Journal of

The Chemical Society,

Chemical Communications

NUMBER 16/1974 21 AUGUST

Preparation and Crystallographic Characterization of $(B_9H_8S)_2$ Thiaboranes

By WAYNE R. PRETZER and RALPH W. RUDOLPH*

(*Department of Chemistry, University of Michigan, Ann Arbor, Michigan* 48104)

Summary The pyrolysis of $B_9H_{11}S$ gives three isomeric forms of $(B_9H_8S)_2$ among the products; *X*-ray crystallography established the structure of one isomer to be $2,2'$-$(1\text{-}B_9H_8S)_2$ and allows the other two isomers to be identified as $2,6'$-$(1\text{-}B_9H_8S)_2$ and $6,6'$-$(1\text{-}B_9H_8S)_2$ from ^{11}B n.m.r. evidence.

WE report the synthesis of $(B_9H_8S)_2$ thiaboranes and a single-crystal *X*-ray analysis of $2,2'$-$(1\text{-}B_8H_8S)_2$, the first for a non-metallo heteroborane other than a carborane. The analysis revealed two *closo* thiaborane units joined by a 2-centre B–B bond. Although other reports have appeared describing various borane and heteroborane cages joined by such a 2-centre bond,[1,2] only the characterization of the *nido* bis-pentaborane $1,1'$-$(B_5H_8)_2$ includes an *X*-ray structure.[1]

Analysis by g.c. and m.s. showed that three of the six possible $(1\text{-}B_9H_8S)_2$ isomers are produced in 5% yield as side products during the pyrolytic conversion of $B_9H_{11}S$ into B_9H_9S. Separation of the $2,2'$-isomer from the others was accomplished by elution with heptane–chloroform (9:1) on preparative silica gel t.l.c. plates. The ^{11}B n.m.r. spectrum at 70·6 MHz shows three regions of resonance; a low field doublet of intensity 2 at $-71·5$ p.p.m., several overlapping doublets and a singlet of composite intensity 8 centred around $+5$ p.p.m., and two overlapping doublets each of intensity 4 at $+18·2$ and $+19·2$ p.p.m., relative to $BF_3{\cdot}OEt_2$. These data are very similar to those for $1\text{-}B_9H_9S$ for which an Archimedean antiprism skeleton is proposed.[4] The chemical shift of the singlet suggests either the $6,6'$- or $2,2'$-isomer of $(1\text{-}B_9H_8S)_2$; the *X*-ray study resolves this in favour of the $2,2'$-isomer and provides the first unequivocal structural data for a non-metallo thiaborane.

Crystal data: $2,2'$-$(1\text{-}B_9H_8S)_2$ crystallizes from CH_2Cl_2 as monoclinic crystals (m.p. 159·5—161·0°) with unit cell dimensions $a = 12·184(4)$, $b = 9·777(3)$, $c = 6·601(1)$ Å, and $\beta = 95·72(2)°$, space group $P2_1/n$. The observed density of $1·166\ g\ cm^{-3}$ (flotation method using water and KCl) agrees well with that calculated for 2 molecules per unit cell ($1·165\ g\ cm^{-3}$) so that the centre of symmetry in each molecule resides at a special position. The structure was solved using Patterson and Fourier difference methods and refined to a residual *R* factor of 0·041 using all 1140 reflections

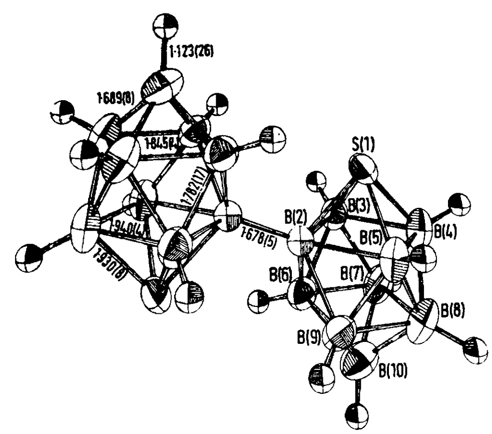

FIGURE. ORTEP plot depicting the molecular structure and thermal ellipsoids for $2,2'$-$(1\text{-}B_9H_8S)$. All terminal hydrogens are included. The skeletal-atom symbol and atom-numbering convention is given on one half of the molecule, while selected interatomic distances (Å) are given on the other, symmetry equivalent, half.

collected. The final least-squares cycle included refinement of the overall scale factor, all positional parameters, anisotropic temperature factors for sulphur and boron, and isotropic temperature factors for hydrogen. The final Fourier difference map was very flat and indicated no missing or misplaced atoms. No correction for absorption was made. The molecular structure is shown in the Figure which also includes representative bond lengths. Of interest are the B–S distances and the B–B bond lengths occuring between the boron atoms of the belt adjacent to the sulphur atom. The B–S distance is shorter than the average B–S bond length of 2·02(5) reported for the metallo thiaborane $[(C_2H_5)_3P]_2Pt(H)B_9H_{10}S$.[5] The upper belt B–B bond lengths are somewhat larger than typical for polyhedral boranes, in particular, 10-vertex *closo* cages, perhaps accounting for the observed easy nucleophilic attack by methoxide and amines on the parent B_9H_9S [whose bond lengths should not vary significantly from those in $(B_9H_8S)_2$.] The B–B bond coupling the two B_9H_8S units is 1·678(5) Å, slightly shorter than the 1·74(6) Å B–B distance joining the two pyramids of 1,1′-$(B_5H_8)_2$.

With the structure of $(B_9H_8S)_2$ established, n.m.r. assignments for 1-B_9H_9S and similar molecules are readily apparent. The belts of 4 boron atoms numbered 2,3,4,5 and 6,7,8,9 (Figure) give signals in the +5 and +18 p.p.m. regions, respectively. ^{11}B n.m.r. spectra also show that the other two isomers isolated from the $B_9H_{11}S$ pyrolysis are 2,6′- and 6,6′-(1-$B_9H_8S)_2$.†

We thank the National Science Foundation for support, Marianna Strumpel for assistance with the *X*-ray analysis, and Lee Todd (Indiana University) for the 70·6 MHz n.m.r. spectra.

(*Received*, 29*th April* 1974; *Com.* 472.)

† The singlets expected in the +6 and +18 p.p.m. regions for the 2,6′-isomer and in the +18 p.p.m. region for the 6,6′-isomer could not be restored because of coincidence with doublet features of the spectra; however, 2,6′-(1-$B_9H_8S)_2$ exhibits two low-field doublets, each of intensity 1, at −72·2 and −69·5 p.p.m. (axial borons coupled to hydrogen), and the 6,6′-isomer gives a doublet of intensity 2 at −72·5 p.p.m.

[1] R. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U.S.A.*, 1961, **46**, 996.
[2] D. F. Gaines, T. V. Iorns, and E. N. Clevenger, *Inorg. Chem.*, 1971, **10**, 1096; J. Dobson, R. Maruca, and R. Schaeffer, *ibid.*, 1970, **9**, 2161; R. J. Wiersema and M. F. Hawthorne, *ibid.*, 1973, **12**, 785; 1969, **8**, 2074.
[3] W. R. Pretzer and R. W. Rudolph, *J. Amer. Chem. Soc.*, 1973, **95**, 931.
[4] R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, 1972, **11**, 1974.
[5] A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 2571.