

**Other Complexes.**—Four of the five monomeric complexes isolated in the present work are capable of exhibiting geometric isomerism, but no evidence for such isomerism was found. Changes were sought in the visible absorption spectra of complexes as they were eluted from ion-exchange columns; failure to find such changes does not rule out the existence of isomers, but may be due to the insensitivity of the spectra to variations in structure.

Two other cationic species were observed during the study. One of these was absorbed by cation-exchange resins so tenaciously that it could only be removed by drastic conditions, while the other was eluted with very dilute acid. The former was probably  $\text{RuNO}(\text{H}_2\text{O})_5^{+3}$ ,

since its behavior was similar to that observed for the pentaquo complex in a study of the nitrate complexes of nitrosylruthenium.<sup>9</sup> The second species had an apparent chloride to ruthenium mole ratio of 1.64 and a spectrum different from either the dichloro or the monochloro complex. This species may be a polymeric complex, but we were not able to obtain sufficient quantities for a complete characterization.

**Acknowledgment.**—The authors are indebted to W. R. Cornman and E. G. Orebaugh, who developed and performed the analyses by X-ray fluorescence, to R. N. Wilhite for the infrared spectra, and to D. E. Harrington for the nitrogen analyses.

CONTRIBUTION FROM THE EVANS LABORATORY OF CHEMISTRY,  
THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO

## Boron Heterocycles. II. Reactions of Diborane with Ethanedithiol; Preparation and Properties of 1,3,2-Dithiaborolane<sup>1</sup>

BY B. Z. EGAN, S. G. SHORE, AND J. E. BONNELL

Received November 25, 1963

Depending upon the mole ratio of reactants,  $\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2$ ,  $(\text{CH}_2\text{S})_2\text{BH}$ , and  $(\text{CH}_2\text{S})_2\text{BSCH}_2\text{CH}_2\text{SB}(\text{SCH}_2)_2$  are prepared through the reaction of  $\text{B}_2\text{H}_6$  with  $\text{HSCH}_2\text{CH}_2\text{SH}$  in ether. Infrared spectra indicate that  $\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2$  and  $(\text{CH}_2\text{S})_2\text{BH}$  are not simple, molecular species in the condensed state, but are associated through intermolecular boron-sulfur coordinate bonds. No evidence is observed for hydrogen bridges between boron atoms. In the vapor phase  $(\text{CH}_2\text{S})_2\text{BH}$  is a monomer which does not disproportionate at elevated temperatures (90°). The addition compounds  $(\text{CH}_3)_3\text{NBH}_2\text{SCH}_2\text{CH}_2\text{SBH}_2\text{N}(\text{CH}_3)_3$ ,  $(\text{CH}_2\text{S})_2\text{HBN}(\text{CH}_3)_3$ , and  $(\text{CH}_2\text{S})_2\text{HBP}(\text{CH}_3)_3$  are stable *in vacuo* at room temperature. Oxygen bases such as ether do not cause significant dissociation of boron-sulfur coordinate bonds in  $[\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2]_x$  and  $[(\text{CH}_2\text{S})_2\text{BH}]_x$ .

### Introduction

The present investigation is part of a systematic program to study the preparation and properties of selected boron heterocycles. Of particular interest is the effect of substituent ring atoms on the apparent stability of the heterocycle and the nature of the boron as an electron pair acceptor. A previous investigation<sup>1</sup> showed that the heterocycle 1,3,2-dioxaborolane,  $(\text{CH}_2\text{O})_2\text{BH}$ , is a monomer in the vapor phase. It is a weak Lewis acid which disproportionates readily into more symmetrical species. Although a variety of alkylthioboranes have been reported,<sup>2-5</sup> the effect of sulfur on boron as a Lewis acid and the ability of boron to participate in hydrogen bridge bonds had not been established. In view of these considerations, we have prepared and examined some sulfur-substituted boron compounds which are derived from the reaction of diborane with ethanedithiol.

(1) For I, see S. H. Rose and S. G. Shore, *Inorg. Chem.*, **1**, 744 (1962).

(2) B. M. Mikhailov and T. A. Shchegoleva, *Izv. Akad. Nauk SSSR Old. Khim. Nauk*, 1868 (1959).

(3) B. M. Mikhailov and T. A. Shchegoleva, *Dokl. Akad. Nauk SSSR*, **131**, 843 (1960).

(4) T. A. Shchegoleva and E. M. Belyavskaya, *ibid.*, **136**, 638 (1961).

(5) B. M. Mikhailov, T. A. Shchegoleva, E. M. Shaskova, and V. D. Sheludiyakov, *Izv. Akad. Nauk SSSR, Old. Khim. Nauk*, 1163 (1961).

### Experimental

(A) **Materials.**— $\text{B}_2\text{H}_6$  was obtained from the Callery Chemical Co.; it was purified by trap-to-trap distillation at  $-120^\circ$ .  $\text{HSCH}_2\text{CH}_2\text{SH}$  was obtained from the Aldrich Chemical Co.; it was distilled at room temperature *in vacuo*. Commercial  $\text{N}(\text{CH}_3)_3$  was dried over  $\text{CaH}_2$  and distilled *in vacuo*.  $\text{P}(\text{CH}_3)_3$  was prepared by treating  $\text{CH}_3\text{MgI}$  in ether with  $\text{PCl}_3$ .<sup>6</sup> It was isolated as the solid  $((\text{CH}_3)_3\text{P}(\text{AgI}))_4$  complex. Gaseous  $\text{P}(\text{CH}_3)_3$  was obtained by heating the solid, anhydrous complex to  $100^\circ$  *in vacuo*.  $(\text{C}_2\text{H}_5)_2\text{O}$  and tetrahydrofuran were distilled from  $\text{LiAlH}_4$  *in vacuo*.

(B) **Apparatus.**—Standard high vacuum techniques were used for handling air-sensitive materials.<sup>7</sup> Outside of the vacuum line, these materials were handled in a drybox under a dry nitrogen atmosphere. The reaction system depicted in Fig. 1 was used for preparing large quantities (30–50 mmoles) of  $\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2$ ,  $(\text{CH}_2\text{S})_2\text{BH}$ , and  $(\text{CH}_2\text{S})_2\text{BSCH}_2\text{CH}_2\text{SB}(\text{SCH}_2)_2$ . The 2-l. metal bulb was of sufficient volume to accommodate gaseous reactants and products; the system could be closed off at the valve and removed from the vacuum line to a safety area where the reaction was allowed to take place. Perkin-Elmer Models 21, 221-g, and 337 recording spectrophotometers were used to obtain infrared spectra. The instruments were calibrated with polystyrene. Mass spectra were obtained on a Consolidated Engineering Model 21-32 mass spectrometer.

(C) **Ethylenedithiobisborane.** (1) **Synthesis.**— $\text{H}_2\text{BSCH}_2$ -

(6) F. G. Mann and A. F. Wells, *J. Chem. Soc.*, 1829 (1937).

(7) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

TABLE I

## INFRARED FREQUENCIES OF SOME COMPOUNDS CONTAINING BORON-SULFUR BONDS

$\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2(\text{s})$		$(\text{CH}_3)_3\text{NBH}_2\text{SCH}_2\text{CH}_2\text{SBH}_2\text{N}(\text{CH}_3)_3(\text{s})$		$(\text{CH}_2\text{S})_2\text{BH}(\text{s})$		$(\text{CH}_2\text{S})_2\text{BHN}(\text{CH}_3)_3(\text{s})$		$(\text{CH}_2\text{S})_2\text{BHP}(\text{CH}_3)_3(\text{s})$	
cm. <sup>-1</sup>	I (rel.) <sup>a</sup>	cm. <sup>-1</sup>	I (rel.) <sup>a</sup>	cm. <sup>-1</sup>	I (rel.) <sup>a</sup>	cm. <sup>-1</sup>	I (rel.) <sup>a</sup>	cm. <sup>-1</sup>	I (rel.) <sup>a</sup>
3195	m	2992	w	2915	w, sp	2940	w	2930	w, sp
2920	w	2923	m	2849	w	2710	w	2365	m
2460	s	2367	s	2435	s	2414	w	1417	s
2409	s	2277	w			1525	sh	1310	m
1412	s	1482	s			1515	sh	1289	m
1279	w	1457	s	1475	sh	1477	sh	1147	br
1249	m	1397	w	1460	sh	1460	sh	1095	w
1191	w	1247	m	1380-1415	s, br	1400-1415	s, br	1013	w, br
1144	s	1188	w	1210-1270	s	1378	w	945	s
1134	s	1134	m	1155	w	1310-1325	s, br	918	sh
1048	s	1120	s	1120	w	1270	sh	848	m, sp
1028	s	1073	s	978	s	1255	w	763	w, sp
981	s	1015	w	937	w	1210	sh	703	w, br
946	sh	982	m	891	w	1165-1155	w, br		
834	s	962	w	836	m	1128	w, sp		
695	w	833	s	729	m	1082	sp		
658	w	705	m	660	w	910-925	w, br		
		668	m			832	w		
						782	w		

<sup>a</sup> s, strong; m, medium; w, weak; br, broad; sp, sharp; sh, shoulder.

$\text{CH}_2\text{SBH}_2$  was prepared in  $(\text{C}_2\text{H}_5)_2\text{O}$  and pentane. Best samples were isolated from ether in which  $\text{B}_2\text{H}_6$  was in excess by 50 mole %. Small-scale runs using 2-4 mmoles of  $\text{HSCH}_2\text{CH}_2\text{SH}$  were carried out in order to establish the reaction stoichiometry from hydrogen evolution and recovery of excess diborane (see eq. 1). In a typical large-scale run, about 75 ml. of anhydrous ether was condensed in the reaction system (Fig. 1). A 25-mmole quantity of  $\text{HSCH}_2\text{CH}_2\text{SH}$  was distilled on top of the ether and the mixture was stirred at room temperature for several minutes to ensure homogeneity. A 38-mmole quantity of  $\text{B}_2\text{H}_6$  was then condensed in the reaction tube and the system was allowed to warm up, with continuous stirring, from  $-78^\circ$  to room temperature over a period of approximately 10 hr. During the reaction a white solid separated from solution. After  $\text{H}_2$  evolution ceased, ether was distilled from the system at  $-40^\circ$ , leaving behind the white, solid, crystalline product. The last traces of solvent were removed by pumping on the product for several hours at room temperature.

*Anal.* Calcd. for  $\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2$ : H (hydridic), 3.42; B, 18.35. Found: H (hydridic), 3.28; B, 18.5.

The infrared spectrum of  $\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2$  is given in Table I. Ethylenedithioborane is insoluble in common organic solvents. Although its solubility in tetrahydrofuran is slight, it is even less soluble in ether.

(2) **Pyrolysis.**— $\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2$  decomposes *in vacuo* at  $70^\circ$ . A 1.32-mmole quantity was pyrolyzed at  $85-95^\circ$  for about 2.5 hr. Diborane, 0.53 mmole, and  $(\text{CH}_2\text{S})_2\text{BH}$  were formed. The pyrolysis products were identified from their infrared spectra. Only a trace quantity of  $\text{H}_2$  was produced.

(3) **Trimethylamine Adduct.**—A 0.44-mmole sample of  $\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2$  was placed in a tube on the vacuum line and a measured tenfold excess of  $\text{N}(\text{CH}_3)_3$  was condensed above the solid. The system was allowed to stand at  $0^\circ$  for 3 days. Excess  $\text{N}(\text{CH}_3)_3$  was then distilled away at room temperature, leaving behind 0.92 mmole of amine in the addition compound ( $\text{N}(\text{CH}_3)_3:\text{BH}_2 = 1.04$ ). The product,  $(\text{CH}_3)_3\text{NBH}_2\text{SCH}_2\text{CH}_2\text{SBH}_2\text{N}(\text{CH}_3)_3$ , proved to be a stable, nonvolatile, solid at room temperature *in vacuo*. An improved synthesis involved adding excess  $\text{N}(\text{CH}_3)_3$  to a suspension of  $\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2$  in tetrahydrofuran and stirring for 3 days at  $0^\circ$ .

The infrared spectrum of  $(\text{CH}_3)_3\text{NBH}_2\text{SCH}_2\text{CH}_2\text{SBH}_2\text{N}(\text{CH}_3)_3$  is given in Table I.

(D) **1,3,2-Dithiaborolane.** (1) **Synthesis.**—Pure  $(\text{CH}_2\text{S})_2\text{BH}$  was prepared in  $(\text{C}_2\text{H}_5)_2\text{O}$  and pentane. Best samples were prepared in ether in which the mole ratio of reactants was main-

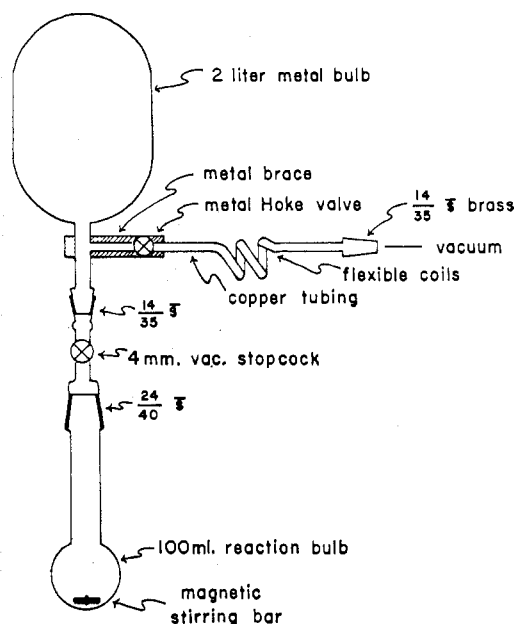


Fig. 1.—Reaction system.

TABLE II  
MASS SPECTRUM OF  $(\text{CH}_2\text{S})_2\text{BH}$ 

<i>m/e</i>	Rel. abundance	<i>m/e</i>	Rel. abundance	<i>m/e</i>	Rel. abundance
104	33.63	59	17.18	33	4.09
103	13.18	58	10.36	32	6.91
77	4.18	57	4.91	28	6.72
76	22.90	47	6.50	27	18.72
75	11.18	46	6.81	26	8.27
62	4.36	45	22.70	11	10.87
61	5.00	44	4.54		
60	100.00	34	7.18		

tained at  $2\text{HSCH}_2\text{CH}_2\text{SH}:\text{B}_2\text{H}_6$ . Small-scale runs using 2-4 mmoles of  $\text{HSCH}_2\text{CH}_2\text{SH}$  were carried out in order to establish the reaction stoichiometry from hydrogen evolution (see eq. 2.). Large-scale runs using approximately 50-mmole quantities of  $\text{B}_2\text{H}_6$  were carried out in the apparatus shown in Fig. 1. The

procedure used was identical with that employed for the synthesis of  $H_2BSCH_2CH_2SBH_2$ . The isolated product was purified by sublimation *in vacuo* at 55°.

*Anal.* Calcd. for  $(CH_2S)_2BH$ : H (hydridic), 0.97; B, 10.40. Found: H (hydridic), 0.93; B, 10.4.

(2) **Physical Properties.**— $(CH_2S)_2BH$  is a white crystalline solid which shows little solubility in common organic solvents. Although its solubility in tetrahydrofuran is small, it is larger than that in ether.

The molecular weight of  $(CH_2S)_2BH$  was determined in the vapor phase by the Dumas method at 82.3° and 40 mm. pressure, and by a Graham's law experiment which measured the relative rate of effusion of the gas through a pinhole at room temperature.<sup>8</sup> The latter method was not especially accurate, but gave an order of magnitude of the molecular weight, indicating a monomeric material in the vapor phase at room temperature.

*Anal.* Calcd. for  $(CH_2S)_2BH$ : mol. wt., 104. Found: mol. wt. (vapor density),  $107 \pm 3$ ; mol. wt. (effusion), 99.

Mass-to-charge ratios in the mass spectrum of  $(CH_2S)_2BH$  are given in Table II. The parent mass is 104.

The vapor pressure of  $(CH_2S)_2BH$  was determined in an apparatus similar to the one described by Brown, Taylor, and Gerstein.<sup>9</sup> Although  $(CH_2S)_2BH$  sublimes *in vacuo*, liquid-vapor equilibrium is achieved by allowing the vapor to condense on the warm (40° or higher) walls of the system. The liquid can exist at room temperature for several days before it eventually crystallizes. Temperature and pressure readings for the liquid-vapor equilibrium were taken over the temperature range 303–333°K. A plot of  $\log p$  vs.  $1/T$  was linear, allowing the data to be reduced to the equation:  $\log p = -2.46 \times 10^3/T + 8.86$ . The heat of vaporization was found to be  $11.3 \pm 0.1$  kcal./mole.

An infrared spectrum of the vapor was obtained by placing a small amount of sample in a 10-cm. gas cell and warming the cell in order to vaporize the solid. Care was taken to prevent condensation of solid on the cell windows. In view of the low gas pressure in the cell (15 mm. estimated), only the predominant features of the spectrum were observed. The important difference between the vapor spectrum and the solid spectrum was a shift in the B–H stretching frequency from 2435  $cm^{-1}$  (solid) to a sharp intense peak at 2595  $cm^{-1}$  (vapor). No evidence for B–H–B bridge absorptions were observed in the vapor. B–H–B bridge absorptions occur at 1618, 1603, and 1585  $cm^{-1}$  in  $B_2H_6$ .<sup>10,11</sup> In general, such absorptions are strong; they are the most intense features of the  $B_2H_6$  spectrum and can be observed at a pressure of less than 1 mm. in a 10-cm. cell.

(3) **Trimethylamine Adduct.**—A 3.20-mmole sample of solid  $(CH_2S)_2BH$  was placed in a tube on the vacuum line. Tetrahydrofuran, 10 ml., was condensed onto the solid, resulting in a cloudy suspension. A measured excess of  $N(CH_3)_3$  was distilled onto the suspension and the system was maintained at 0°, with constant stirring, for 3 days. Tetrahydrofuran and unreacted  $N(CH_3)_3$  were distilled from the reaction tube at 0° into a measured excess of aqueous HCl solution, which was then back-titrated with standard NaOH. Stoichiometrically,  $(CH_2S)_2BH$  and  $N(CH_3)_3$  reacted in the mole ratio 1.03:1.

A second procedure for preparing  $(CH_2S)_2BHN(CH_3)_3$  was carried out in the following way: A solution of  $(CH_2S)_2BH$ , 20 mmoles, in 20 ml. of tetrahydrofuran was prepared according to the procedure in section D1. It is of interest to note that although  $(CH_2S)_2BH$  (solid) is only slightly soluble in tetrahydrofuran, an apparently stable solution of  $(CH_2S)_2BH$  results from the reaction of  $B_2H_6$  with  $HSCH_2CH_2SH$  in tetrahydrofuran. An excess quantity of  $N(CH_3)_3$  was condensed into the solution, which was then maintained at 0°, with constant stirring, for 4 hr. The bulk of the tetrahydrofuran and excess  $N(CH_3)_3$  were

distilled from the reaction bulb at 0°. Final traces of liquid were pumped away at room temperature, leaving behind the crystalline, white product.

*Anal.* Calcd. for  $(CH_2S)_2BHN(CH_3)_3$ : H (hydridic), 0.63; N, 8.59. Found: H (hydridic), 0.62; N, 8.35.

Samples prepared from the two procedures gave identical infrared spectra and X-ray powder diffraction patterns.  $(CH_2S)_2BHN(CH_3)_3$  is insoluble in common organic solvents. It is stable *in vacuo* at room temperature and can be sublimed without apparent decomposition. Its infrared spectrum is given in Table I.

(4) **Trimethylphosphine Adduct.**— $(CH_2S)_2BHP(CH_3)_3$  was prepared according to procedures which were identical with those used to prepare  $(CH_2S)_2BHN(CH_3)_3$ .

*Anal.* Calcd. for  $(CH_2S)_2BHP(CH_3)_3$ : H (hydridic), 0.56; B, 6.01. Found: H (hydridic), 0.54; B, 5.94.

$(CH_2S)_2BHP(CH_3)_3$  is a white crystalline solid which is insoluble in common organic solvents. It is stable *in vacuo* at room temperature and can be sublimed without apparent decomposition. Its infrared spectrum is given in Table I.

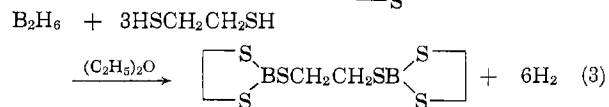
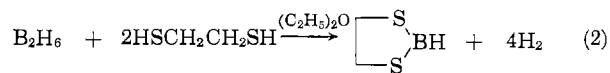
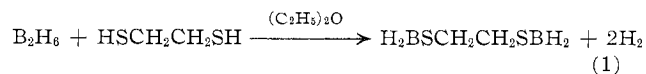
(E) **2,2'-(Ethylenedithio)bis-(1,3,2-dithiaborolane).**— $(CH_2S)_2BSCH_2CH_2SB(SCH_2)_2$  was prepared in ether solution in which the mole ratio of reactants was maintained at  $3H_2SCH_2CH_2SH : B_2H_6$ . Large-scale runs using approximately 50-mmole quantities of  $B_2H_6$  were carried out in the apparatus shown in Fig. 1. The procedure was identical with that employed for the synthesis of  $H_2BSCH_2CH_2SBH_2$ .

*Anal.* Calcd. for  $(CH_2S)_2BSCH_2CH_2SB(SCH_2)_2$ : H (hydridic), 0.00; B, 7.26; S, 64.53. Found: H (hydridic), 0.00; B, 7.30; S, 64.0.

$(CH_2S)_2BSCH_2CH_2SB(SCH_2)_2$  is a white crystalline solid. It is insoluble in common organic solvents.

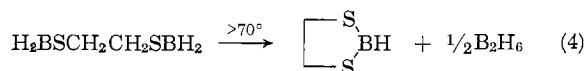
## Results and Discussion

The product formed from the reaction of diborane with 1,2-ethanedithiol depends upon the mole ratio of reactants used.



In several respects the properties of these compounds are markedly different from the characteristics of analogs derived from the ethylene glycol-diborane reaction.

In appearance the ethanedithiol derivatives are crystalline solids at room temperature, while their counterparts derived from ethylene glycol are viscous, glassy substances. Ethylenedithiobisborane,  $H_2BSC_2H_4SBH_2$ , is stable to 70°.



On the other hand,  $H_2BOCH_2CH_2OBH_2$  could not be isolated at room temperature due to apparent instability.<sup>2</sup> 1,3,2-Dithiaborolane has been heated to 90° without significant disproportionation into  $B_2H_6$  and  $(CH_2S)_2BSCH_2CH_2SB(SCH_2)_2$ ; its analog  $(CH_2O)_2BH$  undergoes disproportionation at room temperature.<sup>1</sup>

(8) The authors are indebted to Professor R. C. Taylor of the University of Michigan for the use of this apparatus.

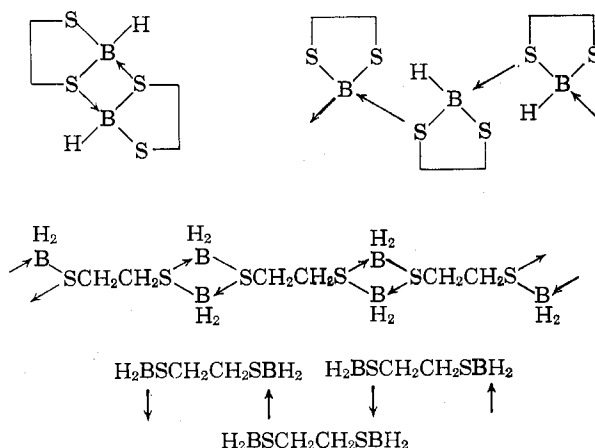
(9) H. C. Brown, M. D. Taylor, and M. Gerstein, *J. Am. Chem. Soc.*, **66**, 431 (1944).

(10) W. C. Price, *J. Chem. Phys.*, **16**, 894 (1948).

(11) W. C. Price, R. D. B. Fraser, T. S. Robinson, and H. C. Longuet-Higgins, *Discussions Faraday Soc.*, **9**, 131 (1950).

These observations parallel reports on  $\text{CH}_3\text{OBH}_2$ <sup>12</sup> and  $\text{CH}_3\text{SBH}_2$ .<sup>13</sup> Both  $(\text{CH}_2\text{S})_2\text{BSCH}_2\text{CH}_2\text{SB}(\text{SCH}_2)_2$  and  $(\text{CH}_2\text{O})_2\text{BOCH}_2\text{CH}_2\text{OB}(\text{OCH}_2)_2$  are stable solids at room temperature.

Molecular weight and mass spectrometric data show that  $(\text{CH}_2\text{S})_2\text{BH}$  is monomeric in the vapor phase. The infrared spectrum of  $(\text{CH}_2\text{S})_2\text{BH}$  vapor shows that the stretching frequency of the terminal B-H bond is  $2595\text{ cm}^{-1}$  (Table I), which is in good agreement with the value for  $(\text{CH}_2\text{O})_2\text{BH}$  vapor.<sup>1</sup> Absorptions corresponding to hydrogen-bridged borons are not observed.<sup>10</sup> Solid  $(\text{CH}_2\text{S})_2\text{BH}$  shows a shift in B-H stretching frequency to  $2435\text{ cm}^{-1}$ . A shift to a lower frequency is a sensitive indication of quaternization of boron.<sup>11</sup> No evidence for hydrogen-bridged borons is observed. The symmetric and asymmetric B-H stretching frequencies,  $2409$  and  $2460\text{ cm}^{-1}$ , of  $\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2$  are sufficiently low to be indicative of quaternary boron. Hydrogen-bridged borons are not observed.<sup>10</sup> In view of these observations, it is reasonable to suggest that in the condensed state quaternization of boron occurs through intermolecular coordinate bonds between boron and sulfur. Possible species are



The physical properties of 1,3,2-dithiaborolane suggest that it can exist in more than one associated form in the condensed state. The liquid form at room temperature might be a relatively low molecular weight species which very slowly polymerizes to form a higher molecular weight solid. A series of polymers has been observed for species of composition  $\text{CH}_3\text{SBH}_2$ .<sup>13,14</sup>

Oxygen bases such as ethers do not appear to cause significant depolymerization. Mikhailov and co-workers<sup>2-5</sup> assign dimeric formulas to  $(n\text{-C}_3\text{H}_7\text{S})_2\text{BH}$  and  $(n\text{-C}_4\text{H}_9)_2\text{BH}$  assuming the existence of hydrogen-bridged boron atoms. However, their experimental

evidence, which is restricted to cryoscopy in benzene, does not necessarily demonstrate the existence of such bonds. We believe that the apparent association of their compound is due to boron-sulfur coordinate bond formation. In fact, in a more recent work,<sup>14</sup> these investigators reported the species  $(\text{CH}_3\text{SBH}_2)_3$  which they assumed to be a six-membered ring containing boron-sulfur coordinate bonds.

The ability of boron, in the boron hydrides, to employ all four of its orbitals in bonding is exemplified by the existence of hydrogen-bridged boron atoms in diborane. Substitution of alkyl groups for terminal hydrogens does not destroy the bridge.<sup>15</sup> On the other hand, substitution by alkoxy groups renders the bridge unstable. Thus dimethoxyborane<sup>10</sup> and 1,3,2-dioxaborolane are monomeric in the vapor phase. If one accepts the "time-honored" rationale that the monomeric character of the latter two species is due to oxygen  $\pi$ -bonding or back bonding with the fourth boron orbital, thereby causing hydrogen-bridge formation to be relatively unfavorable,<sup>14</sup> then it is of interest to consider the ability of sulfur to  $\pi$ -bond with boron. It is expected that sulfur should show less tendency to  $\pi$ -bond with boron than oxygen.<sup>16</sup> Indeed, insofar as chemical shifts in  $\text{B}^{11}$  n.m.r. spectra can be considered to be criteria,  $\pi$ -bonding between boron and sulfur is "nearly absent" in thioborane derivatives.<sup>17</sup> To be consistent with the rationale which accounts for the monomeric character of  $(\text{CH}_2\text{O})_2\text{BH}$ , it would be expected that the near absence of  $\pi$ -bonding between boron and sulfur could lead to hydrogen bridges in  $(\text{CH}_2\text{S})_2\text{BH}$  vapor as a means of employing all four boron orbitals in bonding. Therefore, it is of special interest that this investigation demonstrated the absence of such bridges.

While the monomeric character of  $(\text{CH}_2\text{S})_2\text{BH}$  vapor does not lend credence to  $\pi$ -bonding arguments, the apparent stabilities of the adducts  $(\text{CH}_3)_3\text{NBH}_2\text{-SCH}_2\text{CH}_2\text{SBH}_2\text{N}(\text{CH}_3)_3$ ,  $(\text{CH}_2\text{S})_2\text{BHN}(\text{CH}_3)_3$ , and  $(\text{C}_6\text{H}_5)_2\text{BHP}(\text{CH}_3)_3$  are consistent with such rationale. Substitution of sulfur for oxygen appears to enhance the acceptor character of boron. The oxygen analog  $(\text{CH}_3)_3\text{NBH}_2\text{OCH}_2\text{CH}_2\text{OBH}_2\text{N}(\text{CH}_3)_3$  could not be isolated because of apparent instability.<sup>1</sup> The analog  $(\text{CH}_2\text{O})_2\text{BHN}(\text{CH}_3)_3$  is completely dissociated in the vapor phase,<sup>1</sup> while  $(\text{CH}_2\text{S})_2\text{BHN}(\text{CH}_3)_3$  and  $(\text{CH}_2\text{S})_2\text{-BHP}(\text{CH}_3)_3$  show no tendency to dissociate at room temperature and can be sublimed *in vacuo* without apparent dissociation.

**Acknowledgment.**—We wish to acknowledge, gratefully, the support of this work by the National Science Foundation.

(12) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **55**, 4020 (1933).

(13) A. B. Burg and R. I. Wagner, *ibid.*, **76**, 3307 (1954).

(14) B. M. Mikhailov, T. A. Shegoleva, E. M. Shashkova, and V. D. Sheludyakov, *Izv. Akad. Nauk SSSR, Old. Khim. Nauk*, **7**, 1218 (1962).

(15) F. G. A. Stone, *Quart. Rev. (London)*, **9**, 174 (1955).

(16) A. B. Burg, *J. Chem. Educ.*, **37**, 482 (1960).

(17) M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 1345 (1961).