A New Heteroborane, 1-Thia-*closo*-decaborane(9), B_9H_9S

Sir:

Various authors have recently emphasized the classification of known heteroboranes in terms of the number of electrons which are assignable to the framework bonding.[1,2] Such classification led to a prediction of the existence of B_9H_9S as a new closo[3] heteroborane with a bicapped Archimedean antiprism structure.[1] We wish to report a verification of this prediction with the synthesis and characterization of the subject thiaborane. The only previous report of closo thiaboranes is that for two B-substituted phenyl derivatives of the parent $B_{11}H_{11}S$, most likely icosahedral molecules, although structural characterization was not definitive.[4]

The preparation of 1-thia-*closo*-decaborane(9) was effected by pyrolysis of $B_9H_{11}S$[4] at 375° *in vacuo*. The desired product was conveniently separated from the small amount of unreacted $B_9H_{11}S$ in the volatile pyrolysate by conversion of the latter to $(C_2H_5)_3N \cdot B_9H_{11}S$ followed by vacuum sublimation at 30–40° to give a 50% yield of pure 1-B_9H_9S (mp 216.5–217.0°. *Anal.* Calcd: B, 70.31; H, 6.56; S, 23.15. Found: B, 70.47; H, 6.39; S, 22.96). The low-resolution mass spectrum shows typical boron envelopes;[5] the parent-peak profile is the most intense feature with a cutoff at *m/e* 140 corresponding to $^{11}B_9{}^1H_9{}^{32}S_1{}^+$ and a weaker cutoff in the correct relative intensity to correspond to $^{11}B_9{}^1H_9{}^{34}S_1{}^+$ at *m/e* 142. The infrared spectrum exhibits peaks at 2600 vs, 2560 vs, 1011 w, 972 m, sh, 958 s, 910 w, sh, 902 m, 873 vw, 810 s, 750 w, sh, 738 m, 721 m, 685 s, 660 w, 610 s, 603 s, and 532 m in the 4000–250-cm^{-1} region (KBr disk; s = strong, m = medium, w = weak, sh = shoulder, v = very).

The ^{11}B nmr spectrum of 1-B_9H_9S in benzene is identical in appearance at 32.1 and 70.6 MHz,[6] consisting of doublets at −74.5 (171), 4.8 (178), and 17.6 (152) ppm [chemical shifts are relative to external $BF_3 \cdot O(C_2H_5)_2$ followed by coupling constants (hertz) in parentheses] in intensity ratios of 1.0:4.1:4.0, respectively. These data are entirely consistent with an axial placement of the sulfur atom in the bicapped Archimedean antiprism structure of C_{4v} symmetry shown in Figure 1. The other possible isomer of thiadecaborane consistent with the structural trends evident among heteroboranes[1,3] places the sulfur in an equatorial site (C_s symmetry, 2 position of Figure 1) and would be expected to give a ^{11}B nmr spectrum with six doublets, three of intensity one and three of intensity two.

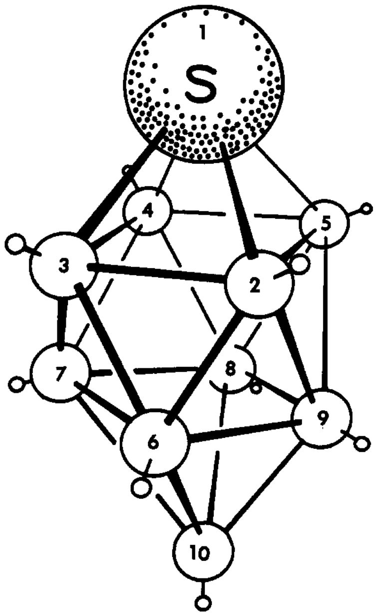

Figure 1. Proposed structure for 1-thia-*closo*-decaborane(9).

In a given heteroborane, the borons with a lower coordination number have been noted to give lower field resonance signals.[5] The axial boron in 1-B_9H_9S occupies a low-coordination site; however, the low-field shift is unexpectedly large, 50.2 ppm further than the lowest field resonance in any other reported thiaborane[7] and 44.6 ppm further than that in any other reported deltahedral borane.[7] Since deltahedral boranes[1] have sometimes been termed "superaromatic,[8,9]" it is tempting to try to relate this low-field shift to ring-current effects similar to those described for various aromatic organic molecules.[10,11] The present effect operates in the wrong direction to be ascribed to such diamagnetic currents. Also, the paramagnetic contribution is usually thought to be dominant in determining ^{11}B chemical shifts.[12] Based on molecular orbital considerations,[13] we feel that the paramagnetic contribution for the axial borons is larger than that for the other boron environments in the related molecules $B_{10}H_{10}{}^{2-}$, 1-$B_9CH_{10}{}^-$, and 1-B_9H_9S, but the axial-boron contribution is unusually large in the case of the thiaborane.

Pure 1-B_9H_9S is a volatile white solid with a distinctly "sweet" odor not unlike that of carborane and exhibiting no repulsive "sulfur" smells. The closo structure of the molecule seems to render it remarkably robust in comparison to nido[3] thiaboranes. It is reasonably air-stable with decomposition occurring only over a period of several weeks. Dilute and concentrated mineral acids have little short-time effect on 1-B_9H_9S as does aqueous base perhaps because of its lack of solubility in water. However, it does dissolve in a wide variety of organic solvents. Attempts to exploit the potential donor properties of 1-B_9H_9S with

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(1) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, **11**, 1974 (1972).

(2) K. Wade, *Inorg. Nucl. Chem. Lett.*, **8**, 559 (1972); *Chem. Commun.*, 792 (1971).

(3) R. E. Williams, *Inorg. Chem.*, 10, 210 (1971).

(4) W. R. Hertler, F. Klanberg, and E. L. Muetterties, *ibid.*, **6**, 1696 (1967).

(5) R. E. Williams, *Progr. Boron Chem.*, 2, 37 (1970).

(6) We thank Professor R. Schaeffer for the opportunity to use the Indiana University 70.6-MHz spectrometer.

(7) The $B_9H_{11}S$ molecule shows a low-field doublet at −24.3;[4] the unique boron in 1-$B_9H_9CH^-$ appears at −29.9 ppm [W. H. Knoth, *J. Amer. Chem. Soc.*, **89**, 1274 (1967)].

(8) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962).

(9) E. L. Muetterties and W. H. Knoth, *Chem. Eng. News*, **44**, 88 (May 9, 1966).

(10) For example, see J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon, Oxford, 1965.

(11) "Ring current" effects may also account for the rather high-field shift found for the apical borons in the $C_nB_{6-n}H_{10-n}$ series (n = 0–4): T. Onak and J. Spielman, *J. Magn. Resonance*, 3, 122 (1970).

(12) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

(13) W. R. Pretzer and R. W. Rudolph, unpublished results.

assorted Lewis acids and metal carbonyls have thus far met with frustration. The molecule quantitatively consumes 2 mol of sodium in tetrahydrofuran, probably yielding the nido anion $B_9H_9S^{2-}$. Degradation of 1-B_9H_9S is facile in methanolic KOH and gives various air and moisture sensitive thiaborane anions which have thus far eluded very definitive characterization. We feel that such degradation reactions and oxidative closure of the resulting deltahedral fragments[1] portend the isolation of an entire series of new thiaboranes. Such reaction chemistry is now under investigation as is a small yield of a less volatile pyrolysate of $B_9H_{11}S$ which contains a mixture of higher thiaboranes as shown by mass spectral analysis.

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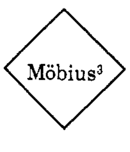
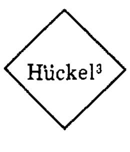
Electron Repulsion in Pericyclic Transition States

Sir:

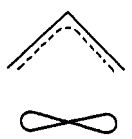
In a recent communication[1] Berson and Salem have shown that subjacent orbital interactions should, in principle, favor concerted "symmetry-forbidden"[2] over purely nonconcerted diradical pathways in certain pericyclic reactions. The one-electron energies of three model transition states for a 1,3-sigmatropic shift were found to be in the order: **1a**, symmetry allowed, aromatic Möbius array[3] ($4\sqrt{2}\beta$) < **1b**, symmetry forbidden, antiaromatic cyclobutadienoid ring (4β) < **1c**, noninteracting allyl plus p, diradical ($2\sqrt{2}\beta$). Berson and Salem point out, however, that "it is not inconceivable that the important two-electron energies characteristic of open shells could reverse, in certain cases, the ordering of the nonconcerted and forbidden transition-state energies."[1] In this communication we investigate the effect of electron repulsion on the relative energies of model aromatic, antiaromatic, and diradical transition states. We show that, in both $4n$ Hückel and $4n + 2$ Möbius "forbidden" transition states, the open-shell electrons can correlate their positions so as to interact with minimal repulsion, thereby making such a reversal of energies unlikely. In contrast, in a planar trimethylenemethane model transition state the open-shell electrons cannot avoid each other, and the large resulting repulsion is responsible for raising the total energy above that of a twisted biradical.



1a



1b



1c

The electron repulsion energies of **1a–c** were calculated from the orbital coefficients using the standard approximation of zero differential overlap.[4] The coefficients were obtained by assuming all β's equal in **1a** and **1b** and a value of zero for the resonance integral between the p and allyl π orbitals in **1c**. The calculated two-electron energies for the *lowest singlet* state of each system are tabulated below, where γ_{11} is the one-center repulsion integral, while γ_{12} and γ_{13} are respectively the repulsion integrals between adjacent and nonadjacent orbitals.

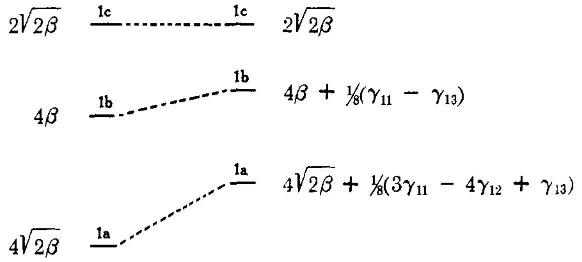
$$\textbf{1a}: \quad \gamma_{11} + 3\gamma_{12} + 2\gamma_{13}$$

$$\textbf{1b}: \quad {}^3/_4\gamma_{11} + {}^7/_2\gamma_{12} + {}^7/_4\gamma_{13}$$

$$\textbf{1c}: \quad {}^5/_8\gamma_{11} + {}^7/_2\gamma_{12} + {}^{15}/_8\gamma_{13}$$

Assuming that the latter two integrals are independent of the orientation of the orbitals involved, the two-electron energies of **1a** and **1b** relative to **1c** are easily computed. Employing typical[5] values of the repulsion integrals, the electron repulsion energy in **1a** is found to be 0.6 eV and in **1b** 1.2 eV *greater* than that in **1c**. The lower two-electron energy of **1c** can be ascribed to the fact that in this system one electron is "isolated." Therefore, it cannot at any time appear simultaneously in a p orbital with an electron of opposite spin.[6]

The most important question now is whether the subjacent orbital stabilization of **1b** relative to **1c** can be reversed by the greater electron repulsion energy present in the former, and the answer depends on the relative values of $(4 - 2\sqrt{2})\beta$ and $^1/_8(\gamma_{11} - \gamma_{13})$. However, even for a conservative value of $\beta = -1.0$ eV the subjacent orbital stabilization of **1b** predominates, and the forbidden concerted transition state model **1b** is lower in total energy than the model for the diradical **1c**. The effect of the one- and two-electron terms in the Hamiltonian on the stability of **1a–c** is shown schematically below.



The dominance of the subjacent orbital effect in determining the relative stability of **1b** and **1c** does not mean that in other systems a reversal of the one-electron energy ordering cannot occur when electron repulsion is included. Comparison of **2a**, a trimethylenemethane model for the transition state in the Woodward–Hoffmann "forbidden" $_\sigma2_s + _\pi2_s$ concerted pathway for the degenerate rearrangement of methylenecyclopro-

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(1) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972).

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(3) H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971).

(4) For a discussion see R. G. Parr, "The Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York, N. Y., 1963.

(5) Calculated for the cyclobutadienoid geometry as suggested by M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969). Any reasonable set of repulsion integrals gives approximately the same quantitative result.

(6) The simultaneous occupancy of an orbital by two electrons of opposite spin is, of course, not prohibited by the Pauli principle and gives rise to ionic terms in the wave function. These terms have high two-electron energy because of the large value of the one-center repulsion integral.