was dissolved in chloroform, and the infrared spectrum was recorded. A second weighed portion was dissolved in cyclohexane and the ultraviolet and visible spectra were determined. A third portion was redissolved in benzene and examined in the nmr. The singlet at τ 4.92 was still present, showing that removal of the benzene from the original solution did not cause any significant destruction of the intermediate.

In a separate experiment a 0.20 *M* solution of **1b** in benzene, containing a small but known amount of cyclohexane, was also examined in the nmr with time in the same fashion as in the earlier experiment. The integrated intensity of the singlet at τ 4.92 was compared with that of the added cyclohexane.

Kinetic Study of the Decomposition of 1b. Sulfur Dioxide Evolution Method.—The same apparatus and procedure used to follow the decomposition of **1c**[4] was employed.

Nmr Method.—A *ca.* 0.20 *M* solution of **1b** in benzene, to which 1 drop of cyclohexane per 1 ml of solution had been added to serve as an internal proton standard, was transferred to an nmr tube having a constricted neck. The solution was then deaerated, and the tube was finally sealed off under *ca.* 100 mm pressure of prepurified nitrogen. The tube was then transferred to the thermostated nmr probe and the relative intensities of the singlet at τ 5.75 and the cyclohexane standard were determined as a function of time by integration.

Rate of Free-Radical Production in the Decomposition of 1b.—This was followed, using the Koelsch radical[7] as the radical counting reagent, in the same way as for the decomposition of **1c** in the accompanying paper.[4]

Registry No.—**1b,** 23264-06-4.

The Reaction of Diborane and Bistriphenylmethyl Disulfide to Give a Carbon–Sulfur Bond Cleavage

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Diborane has been found to cleave the carbon–sulfur bond in bistriphenylmethyl disulfide to produce triphenylmethane, hydrogen, and $(HBS)_x$ polymer. Triphenylmethyl mercaptan reacted with diborane in benzene solution to yield the identical products. Hydrogen sulfide in benzene solution was found to react with diborane much more rapidly to form the $(HBS)_x$ polymer than previously reported for the vapor-phase reaction. The $(HBS)_x$ polymer prepared by these methods was a white, amorphous solid. No characteristic X-ray powder pattern could be obtained. The infrared spectrum corresponded to that reported in the literature. The elemental analysis and hydridic hydrogen determination confirm the stoichiometry. The ion fragments observed in the mass spectrum are consistent with the proposed formulation. The broad-line nmr of the solid indicated tetrahedral coordination of the boron.

Reactions of boron hydrides with elemental oxygen were studied soon after the discovery of the boron hydrides because of the spontaneous nature of the reaction.[1] This was followed by the study of the reactions with oxygen-containing compounds.[2] The study of the reactions with the analogous sulfur compounds, on the other hand, has lagged. For example, in Steinberg's comprehensive monograph,[3] boron–oxygen chemistry requires some 800 pages compared with 20 pages for boron–sulfur chemistry. Recently, however, interest in boron–sulfur chemistry has been increasing.[4–6]

In general, sulfur compounds do not react so fast as their oxygen analogs. Experience in our laboratories indicates that many organic disulfides are unreactive with diborane at −65°. Because of the relative stability of the sulfur–sulfur bond, it was felt that a preferential sulfur–carbon bond cleavage might be observed by properly selecting the carbon group. Furthermore, it was of interest to see whether the sulfur–sulfur bond might not be a sufficiently weak oxidizing agent that it could coexist in the same molecule with a boron–hydrogen bond.

Experimental Section

Reagents.—The benzene, toluene, and diethyl ether were reagent grade solvents stored in glass over calcium hydride. These were transferred by distillation into the vacuum line as needed.

Diborane.—The diborane was prepared by slowly adding 0.5 g of sodium borohydride to 20 ml of concentrated H_2SO_4. It was purified by distilling successively through a −111° trap and two −126° traps.

Triphenylmethyl Mercaptan.—The compound was used as obtained from the Aldrich Chemical Co.

Bistriphenylmethyl Disulfide.—The method of Vorlander and Mittag[7] which involves the treatment of triphenylmethyl mercaptan in alcoholic alkali solution with sulfuryl chloride was used. The sulfuryl chloride was purified by distilling the practical grade from Matheson Coleman and Bell into glass ampoules. These ampoules were sealed and not reopened until just prior to use.

The product obtained directly from the synthesis was a crystalline material, with mp 155–156°. Recrystallization of the disulfide from benzene, toluene–ethanol, and ether–benzene gave rise to some decomposition products and low recoveries. The disulfide used for all of these experiments was, therefore, unrecrystallized.

Bistriphenylmethyl Tetrasulfide.—The method described by Nakabayashi and coworkers[8] involving the reaction of triphenylmethyl mercaptan with sulfur monochloride was used. The product was recrystallized from chloroform–ethanol.

Reaction of Bistriphenylmethyl Disulfide with Diborane.—The reaction was carried out in an inverted U tube which could be sealed off under vacuum and which also contained a break-off so that it could be opened under vacuum. These tubes varied in size. The standard tubes, which were used for most of the experiments, had legs 300 mm long and 18 mm in diameter. The legs were *ca.* 80 mm apart. At the top, perpendicular to the plane of the inverted U, a 14/35 through joint with a 3-mm extension tube was attached. The volatile contents of the tube could be removed by breaking this 3-mm tube with a tube breaker. An accurately weighed amount of 0.3–0.5 g of bis-

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(1) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1957, p 55.

(2) R. M. Adams, "Boron, Metallo-Boron Compounds and Boranes," Interscience Publishers, Inc., New York, N. Y., 1964, pp 596–603.

(3) H. Steinberg, "Orgaoboron Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1964.

(4) H. Cragg, *Quart. Rept. Sulfur Chem.*, **3**, 1 (1968).

(5) R. W. Kirk and R. L. Timms, *Chem. Commun.*, 18 (1967).

(6) B. F. Spielvogel and E. F. Rothgery, *ibid.*, 765 (1966).

(7) D. Vorlander and E. Mittag, *Chem. Ber.*, **46**, 3453 (1913).

(8) T. Nakabayashi, J. Tsurugi, and T. Yabuta, *J. Org. Chem.*, **29**, 1236 (1964).

triphenylmethyl disulfide was put into one arm of the tube along with a glass-covered iron stirrer (*ca.* 10 × 3 mm. The tube was then placed on the vacuum line and evacuated thoroughly. *Ca.* 10 ml of dry benzene was then transferred into this leg by condensation of the vapor with liquid nitrogen. Diborane was measured in the vacuum line and a quantity in excess of an equimolar amount was added. The reaction tube was then opend to the vacuum while keeping the volatiles frozen with liquid nitrogen. The apparatus was then sealed off. The ratio between the volume of the reaction vessel and the amount of the reagents used was chosen so that the diborane pressure at room temperature would fall roughly in the calculated range of 500–700 mm, neglecting solubility or complexing phenomena. On some runs a small amount of solid failed to go into solution. If solution was not effected after 2 days, the residue was assumed to be an impurity and the liquid was carefully decanted to the other arm of the reaction tube. This precipitate when it occurred was a deep red-brown solid which was estimated to be no more than 1 or 2 mg. By the third or fourth day a white precipitate had started to form. After *ca.* 1 week, the reaction mixture was opened and analyzed. With liquid nitrogen cooling the appropriate arm of the reaction tube, the vessel was opened to the line and the hydrogen was tranferred with a Toepler pump and measured. The tube was then allowed to warm, and the benzene solution was decanted from the precipitate to the opposite leg by swinging the apparatus about the 14/35 joint. All the volatiles were then removed to the vacuum line. By distillation through −63.5 and −126° traps, the benzene was separated from the excess diborane. Triphenylmethane was the major benzene-soluble, nonvolatile product.

Hydrogen was identified by mass spectrometry. Diborane was characterized by its infrared spectrum. Triphenylmethane was identified by its melting point, 88–94° (lit. mp 92°), comparisons of its infrared spectrum with that of a known sample, its characteristic behavior in a column chromatogram with alumina and Skelly B, and its characteristic mass spectrum.

Purification and Characterization of $(HBS)_x$.—The insoluble precipitate formed in the reaction was washed as free of triphenylmethane as possible by transferring benzene from the vacuum line, decanting to the other arm, and reevaporating the solvent back to repeat the process. Even after three of these wash operations, the product could not be freed completely from triphenylmethane.

The infrared spectrum of this solid was determined by preparing a KBr pellet in an inert atmosphere. The bands were generally broad (4000–670 cm^{-1}): 3300–3000 (m), 2450 (s), 1350 (s), 1125 (w), and 975 cm^{-1} (s) and a strong band that starts at 750 cm^{-1} and continues off the scale of the instrument.

X-Ray powder diffraction was carried out in a capillary using a Deybe–Scherrer powder camera. Several determinations on products from different runs indicated an amorphous material.

Elemental analysis of a precipitate obtained from the bistriphenylmethyl disulfide reaction gave the following results: C, 15.24: H, 4.92; S, 54.18; B, 18.18 (Calcd: B:S, 1:1. Found: B:S, 0.99:1). The presence of carbon indicates triphenylmethane impurities.

Reaction of Triphenylmethyl Mercaptan with Diborane.—A reaction mixture containing 1.61 mmol of diborane and 1.02 mmol of triphenylmethyl mercaptan in benzene was placed in the apparatus described for the bistriphenylmethyl disulfide reaction. The original yellow color increased in intensity after 2.5 hr. After 4 hr the solution became cloudy but was still quite yellow. *Ca.* 24 hr later the usual copious white precipitate had formed and the solution was colorless. Because of the press of other work, the reaction was not worked up for 20 days. At that time 1.14 mmol of hydrogen were recovered and 0.89 mmol of diborane were collected and identified by its infrared spectrum. Benzene extraction of the solid residue yielded 0.914 mmol of triphenylmethane, which was identified by melting point and infrared spectrum. The infrared spectrum of the $(HBS)_x$ precipitate was identical with that obtained from the bis(triphenylmethyl)disulfide reaction. The $(HBS)_x$ precipitate obtained from a similar reaction gave hydrogen and hydrogen sulfide in a molar ratio of 1:1.18 on hydrolysis. Identification of the gases was by mass spectrometry. Elemental analysis gave the following results: S, 44.85; B, 17.18 (Calcd: B:S, 1:1. Found: B:S, 1.13:1).

Reaction of Hydrogen Sulfide with Diborane.—A reaction was carried out with 0.74 mmol of diborane and 1.03 mmol of hydrogen sulfide in benzene using a reaction apparatus of sufficient volume to give a calculated pressure of 488 mm at 25°, ignoring solubility effects. In 2 days the white precipitate started to form. After 9 days the reaction yielded 2.38 mmol of hydrogen and 0.18 mmol of diborane. The white residue gave the infrared bands for the $(HBS)_x$ polymer. Elemental analysis gave the following results: S, 53.60; B, 23.3 (Calcd: B:S, 1:1. Found: B:S, 1.28:1).

Reaction of Bistriphenylmethyl Tetrasulfide with Diborane.—A reaction of 0.51 mmol of bistriphenylmethyl tetrasulfide with 1.63 mmol of diborane was carried out in a benzene solution under the same conditions as described for the bistriphenylmethyl disulfide reaction. A precipitate formed in *ca.* 2 days, and the original yellow color of the solution changed to colorless in *ca.* 4 days. The volatle fraction consisted of 1.62 mmol of hydrogen and 0.4 mmol of diborane. Triphenylmethane and $(HBS)_x$ were isolated from the residue.

Analytical Methods.—The mass spectral data were obtained for all the solid samples and some of the gases with an AEI MS-12 single-focusing mass spectrometer operated with a nominal resolution of 1000 and an ionizing voltage of 70 eV. Some of the hydrogen and hydrogen sulfide qualitative identifications were determined with an AEI MS-10.

The quantitative analyses of hydrogen, hydrogen sulfide, and diborane were accomplished by standard vacuum-line techniques. Microanalyses of boron and sulfur were carried out by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Nuclear Magnetic Resonance Spectra.—The ^{11}B nmr spectrum, in powdered $(HBS)_x$ was observed at room temperatues using a Varian nuclear induction crossed-coil apparatus. The measurements were carried out at transmitter frequencies of 16 and 22 MHz, corresponding to polarizing fields of *ca.* 11.8 and 16.2 kG. Excellent signal to noise ratios were possible with the high magnetic fields obtainable with a 15-in. Varian electromagnet. The transmitter frequency was crystal controlled while the external field was swept through the resonance value. Quartz sample tubes were used to eliminate the strong background signals arising from boron nuclei in the usual glass sample tubes.

Results and Discussion

The early experiments in unsealed systems indicated a slow reaction, as evidenced by a gradual increase in hydrogen pressure. Triphenylmethane was also separated from these reaction mixtures by column chromatography. This indicated a carbon–sulfur bond cleavage in the early stages of the reaction. The reactions carried out in the sealed reaction tubes indicated, as shown in Table I, a stoichiometry of 1 mol of diborane reacting with 1 mol of bistriphenylmethyl disulfide to yield 1 mol of hydrogen and 2 mol of triphenylmethane. The insoluble reaction product was characterized as having a hydridic hydrogen and a sulfur atom which could be easily hydrolyzed with water to form hydrogen sulfide. Strangely, hydrolysis with dilute HCl is very slow. The reason for this observation has not been

Table I

Expt no.	Calcd pressure of B_2H_6 at start, mm	Molar ratio,[a] B_2H_6 used to $C_{38}H_{30}S_2$ added	Molar ratio, B_2H_6 used to H_2 collected	Molar ratio, triphenylmethane recovered to $C_{38}H_{30}S_2$ used
G-1	688	1.09:1	1.20:1	
G-4	509	0.77:1	1.50:1	
G-5	465	1.18:1	0.855:1	
G-6	436	1.20:1	0.839:1	
G-9	509	1.14:1	0.934:1	
G-10	507	1.26:1	1.00:1	
G-11	477	1.02:1	1.10:1	1.83:1
G-12	496	1.11:1	1.09:1	1.73:1
G-13	486	1.12:1	1.11:1	1.88:1

[a] The amount of diborane used was determined by subtracting the excess diborane collected from the amount originally used.

elucidated. Quantitative studies are summarized in Table II. These determinations pointed to the possibility that the boron-sulfur product reacts with water to produce hydrogen and hydrogen sulfide in a 1:1 molar ratio. The low hydrogen sulfide ratios for the larger samples may be due to incomplete conversion of the sulfur into hydrogen sulfide.

TABLE II

Wt, mg	H_2S, mmol	H_2, mmol	Molar ratio, H_2:H_2S
172.6	0.32	0.48	1.5:1
142.8	0.22	0.26	1.2:1
88.3	0.16	0.18	1.1:1

The mass spectra (Table III) were obtained by transferring the sample to the solid probe of the instrument in a nitrogen-filled glove bag. The spectra were usually run with a source temperature of 200–250°. The largest peak in the spectrum was at m/e 78, which is the parent peak of the solvent benzene. The m/e 44 peak was attributed to the ion HBS^+ and is the largest peak in the spectrum except for the m/e 78 peak from benzene and the m/e 32, 33 and 34 peaks which correspond to the ions S^+, HS^+, and H_2S^+. The m/e 131–132 group is essentially due to $(BSH)_3{}^+$ with very little contribution from ions where hydrogen has been lost. The other B_3 and B_2 groupings are overlaps of patterns from several ions which differ in number of hydrogens. The significant peaks are summarized in Table III. The normalization is based on m/e 44 and includes peaks which are major fragments that cannot be assigned to benzene or hydrogen sulfide. In many cases the boron-sulfur peaks could be distinguished from the carbon peaks by their mass defect, many of the peaks appearing as doublets or triplets. Assignment was also aided by the isotope distribution of the boron-containing peaks.

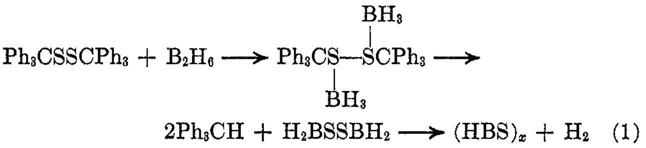
TABLE III

m/e	Normalized peak height	Isotope distribution patterns			Fragment assignment
133	2.0				
132	10.4	10.4 →			$(BSH)_3{}^+$
131	7.8	7.2			$B_3S_3H_2{}^+$
130	2.6	1.6			$B_3S_3H^+$
129	1.3				$B_3S_3{}^+$
102	22.1	22.1 →			$B_3S_2H_5{}^+$
101	16.9	15			$B_3S_2H_4{}^+$
100	26.0	3.6	26.0 →		$B_3S_2H_3{}^+$
99	24.7		18		$B_3S_2H_2{}^+$
98	13.0		4.2	24.7 →	$B_3S_2H^+$
97	6.5			17	$B_3S_2{}^+$
96	2.6			4	
92	3.9				
91	6.5				
90	2.6				
89	3.9				$B_2S_2H_3{}^+$
88	28.6	28.6 →			$(BSH)_2{}^+$
87	38.4	13.2	38.4 →		$B_2S_2H^+$
86	24.7	1.5	17.8	24.7 →	$B_2S_2{}^+$
85	7.8		2	10.4	
84	0			1.3	
83	3.9				
82	2.6				
77 d[a]	11.6	11.6 →			$H_2BS_2{}^+$
76 d[a]	12.7	2.7	12.7 →		$BHS_2{}^+$
75 d[a]	12.6		2.9		$BS_2{}^+$
58	2.6				$B_2SH_4{}^+$
57	23.4	23.4 →			$B_2SH_3{}^+$
56	24.7	10.9	24.7 →		$B_2SH_2{}^+$
55	23.4	1.2	11.5		B_2SH^+
54	11.7		1.3		B_2S^+
47	5.2				
46	44.9				H_3BS^+
45	87.2				H_2BS^+
44	10.0				HBS^+
43	40.4				BS^+
42	5.8				${}^{10}BS^+$
24	2.6				$B_2H_2{}^+$, $C_2{}^+$
23	7.8				${}^{11}B_2H^+$
22	14.3				${}^{11}B_2{}^+$
13	9.1				${}^{11}BH_2{}^+$, CH^+
12	7.8				${}^{11}BH^+$, ${}^{10}BH_2{}^+$, C^+
11	14.3				${}^{11}B^+$, ${}^{10}BH^+$
10	3.9				${}^{10}B^+$

[a] Low mass.

These results, along with the elemental analysis of boron and sulfur, led to the identification of the insoluble precipitate as $(HBS)_x$ polymer. This substance had been described by Burg and Wagner[9] as a product obtained from a 137-day gas-phase reaction of hydrogen sulfide and diborane and by Kirk and Timms[5] as a high-temperature reaction product of hydrogen sulfide on boron. The infrared spectrum reported by Kirk and Timms agreed with the infrared spectrum obtained in a KBr pellet on our product except for a weak band at 1125 cm^{-1} and the final band that drops off scale at *ca.* 750 cm^{-1}, which were observed in these studies but were not reported by Kirk and Timms.

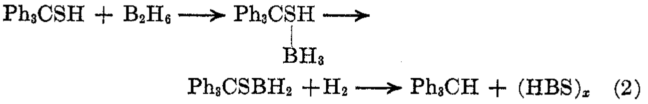
On the basis of these experimental results, the reaction was postulated to proceed by an initial Lewis acid–Lewis base adduct of borane to sulfur, the transfer of hydride from the borohydride to triphenylmethyl, and the loss of hydrogen by an internal redox reaction involving a sulfur-sulfur bond cleavage (eq 1). It is



$$\mathrm{Ph_3CSSCPh_3 + B_2H_6 \longrightarrow Ph_3C\underset{\underset{BH_3}{|}}{S}-\overset{\overset{BH_3}{|}}{S}CPh_3 \longrightarrow}$$
$$\mathrm{2Ph_3CH + H_2BSSBH_2 \longrightarrow (HBS)_x + H_2} \quad (1)$$

quite evident that the sulfur-sulfur bond cannot coexist in the same molecule as a boron-hydrogen bond. Because there is still the possibility that the sulfur-sulfur bond may be undergoing cleavage before the carbon-sulfur bond, a similar experiment was carried out with diphenyl disulfide. There appears to be a slow reaction which is as yet uncharacterized, but it is evident that the sulfur-sulfur bond cleavage is not a fast initial step.

On the basis of this mechanism, it was predicted that triphenylmethyl mercaptan would also form the $(HBS)_x$ polymer (eq 2). This was found to be the case.



$$\mathrm{Ph_3CSH + B_2H_6 \longrightarrow Ph_3C\underset{\underset{BH_3}{|}}{S}H \longrightarrow}$$
$$\mathrm{Ph_3CSBH_2 + H_2 \longrightarrow Ph_3CH + (HBS)_x} \quad (2)$$

A repetition of Burg and Wagner's experiment in our reaction vessel in the presence of benzene indicated that

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[9] A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, **76**, 3307 (1954).

the $(HBS)_x$ polymer could be formed much faster in solution than in the gas phase. The reaction in solution was certainly complete after 9 days. Judging from the appearance of the reaction tube, it may well have been complete after 4 days.

The infrared spectrum of the $(HBS)_x$ polymer from all the reactions was identical. The boron–sulfur elemental analysis was not so satisfying. The results are summarized in Table IV. The high boron content very likely reflects loss of hydrogen sulfide by hydrolysis. Boron, forming a nonvolatile boric acid or an intermediate, is not lost to the analysis. The low percentages found for the boron–sulfur analyses of the products obtained from the triphenylmethyl derivatives indicate a triphenylmethane contaminant. This was substantiated not only by the presence of carbon in the sample but also by the triphenylmethane lines in the X-ray powder pattern and the characteristic triphenylmethane peaks in the mass spectrum.

TABLE IV

Reactant	Expt no.	Boron, %	Sulfur, %	Ratio, boron:sulfur
Bistriphenylmethyl disulfide	G-9	18.18	54.18	0.99:1
Triphenylmethyl mercaptan	G-14	17.18	44.85	1.13:1
Hydrogen sulfide	G-20	23.37	53.60	1.29:1
Bistriphenylmethyl tetrasulfide	G-16	22.60	51.17	1.40:1

The reaction of diborane with bistriphenylmethyl tetrasulfide has been initiated. Hydrogen, triphenylmethane and $(HBS)_x$ polymer are formed. Preliminary experiments seem to indicate that all the sulfur atoms are converted into $(HBS)_x$, but this remains to be proven.

The $(HBS)_x$ polymer did not give evidence of dissolving in chloroform, benzene, toluene, ether, carbon disulfide, triglyme, or dioxane. The only X-ray powder pattern lines which could be seen were the lines from the triphenylmethane contaminant. After hydrolysis boric acid lines appeared.

Because an appropriate solvent could not be found for high-resolution nmr studies, only the broad-line spectrum of the solid was studied. The ^{11}B nmr spectrum consisted of three lines resulting from the nuclear quadrupole interaction. The nuclear spin of ^{11}B is $^3/_2$ and thus the three-line spectrum is expected from the interaction of the quadrupole moment with electric field gradients which exist in the vicinity of a boron nucleus. The field dependence of the absorption indicated that the two satellite lines were indeed a result of first-order quadrupole interaction and were not a splitting of the central line. A small amount of second-order quadrupole broadening was observed in the central line. In addition it is believed that the central line is a composite line with two components, reflecting boron atoms at two crystallographically inequivalent sites. From the splitting of the satellites the quadrupole coupling constant *eqQ* was determined to be *ca.* 0.07 MHz.

The ^{11}B nuclear quadrupole interaction is a sensitive internal probe of the electron environment of the boron nucleus. The main contribution to the electric field gradient is expected to arise from incomplete filling of the 2p orbitals. The atomic quadrupole coupling constant for the boron atom has been calculated[10] to be 5.39 MHz from atomic beam experiments. The reduction by a factor of *ca.* 100 of the value of *eqQ* given in the preceding paragraph compared with the atomic value indicated high symmetry in the structural arrangement of HBS. The small value of *eqQ* strongly favors tetrahedral coordination as opposed to planar trigonal sp^2 hybrid covalent bonding. The ^{11}B quadrupole coupling constants of trigonal compounds, with few exceptions, have been found to lie in the range of 2.5–2.8 MHz.[11] These results should be compared with the tetrahedral borates, in which *eqQ* was in the range of 0.05–0.09 MHz.

Another structural possibility that has not been ruled out is that involving a double-bond character, which would also greatly decrease the quadrupole interaction. The mechanism in this case would be that of boron atoms attracting electrons from neighboring atoms into the vacant boron orbitals to form double bonds which exhibit resonance. Further work is being done on the broad-line nmr spectra of boron compounds and will be reported by R. J. Snodgrass at a later date.

Registry No.—Diborane, 19287-45-7; bistriphenylmethyl disulfide, 15446-31-8; triphenylmethyl mercaptan, 33695-77-0; bistriphenylmethyl tetrasulfide, 23264-36-0.

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[10] G. Wessel, *Phys. Rev.*, **92**, 158 (1963).

[11] P. J. Bray, J. O. Edwards, J. G. O'Keefe, V. F. Ross, and I. Tatsuzaki, *J. Chem. Phys.*, **35**, 435 (1961).