1)	-0.0412 (1)	0.2292 (1)	0.0479
S(5)	0.4274 (1)	0.0715 (1)	0.1503 (1)	0.0403
S(6)	0.8960 (1)	0.1243 (1)	0.2429 (1)	0.0478
B(1)	0.2596 (6)	0.2594 (5)	-0.0057 (3)	0.0464
B(2)	0.1016 (7)	0.1656 (6)	-0.0264 (4)	0.0578
B(3)	0.0988 (6)	0.2934 (5)	0.0507 (4)	0.0542
B(4)	0.4445 (8)	0.0303 (5)	0.2788 (4)	0.0628
B(5)	0.4456 (7)	0.1503 (5)	0.1937 (3)	0.0518
B(6)	0.4968 (7)	-0.0067 (5)	0.1755 (3)	0.0509
C(1)	0.2652 (6)	0.3722 (5)	0.0721 (3)	0.0627
C(2)	0.3617 (6)	0.3630 (5)	0.0803 (4)	0.0810
C(3)	0.2467 (7)	0.4257 (5)	0.0306 (4)	0.0855
C(4)	0.2205 (7)	0.3975 (5)	0.1184 (4)	0.0892
C(5)	0.2706 (6)	0.1332 (5)	-0.0747 (3)	0.0545
C(6)	0.3668 (6)	0.1273 (6)	-0.0676 (3)	0.0865
C(7)	0.2490 (7)	0.1888 (6)	-0.1127 (3)	0.0868
C(8)	0.2307 (7)	0.0593 (5)	-0.0881 (3)	0.0940
C(9)	0.0380 (7)	0.1349 (5)	0.0798 (3)	0.0705
C(10)	0.1241 (14)	0.1202 (11)	0.1038 (7)	0.0747
C(11)	0.0068 (14)	0.0599 (9)	0.0526 (7)	0.0827
C(12)	-0.0356 (12)	0.1651 (11)	0.1109 (7)	0.0874
C(13)	0.4863 (7)	-0.1235 (5)	0.2535 (4)	0.0684
C(14)	0.5807 (8)	-0.1065 (6)	0.2643 (4)	0.1061
C(15)	0.4395 (8)	-0.1468 (6)	0.2991 (4)	0.1030
C(16)	0.4773 (8)	-0.1812 (5)	0.2140 (4)	0.0975
C(17)	0.4826 (6)	0.1029 (4)	0.0946 (3)	0.0442
C(18)	0.4355 (6)	0.1711 (5)	0.0785 (3)	0.0685
C(19)	0.5772 (6)	0.1172 (6)	0.1025 (3)	0.0782
C(20)	0.4691 (7)	0.0420 (5)	0.0583 (3)	0.0752
C(21)	0.2752 (6)	0.1228 (5)	0.2555 (4)	0.0717
C(22)	0.2385 (14)	0.0738 (13)	0.2161 (8)	0.0701
C(23)	0.2470 (13)	0.1980 (11)	0.2282 (8)	0.0976
C(24)	0.2463 (13)	0.1287 (13)	0.3079 (7)	0.1007
C(X1)	0.0166 (19)	0.1794 (17)	0.1292 (11)	0.0261
C(X2)	-0.0330 (21)	0.0799 (19)	0.0672 (12)	0.0214
C(X3)	0.1294 (21)	0.0991 (15)	0.0864 (11)	0.0274
C(Y1)	0.2403 (27)	0.0506 (21)	0.2338 (12)	0.0174
C(Y2)	0.2504 (24)	0.2047 (20)	0.2599 (11)	0.0357
C(Y3)	0.2508 (22)	0.0824 (16)	0.3056 (12)	0.0269

Table 2. Bond distances (Å) and angles (°)

S(1)—B(1)	1.917 (9)	S(1)—C(1)	1.865 (9)
S(1)—B(3)	1.926 (10)	S(2)—C(5)	1.855 (8)
S(2)—B(1)	1.932 (10)	S(3)—C(9)	1.898 (8)
S(2)—B(2)	1.934 (10)	S(4)—C(13)	1.873 (9)
S(3)—B(3)	1.925 (10)	S(5)—C(17)	1.860 (8)
S(3)—B(2)	1.923 (10)	S(6)—C(21)	1.878 (8)
S(4)—B(4)	1.915 (10)	C(5)—C(6)	1.513 (11)
S(4)—B(6)	1.931 (10)	C(5)—C(7)	1.504 (12)
S(5)—B(5)	1.899 (10)	C(5)—C(8)	1.533 (12)
S(5)—B(6)	1.923 (10)	C(9)—C(10)	1.519 (21)
S(6)—B(4)	1.973 (10)	C(9)—C(11)	1.536 (18)
S(6)—B(5)	1.978 (10)	C(9)—C(12)	1.640 (19)
C(1)—C(2)	1.527 (12)	C(9)—C(X1)	1.628 (31)
C(1)—C(3)	1.547 (12)	C(9)—C(X2)	1.534 (36)
C(1)—C(4)	1.532 (12)	C(9)—C(X3)	1.576 (33)
B(1)—S(1)—B(3)	103.3 (4)	S(1)—B(1)—S(2)	103.0 (5)
B(1)—S(2)—B(2)	104.3 (4)	S(2)—B(2)—S(3)	110.8 (5)
B(2)—S(3)—B(3)	110.9 (4)	S(3)—B(3)—S(1)	111.1 (5)
B(4)—S(4)—B(6)	105.4 (5)	S(4)—B(4)—S(6)	109.0 (5)
B(5)—S(5)—B(6)	104.4 (4)	S(5)—B(5)—S(6)	109.0 (5)
B(4)—S(6)—B(5)	109.4 (5)	S(4)—B(6)—S(5)	102.6 (5)
C(1)—S(1)—B(1)	104.4 (4)	C(13)—S(4)—B(4)	103.3 (5)
C(1)—S(1)—B(3)	105.6 (4)	C(13)—S(4)—B(6)	106.4 (4)
C(5)—S(2)—B(1)	105.0 (4)	C(17)—S(5)—B(5)	103.0 (4)
C(5)—S(2)—B(2)	105.1 (4)	C(17)—S(5)—B(6)	105.8 (4)
C(9)—S(3)—B(2)	111.6 (4)	C(21)—S(6)—B(4)	112.2 (4)
C(9)—S(3)—B(3)	111.5 (4)	C(21)—S(6)—B(5)	111.9 (4)
C(2)—C(1)—S(1)	107.1 (6)	C(10)—C(9)—S(3)	113.4 (10)
C(3)—C(1)—S(1)	110.8 (6)	C(11)—C(9)—S(3)	103.6 (8)
C(4)—C(1)—S(1)	106.1 (6)	C(12)—C(9)—S(3)	102.2 (8)
C(6)—C(5)—S(2)	106.7 (6)	C(X1)—C(9)—S(3)	107.3 (12)
C(7)—C(5)—S(2)	111.1 (6)	C(X2)—C(9)—S(3)	107.9 (12)
C(8)—C(5)—S(2)	106.6 (6)	C(X3)—C(9)—S(3)	108.6 (13)
C(14)—C(13)—S(4)	111.2 (7)	C(22)—C(21)—S(6)	113.9 (7)
C(15)—C(13)—S(4)	107.3 (7)	C(23)—C(21)—S(6)	105.2 (8)
C(16)—C(13)—S(4)	104.6 (7)	C(24)—C(21)—S(6)	105.8 (8)
C(18)—C(17)—S(5)	106.0 (6)	C(Y1)—C(21)—S(6)	110.9 (13)
C(19)—C(17)—S(5)	112.4 (6)	C(Y2)—C(21)—S(6)	104.6 (13)
C(20)—C(17)—S(5)	105.2 (5)	C(Y3)—C(21)—S(6)	102.9 (13)

Fig. 1. ORTEP (Johnson, 1965) view and labelling scheme for the [(Bu'S)BH₂]₃ trimer. Only one set of CH₃ groups is shown for the disordered Bu' group [C(9)].Fig. 2. The orientation of the Bu' groups relative to the B₃S₃ 'chairs' in the two independent molecules.

(Trefonas, Mathews & Lipscomb, 1961) and the boron-phosphorus ring in [(CH₃)₂PBH₂]₃ (Hamilton, 1955). The B—S distances range from 1.899 (10) to 1.978 (10) Å, with a mean value of 1.931 (7) Å. This distance is considerably longer than the B—S distance (1.82 Å) in the trimeric (BrBS)₃ compound containing the cyclic B₃S₃ core (Zronkova, 1959). It should be noted, however, that the latter is a rather inaccurate structure and the B—S values are highly uncertain. (BrBS)₃ is the only other crystallographically characterized compound which contains a similar but apparently not identical B₃S₃ core (the B₃S₃ ring was found to be planar). The average B—S bonds in [(Bu'S)BH₂]₃ are also longer than the ones found for the cyclic B₈S₁₆ (Krebs & Hürter, 1980) which has a porphyrin-like structure, B—S 1.805 (11) Å [range 1.789 (3)–1.822 (3) Å] and polymeric BS₂ (Krebs & Hürter, 1981) with B—S = 1.802 (13) Å. This increase by ~0.13 Å is as expected for going from bridging sulfide to bridging mercaptide ligands.

The disposition of the Bu' groups relative to the B₃S₃ chair ring is identical in both [(Bu'S)BH₂]₃ molecules.

Two Bu' groups in each of the two independent molecules occupy equatorial positions [groups attached to S(1), S(2) and S(4), S(5)]. The third Bu' group in each of the two molecules occupies an axial position [on S(3) and S(6)]. The orientation of these groups is depicted in Fig. 2. This arrangement of the Bu' substituents apparently is a solid-state effect. In solution and at room temperature the Bu' groups are indistinguishable and only a single ^1H NMR resonance is observed in CH_2Cl_2 solution with a δ value of 2.01.

The B—S—B angles range from 103.3 (4) to 110.9 (4)°. The S—B—S angles range from 102.6 (5) to 111.1 (5)°. The disposition of the Bu' groups (axial *vs* equatorial, Fig. 2) seems to affect the magnitude of the B—S—B and S—B—S angles in a systematic fashion. The B—S—B angles adjacent to the axially-disposed Bu' groups in each of the two independent molecules [at 110.9 (4) and 109.4 (5)° respectively for B(2)—S(3)—B(3) and B(4)—S(6)—B(5)] are significantly larger than the B—S—B angles associated with the equatorial Bu' groups. The latter are found at 103.3 (4) and 104.3 (4)° and at 104.4 (5) and 105.4 (4)° in the two independent molecules.

In a similar systematic fashion, the S—B—S angles opposite to the S atoms with axial Bu' groups [S(1)—B(1)—S(2) and S(4)—B(6)—S(5), Fig. 2] are small [103.0 (5) and 102.6 (5)°]. In contrast, the remaining S—B—S angles are larger with values of

110.8 (5), 111.1 (5), 109.0 (5) and 109.0 (5)° (Table 2).

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1,6-Dimethyl-1 α ,4 α ,4 α ,5 α ,8 β ,8 $\alpha\alpha$ -hexahydro-1,4-methanonaphthalene-5,8-diol

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Abstract. $\text{C}_{13}\text{H}_{18}\text{O}_2$, $M_r = 206.26$, monoclinic, $P2_1/c$, $a = 9.830$ (2), $b = 9.618$ (3), $c = 12.584$ (4) Å, $\beta = 111.29$ (2)°, $V = 1108.5$ (6) Å³, $Z = 4$, $D_x = 1.24$ Mg m⁻³, D_m not measured, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å, $\mu = 0.61$ mm⁻¹, $F(000) = 448$, $T = 295$ K, $R = 0.077$ for 1252 unique observed data. The X-ray study showed that the hydroxyl groups are on the same side of the six-membered ring and also showed the relative positions of the two methyl groups. There is a *cis* junction between the two six-membered rings, both of which are in a boat conformation. There is one intramolecular OH...O hydrogen bond (O...O =

2.82 Å) and one intermolecular OH...O hydrogen bond (O...O = 2.80 Å).

Introduction. A study of the Diels–Alder reaction of substituted cyclopentadienes with substituted *p*-benzoquinones has been undertaken as part of a program that involves the synthesis of novel substituted polycyclic 'cage' molecules (Marchand, Suri, Earlywine, Powell & van der Helm, 1984; Marchand, 1987). Thermolysis of methylcyclopentadiene dimer affords a mixture of 1- and 2-methylcyclopentadienes (Csicsery, 1960). Diels–Alder cycloaddition of this diene mixture to 2-methyl-