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Reactions of Atomic (^{1}D) Sulfur: Synthesis of *B*-Mercaptocarboranes and *B*-Disulfidocarboranes

Jeffrey S. Plotkin and Larry G. Sneddon*

Contribution from the Department of Chemistry and the Laboratory for Research in the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174. *Received September 28, 1976*

Abstract: The reactions of atomic sulfur (^{1}D), generated by the gas phase photolysis of carbonyl sulfide, with the small closo carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ were studied and found to be a convenient method of preparing the corresponding *B*-mercaptocarboranes, including: 2-SH-1,5-$C_2B_3H_4$, 2-SH-1,6-$C_2B_4H_5$, 5-SH-2,4-$C_2B_5H_6$, 1-SH-2,4-$C_2B_5H_6$, and 3-SH-2,4-$C_2B_5H_6$. In addition, the photolytic decomposition of the *B*-mercapto derivatives of 2,4-$C_2B_5H_7$ results in the formation of several isomers containing boron bonded bridging disulfide groups: 5,5′-S_2-(2,4-$C_2B_5H_6$)$_2$, 1,1′-S_2-(2,4-$C_2B_5H_6$)$_2$, and 3,3′-S_2-(2,4-$C_2B_5H_6$)$_2$.

The use of atomic species as synthetic reagents has seen a resurgence in recent years mainly due to the development of high temperature methods,[1] and these techniques are now widely used[2] for those elements, particularly the transition metals, which vaporize as monoatomic species. Alternatively, a number of atomic species which may be useful for synthetic purposes, but impossible or difficult to generate using high temperatures, may be generated with the use of photochemical techniques.

In particular, Gunning and Strausz[3] have shown in a series of papers that sulfur atoms in the ^{1}D excited state may be produced by the photolysis of carbonyl sulfide at 2537 Å. Their studies have also revealed that these sulfur atoms are extremely reactive and undergo reactions reminiscent of single methylene. For example, ^{1}D sulfur atoms readily insert[4] into the C–H bonds of an alkane to form the corresponding mercaptan. Although the reactions of ^{1}D sulfur atoms with a wide variety of organic compounds have been studied, there has been little application to the synthesis of inorganic compounds. Recent studies in this laboratory have shown that atomic sulfur is a useful reagent for the synthesis of inorganic and organometallic compounds, and we now wish to report our studies of the reaction of sulfur ^{1}D atoms with the small closo carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$.

Experimental Section

All reactions and operations were performed using standard high vacuum techniques except where otherwise indicated. All photochemical reactions were performed in a cylindrical quartz tube (30 × 7 cm diameter) equipped with a greaseless stopcock. Attached to the bottom of the reactor was a small cold finger which was shielded to prevent photolysis of the liquid phase. The radiation source was a Griffin-Rayonet photochemical reactor equipped with 16 2537-Å lamps. Gas–liquid chromatography was conducted on a homemade evacuatable chromatograph equipped with a gas density detector and using 6 ft × 0.25 in., 20% tricresylphosphate (TCP) on Chromosorb W (60/80 mesh) column. Chromatographic retention volumes, R_v, are relative to 2,4-$C_2B_5H_7$ = 1.0. Preparative thin layer chromatography was conducted on silica gel plates (Brinkman) in air. Melting points were determined by Stock's ring method.

Boron-11 NMR spectra at 32.1 MHz and proton NMR spectra at 100 MHz were obtained on either a Varian HA-100 spectrometer or a JEOL PS-100 pulse Fourier transform spectrometer and are presented in Tables I and II, respectively. The ^{11}B chemical shifts were measured relative to an external BF_3:O(C_2H_5)$_2$ (0 ppm) standard, while ^{1}H shifts are relative to external Me_4Si. Infrared spectra (Table III) were obtained on a Perkin-Elmer Infracord spectrophotometer. Mass spectra were recorded on a Perkin-Elmer RMU-6E mass spectrometer.

The 1,5-dicarba-*closo*-pentaborane(5) (1,5-$C_2B_3H_5$), 1,6-dicarba-*closo*-hexaborane(6) (1,6-$C_2B_4H_6$), and 2,4-dicarba-*closo*-heptaborane(7) (2,4-$C_2B_5H_7$) were purchased from Chemical Systems, Inc., and purified by vacuum line fractionation or GLC before use. Carbonyl sulfide (COS) was purchased from Matheson Gas Products. All solvents were reagent grade.

Reaction of 1,5-$C_2B_3H_5$ and ^{1}D Sulfur Atoms. A 10.0-mmol mixture of 1,5-$C_2B_3H_5$ and COS in approximate 2:1 mole ratio was irradiated for 1 h at 35 °C while the cold finger of the photolysis reactor was maintained at 0 °C. During this time the tube became coated with a fine white deposit. The tube was then opened and the volatile material fractionated through a −95 °C trap to remove unreacted COS and 1,5-$C_2B_3H_5$. The material retained at −95 °C was further purified by gas chromatography on the TCP column at 108 °C to give 2.3 mg of 2-SH-1,5-$C_2B_3H_4$, R_v = 1.70. The mass spectrum shows a three-boron pattern with a cutoff at *m/e* 94 corresponding to the formula ${}^{12}C_2{}^{11}B_3{}^{32}S^1H_5$. This compound slowly decomposes in the liquid phase and an accurate melting point could not be obtained.

Reaction of 1,6-$C_2B_4H_6$ and ^{1}D Sulfur Atoms. In a typical reaction, a mixture of 9.9 mmol of 1,6-$C_2B_4H_6$ and 3.9 mmol of COS was irradiated for 3.5 h at 35 °C with the cold finger on the reactor maintained at 0 °C. As in the 1,5-$C_2B_3H_5$ reaction, the tube became coated with a fine white powder. The tube was then opened to the vacuum line and the volatile material was separated by trap-to-trap fractionation. The material retained at −78 °C was purified by GLC on the TCP column at 112 °C to give 3.0 mg of 2-SH-1,6-$C_2B_4H_5$, R_v = 5.0. The yield was 1.5% based on 1,6-$C_2B_4H_6$ consumed. The mass spectrum shows a four-boron pattern with a cutoff at *m/e* 106 corresponding to the formula ${}^{12}C_2{}^{11}B_4{}^{32}S_1{}^1H_6$. The melting point is −6.5 °C.

Reaction of 2,4-$C_2B_5H_7$ and ^{1}D Sulfur Atoms. A mixture of 10.6 mmol of 2,4-$C_2B_5H_7$ and 2.3 mmol of COS was irradiated for 2.5 h at 35 °C, while the cold finger of the reaction tube was maintained at 25 °C. The tube was opened to the vacuum line and the volatile materials were separated by trap-to-trap fractionation. The material retained in a −63 °C trap, but passing a −30 °C trap, consisted of a mixture of compounds of the formula $C_2B_5H_7S$ (25.4 mg, 8.8% yield, based upon 2,4-$C_2B_5H_7$ consumed). The isomers were separated by

Table I. 32.1-MHz ^{11}B NMR Data

Compound	δ, ppm (*J*, Hz)[a]	Relative areas
1,5-$C_2B_3H_5$[b]	−1.1	
2-SH-1,5-$C_2B_3H_4$[d]	−7.6 (175), −6.0	2:1
1,6-$C_2B_4H_6$[b]	19.0	
2-SH-1,6-$C_2B_4H_5$[d]	12.2, 16.8 (191), 22.6 (186)	1:2:1
2,4-$C_2B_5H_7$[c]	−5.0 (187), −2.0 (170), 23.5 (178)	1:2:2
1-SH-2,4-$C_2B_5H_6$[d]	−4.4 (161), −1.2 (170), 18.7, 31.0 (180)	1:2:1:1
3-SH-2,4-$C_2B_5H_6$[d]	−13.1, −2.3 (169), 18.4 (180)	1:2:2
5-SH-2,4-$C_2B_5H_6$[d]	−7.3, −1.9 (186), 3.5 (161), 23.3 (185)	1:1:1:2
5,5′-S_2-(2,4-$C_2B_5H_6$)$_2$[e]	−13.3, −4.6 (189), 0.7 (145) 19.6 (183)	1:1:1:2
1,1′-S_2-(2,4-$C_2B_5H_6$)$_2$[e]	−6.5 (181), −2.9 (153), 13.2, 27.9 (188)	1:2:1:1
3,3′-S_2-(2,4-$C_2B_5H_6$)$_2$[e]	−15.1, 2.8 (178), 18.1 (185)	1:2:2

[a] Shifts relative to external $BF_3{:}O(C_2H_5)_2 = 0$ ppm. [b] References 5 and 6. [c] Reference 6 and assigned to boron positions 3; 5,6; and 1,7, respectively. [d] Neat liquids. [e] Carbon disulfide solution.

gas chromatography on the TCP column at 112 °C to give the following three compounds: 1-SH-2,4-$C_2B_5H_6$ (8.9 mg, $R_v = 10.3$), 5-SH-2,4-$C_2B_5H_6$ (12.7 mg, $R_v = 15.5$) and 3-SH-2,4-$C_2B_5H_6$ (3.8 mg, $R_v = 17.0$). The melting points were −2.0, −2.4, and −1.1 °C, respectively. All three compounds have similar mass spectra showing cutoffs at *m/e* 118 corresponding to the formula $^{12}C_2{}^{11}B_5{}^{32}S_1{}^{1}H_7$.

The viscous oil which had remained in the reaction tube was extracted with tetrahydrofuran and separated on thin layer silica gel plates in air, using hexane as the eluent to give the following compounds: 5,5′-S_2-(2,4-$C_2B_5H_6$)$_2$ (R_f 0.36, 19 mg, 3.3% yield) and 1,1′-S_2-(2,4-$C_2B_5H_6$)$_2$ (R_f 0.56 <5 mg). The mass spectra of both compounds showed cutoffs at *m/e* 234 corresponding to the formula $^{12}C_4{}^{11}B_{10}{}^{32}S_2{}^{1}H_{12}$. Both compounds were oily liquids and melting points could not be obtained. Several additional compounds of this formula were isolated in only trace amounts which precluded complete characterization.

Direct Synthesis of 1,1′-S_2-(2,4-$C_2B_5H_6$)$_2$ and 3,3′-S_2-(2,4-$C_2B_5H_6$)$_2$. In a typical reaction a 13.5-mg sample of 1-SH-2,4-$C_2B_5H_6$ was irradiated in a small quartz tube (25 mm dia × 350 mm) at 35 °C for 1.5 h, with the lower end of the tube maintained at 25 °C. Separation of the products gave 4.7 mg (46% yield) of 1,1′-S_2-(2,4-$C_2B_5H_6$)$_2$ and 3.2 mg of unreacted 1-SH-2,4-$C_2B_5H_6$. An analogous reaction with 3-SH-2,4-$C_2B_5H_6$ gave 3,3′-S_2-(2,4-$C_2B_5H_6$)$_2$ in similar yields.

Results

All photochemical reactions were conducted in the vapor phase without solvent in an evacuated quartz tube described in the Experimental Section. Typically, reactions were performed with an approximate 3:1 mole ratio of carborane to carbonyl sulfide (COS). The concentration of COS was purposely kept low, since previous work[3,4] has shown that at higher concentrations collisional deactivation of ^{1}D sulfur atoms to the $^3P_1$ ground state occurs. The new compounds were characterized by their ^{11}B and ^{1}H NMR, infrared (Tables I, II, and III, respectively) and mass spectra, as also described in the Experimental Section.

1,5-$C_2B_3H_5$. 1,5-$C_2B_3H_5$ reacts readily with ^{1}D sulfur atoms to give a compound of the formula $C_2B_3H_5S$, *m/e* 94, in low yields. The 32.1-MHz ^{11}B NMR spectrum consists of a doublet at −7.6 ppm (B 3,4) and a singlet at −6.0 ppm (B 2) in a 2:1 ratio and is characteristic of 2-substituted derivations of 1,5-$C_2B_3H_5$. Both resonances are shifted to lower field compared to the boron resonances in 1,5-$C_2B_3H_5$ (Table I). The 100-MHz ^{1}H NMR spectrum shows the expected C–H singlet and B–H quartet (B(3,4)–H), each of intensity 2, as well as a resonance at 0.73 ppm (intensity = 1) which may be assigned to the –SH proton. As might be expected, based on the relative stabilities of 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$, the 2-SH-1,5-$C_2B_3H_4$ was found to be the least stable of the *B*-mercaptocarboranes and appears to decompose in the liquid phase to give a white solid and 1,5-$C_2B_3H_5$. In a separate experiment a pure sample of 2-SH-1,5-$C_2B_3H_4$ was irradiated in an attempt to form a disulfide bridged species; however, only decomposition resulted. This photolytic decomposition of the mercaptan probably accounts for the low yields of 2-SH-1,5-$C_2B_3H_4$ formed in the original reaction.

1,6-$C_2B_4H_6$. As in the 1,5-$C_2B_3H_5$ case, 1,6-$C_2B_4H_6$ reacts with ^{1}D sulfur atoms to give only one product, the corresponding boron substituted mercaptocarborane 2-SH-1,5-$C_2B_4H_5$, *m/e* 106. The ^{11}B NMR spectrum consists of a singlet (12.2 ppm) and two doublets (16.8 and 22.6 ppm) of intensity 1:2:1 which may be assigned to the 2; 3,5; and 4 boron positions, respectively. The mercapto group shifts the 2-position downfield 6.8 ppm and the "trans" 4-position upfield 3.6 ppm relative to the resonances of the parent 1,6-$C_2B_4H_6$ (Table I). A similar "trans" effect is observed for the 2,4-$C_2B_5H_7$ derivatives and is discussed below. The ^{1}H NMR spectrum shows the expected C–H (3.47 ppm) and SH (1.26 ppm) resonances; however, the resonances attributable to the B 3,5-H and B 4-H protons were overlapped and could not be resolved, even in the ^{11}B decoupled spectrum.

2,4-$C_2B_5H_7$. 2,4-$C_2B_5H_7$ reacts with ^{1}D sulfur atoms to give two sets of products of mass 118 and 234, respectively. The first more volatile set was found to be an isomeric mixture of *B*-mercaptocarboranes which were separated by vacuum line fractionation and GLC to give 1-SH-2,4-$C_2B_5H_6$, 5-SH-2,4-$C_2B_5H_6$ and 3-SH-2,4-$C_2B_5H_6$ in 3.08, 4.40, and 1.32% yields, respectively, based upon 2,4-$C_2B_5H_7$ consumed. The ^{11}B NMR spectra and assignments for these mercaptans are

Table II. 100-MHz ^{1}H NMR Data

Compound	δ(ppm)[a] S–H	C–H	B–H (*J*, Hz)[b]	Intensity
2-SH-1,5-$C_2B_3H_4$[c]	0.73	4.37	3.42 (193)	1:2:2
2-SH-1,6-$C_2B_4H_5$[c]	0.78	3.47	2.15 (194)[e]	1:2:3
1-SH-2,4-$C_2B_5H_6$[c]	0.05	5.92	4.97, 4.16, 0.05	1:2:1:2:1
3-SH-2,4-$C_2B_5H_6$[c]	1.12	4.52	4.22, 0.39 (184)	1:2:2:2
5-SH-2,4-$C_2B_5H_6$[c]	1.17	4.90	4.53, 3.82, 0.47 (182)	1:2:1:1:2
5,5′-S_2-(2,4-$C_2B_5H_6$)$_2$[d]	—	5.69	4.88, 4.05, 0.60 (184)	2:1:1:2
1,1′-S_2-(2,4-$C_2B_5H_6$)$_2$[d]	—	5.73	5.01, 4.40 0.27	2:1:2:1
3,3′-S_2-(2,4-$C_2B_5H_6$)$_2$[d]	—	5.18	4.21, 0.57	1:1:1

[a] Shifts relative to external Me_4Si. [b] Shifts are reported from the boron decoupled spectrum, coupling constants are given only when they could be accurately measured in the coupled spectrum. [c] Benzene-d_6 solution. [d] Carbon disulfide solution. [e] Overlapping resonances from protons attached to the 3,5 and 4 positions.

Table III. Infrared Data

2-SH-1,5-$C_2B_3H_4$[a]	2900 (w), 2620 (vs), 1300 (m), 1225 (sh), 1180 (s), 1130 (s), 910 (m), 830 (w), 750 (w)
2-SH-1,6-$C_2B_4H_5$[a]	2630 (vs), 1340 (w), 1250 (s), 1200 (s), 1160 (m), 1125 (sh), 1035 (w), 940 (w), 885 (m)
1-SH-2,4-$C_2B_5H_6$[a]	3080 (w), 2600 (vs), 2000 (w), 1730 (w), 1450 (w), 1375 (w), 1270 (w), 1200 (s), 1110 (sh), 1080 (s, br), 980 (m), 935 (w), 900 (m), 895 (w), 720 (m)
3-SH-2,4-$C_2B_5H_6$[a]	2610 (vs), 1380 (w), 1320 (sh), 1290 (vs), 1160 (sh), 1125 (sh), 1100 (sh), 1055 (m), 955 (w), 910 (w), 830 (m)
5-SH-2,4-$C_2B_5H_6$[a]	2590 (vs), 1260 (s), 1130 (s), 1060 (m), 985 (m), 895 (m), 865 (m), 820 (w), 715 (m, br)
5,5′-S_2-(2,4-$C_2B_5H_6)_2$[b]	3120 (w), 2600 (vs), 1300 (sh), 1275 (sh), 1240 (s), 1120 (s), 1060 (s), 1030 (sh), 975 (m), 925 (m), 885 (s), 855 (m), 820 (m), 715 (w, br)
1,1′-S_2-(2,4-$C_2B_5H_6)_2$[b]	3100 (w), 2630 (vs), 1250 (w), 1190 (s), 1135 (s, br), 965 (m), 920 (w), 875 (m), 850 (w), 815 (sh), 805 (w), 785 (w), 705 (m)
3,3′-S_2-(2,4-$C_2B_5H_6)_2$[b]	3100 (w), 2620 (vs), 1275 (m), 1250 (vs), 1220 (sh), 1110 (sh), 1080 (m), 1045 (s), 945 (w), 900 (w), 875 (w), 820 (m), 800 (sh)

[a] Gas phase in 10-cm NaCl cell. [b] Thin film on NaCl plates.

presented in Figure 1 and several trends are apparent. In all cases the boron attached to the mercapto group is shifted downfield 2–6 ppm from its position in the parent 2,4-$C_2B_5H_7$ (Table I). Similar shifts have been reported for fluoro,[7] chloro,[8] and methyl[9] derivatives of 2,4-$C_2B_5H_7$. It has also been noted previously that the downfield shift of the substituted boron is often accompanied by significant shifts elsewhere in the carborane. This is also true for the *B*-mercaptocarboranes. For example, substitution at the 1 position shifts the "trans" 7 position upfield 10 ppm and the 3 and 5,6 positions upfield 2.8 ppm. Substitution at the 5-position causes upfield shifts in the 6 position (7.5 ppm), 3 position (5.3 ppm), and 1,7 positions (2.1 ppm). Substitution at the 3 position shifts the 5,6 positions slightly upfield (1.7 ppm) while shifting the 1,7 positions downfield (−2.8 ppm).

The ^1H NMR spectra of these compounds each showed the expected resonances, but the SH resonance from the 1-SH-2,4-$C_2B_5H_6$ compound is considerably upfield when compared to the mercaptoproton resonances in 3-SH-2,4-$C_2B_5H_6$ and 5-SH-2,4-$C_2B_5H_6$ (Table II). This chemical shift difference is in agreement with predictions based on ring current calculations[10] for the 2,4-$C_2B_5H_7$ cage. Similarly the C–H resonances of 1-methyl-substituted 2,4-$C_2B_5H_7$ derivatives also appear[9] 1.0–1.3 ppm upfield in comparison to the 3- or 5-methyl-substituted compounds.

The second set of products from this reaction consisted of an oily material which was extracted from the photolysis tube and separated by thin layer chromatography. Two compounds containing carborane cages connected by bridging disulfide groups were isolated: 1,1′-S_2-(2,4-$C_2B_5H_6)_2$ and 5,5′-S_2-(2,4-$C_2B_5H_6)_2$. Several additional isomers of these compounds were also produced in the reaction, but in quantities insufficient for complete characterization. In separate experiments 1,1′-S_2-(2,4-$C_2B_5H_6)_4$ and the new compound 3,3′-S_2-(2,4-$C_2B_5H_6)_2$ were produced in good yields by the direct photolysis of 1-SH-2,4-$C_2B_5H_6$ and 3-SH-2,4-$C_2B_5H_6$, respectively.

Upon formation of the disulfide bridged compounds all ^{11}B resonances appeared to be shifted to slightly lower fields when compared to the corresponding *B*-mercaptocarborane, but the appearance of the spectra is very similar and the assignments are the same as those given for the mercaptans. The ^1H NMR also showed that most resonances were shifted to lower field and the absence of the SH resonance was consistent with the proposed disulfide structure.

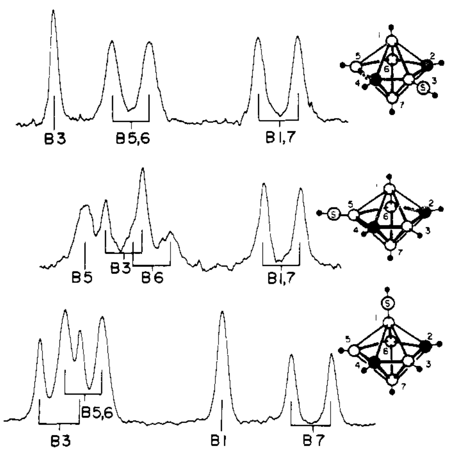

Figure 1. The 32.1-MHz ^{11}B NMR spectra of 3-SH-2,4-$C_2B_5H_6$, 5-SH-2,4-$C_2B_5H_6$, and 1-SH-2,4-$C_2B_5H_6$.

Discussion

The reaction of ^1D sulfur atoms, produced by the gas phase photolysis of carbonyl sulfide, with the small closo carboranes, 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$, has been found to be a convenient method of preparing the corresponding boron-substituted mercaptocarboranes. Several examples[11,12] of icosahedral carboranes containing C-substituted mercapto groups have been prepared by the reaction of the alkali metal salt of the carborane anion with elemental sulfur followed by hydrolysis, but no examples of boron-substituted mercaptocarborane have been previously reported. The reaction with ^1D sulfane atoms is a one-step reaction and the simplicity of the technique, along with the absence of competing side reactions, makes this method particularly useful. Only boron-substituted products have been isolated in these reactions,[13] and no evidence for the formation of C-substituted derivatives was obtained, which is consistent with the estimated relative bond strengths of C–H bonds (98 kcal)[14] vs. B–H bonds (91 kcal)[14] and with the established[3,4] electrophilic nature of ^1D sulfur atoms. Similarly other photochemical substitution reactions of carboranes, such as the photochemical halogenation of *o*-carborane,[15] also give only boron substitution.

The previous studies[3,4] of the reactions of ^1D sulfur atoms with alkanes had supported an insertion mechanism involving the single-step attack of the sulfur atom on the C–H bond, such as has been proposed for the reactions of singlet methylene. For such an insertion type mechanism an indiscrimiate attack of the sulfur atoms on the various bonds of similar energies would be predicted. This appears consistent with our results, since the isomer distribution of mercaptans from the 2,4-$C_2B_5H_7$ reaction was near, within experimental error, the statistical distribution of like B–H bonds in the molecule. Similarly, the absence of any radical recombination products, which would be expected if an alternative abstractive type of mechanism were important, also supports a single-step mechanism.

That ^1D sulfur atoms are definitely involved was demonstrated by performing the same reactions in the presence of mercury vapor. Excited mercury atoms have been shown[4] to promote the deactivation of ^1D sulfur atoms to the ^3P ground state.

$$S(^1D) + Hg(^3P_1) \rightarrow S(^3P_1) + Hg(^1S)$$

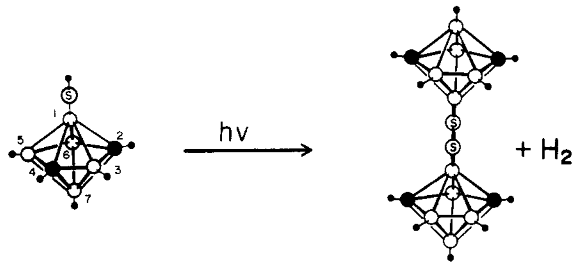

Figure 2. Synthesis of 1,1′-$(2,4\text{-}C_2B_5H_6)_2$ from 1-SH-2,4-$C_2B_5H_6$.

As mentioned above, the studies[4] of the reactions of atomic sulfur with alkanes demonstrated that only ^1D sulfur atoms gave C–H insertion products, while $^3P_1$ sulfur atoms did not react with alkanes. Our studies are analogous to the studies on alkanes, since mercury sensitizing the reactions suppresses the formation of mercaptocarborane products.

The reaction of ^1D sulfur atoms with 2,4-$C_2B_5H_7$ also gave several compounds which are the first examples of boron bonded bridging disulfide groups: 1,1′-S_2-$(2,4\text{-}C_2B_5H_6)$, 5,5′-S_2-$(2,4\text{-}C_2B_5H_6)_2$, and 3,3′-S_2-$(2,4\text{-}C_2B_5H_6)$. Although we have isolated only three such compounds, we have evidence that all possible linked combinations exist, but the small amounts produced, or difficult separations, precluded complete characterization of all such compounds. The formation of the disulfides in the original reaction suggested that the mercaptans formed may have been undergoing some secondary photolytic decomposition, followed by recombination of the resulting radicals:

$$C_2B_5H_6SH \xrightarrow{h\nu} C_2B_5H_6S\cdot + H\cdot$$

$$2\,H\cdot \rightarrow H_2$$

$$2C_2B_5H_6S\cdot \rightarrow S_2\text{-}(C_2B_5H_6)_2$$

To test this possibility separate pure samples of 1-SH-2,4-$C_2B_5H_6$ and 3-SH-2,4-$C_2B_5H_6$ were photolyzed and were found to convert to the corresponding disulfides 1,1′-S_2-$(2,4\text{-}C_2B_5H_6)_2$ and 3,3′-S_2-$(2,4\text{-}C_2B_5H_6)_2$ in good yields (Figure 2).

The disulfides are especially interesting since they appear to be both hydrolytically and thermally stable. Also, like the mercaptans, the disulfides are boron-substituted, therefore leaving the cage carbon positions open for substitution or polymerization reactions. We hope to explore the chemistry of these compounds, as well as their possible applications, in the future.

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Electronic Structure of Macrocyclic Compounds Revealed by X-Ray Photoelectron Spectroscopy

Manabu Senō,* Shinji Tsuchiya, and Shojiro Ogawa

Contribution from the Institute of Industrial Science, The University of Tokyo, 7-22, Roppongi, Minato-Ku, Tokyo 106, Japan.

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Abstract: The electronic and stereochemical structures of tetraaza macrocycle, hexaaza macrocycle, and their metal complexes have been clarified by x-ray photoelectron spectroscopy and magnetic susceptibility measurements. These macrocycles have the delocalized structure of inner hydrogens, whereas tetraphenylporphine has the bonded structure. Most of the metal complexes, except for the cobalt complex, have square planar structure. The structure of the cobalt complex over the temperature range 140–210 K is supposed to be square planar, but there was observed a transition temperature at about 210 K.

A high level of interest has been directed recently to the chemistry of porphyrins and metalloporphyrins owing to their biological importance, and the properties and the structure of these compounds have been studied by many physical methods.[1] For example, the extensive x-ray data on single crystals indicated that the atoms of the inner ring are individually planar and the bond distances of this ring resemble those of a heterocyclic aromatic system.[2] The measurements of x-ray photoelectron spectroscopy (XPS) showed a bonded structure of the inner hydrogens and elucidated the difference in the electron densities between the aza nitrogen and the pyrrole nitrogen in the metal-free tetraphenylporphine.[3]

Some synthetic tetraaza macrocycles have been also studied as porphyrin models.[4] An elucidation of the electronic and stereochemical properties of these macrocycles may give some useful information regarding the behavior of metalloporphyrins